Electronic Supplementary Material (ESI) for Polymer Chemistry.

Supporting Information

Chain-Growth Polycondensation of Perylene Diimide-based copolymers: a New Route to regio-regular Perylene Diimide-Based Acceptors for All-Polymer Solar Cells and n-type transistors.

Wei Liu, Roman Tkachov, Volodymyr Senkovskyy, Marcel Schubert, Zhao Wei, Antonio Facchetti,* Dieter Neher and Anton Kiriy[1]*

Instrumentation

^{1}H NMR spectra were recorded on a Bruker Avance III 500 spectrometer operating at 500.13 MHz for ^{1}H using a 5 mm ^{1}H/^{13}C/^{19}F/^{31}P gradient probe. The samples were measured in $C_2D_2Cl_4$ as solvent at 120°C. The spectra were referenced on the residual solvent peak ($\delta(^1H) = 5.98$ ppm). Signal assignments were deduced from chemical shift values, J coupling constants and NOESY/ROESY measurements giving trough-space correlations to distinguish $H_{5/11}$ and $H_{6/12}$ and H_a and H_b, respectively.

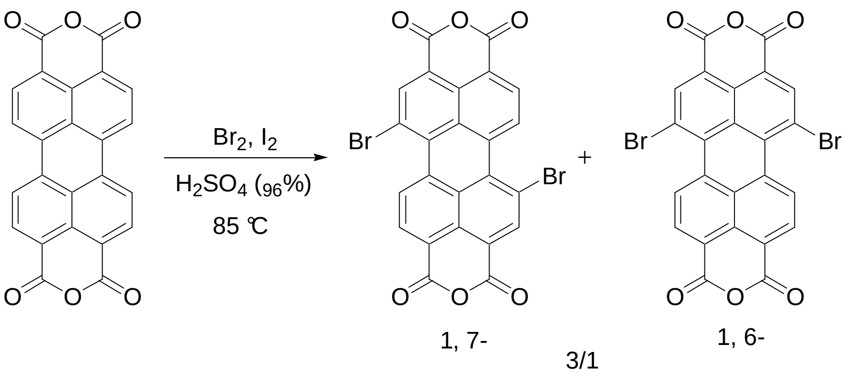
The ESR measurements were conducted in the X-band using a Bruker EMX spectrometer and a rectangular cavity (ER4104OR). The modulation frequency was 100 kHz.

GPC measurements were carried out on an Agilent 1100 Series (Agilent, USA) normal-temperature size exclusion chromatograph, equipped with refractive index detector and one column PL Gel MIXED-B (Polymer Laboratories, UK). Chloroform was used as eluent and the flow rate was 1 mL/min. Number average molecular weights (M_n) and polydispersity indexes (PDI) of obtained polymers were determined based on calibration with polystyrene standards obtained from Polymer Standards Service (PSS, Germany).

Materials.

Active zinc was prepared by the reduction of $ZnCl_2$ with sodium naphthalenide.[1] Tetrahydrofuran (THF) was distilled over sodium benzophenone ketyl. All other chemicals were purchased from Aldrich and used as received.

Synthesis of Br-TPDIT-Br.



1 **2a** **2b**

Step 1:
Ref: F. Würthner, V. Stepanenko, *J. Org. Chem.* 2004, *69*, 7933.
A mixture of **1** (31.3 g, 80 mmol) and 270 mL 96% sulfuric acid was stirred for 12 h at room temperature, and subsequently iodine (0.77 g, 3 mmol) was added. The reaction mixture was heated to 85 C. And bromine (28.2 g, 9 mL, 176 mmol) was added dropwise over a time period of 8 h. The mixture was heated overnight at 85 C and then cooled to room temperature. The excess bromine was removed by gentle stream of air. Water (65 mL) was added carefully. The resulting precipitate was separated by filtration through a G4 funnel, washed with 86% sulfuric acid (300 g) and large amount of water, some acetone (about 50 mL), and dried in a vacuum to give mixture of 2a and 2b (3/1 ratio by NMR) as a red powder.

