Influence of Molecular Weight on the Organic Electrochemical Transistor Performance of Ladder-Type Conjugated Polymers

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Organic electrochemical transistors (OECTs) hold promise for developing a variety of high-performance (bio-)electronic devices/circuits. While OECTs based on p-type semiconductors have achieved tremendous progress in recent years, n-type OECTs still suffer from low performance, hampering the development of power-efficient electronics. Here, it is demonstrated that fine-tuning the molecular weight of the rigid, ladder-type n-type polymer poly(benzimidazobenzophenanthroline) (BBL) by only one order of magnitude (from 4.9 to 51 kDa) enables the development of n-type OECTs with record-high geometry-normalized transconductance ($g_{m,norm} \approx 11 \text{ S cm}^{-1}$) and electron mobility × volumetric capacitance ($\mu C^* \approx 26 \text{ F cm}^{-1} \text{ V}^{-1} \text{s}^{-1}$), fast temporal response (0.38 ms), and low threshold voltage (0.15 V). This enhancement in OECT performance is ascribed to a more efficient intermolecular charge transport in high-molecular-weight BBL than in the low-molecular-weight counterpart. OECT-based complementary inverters are also demonstrated with record-high voltage gains of up to 100 V V$^{-1}$ and ultralow power consumption down to 0.32 nW, depending on the supply voltage. These devices are among the best sub-1 V complementary inverters reported to date. These findings demonstrate the importance of molecular weight in optimizing the OECT performance of rigid organic mixed ionic–electronic conductors and open for a new generation of power-efficient organic (bio-)electronic devices.

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In OECTs, the application of a gate voltage ($V_G$) enables the penetration of ions from the electrolyte into the OMIEC channel layer. Charges are then accumulated/depleted throughout the entire bulk of the OMIEC layer, with a consequent large variation in the source–drain current ($I_{DS}$).[13] This volumetric charging/discharging of the OMIEC layer makes the working mechanism of OECTs very different from traditional organic field-effect transistors (OFETs), where charge accumulation/depletion is confined at the semiconductor/dielectric interface.[16] The figures of merit quantifying the efficiency of this ion-to-electron transduction are the transconductance ($g_m = \frac{\partial I_D}{\partial V_G}$) and the product of charge-carrier mobility and volumetric capacitance ($\mu C_v^\ast$), which are interrelated in the saturation regime according to the equation

$$g_m = \frac{Wd}{L} \mu C_v^\ast (V_G - V_th)$$  \hspace{1cm} (1)

where $L$ is the channel length, $W$ is the channel width, $d$ is the film thickness, $\mu$ is the charge-carrier mobility, $C_v^\ast$ is the volumetric capacitance, and $V_th$ is the threshold voltage. As $g_m$ depends on the volume of the OECT channel material,[17] a geometry-normalized transconductance $g_{m,norm} = g_m \frac{L}{Wd}$ is often used to compare the performance of different OMIECs.

While p-type (hole-transporting) OMIECs can routinely reach $g_{m,norm} > 100 \text{ S cm}^{-1}$ and $\mu C_v^\ast > 300 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ in OFETs,[18] n-type (electron-transporting) OMIECs lag far behind in terms of performance with $g_{m,norm} < 2 \text{ S cm}^{-1}$ and $\mu C_v^\ast$ values of $< 7 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$ (see Table 1). This performance mismatch between p-type and n-type OECTs hinders the development of power-efficient complementary devices/circuits, essential to many of the applications mentioned above. Several material and device design strategies, including introduction of oligo(ethylene glycol) side chains,[19] planarization/rigidification of the OMIEC polymer backbone,[20] modification of the source/drain electrode surface,[21] and use of molecular[22] or polymeric[23] dopants, are currently being explored. In the pioneering work by Giovannitti et al.,[24] naphthalenediimide (NDI)-based polymers were functionalized with oligo(ethylene glycol) side chains to yield n-type OECTs with $g_{m,norm} = 0.1 \text{ S cm}^{-1}$ and $\mu C_v^\ast = 0.1 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$. The only modest performance of these NDI-based OECTs was attributed to a low $\mu < 10^{-5} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, most likely due to the highly localized nature of polarons in this class of donor–acceptor polymers.[25] Recently, we suggested that the use of highly planar and rigid conjugated polymers such as the ladder-type poly(benzimidazobenzophenanthroline) (BBL) might help overcome this limitation[26] and demonstrated n-type OECTs with high $g_{m,norm}$ of 0.3 S cm$^{-1}$ and $\mu C_v^\ast$ of 1–2 F cm$^{-1}$ V$^{-1}$ s$^{-1}$.[27] Remarkably, it was also found that the lack of side chains does not affect the BBL-based OECT’s temporal response.[28] This has motivated further research toward developing other rigid conjugated polymers possessing high electron mobility, like those based on fused electron-deficient lactam rings,[29] which own $\mu = 6.5 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ and $g_{m,norm} = 0.2 \text{ S cm}^{-1}$. Despite significant progress, the best n-type OECTs do not yet meet the performance comparable to the p-type counterparts.

