



# Flexible complementary circuits operating at sub-0.5 V via hybrid organic–inorganic electrolyte-gated transistors

Yao Yao<sup>a,b,c</sup>, Wei Huang<sup>b,c,d,1</sup>, Jianhua Chen<sup>b,c</sup>, Gang Wang<sup>b,c</sup>, Hongming Chen<sup>b,c</sup>, Xinming Zhuang<sup>b,c</sup>, Yibin Ying<sup>a</sup>, Jianfeng Ping<sup>a,1</sup>, Tobin J. Marks<sup>b,c,1</sup>, and Antonio Facchetti<sup>b,c,e,1</sup>

<sup>a</sup>School of Biosystems Engineering and Food Science, Zhejiang University, Hangzhou 310058, People's Republic of China; <sup>b</sup>Department of Chemistry, Northwestern University, Evanston, IL 60208; <sup>c</sup>Materials Research Center, Northwestern University, Evanston, IL 60208; <sup>d</sup>School of Automation Engineering, University of Electronic Science and Technology of China, Chengdu 611731, People's Republic of China; and <sup>e</sup>Flexterra Inc., Skokie, IL 60077

Contributed by Tobin J. Marks, September 23, 2021 (sent for review June 28, 2021; reviewed by George Malliaras, Catherine J. Murphy, and Peidong Yang)

Electrolyte-gated transistors (EGTs) hold great promise for next-generation printed logic circuitry, biocompatible integrated sensors, and neuromorphic devices. However, EGT-based complementary circuits with high voltage gain and ultralow driving voltage (<0.5 V) are currently unrealized, because achieving balanced electrical output for both the p- and n-type EGT components has not been possible with current materials. Here we report high-performance EGT complementary circuits containing p-type organic electrochemical transistors (OECTs) fabricated with an ion-permeable organic semiconducting polymer (DPP-g2T) and an n-type electrical double-layer transistor (EDLT) fabricated with an ion-impermeable inorganic indium–gallium–zinc oxide (IGZO) semiconductor. Adjusting the IGZO composition enables tunable EDLT output which, for In:Ga:Zn = 10:1:1 at%, balances that of the DPP-g2T OECT. The resulting hybrid electrolyte-gated inverter (HCIN) achieves ultrahigh voltage gains (>110) under a supply voltage of only 0.7 V. Furthermore, NAND and NOR logic circuits on both rigid and flexible substrates are realized, enabling not only excellent logic response with driving voltages as low as 0.2 V but also impressive mechanical flexibility down to 1-mm bending radii. Finally, the HCIN was applied in electrooculographic (EOG) signal monitoring for recording eye movement, which is critical for the development of wearable medical sensors and also interfaces for human–computer interaction; the high voltage amplification of the present HCIN enables EOG signal amplification and monitoring in which a small ~1.5 mV signal is amplified to ~30 mV.

electrolyte-gated transistor | complementary circuit | flexible electronics | EOG sensing

Electrolyte-gated transistor (EGT) microelectronics offer great promise, taking advantage of low power consumption, mechanical flexibility, and excellent biocompatibility. They are envisioned to play a major role in the future development of the flexible electronics, medical applications in clinical diagnostics/therapeutics, and electronic skins (1–6). To fully take advantage of the potential of EGTs for signal amplification in applications enabled by unique ionic–electronic interactions (7–10), integration into various logic gates and especially inverters, the basic building blocks of modern logic circuitry, is essential. To date, EGT-based circuits have mainly been constructed with unipolar inverters comprising either organic electrochemical transistors (OECTs) having an ion-permeable semiconducting polymer as the channel layer (11–13) or electrical double-layer transistors (EDLTs) based on ion-impermeable semiconductors (14–16). However, the vast majority of OECT organic (semi)conducting polymers for OECTs are hole-transporting (p-type), while electron-transporting (n-type) semiconducting polymers are sparse, typically unstable, and yield far lower performance than their p-type counterparts (17). In contrast, n-type oxide semiconductor mobilities as high as ~100 cm<sup>2</sup>/Vs are known, and indium–gallium–zinc oxide (IGZO) has been commercialized in

displays and flexible electronics (18–20). This is not the situation with oxide p-type semiconductors (21, 22), where mobilities far lower than 10 cm<sup>2</sup>/Vs are typical (23), and there are long-term stability issues (24, 25). Consequently, circuits based on both kinds of EGTs constructed with unipolar inverters and a resistor as load (26, 27) operated with constant power dissipation and low voltage gain (28, 29). Thus, the goal of complementary logic circuits for low power consumption and high voltage gain with sub-1 V driving voltage for bioelectronics, portable electronics applications, and low power dissipation had not been achieved with these materials (30, 31). Furthermore, devices with complementary circuits based on p- and n-type OECTs only delivered limited performance (voltage gain <11 for a driving voltage of 0.6 V) and required large device footprints for the n-type EGTs due to the mismatched transistor performance (11).

In this work, for the reasons cited above, we investigate integrating in a single device the intrinsically high performance of p-type OECTs with n-type oxide EDLTs. It will be seen that well-matched p- and n-type EGTs are realized, enabling their

## Significance

Electrolyte-gated transistor (EGT)-based inverter circuits are the basic building blocks of next-generation flexible electronic devices. However, constructing high-performance complementary inverters is challenging due to the unbalanced electrical performances of available p- and n-type EGT semiconducting materials. Here we report high-performance EGT complementary inverters achieved by combining p-type organic electrochemical transistors based on an ion-permeable semiconducting organic polymer and n-type electric double-layer transistors based on an ion-impermeable metal oxide semiconductor. The resulting closely balanced complementary inverters achieve ultrahigh voltage gain (>110) under a low supply voltage of only 0.7 V and have been successfully used to achieve flexible logic circuits and sensitive electrophysiological signal amplification suitable for ophthalmologic diagnostics and measuring eye movement.

Author contributions: Y. Yao, W.H., J.P., T.J.M., and A.F. designed research; Y. Yao, J.C., G.W., H.C., X.Z., and Y. Ying performed research; Y. Yao, W.H., and J.C. analyzed data; and Y. Yao, W.H., J.C., T.J.M., and A.F. wrote the paper.

Reviewers: G.M., University of Cambridge; C.J.M., University of Illinois at Urbana–Champaign; and P.Y., University of California, Berkeley University Health Services.

The authors declare no competing interest.

Published under the PNAS license.

<sup>1</sup>To whom correspondence may be addressed. Email: w Huang@uestc.edu.cn, jfping@zju.edu.cn, t-marks@northwestern.edu, or a-facchetti@northwestern.edu.

This article contains supporting information online at <http://www.pnas.org/lookup/suppl/doi:10.1073/pnas.2111790118/-DCSupplemental>.

Published October 29, 2021.