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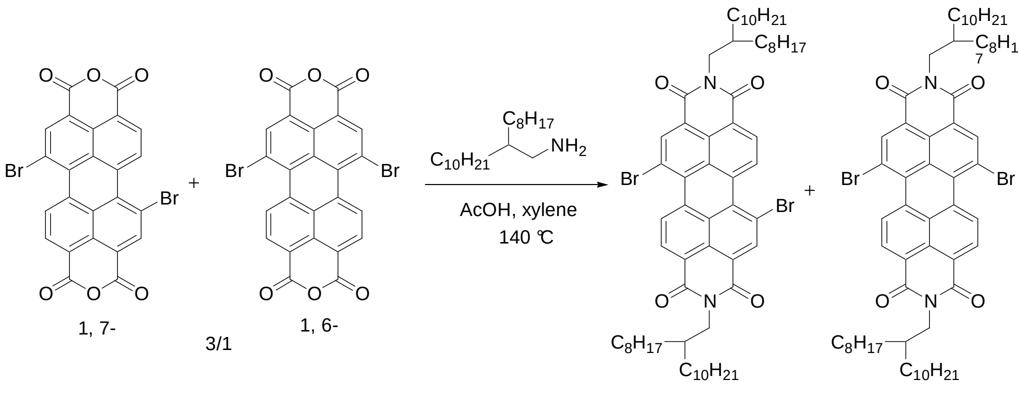
[1] Sodium naphthalenide was prepared according to the protocol published in the work of Rieke with the only difference that sodium was used instead of lithium: Chen, T.; Wu, X.; Rieke, R. D. *J. Am. Chem. Soc.* **1995**,*117*, 233-244.

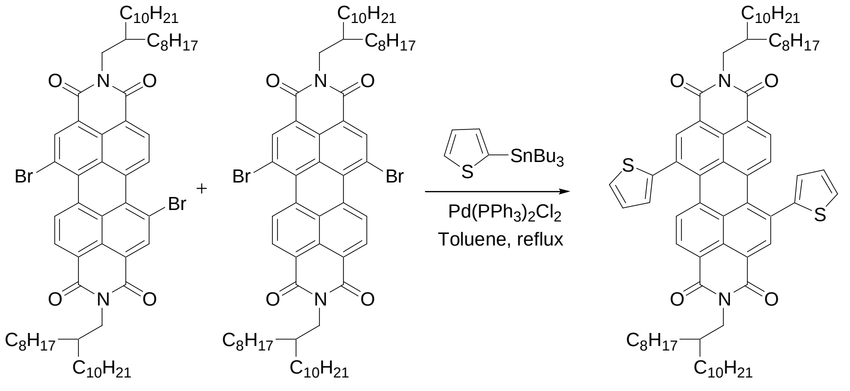


3a **3b**

Step 2:

Ref: JACS, 2009, 131, P8, sup.

A mixture of **2** (25.9 g, 47 mmol, 1 equiv., mixture of isomers), 2-octyldodecylamine (35 g, 117.5 mmol, 2.5 equiv.), xylene (160 mL), and propionic acid (52 mL) was stirred at 145 C for 4 h. After cooling to room temperature, most of solvents were removed by rotary evaporator, and the residue was purified by column chromatography on silica gel with a mixture of hexane:ethyl acetate (40:1 to 20:1, v/v) as eluent, affording 3 (mixture of isomers) as a red solid product.



1,7-H-TPDIT-H

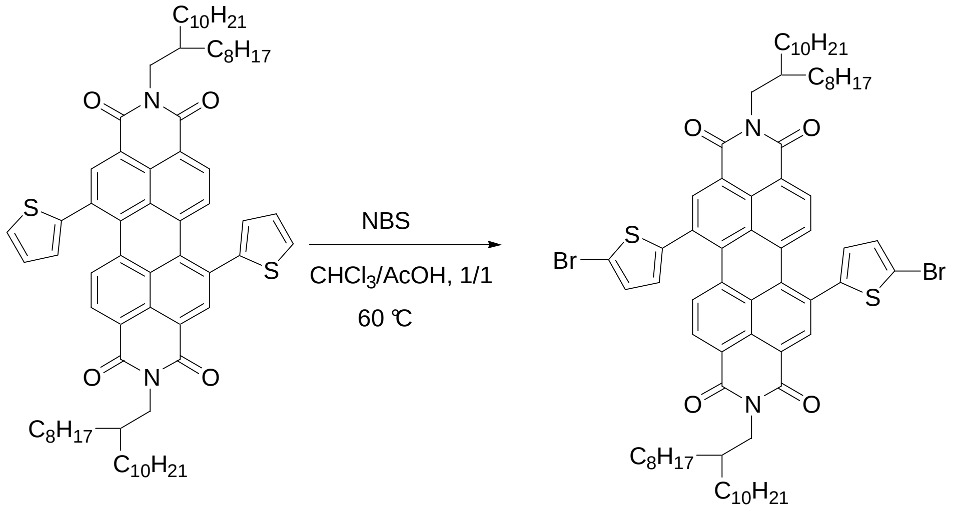
Step 3:

Ref: Adv. Mater. 2012, 24, P3678.

