

Impact of Backbone Fluorination on Self-Assembly and Mixed Conduction of Isoindigo-Based Polymers

Rebecca F. Meacham, Camille E. Cunin, Geon Gug Yang, Saroj Upreti, Wenhao Li, Sanket Samal, Robert Posey, Joshua Tropp, Yan Zhao, Xiaodan Gu, and Aristide Gumyusenge*



Cite This: <https://doi.org/10.1021/acs.macromol.6c01586>



Read Online

ACCESS |



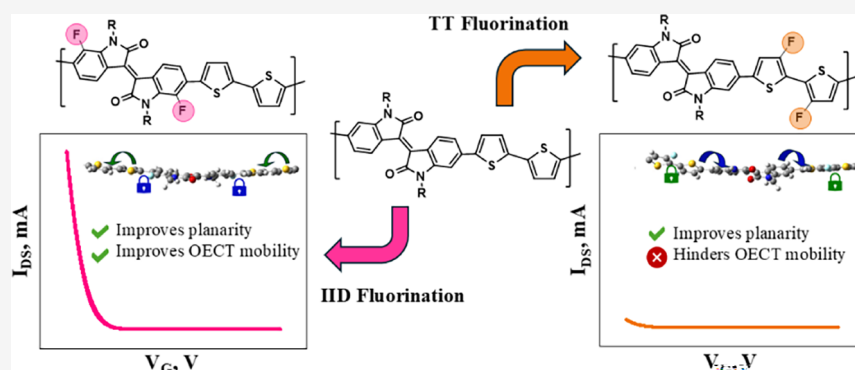
Metrics & More



Article Recommendations



Supporting Information



ABSTRACT: Fluorination is a common method to induce backbone planarity in semiconducting polymers via noncovalent interactions that effectively lock the rotation of single bonds along the backbone. Often explored in dry-state devices, fluorination of isoindigo polymer backbones in mixed conductors remains relatively unexplored. Herein, we investigated systematic fluorination of a family of isoindigo-based mixed conducting polymers with hybrid ethylene glycol-based side chains to probe the impact of fluorination on the resulting assembly and electrochemical performance. Through UV–Vis–NIR, FTIR, Raman spectroscopy, and electrochemical methods, we showed that fluorination effectively planarizes portions of the backbone depending on the fluorination location, even with ethylene glycol side chains, and the placement of fluorine atoms along the backbone is crucial toward organic electrochemical transistor (OECT) device performance. Electronic conduction was found to be improved upon fluorinating the isoindigo acceptor unit in OECTs, but it came at the cost of decreased volumetric ionic capacitance. Further, fluorinating the bithiophene donor inhibited p-type conduction in OECTs. As a result, systematic fluorination revealed the importance of understanding the nuanced design requirements of isoindigo-based mixed conductors for the optimal balance of both modes of conduction in aqueous environments.

INTRODUCTION

Semiconducting polymers combine chemical tunability and mechanical deformability, making them attractive for biointerfacing and other soft-electronic applications.^{1–5} In particular, appending hydrophilic side-chains onto conjugated polymer backbones enables mixed ionic-electronic conduction, allowing intimate interaction with aqueous and ionic species, thus enabling electronic applications at liquid interfaces in devices such as organic electrochemical transistors (OECTs).^{6–9} Designing these materials requires balancing competing transport modes: electronic conduction benefits from tightly packed polymer chains and ordered backbones, whereas ionic conduction requires free volume for ions and their solvation shells that can disrupt the electronic pathways.^{10,11} As a result, parameters such as backbone planarity, hydrophilicity, and side-chain flexibility, as well as their impact on polymer assembly, must be

considered when designing mixed ionic-electronic conducting polymers.

Noncovalent interactions between the lone pair of fluorine atoms and nonbonding orbitals of sulfur atoms in conjugated backbones have been investigated as a method to “lock” single bonds, preventing rotation and thus planarizing conjugated polymer backbones.^{12,13} This interaction has been utilized to design many polymers for operation in dry-state devices (e.g., organic field-effect transistors (OFETs) and organic solar cells

Received: June 6, 2026

Revised: October 4, 2026

Accepted: October 5, 2026

(OSCs)).^{13–17} Planarization is favorable for electronic conduction as it creates favorable charge transport pathways. Isoindigo-based polymers have been explored for fluorination studies due to the ease of synthesis and functionalization with fluorine atoms on the 7 and 7' positions of the benzene rings and side-chain addition to the lactam.^{13–15,17} In addition to planarizing bonds, fluorine's strong electron-withdrawing character can alter orbital energy levels, and in some cases, ambipolar or n-type conduction may be achieved. In these dry-state devices, electronic charge carrier mobility is often seen to improve upon fluorination due to increased aggregation, and increased hydrophobicity due to fluorination is advantageous for stability in ambient conditions.

When considering electrochemical applications such as OECTs, additional considerations are required to apply design rules from dry-state counterparts. Increased order and aggregation are still desirable in OECT channel materials to improve mobility and avoid excessive swelling, which limits operational stability.^{10,18,19} Further, hydrophilic side-chains often included in mixed-conducting polymers, particularly ethylene glycol units, add further complexity: their flexible ether bonds strongly influence morphology, yet the interplay between backbone planarity and hydrophilic side-chain ordering is less explored. A few studies have investigated the impact of backbone fluorination on OMIEC performance and are often limited to DPP and thiophene based materials.^{20,21} In these studies, fluorination has been shown to alter both crystallinity and energy level, thus impacting the resulting mixed conduction performance.²⁰ As a result, systematic fluorination of isoindigo-based polymers with hybrid hydrophilic side-chains is worth investigating as new insights that have not been observed in dry-state devices with only hydrocarbon side-chains or with other backbones may be gained. Particularly, understanding the tradeoff between increasing planarity and aggregation due to fluorination with the ionic conduction imparted by hydrophilic side-chains is beneficial to enable the application of dry-state design rules to hydrophilic, mixed conducting polymers.

To this end, we designed a family of isoindigo-based polymers with controlled fluorination: on the bithiophene donor, then on the isoindigo acceptor, and finally on both, with a non-fluorinated parent polymer as a control. We chose a hydrophilic triethylene glycol (TEG) side-chain with a hexyl spacer between the polymer backbone and the polar termini due to the ability to retain stability through balancing hydrophobic and hydrophilic side-chain segments and limiting swelling during ionic insertion reported in the literature.^{10,22–24} We probed the polymer series using morphological and electrochemical assessments to evaluate the impact of the location of fluorination on the resulting polymer assembly and device performance. We observed strong aggregation upon fluorinating the isoindigo unit, which improves electronic charge carrier mobility but hinders volumetric capacitance. Further, fluorination of the bithiophene unit appears to improve planarity but significantly hinders OECT performance. This study reveals the nuanced design of mixed conductors and limitations of applying design parameters from dry-state devices to electrochemical applications.

■ EXPERIMENTAL SECTION

All starting materials were purchased from commercial sources and used without further purification. All reactions were carried out using

air-sensitive synthesis methods and conditions adapted from the literature. ¹H NMR spectra (Figures S1–S6) were recorded using a Bruker Avance-III HD Nanobay at 400 MHz and a Bruker Avance Neo at 500 MHz and analyzed using Bruker Topspin and MestReNova software. Average molecular weights were determined using ¹H NMR Diffusion Order Spectroscopy (DOSY) in CDCl₃ at ambient temperature. DOSY samples were prepared with CDCl₃ and dried over molecular sieves in a N₂ filled glovebox to avoid moisture. Differential scanning calorimetry (DSC) was measured with a TA Instruments DSC 2500 with a scan rate of 10 °C/min. Thermal gravimetric analysis (TGA) was carried out on a TA Instruments Discovery 550 TGA with a scan rate of 10 °C/min. Atomic force microscopy (AFM) images were obtained on a Bruker Dimension Icon XR SPM and processed with Gwyddion software. Contact angle and surface energy were evaluated on a Rame–Hart Contact Angle Apparatus with DROPimage software. Polymer films for all characterizations were spin-coated from 5 mg/mL solutions in chloroform at 1000 rpm for 40 s and annealed at 120 °C for 30 min in a vacuum oven and cooled for at least 10 min before testing.

Gel Permeation Chromatography

Gel permeation chromatography (GPC) was performed on a Dionex Summit equipped with a Thermo Scientific Vanquish variable-wavelength detector (VWD) using two Varian Polypore columns (300 × 7.5 mm) connected in series and maintained at 35 °C. Chloroform containing 0.8% (v/v) triethylamine (TEA) was used as the eluent at a flow rate of 1.0 mL min^{−1}, and elution was monitored at 750 nm. The system was calibrated using narrow-dispersity polystyrene standards.

