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Near-Infrared Absorbing Compounds Based on π-Extended Tetrathiafulvalene Open-Cage Fullerenes

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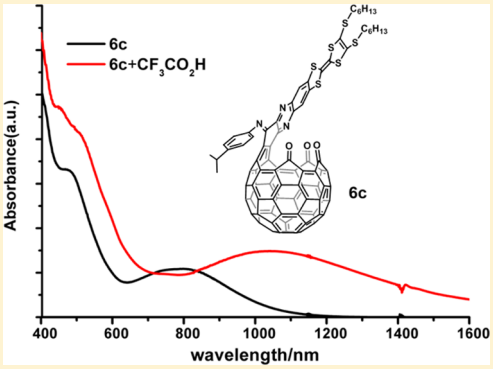
Supporting Information

ABSTRACT: Tetrathiafulvalene (TTF) is attached to open-cage fullerenes through a quinoxaline junction. The resulting linear π-conjugation system shows intense absorption in the near-infrared region. A unique *o*-diaminobenzene-induced furan ring formation process from a conjugated 1,4-dione moiety was observed on the rim of a 18-membered orifice.



INTRODUCTION

Near-infrared (NIR) absorption materials have attracted much attention because of their applications in various fields such as solar-cell, bioimaging, sensing, and nonlinear optics. Organic compounds consist of most of the known NIR absorption materials. Phthalocyanines and naphthalocyanines, metal complex dyes, polyene, polymethine, squaraines, quinines, and azo dyes are among the well-studied organic compounds.[1] Chemical modifications of existing chromophores continue to be a hot topic to optimize their properties for practical applications. For example, (indigo-*N*,*N*′-diarylimine) boron chelate complexes[2] and indeno[2,1-*b*]fluorenes[3] were recently reported as NIR absorption materials. All these organic compounds have a planar conjugated π-system.

Fullerenes have a spherical π-system and show intense absorption in the UV region but have no absorption in the NIR region. Reduction of fullerene results in fullerene radical anion radical $C_{60}^{\bullet-}$ with absorptions at 1075, 1058, and 991 nm and fullerene dianion C_{60}^{2-} with absorptions at 1020−1030 and 933 nm.[4] These anionic species are not stable in air. Dianionic polymeric $(C_{70}^{2-})_n$ chains show absorptions in the NIR region with three main bands at 890, 1200, and 1550 nm.[5] Chemical modification of the spherical π-system has been proven an effective method to prepare fullerene-based NIR materials. Fullerene multiadducts $C_{60}F_{15}R_3$[6] and $C_{60}R_6$[7] show NIR absorption as a result of the change of the spherical π-system. Introduction of a heteroatom into the fullerene cage can also shift the absorption into the NIR region as in the case of azafullerenes.[8] The number of such fullerene-based NIR materials is still quite limited because selective multifunctionalization of fullerene is a challenging problem.

Fullerene derivatives with a covalently linked chromophore can also show absorption in the NIR region.[9] A variety of tetrathiafulvalene (TTF)−fullerene derivatives have been prepared with various linkage strategies.[9c,d] Many of these TTF−fullerene dyads show excellent charge-transfer properties and NIR absorption. The energy gap for a fluorinated fullerene TTF dyad is as low as 0.5 eV.[10] Several fullerene−heptamethine dyads have been synthesized through the Prato reaction, which shows intense absorption around 800 nm.[11] Azulenocyanine fullerene derivatives also show intense NIR absorption.[12]

Open-cage fullerene derivatives[13] with electron-donating group(s) is another type of fullerene-based NIR material. Compound **1** shows intense near-IR absorption as a result of the imino and enamine moieties acting as electron-donating groups.[14] Compound **2** has a linear π-conjugated connection between the thiophene oligomer and the fullerene cage. Cross-talking between the donor and acceptor in the conjugated system leads to intramolecular charge-transfer absorbance in the NIR region.[15]

Compared to the classical planar π-systems, much remains to be done to explore the full potential of fullerene-based NIR materials. We have reported a number of open-cage fullerene

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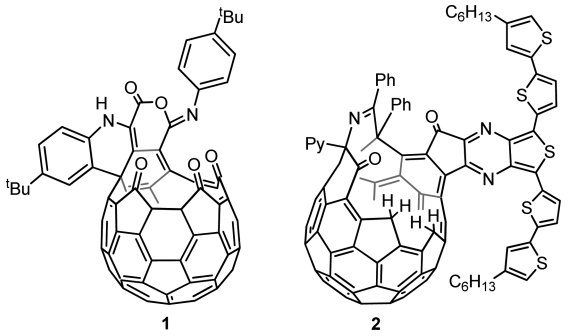

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derivatives through a peroxide-mediated reaction pathway.[16] Most of the open-cage fullerenes show orange-red color. Here, we report the synthesis of π-extended open-cage fullerene derivatives with donor chromophores such as TTF connected through a quinoxaline junction.

