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SYNTHESES OF PARTIALLY BROMINATED DERIVATIVES OF TETRA-2-THIENYLMETHANE FOR THREE-DIMENSIONALLY EXTENDED π-ELECTRON SYSTEMS

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Abstract – Partially α-brominated derivatives of tetra-2-thienylmethane (Br_n-TTM; n = 1–3) were synthesized and isolated in gram quantities. An alternative and more selective preparation of Br_3-TTM was also developed. A new π-electron system based on the tetra-2-thienylmethane framework was synthesized from the monobromo derivative of tetra-2-thienylmethane.

Three-dimensionally extended π-electron systems have attracted much attention due to their potential applications in organic semiconductor and optoelectronic devices.[1] We have studied tetrahedrally extended π-electron systems based on the tetra-2-thienylmethane (TTM) framework, with respect to intramolecular interactions between the thienyl groups in the TTM and intermolecular interactions via S···S contacts and π···π stacking in the crystal state.[2] Envisioning more complex and/or tailor-made π-electron systems based on the TTM framework, it became clear that partially brominated TTM derivatives (Br_n-TTM; n = 1–3) would be useful as key intermediates. Such Br_n-TTM compounds are expected to show high synthetic utility through both the electrophilic substitution of the thienyl groups and the cross-coupling reactions of the bromothienyl groups. Here, we describe the gram-scale synthesis of three partially α-brominated TTM derivatives, and especially, the selective synthesis of Br_3-TTM. To

demonstrate the utility of these intermediates, the synthesis of a new π-electron system based on the TTM framework using Br-TTM is also described.

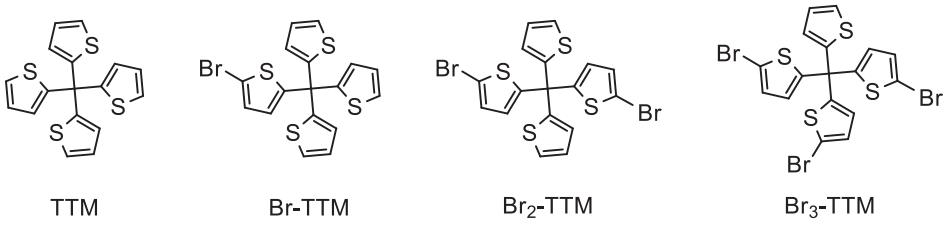
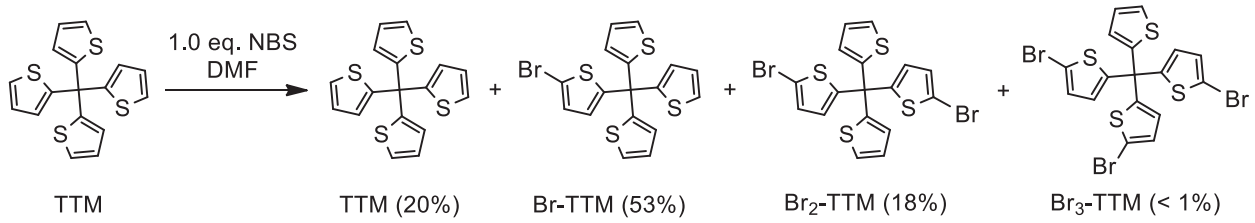


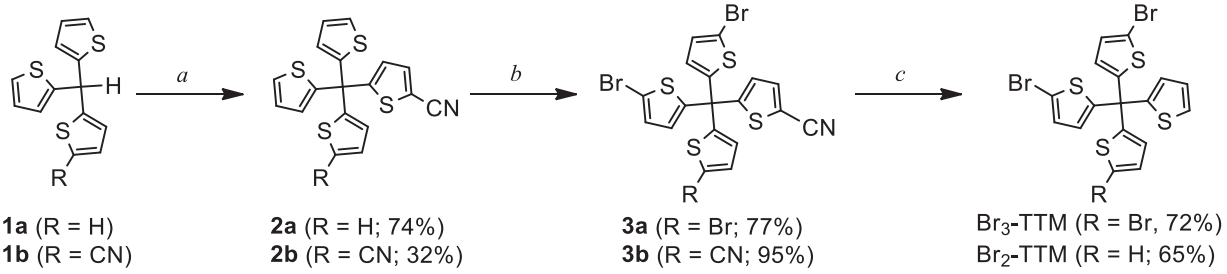
Figure 1. Tetra-2-thienylmethane (TTM) and its partially α-brominated derivatives: Br-TTM, Br_2-TTM, and Br_3-TTM

