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# SYNTHESIS, MOLECULAR STRUCTURE, AND MORPHOLOGICAL PROPERTIES OF DENDRITIC TETRA-2-THIENYLMETHANE

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**Abstract** – Tetrakis(5-(tri-2-thienyl)methyl-2-thienyl)methane, in which as many as 16 thiophene rings connected with five *sp3* carbon atoms, has been synthesized from tetra-2-thienylmethane in four steps. This compound can take both and glass state. Although a deformed structure is taken in the crystal, but it turns be a metastable state. The second polymorph exhibits the melting point more than 30 °C higher than that of the metastable state, suggesting the effective intermolecular interaction.

## INTRODUCTION

Due to their potential applications to the various optoelectronic devices, a number of the novel π-electron systems are designed and studied intensively. Among the strategies of the molecular design for the novel π-electron systems, one of the trends is toward the non-linear system and the various three dimensional (3D) architectures have been explored.[1] One of the characteristics of these non-linear π-systems is the intramolecular interaction between π-conjugation systems. In this context, we have studied the tetrahedral system based on tetra-2-thienylmethane (**G0-Th$_4$**),[2] and it was found that the intramolecular interaction between thiophene rings in the tetra-2-thienylmethane framework exists in the several derivatives of **G0-Th$_4$**. On the other hand, for the bulk properties toward organic semiconductor, the intermolecular interaction such as S···S contact and π···π stacking is crucial. The improvement of the dimensionality of these intermolecular interaction, *bulk dimensionality*,[1d] should be considered in the molecular design. However, the realization of the high bulk dimensionality seems not to be easy because the strong intermolecular interaction makes the molecule insoluble, which in turn causes the problems in synthesis and purification of the desired molecules. Generally, the intermolecular interaction and the solubility are in the relation of trade-off. For example, long alkyl groups are often introduced for the solubility of the molecule, but this modification is apparently not good with respect to the intermolecular interaction. For the model compound for high *bulk dimensionality* with good solubility, we envision that the molecular shape should be approached to ball-like and are interested in the first generation of dendritic tetra-2-thienylmethane (**G1-Th$_{16}$**, Figure 1). This molecule is expected both the intramolecular interaction between the thiophene rings in the tetra-2-thienylmethane frameworks and the intermolecular interaction between the peripheral thiophene rings of the neighboring molecule. Compared to a number of the reported star-shaped[3] and dendritic[4] oligothiophenes, **G1-Th$_{16}$** has the highly symmetric molecular structure and expected to show the good crystallinity. The substance with good crystallinity is expected to show the specific and effective intermolecular interaction. Now we report the synthesis, and characterization of the dendritic tetra-2-thienylmethane **G1-Th$_{16}$**.

