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# Synthesis and optical properties of tetraphenylmethane-based tetrahedral fluorescent compounds and their water-soluble PEG-linked polymers

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**Abstract**—The synthesis and optical properties of tetrahedral fluorescent compounds comprising of tetraphenylmethane as the core and oligothiophenes as the chromophoric arms, and their water-soluble poly(ethylene glycol)-linked polymers are reported.

Tetrahedral organic compounds have attracted much attention in the areas of chemistry and material sciences. They have been investigated as light-emitting materials,[1] electronically active materials,[2] and as a molecular caltrop in scanning probe microscopy, etc.[3] To date, most tetrahedral light-emitting organic compounds have been made from a tetraphenylmethane core, and several chromophores such as vinylstilbene,[1c] triphenylethene,[1c] and oxadiazolyl[4] have been conjugated with the core. In addition, water-soluble fluorescent tetrahedral and dendritic materials derived from tetraphenylmethane have drawn attention in the area of diagnostics and sensoring.[5] We herein report a novel class of tetrahedral fluorescent organic compounds prepared from C($p$-$C_6H_4Br)_4$ and oligothiophenes by Grignard and Suzuki coupling reactions. We chose α-oligothiophenes as fluorescent side arms in view of their well-established optical and electronic properties,[6] and their reactive α-carbon sites that are useful handles for further structural modification. The tetraphenylmethane–oligothiophene fluorophores were conjugated with poly(ethylene glycol) (PEG) to synthesize further water-soluble fluorescent polymers. Such polymers with the tetrahedral hydrophobic fluorescent core being blocked by hydrophilic PEG arms have shown good water solubility and minimized aggregation in aqueous media.

The synthesis of compounds **1**–**9** is shown in Scheme 1. All the newly synthesized compounds were fully characterized.[7] Firstly, the classic Grignard coupling method was employed to synthesize the precursor compounds.[†] Compound **1** was obtained as a major product in 38% yield. In addition, the di-substituted by-product **8** was also isolated in 10% yield. The $^1$H NMR spectrum of **1** in $CDCl_3$ exhibited one doublet–doublet (dd) signal at $\delta$ 7.07 (${}^3J_{HHa} = {}^3J_{HHb} = 3.6$ Hz, β-$H$ of thienyl), and a doublet signal at $\delta$ 7.54 (${}^3J_{HH} = 8.4$ Hz, phenyl-$H$). The $^1$H NMR spectrum of **8** in $CDCl_3$ showed a well-resolved dd signal (β-$H$ of thienyl) and six doublet signals (thienyl-$H$ and Ph-$H$). The Grignard coupling between C($p$-$C_6H_4Br)_4$ and 2,2′-bithiophene-5-MgBr gave **2** and a tri-substituted by-product **9** in 10% and 5% yields, respectively. When a higher excess of the Grignard reagent was used, **9** was still obtained and the yields of both products were not changed significantly. The $^1$H NMR spectrum of **2** in $CDCl_3$ exhibited a dd

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[†] A general procedure for the Grignard coupling reactions. The α-bromo-oligothiophene (12 mmol) dissolved in 50 mL of dry THF was added dropwise into a magnesium (0.35 g, 14.4 mmol) suspension in dry THF (10 mL). After the addition, the reaction mixture was heated at 65 °C for 1 h. The Grignard solution was then added to a mixture of C($p$-$C_6H_4Br)_4$ (1.0 g, 1.6 mmol) and [$NiCl_2$(dppp)] (50 mg) in 20 mL of THF. After being heated at 85 °C for 3 days, the solvent was removed and the residue was re-dissolved in dichloromethane. The dichloromethane solution was washed with a saturated aqueous $NH_4Cl$ solution and dried ($MgSO_4$). The crude product was purified by silica gel column chromatography (first with hexanes, then with hexanes/ethyl acetate 8:1) to give compounds **1**, **2**, **8**, and **9** as light yellow solids in 5–38% yields.