DFT Calculations

All density functional theory (DFT) calculations were performed on the software package Gaussian 16.²⁵ The polymer chains were optimized at the B3LYP[2,3]^{26,27}/6-31G(d)²⁸ level of theory. Oligomers of 4 repeat units and methyl groups in place of side chains were used to reduce the computational time of geometry optimization. Optimized structures and electron cloud distributions were visualized using GaussView 6.1.

GIWAXS Measurements

Room temperature grazing incidence wide angle X-ray scattering (GIWAXS) measurements of thin film samples were carried out using the Xenocs Xeuss 2.0 SAXS/WAXS beamline. The beamline features a GeniX 3D copper (Cu) anode source of wavelength 1.54 Å at 8.0 keV. The samples were placed in a vacuum environment to avoid air scattering. Silver behenate was used as the calibrant to obtain the sample to detector distance. A beam size of 0.8 mm × 1.2 mm and an incidence angle of 0.18° were used. The data was reduced using Igor Pro's Nika and Irena software.

Temperature dependent GIWAXS measurements were carried out at the BL15U beamline of the Shanghai Synchrotron Radiation Facility (SSRF) in China. The beam grazed the spin-coated film samples at an incidence angle of 0.15° for 10 s with a beam energy of 18 keV. The distance between the sample and the detector, as well as the scattering vector were calibrated by lanthanum hexaboride as reference polycrystalline material.

Spectroscopic Characterization

UV–vis–NIR absorbance was measured using a Perkin Elmer 1050 UV–vis–NIR spectrophotometer. ATR-FTIR spectra were collected with a Thermo Fisher Nicolet iS50 FTIR microscope, and baseline correction and peak position assignment were carried out in OMNIC software. Raman spectra were collected on a Renishaw Invia Reflex Micro Raman with a 532 nm source and at low power to avoid damaging the polymer films.

Electrochemical Characterization

CV measurements were carried out using a conventional three-electrode setup with a 4.5 cm wide electrochemical cell to contain the liquid electrolytes during the measurements. The polymer film was coated onto ITO to serve as a working electrode, and a spiral Pt wire was used as a counter electrode vs a Ag/AgCl reference electrode. Spectroelectrochemical absorption responses were then collected using a Perkin Elmer 1050 UV–vis–NIR spectrophotometer in combination with an SP-300 potentiostat (Biologic), using a cuvette to incorporate the same three-electrode setup. A scan rate of 20 mV/s was used. Electrochemical impedance spectroscopy was carried out in the same setup as CV measurements.

OECT Fabrication and Measurement

OECT devices with dimensions of $L = 5\ \mu\text{m}$ and $W = 400\ \mu\text{m}$ were fabricated in a cleanroom environment. Source and drain electrodes were patterned using photolithography with a AZnLOF2020 photoresist and a mask-less aligner (Heidelberg MLA 150). A 10 nm layer of Ti followed by a 100 nm layer of Au was deposited using an e-beam evaporator (Temescal FC2000). Subsequently, a first layer of Parylene-C was deposited using a Specialty Coating Systems PDS 2010, employing Silane A 174 (procured from Sigma Aldrich) as an adhesion promoter. A sacrificial layer of soap was spin-coated onto the wafer before depositing a second layer of Parylene-C. The channel and electrode pads were then defined using the same mask-less aligner with an AZ10XT photoresist and a reactive ion etching process (SAMCO 230iP). Channels were formed by spin-coating 5 mg/mL solutions of polymers in chloroform onto the devices at 1000 rpm for 40 s via dynamic spin-coating. Following a peel-off step, the devices were baked inside a glovebox at 120 °C for 30 min and allowed to cool for at least 1 h before characterization. A PDMS sheet was cut to form a well and used to contain the electrolyte. The output and transfer characteristics of the OECT devices were then measured with a Ag/AgCl pellet as the gate using a Keithley 4200A and analyzed using OriginLab software. A source-drain voltage of 0.6 V was applied with

0.1 M KPF₆ as the electrolyte. The film thicknesses are included in the Supporting Information.

RESULTS AND DISCUSSION

The polymer series was synthesized via palladium-catalyzed Stille coupling, yielding four dark solids with systematic introduction of fluorine atoms onto the parent polymer (IID-TT): fluorine substituted onto bithiophene (IID-TT2F), fluorine substituted onto isoindigo (FIID-TT), and fluorine substituted onto both bithiophene and isoindigo (FIID-TT2F) (Figure 1A). The side-chain and isoindigo monomers were synthesized via modifications to previously reported methods, while the bithiophene monomers were obtained from commercial sources.^{15,29} Full synthetic details and ¹H NMR spectra of the monomers and polymers are included in the Supporting Information. All polymers were thermally stable with 5% mass loss occurring at or above 350 °C as measured by TGA (Figure S7 and Table S1). To evaluate the molecular weights of the studied polymers, we employed two methods: diffusion ordered NMR spectroscopy (DOSY) and gel permeation chromatography (GPC) as detailed in Supporting Information, Section S4. Weight averages of 72.3 kg/mol, 38.4 kg/mol, 23.7 kg/mol, and 26.1 kg/mol were obtained for IID-TT, IID-TT2F, FIID-TT, and FIID-TT2F, respectively, from DOSY measurements in dry conditions (Table S2). GPC measurements resulted in number averages (M_n) of 46.7 kg/mol, 40.7 kg/mol, 87.1 kg/mol, and 44.6 kg/mol with polydispersity values ($\bar{D}$) of 1.9, 1.8, 1.8, and 1.5, respectively (Table S3 and Figure S8). With these dispersity values, we believe that the four polymers are in a reasonable molecular weight range for comparison of properties, although FIID-TT does have a higher molecular weight (based on GPC values), which may influence its properties as discussed in later sections.^{30–33} Additionally, the

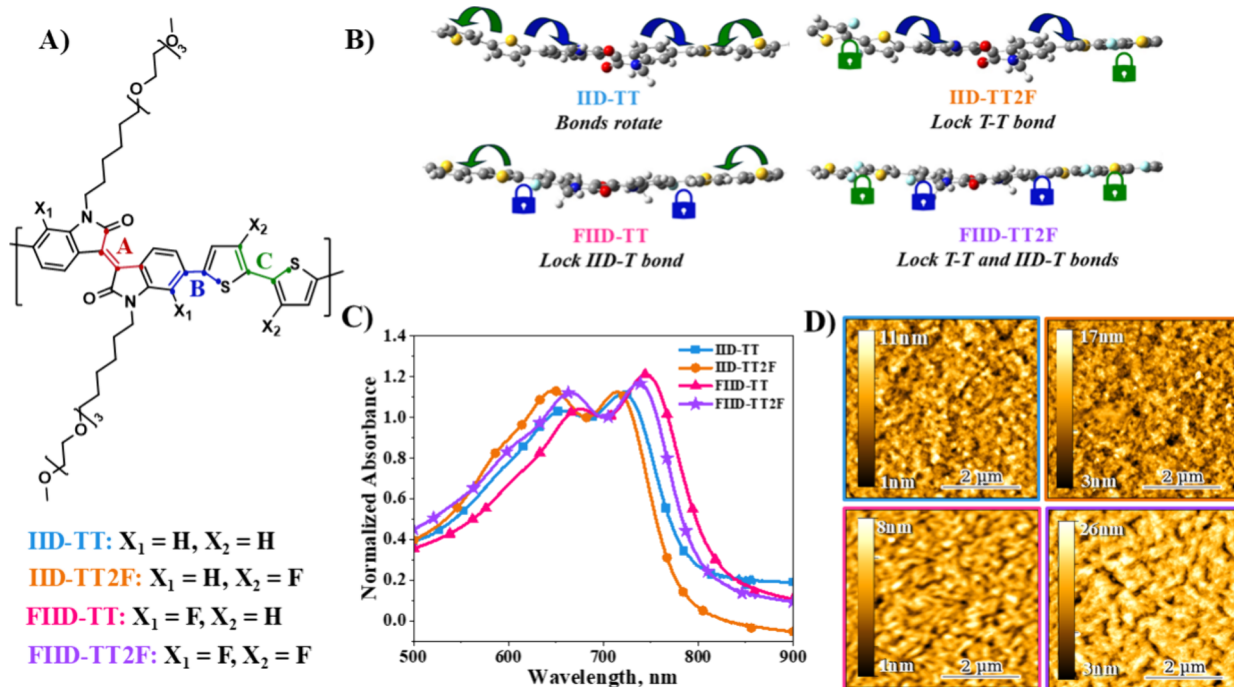


Figure 1. (A) Structures of the polymer series with systematic fluorination. Dihedral angles A, B, and C are labeled. (B) DFT of the polymer backbone showing fluorine-induced planarization. (C) UV–vis–NIR absorption spectra of polymer thin films. (D) AFM height profiles of polymer thin films (top left, blue – IID-TT, top right, orange – IID-TT2F, bottom left, pink – FIID-TT, bottom right, purple – FIID-TT2F).

