Supporting Information

“Semi-Random” Multichromophoric rr-P3HT analogues for Solar Photon Harvesting

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Materials and Methods: All reagents from commercial sources were used without further purification, unless otherwise noted. All reactions were performed under dry N\textsubscript{2}, unless otherwise noted. All dry reactions were performed with glassware that was oven dried and then flamed under high vacuum and backfilled with N\textsubscript{2}. Flash chromatography was performed using Sorbent Technologies 60 (230-400 mesh) silica. Solvents were purchased from VWR and used without further purification except for THF which was dried over sodium/benzophenone before being distilled.
All compounds were characterized by $^1$H NMR (400 MHz) and $^{13}$C NMR (100 MHz) on a Mercury 400. MALDI data was obtained using an Applied Biosystems Voyager-DE STR mass spectrometer and 2,5-dihydroxybenzoic acid as matrix.

Polymer $^1$H NMRs (500 MHz) were obtained on a Varian VNMRS-500. For polymer molecular weight determination, polymer samples were dissolved in HPLC grade o-dichlorobenzene at a concentration of 1 mg/ml, briefly heated and then allowed to turn to room temperature prior to filtering through a 0.2 μm PTFE filter. SEC was performed using HPLC grade o-dichlorobenzene at a flow rate of 1 ml/min on one 300 x 7.8 mm TSK-Gel GMH_H column (Tosoh Corporation) at 70 °C using a Viscotek GPC Max VE 2001 separation module and a Viscotek TDA 305 RI detector. The instrument was calibrated vs. polystyrene standards (1,050 – 3,800 000 g/mol) and data was analyzed using OmniSec 4.6.0 software.

DSC traces were obtained using a Perkin Elmer DSC 7 with a scan rate of 10 °C/min. Sample size was ~ 3 mg and polymers were used as obtained after purification.

Cyclic voltammetry was collected using an EG&G instruments Model 263A potentiostat under the control of PowerSuite Software. A standard three electrode cell based on a Pt wire working electrode, a silver wire pseudo reference electrode (calibrated vs. Fc/Fc$^+$ which is taken as 5.1 eV vs. vacuum)$^1$ and a Pt wire counter electrode was purged with nitrogen and maintained under nitrogen atmosphere during all measurements. Acetonitrile was distilled over CaH$_2$ prior to use and tetrabutyl ammonium hexafluorophosphate (0.1 M) was used as the supporting electrolyte. Polymer films were made by repeatedly dipping the Pt wire in a 1% (w/w) chloroform or o-dichlorobenzene solution and dried under nitrogen prior to measurement.
UV-vis absorption spectra were obtained on a Perkin-Elmer Lambda 950 spectrophotometer. Thickness of the samples and GIXRD measurements were obtained using Rigaku Diffractometer Ultima IV in the reflectivity and grazing-incidence X-Ray diffraction mode, respectively. For thin film measurements polymers were spin coated onto pre-cleaned glass slides from chlorobenzene and dichlorobenzene solutions (7 mg/ml).

**Synthetic Procedures:**

**Scheme S1.**

2,5-Dibromo-3,4-dinitrothiophene (1) Compound was prepared through a previously reported procedure.² 80 ml sulphuric acid, 120 ml fuming sulphuric acid and 70 ml fuming nitric acid were combined in a 500 ml round bottom flask. The solution was cooled with an ice bath to 15 °C. 46.09 g (0.19 mol) 2,5-dibromothiophene was added slowly to keep the temperature below 30 °C. The solution turned orange and a precipitate formed. It was than warmed to r.t. and stirred for 3 h. The yellow precipitate was filtered and recrystallized from MeOH. 29.96 g (0.09
mol, 47 %) of light yellow solid was obtained. $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 112.81, MALDI 389.4 (331.9 + 57).

**3,4-Diaminothiophene hydrochloride (2)** Compound was prepared through a previously reported procedure. $^3$ 10.00 g (30 mmol) 2,5-dibromo-3,4-dinitrothiophene was suspended in 180 ml conc. HCl. The suspension was cooled with an ice bath. 24.90 g (200 mmol) tin was added in small portions to keep the temperature between 15 and 20 °C. The suspension was than stirred over night in an ice bath. The solid was separated by vacuum filtration and washed with Et$_2$O and acetonitrile. 4.85 g of 3,4-diaminothiophene hydrochloride was obtained as a white solid. $^1$H NMR (400 MHz, DMSO-d$_6$) $\delta$ 8.43 (br s, 6 H), 7.10 (s, 2H).

