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2,7,12,17-Tetra(2,5-thienylene)-substituted porphycenes

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ABSTRACT: We report syntheses of thiophene and dithiophene-substituted porphycenes (**ThPc** and **DThPc**) at 2,7,12,17-positions by McMurry coupling. The crystal structure of **ThPc** revealed that the porphycene plane shows a highly planar structure, and the dihedral angles between the porphycene core and thiophene are relatively small at 21° and 18°. **ThPc** and **DThPc** exhibit red-shifted and broadened absorption because of the extension of π conjugations through porphycene to the substituted thiophenes. We found that introduction of thiophene units onto porphycene results in decreasing the HOMO–LUMO differences effectively.

KEYWORDS: porphycene, thiophene, NIR absorption.

INTRODUCTION

Porphycene, which consists of two bipyrroles and two ethylene bridges, is the first constitutional isomer of porphyrin, as reported by Vogel in 1986 [1]. Compared to porphyrin, porphycene shows specific optical properties such as red-shifted absorption, relatively strong red-colored fluorescence and efficient singlet oxygen generation [2, 3]. These properties allow us to apply it to photodynamic therapy [4, 5], protein mimicry [6–9], catalysis [10, 11] and materials sciences [12–18]. The mechanism of tautomerism of the NH in the cavity has also been studied [19–24]. In order to modify the optical and electronic properties of porphycenes, various modification methods have been reported [25, 26], such as metallations [27–35], alkylations at pyrrolic β-positions and/or *meso*-positions [36–40], dimerizations [18, 41], π expansions [42–47], introductions of functional groups [48–57], and core modifications [58–63]. Porphycene is mainly synthesized by two methods. One is the McMurry coupling of diformylated bipyrroles, which is suitable for the synthesis of β-substituted porphycenes. The other is an acid-catalyzed homocoupling of dipyrrolyl-ethane derivatives [24, 64], which is suitable for the synthesis of *meso*-substituted porphycenes. Among these, the introduction of aryl groups to porphycene is simple and effective to control the optical and electronic properties of porphycenes. 2,7,12,17-Tetraphenylporphycene (**β-PhPc**) [65, 66] and 9,10,19,20-tetraphenylporphycene (***m*-PhPc**) [67] have been reported. Comparing these two porphycenes, absorption and fluorescence of **β-PhPc** are slightly red shifted compared to ***m*-PhPc** because the phenyl rings of ***m*-PhPc** are perpendicularly tilted in the crystal structure, whereas **β-PhPc** forms relatively small dihedral angles between porphycene and phenyl rings at 33° and 48°.

Inspired by these phenomena, we designed 2,7,12,17-thiophene- and dithiophene-substituted porphycenes (**ThPc** and **DThPc**, respectively) to achieve the creation of π-expanded porphycenes (Fig. 1). Introductions of thiophene units to porphyrins [68–70] and subporphyrins [71, 72] are known to extend their π conjugations efficiently to give unique optical and electrochemical properties. In contrast, thiophene-substituted porphycenes have not yet been reported except as core-modified porphycenes. In this context, we report the synthesis of **ThPc** and **DThPc** from corresponding diformylated

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[◊] SPP full member in good standing

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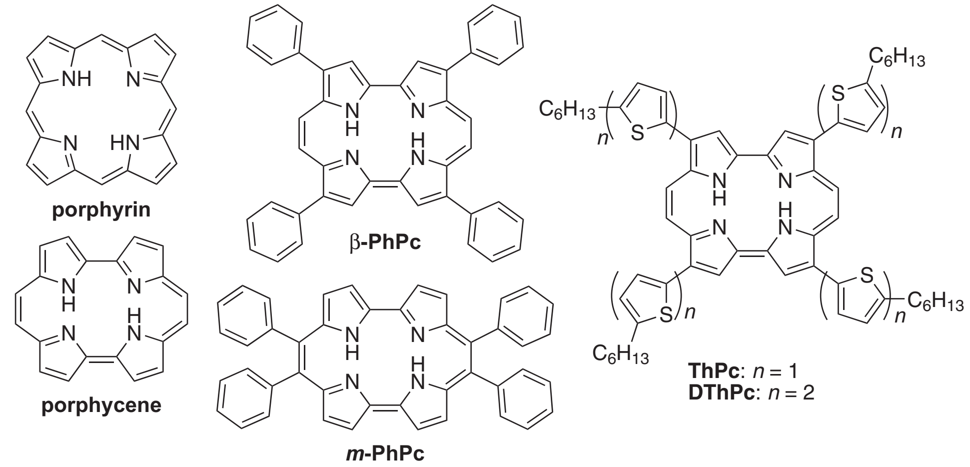
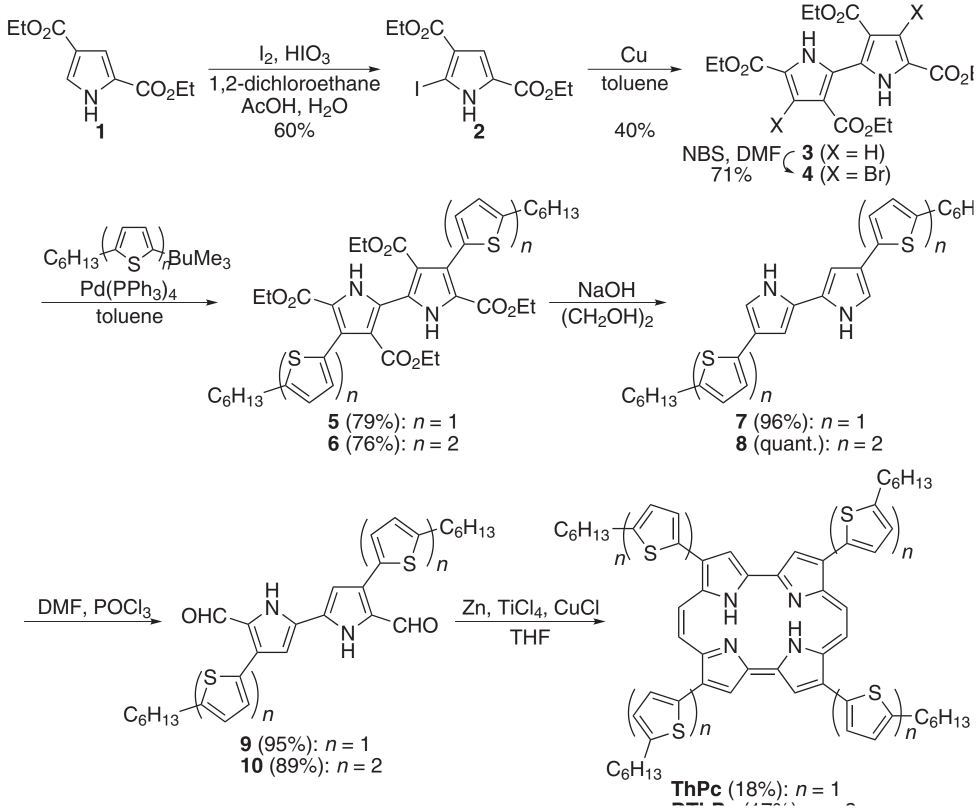


