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Synthesis and study of conjugated polymers containing di- or triphenylamine

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Synthesis and study of conjugated polymers containing di- or triphenylamine

by

Mongkol Sukwattanasinitt

A dissertation submitted to the graduate faculty

in partial fulfillment of the requirments for the degree of

DOCTOR OF PHILOSOPHY

Department: Chemistry

Major: Organic Chemistry

Major Professor: Thomas J. Barton

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1996

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Major Professor

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For the Major Department

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For the Graduate College

DEDICATION

TO MY PARENTS,

TO ANN

TABLE OF CONTENTS

GENERAL INTRODUCTION

This thesis consists of two separate parts. The first part addressess the synthesis and study of conjugated polymers containing di- or triphenylamine. Two types of polymers: linear polymers and dendrimers, were synthesized. The polymers were characterized by NMR, IR, UV, GPC, TGA and DSC. Electronic and optical properties of the polymers were studied through the conductivity measurements and excitation-emisson spectra. The second part of this thesis deals with a reaction of electron-rich acetylenes with TCNE. The discovery of the reaction from charge transfer complex studies and the investigation of this reaction on various electron-rich acetylenes are presented.

PART I

SYNTHESIS, CHARACTERIZATION AND ELECTRONIC PROPERTIES OF N-INTERRUPTED CONJUGATED POLYMERS

INTRODUCTION

Introductory Remarks

As part of a steadily growing interest in the electronic properties of organic materials, a number of intriguing electronic properties and possible applications of arylamine compounds have been discovered. Phenylamines are interesting in their own right because of their charge transporting properties.[1,2] Polymers containing these moieties are even more attractive as the polymers would be more readily processable and provide better mechanical properties. A number of non-conjugated polymers of di- and triphenylamine have been synthesized and used effectively as hole transporting materials[2b] in organic electroluminescent devices. Conjugated polymers containing diphenylamine and triphenylamine are rare. Polyaniline is the only well known example of a conjugated diphenylamine polymer due to its high electrical conductivity and environmental stability in the doped state. After extensive literature searches, we found that no well-characterized diphenylamine and triphenylamine conjugated polymers, besides derivatives of polyaniline, have been synthesized or studied. In this chapter of the thesis, syntheses, characterizations, and preliminary studies of a series of conjugated polymers containing diphenylamine and triphenylamine will be discussed.

Conjugated Polymers

Conjugated polymers are polymers which contain overlapping p-orbitals throughout the polymer chain. Three types of p-orbital providing units have been used to construct conjugated polymers: aromatic segments, non-aromatic segments and hetero atoms.

Arrangements of these units in the polymer chains can be used to classify most of the currently known conjugated polymers into five groups (Figure 1). Polyacetylene (PA)[3,4] and polydiacetylene (PDA)[3d,5] consist solely of conjugated double bonds or triple bonds. Polyparaphenylene (PPP)[3b,6] and polythiophene (PT)[3a,3b,3d,7] consist of conjugated aromatic rings. Examples of copolymers of aromatic and non-aromatic segments are polyparaphenylenevinylene (PPV)[3,8] and polyparaphenyleneethynylene (PPE).[9] Polyaniline (PANI)[3] and polyphenylenesulfide (PPS)[3b] are examples of polymers with alternating benzene ring and hetero atoms. The last class is the polyacenes[10] which consist of fused aromatic rings.

Conjugated polymers are often capable of being doped, through chemical (or electrochemical) oxidation or reduction, to states of higher electrical conductivity.[3,4] The very first synthesis and study of conducting polymers involved PA and PANI. Oxidatively doped trans-PA is the most conductive ($\sigma = 10^3$-10^5 S cm^{-1})[11] among conducting polymers. However, due to its poor environmental stabilities, PA is still only of academic interest. As an environmentally stable material, doped PANI which possesses a lower conductivity ($\sigma = 1$-100 S cm^{-1})[12] has been developed to the point of being a commercialized conducting polymer. Other examples of conducting polymers are PT, PPP and PPV.

Even though electrical conductivity was the initial interest in conjugated polymers, presently the underlying chemistry and physics of these materials in their undoped state seem to be even more interesting. A number of new conjugated polymers have been synthesized and studied in the past two decades. In 1990, physicists and chemists from the University of Cambridge reported the first observation of electroluminescence from polymeric devices.[13]

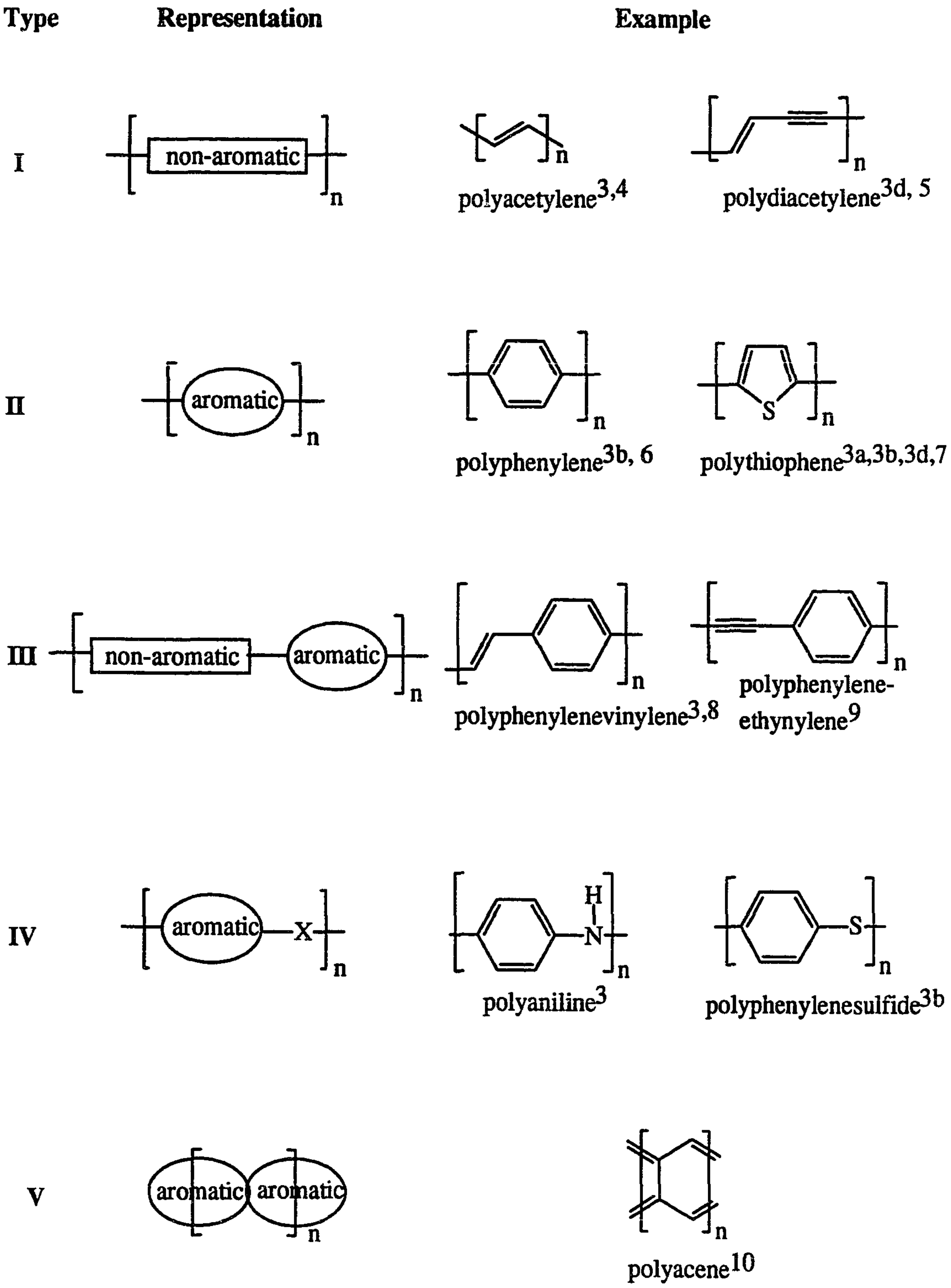


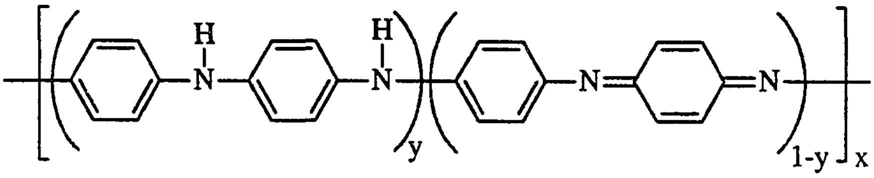
Figure 1 Illustration of various types of conjugated polymers.

The device was constructed sandwiched between indium tin oxide (ITO) and aluminum electrodes. Conjugated polymers have also been studied for nonlinear optical properties, magnetism, photoconductivity, chromism, and sensoring.[3] Relationships between the structure of polymers and their properties are always of great interest.

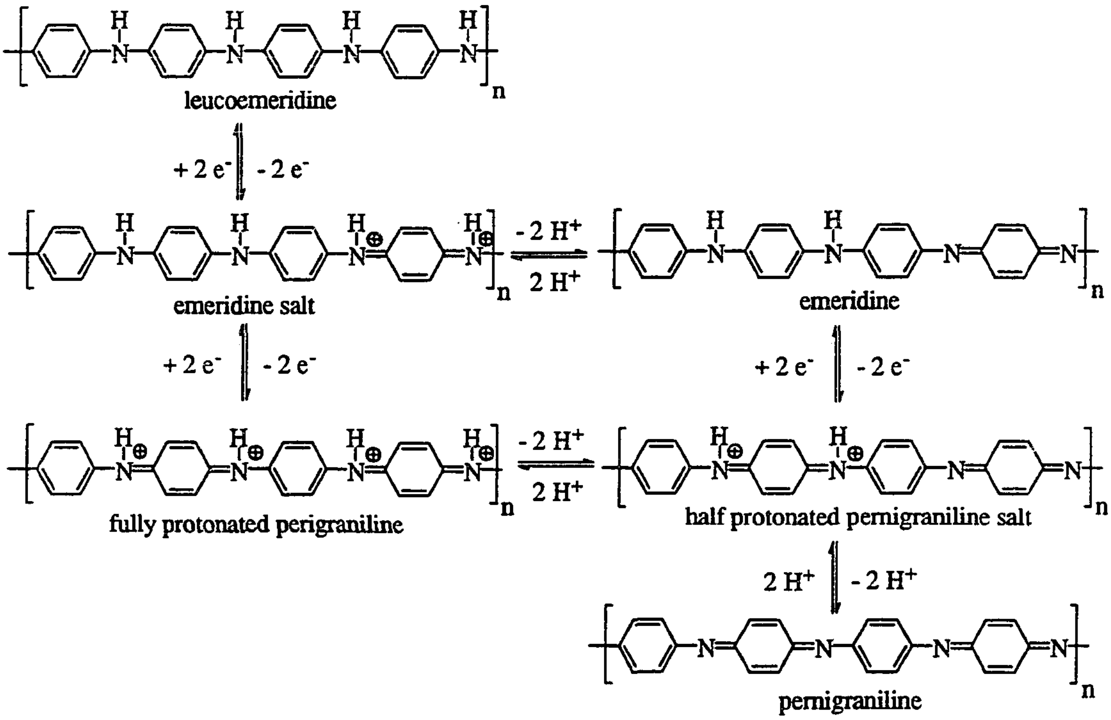
This dissertation involves the synthesis and studies of nitrogen containing polymers whose structures are closely related to PANI, PPV and PPE. The following sections are thus devoted to the discussion of these polymers in more detail.

Polyaniline and Its Conductivity

Polyaniline (PANI) was known long before its current interest as aniline blacks which are undesirable black deposits formed on the anode in electrolyses involving aniline. Recent studies of polyaniline have shown that the polymer can exist in a wide range of structures depending on the environment.[14] Under basic conditions, the polymer has the generalized composition consisting of amine and imine repeating units as shown below.

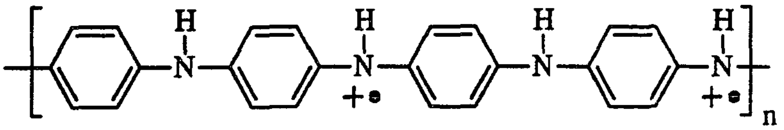


The oxidation state of the polymer is determined by 1-y which can be varied from 0 to 1. The fully reduced form, (1-y) = 0, is called 'leucoemeraldine', the half oxidized form, (1-y) = 0.5 is called 'emeraldine' and the fully oxidized form, (1-y) = 1 is called 'pernigraniline'. The imine nitrogen atoms can be protonated in whole or in part to give the corresponding salts (Scheme 1). The degree of protonation of the polymeric base depends on its oxidation state and on the pH. A complete protonation of imine nitrogen atoms in emeraldine base by aqueous HCl, for example, results in the formation of emeraldine hydrochloride salt which has a conductivity about 9 to 10 orders of magnitude higher. This fully protonated emeraldine salt is the most highly conductive form of polyaniline.[12]

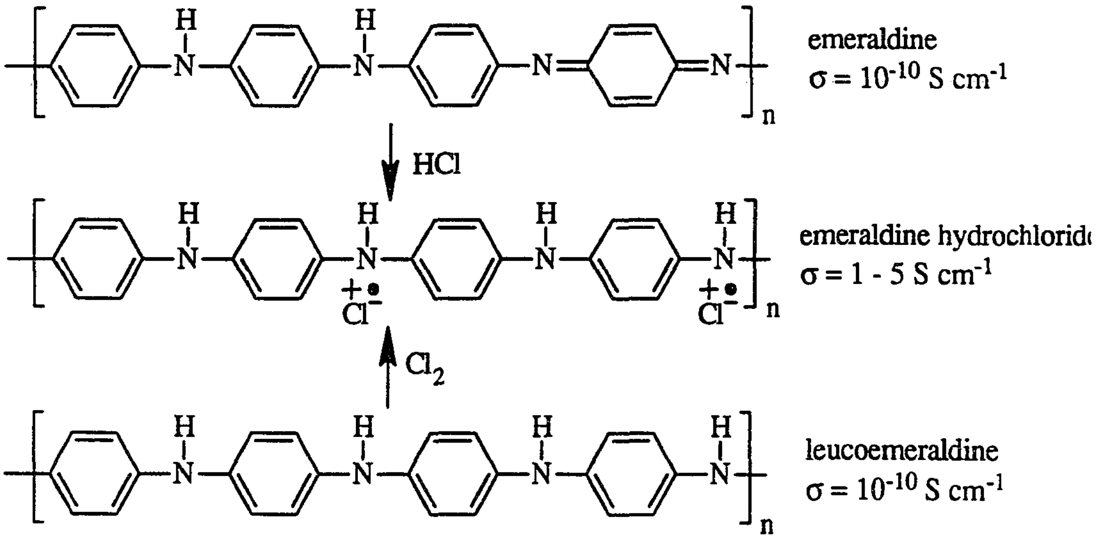


Scheme 1

If the emeraldine salt had the above cationic bipolaron constitution as shown in Scheme 1, it would be diamagnetic. However, extensive magnetic studies have shown that it is strongly paramagnetic and that its Pauli (temperature-independent) magnetic susceptibility increases linearly with the extent of protonation.[14] These observations and earlier studies[15] showed that the protonated polymer is actually a delocalized polysemiquinone radical cation, one resonance form consisting of two separated polarons:

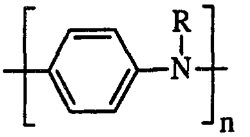


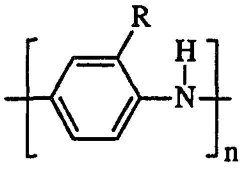
Polyaniline is a special conducting polymer in that its most highly conducting doped form, emeraldine salt, can be reached by two completely different processes, protonic acid doping and oxidative doping (Scheme 2). For example, emeraldine hydrochloride salt can be obtained from the addition of 1 M hydrochloric acid to emeraldine base or from the oxidation of leucoemeraldine by chlorine gas.



Scheme 2

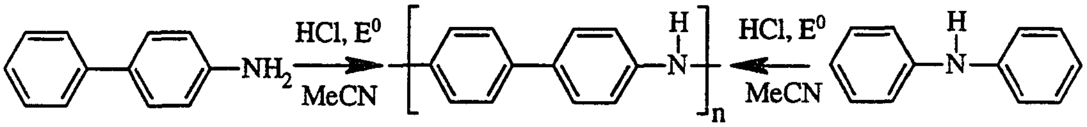
Alkyl derivatives of polyaniline were also synthesized in order to improve the solubility of the polymers in common organic solvents. Poly(N-alkylanilines)[16] and polyalkylaniline[17] were prepared from either chemical oxidative polymerization or electrochemical oxidative polymerization of N-alkylanilines and o-alkylanilines (or m-alkylanilines).


Poly(N-alkylaniline)


Poly(alkylaniline)

The conductivity studies showed that doped poly(N-alkylanilines) have conductivities of 10^{-7}-10^{-6} S cm^{-1} and doped poly(alkylaniline) have conductivities of 0.3-1 S cm^{-1}.

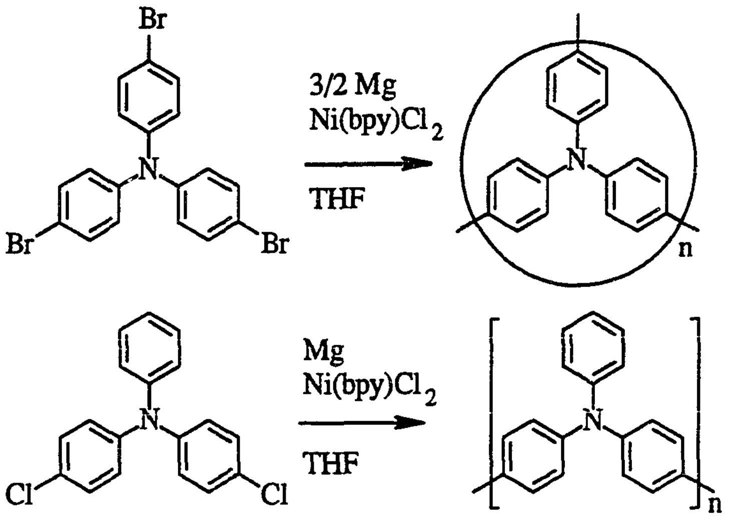
Although the radical cations of arylamines are known to be especially stable, polyaniline is the only conjugated polymer containing diphenylamine units which has been extensively studied. Only a few synthetic attempts for other conjugated polymers containing diphenylamine have been reported. In 1989, electropolymerizations of 4-aminobiphenyl and diphenylamine were reported (Scheme 3).[18] The resulting insoluble film from both polymerizations was proposed to be poly(4-phenylaniline) based on IR.



Scheme 3

The nonlinear optical properties of this polymer were studied and the third-order nonlinear susceptibility, $\chi^{(3)}$, of 1.3×10^{-10} esu was reported.[19]

Triphenylamine conjugated polymers were synthesized in 1991 by Ni-catalyzed coupling polymerization.[20] The polymerization of 4,4',4''-tribromotriphenylamine yielded an insoluble network polymer and the polymerization of 4,4'-dichlorotriphenylamine yielded a low molecular weight (M_w = 2500-3000) linear polymer (Scheme 4).

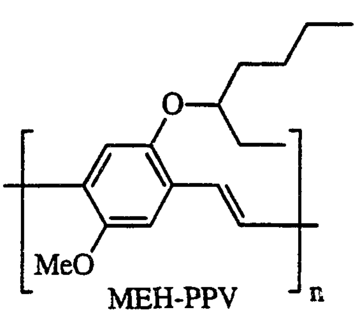


Scheme 4

The proposed structures of the polymers were based on IR and elemental analysis. A film of these polymers were doped by I_2 vapor to reach a maximum conductivity of 0.7-1.2 S cm^{-1} after an 18 h exposure period. An electrochemical study indicated that the maximum conductivity corresponded to a 50% doping level.

Polyparaphenylenevinylene and Light Emitting Diodes

Unlike polyacetylene and polyaniline, polyparaphenylenevinylene (PPV) is a strongly photoluminescent conjugated polymer. The current interest in PPV focuses upon its photophysics and opto-electronic applications. Following the first observation of electroluminescence (EL) of the polymer-based LED constructed from PPV,[13] a number of PPV derivatives have been synthesized. With an introduction of an alkoxy chain, poly (2-methoxy, 5-(2'-ethylhexoxy)-1,4-phenylenevinylene, MEH-PPV, is soluble in organic solvent that greatly simplifies the fabrication.[21]



A device constructed from MEH-PPV also emits light at longer wavelengths than that of the PPV device due to the smaller energy gap between HOMO and LUMO produced by the electron donating alkoxy groups.

There are a number of advantages of the polymer-based LEDs: low cost, simple fabrication, the possibility of color tuning through rational structural designs,[22] the accessibility to large area devices, and flexible LEDs.[23] An example of a flexible LED consisting of poly(ethylene pthalate) (PET) as a substrate, conducting PANI as a hole injector, MEH-PPV as an emissive layer and calcium, Ca, as an electron injector is shown in Figure 2.

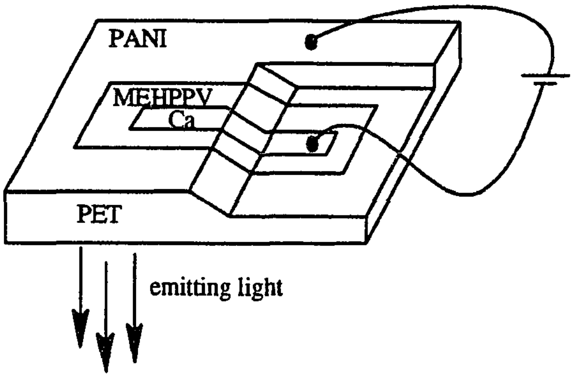


Figure 2 A flexible LED

Currently, research in the area of polymer-based LEDs is focused on the improvement of environmental stabilities and EL quantum efficiencies, η_ϕ, of the devices. In order to achieve this, mechanisms of the electroluminescence must be understood. There are at least four steps involved in electroluminescence: charge injection, charge transport, charge recombination, and light emission (Figure 3).[3c]

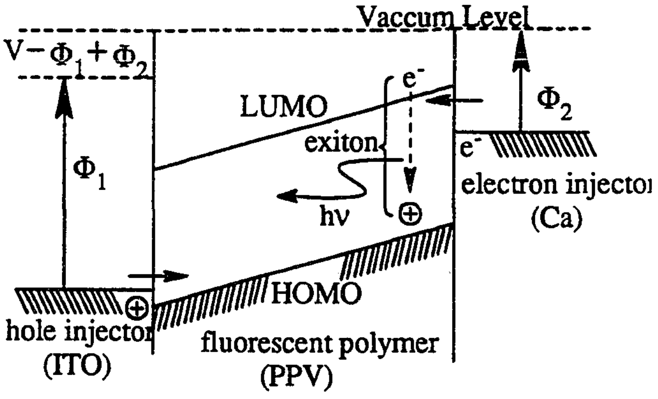


Figure 3 Schematic EL process in a V volts forward biased LED constructed from PPV, ITO with work function of Φ_1 and Ca with work function of Φ_2.

Charge injection consists of two processes occurring at both interfaces of the fluorescent polymer layer: (1) electron injection from an electron injector to the fluorescent polymer, and (2) hole injection from a hole injector to the fluorescent polymer. An electron injector is usually a low ionization energy (work function, Φ_2) metal such as Ca and Al. A hole injector is usually a high ionization energy (Φ_1) conductor such as indium tin oxide (ITO) and conducting PANI. According to Figure 3, the lower the energy barrier between the Fermi level of the hole injector and HOMO of the polymer the easier the holes can be injected. A lower barrier between the Fermi level of the electron injector and LUMO of the polymer allows for easier electron injection. The efficiency of the hole injection is thus dependent upon the difference between the ionization energy of the polymer and the work function of the hole injector ($I-\Phi_1$). The efficiency of electron injection is dependent upon the difference of the work function of the electron injector and electron affinity E_A of the polymer (Φ_2-I).[8] These two values, ($I-\Phi_1$) and (Φ_2-I), can be varied by changing the metal electrodes or structural design of the fluorescent polymers.

Charge transport in the fluorescent polymer film is accomplished through two types of carriers: (1) electrons carrying negative charges and (2) holes carrying positive charges. In most conjugated polymers including PPV, the mobility of holes is faster than the mobility of electrons.[8] The differences in mobilities cause an imbalanced charge in the polymer film and the charge recombinations occur close to or inside the negative electrode. If the recombinations occur close to the negative electrode, the EL quantum efficiency is diminished by the self-absorption. The recombinations inside the metal electrode give no radiative decay. The low quantum efficiency caused by this imbalanced charge transport can be improved by adding an electron-transporting layer[25] between the polymer and electron injector or by blending an electron transporting material with the polymer.[22b,26] Hole-transporting materials[1,2] such as arylamines have also been used to improve the EL efficiencies in polymer-based blue LEDs[22a,b,27].

Charge recombinations in a fluorescent polymer yield excitons when traveling holes and traveling electrons meet (Figure 3). The recombinations of electrons and holes are random in mutiplicities. Statistically, only one fourth of the excitons are singlet excitons which are responsible for the EL. The maximum quantum efficiency of the EL would thus be about one-fourth of the PL. As mentioned earlier, the positions of the charges recombinations depend on the mobilities of the carriers. The charge recombinations are useful only when they occur in the polymer film and the emitted light will have a greater chance to be observed if the recombinations occur closer to the transparent electrode.

Light emission in EL is derived mainly from radiative decay of singlet excitons, as in PL, after the charge recombinations. The theory on structure-fluorescence dependence has not been conclusive and is still a topic of great debate.[28] However a few mechanisms[8a] responsible for non-radiative decay are well-known in organic solids. Intersystem crossing from singlet to triplet, exciton-exciton fusion at high excitation densities, and exciton migration to quenching sites are all mechanisms which affect the photoluminescent quantum yield of PPV. The last mechanism, exciton migration, accouts for the lower quantum yields of longer conjugated PPVs compared to the shorter ones.[29] The PL quantum yields of PPV and its derivatives are 5-25% while the PL quantum yields of the corresponding dimers, stilbenes, are 90-100%. An improvement of EL quantum efficiency was also observed when PPV was replaced by a partial conjugated PPV.[22d]

The EL quantum efficiency (η_ϕ) can be described in terms of the double charge injection factor (γ), efficiency of production of a singlet excitation from a hole-electron pair (η_r), and the quantum efficiency of fluorescence (ϕ_f), as shown in the equation below:[2a]

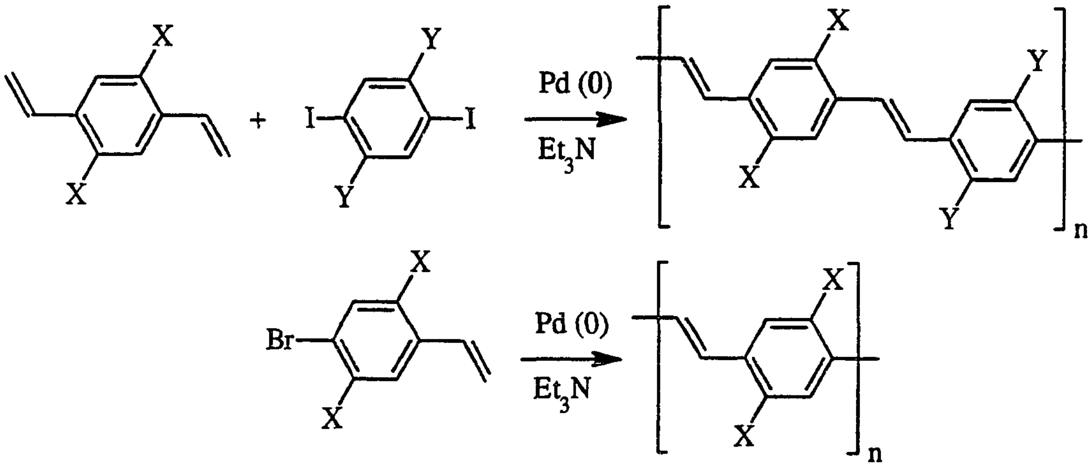
$$\eta_\phi = \gamma\, \eta_r\, \phi_f$$

This equation indicates that the high quantum efficiency requires efficient injections of both carriers as well as hole-electron recombination leading to a singlet exciton, and high fluorescence quantum yield.

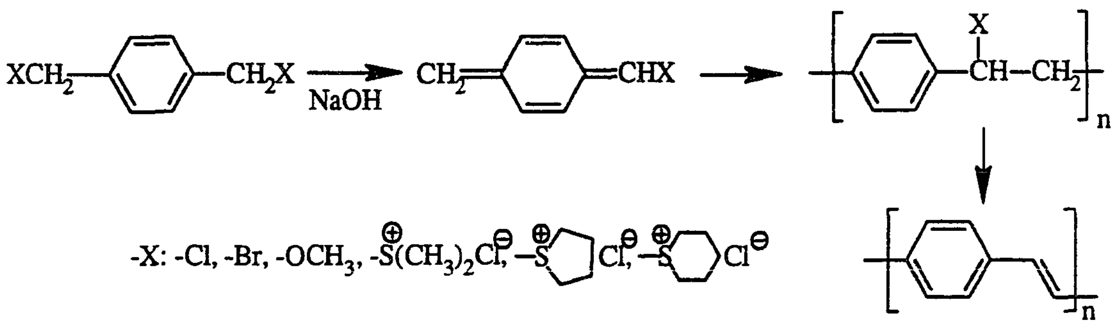
Environmental stability of the polymers is another consideration in developing a new polymer-based LED. There are two recognized sources, from electron injecting metal and emissive polymer layer, responsible for instability of the polymer-based LEDs. A good electron injector such as Ca is usually not stable to O_2 oxidation. Using a more stable metal is one solution but this also poses other problems such as lower EL quantum efficiency and a higher threshold voltages. The higher threshold voltages can cause damage to the polymer layer through electrochemical reactions and local heat. The design and synthesis of new electrochemically stable polymers which have an ionization energy and electron affinity matching the work functions of the electrodes are thus extremely important.

The synthesis of PPV and related stilbenoid compounds were recently reviewed.[9,30] Therefore, only a list of polymerization reactions and references of recent syntheses are given below.

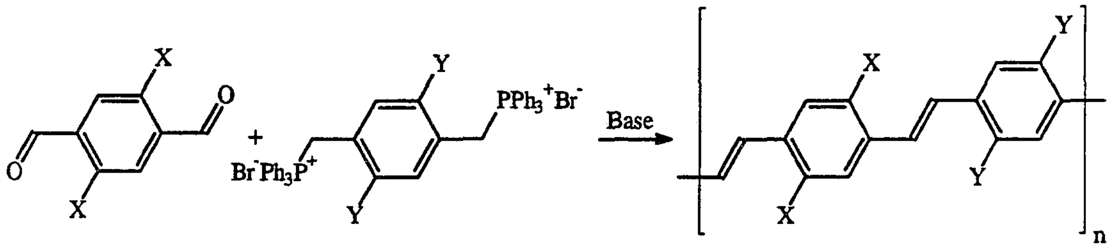
Heck reaction polymerization:[31]



Precursor Route (Wessling Reaction):[22d,32]



Wittig reaction polymerization:[33a,b]



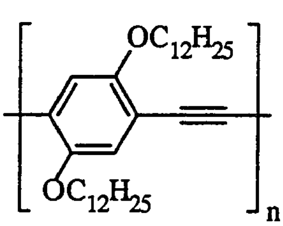
McMurry reaction and ring-opening metathesis polymerizations were also reported for the synthesis of PPV and its derivatives.[33c]

Polyphenyleneethynylene

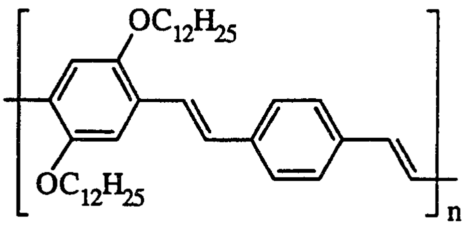
PPE and PPV are very similiar in their structures with the only difference being that PPE has a triple bond, while PPV has a double bond, as a bridge between two phenylene rings. Both polymers also possess many similar properties but with different merits. Studies of the PPE system started over a decade after the PPV system. Studies of PPE systems have developed slowly due to synthetic inaccessibility of processable PPE polymers.

The syntheses of PPE and its derivatives were recently reviewed[9,34] and will not be discussed here. This section will focus on the opto-electronic properties of the conjugated phenyleneethynylene (PE) system with some comparisons with the phenylenevinylene (PV) system. The progress in recent applications and chemistry in the conjugated PE system will also be surveyed.

Electron delocalizations through a triple bond in PE and a double bond in PV were compared theoretically and experimentally. Some evidence indicates that the double bond allows better electron delocalization than the triple bond. The direct observation is that the wavelengths of electronic absorption maxima (λ_{max}) of the PE compounds are shorter than that of the PV analogues.

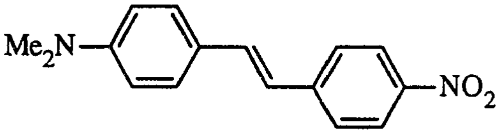


λ_{max}(THF) = 425 nm[34]

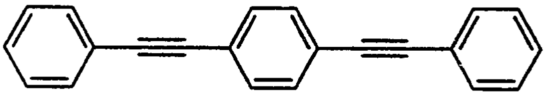


$\lambda_{max}(CHCl_3)$ = 459 nm[31b]

$\lambda_{max}(CHCl_3)$ = 415 nm[35]

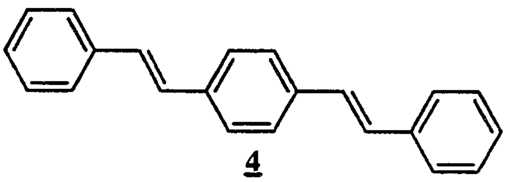


$\lambda_{max}(CHCl_3)$ = 430 nm[35]



3

$\lambda_{max}(CHCl_3)$ = 322 nm[36a]



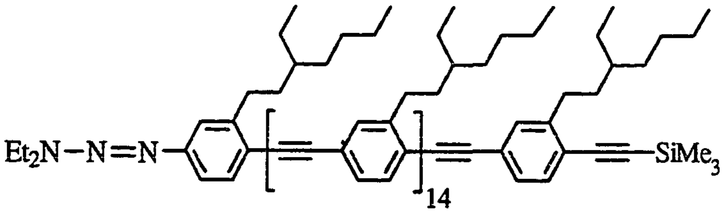
4

$\lambda_{max}(CHCl_3)$ = 356 nm[36b]

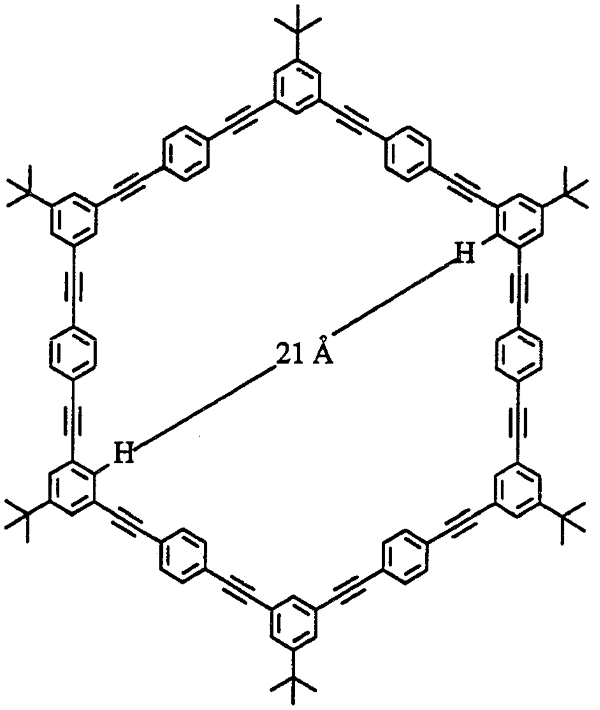
Indirect observations, such as the first hyperpolarizabilities (β), were also reported. The β values of PE derivatives are lower than those of the analogous PV derivatives,[35] indicating the lower molecular polarizabilities of the PE system.

Photoluminescent properties of PE derivatives and PV derivatives were studied.[36] The reported quantum yields of many of the PE derivatives are comparable to those of the PV analogues. The quantum yield of alkoxy PPE in toluene[37] was reported to be as high as 50%, which is about two times higher than that of PPV. Despite being highly fluorescent, studies of electroluminescence of the PPE system have not yet shown satisfactory results[9] compared to the PPV system.

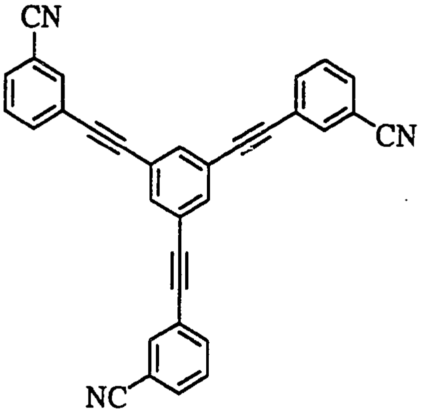
PPE and its derivatives are interesting due mainly to its unique rod-like structure. By taking advantage of the rod-like structure of PPE, Swager[38] was able to unambiguously demonstrate an increase in sensitivity of fluorescent chemosensors based on energy migration. The rod-like structure of PE-based molecules allows predictable geometries which are important for molecular architecture in supramolecular chemistry and nanomolecular chemistry.[39] The PE units have been utilized as building blocks for the construction of defined length molecular wires,[40] precise size macrocylics,[41] shape persistent organic lattices,[42] and defined shape dendrimers,[43] for examples:



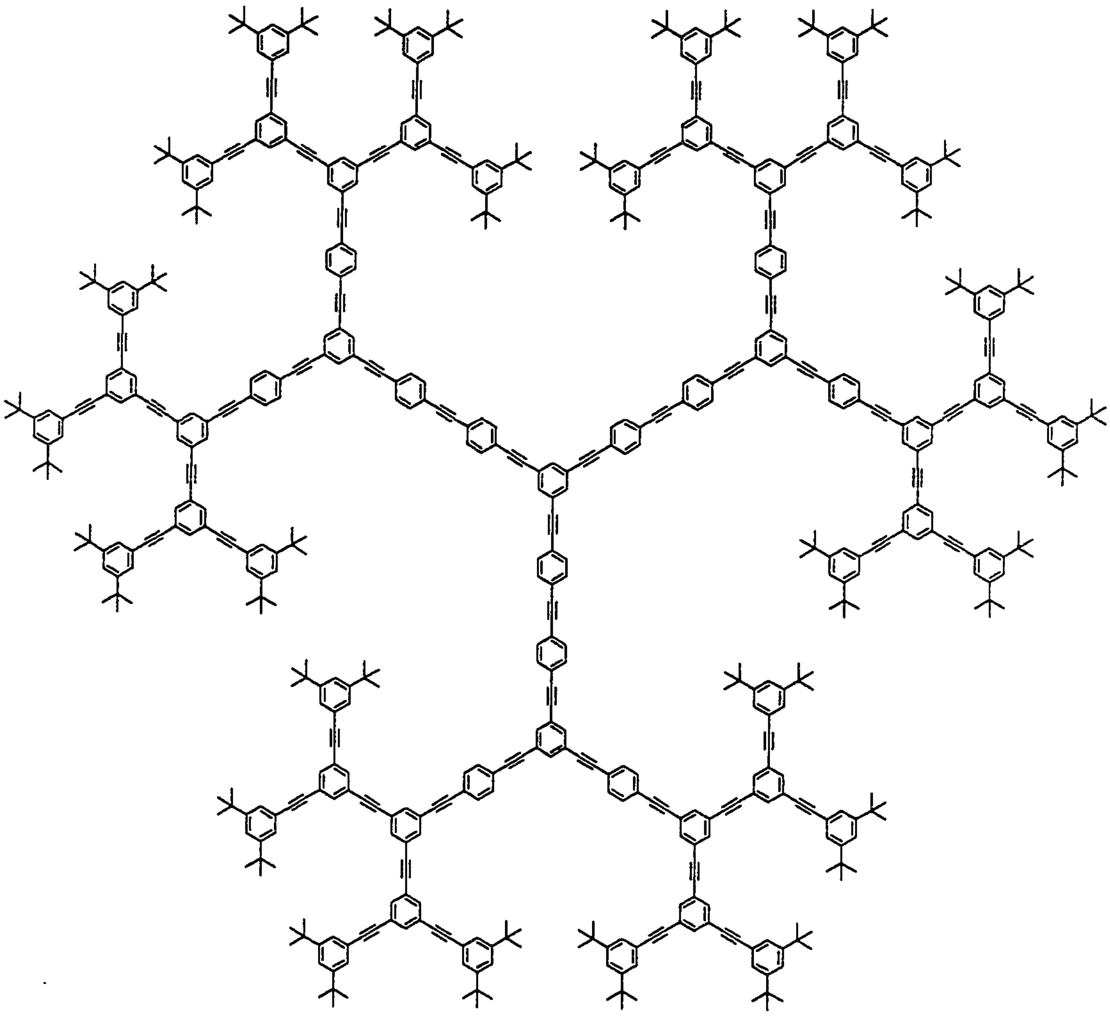
a molecular wire consisting of 16 PE units with a molecular length of 128 Å[40]



a rigid macrocycic consisting of 12 PE units with a diameter of 21 Å[41]



a molecule which can from a shape persistent, zeolite-like, lattice[42]



a dendrimer consisting of 58 PE units with a diameter of 85 Å[43]

RESULTS AND DISCUSSION

Linear conjugated polymers containing diphenylamines

Incorporating of diphenylamine units into a conjugated polymer chain forms N-interrupted conjugated polymers consisting of all three types of conjugated segments, hetero atom, aromatic, and non-aromatic segments. Rapresentation and examples of N-interrupted conjugated polymers are shown in Figure 4.This class of polymers may possess the combined properties of types I, II, III and IV (see Figure 1) and/or other interesting properties.

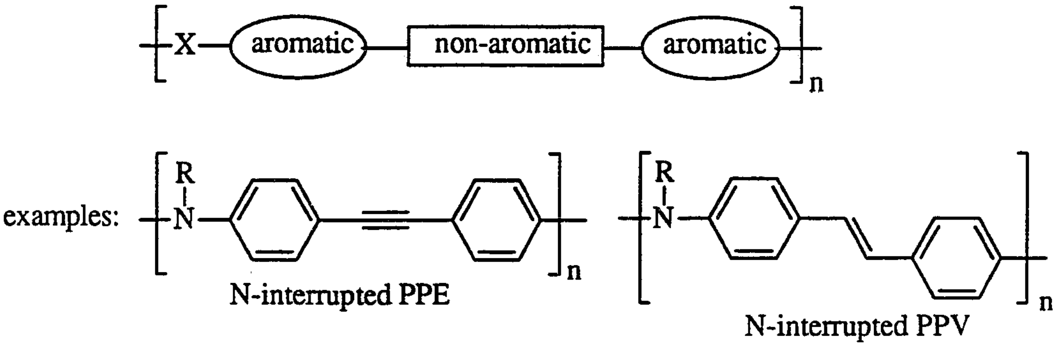
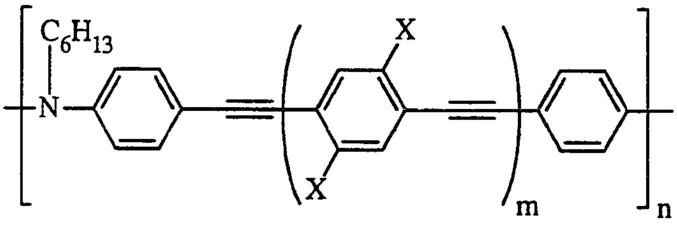


Figure 4 Representation and examples of N-interrupted conjugated polymers.

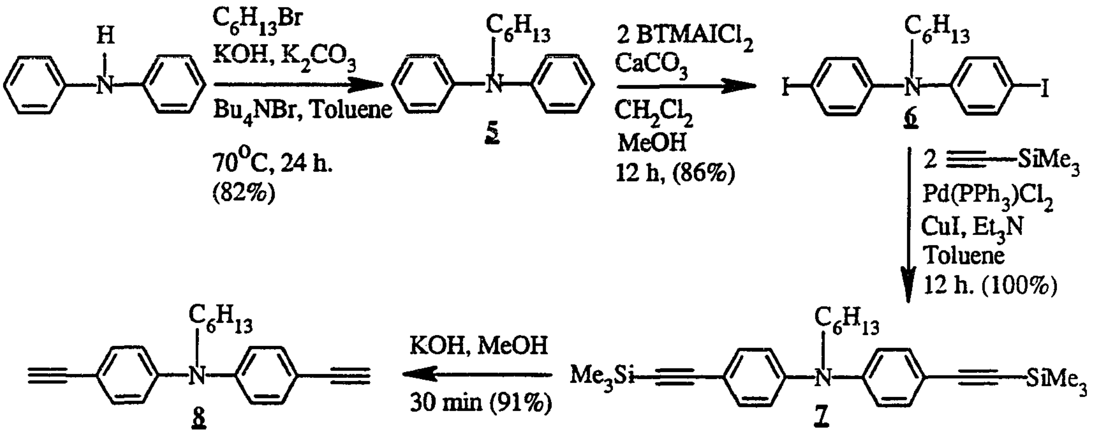
The electronic and optical properties of acetylene-based polymers is an area of considerable interest in our research group.[9,44] Thus, diphenylamine was incorporated first into PPE to give N-interrupted PPE.



Series of N-interrupted PPE

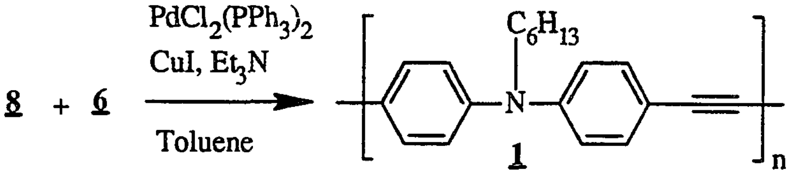
1 m = 0
2 m = 1, X = H
3 m = 1, X = OC_6H_{13}
4 m = 1, X = OC_8H_{17}

A series of N-interrupted PPEs (1, 2, 3 and 4) were synthesized. A key monomer for the synthesis of these N-interrupted PPE is 4,4'-diethynyl-N-hexyldiphenylamine, 8, which was synthesized in four steps from diphenylamine (Scheme 5). Phase transfer N-alkylation[45] of diphenylamine with bromohexane yielded N-hexylamine, 5 in 82% yield. Double iodination[46]



Scheme 5

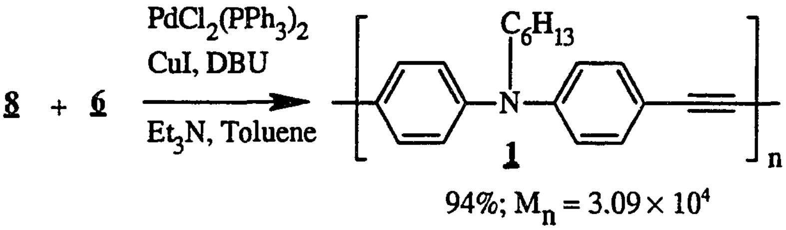
of 6 with a mild iodinating reagent, benzyltrimethylammonium chloroiodate ($BTMAICl_2$), gave diiodo compound 6 in 86% yield. Pd-coupling[47] (100% yield) of 7 with two equivalents of trimethylsilylacetylene followed by deprotection (91% yield) of the trimethylsilyl group afforded the desired monomer 8. In our early attempts to synthesize polymer 1, a typical Pd-coupling condition[9, 34a] was utilized to polymerize monomer 8 with monomer 6 (Scheme 6).



80-85%; $M_n = 3 \times 10^3 - 6 \times 10^3$

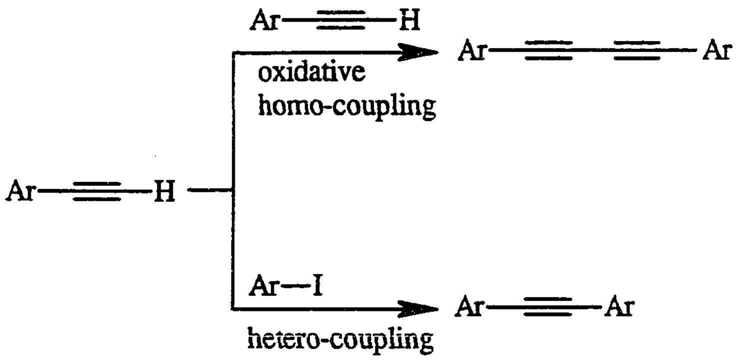
Scheme 6

The polymerizations used 4% mole equivalents of $PdCl_2(PPh_3)_2$ as a catalyst, 8% mole equivalents of CuI as a co-catalyst (Sonogashira's catalyst system),[47a] and triethylamine as a base and co-solvent, in toluene at room temperature or slightly elevated temperature (40-50°C). After 24 h, polymer 1 was obtained in high yield (80-85%). The polymer however possessed low molecular weight ($M_n \approx 6.0 \times 10^3$, GPC against standard polystyrene), corresponding to a degree of polymerization (DP) of 21. Neither the addition of more catalysts during polymerization nor extending the reaction period improved the molecular weight. Raising the reaction temperature above 50°C caused crosslinking resulting in low yields of the soluble polymer. However, with an addition of two equivalents of a stronger base, 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU), the polymerization (Scheme 7) appeared to proceed faster. Polymer 1 was obtained as a pale yellow fibrous solid in excellent yield (94%). The molecular weight was about five times higher (3.09×10^4, DP = 111) than when the polymerization was conducted in an absence of DBU.



Scheme 7

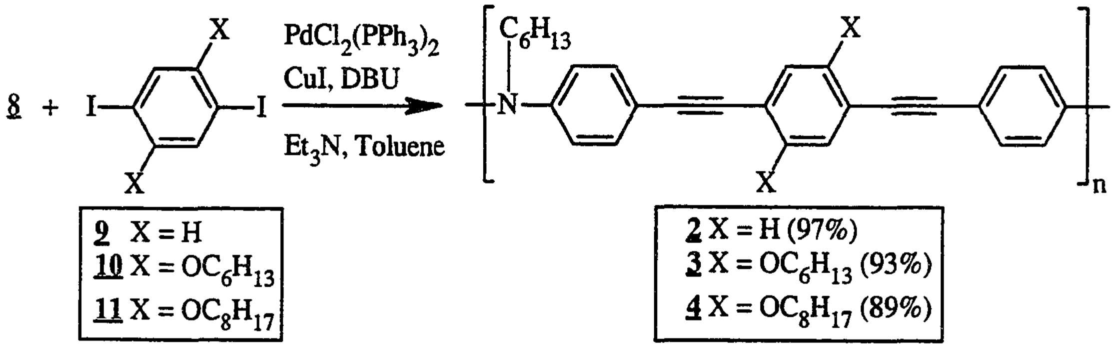
It is known that electron-rich aromatic halides are not very reactive toward the Pd-coupling reaction.[47b] Oxidative homo-coupling of two terminal acetylenes was reported to be competitive with Pd-coupling of halides and acetylenes (Scheme 8).[9, 43a,b] A stronger base such as DBU presumably increases the rate of the hetero-coupling reaction between 8 and 6.



Scheme 8

This faster coupling results in the reduction of the homo-coupling, which leads to an improper stoichiometric ratio of the acetylene and iodide and thus a low molecular weight polymer.

Polymers 2, 3 and 4 (bright-yellow, fibrous solids) were obtained from the polymerization of diethynyl monomer 8 with diiodo compounds 9, 10 and 11 respectively (Scheme 9). The polymerizations proceeded extremely well in the presence of two equivalents of DBU as indicated by the yields (89-97%) and number average molecular weights (> 1×10^4, Table 1). Polydispersities of the polymers were 1.70-3.07, which are typical for step growth polymerizations. Polymerization in the presence of DBU at a lower



Scheme 9

Table 1 Number average molecular weight (M_n), degree of polymerization (DP), weight average molecular weight (M_w), polydispersity (PD), and intrinsic viscosity (IV) of polymers **1**, **2**, **3** and **4**.

Polymer	M_n	DP	M_w	PD = M_w/M_n	IV (dL/g)
1	3.09×10^4	111	5.24×10^4	1.70	0.63
2	1.03×10^4	55	3.16×10^4	3.07	0.96
3	1.68×10^4	57	3.16×10^4	1.60	0.62
4	2.58×10^4	81	6.27×10^4	2.58	0.38

amounts of the catalysts (2% $PdCl_2(PPh_3)_2$/4% CuI) was also as effectivein the presence of DBU. Two equivalents of DBU could also be utilized in the absence of triethylamine in the polymerizations to give polymers with similar molecular weight.

The degree of polymerization likely was controlled by the solubilities of the polymers. Among these four polymers, polymer **2** was obtained in the lowest molecular weight because its rigid structure limited its solubility. Despite possessing the lowest molecular weight, polymer **2** had the highest intrinsic viscosity (0.96 dL/g) which again due to its rigidity. With hexoxy and octoxy chains, polymers **3** and **4** possess higher molecular weights (1.68×10^4 and 2.58×10^4) and lower intrinsic viscosities (0.68 and 0.38 dL/g). The alkoxy chains increased the flexibility of the polymer molecules as well as their solubilities. The solubilities of polymers **1**, **3** and **4** were 35-40 mg/mL in toluene and about 100 mg/mL in THF which were two to three times higher than that of polymer **2**.

Structural assignment of the polymers was achieved by ^{1}H and ^{13}C-NMR. Figure 5 shows ^{1}H-NMR spectra of polymers **1** and **2** compared to that of diethynyl monomer **8**. A singlet signal of two protons on the terminal acetylenes of monomer **8** was absent in the spectrum of the polymers, indicating that all the terminal acetylenes underwent a complete coupling reaction. A small doublet signal at 7.7 ppm belongs to the aromatic protons of the iodo monomer at the end of the polymer chains. The signal was more pronounced in polymer **2** than in polymer **1**, supporting the GPC results of their relative molecular weights. The ^{13}C-NMR spectrum of monomer **8** contained two sp-C signals at 76.2 and 83.8 ppm corresponding to the terminal acetylene carbon and the internal acetylene carbon, respectively (Figure 6). For polymer **1**, only one sp-C signal (at 88.8 ppm) was observed, corresponding to symmetrical acetylenic carbons. In polymer **2**, the two acetylene carbons were not equivalent and they are observed at 88.5 and 91.5 ppm.

Diethynyl monomer **8** was also polymerized by oxidative homo-coupling[48] to produce diacetylene polymer **12** (Scheme 10). A high yield (86%) of polymer **12** with high molecular weight (4.99×10^4) and low polydispersity (1.40) was obtained, demonstrating that electron-rich diethynyl monomers are quite suitable for oxidative coupling polymerization.

The repeating unit of polymer **12** consisted of one more rigid acetylene unit than that of polymer **1**. However, the chain rigidities of these two polymers are apparently not much different, as their solubilities and the intrinsic viscosities (0.78 dL/g for **12** and 0.63 dL/g for **1**) are quite similar, especially when the difference in the molecular weights is taken into account.