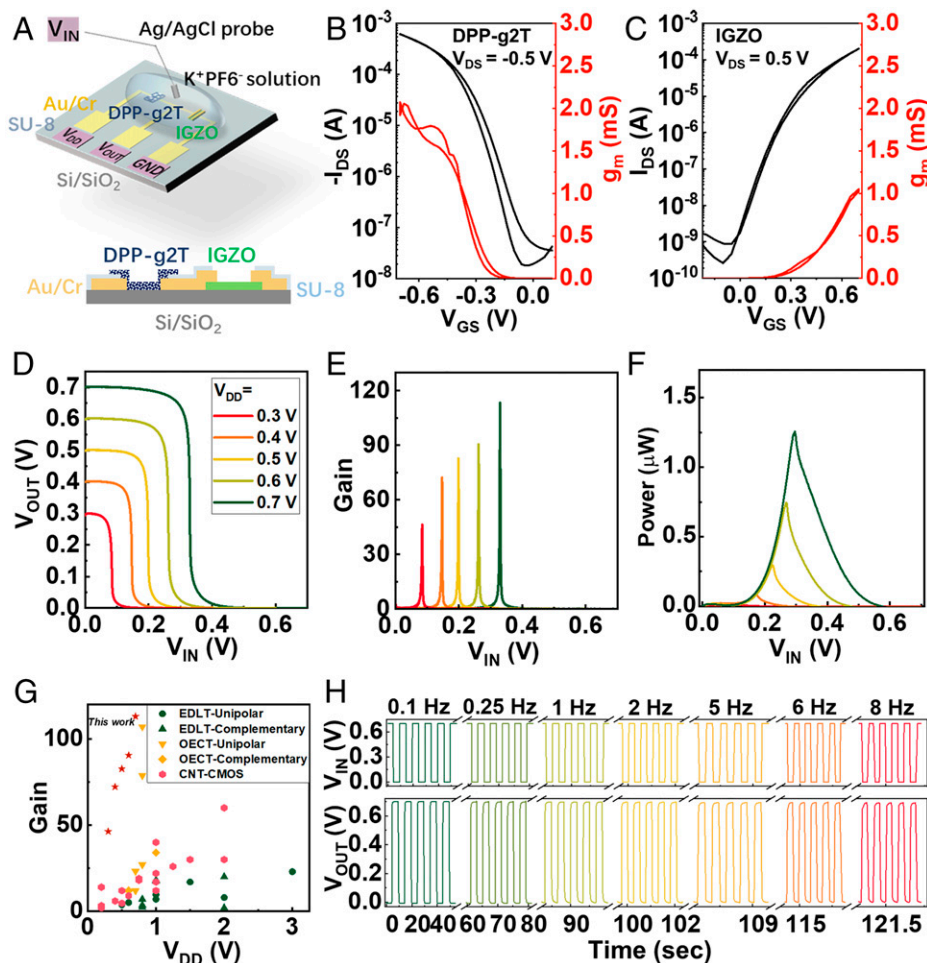
integration into high-performance hybrid organic/inorganic complementary circuitry. Specifically, DPP-g2T (SI Appendix, Fig. S1) having a honeycomb film microstructure is adopted as the channel of the p-type OECT, while IGZO (In:Ga:Zn = 10:1:1 at %) acts as the channel material of an n-type EDLT. The resulting optimized hybrid inverters deliver a high voltage gain of more than 110 under driving voltage of only 0.7 V and static power consumption as low as 15 nW. Furthermore, successful construction of mechanically flexible NAND and NOR logic gates on both rigid and flexible substrates are demonstrated operating at a voltage as low as 0.2 V. Most importantly, real-time monitoring of human electrooculogram (EOG) signals is demonstrated using the present inverter exhibiting voltage amplification gain of ~20, which makes the inverter suitable for the development of wearable EOG sensors for medical research.

## Results and Discussion

**Hybrid Inverter Based on p-Type OECT and n-Type Oxide EDLT.** The structure of the hybrid complementary inverter (HCIN) consisting of a p-type DPP-g2T OECT and an n-type IGZO EDLT is shown in Fig. 1A. Details of HCIN fabrication can be found in *Materials and Methods* and *SI Appendix*. Briefly, as illustrated in *SI Appendix*, Fig. S2, a spin-coated IGZO film was first

patterned on a Si/SiO<sub>2</sub> substrate. Then, 50-nm Au electrodes with a 3-nm Cr adhesion layer were patterned with a lift-off process. Next, an SU-8 layer was patterned on the electrode while leaving the p- and n- type transistor channel area open; a porous DPP-g2T film prepared by the breath figure method (SI Appendix, Fig. S3) was then transferred on top of the p-type transistor channel area. Finally, an aqueous electrolyte (0.1 M KPF<sub>6</sub>) and an Ag/AgCl gate electrode were applied. Note that the OECT DPP-g2T film has a porous morphology to enhance device performance by favoring ion intercalation in/extrusion from the semiconductor layer bulk. In contrast, in an EDLT the electrolyte ions remain at the interface with the semiconductor, and thus a smooth/dense IGZO semiconductor film morphology is optimal for maximizing this device's performance.

Before fabricating HCINs, the p- and n-type transistor characteristics were first evaluated individually and optimized to balance overall device performance. A representative transfer plot of the DPP-g2T OECT (channel length  $L = 10 \mu\text{m}$ ; channel width  $W = 100 \mu\text{m}$ ) is shown in Fig. 1B. Due to the porous DPP-g2T film morphology, minimal hysteresis (~0.05 V) and a large on/off current ratio ( $I_{\text{on}}/I_{\text{off}} = 10^5$ ) are achieved. In contrast, OECTs based on dense DPP-g2T films of similar thickness (~100 nm) exhibit far larger hysteresis (~0.4 V) and a lower  $I_{\text{on}}/I_{\text{off}}$  of  $10^3$  (SI Appendix, Fig. S4). A peak transconductance ( $g_{\text{m,p}}$ ) of  $2.5 \pm 0.8 \text{ mS}$  is obtained for the porous DPP-g2T OECTs,



**Fig. 1.** Hybrid inverter design and performance. (A) Illustration of the hybrid inverter on rigid Si/SiO<sub>2</sub> substrate with top and cross-section views. Representative transfer and transconductance data for (B) p-type OECT and (C) IGZO EDLT. (D) Voltage transfer curves of the HCIN with  $V_{\text{DD}}$  from 0.3 to 0.7 V, and the corresponding (E) voltage gain and (F) power consumption. (G) Comparison of device voltage gain and  $V_{\text{DD}}$  of this work to literature EGT-based inverters (EDLT-based unipolar inverters, EDLT-based complementary inverters, OECT-based unipolar inverters, and OECT-based complementary inverters). (H) Dynamic performance of the HCIN with  $V_{\text{DD}} = 0.7 \text{ V}$  over a frequency range from 0.1 Hz to 8 Hz.

which is  $\sim 250$  times greater than that of the corresponding dense film-based devices ( $0.010 \pm 0.006$  mS) and comparable to that of other reported high-performance p-type OECTs (32). The enhanced OECT performance with porous DPP-g2T reflects greater wettability and surface area of the channel, which facilitates the ion diffusion from the electrolyte to the semiconductor bulk (33). Representative output curves of the OECT based on porous DPP-g2T (SI Appendix, Fig. S5) demonstrate distinct linear and saturation regions, indicating excellent charge injection from the source/drain electrodes (34).

To match the performance of the p-type OECTs, a series of IGZO EDLTs ( $L = 10$   $\mu\text{m}$ ,  $W = 300$   $\mu\text{m}$ ) with systematically varied In/Ga/Zn atomic ratios were fabricated and characterized. Previous research demonstrated that as the indium atomic ratio is increased, negatively shifted transfer curves and increased IGZO EDLT on-currents are observed, which is attributable to the increased electron concentrations and enhanced mobilities (35, 36). Thus, as the In/Ga/Zn atomic ratio is varied from 7:1:2 to 10:1:1 the on-current increases from  $5.0 \times 10^{-5}$  A to  $8.9 \times 10^{-4}$  A, and the turn-on voltage ( $V_{\text{ON}}$ ) shifts from  $\sim 0.1$  V to  $\sim 0.0$  V. The optimal composition (In:Ga:Zn = 10:1:1) (Fig. 1C and SI Appendix, Fig. S6) affords a small turn-on voltage ( $V_{\text{ON}}$ ) of  $\sim 0.0$  V and a higher  $g_{\text{m,p}}$  of  $\sim 0.6$  mS. Note that the data presented in SI Appendix, Fig. S6 are based on unpatterned IGZO channels, which exhibit relatively high off-currents ( $I_{\text{off}}$ ,  $10^{-6}$ – $10^{-5}$  A). However, upon patterning the IGZO and using SU-8 passivated source/drain electrodes, a substantially reduced  $I_{\text{off}}$  of only  $10^{-9}$  A and a slightly enhanced  $g_{\text{m,p}}$  of  $1.2 \pm 0.3$  mS are realized (Fig. 1C). Note that the performance of the present IGZO-based EDLTs includes far larger  $g_{\text{m}}$  values than those of n-type OECTs with similar channel  $W/L$  ratios (37). For example, a recently reported high-performing n-type PgNaN OECT has a  $g_{\text{m,p}} = 0.21$  mS for  $W/L = 10$  (38).