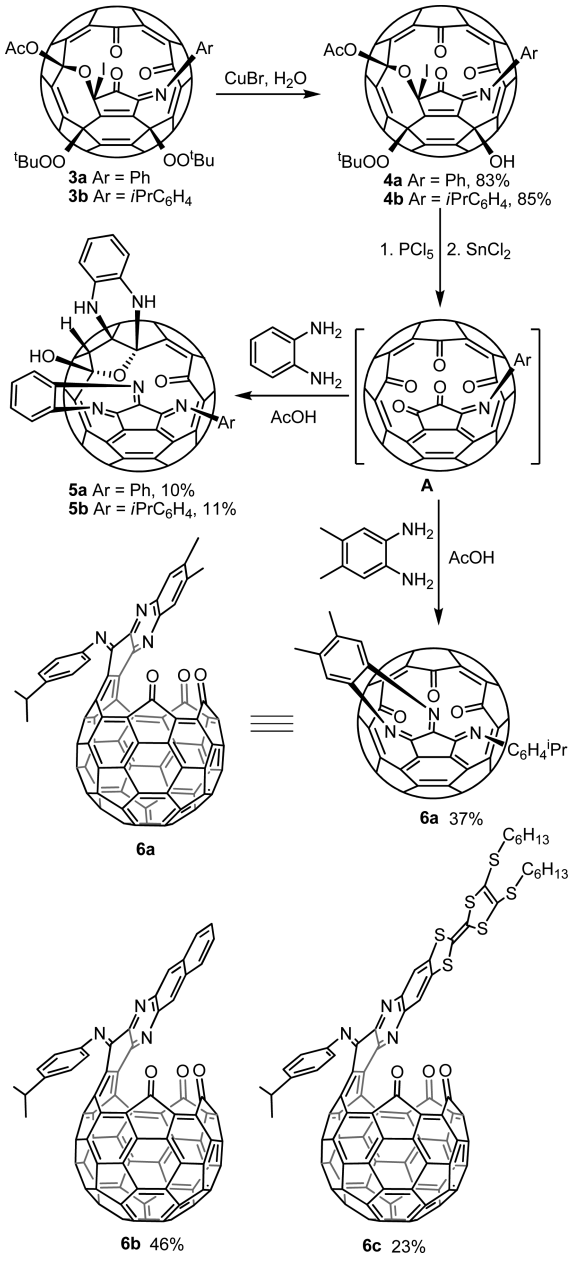
RESULTS AND DISCUSSION

Compounds **3a** and **3b** were prepared as we have previously reported.[17] To remove the two *tert*-butyl peroxo groups in compounds **3a** and **3b**, they were reduced with cuprous bromide to form compounds **4a** and **4b**, respectively (Scheme 1). The regioselectivity is due to H-bonding between the resulting hydroxyl group and the imino nitrogen. Coordination of the imino nitrogen to copper in the transition state of the reduction process probably also played a role in the observed regioselective reduction of the *tert*-butyl peroxo groups. Sequential treatment of compound **4** with PCl_5 and $SnCl_2$ resulted in formation of compound **A** through reductive aromatization[18] and opening of the iodo acetal moiety. It was not possible to purify the intermediate product of the PCl_5 reaction and compound **A**. Presumably, the hydroxyl group was replaced by chlorine after treatment with PCl_5, and aqueous workup resulted in the opening of the iodo acetal moiety. The same procedure was applied to a similar compound before to remove the two *tert*-butyl peroxo groups.[17a]

The crude product **A** was used directly to react with the *o*-diaminoaromatic compounds. Steric hindrance is an important factor for this amination reaction. The bis-adducts **5a** and **5b** were obtained for the less bulky 1,2-diaminobenzene. Monoadducts **6a**, **6b**, and **6c** were obtained for the bulky *o*-diaminoaromatic compounds. Formation of compounds **6a**–**c** suggests that condensation between the vicinal dione and 1,2-diaminobenzene took place before the addition on the rim of the orifice in the formation of bisadducts **5a** and **5b**. Regioisomer of compounds **5a** and **5b** with the diaminophenyl group on the same side as the imino ArN group was detected but could not be fully characterized. The cooperative action of the *o*-diamino groups was necessary for selective formation of isolable products. Treating compound **A** with aniline and aniline derivatives gave complex mixtures.

To get more information about the structure of compound **A**, we treated compound **4** with trifluoromethanesulfonic acid and obtained a mixture of compounds **7** and **8** (Scheme 2). A nonoxidizing silver salt such as $AgSbF_6$ could also give a mixture of **7** and **8**, but $AgClO_4$ resulted in oxidation of the vicinal dione and decarboxylation which is analogous to the decarboxylation of **3** by $AgClO_4$.[17a] Separation of compounds **7** and **8** was difficult because of easy conversion between them on the silica gel column. *o*-Diaminobenzene reacted with **7** and **8** to form compound **9** in the same way as the reaction with compound **A**.

Scheme 1. Preparation of Open-Cage Compounds with Extended π-Systems



Single crystals of compounds **5b** and **7a** were obtained from slow evaporation of their solution in CH_2Cl_2/hexane and $CDCl_3$, respectively. The structure of **5b** showed that the hydroxyl group forms intramolecular H-bonding with one of the quinoxaline nitrogen atoms. The H-bond distance O–H··· N is 2.66 Å. The isopropylphenyl group points toward the fullerene cage. The fullerene pentagon baring the quinoxaline is planar with the quinoxaline ring. The phenyl group bound to the furan ring is in a 45° orientation with respect to the quinoxaline ring. Such an orientation explains the selective formation of monoadduct with more bulky *o*-diaminoaromatic compounds as in the case of compounds **6a**–**c**. The space-filling model of **5b** shows close contact between the *o*-diaminoaryl groups.

The X-ray structure of compound **7a** showed clearly the presence of the hydrate moiety (Figure 1). The space-filling

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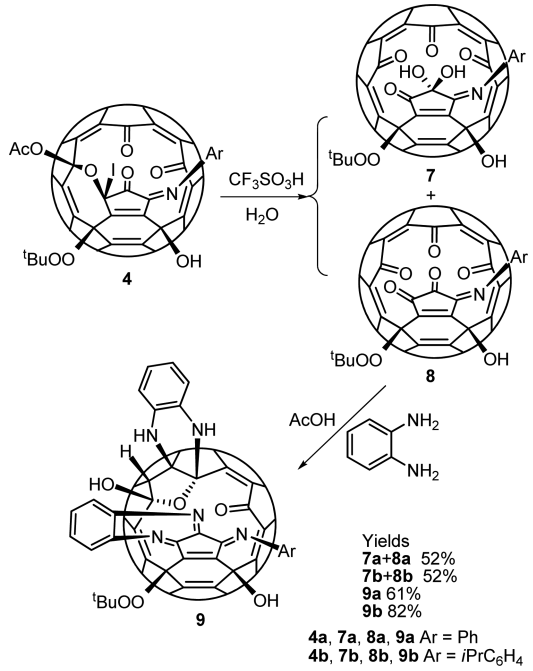
Scheme 2. Addition of *o*-Diaminobenzene to Open-Cage Fullerenes