Under argon, a mixture of **3** (23.17 g, 20.9 mmol, 1 equiv.), 2-tributylstannyl-thiophene (23.4 g, 62.7 mmol, 3 equiv.), and Pd(PPh3)2Cl2 (0.74 g, 0.05 equiv.) in anhydrous toluene (250 mL) was stirred at reflux overnight. After cooled to room temperature, solvent was removed by rotary evaporator, and the residue was purified by column chromatography on silica gel with a mixture of hexane:ethyl acetate (40:1 v/v) as eluent, affording a purple solid. The solid was then recrystallized in ethanol to get pure **1,7-TPDIT** (20 g).

^{1}H NMR ($CDCl_3$, 303 K): 8.65 (2H, s, $H_{2/8}$), 8.24 (2H, d, $H_{5/11}$), 8.06 (2H, d, $H_{6/12}$), 7.50 (2H, dd with $^3J_{HH}$ = 5.2 Hz and $^4J_{HH}$ = 1.2 Hz, H_c), 7.32 (2H, dd with $^3J_{HH}$ = 3.5

Hz and $^{4}J_{HH}$ = 1.2 Hz, H_a), 7.19 (2H, dd with $^{3}J_{HH}$ = 5.2 Hz and $^{3}J_{HH}$ = 3.5 Hz, H_b), 4.11 (4H, d, NCH_2), 1.99 (2H, m, CH), 1.5 – 1.1 (64H, CH_2), 0.86 ppm (12H, CH_3).
^{1}H NMR ($C_2D_2Cl_4$, 393 K): 8.71 (2H, s, $H_{2/8}$), 8.29 (2H, d, H $_{5/11}$), 8.18 (2H, d, $H_{6/12}$), 7.57 (2H, dd with $^{3}J_{HH}$ = 5.2 Hz and $^{4}J_{HH}$ = 1.2 Hz, H_c), 7.35 (2H, dd with $^{3}J_{HH}$ = 3.5 Hz and $^{4}J_{HH}$ = 1.2 Hz, H_a), 7.24 (2H, dd with $^{3}J_{HH}$ = 5.2 Hz and $^{3}J_{HH}$ = 3.5 Hz, H_b), 4.17 (4H, d, NCH_2), 2.10 (2H, m, CH), 1.6 – 1.2 (64H, CH_2), 0.92 ppm (12H, CH_3).



Step 4:

1,7-H-TPDIT-H (9.01g, 8.12 mmol, 1 equiv.) was dissolved in $CHCl_3$ (100 mL), acetic acid (50 mL) was added, and NBS (4.34 g, 24.36 g, 3 equiv.) was added. Then the mixture was heated to 60 C and stirred overnight. Most of the solvent removed by rotary evaporator, the left acetic acid was poured out and the residue was washed with methanol and purified by column chromatography on silica gel with a mixture of hexane:ethyl acetate (40:1 v/v) as eluent, affording pure **Br-TPDIT-Br** as a purple solid as a pure1,7-isomer. The solid was then recrystallized in ethanol.
^{1}H NMR ($CDCl_3$, 303 K): 8.60 (2H, s, $H_{2/8}$), 8.33 (2H, d, $H_{5/11}$), 8.20 (2H, d, $H_{6/12}$), 7.16 (2H, d with $^{3}J_{HH}$ = 5.2 Hz, H_b), 7.11 (2H, d, H_a), 4.12 (4H, d, NCH_2), 1.99 (2H, m, CH), 1.5 – 1.1 (64H, CH_2), 0.86 ppm (12H, CH_3).
^{1}H NMR ($C_2D_2Cl_4$, 393 K): 8.66 (2H, s, $H_{2/8}$), 8.38 (2H, d, $H_{5/11}$), 8.31 (2H, d, $H_{6/12}$), 7.20 (2H, d with $^{3}J_{HH}$ = 5.2 Hz, H_b), 7.13 (2H, d, H_a), 4.18 (4H, d, NCH_2), 2.10 (2H, m, CH), 1.6 – 1.2 (64H, CH_2), 0.92 ppm (12H, CH_3).

Table S1. Polycondensation results (initial concentration of 6.7 mM).

Entry /batch	Purity of Br-TPDIT-Br, %	[Br-TPDIT-Br/Zn]$_o$/[Pd]	*t*	**P** [%]	M_n^{GPC} [gmol^{-1}]	PDI
1/A	95	100/1	2 h	91	15 000	1.8
2/B	99	20/1	2 min	27	11 900	1.3
3/B	99	20/1	5 min	62	16 100	1.5
4/B	99	20/1	10 min	74	18 300	1.7
5/B	99	20/1	20 min	78	21 600	2.0
6/B	99	20/1	40 min	85	23800	2.2
7/B	99	20/1	2h	92	25 100	2.3
8/B	99	100/1	10 min	24	10 800	1.3
9/B	99	100/1	20 min	38	12 500	1.4
10/B	99	100/1	40 min	61	17 800	1.6
11/B	99	100/1	80 min	72	19 200	1.8
12/B	99	100/1	200 min	78	19 900	1.9
13/B	99	100/1	10 h	94	25 100	2.1

