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Facile Approach to Perylenemonoimide with Short Side Chains for Nonfullerene Solar Cells

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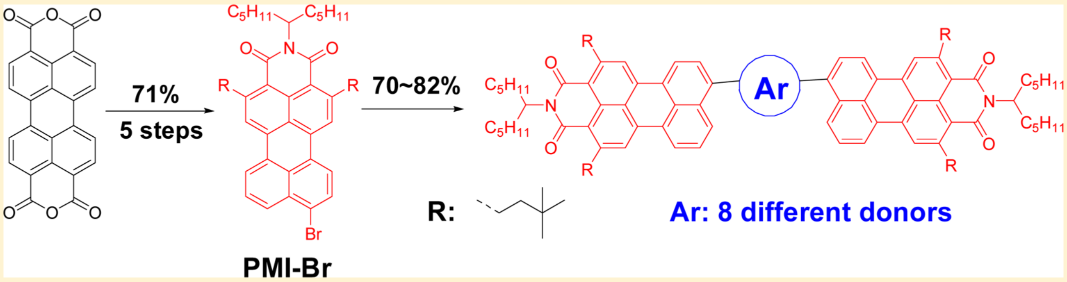
Supporting Information



ABSTRACT: Electron acceptors based on perylene monoimide (PMI) are rare due to the synthetic challenge. Herein, starting from commercially available perylene dianhydride, brominated perylene monoimide (PMI-Br) with short side chains and good solubility was efficiently synthesized in a high overall yield of 71%. With PMI-Br as the intermediate, acceptor−donor−acceptor type electron acceptors with low-lying LUMO energy levels and strong visible absorption were successfully obtained. The nonfullerene bulk heterojunction solar cells based on these acceptors were fabricated with the highest PCE of 1.3%.

Perylene diimides (PDI) and their derivatives as electron acceptors (n-type semiconductors, electron transporting materials) demonstrate various applications in nonfullerene bulk heterojunction (BHJ) solar cells,[1] organic field-effect transistors (OFET),[2] and self-assembly systems.[3] However, perylene monoimide (PMI, Figure 1) with the similar structure, absorption,[4,5] and energy levels[6] as PDI is paid only limited attention. The main reason lies in difficult modification of PMI.[7,8]

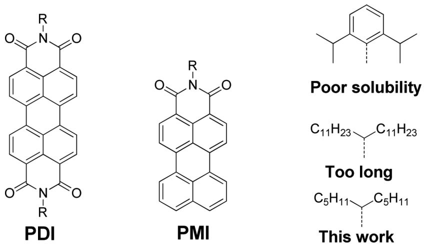


Figure 1. Structures of PDI and PMIs with 2,6-diisopropylphenyl, 1-undecyldodecyl, and 1-pentylhexyl side chains.

PMI derivatives have been used as electron acceptors in nonfullerene BHJ solar cells with the highest power conversion efficiency (PCE) of 2.3%.[9,10] They also showed applications in the field of dyes,[5,11] fluorescent probes,[12,13] self-assemblies,[14−16] organic light-emitting diodes,[17] and molecular fluorophores.[18,19] Since PMI has advantages of PDI such as high stability, low-lying lowest unoccupied molecular orbital (LUMO) energy level, and strong visible absorption,[4,5] it deserves more important applications in semiconductors.[6,20,21]

Due to serious $\pi-\pi$ stacking, PMI has poor solubility, which makes its purification and further application difficult.[22] To increase solubility, Muellen et al. introduced bulky 1-undecyldodecyl to PMI. However, long insulated chains decrease the crystallization of the compound and limit the efficient charge transfer.[23] The corresponding PMI derivatives do not show any performance in the OFET or BHJ solar cells. In addition, it started from commercially unavailable *N*-(2,6-diisopropylphenyl)-PMI whose conversion to soluble PMI is in low yield of 17%. So we are interested in efficient synthesis of soluble PMI with short alkyl chains and its further applications in the optoelectronic field.

Herein, starting from commercially available perylene dianhydride, soluble brominated PMI (PMI-Br) with short side chains was synthesized in five steps with an overall high yield of 71%. 1-Pentylhexyl group was chosen as the side chain due to its excellent application in PDI-based acceptors.[24] The short branched chains not only increase the solubility of the conjugated cores but also keep their effective intermolecular charge transfer.[25] Since the solubility of PMI with one 1-pentylhexyl group is still limited, we introduced 3,3-dimethylbutyl groups at its *ortho* positions, through which a