Fig. 1. Structure of 2,7,12,17-tetrathienyl-porphycenes with reference compounds



Scheme 1. Synthesis of 2,7,12,17-tetrathienyl-porphycenes

bipyrroles by McMurry coupling. The substitution of thiophenes induces the efficient π extensions leading to the NIR absorption properties

RESULTS AND DISCUSSION

Synthesis and characterization

The synthetic procedure of thiophene- and dithiophene-substituted porphycenes is shown in Scheme 1. The starting material of diethyl 1H-pyrrole-2,4-dicarboxylate 1 was synthesized from ethyl propiolate and ethyl 2-isocyanoacetate by a copper(I) oxide and 1,10-phenanthroline mediated cyclization method [73]. The iodination of **1** with iodine and HIO_3 gave pyrrole **2** in 60% yield. Ullmann coupling of **2** provided 2,2-bipyrrole **3** in 40%, and then bromination with *N*-bromosuccinimide (NBS) in DMF afforded **4** in 71% yield. The brominated bipyrrole **4** is a key intermediate for introduction of the thiophene and bithiophene moieties onto the bipyrrole

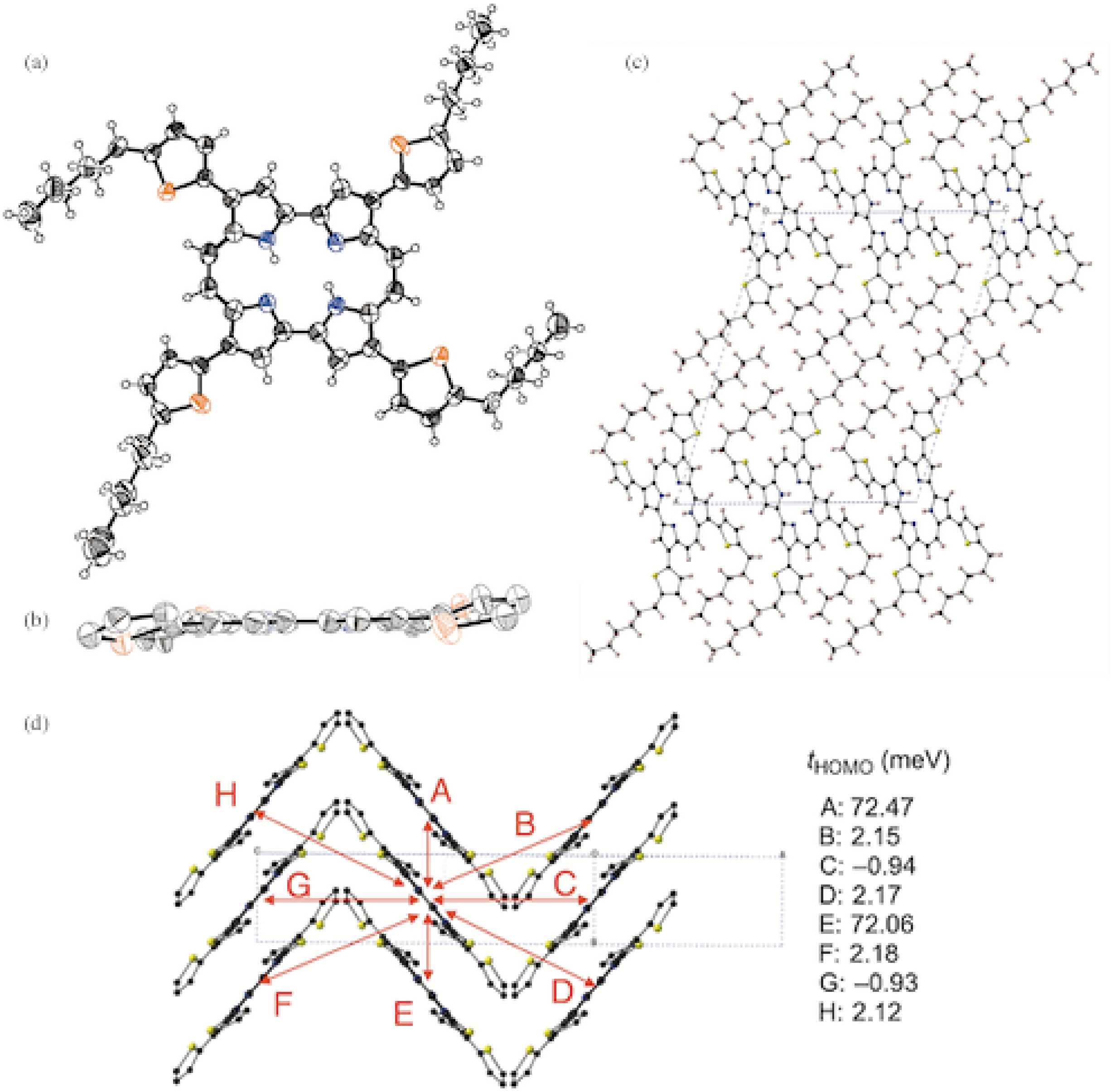


Fig. 2. Crystal structure of **ThPc**. (a) top view and (b) side view. In the side view, the alkyl chains and hydrogen atoms are omitted clarity. Thermal ellipsoids are shown at the 50% probability level. (c) packing structure, (d) transfer integrals for the nearest neighboring molecular pairs