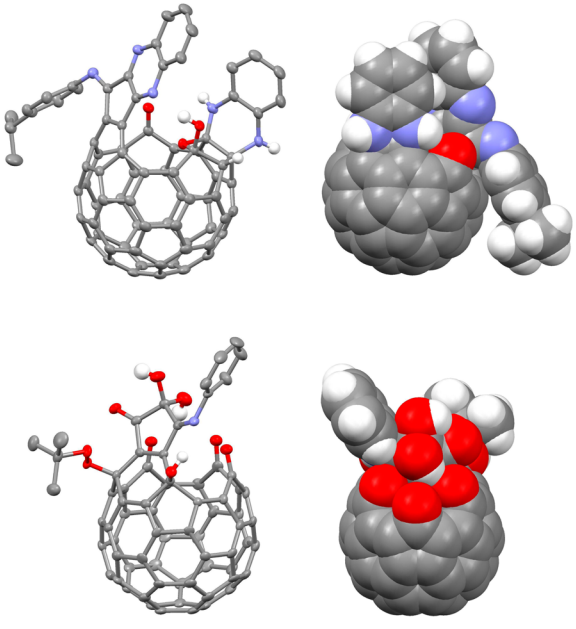


Figure 1. X-ray structure of **5b** (above) and **7a** (below). For clarity, hydrogen atoms on the alkyl and aryl groups for the ellipsoid models were not drawn. Ellipsoids were at 50%. Color scheme: gray = C, blue = N, red = O, white = H.

model indicates that the hydroxyl group above the orifice acts like a stopper and blocks the orifice. There is no apparent H-bond for the two hydroxyl groups in the hydrate moiety. The other hydroxyl group at the *para* position to the *tert*-butyl peroxo group forms intramolecular H-bond with the imino hydrogen atom as mentioned above to explain the regioselective reduction of compounds **3a** and **3b**. Unlike the case in compound **5b**, the phenyl group in **7a** points away from the fullerene cage. The carbonyl bond distance (1.21 Å) in **5b** is virtually the same as that of the corresponding carbonyl group in compound **7a** (1.20 Å), indicating that the orifice is quite rigid and not affected by the addition of different groups. In the unit cell of both compounds **5b** and **7a**, there is a pair of enantiomers.

The presence of a mixture of compounds **7** and **8** were evident on their ^{1}H NMR spectra. The ratio can be easily determined from integration of the corresponding OH group or phenyl protons. For the aniline derivatives the ratio is 40:60 for **7a** and **8a** (Figure 2); for the *p*-isopropylaniline derivatives

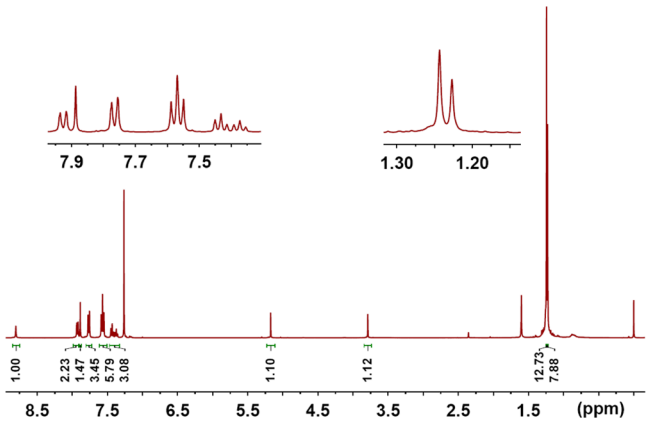


Figure 2. ^{1}H NMR spectrum of compounds **7a** and **8a** in $CDCl_3$.

the ratio is 13:87 for **7b** and **8b**. The two hydroxyl groups on the hydrated carbon appear at 3.79 and 5.17 ppm for **7a** and at 3.84 and 5.15 ppm for **7b**. The difference of the two hydroxyl groups probably results from the shielding effect of the cage; thus, the chemical shift at 3.79 and 3.84 ppm should be assigned to the hydroxyl group above the orifice for compounds **7a** and **7b** ,respectively. The other hydroxyl group on the hexagon appears at 8.80 and 8.97 ppm, respectively, for **7a** and **7b**, which are comparable to that for compounds **8a** (7.89 ppm) and **8b** (8.08 ppm).

UV−vis−NIR spectra revealed clear conjugation effect between the spherical π-system and the planar diaminoaromatic ring in compounds **5** and **6** (Figure 3). Compound **9b** with two sp^3 carbons separating the spherical π-system and the quinoxaline π-system has an orange-red color and showed

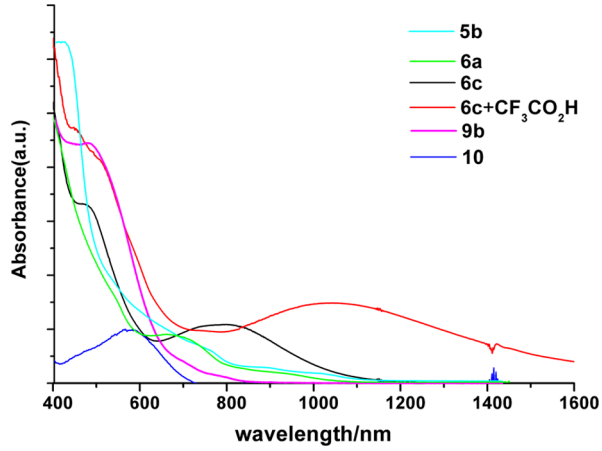


Figure 3. UV−vis−NIR spectra of compounds **5b**, **6a**, **6c**, **9b**, and **10** in $CHCl_3$. Absorption coefficient for **6c** at 790 nm in a 1.0×10^{-4} mol·L^{-1} solution is 6.0×10^3 L·mol^{-1}·cm^{-1}.

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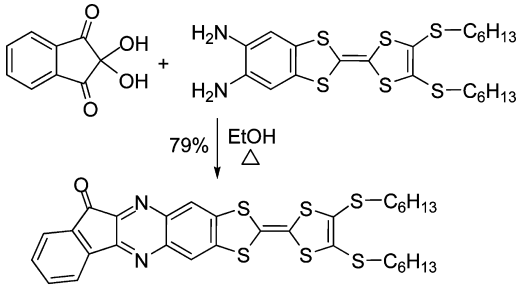
strong absorption in the UV region but has weak absorption above 800 nm. In contrast, the analogous compound **5b** without the hydroxyl and *tert*-butylperoxo groups has a greenish color and showed broad absorption peaks at 680 and 760 nm. Compared to compound **5b**, compound **6a** has a similar conjugation π-system but without the diaminobenzene on the rim of the orifice. The UV−vis absorption spectrum of **6a** is very similar to that of **5b**, indicating the diaminobenzene addend on the rim of the orifice has little effect on the π-system. The UV−vis absorption spectrum of the diaminonaphthalene derivative **6b** is slightly red-shifted due to extended π-conjugation compared to the 4,5-dimethyl-1,2-diamino derivative **6a** (see the Supporting Information for the spectrum of **6b**).