Benefiting from the more balanced p- and n-type EGT performance ( $V_{\text{ON}} \sim 0.0$  V,  $I_{\text{off}} = 10^{-9}$ – $10^{-8}$  A,  $I_{\text{on}} = 10^{-4}$ – $10^{-3}$  A) in the same operational voltage range ( $< \pm 0.7$  V; Fig. 1B and C and SI Appendix, Figs. S5 and S7), the combined DPP-g2T

OECT + IGZO EDLT is ideal for complementary inverters. Here the characteristic response curves (Fig. 1D) exhibit an ideal rail-to-rail voltage behavior with a switching voltage ( $V_{\text{SW}}$ ) centered in a narrow range near  $V_{\text{DD}}/2$  (for 0.3, 0.4, 0.5, 0.6, and 0.7 V  $V_{\text{DD}}$ , the  $V_{\text{SW}}$ s are 0.08, 0.15, 0.20, 0.26, and 0.33 V, respectively), due to the balanced p- and n-type EGT performance. Moreover, a voltage gain up to 113 is obtained with a  $V_{\text{DD}} = 0.7$  V (Fig. 1E), which exceeds previously reported values for either unipolar or complementary inverter EGTs and carbon nanotube-metal oxide complementary metal-oxide-semiconductor circuits (Fig. 1G) (11, 15, 16, 28, 29, 39–56). Note that while the above unipolar OECT inverter reaches a voltage gain  $> 100$  with  $V_{\text{DD}} = 0.8$  V (46), the static power consumption, caused by the leakage current that exists when the inverter is not switching and on a steady state, is  $> 7 \times 10^{-6}$  W, which is far higher than that of the present HCIN reported in Fig. 1F. Due to the low driving voltage of both EGTs, the HCIN has a very low static power consumption of only  $2 \times 10^{-9}$  W at  $V_{\text{DD}} = 0.3$  V. Note that the static power consumption rises with increasing  $V_{\text{DD}}$  from 0.3 to 0.7 V, so that it is  $1.5 \times 10^{-8}$  W at  $V_{\text{DD}} = 0.7$  V. Fig. 1H shows the present HCIN dynamic performance where  $V_{\text{IN}}$  is a square input of 0.7 V (logic state of “1”) and a low voltage input of 0.0 V (logic state of “0”) over the frequency range of 0.1–8 Hz.  $V_{\text{OUT}}$  shows typical inverter characteristics with “0” or “1”  $V_{\text{OUT}}$  obtained with “1” or “0”  $V_{\text{IN}}$ , respectively. Moreover, stable rail-to-rail  $V_{\text{OUT}}$  swings between 0 V and 0.7 V is obtained at a  $V_{\text{IN}}$  frequency of  $\sim 8$  Hz. A stage delay of 0.025 s is achieved by measuring the time between the input falling edge and the point where  $V_{\text{OUT}} = 95\%$   $V_{\text{DD}}$ . Such a stage delay is relatively slow compared to ion-gel-gated EGTs but is above the average (0.9 s) reported for EGT inverters with aqueous electrolytes (15, 28).

**Real-Time EOG Monitoring and Logic Gates Using HCINs.** The high voltage gain of the HCIN developed here should be ideal for wearable/skin-compatible electrophysiological single amplification and monitoring, since these signals are weak in nature (millivolt range) (57). Here we apply the HCIN for real-time monitoring of EOG signals (Fig. 2 and SI Appendix, Fig. S8A).