units. The crystal structure of **4** is shown in Fig. S1 in the Supporting information. The Stille coupling of **4** with 5-hexyl-2-tributylstannyl-thiophene or tributyl(5′-hexyl-[2,2′-bithiophen]-5-yl)stannane in the presence of $Pd(PPh_3)_4$ gave **5** or **6** in 79% or 76% yields, respectively. Bipyrroles **5** and **6** were decarboxylated with NaOH in ethylene glycol at 170 °C and formylated by Vilsmeier–Haack reaction to give **9** and **10** in 95 and 89% yield, respectively. Finally, McMurry coupling of **9** and **10** gave the thiophene- and dithiophene-substituted porphycenes **ThPc** and **DThPc** in 18% and 17% yields, respectively. The synthesized porphycenes were characterized with ^{1}H and ^{13}C NMR spectroscopy and high-resolution mass spectroscopy (HRMS), Figs S2–S13.

Figure 2 shows the crystal structure of **ThPc**. The single crystal was obtained from a slow diffusion of isopropanol into a chlorobenzene solution of **ThPc**. Thiophenes are positioned as propeller-like structures. The porphycene core forms a highly planar macrocyclic structure with mean–plane deviation with respect to the macrocyclic atoms of 0.021 Å. The dihedral angles between thienyl groups and porphycene are 21° and 18°. Previously, we reported the crystal structure of **β-PhPc**, with dihedral angles between phenyl groups and porphycene core at 48° and 33° [66]. These results indicated that the whole of the molecular planarity of **ThPc** increases compared with that of **β-PhPc** due to the small five-membered ring unit of thiophene relative to benzene.

The inside *N–N* distances are 2.642 and 2.838 Å, which are comparable to that of **β-PhPc** (2.635 and 2.843 Å). The stacking structure of **ThPc** is a herringbone pattern and the intermolecular distance of each porphycene core is 3.39 Å, which is slightly shorter than the sum of van der Waals radii of carbon atoms. Intermolecular transfer integral values between the HOMOs of neighboring molecules were calculated with the Amsterdam density functional (ADF) program package [74, 75]. Calculated values are shown in Fig. 2d. The transfer integral value is correlated to the charge carrier mobility and the possibility of application for organic thin-film transistors. Transfer integral values in the stacking direction (A and E) are large (*ca.* 72 meV), whereas other directions are negligible, indicating that **ThPc** is expected to exhibit a one-dimensional transportation property. The transfer integral of **ThPc** is similar to that of pentacene (79 meV) [76], so that **ThPc** may work as a good semiconducting material.

Electronic properties

Absorption spectra of **ThPc** and **DThPc** in CH_2Cl_2 are shown in Fig. 3. Generally, porphycene exhibits slightly split strong Soret bands and three Q-band peaks in the visible regions. **ThPc** and **DThPc** keep typical porphycene-type absorption features. The **ThPc** shows absorption peaks at 403 nm as broadened Soret bands and at 601, 658 and 694 nm as Q-like bands. With additional thiophene rings, **DThPc** shows red-shifted and broadened absorption at 363, 424, 684 nm. In comparison of the absorption property of **β-PhPc**, both Soret and Q bands of **ThPc** and **DThPc** are significantly red shifted and broadened because of the extension of the π conjugations. These results indicate that thiophene moieties strongly perturb the electronic property of porphycene. To evaluate the electronic structures, DFT calculation was examined at the B3LYP/6-31G** level. Geometry optimization calculations were carried out using the structure of **ThPc′** and **DThPc′** with methyl groups instead of hexyl groups for simplicity. The molecular orbitals and energy levels are illustrated in Fig. 4. The parent porphycene has degenerated HOMO and HOMO-1, and non-degenerated LUMO and LUMO+1 because of its lower symmetric structure. When thienyl groups are introduced on porphycene at 2,7,12,17-positions, the LUMO level is comparable and the HOMO level increases to that of the parent porphycene because the HOMO orbital of **ThPc** is distributed on porphycene and thiophenes, resulting in a decrease in the HOMO–LUMO difference. In the case of **DThPc**, HOMO and LUMO levels are slightly up and down, respectively, giving a smaller HOMO–LUMO difference than that of **ThPc**. These trends are consistent with results of the absorption spectra of **ThPc** and **DThPc**. We also measured fluorescence spectra; however, both **ThPc** and **DThPc** have no fluorescence, even in degassed solutions.

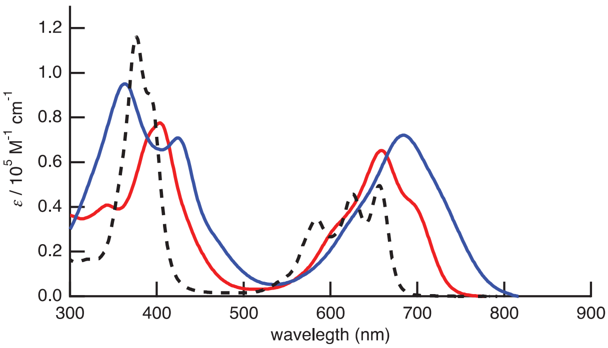


Fig. 3. UV-vis-NIR absorption spectra of **ThPc** (red), **DThPc** (blue) and **β-PhPc** (black dotted) in CH_2Cl_2

To investigate the electrochemical properties of **ThPc** and **DThPc**, cyclic voltammetry was measured in benzonitrile containing 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) as a supporting electrolyte at room temperature (Fig. 5). **ThPc** shows one irreversible oxidation peak at 0.52 V and two reversible reduction peaks at -1.12 and -1.37 V (*vs*. ferrocene/ferrocenium cation). **DThPc** also shows one irreversible oxidation peak at 0.32 V and two reversible reduction peaks at -1.05 and -1.27 V (*vs*. ferrocene/ferrocenium cation). The resulting band-gap energies of **ThPc** (1.60 V) and **DThPc** (1.37 V) are much smaller than that of **β-PhPc** (1.80 V), indicating the extension of the π conjugations through porphycene and thiophene units.