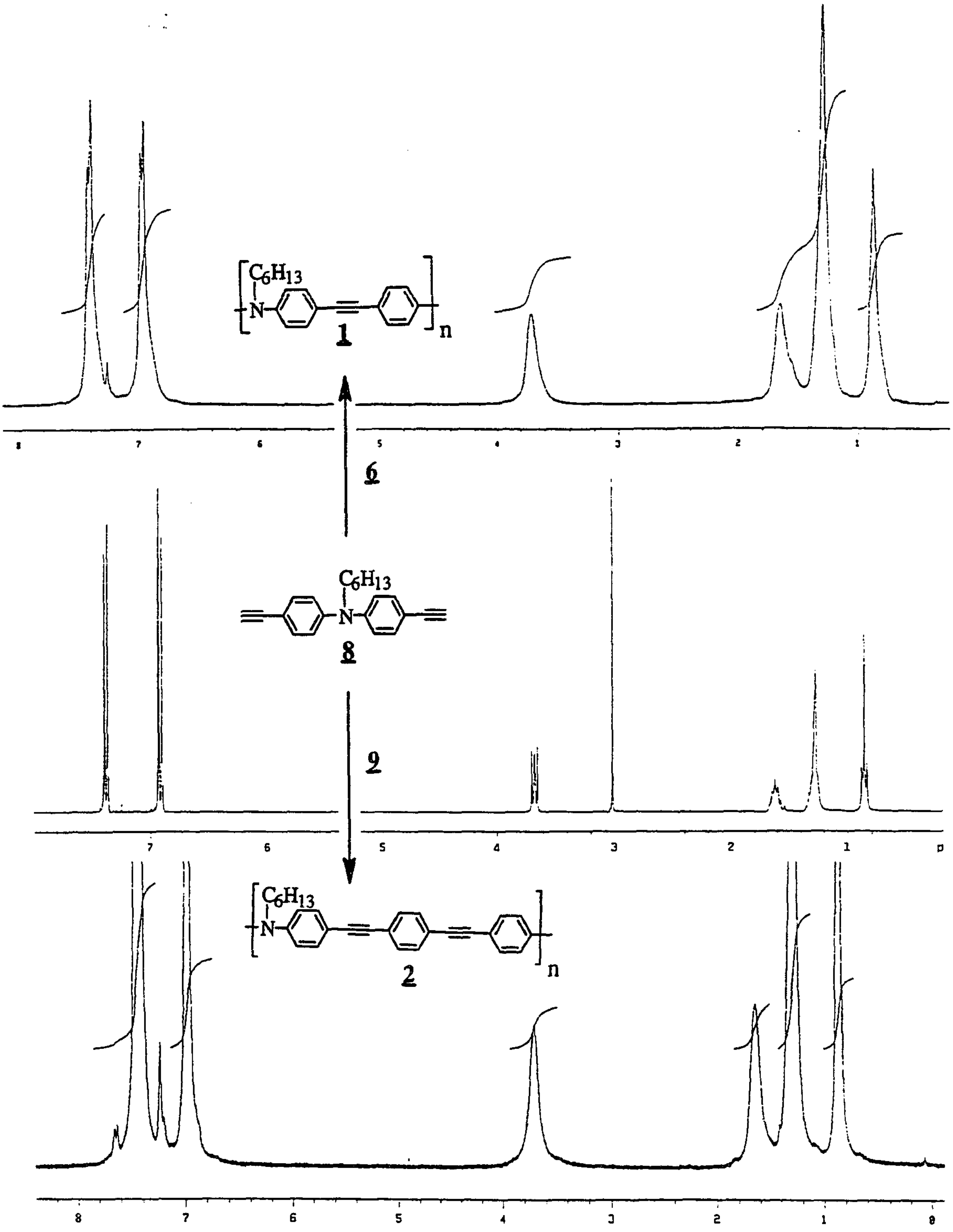


Figure 5 ^{1}H-NMR of polymer 1, polymer 2 and monomer 8 in CDCl$_3$.

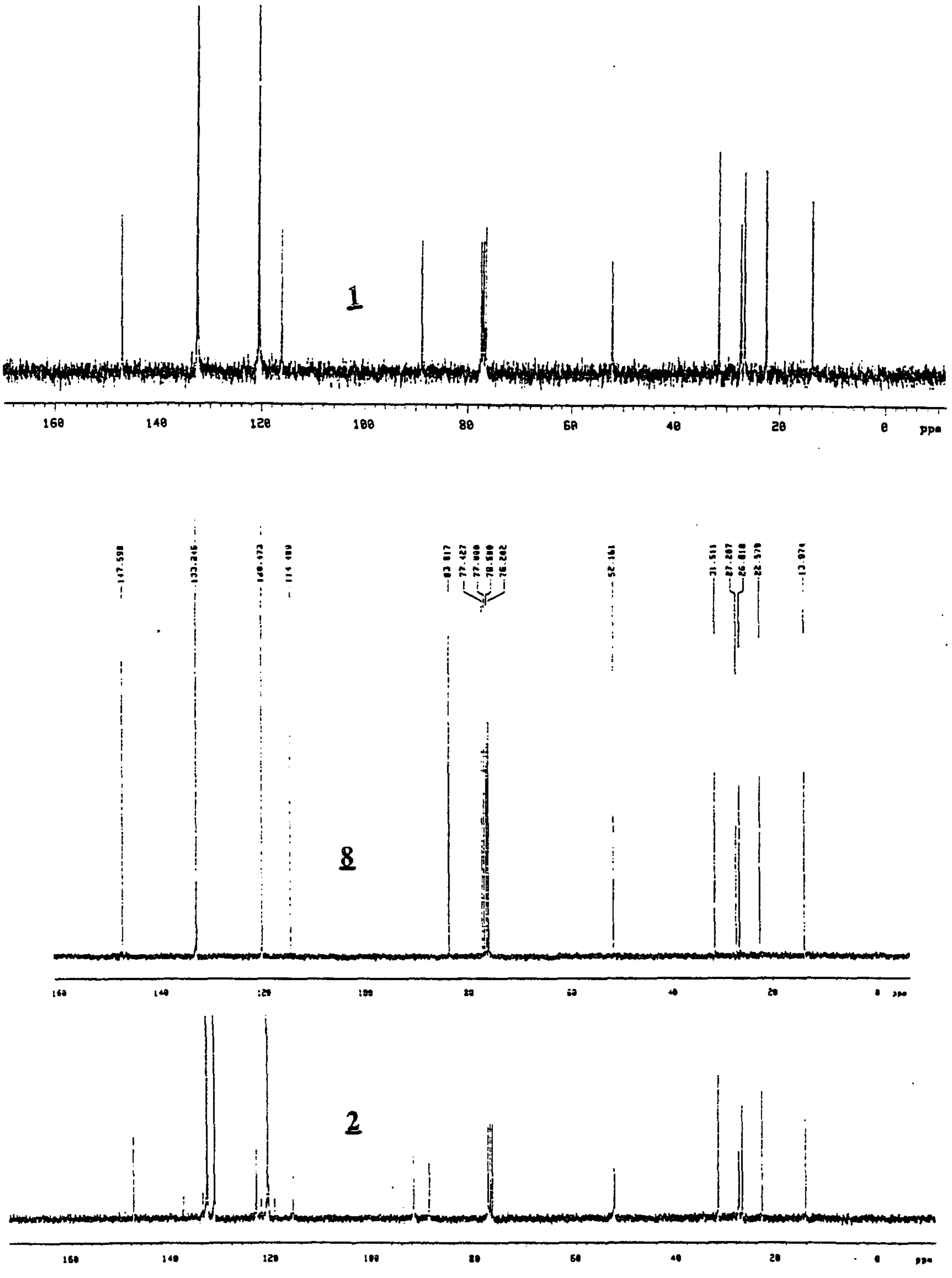
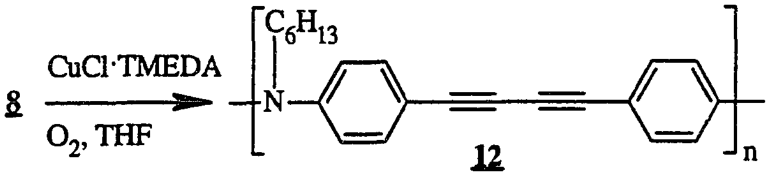


Figure 6 ^{13}C-NMR of polymer **1**, polymer **2** and monomer **8** in $CDCl_3$.



86%, $M_n = 4.99 \times 10^4$, DP = 166
PD = 1.40, IV = 0.78 dL/g

Scheme 10

The chain-ended ^1H-NMR signals of polymer 12 at 6.7 and 7.1 ppm are almost unnoticeable and no detectable chain-ended signal observed in ^{13}C-NMR (Figure 7). This confirms the high molecular weight of this polymer. The ^{13}C-NMR signals at 73.6 and 81.9 ppm correspond to sp-carbons attached to the acetylene and the phenyl ring, respectively.

Ethynylene conjugated polymers containing carbazole, a well known hole transporting molecule,[1,2] were also synthesized. The key monomer, 3,6-diethynyl-N-octylcarbazole, 16 was synthesized in four steps (total yield = 51%) from carbazole through a reaction series similar to that used in the synthesis of monomer 8 (Scheme 11). Double iodination of carbazole was however required a stronger iodinating reagent, iodinemonochloride (ICl).

The Pd-coupling polymerization of monomer 16 with diiodo monomer 14 produced a white polymer, 17, in 79% (Scheme 12). This polymerization was not as successful as the polymerization of monomer 8, previously described, indicated by the lower yields and the molecular weight distribution of this polymer. Polymer 17 has lower molecular weight (M_n = 1.19×10^4) and broader polydispersity (PD = 3.73, Table 2) than its diphenylamine analogue, polymer 1. It was first assumed that the lower molecular weight and broader polydispersity

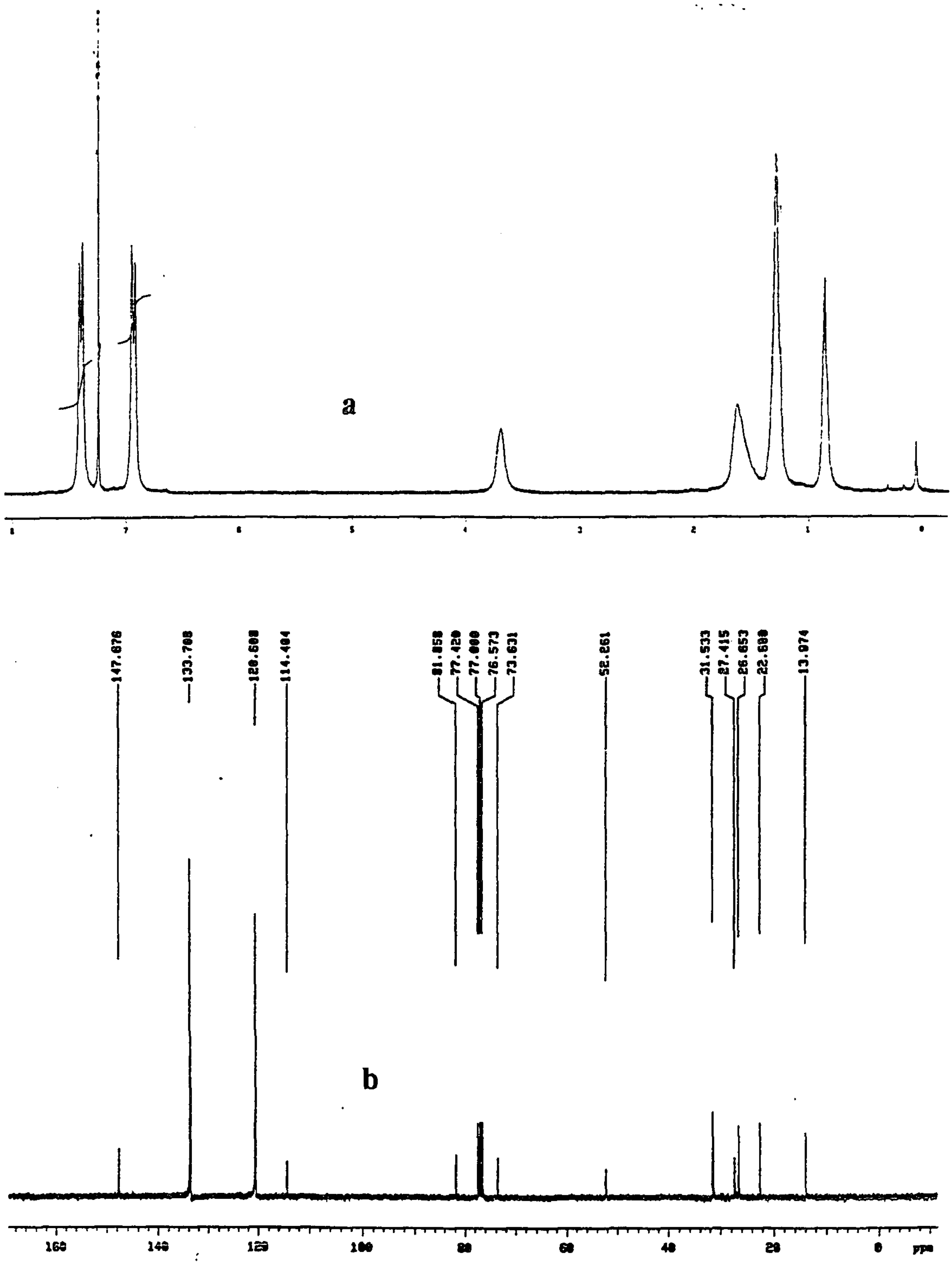
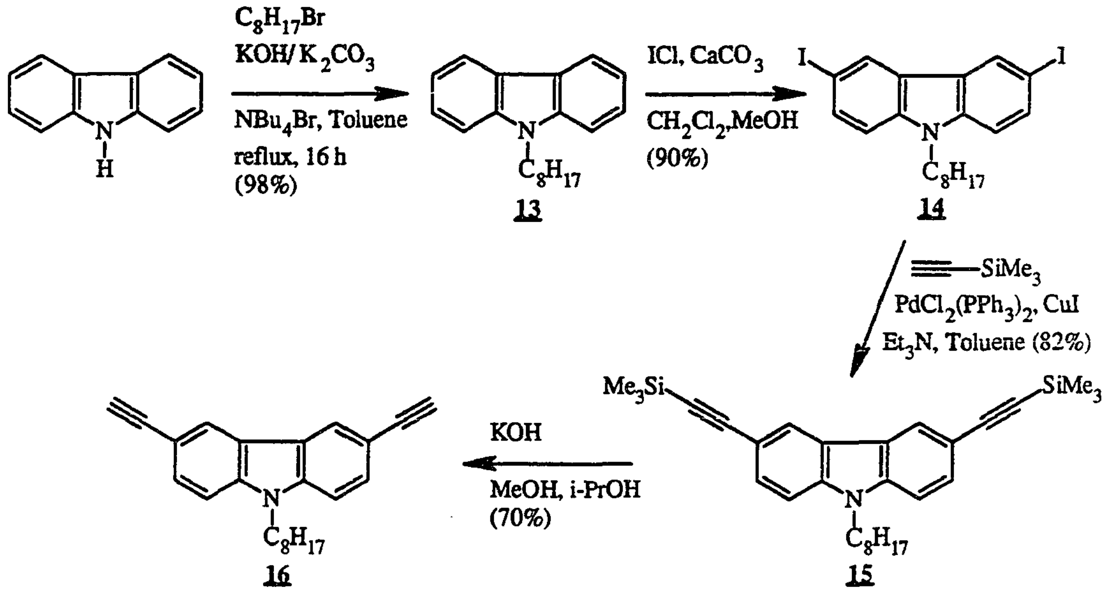


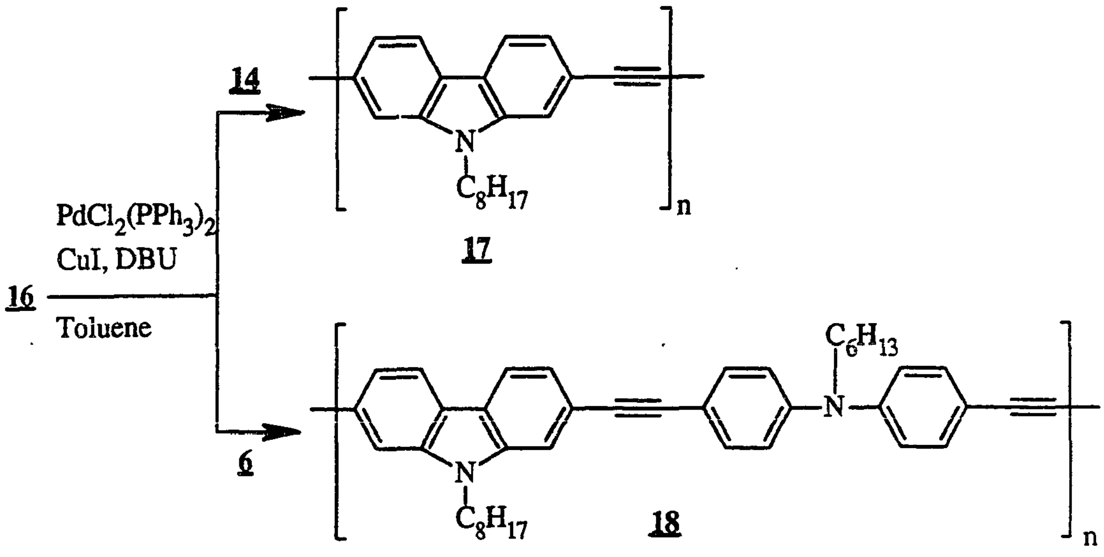
Figure 7 a) ^{1}H-NMR and b) 13C-NMR of polymer 12 in $CDCl_3$



Scheme 11

were due to the low solubility of polymer 17 (about 10 mg/ mL toluene). An attempt to increase the solubility and thus the molecular weight was done by incorporating the more flexible segment, N-hexyldiphenylamine, into the ethynylenecarbazolene chain to form copolymer 18. Even though this copolymer has higher solubility (about 20 mg/ mL toluene) than polymer 17, the polymerization did not give a notably better result, as a polymer with $M_n = 1.08 \times 10^4$ and PD = 3.41 (Table 2) was obtained in 84% yield. Due to the lower molecular weights of polymers 17 and 18, the intrinsic viscosities of these polymers (0.21 and 0.24) are also lower than that of polymer 1.

All the polymers, except for polymer 17, can be cast into flexible free-standing films unlike poly-2,5-dialkoxyphenyleneethynylenes[9] which form brittle films. The films remained flexible over two years. The films cast from toluene solutions (10 mg/ mL - 30 mg/ mL) are particularly homogeneous and transparent (Figure 8).

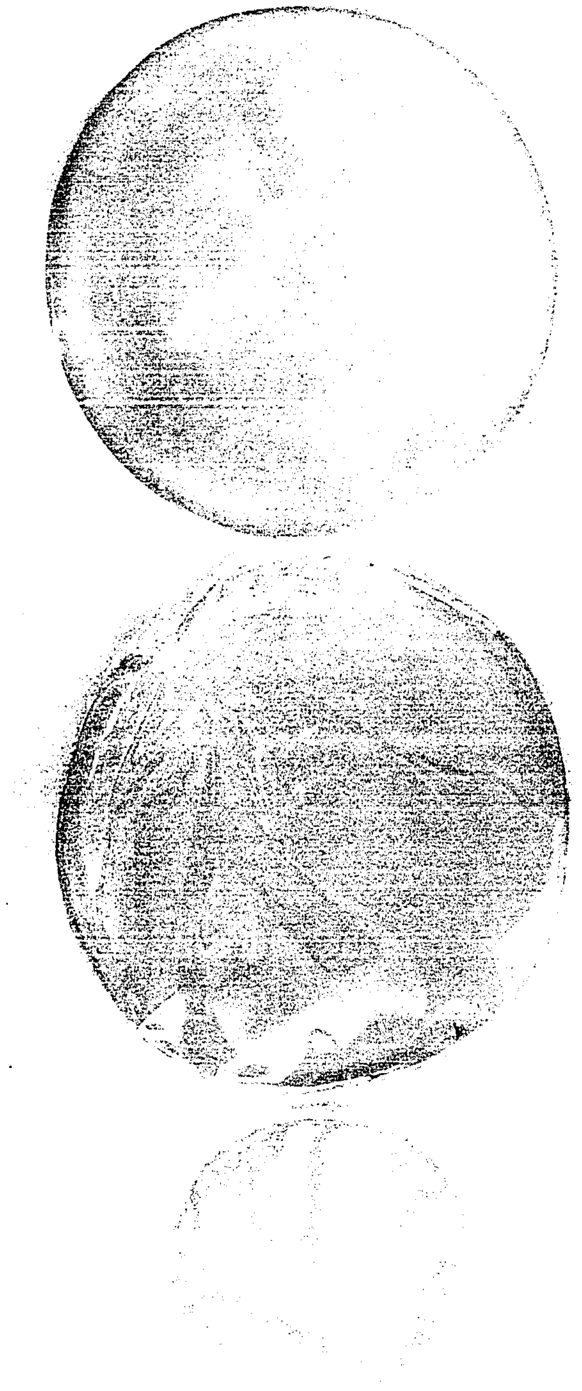


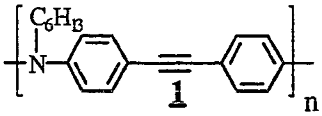
Scheme 12

Table 2 GPC results of polymers **17** and **18**.

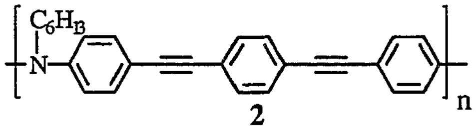
Polymer	M_n	DP	M_w	PD = M_w/M_n	IV (dL/g)
17	1.19×10^4	38	4.43×10^4	3.73	0.21
18	1.08×10^4	42	3.70×10^4	3.41	0.24

Thermal behaviors of these polymers were studied by Thermogravimetric Analysis (TGA) and Differential Scanning Calorimetric Analysis (DSC) under nitrogen atmosphere. The TGA was performed from room temperature to 1100°C with a ramp of 20°C/min. All polymers showed a single weight loss. Thermal degradation of polymers containing diphenylamine (**1**, **2**, **4**, **12**) started (5% weight loss) at temperatures over 370°C (Table 3).





1



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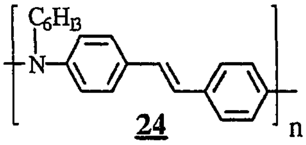


24

Figure 8 Photograph of free-standing films of polymers 1, 2 and 24 shown actual sizes.

Table 3 TGA and DSC results of N-interrupted PPEs.

	TGA		DSC
Polymer	Temperature (°C) (% remaining weight)	% remaining weight at 1100°C	Crosslinking Temperature (°C)
1	410 (94)	53	225
2	383 (96)	60	254
3	373 (96)	44	270
4	386 (96)	40	273
12	423 (96)	58	195
17	287 (96)	51	224
18	343 (95)	55	178, 231

The polymers containing carbazole were less withstanding to thermal degradation as homopolymer 17 and copolymer 18 had 4-5% weight loss at 287°C and 343°C, respectively. The DSC thermogram (Figure 9) indicated that all synthesized polymers did not melt before an exothermic reaction, likely crosslinking, ocurred. Only broad and shallow endothermic transitions were observed before the crosslinking temperature, presumably corresponding to the sidechain softening. Small endothermic peaks at 50°-75°C were possibly due to evaporations of trace solvents in polymer samples.

The electronic absorption spectra (Figure 10) of these polymers in THF were recorded. Absorption peaks (λ_{max}) were determined and absorption edges (λ_e) were estimated within ± 5 nm (Table 4). As expected, the λ_{max} and λ_e increase with an increasing conjugation

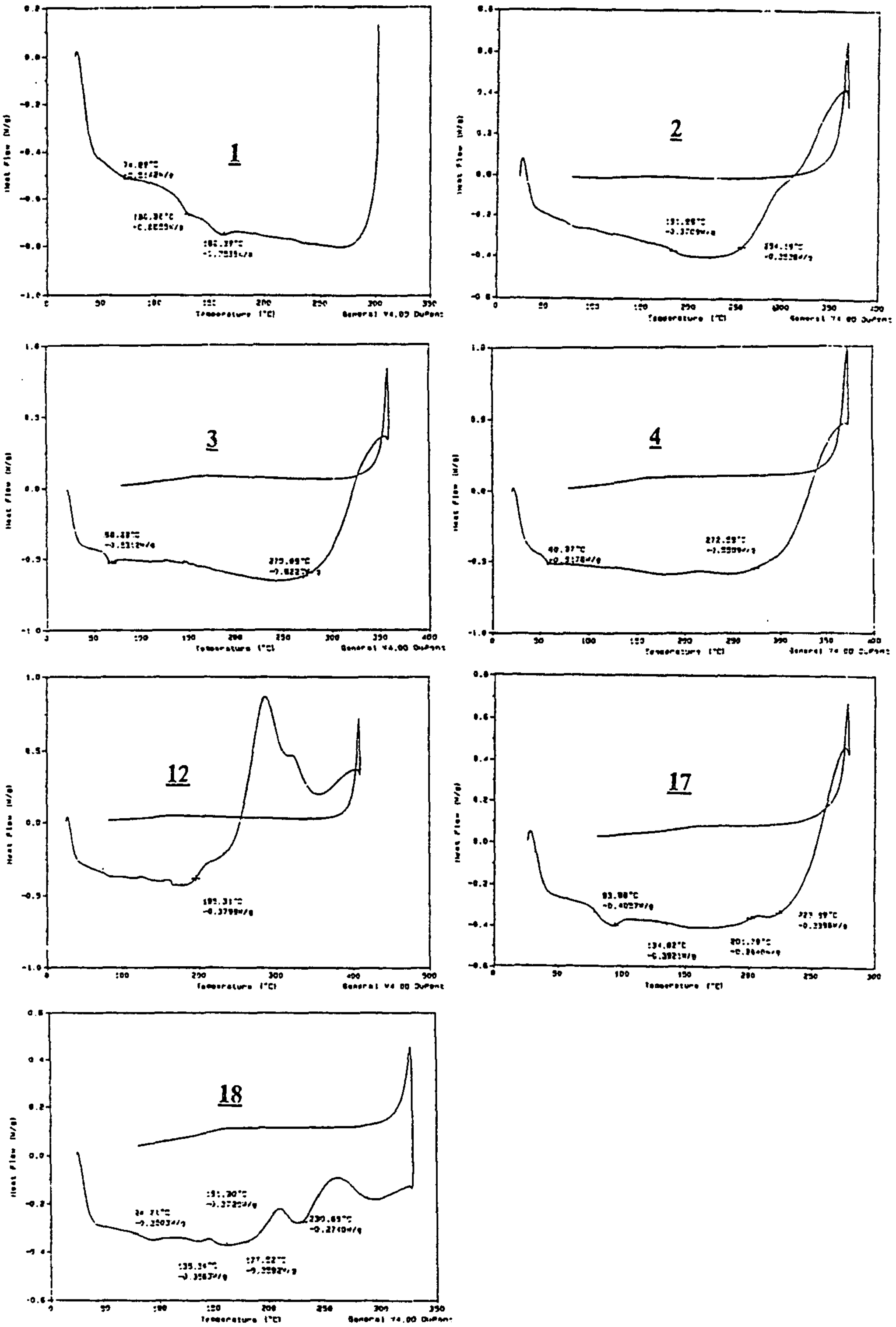


Figure 9 DSC thermograms of polymers **1**, **2**, **3**, **4**, **12**, **17** and **18**.

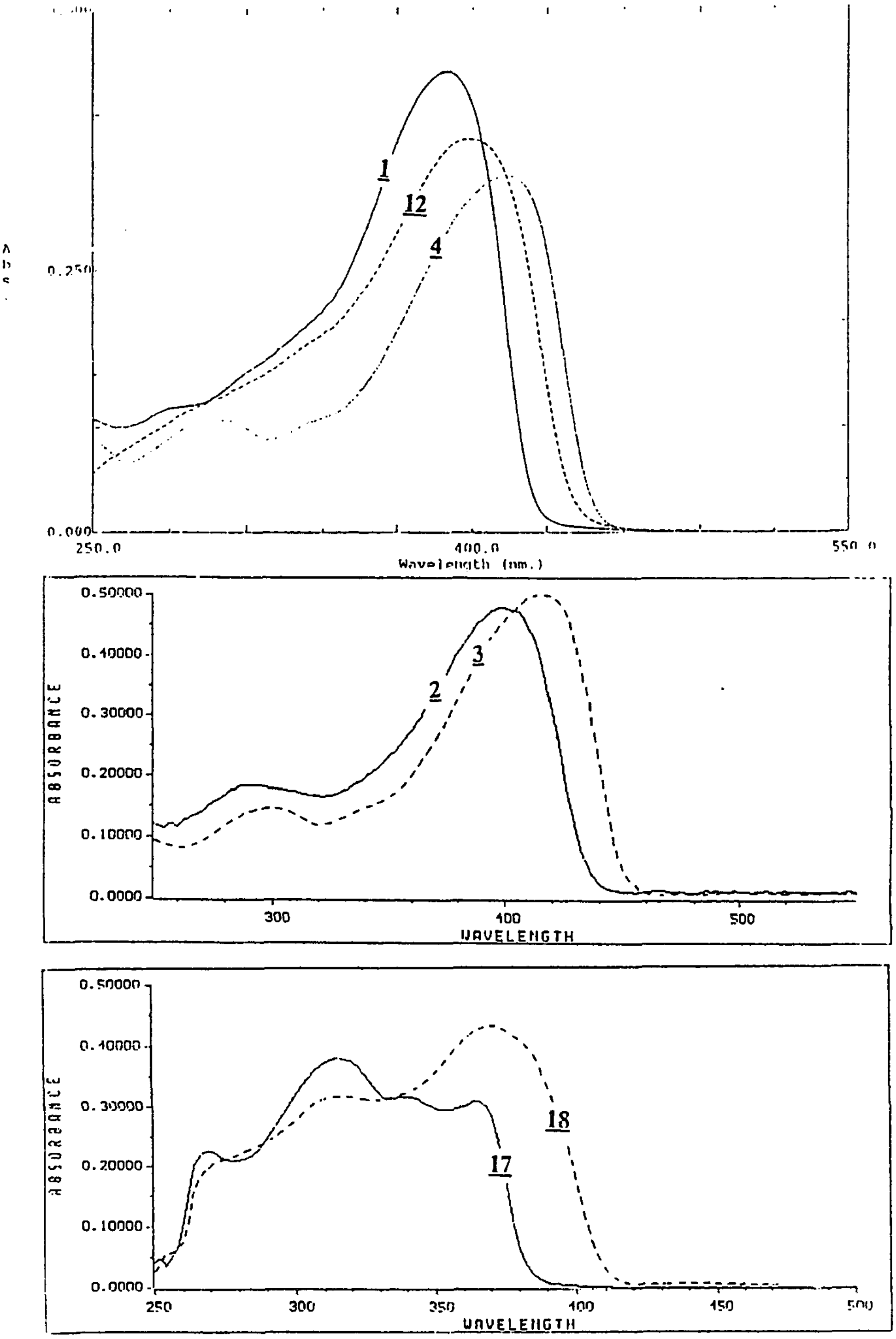


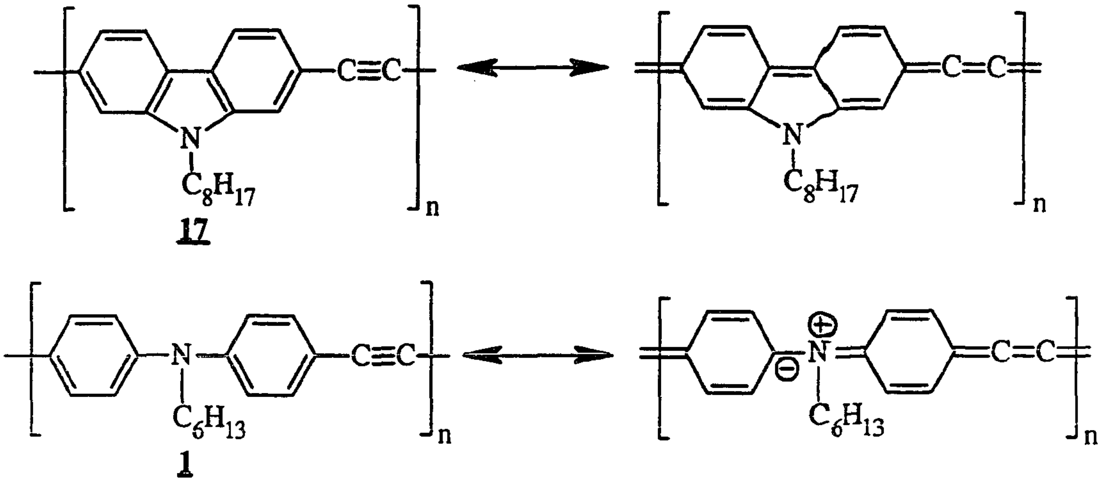
Figure 10 Electronic absorption spectra of polymers **1**, **2**, **3**, **4**, **17** and **18** in THF.

Table 4 UV-Vis absorption maxima (λ_{max}) and band edges (λ_e) of the N-interrupted polymers in THF solution and their films.

Polymer	THF solution		Film	
	λ_{max} (nm)	λ_e (nm)	λ_{max} (nm)	λ_e (nm)
1	389	430	390	450
2	292, 400	445	296, 408	465
3	300, 416	455	298, 420	475
4	302, 415	455	304, 408	475
12	399	450	417	475
17	270, 316, 366	395	250, 320, 366	405
18	270, 314, 368	415	252, 322, 372	425

(compare λ_{max} of polymer **1** with those of polymers **2**, and **12**). Electron-donating substituents, in this case alkoxy groups, also increase the λ_{max} (compare λ_{max} of polymer **2** with those of polymers **3** and **4**).

Surprisingly, polymer **17**, despite having a through conjugation and a more planar repeating unit, has a λ_{max} and λ_e shorter than that of polymer **1**. Polymer **1** is not a through conjugation and its repeating unit is not planar (Scheme 13). We have not produced a satisfactory explanation for this contrary result. The UV-Vis spectrum of copolymer **18** appears to be a spectrum of polymer **17** modified by the spectrum of **1**. The spectrum of **18** has the same three bands as that of **17** but the λ_e is about 20 nm longer (15 nm shorter than

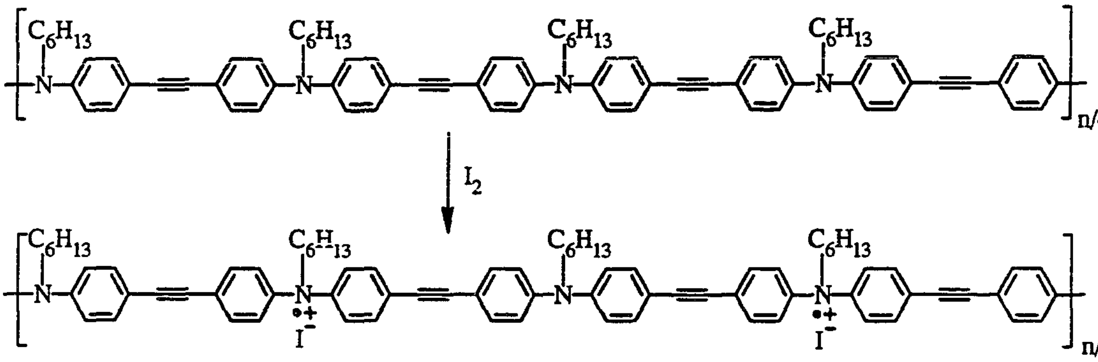


Scheme 13

that of **1**). The relative intensities of the three bands were also altered. The highest intensity band in the spectrum of **18** is 368 nm, while in the spectrum of **17** it is 316 nm. Thus, copolymers may be used to modify electronic absorption spectra.

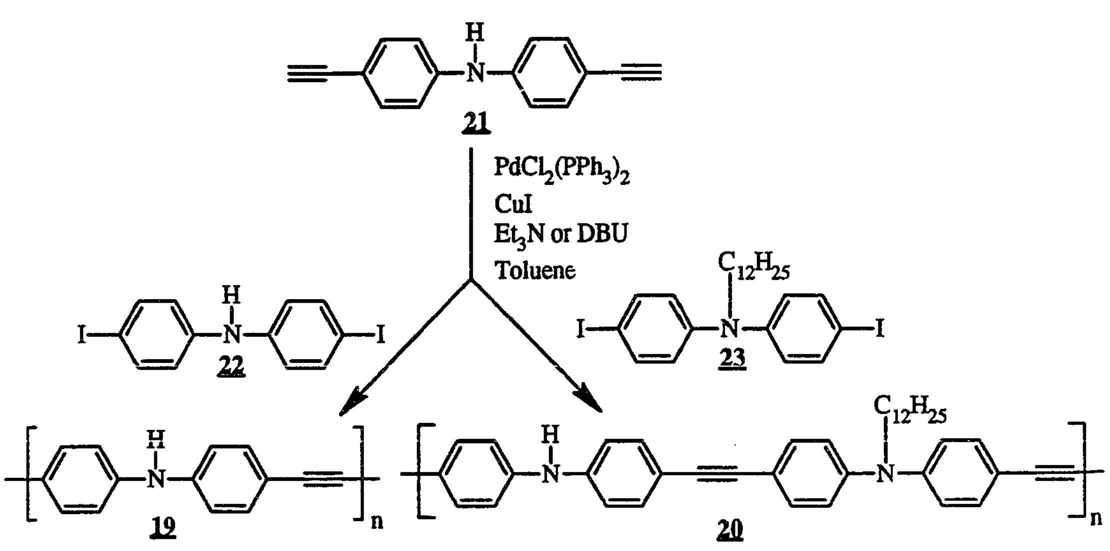
The UV-Vis absorption of films of the polymers were also measured. Except for polymer **12**, the films of polymers have the same absorption peaks (Table 4) as their solutions. The tails of absorption bands of the polymer films extended about 20 nm longer than when in solution. The same λ_{max} but with a longer tail suggests that the conformation of the conjugated segments in the polymer chains in the film state are mostly the same when in solution. A film of polymer **12** gave a λ_{max} which was 18 nm longer than when in solution, which was previously observed in PPE.[9, 34b] This implies that the conformation in the film state allows better conjugation.

The structures of N-interrupted polymers are similar to the leucoemeraldine form of polyaniline (see introduction section). Electrical conductivities of the polymers measured by two in-line probes were lower than the equipment threshold (≤ 10^{-9} S cm^{-1}). Oxidation of these N-interrupted polymers by iodine should yield a polymer with a similar structure as the conductive form of polyaniline, emeraldine salts (for example: Scheme 14). However, when the polymers were doped by iodine vapor, only polymer **1** showed any conductivity at all, and that was only a mere 10^{-7}-10^{-6} S cm^{-1}.



Scheme 14

During this conductivity study, a conductivity of the same order of magnitude was also reported for poly(N-alkylaniline)[16]. The low conductivity of N-alkylated polymers such as our N-interrupted conjugated polymers and poly(N-alkylaniline) can be inferred to be a result of steric hindrance of the alkyl groups. The alkyl chains prevent the polymer chains from being planar and shorten the conjugation lengths which are important for migrations of charge carriers. The obvious solution is to synthesize an analogue of polymer **1** without a substituent on N such as **19** (Scheme 15). Our attempts at synthesis of a non-substituted N-interrupted conjugated polymer, **19** and its copolymer **20** from Pd-coupling polymerization of corresponding monomers yielded only insoluble gels. It is possible that, during the polymerization, a minor side reaction such as Pd-catalyzed amination[49] caused a slight crossslinking. The resulting gel could not be separated from the ammonium salt formed



Scheme 15

during the polymerization. The insolubility and the presence of the salt in the polymers prevented any meaningful property studies.

All the N-interrupted conjugated polymers are photoluminescent in both solution and solid state. Excitation and emission spectra of THF solutions of polymers 1, 2, 3, 12, 17 and 18 are shown in Figure 11. The emission spectra were acquired by using the λ_{ex} 20 nm lower than the lower limits of the scanning ranges. The excitation spectra were recorded while the emissions were monitored at 20 nm (λ_{em}) higher than the upper limits of the scanning ranges. The excitation spectra are similar to absorption spectra but the excitation bands are broader. For polymers 17 and 18, only a single broad band was observed in the excitation spectra (Figure 11) while three bands were observed in the absorption spectra (Figure 10). The emissions of polymers 1, 2, 4, 12 and 18 tailed beyond 600 nm with peaks at 400-450 nm corresponding to blue to green light. Polymer 17 however tails only to 500 nm with the emission peak at 380-400 nm and the observed emission is blue. Emission spectra of polymer

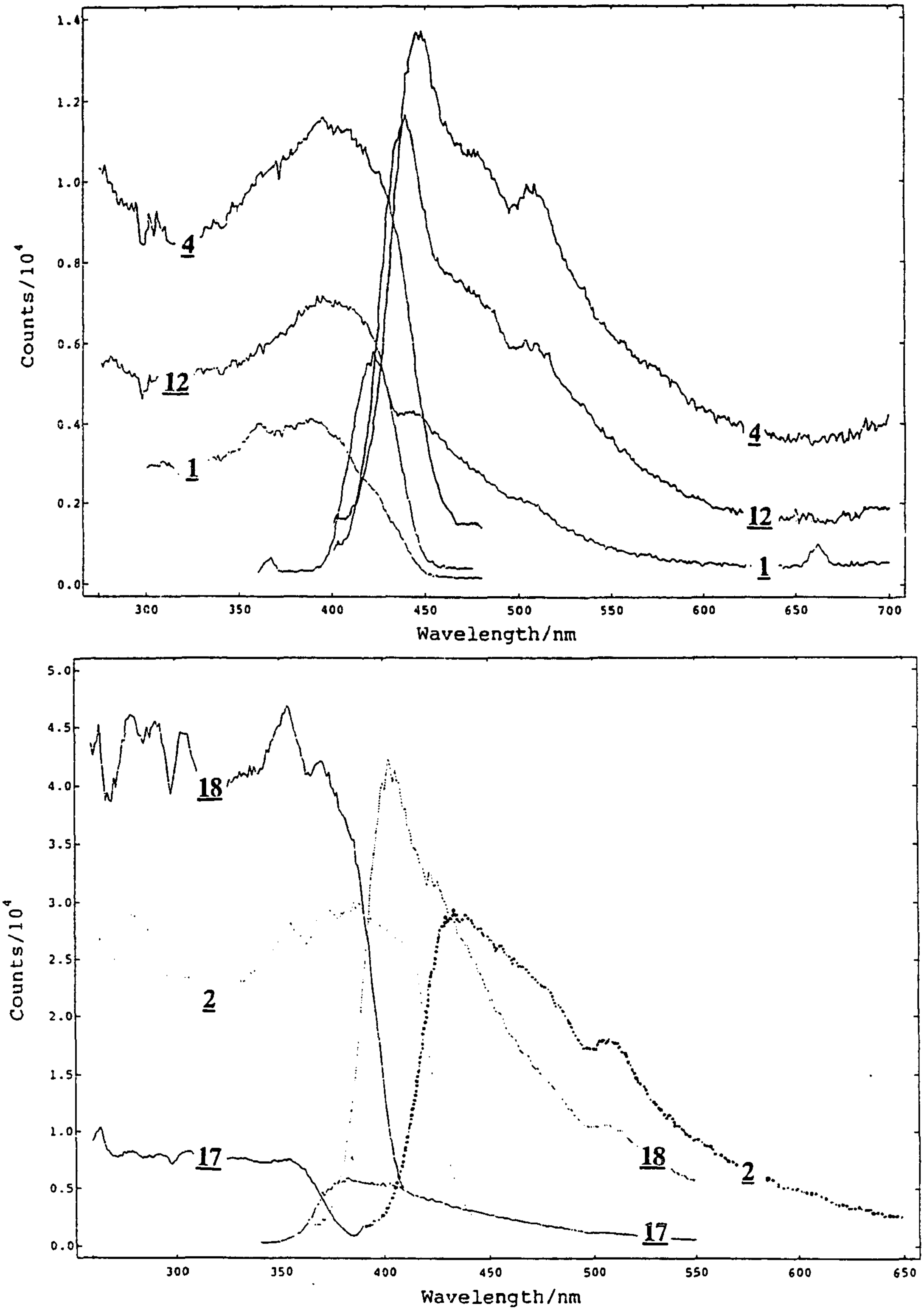


Figure 11 Emission and Excitation spectra of polymers **1**, **2**, **4**, **12**, **17** and **18** in THF

films of **1**, **4** and **12** on quartz substrates were also recorded (Figure 12). The spectra tail over 600 nm with the bands in the same range as the solution spectra. Even the peaks in film spectra seem to be broader than the solution spectra, the film spectra showed more defined electrovibronic coupling structures due to the fixed conformation in the solid state. Only the film spectrum of polymer **4** is sufficiently resolved for an estimation of the vibration frequency. The estimated vibrational frequency of ≈ 2000 cm^{-1} corresponds to the stretching of the triple bond (2200 cm^{-1}).

The electroluminescent property of polymers **4** and **17** were studied by Dr. Shinar's group using single layer light emitting diodes (LED) with ITO hole injector and Al electron injector. The devices from polymer **3** emitted yellow green light while the devices from

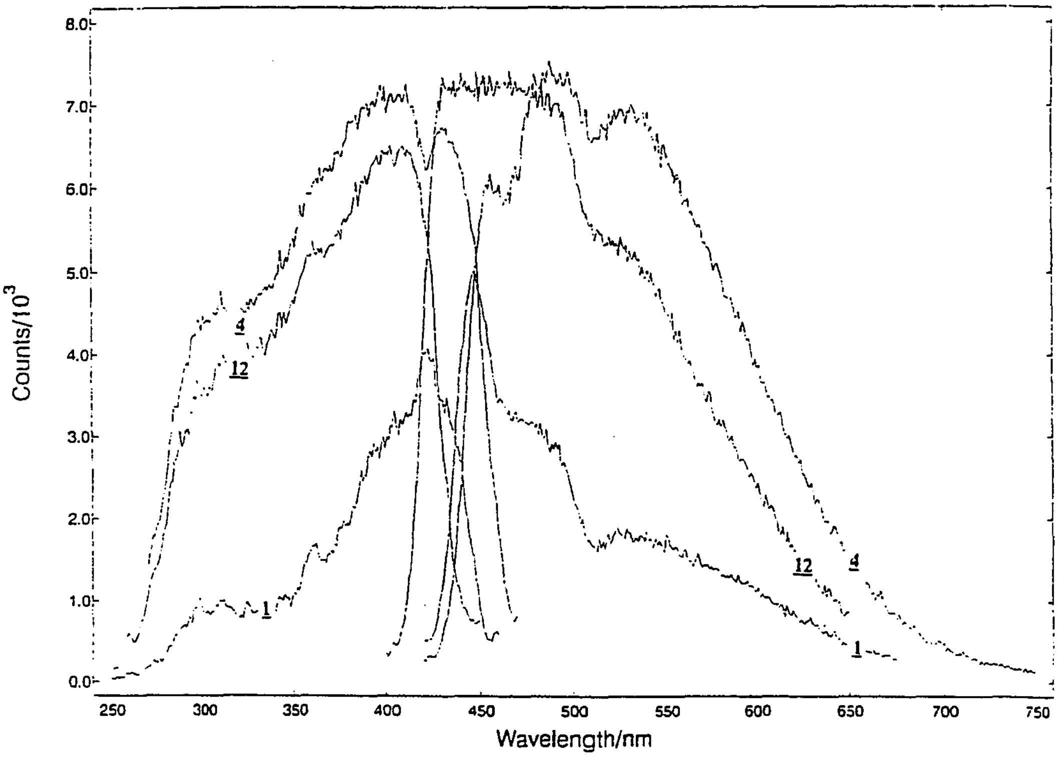


Figure 12 Emission spectra of polymer films of **1**, **4** and **12**.

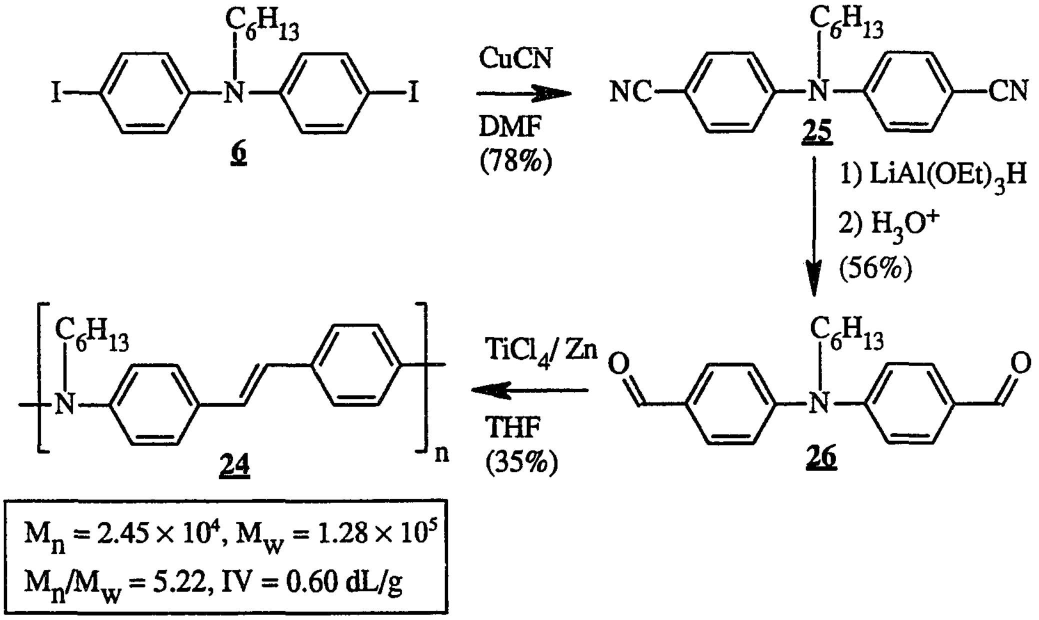
polymer **17** emitted blue light. The efficiencies of these single layer devices were quite low and the driving voltage was relatively high (≥ 20 V). These may due to an inefficient electron injection and imbalanced charge transportation.

Ionization energy of electron donors can be estimated from a UV-Vis spectrum of electron donor-acceptor (EDA) complex with I_2 according to a linear relationship between charge transfer energy ($h\nu_{CT}$) and ionization energy (I^D):[50]

$$h\nu_{CT} = aI^D + b$$

McConnell[51] reported the coefficients $a = 0.67$ and $b = -1.9$ but Mulliken[52] reported another set of these coefficients where $a = 0.87$ and $b = -3.6$. The EDA complex of polymer **3** with I_2 has a charge transfer band at 660 nm (1.87 eV) which gives ionization energy of 4.7 eV and 5.8 eV from McConnell's coefficients and Mulliken's coefficients respectively. This ionization energy well matches with the hole injector ITO workfunctions ($\Phi_{ITO} \approx 4.8$ eV).[8] Electron affinity (E_A) of the polymers can be calculated from the subtraction of ionization energy with band edge energy. Polymer **3** has the band edge at 475 nm (2.6 eV) and the E_A in the range of 2.1 eV to 3.2 eV. This E_a is a little too low compared to the workfunction of Al ($\Phi_{Al} \approx 4.2$ eV).[8] It is also reasonable to assume that the holes travel through the polymer films faster than the electrons because the polymers contain hole transporting moieties, diphenylamine and carbazole, throughout the chain. However, this may not be conclusive as UV-excited optically detected magnetic resonance (ODMR) studies, by Dr. Shinar's group, of polymers **1**, **4** and **12** suggesting structural defects of the polymer chains in the film state.[53] The structural defect may reduce charge recombinations and stabilize triplet excitons resulting in poor electroluminescent quantum efficiencies. Further investigation such as studies of

Electrical conductivity of I_2 doped PPE ($\sigma \approx 10^{-5}$ S cm^{-1})[54] is about seven orders of magnitude lower than that of I_2 doped PPV ($\sigma \approx 10^{2}$ S cm^{-1}).[55] It is thus interesting to see whether this difference exists between N-interrupted polyphenylenevinylene, 24, and N-interrupted PPE, 1. Polymer 24 was synthesized according to scheme 16.



$M_n = 2.45 \times 10^4$, $M_w = 1.28 \times 10^5$
$M_n/M_w = 5.22$, IV = 0.60 dL/g

Scheme 16

The key monomer, a dialdehyde 26, was obtained in 56% from a reduction of dicyano 25 with triethoxylithiumaluminiumhydride.[56] The dicyano compound 25 was synthesized in 78% from a double cyanylation of diiodo compound 6 (see Sheme 5 for the synthesis of this compound) with CuCN.[57] A reductive McMurry coupling polymerization[58] of monomer 26 yielded the desired polymer as a bright yellow solid in 35%. The polymer was first purified by precipitation of methylene chloride solution of the polymer in methanol. The obtained chloride solution by methanol. The obtained polymer has a distinct bimodal molecular weight distribution. The lower molecular weight portion (< 10^{4}) can be largely removed by precipitation of the polymer solution in acetone (Figure 13). The polymer obtained from precipitation (twice in acetone) had M_n of 2.45×10^4 (DP = 87) with a broad polydispersity, 5.21. The intrinsic viscosity of this polymer was 0.60 dL/g. This polymer had poorer solubility in organic solvents than its ethynylene analogue, polymer 1. A solution of polymer 24 in common organic solvents such as chloroform and THF became colloidal when the concentration was over 10 mg/mL. The structural assignment of the polymer was achieved by ^{1}H- and ^{13}C-NMR. The ^{1}H-NMR spectrum (Figure 14) of 24 was fairly clean and fit well with the expected structure with no significant signal of the polymer chain-ended, which implying its high molecular weight.

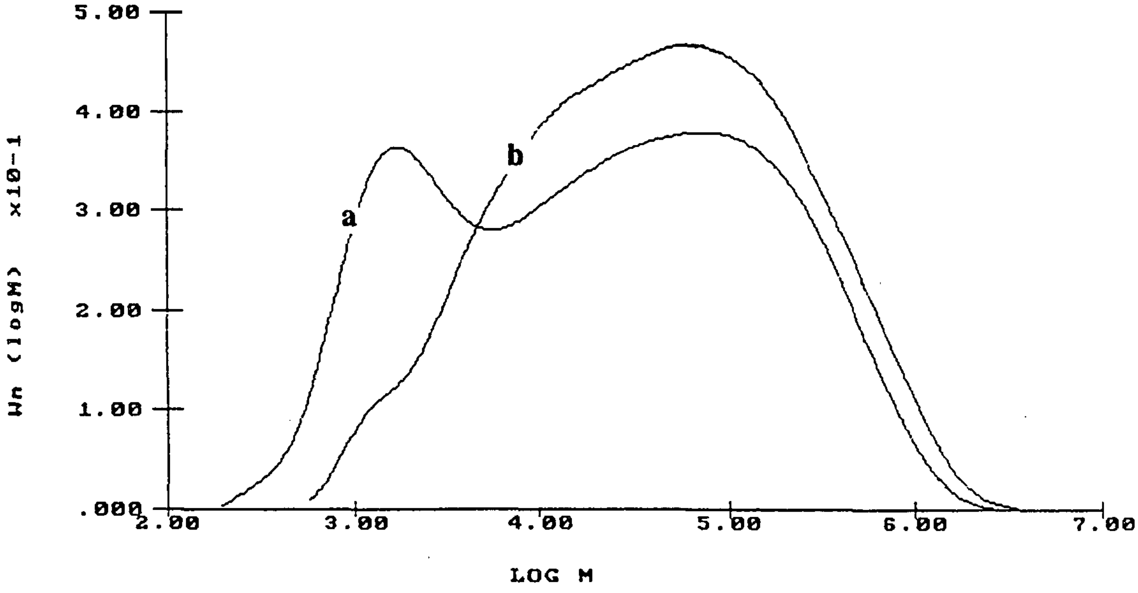


Figure 13 Molecular weight distribution of polymer 24 obtained from a) a precipitation in methanol and b) a precipitation in acetone.

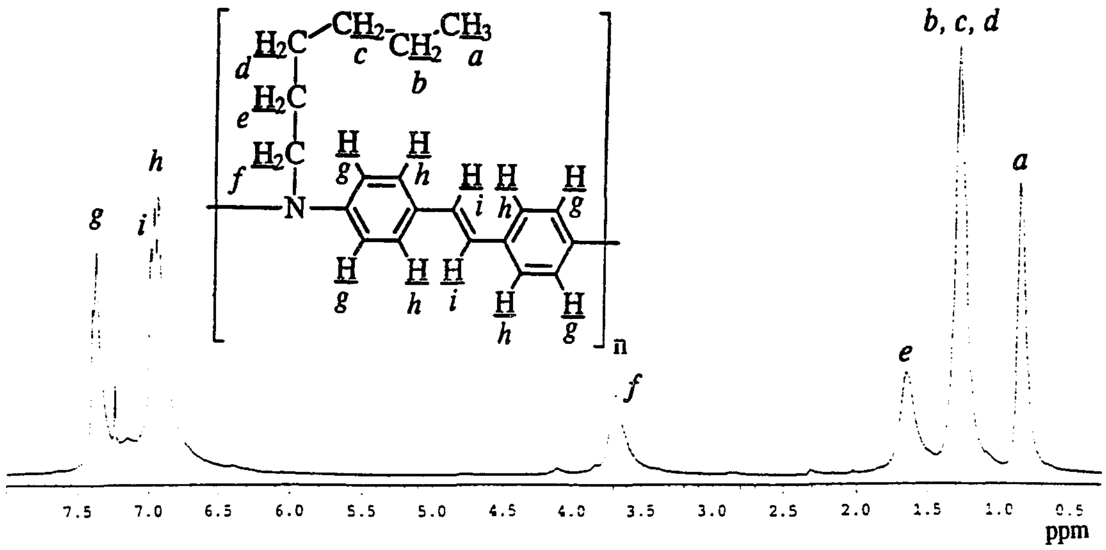


Figure 14 ^{1}H-NMR spectrum of polymer 24 in $CDCl_3$.