**Thieno [3,4-b]pyrazine (3)** Compound was prepared through a modified literature procedure. $^4$ 850 mg (4.54 mmol) 3,4-diaminothiophene hydrochloride was dissolved in 17 ml 5 % Na$_2$CO$_3$ (degassed) solution. 0.23 ml (5.00 mmol) glyoxal was added and the solution was left stirring for one hour. It was than extracted with Et$_2$O several times. The combined organic phases were washed with water and dried over Na$_2$SO$_4$. The solvent was evaporated in vacuo. The product was obtained as a dark brown solid (230 mg, 45 % yield). $^1$H NMR (400 MHz, CDCl$_3$) $\delta$ 8.51 (s, 1H), 8.03 (s, 1H); $^{13}$C NMR (100 MHz, CDCl$_3$) $\delta$ 144.44, 142.69, 117.92.

**5,7-Dibromo-thieno[3,4-b]pyrazine (4)** 200 mg (1.47 mmol) thieno [3,4-b]pyrazine 3 was dissolved in 30 ml DMF and cooled to -20 °C. 547 mg (3.08 mmol) N-bromosuccinimide was added in one portion. The reaction mixture was stirred for 2 h at -20 °C. Water was added and the precipitate was redissolved in diethyl ether. The organic phase was washed several times
with water, dried with MgSO₄ and the solvent was evaporated in vacuo. The crude product was purified using flash chromatography (DCM) to give a yellow solid (212 mg, 49 %). ¹H NMR (400 MHz, CDCl₃) δ 8.53 (s, 1H); ¹³C NMR (100 MHz, CDCl₃) δ 145.61, 140.60, 105.78.

Scheme S2.

2,1,3-Benzothiadiazole (5) 5.00 g (46.23 mmol) o-phenylenediamine was dissolved in 150 ml DCM and 26 ml triethylamine. 6.05 g (3.7 ml, 50.85 mmol) thionyl chloride was added slowly via addition funnel and the resulting mixture was refluxed for 20 h. After washing several times with 1 M HCl the organic phase was dried over MgSO₄ and the solvent was removed in vacuo. The product was obtained as a brown solid (3.33 g, 24.23 mmol, 53 %) and was used without further purification for the next step. ¹H NMR (400 MHz, CDCl₃) δ 8.01 (m, 2H), 7.60 (m, 2H).

4,7-Dibromo-2,13-benzothiadiazole (6) To a solution of 3.00 g (22.00 mmol) 2,1,3-benzothiadiazole in 45 ml HBr (48 %) a solution of 10 g (65.00 mmol) Br₂ in 30 ml HBr (48 %) was added very slowly. After complete addition the mixture was refluxed for 6 h during which time an orange precipitate formed. After cooling to r.t. a saturated solution of Na₂SO₃ was added and the suspension was filtered to obtain a light yellow solid. Recrystallization from hexanes in the presence of activated charcoal gave the product as a white solid (6.08 g, 20.68 mmol, 94 %).
$^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.73 (s, 2H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 152.93, 132.32, 113.89.

Scheme S3.

2-Bromo-3-hexylthiophene (7) 10.29 g (61.25 mmol) 3-hexylthiophene was dissolved in 83 ml acetic acid. 10.9 g (61.25 mmol) NBS was added in one portion. After all the NBS dissolved the reaction mixture turned yellow and warmed up to 35 °C. After approximately 10 min the color turned back to colorless and the solution was left to cool to rt. The reaction mixture was poured in water and extracted with Et$_2$O. The combined organic phases were washed multiple times with 10 % NaOH, dried over MgSO$_4$ and the solvent was removed in vacuo. The product was obtained as a clear oil after vacuum distillation (13.42 g, 88 %). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.18 (d, 1H), 6.79 (d, 1H), 2.56 (t, 2H), 1.57 (m, 2H), 1.31 (m, 6H), 0.89 (t, 3H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 142.02, 128.22, 125.06, 108.70, 31.59, 29.71, 29.39, 28.85, 22.55, 14.07.

2-Bromo-5-trimethyltin-3-hexylthiophene (8) Two 3-neck flasks were flame dried. In flask number one a LDA solution was prepared by dissolving 1.5 ml freshly distilled diisopropylamine
in 7.5 ml dry THF. The solution was cooled to -78 °C, 5.7 ml (9.13 mmol) n-BuLi was added dropwise and the mixture was stirred for 30 min at -78 °C. In flask number two 2.169 g (8.78 mmol) 2-bromo-3-hexylthiophene was dissolved in 16 ml dry THF and cooled to -78 °C. Then the contents of flask number one were transferred via cannula to flask number two. The reaction mixture was stirred for 45 min at -78 °C and then 10.79 ml (10.79 mmol) trimethyltin chloride was added slowly. The mixture was allowed to come to r.t. and stirred overnight. Water was added to quench the reaction and the aqueous phase was extracted several times with Et₂O. The combined organic phases were dried over MgSO₄ and the solvent was evaporated in vacuo. Vacuum distillation gave the product (2.843 g, 6.93 mmol, 79 %) as a colorless liquid. \(^1\)H NMR (400 MHz, CDCl₃) δ 6.85 (s, 1H), 1.57 (m, 2H), 1.32 (m, 6H), 0.89 (m, 3H), 0.35 (s, 9H). \(^{13}\)C NMR (100 MHz, CDCl₃) δ 143.14, 137.96, 136.32, 113.45, 31.67, 29.91, 29.29, 29.10, 22.64, 14.13, -8.19.