In conclusion, thiophene- and dithiophene-substituted porphycenes, **ThPc** and **DThPc**, were successfully synthesized by McMurry coupling from corresponding diformyl-bipyrroles. The crystal structure revealed that **ThPc** forms a highly planar structure through the porphycene core to thiophenes because of less steric hinderance between porphycene and thiophene units. **ThPc** and **DThPc** exhibit the extension of the π conjugations between porphycene and thiophene units, resulting in the red-shifted absorption in NIR regions. These results demonstrate that porphycene-based NIR absorbing dyes can be used in practical applications for PDT and non-linear optical materials. The optical and electrochemical properties and herringbone-type packing structures with high one-dimensional transfer integrals of **ThPc** and **DThPc** signal superior performance as organic semiconducting materials for organic solar cells and transistors. Fabrication of solution-processed organic field effect transistors to evaluate the charge carrier mobility of **Pc** and **DThPc** is underway.

EXPERIMENTAL

General

Absorption spectra were measured with a JASCO UV/vis/NIR Spectrophotometer V-670. ^{1}H NMR and

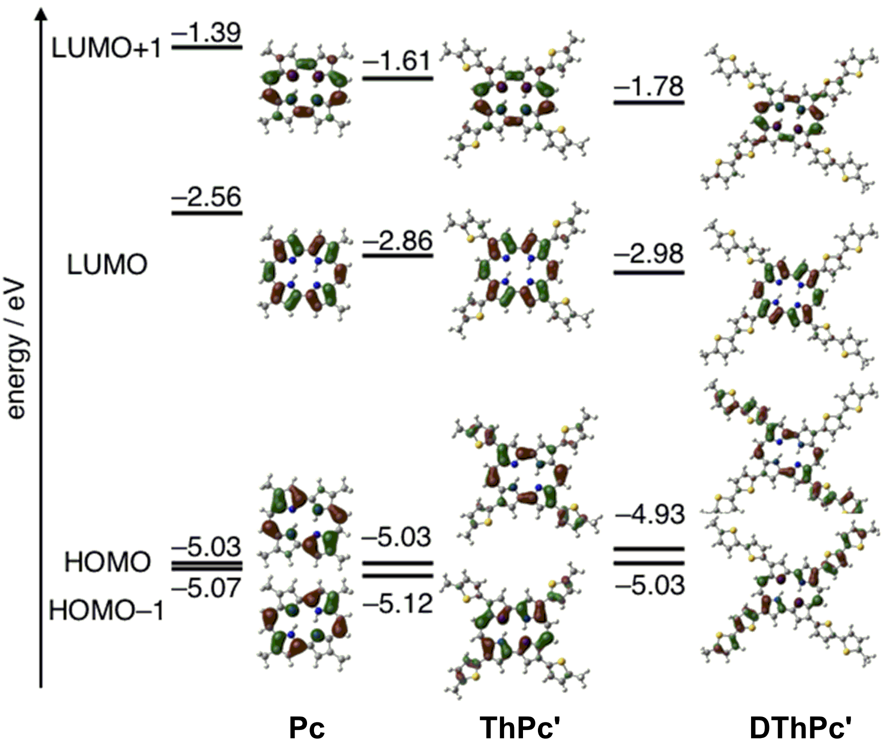


Fig. 4. Calculated energy diagrams and Kohn–Sham molecular orbitals of porphycene (**Pc**), **ThPc′**, and **DThPc′** at the B3LYP/6-31G** level

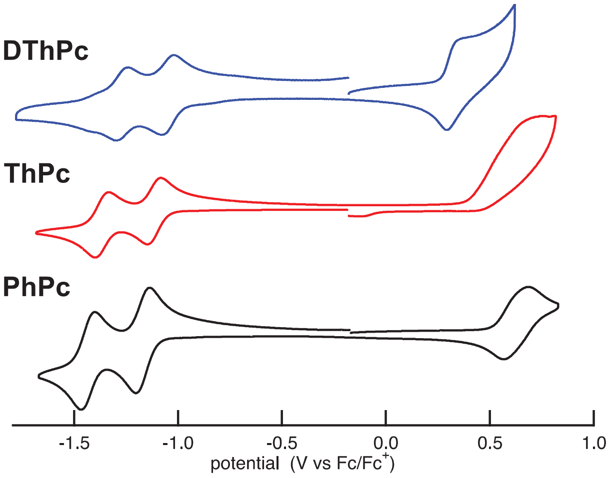


Fig. 5. Cyclic voltammograms of **ThPc**, **DThPc** and β-**PhPc** in benzonitrile containing 0.1 M TBAPF$_6$. Scan rate = 100 mV s^{-1}

^{13}C NMR spectra were recorded on a JNM-ECX 400 spectrometer (operating as 400 MHz for ^{1}H and 100 MHz for ^{13}C) using the residual solvent as the internal reference for ^{1}H ($\delta = 7.26$ ppm in CDCl$_3$, $\delta = 5.32$ ppm in CD$_2$Cl$_2$, and $\delta = 2.50$ ppm in DMSO-d_6). Electrospray ionization (ESI) mass spectra were recorded on a JEOL JMS-MS T100LC spectrometer. Matrix-assisted laser desorption/ionization (MALDI)-TOF-MS spectra were recorded on a JEOL SpiralTOF JMS-S3000 spectrometer (JEOL Akishima, Japan). FAB mass spectra were measured on a JEOL JMS-700 MStation spectrometer. CV measurement was conducted in a solution of 0.1 M TBAPF$_6$ in dry benzonitrile with a scan rate of 100 mV s^{-1} in an argon-filled cell. A glassy carbon electrode and a platinum wire were used as a working and a counter electrode, respectively. Ag/AgNO$_3$ electrodes were used as reference electrodes, which were normalized with the half-wave potential of the ferrocene/ferrocenium (Fc/Fc$^+$) redox couple. All solvents and chemicals were reagent-grade quality, obtained commercially, and used without further purification except as noted. For spectral measurements, spectral-grade dichloromethane was purchased from Nakalai Tesque Co. Thin-layer chromatography (TLC), flush column chromatography, and gravity column chromatography were performed on Art. 5554 (Merck KGaA), Silica Gel 60 (Merck KGaA) and Silica Gel 60N (Kanto Chemical Co.), respectively.