Compound **6c** has an extended π-conjugation system from the TTF moiety to the fullerene cage. It showed intense absorption in the near-infrared region with absorption onset at 1352 nm in chloroform (Figure 3). Changing the solvent to toluene and 1,4-dioxane resulted in a blue-shift of the absorption centered at 797 nm by 45 and 60 nm, respectively. Such a solvatochromism phenomenon indicates possible intramolecular charge transfer. Addition of trifluoroacetic acid to the solution of compound **6c** resulted in gradual red-shift of the absorption band at 797 to 1035 nm while other bands in the UV region remained almost unaffected. The red-shift could be reversed upon addition of pyridine. This halochromic phenomenon further supports the charge transfer nature of the band in the near-infrared region for the TTF derivative **6c**. Addition of trifluoroacetic acid to compounds **5a**, **5b**, **6a**, and **6b** did not show noticeable shift of absorption bands. For comparison, the ninhydrin analogue **10** was synthesized by treating ninhydrin with the diamino TTF derivative (Scheme 3). The absorption of compound **10** in chloroform starts at 710 nm with a broad band centered at 572 nm.

Scheme 3. Synthesis of Compound 10



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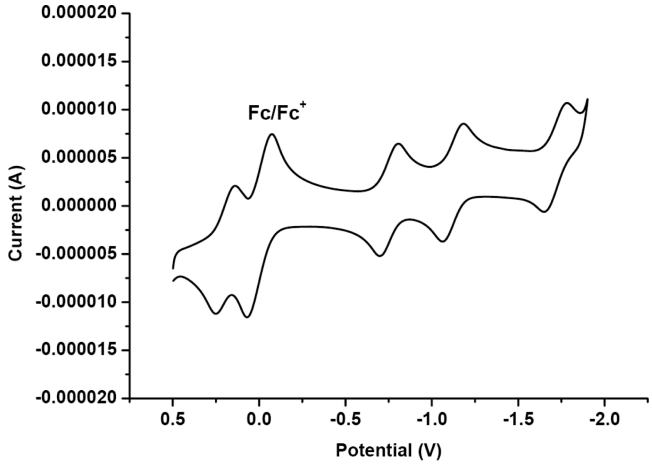
Cyclic voltammetry measurements for compounds **6a**, **6b**, and **6c** showed three reduction peaks with reduction onset at −0.67, −0.59, and −0.68 V (vs Fc/Fc^+), respectively. A reversible oxidation peak with onset at 0.16 V (vs Fc/Fc^+) was also observed for compound **6c** corresponding to the oxidation of the TTF moiety (Figure 4). The calculated HOMO−LUMO gap for compound **6c** is 0.84 eV.

The linear π-conjugated system in compounds **5** and **6** is analogous to that in compound **2**[15] reported by Xiao et al. in that they have the same quinoxaline junction between the addend chromophore and the open-cage fullerene. Comparison of their UV−vis−NIR spectra and the HOMO−LUMO gap indicate that the present TTF-open-cage fullerene derivative shows stronger donor−acceptor interaction than the thiophene



E_{ox}^{on} V	$E_{1/2}^{Ox}$ V	E_{red}^{on} V	$E_{1/2}^{Red1}$ V	HOMO eV	LUMO eV	E_g eV
0.16	0.19	-0.68	-0.75	-5.26	-4.42	0.84

Figure 4. Cyclic voltammogram of **6c** in 1,2-dichlorobenzene solution containing tetrabutylammonium hexafluorophosphate (Bu_4NPF_6, 0.1 M) as a supporting electrolyte at 25 °C with a scan rate of 0.1 V/s.

attached compound **2**, which has a band gap of 1.05 eV. Hummelen et al. reported the first fullerene derivative with the addend connected to the fullerene sphere via alternating double-single bonds.[19] But the overlap between the addend orbitals and the cage orbitals is quite limited due to orbital misalignment. A maximal red-shift of 11 nm was observed for a benzylidene [5,6] fulleroid.

CONCLUSIONS

In summary, *o*-diaminoaromatic compounds react readily with carbonyl groups on the rim of open-cage fullerenes. The conjugated 1,4-dione moiety forms a furan ring upon addition of the *o*-diaminobenzene. The vicinal dione moiety forms quinoxaline ring connecting planar chromophores with the spherical π-system in a linear π-conjugation pattern. The redox active fullerene-based NIR materials may have potential applications in areas such as photodynamic therapy.

EXPERIMENTAL SECTION

All the reagents were used as received. Dichloromethane was distilled over phosphorus pentaoxide. Compound **3** was prepared according to the reported procedure.[17a] The reactions were carried out under atmospheric conditions. NMR spectra were recorded at room temperature (298 K). Chemical shifts are given in ppm relative to TMS or $CDCl_3$ (for ^{13}C NMR). ESI-FT-ICR-HRMS spectra were recorded with $CHCl_3/CH_3OH$ or $CDCl_3/CH_3OH$ as the solvent, and positive-mode spectra were recorded. FTIR spectra were recorded in the microscope mode. Chromatographic purifications were carried out with silica gel of mesh 200−300.

Caution: A large amount of peroxide is involved in some of the reactions. Care must be taken to avoid possible explosion.

Preparation of Compounds 4. CuBr (0.5 mmol) and H_2O (0.3 mmol) were added to a solution of **3b** (325 mg, 0.25 mmol) in CH_2Cl_2 (20 mL) at room temperature. The mixture was stirred in the dark, and progress of the reaction was monitored by TLC. When the starting material **3b** vanished and the desired product **4b** reached its maximum yield, the reaction mixture was directly chromatographed on a silica gel column and eluted with toluene/ethyl acetate = 100:1. The

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orange band was collected and evaporated to give **4b**. Compound **4a** was prepared using the same procedure (Table 1).

Table 1. Preparation of Compounds 4a and 4b

entry	**3** (mg)	product	Ar	mg (yield, %)
1	73	**4a**	Ph	56.8 (83)
2	325	**4b**	*p*-^{i}Pr-C_6H_4	266 (85)

Characterization Data for ***4a***. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.75 (d, J = 7.5 Hz, 2H), 7.53 (t, J = 7.7 Hz, 2H), 7.39 (t, J = 7.4 Hz, 1H), 7.35 (s, 1H), 2.34 (s, 3H), 1.33 (s, 9H). ^{13}C NMR spectrum could not be obtained due to low solubility. ESI-FT-ICR-HRMS: $C_{72}H_{19}INO_9$ (M + H^+) calcd 1168.0099, found 1168.0075.