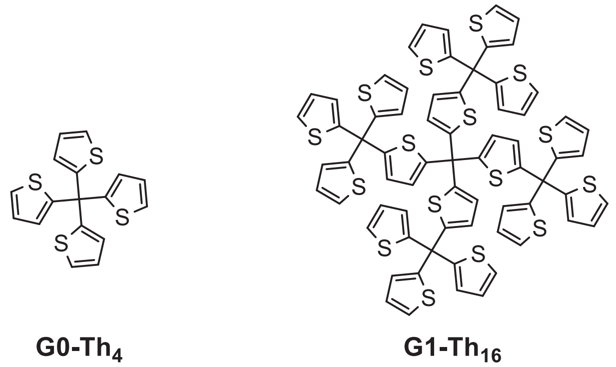
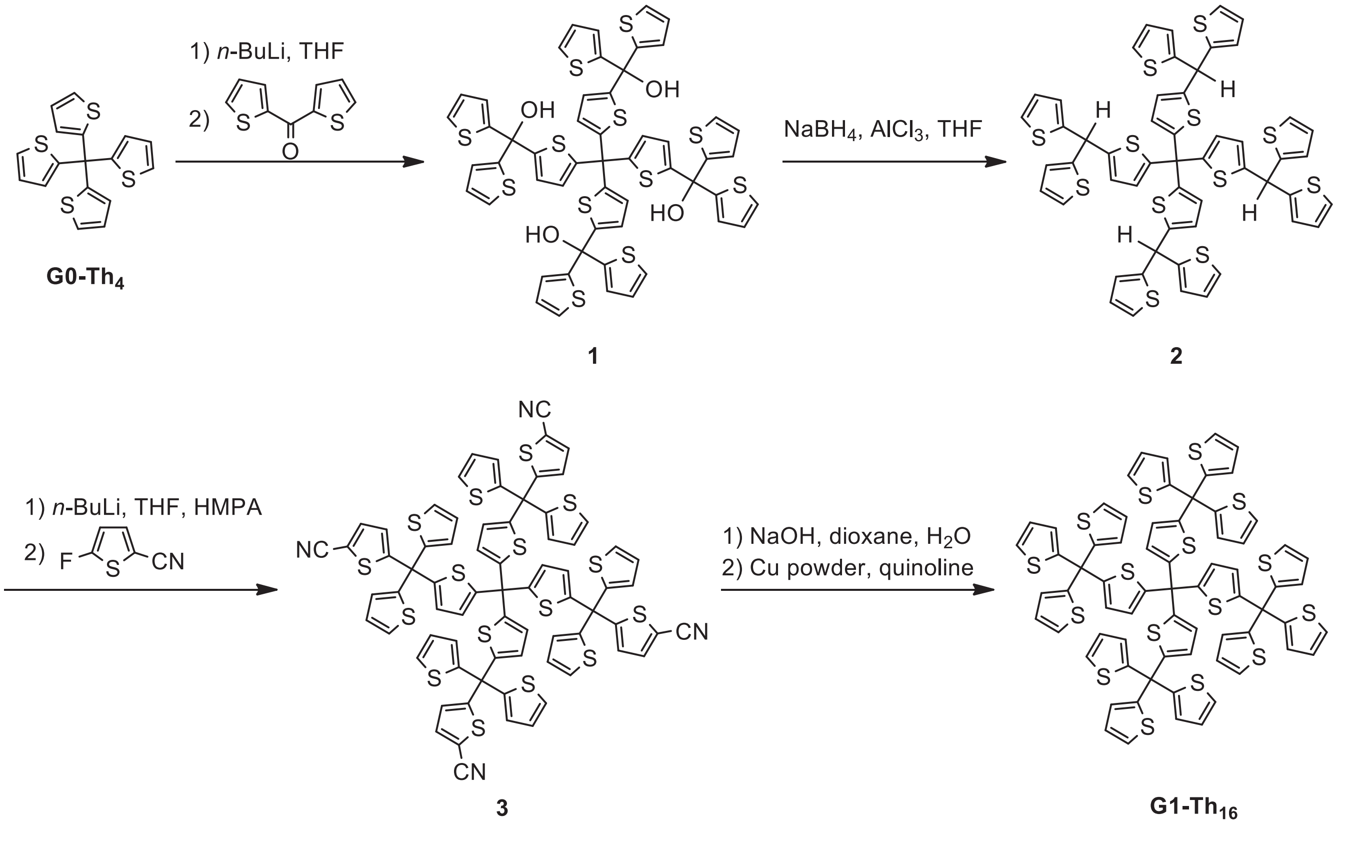


**Figure 1.** Structures of tetra-2-thienylmethane (**G0-Th$_4$**) and the first generation of dendritic tetra-2-thienylmethane (**G1-Th$_{16}$**)