GPC traces show shoulders, particularly for **FIID-TT**, which is likely due to solubility limitations in chloroform at 35 °C.

The impact of fluorine placement on planarity of polymer backbones was first evaluated using density functional theory (DFT) calculations (Figures S9 and S10). The dihedral angles highlighted in the structure in Figure 1A were evaluated, and the values are reported in Table 1. The dihedral angles of interest include the angle across the central double bond in the isoindigo core (dihedral A), the angle between the isoindigo and bithiophene (dihedral B), and the angle between the two thiophenes (dihedral C). Dihedral angle A remained relatively unaffected by the fluorination, showing a 1° increase when isoindigo is fluorinated. Dihedral angle B showed a significant decrease from ~20° in the **IID-TT** and **IID-TT2F** polymers to less than 7° in **FIID-TT**, indicating that the fluorination of isoindigo in the 7 and 7' positions effectively decreases the rotational freedom between the isoindigo and bithiophene units in the polymer backbone. This bond is further restricted by fluorinating bithiophene in **FIID-TT2F** as dihedral angle B further decreased to 2°, indicating that the multifluorination (i.e., fluorinating both isoindigo and bithiophene) is working together to lock the bonds between the two monomers. Dihedral angle C decreased from 14.7° in **IID-TT** to 0.8° in **IID-TT2F**, indicating that fluorinating bithiophene effectively eliminates the rotation of the single bond between the two thiophenes, essentially locking the bithiophene unit in a planar configuration (Figure 1B and Figure S9). A similar impact is seen in **FIID-TT** and **FIID-TT2F**, where the fluorination of bithiophene decreased dihedral angle C. Interestingly, fluorinating isoindigo alone also aids in limiting the rotation of the single bond between the two thiophenes in bithiophene as indicated in the decreased dihedral angle C in **FIID-TT** (7°) compared to the parent polymer (14.7°).

The impact of the planarization induced by fluorination on solid-state properties can be seen experimentally in UV–Vis–NIR absorbance spectra of annealed polymer thin films (Figure 1C). All polymers showed aggregation in dilute solution with an increase in aggregation upon casting into thin films (Figure S11). The polymer films in the series showed characteristic 0–0 and 0–1 vibronic peaks expected of isoindigo polymers.³⁴ Two main findings were concluded from the shifts associated with these peaks across the polymer series. First, fluorinating isoindigo gives rise to an increase in the 0–0 peak intensity, which is attributed to increased intrachain planarity in the backbones,³⁵ and the chain planarity further showed enhanced local aggregation and π – π stacking. The increase in intensity was paired with a ~25 nm redshift, further supporting increased aggregation in the **FIID-TT** and **FIID-TT2F** polymers (Table 1). Second, a blueshift occurred when bithiophene was fluorinated as well as a slight decrease in 0–0 peak intensity

(Figure 1C and Table 1). We attribute this blueshift to a decrease in the electron donating ability of the electron-rich donor bithiophene as a result of appending electron withdrawing fluorine atoms. The impact of bithiophene fluorination will be further discussed in later sections. The slight decrease in 0–0 peak intensity may hint at some structural disruption caused by the locked bithiophene unit, which has been reported to create a more rigid backbone but also disrupt lamellar stacking in other reports.^{16,36} Atomic force microscope (AFM) height images further show the increased aggregation of **FIID** containing polymers as **IID-TT** and **IID-TT2F** remain relatively featureless and **FIID-TT** and **FIID-TT2F** show increasingly aggregated and scale-like surface features (Figure 1D).

The fluorination-enhanced crystallinity was corroborated by grazing incidence wide-angle X-ray scattering (GIWAXS) measurements on annealed polymer thin films. As shown in Figure 2A, all four polymers exhibit a predominantly edge-on orientation, characteristic of isoindigo polymers.³⁴ Upon fluorination, the diffraction patterns and corresponding linecuts revealed stronger lamellar-stacking peaks in the out-of-plane direction and the appearance of a bright π – π stacking peak in the in-plane direction around 1.8 Å^{–1}, most prominent in the **FIID-TT** and **FIID-TT2F** polymers. Scherrer analysis was carried out using the 1D line cut peak positions and full widths at half-maximum (FWHM) of the (010) and (200) peaks to calculate the *d*-spacing and coherence length in the lamellar and π – π stacking directions (Figure 2B–D). 1D line cuts and calculation details are included in the Supporting Information (Figure S12 and Table S4). An important note is based on this analysis: the coherence length obtained is related to, but not exactly, the crystalline domain size.³⁷ However, the trend proves useful to evaluate differences in this polymer series, measured under the same conditions. The *d*-spacing in the lamellar direction decreases slightly upon fluorination (Figure 2C); however, the π – π *d*-spacing remains relatively unchanged (Figure 2D), indicating that the distance between the polymer chains is relatively unchanged. The coherence length in the lamellar direction shows little change upon fluorinating the bithiophene in **IID-TT2F** compared to the parent polymer **IID-TT**. However, fluorination of isoindigo in **FIID-TT** and **FIID-TT2F** showed an increase in lamellar coherence length, indicating larger ordered domains, consistent with the scale-like features revealed in AFM. In the π – π direction, fluorination of either bithiophene or isoindigo led to an increase in coherence length, indicating improved order and π – π stacking in the fluorinated polymers. While larger than the parent polymer, the coherence length of **FIID-TT2F** decreased both the lamellar and π – π directions compared to **FIID-TT**, indicating that some disruption may be occurring in the fully fluorinated polymer, which is similar to other reported polymer systems.^{16,36} A similar trend is observed in the paracrystalline disorder parameter, indicating that the increase in the coherence length is likely due to decreased disorder in the polymer domains as a result of planarization through fluorination, particularly when **IID** is fluorinated compared to the parent polymer (Figure S13). Compared to isoindigo-based analogues with hydrocarbon side-chains, similar *d*-spacing and coherence lengths are obtained in both directions for this polymer series.¹⁴ This suggests that fluorination remains a successful design handle for improving aggregation and order even with the more flexible ethylene glycol side-chains, which have been shown to disrupt backbone order in other reports.^{6,23,24,29,38} It is likely that the

Table 1. Backbone Dihedral Angles and Maximum Absorbance Wavelengths for Polymer Series

polymer	^a A, °	^a B, °	^a C, °	^b $\lambda_{00, \text{max}}$ nm	^b $\lambda_{01, \text{max}}$ nm
IID-TT	11.4	20.8	14.7	719	651
IID-TT2F	11.4	20.5	0.8	714	647
FIID-TT	12.4	6.8	6.8	744	675
FIID-TT2F	12.3	2.3	0.1	738	665

^aCalculated with DFT. ^bObtained from thin film UV–vis–NIR absorbance.