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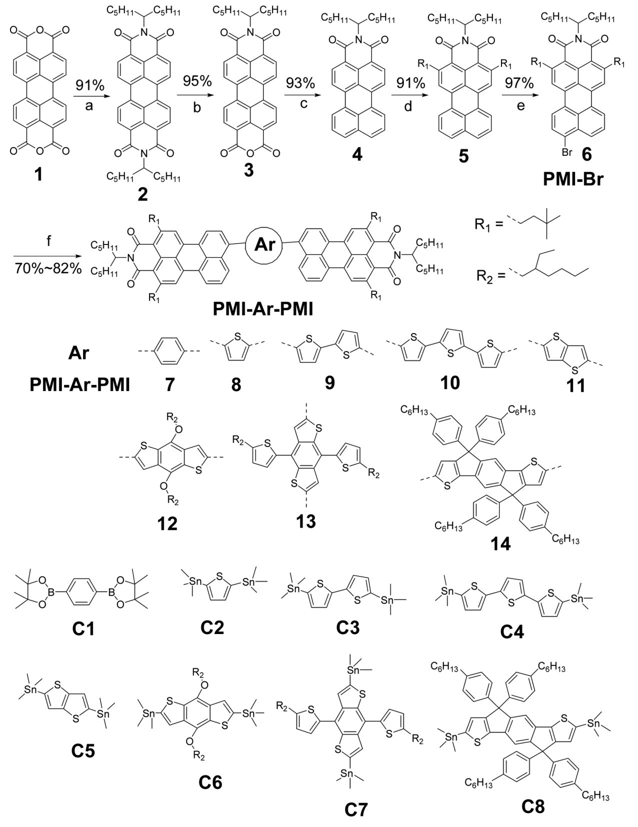
highly soluble 2,5-di(3-dimethylbutyl)-*N*-(1-pentylhexyl)-PMI was obtained.

Scheme 1. Synthesis of Electron Acceptors 7−14[a]



[a]Conditions: (a) 1-pentylhexylamine, imidazole, 145 °C, 4 h; (b) KOH, *t*-BuOH reflux,1 h; (c) copper power, 3-picoline, reflux, 10 h; (d) *tert*-butylethene, toluene, $RuH_2(CO)$ $(PPh_3)_3$, 160 °C, 6 h; (e) Br_2, CH_2Cl_2, K_2CO_3, 0 °C, 15 min; (f) C1, K_2CO_3, $Pd(dppf)Cl_2$, THF, H_2O, 60 °C, 6 h or C2−C8, $Pd(PPh_3)_4$, toluene, 100 °C, 6 h.

As shown in Scheme 1, starting from perylene dianhydride (**1**), *N*,*N*′-di(1-pentylhexyl)-perylene diimide (**2**) was synthesized according to a literature method in the yield of 91%.[24] Branched 1-pentylhexylamine was synthesized from commercial available 6-undecanone, as shown in Supporting Information. Selective hydrolysis of **2** with KOH in refluxed *tert*-butanol afforded **3** with the high yield of 95% under optimized condition.[24]

Decarboxylation of **3** was carried out in refluxed 3-picoline under argon with freshly prepared copper powder as the catalyst. The copper powder was prepared by the reduction of $CuSO_4$ in the water, and the detailed procedure is in the Supporting Information. *N*-(1-pentylhexyl)-perylene monoimide (**4**) was obtained in the isolated yield of 93%. In the literature, the similar reaction has a yield of 28%, without protection by the inert gas and using commercial copper powder as the catalyst.[5]

A ruthenium-catalyzed alkylation by the complex Ru-$[H_2(CO)\ (PPh_3)_3]$ was then carried out to synthesize **5**. The reaction occurs smoothly in the toluene at 160 °C in a sealed tube with an excellent yield of 91%. Nevertheless, it does not work in the refluxed toluene with the common reflux equipment. This type reaction was usually done in trimethylbenzene, in which the solvent with a high boiling point is difficult to remove.[26]

Bromination of **5** at 0 °C in CH_2Cl_2 leads to **6** (PMI-Br) in nearly quantitative yield. The suitable reaction time, reaction temperature, and the concentration of Br_2 are essential. Longer time, higher temperature, or higher concentration leads to multibrominaton of **5**.

With PMI-Br as the intermediate, A−D−A type electron acceptors (**7−14**) were obtained with Suzuki or Stille coupling reactions in good yield of 70−82%. All the new compounds **4−14** were characterized unambiguously by ^1H NMR, ^{13}C NMR, and HRMS. Their purity was confirmed by HPLC analysis with a silica column, and the corresponding spectra were listed in the Supporting Information. Compounds **7−14** are readily soluble in common solvents like $CHCl_3$, THF, and toluene, which guarantees their solution process. Their optical and electrochemical properties and application in nonfullerene solar cells were also investigated.

Cyclic voltammetry of **7−14** was measured in acetonitrile in solid state. All the compounds show a semireversible reduction wave (Figure S1). According to the reduction potential observed in the measurement, the LUMO energy levels of these compounds were calculated to be −3.67 to −3.76 eV (Table 1), which is similar to PDI (−3.71 eV).[27] The low-lying LUMO energy levels indicate their strong electron-accepting ability, which make them suitable candidates as electron acceptors. The reason for almost constant LUMO levels in these molecules attributes to the strong electron-withdrawing carbonyl group, which is confirmed in our previous study.[27]

