Supplementary Information

Dramatically Enhanced Molecular Ordering and Charge Transport of a DPP-based Polymer Assisted by Oligomers through Antiplasticization

Bin Sun,‡,a Wei Hong,‡,a Hany Aziz,a,b Nasser Mohieddin Abukhdeir,a and Yuning Li*

a Department of Chemical Engineering and Waterloo Institute for Nanotechnology (WIN), 200 University Ave W, Waterloo, Ontario, N2L 3G1, Canada; Fax: +1 519-888-4347; Tel: +1 519-888-4567 ext. 31105; Email: yuning.li@uwaterloo.ca.

b Department of Electrical and Computer Engineering and Waterloo Institute for Nanotechnology (WIN), 200 University Ave W, Waterloo, Ontario, N2L 3G1, Canada.

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1. Experimental details

Instrumentation and Methods. High-temperature gel-permeation chromatography (HT-GPC) measurements were performed on a Malvern 350 HT-GPC system using 1,2,4-trichlorobenzene as an eluent with polystyrene as standards at column temperature of 140 °C. HT-GPC data were fitted to the following trial function:

\[ f(x) = a_1 \exp \left( -\frac{1}{2} \left( \frac{x-b_1}{c_1} \right)^2 \right) + a_2 \exp \left( -\frac{1}{2} \left( \frac{x-b_2}{c_2} \right)^2 \right) + d \]

using the method of least-squares for minimization of the residual. In order to maximize accuracy of the nonlinear fit, initial parameters for \( f(x) \) were first found for a smoothed form of the data which was computed using the discrete Fourier transform. These values were used as initial values for the least-squares fit of the full (noisy) data. For the filtered and final fit, the value of \( b_2 \) was fixed to that determined for the PQDT-L sample alone with all other parameters determined through minimization of the residual. UV-Vis spectra were recorded on a Thermo Scientific Genesys 10 UV instrument. Cyclic voltammetry (CV) measurements were performed on a Digi-Ivy model DY2111 Potentiostat using an Ag/AgCl reference electrode, a platinum wire counter electrode, and a platinum foil working electrode in 0.1 M tetrabutylammonium hexafluorophosphate in dry acetonitrile using ferrocene/ferrocenium (Fc/Fc⁺) couple as a standard. The HOMO energy levels were calculated using the equation:

\[ E_{\text{HOMO}} (eV) = - (E_{\text{oxy \text{onset}}} - E_{\text{Fc/Fc+ onset}}) - 4.80 \text{ eV} \]

where \( E_{\text{oxy \text{onset}}} \) and \( E_{\text{Fc/Fc+ onset}} \) are the onset oxidation potentials for the polymer sample and ferrocene relative to Ag/AgCl electrode, while the value – 4.8 eV is the HOMO energy level of ferrocene. X-ray diffraction patterns were conducted on polymer powders or thin films (~35 nm) spin-coated on dodecyltrichlorosilane (DTS)-modified Si/SiO₂ substrates with a Bruker D8 Advance diffractometer with Cu \( K_\alpha \) radiation (\( \lambda = 1.5406 \text{ Å} \)). Atomic force microscopy (AFM) images were obtained on a Dimension 3100 Scanning Probe Microscope.
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Synthesis of PDQT. To a 100 mL dry three-necked flask were added 3,6-bis(5-bromothiophen-2-yl)-2,5-bis(2-octyldodecyl)pyrrolo[3,4-c]pyrrole-1,4(2H,5H)-dione (0.6115 g, 0.6 mmol), \(^2\) 5,5'-bis(trimethylstannyl)bithiophene (0.2951 g, 0.6 mmol) and tri(o-totyl)phosphine (P(tolyl)_3 ) (14.6 mg, 8 mol %, 0.048 mmol). After de-gassing and filling argon for 3 times, tris(dibenzylideneacetone)-dipalladium (Pd_2(dba)_3 ) (2 mol %, 0.012 mmol) and anhydrous chlorobenzene (60 ml) was added under argon protection. The flask was sealed and the mixture stirred for 72 h at 130 °C. After cooling to room temperature, the reaction mixture was poured into a stirring mixture of methanol (300 ml) and concentrated hydrochloric acid (~12 N HCl, 24 ml) and stirred for 16 h. The precipitates were collected by filtration, washed extensively with methanol, dried, and subjected to Soxhlet extraction with acetone, hexane, and then chloroform. The final fraction extracted with chloroform was dried under a reduced pressure to afford a polymer as PDQT-M (607 mg 98.8 %). A portion (207 mg) of PDQT-M was subjected to further Soxhlet extraction with toluene and then chloroform. After removal of solvents, the toluene extracted fraction gave a polymer as PDQT-L (82 mg, 40%), while the chloroform extracted fraction gave a polymer as PDQT-H (125 mg, 60%).