An important parameter of conjugated polymers is the molecular weight, which is known to significantly affect their (opto-) electronic and charge transport properties.[29] In the context of OFETs, charge-carrier mobility is typically found to increase with increasing molecular weight.[10] For example, when the molecular weight of the p-type semiconductor poly(3-hexylthiophene) is increased from 3 to 40 kDa, the field-effect mobility increases by up to four orders of magnitude due to improved connectivity between crystalline regions.[31] Similar trends have been observed for other polymers, such as those based on diketopyrrolopyrrole.[12] Despite the beneficial effect high molecular weight has on the field-effect charge transport properties of conjugated polymers, its role on the OECT electrical characteristics of electrochemically doped OMIECs remains unexplored and poorly understood.

Here, we investigate the influence of molecular weight on the charge transport properties of electrochemically doped BBL and the electrical characteristic of OECTs made thereof. We chose to work with BBL, being this is the best-performing n-type OMIEC for OECTs. We found that increasing the molecular weight of BBL from 4.9 to 51 kDa (i.e., the number of repeating units increases from 15 to 152) enables the development of n-type OECTs with record-high $g_{m,norm}$ (11.1 S cm$^{-1}$) and $\mu C_v^\ast$ (25.9 F cm$^{-1}$ V$^{-1}$ s$^{-1}$). We ascribed the observed enhancement in OECT performance to a stronger $\pi-\pi$ interaction and higher crystallinity. As a result of a more efficient intermolecular charge transport, high-molecular-weight BBL shows electron mobility over one order of magnitude higher than the low-molecular-weight counterpart, fast transient response down to 0.38 ms, and threshold voltage of 0.15 V. By combining electrochemical analysis, UV–vis spectrophotometry, dynamic light scattering (DLS), and X-ray diffraction data, we quantitatively characterized the impact of molecular weight on energetics, crystallinity, and charge transport properties of BBL. Finally, we demonstrated OECT-based complementary inverters with a record-high voltage gain of up to 100 V V$^{-1}$ and ultralow power consumption down to 0.32 nW, depending on the supply voltage. These devices are among the best performing sub-1 V complementary inverters reported to date. These findings demonstrate the importance of molecular weight to optimize the OECT performance of rigid OMIEC polymers.

2. Results and Discussion

BBL was synthesized by polycondensation reaction of 1,4,5,8-naphthalenetetracarboxylic dihydride (NDA) and 1,2,4,5-tetraaminobenzene tetrahydrochloride (TABH) in poly(phosphoric acid) (PPA) at high temperature (Figure 1a). By controlling the polycondensation reaction time, we obtained BBL with different viscosity-average molecular weights ($M_v$) of 4.89, 20.0, 32.8, and 50.8 kDa. Based on the $M_v$, their repeating units were calculated to be 15, 60, 98, and 152 (Figure 1b), so we hereafter refer to BBL15, BBL60, BBL98, and BBL152, respectively. Regardless of $M_v$, these BBL have good solubility in methanesulmonic acid (MSA), and can be spin-cast on different substrates (e.g., gold, silicon, glass, and even polyethylene terephthalate) to form thin films with thickness ranging from 20 to 200 nm. By controlling the BBL-MSA solution concentration (from 1.40 to 775 mg mL$^{-1}$) and spin coating conditions (1000 rpm for 1 min on glass substrates), the BBL film thickness
can be accurately adjusted to be 20.2 ± 1.6 nm for BBL15, 19.9 ± 1.3 nm for BBL60, 20.2 ± 1.4 nm for BBL98, and 20.1 ± 1.2 nm for BBL152. UV–vis spectra show that all BBL polymers have two absorption peaks: 1) peak I located at shorter wavelengths (300–400 nm) and ascribed to the $\pi - \pi^*$ transition, and 2) peak II located at longer wavelengths (400–800 nm) and ascribed to the $\pi - \pi^*$ transition (Figure 1c).[33] The peak II/peak I intensity ratio increases, and the center of peak II redshifts as the number of repeating units increases, suggesting that the effective conjugation length increases as the molecular weight increases.[34] All BBL polymers have a comparable $\lambda_{onset}$ of about 716 nm, indicating similar optical bandgaps ($E_{\text{gap}}$ = 1.74 eV). As measured by cyclic voltammetry (CV), the lowest unoccupied molecular orbital energy level is estimated to be around −4.38 eV and independent of molecular weight (Figure 1d and Figure S1, Supporting Information). The highest occupied molecular orbital energy level is calculated to be −6.12 eV. For dilute MSA solution (0.02–0.4 mg mL$^{-1}$), the UV–vis spectra and DLS measurements show that BBL does not form aggregates and is in a single polymer chain regime (Figures S2 and S3, Supporting Information).[35] In addition, the DLS decay rate ($\Gamma$) decreases as the number of repeating units increases (Figure 1e and Table 1. Summary of n-type accumulation-mode OECT performance.