Table 1. Optical and Electrochemical Data for 7−14

	λ_{max} (nm)	ε (M^{-1} cm^{-1})	λ_{em} (nm)	S (nm)[a]	Φ_f (%)[b]	LUMO (eV)	E_g (eV)
7	513	75400	551	38	50.1	−3.68	2.09
8	519	82200	599	80	6.0	−3.76	2.01
9	520	89100	613	93	1.3	−3.72	1.91
10	518	79900	636	118	0.2	−3.69	1.92
11	521	68500	605	84	9.3	−3.70	1.97
12	514	92000	565	51	0.3	−3.68	1.95
13	514	118000	590	76	1.1	−3.67	1.99
14	542	110600	643	101	0.3	−3.67	1.89

[a]Stokes shift. [b]Standard for fluorescence quantum yield is *N*,*N*′-di(2,6-isopropylphenyl)-PDI.[30]

The absorption spectra of **7−14** in solution and solid state are shown in Figure 2. The optical data are summarized in Table 1. In solution, compound **7** with a phenylene group (weak donor) shows prominent absorption in the range of 400−550 nm. Absorption edges of **8−13** (with moderate donor) red-shift by about 50 nm compared with **7**. Compound **14** with electron-rich donor shows broad absorption between

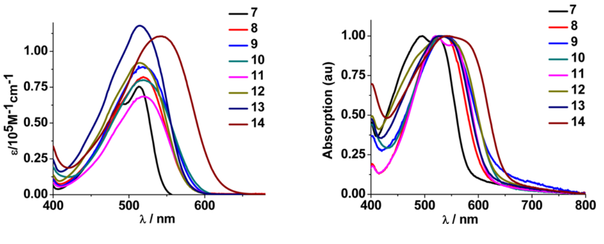


Figure 2. Absorption of **7−14** in THF (left) and in film (right).

400 and 650 nm, deriving from strong pull−push structure of the chromophore.[28,29] All the compounds show strong absorption in the visible region with a maximum extinction coefficient (ε_{max}) higher than 68,500. Compound **13** displays the highest ε_{max} of 118,000 at 514 nm. All the absorption in the solid state red-shifts obviously with comparison to their counterparts in solution due to the intermolecular aggregation of these molecules in the solid film. Calculated optical band gaps of these compounds are between 1.89 and 2.09 eV.

The emission spectra of **7**−**14** in THF were listed in Figure S3, and the corresponding data was summarized in Table 1. Compound **7** shows strong fluorescence with the quantum yield of 50.1%, while the other acceptors display the quantum yield <10%. Since the intramolecular charge transfer (ICT) could quench the fluorescence, the weak donor of **7** leads to weak ICT, which may be responsible for its stronger fluorescence.[31] Compounds **8**−**14** have large Stokes shifts between 51 and 118 nm, which may result from their strong ICT.[6,32]

Organic bulk heterojunction (BHJ) solar cells have become a research focus in the past decade because of their lightweight, low cost, and ability to construct large flexible devices.[33] Compared with their counterpart donors, excellent acceptors are very rare. Nonfullerene acceptors could overcome the shortcomings of fullerene derivatives such as insufficient visible absorption, difficult modification, and high cost, so it has become a promising topic in the past several years.[34,35]

In this research, acceptors **7**−**14** were used in nonfullerene solar cells. The devices were fabricated with an inverted architecture of ITO/ZnO (30 nm)/donor:acceptor (100 nm)/MoO_3 (7 nm)/Ag (100 nm). Commercial available polymer PCE10 (the structure is in Figure S2) was selected as the donor, because it has matched energy levels and complementary absorption with these acceptors.[36] The blending ratio of the donor and acceptor is 1:1. The corresponding current density−voltage (*J*−*V*) curves of the studied devices are illustrated in Figure 3, and the detailed solar parameters are listed in Table 2. All the compounds show typical *J*−*V* curves of solar cells. Compound **9** displays the best PCE of 1.3% with current density (J_{sc}) of 6.73 mA cm^{-2}, open-circuit voltage (V_{oc}) of 0.80 V, and fill factor (FF) of 22%. The excellent morphology and phase separation of its active layer contributes to above high performance. The other acceptors have low PCE of 0.1−0.2%, due to a too low J_{sc} of 0.2−0.4 mA cm^{-2}.

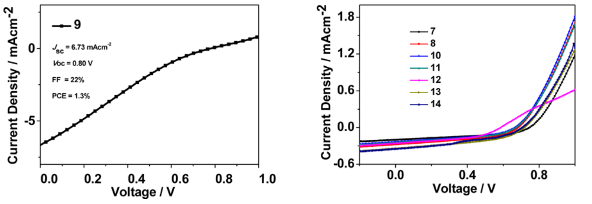
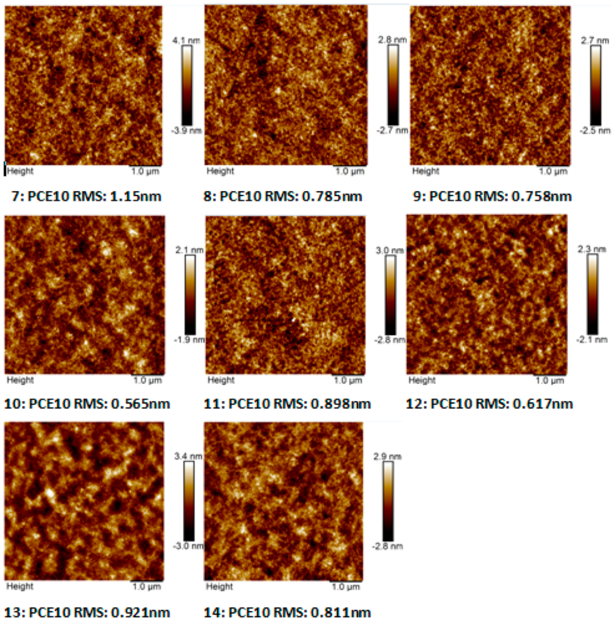


Figure 3. *J*−*V* curves of solar cells based on **7**−**14**.