## RESULTS AND DISCUSSION

Dendritic tetra-2-thienylmethane **G1-Th$_{16}$** was synthesized from **G0-Th$_4$** in four steps illustrated in Scheme 1. Although the synthetic strategy of **G1-Th$_{16}$** is similar to that of **G0-Th$_4$** from thiophene-2-carboxyaldehyde,[2b] two major modifications were needed. First, the key precursor **2** could not be obtained by the reaction of tetrakis(5-formyl-2-thienyl)methane with excess amount of thiophene in the presence of acid catalysis whereas tri-2-thienylmethane was obtained in moderate yield from thiophene-2-carboxyaldehyde under the similar conditions.[5] So we decided to synthesize **2** by another synthetic approach. We first synthesized tetraol **1** in 78% yield by four-fold lithiation of **G0-Th$_4$** with *n*-BuLi followed by the treatment with di-2-thienylketone. Then, the reduction of four hydroxyl groups was carried out with the excess amount of sodium borohydride and anhydrous aluminum chloride in THF-toluene in 78% yield. Second, the four-fold lithiation of **2** did not proceed under the condition similar to the lithiation of tri-2-thienylmethane, and therefore, the detailed investigation for the optimized reaction condition was needed. The major problem seemed to be the formation of precipitate probably due to the partially lithiated species of **2** when *n*-BuLi was added to the solution of **2** in THF. We tried this reaction under the various conditions and finally we found that the addition of hexamethylphosphoric triamide (HMPA) was critical for the effective lithiation of **2**. The intractable precipitate was not formed by the addition of HMPA and the four-fold lithiation of **2** proceeded smoothly, which was confirmed by the reaction with 5-fluorothiophene-2-carbonitrile to give **3** in 73% yield. Alkaline hydrolysis of the cyano groups of **3** followed by the decarboxylation of the resulting tetracarboxylic acid afforded the desired dendritic tetra-2-thienylmethane **G1-Th$_{16}$** in 40% yield. **G1-Th$_{16}$** is a stable, crystalline substance. Good solubility in chloroform and dichloromethane helps the purification and characterization of **G1-Th$_{16}$**. Nakayama *et al*. reported that the corresponding organosilicon dendrimer, in which the five *sp3* carbons of **G1-Th$_{16}$** were replaced with silicon atoms, often formed the inclusion complexes with the various organic solvents,[6] but any behaviors to form the inclusion complexes were not observed in the case of **G1-Th$_{16}$**.



**Scheme 1**. Synthesis of G1-Th$_{16}$

Figure 2 shows the aromatic region of the $^1$H NMR spectra of **G1-Th16** and the related compounds. Reflecting the high symmetry of the molecular structure, **G1-Th16** shows the simple $^1$H NMR spectra (Figure 2a). Namely, **G1-Th16** exhibited only five sets of signals and all central and peripheral thiophene ring protons were observed as equivalent, respectively. The high field shifts of the protons on the central thiophene rings are understandable as the result of the substituent effect of tri-2-thienylmethyl group, considering the substituent effect of the methyl groups in tetrakis(5-methyl-2-thienyl)methane (**4**)[2e] (Figure 2c and 2d). The protons on the peripheral thiophene rings are also observed at higher field than those of **G0-Th4** (Figure 2a and 2d), probably due to the same reason. The $^{13}$C NMR spectrum of **G1-Th16** was also as simple as 10 signals, also reflecting the highly symmetric structure. The chemical shifts of the central and peripheral *sp3* carbon atoms are observed at 53.8 and 53.2 ppm, respectively, which are similar to that of **G0-Th4** (53.2 ppm).