*Keywords*: Tetrahedral material; Tetraphenylmethane; Oligothiophenes; Fluorescence.

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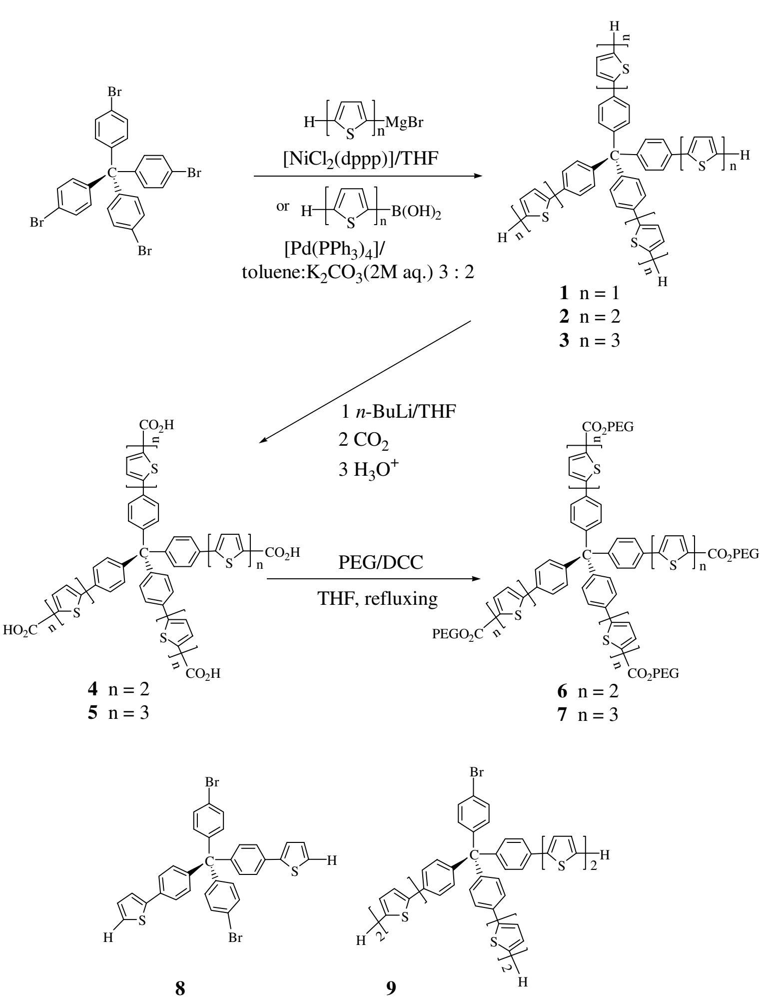

**Scheme 1.**

signal at $\delta$ 7.03 ($^3J_{HHa} = 3.6$ Hz, $^3J_{HHb} = 5.2$ Hz, $H_\beta$ of bithienyl), and two doublet signals from the two sets of Ph-*H*. The $^1$H NMR spectrum of **9** in acetone-$d_6$ showed two doublets at $\delta$ 7.34 ($^3J_{HH} = 8.4$ Hz) and 7.44 ($^3J_{HH} = 8.8$ Hz) in a ratio of 3:1, which are assigned to the two kinds of phenyl groups of the core. Attempts to synthesize **3** by the Grignard coupling method were not successful even when a higher temperature and a longer reaction time were used, and may be due to the difficulty in forming the Grignard reagent of terthiophene.[8] Alternatively, the Suzuki coupling method was employed to prepare the precursor compounds **1**–**3** in improved yields.[‡] The $^1$H NMR spectrum of **3** in CDCl$_3$ exhibited characteristic dd signal at $\delta$ 7.03 ($^3J_{HHa} = 3.6$ Hz, $^3J_{HHb} = 5.2$ Hz, $H_\beta$ of terthienyl), and two doublet signals at $\delta$ 7.39 ($^3J_{HH} = 7.6$ Hz) and 7.60 ($^3J_{HH} = 7.6$ Hz), which were unambiguously assigned to the two sets of Ph-*H* from the tetraphenylmethane unit.