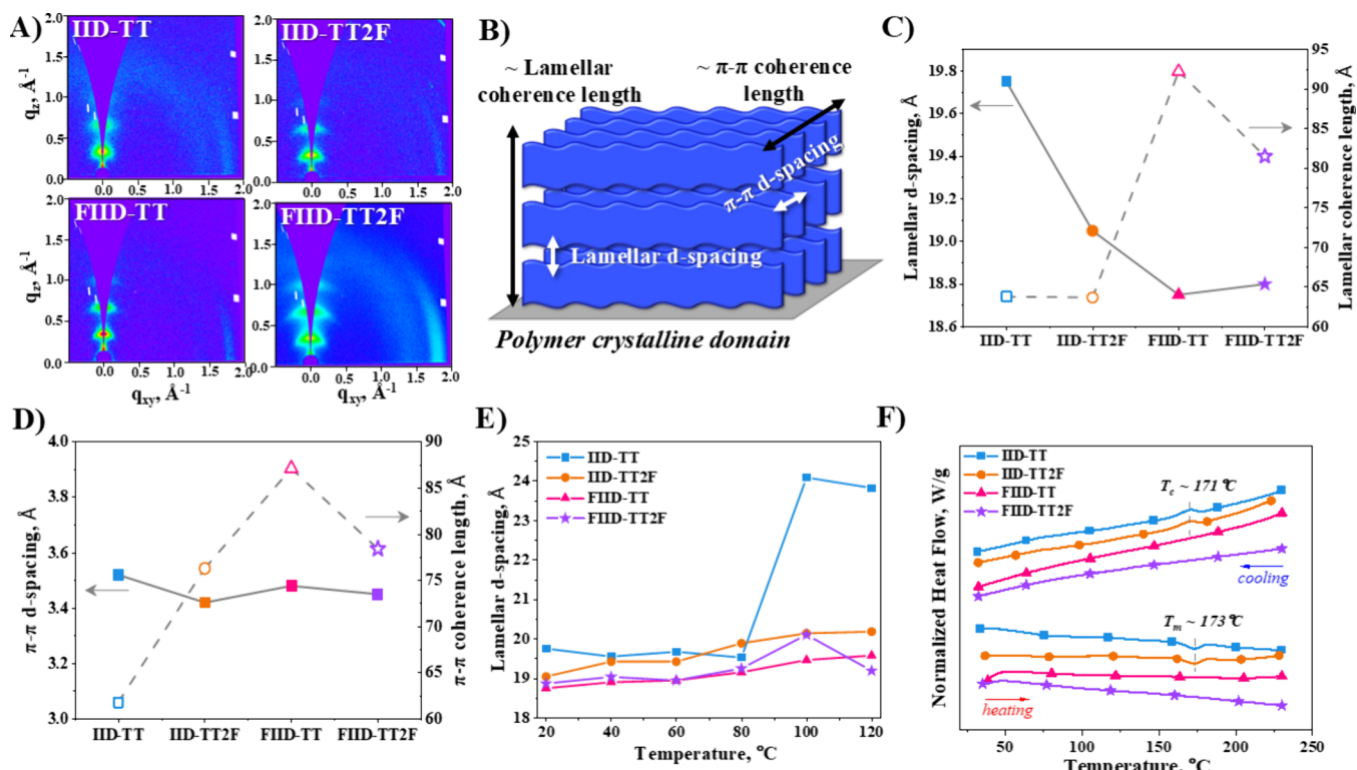


Figure 2. (A) 2D diffraction images obtained from polymer films. (B) Scheme of the edge-on polymer crystalline domain indicating relevant lengths including d -spacing and coherence lengths in both lamellar and π - π directions. (C) Lamellar d -spacing and coherence length and (D) π - π d -spacing and coherence lengths obtained from 1D diffraction line cuts. (E) Lamellar d -spacing over the annealing temperature range. (F) DSC of polymer solids indicating crystalline domain melt and crystallization in IID-TT and IID-TT2F at the tested scan rate.

hexyl spacer region improves the backbone order and limits disruption by extending the more flexible EG region from the backbone. Molecular dynamics simulations were carried out based on the spacing obtained from GIWAXS and supported the increase in planarity and π - π stacking (Figure S14).

Thermal analysis further suggests increased aggregation across the fluorinated polymer series observable in temperature dependent GIWAXS and differential scanning calorimetry (DSC) of polymer solids. Upon heating the parent polymer thin film, an increase in lamellar d -spacing is seen at temperatures above 100 °C (Figure 2E and Figure S15). The fluorinated polymers do not show an expansion indicating that the increased aggregation due to fluorination likely contributes to decreased thermal expansion and retention of lamellar structure at elevated temperatures. Further, in DSC of polymer solids, melting and crystallization temperatures are observed in IID-TT and IID-TT2F but not in FIID-TT and FIID-TT2F, indicating that within the temperature range and rate tested, melting may be suppressed in the backbone region due to increased aggregation strength when isoindigo is fluorinated.

To further unveil the impact of fluorination on the polymer backbone and side-chain assembly, we used attenuated total reflectance Fourier transform infrared (ATR-FTIR) and Raman spectroscopy. As shown in Figure 3A, regions of interest include C=C/C-C stretching and C=O stretching (1400–1700 cm^{-1}) to elucidate backbone behavior and C–O–C, C–N, and C–H stretching and bending (1000–1200 cm^{-1}) and CH_2 stretching (2800–3000 cm^{-1}) regions to probe side-chain behavior. ATR-FTIR spectra were obtained using

polymer solids, and Raman spectra were obtained using annealed polymer films on glass. DFT was used to assist in assigning the peaks for both ATR-FTIR and Raman spectroscopy. The predicted traces and vibrational modes are included in the Supporting Information (Figures S16–S20).

FTIR peaks between 1600 cm^{-1} and 1700 cm^{-1} were observed for all polymers due to the benzene and carbonyl stretching modes in the isoindigo units. Full spectra and peak assignments are included in the Supporting Information (Figures S15–S18). The C=C band occurs at 1605 cm^{-1} for IID-TT, with a 1 cm^{-1} shift to 1606 cm^{-1} upon fluorinating the bithiophene in IID-TT2F. A 13 cm^{-1} shift occurs upon fluorinating the isoindigo with the C=C band occurring at 1692 cm^{-1} and 1693 cm^{-1} for FIID-TT and FIID-TT2F, respectively. These increased shifts arise from increased stiffness and planarity imparted by fluorination, supporting increased aggregation as isoindigo is fluorinated.

Raman spectroscopy was used to probe chain aggregation and order in polymer thin films due to its sensitivity to delocalization and local order.^{17,39–41} Increased delocalization in conjugated polymers causes an effective softening of the polymer bonds, causing a downshift in Raman spectra.^{17,42} Thus, Raman shifts can be used to infer the impact of fluorination on conjugation, revealing two prominent effects in this polymer series: (1) increased planarization due to fluorination extends the conjugation and delocalization, and (2) when appending electron withdrawing fluorine atoms to the donor thiophene units, there is a negative impact on charge delocalization. In IID-TT, IID-TT2F, FIID-TT, and FIID-TT2F polymer thin films, the Raman active C=C/C–C

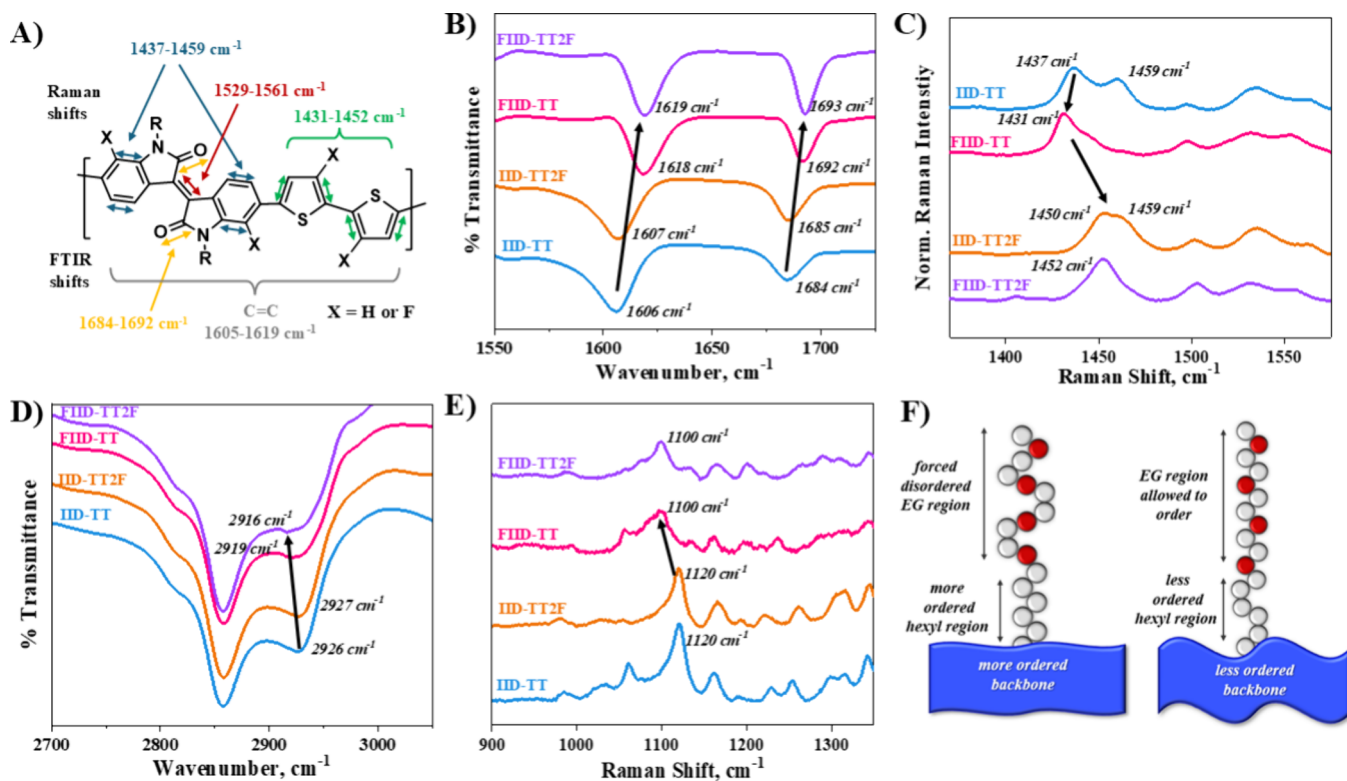


Figure 3. Spectroscopy of polymer solid and films indicating backbone order and side-chain assembly. (A) Polymer structure with relevant Raman shifts and FTIR absorption wavelengths assigned from literature. (B) ATR-FTIR spectra of solids showing the C=O and C=C stretching regions of the isoindigo core. (C) Raman spectra of C=C/C-C backbone stretching. (D) ATR-FTIR of the CH₂ stretching region associated with the alkyl spacer region of the side chain. (E) Raman spectra of side-chain related peaks. (F) Side-chain structure with the proposed assembly scheme.