X-ray analysis

X-ray crystallographic data for **ThPc** was recorded at 103 K on a Rigaku R-AXIS RAPID/S using Mo–Kα radiation from the corresponding set of confocal optics. The structures were solved by direct methods and refined on F^2 by full-matrix least-squares using the CrystalClear and SHELXS–2000 programs [77].

Theoretical calculations

All density functional theory calculations were achieved with the Gaussian 09 program package. The geometry was optimized at the Becke's three-parameter hybrid functional combined with the Lee–Yang–Parr correlation functional abbreviated as the B3LYP level of density functional theory with the 6-31G(*d*,*p*) basis set.

Charge transfer integral calculation

Charge transfer integrals were calculated by the fragment orbital method with the PW91/DZ2P level of theory using the Amsterdam Density Functional (ADF) program. Charge transfer integrals were obtained from one of the disordered structures of **ThPc** with a larger occupancy rate.

Synthesis

***Diethyl 1H-pyrrole-2,4-dicarboxylate* (1).** To a 1,4-dioxane solution (200 ml) of Cu_2O (0.74 g, 5.1 mmol) and 1,10-phenanthroline (1.82 g, 10 mmol) were added ethyl propiolate (10.2 ml, 100 mmol) and ethyl isocyanoacetate (12.0 ml, 110 mmol) under argon atmosphere. The solution was stirred at 100 °C for 1 h. The reaction mixture was cooled to room temperature and filtered through a short Florisil pad and concentrated. The residue was purified by flash silica gel column chromatography (hexane/AcOEt 20:1 to 3:1) to give **1** as white powder. Yield: 83% (17.5 g, 82.7 mmol). ^{1}H NMR (DMSO-d_6; 400 MHz; Me_4Si) δ_H, ppm 12.53 (brs, 1H), 7.56 (s, 1H), 7.07 (s, 1H), 4.28–4.17 (*q* + *q*, 4H), 1.31–1.25 (*t* + *t*, 6H). ^{13}C NMR (DMSO-d_6; 100 MHz; Me_4Si) δ_C, ppm 163.16, 159.90, 127.76, 123.40, 116.56, 115.09, 60.04, 59.38, 14.22, 14.18. HRMS (ESI): *m/z* = 211.09228. calcd for $C_{10}H_{14}NO_4$:211.09299 [M + H]$^+$.

***Diethyl 5-iodo-1H-pyrrole-2,4-dicarboxylate* (2).** A solution of **1** (12.1 g, 57.1 mmol), iodine (14.5 g, 57.2 mmol), HIO_3 (2.63 g, 15.0 mmol), AcOH (78 ml) and H_2O (10 ml) in DCE (183 ml) was refluxed for 15 h. The reaction was quenched with $NaHSO_3$ aq. The separated organic layer was washed with water, sat. $NaHCO_3$ aq. and brine, and then dried over Na_2SO_4. The solution was removed under reduced pressure, then filtrated and rinsed with 2-propanol. The crude product was purified by silica gel column chromatography (CH_2Cl_2) and recrystallized from $CHCl_3$/2-propanol to give **2** as white crystals. Yield: 60% (11.56 g, 34.3 mmol). ^{1}H NMR (DMSO-d_6; 400 MHz; Me_4Si) δ_H, ppm 13.08 (s, 1H), 7.09 (s, 1H), 4.28–4.18 (m, 4H), 1.31–1.08 (t, 6H). ^{13}C NMR (DMSO-d_6; 100 MHz; Me_4Si) δ_C, ppm 162.30, 159.02, 127.05, 119.43, 116.98, 82.06, 60.17, 59.53, 14.13. HRMS (ESI): *m/z* = 359.97087. calcd for $C_{10}H_{12}INNaO_4$:359.97162 [M + Na]$^+$.

***Tetraethyl 1H,1′H-[2,2′-bipyrrole]-3,3′,5,5′-tetracarboxylate* (3).** A mixture of **2** (14.1 g, 42.4 mmol) and activated Cu (18.1 g) in toluene (90 ml) was refluxed for 24 h under argon atmosphere. The precipitate was filtered out on a Celite pad and washed with CH_2C_{12}. The solvent was concentrated under a reduced pressure. The crude product was purified by silica gel column chromatography (CH_2Cl_2) and recrystallized from $CHCl_3$/MeOH to give **3** as white solids. Yield: 40% (3.53 g, 8.40 mmol). ^{1}H NMR ($CDCl_3$; 400 MHz; Me_4Si) δ_H, ppm 14.33 (s, 2H), 7.46 (s, 2H), 4.45–4.37 (m, 8H), 1.43–1.40 (t, 12H). ^{13}C NMR ($CDCl_3$; 100 MHz; Me_4Si) δ_C, ppm 166.75, 160.40, 130.18, 122.65, 118.99, 113.76, 61.52, 60.94, 14.39, 14.30. HRMS (ESI): m/z = 443.1430. calcd for $C_{20}H_{24}N_2NaO_8$: 443.14380 [M + Na]$^+$.

