

# Near 14 cm<sup>2</sup> V<sup>-1</sup> s<sup>-1</sup> Charge Carrier Mobility Enabled by Amorphous Indacenodithiophene-based Polymers with Controlled Regioregularity

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## Article

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# Abstract

Herein, we report the synthesis and characterization of four regioregular, well-defined donor–acceptor polymers (P1, P2, P3, and P4), comprising different compositions of axisymmetric cyclopentadithiophene (CDT) and centrosymmetric indacenodithiophene (IDT) donors in conjugation with the asymmetric 5-fluoro-2,1,3-benzothiadiazole acceptor that is precisely oriented in the regular pattern along the backbone. Morphological analyses of the above polymer series show that exclusive CDT donor-containing P1 is semicrystalline, whereas the others (IDT donor-containing ones) are near-amorphous in nature. Comparatively, IDT donor-containing polymers have superior hole mobilities; in particular, exclusive IDT donor-containing polymer P4 offers an ultra-high mobility of  $13.82 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at a channel length of  $200 \text{ }\mu\text{m}$ , which is comparable to the recently reported values for state-of-the-art semicrystalline semiconductors. In addition, the near-amorphous characteristics render the IDT donor-containing polymer films highly ductile and stretchable. Such superior features, which are associated with excellent charge transport and ductility, demonstrate a promising possibility for application in viable stretchable electronics.

## Introduction

$\pi$ -conjugated polymers have been extensively studied for their application in printing organic field-effect transistor (FET) arrays and circuits to realize low-cost, large-area, flexible, and even stretchable next-generation electronics that cannot be realized using traditional silicon technologies.<sup>1–7</sup> On the basis of the principle that charge carrier mobility is unambiguously linked to the degree of order in the packing, more than a decade of research has focused on increasing the crystallinity of  $\pi$ -conjugated polymers as a strategy for improving charge transport; this has reliably boosted mobility to exceed  $10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ .<sup>8–13</sup> Three major design strategies exist for enforcing polymer crystallinity: (i) donor–acceptor architecture in the backbone induces a strong intramolecular charge transfer (ICT) effect as an attractive force between the donor and acceptor units, resulting in a more planar configuration that facilitates  $\pi$ -electron delocalization along the backbone;<sup>14–17</sup> (ii) the incorporation of fused aromatic building segments into the backbone generates a large  $\pi$ -orbital overlapping area, formulating large crystalline domains with only few disordered domain boundaries;<sup>12, 18–21</sup> and (iii) a precise regioregularity in the polymer repeating units realizes enhanced structural arrangement of the chains, thus promoting self-organization.<sup>16, 22–24</sup> As a successful example that integrates all of the abovementioned concepts for FET applications, Bazan et al. have reported a semicrystalline polymer with the donor–acceptor structure comprising cyclopentadithiophene (CDT) as the fused aromatic donor unit and 5-fluoro-2,1,3-benzothiadiazole (FBT) acceptor with the regioregular orientation of F atoms.<sup>23</sup>

Compared to the axisymmetric CDT unit, indacenodithiophene (IDT), which contains peripheral thiophene rings held in a rigid arrangement through a central phenyl ring, is recognized as part of the extended CDT analogue centrosymmetric structure. Interestingly, polymers based on the extended fused-ring IDT core display high FET mobilities with high backbone coplanarity despite the lack of long-range crystalline

order in the solid state.<sup>2, 3, 25–28</sup> This intriguing feature considerably differs from the abovementioned theory and provides a new molecular-design guideline for achieving high mobilities in near-amorphous polymers, thus facilitating the development of intrinsically stretchable semiconducting polymers toward next-generation electronics. Driven by their unique, yet different properties, many polymers based on CDT and IDT units have been incorporated into high-performance FETs and continue to be studied (see Fig. 1 and **Table S1**).<sup>2, 14, 16, 23, 26, 28–36</sup> However, there is no systematic comparison study between CDT and IDT polymer systems with backbone regioregularity in terms of optoelectronic and morphological properties.

Herein, we aim to synthesize and characterize four donor–acceptor regioregular polymers (P1, P2, P3, and P4) with varied compositions of CDT and IDT donor subunits in conjugation with the regularly arranged FBT acceptor along the backbone; then, we investigate their intrinsic properties including their optical property, energetics, morphology, molecular packing, and charge transport. Notably, we discovered that in addition to their higher ductility, as evidenced by the crack onset strain measurement, FETs prepared using IDT donor-containing near-amorphous polymers show higher mobilities than those of exclusive CDT donor-containing semicrystalline P1. In particular, P4 exhibited an unprecedentedly high hole mobility of up to  $13.82 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at a channel length of  $200 \text{ }\mu\text{m}$ . To the best of our knowledge, this is the highest mobility value among near-amorphous polymers reported to date.

## Results And Discussion

### Synthesis, Characterization, and Computational Analysis

Density functional theory (DFT, B3LYP/6-31G+\*\*) was first performed to gain insight into the structural difference (*e.g.*, conjugation lengths, electrostatic potentials, and net dipole moments) between the axisymmetric CDT and centrosymmetric IDT units, as shown in Figs. 2a,b. Compared with three-rings-fused CDT (with an effective  $\pi$ -conjugated length of  $9.80 \text{ }\text{\AA}$  and a net dipole moment of  $1.75 \text{ D}$ ), the five-rings-fused IDT shows a larger effective  $\pi$ -conjugated length ( $15.47 \text{ }\text{\AA}$ ) and zero net dipole moment. In addition, in cyclic voltammetry (CV) measurement, the oxidation potential ( $E_{\text{oxi}}$ ) of IDT is higher than that of CDT (see Fig. 2c), evidencing the relatively weaker electron-donating nature of the IDT unit.<sup>37, 38</sup>

With theoretical understanding of the structural features of axisymmetric CDT vs. centrosymmetric IDT units, 7,7'-(4,4-dihexadecyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophene-2,6-diyl)bis(4-bromo-5-fluorobenzo[*c*][1, 2, 5]thiadiazole) (**M2**) and 7,7'-(4,4,9,9-tetrahexadecyl-4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene-2,7-diyl)bis(4-bromo-5-fluorobenzo[*c*][1, 2, 5]thiadiazole) (**M4**) were prepared as key symmetrical monomers by the Still coupling reaction of 4,7-dibromo-5-fluoro-2,1,3-benzothiadiazole (FBT-Br<sub>2</sub>) with (4,4-dihexadecyl-4*H*-cyclopenta[1,2-*b*:5,4-*b'*]dithiophene-2,6-diyl)bis(trimethylstannane) (**M1**) and (4,4,9,9-tetrahexadecyl-4,9-dihydro-*s*-indaceno[1,2-*b*:5,6-*b'*]dithiophene-2,7-diyl)bis(trimethylstannane) (**M3**) in yields as high as  $\sim 70\%$ . The structures and purities of the final monomers were clearly verified using various analytical technologies such as nuclear magnetic resonance (NMR) spectroscopy and elementary analysis (EA) (see the experimental procedure and **Figures S10–13**). Four regioregular polymers with the

FBT units facing the same regular pattern along the backbones yet different backbone compositions were synthesized from the corresponding monomers under the same conditions ( $\text{Ph(PPh}_3)_4$  as the catalyst in *o*-xylene under microwave heating at 220°C), as shown in Scheme 1. P1 and P4 exclusively contain CDT and IDT donor units on the backbones and alternately arranged FBT counterparts as acceptor units. However, both P2 and P3 are based on alternating CDT and IDT units with a different F-atom configuration of FBT (F-atoms pointing toward CDT for the former and toward IDT for the latter, respectively).