We initially attempted the direct synthesis of the partially brominated derivatives by the bromination of TTM (Scheme 1). Thus, a solution of TTM in *N*,*N*-dimethylformamide (DMF) was treated with 1.0 equivalent *N*-bromosuccinimide (NBS) under dark conditions. After repeated runs of column chromatography on silica gel, with hexane as the eluent, Br-TTM was isolated as the main product in 53% yield, accompanied by Br_2-TTM (18%) and the recovered TTM (20%). Consequently, gram quantities of Br-TTM and Br_2-TTM were obtained by this one-step synthesis. Although Br_3-TTM could be obtained by increasing the amount of NBS in the reaction, its purification would be much more difficult than those for Br-TTM and Br_2-TTM. For example, tetrakis(5-bromo-2-thienyl)methane[2a,2c] (Br_4-TTM), which would be a main by-product in the synthesis of Br_3-TTM, exhibits much higher crystallinity and a slightly larger R_f value than Br_3-TTM. These would complicate the purification of Br_3-TTM from Br_4-TTM by either recrystallization or column chromatography on silica gel.



Scheme 1. Bromination of TTM with 1.0 equivalent NBS in DMF

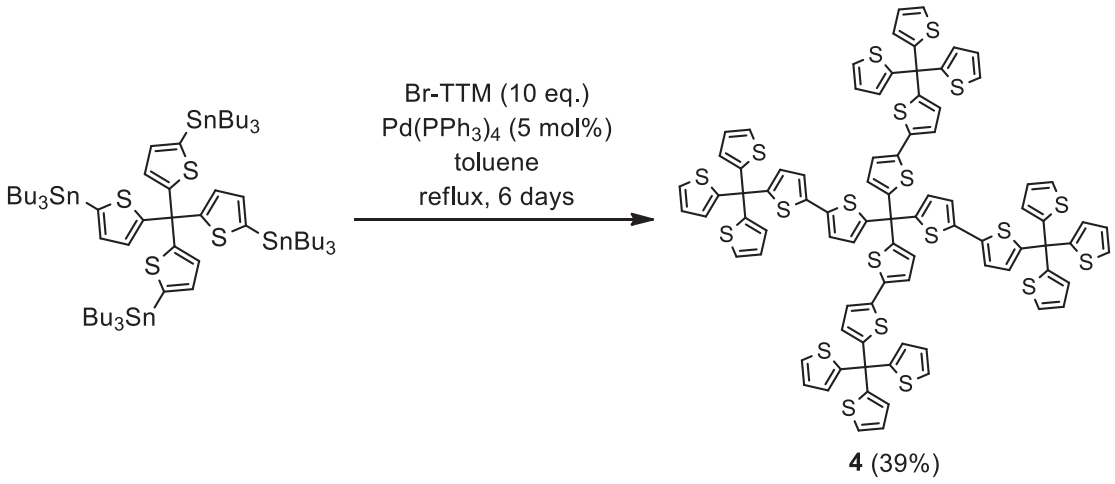
Therefore, we examined the selective synthesis of Br_3-TTM by a modification of the synthetic route to TTM. Since TTM is synthesized by the decyanation of 5-(tri-2-thienylmethyl)thiophene-2-carbonitrile (**2a**), Br_3-TTM could be obtained by the tribromination of **2a** before the removal of the cyano group (Scheme 2). Since Br_4-TTM is never formed by this route, the purification of Br_3-TTM would be easier, because Br_3-TTM is first eluted during silica gel chromatography. As expected, Br_3-TTM was successfully obtained and isolated in gram quantities by the synthetic route shown in Scheme 2.



Scheme 2. Synthesis of Br_3-TTM and Br_2-TTM. *Reaction conditions*: (*a*) (i) *n*-BuLi (1.0 eq.), THF, hexamethylphosphoric triamide (HMPA), –60 °C, 1 h, (ii) 5-fluorothiophene-2-carbonitrile (3 eq.), –60 °C then rt, overnight; (*b*) (i) NBS (4.5 eq. for **3a**, 2.5 eq. for **3b**), DMF, in the dark, rt, 24 h, (ii) NBS (0.5 eq. for **3a**, 2.5 eq. for **3b**), in the dark, rt, 24 h; (*c*) 1,4-dioxane, EtOH, NaOH aq., reflux, 12 h; Cu powders (0.1 eq.), quinolone, 200 °C, 2 h (for Br_3-TTM) or 180 °C, 1 h (for Br_2-TTM).