| Materials          | $V_{th}$ [V] | $\mu_{on}$ [S cm$^{-1}$] | $\tau_{on}$ [ms] | $I_{on}/I_{off}$ | $\mu C^*$ [F cm$^{-1}$ V$^{-1}$ s$^{-1}$] | Year | Reference |
|--------------------|--------------|---------------------------|-----------------|-----------------|---------------------------------------|------|-----------|
| p(gNDI-gT2)        | 0.28*        | 0.1085                    | 5               | $3.2 \times 10^3$ | NA                                    | 2016 | [24]      |
| BBL                | 0.21         | 0.359                     | 900             | $6.0 \times 10^3$ | NA                                    | 2018 | [27]      |
| P-50               | 0.36*        | 0.067                     | NA              | $5.0 \times 10^2$ | NA                                    | 2018 | [19]      |
| P-75               | 0.29*        | 0.141                     | NA              | $5.5 \times 10^2$ | NA                                    | 2018 | [19]      |
| P-90               | 0.26*        | 0.21                      | NA              | $4.0 \times 10^3$ | NA                                    | 2018 | [19]      |
| P-100              | 0.25*        | 0.204                     | NA              | $1.1 \times 10^1$ | NA                                    | 2018 | [19]      |
| C60-TEG            | 0.55         | 0.0146                    | 80              | $2.5 \times 10^4$ | 7                                     | 2019 | [47]      |
| P90, PFBT          | 0.29         | 0.0111                    | NA              | NA              | 0.0008                                | 2019 | [21]      |
| P90, MBT           | 0.27         | 0.0059                    | NA              | NA              | 0.0023                                | 2019 | [21]      |
| p(NDI-T2-L2)       | 0.22         | 0.0084                    | 40              | $2.2 \times 10^2$ | 0.046                                 | 2020 | [48]      |
| P-90               | 0.25         | 0.0113                    | NA              | $1.9 \times 10^2$ | NA                                    | 2020 | [22]      |
| P-90:TBAF(10%)     | 0.25         | 0.0299                    | NA              | $1.7 \times 10^2$ | NA                                    | 2020 | [22]      |
| P-90:TBAF(40%)     | 0.22         | 0.0905                    | 24              | $1.2 \times 10^3$ | NA                                    | 2020 | [22]      |
| P-90:TBAF(80%)     | 0.25         | 0.0833                    | NA              | $2.0 \times 10^2$ | NA                                    | 2020 | [22]      |
| BBL                | 0.19         | 0.815                     | 5.2             | $1.6 \times 10^3$ | 1.99                                  | 2021 | [28]      |
| P90                | 0.24         | 0.0099                    | 41              | $1.9 \times 10^3$ | 0.0343                                | 2021 | [28]      |
| PgNaN              | 0.37         | 0.212                     | 127             | $1.0 \times 10^4$ | 0.662                                 | 2021 | [20]      |
| PgNgN              | 0.21         | 0.007                     | NA              | $1.0 \times 10^3$ | 0.037                                 | 2021 | [20]      |
| p(gNDI-gT2)        | 0.26         | 0.13                      | NA              | $1.4 \times 10^1$ | 0.06                                  | 2021 | [49]      |
| p(C3-gNDI-gT2)     | 0.25         | 0.34                      | NA              | $2.0 \times 10^3$ | 0.13                                  | 2021 | [49]      |
| p(C6-gNDI-gT2)     | 0.37         | 0.37                      | NA              | $2.0 \times 10^3$ | 0.16                                  | 2021 | [49]      |
| p(C4-T2-O-Me)      | 0.46         | 0.10                      | NA              | NA              | 0.07                                  | 2021 | [50]      |
| p(C4-T2-C3-EG)     | 0.32         | 0.31                      | 24.6            | NA              | 0.22                                  | 2021 | [50]      |
| p(C4-T2-C3-EG)     | 0.30         | 0.02                      | 6.2             | NA              | 0.01                                  | 2021 | [50]      |
| p(C4-T2-C2-EG)     | 0.33         | 0.01                      | 12.5            | NA              | 0.006                                 | 2021 | [50]      |
| p(C6-T2)           | 0.27         | 0.40                      | 6.3             | NA              | 0.2                                   | 2021 | [50]      |
| (C4-T2)            | 0.24         | 0.63                      | 7.5             | NA              | 0.3                                   | 2021 | [50]      |
| (C4-T2)            | 0.30         | 2.28                      | 9.6             | NA              | 1.29                                  | 2021 | [50]      |
| (C4-T2)            | 0.37         | 0.15                      | 12.7            | NA              | 0.13                                  | 2021 | [50]      |
| 2DPP-OD-TEG        | 0.89         | 0.73                      | 500             | $2.0 \times 10^3$ | 7                                     | 2021 | [51]      |
| BBL15              | 0.27         | 0.617                     | 0.89            | $2.9 \times 10^3$ | 1.94                                  | 2021 | This work |
| BBL40              | 0.21         | 1.92                      | 0.52            | $8.3 \times 10^4$ | 4.90                                  | 2021 | This work |
| BBL98              | 0.18         | 4.04                      | 0.43            | $2.0 \times 10^3$ | 10.2                                  | 2021 | This work |
| BBL152             | 0.15         | 11.1                      | 0.38            | $4.4 \times 10^5$ | 25.9                                  | 2021 | This work |