As shown in Fig. 3 and **Figures S14–17**, in addition to the accurate peak area integrations, high-temperature  $^1\text{H}$  NMR of the polymers reveals four proton peaks in the aromatic region (three signals from the terminal thiophenes of CDT and IDT moieties in the down-field region and one from the flanking benzene of the IDT unit in the most up-field region), except for P1 having only three peaks owing to the absence of an IDT unit on its backbone. Notably, the chemical shifts of thiophene protons are very sensitive to the F-atom pointing direction of FBT, whereas a similar chemical shift ( $\sim 8.05$  ppm) is observed for the proton peaks of FBT units, regardless of the flanking donor building subunits (CDT and IDT). Overall, these data can elucidate the polymer structures with regioregularity but different backbone compositions. In addition to their good solubility in various organic solvents, all polymers have similar number-average molecular weight ( $M_n$ ) of 88.4–93.5 kDa and polydispersity index (PDI) of 1.3–1.8, as determined by high-temperature gel-permeation chromatography (HT-GPC, 100 °C), which can minimize the influence of molecular weights on their photophysical and optoelectronic properties.

The ultraviolet–visible (UV–Vis) absorption spectra of the polymers in chloroform solutions and thin films are shown in Figs. 4a,b and the detailed relevant data are summarized in Table 1. All polymers have  $\pi$ – $\pi^*$  transition bands that are centered at approximately 410 nm and broad ICT transition bands ranging from 450 to 1000 nm. Notably, upon transitioning from solution to thin films, slight red-shifts occur for IDT donor-containing polymers (P2, P3, and P4), whereas no distinct absorption difference is observed for exclusive CDT donor-based P1. This suggests a breakup of the solid-state structural order within polymer chains to some extent with the incorporation of centrosymmetric IDT into the backbone.<sup>30, 39</sup> In addition, one can observe that absorption spectra shift toward longer wavelengths with increasing CDT content in the repeating polymer unit. Therefore, optical bandgaps ( $E_g^{\text{opt}}$ ) determined by the onsets of absorptions in the films are in the order of  $\text{P1} < \text{P2} \cong \text{P3} < \text{P4}$ , indicating that CDT is a stronger electron donor relative to IDT; this result is consistent with the abovementioned CV-derived oxidation potentials.

Table 1  
Optical and electrophysical properties of the Polymers.

	$\lambda_{\text{sol}}^{\text{max}}$ [nm]	$\lambda_{\text{film}}^{\text{max}}$ [nm]	$\lambda_{\text{onset}}$ [nm]	$E_{\text{g}}^{\text{opt}}$ [eV]	$E_{\text{g}}^{\text{CV}}$ [eV]	$E_{\text{HOMO}}$ [eV]	$E_{\text{LUMO}}$ [eV]	Mn [kDa]	PDI
P1	433, 785	434, 786	948.6	1.31	1.67	-4.93	-3.26	88.4	1.31
P2	415, 693	424, 716	788.5	1.58	1.82	-5.17	-3.35	90.3	1.43
P3	418, 696	423, 719	791.2	1.57	1.82	-5.20	-3.38	84.0	1.50
P4	418, 666	422, 683	734.5	1.69	1.92	-5.31	-3.39	93.5	1.80

The CV measurement of all polymers in thin films was used to evaluate their electronic energy levels (highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO)). Figure 4c shows that all polymers displayed strong quasi-reversible oxidation peaks accompanied by irreversible reduction ones, indicating their *p*-type dominant character (*vide infra*).<sup>40, 41</sup> Based on oxidation and reduction onset potentials against the Fc/Fc<sup>+</sup> standard (− 4.8 eV), the calculated HOMO/LUMO levels of P1, P2, P3, and P4 are − 4.93/− 3.26, − 5.17/− 3.35, − 5.20/− 3.38, and − 5.31/− 3.39 eV, respectively (Table 1). As schematically visualized in their energy level diagram in Fig. 4d, the IDT donor-containing polymers (P2, P3, and P4) showed similar, deeper-lying LUMO levels compared to exclusive CDT donor-based P1 as well as gradual push-down HOMO levels with higher IDT content within the polymer repeating unit. Notably, the considerably higher-lying HOMO of P1 over the other polymers is attributed to the stronger electron-donating ability of CDT over IDT, which is in good agreement with the optical and electrochemical properties of CDT vs. IDT described above.

The DFT calculations of dimers of each polymer were modeled using the B3LYP/6-31G\* basis set, with the long side chains replaced with methyl groups to reduce computation time (Figs. 5, S1, S2, **Table S2**). In addition to a similar trend of HOMO/LUMO levels with CV-derived data, for all cases, the LUMOs are centralized on electron deficient FBT units; however, the HOMOs are well-delocalized on molecular backbones. In the side view, it is observed that all dimers adopt almost coplanar backbones in the minimum-energy configuration most likely owing to noncovalent F⋯S and N⋯H intramolecular interactions within regular, alternating patterns between donor (CDT and/or IDT) and acceptor (FBT) units.<sup>36, 42</sup> Further, the different conformation (syn (CDT) vs. anti (IDT)) of the S-atoms of thiophenes within the donor building blocks favors different optimized ground-state structures. For example, the P1 dimer can be described as a bent, banana-type structure; both P2 and P3 dimers adopt a sigmoid-like shape, whereas P4 forms a rather linear geometry. This observation suggests that P4 has a lower degree of energetic disorder compared to others.<sup>27, 43</sup> Such varied conformations can significantly impact the magnitude and direction of dipole moments of dimer models, as summarized in **Figure S2** and **Table S2**. Note that relative to the models simulated for IDT-containing polymers, the P1 dimer has an overall higher dipole moment, which may increase the dipole–dipole interaction for better polymer chain assembly in the solid state.<sup>44, 45</sup>

# Thin-Film Microstructure Analysis

Tapping-mode atomic force microscopy (AFM) was used to investigate the surface morphology of polymer films (Figs. 6a–d). To accurately compare the morphology with transistor characteristics, we passivated silicon dioxide ( $\text{SiO}_2$ ) surfaces with *n*-decyltrichlorosilane (*n*-DTS) as a self-assembled monolayer before casting polymer solutions, which is described in detail in the experimental procedure. In addition, thin films were spin cast from chlorobenzene (CB) solution and annealed at each optimal temperature determined from the following FET tests. All films annealed at each optimal temperature reveal overall uniform and smooth surfaces with root mean square (RMS) values below 1.0 nm. Notably, the P1 film forms a more pronounced fibrillar microstructural feature with a relatively larger RMS (0.99 nm) compared to other films (0.31–0.39 nm), evidencing its high-order bulk organization structure, at least on the surface.<sup>46</sup> We further characterized the molecular orientation and crystallinity in the optimally annealed films using grazing-incidence wide angle X-ray scattering (GIWAXS) analysis. Figures 6e–l show the 2D GIWAXS patterns and corresponding line cut profiles; the relevant data are listed in **Table S3**.