Scheme S4.

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\text{\textbf{2,5-Bis(trimethyltin)thiophene (9)}} \quad 1.40 \text{ g (16.7 mmol)} \text{ freshly distilled thiophene was combined with 4.06 g (35 mmol) TMEDA in a 100 ml 3-neck flask. 12.1 ml (35 mmol) n-Buli was added slowly and the solution was refluxed for 90 min. It was then cooled to -78 °C and 35 ml (35 mmol) Me₃SnCl was added. After stirring at -78 °C for 10 min the reaction mixture was brought to r.t. and left stirring over night. It was then poured in water and extracted with Et₂O.}
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The combined organic phases were washed with water, dried and the solvent was evaporated in vacuo. After recrystallization from EtOH a white solid was obtained (4.5239 g, 66 %). $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 7.38 (s, 2H), 0.37 (s, 18H).

Scheme S5.
**General Procedure for Stille Polymerization** All monomers were dissolved in dry DMF to give a 0.04 M solution. The solution was then degassed for 20 min. 4 mol% Pd(PPh₃)₄ was added in one portion, the solution was degassed for 10 additional minutes and then heated for 48 hours at 95 °C. Then the reaction mixture was cooled to r.t. and precipitated in MeOH. Purification was achieved via soxhlet extraction using MeOH, hexanes and chloroform for all polymers. For **P3HTT, P3HTT-BTD, P3HTT-TP** and **P3HTT-TP-BTD** an additional extraction with DCM was used prior to the CHCl₃ step. For **P3HTT-TP-BTD** chlorobenzene was used as a final soxhlet solvent. The polymer was then filtered over celite, reprecipitated in MeOH, vacuum filtered and dried. **P3HT**: Yield: 92 %, Mₙ = 17,178, PDI = 2.74. ¹H NMR (500 MHz, CDCl₃) δ 6.97 (s, 0.1H), 2.80 (m, 2H), 2.55 (s, 0.2H), 1.70 (m, 2H), 1.43 (m, 2H), 1.35 (m, 4H), 0.89 (m, 3H). **P3HTT**: Yield: 48 %, Mₙ = 47,853, PDI = 1.75. ¹H NMR (500 MHz, CDCl₃) δ 7.11 – 6.98 (m, 1.55 H), 2.80 (s, 2H), 2.57 (0.08H), 1.71 (s, 2.16H), 1.42, 1.34 (m, 7H), 0.92, (s, 3.4H). **P3HTT-BTD**: Yield: 84 %, Mₙ = 15,308, PDI = 2.45. ¹H NMR (500 MHz, CDCl₃) δ 7.98 (s, 0.25H), 7.82 (s, 0.25H), 7.08, 6.98 (m, 1H), 2.81 (m, 2H), 2.59 (s, 0.09H), 1.71 (s, 2.21H), 1.36 (m, 6.9H), 0.92 (s, 3.4H). **P3HTT-TP**: Yield: 73 %, Mₙ = 16,683, PDI = 2.35. ¹H NMR (500 MHz, CDCl₃) δ 8.52 (s, 0.22H), 7.44 (s, 0.22 H), 7.11 (m, 0.45H), 6.97 (s, 0.65H), 2.80 (s, 2H), 2.57 (s, 0.1H), 1.71 (s, 2.22H), 1.35-1.44 (m, 8H), 0.91 (s, 4H). **P3HTT-TP-BTD**: Yield: 66 %, Mₙ = 16,320, PDI = 2.05. ¹H NMR (500 MHz, Tetrachloroethane-d₂, 100 °C) δ 8.47 (s, 0.24H), 7.96 (s, 0.25H), 7.80 (s, 0.27H), 7.49 (s, 0.26H), 6.99-7.18 (m, 1H), 2.81 (s, 2H), 2.60 (s, 0.07H), 1.72 (s, 2.11H), 1.35-1.45 (m, 7.7H), 0.90 (s, 2.91H).
Figure S1. NMR of P3HT in CDCl₃.
Figure S2. NMR of P3HTT in CDCl₃.
Figure S3. NMR of P3HTT-BTD in CDCl$_3$. The peak at 1.55 is from trace amounts of H$_2$O (from CDCl$_3$) and the peak at 1.25 is an unknown impurity in CDCl$_3$. 
Figure S4. NMR of P3HTT-TP in CDCl₃.
Figure S5. NMR of P3HTT-TP-BTD in Tetrachloroethane-d$_2$
Figure S6. CV traces for the oxidation of P3HT, P3HTT, P3HTT-BTD, P3HTT-TP and P3HTT-TP-BTD.
Figure S7. DSC traces of P3HTT and P3HTT-BTD.
Device fabrication and characterization ITO-coated glass substrates (20 Ω/ , Thin Film Devices Inc.) were sequentially cleaned by sonication in detergent, de-ionized water, tetrachloroethylene, acetone, and isopropyl alcohol, and dried in a nitrogen stream. A thin layer of PEDOT:PSS (Baytron® P VP AI 4083, filtered at 0.45 μm) was first spin-coated on the pre-cleaned ITO-coated glass substrates and baked at 130°C for 60 minutes under N₂. Separate solutions of polymer and PC₆₀BM were prepared in dichlorobenzene or trichlorobenzene solvents. The solutions were stirred for 24 hrs before they were mixed at the desired ratios and stirred for 24 hrs to form a homogeneous mixture. Subsequently, the polymer:PC₆₀BM active layer was spin-coated on top of the PEDOT:PSS layer. The P3HTT-TP:PC₆₀BM layer was spin cast from a solution of 1.7% octanedithioli (by volume) in dichlorobenzene containing 7 mg/ml P3HTT-TP and 5.53 mg/ml PC₆₀BM. The solution of P3HTT-BTD:PC₆₀BM was prepared by dissolving the polymer (7 mg/ml) and PCBM (35 mg/ml) in a dichlorobenzene solvent. The solution of P3HTT-TP-BTD:PC₆₀BM was prepared by dissolving the polymer (10 mg/ml) and PCBM (8 mg/ml) in trichlorobenzene. The substrates with P3HTT-TP-BTD:PC₆₀BM blend were annealed at 100°C for 30 minutes under vacuum and cooled to room temperature prior to electrode deposition. At the final stage, the substrates were pumped down to high vacuum (< 7×10⁻⁷ Torr) and aluminum (100 nm) was thermally evaporated at 2-3 Å/sec using a Denton Benchtop Turbo IV Coating System onto the active layer through shadow masks to define the active area of the devices as of 4.9 mm². Thermal annealing of P3HTT-BTD:PC₆₀BM blends was carried out by directly placing the completed devices in the vacuum oven for 10 min at 100°C. After annealing, the devices were cooled down to the room temperature before measurements were carried out. P3HTT-TP:PC₆₀BM BHJ solar cell was tested without thermal treatment.
The current-voltage (J-V) characteristics of photovoltaic devices were measured under ambient conditions using a Keithley 2400 source-measurement unit. An Oriel® Sol3A class AAA solar simulator with xenon lamp (450 Watt) and an AM1.5 G filter was used as the solar simulator. An Oriel PV reference cell system 91150V was used as the reference cell. To calibrate the light intensity of the solar simulator, the power of the xenon lamp was adjusted to make the short-circuit current \( J_{SC} \) of the reference cell under simulated sun light as high as it was under the calibration condition.