*Calculated from transfer curves; †Calculated from transient response.
The apparent hydrodynamic diameters of BBL 15, BBL 60, BBL 98, and BBL 152 are calculated to be 3.9, 18, 30, and 50 nm, respectively. Interestingly, the apparent hydrodynamic diameter increases linearly with the theoretical 1D length (BBL repeating unit length = 1.23 nm) calculated by density functional theory (DFT, Figure 1f). This suggests that BBL chains retain a semi-rigid character even in solution, and the increase in molecular weight does not lead to a decrease in polymer chain rigidity. Hence, we expect that increasing BBL’s molecular weight would result in enhanced charge transport properties.

Grazing-incidence wide-angle X-ray scattering (GIWAXS) was employed to analyze BBL thin-film microstructures when spin-cast from MSA (Figure 2a–f). BBL 15 shows mixed edge-on and face-on bimodal orientation with respect to the substrate, while BBL 60, BBL 98, and BBL 152 present a predominant edge-on orientation. All the BBL polymers show strong lamellar (100) diffraction peak at around \( q_z = 0.75 \text{ Å}^{-1} \) (d-spacing = 8.4 Å) and a strong \( \pi-\pi \) stacking (010) peak at around \( q_x = 1.86 \text{ Å}^{-1} \) (d-spacing = 3.4 Å). As the molecular weight increases, the \( \pi-\pi \) stacking distance slightly decreases from 3.40 Å for BBL 15 to 3.38 Å for BBL 152. The moderate decrease in \( \pi-\pi \) stacking distance is indicative of a stronger \( \pi-\pi \) interaction in the case of longer BBL polymer chains (Figure 2g,h and Figure S6, Supporting Information). The \( \pi-\pi \) stacking and lamellar packing crystallinities are also enhanced as the molecular weight increases, as suggested by the longer coherence lengths and lower paracrystalline disorder (Figure 2i,j and Figures S6–S8, Supporting Information). Atomic force microscopy (AFM) analysis (Figure 2k–n) shows that the spin-cast BBL forms polycrystalline-like thin films, with roughness ranging from 4.87 nm for BBL15 to 2.91 nm for BBL 152. All these results suggest that higher molecular weight of BBL results in stronger \( \pi-\pi \) interaction, higher crystallinity, and smoother thin films, which could facilitate intermolecular charge transport.

