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Low bandgap poly(fluorinated metallophthalocyanine-*alt*-diketopyrrolopyrrole)s with outstanding thermal stability

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ABSTRACT

This paper reports on a novel synthesis of conjugated alternating polymers composed of a phthalocyanine (Pc) and a diketopyrrolopyrrole (DPP) by combining ABAB-type diiodo-substituted Pc and DPP-boronic acids *via* a Suzuki-Miyaura cross-coupling reaction. The resulting Pc-DPP alternating polymers exhibit a low bandgap of around 1.7 eV and the high level thermal stability. Owing to the potential intriguing properties of these compounds, they can find promising applications in electronic and optoeletronic devices.

1. Introduction

Over the past years diverse electron donor-acceptor (D-A) conjugates have been designed, synthesized, and investigated [1]. Among the various D-A architectures, phthalocyanines (Pc), as an extended electron-rich aromatic moiety containing 18 π-electrons, hold an exceptional position due to their outstanding physicochemical properties and high molar extinction coefficients in the red to near infrared region. However, very few examples of *trans*-disubstituted Pc subunits being connected through π-conjugated pathways have been described and investigated for expanding the application of these materials for useful optoelectronic applications [2]. As far as we know, no conjugated D-A alternating polymerization based on covalent reactions on Pcs has been achieved, which restricts the final structure to rather simple architectures [2c]. Meanwhile, derivatives of diketopyrrolopyrrole (DPP) are frequently employed as acceptors in molecular D-A systems due to their exceptional absorbance properties in the long wavelength region, strong fluorescent performance, and high thermal stability [3]. Therefore, it has been intuitively envisaged that conjugated alternating D-A polymers based on the Pc and DPP can offer excellent ambient stability, accompanied by strong absorption properties and high charge transport efficiency.

Here we report the synthesis of a novel zinc-phthalocyanine (ZnPc)-diketopyrrolopyrrole (DPP) ambipolar polymer containing two bulky bis(trifluoromethyl)phenyl groups at the nonperipheral positions on the Pc. Our synthetic procedure was designed for polymerization of alternating subunits in a Suzuki-Miyaura cross-coupling reaction to iodo-ABAB-Pc (**2**) with DPP-boronic acids (**3**). It is reasonably envisaged, based on the current approach, that this alternating subunit should provide a linearly conjugated alternating polymer backbone made of Pc and DPP.

2. Experimental

2.1. Property investigation

For structure identification, NMR and mass spectra of intermediates and resulting polymers were measured (Figs. S1–S7, in supporting information). The UV absorbance and photoluminescence spectra were collected using a UV-1800 spectrometer (Perkin Elmer) and a Perkin Elmer LS-45 spectro-fluorophotometer

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(Perkin Elmer), respectively, using a 1 cm cuvette. Number average molecular weight (M_n) and weight average molecular weight (M_w) of polymers were determined using gel permeation chromatography (GPC, YL9100 HPLC, Younglin) at 35 °C using THF as the eluent (0.8 mL/min), which was equipped with a refractive index (RI) detector (YL9170, Younglin) and fitted with a Styragel HR3/4 column (Waters) calibrated using linear polystyrene standards with molecular weight ranging 890–42400. A cyclic voltammetry (CV) was carried out on a Biologic SP-150 potentiostat. Measurements were carried at 25 °C in a THF solution containing tetrabutylammonium tetrafluorophosphate (0.1 M) as a support, with a scan rate of 100 mV/s. The potentials were measured versus Ag/Ag + as the quasi-reference electrode, and after each experiment, the potential of the Ag/Ag + electrode was calibrated against the ferrocene/ferrocenium (Fc/Fc+) redox couple.