Compounds **2** and **3** showed maximum emission wavelengths in the visible spectral area, and so they were converted to the corresponding carboxylic acids **4** and **5** by deprotonation of the α-protons of the thiophene moieties and subsequent reactions with carbon dioxide.[9,§] The IR spectra of **4** and **5** exhibited the characteristic absorptions of –COOH at $\nu$ (cm$^{-1}$): 3417, 1665,

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[‡] A general procedure for the Suzuki coupling reactions. The C($p$-C$_6$H$_4$Br)$_4$ (0.4 g, 0.6 mmol), oligothiophene-α-B(OH)$_2$ (3.0 mmol) and [Pd(PPh$_3$)$_4$] (72 mg, 0.06 mmol) were dissolved in 20 mL of toluene and 32 mL of 2 M K$_2$CO$_3$ (aqueous). The mixture was degassed by bubbling with nitrogen for 15 min and then refluxed for three days under nitrogen. Upon completion, the reaction mixture was diluted with 100 mL dichloromethane, the organic layer was isolated and was washed with water, then dried (Mg$_2$SO$_4$). The crude products **1**–**3** were purified by silica gel column chromatography as described in the Grignard coupling method and were obtained as light yellow solids in 40%, 25% and 20% yield, respectively.

[§] A general procedure for the synthesis of **4** and **5**. Compound **2** or **3** (0.4 mmol) was dissolved in 30 mL of THF and was cooled to −70 °C. The $n$-BuLi/$n$-hexane solution (1.6 M, 0.5 mmol) was added to the above solution dropwise through a syringe. The reaction mixture was stirred for 2 h, during this period precipitates appeared. The mixture was then bubbled with dry CO$_2$ for 10 min, and a precipitate formed immediately. The mixture was then allowed warm to r.t. and was stirred for 1 h. The resultant suspension was acidified with 1 M HCl to give a clear yellow solution. The organic layer was separated. The aqueous layer was extracted with dichloromethane three times. The combined organic layer was washed with water and dried (Mg$_2$SO$_4$). Removal of the solvent gave the desired products as yellow solids. The products were used directly without further purification.

and 3432, 1661, respectively. Unlike similar tetrahedral compounds derived from tetraphenylmethane,[1d,4] compounds **1**–**5**, **8**, and **9** did not show any glass transitions as revealed by differential scanning calorimetry studies. Interestingly, **2** exhibited a much higher melting point than **1** and **3**. Finally, reaction of **4** and **5** with excess PEG using dicyclohexylcarbodiimide (DCC) as a dehydrating agent and 4-(dimethylamino)pyridinium *p*-toluenesulfonate (DAPT) as a catalyst, yielded polymers **6** and **7** in good yields, following a literature method.[10,¶] The products were purified efficiently by ultra-filtration and were obtained as yellow semi-solids. The polymers were very soluble in both common organic solvents and water. The $^1$H NMR spectra of **6** and **7** in acetone-$d_6$ exhibited singlet signals due to PEG-*H* at $\delta$ 3.60 and 3.70, respectively. The aromatic signals of the polymers exhibited similar patterns to the starting compounds **4** and **5**, indicating successful reactions of all the four carboxylic groups with PEG and the near symmetrical structures of both polymers. The complete esterification of all the carboxylic groups by PEG was proved further by the integration ratio of PEG-*H* to aromatic-*H*. The IR spectra of **6** and **7** exhibited characteristic strong absorptions at 1097 and 1099 cm$^{-1}$ ($\nu_{C–O–C}$), respectively.

