

Electron-Rich Pyrroloindacenodithiophenes: Synthesis, Characterization, and Spectroscopic Studies

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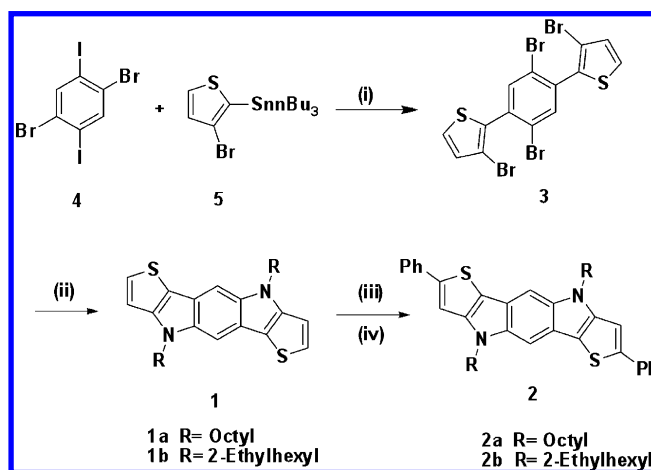
S Supporting Information

ABSTRACT: *N*-Alkyl substituted pyrroloindacenodithiophene (PIDT) and their phenyl substituted derivatives were synthesized. Their single-crystal structures and electrochemical and spectroscopic properties were investigated. Experimental results showed PIDT displayed strong electron-donating properties, reversible redox behaviors, and strong fluorescence and could be controlled to oxidize to radical cation and dication with distinctive optical changes. These attractive properties demonstrated the potential applications of PIDT in the field of switches, molecular machines, and information memories.



Electron donors with reversible redox properties have attracted a great deal of attention due to their wide applications in the fields of switches,¹ sensors,² molecular machines,³ and information memories.⁴ An ideal electron donor for these fields should (i) have high HOMO energy level (larger than -5.3 eV, so that it can be easily oxidized by electrochemical technique or chemical species); (ii) exhibit optical (absorption and/or emission) changes with the oxidation; (iii) provide easy synthesis, purification and modification; and (iv) have good solubility in organic solvents. Though great effort has been taken, to date, the most common electron donors used are tetrathiafulvalene (TTF)⁵ and ferrocene (Fc),⁶ so there is a great need to develop new type of strong electron donors with reversible redox property.

Pyrroloindacenodithiophene (PIDT), as a π -conjugated unit, was synthesized by Donaghey and coauthors with the aim to copolymerize with electron-deficient units and investigate the applications of these donor–acceptor (D–A) type polymers in transistors and organic solar cells.⁷ Devices characteristics suggested PIDT was a good conjugated block for polymer semiconductors. However, till now the physicochemical properties of PIDT had not been reported. Herein, a series of new type of *N*-alkyl substituted PIDTs (**1**) and their phenyl substituted derivatives (**2**) were synthesized (Scheme 1). Their physicochemical properties as well as single crystal structures were thoroughly investigated. Experimental results showed that **1** and **2** (i) displayed two reversible redox peaks in cyclic voltammetry with HOMO levels ranging from -4.9 to -5.1 eV; (ii) with the titration of oxidant FeCl_3 , displayed new absorption bands, with one of them located at the near-infrared (NIR) region; and (iii) exhibited strong fluorescence in solution. These results demonstrated the potential applications

Scheme 1^a

^a(i) CuCl , LiCl , $\text{Pd}(\text{PPh}_3)_4$, DMF; (ii) 5 mol % Pd_2dba_3 , 10 mol % BINAP, NaOtBu , alkylamine, *p*-xylene, 150°C , 2 h; (iii) NBS, THF/DMF, -78°C ; (iv) $\text{PhB}(\text{OH})_2$, $\text{Pd}(\text{PPh}_3)_4$, K_2CO_3 , toluene, reflux for 6 h.

of PIDTs in molecular machines, switches, and information memories.

The syntheses of compounds **1** and **2** are illustrated in Scheme 1. The pyrroloindacenodithiophene (PIDT) core was obtained following a recent reported method with a little modification.⁷ Compound **3** was synthesized through Stille coupling reaction and further reacted with alkylamine in the presence of Pd catalyst (Buchwald amination reaction) to

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afford compound **1**. The Buchwald amination reaction was carried out in refluxing *p*-xylene solvent instead of toluene, which was used as solvent in Donaghey's procedure. With this modification, the PIDT core was prepared efficiently with great yield improvement. Compound **1** reacted with NBS followed by Suzuki coupling reaction with phenylboronic acid to give **2** in moderate yield. It should be noted, because of the strong electron-donating property, the bromination of compound **1** needed to be carried out at low temperature. Compounds **1** had good solubility in common organic solvents (such as CH₂Cl₂, THF, and CHCl₃), and compound **2** had low solubility in organic solvents. Compounds **1** and **2** were fully characterized by NMR, MS, and elemental analysis.