**Mobility measurements** Polymer mobility was measured using a hole-only device configuration of ITO/PEDOT:PSS/Polymer/Al in the space charge limited current regime. The devices preparations were the same as described above for solar cells. The dark current was measured under ambient conditions. At sufficient potential the mobilities of charges in the device can be determined by fitting the dark current to the model of SCL current and described by:

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J_{SCLC} = \frac{9}{8} \varepsilon_R \varepsilon_0 \mu \frac{V^2}{L^3}
\]

where \( J_{SCLC} \) is the current density, \( \varepsilon_0 \) is the permittivity of space, \( \varepsilon_R \) is the dielectric constant of the polymer (assumed to be 3), \( \mu \) is the zero-field mobility of the majority charge carriers, \( V \) is the effective voltage across the device \( (V = V_{applied} - V_{bi} - V_r) \), and \( L \) is the polymer layer thickness. The series and contact resistance of the device (25-35 \( \Omega \)) was measured using a blank (ITO/PEDOT/Al) configuration and the voltage drop due to this resistance \( (V_r) \) was subtracted from the applied voltage. The built-in voltage \( (V_{bi}) \), which is based on the relative work function difference of the two electrodes, was also subtracted from the applied voltage. The built-in
voltage can be determined from the transition between the ohmic region and the SCL region and is found to be about 1 V. Polymer film thickness was measured using GIXRD.

Figure S8. J-V curves of solar cells based on P3HT, P3HTT-TP, P3HTT-BTD and P3HTT-TP-BTD.

References