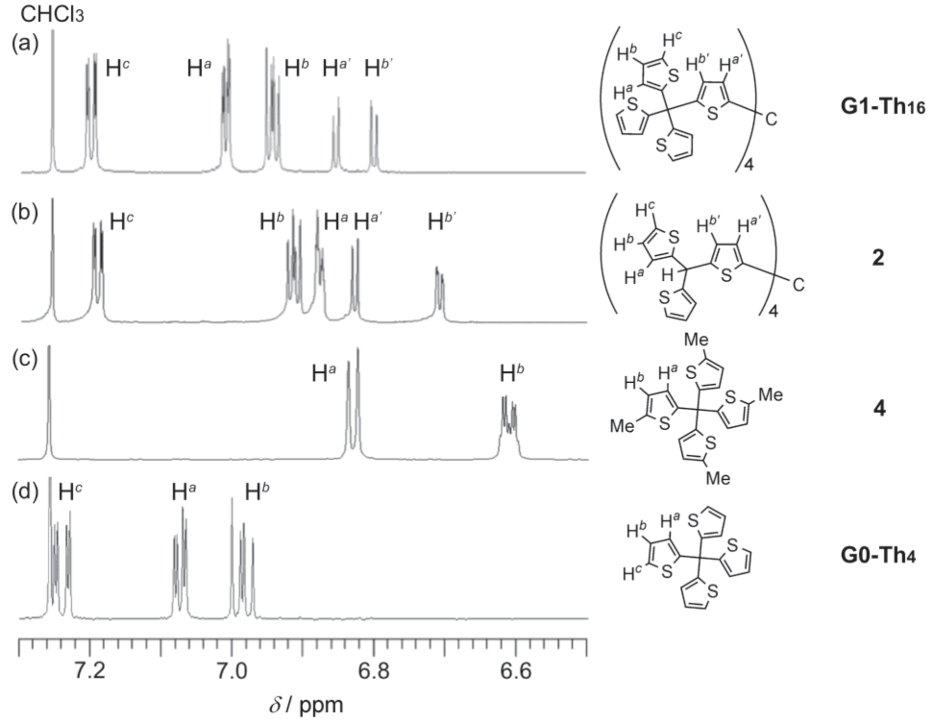


**Figure 2.** Aromatic region of $^1$H NMR spectra of (a) **G1-Th16**, (b) **2**, (c) tetrakis(5-methyl-2-thienyl)methane (**4**), and (d) **G0-Th4** (in $CDCl_3$, 25 °C)

Figure 3 shows the UV spectra of **G1-Th16**, **2**, and **4**. Although remarkable bathochromic shifts of the absorption maxima $\lambda_{max}$ (**G1-Th16**; 242, **2**; 240, **4**; 245 nm) are not observed, the shoulder around 265 nm observed in **4** are slightly red shifted in **2** and **G1-Th16** (around 270 nm). This might suggest the intramolecular interactions of thiophene rings. Unfortunately, **G1-Th16** shows no fluorescence properties similar to **G0-Th4**.