The P1 polymer shows distinct long-range ordered (*n*00) lamellar diffraction peaks in the out-of-plane (OOP) and (010)  $\pi$ – $\pi$  interchain diffraction peak in the in-plane (IP) direction ( $d_{(100)} = 24.0 \text{ \AA}$  and  $d_{(010)} = 3.57 \text{ \AA}$ ), which suggests the highly crystalline microstructure (so-called crystalline polymer) with a clear edge-on dominant packing orientation. In addition, compared to IDT donor-containing polymers ( $\text{CCL}_{100} = 8.83\text{--}13.6 \text{ nm}$  and  $\text{CCL}_{010} = 1.51\text{--}1.65 \text{ nm}$ ), P1 has larger lamellar and  $\pi$ – $\pi$  stacking crystallite coherence lengths ( $\text{CCL}_{100} = 26.8 \text{ nm}$  and  $\text{CCL}_{010} = 5.1 \text{ nm}$ ), as determined by the Scherrer equation, which is indicative of the formation of larger crystallites in P1. Thus, we anticipate that P1 is typically favorable for efficient charge transport through the lateral charge-hopping mechanism.<sup>47–49</sup>

However, IDT donor-containing polymers tend to adopt a face-on/edge-on coexisting bimodal texture, as confirmed by the strong (010)  $\pi$ – $\pi$  peak in the OOP direction together with multiple (*n*00) lamellar peaks, which correspond to  $d_{(010)} = 4.06\text{--}4.08 \text{ \AA}$  and  $d_{(100)} = 24.0\text{--}24.2 \text{ \AA}$ , respectively. In particular, note that the ring-like halos surrounding the (010)  $\pi$ – $\pi$  peak, as previously observed in other reported polymers employing an IDT unit, clearly appeared in IDT donor-containing polymers, which indicates their near-amorphous microstructure.<sup>2, 25, 29, 33</sup>

In addition, changes occur in the diffraction patterns among IDT donor-containing polymers. For example, both P2 and P3 possess (100) and (200) peaks in the IP direction ( $d_{(100)} = 24.4\text{--}24.5 \text{ \AA}$ ), whereas P4 shows a clear presence of multi-ordered (00 *l*) diffraction peaks along the IP direction ( $d_{(001)} = 16.0 \text{ \AA}$  and  $\text{CCL}_{001} = 15.3 \text{ nm}$ ) rather than lamellar ones. Such multi-ordered (00 *l*) peaks are indicative of significant ordering along the backbone direction induced by the planarity, possibly acting to yield a strong ICT character as a positive effect on the charge transport property; this is corroborated by a series of previous studies on the amorphous IDT-BT polymer.<sup>2</sup>

## Electrical Characterization

To evaluate the electrical properties of the polymers, two types of FET geometries, *i.e.*, bottom-gate/top-contact (BGTC) and bottom-gate/bottom-contact (BGBC), were fabricated and characterized, wherein Au was used as source and drain contact electrodes. Both device architectures are schematically shown in Fig. 7a. The devices were subjected to the thermal annealing process ranging from 180 °C to 240 °C, which showed the optimal device performance at different annealing temperatures for each polymer, *e.g.*, P1 (240 °C), P2 (180 °C), P3 (180 °C), and P4 (200 °C). Figure 7b and **Figures S3–S4** show a representative transfer and output characteristics of the best-performing FETs fabricated with the polymers, and detailed FET parameters are summarized in Table 2. Additional details of the FETs examined herein are included in the Supplementary Information. All FETs show conventional characteristics of *p*-type transistors with low threshold voltages ( $V_T$ ) and high on–off ratios. For BGTC FETs with Au, P4 produced the maximum hole mobility as high as  $2.22 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ , which was approximately 4–10 times higher than those of other polymers ( $0.22 \sim 0.60 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ ).

$\text{MoO}_3$  hole injection and/or the electron blocking layer is required to produce ideal (*i.e.*, gate-bias ( $V_{GS}$ )-independent) transistor characteristics with small hysteresis. Therefore, we also screened the BGTC-type FET performance by utilizing  $\text{MoO}_3$  interfacial layers. Figure 7c shows that FETs with  $\text{MoO}_3$  showed nearly ideal transistor characteristics with mobility values that are relatively constant over the entire  $V_{GS}$  region, presumably owing to reduced contact resistance of  $\text{MoO}_3/\text{Au}$  devices. Figure 7d and **Figures S5–S6** show contact resistance values of the P4 device at various  $V_{GS}$  extracted by the transfer-line method.<sup>50</sup> P4 was chosen as the transporting layer material owing to the lowest HOMO energy. The FET with  $\text{MoO}_3/\text{Au}$  yielded a relatively lower contact resistance compared to those of FET with Au electrodes over the entire  $V_{GS}$  range (–20 to –60 V). Notably, compared to FET with Au, FETs with  $\text{MoO}_3$  showed somewhat reduced electrical properties similar to the trend observed in the polymer film series (Table 2). The observed highest mobility of P4 is attributed to reduced trap densities of P4 thin films. To compare trap densities of the polymers, we calculated deep trap densities ( $N_{tr}$ ) from subthreshold swings ( $S$ ) of BGTC FETs with  $\text{MoO}_3/\text{Au}$  using the following equation,<sup>6</sup>

$$N_{tr} = \frac{C_i}{e^2} \left( \frac{eS}{kT \ln 10} - 1 \right), \quad (1)$$

where  $C_i$  is the capacitance of the gate dielectric per unit area,  $e$  is the elementary charge,  $k$  is the Boltzmann constant, and  $T$  is the measured temperature. **Table S4** shows that the estimated  $N_{tr}$  value of P4 was  $8.64 \cdot 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$ , which is smaller than those of other polymers,  $(1.36\text{--}1.92) \cdot 10^{12} \text{ eV}^{-1} \text{ cm}^{-2}$ . Such reduced deep trap density of P4 corroborates the DFT results that P4 has the lower degree of energetic disorders than other polymers.

However, BGBC FET with Ni/Au electrodes for the polymer family performed better than BGTC FET ones for the corresponding polymers. Specifically, in BGBC FETs, hole mobilities were as high as  $0.47 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for P1,  $0.49 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for P2,  $1.13 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for P3, and  $4.13 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  for P4 (**Table 2** and

**Figure S7).** Performance dependence on device geometry is most likely due to the morphological change between bulk and surface regions of polymer films. A similar phenomenon has also been observed in our previous study on thienoisindigo–naphthalene polymer.<sup>12</sup> However, we cannot rule out the influence of Ni/Au source/drain contact resistance on the electrical property of the BGBC structure.

Driven by the significantly improved performance of the BGBC structure, we further characterized the FET properties of polymers by varying the channel length from 20 to 200  $\mu\text{m}$ . (**Figure S8**) We determined that the mobilities of IDT donor-containing polymers (P2, P3, and P4) increased with longer channel length, whereas P1 showed nearly constant mobility values regardless of the channel length (**Table 2** and **Table S5**). Because IDT donor-containing polymers have deeper-lying HOMOs than P1, their mobility enhancement is partially due to the decreased portion of contact resistance in the total resistance of long-channel FETs. In addition, we determined that P4-based devices with varied channel lengths outperformed other devices, as has been observed in the abovementioned studies. Notably, an unprecedented mobility of up to  $13.82\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$  is achieved for P4-based BGBC FET at the channel length of 200  $\mu\text{m}$  (**Figure 7e** and **Table 2**). Thus far, this mobility is the highest value among amorphous polymers reported in the literature and is approximately comparable to the values obtained from the recently reported highly ordered crystalline polymers. Assuming that the highest mobility can be obtained with minimized contact resistance, this result implies that P4 can produce hole mobility that is higher than the current highest value reported herein (*i.e.*,  $13.82\text{ cm}^2\text{ V}^{-1}\text{ s}^{-1}$ ) when ohmic contacts are favorably formed at semiconductor/contact interfaces. We anticipate that interfacial doping of the semiconducting polymer area adjacent to contact electrodes is a promising approach to obtain high mobility of short-channel IDT-based FETs.<sup>51</sup> These results open up possibilities for achieving high mobility of IDT-based polymers by forming optimal contact junctions in FET configurations.