Table 2. Device Parameters of Solar Cells with PMI Acceptor:PCE10 as the Active Layer

active layer	J_{sc} (mA cm^{-2})	V_{oc} (V)	FF (%)	PCE (%)
7	0.2	0.75	44	0.1
8	0.2	0.68	44	0.1
9	6.73	0.80	22	1.3
10	0.3	0.66	42	0.1
11	0.3	0.67	44	0.2
12	0.3	0.66	42	0.1
13	0.4	0.70	40	0.1
14	0.4	0.70	38	0.1

To investigate the morphology of the active layer, atomic force microscopy (AFM) scans were carried out for a blended film of PCE10 and the acceptor (1:1, w/w). The height images and phase images are shown in Figures 4 and S4. Compound **9** and PCE10 could form a cross interpenetrating structure with phase separation in the tens of nanometers, which is favorable for efficient BHJ solar cells.[37] Compounds **10**, **13**, and **14** form a blended film with a large phase separation scale in the hundreds nanometers, which contribute to their low performance in solar cells. The film of **7** and PCE10 demonstrates the roughest surface morphology with the average root-mean-square (RMS) roughness of 1.15 nm, which could be attributed to strong intermolecular aggregation of the compound. The strong aggregation also causes **7** to have a lower solubility compared with other compounds. All the other compounds show smooth surface morphology with a RMS of 0.565−0.921 nm.



7: PCE10 RMS: 1.15nm **8: PCE10 RMS: 0.785nm** **9: PCE10 RMS: 0.758nm**
10: PCE10 RMS: 0.565nm **11: PCE10 RMS: 0.898nm** **12: PCE10 RMS: 0.617nm**
13: PCE10 RMS: 0.921nm **14: PCE10 RMS: 0.811nm**

Figure 4. AFM height images (5 μm × 5 μm) of the spin-cast active layers with 1:1 weight ratio of PCE10 and the acceptor.

In conclusion, soluble brominated PMI (PMI-Br) with short alkyl chains was synthesized with a highly efficient synthetic route from commercially available starting material. A−D−A type electron acceptors (**7**−**14**) with strong visible absorption and low-lying LUMO energy levels were obtained with PMI as the electron-accepting part. All the acceptors can be used in the nonfullerene solar cells. Their further applications in optoelectronic devices are in progress in our laboratory.

■ EXPERIMENTAL SECTION

General Experimental Methods. Compound 1-pentylhexylamine was synthesized according to literature method.[31] The other reagents were purchased from commercial resources. Cyclic voltammetry (CV) was performed with an electrochemical analyzer with a three-electrode system. Working electrode: glassy carbon; reference electrode: Ag/Ag$^+$; auxiliary electrode: Pt wire; electrolyte:

tetrabutylammonium hexafluorophosphate (Bu_4NPF_6); internal standard: ferrocene (Fc). CV was conducted with the working electrode coated with thin solid film of compounds in acetonitrile. LUMO energy levels were calculated based on the assumption that the energy of Fc/Fc^+ is −4.8 eV vs vacuum.[2] NMR spectra were recorded on 400 MHz spectrometers. Chemical shifts are reported in ppm (δ) with tetramethylsilane as the internal standard. MALDI-TOF mass spectra were measured with commercial spectrometers either in the positive or negative reflector mode. The purity of the compounds **7**−**14** was determined by HPLC analysis using an Agilent-1100 instrument equipped with ZORBAX RX-SIL column (4.6 × 250 mm) and with a mobile phase of hexane/isopropanol (98.5:1.5), flow rate of 1.0 m L/min, and detection wavelength of 450 nm. The fluorescence quantum yield was determined with the standard *N,N′*-di(2,6-isopropylphenyl)-PDI.[30]

*Synthesis of **2**.*[5] A mixture of perylene-3,4,9,10-tetracarboxylic dianhydride (5.88 g, 15 mmol), 1-pentylhexylamine (10.26 g, 60 mmol), and imidazole (60 g) was stirred at 145 °C for 4 h under argon. After cooling, the mixture was poured into 2 M HCl (350 mL) and stirred overnight. The product was extracted with CH_2Cl_2, washed with water, dried with $MgSO_4$, and concentrated. The product **2** (9.5 g, 91%) was obtained through a short silica gel column with the eluent of CH_2Cl_2. Mp 182−185 °C; MS (MALDI-TOF): Calcd for $C_{46}H_{54}N_2O_4$ 698.40, found: 698.37 (M^-); UV−vis (THF): λ_{max} (ε) = 523 (108000), 486 nm (64700 M^{-1} cm^{-1}); ^{1}HNMR (400 MHz, $CDCl_3$) δ 8.60 (t, 8H), 5.18 (m, 2H), 2.25 (m, 4H), 1.86 (m, 4H), 1.27−1.58 (m, 24H), 0.82 ppm (t, 12H).