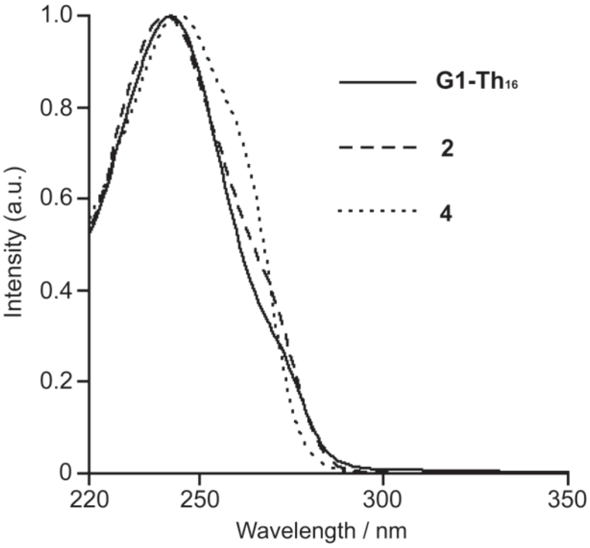


**Figure 3**. Normalized UV spectra of **G1-Th16**, **2**, and **4** in $CH_2Cl_2$

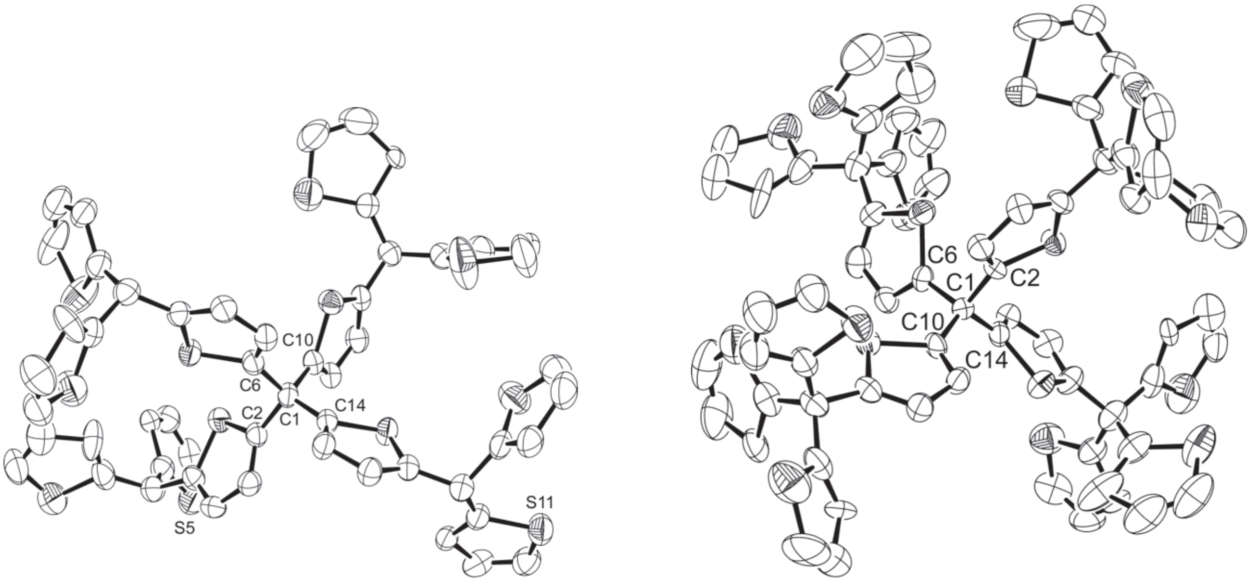


**Figure 4.** ORTEP drawing of **2** (left) and **G1-Th16** (right) drawn at 50% probability ellipsoid. Hydrogen atoms are omitted for clarity.

Single crystals of **2** and **G1-Th16** were obtained by the recrystallization from dichloromethane–hexane.[7] The ORTEP drawings of **2** and **G1-Th16** are shown in Figure 4. In spite of the high symmetry of the molecular structure, **G1-Th16** takes a deformed structure in the crystal probably due to the packing force and/or the disorder of the peripheral thiophene rings. Interestingly, this deformed structure includes not only the asymmetric orientation of the thiophene rings but also the different central C–C bond lengths. Thus, C1–C10 bond length (1.513(9) Å) is shorter than the three other bonds (C1–C2; 1.548(10), C1–C6; 1.545(7), C1–C14; 1.543(12) Å). The same tendency is observed in **2** (The four bond lengths of the central *sp3* atom are C1–C2 1.548(8), C1–C6 1.551(7), C1–C10 1.539(7), C1–C14 1.508(7) Å). There are no intermolecular S···S contacts closer than the sum of the van der Waals radii whereas one S···S contact (S5···S11$^{i}$ 3.526(3) Å; symmetry code: 2–x, –y, 2–z) is observed in **2**.

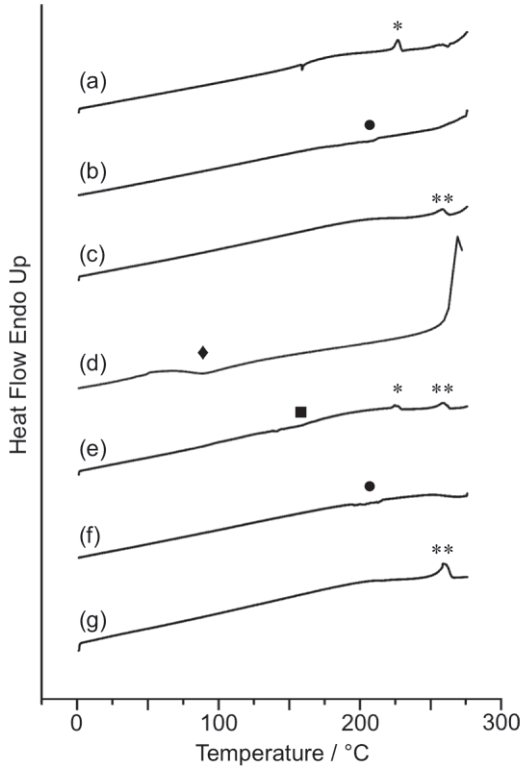


**Figure 5.** DSC traces of **G1-Th$_{16}$**. (a) 1st cycle, heating scan, 10 °C min$^{-1}$, (b) 1st cycle, cooling scan, 10 °C min$^{-1}$, (c) 2nd cycle, heating scan, 10 °C min$^{-1}$, (d) 2nd cycle, cooling scan, 200 °C min$^{-1}$, (e) 3rd cycle, heating scan, 10 °C min$^{-1}$, (f) 3rd cycle, cooling scan, 5 °C min$^{-1}$, (g) 4th cycle, heating scan, 10 °C min$^{-1}$. ∗; melting of the crystal, ●; exothermic peak due to crystallization, ∗∗; melting of the second polymorph, ♦; glass transition, ■; exothermic peak due to the transition from glass to crystal.