Characterization Data for ***4b***. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.78 (d, J = 7.5 Hz, 2H), 7.47 (s, 1H), 7.38 (d, J = 7.0 Hz, 2H), 2.93−3.10 (m, 1H), 2.33 (s, 3H), 1.33 (d, J = 6.7 Hz, 6H), 1.31 (s, 9H). ^{13}C NMR ($CDCl_3$, 100 MHz) all signals represent 1C except noted, δ: 187.55, 183.99, 179.90, 166.91, 154.24, 149.99, 149.81, 149.58, 149.55, 149.50, 149.44, 149.25, 149.15 (2C), 149.07, 149.01, 148.46, 148.31, 148.19, 148.13, 147.88, 147.83, 147.58 (2C), 147.30, 147.14, 146.59, 146.04, 145.79, 145.22, 145.14, 144.63 (2C), 143.58 (2C), 143.45, 143.35 (2C), 143.27 (2C), 143.20, 142.98, 142.56, 142.53, 142.39, 142.26, 141.98, 141.64, 141.21, 141.13, 140.64, 140.21 (2C), 138.07, 136.00, 133.17, 132.66, 129.50, 128.88, 126.86 (2C), 124.40 (2C), 108.56, 82.31, 82.24, 79.56, 58.40, 34.13, 26.92 (3C), 24.15 (2C), 22.12. ESI-FT-ICR-HRMS: $C_{75}H_{25}INO_9$ (M + H^+) calcd 1210.0569, found 1210.0581.

Preparation of Compounds 5. PCl_5 (1.2 equiv of **4b**) was added to a solution of **4b** (120 mg, 0.099 mmol) in CH_2Cl_2 (20 mL) at room temperature. The mixture was stirred vigorously, and progress of the reaction was monitored by TLC. When the starting material **4b** vanished and the desired product reached its maximum yield (about 5 min), 10 mL of water was added to the reaction mixture, and the reaction was quenched. Then the water layer was extracted with dichloromethane three times. The dichloromethane extraction solutions were combined and dried with anhydrous sodium sulfate. Then the solution was concentrated to 20 mL. $SnCl_2$ (1.5 equiv of **4b**) was added to the concentrated solution under vigorously stirring. When the starting material vanished and the desired intermediate reached its maximum yield (about 10 min), 10 mL of 1 M HCl aqueous solution was added to the reaction mixture, and the reaction was quenched. The aqueous layer was extracted with dichloromethane three times. The dichloromethane extraction solutions were combined and dried with anhydrous sodium sulfate and evaporated to give the crude intermediate **A**. Acetic acid (2 mL) and diaminobenezene (10 equiv of **4b**) was added to a solution of intermediate **A** in CH_2Cl_2 (20 mL) at room temperature. The mixture was stirred vigorously, and progress of the reaction was monitored by TLC. When the desired product **5b** reached its maximum yield (about 6 h), the reaction mixture was washed with water and extracted with dichloromethane three times. The dichloromethane extraction solutions were combined and dried with anhydrous sodium sulfate, concentrated to about 2 mL by rotary evaporator. and chromatographed on a silica gel column and eluted with toluene/ethyl acetate = 100:1 (volume ratio). The green band was collected and evaporated to give **5b**. Compound **5a** was prepared using the same procedure (Table 2).

Characterization Data for ***5a***. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.74 (d, J = 8.5 Hz, 1H), 8.65 (s, 1H), 8.13−8.07 (m, 2H), 8.03−7.92 (m, 1H), 7.41−7.28 (m, 2H), 7.06−7.00 (m, 3H), 6.91 (d, J = 7.3 Hz, 1H), 6.75 (t, J = 7.5 Hz, 1H), 6.35 (t, J = 7.4 Hz, 1H), 5.32 (s, 1H), 5.30 (d, J = 8.2 Hz, 1H), 4.48 (s, 1H), 4.47 (s, 1H). ^{13}C NMR spectrum could not be obtained due to low solubility. ESI-FT-ICR-HRMS: $C_{78}H_{18}N_5O_3$ (M + H^+) calcd 1072.1404, found 1072.1414.

Table 2. Preparation of Compounds 5a and 5b

entry	**4** (mg)	product	Ar	mg (yield, %)
1	94	**5a**	Ph	9.1 (10)
2	120	**5b**	*p*-^{i}Pr-C_6H_4	12.7 (11)

Characterization Data for ***5b***. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.72 (d, J = 8.2 Hz, 1H), 8.59 (s, 1H), 8.18−8.01 (m, 2H), 7.95 (t, J = 7.4 Hz, 1H), 7.17 (d, J = 8.1 Hz, 2H), 6.97 (d, J = 8.1 Hz, 2H), 6.88 (d, J = 7.4 Hz, 1H), 6.73 (t, J = 7.5 Hz, 1H), 6.34 (t, J = 7.5 Hz, 1H), 5.32 (d, J = 7.7 Hz, 1H), 5.30 (s, 1H), 4.45 (s, 2H), 2.81−2.76 (m, 1H), 1.12−1.09 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) all signals represent 1C except as noted, δ: 191.04, 161.27, 154.80, 152.18, 151.75, 151.01, 150.46, 150.44, 150.41, 150.38, 149.75, 149.73, 149.41, 149.15, 148.85, 148.71, 148.62, 147.97, 147.78, 147.75, 147.32, 147.11, 146.99, 146.32, 146.24, 146.11, 146.03, 145.34, 144.92, 144.90, 144.85, 144.70, 144.21, 144.04, 143.98, 143.96, 143.45, 143.36, 143.13, 142.98, 142.82, 142.61, 142.42, 141.26, 140.35, 140.24, 139.70, 139.04, 138.64, 138.16, 137.70, 136.24, 135.44, 135.12, 134.99, 134.97, 134.04, 131.84, 131.65, 131.12, 131.01, 130.78, 130.28, 129.41, 128.79(2C), 127.58(2C), 122.52, 119.99, 117.98(2C), 117.46, 115.58, 114.40, 108.63, 80.21, 65.04, 33.74, 24.04, 23.95. ESI-FT-ICR-HRMS: $C_{81}H_{24}N_5O_3$ (M + H^+) calcd 1114.1874, found 1114.1903.