*Synthesis of **3**.*[5] A mixture of compound **2** (3.42 g, 4.9 mmol), KOH (0.8 g), and 120 mL *t*-BuOH was stirred at reflux for 1 h. The mixture was poured into 25 mL CH_3COOH and 100 mL H_2O and stirred at reflux for 0.5 h. After cooling to the room temperature, it was extracted with CH_2Cl_2, washed with water, dried with $MgSO_4$, and concentrated. Pure **3** as a red solid (2.54 g, 95%) was obtained after purification through a silica gel column (eluent, CH_2Cl_2). Mp > 300 °C; MS (MALDI-TOF): Calcd for $C_{35}H_{31}NO_5$ 545.22, found: 545.16 (M^-); UV−vis (THF): λ_{max} (ε) = 518 (92900), 483 nm (57900 M^{-1} cm^{-1}); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.64 (m, 8H), 5.17 (m, 1H), 2.24 (m, 2H), 1.86 (m, 2H), 1.26 (m, 12H), 0.82 ppm (t, 6H).

Preparation of Copper Powder. A mixture of $CuSO_4{\cdot}5H_2O$ (10 g, 0.04 mol), zinc powder (3.5 g, 0.054 mol), and 40 mL of H_2O was stirred at room temperature for 2 h. The mixture was washed with water, and then 5.8% HCl (40 mL) was added to the mixture and stirred for 2 h. The mixture was washed with water to neutral and then washed with acetone. Copper powder (2.4 g, 94%) was obtained as brown powder after drying.

*Synthesis of **4**.*[4] A mixture of copper power (2.6 g, 41.0 mmol), compound **3** (3 g, 5.5 mmol), and 300 mL of dry 3-picoline was stirred at reflux for 10 h under argon. After cooling to the room temperature, the mixture was poured into 2 M HCl (750 mL) and stirred for 1 h. The product was extracted with CH_2Cl_2, washed with water, dried with $MgSO_4$, and concentrated. Pure **4** (2.45 g, 93%) was obtained as a red solid after purification through a silica gel column (eluent, CH_2Cl_2/petroleum ether = 4:1, v/v). Mp 225−226 °C; HRMS (MALDI-TOF): Calcd for $C_{33}H_{33}NO_2$ 475.2511, found: 475.2557 (M^-); UV−vis (THF): λ_{max} (ε) = 502 (40900), 477 nm (41300 M^{-1} cm^{-1}); ^{1}H NMR (400 MHz, $CDCl_3$) δ8.46 (m, 2H), 8.24 (m, 4H), 7.78(d, 2H), 7.52 (t, 2H), 5.19 (m, 1H), 2.26 (m, 2H), 1.87 (m, 2H), 1.29 (m, 12H), 0.83 ppm (t, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 165.0, 136.6, 134.1, 131.7, 130.9, 130.6, 129.7, 129.0, 127.7, 126.8, 126.4, 123.4, 119.9, 54.3, 32.3, 31.8, 26.6, 22.5, 14.0 ppm.

*Synthesis of **5**.*[23] A mixture of compound **4** (2.16 g, 3.4 mmol), dry *tert*-butylethene (5.6 g, 68 mmol), dry toluene (100 mL), and $RuH_2(CO)$ $(PPh_3)_3$ (50 mg) was stirred at 160 °C for 6 h under argon. The solvent was removed by rotavapor. Compound **5** (1.98 g, 91%) was obtained as a red solid after purification through a silica gel column (eluent, CH_2Cl_2/petroleum ether = 1:3, v/v). Mp 154−156 °C; HRMS (MALDI-TOF): Calcd for $C_{45}H_{57}NO_2$ 643.4389, found: 643.4384 (M^-); UV−vis (THF): λ_{max} (ε) = 496 (34900), 470 nm (37300 M^{-1} cm^{-1}); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.33 (d, 2H), 8.05 (s, 2H), 7.78(d, 2H), 7.54 (t, 2H), 5.20 (m, 1H), 3.44 (m, 4H), 2.31 (m, 2H), 1.79 (m, 2H), 1.29 (m,16H), 1.06 (s, 18H), 0.83 ppm (t, 8H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 150.8, 134.8, 134.0, 132.2, 130.0, 129.1, 127.8, 126.7, 124.2, 122.8, 53.8, 45.8, 32.4, 32.3, 31.9, 30.9, 29.4, 26.6, 22.6, 14.1 ppm.