***Tetraethyl 4,4′-dibromo-1H,1′H-[2,2′-bipyrrole]-3,-3′,5,5′-tetracarboxylate* (4).** A solution of bipyrrole **3** (3.5 g, 8.4 mmol) and *N*-bromosuccinimide (4.5 g, 25 mmol) in DMF (170 ml) was heated at 100 °C for 48 h under argon atmosphere. After cooling to room temperature, the reaction was quenched with aqueous $NaHSO_3$. After removal of the solvent, the residue was extracted with CH_2Cl_2. The extract was washed with 1 M HCl, water and brine, and then dried over Na_2SO_4. After removal of the solvent, the residue was purified by silica gel column chromatography (CH_2Cl_2) and recrystallized from $CHCl_3$/hexane to give **4** as greenish-white solids. Yield: 71% (3.4 g, 5.9 mmol). ^{1}H NMR ($CDCl_3$; 400 MHz; Me_4Si) δ_H, ppm 14.31 (brs, 2H), 4.48 (q, *J* = 7 Hz, 4H), 4.43 (q, *J* = 7 Hz, 4H), 1.47 (t, *J* = 7 Hz, 6H), 1.44 (t, *J* = 7 Hz, 6H). ^{13}C NMR ($CDCl_3$; 100 MHz; Me_4Si) δ_C, ppm 166.63, 159.37, 129.21, 121.61, 114.72, 106.18, 62.38, 61.39, 14.33, 14.16. HRMS (ESI): *m/z* = 607.11848. calcd. for $C_{28}H_{28}N_2O_8S_2Na$: 607.11867 [M + Na]$^+$. Crystal data: $C_{20}H_{22}Br_2N_2O_8$, Fw 578.21, monoclinic, space group $P2_1/c$, a = 14.2510 (5), b = 5.51633 (16), c = 14.7039 (5) Å, β = 109.8223 (9), V = 1087.43 (6) Å^3, Z = 2, T = 103 K, D_{calc} = 1.766 g cm^{-3}, GOF = 1.086, R_1 ($I > 2\sigma(I)$) = 0.0292 and wR_2 = 0.0737 (all data), CCDC 1917992.

***Tetraethyl 4,4′-bis(5-hexylthiophen-2-yl)-1H,1′H-[2,2′-bipyrrole]-3,3′,5,5′-tetracarboxylate* (5).** A solution of **4** (1.74 g, 3.0 mmol) and 5-hexyl-2-tributylstannyl-thiophene (8.23 g, 18 mmol) in toluene (45 mL) was degassed by bubbling with argon for 30 min. To the resulting mixture was added $Pd(PPh_3)_4$ (376 mg, 0.30 mmol) and refluxed for 18 h. The solvent was removed under reduced pressure. The crude product was purified by column chromatography (10% K_2CO_3 in silica gel, hexane/CH_2Cl_2 9:1 to 1:9) to give **5** as yellowish-white solids. Yield: 79% (1.78 g, 2.37 mmol). ^{1}H NMR ($CDCl_3$; 400 MHz; Me_4Si) δ_H, ppm 14.10 (brs, 2H, –NH), 6.72 (d, 2H, *J* = 4 Hz), 6.70 (d, 2H, *J* = 4 Hz) 4.25 (q, 4H, *J* = 7 Hz), 4.14 (q, 4H, *J* = 7 Hz), 2.83 (t, 4H, *J* = 7 Hz), 1.73–1.65 (m, 4H), 1.43–1.30 (m, 12H) 1.22 (t, 6H, *J* = 7 Hz), 0.97 (t, 6H, *J* = 7 Hz), 0.90 (t, 6H, *J* = 7.3 Hz). ^{13}C NMR ($CDCl_3$; 100 MHz; Me_4Si) δ_C, ppm 167.50, 160.08, 145.96, 132.22, 128.92, 127.17, 126.36, 123.13, 121.73, 115.23, 61.33, 60.71, 31.99, 31.65, 30.16, 28.85, 22.65, 14.12, 13.96, 13.26. HRMS (ESI) : *m/z* = 775.30628. calcd. for $C_{40}H_{52}N_2O_8S_2Na$: 775.30472 [M + Na]$^+$.

Tetraethyl 4,4′-bis(5′-hexyl-[2,2′-bithiophen]-5-yl)-1H,1′*H*-[2,2′-bipyrrole]-3,3′,5,5′-tetracarboxylate

(6). A solution of **4** (1.74 g, 3.0 mmol) and 5-hexyl-2-tributylstannyl-thiophene (8.23 g, 18 mmol) in toluene (45 mL) was degassed by bubbling with argon for 30 min. To the resulting mixture was added $Pd(PPh_3)_4$ (376 mg, 0.30 mmol) and refluxed for 18 h. The solvent was removed under reduced pressure. The crude product was purified by column chromatography (10% K_2CO_3 in silica gel, hexane/CH_2Cl_2 9:1 to 1:9) to give **6** as yellowish-white solids. Yield: 79% (1.78 g, 2.37 mmol). ^{1}H NMR ($CDCl_3$; 400 MHz; Me_4Si) δ_H, ppm 14.24 (brs, 2H), 7.05 (d, $J = 4$ Hz, 2H), 6.97 (d, $J = 4$ Hz, 2H), 6.82 (d, $J = 4$ Hz, 2H), 6.69 (d, $J = 4$ Hz, 2H), 4.26 (q, $J = 7$ Hz, 4H), 4.18 (q, $J = 7$ Hz, 4H), 2.80 (t, $J = 7$ Hz, 4H), 1.70 (m, 4H), 1.44–1.30 (m, 12H), 1.23 (t, $J = 7$ Hz, 6H), 1.00 (t, $J = 7$ Hz, 6H), 0.90 (t, $J = 7$ Hz, 6H). ^{13}C NMR ($CDCl_3$; 100 MHz; Me_4Si) δ_C, ppm 167.50, 160.08, 145.96, 132.22, 128.92, 127.17, 126.36, 123.13, 121.73, 115.23, 61.33, 60.71, 31.99, 31.65, 30.16, 28.85, 22.65, 14.12, 13.96, 13.26; HRMS (ESI) : $m/z = 775.30628$. calcd. for $C_{40}H_{52}N_2O_8S_2Na$: 775.30472 $[M + Na]^+$.