A crystal of **5b** suitable for X-ray diffraction was obtained from a mixture of dichloromethane and hexane. Crystal data: triclinic, P-1. Unit cell dimensions: a = 13.809(4) Å, α = 100.669(3)°, b = 14.082(4) Å, β = 106.061(2)°, c = 16.063(5) Å, γ = 107.353(3)°, volume = 2740.2(13) Å^3. Final R indices [$I > 2\sigma(I)$]: R_1 = 0.0707 wR_2 = 0.1793. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as deposition no. CCDC-967768.

Preparation of Compounds 6. PCl_5 (1.2 equiv of **4a**) was added to a solution of **4a** (32 mg, 0.0264 mmol) in CH_2Cl_2 (10 mL) at room temperature. The mixture was stirred vigorously, and progress of the reaction was monitored by TLC. When the starting material **4a** vanished and the desired product reached its maximum yield (about 10 min), 10 mL water was added to the reaction mixture and the reaction was quenched. Then the water layer was extracted with dichloromethane three times, the extractions were combined and dried with anhydrous sodium sulfate. Then the solution was concentrated to 10 mL. $SnCl_2$ (1.5 equiv of **4a**) was added to the concentrated solution under vigorously stirring. When the starting material vanished and the desired intermediate reached its maximum yield (about 10 min), 10 mL of 1 M HCl aqueous solution was added to the reaction mixture and the reaction was quenched. Then aqueous layer was extracted with dichloromethane three times. The dichloromethane extractions were combined and dried with anhydrous sodium sulfate and evaporated to give the crude intermediate **A**. Acetic acid (2 mL) and diaminobenezene (2 equiv of **4a**) were added to a solution of intermediate **A** in CH_2Cl_2 (10 mL) at room temperature. The mixture was stirred vigorously, and progress of the reaction was monitored by TLC. When the desired product **6a** reached its maximum yield (about 6 h), the reaction mixture was washed with water and extracted with dichloromethane three times. The dichloromethane extractions were combined and dried with anhydrous sodium sulfate, concentrated to about 2 mL by rotary evaporator, and then chromatographed on a silica gel column and eluted with toluene/ethyl acetate = 100:1. The green band was collected and evaporated to give **6a**. Compounds **6b** and **6c** were prepared using the same procedure (Table 3).

Characterization Data for ***6a***. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.32 (s, 1H), 8.04 (s, 1H), 7.10 (d, J = 8.3 Hz, 2H), 6.98 (d, J = 8.3 Hz, 2H), 2.73−2.66(m, 1H), 2.63 (s, 3H), 2.57 (s, 3H), 1.00 (d, J = 6.4 Hz, 3H), 0.98 (d, J = 6.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$)

Table 3. Preparation of compounds 6a−6c[a]

entry	**4** (mg)	product	Ar	Ar′	mg (yield, %)
1	32	**6a**	*p*-^{i}Pr-C_6H_4	A	10.1 (37)
2	63.6	**6b**		B	25.7 (46)
3	38.8	**6c**		C	10.0 (23)

[a]A = 4,5-dimethyldiaminobenezene; B = 2,3-diaminonaphthalene; C = 5,6-diamino-2-(4,5-bis(hexylthio)-1,3-dithio-2-ylidene)benzo[*d*]-1,3-dithiole.

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all signals represent 1C except noted, δ: 185.56, 185.26, 183.96, 160.67, 155.14, 151.81, 150.38, 150.36, 149.71, 149.68, 149.57, 149.48, 149.23, 149.22, 149.19, 149.18, 148.65, 147.26, 146.97, 146.77, 146.67, 146.57, 146.51, 146.45, 146.09, 146.01, 145.97, 145.94, 145.92, 145.82, 145.78, 145.36, 145.20, 144.54, 143.94, 143.84, 143.55, 143.39, 143.24, 143.15, 143.11, 143.04(2C), 142.85(2C), 142.81, 142.47, 142.10, 141.85, 141.33, 141.15, 140.39, 140.12, 139.77, 137.41, 137.29, 137.14, 136.95, 136.45, 133.99, 133.03, 131.39, 131.24, 130.56(2C), 129.19(2C), 127.15(3C), 118.72(2C), 33.62, 23.91, 22.64, 20.54, 20.50. FT-IR (microscope): 3362, 2955, 2922, 2852, 1743, 1660, 1634, 1567, 1493, 1462, 1373, 1218, 1125, 1097, 1082, 1022, 870, 844, 741 cm^{-1}. ESI-FT-ICR-HRMS: $C_{77}H_{20}N_3O_3$ (M + H^+) calcd 1034.1499, found 1034.1488.

Characterization Data for ***6b***. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 9.15 (s, 1H), 8.84 (s, 1H), 8.25 (d, *J* = 7.8 Hz, 1H), 8.13 (d, *J* = 7.8 Hz, 1H), 7.93−7.56 (m, 2H), 7.12 (d, *J* = 8.1 Hz, 2H), 7.00 (d, *J* = 8.1 Hz, 2H), 2.65−2.74 (m, 1H), 1.01 (d, *J* = 6.4 Hz, 3H), 0.99 (d, *J* = 6.4 Hz, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) all signals represent 1C except noted, δ: 185.56, 185.31, 183.90, 160.10, 155.40, 151.72, 151.26, 150.33(2C), 149.70, 149.59, 149.51, 149.26(2C), 149.22(2C), 148.68, 146.93, 146.85, 146.64, 146.60, 146.53, 146.49, 146.38, 146.05, 145.96, 145.92(2C), 145.91, 145.87, 145.81, 145.34, 145.13, 144.66, 143.83, 143.78, 143.51, 143.37, 143.12, 143.00(2C), 142.98(2C), 142.83(2C), 142.80, 142.40, 141.20, 140.49, 139.97, 139.82, 139.66, 139.47, 138.93, 137.33(2C), 137.13, 136.99, 136.25, 134.76, 134.35, 134.03, 133.01, 131.26, 131.12, 130.42, 129.03, 128.79, 128.59, 128.47, 127.41, 127.27(2C), 127.09, 126.17, 118.48, 33.62, 23.92(2C). FT-IR (microscope): 2956, 2923, 2852, 1743, 1561, 1494, 1460, 1381, 1337, 1217, 1160, 1125, 1079, 1052, 882, 842, 750 cm^{-1}. ESI-FT-ICR-HRMS: $C_{79}H_{18}N_3O_3$ (M + H^+) calcd 1056.1325, found 1056.1323.