## Stretchability

To demonstrate a certain unique feature, which originates from amorphous IDT-containing polymers over semicrystalline P1, we performed crack onset strain measurements for all polymer thin films. First, the polymer thin films were spin-cast onto  $\text{SiO}_2$  substrates and then transferred to PDMS substrates (approximately 500- $\mu\text{m}$  thickness). The polymer/PDMS films were stretched at discrete strain values ( $\varepsilon = 30\%$ ,  $60\%$ , and  $100\%$ ) and then monitored under strain via optical microscopy. **Figure 8** shows optical microscope images of annealed polymer thin films at each strain value. Pristine ( $\varepsilon = 0\%$ ) P1 shows a rough, nonuniform surface with some gross aggregation, most likely due to its high crystalline nature. Numerous microcracks begin to form even at  $\varepsilon = 30\%$ . However, pristine IDT-containing polymers appear to be featureless with a uniform surface and exhibit highly ductile behavior during stretching tests. Both P3 and P4 did not exhibit diamond-shaped cracks at  $\varepsilon = 60\%$  strain, particularly for P3 with mechanical robustness up to  $\varepsilon = 100\%$ . Although further investigation is required to understand reasons for the highest ductility of P3, we attributed such high stretchability to the amorphous nature of IDT-based polymers and more entangled IDT polymer chains. Notably, upon relaxation after being stretched at  $\varepsilon =$



30% and 60%, amorphous IDT donor-containing polymers exhibit a wrinkled surface; in contrast, the P1 film does not exhibit wrinkles but contains chunked lumps to some extent (**Figure S9**).

In summary, we designed and synthesized four regioregular donor–acceptor polymers (P1, P2, P3, and P4) based on axisymmetric CDT and centrosymmetric IDT donors with the precise orientation of the asymmetric FBT counterpart acceptor relative to the backbone vector. The different backbone composition with the same regioregularity modifies photophysical and electrochemical properties and electronic structure of the polymers. Relative to the exclusive CDT donor-containing semicrystalline P1, IDT donor-containing amorphous polymers (P2, P3, and P4) exhibit higher hole mobilities in different FET configurations tested herein, despite their lower degree of structural order within the films, as indicated by the GIWAXS characterization. Specifically, P4-based BGBC FET reached an unprecedented value up to  $13.82 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  at the channel length of  $200 \text{ }\mu\text{m}$ ; this value was approximately comparable to the values obtained from recently reported highly ordered top-performing crystalline polymers. Moreover, amorphous IDT donor-containing polymer films exhibit superior deformability and ductility, particularly for P3 that has a stretchability up to  $\varepsilon = 100\%$ . The systematic study described herein reinforces the current understanding of the structure–property relationship in terms of backbone symmetry, composition, and regioregularity; in addition, this study upgrades the FET performance level of sporadically reported amorphous polymers, which can facilitate the rational designing of top-performing polymers for stretchable electronics applications.

## Declarations

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### Author Contributions

Y. C. and S. P. contributed equally. C. Y. and B. H. L. conceptualized the project. Y. C. synthesized and characterized materials, as well as analyzed the data. S. P. and H. Y. carried out the device fabrication and measurement. S. J. measured UV and CV. B. L. and S. M. performed DFT calculation. Y. C. and C. Y. wrote the manuscript.

### Competing financial interests:

The authors declare no competing interests.

## Data availability.

The authors declare that the data supporting the findings of this study are available within the article and its Supplementary Information Files.

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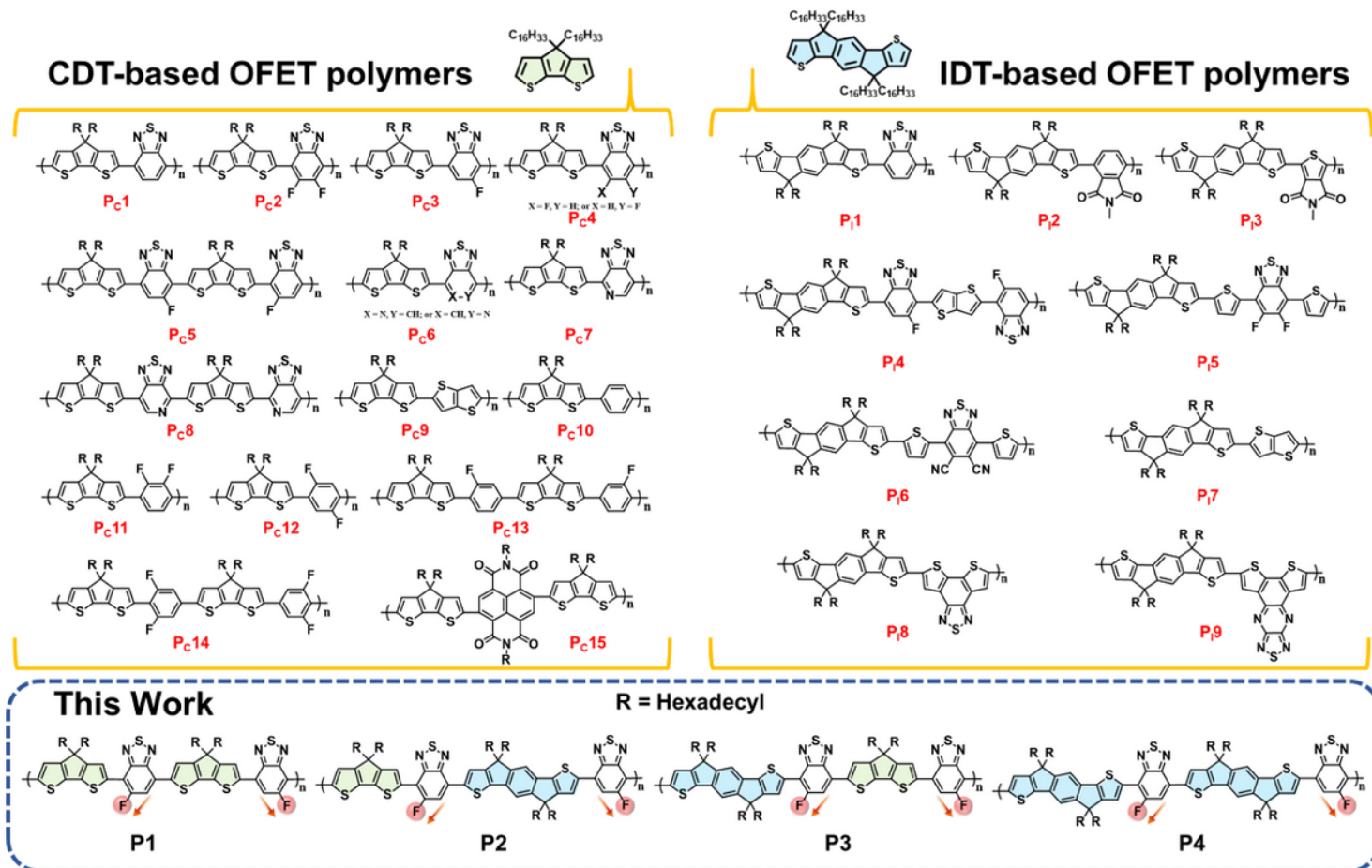
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## Tables And Schemes

Due to technical limitations, full-text HTML conversion of Scheme 1 and Table 2 could not be completed. However, they can be accessed in the Supplementary Files.