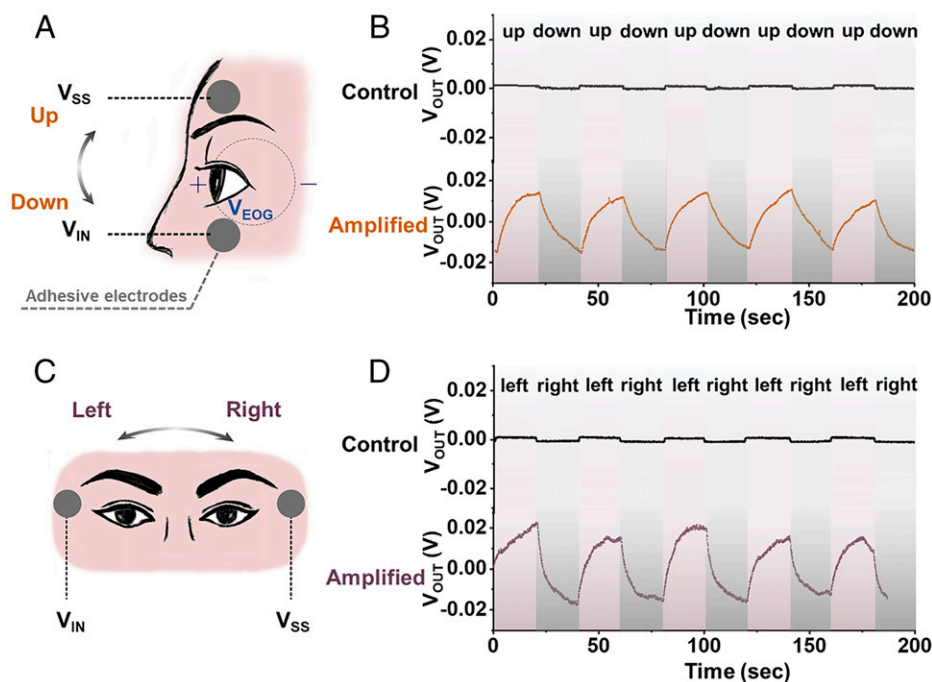


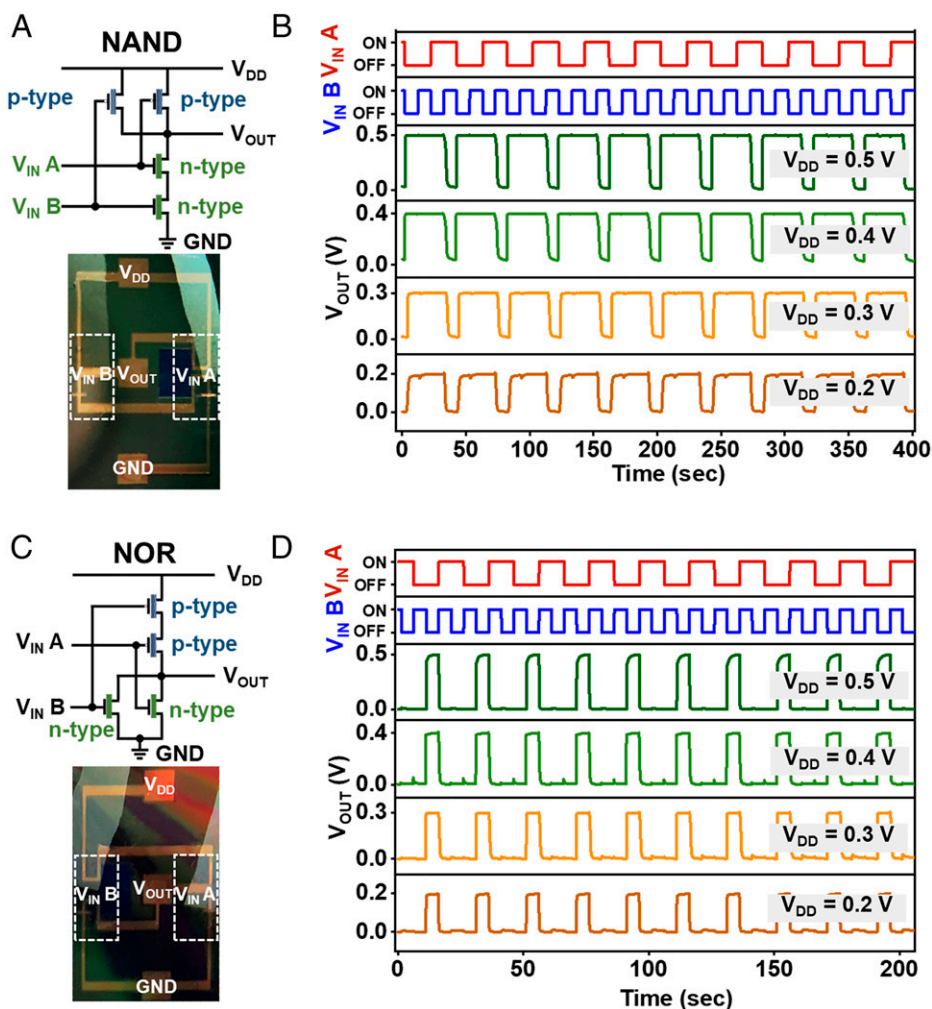
Fig. 2. EOG signals monitored by hybrid complementary circuits. Operating principle of the hybrid circuit in EOG signals monitoring during (A) up–down and (C) left–right eye movements. EOG signals obtained from the control group and the hybrid circuits during (B) up–down and (D) left–right eye movements.

As an example, EOG signal is of great significance for virtual and augmented reality, as well as medical research, such as the monitoring of reading speed, drowsiness detection, and diagnosis of sleep disorders (58, 59). Various current monitoring methods achieve cost-effective wearable sensing and high signal amplification metrics (60). However, these techniques require complex circuitry and/or specialized instrumentation for processing the recorded EOG signals (61, 62). In contrast, our HCIN can measure and amplify EOG signals simultaneously, which is advantageous in terms of directness of evaluation, fabrication simplicity, and low cost.

The EOG signal originates from the potential difference between the cornea and retina ( $V_{EOG}$ ), where eye movement leads to potential variations along vertical or horizontal directions of the eye on the nearby skin with up/down or left/right eye movement (Fig. 2) (63, 64). By placing two 3M-2560 electrodes on the top and bottom sides of the eye,  $V_{EOG}$  is directly measured and exhibits small voltage fluctuations (1~1.5 mV) with up and down eye movement (Fig. 2B). However, by connecting one electrode to  $V_{IN}$  and the other to  $V_{SS}$  (SI Appendix, Fig. S8B), the HCIN  $V_{OUT}$  exhibits voltage variations as large as 30 mV (Fig. 2B). Note that  $V_{DD}$  and  $V_{SS}$  are properly adjusted to ensure  $V_{SW}$  is ~0 V (see Materials and Methods for details). Moreover, horizontal eye movement is also tracked, showing less than a 1.5-mV variation by direct voltage measurement (Fig. 2D). However, an amplified voltage variation of up

to ~40 mV is achieved by the HCIN in monitoring horizontal eye movement (Fig. 2D and SI Appendix, Fig. S8C). The proposed hybrid circuit exhibits satisfactory performance in tracking eye movement, which demonstrates the signal amplification capacity of the HCIN and its potential for further applications in wearable integration systems for health monitoring.

Based on the high HCIN performance, we next explored the integration of complementary NAND and NOR gates; the circuit diagrams and circuit photographs are shown in Fig. 3. From the voltage input–output characteristics of the NAND gate in SI Appendix, Fig. S9A,  $V_{OUT}$  remains at a high voltage (logic “1”), as long as  $V_{IN A}$  and/or  $V_{IN B}$  are at low voltage state (logic “0”), while  $V_{OUT}$  switches to logic “0” only when both of the inputs are at logic “1.” SI Appendix, Fig. S9B shows the dynamic output of a NOR gate with  $V_{DD} = 0.7$  V, in which  $V_{OUT}$  switches to logic “1” only when both of the inputs are at logic “0.” These logic gates exhibit correct  $V_{OUT}$  with a rail-to-rail behavior corresponding to their  $V_{IN}$ , which then suggests the possibility of operating the logic gates at lower driving voltages. Fig. 3 C and D illustrate the dynamic performance of both NAND and NOR logic circuits with  $V_{DD}$  from 0.5 to 0.2 V. Typical rail-to-rail behavior of outputs are obtained even for driving voltage as low as 0.2 V, which is attributable to the well-balanced transistor performance, especially near 0 V  $V_{ON}$  in both EGTs. This is among the lowest reported driving voltage of EGT-based logic circuits and is comparable to technologically mature Si technologies

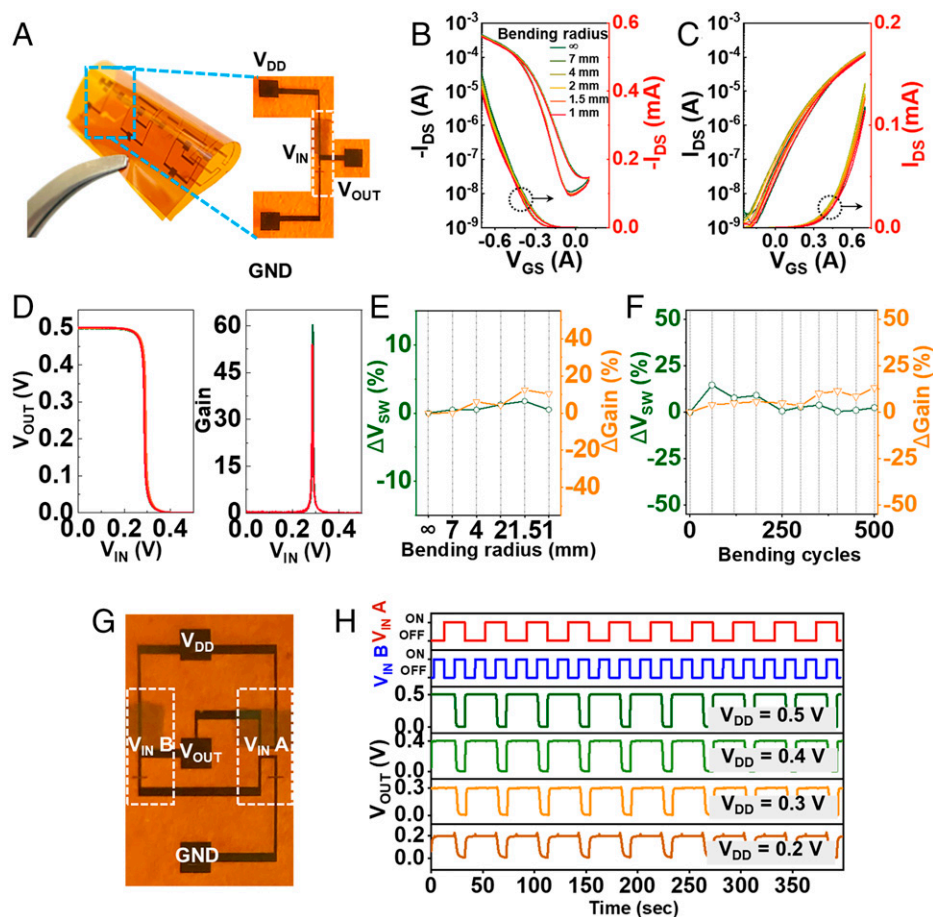


**Fig. 3.** Logic gates based on hybrid complementary circuits. Circuit diagrams and corresponding images of the (A) NAND and (C) NOR logic gates. Voltage input–output characteristics of the (B) NAND and (D) NOR logic gates, with  $V_{DD} = 0.2, 0.3, 0.4,$  and  $0.5$  V, respectively.