Signals in the ^{13}C-NMR spectrum of polymer 24 can be assigned by comparing the spectrum to that of the corresponding dimer 27 (Figure 15). Dimer 27 was obtained in two steps from N-hexyldiphenylamine, 5 (Scheme 17). A Vilsmeier-Haack formylation of 5 yielded exclusively (95% yield) monoaldehyde 28 which was subjected to a reductive McMurry coupling reaction to produce the desired dimer in 55%. The ^{13}C-NMR spectra had number of signals as expected, 11 and 15 for 24 and 27, respectively. The clean ^{13}C-NMR spectrum of 24 confirmed that the polymer was pure and its molecular weight was high. The observation of exactly the same number of signals as expected for polymer 24 also strongly suggested that the polymer chains contain only one geometrical isomer, presumably trans. The six peaks observed between 10 to 55 ppm in both spectra corresponded to six carbons of the hexyl side chain. The sp^2-C signals were observed between 120-150 ppm with vinyl carbon at 126 ppm.

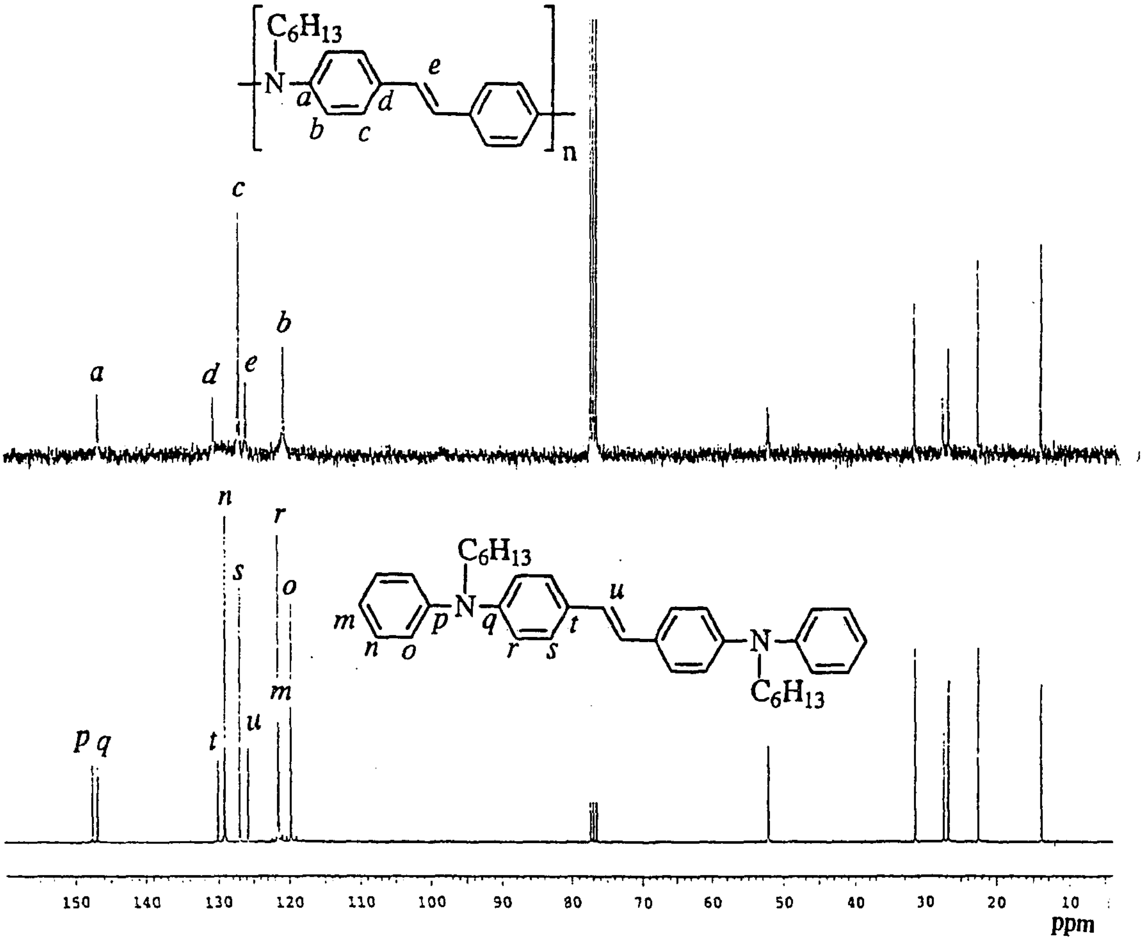
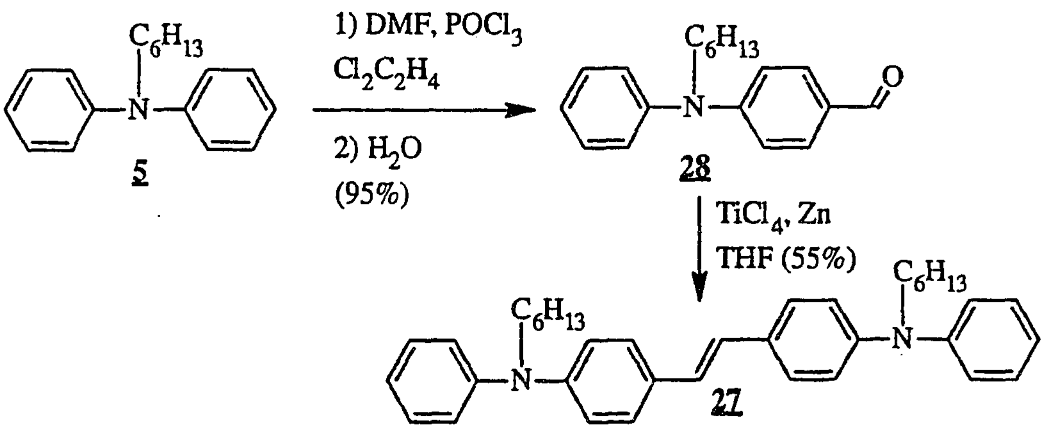


Figure 15 ^{13}C-NMR spectra of polymer 24 and dimer 27.



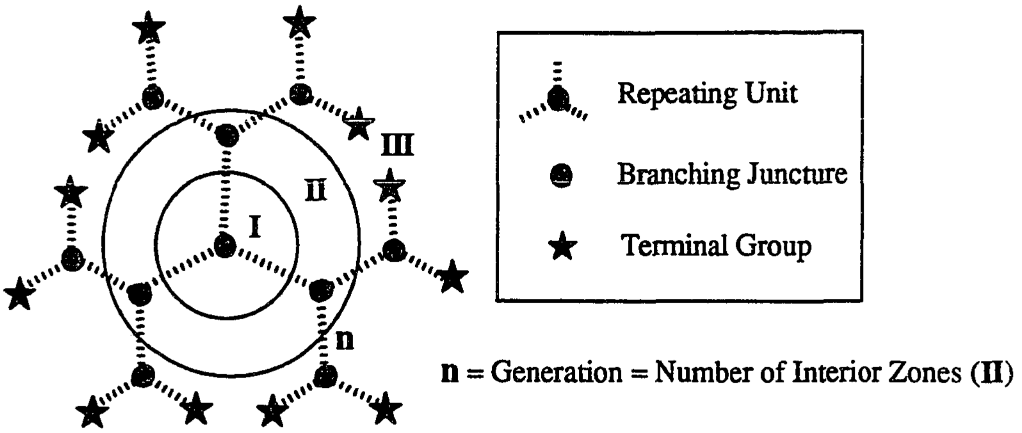
Scheme 17

TGA showed a single weight loss at 392°C (95% remaining weight) and only 9% remaining weight at 1000°C. A UV-Vis absorption spectrum of polymer **24** in THF showed a broad band with a λ_{max} at 400 nm. Visibly, this polymer showed much stronger luminescence than its ethynylene analogue, polymer **1**. An emission spectrum of the THF solution showed three emission peak at 457, 488 and 515 nm. The energy differences between these three peaks are 1390 and 1075 cm^{-1} which are considerably lower than the stretching energy of the double bonds (1600-1650 cm^{-1}) in the stilbene units. The differences in these energy remains unexplained. Polymer **24** can form a homogeneous free standing film with bright yellow color (Figure 8). This film is not as transparent as a film of polymer **1**.

Electrical conductivities of polymer **24** measured by two in-line probes were lower than the equipment threshold ($\leq 10^{-9}$ S cm^{-1}). Doping this polymer by iodine vapor was very slow, but a conductivity of 1-10 S cm^{-1} was obtained after one day. The doping was irreversible by vacuum but, upon exposure to air the conductivity dropped below 10^{-9} S cm^{-1} within 5 minutes. The origin of this conductivity remains unclear but the slow oxidation of the polymer by I_2 to form tight radical ion pairs seems reasonable.

Ethynylene dendrimers containing triphenylamines

Dendrimers, sometimes called starburst dendrimers, refer to a class of well defined oligomeric or polymeric compounds with highly branched structures.[60] This new class of compounds is composed of three distinct architectural features: an initiator core (**I**), interior zones (**II**), and a surface region (**III**) (Figure 16). Repeating units in dendrimers possess three or more linkages instead of two as in conventional linear polymers. In both the initiator core and interior zones, the repeating units are attached to branching junctures. The propagating repeating units of the interior zone will be capped with a terminal group to form the surface region. Besides molecular weights (M_n and M_w), sizes of the dendrimers can be designated by the number of interior zones called generations (n).



n = Generation = Number of Interior Zones (II)

Figure 16 Architectural features of dendrimers.

Syntheses of dendrimers have become more intensive in the past decade, although the concepts of dendritic structures[61] and the first observation of dendritic structures in natural proteins[62] date back to 1943 and 1953, respectively. Due to their unique features, dendrimers should possess special properties and offer diverse applications. Mechanical properties of the dendrimers are usually inferior to those of the linear polymers. However, their employment as composite additives in siloxane rubbers has lead to significant increases in their tensile strengths.[63] Better solubility of dendrimers in common solvents compared to linear polymers containing similar repeating units were observed and rationalized.[64] The solubilities in various solvents can be altered by modification of the terminal groups at the surface.[65] This surface region can also provide a rich chemistry for the dendrimers. A pH-dependent aggregation of acid-functionalized semi-dendrimers has been reported.[66] Complexation of gold with dendritic polyphosphines was reported to occur at the surface region with no marked difference in reactivity when the generations of the dendrimers increase from 1 to 10.[67] Electrochemical studies of dendritic organosilicon containing peripheral ferrocenyl groups shows that all of the ferrocenyl group can be oxidized at the same potential.[68] Homogeneous catalysts based on silane dendrimer-functionalized arylnickel (II) complexes are shown to be effective for Kharasch addition.[69] With precise sizes and shapes, these dendrimer-based catalysts offer some advantages over conventional polymer-based catalysts, such as an all metal catalytic site exposed to the reagents and substrate, an easy control of catalytic quality, and easy separation and good recovery from the reaction mixture. While the surface region may provide several varieties of interesting chemistry, the internal zones of the dendrimers have been the target of research in guest-host chemistry.[70] The internal zones contain many rigid or semi-rigid cavities with precise sizes and shapes which can be utilized to selectively trap guest molecules with proper sizes and shapes.

The choice of the repeating units and terminal groups can considerably alter the properties of dendrimers as a whole. However, changing the generations of the dendrimers can be used to fine tune these properties. This was observed, for example, in thermal properties of the dendrimers, that lead to the design and synthesis of a novel class of liquid crystalline macromolecules.[71] Studies on the optical and electronic properties of dendrimers began in 1994. UV-Vis absorption and emission of dendritic polysilanes and linear polysilane have been compared.[72] Moore modified his phenylacetylene-based dendrimers for a molecular light funneling device.[73] The molecule consists of peripheral diphenylacetylene chromophores and longer conjugated phenylacetylene segments moving inward toward its center (Figure 17).The ends of each of these units are *meta*-linked to interrupt the conjugation between the units. This design results in a smooth decrease in energy levels from the surface region to the initiator core attached with a fluorescent probe, perylene.

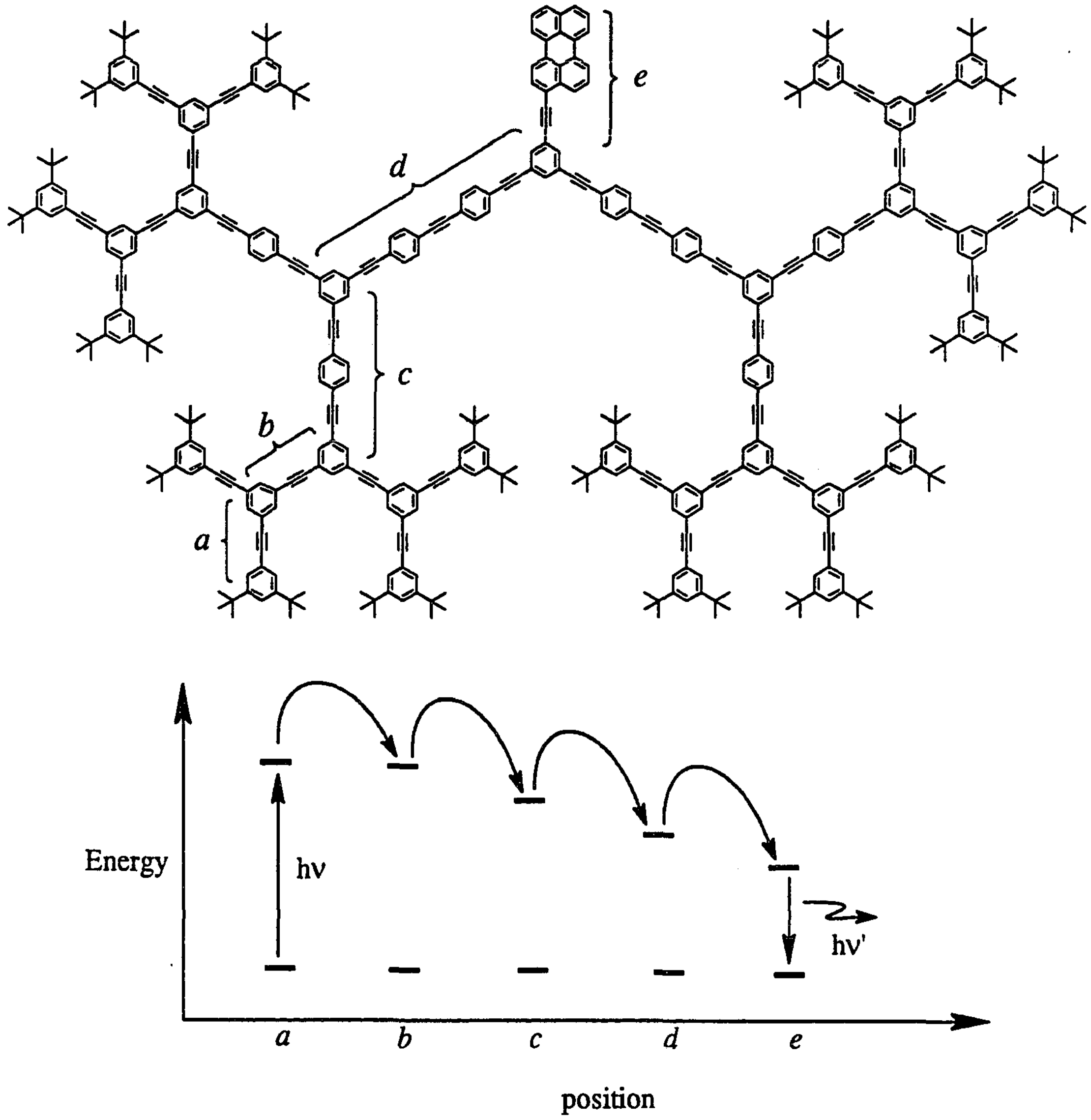


Figure 17 Illustration duplicated from reference 73 showing structure and conceptual design of the molecular light funneling device.

Replacing the diphenylamine basic units in our linear N-interrupted polyphenylene-ethynylene with triphenylamine would provide appropriate building blocks for the dendrimers whose repeating units are closely related to those of the linear system. Comparing the conductivity and photophysics of the dendrimers to those of the linear polymers should confirm the effect of molecular shapes and dimensions on these properties. Thus, the dendrimers containing 4,4',4"-tricarbynyltriphenylamine repeating units (Figure 18) were synthesized.

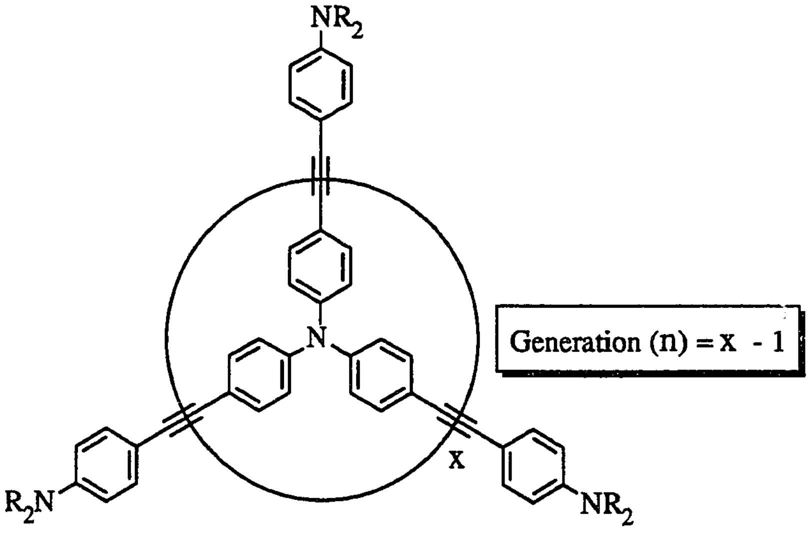
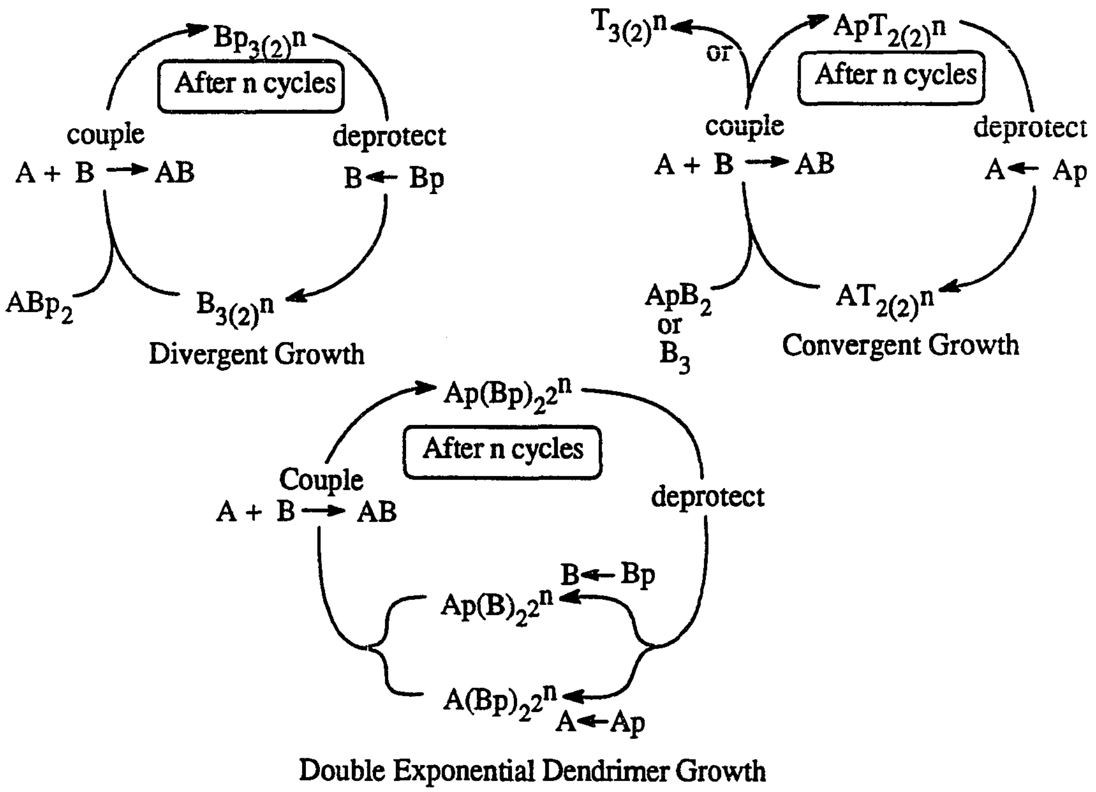


Figure 18 General structure of dendritic 4,4',4"-carbynyltriphenylamine.

Dendrimers can be obtained by two different approaches: single stage synthesis and repetitive synthesis. Single stage synthesis involves polymerization of monomers containing at least three polymerizable functional groups.[63] Repetitive synthesis usually consists of repetitive cycles of multisteps: protecting, coupling, and deprotecting. The former approach is simpler and faster, but the resulting polymers are not structurally precise. Thus, it was decided to utilize the second approach in our dendrimer syntheses.

Three major dendrimer growth schemes (Scheme 18), known as the "divergent",[74] "convergent",[75] and "double exponential growth",[76] have been devised for repetitive synthesis. For syntheses of dendrimers whose repeating units possess three branches, a key monomer,



Divergent Growth

Convergent Growth

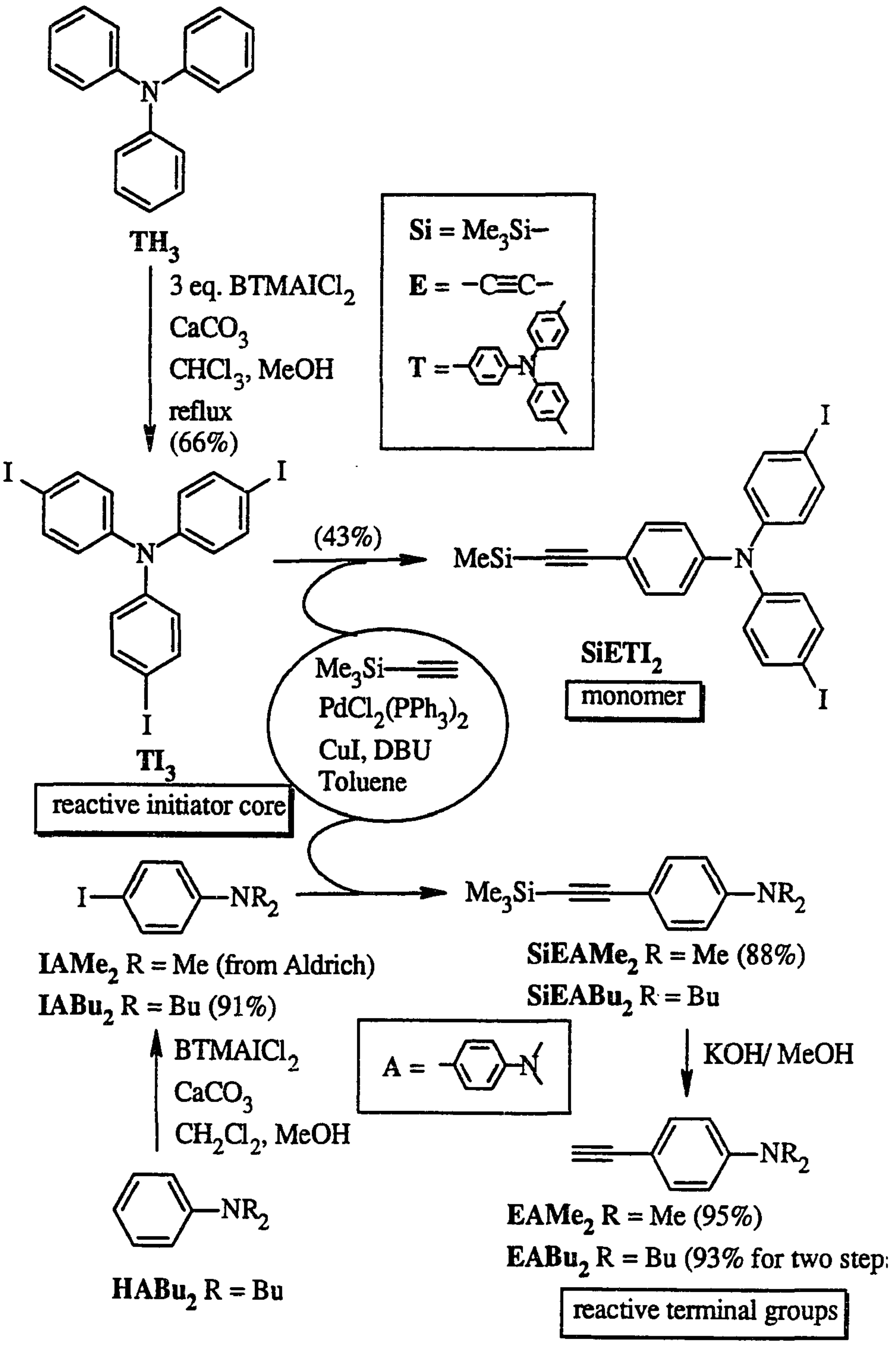
Double Exponential Dendrimer Growth

Scheme 18

represented as AB_2, generally contains two types of functional groups, A and B. The coupling between these two functional groups should be virtually quantitative. Either A or B functional groups needs to be protected and is represented by Ap or Bp. Therefore, two kinds of monomers, ABp_2 or ApB_2, can be used. An ABp_2 monomer is appropriate for the divergent scheme while ApB_2 is used for the convergent scheme. Both types of monomers are required for the double exponential dendrimer growth. In the divergent scheme, three equivalents of ABp_2 react with an initiator core containing three B functional groups, B_3, producing Bp_6. After deprotection, the resulting B_6 can again couple with six equivalents of ABp_2 monomer generating a bigger dendrimer. The cycle can be repeated until the surface region becomes too congested. For a rigid systems, however, this synthetic scheme is stopped rapidly, usually after the first cycle, by the poor solubility of the products.[43b] The convergent scheme has been used successfully for the synthesis of rigid dendrimers because the flexible terminal groups, T, are introduced into the dendritic product from the first step.[43] In fact, the number of these flexible groups increases as the cycle is repeated. The products from the later cycles thus generally possess greater solubilities.

The double exponential growth scheme allows the fastest dendritic growth per each cycle. However, it requires two types of monomers and two compatible protecting-deprotecting reactions. The convergent scheme seems to best fit our system since we are interested in the properties of the dendrimers. From the convergent scheme, three major building blocks are required: a reactive initiator core (B_3), a monomer (ApB_2), and a reactive terminal group (T_3).

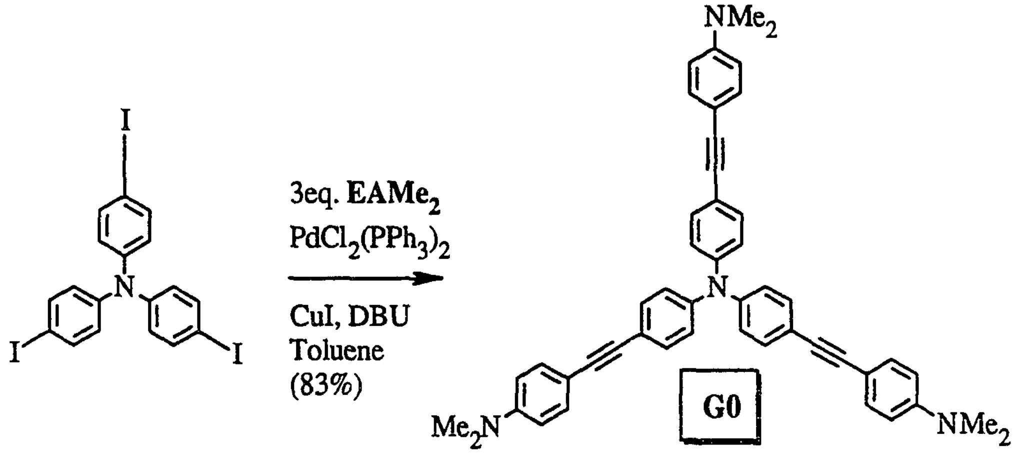
In the synthesis of our dendritic 4,4',4"-tricarbynyltriphenylamine, the reactive initiator core is 4,4',4"-triiodotriphenylamine, **TI_3**, the monomer is 4,4'-diiodo-4"-trimethylsilyl-ethynyltriphenylamine, **$SiETI_2$**, and the reactive terminal groups are 4-ethynyl-N,N-dialkylaniline, **$EAMe_2$** or **$EABu_2$** (Scheme 19). The synthesis of these building blocks used the same reactions, with some modifications, as the synthesis of the monomers of the linear polymers. The reactive initiator core, **TI_3**, was obtained in 66% yield from the triple


TH$_3$
3 eq. BTMAICl$_2$
CaCO$_3$
CHCl$_3$, MeOH
reflux
(66%)
Si = Me$_3$Si–
E = –C≡C–
T =
TI$_3$
reactive initiator core
(43%)
MeSi
SiETI$_2$
monomer
Me$_3$Si
PdCl$_2$(PPh$_3$)$_2$
CuI, DBU
Toluene
NR$_2$
IAMe$_2$ R = Me (from Aldrich)
IABu$_2$ R = Bu (91%)
SiEAMe$_2$ R = Me (88%)
SiEABu$_2$ R = Bu
BTMAICl$_2$
CaCO$_3$
CH$_2$Cl$_2$, MeOH
A =
KOH/ MeOH
HABu$_2$ R = Bu
EAMe$_2$ R = Me (95%)
EABu$_2$ R = Bu (93% for two step
reactive terminal groups

Scheme 19

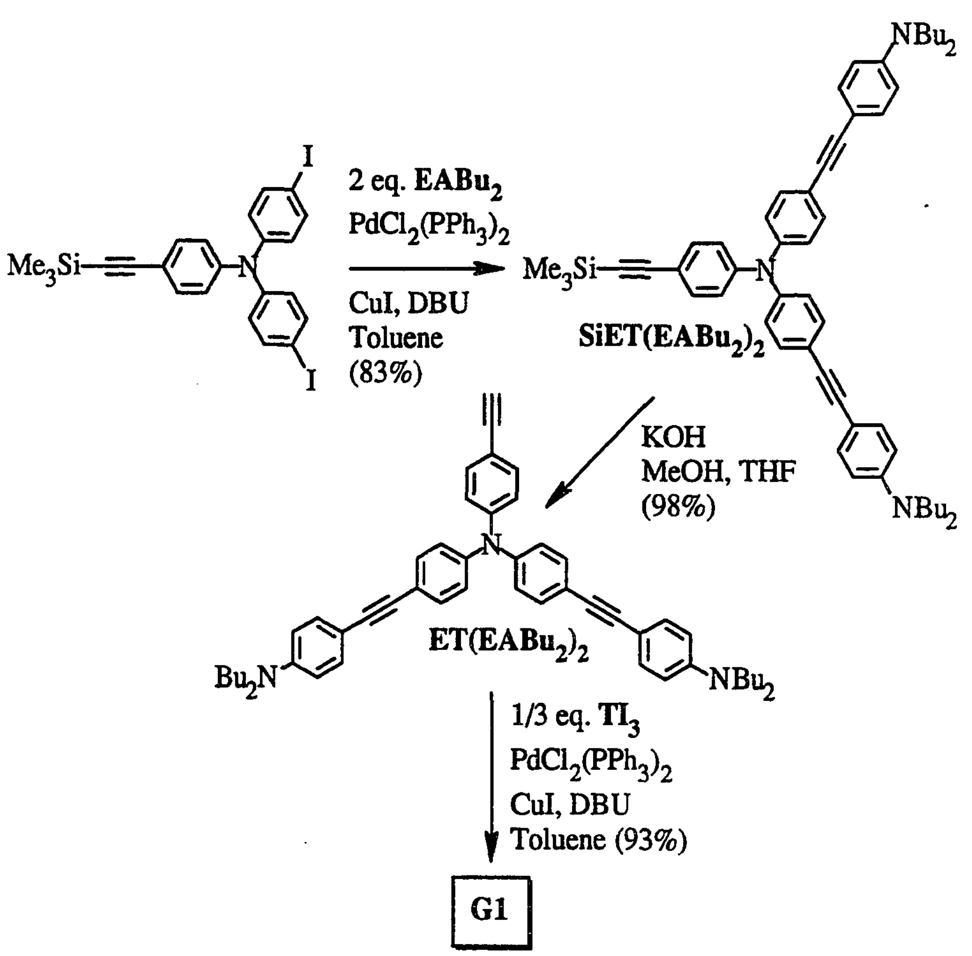
iodination of triphenylamine, **TH_3**, by three equivalents of $BTMAICl_2$ under reflux temperature of $CHCl_3$ for 72 h. An attempt to shorten the reaction time by use of a stronger iodinating agent, ICl, did not yield the desired product. It is worth mentioning that the direct Pd-coupling of one equivalent of trimethylsilylacetylene with **TI_3** is a statistical reaction. However, the desired monomer **$SiETI_2$** was obtained in satisfactory yield (43% isolated) along with 18% recovery of starting material **TI_3**, 17% of 4-iodo-4',4"-bistrimethylsilylethynyltriphenylamine, **$(SiE)_2TI$**, and 2 % of 4,4',4"-tristrimethylsilylethynyltriphenylamine, **$T(ESi)_3$**.The isolation of the monomer was achieved by repetitive flash chromatography. The synthesis of the reactive terminal groups was straightforward and the desired compounds were obtained in excellent yields.

The synthesis of the zero generation (**G0**) dendrimer was accomplished by a Pd-coupling of **TI_3** with three equivalents of **$EAMe_2$** (Scheme 20). For higher generations, the **$EABu_2$** was utilized as the reactive terminal group to ensure solubilities of the products. A Pd-coupling of two equivalents of **$EABu_2$** with monomer **$SiETI_2$** yielded the protected

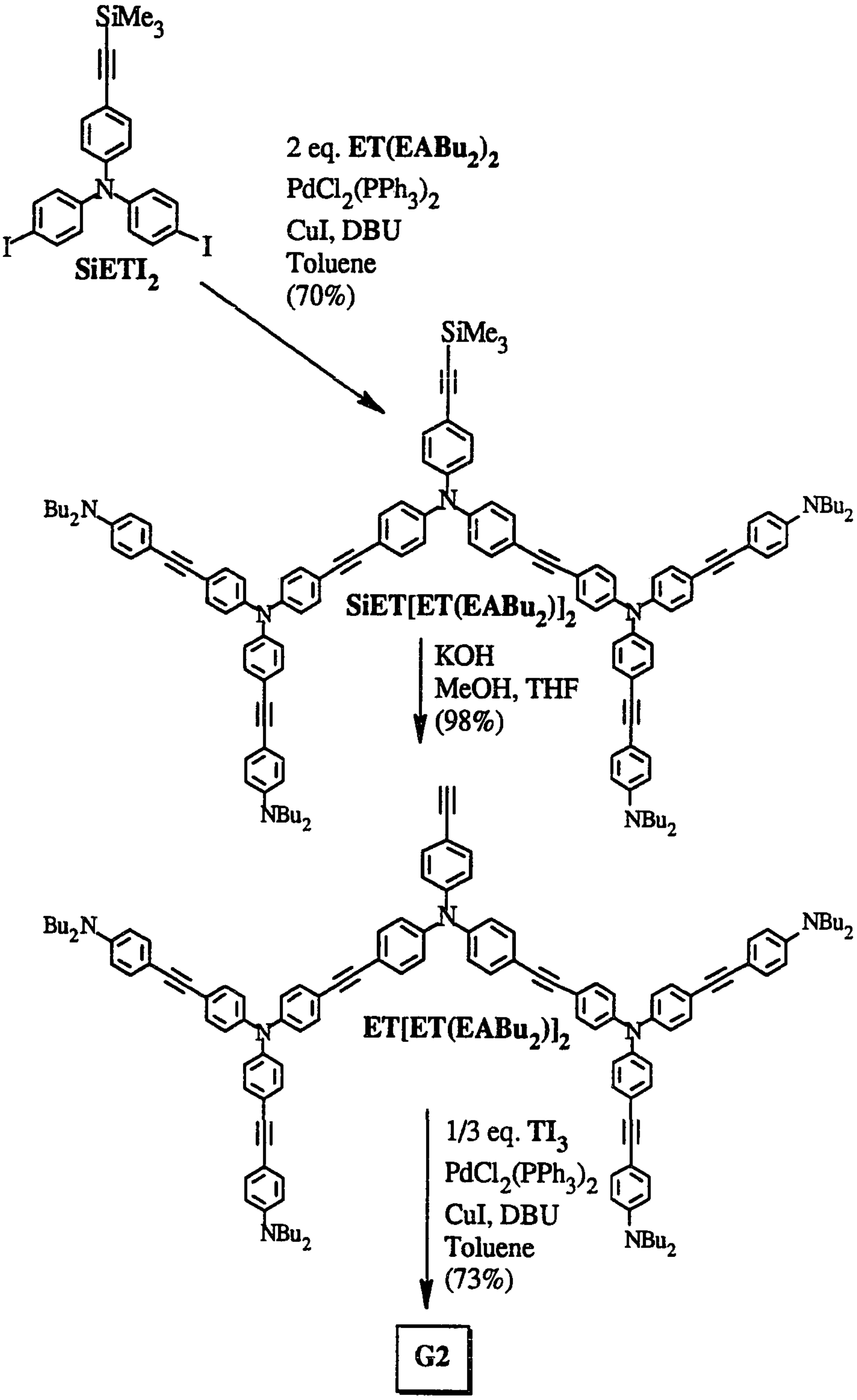


Scheme 20

monodendron **SiET(EABu$_2$)$_2$** in 77% yield. The monodendron **ET(EABu$_2$)$_2$** was obtained from base-catalyzed desilylation of **SiET(EABu$_2$)$_2$** in 98% yield. A Pd-coupling of three equivalents of this monodendron with **TI$_3$** gave the desired **G1** in 93% yield (Scheme 21). The synthesis of **G2** involved repeating coupling-deprotecting sequences. The monomer **SiETI$_2$** was coupled with two equivalents of **ET(EABu$_2$)$_2$** to form **SiET[ET(EABu$_2$)$_2$]$_2$** (Scheme 22). The desilylation of **SiET[ET(EABu$_2$)$_2$]$_2$** yielded **ET[ET(EABu$_2$)$_2$]$_2$**, another monodendron, which can be coupled with one third equivalent of **TI$_3$** to give the desired **G2**.



Scheme 21


SiMe3
I
I
SiETI2
2 eq. ET(EABu2)2
PdCl2(PPh3)2
CuI, DBU
Toluene
(70%)
SiMe3
N
Bu2N
NBu2
N
N
SiET[ET(EABu2)]2
KOH
MeOH, THF
(98%)
NBu2
NBu2
N
Bu2N
NBu2
N
N
ET[ET(EABu2)]2
1/3 eq. TI3
PdCl2(PPh3)2
CuI, DBU
Toluene
(73%)
NBu2
NBu2
G2

Scheme 22

Structural assignments of G1 and G2 were accomplished by ^{13}C-NMR. The spectra of G1 and G2 showed four and six characteristic peaks, respectively. The peaks at 146-148 ppm corresponded to sp^2-C's attached to N and the peaks at 86-91 ppm corresponded to the acetylene carbons (Figure 19). Molecular weights of the dendrimers were determined by GPC

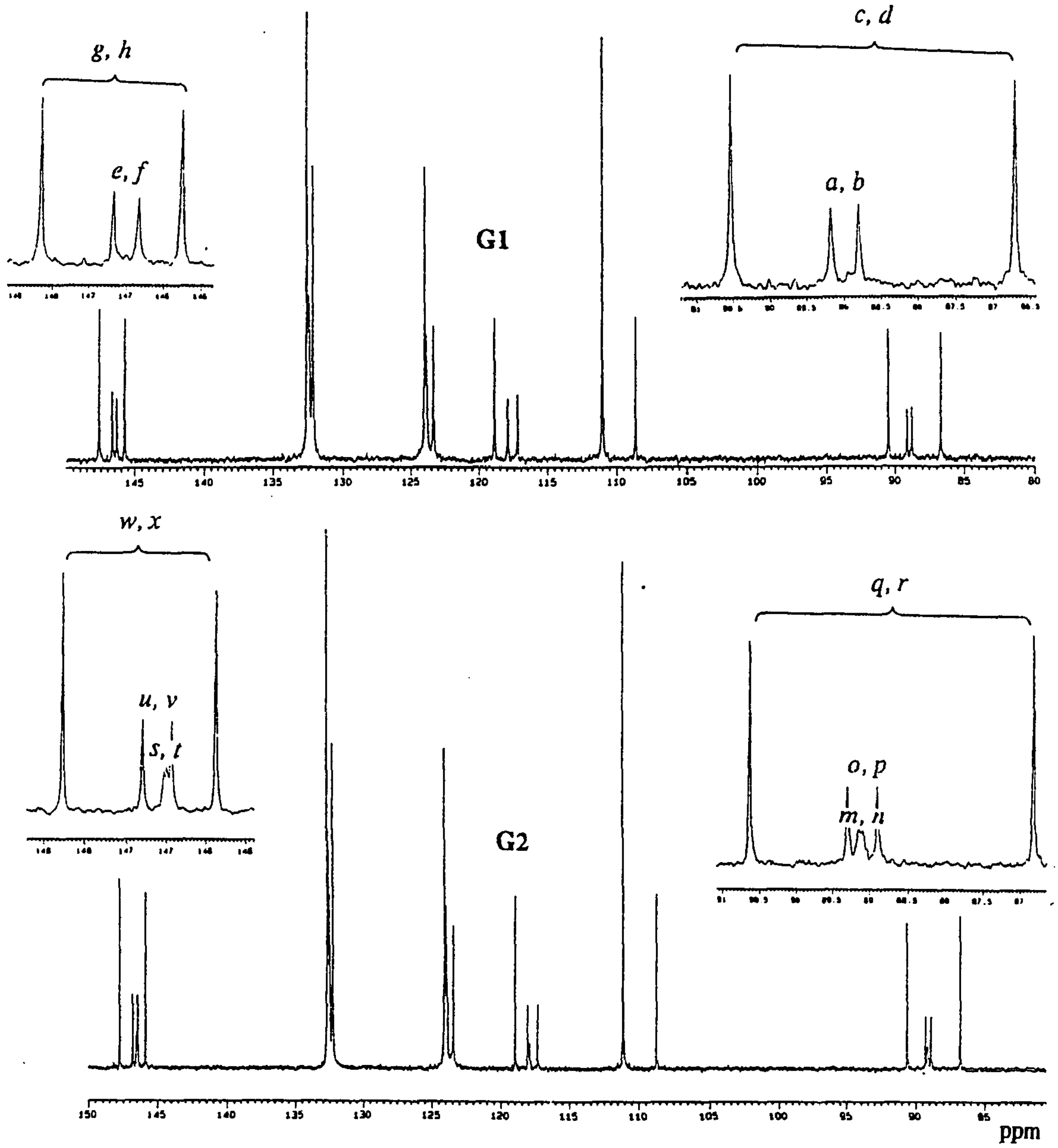


Figure 19 ^{13}C-NMR spectra of G1 and G2 and their characteristic peaks assignments

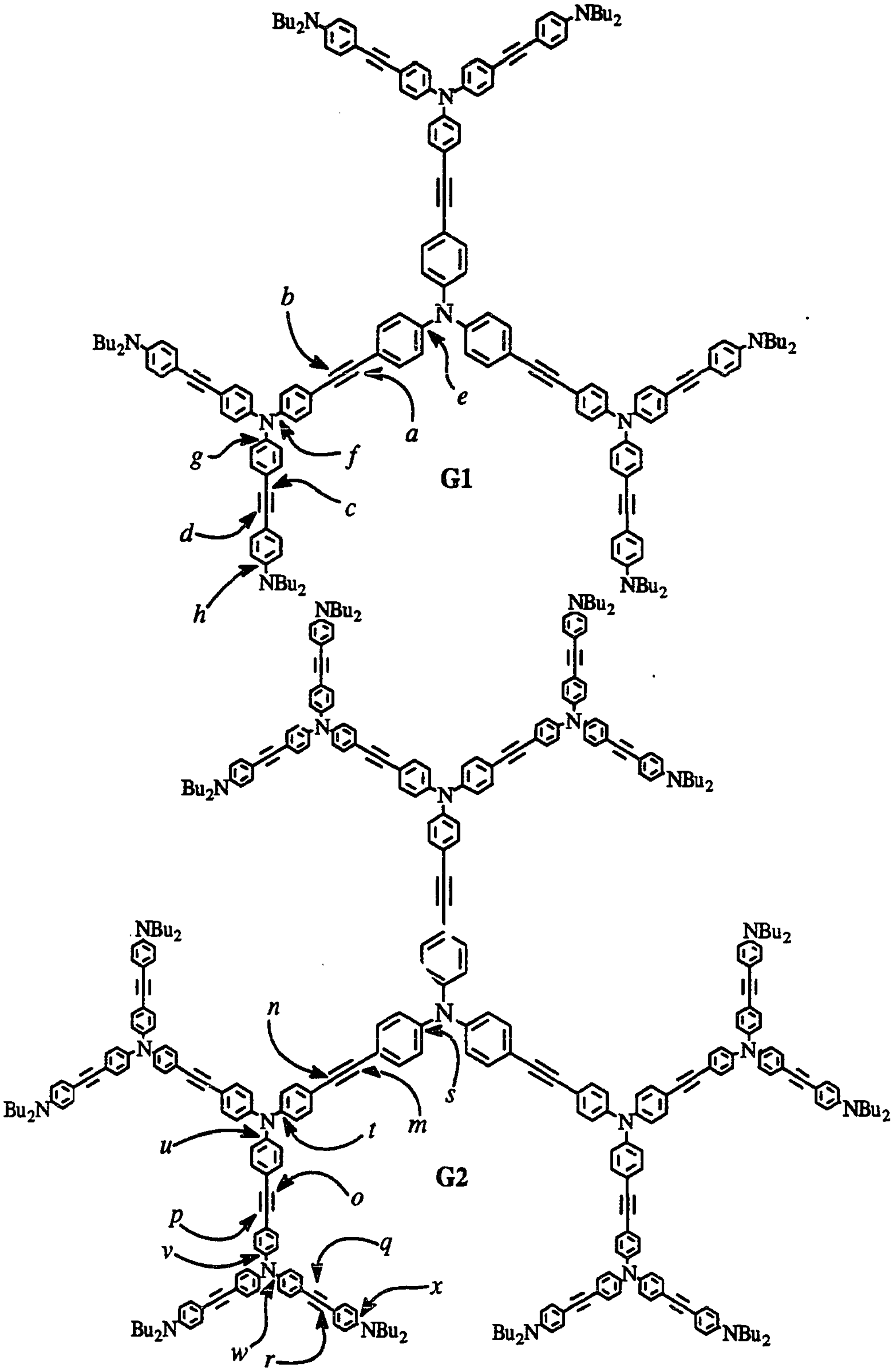


Figure 19 (continued)

Table 5 Formulas, formula weights (F.W.), and observed molecular weights from GPC (M_n, M_w) and MS (M^+) of synthesized dendrimers.

Dendrimer	Formula	F.W.	observed molecular weight		
			Mn	Mw	M^+
G0	$C_{48}H_{42}N_4$	674.34	NA	NA	674.3414
G1	$C_{174}H_{180}N_{10}$	2,411.45	2,400	2,470	2,411.47
G2	$C_{390}H_{384}N_{22}$	5,379.49	5,210	5,250	5,374.2

and MS (Table 5). For **G0**, an exact mass of 674.3414 (calc. 674.3410) was obtained from high resolution EI. The molecular weight of G1 obtained from low resolution EI was comparable to the formula weight. A matrix assisted laser desorption/ ionization (MALDI) technique was required to obtain the molecular ion mass of **G2**. An acceptable mass (5374.2) was obtained when α-cyano-4-hydroxycinamic acid was used as a matrix and **G1** was used as a reference. The GPC gave satisfactory M_n with very narrow polydispersities (1.02 and 1.01 for **G1** and **G2**, respectively) indicating the precise sizes of these dendrimers. Geometry optimizations of **G0**, **G1** and **G2** were performed on HyperChem™ using MM$^+$ molecular mechanics calculation. For **G1** and **G2**, the butyl groups were replaced by methyl groups for simplicity of the calculation. The resulting three dimensional structures of these three dendritic molecules displayed that the molecular structure of **G0** and **G1** were almost two dimensional whereas G2 developed an extensive three dimensional structure (Figure 20). The radii from the N of the initiator core to the peripheral N of **G0**, **G1**, and **G2** were 12.1 Å, 21.1 Å and 28.6 Å, respectively.

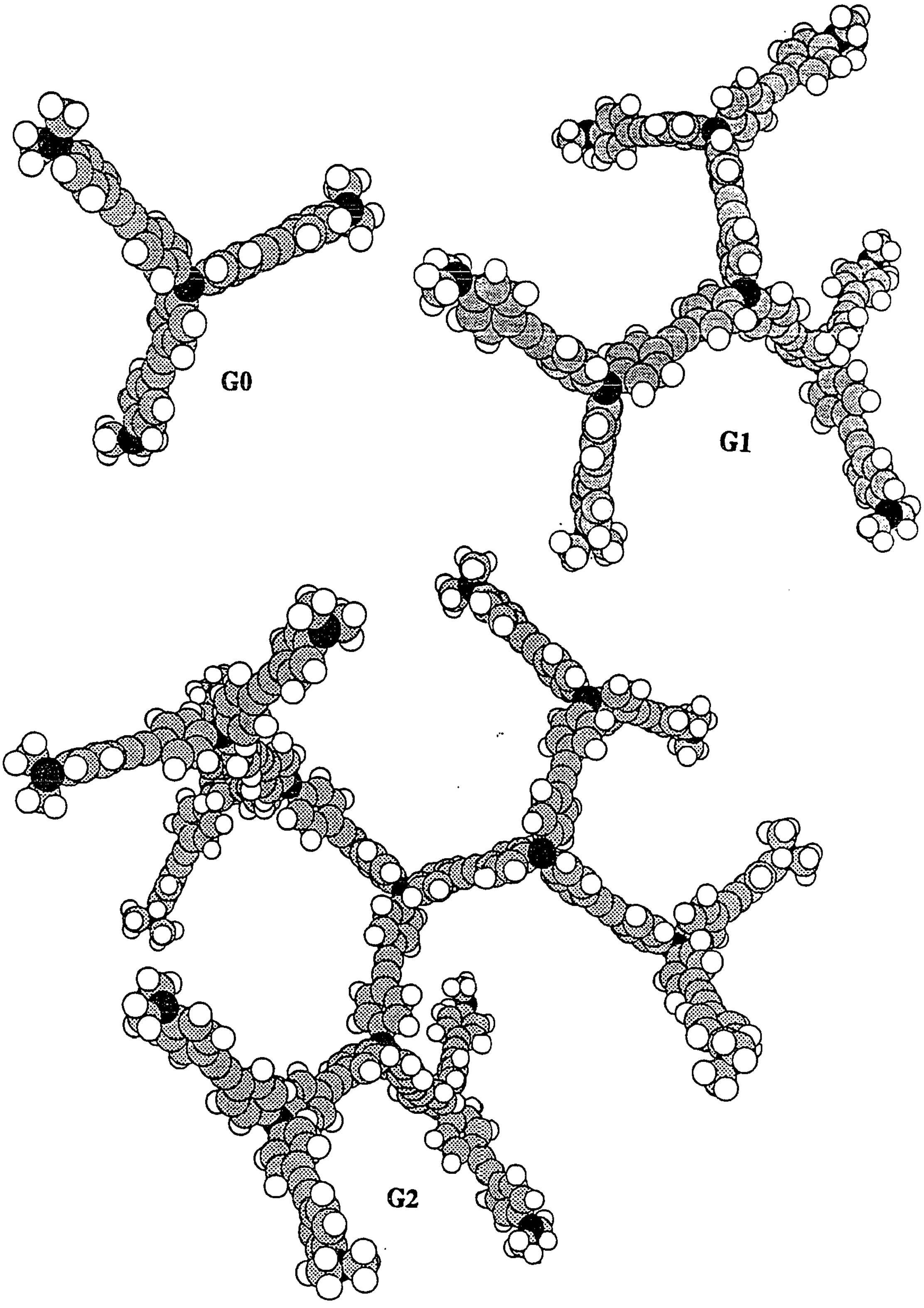


Figure 20 Three dimensional structures of **G0**, **G1** and **G2**.

The UV-Vis absorption spectra showed that **G0** had a λ_{max} at 378 nm, and both **G1** and **G2** had the same λ_{max} at 386 nm. The same λ_{max} of **G1** and **G2** suggests no extensive conjugation beyond the dimer of 4-carbynyltriphenylamine. The 8 nm difference in the λ_{max} is likely due to the difference in their basic chromophores, not the extension of the conjugation. **G1** and **G2** contain a chromophore, bis(4,4′-triphenylamine) acetylene, which was not present in **G0**. The absorption maxima of **G1** and **G2** were close to the λ_{max} (389 nm) of the linear polymer **1** suggesting the similarity of electronic properties of these two types of polymers.

G1 and **G2** were photoluminescent and excitation and emission spectra of their THF solutions were recorded (Figure 21). The emission spectra contained three partially resolved peaks spreading from 375 to 575 nm, similar to those observed in polymer **1**. The photoluminescence of the dendrimers appeared much stronger than that of polymer **1**. This result was opposite to what was observed in the silane system.[72] **G2** also showed electroluminescence, but the stabilities and quantum efficiencies of the devices based on this dendrimer have not been satisfactory yet.

The electrical conductivity of **G2** was similar to that of polymer **1**. The conductivity increased from $< 10^{-9}$ to $\approx 10^{-6}$ when the dendrimer was doped with iodine vapor. This result indicated no effect of shapes, dimensions, or conformations on the conductivity of this polymer system. Therefore, it was reasonable to assume that electron hopping, rather than the electron migration through the π-conjugated bonds, was responsible for conductivity in these polymers. The previously described spectroscopic data also indicated that the electronic properties of these polymers depended mostly on individual repeating units.

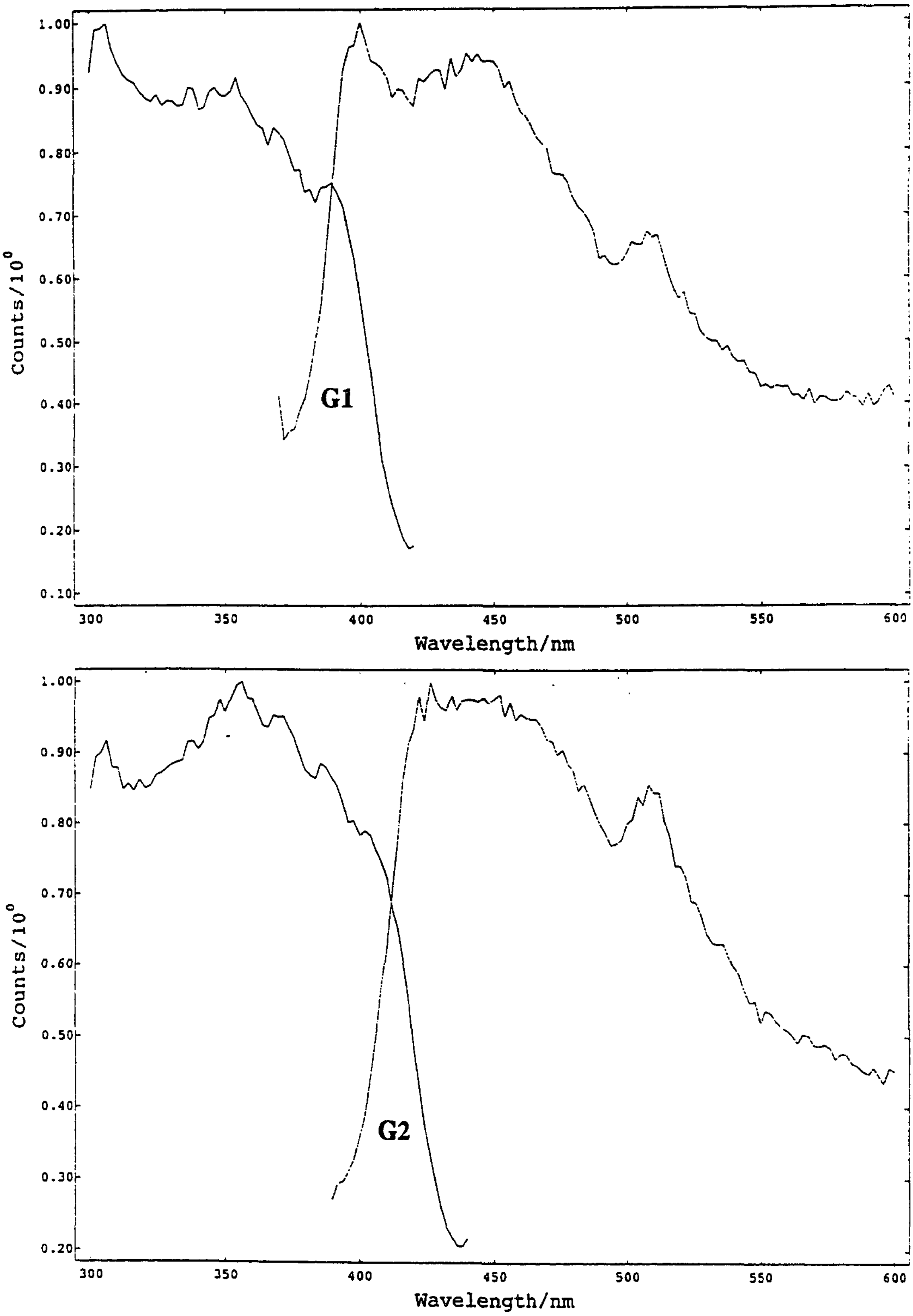


Figure 21 Excitation and emission spectra of **G1** and **G2**.