## Figures



**Figure 1**

Chemical structures of CDT- and IDT-based OFET polymers reported in the literatures and this work.

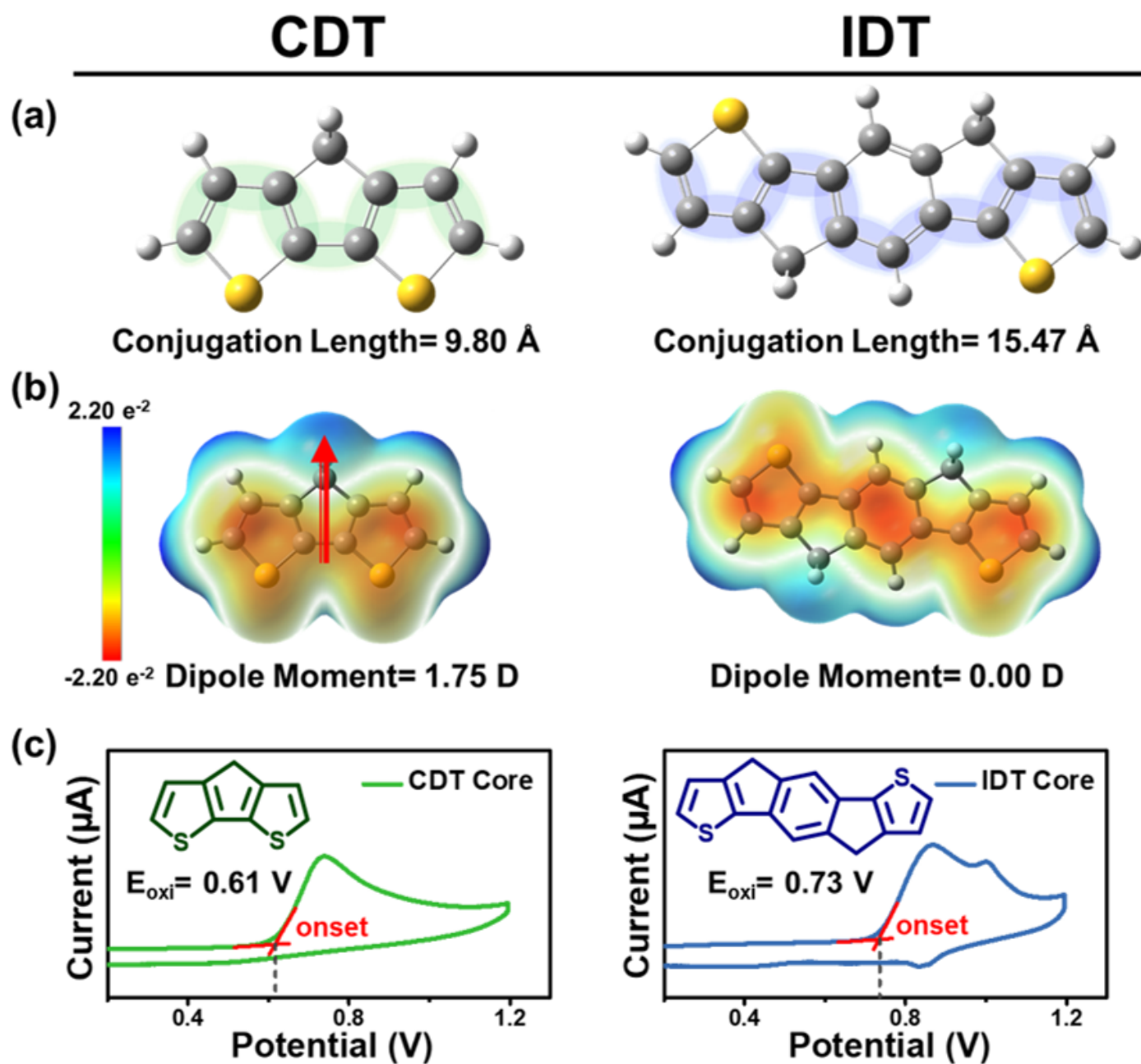
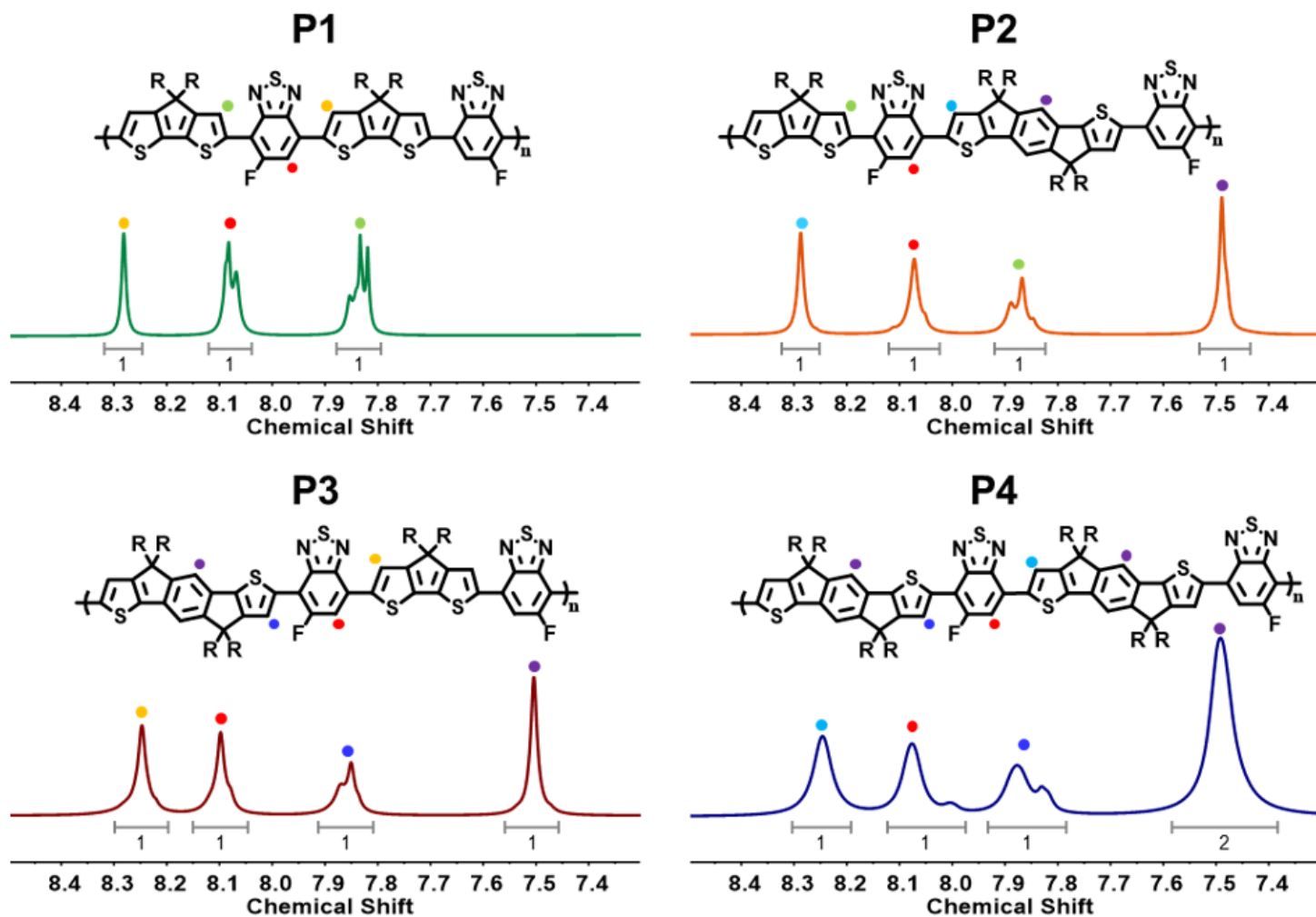