(15, 28, 65). Low driving voltages are essential for electronics where the power source is limited, indicating that the hybrid complementary circuit holds great potential for next-generation applications including bioelectronics, wearable/portable electronics, and artificial intelligence.

**Flexible Hybrid Complementary Circuits.** Since HCIN fabrication is compatible with flexible substrates (66, 67), and considering the need for mechanical flexibility in bioelectronics and wearable/portable electronics (19), complementary circuits are constructed here on flexible polyimide (PI) substrates (Fig. 4A; details in *SI Appendix*). First, the DPP-g2T OECT and IGZO EDLT on PI transistor performances were individually assessed (*SI Appendix*, Fig. S10) and indicated performances similar to these EGTs on Si/SiO<sub>2</sub> substrates. The transfer curve of the porous DPP-g2T OECT ( $L = 10 \mu\text{m}$ ;  $W = 100 \mu\text{m}$ ) (*SI Appendix*, Fig. S10) shows an  $I_{\text{on}}/I_{\text{off}}$  of  $10^4$  and  $V_{\text{ON}}$  of  $\sim 0.0$  V, with  $g_{\text{m,p}} = 1.7 \pm 0.5$  mS, while the IGZO EDLT ( $L = 10 \mu\text{m}$ ;  $W = 300 \mu\text{m}$ ) (*SI Appendix*, Fig. S10B) exhibits an  $I_{\text{on}}/I_{\text{off}}$  of  $10^5$  and  $V_{\text{ON}}$  of  $\sim -0.3$  V, with  $g_{\text{m,p}} = 0.6 \pm 0.3$  mS. The corresponding HCIN performance on PI (*SI Appendix*, Fig. S11) demonstrates good voltage transfer properties for  $V_{\text{DD}}$  from 0.3 V to 0.7 V. Moreover, a voltage gain of 95 is achieved at 0.7 V, slightly lower than 113 on a rigid substrate. The static power consumption is  $3.3 \times 10^{-9}$  W with  $V_{\text{DD}} = 0.3$  V and increases to  $2 \times 10^{-8}$  W with  $V_{\text{DD}} = 0.7$  V.

For flexible electronics applications, circuit electrical metrics should remain stable under mechanical deformation. Thus, a single EGT and HCIN electrical response was next investigated on bending about radii ( $R$ ) from  $\infty$  (no bending stress) to 1 mm (stress  $\sim 1.3\%$  for EGT active layers) both parallel and perpendicular to the channel length direction as flexible electronics. As shown in Fig. 4B and C, representative transfer curves for DPP-g2T OECTs and IGZO EDLTs on different degrees of bending along the direction parallel to the channel length indicate that transistor performance is extremely stable after bending down to 1 mm. For example,  $V_{\text{ON}}$  of the DPP-g2T OECT and IGZO EDLT shift slightly from  $-0.03$  to  $-0.02$  V and from  $-0.15$  to  $-0.18$  V, respectively. The OECT  $I_{\text{on}}$  (from  $3.2 \times 10^{-5}$  to  $1.1 \times 10^{-5}$  A) and  $I_{\text{off}}$  (from  $8.5 \times 10^{-9}$  to  $1.1 \times 10^{-8}$  A) exhibit negligible variations. Similarly, the IGZO EDLT  $I_{\text{on}}$  and  $I_{\text{off}}$  after bending deteriorate minimally from  $1.17 \times 10^{-4}$  to  $1.14 \times 10^{-4}$  A and from  $2.4 \times 10^{-9}$  to  $1.2 \times 10^{-9}$  A, respectively. Similar stable transistor behaviors are also obtained on bending along the direction perpendicular to the channel length (*SI Appendix*, Fig. S12). Specifically, the DPP-g2T OECT exhibits stable operation performance on bending (*SI Appendix*, Fig. S12A), while slightly positive shifted IGZO EDLT transfer curves are evident for bending radii smaller than 1.5 mm, where  $V_{\text{ON}}$  shifts from  $-0.14$  to  $-0.04$  V and  $I_{\text{on}}$  and  $I_{\text{off}}$  decrease substantially from  $1.5 \times 10^{-4}$  to  $5.0 \times 10^{-5}$  A and from  $1.0 \times 10^{-9}$  to  $4.5 \times 10^{-9}$  A, respectively (*SI Appendix*, Fig. S12B). Nevertheless, the IGZO EDLT remains functional



**Fig. 4.** Mechanically flexible hybrid complementary circuits. (A) Photo of the flexible hybrid circuits, along with a zoomed-in part of the inverter. Transfer curves of the flexible (B) DPP-g2T OECT and (C) IGZO EDLT when bended at the indicated radius (from 7 mm to 1 mm) along the direction perpendicular to channel length. (D) Corresponding voltage transfer characteristics and voltage gain of the flexible complementary inverter after bended under the indicated radius (from 7 mm to 1 mm). Switch voltage ( $V_{\text{sw}}$ ) and voltage gain variation of flexible hybrid inverter (E) after different bending radius and (F) after multiple bending cycles (bending radius = 4 mm) along the direction perpendicular to channel length. (G) Photo of the NAND gate on PI substrate, along with (H) the dynamic performance of the NAND logic gate with  $V_{\text{DD}}$  from 0.2 V to 0.5 V.

after bending to a 1-mm radius along the direction perpendicular to the channel length. Thus, the above transistor performances after bending indicate that circuits based on such transistors should also show stable performance down to  $\sim 1.5$ -mm radii. As shown in Fig. 4D and *SI Appendix, Fig. S12C*, HCIN voltage transfer curves after bending to different radii exhibit identical characteristics, where the voltage gains only fall from 60 to 54 and from 50 to 43, after bending from  $\infty$  to 1 mm in the parallel and perpendicular direction, respectively ( $V_{DD} = 0.5$  V). Variations of  $V_{SW}$  and voltage gain (gain) of the circuit (normalized value) as a function of bending radius are summarized in Fig. 4E and *SI Appendix, Fig. S13A*. No significant changes are observed on bending in both directions, with the  $V_{SW}$  and voltage gains of hybrid circuit varying only  $\sim 0.5\%$  and  $\sim 10\%$ , respectively, after bending to a 1-mm radius (Fig. 4E). For the bending direction perpendicular to channel length,  $\sim 2.8\%$  and  $\sim 13.9\%$  variations in  $V_{SW}$  and voltage gain are observed after bending at  $R$  of 1 mm (*SI Appendix, Fig. S13A*).