Characterization Data for ***6c***. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.28 (s, 1H), 8.00 (s, 1H), 7.09 (d, *J* = 7.9 Hz, 2H), 6.96 (d, *J* = 7.9 Hz, 2H), 2.93 (t, *J* = 7.1 Hz, 2H), 2.87 (t, *J* = 7.1 Hz, 2H), 2.72−2.66 (m, 1H), 1.82−1.63 (m, 4H), 1.53−1.40 (m, 4H), 1.42−1.25 (m, 8H), 1.00 (d, *J* = 6.4 Hz, 3H), 0.98 (d, *J* = 6.4 Hz, 3H), 0.96−0.87 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) all signals represent 1C except noted, δ: 185.68, 185.37, 183.98, 160.17, 155.75, 151.57, 150.35(2C), 150.05, 149.71, 149.63, 149.51, 149.20(4C), 148.63, 147.02, 146.91, 146.71, 146.65, 146.55, 146.47, 146.37, 146.14, 145.98(2C), 145.87(2C), 145.85, 145.32, 145.18, 144.79, 143.92, 143.81, 143.53, 143.38, 143.19, 143.07(2C), 143.06(2C) 143.00, 142.89(2C), 142.84(2C), 142.34, 142.01(2C), 141.22, 140.20, 139.51, 139.48, 138.80, 137.45, 137.27, 137.01(2C), 136.26, 133.88, 133.02, 131.31, 131.23, 128.16, 127.97, 127.43, 127.22(2C), 125.58, 121.91, 120.68, 118.69(2C), 115.08, 109.04, 36.49, 36.44, 33.64, 31.40, 31.36, 29.87, 29.79, 28.34, 28.29, 23.92(2C), 22.63, 22.58, 14.10, 14.06. FT-IR (microscope): 2954, 2924, 2853, 1743, 1560, 1493, 1456, 1342, 1157, 1125, 1098, 1052, 1019, 868, 840, 775, 755 cm^{-1}. ESI-FT-ICR-HRMS: $C_{91}H_{40}N_3O_3S_6$ (M + H^+) calcd 1414.1388, found 1414.1360.

Preparation of Compounds 7 and 8. CF_3SO_3H (1.5 equiv of **4b**) in 2 mL of dichloromethane was added to a solution of **4b** (34.7 mg, 0.0286 mmol) in CH_2Cl_2 (10 mL) at room temperature. The mixture was stirred vigorously, and progress of the reaction was monitored by TLC. When the starting material **4b** vanished and the desired product **7b** and **8b** reached its maximum yield (about 0.5 h), the reaction mixture was directly chromatographed on a silica gel column and eluted with dichloromethane/ethyl acetate = 20:1. The orange band was collected and evaporated to give **7b** and **8b**. Compounds **7a** and **8a** were prepared using the same procedure (Table 4).

Characterization Data for ***7a***. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.80 (s, 1H), 7.93 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 2H), 7.37 (t, *J* = 7.4 Hz, 1H), 5.17 (s, 1H), 3.79 (s, 1H), 1.23 (s, 9H). ESI-FT-ICR-HRMS: $C_{70}H_{18}NO_9$ (M + H^+) calcd 1016.0982, found 1016.0969.

A crystal of **7a** suitable for X-ray diffraction was obtained by slow evaporation of chloroform-*d*. Crystal data: triclinic, *P*-1. Unit cell dimensions: *a* = 13.942(3) Å, α = 68.08(3)°, *b* = 14.382(3) Å, β = 71.71(3)°, *c* = 15.520(3) Å, γ = 71.78(3)°, volume = 2672.8(9) $Å^3$. Final *R* indices [$I > 2\sigma(I)$]: R_1 = 0.1397 wR_2 = 0.3273. Crystallographic data have been deposited in the Cambridge Crystallographic Data Centre as deposition no. CCDC-967767.

Characterization Data for ***7b***. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.97 (s, 1H), 7.91 (d, *J* = 7.9 Hz, 2H), 7.43 (d, *J* = 7.9 Hz, 2H), 5.15 (s, 1H), 3.84 (s, 1H), 3.02−3.07 (m, 1H), 1.35 (d, *J* = 6.6 Hz, 6H), 1.22 (s, 9H). ESI-FT-ICR-HRMS: $C_{73}H_{24}NO_9$ (M + H^+) calcd 1058.1446, found 1058.1423.

Characterization Data for ***8a***. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.89 (s, 1H), 7.76 (d, *J* = 7.5 Hz, 2H), 7.57 (t, *J* = 7.8 Hz, 2H), 7.43 (t, *J* = 7.4 Hz, 1H), 1.24 (s, 9H). ESI-FT-ICR-HRMS: $C_{71}H_{20}NO_9$ (M + CH_3OH + H^+) calcd 1030.1109, found 1030.1114.

Characterization Data for ***8b***. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.08 (s, 1H), 7.79 (d, *J* = 7.9 Hz, 2H), 7.43 (d, *J* = 7.9 Hz, 2H), 3.02−3.07 (m, 1H), 1.35 (d, *J* = 6.6 Hz, 6H), 1.24 (s, 9H). $C_{74}H_{26}NO_9$ (M + CH_3OH + H^+) calcd 1072.1602, found 1072.1590.

Preparation of Compounds 9. Acetic acid (1 mL) and diaminobenezene (5 mg, 0.046 mmol)) were added to a solution of **7b** and **8b** (15.0 mg) in CH_2Cl_2 (10 mL) at room temperature. The mixture was stirred vigorously, and progress of the reaction was monitored by TLC. When the desired product **9b** reached its maximum yield (about 4 h), the reaction mixture was washed with water and extracted with dichloromethane three times. The dichloromethane extraction solutions were combined and dried with anhydrous sodium sulfate, concentrated, and chromatographed on a silica gel column eluting with dichloromethane/ethyl acetate = 100:1. The first red-orange band was collected and evaporated to give **9b**. Compound **9a** was prepared using the same procedure (Table 5).