*Synthesis of **6**.*[23] A mixture of compound **5** (1.58 g, 2.45 mmol), CH_2Cl_2 (76 mL), and K_2CO_3 (2.88 g) was stirred at 0 °C. Br_2 solution (0.2 mL Br_2 in 2 mL CH_2Cl_2) was added to the mixture. The reaction lasted for 15 min. Then the reaction mixture was added to an ice-Na_2SO_3 (2.45 g)-H_2O mixture with stirring. The product was extracted with CH_2Cl_2, washed with water, and dried with $MgSO_4$. Compound **6** (1.72 g, 97%) was obtained as a red solid after the removal of the solvent. Mp 177−178 °C; HRMS (MALDI-TOF): Calcd for $C_{45}H_{56}BrNO_2$ 721.3494, found: 721.3474 (M^-); UV−vis (THF): λ_{max} (ε) = 498 (42000), 470 nm (42000 M^{-1} cm^{-1}); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.28 (d, 1H), 8.14(d, 1H), 7.99 (t, 2H), 7.91 (s, 1H), 7.74 (d, 1H), 7.57 (t, 1H), 5.22 (m, 1H), 3.41(m, 4H), 2.30 (m, 2H), 1.82 (m, 2H), 1.28−1.56(m, 16H), 1.07 (s, 18H), 0.84 ppm (t, 6H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.2, 151.0, 134.0, 133.9, 132.5, 132.0, 130.7, 129.4, 129.0, 128.9, 127.7, 125.0, 124.7, 124.4, 123.7, 123.3, 122.7, 53.8, 45.7, 32.4, 31.9, 30.9, 29.4, 26.6, 22.6, 14.1 ppm.

*Synthesis of **7**.*[38] A mixture of compound **6** (0.78 g, 1.08 mmol), 1,4-benzenediboronic acid bis(pinacol)ester (**C1**, 0.15 g, 0.48 mmol), K_2CO_3 (1.53 g, 11.4 mmol), Pd(dppf)Cl_2 (40 mg), THF (21 mL), and H_2O (9 mL) was stirred at 60 °C for 6 h under argon. After cooling to room temperature, the product was extracted with CH_2Cl_2, washed with water, dried with $MgSO_4$, and concentrated. Compound **7** (0.462 g, 76%) was obtained as a red solid after purification through a silica gel column (eluent, CH_2Cl_2/petroleum ether = 1:4, v/v). Mp 298−300 °C; HRMS (MALDI-TOF): Calcd for $C_{96}H_{116}N_2O_4$ 1360.8935, found: 1360.8957 (M^-); UV−vis (THF): λ_{max} (ε) = 513 (75400), 489 nm (63200 M^{-1} cm^{-1}); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48 (m, 4H), 8.15(m, 6H), 7.72 (s, 4H), 7.66 (m, 4H), 5.22 (m, 2H), 3.48(m, 8H), 2.30 (m, 4H), 1.81 (m, 4H), 1.29 (m, 32H), 1.08 (s, 36H), 0.84 ppm (t, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.1, 150.8, 141.7, 139.5, 135.0, 134.8, 132.4, 132.2, 130.1, 129.5, 128.8, 128.4, 128.0, 126.8, 124.5, 124.2, 123.0, 122.6, 53.8, 45.8, 32.4, 31.9, 30.9, 29.4, 26.6, 22.6, 14.1 ppm.

*Synthesis of **8**.*[39] A mixture of compound **6** (0.432 g, 0.6 mmol), 2,5-bis(trimethylstannanyl)thiophene (**C2**, 0.102 g, 0.252 mmol), $Pd(PPh_3)_4$ (40 mg), and dry toluene (42 mL) was stirred at 100 °C for 6 h under argon. The solvent was removed by rotavapor. Compound **8** (0.252 g, 72%) was obtained as a red solid after purification through a silica gel column (eluent, CH_2Cl_2/petroleum ether = 1:4, v/v). Mp 161−162 °C; HRMS (MALDI-TOF): Calcd for $C_{94}H_{114}N_2O_4S$ 1366.8499, found: 1366.8411 (M^-); UV−vis (THF): λ_{max} (ε) = 519 nm (82200 M^{-1} cm^{-1}); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.48−8.40 (m, 6H), 8.12(s, 4H), 7.79 (d, 2H), 7.64 (t, 2H), 7.45(s, 2H), 5.22 (m, 2H), 3.48(m, 8H), 2.31 (m, 4H), 1.82 (m, 4H), 1.24−1.56(m, 32H), 1.07 (s, 36H), 0.84 ppm (t, 12H); ^{13}C NMR (100 MHz, $CDCl_3$), δ 164.7, 151.2, 142.2, 134.5, 133.9, 132.3, 132.2, 129.5, 129.2, 128.9, 128.6, 128.5, 127.9, 127.2, 124.6, 124.5, 124.1, 123.2, 122.4, 53.8, 45.8, 45.8, 32.4, 31.9, 30.9, 29.6, 29.4, 26.6, 22.6, 14.1 ppm.