Device Fabrication. A bottom-contact, bottom-gate OTFT structure was used to evaluate the polymer semiconductors. Heavily n-doped Si wafer was used as gate electrode. A 200 nm thermally grown SiO\(_2\) layer on top of the Si wafer was utilized as a gate dielectric layer with a capacitance of \(~17\) nF·cm\(^{-2}\). Gold source and drain patterns were deposited by thermal evaporation on the SiO\(_2\) layer using a conventional lithography technique. The substrate surface was cleaned with O\(_2\) plasma, acetone, and isopropanol sequentially, and then modified with DTS in toluene (10 mg.mL\(^{-1}\)) at 60 °C for 20 min. Subsequently the substrate was washed with toluene, and dried under a nitrogen flow. A PDQT film (~35 nm) was deposited on the substrate by spin-coating a 5 mg/mL polymer solution in tetrachloroethane and 1,2-dichlorobenzene (1/1, v/v) at 2000 rpm for 90 s. After annealing on a hotplate in a glove box at 150 or 200 °C for 15 min, the devices were encapsulated with a 500 nm PMMA film
by spin coating an 8 wt % of PMMA solution in butyl acetate at 3000 rpm for 50 s, and dried at 80°C for 30 min in a glove box. The devices were characterized in air using an Agilent 4155C Semiconductor Parameter Analyzer. The carrier mobility in the saturated regime, $\mu$, was calculated from the slope of the $(I_{DS})^{1/2}$ versus $V_{GS}$ plot according to the equation of $I_{DS} = \mu C_i W (V_{GS} - V_T)^2 / 2L$, where $I_{DS}$ is the drain current, $C_i$ is the capacitance per unit area of the gate dielectric, $V_{GS}$ is the gate voltage, and $V_T$ is the threshold voltage. The channel length ($L$) and channel width ($W$) are 30 μm and 1000 μm, respectively.

2. Additional data

Table S1 Summary of properties of three PDQT polymers with different molecular weights and distributions.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>HT-GPC</th>
<th>UV-Vis</th>
<th>CV</th>
<th>OTFT mobility, Average$^d$ (STD$^e$) / range$^f$</th>
<th>cm$^2$V$^{-1}$s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$M_a$, kDa $M_p$, kDa PDI Oligo, wt%$^a$ Sol.$^b$ r. t.$^c$ 150 °C 200 °C</td>
<td>E$_{\text{HOMO}}$, eV 150 °C 200 °C</td>
<td></td>
<td></td>
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</tr>
<tr>
<td>PDQT-L</td>
<td>34 113 8.8 3.85 20 784 786 795 796 -5.24</td>
<td>0.76 (0.11) /0.63-0.90</td>
<td>1.14 (0.24) /0.86-1.45</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PDQT-H</td>
<td>61 129 2.49 7 784 792 795 795 -5.24</td>
<td>1.28 (0.19) /1.09-1.55</td>
<td>2.44 (0.13) /2.26-2.55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PDQT-M</td>
<td>40 121 3.22 12 784 786 792 793 -5.24</td>
<td>1.58 (0.36) /1.24-2.10</td>
<td>3.57 (1.11) /2.70-5.50</td>
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<td></td>
</tr>
</tbody>
</table>

$^a$ The oligomeric component calculated by fitting the HT-GPC curves with two Gaussian distributions (see Figure 1). $^b$ Measured in chloroform. $^c$ Measured using thin films annealed at different temperatures. $^d$ Average hole mobility in the saturation region at a drain-source voltage ($V_{DS}$) of -80 V. $^e$ Standard deviation. $^f$ Mobility range with the minimum and maximum value.
**Fig. S1.** UV-Vis spectra of polymer solutions in chloroform and thin films annealed at different temperatures.
**Fig. S2.** Cyclic voltammograms of polymer thin films showing the oxidative cycles at a scan rate of 0.05 Vs\(^{-1}\). The electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate in anhydrous acetonitrile. The HOMO energy levels (E\(_{\text{HOMO}}\)) are \(-5.24\) eV for PDQT-M and PDQT-H, and \(-5.28\) eV for PDQT-L, using ferrocene (Fc) (E\(_{\text{HOMO}} = -4.8\) eV) as a standard.
Fig. S3. AFM height images (1 μm × 1 μm) of polymer thin films annealed at 150 °C/200 °C: (a)/(d) PDQT-M, (b)/(e) PDQT-L, and (c)/(f) PDQT-H.
**Fig. S4.** Mobility values of OTFT devices using PDQT-L (100 wt% of PDQT-L), PDQT-H (0 wt% of PDQT-L), and their mixtures. The polymer mixtures with PDQT-L contents of 25 wt%, 50 wt%, and 75 wt% were prepared by mixing PDQT-L and PDQT-H at weight ratios of 1/3, 1/1, and 3/1, respectively. The concentrations of oligomers (highlighted in blue) in the polymer mixtures were calculated based on the contents of oligomers in PDQT-L (20 wt%) and PDQT-H (7 wt%). The polymer thin films were annealed at 200 °C for 15 min. The data at PDQT-H % = 60% were obtained from OTFT devices using the original polymer PDQT-M (12 wt% of oligomers) before fractional separation. It can be clearly seen that the polymer mixture with 75 wt% of PDQT-L showed exhibited mobility very similar to that of 100% PDQT-L, while the mixtures with 50 wt% and 25 wt% of PDQT-L showed an obvious enhancement in mobility as observed for PDQT-M (40% PDQT-L).

3. **References**