Table 4. Preparation of Compounds 7a+8a and 7b+8b

entry	**4** (mg)	product	Ar	mg (yield, %)
1	46	**7a+8a**	Ph	21.1 (52)
2	34.7	**7b+8b**	*p*-^{i}Pr-C_6H_4	15.0 (50)

Table 5. Preparation of Compounds 9a and 9b

entry	**7** and **8** (mg)	product	Ar	mg (yield, %)
1	52.2	**9a**	Ph	36.7 (61)
2	15.0	**9b**	*p*-^{i}Pr-C_6H_4	14.6 (82)

Characterization Data for ***9a***. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 8.44 (s, 1H), 8.15 (d, *J* = 6.0 Hz, 1H), 8.14 (s, 1H), 7.95−7.82 (m, 3H), 7.76 (d, *J* = 7.6 Hz, 2H), 7.62 (t, *J* = 7.8 Hz, 2H), 7.45 (t, *J* = 7.4 Hz, 1H), 6.78 (d, *J* = 7.4 Hz, 1H), 6.67 (t, *J* = 7.4 Hz, 1H), 6.23 (t, *J* = 7.4 Hz, 1H), 4.89 (d, *J* = 7.5 Hz, 1H), 4.61 (s, 1H), 4.22 (s, 1H), 4.15 (s, 1H), 1.06 (s, 9H). ^{13}C NMR ($CDCl_3$, 125 MHz): all signals represent 1C except noted, δ: 190.62, 162.41, 154.97, 151.25, 150.93, 150.86, 150.84, 150.41, 150.04, 149.61, 149.44, 149.18, 148.93(2C), 148.85, 148.80, 148.71, 148.41, 148.34, 148.27(2C), 148.23, 147.97, 147.88, 147.84, 147.71, 147.61, 147.53, 147.23, 147.13(2C), 146.23, 145.39, 145.34, 145.21, 144.41, 144.25, 143.94, 143.66, 143.27, 143.04, 142.51, 142.29, 141.38, 141.07, 141.03, 140.65, 139.42, 139.21, 139.06, 138.85, 137.88, 136.31, 135.98, 134.86, 134.27, 131.98, 131.17, 130.73, 130.31, 130.09, 129.01, 128.49, 128.44(2C), 126.94, 122.60(2C), 122.38, 120.08, 117.48, 114.50, 114.12, 108.10, 86.56, 81.32, 79.08, 76.52, 64.81, 26.60(3C). ESI-FT-ICR-HRMS: $C_{82}H_{28}N_5O_6$ (M + H^+) calcd 1178.2034, found 1178.2002.

Characterization Data for ***9b***. ^{1}H NMR (500 MHz, $CDCl_3$) δ: 8.45 (s, 1H), 8.32 (s, 1H), 8.20 (d, *J* = 8.2 Hz, 1H), 7.99−7.88 (m, 2H), 7.86−7.83 (m, 3H), 7.49 (d, *J* = 8.0 Hz, 2H), 6.77 (d, *J* = 7.4 Hz, 1H), 6.66 (t, *J* = 7.4 Hz, 1H), 6.24 (d, *J* = 7.4 Hz, 1H), 4.91 (d, *J* = 7.6 Hz, 1H), 4.60 (s, 1H), 4.20 (s, 1H), 4.15 (s, 1H), 3.15−3.07 (m, 1H), 1.42 (d, *J* = 6.8 Hz, 6H), 1.04 (s, 9H). ^{13}C NMR (125 MHz, $CDCl_3$) all signals represent 1C except noted, δ: 190.58, 161.60, 154.97, 151.28, 150.96, 150.88, 150.86, 150.44, 150.09, 149.64, 149.47, 149.20, 148.96(2C), 148.88, 148.83(2C), 148.75, 148.44, 148.36, 148.30(2C), 148.29, 148.11, 148.04(2C), 147.92, 147.63, 147.57, 147.30, 147.18, 146.31, 145.42, 145.36, 145.24, 144.55, 144.47, 144.40, 143.99, 143.73,

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143.34, 143.04, 142.92, 142.60, 142.34, 141.38, 141.11, 140.68, 140.34, 139.45, 139.23, 139.09, 138.87, 137.89, 136.41, 136.00, 134.93, 134.38, 131.88, 131.12, 130.72, 130.35, 130.01, 129.04, 126.47(2C), 123.86(2C), 122.39, 120.07, 117.50, 114.54, 114.16, 108.07, 86.59, 81.26, 79.09, 76.63, 64.89, 34.14, 26.61(3C), 24.17, 24.14. ESI-FT-ICR-HRMS: $C_{85}H_{34}N_5O_6$ ($M + H^+$) calcd 1220.2504, found 1220.2527.

Procedure for Preparation of Compounds 10. 5,6-Diamino-2-(4,5-bis(hexylthio)- 1,3-dithio-2-ylidene)benzo[*d*]-1,3-dithiole (158 mg, 0.306 mmol) and ninhydrin (54.5 mg, 0.306 mmol) were dispersed in EtOH (20 mL). The mixture was heated to reflux for 2 h. A deep blue solid was observed in the solution. The reactants were cooled to room temperature, and the resulting solid was obtained by filtration. After the solid was washed with EtOH several times, pure product **10** was obtained (155.6 mg, yield: 79%). Characterization data for **10**. ^{1}H NMR (400 MHz, $CDCl_3$) δ: 7.81 (d, J = 7.1 Hz, 1H), 7.70 (d, J = 7.1 Hz, 1H), 7.66−7.54 (m, 2H), 7.47−7.40 (2H), 2.80 (t, J = 7.2 Hz, 4H), 1.77−1.52 (m, 4H), 1.45−1.40 (4H), 1.31−1.29 (8H), 0.90 (t, J = 6.5 Hz, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) all signals represent 1C except noted, δ: 188.99, 156.28, 148.25, 144.43, 141.64, 141.57, 141.13, 140.77, 136.31, 136.25, 131.96, 127.45, 127.26, 124.26, 122.04, 121.37, 119.90, 114.10, 106.77, 36.16(2C), 31.24(2C), 29.65, 29.63, 28.16(2C), 22.46(2C), 13.95(2C). FT-IR (microscope): 2955, 2926, 2855, 1731, 1608, 1465, 1448, 1330, 1191, 1171, 1140, 1094, 1045, 914, 888, 866, 776, 731 cm^{-1}. ESI-FT-ICR-HRMS: $C_{31}H_{32}N_2OS_6$ (M^+) calcd 640.0833, found 640.0841.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Selected spectroscopic data for all new compounds and crystallographic data for **5b** and **7a** (CIF). 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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