

Supporting Information

Hydrophobic Polythiophene Hole-Transport Layers to Address the Moisture-Induced Decomposition Problem of Perovskite Solar Cells

*Soumya Kundu, Timothy L. Kelly**

Department of Chemistry, University of Saskatchewan, 110 Science Place, Saskatoon, Saskatchewan S7N
5C9, Canada

* E-mail: tim.kelly@usask.ca

EXPERIMENTAL SECTION

Materials. All solvents were analytical grade and were purchased from Fisher Chemicals and used as received, except where noted below. All other reagents were used as received, without further purification. All reactions were carried out under an argon atmosphere using standard Schlenk techniques, unless otherwise stated. Toluene, DMF, and THF were dried over activated 3 Å molecular sieves and stored under nitrogen. 3-Methoxythiophene, 1H,1H,2H,2H-perfluorohexan-1-ol, 1-dodecanol, 1-hexanol, 2-(2-(2-methoxyethoxy)ethoxy)ethanol, *p*-toluenesulfonic acid monohydrate, copper(I) chloride, sodium metal, 1,3-dibromo-5,5-dimethylhydantoin, [1,3-bis(diphenylphosphino)propane]dichloronickel(II), lead(II) iodide (99%), methylamine (37% in absolute ethanol), hydriodic acid (57% in H₂O), 4-*tert*-butylpyridine (96%) and lithium bis(trifluoromethanesulfonyl)imide (Li-TFSI, 99%) were purchased from Sigma-Aldrich. Zinc acetate dihydrate was purchased from Alfa Aesar. 3-Bromothiophene was purchased from Matrix Scientific. Poly(3-hexylthiophene) (P3HT, electronic grade, $M_w \sim 50$ kDa) was purchased from Rieke Metals Inc. ITO-coated glass ($R_s = 20 \Omega \cdot \text{sq}^{-1}$) substrates were purchased from Delta Technologies, Ltd. Ag pellets (99.99%) were purchased from Kurt J. Lesker.

Characterization. NMR spectra were recorded using Bruker Avance 500 MHz and 600 MHz spectrometers. UV-visible spectra were obtained using a Cary 6000i UV-visible spectrophotometer. Polymer molecular weights were measured by triple-detection gel permeation chromatography (GPC) using a Viscotek 350 HT-GPC system (Malvern) using tetrahydrofuran as the eluent at a 1.0 mL min⁻¹ flow rate. The instrument was equipped with an autosampler (Model 430 Vortex), a degasser (model 7510), two pumps (model 1122), 7 and 90° light-scattering detectors, refractometer, and viscometer. GPC columns (three main columns: Plgel 10 mm MIXED-B LS 300 × 7.5 mm; one guard column: 10 mm GUARD 50 × 7.5 mm; Agilent Technologies) covering the M_w range of 500 to 10,000,000 g mol⁻¹ were used. The column temperature was 37 °C. To prepare samples for analysis, the polymers were first dissolved in THF by stirring overnight. They were then filtered through 0.45 μm PTFE syringe filters

immediately prior to measurement. The molecular weights and dispersities ($D = M_w/M_n$) were calculated using a calibration curve based on linear polystyrene standards.

Synthesis of 3-((3',3',4',4',5',5',6',6',6'-nonafluorohexyl)oxy)thiophene (**1**)

3-((3',3',4',4',5',5',6',6',6'-nonafluorohexyl)oxy)thiophene (**1**) was synthesized according to previously reported procedures.¹ 3-Methoxythiophene (1.70 mL, 17.5 mmol) was placed in a 100 mL two-necked round bottom flask and dissolved in 15 mL of dry toluene. 3',3',4',4',5',5',6',6',6'-Nonafluorohexan-1-ol (5.81 mL, 35.0 mmol) was added, followed by the addition of *p*-toluenesulfonic acid (0.33 g, 1.80 mmol). Then the reaction mixture was heated at reflux under an argon atmosphere for 24 hours. The reaction mixture was cooled, extracted with CH₂Cl₂ (50 mL), and washed with distilled water (2 × 30 mL). The organic layer was dried over anhydrous magnesium sulfate and concentrated to dryness. The crude product was purified by column chromatography using hexane as the eluent to yield **1** as a colorless liquid (1.81 g, 5.25 mmol, 30%). ¹H NMR (500 MHz, CDCl₃, δ ppm): 7.21 (dd, 1H), 6.76 (dd, 1H), 6.30 (dd, 1H), 4.27 (t, $J = 6.85$ Hz, 2H), 2.68-2.58 (m, 2H).

Representative synthesis of 3-(alkoxy)thiophenes (2-4)

3-Hexyloxythiophene (**3**) was synthesized according to previously reported procedures.² First, sodium hexoxide was prepared *in situ* by slowly adding sodium (3.38 g, 147 mmol) to dry 1-hexanol (75 mL). After all of the metallic sodium had disappeared, dry DMF (20 mL) was added to the reaction mixture as a co-solvent. 3-Bromothiophene (6.89 mL, 73.6 mmol) was slowly added to the reaction mixture, followed by a catalytic amount of copper(I) chloride (1.09 g, 11.0 mmol). The reaction mixture was stirred for 0.5 hours at 110 °C under an argon atmosphere. The reaction mixture was poured into water, extracted with diethyl ether, and concentrated under vacuum. The product was purified by fractional distillation yield 3-hexyloxythiophene (**3**) (11.53 g, 62.56 mmol, 85%). ¹H NMR (500 MHz, CDCl₃, δ ppm): 7.16 (dd, 1H),

6.75 (dd, 1H), 6.22 (dd, 1H), 3.94 (t, $J = 6.53$ Hz, 2H), 1.80-1.74 (m, 2H), 1.36-1.31 (m, 6H), 0.92-0.89 (m, 3H).

Analogous procedures were used to prepare 3-dodecyloxythiophene (**2**) from 1-dodecanol (17.58 g, 65.50 mmol, 89%). ^1H NMR (500 MHz, CDCl_3 , δ ppm): 7.18 (dd, 1H), 6.78 (dd, 1H), 6.24 (dd, 1H), 3.96 (t, $J = 6.75$ Hz, 2H), 1.83-1.77 (m, 2H), 1.51-1.45 (m, 2H), 1.40-1.32 (m, 16H), 0.93 (t, $J = 7.00$, 3H).