Considering the troublesome and time-consuming chromatographic separation of Br_2-TTM from Br-TTM and Br_3-TTM, an approach similar to that for Br_3-TTM was considered for the synthesis of Br_2-TTM (Scheme 2). However, this synthetic route was less effective because of the low yield in the conversion to **2b**. The reactivity of the corresponding tri-2-thienylmethyl anion of **1b** was lowered by the electron-withdrawing cyano group. On the other hand, **2b** and **3b** are regarded as useful compounds for the synthesis of non-symmetrical derivatives of TTM, such as push-pull derivatives, by the introduction of electron-donating groups.

As a typical example, the new dendritic oligothiophene, **4**, in which as many as 20 thiophene rings are connected by five sp^3 carbon atoms, was synthesized from Br-TTM and tetrakis(5-tributylstannyl-2-thienyl)methane[2e] (Scheme 3). Compound **4** is difficult to synthesize without monobromo- or monometalated-TTM derivatives.



Scheme 3. Synthesis of dendritic oligothiophene **4**

Compound **4** is a stable, colorless crystalline substance. The crystals of **4** shows good solubility in chloroform and dichloromethane, which helps the purification and characterization of **4**. Reflecting the high symmetry of its molecular structure, **4** shows simple ^{1}H and ^{13}C NMR spectra as previously reported for a dendritic TTM derivative.[2f] The solution of **4** in dichloromethane shows two absorption bands at the range of 250–280 and 300–370 nm, due to the absorption of the peripheral tri-2-thienylmethane moieties and the central tetrakis(5-(2-thienyl)-2-thienyl)methane moiety, respectively. The fluorescence maximum (420 nm) and the Stokes shift (4400 cm^{-1}) of **4** are comparable with related compounds having the tetrakis(5-(2-thienyl)-2-thienyl)methane skeleton.[2d,2e] Interestingly, the crystals of **4** also exhibit blue emission under irradiation at 365 nm. This suggests that the bulky tri-2-thienylmethyl groups prevent the intermolecular interaction between tetrakis(5-(2-thienyl)-2-thienyl)methane cores even in the solid state. More detailed properties for **4**, along with those of related compounds, will be reported in future.

In summary, three partially α-brominated TTM derivatives, Br$_n$-TTM (n = 1–3), were synthesized and isolated in gram quantities. Using these partially brominated compounds, tailor-made π-electron systems based on the TTM framework could be synthesized efficiently. This new family of TTM derivatives, including **4**, is now under investigation.

EXPERIMENTAL

Bromination of tetra-2-thienylmethane (TTM) with 1.0 equivalent NBS. A solution of NBS (2.51 g, 1.0 equiv) in DMF (14 mL) was added dropwise to a solution of TTM (4.83 g, 14 mmol) in DMF (80 mL) at room temperature under dark conditions. Water (100 mL) was added after the reaction mixture was stirred 24 h at room temperature. The reaction mixture was extracted with benzene three times (100 mL, 50 mL×2). The combined organic layers were washed with water (100 mL), 10% sodium hydrogen sulfite aq. (100 mL), water (100 mL), and brine (50 mL). The organic layer was dried over anhydrous sodium sulfate. After the filtration and concentration the residue was purified by the iterative column chromatography on silica gel eluted with hexane to isolate 3.16 g (53%) of (5-bromo-2-thienyl)-tri-2-thienylmethane (Br-TTM), 1.25 g (18%) of bis(5-bromo-2-thienyl)-di-2-thienylmethane (Br$_2$-TTM), 50 mg (0.6%) of tris(5-bromo-2-thienyl)-2-thienylmethane (Br$_3$-TTM), and 980 mg (20%) of the starting TTM.