In order to investigate the thermal properties, we performed the differential scanning calorimetry (DSC) measurement of **G1-Th$_{16}$** (Figure 5). By heating the crystals determined by X-ray analysis, a single endothermic peak due to melting was observed at 235 °C (Figure 5a). Then the sample was cooled slowly (10 °C min$^{-1}$), the weak exothermic peak at around 200 °C due to crystallization was observed (Figure 5b). This showed that the sample returned to the crystalline state. But surprisingly, the second heating of the sample gave the endothermic peak at more than 30 °C higher temperature (271 °C), than the initially observed endothermic peak (Figure 5c). This indicates that the initial crystalline state is a metastable state and the second polymorph would take the effective intermolecular interaction because of the higher melting point. These behaviors are in contrast with those of **4** and tetrakis(5’’-hexyl-2’’,5’:2’,5-terthiophene-2-yl)methane, which were obtained as the most stable crystalline state and the melting points of the metastable state were observed only at 2–3 °C lower temperature than the initial crystalline state.[2e] On the other hand, when the sample was cooled quickly (200 °C min$^{-1}$), the glass transition was clearly observed ($T_g$ = 88 °C, Figure 5d). Therefore, the crystalline and glass states are controllable by the cooling rate. In addition to the nonplanar molecular structure, the existence of many conformers would facilitate the glass formation.[8] This glass state was stable up to 150 °C (Figure 5e) and no decomposition over DSC measurements were confirmed by the return to the crystalline state (Figure 5f). The molecular and crystal structure of the most stable crystalline state is now under investigation.

In summary, the first generation of tetra-2-thienylmethane **G1-Th$_{16}$** have successfully obtained as a stable, crystalline substance. In solution, the thiophene rings of **G1-Th$_{16}$** can rotate freely on the NMR time scale and the intramolecular interaction between thiophene rings is negligible. In contrast, **G1-Th$_{16}$** takes a deformed structure in the crystal. Although any notable intermolecular interaction is not observed, this crystal state is a metastable state according to DSC measurements. The second polymorph exhibits the melting point more than 30 °C higher than that of the metastable crystal, suggesting the effective intermolecular interaction. **G1-Th$_{16}$** can also take a stable glass state by fast cooling. The detailed investigation of the structure of the second polymorph as well as further modified new π-conjugation molecules are now in progress.

## EXPERIMENTAL

Melting points were taken on a Yanako MP 500D apparatus and were uncorrected. $^1$H and $^{13}$C NMR spectra were recorded on a JEOL GSX400 (400 MHz) and JEOL LA-500 (500 MHz) spectrometers. Chemical shifts were recorded in units of parts per million downfield from tetramethylsilane as an internal standard and all coupling constants are reported in Hz. Data collection for X-ray crystal analysis was performed on Rigaku/Varimax diffractometer (Mo$_{K\alpha}$, $\lambda$ = 0.71069 Å). The structures were solved with direct methods and refined with full-matrix least squares (SHELXL-97[9]). Electronic spectra were taken in $CH_2Cl_2$ solution on a JASCO V-570 spectrophotometer. Mass spectra were recorded with Applied Biosystems Japan Ltd. QSTAR Elite by ESI method. Thermal analyses were performed using a Perkin Elmer Pyris Diamond DSC differential scanning calorimeter. Elemental analyses were performed at the Elemental Analysis Center in the Faculty of Science, Osaka University. Column chromatography was performed using Merck Kieselgel 60 (0.063–0.200 mm). All of the organic solvents used in this study were dried over appropriate drying agents and distilled prior to use.

**Starting Materials.** Tetra-2-thienylmethane,[2b] di-2-thienylketone,[10] and 5-fluorothiophene-2-carbonitrile[11] were prepared by previously reported procedures.