2.2. Synthetic method

2.2.1. 3,3″,5,5″-Tetrakis(trifluoromethyl)-[1,1′:4′,1″-terphenyl]-2′,3′-dicarbonitrile (**1**)

Deaerated solution of (3,5-bis(trifluoromethyl)phenyl)boronic acid (**1**) (1.5 g, 6.12 mmol) and sulfonic ester of phthalonitrile (1 g, 2.35 mmol) in anhydrous 1,2-Dimethoxyethane (30 mL) was placed in to preheated oil bath at 80 °C, and then $Pd(PPh_3)_4$ (136 mg, 0.12 mmol), Na_2CO_3 (1.99 g, 18.9 mmol) were added respectively at 80 °C. The resulting reaction mixture was stirred at 80 °C for 16 h. After cooling to room temperature, the solvent was rotary evaporated. The residue was diluted in EtOAc and washed with water and saturated NaCl solution. The organic phase was dried with Na_2SO_4 and the solvent was rotary evaporated. The resulting crude solid was purified on silica gel using EtOAc/Hexane (2/8) as an eluent to produce 1.130 g (86%) of **1** as a white solid. ^{1}H NMR (500 MHz, $CDCl_3$), δ (ppm): 8.08 (s, 2 H), 8.05 (s, 4 H), 7.94 (s, 2 H) [4]. FT-IR (KBr, cm^{-1}): 3438 (w), 3074 (m), 2928 (s), 2341 (m), 2230 (m), 1620 (m), 1457 (s), 1380 (s), 1280 (s), 1187 (m), 1140 (m), 899(m), 835 (m), 782 (m), 706 (m), 677 (m), 442 (m).

2.2.2. 1,4,15,18-Tetrakis(3,5-bis(trifluoromethyl)phenyl)-9[10],23[24]-diiodo-5,28:14,19-diimino-7,12:21,26-dinitrilotetrabenzo[c, h, m, r] [1, 6, 11, 16] tetraazacycloeicosinato-(2-)-N29, N30, N31, N32 zinc (II) (**2**)

4-iodophthalonitrile (0.905 mmol, 230 mg), **1** (0.905 mmol, 500 mg) and anhydrous $Zn(AcO)_2$ (0.597 mmol, 166 mg) were dissolved in *o*-dichlorobenzene/DMF 2:1 (12 mL). The mixture was placed in preheated oil bath (160 °C) and stirred for 16 h under nitrogen atmosphere. Reaction mixture was cooling to room temperature, and then solvent was removed under vacuum. The crude was purified by silica-gel column chromatography (hexane/THF 4:1). The obtained solid was washed with methanol/water (5:1). Yield: 231 mg, 15%. ^{1}H NMR (500 MHz, THF-d_8), δ (ppm): 8.72 (d, 4H, J = 1.5 Hz), 8.71 (d, 4H, J = 1.5 Hz), 8.66 (d, 4H, J = 1.4 Hz), 8.65 (d, 4H, J = 1.4 Hz), 8.52 (d, 4H, J = 1.5 Hz), 8.46 (d, 4H, J = 1.4 Hz), 8.43 (s, 2H), 8.41 (s, 2H), 8.20–8.16 (m, 14H), 7.92 (d, 2H, J = 7.8 Hz), 7.90 (d, 2H, J = 7.8Hz) [4].

2.2.3. 1,4,15,18-Tetrakis(3,5-bis(trifluoromethyl)phenyl)-9[10],23[24]-diiodo-5,28:14,19-diimino-7,12:21,26-dinitrilotetrabenzo[c, h, m, r] [1, 6, 11, 16] tetraazacycloeicosinato-(2-)-N29, N30, N31, N32 (**2′**)

Diiodo ABAB ZnPc (**2**) (200 mg, 0.119 mmol), pyridine (10 mL), pyridine-HCl (2 g) were stirred at 120 °C for 4 h. After cooling to room temperature, the solvent was rotary evaporated. The crude solid was suspended in water (20 mL), sonicated for 10 min and filtered. The resulting solid was washed with methanol/water (9/1) and collected by centrifugation. The resulting blue solid was purified on silica gel using THF/Hexane (2/8) as an eluent to produce 146 mg (76%) of **2′** as a blue solid [5]. ^{1}H NMR (500 MHz, THF-d_8), δ (ppm): 8.52 (s, 4H), 8.48–8.46 (m, 4H), 8.31–8.29 (m, 2H), 8.25–8.19 (m, 5H), 7.98 (d, J = 7.4 Hz, 1 H), 7.91 (d, J = 7.8 Hz, 1 H). ^{19}F NMR (282 MHz, THF-d8), δ (ppm): −62.25(m). MALDI-MS calculated for $C_{64}H_{24}F_{24}I_2N_8$ = 1613.9830, found m/z 1613.9270; Q-band λ_{max} 694 nm, and a B-band λ_{max} 342 nm (THF).