(5-Bromo-2-thienyl)-tri-2-thienylmethane (Br-TTM): colorless crystals, mp 104–105 °C; MS (EI) *m/z* (rel intensity) 424 (M$^+$, ^{81}Br, 78), 422 (M$^+$, ^{79}Br, 67), 343 ([M–Br]$^+$, 100); UV/Vis (in CH_2Cl_2) λ_{max} / nm (log ε) 270sh (3.81), 241 (4.42); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.81 (d, J = 3.9 Hz, 1H), 6.93 (d, J = 3.9 Hz, 1H), 6.97 (dd, J = 5.2, 3.6 Hz, 3H), 7.06 (dd, J = 3.6, 1.3 Hz, 3H), 7.23 (dd, J = 5.2, 1.3 Hz, 3H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 53.3, 112.3, 125.5, 126.5, 127.8 (Two signals were overlapped), 129.3, 151.7, 153.8. Anal. Calcd for $C_{17}H_{11}BrS_4$: C, 48.22; H, 2.62. Found: C, 48.14; H, 2.54.

Bis(5-bromo-2-thienyl)-di-2-thienylmethane (Br_2-TTM): colorless crystals, mp 134–135 °C; MS (EI) *m/z* (rel intensity) 504 (M^+, $^{81}Br_2$, 45), 502 (M^+, $^{79}Br\cdot^{81}Br$, 78), 500 (M^+, $^{79}Br_2$, 36), 423 ($[M–Br]^+$, ^{81}Br, 100), 421 ($[M–Br]^+$, ^{79}Br, 84), 342 ($[M–Br_2]^+$, 62); UV/Vis (in CH_2Cl_2) λ_{max} / nm (log ε) 272sh (4.03), 243 (4.43); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.81 (d, J = 3.9 Hz, 2H), 6.94 (d, J = 3.9 Hz, 2H), 6.98 (dd, J = 5.2, 3.6 Hz, 2H), 7.06 (dd, J = 3.6, 1.3 Hz, 2H), 7.25 (dd, J = 5.2, 1.3 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 53.4, 112.6, 125.7, 126.6, 127.9 (Two signals were overlapped), 129.4, 150.9, 153.0. Anal. Calcd for $C_{17}H_{10}Br_2S_4$: C, 40.65; H, 2.01. Found: C, 40.81; H, 2.06.

Tris(5-bromo-2-thienyl)-2-thienylmethane (Br_3-TTM): colorless crystals, mp 156–157 °C; MS (EI) *m/z* (rel intensity) 584 (M^+, $^{81}Br_3$, 25), 582 (M^+, $^{79}Br\cdot^{81}Br_2$, 69), 580 (M^+, $^{79}Br_2\cdot^{81}Br$, 62), 578 (M^+, $^{79}Br_3$, 15), 503 ($[M–Br]^+$, $^{81}Br_2$, 67), 501 ($[M–Br]^+$, $^{79}Br\cdot^{81}Br$, 100), 499 ($[M–Br]^+$, $^{79}Br_2$, 58), 422 ($[M–Br_2]^+$, ^{81}Br, 77), 420 ($[M–Br_2]^+$, ^{79}Br, 70), 341 ($[M–Br_3]^+$, 29); UV/Vis (in CH_2Cl_2) λ_{max} / nm (log ε) 274sh (4.10), 247 (4.42); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.80 (d, J = 3.9 Hz, 3H), 6.94 (d, J = 3.9 Hz, 3H), 6.99 (dd, J = 5.2, 3.7 Hz, 1H), 7.05 (dd, J = 3.7, 1.3 Hz, 1H), 7.26 (dd, J = 5.2, 1.3 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 53.6, 112.9, 126.0, 126.7, 127.96, 128.00, 129.5, 150.0, 152.1. Anal. Calcd for $C_{17}H_9Br_3S_4$: C, 35.13; H, 1.56. Found: C, 35.15; H, 1.52.