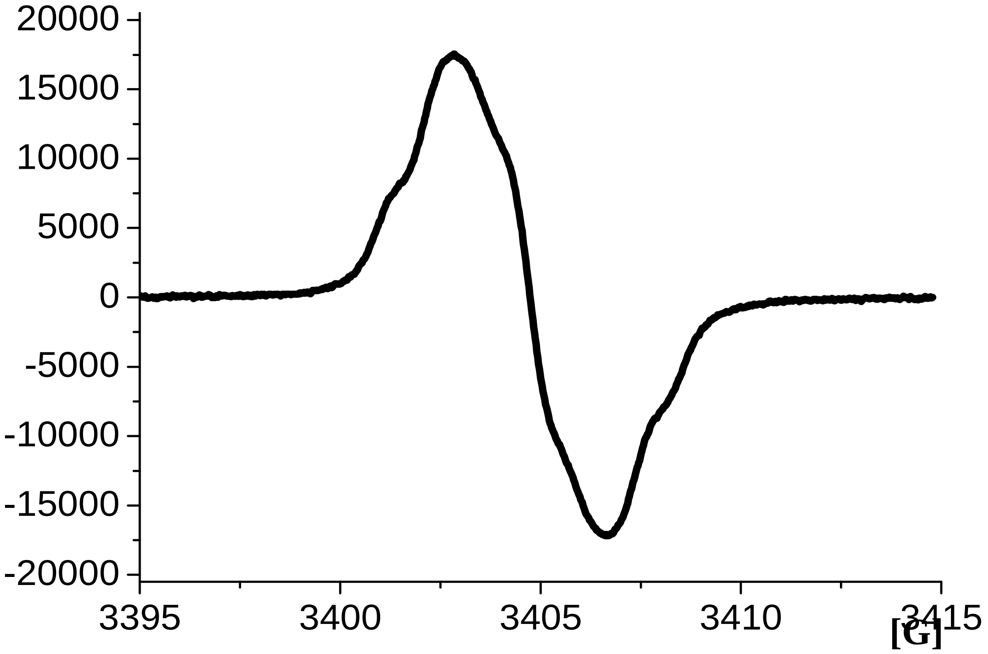


Figure S1. EPR spectrum of the radical anion of Br-TPDIT-Br/Zn in THF solution.

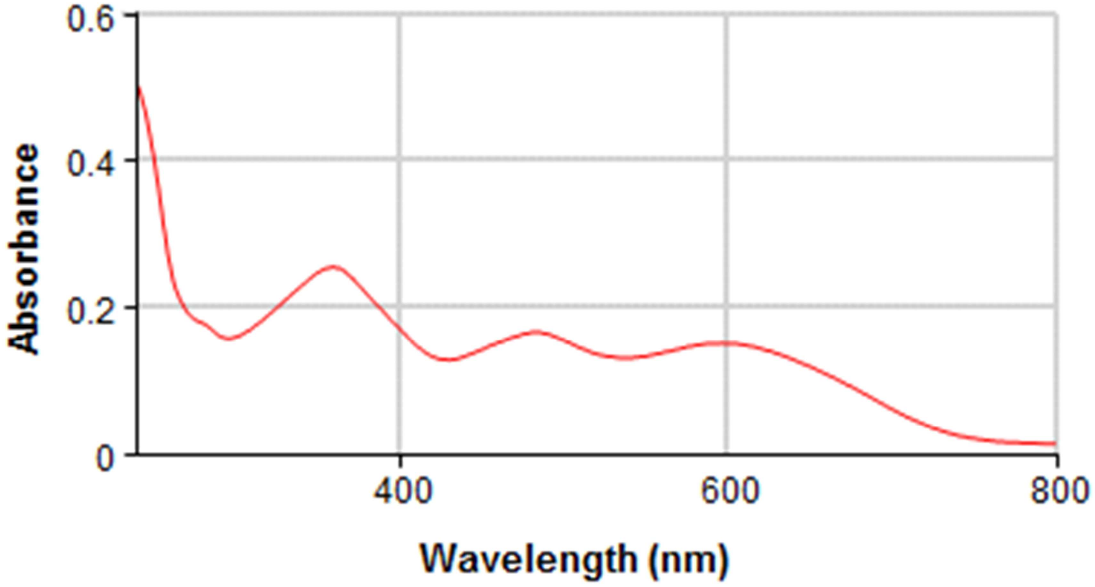


Figure S2. UV-vis absorption spectrum of PPDIT2 taken in chloroform ([PPDIT2]=1 mg/L).