2.2.4. ABAB Phthalocyanine(Zn)-diketopyrrolopyrrole polymer (**4**)

Diiodo ZnPc **2** (20 mg, 0.0119 mmol), 2,5-dihexyl-3,6-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrrolo [3,4-c]pyrrole-1,4(2*H*,5*H*)-dione (8.4 mg, 0.0119 mmol), Na_2CO_3 (10 mg, 0.0953 mmol), $PdCl_2$(dppf) (1 mg, 0.00119 mmol) were dissolved in 1,2-Dimethoxyethane (9 mL) and water (1 mL) and degassed with nitrogen for 10 min. The reaction mixture was heated to 80 °C and stirred for 48 h under nitrogen atmosphere. After cooling to room temperature, the solvent was rotary evaporated. The crude solid was suspended in 10 mL of water and sonicated for 10 min and the solid was collected by centrifugation. The blue solid was washed several times with methanol/water (9/1) and THF/hexane (2/8). The resulting solid was dissolved in THF (20 mL) and passed through a short pad of silica gel, and the evaporation of the solvent produced the polymer **4** in 83% yield as blue solid (19 mg). We did not obtain a good quality of ^{1}H NMR of Pc-DPP polymer **4** from a broadening and overlap of the aromatic signals, which might be due to the extended conjugation. Number average molecular weight (M_n) 6500 and weight average molecular weight (M_w) 14,100, with polydispersity index (PDI) value of 2.17, were obtained. Q-band λ_{max} 692 nm, B-band λ_{max} 498 (THF). FT-IR (KBr, cm^{-1}): 3438 (w), 2928 (m), 2851 (w), 1673 (s), 1609 (m), 1457 (m), 1380 (s), 1280 (s), 1175(m), 1128 (m), 893 (s), 829 (m), 747 (m), 706 (m), 677 (m), 566 (m).

2.2.5. ABAB phthalocyanine-diketopyrrolopyrrole polymer (**5**)

Diiodo Pc **2′** (19 mg, 0.0119 mmol), 2,5-dihexyl-3,6-bis(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)pyrrolo [3,4-c]pyrrole-1,4(2*H*,5*H*)-dione (8.4 mg, 0.0119 mmol), Na_2CO_3 (10 mg, 0.0953 mmol), $PdCl_2$(dppf) (1 mg, 0.00119 mmol) were dissolved in 1,2-Dimethoxyethane (9 mL) and water (1 mL) and degassed with nitrogen for 10 min. The reaction mixture was heated to 80 °C and stirred for 48 h under nitrogen atmosphere. After cooling to room temperature, the solvent was rotary evaporated. The crude solid was suspended in water (10 mL) and sonicated for 10 min and the solid was collected by centrifugation. The dark blue solid was several times washed with methanol/water (9/1) and THF/hexane (2/8). The resulting solid was dissolved in THF (20 mL) and passed through a short pad of silica gel, and evaporation of the solvent produced the polymer **4** in 76% yield as dark blue solid (17 mg) with M_n 8817, M_w 20830, and PDI 2.36. We did not obtain a good quality of ^{1}H NMR of Pc-DPP polymer **5** from the broadening and overlap of the aromatic signals, which might be due to the extended

Table 1
Reaction conditions of Suzuki-Miyaura cross-coupling of sulfonic ester with 3,5-bis(trifluoromethyl)phenylboronic acid (**1**).

Entry	Catalyst 10 mol%	Base	Solvent	Yield of 1
1	$Pd(PPh_3)_4$	Na_2CO_3	DME/water[a]	6%
2	$Pd(PPh_3)_4$	Na_2CO_3	DME/water[a]	Trace
3	$Pd(PPh_3)_4$	Na_2CO_3	1,4-Dioxane/water[a]	3%
4	$Pd(PPh_3)_4$	Na_2CO_3	DMF[a]	Trace
5	$Pd(PPh_3)_4$	Na_2CO_3	DME[a]	10%
6	$Pd(PPh_3)_4$	Na_2CO_3	DME/water[b]	30%
7	$Pd(PPh_3)_4$	Na_2CO_3	DME[b]	86%

Reaction conditions.
[a] Reaction starts at 80 °C, and maintain for 16 h.
[b] Na_2CO_3 is added at 80 °C, and reacted for 16 h.