Figure 2

Comparison of CDT and IDT core units. DFT-calculated (a) optimized geometries with conjugation length, (b) electrostatic potential, and (c) CV-derived oxidation potential of CDT and IDT cores.



**Figure 3**

$^1\text{H}$  NMR spectra of the polymers.



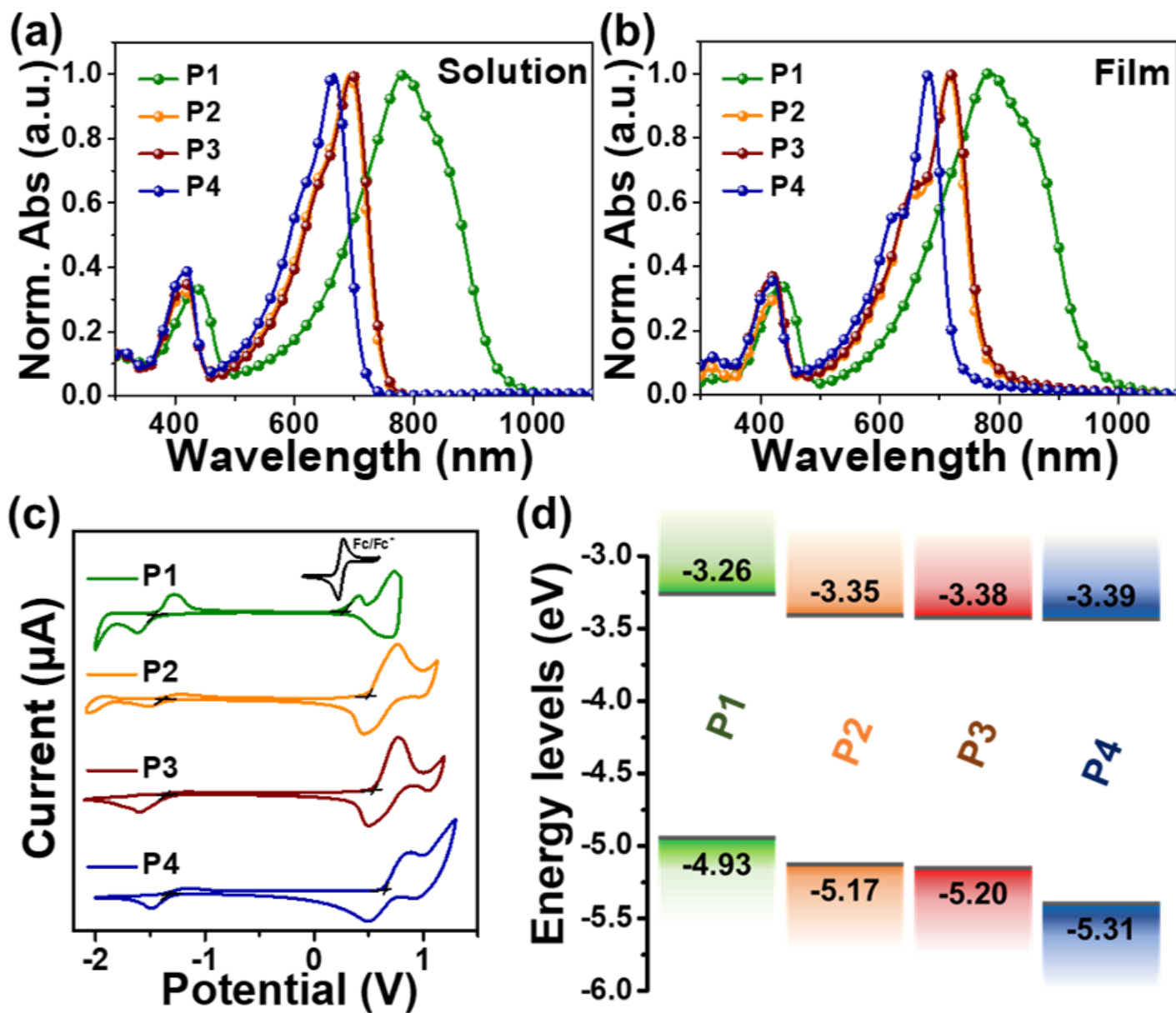


Figure 4

Optoelectrical properties of polymers. Normalized UV-vis-NIR absorption spectra in (a) thin film and (b) CF solution, (c) CV, and (d) energy level diagram of the polymers.