Analogous procedures were used to prepare 3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)thiophene (**4**) from 2-(2-(2-methoxyethoxy)ethoxy)ethanol (14.86 g, 60.35 mmol, 82%). ^1H NMR (500 MHz, CDCl_3 , δ ppm): 7.16 (dd, 1H), 6.77 (dd, 1H), 6.26 (dd, 1H), 4.12 (t, $J = 4.7$ Hz, 2H), 3.84 (t, $J = 4.9$ Hz, 2H), 3.74-3.72 (m, 2H), 3.79-3.65 (m, 4H), 3.56-3.54 (m, 2H), 3.38 (s, 3H).

Representative synthesis of 2,5-dibromo-3-alkoxythiophene (5-8)

Bromination of the 3-alkoxythiophenes was performed using dibromatin as a brominating agent according to previously reported procedures.³ 3-Hexyloxythiophene (**3**) (3.15 g, 17.0 mmol) was dissolved in 50 mL of anhydrous THF and the reaction mixture was cooled to -78 °C. 1,3-Dibromo-5,5-dimethylhydantoin (5.35 g, 18.7 mmol) was added, and the reaction mixture stirred for 0.5 hours at -78 °C under an argon atmosphere. The low-temperature bath was removed and the reaction mixture stirred for another 2 h at room temperature, after which the solvent was removed by rotary evaporation. The residue was transferred onto filter paper and washed several times with hexanes to extract the product. The filtrate was concentrated by evaporation under reduced pressure, and the product purified by column chromatography using hexanes as the eluent to yield 2,5-dibromo-3-hexyloxythiophene (**7**) as an oil (5.22 g, 15.3 mmol, 90%). In order to prevent radical-initiated self-polymerization, the product was stored over charcoal at 4 °C in the dark; the oil was decanted from the charcoal immediately prior to use. ^1H NMR (500 MHz, CDCl_3 , δ ppm): 6.76 (s, 1H), 3.99 (t, $J = 6.60$ Hz, 2H), 1.76-1.70 (m, 2H), 1.46-1.42 (m, 6H), 0.92-0.89 (m, 3H).

Analogous procedures were used to prepare 2,5-dibromo-3-((3',3',4',4',5',5',6',6',6'-nonafluorohexyl)oxy)thiophene (**5**) from **1** (7.28 g, 14.5 mmol, 85%). ¹H NMR (500 MHz, CDCl₃, δ ppm): 6.75 (s, 1H), 3.99 (t, *J* = 6.65 Hz, 2H), 1.76-1.71 (m, 2H).

Analogous procedures were used to prepare 2,5-dibromo-3-dodecyloxythiophene (**6**) from **2** (6.52 g, 15.3 mmol, 90%). ¹H NMR (500 MHz, CDCl₃, δ ppm): 6.75 (s, 1H), 3.98 (t, *J* = 6.65 Hz, 2H), 1.76-1.71 (m, 2H), 1.47-1.41 (m, 2H), 1.35-1.27 (m, 16H), 0.89 (t, *J* = 6.9, 3H).

Analogous procedures were used to prepare 2,5-dibromo-3-(2-(2-(2-methoxyethoxy)ethoxy)ethoxy)thiophene (**8**) from **4** (5.84 g, 14.5 mmol, 85%). ¹H NMR (500 MHz, CDCl₃, δ ppm): 6.79 (s, 1H), 4.15 (t, *J* = 3.9 Hz, 2H), 3.79 (t, *J* = 4.0 Hz, 2H), 3.72-3.71 (m, 2H), 3.67-3.64 (m, 4H), 3.56-3.54 (m, 2H), 3.38 (s, 3H).

Synthesis of ZnO nanoparticles

ZnO nanoparticles were synthesized according to previously reported procedures.⁴⁻⁵ In a 500 mL three-necked round bottom flask zinc acetate dihydrate (2.95 g, 13.4 mmol) was first dissolved in methanol (125 mL) at 70 °C. Then a solution of KOH (1.48 g, 23 mmol) in methanol (65 mL) was added dropwise over a period of 10-15 minutes. The reaction mixture was allowed to stir continuously at 65 °C for an additional 2.5 h. The reaction mixture was then allowed to cool to room temperature without stirring. The supernatant was decanted and the precipitate was washed twice with methanol (2 × 50 mL) to remove residual KOH. Finally, chloroform (10 mL), n-butanol (50 mL) and methanol (5 mL) were added to prepare a translucent dispersion of ZnO nanoparticles (~ 6 mg/mL). The solution was filtered using a 0.45 μm PVDF syringe filter prior to use.

Synthesis of methylammonium iodide

Methylammonium iodide was synthesized according to previously reported procedures.⁶⁻⁷ A methylamine solution (30 mL, 37% in EtOH) was added to 200 mL of ethanol and cooled to 0 °C in an

ice bath. Then 30 mL of hydriodic acid was added dropwise with vigorous stirring. The reaction mixture was allowed to stir continually at 0 °C for 2 h, after which the solvent was removed by evaporation under reduced pressure. The resulting residue was washed with diethyl ether (3 × 50 mL). The crude product was dissolved in ethanol (50 mL) and reprecipitated in diethyl ether to obtain methylammonium iodide as a white, crystalline powder. The powder was dried under high vacuum for 24 hours at 65 °C.