*Synthesis of **9**.*[39] A mixture of compound **6** (0.450 g, 0.625 mmol), 2,2′-bis(trimethylstannyl)-5,5′-bithiophene (**C3**, 0.105 g, 0.21 mmol), $Pd(PPh_3)_4$ (40 mg), and dry toluene (35 mL) was stirred at 100 °C for 6 h under argon. The solvent was removed by rotavapor. Compound **9** (0.23 g, 77%) was obtained as a red solid after purification through a silica gel column (eluent, CH_2Cl_2/petroleum ether = 1:4, v/v). Mp 171−174 °C; HRMS (MALDI-TOF): Calcd for $C_{98}H_{116}N_2O_4S_2$ 1448.8377, found: 1448.8463 (M^-); UV−vis (THF): λ_{max} (ε) = 519 nm (89100 M^{-1} cm^{-1}); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.36 (m, 6H), 8.09 (d, 4H), 7.70 (d, 2H), 7.61 (t, 2H), 7.38(d, 2H), 7.28(d, 2H), 5.23 (m, 2H), 3.47(m, 8H), 2.31 (m, 4H), 1.83 (m, 4H), 1.24−1.29(m, 32H), 1.07 (s, 36H), 0.84 ppm (t, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.3, 151.1, 140.5, 138.0, 134.7, 134.4, 133.8, 132.2, 132.2, 129.4, 129.2, 128.9, 128.7, 128.4, 127.8, 127.1, 124.6, 124.4, 124.4, 124.1, 123.2, 122.4, 45.8, 32.4, 31.9, 30.9, 29.6, 29.4, 26.6, 22.6, 14.1 ppm.

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Synthesis of 10.[40] A mixture of compound **6** (0.432 g, 0.6 mmol), **C4** (0.144 g, 0.252 mmol), $Pd(PPh_3)_4$ (40 mg), and dry toluene (42 mL) was stirred at 100 °C for 6 h under argon. The solvent was removed by rotavapor. Compound **10** (0.294 g, 78%) was obtained as a red solid after purification through a silica gel column (eluent, CH_2Cl_2/petroleum ether = 1:4, v/v). Mp 230–232 °C; HRMS (MALDI-TOF): Calcd for $C_{102}H_{118}N_2O_4S_3$ 1530.8254, found: 1530.8145 (M^-); UV–vis (THF): λ_{max} (ε) = 518 nm(79900 M^{-1} cm^{-1}); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.34–8.41 (m, 6H), 8.10(d, 4H), 7.68 (d, 2H), 7.60 (t, 2H), 7.31(d, 2H), 7.26(d, 2H), 7.21(s, 2H), 5.21 (m, 2H), 3.47(m, 8H), 2.31 (m, 4H), 1.80 (m, 4H), 1.28–1.56(m, 32H), 1.07 (s, 36H), 0.84 ppm (t, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 151.1, 140.3, 138.0, 136.1, 134.8, 134.4, 133.8, 132.2, 132.2, 129.4, 129.1, 128.9, 128.7, 128.4, 127.8, 127.1, 124.6, 124.6, 124.4, 124.2, 124.1, 123.2, 122.4, 53.8, 45.8, 32.4, 31.9, 30.9, 29.6, 29.4, 26.6, 22.6, 14.1 ppm.

Synthesis of 11.[41] A mixture of compound **6** (0.432 g, 0.6 mmol), **C5** (0.120 g, 0.252 mmol), $Pd(PPh_3)_4$ (40 mg), and dry toluene (42 mL) was stirred at 100 °C for 6 h under argon. The solvent was removed by rotavapor. Compound **11** (0.258 g, 72%) was obtained as a red solid after purification through a silica gel column (eluent, CH_2Cl_2/petroleum ether = 1:4, v/v). Mp > 300 °C; HRMS (MALDI-TOF): Calcd for $C_{96}H_{114}N_2O_4S_2$ 1422.8220, found: 1422.8214 (M^-); UV–vis (THF): λ_{max} (ε) = 521 nm (68400 M^{-1} cm^{-1}); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.40 (t, 6H), 8.12(d, 4H), 7.76(d, 2H), 7.61(t, 2H), 7.56(s, 2H), 5.23 (m, 2H), 3.48(m, 8H), 2.32(m, 4H), 1.81 (m, 4H), 1.24–1.56(m, 32H), 1.07 (s, 36H), 0.84 ppm (t, 12H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.7, 151.1, 143.1, 140.0, 134.2, 132.4, 132.2, 129.5, 129.4, 129.1, 128.4, 127.2, 124.6, 124.5, 124.1, 123.2, 122.3, 120.3, 45.8, 32.4, 31.9, 30.9, 29.6, 29.5, 29.4, 26.6, 22.6, 14.1 ppm.