We then performed spectroelectrochemistry measurements to explore how molecular weight affects the electronic band structure (i.e., optical properties) of BBL upon electrochemical doping in 0.1 m \( \text{NaCl} \) aqueous electrolyte. Figure 3a–d shows that all BBL samples can be electrochemically doped at low voltage (<0.7 V vs Ag/AgCl), with a clearly visible ground-state bleaching occurring at 320–375 nm and 440–656 nm, and the formation of two polaron bands at 375–440 nm and 656–1200 nm (see also Figure S9, Supporting Information). This indicates that a positive bias drives sodium ions (\( \text{Na}^+ \)) from the electrolyte into the bulk of the BBL films and promotes the injection/accumulation of negative charges into the BBL conjugated polymer backbone. For all BBL batches, the relative absorption intensity of the polaron band induced by electrochemical doping reaches 0.3 a.u. in the thickness-normalized differential absorbance spectra. These significant changes in the electronic band structure of BBL upon electrochemical doping are comparable to those observed by chemical (molecular and polymeric) doping.[23,36] In addition, the formation of polaronic species in BBL 15 starts at voltage >0.2 V vs Ag/AgCl, while for BBL60, BBL98, and BBL152 it starts already at a lower voltage (Figure 3e,f and Figure S10, Supporting Information).
Figure 2. Thin-film microstructures. a–d) 2D GIWAXS patterns of BBL15 (a), BBL40 (b), BBL80 (c), and BBL152 (d) thin films. e,f) Out-of-plane (e) and in-plane (f) GIWAXS line cuts of BBL15, BBL40, BBL80, and BBL152 thin films. g) Overlap of \(\pi-\pi\) stacking (010) diffraction peaks of BBL15, BBL40, BBL80, and BBL152. h) \(\pi-\pi\) distance \((d_{\pi-\pi})\) of BBL15, BBL40, BBL80, and BBL152. i) Coherence length \((L_{\text{coh}})\) of BBL15, BBL40, BBL80, and BBL152. j) Paracrystalline disorder \((g_{\text{dis}})\) of BBL15, BBL40, BBL80, and BBL152. k–n) AFM height images of BBL15 (k), BBL40 (l), BBL80 (m), and BBL152 (n) films. The root mean square (RMS) surface roughness is also reported.

Figure 3. Differential spectroelectrochemistry. a–d) Differential absorption spectra of BBL15 (a), BBL40 (b), BBL80 (c), and BBL152 (d) scanned between 0 and 0.7 V versus Ag/AgCl electrode in 0.1 M NaCl aqueous solution. e,f) Differential absorption spectra of BBL15 (e) and BBL152 (f) at select wavelengths scanned between 0 and 0.7 V versus Ag/AgCl electrode in 0.1 M NaCl aqueous solution. In all the spectroelectrochemistry tests, the BBL films were grounded, and the voltage was applied to the Ag/AgCl electrode, similar to the gate voltage in OECTs.
Next, we evaluated the OECTs performance of the different BBL batches (Figure 4a–f). The OECTs were fabricated following the description reported in the Experimental Section. In brief, gold source/drain electrodes were deposited on glass substrates and coated by a 4 μm-thick parylene layer. Thin BBL films were cast and patterned using another layer of parylene to define the OECT channel length and width (W/L = 20 μm/10 μm or 100 μm/10 μm). Finally, a 0.1 M NaCl aqueous solution was used as the electrolyte and an Ag/AgCl pellet was dipped into the electrolyte to serve as the gate electrode (Figure 4b,c, inset graphs). All BBL-based OECTs show typical n-type accumulation-mode output and transfer characteristics, as well as excellent reproducibility with an ON current standard deviation of less than 3% for ten different devices (Figure S11, Supporting Information). The ON/OFF ratio increases from 2.9 × 10^3 for BBL15 to 4.4 × 10^5 for BBL152-based OECTs (Figure 4a,b and Figures S12 and S13, Supporting Information). At V_D = V_G = 0.7 V, I_D reaches the maximum value of 0.624 ± 0.018 μA for BBL15 and increases up to 14.2 ± 0.3 μA for BBL152 (Figure 4b). The max g_{m,norm} increases more than one order of magnitude within the series going from 0.617 ± 0.017 S cm^-1 for BBL15 to 11.1 ± 0.2 S cm^-1 for BBL152 (Figure 4c and Tables S1 and S2, Supporting Information), with the latter being the highest transconductance reported to date for n-type OECTs (see Table 1). Based on the transfer curves reported in Figure S11 in the Supporting Information, we then calculated μ_C^+ to be 1.94 ± 0.05, 4.90 ± 0.16, 10.2 ± 0.4, and 25.9 ± 0.9 F cm^-1 V^-1 s^-1 for BBL15, BBL60, BBL98, and BBL152, respectively (Figure 4d). As C^+ does not change significantly within the series, with average values in the range of 500–590 F cm^-3 (Figure S14, Supporting Information), we estimated an increase of more than one order of magnitude in the electron mobility, with μ_{OECT} values ranging from (3.59 ± 0.23) × 10^-2 cm^2 V^-1 s^-1 for BBL15 to (4.40 ± 0.34) × 10^-2 cm^2 V^-1 s^-1 for BBL152 (Figure 4d). This is consistent with the DLS and GIWAXS data, suggesting that a longer rigid polymer backbone with higher crystallinity enhances the BBL charge-transport properties. Interestingly, V_{th} decreases with increasing the molecular weight, going from 0.272 ± 0.002 V for BBL15 to 0.151 ± 0.005 V for BBL152 (Figure 4e and Figure S13, Supporting Information). Note that the drain current in the linear regime (V_D < 0.2 V) decreases at V_G > 0.6 V. The observed drain current evolution at high gate voltages is typical of OECTs and commonly ascribed to either contact resistance[21] or drop in mobility at high charge density.[37]