Thermal behavior of these dendrimers was studied by DSC scanning from room temperature to 400°C for **G0** and to 350°C for **G1** and **G2**, with a 20°C/min ramp. The DSC thermogram of **G0** showed a melting point at 278°C and an interesting endothermic and exothermic peaks at 145 and 157° C (Figure 22). These endo/exothermic peaks were not observed when the compound previously heated (to 200°C) was reheated, indicating an irreversible phase transition. However, these peaks could be restored by recrystallization of the compound in methanol/methylene chloride. The TGA thermogram of **G0** showed no weight loss below 350°C, excluding a loss of solvent from a solvent-inclusion crystal. X-ray powder diffraction of the preheated material and postheated material showed different patterns of sharp diffractions, indicating two types of crystals. Therefore, these endo/exothermic peaks were likely due to melting-crytallization transition.[77] Conformational changes maybe involved in this transition, which should be obvious in X-ray crystallogaphy. Unfortunately, a high quality single crystal could not be obtained. The DSC thermograms of **G1** and **G2** consisting of small endothermic peaks cannot be unambiguously interpreted.

An attempt to synthesize **G3** was also conducted. The repetitive convergent scheme was again utilized (Scheme 23). The coupling of three equivalents (with 20 % excess) of monodendron $\mathbf{ET[ET[ET(EABu_2)_2]_2]_2}$ with $\mathbf{TI_3}$ in the final step yielded an inseparable mixture, possibly the didendron and **G3**. The ^{1}H-NMR spectrum showed the presence of an iodophenyl group. The GPC chromatogram showed two greatly overlapping peaks with $M_n = 1.48 \times 10^4$ and $M_w = 1.61 \times 10^4$ (Figure 23). Presumably, steric hindrance of the branches surrounding the reactive focal point reduces the reactivity of the didendron toward the third coupling.[43b]

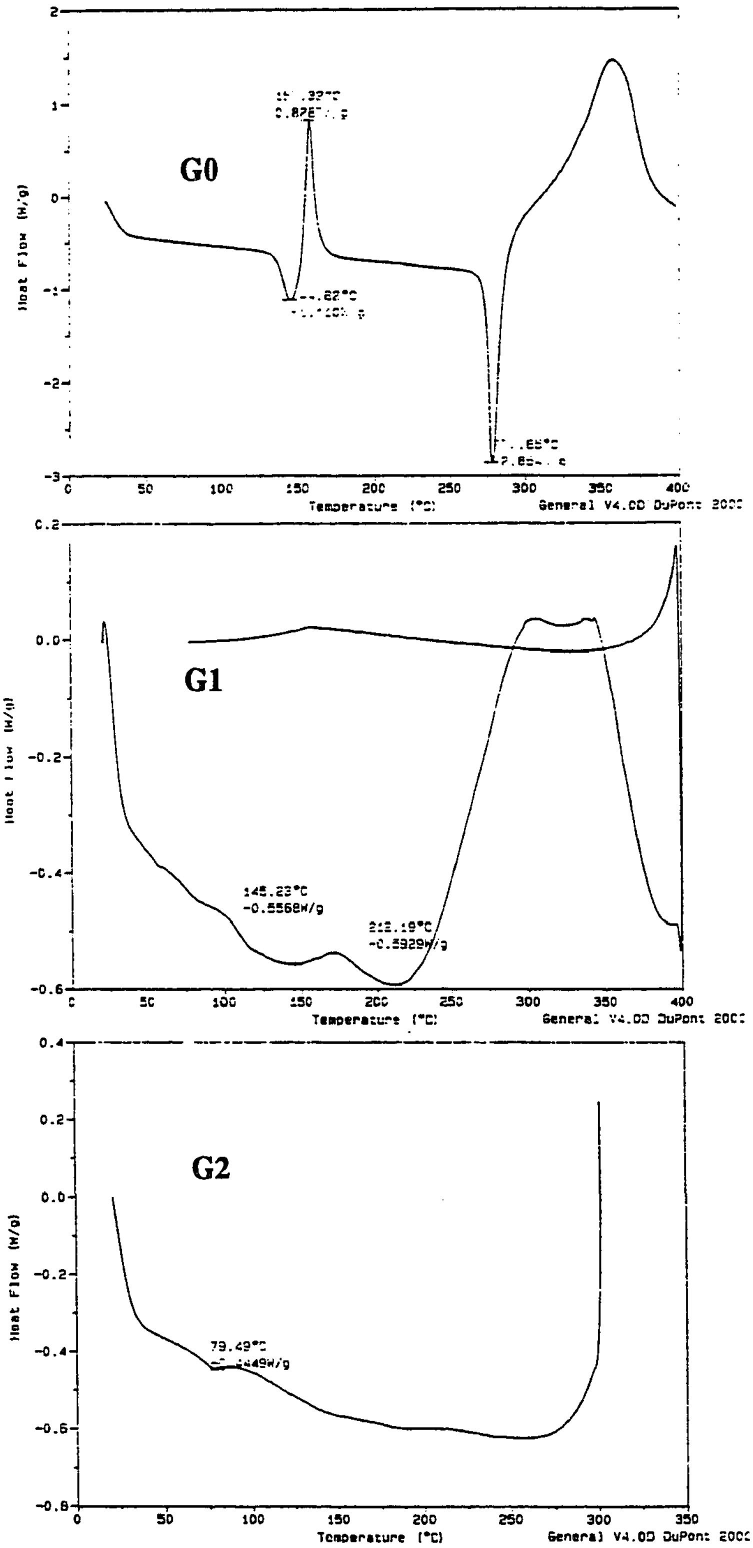
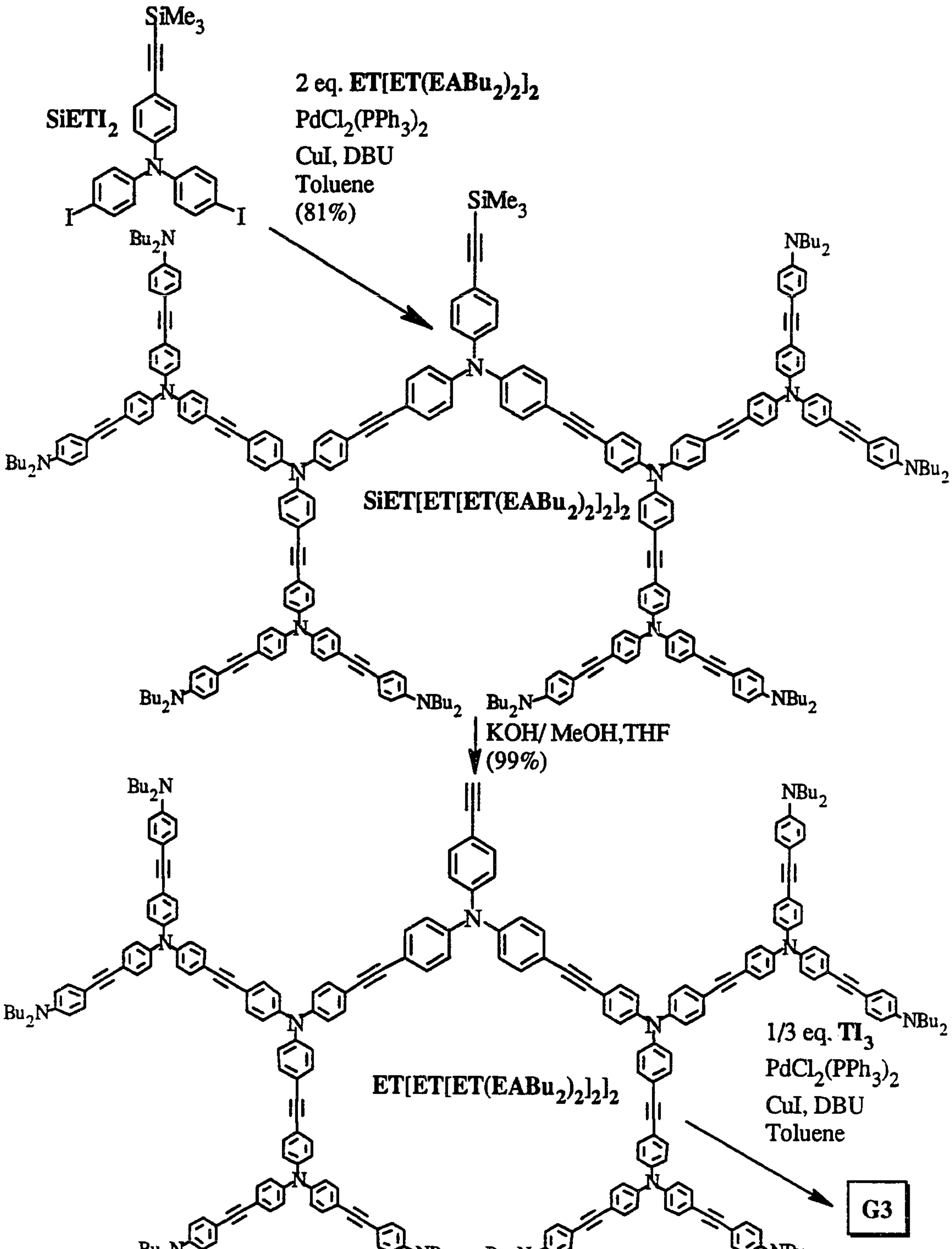


Figure 21 DSC thermograms of **G0**, **G1** and **G2**.


SiMe3
SiETI2
2 eq. ET[ET(EABu2)2]2
PdCl2(PPh3)2
CuI, DBU
Toluene
(81%)
SiMe3
SiET[ET[ET(EABu2)2]2]2
KOH/ MeOH,THF
(99%)
ET[ET[ET(EABu2)2]2]2
1/3 eq. TI3
PdCl2(PPh3)2
CuI, DBU
Toluene
G3

Scheme 23

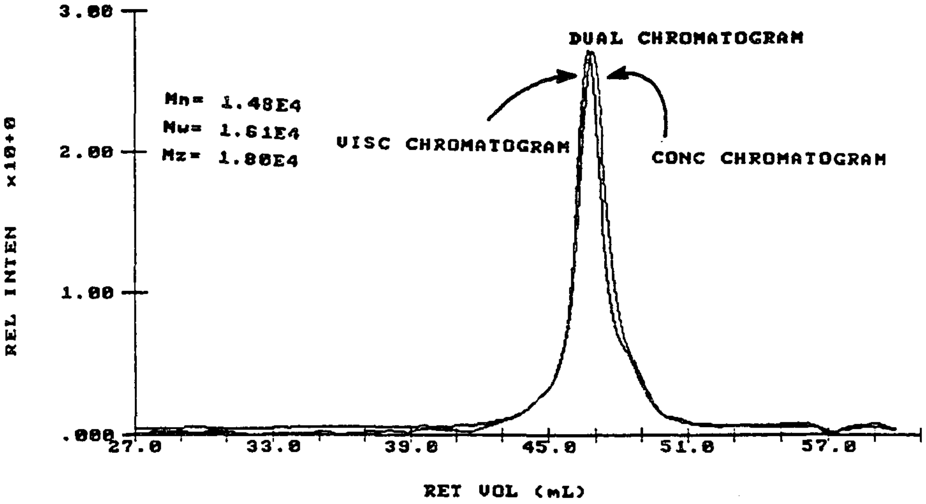


Figure 23 GPC chromatograms of the product from a Pd-coupling of two equivalents of $ET[ET[ET(EABu_2)_2]_2]_2$ with TI_3.

EXPERIMENTAL

Characterizations of all synthesized compounds were based on exact mass, IR, UV/Vis, ^{1}H-NMR and ^{13}C-NMR.. The exact masses were obtained from a Kratos MS 50 mass spectrometer with 10,000 resolution. The infrared spectra were recorded on a Bio-Rad Digilab FTS-7 spectrometer from neat samples. The UV/Vis spectra were acquired on a Hewlett Packard 8452A diode array UV/Vis spectrometer and λ_{max} were determined at optical densities of 0.2-0.5. The ^{1}H and ^{13}C NMR spectra were collected on a Varian VXR-300 MHz spectrometer in deuterated chloroform solution unless otherwise specified. Tentative signal assignments of ^{13}C-NMR spectra are given in parentheses after each chemical shift. Reactions were monitors by Hewlett Packard 5890 series II GC and Hwelett Packard tandem GC-IR-MS (5890A GC-5965A IR-5970 Series MS).

The thermal responses of polymers were studied on Du Pont Instruments 951 Thermogravimetric Analyzer (TGA) and 910 Differential Scanning Calorimeter (DSC) with a scanning rate of 20°C/min for both analyses. Molecular weight distribution of polymers were detemined by gel permeation chromatograph (GPC) system using universal calibration against polystyrene standards (M_n = 2,000 - 170,000). The GPC system consisted of a Beckman 110B solvent derivery system, a Perkin-Elmer 601 liquid chromatograph equipped with six Beckman 10 μ U-spherogel (7.7 mm × 30 cm) columns, a Viscotek 110 differential viscometer and a Waters Associates R401 differential refractometer. The viscometer and refractometer were parallel connected. The GPC analysis was performed at a flow rate of 1.0 mL/min of THF.

THF was distilled over Na-benzophenone and ether was distilled over CaH_2 immediately before use. Commercially available reagents were used as receivedd unless otherwise specified. Scientific Adsorbents 40 μ silica gel was utilized in flash chromatography.

N-Hexyldiphenylamine, 5

A 500 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with diphenylamine (8.46 g, 50 mmol), pulverized 87% KOH (19.35 g, 300 mmol), K_2CO_3 (10.37 g, 75 mmol) and tetrabutylammoniumbromide (1.61 g, 5 mmol) and toluene (100 mL). Bromohexane (9.25 g, 56 mmol) was added slowly to this stirred mixture. After 24 h, of reflux the mixture was filtered and the filtrate was washed with 1M HCl (2 × 100 mL). The solvent was removed and the remaining yellow oil was eluted through a flash silica gel column by hexane. The product was collected and the solvent was removed to give the desired product (10.53 g, 82 %) as a colorless liquid. **IR** (**cm^{-1}**) 1497, 2937, 3073; **^{1}H-NMR:** δ 0.90 (3 H, t *J* 7.0), 1.32 (6 H, m), 1.68 (2 H, qui *J* 8.0), 3.70 (2 H, t *J* 8.0), 6.95 (2 H, t *J* 9.0), 7.01 (4 H, d *J* 9.0), 7.27 (4 H, t *J* 9.0); **^{13}C-NMR:** δ 14.0 (CH_3), 22.6 (CH_2), 26.7 (CH_2), 27.4 (CH_2), 31.6 (CH_2), 52.3 (CH_2), 120.8 (4 sp^2-CH), 121.0 (2 sp^2-CH), 129.2 (4 sp^2-CH), 148.1 (2 sp^2-C).

4,4′-diiodo-N-hexyldiphenylamine, 6

A 1000 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with N-hexyldiphenylamine (10.21 g, 40 mmol) in methylene chloride (300 mL) and methanol (100 mL). Benzyltrimethylammonium chloroiodate,[47] BTMAICl$_2$, (30.64 g, 88 mmol) and CaCO$_3$ (11 g, 0.11 mol) was added quickly to this stirred solution. After 20 h, 20% NaHSO$_3$ solution was added to this mixture until the mixture became colorless. The organic layer was separated and the aqueous layer was extracted with methylene chloride (2 × 50 mL). The combined organic layer was washed with water (2 × 100 mL) and dried over anhydrous MgSO$_4$. The mixture was concentrated and the residue was eluted through a flash silica gel column by hexane. The solvents was removed the resulting yellow oil was dried under vacuum at 65 °C for 24 h. to give the desired product (4.40 g, 86%). **HIRES EI:** calcd for $C_{18}H_{21}NI_2$ 504.9763, measured 504.9694; **IR (cm^{-1}):** 1484, 1557, 1589, 2924,2952, 3028, 3060; **^{1}H-NMR:** δ 0.86 (3 H, t *J* 7.0), 1.26 (6 H, m), 1.54 (2 H, qui *J* 7.0), 3.60 (2 H, t *J* 7.0), 6.73 (4 H, d *J* 9.0), 7.51 (4 H, d *J* 9.0); **^{13}C-NMR:** δ 14.0 (CH$_3$), 22.6 (CH$_2$), 26.6 (CH$_2$), 27.1 (CH$_2$), 31.5 (CH$_2$), 52.2 (CH$_2$), 83.9 (2 sp^2-C), 129.0 (4 sp^2-CH), 138.1 (4 sp^2-CH), 147.1 (2 sp^2-C).

4,4′-bistrimethylsilylethynyl-N-hexyldiphenylamine, 7

A 1000 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with 4,4′-diiodo-N-hexyldiphenylamine (6.00 g, 11.9 mmol), PdCl$_2$(PPh$_3$)$_2$ (82 mg, 0.12 mmol) and CuI (22 mg, 0.12 mmol) in triethylamine (25 mL) and toluene (20 mL). Trimethylsilylacetylene (2.56 g, 26.1 mmol) was added dropwise to this stirred solution. After 12 h, the mixture was filtered and the filtrate was washed with 1 M HCl (2 × 30 mL). The solvent was removed and the residue was eluted through a flash silica gel column by hexane. The product was collected and the solvent was removed. The product was dried under vacuum for 24 h to give the desired product (5.29 g, 100%) as a yellow oil. **HIRES EI:** calcd for $C_{24}H_{39}NSi_2$ 445.2621, measured 445.2633; **IR (cm^{-1}):** 1498, 1594, 2188, 2856, 2927, 2953, 3038; **^{1}H-NMR:** δ 0.22 (18 H, s), 0.85 (3 H, t *J* 7.0), 1.25 (6 H, m), 1.59 (2 H, qui *J* 7.0), 3.65 (2 H, t *J* 7.0), 6.87 (4 H, d *J* 9.0), 7.33 (4 H, d *J* 9.0); **^{13}C-NMR:** δ 0.1 (3 CH_3), 14.0 (CH_3), 22.6 (CH_2), 26.6 (CH_2), 27.3 (CH_2), 31.5 (CH_2), 52.1 (CH_2), 93.0 (2 sp-C), 105.4 (2 sp-C), 115.5 (2 sp^2-C), 120.4 (4 sp^2-CH), 133.1 (4 sp^2-CH), 147.4 (2 sp^2-C).

4,4′-diethynyl-N-hexyldiphenylamine, 8

A 1000 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with 4,4′-bistrimethylsilylethynyl-N-hexyldiphenylamine (4.62 g, 10.4 mmol) in methanol/isopropanol (50 mL/50mL). Saturated KOH aqeous solution (0.2 mL) was added dropwise to this stirred solution. After 30 min the mixture was neutralized by 1M HCl before water (50 mL) and hexane (50 mL) were added. The organic layer was separated and the aqeous layer was extracted with hexane (2 × 30 mL). The combined organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed. The residue was eluted through a flash silica gel column by hexane. The solvent was removed and the product was dried under vacuum for 24 h to give the desired product (2.84 g 91%) as a yellow oil. **HIRES EI:** calcd for $C_{22}H_{23}N$ 301.1839, measured 301.1839; **UV ($CHCl_3$, nm):** 339, 279; **IR (GC-IR):** 1504, 2106, 2938, 3331; **^{1}H-NMR:** δ 0.87 (3 H, t *J* 7.0), 1.28 (6 H, m), 1.63 (2 H, qui *J* 7.5), 3.02 (H, s), 3.68 (2 H, t *J* 7.5), 6.93 (4 H, d *J* 9.0), 7.38 (4 H, d *J* 9.0); **^{13}C-NMR:** δ 14.0 (CH_3), 22.6 (CH_2), 26.6 (CH_2), 27.3 (CH_2), 31.5 (CH_2), 52.1 (CH_2), 76.2 (2 sp-CH), 83.8 (2 sp-C), 114.5 (2 sp^2-C), 120.5 (4 sp^2-CH), 133.2 (4 sp^2-CH), 147.6 (2 sp^2-C).

Poly-4,4′-ethynylene-N-hexyldiphenylamine (Polymer 1)

A 100 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with 4,4′-diethynyl-N-hexyldiphenylamine (0.30 g, 1 mmol), 4,4′-diiodo-N-hexyldiphenylamine (0.50 g, 1 mmol), DBU (1 mL), toluene (20 mL) and triethylamine (20 mL). $PdCl_2(PPh_3)_2$ (14 mg, 0.02 mmol) and CuI (14 mg, 0.07 mmol) were added quickly to this stirred solution, After 16 h, the mixture was warmed to 50°C and the stirring was continued for 6 h. The mixture was allowed to cool to ambient temperature and was then filtered. The solid was washed several times with warm toluene and the combined filtrate was concentrated to 40 mL and was then dropped into methanol (200 mL). The yellow precipitate was collected and reprecipitated in methanol from toluene solution. The yellow precipitate was dried under vacuum at 65°C for 24 h to give the desired polymer (0.52 g, 94%). **UV (THF, nm):** $\lambda_{max} = 389$; **IR (cm^{-1}):** 1510, 1598, 2210, 2856, 2926, 2953, 3038; **^{1}H-NMR:** δ 0.87 (3 H, br.), 1.29 (6 H, br.), 1.64 (2 H, br.), 3.70 (2 H, br.), 6.96 (4 H, d *J* 8.5), 7.39 (4 H, d *J* 8.5); **^{13}C-NMR:** δ 14.0 (CH_3), 22.6 (CH_2), 26.7 (CH_2), 27.4 (CH_2), 31.6 (CH_2), 52.2 (CH_2), 88.8 (2 sp-C), 116.0 (2 sp^2-C) 120.5 (4 sp^2-CH), 132.4 (4 sp^2-CH), 147.0 (2 sp^2-C); **GPC:** $M_n = 3.09 \times 10^4$, $M_w = 5.24 \times 10^4$, $M_w/M_n = 1.70$, IV = 0.63 dl/g.

Polymer 2

A 100 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with 4,4′-diethynyl-N-hexyldiphenylamine (0.30 g, 1 mmol), 1,4-diiodobenzene (0.33 g, 1 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.020 mmol), CuI (10 mg, 0.052 mmol) and toluene (15 mL). DBU (0.8 mL) was added dropwise to this stirred solution. After 20 min., 40 min and

60 min additional toluene (5 mL) was added to the mixture to prevent a precipitation of the forming polymer. After 6 h, the mixture was filtered. The precipitate was washed several times with warm toluene and the combined filtrate was concentrated to 40 mL and then dropped into methanol (200 mL). The yellow precipitate was collected and reprecipitated in methanol from THF (40 mL) solution. The precipitate was dried under vacuum at 65°C for 24 h to give **2** (0.36 g, 97%). **UV (THF, nm):** $\lambda_{max} = 400$; **IR** (cm^{-1}): 1498, 1594, 2210, 2856, 2927, 2954, 3038; **^{1}H-NMR:** δ 0.86 (3 H, br.), 1.29 (6 H, br.), 1.64 (2 H, br.), 3.73 (2 H, br.), 4.01 (4 H, br.), 6.98 (4 H, d *J* 8.0), 7.42 (4 H, d J 8.0), 7.46 (4 H, s); **^{13}C-NMR:** δ 14.0 (CH_3), 22.6 (CH_2), 26.7 (CH_2), 27.4 (CH_2), 31.6 (CH_2), 52.2 (CH_2), 88.5 (2 sp-C), 91.5 (2 sp-C), 115.5 (2 sp^2-C), 120.7 (4 sp^2-CH), 123.0 (2 sp^2-C), 131.3 (4 sp^2-CH), 132.8 (4 sp^2-CH), 147.4 (2 sp^2-C); **GPC:** $M_n = 1.03 \times 10^4$, $M_w = 3.16 \times 10^4$, $M_w/M_n = 3.07$, IV = 0.96 dl/g.

Polymer 3

A 100 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with 4,4′-diethynyl-N-hexyldiphenylamine (0.30 g, 1 mmol), 1,4-diiodobenzene (0.53 g, 1 mmol), $PdCl_2(PPh_3)_2$ (10 mg, 0.014 mmol), CuI (5 mg, 0.026 mmol) and toluene (10 mL). DBU (0.9 mL) was added dropwise to this stirred solution. After 30 min toluene (15 mL) was added to the mixture. After 16 h, the mixture was filtered. The solid was washed several times with warm toluene and the combined filtrate was concentrated to 40 mL by rotating evaporation. The concentrated filtrate was dropped into methanol (200 mL). The yellow precipitate was collected and reprecipitated in methanol from THF (40 mL) solution.

The precipitate was dried under vacuum at 65°C for 24 h to give 4 (0.54 g, 93%).UV (**THF, nm):** $\lambda_{max} = 416$; **^{1}H-NMR:** δ 0.88 (9 H, br.), 1.29-1.34 (14 H, m.), 1.54 (4 H, br.), 1.65 (2 H, br.), 1.83 (4 H, qui *J* 7.0), 3.71 (2 H, br.), 4.01 (4 H, t *J* 7.0.), 6.96 (4 H, d *J* 8.0), 6.98 (2 H, s), 7.42 (4 H, d *J* 8.0); **^{13}C-NMR:** δ 14.1 (3 CH_3), 22.6 (3 CH_2), 25.7 (2 CH_2), 26.7 (CH_2), 27.4 (CH_2), 29.3 (2 CH_2), 31.6 (3 CH_2), 52.2 (CH_2), 69.6 (2 CH_2), 85.3 (2 sp-C), 95.1 (2 sp-C), 114.0 (2 sp^2-C), 116.0 (2 sp^2-C), 116.8 (2 sp^2-CH), 120.5 (4 sp^2-CH), 132.7 (4 sp^2-CH), 147.3 (2 sp^2-C), 153.5 (2 sp^2-C); **GPC:** $M_n = 1.68 \times 10^4$, $M_w = 2.68 \times 10^4$, $M_w/M_n = 1.60$, IV = 0.62 dl/g.

Polymer 4

A 100 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with 4,4′-diethynyl-N-hexyldiphenylamine (0.51 g, 1.7 mmol), 2,5-diiodo-1,4-dioctoxybenzene (0.99 g, 1.7 mmol), DBU (1 mL), toluene (40 mL) and triethylamine (20 mL). $PdCl_2(PPh_3)_2$ (26 mg, 0.037 mmol) and CuI (26 mg, 0.14 mmol) were added quickly to this stirred solution. After 16 h, the mixture was warmed to 50°C and the stirring was continued for 6 more hour. The mixture was allowed to cool to ambient temperature and was then filtered. The solid was washed several times with warm toluene and the combined filtrate was concentrated to 50 mL and was then dropped into methanol (250 mL). The yellow precipitate was collected and reprecipitated in methanol from a toluene solution. The precipitate was dried under vacuum at 65°C for 24 h to give 4 (0.95 g, 89%). **UV (THF, nm):** $\lambda_{max} = 414$; **IR (cm^{-1}):** 1512, 1594, 2142, 2203, 2855, 2925, 2952, 3037; **^{1}H-NMR:** δ 0.85 (9 H, br.), 1.27 (22 H, br.), 1.54 (4 H, br.), 1.64 (2 H, br.), 1.83 (4 H, br), 3.70 (2 H, br.), 4.01 (4 H br.), 6.98 (6 H, br.), 7.40 (4 H, br); **^{13}C-NMR:** δ 14.0 (CH_3), 14.1 (2 CH_3), 22.6 (CH_2), 22.7 (2 CH_2), 26.1 (2 CH_2), 26.6 (CH_2), 27.4 (CH_2), 29.3 (2 CH_2), 29.4 (4 CH_2), 31.6 (CH_2), 31.8 (2 CH_2), 52.3 (CH_2), 69.6 (2 CH_2), 85.3 (2 sp-C), 95.1 (2 sp-C), 114.0 (2 sp^2-C), 116.0 (2 sp^2-C), 116.8 (2 sp^2-CH), 120.5 (4 sp^2-CH), 133.8 (4 sp^2-CH), 147.3 (2 sp^2-C), 153.5 (2 sp^2-C); **GPC:** $M_n = 2.58 \times 10^4$, $M_w = 6.27 \times 10^4$, $M_w/M_n = 2.43$, IV = 0.38 dl/g.

Poly-4,4′-butadiynylene-N-hexyldiphenylamine (polymer 12)

A 25 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with CuCl (0.50g, 5.1 mmol) and 9 mL THF. Tetramethylethylenediamine, TMEDA, (0.25 mL, 1.7 mmol) was added to this stirred solution. After 45 min the solution was allowed to settle, leaving a clear deep blue-green solution of the CuCl·TMEDA complex.

Another 100 mL flask, equipped with a magnetic stirring bar, thermometer, cold-finger condenser and O_2 inlet-outlet tubes, containing THF (10 mL) and 4-ethynyl-N,N-dimethylanilne (1.16 g, 38 mmol) was charged with a rapid stream of O_2. The solution of CuCl·TMEDA complex (2 mL) freshly prepared as described above was added dropwise to this stirred solution. The temperature was maintained at 35^0-45^0. THF (10 mL) was added again after 30 min and 1 h to prevent a precipitation of the polymer. After 5 h, the solution was filtered and the solid was washed several times with THF. The filtrate was combined and concentrated to 50 mL before dropping into methanol (200 mL). The yellow polymer was collected and reprecipitated in methnol from THF solution. The polymer precipitate was dried under vacuum at 65°C for 24 h to yield **12** (0.99 g, 87%). **UV (THF, nm):** $\lambda_{max} = 399$; **IR (cm^{-1}):** 1590, 1605, 2143, 2207, 2858, 2928, 2956, 3038; **^{1}H-NMR:** δ 0.85 (3 H, br.), 1.27

(6 H, br.), 1.59 (2 H, br.), 3.69 (2 H br.), 6.93 (4 H, d *J* 8.0), 7.39 (4 H, d *J* 8.0); **^{13}C-NMR:** δ 14.0 (CH_3), 22.6 (CH_2), 26.6 (CH_2), 27.4 (CH_2), 31.5 (CH_2), 52.3 (CH_2), 73.6 (2 sp-C), 81.9 (2 sp-C), 114.4 (2 sp^2-C) 120.6 (4 sp^2-CH), 133.7 (4 sp^2-CH), 147.0 (2 sp^2-C); **GPC:** $M_n = 4.99 \times 10^4$, $M_w = 7.00 \times 10^4$, $M_w/M_n = 1.40$, IV = 0.78 dl/g.

N-octylcarbazole, 13

A 500 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with carbazole (16.7 g, 0.100 mol), pulverized 87% KOH (38.7 g, 0.600 mol), K_2CO_3 (20.7 g, 0.150 mol), tetrabutylammonium bromide (3.22 g, 10 mmol) and toluene (200 mL). 1-Bromooctane (19.3 g, 0.100 mol) was added slowly to this stirred solution. After 16 h of reflux, the mixture was allowed to cool to room temperature and was filtered. The filtrate was washed with 1M HCl (2 × 100 mL) and dried over anhydrous $MgSO_4$. The solvent was removed and the remaining yellow oil was eluted through flash silica gel columns by hexane. The product was collected and the solvent was removed to give 13 (28.3 g, 98 %) as a light yellow liquid. **^{1}H-NMR:** δ 1.18 (3 H, t *J* 7.0), 1.49-1.57 (10 H, m), 2.04 (2 H, qui *J* 7.0), 4.40 (2 H, t *J* 7.0), 7.50 (2 H, t *J* 8.0), 7.60 (2 H, d *J* 8.0), 7.72 (2 H, t *J* 8.0), 8.37 (2 H, d *J* 8.0); **^{13}C-NMR:** δ 14.3 (CH_3), 22.7 (CH_2), 27.2 (CH_2), 28.9 (CH_2), 29.4 (CH_2), 29.5 (CH_2), 31.9 (CH_2), 42.4 (CH_2), 108.4 (2 sp^2-CH), 118.3 (2 sp^2-CH), 120.1 (2 sp^2-CH), 122.1 (2 sp^2-C), 125.3 (2 sp^2-CH), 139.8 (2 sp^2-C).

3,6-diiodo-N-octylcarbazole, 14

A 500 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with N-octylcarbazole (6.40 g, 23 mmol), $CaCO_3$ (11 g, 0.11 mol), methylene chloride (150 mL) and methanol (50 mL). A solution of iodinemonochloride (ICl) in methylene chloride (1M, 46 mL, 46 mmol) was added dropwise to this stirred solution. After 8 h, another portion of 1 M ICl (10 mL, 10 mmole) was added. After additional 8 h of stirring, the mixture was added with 20% $NaHSO_3$ solution until the mixture became pale yellow. The organic layer was separated and the aqueous layer was extracted with methylene chloride (2 × 50 mL). The combined organic layer was washed with water (2 × 100 mL) and dried over anhydrous $MgSO_4$. The solvents were removed and the resulting solid was crystallized from acetone and dried under vacuum at 65 °C for 24 h to give 14 (10.9 g, 90%) as a white solid. **m.p.:** 96°C; **HIRES EI:** calcd for $C_{20}H_{24}NI_2$ (M+H) 531.9998, measured 531.9792; **IR (cm^{-1}):** 1497, 2852, 2924, 2952; **^{1}H-NMR:** δ 0.85 (3 H, t *J* 7.0), 1.21-1.28 (10 H, m), 1.78 (2 H, qui *J* 7.0), 4.15 (2 H, t *J* 7.0), 7.12 (2 H, d *J* 8.5), 8.27 (2 H, dd *J* 8.5, 1.5), 8.28 (2 H, d *J* 1.5); **^{13}C-NMR:** δ 14.0 (CH_3), 22.6 (CH_2), 27.2 (CH_2), 28.8 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 31.7 (CH_2), 43.2 (CH_2), 81.6 (2 sp^2-C), 110.8 (2 sp^2-CH), 123.9 (2 sp^2-C), 129.3 (2 sp^2-CH), 134.4 (2 sp^2-CH), 139.4 (2 sp^2-C).

3,6-bistrimethylsilylethynyl-N-octylcarbazole, 15

A 250 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with 3,6-diiodo-N-octylcarbazole (5.31 g, 10.0 mmol), $PdCl_2(PPh_3)_2$ (56 mg, 0.080 mmol), CuI (38 mg, 0.20 mmol), triethylamine (35 mL) and toluene (35 mL).

Trimethylsilylacetylene (2.06 g, 21 mmol) was added dropwise to this stirred solution. After 12 h, the mixture was filtered and the filtrate was washed with 1 M HCl (2 × 30 mL). The solvent was removed and the residue was eluted through a flash silica gel column by hexane. The product was collected and the solvent was removed. The product was dried under vacuum for 24 h to give the desired product (3.86 g, 82%) as a white solid. **^{1}H-NMR:** δ 0.31 (9 H, s), 0.87 (3 H, t *J* 7.0), 1.23-1.30 (10 H, m), 1.81 (2 H, qui *J* 7.0), 4.21 (2 H, t *J* 7.0), 7.27 (2 H, d *J* 8.5), 7.57 (2 H, dd *J* 8.5, 1.5), 8.20 (2 H, d *J* 1.5); **^{13}C-NMR:** δ 0.16 (3 CH_3), 14.0 (CH_3), 22.6 (CH_2), 27.2 (CH_2), 28.9 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 31.7 (CH_2), 43.2 (CH_2), 92.0 (sp-C), 106.4 (sp-C), 108.7 (2 sp^2-CH), 113.7 (2 sp^2-C), 122.3 (2 sp^2-C), 124.6 (2 sp^2-CH), 129.9 (2 sp^2-CH), 140.5 (2 sp^2-C)

3,6-diethynyl-N-octylcarbazole, 16

A 100 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with 3,6-bistrimethylsilylethynyl-N-octylcarbazole (1.43 g, 3 mmol) in methanol/ isopropanol (20 mL/ 20mL). Saturated KOH aqueous solution (0.1 mL) was added dropwise to this stirred solution. After 30 min the mixture was neutralized by 1M HCl before water (20 mL), toluene (10 mL) and hexane (20 mL) were added. The organic layer was separated and the aqeous layer was extracted with hexane (2 × 30 mL). The combined organic layer was dried over anhydrous $MgSO_4$ and the solvent was removed. The residue was eluted through a flash silica gel column by hexane. The solvent was removed and the product was dried under vacuum for 24 h to give **16** (0.73 g 70%) as a yellow solid. **mp:** 65°C, **HIRES EI:** calcd for $C_{24}H_{25}N$ 327.1983, measured 327.1987, **IR (cm^{-1}):** 1598, 1630, 2104, 2854, 2926, 2954, 3306, ^{1}**H-NMR:** δ 0.86 (3 H, t *J* 7.0), 1.24-1.29 (10 H, m), 1.78 (2 H, qui *J* 7.0), 3.09 (H, s), 4.16 (2 H, t *J* 7.0), 7.26 (2 H, d *J* 8.5), 7.57 (2 H, dd *J* 8.5, 1.5), 8.18 (2 H, d *J* 1.5); ^{13}**C-NMR:** δ 14.0 (CH_3), 22.5 (CH_2), 27.1 (CH_2), 28.8 (CH_2), 29.1 (CH_2), 29.2 (CH_2), 31.7 (CH_2), 43.2 (CH_2), 75.4 (sp-CH), 84.7 (sp-C), 108.8 (2 sp^2-CH), 112.6 (2 sp^2-C), 122.1 (2 sp^2-C), 124.6 (2 sp^2-CH), 130.0 (2 sp^2-CH), 140.5 (2 sp^2-C)

Polymer <u>17</u>

A 100 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with 3,6-diethynyl-N-octylcarbazole (0.33 g, 1 mmol), 3,6-diiodo-N-octylcarbazole (0.53 g, 1 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.020 mmol), CuI (12 mg, 0.063 mmol) and toluene (20 mL). DBU (1.0 mL) was added dropwise to this stirred solution. Toluene (10 mL) was added after 20 min and 30 min. After 20 h, the mixture was filtered. and the solid was washed several times with warm toluene. The combined filtrate was concentrated to 40 mL and was then dropped into methanol (200 mL). The white precipitate was collected and reprecipitated in methanol from THF (40 mL) solution. The precipitate was dried under vacuum at 65°C for 24 h to give <u>17</u> (0.48 g, 79%). **UV (THF, nm):** λ_{max} = 270, 316, 366; **IR (cm^{-1}):**1601, 1629, 2853, 2925, 2952, 3049; ^{1}**H-NMR:** δ 0.81 (3 H, br.), 1.22-1.25 (10 H, br., m.), 1.75 (2 H, br.), 4.09 (2 H, br.), 7.23 (4 H, d *J* 8.5), 7.64 (2 H, d *J* 8.5), 8.26 (4 H, s); ^{13}**C-NMR:** δ 14.1 (CH_3), 22.6 (CH_2), 27.2 (CH_2), 28.9 (CH_2), 29.2 (CH_2), 29.3 (CH_2), 31.8 (CH_2), 43.1 (CH_2), 89.0 (2 sp-C), 108.8 (2 sp^2-CH), 114.3 (2 sp^2-C), 122.5 (2 sp^2-C), 123.8 (2 sp^2-CH), 129.5 (2 sp^2-CH), 140.0 (2 sp^2-C); **GPC:** $M_n = 1.19 \times 10^4$, $M_w = 4.43 \times 10^4$, $M_w/M_n = 3.73$, IV = 0.21 dl/g.

Polymer 18

A 100 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with 3,6-diethynyl-N-octylcarbazole (0.33 g, 1 mmol), 4,4′-diiodo-N-octylcarbazole (0.50 g, 1 mmol), $PdCl_2(PPh_3)_2$ (14 mg, 0.020 mmol), CuI (10 mg, 0.053 mmol) and toluene (20 mL). 1,8-Diazabicyclo[5.4.0]undec-7-ene DBU (1.0 mL) was added dropwise to this stirred solution. Toluene (10 mL) was added after 10 min and 30 min. After 20 h, the mixture was filtered and the solid was washed several times with warm toluene. The combined filtrate was concentrated to 40 mL and was then dropped into methanol (200 mL). The brownish yellow precipitate was collected and reprecipitated in methanol from THF (40 mL) solution. The precipitate was dried under vacuum at 65°C for 24 h to give 18 (0.49 g, 84%). **UV (THF, nm):** $\lambda_{max} = 270, 314, 368$; **IR(cm^{-1}):** 1507, 1598, 2205, 2853, 2925, 2952, 3037; **^{1}H-NMR:** δ 0.87 (6 H, br.), 1.23-1.30 (16 H, br. m.), 1.67 (2 H, br.), 1.84 (2 H, br.), 3.73 (2 H, br.), 4.24 (2 H, br.), 7.00 (4 H, d *J* 7.5), 7.32 (2 H, d *J* 8.0), 7.48 (4 H, d *J* 7.5), 7.62 (2 H, d *J* 8.0), 8.25 (2 H, s); **^{13}C-NMR:** δ 14.0 (CH_3), 14.1 (CH_3), 22.6 (CH_2), 22.7 (CH_2), 26.7 (CH_2), 27.2 (CH_2), 27.4 (CH_2), 28.9 (CH_2), 29.1 (CH_2), 29.3 (CH_2), 31.6 (CH_2), 31.7 (CH_2), 43.3 (CH_2), 52.2 (CH_2), 88.0 (2 sp-C), 89.7 (2 sp-C), 108.9 (2 sp^2-CH), 114.2 (2 sp^2-C), 116.2 (2 sp^2-C) 120.6 (4 sp^2-CH), 122.5 (2 sp^2-C), 123.9 (2 sp^2-CH), 129.5 (2 sp^2-CH), 132.6 (4 sp^2-CH), 140.2 (2 sp^2-CH) 147.0 (2 sp^2-C); **GPC:** $M_n = 1.08 \times 10^4$, $M_w = 3.70 \times 10^4$, $M_w/M_n = 3.41$, IV = 0.24 dl/g.

4,4′-dicyano-N-hexyldiphenylamine, 25

A mixture of 4,4′-diiododiphenylamine (14.68 g, 30 mmol) and copper cyanide (8.06 g, 90 mmol) in DMF (100 mL) was refluxed under Ar. After 48 h, the mixture was allowed to cool to ambient temperature and was then added with 1 M KOH solution (150 mL) and ether (150 mL). The organic layer was separated and the aqueous was extracted with ether (2 × 100 mL). The combined organic layer was washed with water (2 × 200 mL) and was dried over anhydrous Na_2SO_4. The solvent was removed and the residue was eluted through a flash silica gel column by methylene chloride/hexane, 50/50. The product was collected and the solvent was removed. The obtained solid was crystallized from hexane and dried under vacuum to yield 25 (7.10 g, 78%) as white needles. **mp:** 74.5-75.5°C, **HIRES EI:** calcd for $C_{20}H_{21}N_3$ 303.1736, measured 303.1728; **IR (cm^{-1}):** 1504, 1554, 1595, 1612, 2219, 2858, 2930, 2955, 3046, 3094; **^{1}H-NMR:** δ 0.83 (3 H, t *J* 7.0), 1.27 (6 H, m), 1.62 (2 H, qui *J* 7.0), 3.74 (2 H, t *J* 7.0), 7.04 (4 H, d *J* 9.0), 7.52 (4 H, d *J* 9.0); **^{13}C-NMR:** δ 13.8 (CH_3), 22.4 (CH_2), 26.4 (CH_2), 27.1 (CH_2), 31.3 (CH_2), 52.2 (CH_2), 104.7 (2 CN), 119.0 (4 sp^2-C), 120.9 (2 sp^2-CH), 133.5 (4 sp^2-CH), 150.0 (2 sp^2-C).

4,4′-diformyl-N-hexyldiphenylamine, 26

A 250 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with a solution of 1 M lithium aluminium hydride in ether (24 mL, 24 mmol). Ethyl acetate (36 mL, 36 mmol) was added dropwise to this stirred solution at 3-7 °C. After 1 h at 0 °C, 4,4′-dicyano-N-hexyldiphenyl amine (3.03 g, 10 mmol) in ether (10mL) was added dropwise to the mixture. After an additional 1.5 h at 0 °C, the resulting yellow slurry was then quenched with 1 M sulfuric acid (50 mL). After 30 min the organic layer was separated and the aqueous was extracted with ether (3 × 20 mL). The combined organic layer was washed with saturated $NaHCO_3$ solution (30 mL) and cold water (3 × 30 mL) and was dried over anhydrous Na_2SO_4. The solvent was removed and the residue was eluted through a flash silica gel column by gradient solvents, methylene chloride/ hexane, from 25/75 to 100/0. The product was collected and the solvent was removed. The obtained yellow oil was dried under vacuum to yield <u>26</u> (1.74 g, 56%). **HIRES EI:** calcd for $C_{20}H_{23}NO_2$ 309.1729, measured 309.1732; **IR (cm^{-1}):** 1508, 1561, 1587, 1607, 1691, 2730, 2856, 2928, 2955, 3069; **^{1}H-NMR:** δ 0.84 (3 H, t *J* 7.0), 1.27 (6 H, m), 1.66 (2 H, qui *J* 7.0), 3.81 (2 H, t *J* 7.0), 7.12 (4 H, d *J* 9.0), 7.78 (4 H, d *J* 9.0), 9.85 (2 H, s); **^{13}C-NMR:** δ 13.9 (CH_3), 22.5 (CH_2), 26.5 (CH_2), 27.4 (CH_2), 31.4 (CH_2), 52.5 (CH_2), 120.6 (4 sp^2-CH), 130.5 (2 sp^2-C), 131.5 (4 sp^2-CH), 151.8 (2 sp^2-C), 190.4 (2 sp^2-CHO).

Poly-4,4′-vinylene-N-hexyldiphenylamine (Polymer <u>24</u>)

In a dry 250 mL round bottom flask equipped with a magnetic stirring bar and reflux condenser, titaniumtetrachloride (6.14 g, 32.35 mmol) and THF (50 mL) were carefully mixed at about –40°C. Zinc powder (4.23 g, 64.7 mmol) was added slowly and the mixture was heated to reflux. The reflux was continued for 50 h. The mixture was allowed to cool to ambient temperature and was quenched by 10% K_2CO_3 solution. The resulting solution was filtered through celite and washed several times with methylene chloride. The combined filtrate was concentrated to 50 mL and was then dropped into methanol (200 mL). The yellow precipitate was collected and reprecipitated in acetone from a THF solution. The yellow precipitate was dried under vacuum at 65°C for 24 h to give the desired polymer (0.55 g, 35%). **UV (THF, nm):** $\lambda_{max} = 400$; **IR(cm^{-1}):**1508, 1599, 2854, 2926, 2952, 3025; **^{1}H-NMR:** δ 0.86 (3 H, br.), 1.28 (6 H, br.), 1.64 (2 H, br.), 3.68 (2 H br.), 6.93-6.96 (6 H, m), 7.38 (4 H, br. d); **^{13}C-NMR:** δ 14.0 (CH_3), 22.6 (CH_2), 26.7 (CH_2), 27.4 (CH_2), 31.6 (CH_2), 52.3 (CH_2), 120.9 (4 sp^2-CH), 126.1 (2 sp^2-CH), 127.2 (4 sp^2-CH), 130.8 (2 sp^2-C), 146.9 (2 sp^2-C); **GPC:** $M_n = 2.45 \times 10^4$, $M_w = 1.28 \times 10^5$, $M_w/ M_n = 5.22$, IV = 0.60 dl/g.

4-formyl-N-hexyldiphenylamine, 28

A 100 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with N-hexyldiphenylamine (2.53 g, 10 mmol), anhydrous dimethylformamide (1.60 g, 22 mmol) and 1,2-dichloroethane (25 mL). Phosphorusoxy chloride (3.37 g, 22 mmol) was added dropwise to this stirred solution at 0°C. After the addition was completed, the mixture was allowed to warm to room temperature. The mixture was then heated at 60°C for 4 h. The reaction mixture was allowed to cool to room temperature before it was poured into a precooled sturated sodium acetate solution (100 mL, 0 °C). The organic layer was separated and the aqueous layer was extracted with ether (2 x 30 mL). The combined organic layer was washed with water (50 mL) followed by saturated $NaHCO_3$ solution (2 x 50 mL) and was dried over anhydrous Na_2SO_4. The solvent was removed to yield the product (2.68g, 95%) as a yellow oil. This crude product was quite pure (>95% purity). However, further purification was done by flash chromatography using silica gel column and ethylacetate/ hexane (10/90) eluent. **HIRES EI:** calcd for $C_{19}H_{23}NO$ 281.1780, measured 281.1773; **IR (cm^{-1}):** 1514, 1586, 1602, 1684, 2694, 2728, 2807, 2857, 2928, 2955, 3030, 306; **^{1}H-NMR:** δ 0.86 (3 H, t

J 6.5), 1.28 (6 H, m), 1.68 (2 H, qui *J* 7.5), 3.70 (2 H, t *J* 7.5), 6.68 (2 H, d *J* 9.0), 7.19 (2 H, d *J* 7.5), 7.26 (H, t *J* 7.5), 7.42 (H, t *J* 7.5), 7.64 (2 H, d *J* 9.0), 9.71 (H, s); **^{13}C-NMR:** δ 13.9 (CH_3), 22.5 (CH_2), 26.5 (CH_2), 27.1 (CH_2), 31.5 (CH_2), 52.6 (CH_2), 113.2 (2 sp^2-CH), 126.2 (sp^2-C), 126.4 (sp^2-CH), 127.5 (2 sp^2-CH), 130.0 (2 sp^2-C), 131.7 (2 sp^2-CH), 145.6 (sp^2-C), 153.3 (sp^2-C), 190.1 (sp^2-CHO).

dimer <u>27</u>

The synthesis of dimer <u>27</u> from a reductive McMurry coupling reaction of 4-formyl-N-hexyldiphenylamine was performed in the same fashion as the polymerization of the diformyl monomer <u>26</u> to form polymer <u>24</u>. **Yield:** 55%; **^{1}H-NMR:** δ 0.86 (6 H, t *J* 7.0), 1.27 (12 H, m.), 1.64 (4 H, qui. *J* 7.0), 3.65 (4 H t *J* 7.0), 6.88-6.95 (8 H, m), 7.00 (4 H, d *J* 9.0), 7.22 (4 H, t *J* 9.0), 7.32 (4 H, d *J* 9.0); **^{13}C-NMR:** δ 14.0 (2 CH_3), 22.6 (2 CH_2), 26.7 (2 CH_2), 27.4 (2 CH_2), 31.5 (2 CH_2), 52.2 (2 CH_2), 119.8 (4 sp^2-CH), 121.6 (2 sp^2-CH), 121.7 (4 sp^2-CH), 125.8 (2 sp^2-CH), 127.0 (4 sp^2-CH), 129.2 (4 sp^2-CH), 130.1 (2 sp^2-C), 147.0 (2 sp^2-C); 147.7 (2 sp^2-C).

4,4′,4′′-triiodotriphenylamine, TI_3

A 500 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with triphenylamine (7.36 g, 30 mmol), chloroform (100 mL) and methanol (50 mL). $BTMAICl_2$ (34.47 g, 99 mmol) and $CaCO_3$ (18 g, 0.18 mol) was added quickly to this stirred solution. After 72 h of reflux, 20% $NaHSO_3$ solution was added to the mixture until the mixture became light green. The mixture was filtered and the filtrate was separated. The aqueous layer was extracted with methylene chloride (2 × 50 mL). The combined organic layer was washed with water (2 × 100 mL) and dried over anhydrous $MgSO_4$. The mixture was concentrated and the residue was eluted through a flash silica gel column by hexane. The solvents was removed and the resulting yellow oil was dried under vacuum at 65 °C for 24 h to give **TI_3** (12.30 g, 66%). **^{1}H-NMR:** δ 6.80 (6 H, d *J* 9.0), 7.52 (6 H, d *J* 9.0), **^{13}C-NMR:** δ 86.6 (3 sp^2-C), 126.0 (6 sp^2-CH), 138.4 (6 sp^2-CH), 146.5 (3 sp^2-C).

4-trimethylsilylethynyl-N,N,-dimethylaniline, ($SiEAMe_2$)

A 100 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with 4-iodo-N,N-dimethylaniline (2.47 g, 10 mmol), $PdCl_2(PPh3)_2$ (30 mg), CuI (19 mg), DBU (1.64 g) and toluene (30 mL). Trimethylsilylacetylene (1.08g, 11 mmol). was added dropwise to this stirred solution. After 2 h, the mixture was filtered and the precipitate was washed with toluene (3 × 15 mL). The combined filtrate was concentrated and the residue was eluted through a short alumina column by methylene chloride. The solvent was removed and the resulting yellow solid was dried under vacuum for 24 h to give the desired product (1.91 g, 88 %). The product was characterized only by GC-IR-MS. **IR (cm^{-1}):** 1515, 2150, 2806, 2963; **MS:** 217 (M^+), 202 (100%), 186, 172, 158, 101.

4-ethynyl-N,N-dimethylaniline, $EAMe_2$

A 100 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with trimethylsilylethynyl-N,N-dimethylaniline (1.5 g) and methanol (20 mL). Saturated KOH aqueous solution (0.2 mL) was added dropwise to this stirred solution. After

6 h, potassium bicarbonate solution (10%, 20 mL) and hexane (20 mL) was added to the mixture. The organic layer was separated and the aqueous layer was extracted with hexane (2 × 20 mL). The combined organic layer was washed with water (2 × 20 mL) and was then dried over anhydrous $MgSO_4$. The solvent was removed and the resulting yellow solid was dried under vacuum for 24 h to give **$EAMe_2$** (1.00 g, 95%). **m.p.:** 50-51 °C; **HIRES EI:** clcd for $C_{10}H_{11}N$ 145.0892, measured 145.0891; **UV ($CHCl_3$, nm):** 292; **IR(cm^{-1}):** 1516, 1605, 2814, 2895, 2097, 3266; **^{1}H-NMR (CD_3CN):** δ 2.93 (6 H, s), 3.19 (H, s), 6.65 (2 H, d *J* 9.0), 7.30 (2 H, d *J* 9.0); **^{13}C-NMR (CD_3CN):** δ 40.2 (2 CH_3), 76.2 (sp-CH), 85.3 (sp-C), 109.0 (sp^2-C), 112.6 (2 sp^2-CH), 133.7 (2 sp^2-CH), 151.5 (sp^2-C).

4,4′,4′′-Tris-(4-dimethylaminophenylethynyl)triphenylamine, G0

A 100 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with 4,4′,4′′-triiodotriphenylamine (0.62 g, 1 mmol), $PdCl_2(PPh3)_2$ (10 mg, 0.014 mmol), CuI (5 mg 0.026 mmol), 4-ethynyl-N,N-dimethylaniline (0.44 g, 3 mmol), toluene (20 mL) and THF (10 mL). DBU (0.5 mL) was added dropwise to this stirred solution. After 24 h, methanol (30 mL) was added to the mixture and was then filtered. The obtained yellow solid was reprecipitated in methanol from methylene chloride solution. The precipitate was dried under vacuum for 24 h to give **G0** (0.56 g, 83 %). **DSC(rt-400 °C, rate 20 °C/min):** endothermic at 133-152°C (144°C), exothermic at 152-171 °C (157 °C), m.p.range 268-287 °C (278 °C); **m.p.:** 267-269 °C; **HIRES EI:** $C_{48}H_{42}N_4$ 674.3410, measured 674.3414; **IR(cm^{-1}):** 1501, 1523, 1609, 2208, 2803, 2890, 3037; **UV (THF, nm):** λ_{max} =378; **^{1}H-NMR (CD_3CN):** δ 2.98 (18 H, s), 6.66 (6 H, d *J* 9.0), 7.04 (6 H, d *J* 9.0), 7.40 (6 H, d *J* 9.0), 7.41

(6 H, d *J* 9.0); **^{13}C-NMR (CD_3CN):** δ 40.1 (3 CH_3), 87.2 (3 sp-C), 90.3 (3 sp-C), 110.1 (3 sp^2-C), 111.8 (6 sp^2-CH), 118.6 (3 sp^2-C), 123.8 (6 sp^2-CH), 132.3 (6 sp^2-CH), 132.5 (6 sp^2-CH), 146.1 (3 sp^2-C), 149.9 (3 sp^2-C).