Tris(5-bromo-2-thienyl)-(5-cyano-2-thienyl)methane (3a): A solution of NBS (8.0 g, 4.5 equiv) in DMF (20 mL) was added dropwise to a solution of 5-(tri-2-thienylmethyl)thiophene-2-carbonitrile (**2a**)[2b] (3.7 g, 10 mmol) in DMF (40 mL) at room temperature under dark conditions. The reaction mixture was stirred for 24 h at room temperature. According to the TLC analysis, the reaction mixture contained the considerable amount of dibromo by-product with the desired tribromo compound. NBS (890 mg, 0.5 equiv) was added and stirred for the additional 24 h. Water (150 mL) was added and the resulting white suspension was extracted with benzene (100 mL×3). The combined organic layers were washed with water (100 mL), 10% sodium hydrogen sulfite aq. (100 mL), water (100 mL). The organic layer was dried over anhydrous sodium sulfate. After the filtration and concentration the residue was purified by column chromatography on silica gel eluted with hexane/benzene (1:1 v/v). Recrystallization from benzene gave 4.7 g (77%) of **3a** as pale yellow crystals; mp 177–178 °C; MS (EI) *m/z* (rel intensity) 609 (M^+, $^{81}Br_3$, 26), 607 (M^+, $^{79}Br\cdot^{81}Br_2$, 59), 605 (M^+, $^{79}Br_2\cdot^{81}Br$, 54), 603 (M^+, $^{79}Br_3$, 18), 528 ($[M–Br]^+$, $^{81}Br_2$, 62), 526 ($[M–Br]^+$, $^{79}Br\cdot^{81}Br$, 100), 524 ($[M–Br]^+$, $^{79}Br_2$, 48), 447 ($[M–Br_2]^+$, ^{81}Br, 67), 445 ($[M–Br_2]^+$, ^{79}Br, 60), 366 ($[M–Br_3]^+$, 28); IR (KBr) ν / cm^{-1}: 2222 (CN); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.80 (d, J = 3.8 Hz, 3H), 6.99 (d, J = 3.8 Hz, 3H), 7.10 (d, J = 3.9 Hz, 1H), 7.54 (d, J = 3.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 53.7, 110.2, 113.6, 113.7, 128.1, 128.3, 129.8, 137.2, 150.3, 158.0. Anal. Calcd for $C_{18}H_8Br_3NS_4\cdot0.04C_6H_6$: C, 35.95; H, 1.36; N, 2.30. Found: C, 36.19; H, 1.38; N, 2.38 (The ratio of **3a** and benzene were estimated by the integration ratio of their ^{1}H NMR spectrum).

Synthesis of Br_3-TTM from 3a. A mixture of **3a** (2.43 g, 4.0 mmol), 1,4-dioxane (8 mL), EtOH (8 mL), and 10% NaOH aq. (16 mL) was heated to reflux for 12 h. After cooling, 10% HCl (20 mL) was added and the aqueous layer was extracted with benzene (60 mL and 30 mL×2). The combined organic layers were washed with water (100 mL) and dried over anhydrous sodium sulfate. Filtration and concentration gave the crude 5-(tris(5-bromo-2-thienyl)methyl)-2-thiophene carboxylic acid (2.50 g, > 99%) which was used without further purification. The crude product was heated with copper powder (25 mg, 0.1 equiv) and quinoline (8 mL) at 180 °C under nitrogen atmosphere for 1 h. After cooling, 10% HCl (30 mL) and benzene (20 mL) were added and stirred vigorously. The reaction mixture was passed through a pad of alumina and the alumina was washed thoroughly with benzene (20 mL). The aqueous layer was extracted with benzene (20 mL×2). The combined organic layers was washed with 5% HCl (30 mL×2) and water (30 mL), and then dried over anhydrous sodium sulfate. After filtration and concentration the residue was purified by column chromatography on silica gel eluted with hexane/benzene (1:1 v/v). Recrystallization from cyclohexane gave Br_3-TTM as colorless crystals (1.68 g, 72%).

5-(Di-2-thienylmethyl)-2-thiophenecarbonitrile (1b):[3] A mixture of 5-cyanothiophene-2-carboxyaldehyde[4] (5.0 g, 36.5 mmol), thiophene (200 mL), and the sodium hydrogen sulfate–silica gel catalyst (7.3 g, 1.0 equiv) was refluxed for 3 h. The reaction mixture turned dark red suspension. During the heating the water was removed by using the Dean-Stark apparatus. The excess thiophene was removed by distillation, the reaction mixture passed through a pad of celite to remove the intractable solid materials and the celite was washed thoroughly with Et_2O (150 mL). After the concentration the residue was purified by column chromatography on silica gel eluted with benzene/hexane (1:1 v/v). 6.3 g (60%) of **1b** was obtained as colorless crystals; mp 37–38 °C; MS (EI) *m/z* (rel intensity) 287 (M^+, 100), 286 ($[M–H]^+$, 39), 203 ($[M–H–C_4H_3S]^+$, 51), 178 ($[M–H–C_5H_2NS]^+$, 36); IR (KBr) ν / cm^{-1}: 2218 (CN); ^1H NMR (500 MHz, $CDCl_3$) δ 6.08 (q, J = 0.9 Hz, 1H), 6.89 (dd, J = 3.9, 0.9 Hz, 1H), 6.92 (ddd, J = 3.6, 1.3, 0.9 Hz, 2H), 6.94 (dd, J = 5.0, 3.6 Hz, 2H), 7.23 (dd, J = 5.0, 1.3 Hz, 2H), 7.41 (d, J = 3.9 Hz, 1H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 42.5, 108.8, 114.1, 125.4, 126.2, 126.3, 126.8, 137.3, 145.1, 155.7. HRMS (ESI) calcd for $C_{14}H_9NaS_3$ $[M+Na]^+$ 309.9789, found 309.9790.