Transient response of the OECTs’ drain current plays a crucial role in the development of high-speed (bio-)electronic devices and circuits. The switching speed of BBL-based OECTs was measured by pulsing V_G between 0 and 0.6 V, and measuring the increase/decrease in I_D. The latter was then fitted by using an exponential fit to extract the rise (τ_{ON}) and decay (τ_{OFF}) times. For comparison, we also estimated the OECT’s response time by measuring the time that it takes for I_D to reach 90% of its max (τ_{ON,90%}) and min (τ_{OFF,90%}) value while V_G is pulsed between 0 and 0.6 V. BBL15 shows fast transient response with τ_{ON} = 0.89 ± 0.10 ms (τ_{ON,90%} = 3.76 ± 0.36 ms) and τ_{OFF} = 0.70 ± 0.16 ms (τ_{OFF,90%} = 2.36 ± 0.48 ms). A twofold increase in switching speed is observed for BBL152, with τ_{ON} = 0.38 ± 0.01 ms (τ_{ON,90%} = 1.18 ± 0.03 ms) and τ_{OFF} = 0.15 ± 0.02 ms

Figure 4. OECT performance. a) Output characteristics of a BBL152-based OECT. b) Transfer characteristics of BBL15, BBL60, BBL98, and BBL152-based OECTs. Inset: cross-sectional schematic of the OECTs. c) Transconductance (g_m) and geometry-normalized transconductance (g_{m,norm}) of BBL15, BBL60, BBL98, and BBL152, OECTs. Inset: top-view microscopy photograph of the channel region of a BBL152-based OECT. d) μ_C^+ and μ_{OECT} of BBL15, BBL60, BBL98, and BBL152, calculated from the OECT transfer characteristics. e) Threshold voltage (V_{th}) and τ_{ON} of BBL15, BBL60, BBL98, and BBL152-based OECTs. Inset: cross-sectional schematic of the OECTs. f) Comparison of V_{th}, τ_{ON}, and g_{m,norm} values with the known n-type accumulation-mode OECTs reported in the literature. All the above BBL15, BBL60, BBL98, and BBL152-based OECTs have the same channel geometry (W = 20 μm, L = 10 μm, d = 20 nm). The error bars indicate standard deviation for ten experimental replicates.
Figure 5. OECT-based complementary inverters. a) Schematic of the complementary inverter and chemical structures of P(g42T-T) (p-type) and BBL OECT channel materials. b) Transfer curves of P(g42T-T)-based OECT and BBL152-based OECT, showing fully balanced p-type and n-type transport characteristics. c) Typical voltage transfer characteristics (VTC) of the inverter at various supply voltages (from 0.1 to 0.7 V). d) Voltage gain of the inverter at various supply voltages. e) Power consumption of the inverter at various supply voltages. f) Input and output given by the inverter showing “0” and “1” states. In all the above OECTs and inverters, p-type OECTs have channel geometry W = 100 μm, L = 10 μm, d = 2.7 nm, and n-type OECTs have channel geometry W = 100 μm, L = 10 μm, d = 20 nm.