4-iodo-N,N-dibutylaniline, IABu$_2$

A 500 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with triphenylamine (10.27 g, 50 mmol) $CaCO_3$ (15.02 g, 0.15 mol) and methylene chloride (50 mL). A solution of $BTMAICl_2$ (18.11 g, 52 mmol) in methylene chloride/ methanol (80 mL/ 100 mL) was added dropwise to this stirred solution. After 24 h, 20% $NaHSO_3$ solution was added to the mixture until the mixture became light purple. The mixture was filtered and the filtrate was separated. The aqueous layer was extracted with methylene chloride (2 × 50 mL). The combined organic layer was washed with water (2 × 100 mL) and dried over anhydrous $MgSO_4$. The mixture was concentrated and the residue was eluted through a flash silica gel column by hexane. The solvents was removed and the resulting yellow oil was dried under vacuum at 65 °C for 24 h to give **IABu$_2$** (15.06 g, 91%). **^{1}H-NMR:** δ 0.94 (6 H, t *J* 7.5), 1.32 (4 H, sex *J* 7.5), 1.52 (4 H, qui *J* 7.5), 3.21 (2 H, t *J* 7.5), 6.40 (2 H, d *J* 9.0), 7.40 (2 H, d *J* 9.0); **^{13}C-NMR:** δ 14.0 (2 CH_3), 20.3 (2 CH_2), 29.2 (2 CH_2), 50.7 (2 CH_2), 75.3 (sp^2-C), 114.0 (2 sp^2-CH), 137.6 (2 sp^2-CH), 147.6 (sp^2-C).

4-ethynyl-N,N,-dibuthylaniline, EABu$_2$

A 100 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with 4-iodo-N,N-dibutylaniline (15.0 g, 45.3 mmol), $PdCl_2(PPh3)_2$ (100 mg, 0.142

mmol), CuI (50 mg, 0.263 mmol), trimethylsilyl acetylene (4.50 g, 45.8 mmol) and toluene (30 mL). DBU (7.0 mL) was added dropwise to this stirred mixture. After 24 h, the mixture was filtered and the solid was washed with toluene (3 × 15 mL). The combined filtrate was concentrated and the residue was eluted through a flash silica gel column by hexane. The solvent was removed and the resulting yellow oil was dried under vacuum for 24 h to give 4-trimethylsilylethynyl-N,N-dibutylaminobenzene. This trimethylsilylethynyl-N,N-dibutylaniline was dissolved in methanol (200 mL) and was flushed with Ar (to avoid a possible oxidative coupling reaction). Saturated KOH aqueous solution (0.5 mL) was added dropwise to this solution. After 12 h, water (100 mL) and hexane (50 mL) was added to the mixture. The organic layer was separated and the aqueous layer was extracted with hexane (2 × 50 mL). The combined organic layer was washed with water (2 × 50 mL) and was then dried over anhydrous $MgSO_4$. The solvent was removed and the resulting yellow oil was dried under vacuum for 24 h to give **EABu₂** (9.70 g, 93%). **HIRES EI:** calcd for $C_{16}H_{23}N$ 229.1833, measured 229.1830; **IR(cm^{-1}):** 1516, 1608, 2099, 2931, 2957, 3043, 3094, 3307; **^{1}H-NMR:** δ 0.96 (6 H, t *J* 7.5), 1.35 (4 H, sex *J* 7.5), 1.56 (4 H, qui *J* 7.5), 2.96 (H, s), 3.27 (4 H, t *J* 7.5), 6.54 (2 H, d *J* 9.0), 7.33 (2 H, d *J* 9.0); **^{13}C-NMR:** δ 13.9 (2 CH_3), 20.2 (2 CH_2), 29.2 (2 CH_2), 50.6 (2 CH_2), 74.3 (sp-CH), 85.0 (sp-C), 107.3 (sp^2-C), 111.0 (2 sp^2-CH), 133.3 (2 sp^2-CH), 148.1 (sp^2-C).

4,4′-diiodo-4′′-trimethylsilylethynyltriphenylamine, SiETI$_2$

A 500 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with of 4,4′,4′′-triiodotriphenylamine (24.00 g, 38.5 mmol), $PdCl_2(PPh_3)_2$ (68 mg, 0.097 mmol), CuI (34 mg, 0.18 mmol),trimethylsilyl acetylene (4.54 g, 46 mmol) and toluene (200 mL). DBU (7 mL, 46 mmol) was added dropwise to this stirred solution. After 24 h, the mixture was filtered and the solid was washed with toluene (3 × 30 mL). The combined filtrate was concentrated and the residue was eluted through a flash silica gel column by hexane. The product was collected and the solvent was removed. The resulting white solid was dried at 65 °C under vacuum for 24 h to give **SiETI$_2$** (9.54 g, 43%). **HIRES EI:** calcd for $C_{23}H_{22}NI_2Si$ (M+H) 593.9611, measured 593.9619; **IR(cm^{-1}):** 1483, 1503, 1583, 2153, 2956, 3035; **^{1}H-NMR:** δ 0.23 (9 H, s), 6.80 (4 H, d *J* 8.5), 6.93 (2 H, d *J* 8.5), 7.20 (2 H, d *J* 8.5), 7.52 (2 H, d *J* 8.5); **^{13}C-NMR:** δ 0.03 (3 CH_3), 86.8 (sp^2-C), 93.9 (sp-C), 104.8 (sp-C), 117.5 (2 sp^2-C), 123.1 (2 sp^2-CH), 126.3 (4 sp^2-CH), 133.2 (2 sp^2-CH), 138.4 (4 sp^2-CH), 146.5 (2 sp^2-C), 146.8 (sp^2-C).

4′′-trimethylsilylethynyl-4,4′-bis-(4-N,N-dibutylaminophenylethynyl) triphenyl amine, SiET(EABu$_2$)$_2$

A 250 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with **SiETI$_2$** (5.80 g, 10.0 mmol), $PdCl_2(PPh_3)_2$ (50 mg, 0.071 mmol), CuI (25 mg, 0.13 mmol), 4-dibutylaminoethynylbenzene (5.04 g, 22 mmol) and toluene (75 mL). DBU (4.0 mL, 27 mmol) was added dropwise to this stirred solution. After 36 h, the mixture was filtered and the solid was washed with toluene (3 × 30 mL). The combined filtrate was evaporated and the residue was eluted through a flash silica gel column by gradient solvents from pure hexane to methylene chloride/hexane (30/70). The product was collected and the solvent was removed. The resulting yellow solid was dried at 65 °C under vacuum for 24 h.

to give **SiET(EABu$_2$)$_2$** (6.10 g, 77%). **^{1}H-NMR:** δ 0.29 (9 H, s), 0.99 (12 H, t *J* 7.5), 1.38 (8 H, sex *J* 7.5), 1.58 (8 H, qui *J* 7.5), 3.29 (8 H, t *J* 7.5), 6.59 (4 H, d *J* 9.0), 7.00 (2 H, d *J* 8.5), 7.02 (4 H, d *J* 8.5), 7.36-7.42 (10 H, m); **^{13}C-NMR:** δ 0.07 (3 CH_3), 13.9 (4 CH_3), 20.2 (4 CH_2), 29.3 (4 CH_2), 50.5 (4 CH_2), 86.8 (2 sp-C), 90.7 (2 sp-C), 93.3 (sp-C), 105.1 (sp-C), 108.8 (2 sp^2-C), 111.1 (4 sp^2-CH), 117.0 (sp^2-C), 119.1 (2 sp^2-C), 123.0 (2 sp^2-CH), 124.0 (4 sp^2-CH), 132.2 (4 sp^2-CH), 132.6 (4 sp^2-CH), 132.9 (2 sp^2-CH), 145.6 (2 sp^2-C), 147.0 (sp^2-C), 147.6 (2 sp^2-C).

4″-ethynyl-4,4′-bis-(4-N,N-dibutylaminophenylethynyl)triphenylamine, ET(EABu$_2$)$_2$

A 250 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with **SiET(EABu$_2$)$_2$** (2.50 g, 5.7 mmol), THF (50 mL) and methanol (50 mL). Saturated KOH aqueous solution (0.5 mL) was added dropwise to this stirred solution. After 6 h, water (30 mL) and hexane (30 mL) was added to the mixture. The organic layer was separated and the aqueous layer was extracted with methylene chloride (2 × 30 mL). The combined organic layer was washed with water (2 × 30 mL) and was then dried over anhydrous $MgSO_4$. The solvent was removed and the resulting yellow solid was dried under vacuum for 24 h to give **ET(EABu$_2$)$_2$** (4.02 g, 98%). **^{1}H-NMR:** δ 0.99 (12 H, t *J* 7.5), 1.35 (8 H, sex *J* 7.5), 1.59 (8 H, qui *J* 7.5), 3.06 (H, s), 3.30 (8 H, t *J* 7.5), 6.60 (4 H, d *J* 9.0), 7.03 (2 H, d *J* 8.5), 7.05 (4 H, d *J* 8.5), 7.36-7.42 (10 H, m); **^{13}C-NMR:** δ 14.0 (4 CH_3), 20.2 (4 CH_2), 29.3 (4 CH_2), 50.6 (4 CH_2), 76.6 (sp-CH), 83.6 (sp-C), 86.8 (2 sp-C), 90.7 (2 sp-C), 108.7 (2 sp^2-C), 111.1 (4 sp^2-CH), 115.8 (sp^2-C), 119.2 (2 sp^2-C), 123.1 (2 sp^2-CH), 124.1 (4 sp^2-CH), 132.3 (4 sp^2-CH), 132.7 (4 sp^2-CH), 133.1 (2 sp^2-CH), 145.7 (2 sp^2-C), 147.4 (sp^2-

C), 147.7 (2 sp^2-C)

G1

A 50 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with **$ET(EABu_2)_2$** (0.60 g, 0.83 mmol), $PdCl_2(PPh_3)_2$ (10 mg, 0.014 mmol), CuI (5 mg, 0.026 mmol), 4,4′,4′′-triiodotriphenylamine (0.17 g, 0.27 mmol) and toluene (10 mL). DBU (0.20 mL, 1.4 mmol) was added dropwise to this stirred solution. After 36 h, the mixture was filtered and the solid was washed with toluene (3 × 10 mL). The combined filtrate was concentrated to 10 mL and was then dropped into 200 mL methanol. The obtained yellow precipitate was eluted through a flash silica gel column by methylene chloride/hexane (40/60). The product was collected and the solvent was removed. The resulting yellow solid was dried at 65 °C under vacuum for 24 h to give **G1** (0.610 g, 93%). **EI Mass:** calcd for $C_{174}H_{180}N_{10}$ 2411.45, measured 2411.47; **IR(cm^{-1}):** 1513, 1519, 1606, 2150, 2207, 2870, 2929, 2958, 3037, 3090; **UV (THF, nm):** $\lambda_{max} = 386$; **^{1}H-NMR:** δ 0.95 (36 H, t *J* 7.5), 1.35 (24 H, sex *J* 7.5), 1.58 (24 H, qui *J* 7.5), 3.27 (24 H, t *J* 7.5), 6.57 (12 H, d *J* 9.0), 7.02-7.07 (24 H, m), 7.33-7.42 (36 H, m); **^{13}C-NMR:** δ 14.0 (12 CH_3), 20.3 (12 CH_2), 29.3 (12 CH_2), 50.5 (12 CH_2), 86.8 (6 sp-C), 88.9 (3 sp-C), 89.3 (3 sp-C), 90.6 (6 sp-C), 108.8 (6 sp^2-C), 111.2 (12 sp^2-CH), 117.4 (3 sp^2-C), 118.1 (3 sp^2-C), 119.0 (6 sp^2-C), 123.5 (6 sp^2-CH), 124.0 (6 sp^2-CH), 124.1 (12 sp^2-CH), 132.3 (12 sp^2-CH), 132.6 (6 sp^2-CH), 132.7 (6 sp^2-CH), 132.8 (12 sp^2-CH), 145.9 (6 sp^2-C), 146.5 (3 sp^2-C), 146.8 (3 sp^2-C), 147.8 (6 sp^2-C); **GPC:** $M_n = 2.40 \times 10^3$, $M_w = 2.47 \times 10^3$, $M_w/M_n = 1.03$, IV = 0.08 dl/g; **DSC:** no transition before an exothermic transition (crosslinking) at 300°C

SiET[ET(EABu$_2$)$_2$]$_2$

A 100 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with **ET(EABu$_2$)$_2$** (4.02 g, 5.6 mmol), PdCl$_2$(PPh$_3$)$_2$ (40 mg, 0.057 mmol), CuI (20 mg, 0.11 mmol), **SiETI$_2$** (1.38 g, 2.32 mmol) and toluene (30 mL). DBU (0.90 mL, 6.1 mmol) was added dropwise. After 36 h, the mixture was filtered and the solid was washed with toluene (3 × 30 mL). The combined filtrate was evaporated to dryness. The residue was eluted through a flash silica gel column by gradient solvents, from pure hexane to methylene chloride/hexane (35/65). The product was collected and the solvent was removed. The resulting yellow solid was dried at 65 °C under vacuum for 24 h. to give **SiET[ET(EABu$_2$)$_2$]$_2$** (2.90 g, 70%). **^{1}H-NMR:** δ 0.26 (9 H, t *J* 7.5), 0.97 (24 H, t *J* 7.5), 1.36 (16 H, sex *J* 7.5), 1.58 (16 H, qui *J* 7.5), 3.28 (16 H, t *J* 7.5), 6.57 (8 H, d *J* 9.0), 7.01-7.06 (18 H, m), 7.34-7.42 (26 H, m); **^{13}C-NMR:** δ 0.0 (3 CH$_3$), 14.0 (8 CH$_3$), 20.3 (8 CH$_2$), 29.3 (8 CH$_2$), 50.6 (8 CH$_2$), 86.8 (4 sp-C), 88.8 (2 sp-C), 89.3 (2 sp-C), 90.6 (4 sp-C), 93.8 (sp-C), 104.9 (sp-C), 108.8 (4 sp^2-C), 111.1 (8 sp^2-CH), 117.3 (2 sp^2-C), 117.5 (sp^2-C), 118.2 (2 sp^2-C), 119.0 (4 sp^2-C), 123.4 (4 sp^2-CH), 123.7 (2 sp^2-CH), 124.0 (4 sp^2-CH), 124.1 (8 sp^2-CH), 132.3 (8 sp^2-CH), 132.5 (4 sp^2-CH), 132.6 (4 sp^2-CH), 132.7 (8 sp^2-CH), 133.1 (2 sp^2-CH), 145.8 (4 sp^2-C), 146.4 (2 sp^2-C), 146.8 (2 sp^2-C), 146.9 (sp^2-C), 147.8 (4 sp^2-C).

ET[ET(EABu$_2$)$_2$]$_2$

A 100 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with **SiET[ET(EABu$_2$)$_2$]$_2$** (2.70 g, 1.5 mmol), THF (30 mL) and methanol (20 mL). Saturated KOH aqueous solution (0.2 mL) was added dropwise to this stirred solution. After

6 h, the mixture was added with water (30 mL) and hexane (30 mL). The organic layer was separated and the aqueous layer was extracted with methylene chloride (2 × 30 mL). The combined organic layer was washed with water (2 × 30 mL) and was then dried over anhydrous $MgSO_4$. The solvent was removed and the resulting yellow solid was dried under vacuum for 24 h. to give **ET[ET(EABu$_2$)$_2$]$_2$** (2.55 g, 98%). **^{1}H-NMR:** δ 0.97 (24 H, t *J* 7.5), 1.36 (16 H, sex *J* 7.5), 1.58 (16 H, qui *J* 7.5), 3.28 (16 H, t *J* 7.5), 6.57 (8 H, d *J* 9.0), 7.03-7.06 (18 H, m), 7.34-7.43 (26 H, m); **^{13}C-NMR:** δ 14.0 (8 CH_3), 20.3 (8 CH_2), 29.3 (8 CH_2), 50.6 (8 CH_2), 76.8 (sp-C), 83.5 (sp-C), 86.8 (4 sp-C), 88.8 (2 sp-C), 89.3 (2 sp-C), 90.6 (4 sp-C), 108.8 (4 sp^2-C), 111.1 (8 sp^2-CH), 116.4 (sp^2-C), 117.3 (2 sp^2-C), 118.3 (2 sp^2-C), 119.0 (4 sp^2-C), 123.4 (4 sp^2-CH), 123.6 (2 sp^2-CH), 124.0 (4 sp^2-CH), 124.1 (8 sp^2-CH), 132.3 (8 sp^2-CH), 132.5 (4 sp^2-CH), 132.6 (4 sp^2-CH), 132.7 (8 sp^2-CH), 133.3 (2 sp^2-CH), 145.8 (4 sp^2-C), 146.3 (2 sp^2-C), 146.8 (2 sp^2-C), 147.2 (sp^2-C), 147.8 (4 sp^2-C).

G2

A 250 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with **ET[ET(EABu$_2$)$_2$]$_2$** (0.78 g, 0.43 mmol), $PdCl_2(PPh_3)_2$ (10 mg, 0.014 mmol), CuI (5 mg, 0.026 mmol), 4,4′,4′′-triiodotriphenylamine (80 mg, 0.13 mmol) and toluene (10 mL). DBU (0.10 mL, 0.70 mmol) was added dropwise to this stirred solution. After 36 h, the mixture was filtered and the solid was washed with toluene (3 × 10 mL). The combined filtrate was concentrated to 10 mL and was then dropped into 200 mL methanol. The obtained yellow precipitate was eluted through a flash silica gel column by gradient solvents, methylene chloride/hexane, from 20/80 to 45/55. The product was collected and the solvent was removed. The resulting yellow solid was dried at 65 °C under vacuum for 24 h. to give G2 (0.50 g, 73%). **MALDI Mass:** calcd for $C_{390}H_{384}N_{22}$ 5379, measured 5374; **UV (THF, nm):** $\lambda_{max} = 386$; **^{1}H-NMR:** δ 0.96 (72 H, t *J* 7.5), 1.35 (48 H, sex *J* 7.5), 1.57 (48 H, qui *J* 7.5), 3.27 (48 H, t *J* 7.5), 6.57 (24 H, d *J* 9.0), 7.03-7.08 (60 H, m), 7.33-7.43 (84 H, m); **^{13}C-NMR:** δ 14.0 (24 CH_3), 20.3 (24 CH_2), 29.3 (24 CH_2), 50.6 (24 CH_2), 86.8 (12 sp-C), 88.9 (6 sp-C), 89.1 (3 sp-C), 89.2 (3 sp-C), 89.3 (6 sp-C), 90.6 (12 sp-C), 108.8 (12 sp^2-C), 111.1 (24 sp^2-CH), 117.4 (6 sp^2-C), 117.9 (3 sp^2-C), 118.0 (3 sp^2-C), 118.1 (6 sp^2-C), 119.0 (12 sp^2-C), 123.5 (12 sp^2-CH), 123.9 (6 sp^2-CH), 124.0 (18 sp^2-CH), 124.1 (24 sp^2-CH), 132.3 (24 sp^2-CH), 132.5 (12 sp^2-CH), 132.6 (24 sp^2-CH), 132.7 (24 sp^2-CH), 145.9 (12 sp^2-C), 146.4 (6 sp^2-C), 146.5 (3 sp^2-C), 146.6 (3 sp^2-C), 146.8 (6 sp^2-C), 147.8 (12 sp^2-C); **GPC:** $M_n = 5.21 \times 10^3$, $M_w = 5.25 \times 10^3$, $M_w/M_n = 1.01$, IV = 0.12 dl/g; **DSC:** no transition before an exothermic transition (crosslinking) at 300°C

SiET[ET[ET(EABu$_2$)$_2$]$_2$]$_2$

A 250 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with **ET[ET(EABu$_2$)$_2$]$_2$** (2.50 g, 1.46 mmol), $PdCl_2(PPh_3)_2$ (20 mg, 0.028 mmol), CuI (10 mg, 0.052 mmol) and 4′′-trimethylsilylethynyl-4,4′-diidotriphenylamine (0.35 g, 59 mmol) in toluene (20 mL) under Ar was added dropwise, DBU (0.25 mL, 1.7 mmol). After 48 h. the mixture was filtered and the solid was washed with toluene (3 × 20 mL). The combined filtrate was concentrated to 20 mL and was then dropped into 200 mL methanol. The obtained yellow precipitate was eluted through a flash silica gel column by gradient solvents from methylene chloride/hexane (15/85) to (40/60). The product was collected and the solvent was removed. The resulting yellow solid was dried at 65 °C under vacuum for 24 h. to give **SiET[ET[ET(EABu$_2$)$_2$]$_2$]$_2$** (1.80 g, 81%). **^{1}H-NMR:** δ 0.26 (9 H, s), 0.96 (48 H, t *J* 7.5), 1.36 (32 H, sex *J* 7.5), 1.57 (32 H, qui *J* 7.5), 3.28 (32 H, t *J* 7.5), 6.57 (16 H, d *J* 9.0), 7.03-7.08 (42 H, m), 7.34-7.43 (58 H, m); **^{13}C-NMR:** δ 13.99 (16 CH$_3$), 20.2 (16 CH$_2$), 29.1 (16 CH$_2$), 50.6 (16 CH$_2$), 77.2 (sp-CH), 83.5 (sp-C), 86.8 (8 sp-C), 88.9 (4 sp-C), 89.0 (2 sp-C), 89.2 (2 sp-C), 89.3 (4 sp-C), 90.7 (8 sp-C), 108.8 (8 sp^2-C), 111.1 (16 sp^2-CH), 116.5 (sp-C), 117.4 (4 sp^2-C), 104.9 (sp-C), 117.6 (sp^2-C), 117.9 (2 sp^2-C), 118.0 (2 sp^2-C), 118.1 (4 sp^2-C), 119.0 (8 sp^2-C), 123.4 (8 sp^2-CH), 123.8 (2 sp^2-CH), 123.9 (4 sp^2-CH), 124.0 (12 sp^2-CH), 124.1 (16 sp^2-CH), 132.3 (16 sp^2-CH), 132.5 (8 sp^2-CH), 132.6 (16 sp^2-CH), 132.7 (16 sp^2-CH), 133.1 (2 sp^2-CH), 145.9 (8 sp^2-C), 146.4 (5 sp^2-C), 146.6 (2 sp^2-C), 146.8 (4 sp^2-C), 146.9 (2 sp^2-C), 147.8 (8 sp^2-C).

ET[ET[ET(EA)$_2$]$_2$]$_2$

Into a stirred solution of **SiET[ET[ET(EA)$_2$]$_2$]$_2$** (1.80 g, 0.42 mmol) in THF/methanol (30 mL/ 12 mL) under Ar was added dropwise, saturated KOH aqueous solution (0.1 mL). After 6 h, water (30 mL) and hexane (30 mL) were added to the mixture. The organic layer was separated and the aqueous layer was extracted with methylene chloride (2 × 30 mL). The combined organic layer was washed with water (2 × 30 mL) and was then dried over anhydrous MgSO$_4$. The solvent was removed and the resulting yellow solid was dried under vacuum for 24 h to give **ET[ET[ET(EA)$_2$]$_2$]$_2$** (1.74 g, 99%). **^{1}H-NMR:** δ 1.00 (48 H, t *J* 7.5), 1.38 (32 H, sex *J* 7.5), 1.60 (32 H, qui *J* 7.5), 3.08 (H, t *J* 7.5), 3.30 (32 H, t *J* 7.5), 6.60 (16 H, d *J* 9.0), 7.05-7.08 (42 H, m), 7.37-7.45 (58 H, m); **^{13}C-NMR:** δ 14.0 (16 CH$_3$), 20.3 (16 CH_2), 29.3 (16 CH_2), 50.6 (16 CH_2), 77.2 (sp-C), 83.5 (sp-C), 86.8 (8 sp-C), 88.9 (4 sp-C), 89.0 (2 sp-C), 89.2 (2 sp-C), 89.3 (4 sp-C), 90.6 (8 sp-C), 108.8 (8 sp^2-C), 111.1 (16 sp^2-CH), 116.5 (sp^2-C), 117.3 (4 sp^2-C), 117.8 (2 sp^2-C), 118.1 (6 sp^2-C), 119.0 (8 sp^2-C), 123.4 (8 sp^2-CH), 123.6 (2 sp^2-CH), 123.8 (4 sp^2-CH), 124.0 (12 sp^2-CH), 124.0 (16 sp^2-CH), 132.3 (16 sp^2-CH), 132.5 (8 sp^2-CH), 132.6 (12 sp^2-CH), 132.7 (20 sp^2-CH), 133.2 (2 sp^2-CH), 145.8 (8 sp^2-C), 146.3 (6 sp^2-C), 146.5 (2 sp^2-C), 146.7 (4 sp^2-C), 147.1 (sp^2-C), 147.7 (8 sp^2-C).

G3

Into a stirred solution of **ET[ET[ET(EA)$_2$]$_2$]$_2$** (1.742 g, 0.47 mmol), $PdCl_2(PPh_3)_2$ (25 mg, 0.035 mmol), CuI (10 mg, 0.052 mmol) and 4,4′,4′′-triiodotriphenylamine (82 mg, 0.13 mmol) in toluene (20 mL) under Ar was added dropwise, DBU (0.20 mL, 1.4 mmol). After 72 h, the mixture was filtered and the precipitate was washed with toluene (3 × 10 mL). The combined filtrate was concentrated to 10 mL and was then dropped into 200 mL methanol. The obtained yellow precipitate was eluted through a flash silica gel column by gradient solvents, methylene chloride/hexane, from 20/80 to 60/40. The product was collected and the solvent was removed. The resulting yellow solid was dried at 65 °C under vacuum for 24 h. to give an inseparable mixture of di- and tri- substituted products. **^{1}H-NMR:** δ 0.97 (144 H, t *J* 7.5), 1.34 (96 H, sex *J* 7.5), 1.58 (96 H, qui *J* 7.5), 3.29 (H, t *J* 7.5), 6.58 (48 H, d *J* 9.0), 7.04-7.09 (132 H, m), 7.37-7.45 (180 H, m); **^{13}C-NMR:** δ 14.0 (48 CH_3), 20.3 (48 CH_2), 29.3 (16 CH_2), 50.6 (16 CH_2), 86.8 (24 sp-C), 88.9 (12 sp-C), 89.0 - 89.2 (18 sp-C), 89.3 (12 sp-C), 90.6 (24 sp-C), 108.8 (24 sp^2-C), 111.1 (48 sp^2-CH), unassigned aromatic carbon peaks from 117.3- 132.7, 145.8 (24 sp^2-C), 146.2 (3 sp^2-C), 146.4 (12 sp^2-C), 146.5-146.7 (15 sp^2-C), 146.8 (12 sp^2-C), 147.7 (24 sp^2-C); **GPC:** bimodal with $M_n = 1.03 \times 10^4$, $M_w = 1.08 \times 10^4$, $M_w / M_n = 1.04$, IV = 0.14 dl/g.

PART II

REACTION OF ELECTRON-RICH ACETYLENES WITH TETRACYANOETHYLENE (TCNE)

INTRODUCTION

Introductory Remarks

Interest in organic electron donor-acceptor (EDA) complexes has increased considerably over the past four decades due greatly to the involvement of EDA complexation in numerous organic reactions and biochemical processes. EDA complexes are particularly important in the pioneering work on electrical conductivity of organic compounds. These studies initiated one of the most exciting subjects in materials chemistry; electrically conducting polymers.[1] Organic polymers are normally electrical insulators, but in certain polymers the conductivity can be greatly increased by doping, adding electron acceptors (p-dopants) or electron donors (n-dopants) to the polymers.[2] The dopants form EDA complexes with the polymers which can be observed by UV-Vis or near-IR spectroscopy.

Our design and synthesis of new series of N-interrupted polyphenyleneethynylene was originally intended for electrical conductivity and electroluminescent studies as specified in the previous chapter. Nevertheless, the study of EDA complexation by UV-Vis spectroscopy of various organic acceptors with this new class of polymers has led us to a discovery of a convenient route to synthesize electron donor-acceptor molecules of interest as second-order nonlinear optical (NLO) chromophores. Polymers containing these NLO chromophores arealso interesting as second harmonic generator (SHG) materials. This part of the thesis will be devoted to the discussion of this discovery and the application of this reaction with various electron-rich acetylenes.

Donor-Acceptor Complexes

Foster[3] defined electron donor-acceptor (EDA) complexes (also often referred to as charge-transfer complexes) as "a substance formed by the interaction of two or more component molecules (and/ or ions), which may have an independent crystal structure and which reversibly dissociate into its components, at least partially, in vapor phase and solution. This definition suggests that there is very little or no contribution from covalent binding in the ground state. However, there is a gradation from these weaker interactions to classical covalent bond formation". The interaction between an electron donor (D) and an electron acceptor (A) at ground state can be described in terms of a wave function of the form:[4a]

$$\psi_N(AD) = a\ \psi_0(A,D) + b\ \psi_1(A^- \text{-} D^+) \qquad (1)$$

where: $a^2 + 2\ ab\psi_0\psi_1 + b^2 = 1$

and at the corresponding excited state can be described as:

$$\psi_E(AD) = a^{\neq}\ \psi_1(A^- \text{-} D^+) - b^{\neq}\ \psi_0(A,D) \qquad (2)$$

where: $a^{\neq 2} - 2\ a^{\neq}b^{\neq}\psi_0\psi_1 + b^{\neq 2} = 1$

Two extreme cases of EDA complexes are molecular complexes and ionic complexes.[4a] According to equation (1), an EDA complex is a molecular complex when $a \gg b$ and it is an ionic complex when $b \gg a$. In the molecular complexes, also often called weak complexes, the interaction between a donor and acceptor is a weak intermolecular force such as a dipole-dipole, dipole-induced-dipole, London dispersion force or hydrogen bonding. There is also very little or no transfer of charge in the molecular complexes in the ground state. This type of complex possesses most of the individual molecular character of its components; the donor and the acceptor. The molecular character can be observed through the IR spectra of these complexes which are almost identical to the sum of the IR spectra of their components.[4b] The ionic complexes are the other extreme where there is a completed or almost completed transfer of an electron or electrons from donors to acceptors in the ground state complexes. These complexes have the character of the cations of donors and the anions of the acceptors which also can be observed by IR. Complexes which fall between these two extremes are called strong complexes. The degree of complexation in solution depends on the solvents, the donors, and acceptors. While the molecular complexes are commonly found in poorly ionizing solvents, the ionic complexes are formed from low ionization energy donors and high electron affinity acceptors in better ionizing solvents such as acetonitrile or ethanol.

An EDA complex can be observed spectroscopically (UV-Vis, IR, NMR and X-ray). The simplest and most common technique is UV-Vis spectroscopy. Brackman[4c] observed that a molecular complex still retains the electronic absorption of the components modified to a greater or lesser extent, together with one or more absorption bands characteristic of the complex as a whole. In practice, the absorption characteristics of the molecular complex in solution may not be easily observed since the complex will be partially dissociated into its components. This problem can sometimes be solved experimentally by making the optical measurements at low temperatures or in the solid state which will favor complex formation. The lowest absorption energy is usually the most important and is referred to as a charge-transfer (CT) transition energy. The CT transition energy, E_{CT}, depends on the ionization potential of the donor, I^D, and the electron affinity of the acceptor, E^A. A plot of E_{CT} for a set of complexes of a series of donors with a given acceptor, against the I^D of the donors is often a straight line. This linear relationship is also often found for the plot of E_{CT} for a set of complexes of a series of acceptors with a given donor, against the E^A of a series acceptors. Thus, the CT transition energies can be described as the equations shown below.[4d]

$$E_{CT} = aI^D + b \qquad (3)$$

where *a* and *b* are constant for a given acceptor and

$$E_{CT} = a'E^A + b' \qquad (4)$$

where *a'* and *b'* are constant for a given donor.

Chemistry of aromatic monoamines with electron acceptors

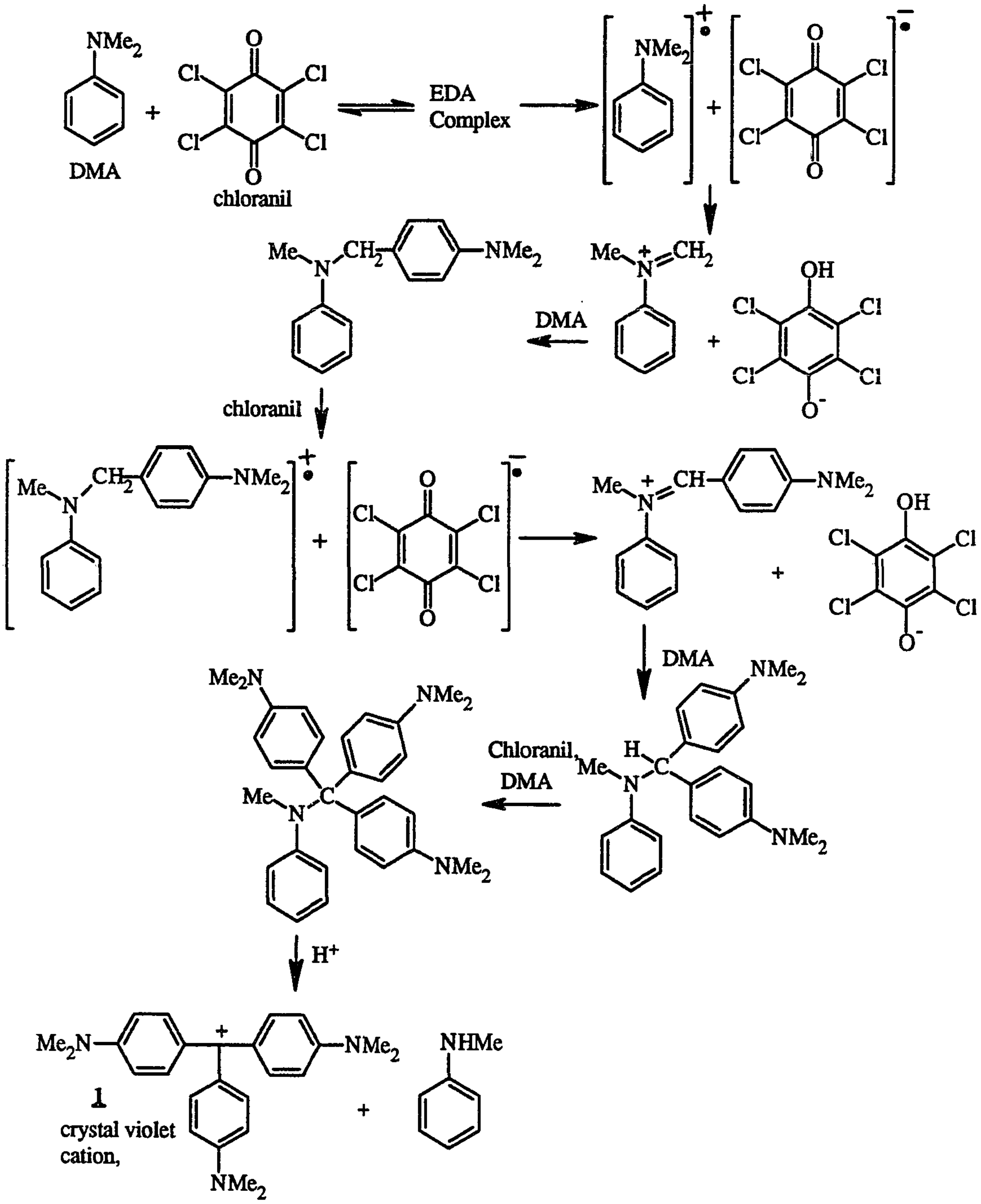
Aromatic amines are good electron donors and can form EDA complexes with most electron acceptors. In some cases, especially with strong electron acceptors, chemical reactions may also occur.

In poorly ionizing solvents, such as cyclohexane and carbon tetrachloride, aromatic monoamines form molecular complexes with iodine[3,4], p-benzoquinone[5], tetracyanoethylene[6] and halogenated organic compounds.[7] In polar solvents, the amines can also form ionic complexes with quinones, with a high electron affinity, such as chloranil. An ionic complex of an amine usually appears as a pair of an amine radical cation with an acceptor radical anion suggesting a single electron transfer between the donor and acceptor. Some experimental results have indicated that the molecular complex is on the reaction path in the formation of the radical-ion pair.[8]

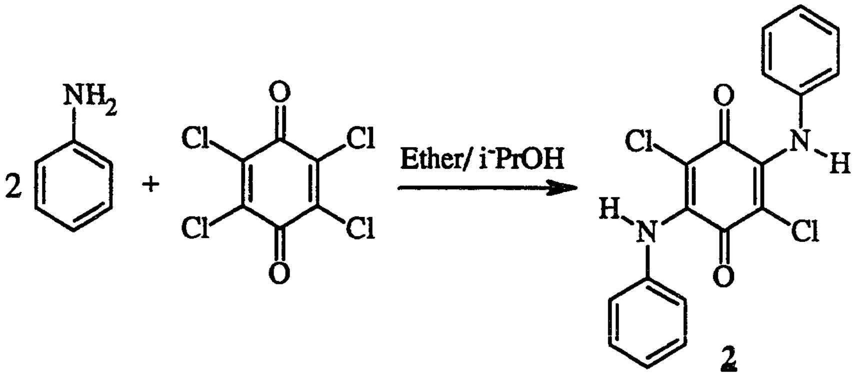
Aromatic amines react with strong electron acceptors through the formation of molecular and ionic EDA complexes in the first two steps. The reaction of N,N-dimethylaniline (DMA) with chloranil in the absence of solvent is of particular interest in that crystal violet, **1**, is formed.[9] The proposed mechanism is shown in Scheme 1. The molecular complex in solution was observed by the electronic absorption at 650 nm immediately after mixing. Upon mixing, no ESR absorption was observed, but with time, it increased to a maximum at about three days and eventually disappeared. This ESR absorption corresponded closely to the absorption of the chloranil semiquinone ion.

The other common reaction between quinones and aromatic amines is the formation of substituted quinones. Typical examples are the reactions of quinones with primary aromatic amines. Chloranil reacts with two equivalents of aniline to form 2,5-di-anilino-3,6-dichloro-p-benzoquinone **2** through the EDA complexes[10] (Scheme 2).

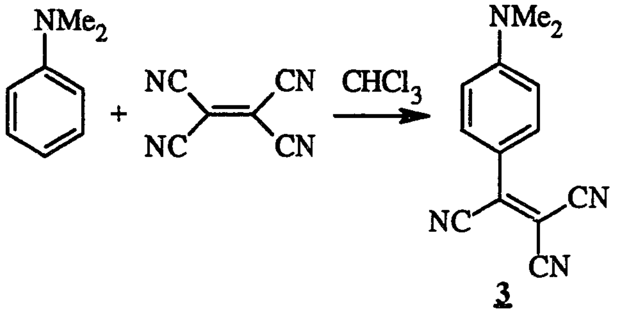
Aromatic amines react with TCNE more readily than the quinones. A substitution reaction of tetracyanoethylene (TCNE), known as tricyanovinylation, is very facile even in poor ionizing solvents. For example: in chloroform, TCNE reacts with dimethylaniline to give 4-tricyanovinyl-N,N-dimethylaniline[11], **3** (Scheme 3). EDA complexation is also believed to be the first step in this reaction.


NMe$_2$
DMA
chloranil
EDA
Complex
DMA
chloranil
Chloranil,
DMA
DMA
H$^+$
1
crystal violet
cation,
NHMe

Scheme 1



Scheme 2



Scheme 3

Chromophores and polymers for second-order nonlinear optics

In recent years, nonlinear optical (NLO) polymers have become one of the most exciting subjects in the area of organic materials.[12,13] The linear and nonlinear optical behavior of a material can be described by a series expansion of the polarization, P, in the material, in powers of applied electric fields, E:

$$P = P_0 + \chi(1)E + \chi(2)EE + \chi(3)EEE + \ldots$$

where P_0 is the permanent (or ground state) polarization, and $\chi^{(\xi)}$ are the susceptibilities. The $\chi^{(1)}$ term describes ordinary linear behavior (refraction and absorption). The $\chi^{(2)}$ and $\chi^{(3)}$ are the second-order and third-order nonlinear susceptibilities respectively. The same kind of expression can be applied to a dipole moment, μ, of an individual chromophore:

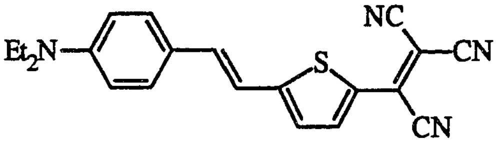
$$\mu = \mu_0 + \alpha E + \beta EE + \gamma EEE + \ldots$$

where β is the second-order susceptibility tensor of the chromophore (also called the quadratic hyperpolarizability, or first hyperpolarizability). Usually $\chi^{(2)}$ is related to the β of the chromophore from second harmonic generation (SHG) measurements in poled NLO films as described in the following equation[14].

$$\chi(2) = N\beta(f^{\omega})^2 f^{2\omega} \langle\cos 3\theta\rangle$$

N is the number of chromophores per unit volume, f^{ω} and $f^{2\omega}$ are the local field factors which are simple functions of the index of refraction at fundamental and second harmonic frequencies, and θ is the average angle between the ground-state dipole moments of the chromophores and the direction in the film they would be pointing if perfectly aligned, e.g., perpendicular to the plane of the polymer film.

The typical second-order NLO chromophores are organic donor-acceptor molecules. A chromophore possessing a large β value is desirable. The β values of the chromophores are generally increased with the molecular conjugated length and the strength of donors and acceptors.[15,16] The superiority of dicyanovinyl and tricyanovinyl groups to the nitro group in enhancing the β values has been established.[17] The synthesis of donor-acceptor π-conjugated chromophores containing tricyanovinyl groups such as 4 and 5 was accomplished by the tricyanovinylation of the corresponding thiophenes.[18,19]



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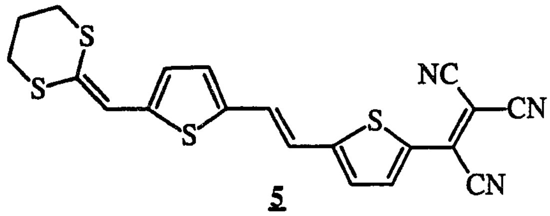

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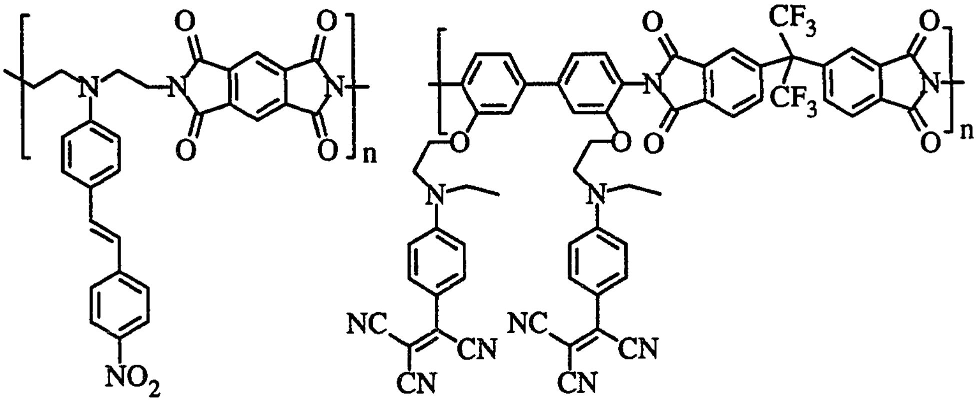
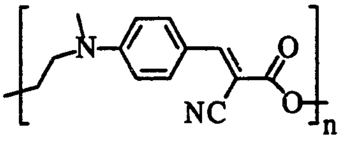
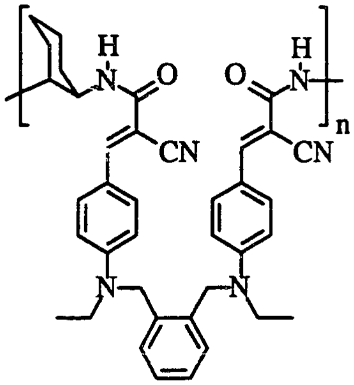
There are four types of NLO polymers, guest-host systems, sidechain polymers, mainchain polymers, and crosslinked polymers, known to date.[14] In the guest-host systems, small unattached chromophores are dissolved in high molecular weight polymers. Generally a guest-host system contains only about 10-30% by weight of the chromophore because the higher levels tend to phase separate causing light scattering. A higher concentration of chromophores can be achieved without causing inhomogeneity by incorporating the chromophore into the polymers as in the sidechain, mainchain and closslinked polymers. The sidechain polymers have one end of the chromophore chemically attached to the backbone while the mainchain polymers have both ends of the chromophore linked in the backbone and the chromophore becomes part of the polymer backbone. The crosslinked polymers are the products from crosslinking of the guest-host systems, sidechain polymers or mainchain polymers. Examples of these three types of NLO polymers are shown beow.

Sidechain Polymers[20]:

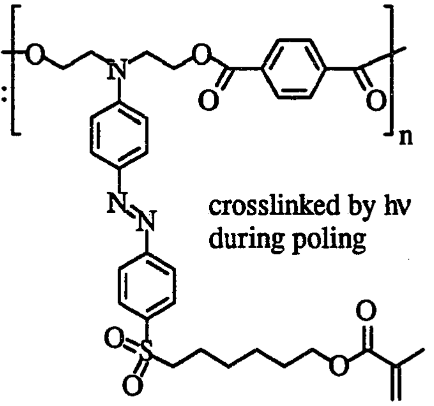


Mainchain Polymers[21]:

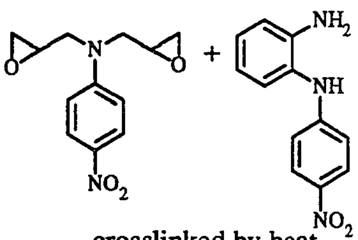




Precursors for crosslinked polymers[22]:



crosslinked by hv during poling



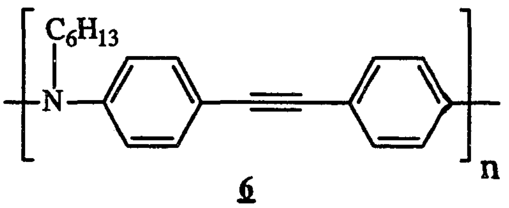
crosslinked by heat during poling

In all types of NLO polymers, the chromophores need to be aligned, usually by electric field poling, near the glass transition temperature.[23] When the polymer is cooled and the field is removed, the alignment can remain frozen. In a crosslinked polymer, a precursor polymer can be crosslinked during poling or after poling. The alignment stability is extremely important for developing commercial devices from the NLO polymers. The stability is generally in the order: guest-host system < sidechain polymers < mainchain polymers < crosslinked polymers.[14] Despite having the highest stability, the crosslinked polymers also possess their own problem since they are more difficult to process and to control the quality.

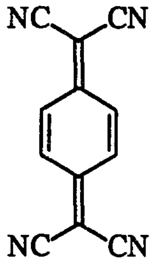
RESULTS AND DISCUSSION

Reaction of electron-rich acetylene with TCNE

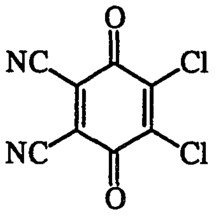
Electron donor-acceptor (EDA) complexes of acetylenic polymer **6** with organic acceptors were studied by UV-Vis absorption spectroscopy. Four organic acceptors, iodine, 7,7,8,8-tetracyanoquino dimethane (TCNQ), 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (DDQ) and tetracyanoethylene (TCNE) were utilized in this experiment.



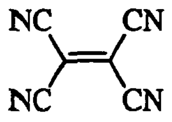
6



TCNQ



DDQ



TCNE

A 1:1 mixture of polymer **6** with I_2, TCNQ or DDQ in chloroform showed new absorption bands at 612 nm, 651 nm and 710 nm respectively along with the modified absorption band of polymer **6** around 375-400 nm (Figure 1). With TCNE, however, the solution showed a very intense band at 512 nm with a disappearance of the absorption band of the polymer. This result suggested that while I_2, TCNQ and DDQ formed EDA complexes with polymer **6**, TCNE reacted with the polymer to form a new polymer.

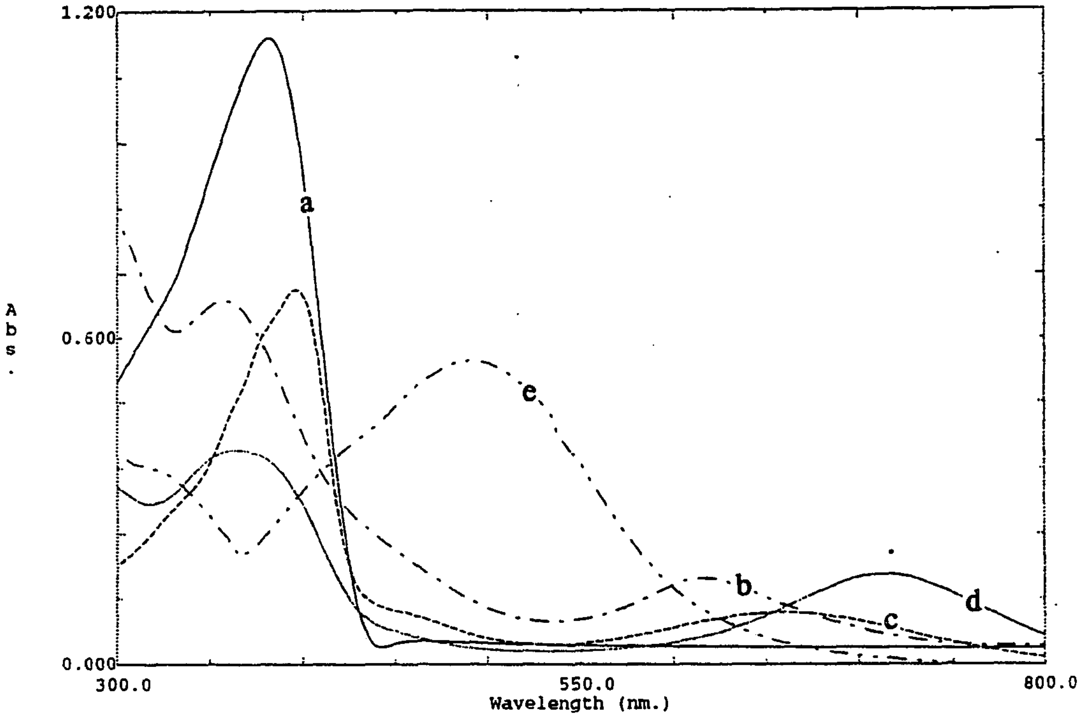


Figure 1 UV-Vis absorption spectra of a) polymer 6 and its 1:1 mixture with b) I_2, c) TCNQ, d) DDQ and e) TCNE in chloroform.

Another interesting feature of the absorption spectra is the absorption energies of the new bands. The energies of these new absorptions of polymer 6 with the acceptors are 2.03 eV for I_2, 1.90 eV for TCNQ, 1.75 eV for DDQ and 2.42 eV for TCNE. The electron affinities (E_A) of the acceptors from the literature are 2.55 eV for I_2,[24] 2.8 eV for TCNQ,[24] 3.12 eV for DDQ[25] and 2.3 eV for TCNE.[24] A plot of the absorption energies against the E_A of the corresponding acceptors is presented in Figure 2. A good linear relationship between the E_A and the absorption energies of the new bands was observed for the mixture of 6 with I_2, TCNQ and DDQ. The absorption energy of the mixture of TCNE and polymer 6 however

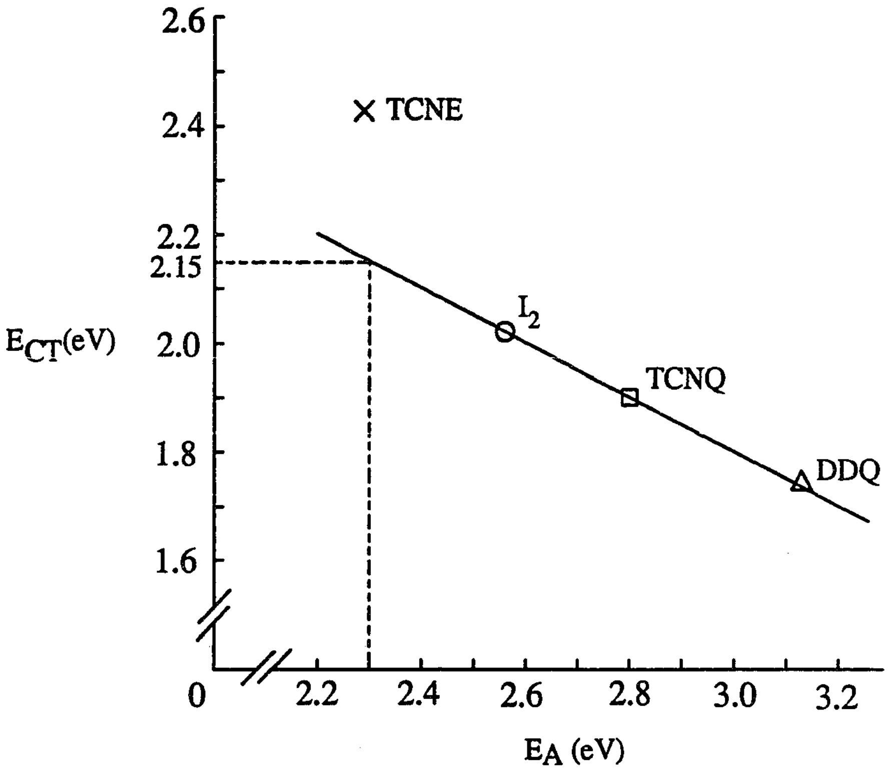


Figure 2 Plot of the energy of the new observed absorption band against electron affinity (E_A) of the acceptors. The dashed line indicates the expected CT transition energy of the EDA complex of TCNE with polymer 6.

deviated considerably from this linear relationship. With an E^A of 2.3 eV, the expected CT transition band of the EDA complex of TCNE with polymer 6 should be at 577 nm (2.15 eV). Thus clearly a chemical reaction was involved in the mixture of TCNE and polymer 6.

An attempt to identify the product of the mixture of TCNE and polymer 6 by NMR spectroscopy was performed. The ^{1}H-NMR of the mixture revealed only that the number of proton resonances remained the same during the reaction. The ^{13}C-NMR spectra was complicated and more information was required to unambiguously characterize the product of this mixture. However, it is very difficult to determine a structure of the polymer product because some of the very useful characterization techniques, such as the mass spectrometry and X-ray crystallography, are not applicable for polymers. Furthermore, if the reaction of polymer 6 with TCNE was not quantitative, the resulting polymer would be a random copolymer complicating its characterization. Thus a small model system was needed and a simple anilinoacetylene, 4,4′-dimethylamino-diphenylacetylene 7, was synthesized.