Single crystals of **1a** and **2a** were grown by slow evaporation of organic solvents at room temperature (Figure 1). XRD

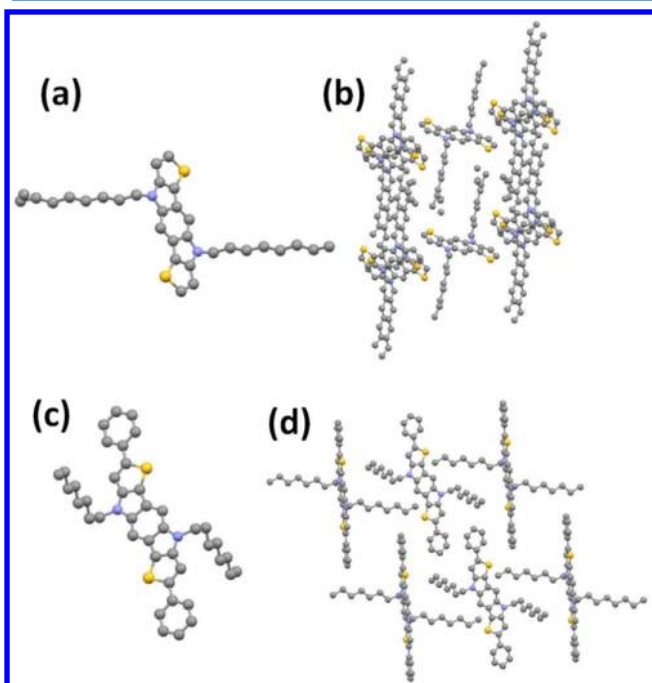


Figure 1. Single crystal and packing of compound **1a** (a,b) and **2a** (c,d).

results revealed that **1a** single crystals belonged to a monoclinic space group $P2_1/n$ with unit cell parameters of $a = 15.003(3)$ Å,

$b = 5.770(11)$ Å, $c = 17.973(4)$ Å, $\beta = 102.020(4)^\circ$. In the single crystal, the PIDT core exhibited planar structure and the alkyl chains were positioned out of the PIDT plane. The C—H $\cdots\pi$ interactions of the hydrogen atoms on the PIDT core and alkyl chain to the adjacent PIDT core were observed. Similar to **1a**, the conjugated backbone of **2a** displayed planar structure and the alkyl substituents were out of the core plane. Strong C—H $\cdots\pi$ interactions of the hydrogen atoms on the PIDT core and alkyl chain to the adjacent PIDT core were also observed. However, the space group of **2a** single crystals were different with that of **1a** and belonged to a monoclinic $C2/C$ group with unit cell parameters of $a = 35.045(3)$ Å, $b = 5.4519(2)$ Å, $c = 24.299(2)$ Å, $\beta = 117.063(2)^\circ$.

Figure 2a illustrated the absorption spectra of **1** and **2** in dilute CH₂Cl₂ solutions. The absorption spectra of **1a** and **2a** were nearly identical to those of **1b** and **2b**, respectively, suggesting the changes of alkyl chains had no influence on the HOMO–LUMO energy gaps. The onset absorptions of **1a,b** were 410 nm, ~ 66 nm blue-shifted compared with those of **2a,b**, indicating the enlarged conjugation length of **2a,b**. The optical energy band gaps calculated from solution were 3.02 eV for **1** and 2.60 eV for **2**. The fluorescence spectra of **1** and **2** are shown in Figure 2b. Similar as the absorption spectra, **1a** and **2a** exhibited identical emission spectra as **1b** and **2b**, respectively. The fluorescence quantum yield estimated from solution (9,10-diphenylanthracene as a reference standard)⁸ were 0.11 for **1a**, 0.12 for **1b**, 0.30 for **2a**, and 0.26 for **2b**.