Table S1. Physical properties of P3HT and the various poly(3-alkoxythiophenes).

| Polymer | M_n (kDa) | M_w (kDa) | \bar{D} | λ_{max} (nm) | Contact Angle |
|----------------|-------------------------------|-------------------------------|-----------------------------|--|----------------------|
| P3OFHT | 7.6 | 10.3 | 1.3 | 495 | 135° |
| P3ODDT | 16.6 | 23.4 | 1.4 | 560 | 119° |
| P3OHT | 6.4 | 8.9 | 1.4 | 620 | 109° |
| P3HT | - | 50-70 | 2.1-2.5 | 445 | 103° |
| P3OEGT | - | - | - | 575 | 37° |

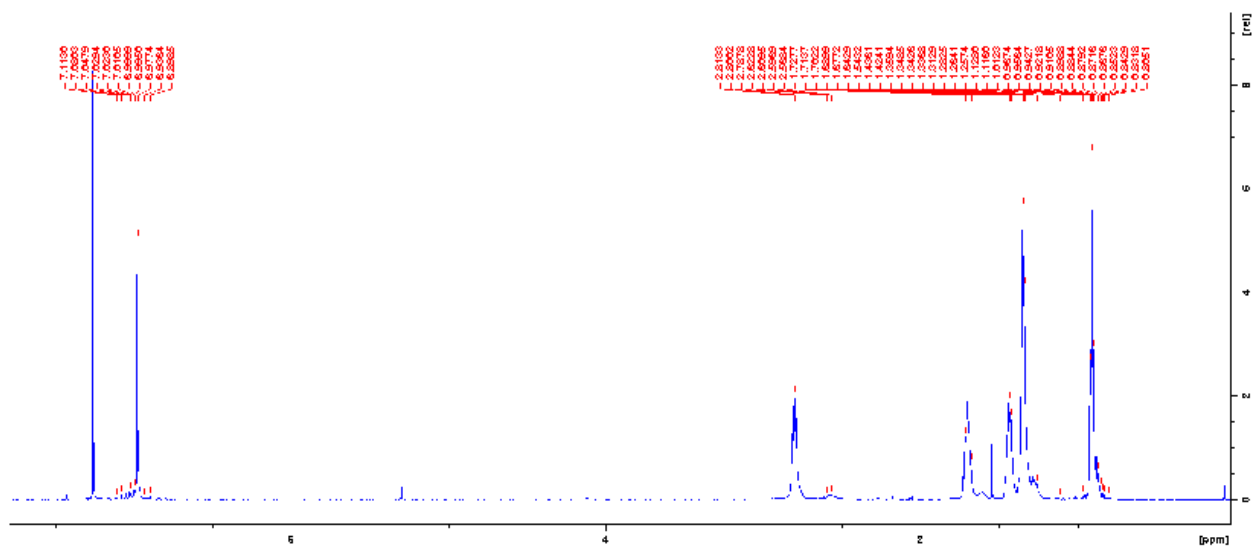


Fig. S1. ^1H NMR spectrum of P3HT in CDCl_3 .

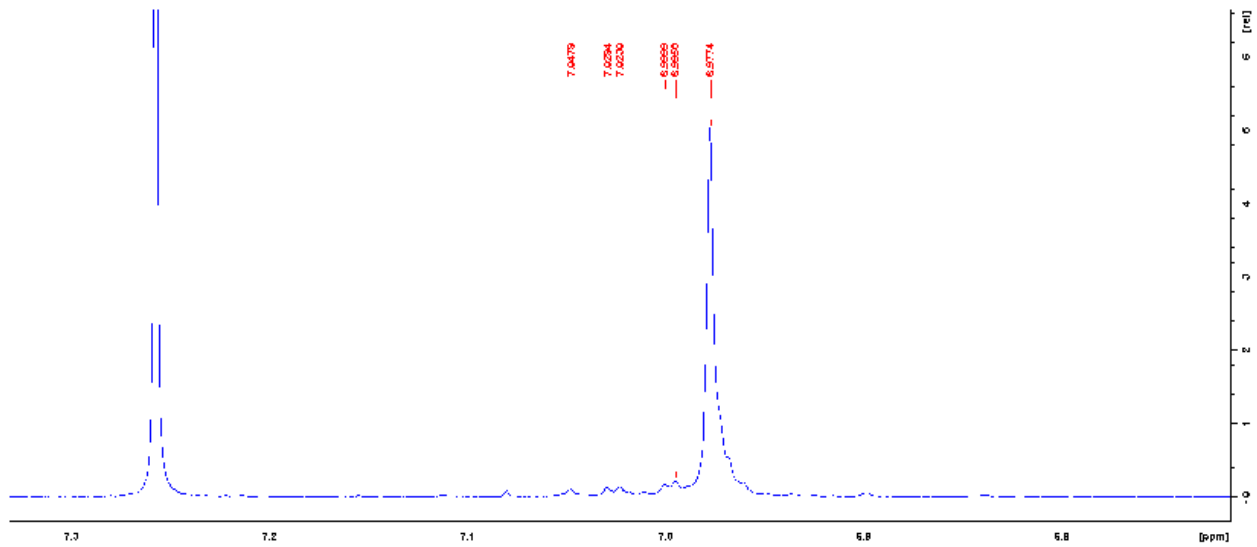


Fig. S2. Expanded view of the aromatic region in the ^1H NMR spectrum of P3HT in CDCl_3 .

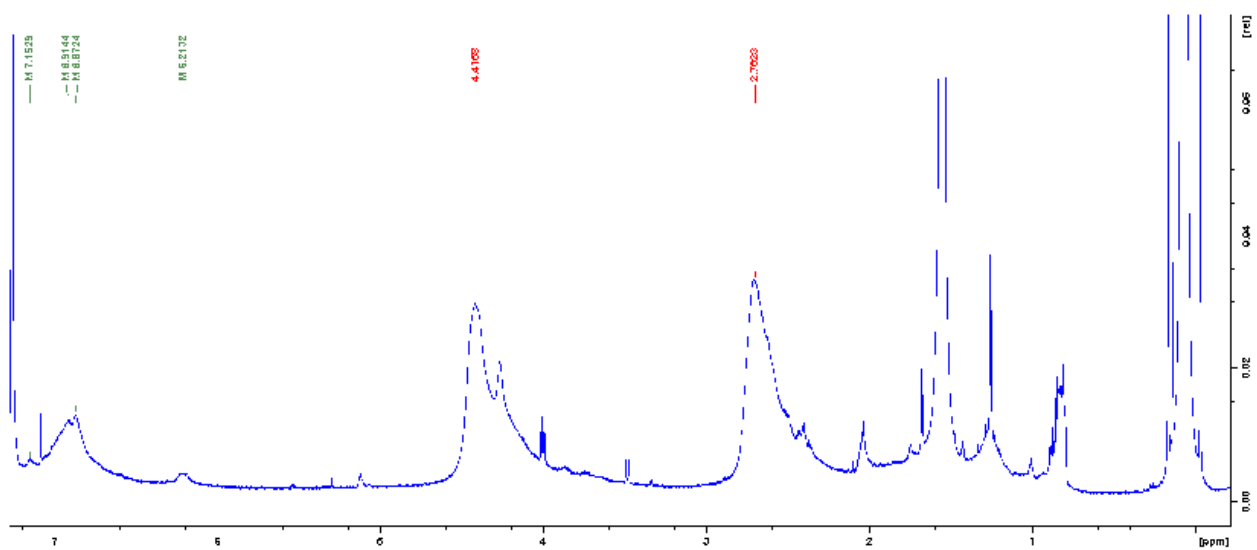


Fig. S3. ^1H NMR spectrum of P3OFHT in CDCl_3 .