7

Like polymer 6, a yellow solution of 7 in chloroform turned intensely red immediately after an addition of one equivalent of TCNE. A UV-Vis absorption spectrum of acetylene 7 has bands at 350 nm and 379 nm(Figure 3). Upon addition of TCNE, these absorption peaks disappeared and only a new, intense peak at 468 nm was observed. This result agrees well with the result obtained from the study of polymer 6 suggesting that model compound 7 and polymer 6 underwent the same chemical reaction. ^{1}H-NMR and ^{13}C-NMR spectra of 7 in chloroform were recorded before and 10 minutes after the addition of TCNE. In the ^{1}H-NMR spectra (Figure 4), the number of protons remained the same and all of the signals shifted downfield upon equivalent addition of TCNE. In the ^{13}C-NMR spectra (Figure 5), the number of carbons increased by six and the acetylenic carbon signals disappeared. Thus the reaction might be a [2 + 2] cycloaddition of the double bond of TCNE with the triple bond of 7. The exact mass obtained from electron impact (EI) high resolution mass spectrometry

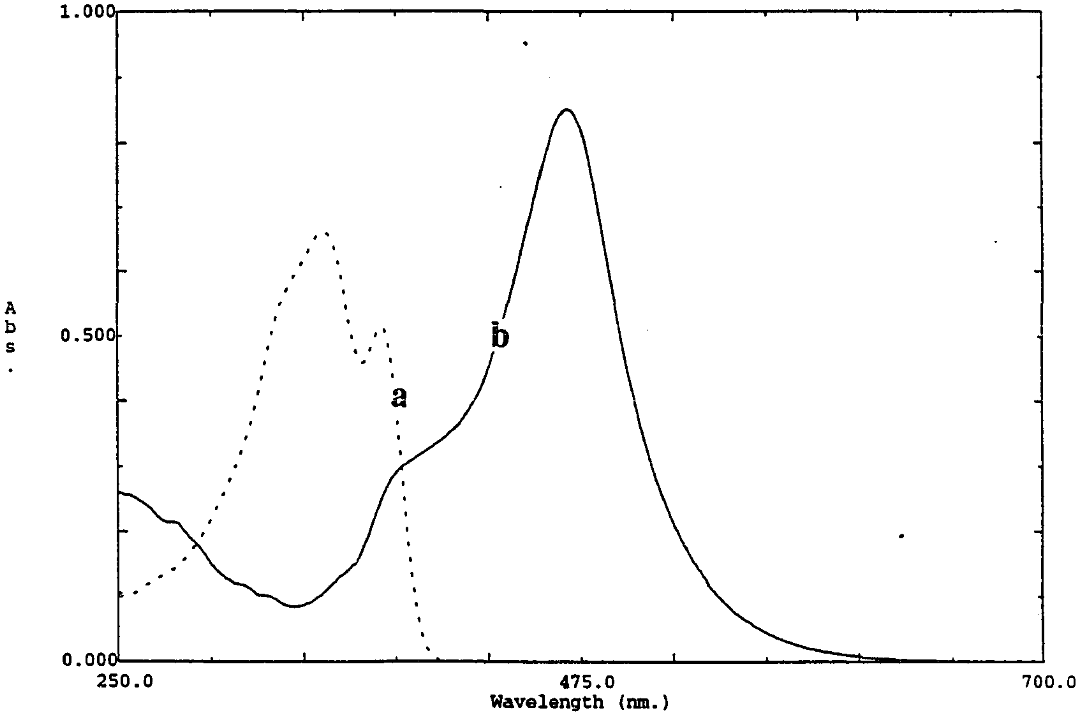


Figure 3 UV-Vis absorption spectra of acetylene 7 in chloroform a) before and b) 10 minutes after the addition of TCNE

(HIRES-MS) was equal to the sum mass of 7 with TCNE supporting a formation of a 1:1 adduct. The product from a [2 + 2] cycloaddition of TCNE to acetylene 7 would be a cyclobutene adduct 8, but ^{13}C-NMR shows no other sp^3-C besides dimethylamino groups. However, the ^{13}C-NMR spectra matched well with butadiene 9 which can be formed from an electrocyclic ring opening of 8 (Scheme 4).[26] A peak at 165 ppm is a dicyanovinylene carbon peak which is very characteristic for this general structure.

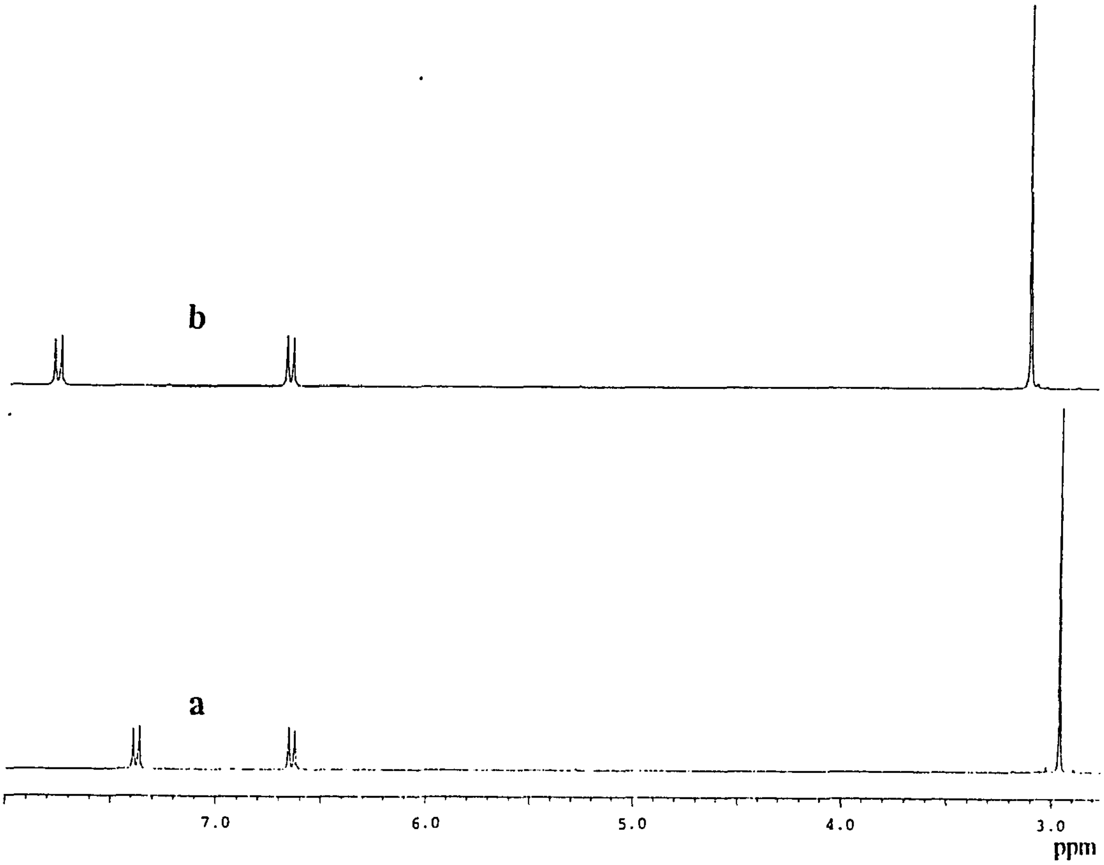


Figure 4 ^{1}H-NMR spectra of acetylene 7 (a) before and (b) 10 minutes after the addition of TCNE.

The structure of 9 was confirmed by X-ray crystallography. Single crystals of the product was grown from a methanol/chloroform solution by allowing the solvents to slowly evaporate. The deep red, shiny, metallic-like orthorhombic crystals were obtained from this crystallization. The molecules of 9 in the crystal are not planar but twisted into an X shape (Figure 6).

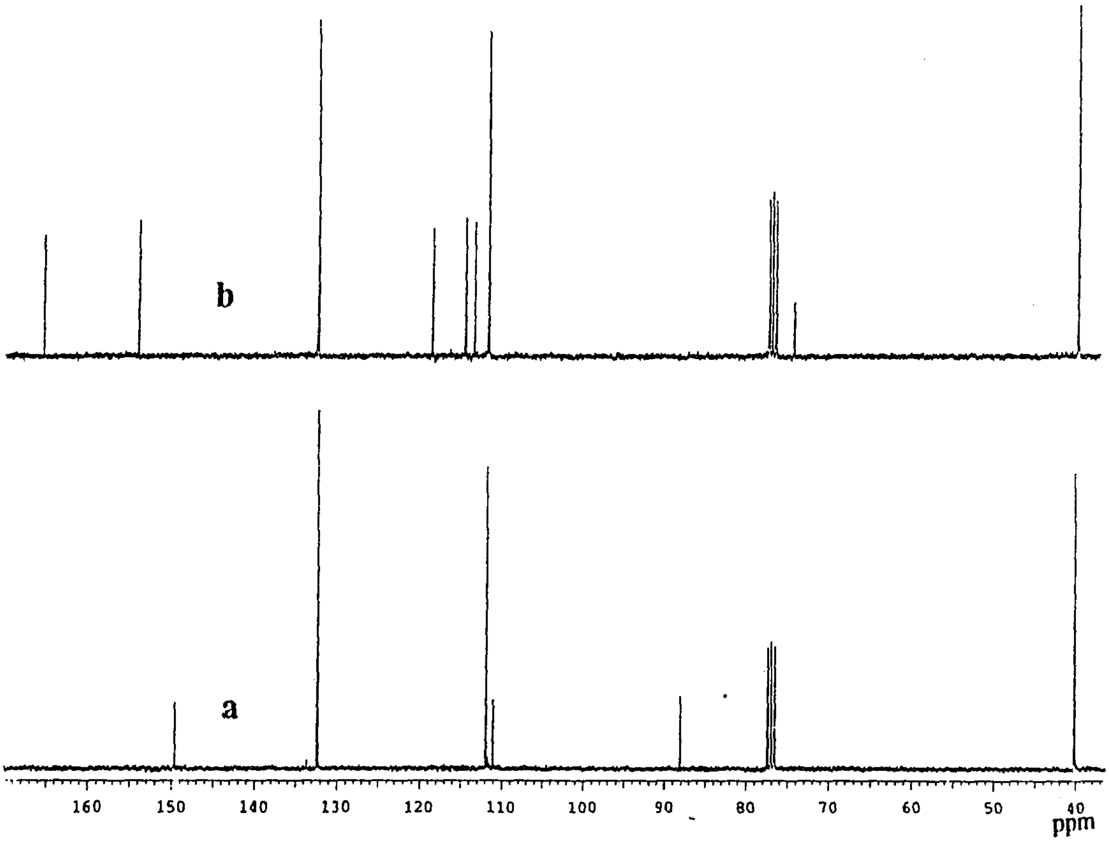
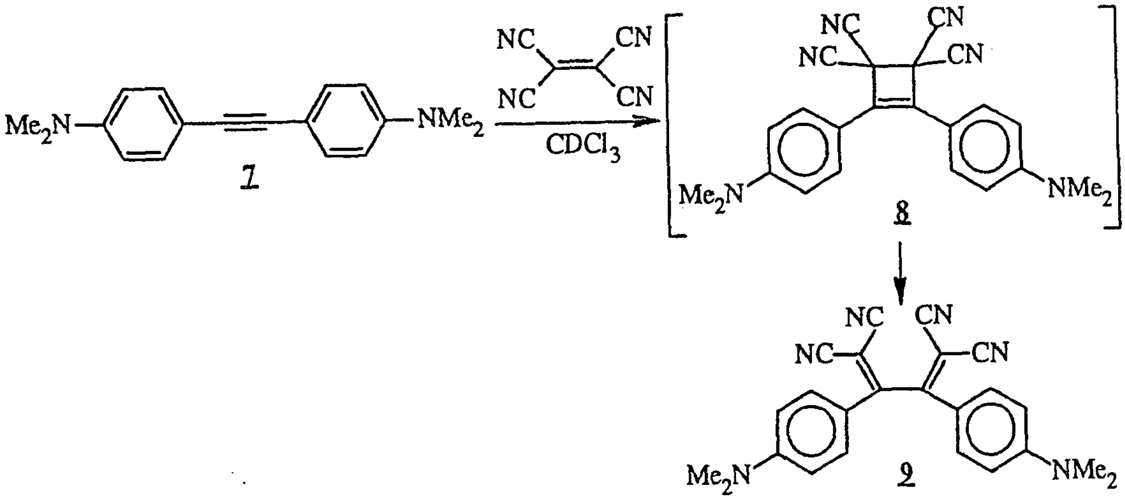


Figure 5 ^{13}C-NMR spectra of acetylene 7 (a) before and (b) 10 minutes after the addition of TCNE.



Scheme 4

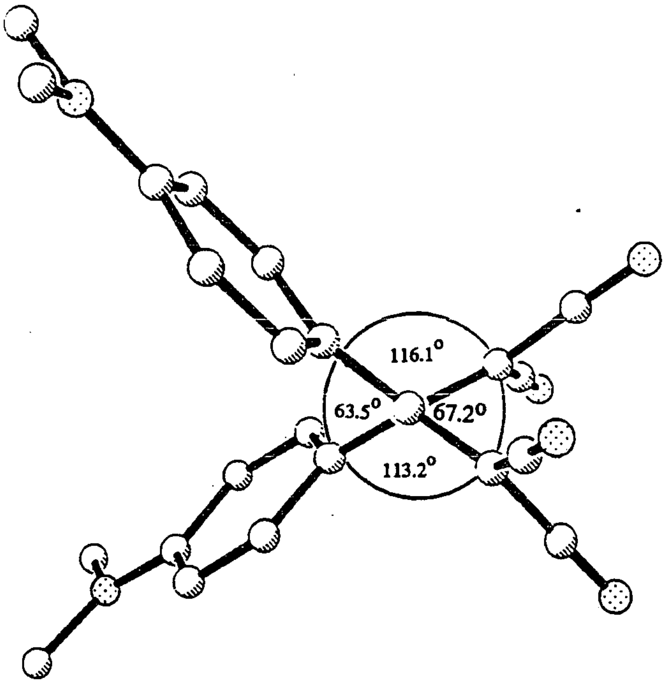
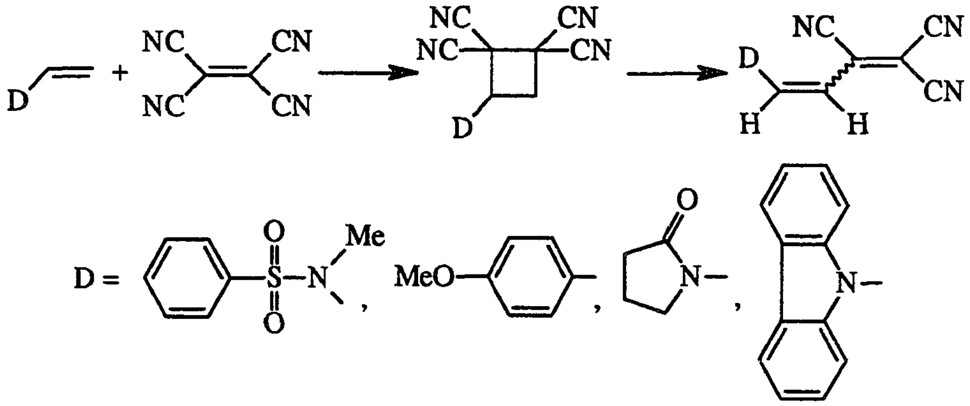


Figure 6 X-ray structure of 9

While a twisted structure is reasonable, resulting from the steric repulsions of four substituents on two center carbons, (C1) and (C1'), the degree of twisting was quite surprising. The dihedral angles between two anilinic groups (67.2°) and between two malononitrile groups (63.5°), supposedly carrying the same partial charges, are about 50° less than the dihedral angles between anilinic groups and malononitrile groups (113.2° and 116.1°) which carry partial positive and negative charges respectively. The surprising small dihedral angles between the same groups may be attributed to a strong intermolecular interaction between anilinic groups and malononitrile groups of neighboring molecules in the crystal.

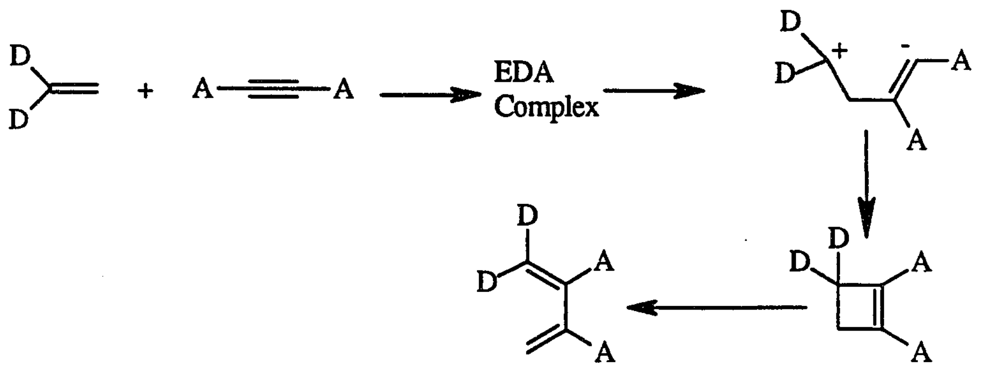
Because of the lack of a center of symmetry, this twisted structure is encouraging in the view of using this unit for a second-order NLO chromophore. After an extensive literature search we confirmed that compound 9 was not known but that the thermal [2+2] cycloadditions of TCNE with alkenes and alkynes have been reported.

Generally, TCNE can form molecular EDA π-complexes with alkenes and alkynes through the interaction of π-orbitals of the donors and acceptors. These π-complexes are usually well behaved as the ionization energy values of the alkenes and alkynes are in good agreement with the CT bands of the complexes.[27,28] For some electron-rich alkenes and alkynes, EDA complexation can eventually result in chemical reactions. A thermal [2 + 2] cycloaddition between electron-rich alkenes with TCNE forming tetracyanocyclobutane was first observed in 1962.[29] The reaction generally occurs rapidly and in high yield at 0-30 °C. The observation of highly colored solution at the beginning of the reaction indicated a formation of a molecular EDA complex in the early step. For some cyclobutane adducts, a ring cleavage with an elimination of HCN producing 1,1,2-tricyanobutadienes readily occur in polar solvents such as alcohols (Scheme 5).[30]



Scheme 5

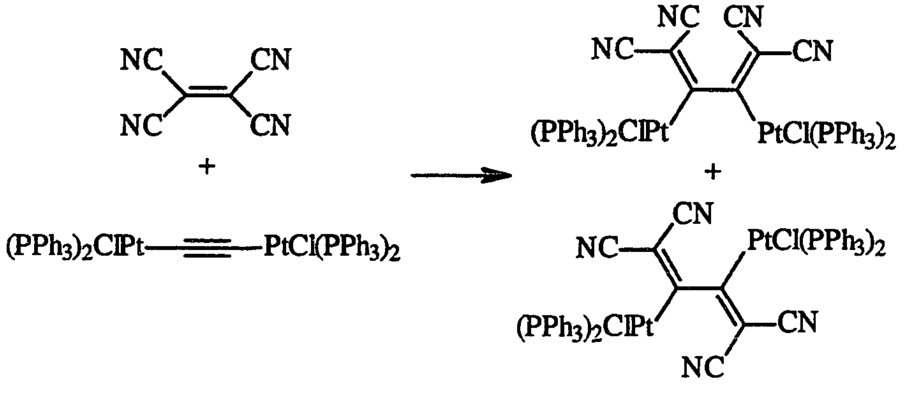
Formation of cyclobutenes from thermal [2 + 2] cycloadditions of electron-rich alkenes and electron-deficient alkynes has been utilized as a synthetic tool in natural product synthesis.[31] The mechanistic work showed that 1,4-dipolar intermediates were formed before the cyclization to form the cyclobutenes. The slow ring opening of the cyclobutene adducts to form butadienes was also observed at room temperature. Scheme 6 shows the proposed mechanism for an alkene containing an electron donor, D = OMe, and an alkyne containing two electron acceptors, A = CO_2Me, COPh, COMe.



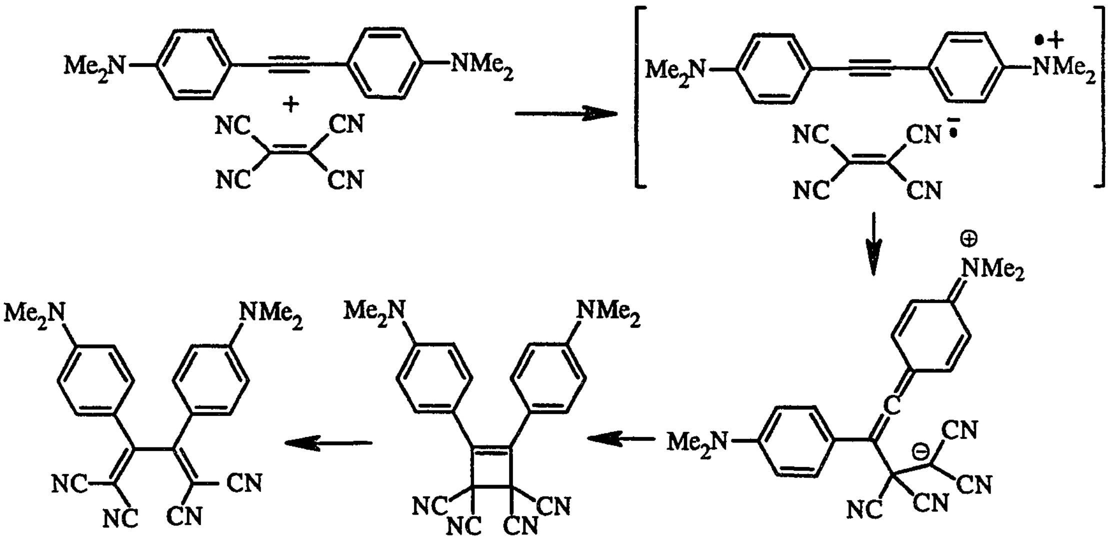
Scheme 6

The thermal [2 + 2] cycloaddition between electron-rich acetylenes and TCNE has only been reported for acetylene σ–complexes of metals such as Pt, Ru or Fe (Scheme 7).[32] The single electron transfer process was proposed to be involved before the formation of a 1,4-dipolar intermediate similar to that in the proposed mechanism in Scheme 6.

The reaction of TCNE with our acetylene 7 is formally a [2 + 2] cycloaddition followed by electrocyclic ring opening to give tetracyanobutadiene (TCBD) 9. Presumably this reaction is also initiated by electron transfer from acetylene 7 to TCNE to form radical cation, $\underline{7}^{\bullet+}$, and TCNE radical anion[29,32] (Scheme 8). A nucleophilic attack of the radical anion



Scheme 7



Scheme 8

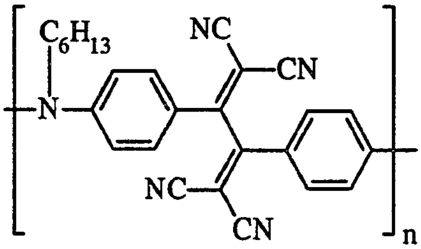
on the triple bond of 7$^{\bullet+}$ gives a 1,4-dipolar intermediate which closes to form cyclobutene.[31] Electrocyclic ring opening of the unstable cyclobutene yields the final product, TCBD.

The synthesis of new chromophores with large β values and incorporating them into polymer chains has been a very important part in the development of optimal second-order

NLO polymers for practical electro-optic devices.[12,13,14] A high concentration of chromophores in the polymer chain without any adverse effect on processibilities, optical properties and mechanical properties of the polymers is highly desirable. In polymer synthesis, incorporating a high concentration of NLO chromophores into a polymer chain is quite a synthetic challenge.

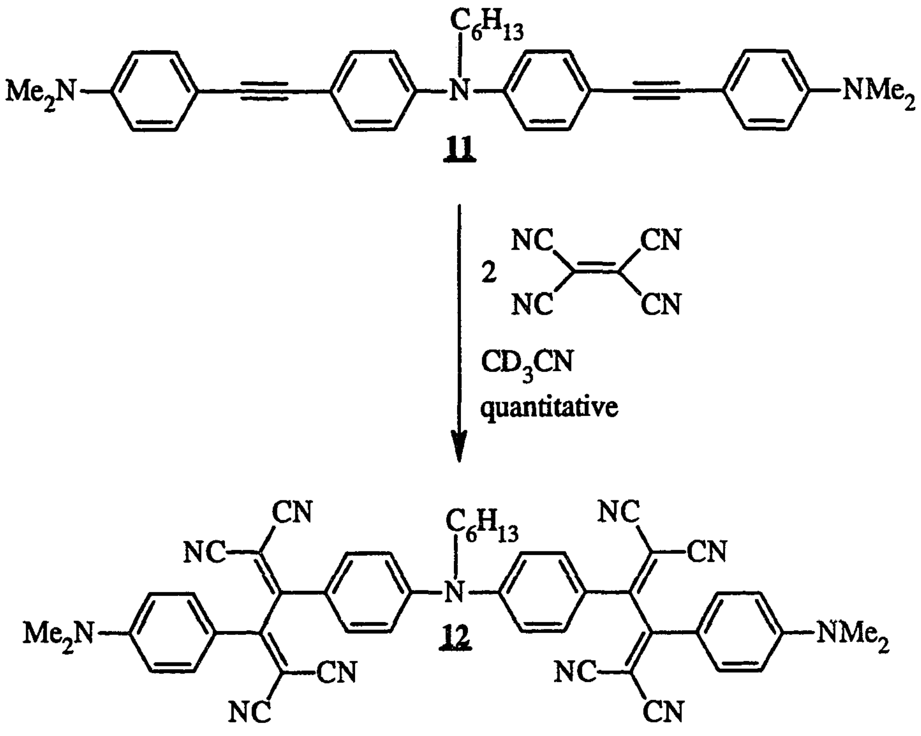
Two synthetic approaches to NLO polymers are: a) polymerization of monomers containing NLO chromophores, and b) introduction of NLO chromophores into a polymer chain by polymer modification. The TCNE reaction with electron-rich acetylenes fits into the second approach and is particularly interesting because of a mild condition and excellent yield of this reaction. The complete conversion of polymer **6** by the reaction with TCNE would yield the interesting mainchain NLO polymer **10**.

As mentioned in a previous section, the structural assignment for the product from the mixture of polymer **6** and TCNE in chloroform was not possible from ^{1}H-NMR and ^{13}C-NMR spectra. The NMR spectra showed more proton and carbon peaks than expected from complete reaction of **6**, implying an incomplete conversion to polymer **10**. Integration of ^{1}H-NMR spectra indicated that only about 50 % of the acetylene units in polymer **6** were reacted. This percent remained unchanged even after 48 hours.



10

A bigger acetylene, **11** resembling two repeating units of polymer **6** was thus synthesized and used as a more representative model system. Acetylene **11** reacted slowly with TCNE in chloroform and did not reach completion even after 24 hours. However, in acetronitrile solution, a quantitative conversion of acetylene **11** to corresponding TCBD, **12**, was observed by ^{1}H-NMR within 10 minutes (Scheme 9). The faster reaction may largely be due to a better solubility of TCNE in acetonitrile. The 1,4-dipolar intermediate is also stabilized by the higher polarity of acetonitrile which should increase the rate of the reaction.



Scheme 9

The reaction of TCNE with polymer 6 however cannot be performed in pure acetronitrile due to the poor solubility of the polymer in this solvent. The reaction was thus performed in a chloroform/ acetronitrile (70:30) mixed solvent. In this mixed solvent, over 95% conversion of acetylene units in polymer 6 to TCBD units in polymer 10 was obtained within 24 hours as observed by ^{1}H-NMR (Figure 7). Less than 5% of unconverted acetylene units can be observed in the ^{1}H-NMR spectrum of polymer 10 through the signals of aromatic protons at 6-8-7.0 ppm and N-CH_2 protons at 4.6-4.8 ppm. However, the ^{13}C-NMR spectrum (Figure 8) of polymer 10 is very clean indicating a virtually quantitative conversion.

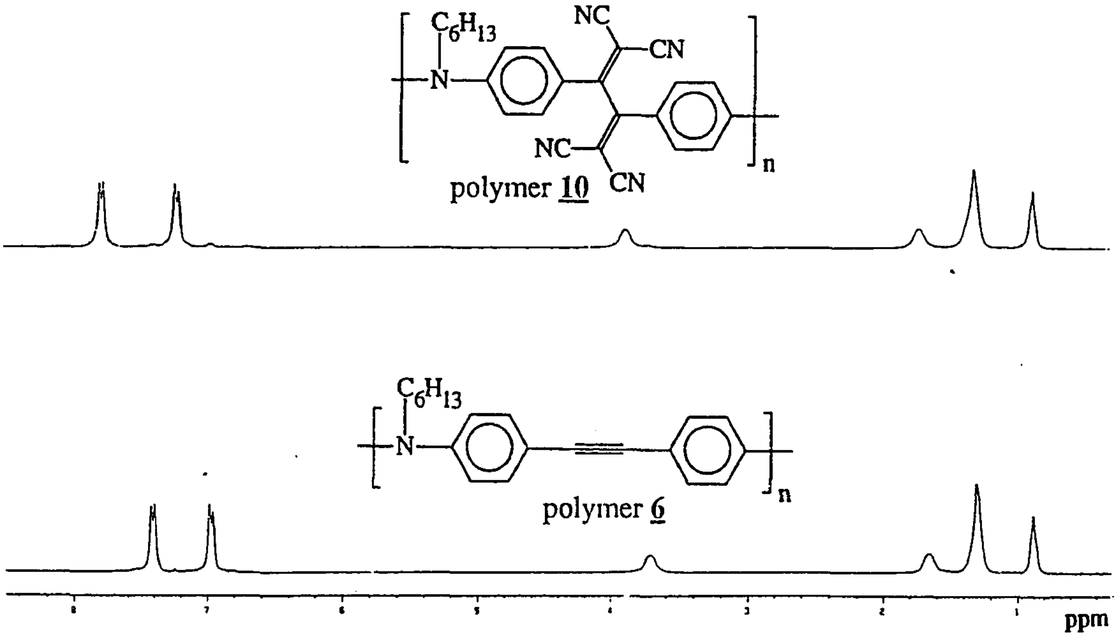


Figure 7 ^{1}H-NMR of polymer 6 and the product, polymer 10, from the reaction with TCNE.

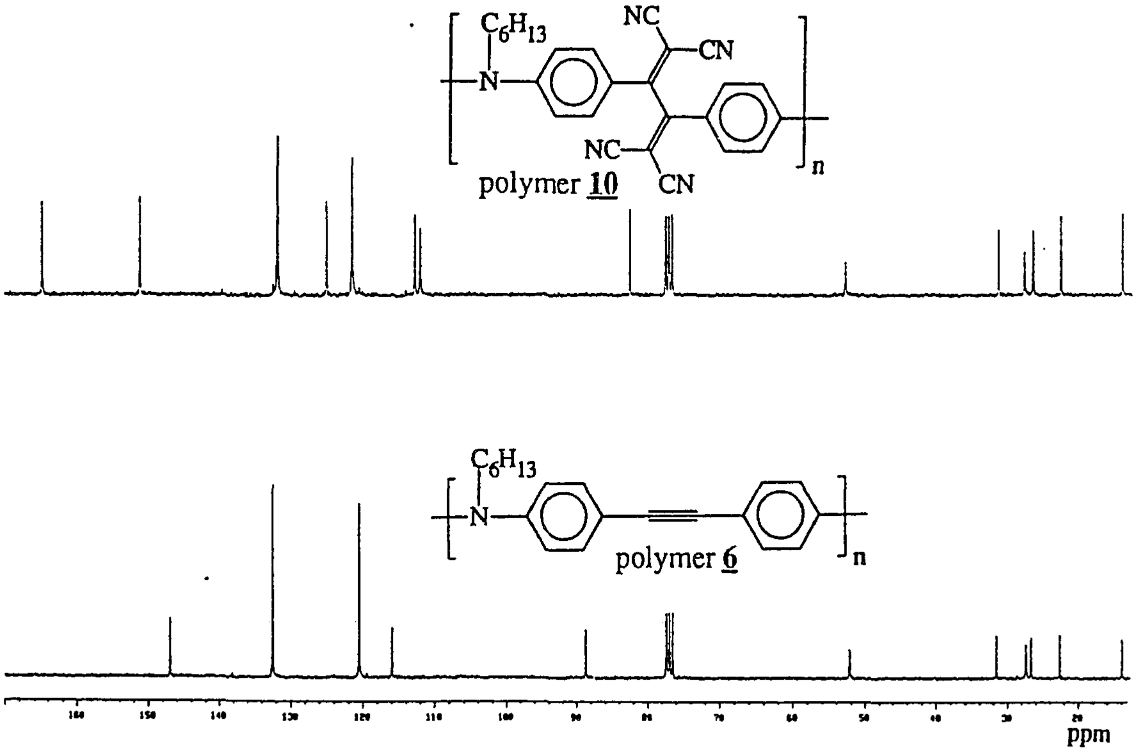


Figure 8 ^{13}C-NMR spectra of polymer 6 and the product, polymer 10, from the reaction with TCNE.

On total conversion of polymer 6 to polymer 10, the molecular weight of the polymer should be increased by 46% (compare the F.W. in Table 1). The GPC results showed that the number average molecular weight of polymer 10 (2.22×10^4) was about 52% higher than that of polymer 6 (1.46×10^4). This higher-than-theoretical value for M_n maybe due to loss of the lower molecular weight polymer during purification by precipitation of the product in methanol. The loss of lower molecular weight polymer can also be observed through a slight decrease (from 2.50 to 2.35) in polydispersity upon the conversion.

Table 1 Formula weight of a repeating unit (F.W.) and GPC results, number average molecular weight (M_n), polydispersity (PD) and intrinsic viscosity (η), of polymers <u>**6**</u> and <u>**10**</u>.

Polymer	F.W.	Mn	Mw/Mn	η (dL/g)
<u>**6**</u>	275.38	1.46×10^4	2.50	0.65
<u>**10**</u>	390.37	2.22×10^4	2.35	0.33

The concentration chromatograms of the polymers obtained from a tandem gel-permeation chromatography-differential refractrometer (GPC-DR) (Figure 9) shows a very similar molecular weight distribution of polymers <u>**6**</u> and <u>**10**</u>. The reasonable increase of the molecular weights of the polymers, and the similarities of the shape of the chromatograms indicate that the addition reaction of TCNE to polymer <u>**6**</u> did not cause detectable chain

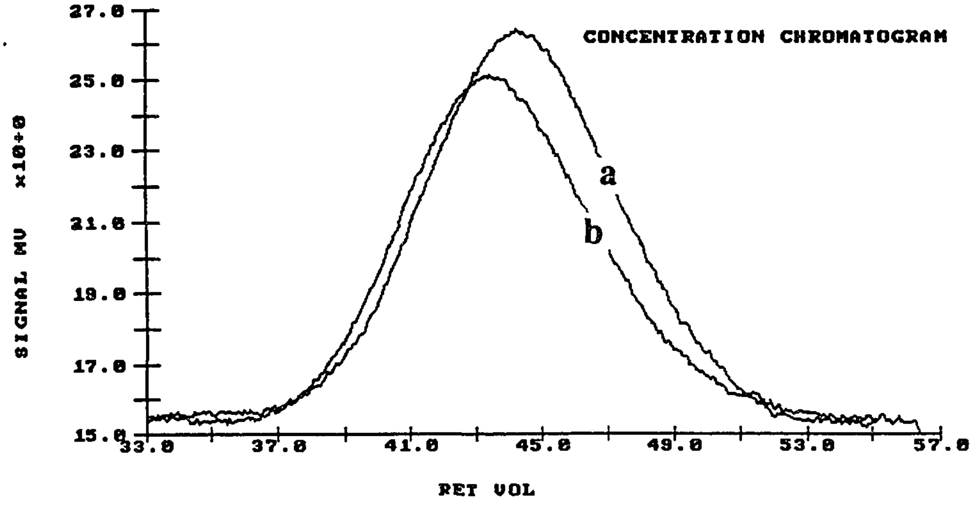
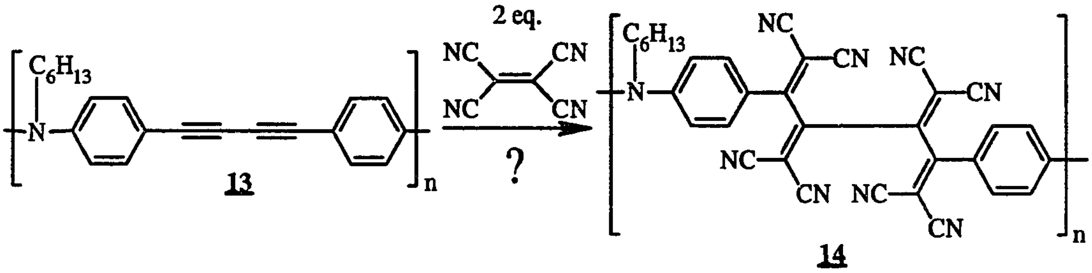


Figure 9 GPC-DR concentration chromatograms of a) polymer <u>**6**</u> and b) polymer <u>**10**</u>.

fission or interchain crosslinking. It is worth noting that upon conversion of polymer **6** to polymer **10** the intrinsic viscosity (η) is decreased by half (Table 1), in spite of the increase in molecular weight, indicating less rigidity in polymer chains of **10**.

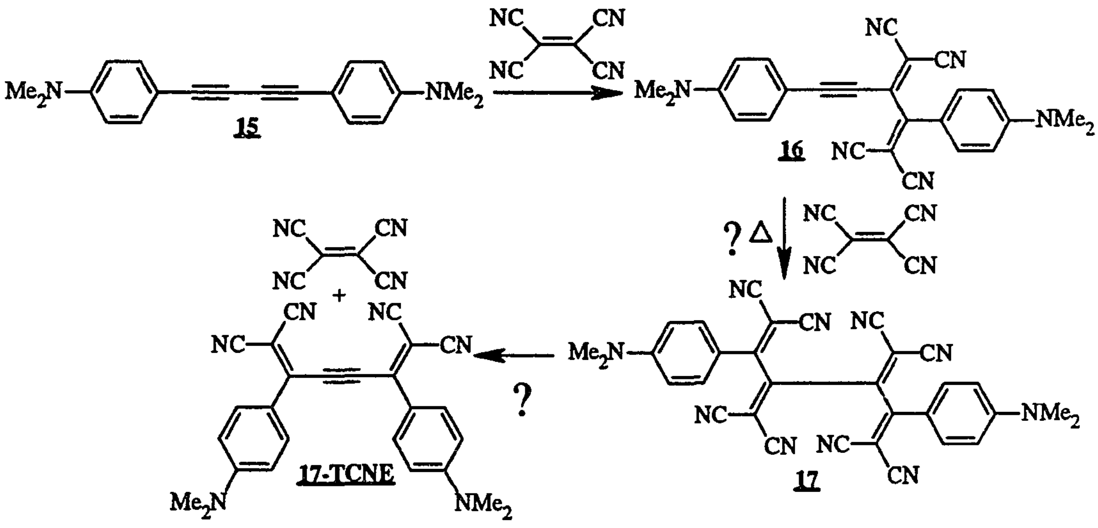
Thermal behaviors of polymer **10** were studied by thermogravimetric analysis (TGA) and differential scanning calorimetric analysis (DSC) under nitrogen atmosphere. The TGA showed the first weight loss at 314°C and 64% weight remaining from 600°C to 1000°C. The second weight loss started at 1000°C and the weight dropped to zero after held for 60 minutes at 1100°C. The DSC showed no glass transition or melting point of the solvent free polymer before crosslinking at 330°C. In order to use this polymer as an NLO polymer, it will need to be aligned at a glass transition temperature. This may require the presence of a small amount of solvent or another polymer with a low glass transition temperature.

The expected product from the total conversion of diacetylene polymer **13** with two equivalents of TCNE was polymer **14**.



The ^{1}H-NMR and ^{13}C-NMR spectra of the mixture of polymer **13** with two equivalents of TCNE in $CDCl_3/CD_3CN$ (70/30) was too complicated to assign a structure. Again, a study of a small model compound was required. Diacetylene **15** was synthesized and used as a model. The reaction of diacetylene **15** with excess TCNE gave a 1:1 adduct, **16** in quantitative yield.

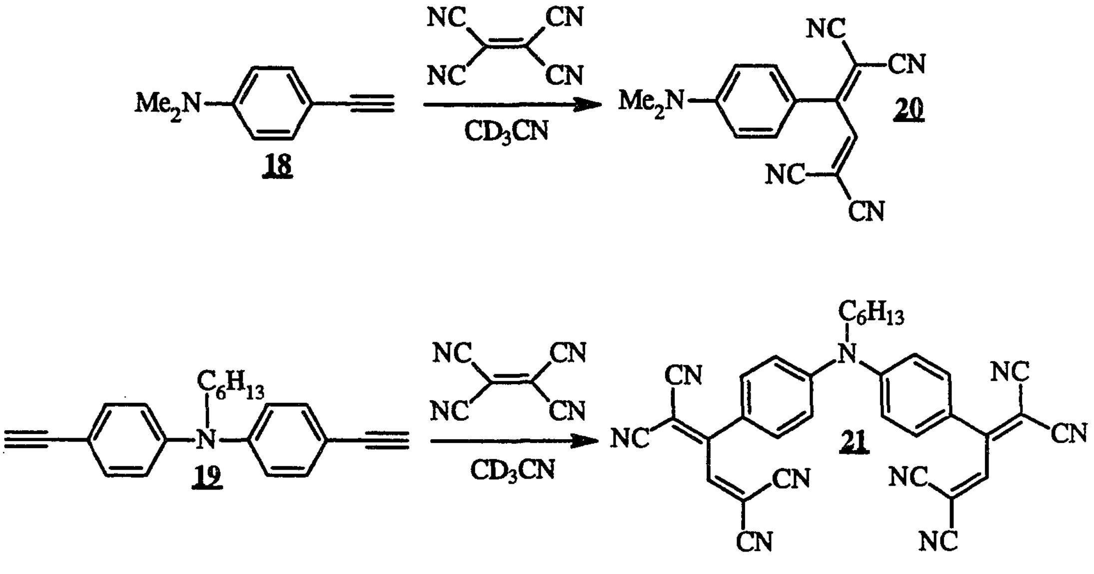
It was hoped that increasing the reaction temperature would drive the reaction further to give a 1:2 adduct, **17** (Scheme 10). It was also anticipated that at higher temperature **17** might undergo an interesting electrocyclic ring-closure and retrocycloaddition to give **17-TCNE** and TCNE. The expected 1:2 adduct, **17**, was however not observed and **16** remained unchanged even when the reaction was conducted in refluxing dioxane. At higher temperatures, the 1:1 adduct, **16**, started to decompose. The limited addition is conceivably caused by a steric hindrance of the bulky tetracyano groups formed in the first addition.



Scheme 10

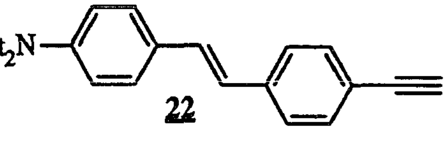
The addition of TCNE to the diacetylene polymer **13** was also likely limited to the 1:1 addition. In the polymer chain, there are two triple bonds for each repeating unit that TCNE can react with. The random addition of TCNE to one of these two triple bonds generated a regio-irregularity in the polymer which was observed by NMR. The NMR spectra consists of many peaks which cannot be assigned to a single structure.

The addition/ring-opening reactions of TCNE with disubstituted electron-rich acetylenes to form disubstituted TCBD electron donor-acceptor molecules is very facile, as previously described. It was interesting to see whether monosubstituted electron-rich acetylenes would undergo the same addition/ring-opening reaction, as the products would be quite attractive since they should possess higher dipole moments and polarizabilities than their disubstituted analogues. Therefore the reactions of TCNE with acetylenes **18** and **19** were studied. Upon addition of one or two equivalents of TCNE to a solution of acetylene **18** or acetylene **19** in acetonitrile, the color of the solution immediately became purple. ^{1}H-NMR and ^{13}C-NMR spectra identified the products as adducts from the addition/ring-opening reactions. The conversion was facile at room temperature and generated the corresponding mono and di-TCBD in quantitative yield (Scheme 11).



Scheme 11

Because the β values of chromophores generally increase with increasing lengths of π conjugation[21], this addition reaction of TCNE to a triple bond would be more valuable if it could be applied to longer π-conjugated acetylenes. An ethynyl derivative of aminostilbene 22 was synthesized and used as a substrate for the reaction with TCNE.



22

When one equivalent of TCNE was added to a solution of 22 in acetone-D6 , the color of the mixture quickly changed from yellow to deep green. After 10 minutes the solution turned light brown and eventually deep brown. This reaction was monitored by ^{1}H-NMR. During the reaction of acetylene 22 with TCNE, new AB-quartet peaks centered at 5.4 ppm gradually emerged at the expense of AB-quartet peaks centered at 7.2 ppm. This result unfortunately corresponded to the formation of undesired tetracyanocyclobutane (TCCB) 23 from an addition of TCNE to the double bond between two phenyl rings. When all the deep green color disappeared, a quantitative conversion of 22 to TCCB 23 was observed by ^{1}H-NMR and ^{13}C-NMR (Figure 10). The color of the solution slowly became dark brown as the product, TCCB 23, decomposed (Scheme 12). ^{1}H-NMR signals corresponding to the desired product, TCBD 24, were not observed during the course of the reaction. The decomposition products could not be identified because the observed ^{1}H-NMR spectra became extremely complicated. This result implied an inefficient delocalization of electron density from the amino group through this π-conjugated system, thus the addition reaction at the triple bond was not preferred.

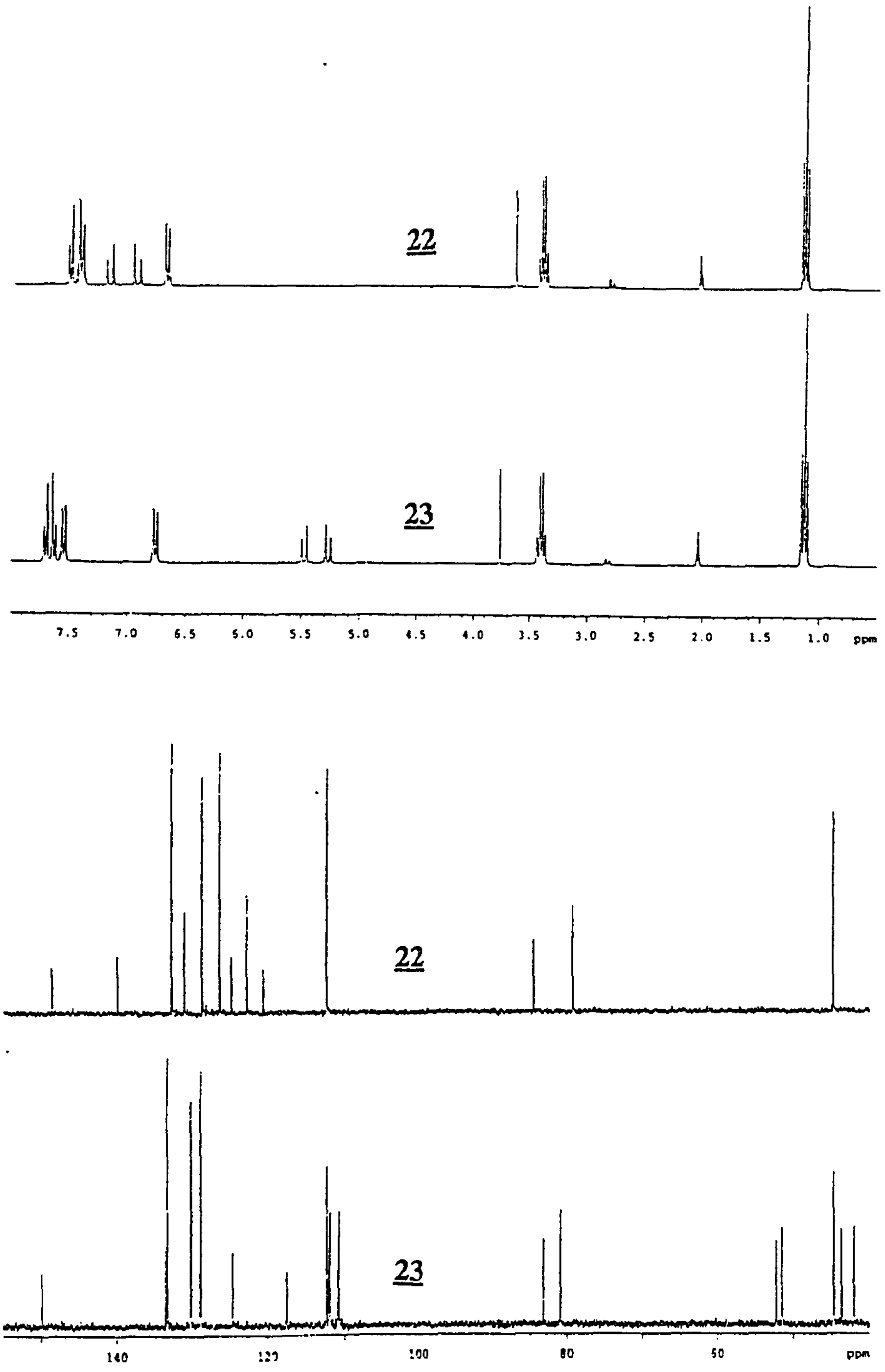
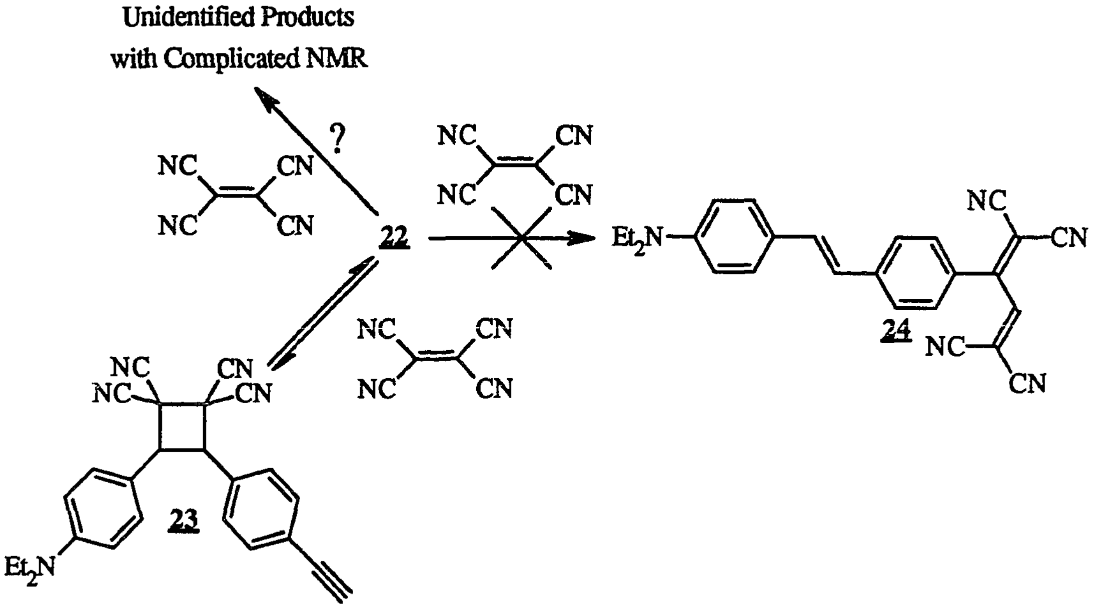
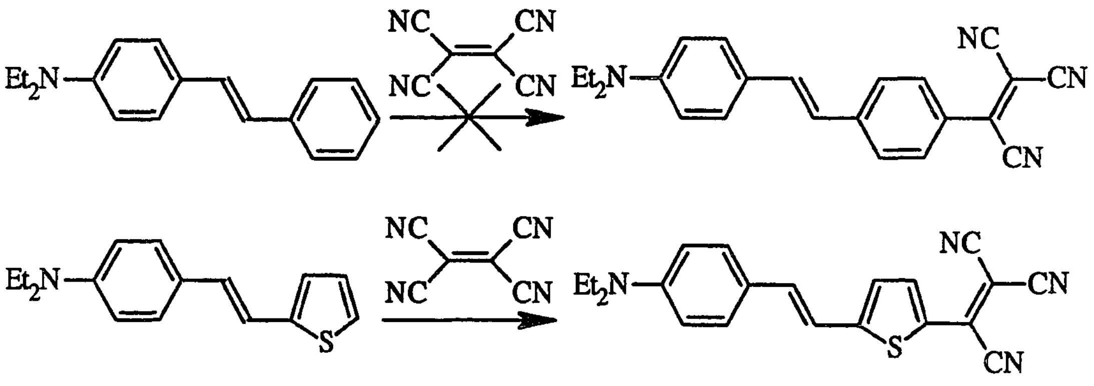


Figure 10 ^{1}H-NMR and ^{13}C-NMR of acetylene 22 and its adduct with TCNE, tetracyanocyclobutane (TCCB) derivative 23.



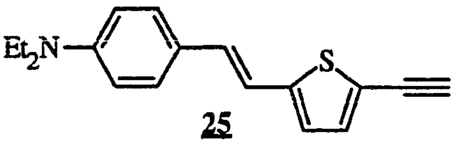
Scheme 12

At this stage of our research a report on tricyanovinylations of extended π-conjugated system (Scheme 13) appeared in Journal of Chemical Society, Chemistry Communication.[18] The study showed that 4-diethylaminostilbene was not reactive toward tricyanovinylation. By replacing the designated benzene ring with thiophene, an electron-rich hetero cyclic, the



Scheme 13

tricyanovinylation was accomplished. Using a similar concept, an ethynylthiophene π-conjugated molecule, 25, was thus synthesized and used as a new substrate. A reaction of TCNE with acetylene 25 in methylene chloride yielded a green solution containing exclusively the desired TCBD product, 28. The reaction of acetylene 25 with TCNE was followed by ^{1}H-NMR (Figure 11). The ^{1}H-NMR of the reaction of 25 with TCNE showed behavior similar to



25

the reaction of 22 with TCNE. New AB-quartet peaks centered at 4.9 ppm were observed which correspond to the attack of TCNE at the central double bond of 25 to form TCCB 26. The intensity of these AB-quartet peaks reached a maximum, then slowly decreased while a singlet peak at 7.87 ppm started to appear with the corresponding reduction of the terminal acetylene proton peak at 3.45 ppm, indicating the formation of the desired TCBD 28. Eventually the AB-quartet peaks of TCCB 26 and the terminal acetylene proton peak disappeared and only the new peaks of TCBD 28 was observed. Intermediates, tetracyanocyclobutene 27 and 26+TCNE were also implicated by a couple of signals at 6.25 and 6.45 ppm, observed after 5 minutes, corresponding to protons on cyclobutene rings. The reaction was completed within 10 minutes and TCBD 28 was the only observed product. ^{13}C-NMR (Figure 12) confirmed the total conversion of acetylene 25 to TCBD 28. The transient observation of intermediate 26 and 26+TCNE implies a reversibility of the addition of TCNE (Scheme 14).

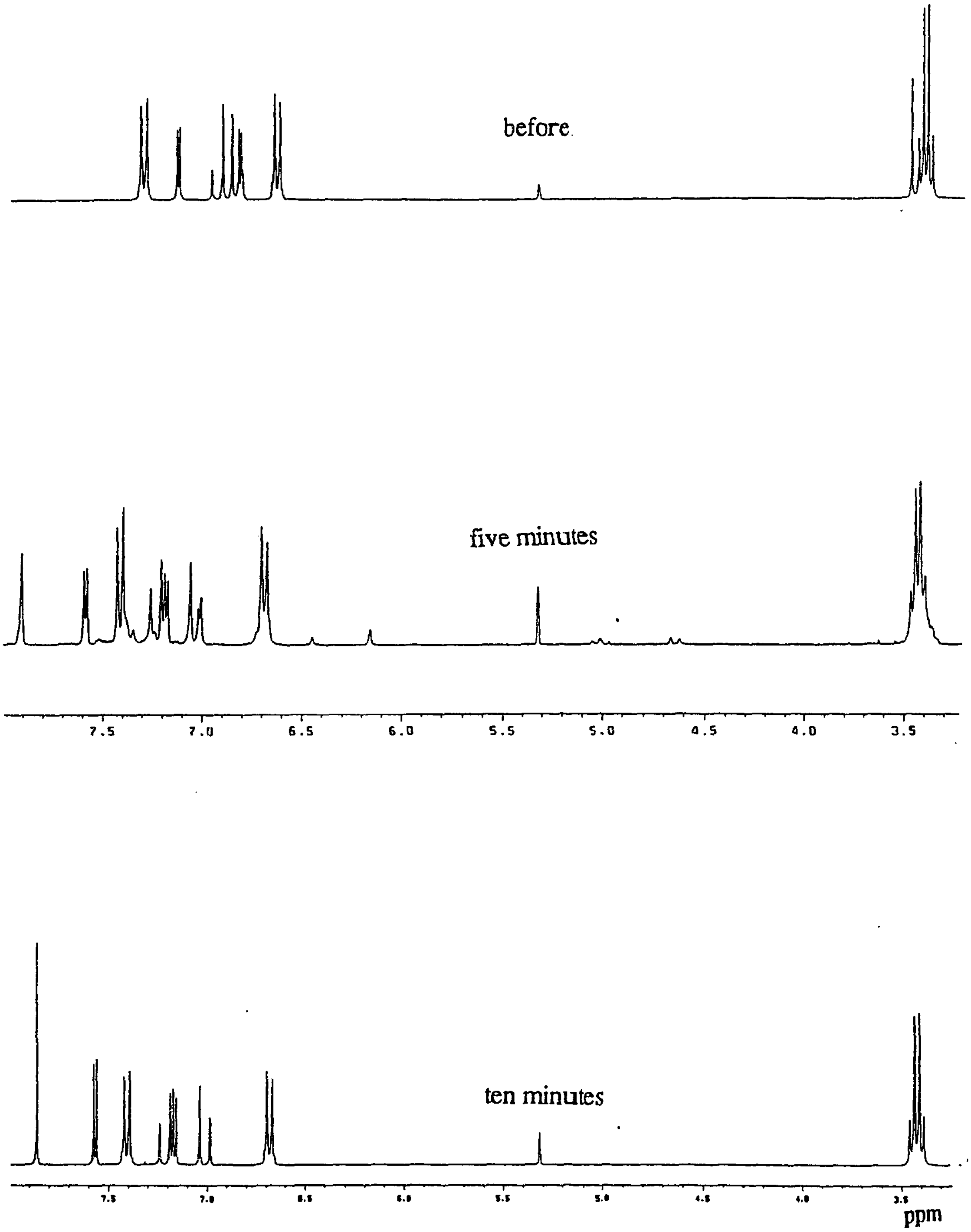


Figure 11 1H-NMR of acetylene <u>25</u> before, five minutes and ten minutes after the addition of TCNE.