The electronic properties of **1a,b** and **2a,b** were examined by cyclic voltammetry. All compounds showed two reversible redox waves (Figure 3). The redox potentials of **1a** and **1b** were determined as $E_{1/2}^1 = 0.59$ V, $E_{1/2}^2 = 1.22$ V from the midpoint of forward and backward scan. The first oxidation potential was close to that of ferrocene ($E_{1/2}^1 = 0.43$ V) and TTF ($E_{1/2}^1 = 0.37$ V),⁹ which suggested PIDT was a strong electron-rich compound and could be sequentially and reversibly oxidized to radical cation and dication within an accessible potential window like TTF.¹⁰ The HOMO energy levels of **1a,b** calculated from CV were -5.03 eV. It is well known TTF derivatives with aromatic substituents usually display a redox potential higher than that of TTF. Surprisingly, the redox potentials of **2a** and **2b** were at $E_{1/2}^1 = 0.54$ V and $E_{1/2}^1 = 1.05$ V and slightly lowered than those of **1a** and **1b**, indicating that the electrons on the phenyl rings were fully delocalized on the whole backbone. The HOMO energy levels of **2a** and **2b** calculated from CV were -4.98 eV.

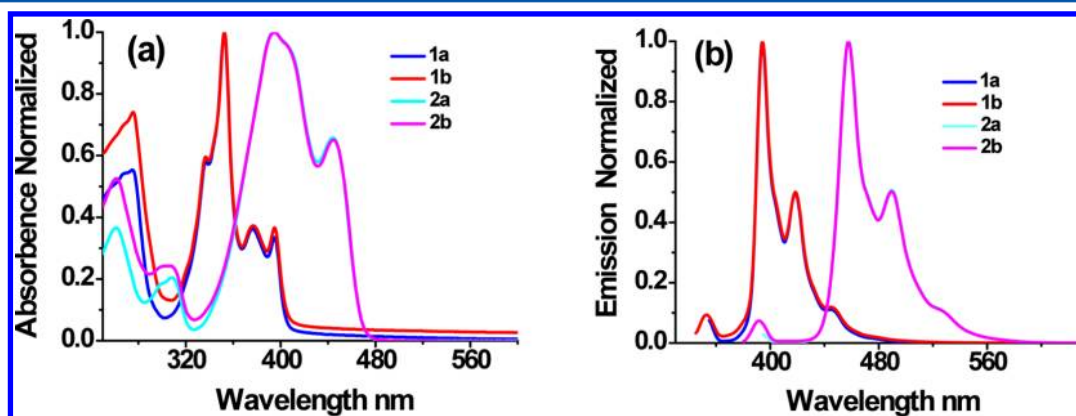


Figure 2. (a) UV–vis absorption spectra of **1a,b** and **2a,b** in CH₂Cl₂ solutions (1×10^{-4} mol/L). (b) Fluorescence spectra of **1a,b** and **2a,b** in cyclohexane solution.

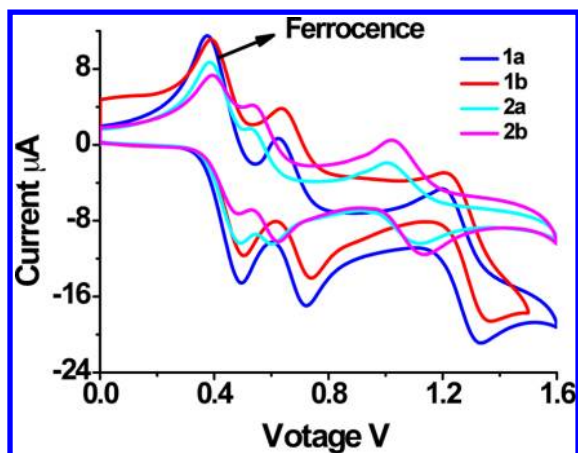


Figure 3. Cyclic voltammograms of 1a,b and 2a,b in CH_2Cl_2 by using $0.1 \text{ M } ^t\text{Bu}_4\text{PF}_6$ as electrolyte and SCE as reference under scan rate 100 mV/s . Fc/Fc^+ was used as internal standard.