**Tetrakis(5-(di-2-thienyl-hydroxymethyl)-2-thienyl)methane (1).** A solution of *n*-BuLi (1.43M hexane solution, 11.2 mL, 16 mmol) was added to a solution of tetra-2-thienylmethane (**G0-Th$_4$**) (689 mg, 2 mmol) in THF (40 mL) over 10 min at –75 °C. After the reaction mixture was stirred at 0 °C for 1 h, cooled to –75 °C again. A solution of di-2-thienylketone (3.89 g, 20 mmol) in THF (20 mL) was added to the reaction mixture over 15 min. The reaction mixture was allowed to room temperature and stirred overnight. Water (60 mL) was added slowly at 0 °C and the aqueous layer was extracted with AcOEt (100 mL×2). The combined organic layers were washed with water (100 mL×2) and brine (100 mL) and dried over anhydrous sodium sulfate. After filtration and concentration the residue was purified by column chromatography on silica gel (3:7 AcOEt–hexane) to give **1** (1.74 g, 78%); pale yellow solid; mp 108–109 °C (AcOEt–hexane); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 3.24 (s, 4H), 6.76 (d, $J$ = 4.0 Hz, 4H), 6.88 (d, $J$ = 4.0 Hz, 4H), 6.90–6.93 (m, 16H), 7.25 (dd, $J$ = 4.5, 1.5 Hz, 8H). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 53.8, 67.0, 125.77, 125.84, 126.4, 126.6, 127.3, 150.5, 150.9, 151.8. HRMS (ESI) calcd for $C_{53}H_{36}NaO_4S_{12}$ $[M+Na]^+$ 1142.9159, found 1142.9104; calcd for $C_{53}H_{36}O_3S_{12}$ $[M–OH]^+$ 1102.9234, found 1102.9180.

**Tetrakis(5-(di-2-thienylmethyl)-2-thienyl)methane (2).** A solution of **1** (4.41 g, 3.9 mmol) in toluene (40 mL) was added to a suspension of anhydrous aluminium chloride (10.48 g, 78.6 mmol) and sodium borohydride (6.69 g, 176 mmol) in THF (70 mL) at room temperature. The reaction mixture was heated at 80 °C for 3 h. After cooling, the reaction mixture was poured into the crashed ice (300 g) and the aqueous layer was extracted with toluene (150 mL×2). The combined organic layers were washed with 2M aqueous solution of HCl (100 mL×2), water (100 mL), and brine (100 mL), then dried over anhydrous sodium sulfate. After filtration, the filtrate was passed through a pad of silica gel (50 g). Concentration to give **2** (3.25 g, 78%); light orange crystals; mp 133–134 °C; UV/Vis (in $CH_2Cl_2$) $\lambda_{max}$/nm (log $\varepsilon$) 264 (4.58), 240 (4.88). $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 5.98 (s, 4H), 6.71 (d, $J$ = 4.0 Hz, 4H), 6.83 (d, $J$ = 4.0 Hz, 4H), 6.88 (dd, $J$ = 3.5, 1.0 Hz, 8H), 6.91 (dd, $J$ = 5.0, 3.5 Hz, 8H), 7.19 (dd, $J$ = 5.0, 1.0 Hz, 8H). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 42.7, 53.8, 124.8, 125.1, 125.9, 126.6, 127.2, 146.7, 147.1, 151.1. HRMS (ESI) calcd for $C_{53}H_{36}NaS_{12}$ $[M+Na]^+$ 1078.9363, found 1078.9436. Anal. Calcd for $C_{53}H_{36}S_{12}$: C, 60.19; H, 3.43. Found: C, 60.34; H, 3.55.

**Tetrakis(5-(di-2-thienyl)(5-cyano-2-thienyl)methyl-2-thienyl)methane (3).** A solution of *n*-BuLi (1.43M hexane solution, 1.18 mL, 1.7 mmol) was added to a solution of **2** (423 mg, 0.4 mmol) in THF (8 mL) and HMPA (2 mL) over 5 min at –75 °C. After the reaction mixture was stirred at 0 °C for 1 h, cooled to –60 °C. A solution of 5-fluorothiophene-2-carbonitrile (305 mg, 2.4 mmol) in THF (2 mL) was added to the reaction mixture at –60 °C and the reaction mixture was stirred for 1 h at the same temperature. Water (50 mL) was added at –60 °C and the aqueous layer was extracted with AcOEt (300 mL×2). The combined organic layers were washed with water (100 mL×5) and brine (100 mL) and dried over anhydrous sodium sulfate. After filtration and concentration the residue was purified by column chromatography on silica gel eluted with hexane/AcOEt (90:10 v/v). Recrystallization from $CH_2Cl_2$–hexane gave **3** (434 mg, 73%); light orange crystals; mp > 130 °C (decomp); $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ 6.85 (d, $J$ = 3.6 Hz, 4H), 6.87 (d, $J$ = 3.6 Hz, 4H), 6.97–7.00 (m, 16H), 7.04 (d, $J$ = 4.0 Hz, 4H), 7.27 (dd, $J$ = 4.4, 2.0 Hz, 8H), 7.47 (d, $J$ = 4.0 Hz, 4H). $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ 53.5, 53.8, 114.1, 109.4, 126.0, 126.7, 127.4, 127.5, 128.1, 128.2, 137.0, 150.5, 150.8, 151.1, 160.5. HRMS (ESI) calcd for $C_{73}H_{40}N_4NaS_{16}$ $[M+Na]^+$ 1506.8682, found 1506.8719.