Performance stability of the flexible HCIN was further investigated by bending the device in both directions at  $R = 4$  mm (stress  $\sim 0.3\%$ ) for 500 cycles, and the variation of  $V_{SW}$  and voltage gain were recorded (Fig. 4F and *SI Appendix, Fig. S13B*).  $V_{SW}$  and voltage gain variations are within  $\sim 2.4\%$  and  $13.1\%$ , respectively, in the bending direction parallel to channel length, while  $\sim 9.3\%$  and  $3.6\%$  variations on  $V_{SW}$  and voltage gain, respectively, are observed in the bending direction perpendicular to the channel length. The present HCIN shows satisfactory stability on flexible substrates under dynamic bending stresses, as a result of the amorphous nature of the IGZO (*SI Appendix, Fig. S14*) and SU-8 encapsulated Au electrodes, preventing them from cracking under bending (*SI Appendix, Fig. S15*) (68). Finally, mechanically flexible NAND and NOR logic gates were demonstrated on PI (Fig. 4G and *SI Appendix, Fig. S16A*). The corresponding dynamic performances are shown in Fig. 4H and *SI Appendix, Fig. S16B*. Both NAND and NOR logic gates exhibit full rail-to-rail behavior, where good logic responses to two square-wave input signals ( $V_{IN A}$  and  $V_{IN B}$ ) are obtained with a power supply as low as 0.2 V. These results further illustrate the potential of implementing the hybrid OECT/IGZO EGT configuration in flexible integrated circuits and wearable sensing electronics.

## Conclusions

Here we demonstrated an approach to achieving high-performance complementary circuits by integrating an organic p-type OECT and an inorganic n-type IGZO EDLT. Balanced transistor performances thereby afford an inverter with ultrahigh voltage gain ( $\sim 113$ ) under a low operating voltage of 0.7 V. Diverse logic circuits on both rigid and flexible substrates are fabricated, demonstrating stable performance output under ultralow driving voltages (0.2 V), and utility is demonstrated in the high-sensitivity monitoring and amplification EOG signals, which is critical for the development of useful diagnostic tool for human health and wearable human-computer interfaces. These results demonstrate considerable potential for the further development of hybrid porous organic OECT/nonporous inorganic EDLT circuits in low-power flexible electronics and wearable sensors.

## Materials and Methods

**Precursor Preparation.** All chemicals were purchased from Sigma-Aldrich; 354.8 mg  $\text{In}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ , 399.6 mg  $\text{Ga}(\text{NO}_3)_3 \cdot x\text{H}_2\text{O}$ , and 297.2 mg  $\text{Zn}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$  were dissolved in 10 mL deionized (DI) water to achieve a concentration of 0.1 M. Then, the well-dispersed precursor solutions were mixed to obtain the IGZO precursor solutions with the desired In:Ga:Zn molar ratio of 7:1:2, 8:1:1, 9:1:1, and 10:1:1, followed by continuous stirring for 8 h. DPP-g2T was synthesized following the procedure described in *SI Appendix, Scheme S1 and Fig. S1*. DPP-g2T (8 mg) was dissolved in 1 mL solvent mixture of chloroform:methyl alcohol = 9:1 in volume, and the prepared DPP-g2T solution was stirred for at least 12 h before use.

**Device Fabrication and Evaluation.**  $n^{++}$ -silicon wafers with 300 nm  $\text{SiO}_2$  coating or 25- $\mu\text{m}$  PI films as substrates were first ultrasonically cleaned in isopropyl alcohol and then treated with an oxygen plasma for 15 min. Next, the IGZO precursor solution was filtered through a 0.2- $\mu\text{m}$  polytetrafluoroethylene syringe filter and spin-coated on the  $\text{Si}/\text{SiO}_2$  substrate at 3,000 rpm for 20 s and annealed at 300 °C for 30 min. This spin-coating and annealing process was repeated for three times on  $\text{Si}/\text{SiO}_2$  substrate or seven times on the PI substrate. Then, patterning of the IGZO layer was achieved by spin coating on S1813 photoresist at 4,000 rpm for 45 s, followed by annealing at 110 °C for 60 s and then exposing in a maskless aligner system (MLA150; Heidelberg Instruments). Next, the sample was developed in AZ400k (Microchemicals) for 40 s, cleaned with DI water, and dried by an  $\text{N}_2$  flow. The exposed oxide film was then etched in an aqueous oxalic acid solution (10% wt/vol) for 40 s and rinsed with DI water. Residual S1813 photoresist was removed by sonicating the sample in acetone and then isopropyl alcohol for 2 min each. The obtained patterned IGZO was further annealed at 300 °C for 5 min to remove residual solvent. The Au/Cr electrodes were next patterned with S1813 in a lift-off process, where S1813 was first patterned with the same process as described above but with a different pattern. Then, 3 nm Cr and 30 nm Au were deposited by thermal evaporation and developed by soaking in acetone for 5 min to remove the S1813. Here, the patterned Au electrodes define the channel dimensions, which for the IGZO EDLT were  $W = 300 \mu\text{m}$  and  $L = 10 \mu\text{m}$ , while those for the DPP-g2T OECT were  $W = 100 \mu\text{m}$  and  $L = 10 \mu\text{m}$ . Next, the device was encapsulated by spin coating SU-8 (2002) at 3,000 rpm for 30 s, followed by exposing to a mask aligner (Suss MABA6) for 15 s through a photo mask. After developing the SU-8 developer, only the channel areas for both transistors were exposed to air. The porous DPP-g2T films were first deposited on polyvinyl alcohol (PVA;  $\sim 30$  nm thick)-coated glass by spin coating the prepared DPP-g2T solution at 5,000 rpm for 10 s in a high-humidity atmosphere (relative humidity =  $\sim 94\%$ ). Next, the free-standing porous DPP-g2T film was obtained by immersing the DPP-g2T/PVA/glass multilayer in water, and the detached DPP-g2T was transferred to the p channel area of the circuit electrodes. Finally, the device was annealed at 110 °C for 5 min before applying the 0.1 M  $\text{KPF}_6$  aqueous electrolyte and Ag/AgCl as gate electrode.

Electrical characterization of the transistors and circuits was performed with an Agilent 1500 semiconductor parameter analyzer on a probe station. For the logic circuit measurements, pulse input signals were generated by a waveform generator (Keysight 33500B).

**Thin Film Characterization.** For the IGZO film characterization, GIXRD measurements were carried out with a Rigaku Smart Lab Thin-film Diffraction Workstation using a high-intensity 9-kW copper rotating anode X-ray source which is coupled to a multilayer optic. The scanning electron microscope (SEM) characterization of the porous DPP-g2T films was carried out on a Hitachi SU8030 FE-SEM.

**EOG Monitoring.** For the EOG monitoring of up-down eye motion (*SI Appendix, Fig. S8A*), a 26-y-old healthy female participated in the experiments and all testing procedures were conducted safely without any external stimulus. Before the experiments, the human subject was trained on the experimental protocol which including vertical and horizontal eyeball movements and was also instructed not to speak to avoid any interference from other body movements. During the testing, two adhesive electrodes (3M Red Dot 2560-5) were placed on the upper and lower sides of the eye socket, respectively. The upper one was connected to the  $V_{SS}$  of the proposed inverter, and the lower one was directly connected to the  $V_{IN}$ . The  $V_{DD}$  and  $V_{SS}$  were supplied by an Agilent 1500 semiconductor parameter analyzer and properly adjusted to make sure that  $V_{SW}$  was  $\sim 0$  V. Next, in a relaxed state, the human subject followed instructions to look up and down (*SI Appendix, Fig. S8B*). First, the subject was asked to look horizontally, then asked to move the eyeballs up and then down. This procedure was repeated during the measurements. The amplified EOG signal was recorded by monitoring  $V_{OUT}$  using a Bio-Logic SP-150. The left-right eye movement tracking was similar to the above operation (*SI Appendix, Fig. S8C*), except that the two adhesive electrodes were placed on the left and right temples, and the human subject was asked to move the eyeballs in the horizontal direction to the left and next to the right directions. The left electrode was connected to  $V_{SS}$ , and the right one was connected to  $V_{IN}$ . This procedure was repeated during the measurements. The EOG experiment involving human subjects described in this research was assigned as "Not Human Research" by the Institutional Review Board at the Northwestern University. A subject consent was signed before participating in the research, and the authors are very grateful to the participant for involvement in this study.