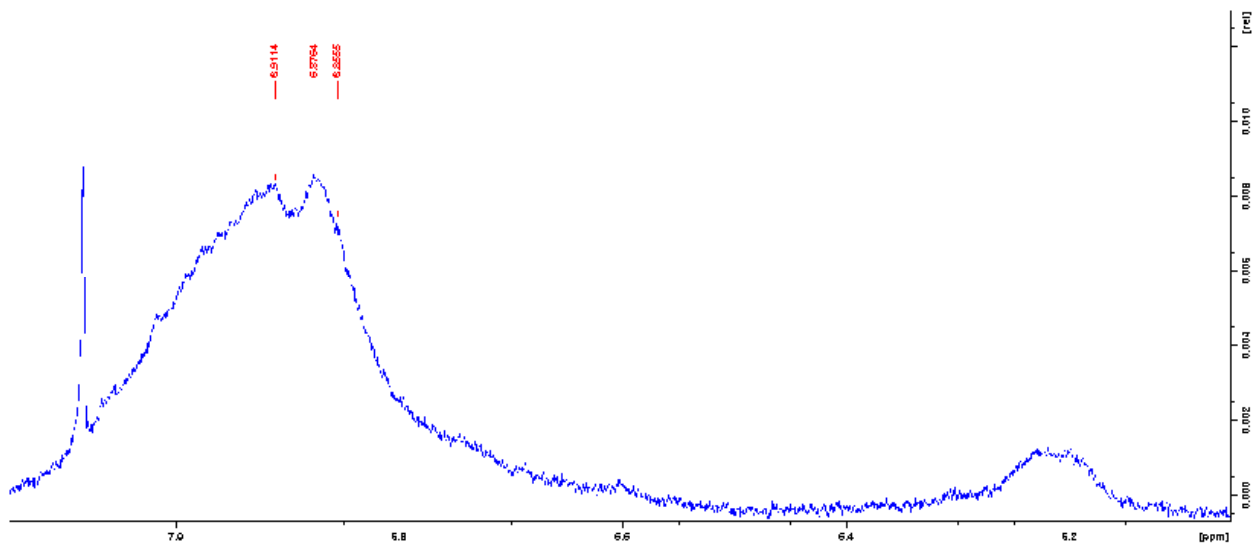


Fig. S4. Expanded view of the aromatic region in the ^1H NMR spectrum of P3OFHT in CDCl_3 .

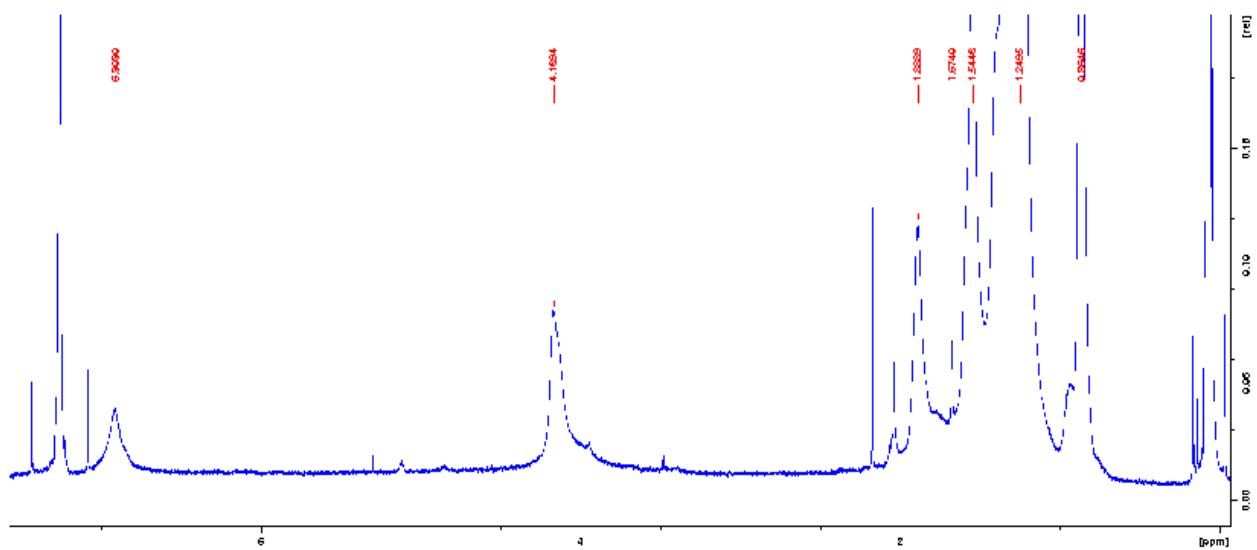


Fig. S5. ^1H NMR spectrum of P3ODDT in CDCl_3 .