4,4′-Bis*(5-*hexylthiophen*-2-*yl*)-1*H*,1′*H*-2,2′-*bipyrrole **(7)**. A mixture of **5** (926 mg, 1.23 mmol) and NaOH (395 mg, 8.0 mmol) in degassed ethylene glycol (17 ml), which was connected to a vacuum line for 20 min, was heated at 170 °C for 2 h under argon atmosphere. After cooling to room temperature, the reaction mixture was diluted with cold water. The resulting precipitate was filtrated and washed with water and MeOH. The product was dried *in vacuo* with P_2O_5 to give **7** as greenish gray solids. This product was directly used for the next step without any further purification. Yield: 96% (549 mg, 1.18 mmol). ^{1}H NMR ($CDCl_3$; 400 MHz; Me_4Si) δ_H, ppm 8.18 (brs, 2H), 6.93 (m, 2H), 6.85 (d, $J = 3.7$ Hz, 2H), 6.65 (d, $J = 3.7$ Hz, 2H), 6.38 (m, 2H), 2.78 (t, $J = 7.3$ Hz, 4H), 1.67 (quint, $J = 7.3$ Hz, 4H), 1.39–1.28 (m, 12H), 0.89 (t, $J = 7.3$ Hz, 6H). ^{13}C NMR ($CDCl_3$; 100 MHz; Me_4Si) δ_C, ppm 142.90, 136.23, 126.17, 124.38, 120.92, 120.58, 114.26, 102.33, 31.78, 31.71, 30.23, 28.89, 22.69, 14.20. HRMS (ESI): m/z = 465.23981. calcd for $C_{28}H_{37}N_2S_2$:465.23879 $[M + H]^+$.

4,4′-Bis*(5′-*hexyl*-[2,2′-*bithiophen*]-5-*yl*)-1*H*,1′*H*-2,2′-*bipyrrole **(8).** A mixture of **6** (1.12 g, 1.23 mmol) and NaOH (380 mg, 9.5 mmol) in degassed ethylene glycol (17 ml), which was connected to vacuum line for 20 min, was heated at 170 °C for 2 h under an argon atmosphere. After cooling to room temperature, the reaction mixture was diluted with cold water. The resulting precipitate was filtrated and washed with water and MeOH. The product was dried *in vacuo* with P_2O_5 to give **8** as greenish-gray solids. This product was directly used for the next step without any further purification. Yield: quant. (773 mg, 1.23 mmol). ^{1}H NMR (DMSO-d_6; 400 MHz; Me_4Si) δ_H, ppm 11.29 (brs, 2H), 7.14 (d, $J = 1$ Hz, 2H), 7.08 (d, $J = 4$ Hz, 2H), 7.02 (d, $J = 4$ Hz, 2H), 7.00 (d, $J = 4$ Hz, 2H), 6.78 (d, $J = 4$ Hz, 2H), 6.55 (d, $J = 1$ Hz, 2H), 2.77 (t, $J = 7$ Hz, 4H), 1.62 (m, 4H), 1.36–1.26 (m, 12H), 0.87 (t, $J = 7$ Hz, 6H); ^{13}C NMR (DMSO-d_6; 100 MHz; Me_4Si) δ_C, ppm 144.38, 138.80, 135.01, 132.69, 127.08, 125.93, 124.39, 123.16, 121.67, 118.46, 115.65, 101.78, 31.60, 31.49, 29.86, 28.62, 22.58, 14.49. HRMS (MALDI-TOF): $m/z = 628.2066$. calcd for $C_{36}H_{41}N_2S_4$: 628.2069$[M]^+$.

4,4′-Bis*(5-*hexylthiophen*-2-*yl*)-1*H*,1′*H*-[2,2′-*bipyrrole*]-5,5′-*dicarbaldehyde **(9).** To a solution of **7** (507 mg, 1.09 mmol) in DMF (11 ml) was slowly added $POCl_3$ (0.45 ml, 4.95 mmol) at 0 °C under argon atmosphere. The reaction mixture was heated at 60 °C for 2 h. After cooling to room temperature, NaOAc aq. (1.2 g/16 ml) was carefully added. The mixture was heated at 85 °C for another 1 h. The solution was poured into cold water, the resulting precipitate was filtrated and rinsed with water and MeOH. The product was dried *in vacuo* with P_2O_5 to give **9** as yellowish-green solids. This product was used for the next step without any further purification. Yield: 95% (539 mg, 1.03 mmol). ^{1}H NMR (DMSO-d_6; 400 MHz; Me_4Si) δ_H, ppm 12.41 (brs, 2H), 9.79 (s, 2H), 7.24 (d, $J = 3$ Hz, 2H), 7.18 (d, $J = 3$ Hz, 2H), 6.97 (d, $J = 3$ Hz, 2H), 2.81 (t, $J = 7$ Hz, 4H), 1.64 (m, 4H), 1.38–1.28 (m, 12H), 0.87 (t, $J = 7$ Hz, 6H). ^{13}C NMR (DMSO-d_6; 100 MHz; Me_4Si) δ_C, ppm 178.55, 146.45, 132.75, 130.67, 129.41, 129.13, 126.94, 126.05, 110.18, 31.62, 31.50, 29.86, 28.67, 22.58, 14.49. HRMS (ESI): m/z = 543.21159. calcd for $C_{30}H_{36}N_2O_2S_2Na$:543.21194 $[M]^+$.