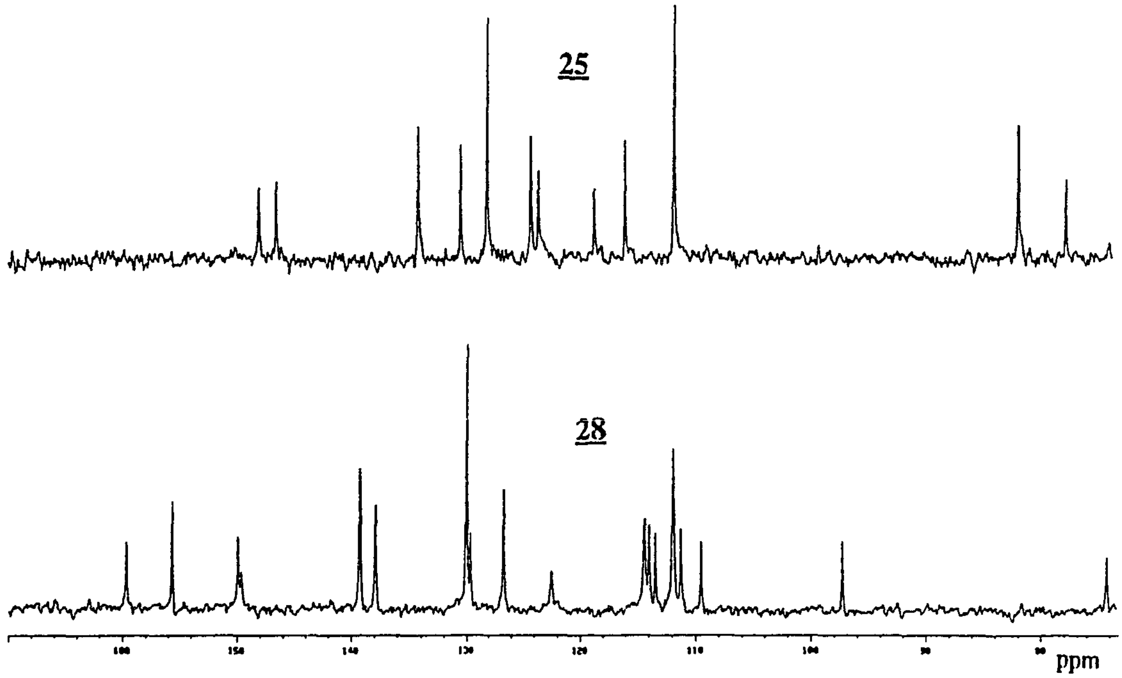
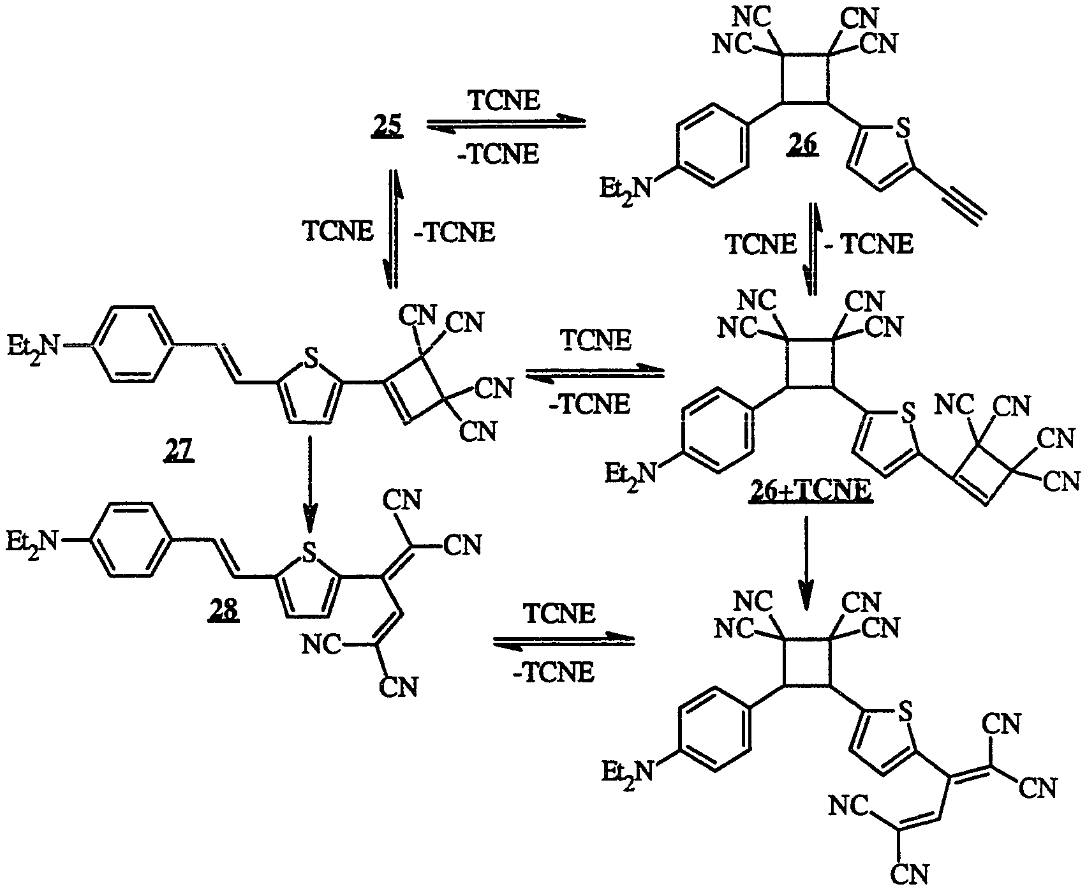


Figure 12 ^{13}C-NMR of acetylene 25 and its adduct with TCNE, tetracyanobutadiene (TCBD) derivative 28.

The observation of TCCB 26 early but not at the end of the reaction indicates that TCCB 26 is a kinetic product. The final product, TCBD 28, should be a thermodynamic product (Figure 13). For acetylene 22, the electron density on the triple bond is not high enough to direct the attack of TCNE to yield the desired TCBD, 24. Only a kinetic product, TCCB 23, was observed. By replacing the phenyl ring between the double bond and the triple bond with an electron-rich heterocyclic thiophene ring, the activation energies of the addition of TCNE on both double bond and triple bond are decreased. Acetylene 25 thus allowed an attack of TCNE on the triple bond to form the thermodynamically stable TCBD 28 as a final product.



Scheme 14

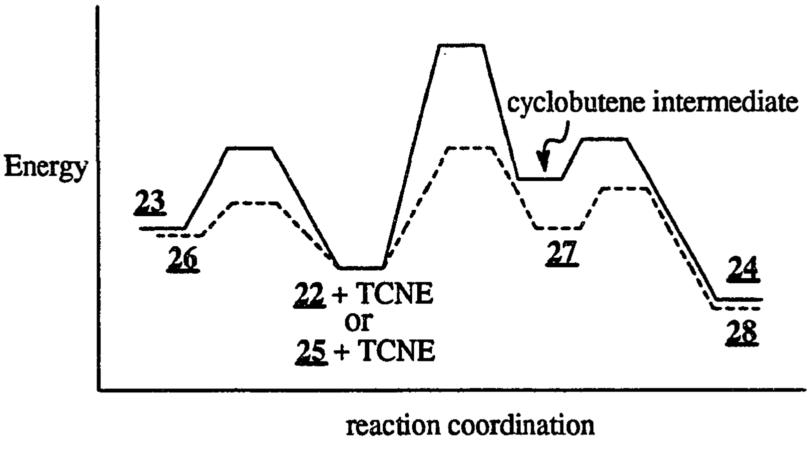
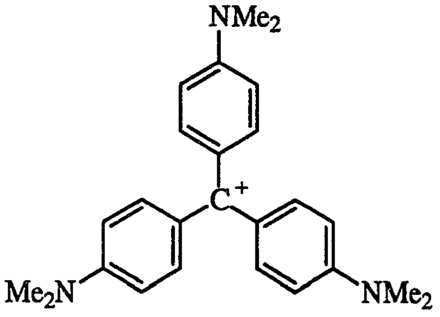
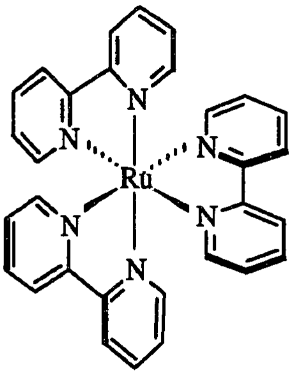


Figure 13 Energy diagram of the reaction of 22 and 25 with TCNE

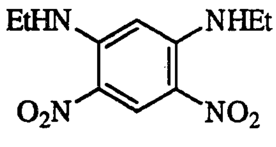
Synthesis of dendrimers containing ethynyltriphenylamine subunits was described in part I of this thesis. The reaction of these dendrimers with TCNE would yield interesting multipolar molecules which recently have attracted attention in the study of organic NLO materials. Second order NLO properties of Multipolar chromophores such as crystal violet, ruthenium tribipyridine complex (RuTB), and N,N'diethyl-4,6-dinitro-1,3-diaminobenzene (DIEDD) were reported.[33]



crystal violet



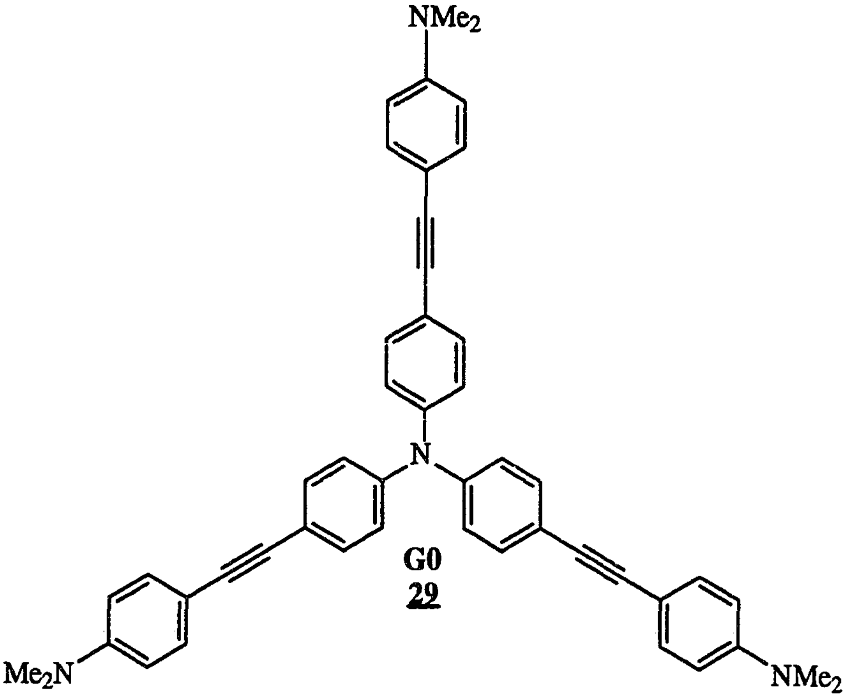
RuTB



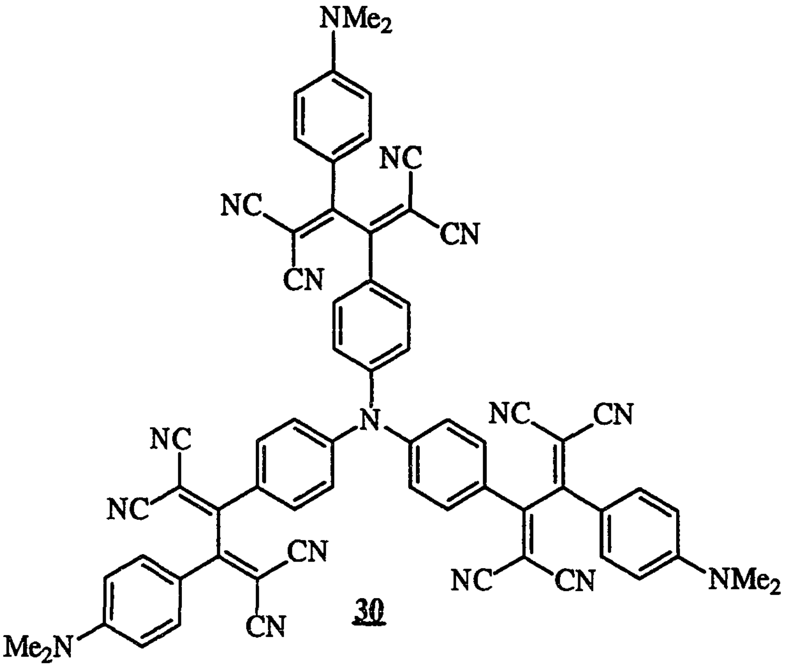
DIEDD

Compared to their dipolar couterparts, these chromophores possess some favorable features: (1) rounded shapes which allow single crystal packing, (2) lack of dipole moments, favoring noncentrosymmetric crystal. (3) trigonal lamellar structures which increase electro-optic modulator capacities, and (4) improved transparency and efficiency.

The reaction of **G0** dendrimer, 29, containing three triple bonds with three equivalents of TCNE was performed in CD_3CN and followed by ^1H and ^{13}C-NMR. A yellow solution of 29 turned deep red immediately after three equivalents of TCNE were added. ^1H and ^{13}C-NMR spectra showed that the reaction produced TCBD 30, in quantitative yield after 10 minutes. All of the three triple bonds were converted into TCBD units.

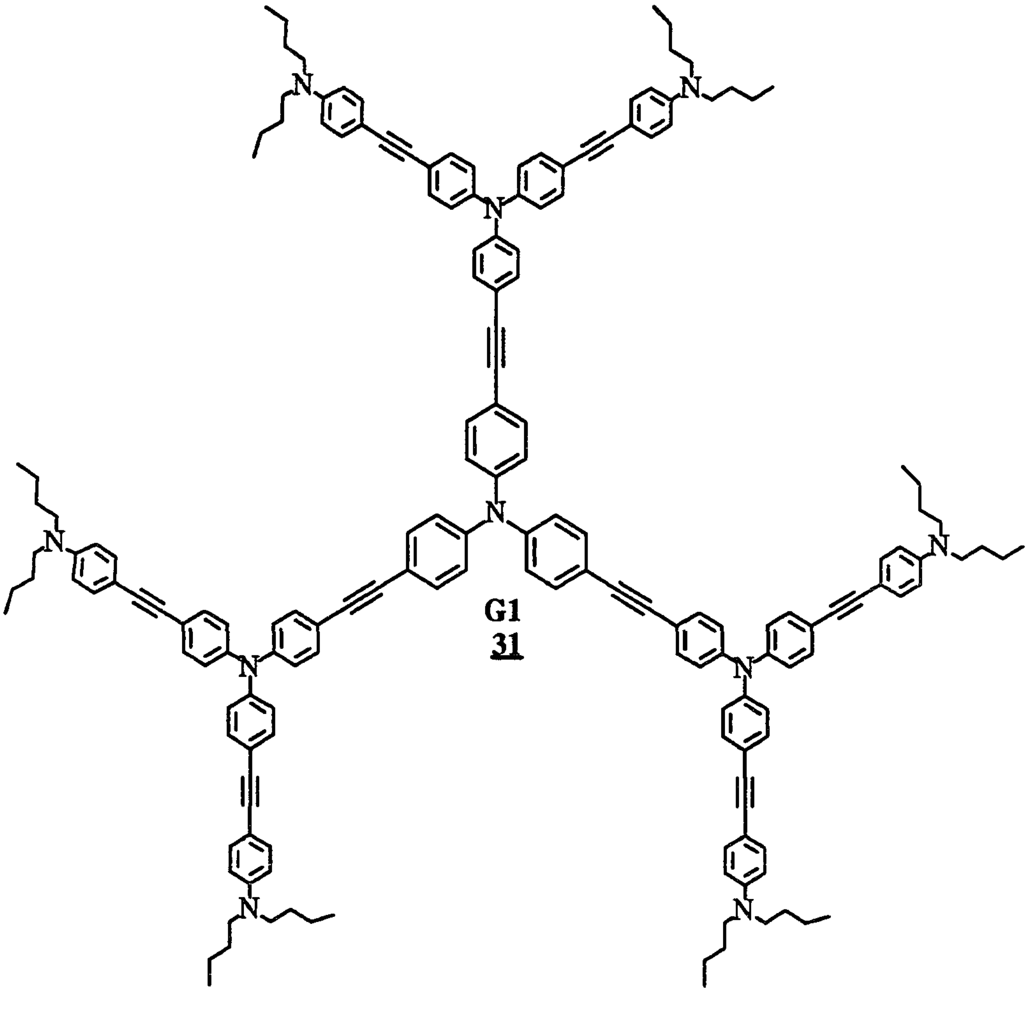

NMe2
N
Me2N
NMe2

G0
29


NMe2
NC
NC
CN
CN
N
NC
CN
NC
NC
CN
CN
NC
CN
NMe2
Me2N

30

The G1 dendritic triphenylamine acetylene, **31**, contains nine triple bonds. According to ^{1}H and ^{13}C-NMR, a reaction of dendrimer **31** with excess TCNE in $CDCl_3/CD_3CN$ did not give the product corresponding to the addition of all nine equivalents of TCNE. ^{1}H-NMR spectrum (Figure 12) of **G1** consists of three groups of greatly overlapped peaks from 6.5 to 7.4 ppm; a doublet at 6.5 ppm corresponding to the 12 outermost ortho (to dibutylamino) protons, the overlapping peaks centered at 7.0 correspond to the 24 inner ortho (to nitrogen) protons, and the peaks at 7.3 ppm correspond to the 36 meta (to nitrogen) protons. Upon the reaction with TCNE, these three groups of peaks were separated and shifted downfield



G1
31

indicating the addition of TCNE to some of the triple bonds. The 36 meta protons of **G1** were split into two groups containing 8 and 28 protons suggesting that an average of seven acetylene units of each **G1** molecule were converted to TCBD units (Figure 14). It however remained uncertain whether the reaction produced a single product, or a mixture of products.

The ^{13}C-NMR spectrum (Figure 15) appeared very complex and it was not possible to assign all the signals. With careful and systematic analysis of this spectrum, a reasonable structure for the product could be deduced. The single N-CH_2 signal at 50.3 ppm indicates full conversion of six outer triple bonds to six TCBD units. There are four possible products,

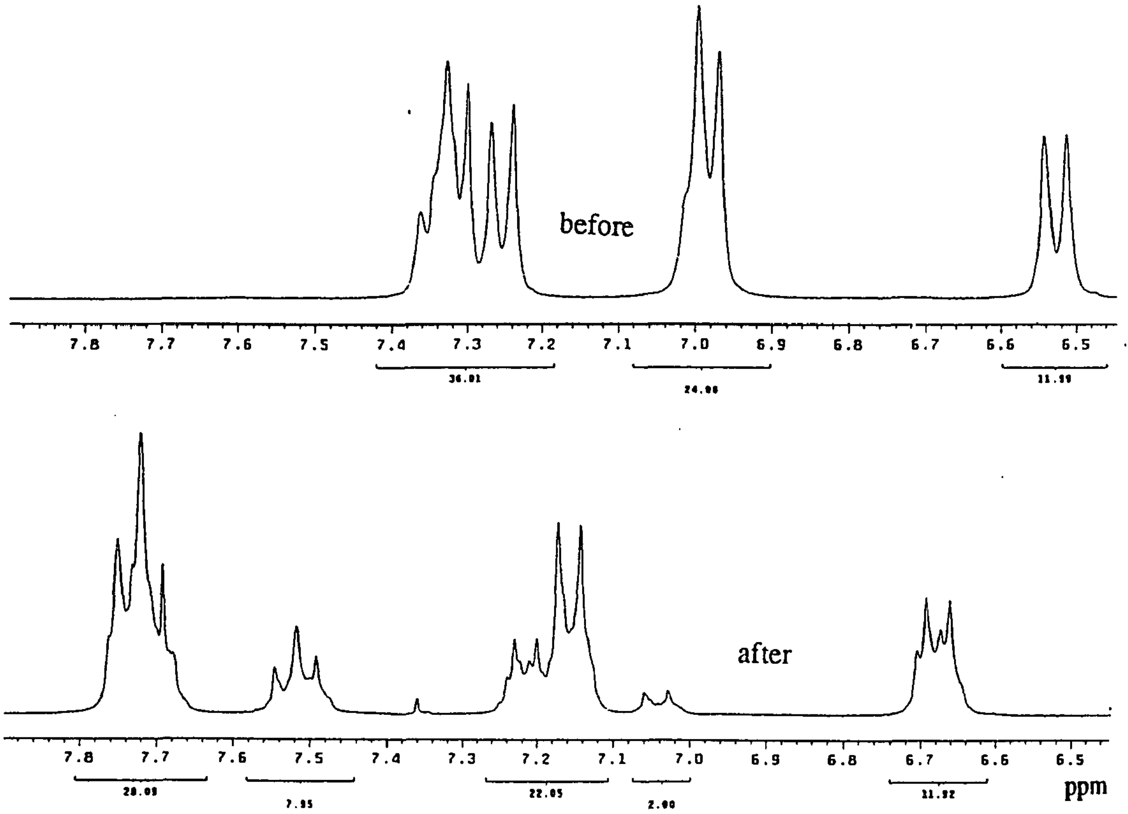


Figure 14 Aromatic ^{1}H-NMR spectra of **G1** in CD_3CN/ $CDCl_3$ before and thirty minutes after the addition of 9 equvalents of TCNE.

1:6 adduct, 1:7 adduct, 1:8 adduct, and 1:9 adduct, each having all of the outer acetylenes converted (Figure 16). The spectrum shows six signals of sp^2-C attached to N (*a, b, c, d, e, f*) and six signals of sp^2-C attached to malanonitrile group (*a', b', c', d', e' f'*) which can be expected from the 1:7 adduct and 1:8 adduct, but not from the 1:6 adduct or 1:9 adduct which requires only 2 and 4 signals, respectively. The ratios of carbons for *a:b:c:d:e:f* and *a' :b' :c:'d' :e' :f* are 4:4:1:1:2:2 and 2:2:2:2:4:4 for the 1:7 and 1:8 adducts, respectively. The ^{13}C-NMR spectrum shows that the integration ratio of 4:4:1:1 :2:2 matches with the 1:7 adduct. Thus, the product of the reaction of <u>31</u> with excess TCNE should be the 1:7 adduct, **<u>31+7TCNE</u>**, exclusively. This deduction agrees with the integration of the ^{1}H-NMR spectum and it is also reasonable based on the steric hindrance argument. The brief structure for 1:7 adduct (Figure 16) showed two seemingly equivalent unreacted diphenylacetylenes.

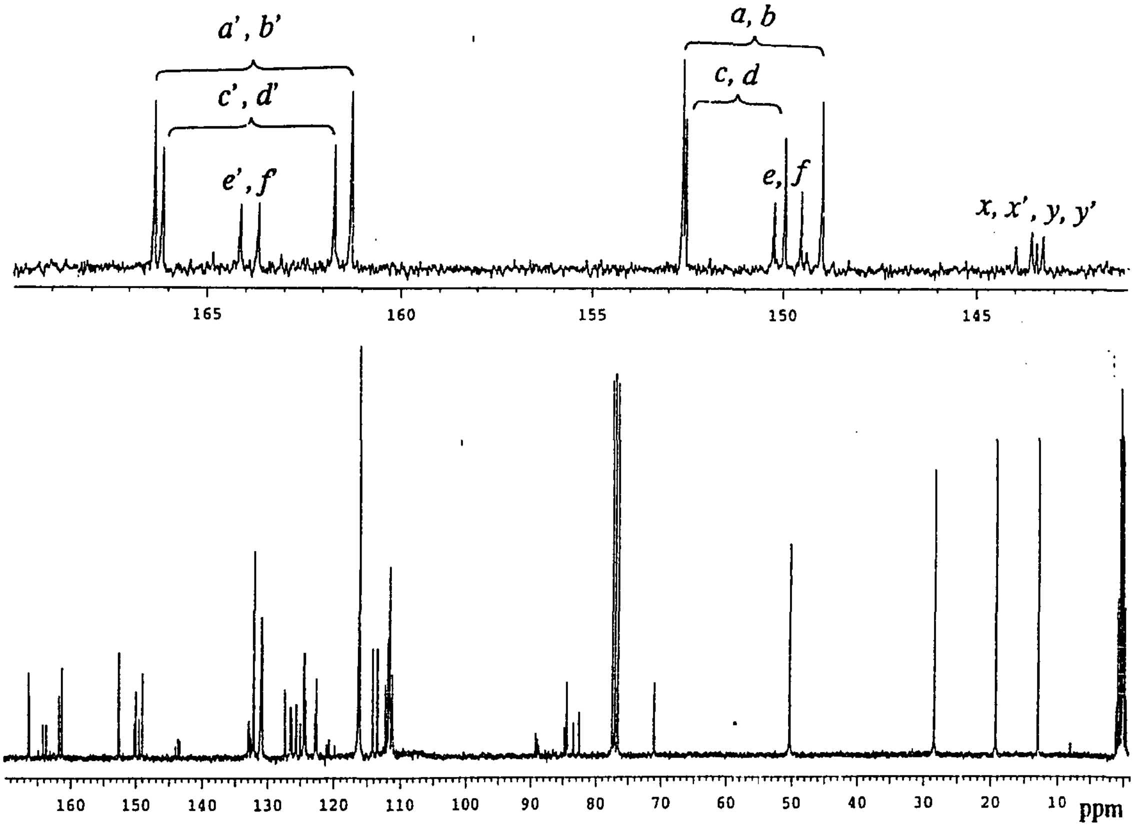
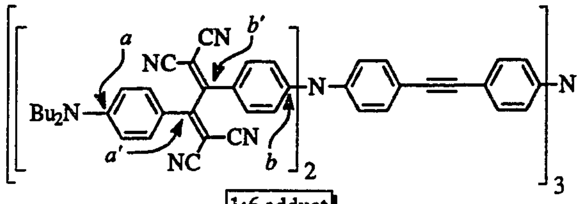
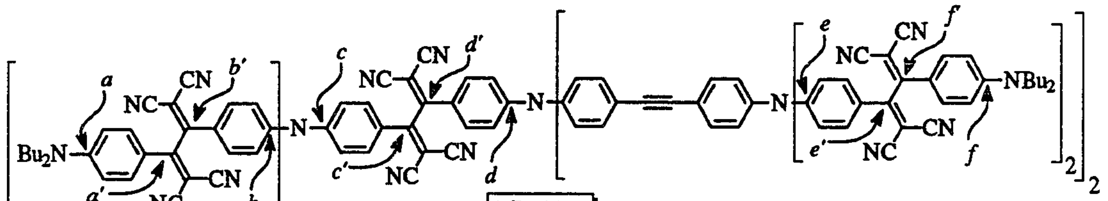


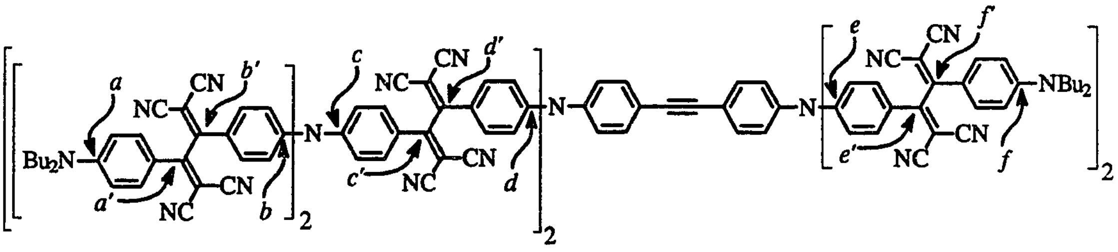
Figure 15 ^{13}C-NMR spectra of the product of the reaction of G1 with TCNE.



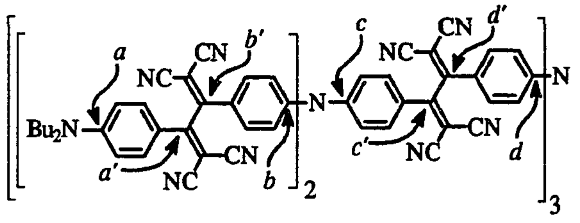
1:6 adduct



1:7 adduct



1:8 adduct



1:9 adduct

Figure 16 Characteristic carbons of 1:6, 1:7, 1:8 and 1:9 adducts of **G1** with TCNE.

However, the ^{13}C-NMR showed four, instead of two, signals (x, x', y, y') of sp^2-C attached to N of these two unreacted diphenylacetylenes (insert in Figure 15). The full structure of **31+7TCNE** showed that the molecule is chiral if the rotation about designated bond is restrained (Figure 17). The four carbons (x, x'; y, y') on these two diphenylacetylenes were thus diastereotopic.

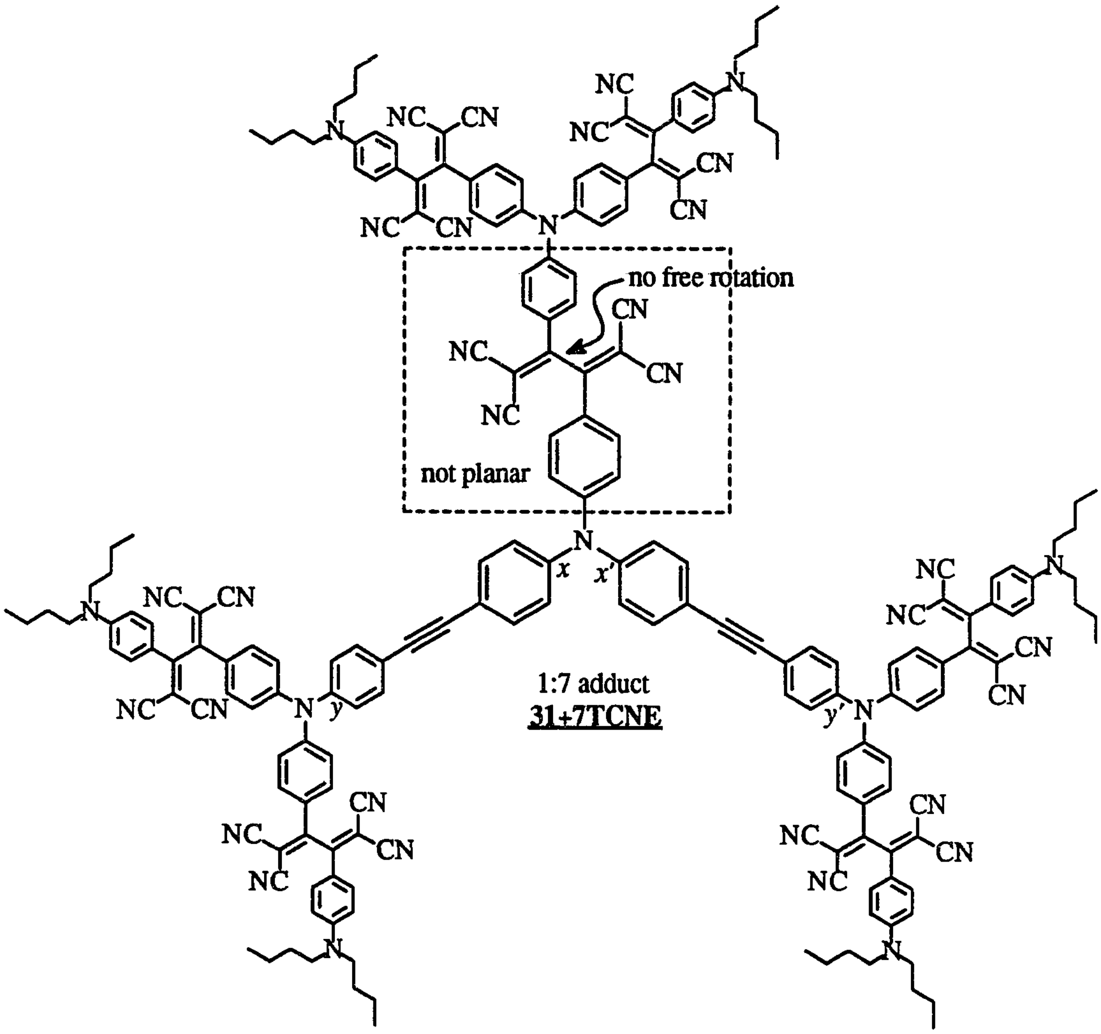
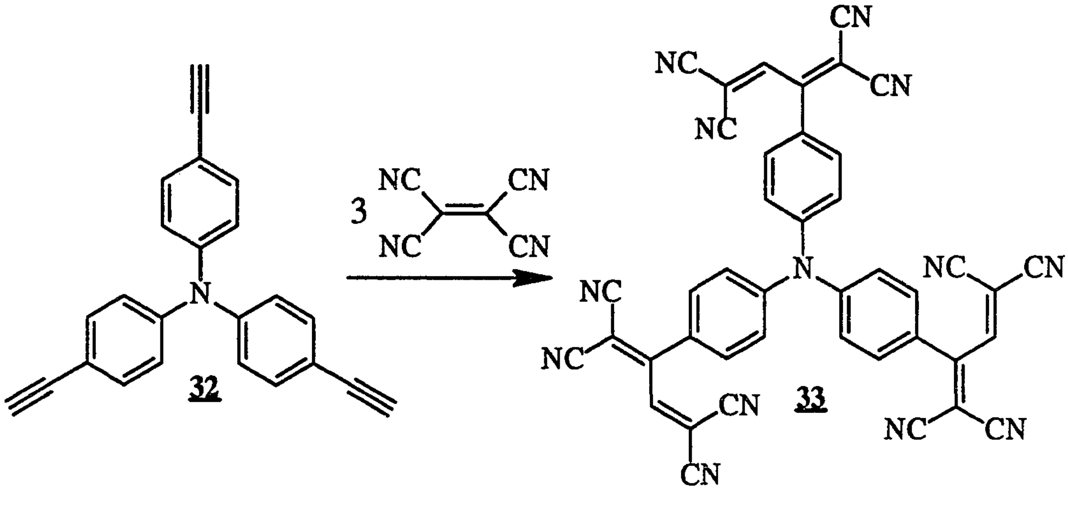


Figure 17 Structure of the 1:7 adduct showing two pairs of diastereotopic (x:x' and y:y') carbons observed in ^{13}C-NMR.

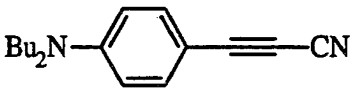
Ethynylbenzene was reported to form a molecular EDA complex with TCNE.[27] Our studies have shown that, with an electron donor substituent such as an amino group on the para position of ethynylbenzene, the triple bond reacts quickly with TCNE to form the TCBD product in quantitative yields at ambient temperature. The monosubstituted electron-rich acetylenes, both ethynylaniline **18** and diethynyldiphenyl-amine **19** were described earlier as reacting readily with one and two equivalents of TCNE, respectively, to form the corresponding mono- and bis-TCBD in quantitative yield. The possible reaction of three equivalents of TCNE with 4,4′,4′′-triethynyltriphenyl amine, **32**, which contains three acetylene groups and only one amino group was thus of interesting. The reaction was conducted in CD_3CN and studied by NMR. Remarkably, all three triple bonds of triacetylene **32** reacted readily with three equivalents of TCNE in acetonitrile to produce the corresponding TCBD **33** in quantitative yield within 10 minutes (Scheme 15). This result was not entirely expected considering that the additions of three molecules of TCNE to the triple



Scheme 15

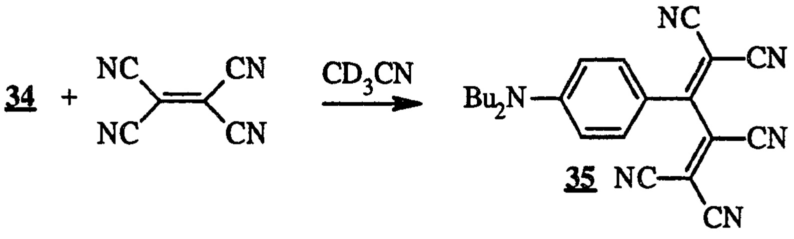
bonds are stepwise, whereas the third equivalent of TCNE must add to the last triple bond of the molecule already containing two strong electron withdrawing groups on the N of the amino group. However, if each addition occurs before any of the cyclobutenes open it could be argued that each addition step gets easier as N becomes more electron donating.

Another interesting and challenging substrate was cyanoacetylene 34, which contains a strong electron withdrawing group (CN) on one extremity of the triple bond. This acetylene presumably possesses a higher ionization energy than any other acetylenes which have been used as substrates in our studies.



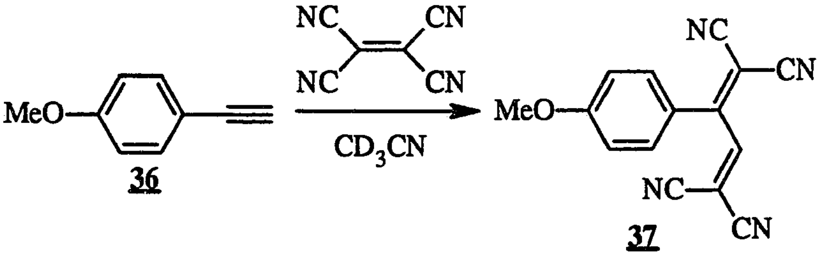
34

The product from the addition/ring-opening reaction of TCNE with cyanoacetylene 34 would be a novel pentacyanobutadiene (PCBD) which is interesting as a high β-value NLO chromophore. Surprisingly, the reaction went rapidly in acetronitrile and a quantitative yield of 35 (Scheme 16) was obtained within 10 minutes as observed by ^{1}H-NMR.



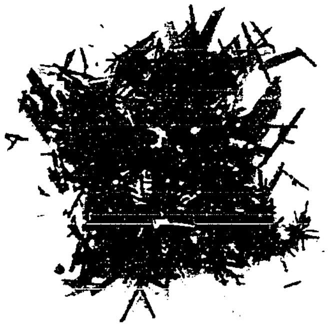
Scheme 16

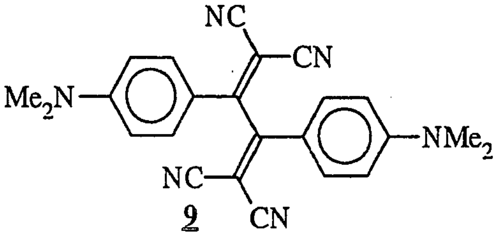
So far, all of our studies have focused solely on the reaction of TCNE with aryl amines containing ethynyl groups. This is because the alkoxy groups are poorer electron donors and provide less diversity in structures as the oxygen is a divalent atom while the nitrogen is a trivalent atom. However, it was of interest to see whether an electron-donating alkoxy group would provide sufficient electron supply to produce the same reaction. Indeed, acetylene 36 was found to react with TCNE to give TCBD 37 in quantitative yield (Scheme 17).



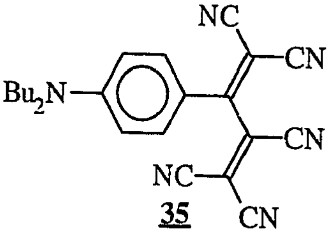
Scheme 17

TCBD 37 can be crystallized from a toluene/chloroform solution to give red hexagonal crystals. A big single crystal (3 mm × 5 mm × 1 mm) was obtained from this mixed solvent. The crystals of TCBD 37 are transparent and glass-like, unlike the crystals of TCBD 20, the amine analogue, or TCBD 35, which are shiny metal-like (Figure 18). Good transparency is also one of the desired properties of the NLO chromophores for optical devices. This result will provide more varieties of the monomer structures for designing new NLO polymers.

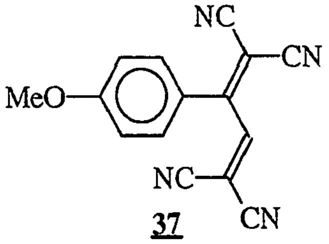




9



35



37

Figure 18 Crystals of 20, 37 and 35 shown 7 × actual sizes.

UV-Vis absorption spectra of the tetracyanobutadienes (TCBD)

In order to be meaningful, NLO properties need to be studied in the region beyond the electronic absorption bands to avoid the possible photochemical reactions and thermal effects from the absorption.[12] Therefore, the absorption characteristics of new NLO chromophores need to be studied before the NLO properties. Furthermore, the absorption energies of the chromophores provide information about the polarizabilities of the molecules as the chromophores with higher polarizability usually absorb the light at lower energy (or longer wavelength).[12] In other words, molecules with lower electronic transition energies are more polarizable. The UV-Vis absorption spectrum of each compound is also useful for characterization, especially for a highly colored compound.

The UV-Vis spectra of all the new TCBDs were recorded and the absorption peaks are presented in Table 2. The structure of the UV-Vis absorption spectra as well as the position of the absorption peaks of disubstituted TCBDs (**9**, **10**, **12**, **30**) are quite different from monosubstituted TCBDs (**20**, **21**, **33**). The spectra of disubstituted TCBDs contained a single broad absorption band in contrast to the spectra of monosubstituted TCBDs which showed multiple absorption bands. The multiple bands observed in the monosubstituted TCBDs still cannot be completely accounted for, but the availability of several conformations in the monosubstituted TCBDs is a possible rationalization. The λ_{max} of disubstituted TCBDs are about 100 nm lower than the longest λ_{max} of monosubstituted TCBDs. The lower absorption energies of monosubstituted TCBDs (**20**, **21** and **33**), relative to the disubstituted ones (**9**, **12** and **30**), suggest higher polarizabilities of the monosubstituted TCBDs.

Table 2 UV-Vis absorption peaks of the tetracyanobutadiene (TCBD) derivatives.

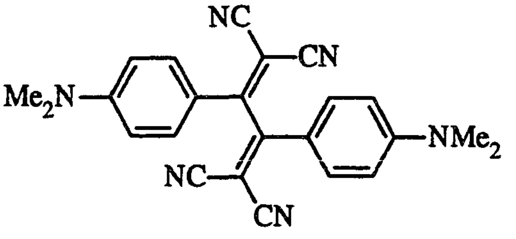
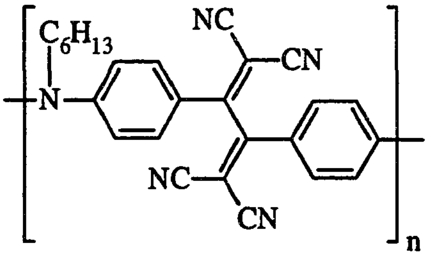
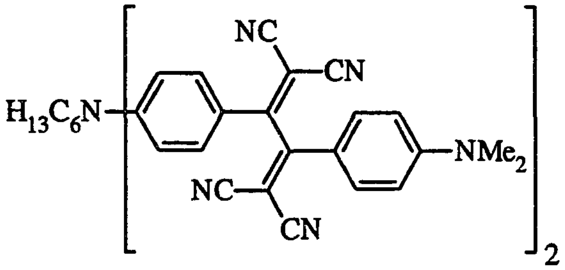
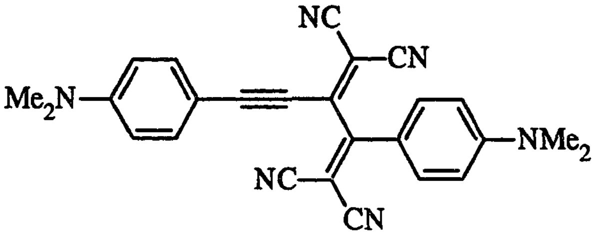
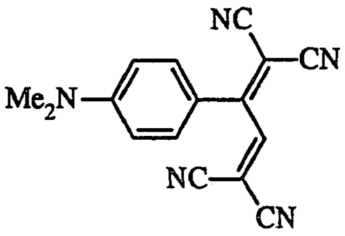
compound	structure	λ_{max}
9		468
10		512
12		468
16		520
20		346, 571

Table 2 (Continued)

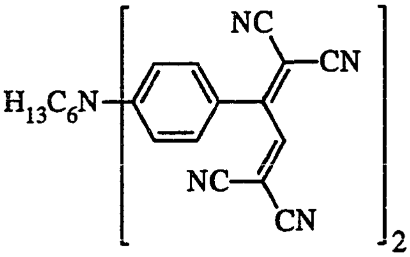
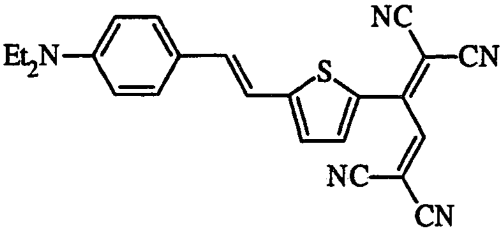
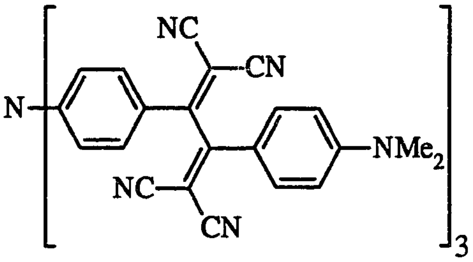
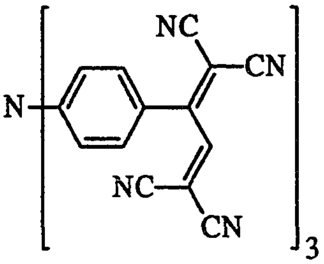
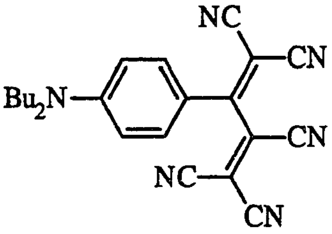
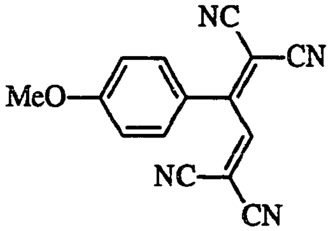
compound	structure	λ_{max}
21		303, 355, 590
28		314, 450, 656
30		464
33		280, 574
35		464

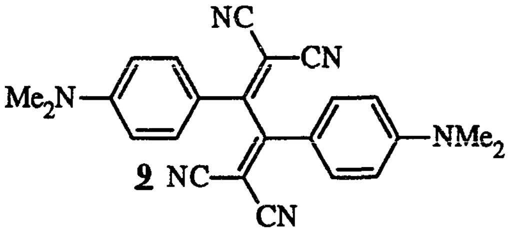
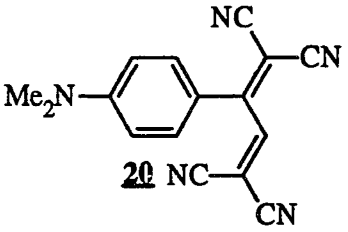
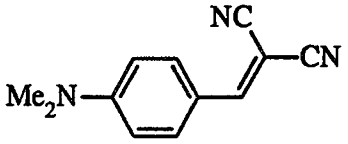
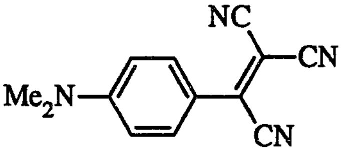
Table 2 (Continued)

compound	structure	λ_{max}
37		292, 444

Due to the lower steric hindrance, the monosubstituted TCBD are more planar than the disubstituted ones. The more planar structure allows better overlap of the π-orbitals and better electron delocalization in the conjugated system resulting in lower band gaps between the HOMO and LUMO.

The λ_{max} of TCBD 9 (468 nm in chloroform) falls between the λ_{max} of 4-dicyanovinyl-N,N-dimethyaniline (420 nm in chloroform)[17] and 4-tricyanovinyl-N,N-dimethylaniline (521 nm in acetone)[18] (Table 3). The longest λ_{max} of TCBD 20 is the highest (571 nm in chloroform). Comparison of these λ_{max} suggests that the molecular polarizabilities of the disubstituted TCBDs should be higher than the dicyanovinyl analogues and the molecular polarizabilities of the monosubstituted TCBDs should be higher than the tricyanovinyl analogues. The longest λ_{max} of the new extended π-conjugated TCBD 28 is 656 nm, which is 85 nm longer than the λ_{max} of the simple TCBD 20. This considerable bathochromic shift indicates that increasing the π-conjugated lengths is indeed a good strategy to increase the polarizabilities of these TCBD chromophores.

Table 3 Absorption peaks of the synthesized TCBD 9 and 20 compared to the known dicyanovinyl and tricyanovinyl analogues.

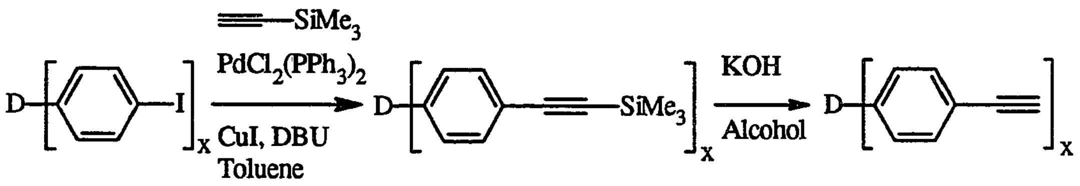
compound	λ_{max} (nm)
9 	468 (chloroform)
20 	571 (chloroform)
	420[17] (chloroform)
	521[18] (acetone)

PCBD 35, containing five cyano groups on butadiene, was expected to absorb light at longer wavelengths than the monosubstituted TCBD 20. The absorption spectrum of PCBD, however, looks just like the absorption spectra of normal disubstituted TCBD, containing only a single broad band with a λ_{max} at 464 nm. This result suggests that the second substituent, even when it is an electron withdrawing group, on TCBD causes a negative effect on the λ_{max} and molecular polarizabilities of the chromophores.

Synthesis of the electron-rich acetylenes

Several reactions utilized in the synthesis of the electron-rich acetylenes in this Chapter are the same as those of acetylene monomers in PART I, so they will be only briefly described in this section. The ethynyl derivatives of anisole, N,N-dimethylaniline, N-hexyldiphenylamine and triphenylamine (**36**, **18**, **19**, **32**) were synthesized from Heck-type coupling[34] reactions of appropriate iodo compounds with trimethylsilylacetylene followed by a base-catalyzed desilyation[35] (Scheme 18).

The iodo compounds **36**-I and **18**-I are commercially available but **19**-I and **32**-I were synthesized from iodination of the N-hexyldiphenylamine[*] by a mild reagent, benzyltrimethylammonium dichloroiodate[36] (Scheme19).



36-I	**36**-TMS	**36** D = MeO, x = 1
18-I	**18**-TMS	**18** D = Me$_2$N, x = 1
19-I	**19**-TMS	**19** D = H$_{13}$C$_6$N, x = 2
32-I	**32**-TMS	**32** D = N, x = 3

Scheme 18

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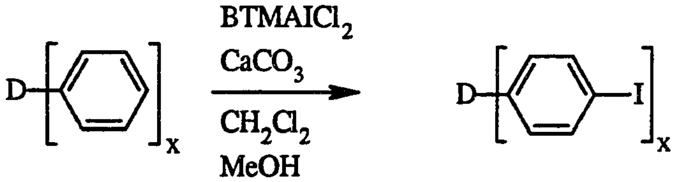
[*] see page 69 for the synthesis and spectroscopic data of this compound.



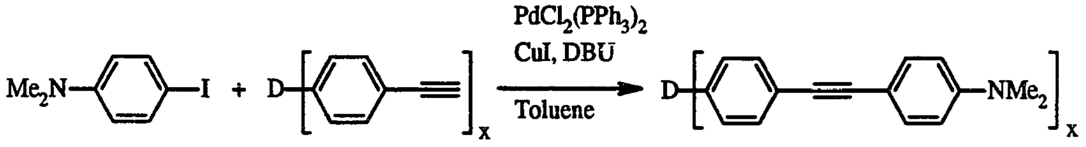
19-I R = $H_{13}C_6N$, x = 2

32-I D = N, x = 3

Scheme 19

The disubstituted acetylenes **7**, **11** and **29** were synthesized from the palladium coupling[34] reaction of 4-iodo-N,N-dimethylaniline with monosubstituted acetylenes **18**, **19** and **32**, respectively (Scheme 20). The yields and spectroscopic data for these compounds are presented in the experimental section.

Diacetylene **15** was synthesized from an oxidative coupling[37] of 4-ethynyl-N,N-dimethylaniline **18** in 87% yield (Scheme 21).

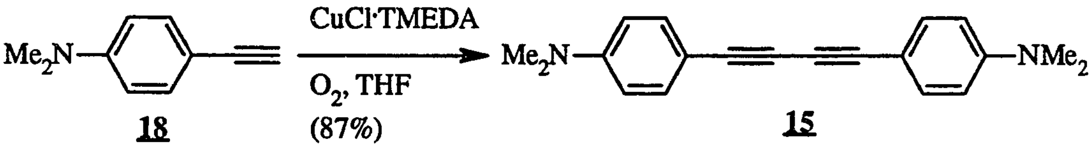


18-I

18 D = Me_2N, x = 1
19 D = $H_{13}C_6N$, x = 2
32 D = N, x = 3

7 D = Me_2N, x = 1
11 D = $H_{13}C_6N$, x = 2
29 D = N, x = 3

Scheme 20

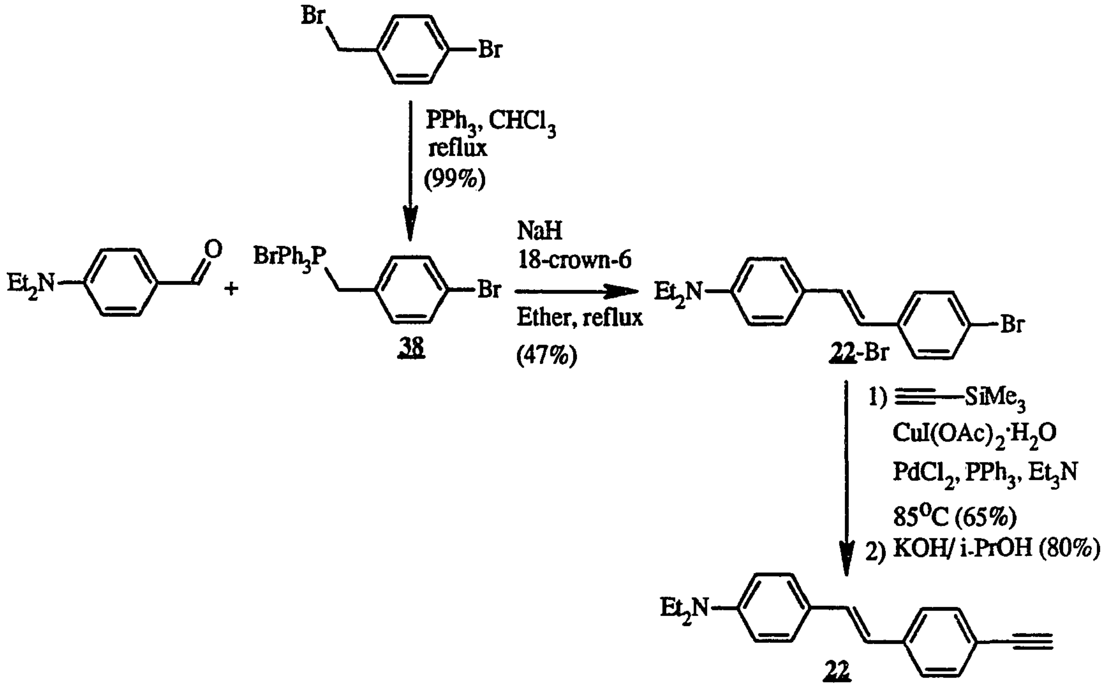


18

15

Scheme 21

Synthesis of extended π-conjugated acetylene 22 is shown in Scheme 22. The Wittig reagent precursor, 38, 4-bromobenzyltriphenylphosphenium bromide, was obtained in quantitative yield by refluxing a chloroform solution of triphenylphosphine and 4-bromobenzylbromide.[38,39] The Wittig reagent,[40,41] generated in situ from the precursor 38 by sodium hydride in presence of 18-crown-6, reacted with 4-diehtylaminobenzaldehyde to give 4-diethylamino-4′-bromo-trans-stilbene, 22-Br, in 47% yield.