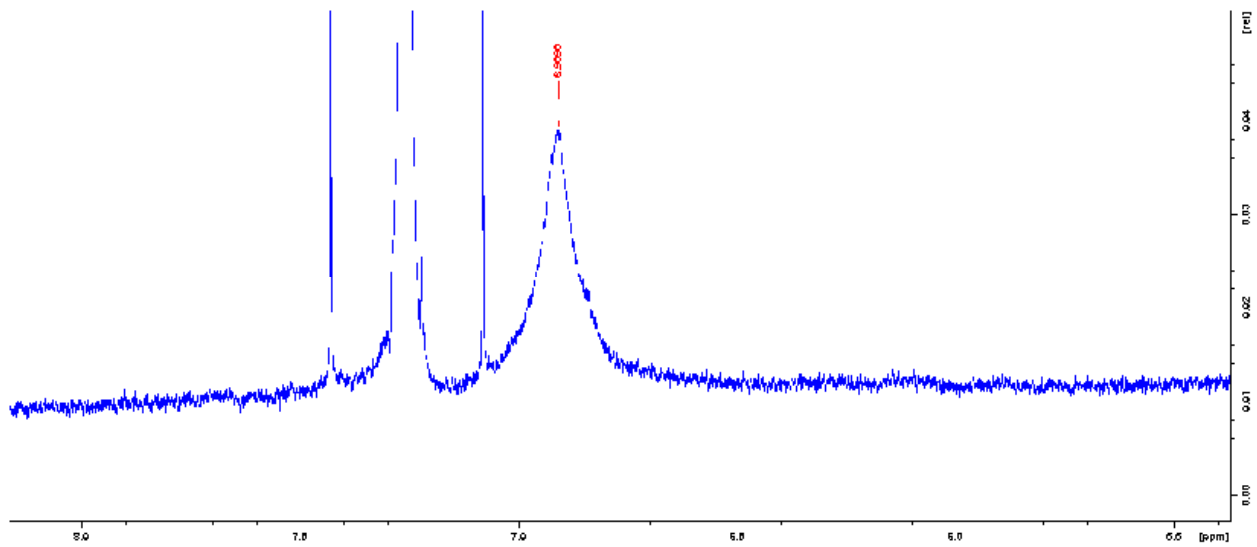


Fig. S6. Expanded view of the aromatic region in the ^1H NMR spectrum of P3ODDT in CDCl_3 .

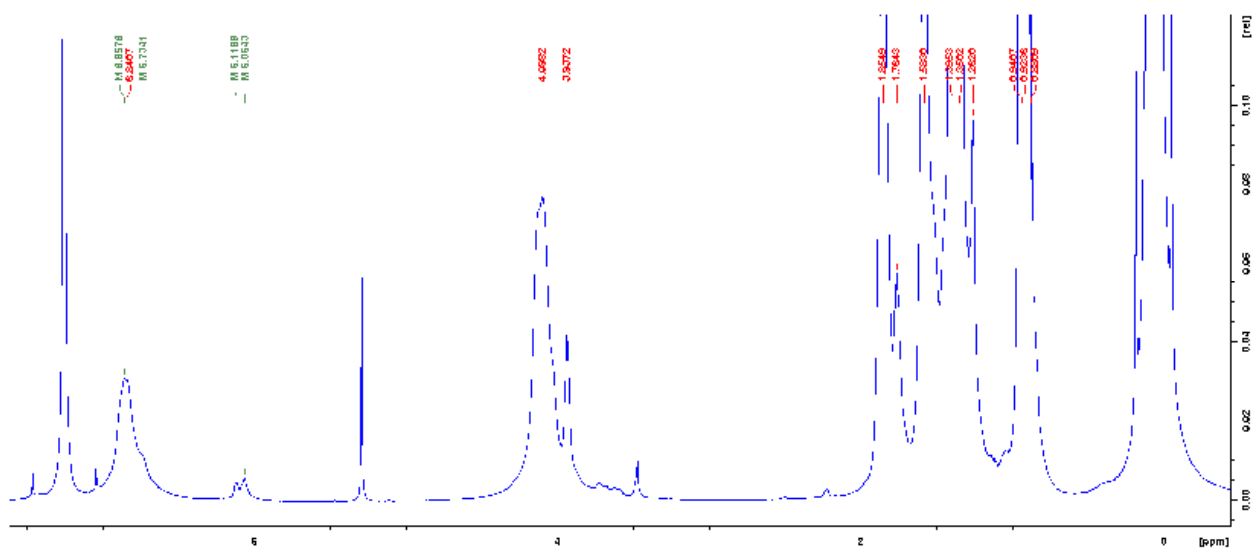


Fig. S7. ^1H NMR spectrum of P3OHT in CDCl_3 .

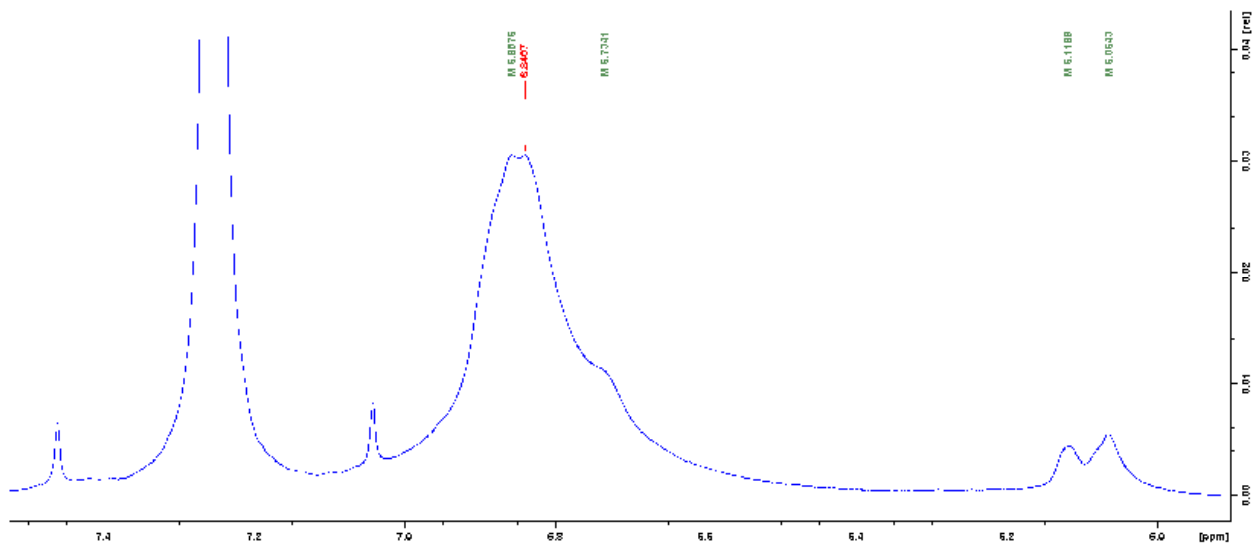


Fig. S8. Expanded view of the aromatic region in the ^1H NMR spectrum of P3OHT in CDCl_3 .