The reversible redox behavior of 1 and 2 suggested that they could be controlled to oxidize to stable radical cation and dication with distinctive optical properties. To confirm this, the titration of 2a with FeCl_3 , as an example, was studied (Figure 4

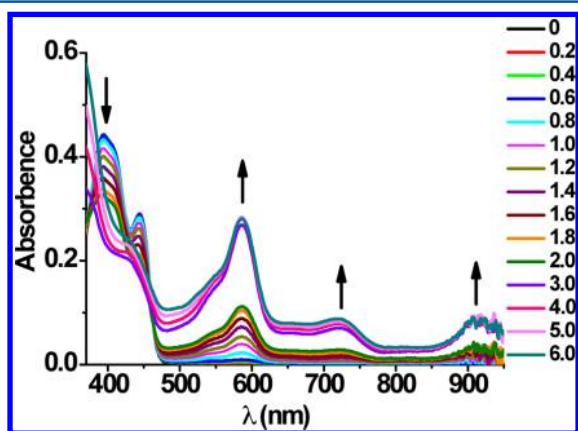


Figure 4. UV-vis absorption spectra of 2a in DCM ($1.43 \times 10^{-5} \text{ M}$) with the titration of FeCl_3 .

and Figure S1 in Supporting Information). With the addition of FeCl_3 , the intensity of the initial absorptions of 2a was decreased, and new bands located at 586, 720, and 910 nm emerged. No other new bands were observed upon the addition of 6.0 equiv of FeCl_3 . Considering the redox potentials of 2a, we inferred that 2a was oxidized to radical cation. To prove this assumption, the absorption spectra of radical cation and dication of 2a were measured by implementing the potentiostatic electrochemical experiment with in situ spectroelectrochemistry measuring technique.¹¹ According to cyclic voltammetry results, oxidation potentials of 0.7 and 1.4 V were applied separately to compound 2a for 200 s before the absorption spectra were conducted (Figure 5). We found when an oxidation voltage of 0.7 V was applied, 2a displayed an identical spectrum as that titrated by FeCl_3 (Figure S2 in Supporting Information.) When an oxidation potential of 1.4 V was used, besides the three new peaks at 586, 720, and 910 nm, a shoulder peak located at 602 nm was also observed in the absorption spectrum. These results evidenced that, unlike TTF (which can be oxidized to radical cation and dication sequentially),¹⁰ PIDT was only oxidized to radical cation by

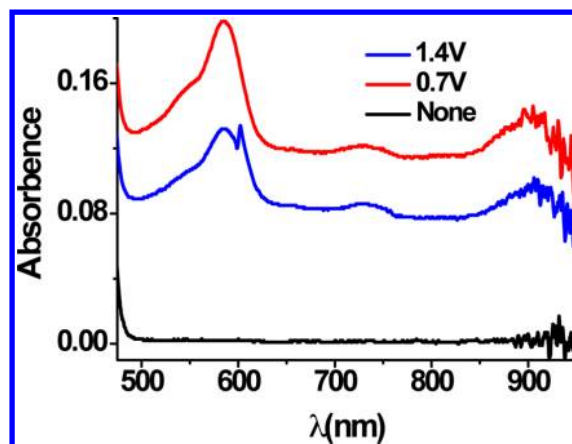


Figure 5. Absorption spectra of radical cation and dication of 2a measured by in situ spectroelectrochemistry.

ferric cation. To further confirm this assumption, the redox potential of FeCl_3 in CH_2Cl_2 solution was measured by cyclic voltammetry. The reduce potential of FeCl_3 was 0.88 V, which is higher than the first redox potential and lower than the second redox potential of compounds 1 and 2 (Figure S3 in Supporting Information3). These results further proved that compounds 1 and 2 can only be oxidized to radical cation by ferric cation. Moreover, when a solution of SnCl_2 was added to the radical cation of 2a, the absorption of neutral 2a was recovered, suggesting compounds 1 and 2 can be reversibly tuned by oxidation and reduction (Figure S4 in Supporting Information).

In summary, *N*-alkyl substituted PIDT (1a,b) and their phenyl substituted derivatives (2a,b) were synthesized. These compounds were strong electron donors with reversible redox behaviors and displayed strong fluorescence. These compounds can be controlled to oxidize to radical cation and dication with distinctive optical changes. These attractive properties demonstrated the potential applications of PIDT in the field of switches, molecular machines, and information memories.

EXPERIMENTAL SECTION

2,5-Dibromo-1,4-diiodobenzene (4).¹² A solution of *p*-dibromobenzene (36.0 g, 152.6 mmol) in concentrated sulfuric acid (450 mL) was heated to $125\text{--}135^\circ\text{C}$. Iodine (114.0 g, 449.2 mmol) was added portion-wise over 2 h. The mixture was held at $125\text{--}135^\circ\text{C}$ for 12 h and then cooled to room temperature. The reaction mixture was quenched into ice, and the resulting blocky solid was collected and washed with a saturated sodium bisulfate solution. The solid was recrystallized from tetrahydrofuran and further from chloroform affording 4 as white crystals: 33.0 g (45%). $^1\text{H NMR}$ (CDCl_3) δ 8.05 (s, 2 H); MS (EI) (m/z) 487.