The UV–vis and fluorescence spectra of **1**–**5**, **8**, and **9** in THF are shown in Figures 1 and 2, respectively. A summary of their optical properties is given in Table 1. All the compounds exhibit two absorption bands, which are assigned in terms of the strong absorption band at longer wavelength being associated with the $\pi \rightarrow \pi^*$ electron transfer of the entire chromophore, and the less intense band with the $\pi \rightarrow \pi^*$ local excitation of the hetero-nucleus.[11] The UV absorptions of the present tetrahedral compounds show a significant red shift relative to their parent oligothiophene chromophores,[11] due to conjugation involving the phenyl groups and a possible weak hyperconjugation within the tetrahedral molecules. As expected, the long wavelength $\pi \rightarrow \pi^*$ absorptions show a red shift with the increase of the conjugation length of oligothiophene arms. Except for the two derivatives of thiophene (**1** and **8**), compounds **2**–**5** and **9** emit bright indigo-blue light. A red shift of the maximum emission wavelength is also observed with the increase of the conjugation length of the oligothiophene arms.

Figure 3 shows the UV–vis and fluorescence spectra of polymer **6** in different organic solvents and water. A summary of the optical properties of **6** and **7** in different solvents is given in Table 2. The polymers **6** and **7**

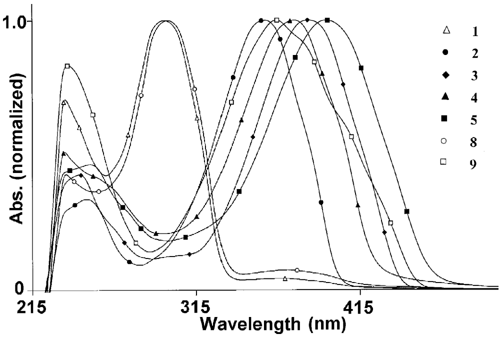

**Figure 1.** Electronic absorption spectra of tetrahedral organic products in THF.

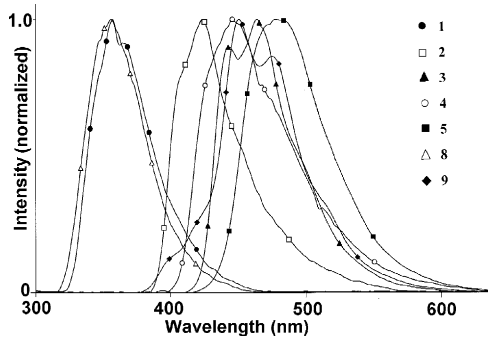

**Figure 2.** Fluorescence spectra of tetrahedral organic products in THF.

**Table 1.** Optical properties of the tetrahedral organic compounds[a]

| | $\lambda_{max}$ (nm) | | $\lambda_{max}$ (nm) Emission | Quantum yield (%) |
|---|---|---|---|---|
| | Absorption | $\varepsilon$ (M$^{-1}$ cm$^{-1}$)$\times 10^4$ | | |
| **1** | 298, 239 | 5.1, 2.8 | 360 | 0.6 |
| **2** | 356, 248 | 11.2, 4.2 | 426 | 1.4 |
| **3** | 383, 244 | 12.5, 5.7 | 467 (447) | 2.7 |
| **4** | 375, 235 | 6.2, 3.2 | 447 | 2.5 |
| **5** | 395, 250 | 11.0, 5.1 | 478 | 4.5 |
| **8** | 297, 239 | 3.1, 2.2 | 358 | 1.5 |
| **9** | 364, 236 | 4.2, 3.5 | 450 (475) | 5.5 |

[a] Data were determined in THF with concentrations of $1\times10^{-5}$ M. The emission spectra were taken by excitation at their longest wavelength absorption maximum.