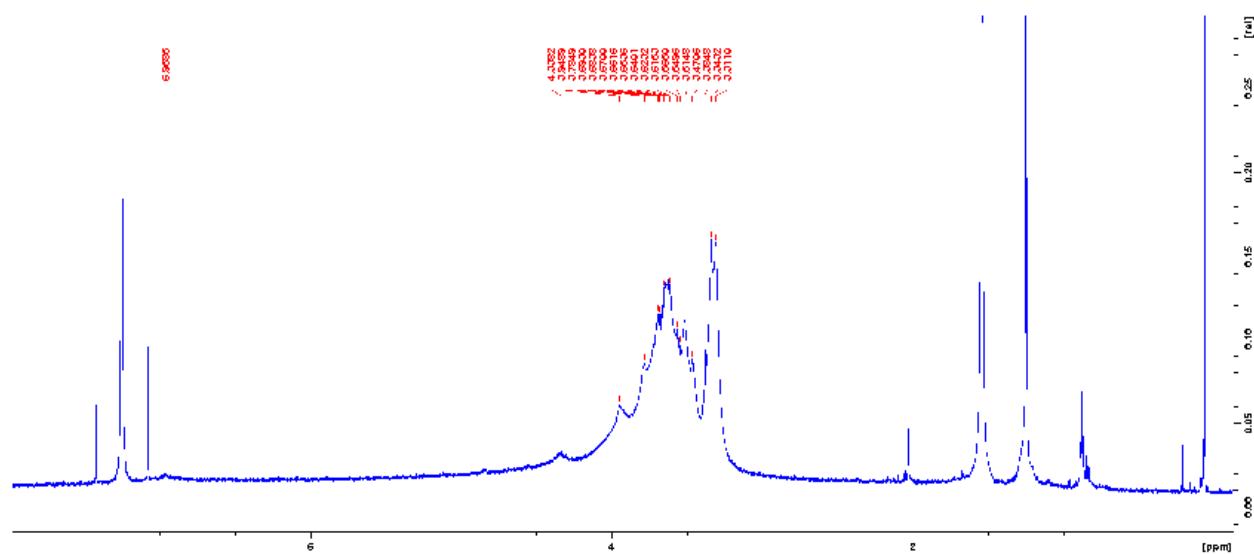


Fig. S9. ^1H NMR spectrum of P3OEGT in CDCl_3 .

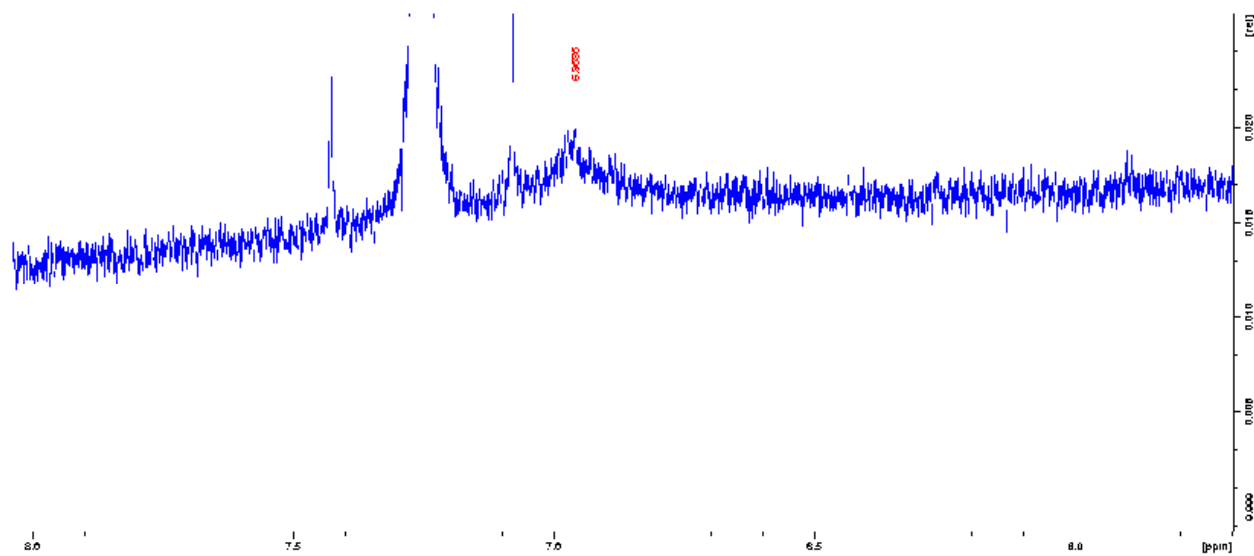


Fig. S10. Expanded view of the aromatic region in the ^1H NMR spectrum of P3OEGT in CDCl_3 .