stretching region revealed 3 main groups of peaks observed across the polymer series (Figure 3C). We assigned the peaks following literature references and DFT calculations (Figures S18–S20) as follows: C=C/C-C backbone stretching localized on the thiophene units at 1431–1452 cm⁻¹,⁴³ C=C/C-C backbone stretching across thiophene and isoindigo at 1459 cm⁻¹,¹⁷ and C=C stretching of the center double bond of isoindigo at 1529–1561 cm⁻¹.⁴³ The Raman spectra of thin films support increased aggregation upon fluorinating isoindigo as seen by downshifts in the thiophene stretching between the parent polymer (1437 cm⁻¹) and FIIID-TT (1431 cm⁻¹) (Figure 3C). Additionally, the second C=C/C-C stretching peak present in IID-TT and IID-TT2F shifts and merges with the lower shift peak in both FIIID-TT and FIIID-TT2F, indicating a stiffening of the isoindigo and backbone vibrations. Despite increasing planarity, both IID-TT2F and FIIID-TT2F show a significant upshift compared to the polymers containing unfluorinated bithiophene, IID-TT and FIIID-TT, which hints that the electron withdrawing effects of the fluorine atoms appended to bithiophene may have negative effects on the overall polymer conjugation.

ATR-FTIR and Raman spectroscopy can also be used to evaluate the effects of backbone planarity on side-chain behavior. We first monitored the hexyl spacer region of the side chain focusing on the differences between the all-trans crystalline and the disordered, liquid-like states. The CH₂ stretching region corresponding to the alkyl groups appears between 2700 cm⁻¹ and 3000 cm⁻¹ in the FTIR. In this region, all four polymer solids exhibit two peaks assigned to the symmetric stretching at 2857 cm⁻¹ and asymmetric stretching between

2916 cm⁻¹ and 2927 cm⁻¹ (Figure 3D). As observed in oligo(ethylene-glycol) monolayer literature, the asymmetric stretching peak at 2917 cm⁻¹ corresponds to a crystalline, all-trans state of an alkyl region and the peak at 2925 cm⁻¹ indicates a more disordered and liquid-like state.^{44,45} IID-TT and IID-TT2F have peaks occurring at 2925 cm⁻¹ and 2927 cm⁻¹, respectively, indicating a disordered alkyl spacer region. FIIID-TT and FIIID-TT2F show peaks at 2919 cm⁻¹ and 2916 cm⁻¹, indicating the presence of more ordered alkyl regions of the side chain. This led us to propose that the increased aggregation and planarity induced by fluorinating isoindigo can extend to the neighboring alkyl chain, resulting in more ordered hexyl regions of the side chain. The ethylene glycol region of the side chain is expected to also produce peaks in the CH₂ stretching region, but they are likely masked by the stronger alkyl spacer region stretching peaks.⁴⁴

We extracted further insight into the ethylene glycol portion of the side chain from the 1000 cm⁻¹ to 1200 cm⁻¹ region of the thin film Raman spectra. Raman peaks in this region are attributed to contributions from the side chains in other conjugated polymer systems.^{18,19} This region includes absorbances from the C–O–C stretching of the ethylene glycol portion of the side chain, the C–N stretching from the side-chain attachment to the IID core, and the CH₃ stretching of the methyl terminus. A peak around 1100 cm⁻¹ occurs in all four of the polymers with a distinct shift when the IID core is fluorinated (Figure 3E). IID-TT and IID-TT2F both exhibit sharp peaks centered around 1120 cm⁻¹, whereas the same peak broadens and is shifted by 20 cm⁻¹ to 1100 cm⁻¹ for both FIIID-TT

and FIID-TT2F. We hypothesize that this shift is due to disorder in the EG side-chain due to both the downshift and broadening observed in the Raman spectra.^{46,47} Additionally, a shoulder appears in the C–O–C stretching region of the ATR-FTIR spectra of both FIID-TT and FIID-TT2F, which could arise due to the gauche defects in the ethylene glycol region (Figure S19).^{44,45} We propose that the rigid alkyl spacer unit seen in FIID-TT and FIID-TT2F limits the ordering of the ethylene glycol region, causing increased defects and disorder, whereas the less ordered alkyl spacer region of IID-TT and IID-TT2F allows the ethylene glycol region to order more independently (Figure 3F).

To investigate how backbone fluorination influenced mixed ionic-electronic performance, the polymer series was evaluated using cyclic voltammetry (CV) and OECT devices using KPF₆ as an aqueous electrolyte, chosen based on previous reports of high performance.⁴⁸ All electrochemical devices were fabricated by spin coating polymer films onto the respective substrates from chloroform solutions and annealing under vacuum, identical to the films prepared for structural analysis. We anticipated two factors to govern mixed conduction: (1) fluorination of the isoindigo unit strengthens its acceptor character, while fluorination of bithiophene reduces its donor strength and likely suppresses electronic transport, and (2) the fluorinated polymers are more crystalline and ordered, which is optimal for more efficient charge carrier transport but causes a tradeoff with bulk ionic uptake. Optimal fluorination is thus needed to maximize D-A character and maintain mixed conduction.

All four polymers exhibit redox behavior at positive and negative voltages in the −0.8 V to 0.8 V testing window and maintained activity upon cycling (Figure 4A and Figure S20). As

expected, fluorination increases the oxidation onset potential and alters the HOMO and LUMO levels depending on the location of the fluorine atoms (Figure 4B and Figure S21).¹⁴ In OECT devices, all polymers exhibited dominantly p-type characteristics under the conditions investigated here. Although no appreciable n-type behavior was observed under our measurement conditions, the electronic structure of the IID series and the increase in reductive current observed from CV suggest that these materials may still have potential for n-type operation. We believe that a more dedicated characterization under carefully controlled inert conditions is warranted to properly assess this behavior. Nonetheless, the measured transfer curves revealed the importance of the location of fluorine atoms on the resulting transistor performance (Figure 4C and Supporting Information, Section S9). When on bithiophene, fluorination significantly hinders p-type conduction, likely due to limiting conjugation and delocalization as seen by lower currents obtained in these devices. IID-TT shows the highest current reached within the tested gate voltage range, but the continued rise in the current in the case of FIID-TT indicates that higher currents may be obtained at higher gate voltage, due to the shifted threshold voltage upon fluorinating the isoindigo core (Figure 4C and Supporting Information Section S9).

The mixed conduction term, μC^* , was extracted from the transfer curves to evaluate the impact of fluorination on mixed conduction (Figure 4D and Supporting Information Section S9). Due to the low current obtained in the devices, it is not surprising that IID-TT2F and FIID-TT2F both underperform in μC^* as well. FIID-TT shows a slightly higher μC^* ($74.3 \pm 18 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$) than IID-TT ($60.2 \pm 24 \text{ F cm}^{-1} \text{ V}^{-1} \text{ s}^{-1}$), but the increase in performance is not significant. Differences in performance