Bis(5-cyano-2-thienyl)-di-2-thienylmethane (2b): A solution of *n*-BuLi (1.43M hexane solution, 7.0 mL, 1.0 equiv) was added to a solution of **1b** (2.87 g, 10 mmol) in THF (40 mL) and HMPA (10 mL) over 20 min below –60 °C. The resulting dark red solution was stirred for 1 h at the same temperature. A solution of 5-fluorothiophene-2-carbonitrile[5] (3.8 g, 3.0 equiv) in THF (15 mL) was added dropwise over 10 min below –60 °C. After the stirring for 1 h at low temperature the reaction mixture was allowed to be stirred overnight at ambient temperature. Water (100 mL) and benzene (50 mL) was added and the reaction mixture was stirred for 1 h. Brine (100 mL) was added and the aqueous layer was extracted with

benzene (100 mL×3). The combined organic layers passed through a pad of celite to remove the tar material and then washed with water (100 mL) and dried over anhydrous sodium sulfate. After filtration and concentration the residue was purified by column chromatography on silica gel eluted with cyclohexane/benzene (1:1 v/v). The crude product obtained by the concentration of the fractions containing the desired material was washed with cyclohexane/benzene (1:1 v/v) gave pure **2b** as pale yellow crystals (1.28 g, 32%); mp 165–166 °C; MS (EI) *m/z* (rel intensity) 394 (M^+, 100), 311 ([M–C_4H_3S]$^+$, 13), 286 ([M–C_5H_2NS]$^+$, 27), 203 ([M–C_4H_3S–C_5H_2NS]$^+$, 89); IR (KBr) ν / cm^{-1}: 2219 (CN); ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.04 (dd, J = 4.9, 3.7 Hz, 2H), 7.06 (dd, J = 3.7, 1.5 Hz, 2H), 7.11 (d, J = 4.1 Hz, 2H), 7.33 (dd, J = 4.9, 1.5 Hz, 2H), 7.55 (d, J = 4.1 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 53.4, 110.0, 113.6, 126.5, 127.0, 128.2, 128.4, 137.1, 149.2, 158.8. Anal. Calcd for $C_{19}H_{10}N_2S_4$: C, 57.84; H, 2.55; N, 7.10. Found: C, 58.01; H, 2.55; N, 7.21.

Bis(5-bromo-2-thienyl)-bis(5-cyano-2-thienyl)methane (3b): A solution of NBS (445 mg, 2.5 equiv) in DMF (2 mL) was added dropwise to a solution of **2b** (395 mg, 1.0 mmol) in DMF (8 mL) at room temperature under dark conditions. The reaction mixture was stirred for 24 h at room temperature. According to the TLC analysis, the reaction mixture contained the considerable amount of the starting materials and monobromo by-product with the desired dibromo compound. NBS (445 mg, 2.5 equiv) was added and stirred for the additional 24 h. Water (50 mL) was added and the resulting white suspension was extracted with $CHCl_3$ (40 mL×3). The combined organic layers were washed with water (50 mL), 10% sodium hydrogen sulfite aq. (50 mL), water (50 mL). The organic layer was dried over anhydrous sodium sulfate. After the filtration and concentration the residue was purified by column chromatography on silica gel eluted with hexane/benzene (2:1 v/v). Pure **3b** was obtained as pale yellow crystals (520 mg, 95%); mp 178–179 °C; MS (EI) *m/z* (rel intensity) 554 (M^+, $^{81}Br_2$, 42), 552 (M^+, $^{79}Br\cdot^{81}Br$, 67), 550 (M^+, $^{79}Br_2$, 31), 473 ([M–Br]$^+$, ^{81}Br, 81), 471 ([M–Br]$^+$, ^{79}Br, 70), 392 ([M–Br_2]$^+$, 36), 202 ([M–C_5H_2NS–C_4H_2Br–Br]$^+$, 100); IR (KBr) ν / cm^{-1}: 2220 (CN); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.81 (d, J = 3.9 Hz, 2H), 7.02 (d, J = 3.9 Hz, 2H), 7.10 (d, J = 4.0 Hz, 2H), 7.57 (d, J = 4.0 Hz, 2H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 53.7, 110.7, 113.3, 114.3, 128.4, 128.8, 130.0, 137.3, 149.5, 157.0. Anal. Calcd for $C_{19}H_8Br_2N_2S_4$: C, 41.32; H, 1.46; N, 5.07. Found: C, 41.52; H, 1.45; N, 5.14.