Synthesis of 12.[42] A mixture of compound **6** (0.432 g, 0.6 mmol), **C6** (0.193 g, 0.252 mmol), $Pd(PPh_3)_4$ (40 mg), and dry toluene (42 mL) was stirred at 100 °C for 6 h under argon. The solvent was removed by rotavapor. Compound **12** (0.306 g, 70%) was obtained as a red solid after purification through a silica gel column (eluent, CH_2Cl_2/petroleum ether = 1:7, v/v). Mp 290–292 °C; HRMS (MALDI-TOF): Calcd for $C_{116}H_{148}N_2O_6S_2$ 1729.0779, found: 1729.0686 (M^-); UV–vis (THF): λ_{max} (ε) = 514 nm (92000 M^{-1} cm^{-1}); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44–8.50 (m, 6H), 8.18 (d, 4H), 7.85 (d, 2H), 7.71 (s, 2H), 7.67 (t, 2H), 5.22 (m, 2H), 4.32 (d, 4H), 3.49 (m, 8H), 2.31 (m, 4H), 1.81 (m, 4H), 1.24–1.56 (m, 42H), 1.08 (s, 36H), 1.01(t, 8H), 0.86 ppm (t, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 151.1, 144.3, 141.0, 134.8, 134.4, 134.3, 132.5, 132.2, 130.2, 129.7, 129.6, 129.3, 128.4, 128.0, 127.3, 124.7, 124.6, 124.2, 123.3, 122.3, 121.2, 53.8, 45.8, 40.6, 32.4, 31.9, 30.9, 30.4, 29.6, 29.4, 29.1, 26.6, 23.8, 23.0, 22.6, 14.1, 11.3 ppm.

Synthesis of 13.[40] A mixture of compound **6** (0.432 g, 0.6 mmol), **C7** (0.228 g, 0.252 mmol), $Pd(PPh_3)_4$ (40 mg), and dry toluene (42 mL) was stirred at 100 °C for 6 h under argon. The solvent was removed by rotavapor. Compound **13** (0.354 g, 74%) was obtained as a red solid after purification through a silica gel column (eluent, CH_2Cl_2/petroleum ether = 1:7, v/v). Mp 146–149 °C; HRMS (MALDI-TOF): Calcd for $C_{124}H_{152}N_2O_4S_4$ 1861.0635, found: 1861.0431 (M^-); UV–vis (THF): λ_{max} (ε) = 514 nm (118000 M^{-1} cm^{-1}); ^{1}H NMR (400 MHz, CDCl3) δ 8.45 (d, 2H), 8.40 (m,4H), 8.15 (d, 4H), 7.90 (s, 2H), 7.80 (d,2H), 7.64 (t, 2H), 7.43 (d, 2H), 6.90 (d, 2H), 5.22 (m, 2H), 3.47 (m, 8H), 2.85 (d, 4H), 2.31 (m, 4H), 1.80 (m, 4H), 1.66 (br, 4H),1.24–1.56 (m, 48H), 1.07 (s, 36H), 0.83–0.90 ppm (br, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 151.1, 146.1, 142.5, 139.6, 137.0, 136.9, 134.8, 134.4, 132.4, 132.2, 129.6, 129.4, 129.3, 128.3, 128.0, 127.9, 127.3, 125.5, 124.7, 124.3, 124.2, 123.8, 123.2, 122.2, 53.8, 45.8, 41.4, 34.2, 32.4, 32.4, 31.8, 30.9, 29.6, 29.4, 28.8, 26.6, 25.6, 22.9, 22.6, 13.9, 10.8 ppm.

Synthesis of 14.[41] A mixture of compound **6** (0.432 g, 0.6 mmol), **C8** (0.312 g, 0.252 mmol), $Pd(PPh_3)_4$ (40 mg), and dry toluene (42 mL) was stirred at 100 °C for 6 h under argon. The solvent was removed by rotavapor. Compound **14** (0.450 g, 82%) was obtained as a red solid after purification through a silica gel column (eluent, CH_2Cl_2/petroleum ether = 1:8, v/v). Mp > 300 °C; HRMS (MALDI-TOF): Calcd for $C_{154}H_{184}N_2O_4S_2$ 2189.3698, found: 2189.3874 (M^-); UV–vis (THF): λ_{max} (ε) = 542 nm (110600 M^{-1} cm^{-1}); ^{1}H NMR (400 MHz, $CDCl_3$) δ 8.44 (d, 2H), 8.37 (t,4H), 8.14 (d, 4H), 7.70 (d, 2H), 7.59 (t, 2H), 7.54 (s, 2H), 7.28 (d, 8H), 7.20 (br, 2H), 7.12 (d, 8H), 5.21 (m, 2H), 3.49(m, 8H), 2.59(t, 8H), 2.31 (m, 4H), 1.79 (m, 4H), 1.24–1.56 (m, 64H), 1.06 (s, 36H), 0.84 ppm (t, 24H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 164.4, 151.1, 146.1, 142.5, 139.6, 137.0, 136.9, 134.8, 134.4, 132.4, 132.2, 129.6, 129.4, 129.3, 128.3, 128.0, 127.9, 127.3, 125.5, 124.7, 124.3, 124.2, 123.8, 123.2, 122.2, 53.8, 45.8, 41.4, 34.2, 32.4, 32.4, 31.8, 30.9, 29.6, 29.4, 28.8, 26.6, 25.6, 22.9, 22.6, 13.9, 10.8 ppm.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.7b00272.

Copy of NMR spectra and cyclic voltammograms (PDF)

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Notes

The authors declare no competing financial interest.

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