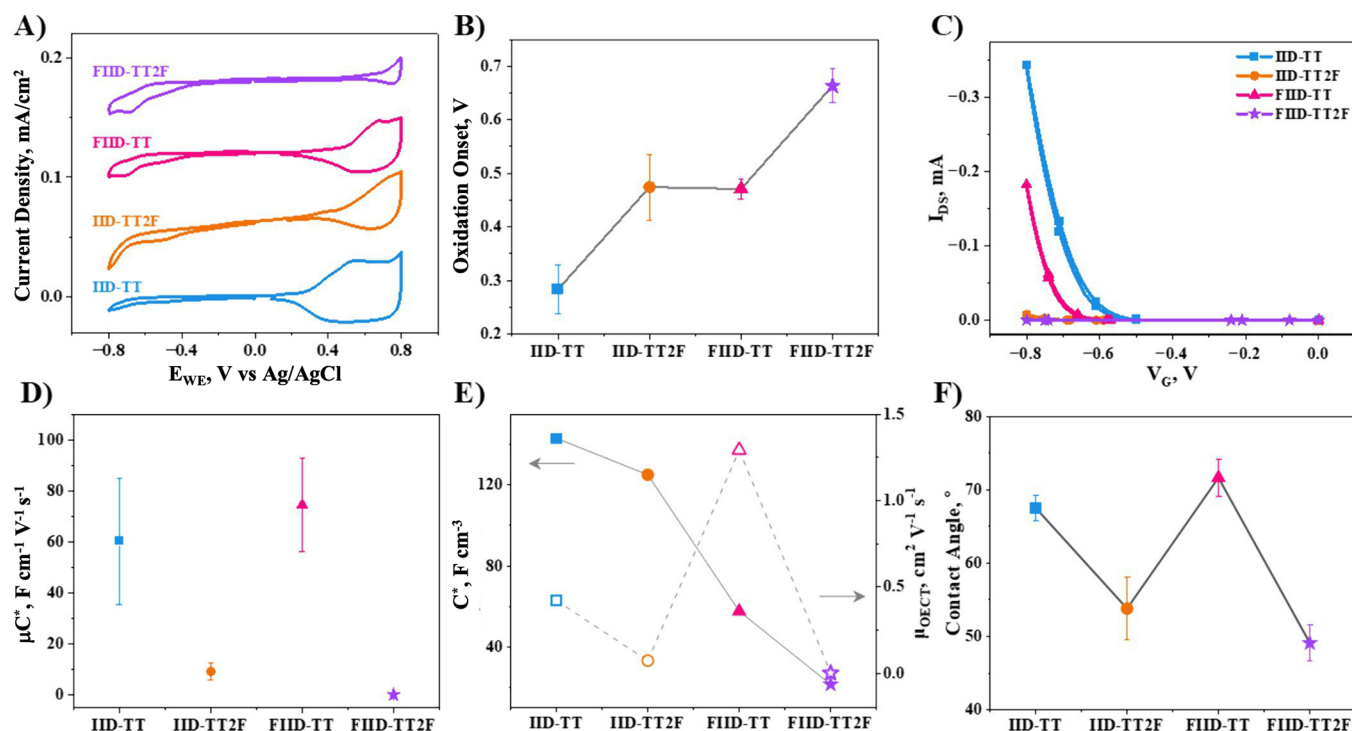


Figure 4. Electrochemical performance in 0.1 M KPF₆. (A) Cyclic voltammetry of polymer films on ITO glass. (B) Extracted oxidation onset in KPF₆. (C) Representative transfer curves of OECTs in 0.1 M KPF₆ with dimensions W : 400 μm , L : 5 μm , D : 30–60 nm. (D) Mixed conduction parameter extracted from OECT transfer curves. (E) Volumetric capacitance (filled) extracted from CV and OECT charge carrier mobility (hollow) calculated from μC^* and C^* . (F) Water contact angles of polymer thin films.

become evident when separating the electronic and ionic components of the mixed conduction term into OECT charge carrier mobility and volumetric capacitance components (Figure 4E). Volumetric capacitance is extracted from cyclic voltammetry, and OECT charge carrier mobility is obtained by dividing the mixed conduction term by volumetric capacitance (Supporting Information Section S9). By isolating these terms, we can see that the charge carrier mobility is highest in FIID-TT, reaching 3 times the parent polymer mobility, indicating that the planarization due to fluorination of the isoindigo unit favorably enhances crystallinity and therefore electronic conduction. Inversely, there is a decrease in volumetric capacitance upon fluorination due to the increase in crystallinity limiting ion uptake. Interestingly, despite fluorination, the IID films in this series remain hydrophilic with water contact angles between 50° and 70°, which is different from literature reports where fluorination increases the contact angle of the resulting polymer film⁴⁹ (Figure 4F). Both IID-TT2F and FIID-TT2F create more hydrophilic thin films; however, this does not directly translate to a higher volumetric capacitance or transistor performance. Note that electrochemical characterizations and OECT measurements were also carried out using an ionic liquid, EMIM:TFSI, and revealed similar trends as the aqueous electrolyte (Figure S28). These results thus underscore that it is important to consider both electronic and ionic conduction when using fluorination as a method to engineer mixed conductors, especially isoindigo-based ones. The new insights garnered here further expand on previous fluorination studies that show enhanced performance in dry-state devices and reveal the nuanced design of mixed conductors compared to their purely electronic conducting counterparts.

CONCLUSIONS

Fluorination was used to tune backbone planarity of polymers flanked with hybrid side-chains, and we investigated the resulting impact on film morphology, backbone and side-chain assembly, and electrochemical performance. We used computational and solid-state spectroscopy and X-ray diffraction to uncover the impact of fluorination on backbone planarity and the resulting increased aggregation and order, particularly when the isoindigo unit is fluorinated at the 7 and 7' positions. Further insight was gained from spectroscopic methods into the increased order in the polymers due to fluorination as well as some evidence that side-chain ordering is impacted by backbone order. Finally, we evaluated the electrochemical response of the polymer series and found that, while fluorinating bithiophene hindered transistor performance, fluorinating isoindigo improved electronic charge carrier mobility but hindered ionic capacitance. Overall, this study was able to expand understanding of backbone order in isoindigo systems in electrochemical environments, applying a design principle from dry-state device literature to a wet state environment. Here, both electronic conduction and ionic conduction need to be considered, thus leading to nuanced material design principles and balancing order and disorder and charge delocalization in channel materials.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acs.macromol.6c01586>.

Synthetic procedures, ¹H NMR, thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), DOSY molecular weight estimates, dihedral angles and HOMO/LUMO distribution from DFT calculations, solution UV–Vis–NIR, GIWAXS parameters and line-cuts, DFT predicted FTIR and Raman spectra and vibration assignments, full ATR-FTIR spectra, cyclic voltammetry, calculated energy levels, transistor-related parameters, and electrochemical characterization with EMIM:TFSI electrolyte (PDF)

AUTHOR INFORMATION

Corresponding Author

Aristide Gumyusenge – Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States;
 orcid.org/0000-0003-4995-5222;
Email: aristide@mit.edu

Authors

Rebecca F. Meacham – Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Camille E. Cunin – Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States;
 orcid.org/0009-0004-1385-0829

Geon Gug Yang – Department of Materials Science and Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, United States

Saroj Upreti – School of Polymer Science and Engineering, University of Southern Mississippi, Hattiesburg, Mississippi 39406, United States

Wenhao Li – Laboratory of Molecular Materials and Devices, College of Smart Materials and Future Energy, Fudan University, Shanghai 200438, P.R. China

Sanket Samal – James Tarpo Jr. and Margaret Tarpo Department of Chemistry, Purdue University, West Lafayette, Indiana 47907, United States

Robert Posey – Department of Chemistry & Biochemistry, Texas Tech University, Lubbock, Texas 79409, United States

Joshua Tropp – Department of Chemistry & Biochemistry, Texas Tech University, Lubbock, Texas 79409, United States;
 orcid.org/0000-0002-1427-1296

Yan Zhao – Laboratory of Molecular Materials and Devices, College of Smart Materials and Future Energy, Fudan University, Shanghai 200438, P.R. China;  orcid.org/0000-0002-4216-2150

Xiaodan Gu – School of Polymer Science and Engineering, University of Southern Mississippi, Hattiesburg, Mississippi 39406, United States;  orcid.org/0000-0002-1123-3673

Complete contact information is available at:

<https://pubs.acs.org/doi/10.1021/acs.macromol.6c01586>

Author Contributions

R.F.M. and A.G. designed the study and analyzed the results. R.F.M. synthesized the materials and conducted the spectroscopic and electrochemical characterization. C.E.C. and G.G.Y. assisted with OECT characterization and data analysis. S.U. and X.G. conducted room temperature GIWAXS measurements.

W.L. and Y.Z. conducted temperature-dependent GIWAXS measurements. S.S. conducted molecular dynamics simulations. R.P. and J.T. carried out GPC measurements. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Funding

R.F.M. acknowledges support by the National Science Foundation Graduate Research Fellowship Program under Grant No. 2141064. A.G. and C.E.C. acknowledge support from the K. Lisa Yang Brain-Body Center at the Massachusetts Institute of Technology (MIT). X.G. and S.U. acknowledge support from the National Science Foundation under award number CHE-2304969.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Part of this work was carried out in the shared experimental facilities at MIT supported by the National Science Foundation (Grant No. DMR-14-19807), the MIT Department of Chemistry Instrumentation Facility (DCIF), and MIT.nano facilities. S.U. and X.G. are grateful for financial support from the Department of Energy under award number DE-SC0024432 to enable the morphology study by X-ray scattering.