(τ_{OFF,90%} = 0.42 ± 0.05 ms) (Figure 4e as well as Figure S15 and Table S6, Supporting Information). Note that the switching speed of the best BBL-based OECTs reported in this study is much higher than that recently reported for photolithography-made BBL-based OECTs (5 ms)[36] and 30x faster than the fully printed BBL-based OECTs.[38] All the BBL-based OECTs show exceptionally high stability in air, with their current retentions being larger than 95% for 1000 switching cycles over a period of about 6 h of continuous operation (Figure S16, Supporting Information). OEECTs with channel W/L = 10 show identical performance to those with channel W/L = 2, and the results are presented in Figures S17 and S19 (Supporting Information) and summarized in Tables S1–S3 of the Supporting Information. A comparison of the performance of the BBL15–BBL152 series and the other n-type accumulation OECT materials reported to date is shown in Figure 4f and summarized in Table 1. BBL152 shows the highest transconductance (g_{dn,norm} = 11.1 S cm^{-1}), fastest transient response (τ_{ON} = 0.38 ms), and lowest threshold voltage (V_{th} = 0.15 V).

Having demonstrated n-type accumulation-mode OECTs with record-high performance, we then moved to fabricate complementary accumulation-mode inverters (Figure 5a). We used the hole-transporting polythiophene P(g42T-T)[39] to construct accumulation-mode pull-up (p-type) OECTs in the complementary inverters. P(g42T-T) shows high ON/OFF ratio of 5.9 × 10^4, low V_{th} of −0.178 ± 0.02 V, high g_{dn,norm} of 80 ± 2 S cm^{-1}, high µC_{IN} = 187 ± 6 F cm^{-1} V^{-1} s^{-1}, and fast transient response with τ_{ON} = 0.074 ± 0.001 ms (τ_{ON,90%} = 0.203 ± 0.003 ms) and τ_{OFF} = 0.025 ± 0.001 ms (τ_{OFF,90%} = 0.039 ± 0.002 ms) (Figure S20, Supporting Information). To achieve balanced driving strengths of the pull-up and pull-down (n-type) transistors, we set the thickness of P(g42T-T) and BBL152 channel layers to be 2.7 and 20 nm, respectively. A channel geometry of W/L = 10 was used for both p-type and n-type OECTs. The pull-up and pull-down OECTs show perfectly balanced electrical characteristics, with comparable current levels even in their sub-threshold region at V_C around ±0.1 V (Figure 5b and Figure S21, Supporting Information). These well-balanced p-/n-type electrical characteristics result in complementary inverters operating at supply voltages (V_{DD}) as low as 0.1 V, with a switching threshold (V_{M}) of 0.037 V, voltage gain over 2.5 V V^{-1}, static power consumption (P_{static}) of 0.12 nW, and dynamic power consumption (P_{dynamic}) of 0.32 nW (Figure 5c–f and Tables S4 and S5 in the Supporting Information). At V_{DD} = 0.7 V, V_{M} approaches the ideal V_{DD}/2 (i.e., V_{M} = 0.344 V at V_{DD} = 0.7 V, see Table S4 in the Supporting Information), voltage gain over 100 V V^{-1}, P_{static} < 2 nW, and P_{dynamic} < 2.2 μW (Figure 5c–f and Tables S4 and S5, Supporting Information). These OECT-based complementary inverters are among the best reported sub-1 V CMOS-like technologies[40] Thus, enhancing the charge transport properties of n-type OMIECs to match that of p-type OMIECs is the key to achieving high-performance complementary OECT circuits.

3. Conclusions

We have investigated the influence of molecular weight on charge transport properties and OECT performance of
the ladder-type polymer BBL. We have demonstrated that increasing the molecular weight of BBL by one order of magnitude (from 4.9 to 51 kDa) yields n-type OECTs with record-high $g_{\text{m,norm}}$ (11.1 S cm$^{-1}$) and $\mu C^2$ (25.9 F cm$^{-1}$ V$^{-1}$ s$^{-1}$). The improvement in OEET performance is ascribed to a strong p–π interaction and high crystallinity. As a result of the improved intermolecular charge transport, the reported OECTs have a fast transient response (0.38 ms) and low threshold voltage (0.15 V).

By combining the best-performing BBL-based OECTs with P(g42T-T)-based p-type OECTs, we demonstrated OECT-based complementary inverters with record-high voltage gain (up to 51 kDa) yields n-type OECTs with record-high $g_{\text{m,norm}}$ (11.1 S cm$^{-1}$) and $\mu C^2$ (25.9 F cm$^{-1}$ V$^{-1}$ s$^{-1}$). The improvement in OEET performance is ascribed to a strong p–π interaction and high crystallinity. As a result of the improved intermolecular charge transport, the reported OECTs have a fast transient response (0.38 ms) and low threshold voltage (0.15 V).