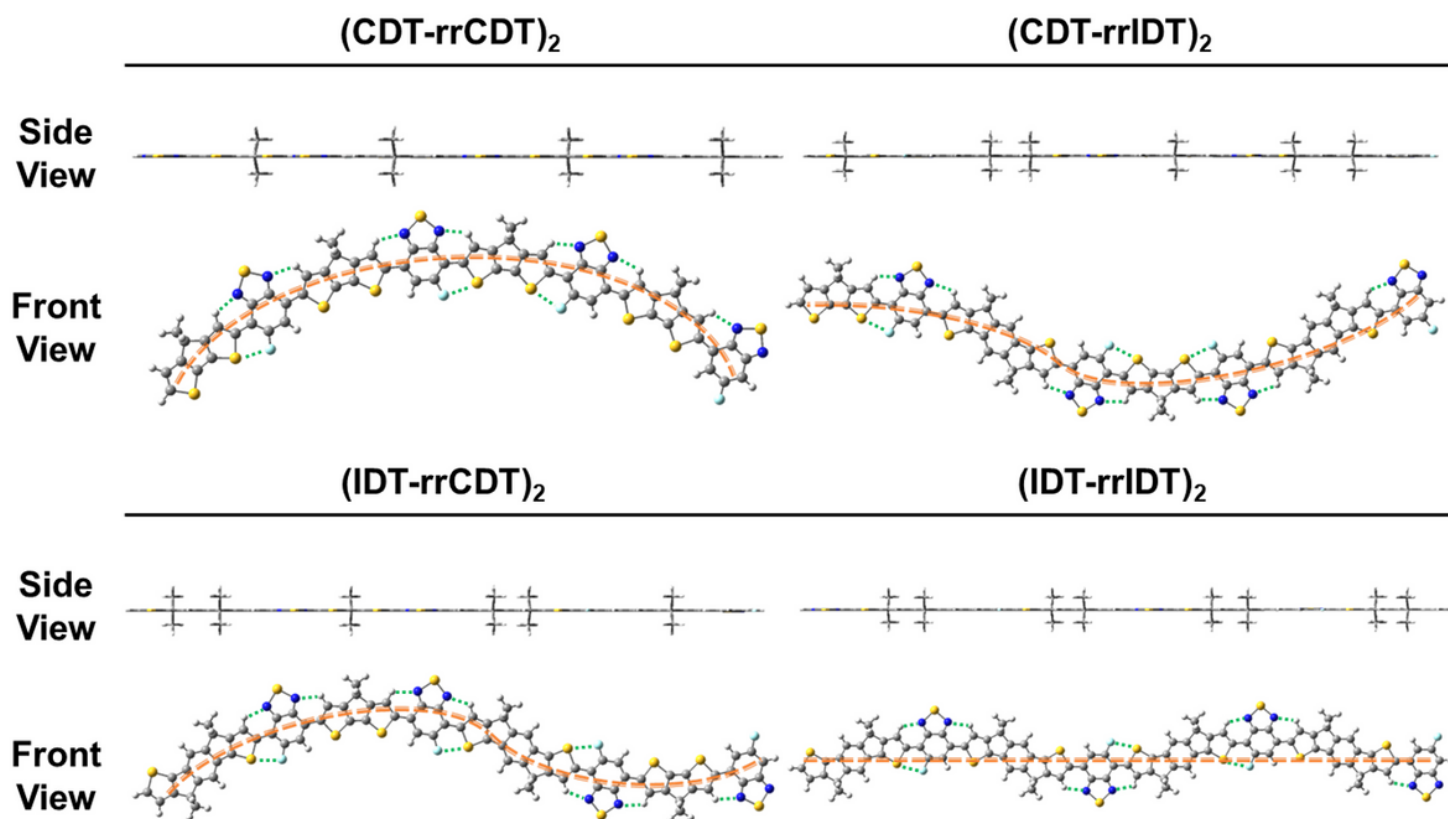
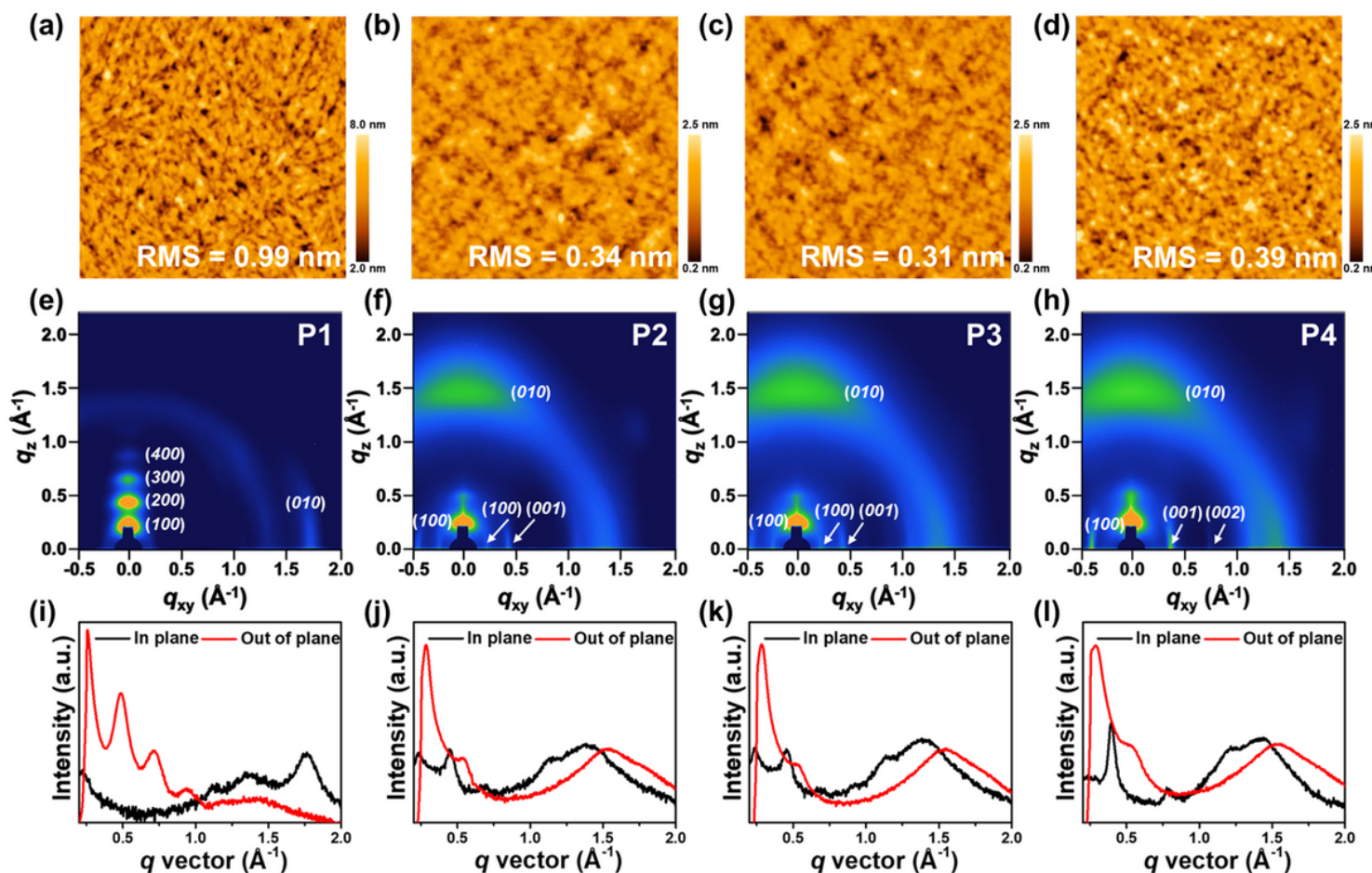