■ REFERENCES

- (1) Saleh, A.; Koklu, A.; Uguz, I.; Pappa, A.-M.; Inal, S. Bioelectronic Interfaces of Organic Electrochemical Transistors. *Nat. Rev. Bioeng.* **2024**, *2* (7), 559–574.
- (2) Strakosas, X.; Bongo, M.; Owens, R. M. The Organic Electrochemical Transistor for Biological Applications. *J. Appl. Polym. Sci.* **2015**, *132* (15).
- (3) Gumyusenge, A. Organic Iono-Electronics, a New Front for Semiconducting Polymers to Shine. *Acc. Mater. Res.* **2022**, *3* (7), 669–671.
- (4) Kim, Y.; Chortos, A.; Xu, W.; Liu, Y.; Oh, J. Y.; Son, D.; Kang, J.; Foudeh, A. M.; Zhu, C.; Lee, Y.; Niu, S.; Liu, J.; Pfattner, R.; Bao, Z.; Lee, T.-W. A Bioinspired Flexible Organic Artificial Afferent Nerve. *Science* **2018**, *360* (6392), 998–1003.
- (5) Someya, T.; Bao, Z.; Malliaras, G. G. The Rise of Plastic Bioelectronics. *Nature* **2016**, *540* (7633), 379–385.
- (6) Moro, S.; Siemons, N.; Drury, O.; Warr, D. A.; Moriarty, T. A.; Perdigão, L. M. A.; Pearce, D.; Moser, M.; Hallani, R. K.; Parker, J.; McCulloch, I.; Frost, J. M.; Nelson, J.; Costantini, G. The Effect of Glycol Side Chains on the Assembly and Microstructure of Conjugated Polymers. *ACS Nano* **2022**, *16* (12), 21303–21314.
- (7) Savva, A.; Hallani, R.; Cendra, C.; Surgailis, J.; Hidalgo, T. C.; Wustoni, S.; Sheelamantula, R.; Chen, X.; Kirkus, M.; Giovannitti, A.; Salleo, A.; McCulloch, I.; Inal, S. Balancing Ionic and Electronic Conduction for High-Performance Organic Electrochemical Transistors. *Adv. Funct. Mater.* **2020**, *30* (11), No. 1907657.
- (8) Nielsen, C. B.; Giovannitti, A.; Sbircea, D.-T.; Bandiello, E.; Niazi, M. R.; Hanifi, D. A.; Sessolo, M.; Amassian, A.; Malliaras, G. G.; Rivnay, J.; McCulloch, I. Molecular Design of Semiconducting Polymers for High-Performance Organic Electrochemical Transistors. *J. Am. Chem. Soc.* **2016**, *138* (32), 10252–10259.
- (9) Rivnay, J.; Inal, S.; Salleo, A.; Owens, R. M.; Berggren, M.; Malliaras, G. G. Organic Electrochemical Transistors. *Nat. Rev. Mater.* **2018**, *3* (2), 1–14.
- (10) Flagg, L. Q.; Bischak, C. G.; Onorato, J. W.; Rashid, R. B.; Luscombe, C. K.; Ginger, D. S. Polymer Crystallinity Controls Water Uptake in Glycol Side-Chain Polymer Organic Electrochemical Transistors. *J. Am. Chem. Soc.* **2019**, *141* (10), 4345–4354.
- (11) Siemons, N.; Pearce, D.; Yu, H.; Tuladhar, S. M.; LeCroy, G. S.; Sheelamantula, R.; Hallani, R. K.; Salleo, A.; McCulloch, I.; Giovannitti, A.; Frost, J. M.; Nelson, J. Controlling Swelling in Mixed Transport Polymers through Alkyl Side-Chain Physical Cross-Linking. *Proc. Natl. Acad. Sci.* **2023**, *120* (35), No. e2306272120.
- (12) Thorley, K. J.; McCulloch, I. Why Are S–F and S–O Non-Covalent Interactions Stabilising? *J. Mater. Chem. C* **2018**, *6* (45), 12413–12421.
- (13) Lei, T.; Dou, J.-H.; Ma, Z.-J.; Yao, C.-H.; Liu, C.-J.; Wang, J.-Y.; Pei, J. Ambipolar Polymer Field-Effect Transistors Based on Fluorinated Isoindigo: High Performance and Improved Ambient Stability. *J. Am. Chem. Soc.* **2012**, *134* (49), 20025–20028.
- (14) Gao, Y.; Deng, Y.; Tian, H.; Zhang, J.; Yan, D.; Geng, Y.; Wang, F. Multifluorination toward High-Mobility Ambipolar and Unipolar n-Type Donor–Acceptor Conjugated Polymers Based on Isoindigo. *Adv. Mater.* **2017**, *29* (13), No. 1606217.
- (15) Yang, J.; Zhao, Z.; Geng, H.; Cheng, C.; Chen, J.; Sun, Y.; Shi, L.; Yi, Y.; Shuai, Z.; Guo, Y.; Wang, S.; Lui, Y. Isoindigo-Based Polymers with Small Effective Masses for High-Mobility Ambipolar Field-Effect Transistors. *Adv. Mater.* **2017**, *29* (36), No. 1702115.
- (16) Lin, Y.-C.; Chen, F.-H.; Chiang, Y.-C.; Chueh, C.-C.; Chen, W.-C. Asymmetric Side-Chain Engineering of Isoindigo-Based Polymers for Improved Stretchability and Applications in Field-Effect Transistors. *ACS Appl. Mater. Interfaces* **2019**, *11* (37), 34158–34170.
- (17) Gámez-Valenzuela, S.; Comi, M.; González, S. R.; Delgado, M. C. R.; Al-Hashimi, M.; Ortiz, R. P. The Fluorination Effect: The Importance of Backbone Planarity in Achieving High Performance Ambipolar Field Effect Transistors. *J. Mater. Chem. C* **2023**, *11* (24), 8027–8036.
- (18) Quill, T. J.; LeCroy, G.; Melianas, A.; Rawlings, D.; Thiburce, Q.; Sheelamantula, R.; Cheng, C.; Tuchman, Y.; Keene, S. T.; McCulloch, I.; Segalman, R. A.; Chabynyc, M. L.; Salleo, A. Ion Pair Uptake in Ion Gel Devices Based on Organic Mixed Ionic–Electronic Conductors. *Adv. Funct. Mater.* **2021**, *31* (47), No. 2104301.
- (19) Savva, A.; Cendra, C.; Giugni, A.; Torre, B.; Surgailis, J.; Ohayon, D.; Giovannitti, A.; McCulloch, I.; Di Fabrizio, E.; Salleo, A.; Rivnay, J.; Inal, S. Influence of Water on the Performance of Organic Electrochemical Transistors. *Chem. Mater.* **2019**, *31* (3), 927–937.
- (20) Wang, T.; Mo, S.; Du, Z.; Cai, S.; Deng, C.; Feng, W.; Peng, Q.; Li, H.; Chen, J. Crystallinity and Energy Level Modulation in Organic Mixed Ion-Electron Conductors: Facilitating High-Performance OECTs and Diverse Applications. *Chem. Eng. J.* **2025**, *522*, No. 167525.
- (21) Yang, W.; Feng, K.; Ma, S.; Liu, B.; Wang, Y.; Ding, R.; Jeong, S. Y.; Woo, H. Y.; Chan, P. K. L.; Guo, X. High-Performance n-Type Polymeric Mixed Ionic-Electronic Conductors: The Impacts of Halogen Functionalization. *Adv. Mater.* **2024**, *36* (4), No. 2305416.
- (22) Giridharagopal, R.; Flagg, L. Q.; Harrison, J. S.; Ziffer, M. E.; Onorato, J.; Luscombe, C. K.; Ginger, D. S. Electrochemical Strain Microscopy Probes Morphology-Induced Variations in Ion Uptake and Performance in Organic Electrochemical Transistors. *Nat. Mater.* **2017**, *16* (7), 737–742.
- (23) Chen, S. E.; Flagg, L. Q.; Onorato, J. W.; Richter, L. J.; Guo, J.; Luscombe, C. K.; Ginger, D. S. Impact of Varying Side Chain Structure on Organic Electrochemical Transistor Performance: A Series of Oligoethylene Glycol-Substituted Polythiophenes. *J. Mater. Chem. A* **2022**, *10* (19), 10738–10749.
- (24) Onorato, J. W.; Wang, Z.; Sun, Y.; Nowak, C.; Flagg, L. Q.; Li, R.; Dong, B. X.; Richter, L. J.; Escobedo, F. A.; Nealey, P. F.; Patel, S. N.; Luscombe, C. K. Side Chain Engineering Control of Mixed Conduction in Oligoethylene Glycol-Substituted Polythiophenes. *J. Mater. Chem. A* **2021**, *9* (37), 21410–21423.
- (25) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Petersson, G. A.; Nakatsuji, H.; Li, X.; Caricato, M.; Marenich, A. V.; Bloino, J.; Janesko, B. G.; Gomperts, R.; Mennucci, B.; Hratchian, H. P.; Ortiz, J. V.; Izmaylov, A. F.; Sonnenberg, J. L.; Williams-Young, D.; Ding, F.;