2-(Tri-*n*-butylstannyl)-3-bromo-thiophene (5). To a solution of diisopropylamine (11.1 g, 110.0 mmol) in anhydrous tetrahydrofuran was added a 2.5 M solution of *n*-butyllithium (44.4 mL, 110.0 mmol) at -20°C under nitrogen. The solution was stirred at -20°C for 5 min. The solution was warmed to room temperature and stirred for another 20 min. The solution was transferred to a stirred solution of 3-bromothiophene in anhydrous tetrahydrofuran at -20°C via a cannula under nitrogen. After 2 h, tributyltin chloride (35.8 g, 110 mmol) was added in one portion, and the reaction mixture was stirred overnight. The reaction mixture was quenched into water (50 mL) and extracted with *n*-hexane (50 mL). The aqueous layer was extracted twice with *n*-hexane ($2 \times 50 \text{ mL}$). The combined organic layers were washed with water ($2 \times 50 \text{ mL}$) and brine (50 mL) and dried over MgSO_4 . Solvent was evaporated in vacuo to give compound 5 as a pale

brown oil. ^1H NMR (CDCl_3) δ 7.49 (d, J = 4.8 Hz, 1H), 7.12 (d, J = 4.8 Hz, 1H), 1.63 (m, 6H), 1.37 (m, 6H), 1.23 (m, 6H), 0.89 (m, 9H).

2,2'-(2,5-dibromo-1,4-phenylene)bis(3-bromothiophene) (3).¹³ A Schlenk tube was charged with LiCl (2.7 g, 60 mmol), compound 4 (4.8 g, 10 mmol), $\text{Pd}(\text{PPh}_3)_4$ (287.5 mg, 0.25 mmol), and CuCl (5.0 g, 50 mmol). The tube was degassed under high vacuum with a nitrogen purge. DMSO (60 mL) was added with concomitant stirring followed by the addition of compound 5 (9.9 g, 11 mmol). The reaction mixture was stirred at room temperature for 1 h and then heated to 50 °C for 3 h. The reaction mixture was cooled, and the precipitation was collected by filtration, affording compound 2. Yield: 2.2 g (40%); ^1H NMR (CDCl_3) δ 7.72 (s, 2H), 7.42 (d, J = 5.1 Hz, 2H), 7.09 (d, J = 5.4 Hz, 2H).

General Procedure for the Synthesis of *N*-Alkyl Pyrroloindacenodithiophenes (1a,b). A Schlenk tube was charged with compound 3 (558.0 mg, 1 mmol), NaO^tBu (768.0 mg, 8 mmol), $\text{Pd}_2(\text{dba})_3$ (92.0 mg, 0.1 mmol), and BINAP (124.0 mg, 0.2 mmol). The tube was degassed under high vacuum with a nitrogen purge. The corresponding amine (516 mg, 4 mmol) and *p*-xylene were successively injected into the tube. The reaction mixture was heated to reflux and stirred for 2 h. After cooling to room temperature, the solid was filtered and washed with dichloromethane. The combined organic phase was washed twice with water (2×50 mL) and then dried over MgSO_4 . The solvents were removed under vacuum, and the residue was purified by column chromatography (silica gel; eluent, hexane/dichloromethane, 8/1, v/v) to afford compounds 1a,b.

Compound 1a Was Collected As a Pale Yellow Solid. Yield: 344 mg (70%); mp 137–139 °C; ^1H NMR (CDCl_3) δ 7.63 (s, 2H), 7.35 (d, J = 4.8 Hz, 2H), 7.08 (d, J = 5.1 Hz, 2H), 4.32 (t, J = 6.9 Hz, 4H), 1.91 (q, J = 7.2 Hz, 4H), 1.24 (m, 20H), 0.86 (t, 6H); ^{13}C NMR (CDCl_3) δ 146.3, 137.7, 125.8, 119.4, 115.0, 110.6, 98.2, 45.5, 31.8, 29.6, 29.4, 29.2, 27.3, 22.6, 14.1; MS (MALDI-TOF) 492.3. Anal. Calcd for $\text{C}_{30}\text{H}_{40}\text{N}_2\text{S}_2$: C 73.12, H 8.18, N 5.68. Found: C 73.43, H 8.22, N 5.66.