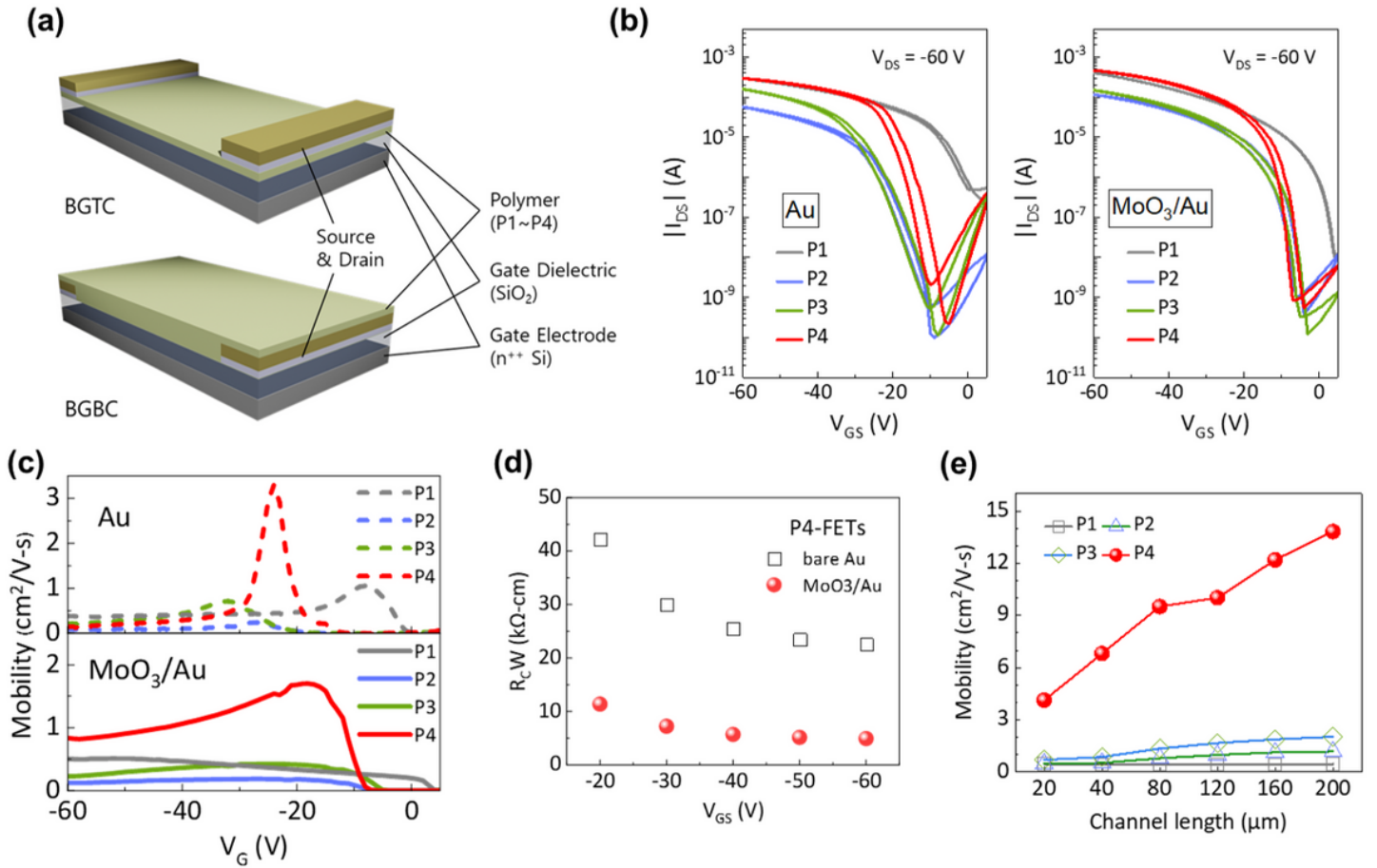
Figure 5

Optimized geometries of dimers by DFT calculation.



**Figure 6**

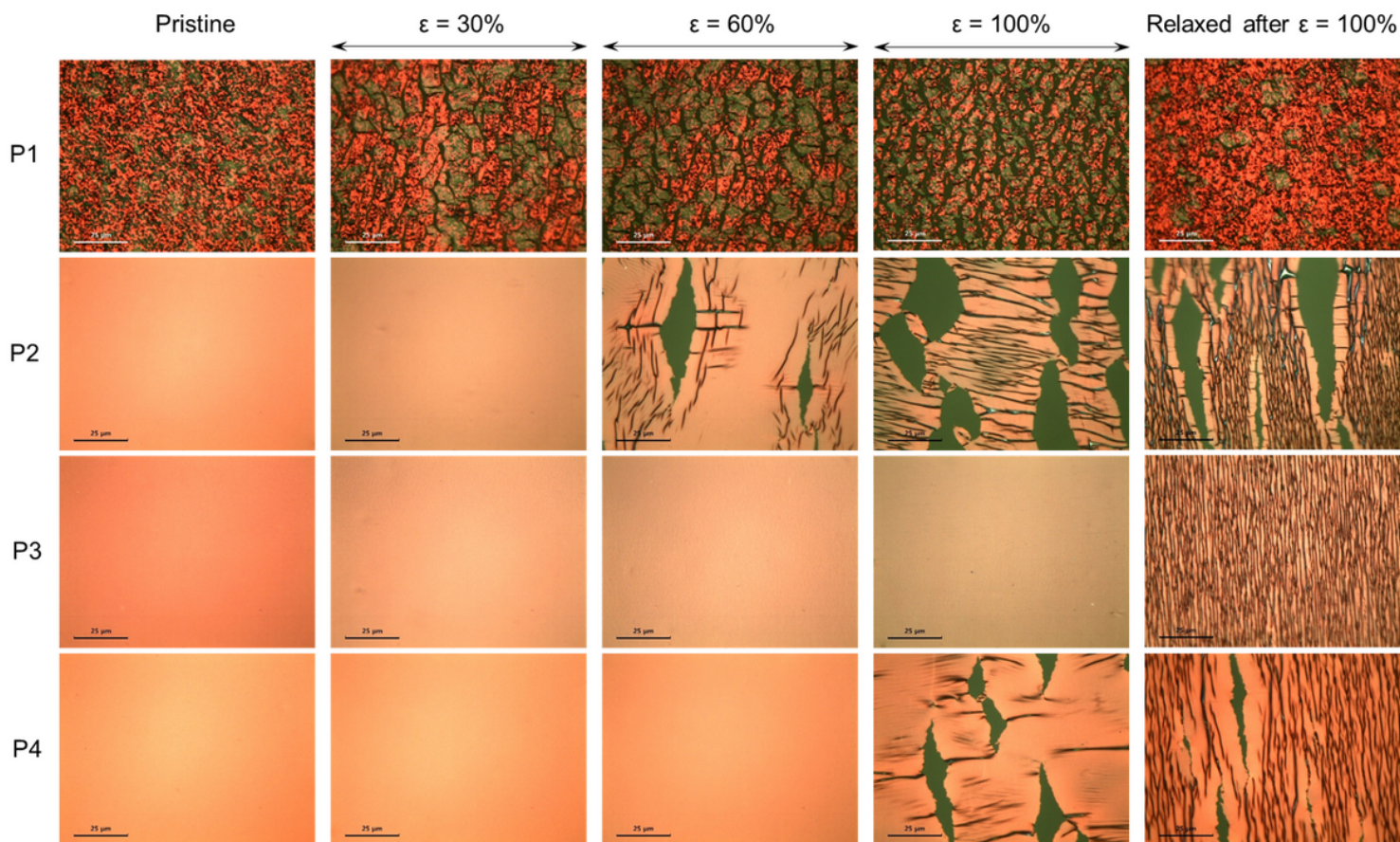
Morphologies and crystalline properties of polymers.  $2\ \mu\text{m} \times 2\ \mu\text{m}$  scaled AFM topographic images of (a) P1, (b) P2, (c) P3, and (d) P4 films annealed under optimized temperatures. The 2D GIWAXS pictures (e-h) and the line cut profiles (i-l) of the P1 (e and i), P2 (f and j), P3 (g and k), and P4 (h and l) films annealed under optimized temperatures.



**Figure 7**

FET characteristics. (a) Schematic architecture of BGTC and BGBC FETs, (b) transfer characteristics of the BGTC devices (Au or MoO<sub>3</sub>/Au source and drain electrodes) annealed at optimal temperatures of 240 oC (for P1), 180 oC (for P2 and P3), and 200 oC (for P4), (c) mobility variation of the polymers, (d) channel width-normalized contact resistance of the P4 FETs with or without a MoO<sub>3</sub> interfacial layer as a function of gate voltages, and (e) mobility variation of the BGBC devices with Ni/Au as a function of channel lengths.





**Figure 8**

Optical microscopic images of the polymer/PDMS films with varying strain values (0 - 100%). The arrows indicate direction parallel to stretching of the films. The scale bars are 25 μm.

## Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- [Scheme1.png](#)
- [Table2.docx](#)
- [SupplementaryInformation.docx](#)