- Lipparini, F.; Egidi, F.; Goings, J.; Petrone, A.; Henderson, T.; Ranasinghe, D.; Zakrzewski, V. G.; Gao, J.; Rega, N.; Zheng, G.; Liang, W.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Throssell, K.; Montgomery, J. A. Jr; Peralta, J. E.; Ogliaro, F.; Berapark, M. J.; Heyd, J. J.; Brothers, E. N.; Kudin, K. N.; Staroverov, V. N.; Keith, T. A.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A. P.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Millam, J. M.; Klene, M.; Adamo, C.; Cammi, R.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Farkas, O.; Foresman, J. B.; Fox, D. J. *Gaussian 16*; Gaussian, Inc.: Wallingford CT, 2016.
- (26) Becke, A. D. Density-Functional Exchange-Energy Approximation with Correct Asymptotic Behavior. *Phys. Rev. A* **1988**, 38 (6), 3098–3100.
- (27) Becke, A. D. Density-Functional Thermochemistry. I. The Effect of the Exchange-Only Gradient Correction. *J. Chem. Phys.* **1992**, 96 (3), 2155–2160.
- (28) Hehre, W. J.; Stewart, R. F.; Pople, J. A. Self-Consistent Molecular-Orbital Methods. I. Use of Gaussian Expansions of Slater-Type Atomic Orbitals. *J. Chem. Phys.* **1969**, 51 (6), 2657–2664.
- (29) Wang, Y.; Zeglio, E.; Liao, H.; Xu, J.; Liu, F.; Li, Z.; Maria, I. P.; Mawad, D.; Herland, A.; McCulloch, I.; Yue, W. Hybrid Alkyl–Ethylene Glycol Side Chains Enhance Substrate Adhesion and Operational Stability in Accumulation Mode Organic Electrochemical Transistors. *Chem. Mater.* **2019**, 31 (23), 9797–9806.
- (30) Koch, F. P. V.; Rivnay, J.; Foster, S.; Müller, C.; Downing, J. M.; Buchaca-Domingo, E.; Westacott, P.; Yu, L.; Yuan, M.; Baklar, M.; Fei, Z.; Luscombe, C.; McLachlan, M. A.; Heeney, M.; Rumbles, G.; Silva, C.; Salleo, A.; Nelson, J.; Smith, P.; Stingelin, N. The Impact of Molecular Weight on Microstructure and Charge Transport in Semicrystalline Polymer Semiconductors–Poly(3-Hexylthiophene), a Model Study. *Prog. Polym. Sci.* **2013**, 38 (12), 1978–1989.
- (31) Wu, H.-Y.; Yang, C.-Y.; Li, Q.; Kolhe, N. B.; Strakosas, X.; Stoeckel, M.-A.; Wu, Z.; Jin, W.; Savvakis, M.; Kroon, R.; Tu, D.; Woo, H. Y.; Berggren, M.; Jenekhe, S. A.; Fabiano, S. Influence of Molecular Weight on the Organic Electrochemical Transistor Performance of Ladder-Type Conjugated Polymers. *Adv. Mater.* **2022**, 34 (4), No. 2106235.
- (32) Li, W.; Yang, L.; Tumbleston, J. R.; Yan, L.; Ade, H.; You, W. Controlling Molecular Weight of a High Efficiency Donor-Acceptor Conjugated Polymer and Understanding Its Significant Impact on Photovoltaic Properties. *Adv. Mater.* **2014**, 26 (26), 4456–4462.
- (33) Zhao, K.; Zhang, T.; Zhang, L.; Li, J.; Li, H.; Wu, F.; Chen, Y.; Zhang, Q.; Han, Y. Role of Molecular Weight in Microstructural Transition and Its Correlation to the Mechanical and Electrical Properties of P(NDI2OD-T2) Thin Films. *Macromolecules* **2021**, 54 (21), 10203–10215.
- (34) Lei, T.; Cao, Y.; Zhou, X.; Peng, Y.; Bian, J.; Pei, J. Systematic Investigation of Isoindigo-Based Polymeric Field-Effect Transistors: Design Strategy and Impact of Polymer Symmetry and Backbone Curvature. *Chem. Mater.* **2012**, 24 (10), 1762–1770.
- (35) Spano, F. C. The Spectral Signatures of Frenkel Polarons in H- and J-Aggregates. *Acc. Chem. Res.* **2009**, 43 (3), 429–439.
- (36) Chang, J.-F.; Hsieh, C.-T.; Su, L.-Y.; Chueh, C.-C. Reducing the Side-Chain Influences of Isoindigo-Based Polymer Donors by Backbone Fluorination in Photovoltaic Applications. *Dyes Pigm.* **2022**, 199, No. 110038.
- (37) Jiao, X.; Statz, M.; Lai, L.; Schott, S.; Jellett, C.; McCulloch, I.; Sirringhaus, H.; McNeill, C. R. Resolving Different Physical Origins toward Crystallite Imperfection in Semiconducting Polymers: Crystallite Size vs Paracrystallinity. *J. Phys. Chem. B* **2020**, 124 (46), 10529–10538.
- (38) Meacham, R. F.; Roh, H.; Cunin, C. E.; Lee, E. R.; Li, W.; Zhao, Y.; Samal, S.; Gumyusenge, A. Contrasting Interchain Order and Mixed Ionic–Electronic Conduction in Conjugated Polymers: An Isoindigo Case Study. *RSC Appl. Polym.* **2024**, 2 (6), 1193–1201.
- (39) Brambilla, L.; Tommasini, M.; Botiz, I.; Rahimi, K.; Agumba, J. O.; Stingelin, N.; Zerbi, G. Regio-Regular Oligo and Poly(3-Hexyl Thiophene): Precise Structural Markers from the Vibrational Spectra of Oligomer Single Crystals. *Macromolecules* **2014**, 47 (19), 6730–6739.
- (40) Gao, Y.; Grey, J. K. Resonance Chemical Imaging of Polythiophene/Fullerene Photovoltaic Thin Films: Mapping Morphology-Dependent Aggregated and Unaggregated C=C Species. *J. Am. Chem. Soc.* **2009**, 131 (28), 9654–9662.
- (41) Sweetnam, S.; Vandewal, K.; Cho, E.; Risko, C.; Coropceanu, V.; Salleo, A.; Brédas, J.-L.; McGehee, M. D. Characterizing the Polymer:Fullerene Intermolecular Interactions. *Chem. Mater.* **2016**, 28 (5), 1446–1452.
- (42) Mosca, S.; Milani, A.; Castiglioni, C.; Hernández Jolin, V.; Meseguer, C.; López Navarrete, J. T.; Zhao, C.; Sugiyasu, K.; Ruiz Delgado, M. C. Raman Fingerprints of π -Electron Delocalization in Polythiophene-Based Insulated Molecular Wires. *Macromolecules* **2022**, 55 (9), 3458–3468.
- (43) Park, K. S.; Kwok, J. J.; Dilmurat, R.; Qu, G.; Kafle, P.; Luo, X.; Jung, S.-H.; Olivier, Y.; Lee, J.-K.; Mei, J.; Beljonne, D.; Diao, Y. Tuning Conformation, Assembly, and Charge Transport Properties of Conjugated Polymers by Printing Flow | Science Advances. *Sci. Adv.* **2019**, 5 (8), No. eaaw7757.
- (44) Harder, P.; Grunze, M.; Dahint, R.; Whitesides, G. M.; Laibinis, P. E. Molecular Conformation in Oligo(Ethylene Glycol)-Terminated Self-Assembled Monolayers on Gold and Silver Surfaces Determines Their Ability To Resist Protein Adsorption. *J. Phys. Chem. B* **1998**, 102 (2), 426–436.
- (45) Valiokas, R.; Malysheva, L.; Onipko, A.; Lee, H.-H.; Ruželė, Ž.; Svedhem, S.; Svensson, S. C. T.; Gelius, U.; Liedberg, B. On the Quality and Structural Characteristics of Oligo(Ethylene Glycol) Assemblies on Gold: An Experimental and Theoretical Study. *J. Electron Spectrosc. Relat. Phenom.* **2009**, 172 (1), 9–20.
- (46) Koh, M.; Kitt, J. P.; Pendergast, A. D.; Harris, J. M.; Minter, S. D.; Korzeniewski, C. Confocal Raman Microscopy for Measuring In-Situ Temperature-Dependent Structural Changes in Poly(Ethylene Oxide) Thin Films. *Appl. Spectrosc.* **2025**, 79 (9), 1334–1345.
- (47) Samuel, A. Z.; Umapathy, S. Energy Funneling and Macromolecular Conformational Dynamics: A 2D Raman Correlation Study of PEG Melting. *Polym. J.* **2014**, 46 (6), 330–336.
- (48) Flagg, L. Q.; Giridharagopal, R.; Guo, J.; Ginger, D. S. Anion-Dependent Doping and Charge Transport in Organic Electrochemical Transistors. *Chem. Mater.* **2018**, 30 (15), 5380–5389.
- (49) Wang, Y.; Zhu, G.; Zeglio, E.; Castillo, T. C. H.; Haseena, S.; Ravva, M. K.; Cong, S.; Chen, J.; Lan, L.; Li, Z.; Herland, A.; McCulloch, I.; Inal, S.; Yue, W. N-Type Organic Electrochemical Transistors with High Transconductance and Stability. *Chem. Mater.* **2023**, 35 (2), 405–415.