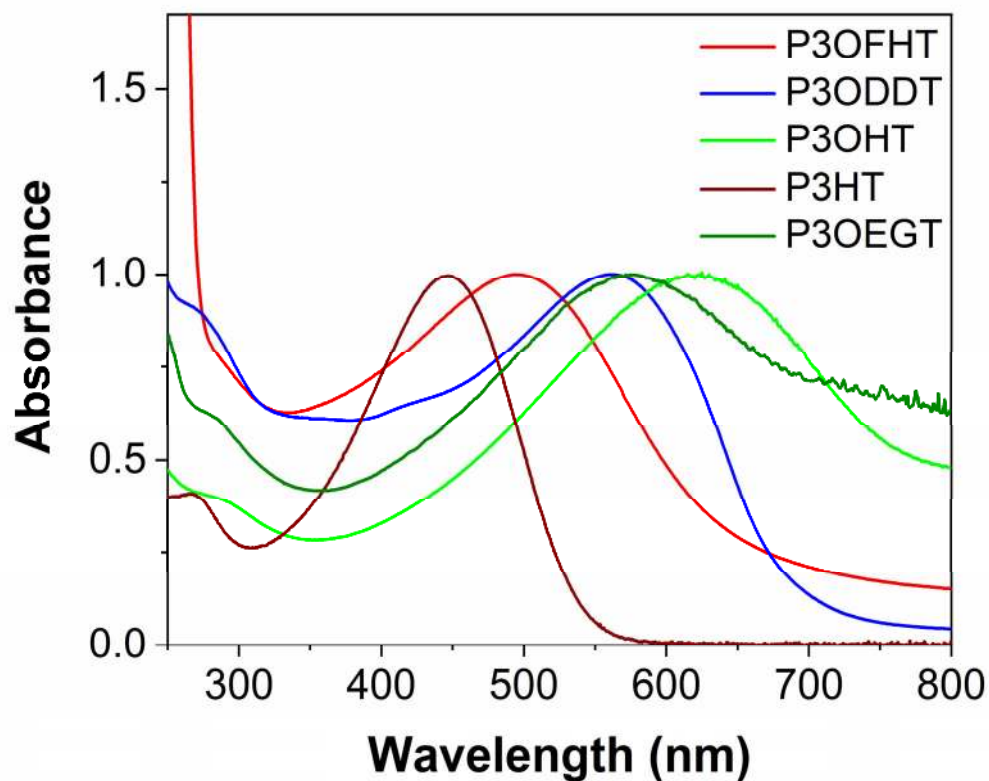


Fig. S11. Normalized UV/vis absorbance spectra of chloroform solutions of the various polymers.

Table S2. Average device performance parameters and number of cells tested (N) for ITO/ZnO/CH₃NH₃PbI₃/HTL/Ag devices. The associated uncertainties represent plus-or-minus one standard deviation from the mean.

| HTL | N | V_{oc} (V) | J_{sc} (mA/cm ²) | FF (%) | PCE (%) | Best PCE (%) |
|--------|-----|-----------------|--------------------------------|------------|----------------|--------------|
| P3OFHT | 27 | 0.87 ± 0.04 | 8.3 ± 1 | 23 ± 1 | 1.7 ± 0.3 | 3.3 |
| P3ODDT | 58 | 0.78 ± 0.03 | 13.0 ± 1 | 53 ± 2 | 5.1 ± 0.5 | 6.7 |
| P3OHT | 23 | 0.73 ± 0.05 | 12.4 ± 0.6 | 48 ± 2 | 4.3 ± 0.4 | 4.7 |
| P3HT | 30 | 0.93 ± 0.03 | 15.9 ± 1 | 64 ± 2 | 9.4 ± 0.3 | 10.2 |
| P3OEGT | 25 | 0.30 ± 0.05 | 4.0 ± 0.8 | 33 ± 3 | 0.4 ± 0.09 | 0.5 |

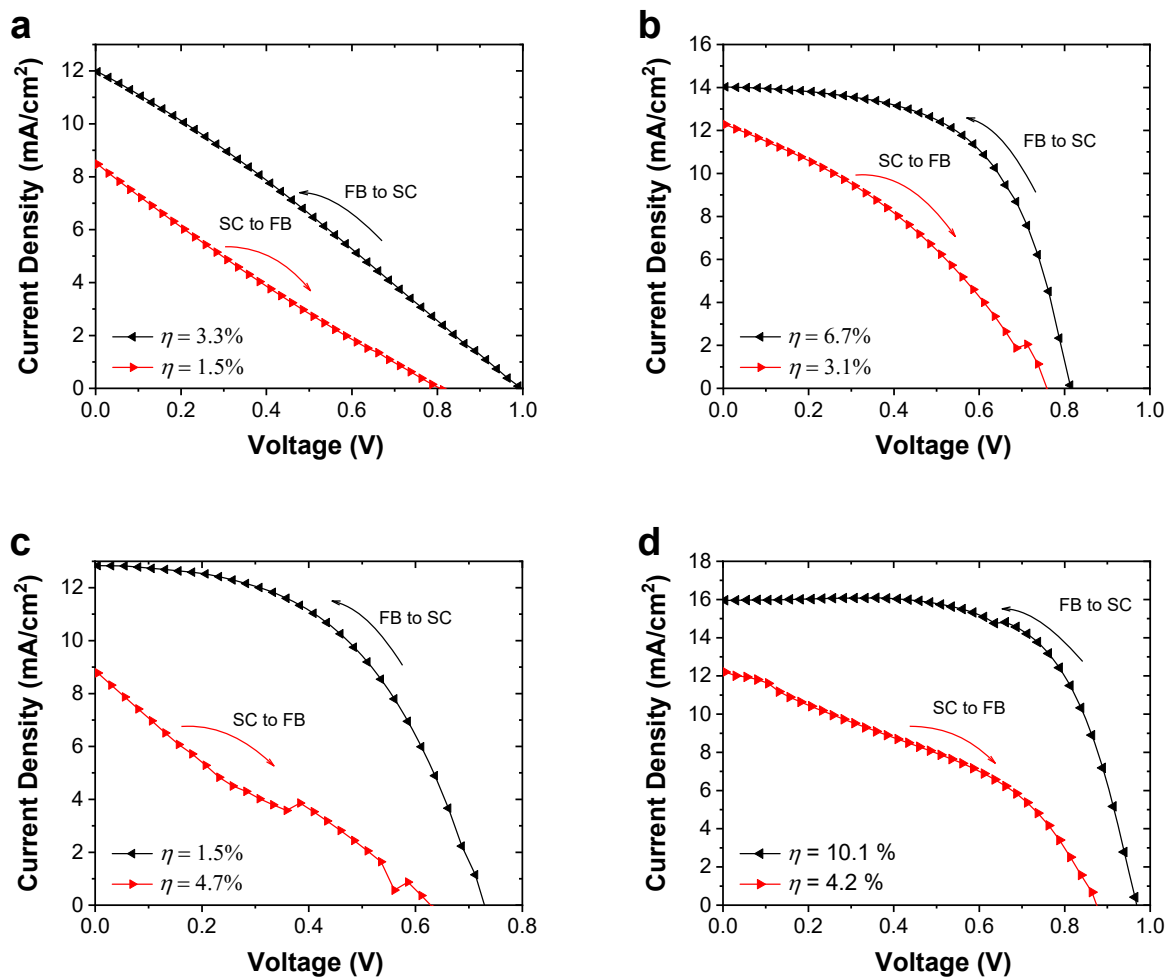


Fig. S12. J - V curves in both scan directions for devices with various HTLs: (a) P3OFHT, (b) P3ODDT, (c) P3OHT, and (d) P3HT. J - V curves were measured at a scan rate of $0.83 \text{ V}\cdot\text{s}^{-1}$.