4,4′-Bis*(5′-*hexyl*-[2,2′-*bithiophen*]-5-*yl*)-1*H*,1′*H*-[2,2′-*bipyrrole*]-5,5′-*dicarbaldehyde **(10).** To a solution of **8** (694 mg, 1.10 mmol) in DMF (11.5 ml) was slowly added $POCl_3$ (0.45 ml, 4.95 mmol) at 0 °C under argon atmosphere. The reaction mixture was heated at 60 °C for 1 h. After cooling to room temperature, NaOAc aq. (1.16 g/16 ml) was carefully added. The mixture was heated at 85 °C for another 1 h. The solution was poured into cold water, the resulting precipitate was filtrated and rinsed with water and MeOH. The product was dried *in vacuo* with P_2O_5 to give **10** as yellowish-green solids. This product was used for the next step without any further purification. Yield: 89% (670 mg, 0.98 mmol). ^{1}H NMR (DMSO-d_6; 400 MHz; Me_4Si) δ_H, ppm 12.53 (brs, 2H), 9.85 (s, 2H), 7.42 (d, $J = 4$ Hz, 2H), 7.26 (s, 2H), 7.26 (d, $J = 4$ Hz, 2H), 7.17 (d, $J = 4$ Hz, 2H), 6.84 (d, $J = 4$ Hz, 2H), 2.80 (t, $J = 7$ Hz, 4H), 1.63 (m, 4H), 1.38–1.24 (m, 12H), 0.87 (t, $J = 7$ Hz, 6H). ^{13}C NMR could not be recorded because of low solubility. HRMS (MALDI-TOF): $m/z = 684.1960$. calcd for $C_{38}H_{41}N_2O_2S_4$: 684.1967 $[M{+}H]^+$.

2,7,12,17-*Tetra*(5-*hexyl-thien*-2-*yl*)*porphycene* (*ThPc*). $TiCl_4$ (1.10 ml, 10 mmol) was added dropwise to a THF (80 mL) solution containing Zn dust (1.31 g) and CuCl (499 mg, 5.0 mmol) at room temperature under argon atmosphere, and then the mixture was refluxed for 3 h. The resulting mixture was added pyridine (0.8 ml). Subsequently a solution of **9** (520 mg, 1.0 mmol) in THF (40 mL) was added dropwise to the boiling reaction mixture. The mixture was stirred at same temperature for another 30 min. After cooling to 0 °C, an aqueous 10% K_2CO_3 solution (140 ml) was added dropwise. After filtration the precipitate was washed with CH_2Cl_2, the combined organic layer was then dried with Na_2SO_4, and the solution was removed under reduced pressure. The crude product was purified by alumina column chromatography (CH_2Cl_2) and silica gel column chromatography (20% CH_2Cl_2 in hexane). Recrystallization from $CHCl_3$/MeOH gave **ThPc** as greenish-purple powder. Yield: 18% (87 mg, 0.09 mmol). ^{1}H NMR (CD_2Cl_2; 400 MHz; Me_4Si) δ_H, ppm 9.77 (s, 4H), 9.23 (s, 4H), 7.82 (d, $J = 4$ Hz, 4H), 7.23 (d, $J = 4$ Hz, 4H), 3.15 (t, $J = 7$ Hz, 8H), 2.59 (brs, 2H), 1.98 (m, 8H), 1.67–1.46 (m, 24H), 1.01 (t, $J = 7$ Hz, 12H). ^{13}C NMR ($CDCl_3$; 100 MHz; Me_4Si) δ_C, ppm 148.24, 140.88, 136.32, 135.65, 133.06, 127.82, 125.74, 121.74, 113.27, 32.09, 31.86, 30.59, 29.19, 22.84, 14.06. HRMS (FAB): $m/z = 975.4556$ calcd for $C_{60}H_{71}N_4S_4$: 975.4568 $[M{+}H]^+$. Crystal data: $C_{60}H_{70}BN_4S_4$, Fw 975.48, monoclinic, space group $P2/c$, $a = 25.6267$ (13), $b = 5.2743$ (2), $c = 20.2390$ (10) Å, $\beta = 107.6630$ (10), $V = 2606.6$ (2) Å^3, $Z = 2$, $T = 103$ K, $D_{calc} = 1.243$ g cm^{-3}, GOF = 1.048, R_1 ($I > 2\sigma(I)$) = 0.0680 and $wR_2 = 0.1890$ (all data), CCDC 1917993.

2,7,12,17-*Tetra*(5′-*hexyl*-[2,2′-*bithiophen*]-5-*yl*) *porphycene* (*DThPc*). $TiCl_4$ (0.80 ml, 7.3 mmol) was added dropwise to a THF (70 mL) solution containing Zn dust (0.963 g) and CuCl (753 mg, 7.4 mmol) at room temperature under argon atmosphere, and then the mixture was refluxed for 3 h. The resulting mixture was added pyridine (0.6 ml). Subsequently a solution of bipyrrole 10 (506 mg, 0.73 mmol) in THF (50 mL) was added dropwise to the boiling reaction mixture. The mixture was stirred at same temperature for another 30 min. After cooling to 0 °C, an aqueous 10% K_2CO_3 solution (140 mL) was added dropwise. After filtration the precipitate was washed with CH_2Cl_2, the combined organic layer was then dried with Na_2SO_4, and the solution was removed under reduced pressure. The crude product was purified by alumina column chromatography (CH_2Cl_2) and silica gel column chromatography (20% CH_2Cl_2 in hexane). Recrystallization from $CHCl_3$/MeOH gave **DThPc** as greenish purple powder. Yield: 17% (83 mg, 0.06 mmol). ^{1}H NMR (CD_2Cl_2; 400 MHz; Me_4Si) δ_H, ppm 8.93 (s, 4H), 9.42 (s, 4H), 7.55 (d, $J = 4$ Hz, 4H), 7.36 (d, $J = 4$ Hz, 4H), 7.21 (d, $J = 4$ Hz, 4H), 6.79 (d, $J = 4$ Hz, 4H), 2.89 (t, $J = 7$ Hz, 8H), 2.66 (brs, 2H), 1.78 (m, 8H), 1.40–1.31 (m, 24H), 0.93 (t, $J = 7$ Hz, 12H); ^{13}C NMR spectrum were not recorded because of poor solubility; HRMS (MALDI-TOF): $m/z = 1303.4075$ calcd for $C_{76}H_{79}N_4S_8$: 1303.4065 $[M + H]^+$.

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Supporting information

Crystal structure for compound **4** and spectral data for Compounds **1–10** and **ThPc** and **DThPc** are given in the supplementary material. This material is available free of charge *via* the Internet at http://www.worldscinet.com/jpp/jpp.shtml.

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