**Data Availability.** All study data are included in the article and/or *SI Appendix*.

**ACKNOWLEDGMENTS.** We thank the Air Force Office of Scientific Research (FA9550-18-1-0320), the Northwestern University Materials Research Science and Engineering Center (MRSEC; NSF grant DMR-1720139), and Flexterra Corp. for support of this research. This work made use of the Northwestern University Micro/Nano Fabrication Facility and Electron Probe Instrumentation Center facility of the Northwestern University Atomic and Nanoscale Characterization Experimental Center at Northwestern University, which has received

support from the Soft and Hybrid Nanotechnology Experimental (ShyNE) Resource (NSF ECCS-2025633), the State of Illinois, and Northwestern's MRSEC program (NSF DMR-1720139). This work made use of the Jerome B. Cohen X-Ray Diffraction Facility supported by the MRSEC program of the NSF (DMR-1720139) at the Materials Research Center of Northwestern University and SHyNE Resource (NSF ECCS-1542205.). Y. Yao thanks the joint-Ph.D. program supported by the China Scholarship Council (201906320346) for a fellowship and acknowledges support from 2019 Zhejiang University Academic Award for Outstanding Doctoral Candidates.

- C. Liao *et al.*, Flexible organic electronics in biology: Materials and devices. *Adv. Mater.* **27**, 7493–7527 (2015).
- B. Wang *et al.*, High-k gate dielectrics for emerging flexible and stretchable electronics. *Chem. Rev.* **118**, 5690–5754 (2018).
- M. Fahlman, S. Fabiano, V. Gueskine, D. Simon, X. Crispin, Interfaces in organic electronics. *Nat. Rev. Mater.* **4**, 627–650 (2019).
- D. T. Simon, E. O. Gabrielson, K. Tybrandt, M. Berggren, Organic bioelectronics: Bridging the signaling gap between biology and technology. *Chem. Rev.* **116**, 13009–13041 (2016).
- T. Someya, Z. Bao, G. G. Malliaras, The rise of plastic bioelectronics. *Nature* **540**, 379–385 (2016).
- T. Sekitani, T. Someya, Stretchable, large-area organic electronics. *Adv. Mater.* **22**, 2228–2246 (2010).
- J. Rivnay *et al.*, Organic electrochemical transistors. *Nat. Rev. Mater.* **3**, 1–14 (2018).
- W. Huang *et al.*, Dielectric materials for electrolyte gated transistor applications. *J. Mater. Chem. C* **9**, 9348–9376 (2021).
- D. A. Bernards, G. G. Malliaras, Steady-state and transient behavior of organic electrochemical transistors. *Adv. Funct. Mater.* **17**, 3538–3544 (2007).
- J. Rivnay *et al.*, Structural control of mixed ionic and electronic transport in conducting polymers. *Nat. Commun.* **7**, 10.1038/ncomms11287 (2016).
- H. Sun *et al.*, Complementary logic circuits based on high-performance n-type organic electrochemical transistors. *Adv. Mater.* **30**, 1704916 (2018).
- L. Travaglini *et al.*, Single-material OECT-based flexible complementary circuits featuring polyaniline in both conducting channels. *Adv. Funct. Mater.* **31**, 2007205 (2020).
- P. A. Ersman *et al.*, Screen printed digital circuits based on vertical organic electrochemical transistors. *Flex. Print. Electron.* **2**, 045008 (2017).
- G. Cadilha Marques *et al.*, Progress report on “from printed electrolyte-gated metal-oxide devices to circuits”. *Adv. Mater.* **31**, e1806483 (2019).
- F. Zare Bidoky *et al.*, Sub-3 V ZnO electrolyte-gated transistors and circuits with screen-printed and photo-crosslinked ion gel gate dielectrics: New routes to improved performance. *Adv. Funct. Mater.* **30**, 1902028 (2020).
- S. Park *et al.*, Sub-0.5 V highly stable aqueous salt gated metal oxide electronics. *Sci. Rep.* **5**, 10.1038/srep13088 (2015).
- H. Sun, J. Y. Gerasimov, M. Berggren, S. Fabiano, N-Type organic electrochemical transistors: Materials and challenges. *J. Mater. Chem. C* **6**, 11778–11784 (2018).
- X. Yu, T. J. Marks, A. Facchetti, Metal oxides for optoelectronic applications. *Nat. Mater.* **15**, 383–396 (2016).
- B. Wang *et al.*, Flexible and stretchable metal oxide nanofiber networks for multimodal and monolithically integrated wearable electronics. *Nat. Commun.* **11**, 2405 (2020).
- W. Huang *et al.*, Metal composition and polyethylenimine doping capacity effects on semiconducting metal oxide–polymer blend charge transport. *J. Am. Chem. Soc.* **140**, 5457–5473 (2018).
- Z. Wang, P. K. Nayak, J. A. Caraveo-Frescas, H. N. Alshareef, Recent developments in p-Type oxide semiconductor materials and devices. *Adv. Mater.* **28**, 3831–3892 (2016).
- W. Huang *et al.*, Experimental and theoretical evidence for hydrogen doping in polymer solution-processed indium gallium oxide. *Proc. Natl. Acad. Sci. U.S.A.* **117**, 18231–18239 (2020).
- J. A. Caraveo-Frescas, H. N. Alshareef, Transparent p-type SnO nanowires with unprecedented hole mobility among oxide semiconductors. *Appl. Phys. Lett.* **103**, 222103 (2013).
- H. Yabuta *et al.*, Sputtering formation of p-type SnO thin-film transistors on glass toward oxide complementary circuits. *Appl. Phys. Lett.* **97**, 072111 (2010).
- H. Zhu, A. Liu, Y.-Y. Noh, Impact of humidity on the performance and stability of solution-processed copper oxide transistors. *IEEE Electron Device Lett.* **41**, 1033–1035 (2020).
- G. Cadilha Marques *et al.*, Digital power and performance analysis of inkjet printed ring oscillators based on electrolyte-gated oxide electronics. *Appl. Phys. Lett.* **111**, 102103 (2017).
- Y. J. Jo, K. Y. Kwon, Z. U. Khan, X. Crispin, T. I. Kim, Gelatin hydrogel-based organic electrochemical transistors and their integrated logic circuits. *ACS Appl. Mater. Interfaces* **10**, 39083–39090 (2018).
- Y. Xia *et al.*, Printed sub-2 V gel-electrolyte-gated polymer transistors and circuits. *Adv. Funct. Mater.* **20**, 587–594 (2010).
- K. Hong, S. H. Kim, K. H. Lee, C. D. Frisbie, Printed, sub-2V ZnO electrolyte gated transistors and inverters on plastic. *Adv. Mater.* **25**, 3413–3418 (2013).
- S. H. Kim *et al.*, Electrolyte-gated transistors for organic and printed electronics. *Adv. Mater.* **25**, 1822–1846 (2013).
- T. Leydecker, Z. M. Wang, F. Torricelli, E. Orgiu, Organic-based inverters: Basic concepts, materials, novel architectures and applications. *Chem. Soc. Rev.* **49**, 7627–7670 (2020).
- M. Moser, J. F. Ponder Jr., A. Wadsworth, A. Giovannitti, I. McCulloch, Materials in organic electrochemical transistors for bioelectronic applications: Past, present, and future. *Adv. Funct. Mater.* **29**, 1807033 (2019).
- X. Zhang *et al.*, Breath figure-derived porous semiconducting films for organic electronics. *Sci. Adv.* **6**, eaaz1042 (2020).
- J. Rivnay *et al.*, Organic electrochemical transistors with maximum transconductance at zero gate bias. *Adv. Mater.* **25**, 7010–7014 (2013).
- S. Jeong, Y. G. Ha, J. Moon, A. Facchetti, T. J. Marks, Role of gallium doping in dramatically lowering amorphous-oxide processing temperatures for solution-derived indium zinc oxide thin-film transistors. *Adv. Mater.* **22**, 1346–1350 (2010).
- G. H. Kim *et al.*, Effect of indium composition ratio on solution-processed nanocrystalline InGaZnO thin film transistors. *Appl. Phys. Lett.* **94**, 233501 (2009).
- A. Giovannitti *et al.*, N-type organic electrochemical transistors with stability in water. *Nat. Commun.* **7**, 13066 (2016).
- X. Chen *et al.*, N-type rigid semiconducting polymers bearing oligo (ethylene glycol) side chains for high performance organic electrochemical transistors. *Angew. Chem. Int. Ed. Engl.* **60**, 9368–9373 (2021).
- K. G. Cho *et al.*, Sub-2 V, transfer-stamped organic/inorganic complementary inverters based on electrolyte-gated transistors. *ACS Appl. Mater. Interfaces* **10**, 40672–40680 (2018).
- S. Joshi *et al.*, Ambient processed, water-stable, aqueous-gated sub 1 V n-type carbon nanotube field effect transistor. *Sci. Rep.* **8**, 11386 (2018).
- H. J. Conley *et al.*, Bandgap engineering of strained monolayer and bilayer MoS<sub>2</sub>. *Nano Lett.* **13**, 3626–3630 (2013).
- G. Gao *et al.*, Triboiontronic transistor of MoS<sub>2</sub>. *Adv. Mater.* **31**, e1806905 (2019).
- L. Herlogsson, X. Crispin, S. Tierney, M. Berggren, Polyelectrolyte-gated organic complementary circuits operating at low power and voltage. *Adv. Mater.* **23**, 4684–4689 (2011).
- R. Porrazzo *et al.*, Water-gated n-type organic field-effect transistors for complementary integrated circuits operating in an aqueous environment. *ACS Omega* **2**, 1–10 (2017).
- S. E. Doris, A. Pierre, R. A. Street, Dynamic and tunable threshold voltage in organic electrochemical transistors. *Adv. Mater.* **30**, e1706757 (2018).
- P. Romele, M. Ghittorelli, Z. M. Kovács-Vajna, F. Torricelli, Ion buffering and interface charge enable high performance electronics with organic electrochemical transistors. *Nat. Commun.* **10**, 3044 (2019).
- G. C. Marques *et al.*, Printed logic gates based on enhancement- and depletion-mode electrolyte-gated transistors. *IEEE Trans. Electron Devices* **67**, 3146–3151 (2020).
- K. G. Cho *et al.*, Printable carbon nanotube-based elastic conductors for fully-printed sub-1 V stretchable electrolyte-gated transistors and inverters. *J. Mater. Chem. C* **8**, 3639–3645 (2020).
- P. Romele *et al.*, Multiscale real time and high sensitivity ion detection with complementary organic electrochemical transistors amplifier. *Nat. Commun.* **11**, 3743 (2020).
- Y. Yang *et al.*, Carbon nanotube network film-based ring oscillators with sub 10-ns propagation time and their applications in radio-frequency signal transmission. *Nano Res.* **11**, 300–310 (2018).
- X. Zhang *et al.*, Flexible CMOS-like circuits based on printed P-type and N-type carbon nanotube thin-film transistors. *Small* **12**, 5066–5073 (2016).
- H. Zhang *et al.*, High-performance carbon nanotube complementary electronics and integrated sensor systems on ultrathin plastic foil. *ACS Nano* **12**, 2773–2779 (2018).
- Y. Yang, L. Ding, J. Han, Z. Zhang, L.-M. Peng, High-performance complementary transistors and medium-scale integrated circuits based on carbon nanotube thin films. *ACS Nano* **11**, 4124–4132 (2017).
- S.-J. Han *et al.*, High-speed logic integrated circuits with solution-processed self-assembled carbon nanotubes. *Nat. Nanotechnol.* **12**, 861–865 (2017).
- C. Qiu *et al.*, Scaling carbon nanotube complementary transistors to 5-nm gate lengths. *Science* **355**, 271–276 (2017).
- Y. Zhao *et al.*, Three-dimensional flexible complementary metal-oxide-semiconductor logic circuits based on two-layer stacks of single-walled carbon nanotube networks. *ACS Nano* **10**, 2193–2202 (2016).
- N. Feltgen *et al.*; EAGLE-Study Group, Multicenter study of the European Assessment Group for Lysis in the Eye (EAGLE) for the treatment of central retinal artery occlusion: Design issues and implications. *Graefes Arch. Clin. Exp. Ophthalmol.* **244**, 950–956 (2006).
- T. C. Chieh, M. M. Mustafa, A. Hussain, S. F. Hendi, B. Y. Majlis, “Development of vehicle driver drowsiness detection system using electrooculogram (EOG)” in *2005 1st*