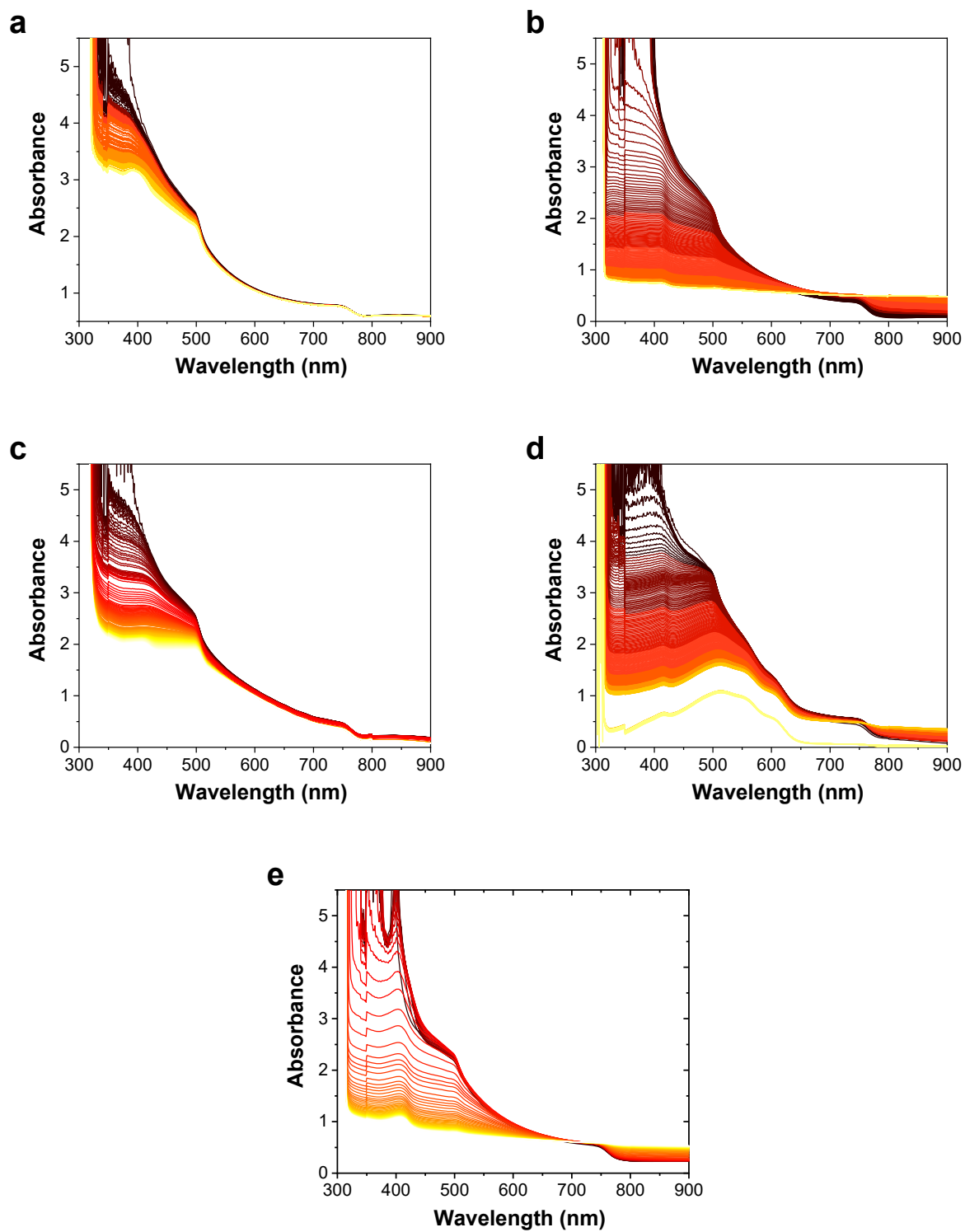


Fig. S13. UV/vis absorption spectra of glass/ $\text{CH}_3\text{NH}_3\text{PbI}_3$ /HTL films in a $\text{RH} = 98 \pm 2\%$ environment, acquired at 15 min intervals: (a) P3OFHT, (b) P3ODDT, (c) P3OHT, (d) P3HT, and (e) P3OEGT.

REFERENCES

1. Guo, X.; Watson, M. D., *Org. Lett.* **2008**, *10*, 5333.
2. Shi, C.; Yao, Y.; Yang; Pei, Q., *J. Am. Chem. Soc.* **2006**, *128*, 8980.
3. Sheina, E. E.; Khersonsky, S. M.; Jones, E. G.; McCullough, R. D., *Chem. Mater.* **2005**, *17*, 3317.
4. Beek, W. J. E.; Wienk, M. M.; Kemerink, M.; Yang, X.; Janssen, R. A. J., *J. Phys. Chem. B* **2005**, *109*, 9505.
5. Liu, D.; Kelly, T. L., *Nat. Photonics* **2013**, *8*, 133.
6. Lee, M. M.; Teuscher, J.; Miyasaka, T.; Murakami, T. N.; Snaith, H. J., *Science* **2012**, *338*, 643.
7. Kim, H.-S.; Lee, C.-R.; Im, J.-H.; Lee, K.-B.; Moehl, T.; Marchioro, A.; Moon, S.-J.; Humphry-Baker, R.; Yum, J.-H.; Moser, J. E.; Grätzel, M.; Park, N.-G., *Sci. Rep.* **2012**, *2*, 591.