Compound 1b Was Collected As a Pale Yellow Solid. Yield: 280 mg (57%); mp 117–119 °C; ^1H NMR (CDCl_3) δ 7.60 (s, 2H), 7.36 (d, J = 4.8 Hz, 2H), 7.06 (d, J = 5.1 Hz, 2H), 4.17 (m, 4H), 2.11 (m, 2H), 1.41–1.24 (m, 16H), 0.95–0.86 (m, 12H); ^{13}C NMR (CDCl_3) δ 146.7, 138.1, 125.7, 119.3, 114.9, 110.8, 98.3, 49.7, 39.6, 30.8, 28.7, 24.3, 23.1, 14.1, 10.8; MS (MALDI-TOF): 492.3. Anal. Calcd for $\text{C}_{30}\text{H}_{40}\text{N}_2\text{S}_2$: C 73.12, H 8.18, N 5.68. Found: C 73.05, H 8.18, N 5.46.

General Procedure for the Synthesis of Diphenyl-pyrroloindacenodithiophenes (2a,b). NBS (391.6 mg, 2.2 mmol) was added portionwise into a solution of compound 1a,b (1.0 mmol) in tetrahydrofuran (THF) and *N,N*-dimethyl formamide (DMF) at –78 °C under nitrogen. The reaction mixture was stirred for 0.5 h. Then the reaction mixture was quenched with water and extracted twice with dichloromethane (2×50 mL). The combined organic phase was dried over MgSO_4 , and solvents were removed in vacuo. The obtained dibromo-pyrroloindacenodithiophenes were purified by column chromatography (silica gel; eluent, hexane).

A Schlenk tube was charged with dibromo-pyrroloindacenodithiophenes (324.0 mg, 0.5 mmol) and phenylboronic acid (134.1 mg, 1.1 mmol). The tube was degassed under high vacuum with a nitrogen purge. A solution of 2 M K_2CO_3 (3 mL), Aliquat (catalytic), and toluene (10 mL) were added successively. The reaction mixture was stirred and purged with nitrogen for 15 min before tetrakis(triphenylphosphine) palladium(0) (28.7 mg, 0.025 mmol) was added. The reaction mixture was heated at 110 °C for 6 h. After cooling down to room temperature, dichloromethane was added, and the organic layer was collected. The organic layer was washed 3 times with water (3×50 mL), and dried over anhydrous MgSO_4 . The solvent was removed under vacuum, and the residue was purified by column chromatography (silica gel; eluent, hexane/dichloromethane, 10/1, v/v) to afford compounds 2a,b.

Compound 2a Was Collected As a Yellow Solid. Yield: 96 mg (30%); mp 189–191 °C; ^1H NMR (CDCl_3) δ 7.72 (m, 6H), 7.40 (m, 6H), 7.32 (s, 2H), 4.32 (t, J = 1.2 Hz, 4H), 1.94 (q, 4H), 1.26 (m, 20H), 0.86 (m, 6H). Anal. Calcd for $\text{C}_{42}\text{H}_{48}\text{N}_2\text{S}_2$: C 78.21, H 7.50, N

4.34. Found: C 78.05, H 7.72, N 4.28. MS (MALDI-TOF): m/z 645. HR-MS (MALDI-MS): m/z 644.3249, calcd for $(\text{C}_{42}\text{H}_{48}\text{N}_2\text{S}_2)^+$ 644.3253. Because of the low solubility, the ^{13}C NMR of 2a could not be obtained.

Compound 2b Was Collected As a Yellow Solid. Yield: 185 mg (58%); mp 213–215 °C; ^1H NMR (CDCl_3) δ 7.72 (m, 6H), 7.40 (m, 6H), 7.32 (s, 2H), 4.17 (m, 4H), 2.11 (m, 2H), 1.41–1.24 (m, 16H), 0.95–0.86 (m, 12H); MS (MALDI-TOF): m/z 645. Anal. Calcd for $\text{C}_{42}\text{H}_{48}\text{N}_2\text{S}_2$: C 78.21, H 7.50, N 4.34. Found: C 78.30, H 7.62, N 4.23. Because of the low solubility, the ^{13}C NMR of 2b could not be obtained.

■ ASSOCIATED CONTENT

Supporting Information

General method for the experiment, absorption spectra, single crystal structure, and CIF files. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Notes

The authors declare no competing financial interest.

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