Yao et al.

Flexible complementary circuits operating at sub-0.5 V via hybrid organic-inorganic electrolyte-gated transistors

PNAS | 7 of 8

<https://doi.org/10.1073/pnas.2111790118>

www.manaraa.com

*International Conference on Computers, Communications, & Signal Processing with Special Track on Biomedical Engineering* (IEEE, 2005), pp. 165–168.

59. S. F. Liang, C. E. Kuo, Y. C. Lee, W. C. Lin, F. Z. Shaw, Development of an EOG-based automatic sleep-monitoring eye mask. *IEEE Trans. Instrum. Meas.* **64**, 2977–2985 (2015).
60. S. Hillaire, A. Lécuyer, R. Cozot, G. Casiez, “Using an eye-tracking system to improve camera motions and depth-of-field blur effects in virtual environments” in *Proceedings of the 2008 IEEE Virtual Reality Conference* (IEEE, 2008), pp. 47–50.
61. A. J. Golparvar, M. K. Yapici, “Wearable graphene textile-enabled EOG sensing” in *2017 IEEE Sensors* (IEEE, 2017), pp. 1–3.
62. J. Heo, H. Yoon, K. S. Park, A novel wearable forehead EOG measurement system for human computer interfaces. *Sensors (Basel)* **17**, 1485 (2017).
63. N. I. Kim *et al.*, Highly-sensitive skin-attachable eye-movement sensor using flexible nonhazardous piezoelectric thin film. *Adv. Funct. Mater.* **31**, 2008242 (2020).
64. C. Jiang *et al.*, Printed subthreshold organic transistors operating at high gain and ultralow power. *Science* **363**, 719–723 (2019).
65. H. Chen, Y. Cao, J. Zhang, C. Zhou, Large-scale complementary macroelectronics using hybrid integration of carbon nanotubes and IGZO thin-film transistors. *Nat. Commun.* **5**, 4097 (2014).
66. Y. Khan *et al.*, A new frontier of printed electronics: Flexible hybrid electronics. *Adv. Mater.* **32**, e1905279 (2020).
67. D. Zhao *et al.*, Engineering intrinsic flexibility in polycrystalline molecular semiconductor films by grain boundary plasticization. *J. Am. Chem. Soc.* **142**, 5487–5492 (2020).
68. W. S. Lee *et al.*, Multiaxial and transparent strain sensors based on synergetically reinforced and orthogonally cracked hetero-nanocrystal solids. *Adv. Funct. Mater.* **29**, 1806714 (2019).