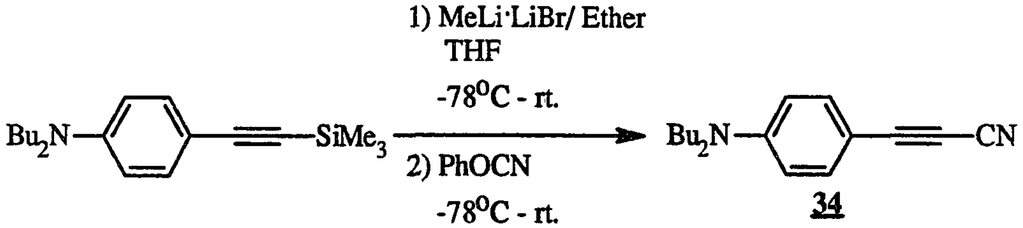


Scheme 22

The reaction also gave 30% of the cis-isomer as a byproduct. The palladium coupling[42] of bromostilbene 22-Br with trimethylsilylacetylene gave 4-diethylamino-4′-bromo-trans-stilbene, 22-TMS. The following base-catalyzed desilylation gave the desired acetylene 22 in 52% yield (for the last two steps).

Another extended π-conjugated acetylene containing a thiophene unit, 25, was synthesized by the same sequences of reactions as for acetylene 22. A Wittig reaction of (5-bromo-2-thenyl)triphenylphosphoniumbromide,[43] 39 with 4-diethylaminobenzaldehyde produced 5-(4-N,N-diethylamino-β-trans-styryl)-2-bromo thiophene, 25-Br in 45%. The subsequent palladium coupling of 25-Br with trimethylsilyl acetylene yielded 2-trimethylsilylethynyl-5-(4-N,N-diethylamino-β-styryl) thiophene, 25-TMS, which was subjected to a base-catalyzed desilylation to give 25.

The synthesis of the cyanoacetylene 34 was performed according to Scheme 23. In a one pot synthesis, 4-trimethylsilylethynyl-N,N-dibutylaniline* was treated with a solution of methyllithium-lithium bromide complex.[44] The reaction was then quenched by phenylcyanate[45] to give the desired product in 65% yield.



Scheme 23

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* see page 87 for the synthesis of this compound.

EXPERIMENTAL

Characterizations of all synthesized compounds were based on exact mass, IR, UV/Vis, ^{1}H-NMR and ^{13}C-NMR.. The exact masses were obtained from a Kratos MS 50 mass spectrometer with 10,000 resolution. The infrared spectra were recorded on a Bio-Rad Digilab FTS-7 spectrometer from neat samples. The UV/Vis spectra were acquired on a Hewlett Packard 8452A diode array UV/Vis spectrometer and λ_{max} were determined at optical densities of 0.2-0.5. The ^{1}H and ^{13}C NMR spectra were collected on a Varian VXR-300 MHz spectrometer in deuterated chloroform solutions unless otherwise specified. Tentative signal assignments of ^{13}C-NMR spectra are given in parentheses after each chemical shift. Reactions were monitored by Hewlett Packard 5890 series II GC and Hwelett Packard tandem GC-IR-MS (5890A GC-5965A IR-5970 Series MS).

The thermal responses of polymers were studied on Du Pont Instruments 951 Thermogravimetric Analyzer (TGA) and 910 Differential Scanning Calorimeter (DSC) with a scanning rate of 20°C/min for both analyses. Molecular weight distribution of polymers were detemined by gel permeation chromatograph (GPC) system using universal calibration against polystyrene standards (M_n = 2,000 - 170,000). The GPC system consisted of a Beckman 110B solvent derivery system, a Perkin-Elmer 601 liquid chromatograph equiped with six Beckman 10 μ U-spherogel (7.7 mm × 30 cm) columns, a Viscotek 110 differential viscometer and a Waters Associates R401 differential refractometer. The viscometer and refractometer were parallel connected. The GPC analysis was performed at a flow rate of 1.0 mL/min of THF.

THF was distilled over Na-benzophenone and ether was distilled over CaH_2 immediately before use. Commercially available reagents were used as received unless otherwise specified. Scientific Adsorbents 40 µ silica gel was utilized in flash chromatography.

4-trimethylsilylethynyl-N,N,-dimethylaniline, 18-TMS

A general procedure of palladium coupling of trimethylsilylacetylene with aryl iodide is presented here. A 100 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with 4-iodo-N,N-dimethylaminobenzene (2.47 g, 10 mmol), $PdCl_2(PPh3)_2$(30 mg), CuI (19 mg) and DBU (1.64 g) and toluene (30 mL). Trimethylsilylacetylene (1.08g, 11 mmol) was added dropwise to this stirred solution. After 2 h the mixture was filtered and the precipitate was washed with toluene (3 × 15 mL). The combined filtrate was concentrated and the residue was eluted through a flash silica gel column by methylene chloride. The solvent was removed and the resulting yellow solid was dried under vacuum for 24 h. to give **18-TMS** (1.91 g, 88 %). **IR (cm^{-1}):** 1515, 2150, 2806, 2963; **MS:** 217 (M^+), 202 (100%), 186, 172, 158, 101.

4-ethynyl-N,N-dimethylaniline, 18

A general procedure of base-catalyzed desilylation is presented here. A 100 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with **18**-TMS (1.5 g) and methanol (20 mL). Saturated KOH aqueous solution (0.2 mL) was added dropwise to this stirred solution. After 6 h 10% potassium hydrogencarbonate solution (20 mL) and hexane (20 mL) was added to the mixture. The organic layer was separated and the aqueous layer was extracted with hexane (2 × 20 mL). The combined organic layer was washed with water (2 × 20 mL) and then dried over anhydrous $MgSO_4$. The solvent was removed and the resulting yellow solid was dried under vacuum for 24 h. to give **18** (1.00 g, 95%). **m.p.:** 50-51 °C; **HIRES EI:** calcd for $C_{10}H_{11}N$ 145.0892, measured 145.0891; UV **($CHCl_3$, nm):** $\lambda_{max} = 292$; **IR (cm^{-1}):** 1516, 1605, 2814, 2895, 2097, 3266; **^{1}H-NMR (CD_3CN):** δ 2.93 (6 H, s), 3.19 (H, s), 6.65 (2 H, d *J* 9.0), 7.30 (2 H, d *J* 9.0); **^{13}C-NMR (CD_3CN):** δ 40.2 (2 CH_3), 76.2 (sp-CH), 85.3 (sp-C), 109.0 (sp^2-C), 112.6 (2 sp^2-CH), 133.7 (2 sp^2-CH), 151.5 (sp^2-C).

4,4′-diodo-N-hexyldiphenylamine, 19-I

A general procedure for the iodination of arylamines by Benzyltrimethylammonium chloroiodate[36], $BTMAICl_2$, is presented here. A 100 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with N-hexyldiphenylamine (10.21 g, 40 mmol), methylene chloride (300 mL) and methanol (100 mL). $BTMAICl_2$ (30.64 g, 88 mmol) and $CaCO_3$ (11 g, 0.11mol) were added quickly to this stirred solution. After 20 h, to the mixture was added 20% $NaHSO_3$ solution until the mixture became colorless. The organic layer was separated and the aqueous layer was extracted with methylene chloride (2 × 50 mL). The combined organic layer was washed with water (2 × 100 mL) and dried over anhydrous $MgSO_4$. The mixture was concentrated and the residue was eluted through a flash silica gel column by hexane. The solvent was removed and the resulting yellow oil was dried under vacuum at 65 °C for 24 h. to give **19-I** (4.40 g, 86%). **HIRES EI:** calcd for $C_{18}H_{21}NI_2$

504.9763, measured 504.9694; ^{1}**H-NMR:** δ 0.86 (3 H, t *J* 7.0), 1.26 (6 H, m), 1.54 (2 H, qui *J* 7.0), 3.60 (2 H, t *J* 7.0), 6.73 (4 H, d *J* 9.0), 7.51 (4 H, d *J* 9.0); ^{13}**C-NMR:** δ 14.0 (CH$_3$), 22.6 (CH$_2$), 26.6 (CH$_2$), 27.1 (CH$_2$), 31.5 (CH$_2$), 52.2 (CH$_2$), 83.9 (2 sp^2-C), 129.0 (4 sp^2-CH), 138.1 (4 sp^2-CH), 147.1 (2 sp^2-C).

4,4′-bis(trimethylsilyethynyl)-N-hexyldiphenylamine, 19-TMS

The palladium coupling of 19-I and two equivalents of TMSA followed the procedure in the synthesis of 18-TMS. **Yield:** quantitative (yellow oil); **HIRES EI:** calcd for $C_{28}H_{39}NSi_2$ 445.2621, measured 445.2633; ^{1}**H-NMR:** δ 0.22 (18 H, s), 0.85 (3 H, t *J* 7.0), 1.25 (6 H, m), 1.59 (2 H, qui *J* 7.0), 3.65 (2 H, t *J* 7.0), 6.87 (4 H, d *J* 9.0), 7.33 (4 H, d *J* 9.0); ^{13}**C-NMR:** δ 0.1 (3 CH$_3$), 14.0 (CH$_3$), 22.6 (CH$_2$), 26.6 (CH$_2$), 27.3 (CH$_2$), 31.5 (CH$_2$), 52.1 (CH$_2$), 93.0 (2 sp-C), 105.4 (2 sp-C), 115.5 (2 sp^2-C), 120.4 (4 sp^2-CH), 133.1 (4 sp^2-CH), 147.4 (2 sp^2-C).

4,4′-diethynyl-N-hexyldiphenylamine, 19

The base-catalyzed desilylation was performed in methanol/ *i*-propanol (1:2) using the same procedure as in the synthesis of 18. **Yield:** 91% (yellow oil); **HIRES EI:** calcd for $C_{22}H_{23}N$ 301.1839, measured 301.1839, 230.1 (100%); **UV (CHCl$_3$, nm):** λ_{max} = 339, 279; **IR(GC-IR, cm^{-1}):** 1504, 2106, 2938, 3331; ^{1}**H-NMR (CD$_3$CN):** δ 0.87 (3 H, t *J* 7.0), 1.28 (6 H, m), 1.63 (2 H, qui *J* 7.5), 3.02 (H, s), 3.68 (2 H, t *J* 7.5), 6.93 (4 H, d *J* 9.0), 7.38 (4 H, d *J* 9.0); ^{13}**C-NMR (CD$_3$CN):** δ 14.0 (CH$_3$), 22.6 (CH$_2$), 26.6 (CH$_2$), 27.3 (CH$_2$), 31.5 (CH$_2$), 52.1 (CH$_2$), 76.2 (2 sp-CH), 83.8 (2 sp-C), 114.5 (2 sp^2-C), 120.5 (4 sp^2-CH), 133.2

(4 sp^2-CH), 147.6 (2 sp^2-C).

4,4′,4″-triiodotriphenylamine, 32-I

The triple iodination of triphenylamine was accomplished by using 3.3 equivalents of the iodinating reagent, BTMAICl$_2$. The reaction was performed at the reflux temperature of mixed solvent of chloroform and methanol (2:1) for 36 h. The procedure and work up were the same as in the synthesis of 19-I. **Yield:** 66%; **^{1}H-NMR:** δ 6.80 (6 H, d *J* 9.0), 7.52 (6 H, d *J* 9.0), **^{13}C-NMR:** δ 86.6 (3 sp^2-C), 126.0 (6 sp^2-CH), 138.4 (6 sp^2-CH), 146.5 (3 sp^2-C).

4,4′,4″-tris(trimethylsilylethynyl) triphenylamine, 32-TMS

The palladium coupling of 32-I and three equivalents of TMSA followed the procedure in the synthesis of 18-TMS. **m.p.:** 166-167 °C; **HIRES EI:** calcd for $C_{33}H_{39}NSi_3$ 533.2395, measured 533.2390; **IR(cm^{-1}):** 1502, 1596, 2155, 2899, 2958, 3038; **^{1}H-NMR (CD$_3$CN):** δ 0.23 (27 H, s), 6.94 (6 H, d *J* 9.0), 7.33 (6 H, d *J* 9.0); **^{13}C-NMR (CDCl$_3$):** δ 0.0 (9 sp-CH$_3$), 93.9 (3 sp-C), 104.8 (3 sp-C), 117.8 (3 sp^2-C), 123.8 (6 sp^2-CH), 133.1 (6 sp^2-CH), 146.7 (3 sp^2-C).

4,4′,4″-triethynyltriphenylamine, 32

The base-catalyzed desilylation was performed in methanol/ diethylether (1:1) with the same procedure as in the synthesis of 18. **Yield:** 92%(yellow solid); **m.p.:** 108-110 °C; **HIRES EI:** calcd for $C_{24}H_{15}N$ 317.1209, measured 317.1204; **IR(cm^{-1}):** 1598, 2104, 3037, 3287; **UV (CHCl$_3$, nm):** λ_{max} = 282; **^{1}H-NMR (CD$_3$CN):** δ 3.33 (3 H, s), 7.36 (6 H, d *J*

9.0), 6.96 (6 H, d *J* 9.0); **^{13}C-NMR:** δ 78.6 (3 sp-CH), 84.0 (3 sp-C), 117.6 (3 sp^2-C), 125.0 (6 sp^2-CH), 134.2 (6 sp^2-CH), 148.0 (3 sp^2-C).

4,4′-dimethylaminotolan, 7

Acetylene **7** was obtained from a palladium coupling of **18** with 4-iodo-N,N-dimethylaniline using the same procedure as in the synthesis of **18**-TMS. **Yield:** 53 %; **m.p.:** 222-224 °C; **HIRES EI:** calcd for $C_{18}H_{20}N_2$ 264.1665, measured 264.1631; **UV (CHCl$_3$, nm):** λ_{max} = 332, 352; **IR(cm^{-1}):** 1527, 1609, 2807, 2888; **^{1}H-NMR:** δ 2.96 (12 H, s), 6.64 (4 H, d *J* 9.0), 7.37 (4 H, d *J* 9.0); **^{13}C-NMR:** δ 40.3 (4 CH$_3$), 88.1 (2 sp-C), 111.1 (2 sp^2-C), 111.9 (4 sp^2-CH), 132.3 (4 sp^2-CH), 149.7 (2 sp^2-C).

bis-N,N-(4-dimethylaminophenylethynylene-p-phenylene) hexylamine, 11

Acetylene **11** was obtained from a palladium coupling of **19** with two equivalents of 4-iodo-N,N-dimethylaniline using the same procedure as in the synthesis of **18**-TMS. **Yield:** 78%; **m.p.:** 146-147 °C; **HIRES EI:** calcd for $C_{38}H_{41}N_3$ 539.330, measured 5539.3299; **UV (CHCl$_3$, nm):** λ_{max} = 332, 360; **IR(neat, cm^{-1}):** 1506, 1523, 1609, 2207, 2803, 2856, 2926, 2951; **^{1}H-NMR (CD$_3$CN):** δ 0.86 (3 H, t *J* 7.0), 1.28 (6 H, m), 1.64 (2 H, qui *J* 7.0), 2.97 (12 H, s), 3.68 (2 H, t *J* 7.0), 6.64 (4 H, d *J* 9.0), 7.94 (4 H, d *J* 9.0), 7.38 (8 H, d *J* 9.0); **^{13}C-NMR (CD$_3$CN):** δ 14.0 (CH$_3$), 22.6 (CH$_2$), 26.7 (CH$_2$), 27.4 (CH$_2$), 31.6 (CH$_2$), 40.2 (4 CH$_3$), 52.2 (CH$_2$), 87.4 (2 sp-C), 89.5 (2 sp-C), 110.5 (2 sp^2-C), 111.8 (4 sp^2-CH), 116.4 (2 sp^2-C), 120.5 (4 sp^2-CH), 132.3 (4 sp^2-CH), 132.5 (4 sp^2-CH), 146.8 (2 sp^2-C), 149.8 (2 sp^2-C).

4,4′,4′′-Tris(4-dimethylaminophenylethynyl) triphenylamine, 29

Acetylene 29 was obtained from a palladium coupling of 29-I with three equivalents of 4-ethynyl-N,N-dimethylaniline using the synthesis procedure of 7. **Yield:** 83%; **m.p.:** 267^0-269 °C; **DSC(rt-400 °C, rate 20 °C/min): HIRES EI:** calcd for $C_{48}H_{42}N_4$ 674.34095, measured 674.34140; **IR(cm^{-1}):** 1501, 1523, 1609, 2208, 2803, 2890, 3037; **UV** ($CHCl_3$, nm) : λ_{max} = 380; **^{1}H-NMR (CD_3CN):** δ 2.98 (18 H, s), 6.66 (6 H, d *J* 9.0), 7.04 (6 H, d *J* 9.0), 7.40 (6 H, d *J* 9.0), 7.41 (6 H, d *J* 9.0); **^{13}C-NMR (CD_3CN):** δ 40.1 (3 sp^3-C), 87.2 (3 sp-C), 90.3 (3 sp-C), 110.1 (3 sp^2-C), 111.8 (6 sp^2-CH), 118.6 (3 sp^2-C), 123.8 (6 sp^2-CH), 132.3 (6 sp^2-CH), 132.5 (6 sp^2-CH), 146.1 (3 sp^2-C), 149.9 (3 sp^2-C).

bis-(4,4′-dimethylaminophenyl) butadiyne, 15

A 100 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with CuCl (0.30g, 3.0 mmol) and THF (5 mL). Tetramethylethylenediamine, TMEDA, (0.20 mL, 1.3 mmol) was added to this stirred suspension. After 45 min the mixture was allowed to settle, leaving a clear, deep blue-green solution of the CuCl·TMEDA complex.

A three-necked 50 mL round-bottomed flask equipped with a magnetic stirring bar, thermometer, cold-finger condenser and O_2 inlet-outlet tubes, containing the solution of 4-ethynyl-N,N-dimethylaniline, 18 (1g, 6.9 mmol) and THF (20 mL) was charged with a rapid stream of O_2. The solution was added dropwise with a CuCl·TMEDA complex solution (2 mL), freshly prepared as described above, and the temperature was maintained at 35-45 °C. After 5 h the solution was filtered and the solid was washed several times with methylene chloride until no more yellow filtrate obtained. The filtrate was combined and the solvent was removed. The yellow residue was eluted through a flash silica gel column by methylene chloride. The product was collected and the solvent was removed. **Yield:** 87 %; **m.p.**: 231 233 °C; **HIRES EI:** calcd for $C_{20}H_{20}N_2$ 288.1627, measured 288.1628; **UV ($CHCl_3$, nm):** λ_{max} = 350, 379; **IR(cm^{-1}):** 1516, 1601, 2125, 2143, 2804, 2921, 2963; **^{1}H-NMR (CD_2Cl_2):** δ 2.97 (12 H, s), 6.59 (4 H, d *J* 9.0), 7.37 (4 H, d *J* 9.0); **^{13}C-NMR (CD_2Cl_2):** δ 40.1 (4 CH_3), 72.6 (2 sp-C), 82.3 (2 sp-C), 108.6 (sp^2-C), 111.6 (4 sp^2-CH), 133.6 (4 sp^2-CH), 150.3 (sp^2-C).

4-cyanoethynyl-N,N-dibutylaniline, 34

A 100 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with 4-trimethylsilylethynyl-N,N-dibutylaniline (3.01g, 10 mmol) and dry THF (20 mL). The solution was cooled to -78°C. A solution of MeLi·LiBr in diethylether (6.7 mL × 1.5 M , 10 mmol) was then added dropwise to this stirred solution.[18] After 1 h the mixture was allowed to warm to room temperature and maintained at this point for 8 h. The mixture was again cooled to -78 °C. Phenyl cyanate[19] (1.3 g, 11 mmol) was then added dropwise to this mixture. The mixture was allowed to warm slowly to room temperature. After 8 h 6M NaOH (40 mL) and ether (80 mL) was then added to the mixture. The organic layer was extracted with 6M NaOH (3 × 40 mL), dried over $MgSO_4$ and the solvent was removed. The residue was eluted through a flash silica gel column by hexane/ethylacetate (90:10). Further purification by crystallization from hexane provided pure 34 (1.6 g, 63 %) as white crystalline needles. **m.p.:** 61-62 °C; **HIRES EI:** calcd for $C_{17}H_{22}N_2$ 254.1780, measured 254.1785;

UV ($CHCl_3$, nm): λ_{max} = 348; **IR(cm^{-1}):** 1598, 2132, 2224, 2254, 2870, 2955; **^{1}H-NMR (CD_3CN):** δ 0.93 (6 H, t *J* 7.5), 1.33 (4 H, sex *J* 7.5), 1.53 (4 H, qui *J* 7.5), 3.309 (4 H, t *J* 7.5), 6.63 (2 H, d *J* 21), 7.43 (2 H, d *J* 21); **^{13}C-NMR (CD_3CN):** δ 14.1 (2 CH_3), 20.7 (2 CH_2), 29.7 (2 CH_2), 51.1 (2 CH_2-N), 62.2 (C6), 87.8(C5) 101.1 (C4), 107.3 (C7), 112.3 (C2), 136.1 (C3), 151.4 (C1).

4-bromobenzyltriphenylphosphinium bromide, 38

A 250 mL round-bottomed flask equipped with a reflux condenser, under Ar, was charged with 4-bromobenzylbromide (5.00 g, 20 mmol) and chloroform (100 mL). Triphenylphosphine (5.25 g, 20 mmol) was added to this stirred solution. After 72 h of reflux, the mixture was allow to cool to room temperature and the solvent was removed. The residue was precipitated in hexane from methylene chloride solution. After drying under vacuum at 65 °C for 24 h, 38 (10.1 g, 99%) was obtained as a white powder. **^{1}H-NMR (DMSO-D6):** δ 5.56 (2 H, d *J* 15.0), 7.09 (2 H, dd *J* 8.5, 2.5), 7.16 (H, d *J* 8.5), 7.58-7.64 (6 H, m), 7.73-7.81 (9 H, m); **^{13}C-NMR ($CDCl_3$):** δ 29.39 (CH_2, d *J* 186.0), 117.20 (3 sp^2-C, d *J* 340.0), 122.21 (sp^2-C, d *J* 19.0), 126.30 (sp^2-C, d *J* 34.0), 129.81 (6 sp^2-CH, d *J* 49.0), 131.33 (2 sp^2-CH, d *J* 11.0), 133.08 (2 sp^2-CH, d *J* 21.5), 134.16 (6 sp^2-CH, d *J* 38.5), 134.69 (3 sp^2-CH, broad).

4-diethylamino-4′-bromostilbene, 22-Br

A 250 mL two-necked round-bottomed flask equipped with a magnetic stirring bar, reflux condenser and additional funnel, under Ar, was charged with 4-bromobenzyltriphenyl phosphenium bromide (18.96 g, 37 mmol) and dry ether (20 mL). A suspension of NaH (41 mmol), 4-N,N-diethylaminobenzaldehyde (4.37 g, 25 mmol) and 18-crown-6 (100 mg, 0.38 mmol) in ether (50 mL) was added dropwise to this stirred solution. After reflux for 8 h the mixture was allowed to cool to room temperature and 3 M NH_4Cl solution (100 mL) was then added. The aqueous layer was extracted with methylene chloride (2 × 50 mL) and the organic layer was combined. The organic layer was washed with water (2 × 50 mL) and dried over anhydrous $MgSO_4$. The solvent was removed. Precipitation of the residue in methanol from methylene chloride solution yielded pure **22-Br** (3.87 g, 47 %). **m.p.:** 149-150 °C; **HIRES EI:** calcd for $C_{18}H_{20}NBr$ 329.0779, measured 329.0788; **IR(cm^{-1}):** 1520, 2968, 2887, 2930; **^{1}H-NMR:** δ 1.20 (6 H, t *J* 7.0), 3.39 (4 H, q *J* 7.0), 6.67 (2 H, d *J* 9.0), 6.81 (H, d *J* 16.0), 7.03 (H, d *J* 16), 7.33 (2 H, d *J* 8.5), 7.39 (2 H, d *J* 9.0), 7.44 (2 H, d *J* 8.5); **^{13}C-NMR:** δ 12.6 (2 CH_3), 44.3 (2 CH_2), 111.5 (2 sp^2-CH), 119.8 (sp^2-C), 122.2 (sp^2-CH), 124.1 (sp^2-C), 127.3 (2 sp^2-CH), 127.9 (2 sp^2-CH), 129.6 (sp^2-CH), 131.5 (2 sp^2-CH), 137.2 (sp^2-C), 147.5 (sp^2-C).

4-diethylamino-4′-trimethylsilylethynyl stilbene, 22-TMS

A 250 mL round-bottomed flask, equipped with a magnetic stirring bar and reflux condenser, was charged with 4-diethylamino-4′-bromostilbene (3.30 g, 10 mmol), $PdCl_2$ (177 mg, 1.0 mmol), $Cu(OAc)_2 \cdot H_2O$ (200 mg, 1.0 mmol), triphenylphosphine (0.86 g, 3.3 mmol) and degassed triethylamine (100 mL). Trimethylsilylacetylene (1.47 g, 15 mmol) was added dropwise to this stirred solution. The mixture was warmed to 85 °C. After 1 h the mixture was allowed to cool to room temperature and then filtered. The filtrate was evaporated and the residue was redissolved in methylene chloride (200 mL). The resulting solution was filtered again and the solvent was removed. The residue was eluted through a flash silica gel column by hexane/methylene chloride (80/20). The bright yellow solution was collected and the solvent was removed. The product was dried under vacuum to give **22-TMS** (2.25 g, 65 %) as a bright yellow powder. **m.p.:** 140-141 °C; **HIRES EI:** calcd for $C_{23}H_{29}NSi$ 347.2069, measured 347.2070; **IR** (cm^{-1}): 1521, 1592, 1606, 2152, 2897, 2966; **^{1}H-NMR:** δ 0.28 (9 H, s), 1.18 (6 H, t *J* 7.0), 3.38 (4 H, q *J* 7.0), 6.65 (2 H, d *J* 9.0), 6.84 (H, d *J* 16), 7.05 (H, d *J* 16), 7.40 (6 H, m); **^{13}C-NMR:** δ 0.02 (3 CH_3), 12.6 (2 CH_3), 44.3 (2 CH_2), 94.3 (sp-C), 105.6 (sp-C), 111.5 (2 sp^2-CH) 120.6 (sp^2-C), 122.7 (sp^2-CH), 124.2 (sp^2-C), 125.6 (2 sp^2-CH), 128.0 (2 sp^2-CH), 129.9 (sp^2-CH), 132.1 (2 sp^2-CH), 138.5 (sp^2-C), 147.5 (sp^2-C).

4-diethylamino-4′-ethynylstilbene, 22

The base-catalyzed desilylation of 24 in methanol/ THF (2:3) gave 18 in 80 %Yield; **m.p.:** 128°-129 °C; **HIRES EI**: calcd for $C_{20}H_{21}N$ 275.1674, measured 275.1678; **IR** (cm^{-1}) : 1521, 1594, 1606, 2098, 2892, 2974, 3280; **^{1}H-NMR (acetone-D6):** δ 1.14 (6 H, t *J* 7.0), 3.41 (4 H, q *J* 7.0), 3.65 (H, s), 6.69 (2 H, d *J* 9.0), 6.94 (H, d *J* 16.5),), 7.17 (2 H, d *J* 16.5), 7.41 (2 H, d *J* 9.0), 7.42 (2 H, d *J* 8.5), 7.51 (2 H, d *J* 8.5); **^{13}C-NMR (acetone-D6):** δ 12.9 (2 CH_3), 44.8 (2 CH_2), 79.3 (sp-CH), 84.5 (sp-C), 112.4 (2 sp^2-CH), 120.7 (sp^2-C), 122.9 (sp^2-CH), 125.0 (sp^2-C), 126.6 (2 sp^2-CH), 128.9 (2 sp^2-CH), 131.2 (sp^2-CH), 133.0 (2 sp^2-CH), 140.0 (sp^2-C), 148.6 (sp^2-C).

(5-bromo-2-thenyl)triphenylphospheniumbromide, 39

A 250 mL round-bottomed flask equipped with a magnetic stirring bar and reflux condenser, under Ar, was charged with NBS (16 g, 90 mmol), benzoylperoxide (12 mg, 0.05 mmol) and carbon tetrachloride (60 mL). 2-Methylthiophene (4 g, 41 mmol) was then added quickly to this solution at 100 °C. After 8 h another portion of NBS (2 g, 11 mmol) and carbon tetrachloride (10 mL) was added to the mixture. After refluxing for 2 additional hours the mixture was allowed to cool to room temperature. Hexane (50 mL) was added to the mixture. The mixture was filtered and the filtrate was evaporated. The residue was redissolved in chloroform (25 mL)/ hexane (25 mL). A solution of triphenylphosphine (10 g, 38 mmol) in 1:1 chloroform/ hexane (50mL) was then added to the solution while swirling. The mixture was kept for 10 h in the open air and then hexane (100 mL) was added. The mixture was then filtered and the precipitate was washed with cold acetone until the yellow color disappeared. The off-white powder was dried under vacuum to give the desired product (10.5 g, 50 %). **m.p.:** 261-263 (Lit. 271-273 °C); **^{1}H-NMR (DMSO-D6):** δ 5.69 (2 H, d *J* 15.0), 6.69 (H, dd *J* 4.0, 3.5), 7.07 (H, dd *J* 4.0, 0.5), 7.76 (12 H, m), 7.91 (3 H, m); **^{13}C-NMR (DMSO-D6):** δ 24.44 (CH_2, d *J* 198.5), 112.26 (sp^2-C, d *J* 21.5), 117.50 (3 sp^2-C, d *J* 342.0), 130.22 (6 sp^2-CH, d *J* 49.0), 130.47 (sp^2-CH, d *J* 13.0), 130.62 (sp^2-CH, d *J* 40.5), 131.53 (sp^2-C, d *J* 33.5), 133.94 (6 sp^2-CH, d *J* 40.0), 135.30 (3 sp^2-CH, d *J* 10.5).

2-bromo-5-(4-N,N-diethylamino-β-styryl)thiophene, 25-Br

A 250 mL round-bottomed flask equipped with a magnetic stirring bar and reflux condenser, under Ar, was charged with (5-bromo-2-thenyl)triphenylphospheniumbromide

(13.5 g, 26 mmol) and dry ether (20 mL). A suspension of NaH (36 mmol), 4-N,N-diethylaminobenzaldehyde (3.54 g, 20 mmol) and 18-crown-6 (80 mg, 0.3 mmol) in ether (40 mL) was added to this stirred solution. The mixture was refluxed for 8 h. The mixture was allowed to cool to room temperature and 3 M NH_4Cl solution (100 mL) was then added. The aqueous layer was extracted with methylene chloride (2 × 30 mL) and the organic layer was combined. The organic layer was washed with water (2 × 50 mL) and dried over anhydrous $MgSO_4$. The solvent was removed and the residue was redissolved in hot hexane. The solution was filtered and the filtrate was evaporated. Precipitation of the residue in methanol from methylene chloride solution yielded a crude product (~ 85% pure). The crude product was eluted through a flash silica gel column by hexane/methylene chloride (19:1 → 3:1). Evaporation of the solvents gave **25-Br** (3.0 g, 45% yield). **m.p.:** 105-107 °C; **HIRES EI:** cald for $C_{16}H_{18}BrNS$ 335.0343, measured 335.0340; **IR(cm^{-1}):** 1514, 1527, 1600, 2869, 2968; **^{1}H-NMR:** δ 1.18 (6 H, t *J* 7.0), 3.37 (4 H, q *J* 7.0), 6.64 (2 H, d *J* 9.0), 6.69 (H, d *J* 3.5), 6.74 (H, d *J* 16), 6.88 (H, d *J* 16), 6.90 (H, d *J* 3.5), 7.31 (2 H, d *J* 9.0); **^{13}C-NMR:** δ 12.6 (2 CH_3), 44.3 (2 CH_2), 109.1 (sp^2-C), 111.5 (2 sp^2-CH), 116.2 (sp^2-CH), 123.7 (sp^2-C), 124.3 (sp^2-CH), 127.7 (2 sp^2-CH), 129.2 (sp^2-CH), 130.2 (sp^2-CH), 145.8 (sp^2-C), 147.5 (sp^2-C).

2-trimethylsilylethynyl-5-(4-N,N-diethylamino-β-styryl) thiophene, 25-TMS

A 100 mL round-bottomed flask equipped with a magnetic stirring bar and reflux condenser 2-bromo-5-(4-N,N-diethylamino-β-styryl)thiophene (2.5 g, 7.4 mmol), $PdCl_2$ (131 mg, 0.74 mmol), Cu(OAc)2·H2O (148 mg, 0.74 mmol), triphenylphosphine (0.639 g, 2.4

mmol) and degassed triethylamine (75 mL). Trimethylsilylacetylene (1.1 g, 11.1 mmol) was added dropwise to the stirred solution. The mixture was warmed to 85 °C. After 1 h the mixture was allowed to cool to room temperature and then filtered. The filtrate was evaporated and the residue was redissolved in methylene chloride (200 mL). The resulting solution was filtered again and the solvent was removed. The residue was eluted through a flash silica gel column by hexane/ methylene chloride (1:0 → 4:1). The bright yellow solution was collected and the solvent was removed. Further purification by precipitation in methanol from methylene chloride solution yielded 25-TMS (1.0 g, 39 %) as a bright yellow powder. **m.p.:** 122-124 °C; **HIRES EI:** calcd for $C_{21}H_{27}NSSi$ 353.1634, measured 353.1630; **IR** (cm^{-1}): 1526, 1601, 2140, 2869, 2966; ^{1}**H-NMR:** δ 0.23 (9 H, s), 1.16 (6 H, t *J* 7.0), 3.36 (4 H, q *J* 7.0), 6.62 (2 H, d *J* 9.0), 6.77 (H, d *J* 3.5), 6.80 (H, d *J* 16), 6.90 (H, d *J* 16), 7.07 (H, d *J* 3.5), 7.30 (2 H, d *J* 9.0); ^{13}**C-NMR:** δ -0.1 (3 CH_3), 12.6 (2 CH_3), 44.4 (2 CH_2), 98.3 (sp-C), 99.2 (sp-C), 111.6 (2 sp^2-CH) 116.3 (sp^2-CH), 119.8 (sp^2-C), 123.7 (sp^2-C), 124.0 (sp^2-CH), 127.9 (2 sp^2-CH), 129.9 (sp^2-CH), 133.4 (sp^2-CH), 146.0 (sp^2-C), 147.6(sp^2-C).

2-ethynyl-5-(4-N,N-diethylamino-β-styryl) thiophene, 25

The base-catalyzed desilylation of 25-TMS in methanol/ THF (2:3) gave 25 in 80% yield; **m.p.:** 99-100 °C; **HIRES EI:** $C_{18}H_{19}NS$ 281.1238, measured 281.1236; **UV** ($CHCl_3$, **nm**): λ_{max} = 402; **IR**(cm^{-1}): 1513, 1524, 1599, 2097, 2871, 2968, 3296; ^{1}**H-NMR:** δ 1.17 (6 H, t *J* 7.0), 3.38 (4 H, q *J* 7.0), 3.45 (H, s), 6.65 (2 H, d *J* 9.0), 6.84 (H, d *J* 3.5), 6.85 (H, d *J* 16), 6.95 (H, d *J* 16), 7.15 (H, d *J* 3.5), 7.32 (2 H, d *J* 9.0); ^{13}**C-NMR:** δ 12.7 (2 CH_3), 44.7 (2 CH_2), 77.8 (sp-C), 81.9 (sp-CH), 111.8 (2 sp^2-CH), 116.1 (sp^2-CH), 118.7 (sp^2-C), 123.7

(sp^2-C), 124.3 (sp^2-CH), 128.2 (2 sp^2-CH), 130.6 (sp^2-CH), 134.2 (sp^2-CH), 146.6 (sp^2-C), 148.1 (sp^2-C).

4-ethynylanisole, 36

Acetylene 36 was synthesized in two steps, palladium coupling with trimethylsilylacetylene followed by base-catalyzed desilylation, from 4-iodoanisole. The procedure of the synthesis is similar to the synthesis of 4-ethynyl-N,N-dimethylaniline. The compound was characterized by only ^{1}H and ^{13}C-NMR. **^{1}H-NMR (CD_3CN):** δ 3.27 (1 H, s), 3.88 (3 H, s), 6.88 (2 H, d *J* 12.0), 7.41 (2 H, d *J* 12.0), 8.20 (1 H, s); **^{13}C-NMR (CD_3CN):** δ 56.0 (CH_3), 77.4 (sp-CH), 84.2 (sp^2-C), 114.8 (sp-C), 134.4 (2 sp^2-CH), 161.0 (sp^2-C).

Polymer 10

A 25 mL round-bottomed flask equipped with a magnetic stirring bar, under Ar, was charged with polymer 6 (200 mg, 0.73 mmol), chloroform (9 mL) and acetonitrile (3 mL). Freshly sublimed TCNE (95 mg, 0.74 mmol) was added to this stirred solution. After 24 h the mixture was added dropwise by a Pasteur pipette into 100 mL methanol. The red precipitate was collected by filtration and reprecipitated in methanol from a methylene chloride solution. The obtained polymer was dried under vacuum at 65 °C for 36 h to yield pure 10 (236 mg, 80%) **^{1}H-NMR:** δ 0.86 (3 H, br.), 1.30 (6 H, br), 1.71 (2 H, br), 3.87 (2 H, br.), 7.20 (4 H, d *J* 8.5), 7.78 (4 H, d *J* 8.5); **^{13}C-NMR :** δ 13.8 (CH_3), 22.4 (CH_2), 26.4 (CH_2), 27.6 (CH_2), 31.2 (CH_2), 52.8 (CH_2), 82.5 (2 sp^2-C), 111.9 (2 CN), 112.7 (2 CN), 121.4 (4 sp^2-CH), 124.9 (4 sp^2-C) 131.8 (4 sp^2-CH), 151.1 (2 sp^2-C), 164.8 (2 sp^2-C).

bis-α,α'-(-4-dimethylamino-β,β-dicyanostyrene), 9

A general procedure for the study of the reaction of TCNE with acetylene 9 and other electron-rich acetylenes is described here. The reaction of TCNE with electron-rich acetylenes was performed in a 5 mL NMR tube. ^{1}H and ^{13}C-NMR spectra of a solution of acetylene 9 (30 mg) in deuterated chloroform were recorded. An equivalent of freshly sublimed TCNE was added to this solution, and the mixture was intermittently agitated. The solution was deep red. After 10 min the ^{1}H and ^{13}C-NMR spectra of the of the mixture were recorded again. Percent conversion and yields were determined by ^{1}H-NMR. The metallic shiny crystalline product were obtained from crystallization of the product in chloroform/methanol. **Yield:** quantitative; **m.p.:** 268-270 °C; **HIRES EI:** calcd for $C_{24}H_{20}N_6$ 392.1749, measured 392.1746; 184.1 (100%); **UV ($CHCl_3$, nm):** λ_{max} = 468; **IR(cm^{-1}):** 1605, 2135, 2216, 2929; **^{1}H-NMR:** δ 3.12 (12 H, s), 6.67 (4 H, d *J* 9.5), 7.77 (4 H, d *J* 9.5); **^{13}C-NMR:** δ 40.0 (4 CH_3), 74.5 (2 sp^2-C), 111.9 (4 sp^2-CH), 113.5 (2 CN), 114.7 (2 CN), 118.7 (2 sp^2-C), 132.5 (4 sp^2-CH), 154.1 (2 sp^2-C), 165.4 (2 sp^2-C).

12

The reaction of 11 with two equivalents of TCNE was performed in deuterated acetonitrile using the same procedure as in the synthesis of 9. The solution was deep red. Evaporation of the solvent gave black powder of 12. **Yield:** quantitative; **m.p.:** 165-167 °C; **EI:** $C_{50}H_{41}N_{11}$ 795.3, 169.8 (100%); **UV-($CHCl_3$, nm):** λ_{max} = 268, 468; **IR(cm^{-1}):** 1589, 1606, 2217, 2859, 2929; **^{1}H-NMR (CD_3CN):** δ 0.86 (3 H, t *J* 7.0), 1.29 (6 H, m), 1.63 (2 H, qui *J* 7.0), 3.15 (12 H, s), 3.82 (2 H, t *J* 7.0), 6.72 (4 H, d *J* 9.0), 7.13 (4 H, d *J* 9.0), 7.74 (4

H, d *J* 9.0), 7.78 (4 H, d *J* 9.0); **^{13}C-NMR (CD$_3$CN):** δ 13.9 (CH$_3$), 22.5 (CH$_2$), 26.5 (CH$_2$), 27.6 (CH$_2$), 31.3 (CH$_2$), 40.2 (4 CH$_3$), 52.6 (CH$_2$), 73.8 (2 sp^2-C), 82.3 (2 sp^2-C), 112.0 (2 CN), 112.2 (4 sp^2-CH), 113.0 (2 CN), 113.5 (2 CN), 114.4 (2 CN), 118.0 (2 sp^2-C), 121.2 (4 sp^2-CH), 125.5 (2 sp^2-C), 131.8 (4 sp^2-CH), 132.5 (4 sp^2-CH), 150.8 (2 sp^2-C), 154.4 (2 sp^2-C), 163.5 (2 sp^2-C), 166.7 (2 sp^2-C).

30

The reaction of **29** with three equivalents of TCNE was performed in deuterated acetonitrile using the same procedure as in the synthesis of **9**. The solution was deep red. Evaporation of the solvent gave black powder of **30**. **Yield:** quantitative; **m.p.:** >300 °C; **IR(cm^{-1}):** 1536, 1605, 2216, 2812, 2921, 3090; **UV (CHCl$_3$, nm):** λ_{max} = 464; **^{1}H-NMR (CD$_3$CN):** δ 3.16 (18 H, s), 6.73 (6 H, d *J* 9.5), 7.21 (6 H, d *J* 9.5), 7.72 (6 H, d *J* 9.5), 7.79 (6 H, d *J* 9.5); **^{13}C-NMR (CD$_3$CN):** δ 40 0 (6 CH$_3$), 73.0 (3 sp^2-C), 84.9 (3 sp^2-C), 111.5 (3 CN), 112.2 (6 sp^2-CH), 113.6 (3 CN), 114.2 (3 CN), 117.3 (3 CN), 124.8 (6 sp^2-CH), 127.8 (3 sp^2-C), 131.5 (6 sp^2-CH), 132.3 (6 sp^2-CH), 149.5 (3 sp^2-C), 154.4 (3 sp^2-C), 162.5 (3 sp^2-C), 166.8 (3 sp^2-C).

2-(p-dimethyaminophenyl)-1,1,4,4-tetracyanobutadiene, 20

The reaction of **18** with an equivalent of TCNE was performed in deuterated acetonitrile using the same procedure as in the synthesis of **9**. The solution was deep blue Evaporation of the solvent gave black powder of **20**. **Yield:** quantitative ; **m.p.:** 152-153 °C; **HIRES EI:** calcd for C$_{16}$H$_{11}$N$_5$ 273.1014, measured 273.1014; **UV (CHCl$_3$, nm):** λ_{max} = 270, 343, 571; **IR(cm^{-1}):** 1537, 1604, 2216, 2317, 2923, 3031; **^{1}H-NMR (CD$_3$CN):** δ 3.10 (6 H, s), 6.80 (2 H, d *J* 9.0), 7.59 (2 H, d *J* 9.0), 8.25 (H, s); **^{13}C-NMR (CD$_3$CN):** δ 40.3 (2 CH$_3$), 78.0 (sp^2-C), 97.5 (sp^2-C), 110.7 (CN), 112.6 (2 sp^2-CH), 112.8 (CN), 114.4 (CN), 115.3 (CN), 118.5 (sp^2-C), 133.2 (2 sp^2-CH), 155.3 (sp^2-C), 158.9 (sp^2-C), 160.8 (sp^2-C).

4,4′-bis (1,1,4,4-Tetracyanobutadien-2-yl)-N-hexyldiphenylamine, 21

The reaction of 21 with two equivalents of TCNE was performed in deuterated acetonitrile using the same procedure as in the synthesis of 9. The solution was deep blue. Evaporation of the solvent gave black powder of 21. **Yield:** quantitative; **m.p.:** 184-186 °C; **HIRES EI:** calcd for $C_{34}H_{23}N_9$ 557.2076, measured 557.2066; base peak 486.1; **UV (CHCl$_3$, nm):** λ_{max} = 303, 355, 590; **IR (cm^{-1}):** 1588, 1609, 1750, 2223, 2859, 2930, 2957, 3036; **^{1}H-NMR (CD$_3$CN):** δ 0.85 (3 H, t *J* 7.0), 1.27 (6 H, m), 1.66 (2 H, qui *J* 7.0), 3.87 (2 H, t *J* 7.0), 7.23 (4 H, d *J* 9.0), 7.55 (4 H, d *J* 9.0), 8.22 (H, s); **^{13}C-NMR (CD$_3$CN):** δ 14.2 (CH$_3$), 23.2 (CH$_2$), 27.0 (CH$_2$), 27.9 (CH$_2$), 32.1 (CH$_2$), 53.2 (CH$_2$), 88.4 (2 sp^2-C), 98.0 (2 sp^2-C), 110.5 (2 CN), 112.8 (2 CN), 113.2 (2 CN), 113.8 (2 CN), 122.4 (4 sp^2-CH), 125.4 (2 sp^2-C), 132.7 (4 sp^2-CH), 152.0 (2 sp^2-CH), 156.0 (2 sp^2-C), 162.1 (2 sp^2-C).

4,4′,4′′-tris(1,1,4,4-tetracyanobutadien-2-yl)triphenylamine, 33

The reaction of 21 with three equivalents of TCNE was performed in deuterated acetonitrile using the same procedure as in the synthesis of 9. The solution was deep blue. Evaporation of the solvent gave black powder of 33. **Yield:** quantitative; **m.p.:** > 300 °C (soften at 140°C); **HIRES EI:** calcd for $C_{42}H_{15}N_{13}$ 701.1573, measured 701.1576; **IR (cm^{-1}):**

1588, 1749, 2226, 3035; **UV ($CHCl_3$, nm)** : complex structure around 250-400 and a broad peak at 574; **^{1}H-NMR (CD_3CN):** δ 7.30 (6 H, d *J* 9.0), 7.52 (6 H, d *J* 9.0), 8.21 (3 H, s); **^{13}C-NMR (CD3CN):** δ 91.8 (3 sp^2-C), 98.2 (3 sp^2-C), 110.4 (3 CN), 112.2 (3 CN), 113.2 (3 CN), 118.3 (3 CN), 126.1 (6 sp^2-CH), 127.7 (3 sp^2-C), 132.5 (6 sp^2-CH), 151.0 (3 sp^2-CH), 154.9 (3 sp^2-C), 162.3 (3 sp^2-C).

1,1-dicyano-2-(p-dimethylamino-β,β-dicyanostyryl)-4-(p-dimethylaminophenyl) but-1-en-3-yne, 16

The reaction of **15** with two equivalents of TCNE was performed in deuterated methylene chloride using the same procedure as in the synthesis of **9**. The solution was deep red. Evaporation of the solvent gave black powder of **16**. **Yield:** quantitative; **m.p.:** 192°-194 °C; **UV ($CHCl_3$, nm):** $\lambda_{max} = 520$; **IR(cm^{-1}):** 1538, 1602, 2133, 2216, 2811, 2917, 3083; **HIRES EI:** calcd for $C_{26}H_{20}N_6$ 416.1749, measured 416.1746; **^{1}H-NMR (CD_2Cl_2):** δ 3.09 (6 H, s), 3.15 (6 H, s), 6.68 (2 H, d *J* 9.0), 6.76 (2 H, d *J* 9.0), 7.49 (4 H, d *J* 9.5), 7.82 (4 H, d *J* 9.5); **^{13}C-NMR (CD_2Cl_2):** δ 40.2 (2 CH_3), 40.3 (2 CH_3), 74.1 (sp^2-C), 87.8 (sp-C), 90.5 (sp-C), 105.1 (sp^2-C), 112.0 (CN), 112.1 (4 sp^2-CH), 113.0 (CN), 113.9 (CN), 115.0 (CN), 117.8 (sp^2-C), 125.6 (sp^2-C), 132.8 (2 sp^2-CH), 136.2 (2 sp^2-CH), 150.2 (sp^2-C), 153.5 (sp^2-C), 154.8 (sp^2-C), 161.6 (sp^2-C).

23

The reaction of **22** with an equivalent of TCNE was performed in deuterated acetone using the same procedure as in the synthesis of **9**. The solution was light brown. The product decomposed slowly and no isolation was attempted. **Yield:** quantitative (^{1}H-NMR); **^{1}H-NMR (acetone-D6) :** δ 1.12 (6 H, t *J* 7.0), 3.40 (4 H, q *J* 7.0), 3.76 (H, s), 5.27 (H, d *J* 13.0), 5.47 (H, d *J* 13.0), 6.76 (2 H, d *J* 9.0), 7.54 (2 H, d *J* 9.0),), 7.62 (2 H, d *J* 8.5), 7.69 (2 H, d *J* 8.5); **^{13}C-NMR (acetone-D6) :** δ 12.3 (2 CH_3), 41.7 (sp^3-C), 43.3 (sp^3-C), 44.3 (2 CH_2), 51.1 (sp^3-CH), 51.8 (sp^3-CH), 80.5 (sp-CH), 82.8 (sp-C), 110.3 (CN), 110.5 (CN), 111.5 (CN), 111.6 (CN), 111.9 (2 sp^2-CH), 117.1 (sp^2-C), 124.4 (sp^2-C), 128.7 (2 sp^2-CH), 129.9 (2 sp^2-CH), 133.1 (2 sp^2-CH), 133.3 (sp^2-C), 149.5 (sp^2-C).

28

The reaction of **25** with an equivalent of TCNE was performed in deuterated acetonitrile using the same procedure as in the synthesis of **9**. The solution was deep puple. Evaporation of the solvent gave black powder of **28**. **Yield:** quantitative (^{1}H-NMR); **m.p.:** 179-181 °C; **HIRES EI:** calcd for $C_{24}H_{19}N_5S$ 409.1361, measured 409.1357; **UV ($CHCl_3$, nm) :** λ_{max} = 656, 450, 314; **IR (cm^{-1}) :** 1511, 1585, 2214, 2972; **^{1}H-NMR (CD_2Cl_2):** δ 1.20 (6 H, t *J* 7.0), 3.43 (4 H, q *J* 7.0), 6.68 (2 H, d *J* 9.0), 7.01 (H, d *J* 16.0), 7.17 (H, d *J* 4.5),), 7.22 (2 H, d *J* 16.0), 7.41 (2 H, d *J* 9.0), 7.57 (H, d *J* 4.5), 7.87 (H, s); **^{13}C-NMR (CD_2Cl_2):** δ 12.7 (2 CH_3), 44.9 (2 CH_2), 74.3 (sp^2-C), 97.4 (sp^2-C), 109.6(CN), 111.2 (CN), 111.9 (2 sp^2-CH), 113.5 (CN), 114.0 (CN), 114.4 (sp^2-CH), 122.6 (sp^2-C), 126.7 (sp^2-CH), 129.7 (sp^2-C), 130.1 (2 sp^2-CH), 137.9 (sp^2-CH), 139.3 (sp^2-CH), 149.7 (sp^2-C), 150.0 (sp^2-C), 155.7 (sp^2-CH), 159.7 (sp^2-C).

4-(1,1,2,4,4-pentacyanobutadien-3-yl)-N,N-dibutylaniline, 35

The reaction of 24 with an equivalent of TCNE was performed in deuterated acetonitrile using the same procedure as in the synthesis of 9. The solution was deep puple. Crystallization of product from methylene chloride/hexane gave shiny deep violet crystals of 35. **Yield:** quantitative; **m.p.:** 103-105 °C; **HIRES EI:** calcd for $C_{23}H_{22}N_6$ 382.1906, measured 382.1906; **UV ($CHCl_3$, nm)** : $\lambda_{max} = 464$; **IR (neat, cm^{-1}):** 1604, 2215, 2873, 2933, 2961; **^{1}H-NMR (CD_3CN):** δ 0.94 (6 H, t *J* 7.5), 1.36 (4 H, sex *J* 7.5), 1.59 (4 H, qui *J* 7.5), 3.46 (4 H, t *J* 7.5), 6.84 (2 H, d *J* 9.5), 7.70 (2 H, d *J* 9.5); **^{13}C-NMR (CD_3CN):** δ 14.0 (2 CH_3), 20.6 (2 CH_2), 29.9 (2 CH_2), 51.7 (2 CH_2), 74.2 (sp^2-C), 107.9 (CN), 109.5 (CN), 110.9 (CN), 112.7 (CN), 113.6(2 sp^2-CH), 114.5 (sp^2-C), 115.4 (CN) 117.4 (sp^2-C), 134.1 (2 sp^2-CH), 139.8 (sp^2-C), 153.8 (sp^2-C) 154.9 (sp^2-C).

4-(1,1,4,4-tetracyanobutadien-2yl) anisole, 37

The reaction of 36 with an equivalent of TCNE was performed in deuterated acetonitrile using the same procedure as in the synthesis of 9. The solution was transparent redish-orange. Crystallization of product from methylene chloride/hexane gave transparent red crystals of 37. **Yield:** quantitative (^{1}H-NMR); **m.p.: HIRES EI:** calcd for $C_{15}H_9N_4O$ (M+H) 261.0778, measured 261.0776; **UV ($CHCl_3$, nm)** : 292, 444; **IR (neat, cm^{-1}):**; **^{1}H-NMR (CD_3CN):** δ 3.88 (3 H, s), 7.11 (2 H, d *J* 9.0), 7.54 (2 H, d *J* 9.0), 8.20 (1 H, s); **^{13}C-NMR:** δ 55.8 (CH_3), 98.1 (sp^2-C), 108.5 (CN), 111.2 (CN), 111.6 (CN), 111.8 (CN), 115.7 (sp^2-CH), 122.3 (sp^2-C), 131.4 (2 sp^2-CH), 153.4 (sp^2-CH), 161.4 (sp^2-C) 164.6 (sp^2-C).

CONCLUSIONS

In the first part, the syntheses of linear and dendritic polymers containing hole transporting units, di- and triphenylamine, were accomplished by Pd-coupling polymerization and oxidative coupling. High molecular weight polymers were obtained in the presence of a strong base such as DBU. Spectroscopic and electrical conductivity studies of these polymers indicated that the electronic properties of these polymers depended mainly on the structure of their individual repeating units. The benzene rings in the linear polymers are likely highly twisted from the p-orbital of N and the polymer chains may develop helical secondary structures prohibiting extensive conjugation. The introduction of N atom into conjugated chain enhanced the solubilities and the flexibility of the polymers. Even though the preliminary results of electroluminescence and conductivity studies have not showed impressive numbers, the modification of conjugation segments by replacing ethynylene to vinylene showed some positive results on the photoluminescence and conductivity.

In the second part, the synthesis of new electron donor-acceptor tetracyanobutadienyl (TCBD) derivatives from a facile thermal cycloaddition-ring opening reaction of TCNE on electron-rich aromatic acetylenes were studied. A very efficient conversion of the substrate to TCBD was found in monosubstituted and disubstituted acetylenic anilines. This reaction offers a new convenient and efficient synthetic route to new NLO chromophores and polymers from acetylenic monomers and polymers. A new mainchain NLO polymer, polymer **10**, was the first example in this regard. Some disubstituted acetylenes with bulky substituents in this study have showed that the most serious problem limiting the addition of TCNE was the steric hindrance. This limitation need to be considered before designing a new acetylenic polymer precursor.

An extended π-conjugated TCBD NLO chromophore can be obtained from a thienyl acetylene derivative. A low electronic absorption energy suggests that this longer π-conjugated TCBD will be a very good candidate for a high β value chromophore. The quantitative conversion of all three triple bonds of 4,4′,4″-triethynyltriphenylamine into three TCBD units has emphasized the remarkable efficiency of this reaction. The reaction of TCNE with higher ionization energy substrates such as 4-ethynyl anisole and 4-cyanoethynyl-N,N-dimethylaniline yields quite interesting anisole TCBD and PCBD providing more selections of the acetylene substrates.

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