Synthesis of Br_2-TTM from 3b. A mixture of **3b** (2.1 g, 3.8 mmol), 1,4-dioxane (30 mL), EtOH (15 mL), and 30% NaOHaq (20 mL) was heated to reflux for 12 h. After cooling, 10% HCl (100 mL) was added and the aqueous layer was extracted with EtOAc (100 mL and 50 mL×2). The combined organic layers were washed with water (100 mL) and brine (50 mL), then dried over anhydrous sodium sulfate Filtration and concentration gave the crude dicarboxylic acid derivative (2.2 g, > 99%) which was used without further purification. 1.1 g (1.9 mmol) of the crude product was heated with copper powder (8 mg, 0.06

equiv) and quinoline (10 mL) at 200 °C under nitrogen atmosphere for 2 h. After cooling, 10% HCl (30 mL) and benzene (20 mL) were added and stirred vigorously. The reaction mixture was passed through a pad of alumina and the alumina was washed thoroughly with Et_2O (20 mL). The aqueous layer was extracted with Et_2O (20 mL×2). The combined organic layers was washed with 5% HCl (30 mL×2), water (30 mL), and brine (30 mL), and then dried over anhydrous sodium sulfate. After filtration and concentration the residue was purified by column chromatography on silica gel eluted with hexane. Pure Br_2-TTM was obtained as colorless crystals (940 mg, 65%).

Tetrakis(5'-(tri-2-thienylmethyl)-2',5-bithiophene-2-yl)methane (4): A mixture of Br-TTM (380 mg, 10 equiv), tetrakis(5-tributylstannyl-2-thienyl)methane[2e] (140 mg, 0.094 mmol), and $Pd(PPh_3)_4$ (52 mg, 5.0 mol%) in toluene (20 mL) was heated to reflux for 6 days under nitrogen atmosphere. The resultant black solution was cooled at room temperature, and 2M HCl (50 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (50 mL×3). The combined organic layers were washed with water (50 mL) and brine (50 mL), and then dried over anhydrous sodium sulfate. After the filtration and concentration the residual green oil was purified by column chromatography on silica gel eluted with hexane/CH_2Cl_2 (2:1 v/v) to give **4** (63 mg, 39%) as colorless crystals; mp > 240 °C (dec.); UV/Vis (in CH_2Cl_2) λ_{max} / nm (log ε) 355sh (4.84), 336 (5.01), 265 (4.50); Emission (in CH_2Cl_2) λ_{em} 420 nm (excited wavelength: 355 nm); ^{1}H NMR (500 MHz, $CDCl_3$) δ 6.92 (d, J = 4.0 Hz, 4H), 6.94 (d, J = 3.5 Hz, 4H), 6.97–6.99 (m, 20H), 7.08 (dd, J = 4.0, 1.2 Hz, 12H), 7.24 (dd, J = 5.1, 1.2 Hz, 12H); ^{13}C NMR (125 MHz, $CDCl_3$) δ 53.2, 53.4, 122.9, 123.0, 125.3, 126.5, 127.8, 128.4, 128.5, 136.8, 137.3, 150.2, 151.7, 152.2; HRMS (ESI) calcd for $C_{85}H_{52}NaS_{20}$ $[M+Na]^+$ 1734.8381, found 1734.8442. Anal. $C_{85}H_{52}S_{20}\cdot 1.4C_6H_6$: C, 61.50; H, 3.33. Found: C, 61.67; H, 3.37 (The ratio of **4** and benzene were estimated by the integration ratio of their ^{1}H NMR spectrum).

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