4. Experimental Section

**Materials:** TABH, NDA, PPA, and MSA were purchased from Sigma-Aldrich. To remove the adsorbed moisture, NDA was washed with acetone then dried in the oven at 150 °C for 1 h, while TABH was dried in the oven at 150 °C for 10 min. Other reagents were used as received. BBL was synthesized following a procedure reported previously.[41] In brief: BBL was synthesized following a procedure reported previously.[41] In brief, BBL 15, BBL 60, BBL 98, and BBL 152 were dissolved in MSA at 100 °C for 12 h, then cooled down to room temperature and filtered through 0.45 µm polypropylene filter to obtain BBL-MSA solution. The scattering signal was measured with an Ubbelohde type viscometer, using a constant phase element, R, is the charge transfer resistance, and M is the restricted diffusion impedance.[44]

**Dynamic Light Scattering:** DLS measurements were performed at Zetasizer Nano ZS90 (laser wavelength $\lambda = 632.8$ nm) at T = 298 K. BBL15, BBL60, BBL98, and BBL152 were dissolved in MSA at 100 °C for 12 h, then cooled down to room temperature and filtered through 0.45 µm polypropylene filter to obtain BBL-MSA solution. The scattering signal was measured with an Ubbelohde type viscometer, using a constant phase element, R, is the charge transfer resistance, and M is the restricted diffusion impedance.[44]

**Grazing-Incidence Wide-Angle X-ray Scattering:** GIWAXS experiments were performed at Beamline 9A at the Pohang Accelerator Laboratory in South Korea. The X-ray energy was 11.08 eV and the incidence angle was 0.12°. Samples were measured in vacuum and the total exposure time was 10 s. The scattered X-rays were recorded by a charge-coupled device detector located 221.9351 mm from the sample. All samples for GIWAXS measurements had a similar thickness of 100 nm.

**OECTs and Complementary Inverters:** OECTs were fabricated following a procedure reported previously.[46] Standard microscope glass slides were cleaned via successive sonication in acetone, deionized water, and isopropyl alcohol, and dried with nitrogen. Source/drain electrodes (5 nm Cr and 50 nm Au) were thermally evaporated onto the glass substrates. A layer of polyethylene terephthalate (PET), deposited as a sacrificial layer. To protect the parylene C interface, a platinum wire was used as the RE, and patterned BBL thin films with a volume of 8.1 × 10$^{-6}$ to 5.1 × 10$^{-5}$ cm$^{3}$ on Cr/Au electrode on glass substrate served as the WE. WE was set to ~0.7 V for volumetric capacitance measurements, and spectra were recorded in the frequency range 0.1 Hz–10 kHz. The capacitance was extracted by fitting to modified Randles circuit model: $\Gamma = C_{\text{tc}} + \text{CPE}/(j\omega R_{\text{ct}})$, where $\Gamma$ is the constant phase element, $R_{\text{ct}}$ is the charge transfer resistance, and $M$ is the restricted diffusion impedance.[44]
channel area were exposed to the air while other areas were still covered with two layers of parylene C. The channel between source and drain were patterned to obtain W/L = 20 µm/10 µm and 100 µm/10 µm. BBL100, BBL400, and BBL1325 MSA solutions were spin-coated to obtain 20 nm thick film, covering the whole substrate surface. The sacrificial layer was peeled off and the BBL film on it was removed, leaving separated pieces of film staying in the wells, consisting of the semiconductor connecting the OECT source/drain electrodes. P(g2T-T)-based OECTs were fabricated using a similar procedure. For all OECTs, 0.1 m NaCl aqueous solution was used as the electrolyte and Ag/AgCl pellet electrode (purchased from VWR) was used as the gate electrode. The complementary inverters were assembled by connecting a P(g2T-T)-based OECT and a BBL152-based OECT using silver paint (Figure 5a). The OECTs and inverters were characterized by Keithley 4200A-SCS (with 4225-PMU Ultra Fast I-V Module and 4225-RPM Remote Amplifier/ Switch Modules).

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
C.-Y.Y., M.-A.S., M.B., and S.F. are the co-founder of n-Ink AB. The other authors declare no competing interests.

Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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complementary circuits, inverters, molecular weight, n-type polymers, organic electrochemical transistors, organic mixed ionic–electronic conductors

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