**Tetrakis(5-(tri-2-thienyl)methyl-2-thienyl)methane (G1-Th$_{16}$).** A mixture of **3** (344 mg, 0.33 mmol), 1,4-dioxane (11 mL), and 50% NaOH aq (23 mL) was heated to reflux for 12 h. After cooling, 6M aqueous solution of HCl (150 mL) was added and the aqueous layer was extracted with AcOEt (150 mL×2). The combined organic layers were washed with 2M aqueous solution of HCl (100 mL), water (100 mL), and brine (100 mL), and dried over anhydrous sodium sulfate. Filtration and concentration gave the crude tetracarboxylic acid which was used without further purification. The crude product was heated with copper powder (17 mg) and quinoline (10 mL) at 180 °C under nitrogen atmosphere for 24 h. After cooling, 2M aqueous solution of HCl (100 mL) was added. The reaction mixture was passed through a pad of alumina and the alumina was washed thoroughly with AcOEt (300 mL). The organic layer was washed with 2M aqueous solution of HCl (100 mL×3), water (100 mL), and brine (100 mL), and dried over anhydrous sodium sulfate. After filtration and concentration the residue was purified by column chromatography on silica gel (1:4 $CH_2Cl_2$–hexane). Recrystallization from $CH_2Cl_2$–hexane gave **G1-Th$_{16}$** (181 mg, 40%); light orange crystals; mp 235–236 °C ($CH_2Cl_2$–hexane); UV/Vis (in $CH_2Cl_2$) $\lambda_{max}$/nm (log $\varepsilon$) 265 (4.58), 242 (4.98); $^1$H NMR (500 MHz, $CDCl_3$) $\delta$ 6.80 (d, $J$ = 4.0 Hz, 4H), 6.86 (d, $J$ = 4.0 Hz, 4H), 6.95 (dd, $J$ = 5.0, 4.0 Hz, 12H), 7.01 (dd, $J$ = 4.0, 1.5 Hz, 12H), 7.20 (dd, $J$ = 5.0, 1.5 Hz, 12H). $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ 53.2, 53.8, 125.0, 126.2, 126.7, 126.9, 127.6, 150.9, 151.7, 152.3. HRMS (ESI) calcd for $C_{69}H_{44}NaS_{16}$ $[M+Na]^+$ 1406.8872, found 1406.8871. Anal. Calcd for $C_{69}H_{44}S_{16}$: C, 59.79; H, 3.27. Found: C, 59.54; H 3.27.

## ACKNOWLEDGEMENTS

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14.2942(9), $c$ = 20.8487(14) Å, $\beta$ = 99.5357(19)°, $V$ = 4897.3(6) Å$^3$, $T$ = 200 K, $Z$ = 4, $\rho$(calcd) =1.434 g cm$^{-3}$, reflections collected = 47255, unique reflections = 11165, $R_{\text{int}}$ = 0.102, param. refined = 587, $R1$ = 0.091 ($I$>2$\sigma$($I$)) $wR2$ = 0.308 (all data), GOF=1.08. CCDC-1422932. Crystal data for **G1-Th16**: $C_{69}H_{44}S_{16}$, $Mw$ = 1386.07, monoclinic, $Cc$ (#9), $a$ = 27.661(3), $b$ = 16.0342(17), $c$ = 15.9700(15) Å, $\beta$ = 115.3636(19)°, $V$ = 6400.2(11) Å$^3$, $T$ = 200 K, $Z$ = 4, $\rho$(calcd) = 1.438 g cm$^{-3}$, reflections collected = 31020, unique reflections = 14033, $R_{\text{int}}$ = 0.077, param. refined = 767, $R1$ = 0.079 ($I$>2$\sigma$($I$)), $wR2$ = 0.2453 (all data), GOF=1.03. CCDC-1422933. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre at www.ccdc.cam.ac.uk/data_request/cif.

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