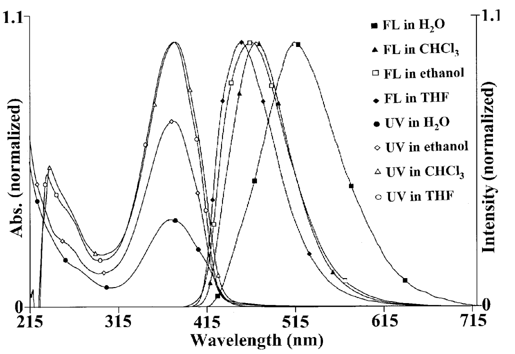

**Figure 3.** Electronic and fluorescence emission spectra of polymer **6** in organic solvents and water.

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[¶] A general procedure for the synthesis of **6** and **7**. Compound **4** or **5** (0.1 g), PEG ($M_n$ 1000, 1.0 g), DAPT (15 mg) and DCC (0.2 g) were dissolved in freshly dried THF (30 mL). The reaction mixture was refluxed under nitrogen for 16 h. Upon completion, the reaction mixture was filtered and the clear filtrate was concentrated to dryness. The crude product was dissolved in 10 mL DMF and dialyzed against water for 72 h using a dialysis bag with a molecular weight cut-off of 2000 (Sigma D-7884). The obtained yellow aqueous solution was again filtered with a 0.2 μm sized syringe filter. Removal of water afforded the product as yellow semi-solids.

**Table 2.** Optical properties of polymers **6** and **7**[a]

| Solvent | **6** | | | **7** | | |
|---|---|---|---|---|---|---|
| | $\lambda_{max}$ (nm) absorption | $\lambda_{max}$ (nm) emission | Quantum yield (%) | $\lambda_{max}$ (nm) absorption | $\lambda_{max}$ (nm) emission | Quantum yield (%) |
| THF | 378, 234 | 455 | 15.4 | 392, 287, 235 | 472 | 34.1 |
| $CHCl_3$ | 380, 238 | 471 | 15.9 | 396, 289, 238 | 477 | 31.0 |
| EtOH | 378 | 466 | 14.1 | 393, 285 | 479 | 30.7 |
| $H_2O$ | 375 | 514 | 3.2 | 392, 284 | 531 | 3.5 |
| Size (nm)[b] | 13.1 ± 5.1 (polydispersity 0.49) | | | 13.3 ± 5.0 (polydispersity 0.45) | | |

[a] Data were determined with concentrations of $1\times10^{-4}$ M. The emission spectra were taken by excitation at their longest wavelength absorption maximum.

[b] The average sizes of aggregates were determined in aqueous media.

exhibit similar maximum absorption wavelengths and maximum emission wavelengths in all the organic solvents tried. Unlike other PEG-linked fluorescent compounds,[12] the present PEG-linked tetrahedral luminescent polymers did not show significant solvent effects. In organic solutions, the quantum yields of polymers **6** and **7** were around 15% and 32%, respectively, which are significantly higher than those of their parent carboxylic acids **4** and **5** in the same solvent. Such significant increases in the quantum yields of the polymers may be attributed to the PEG side arms, which sterically reduce the intermolecular interaction of the chromophoric cores in organic solutions thus decreasing the non-emissive energy loss. In aqueous solutions, the long wavelength absorption maxima of both polymers **6** and **7** are similar to those determined in organic solutions, however, significant red shifts of maximum emission wavelengths and decreases in fluorescence intensities are observed. Such red shift of water-soluble fluorescent compounds in aqueous media has been observed previously and has been attributed to self-aggregation due to the amphiphilic nature of the compounds.[9] This intermolecular aggregation is driven by the hydrophobic–hydrophobic interactions of the chromophores. We examined the self-aggregation of the present tetrahedral polymers by dynamic light scattering (DLS) studies. The DLS studies showed that both polymers existed as nano-aggregates with an average size of 13 nm and with relatively narrow size distributions (Table 2). The results showed that the branched structures with hydrophobic chromophores are located inside and effectively minimized the aggregation of the amphiphilic polymers in aqueous media. It is important to note that good water solubility and non-aggregating properties are important for a fluorescent agent to be used in bio-sensoring.[5] Our preliminary studies showed that the fluorescence intensities of **6** and **7** in pH buffers were significantly enhanced in the presence of bovine serum albumin, indicating they are potential protein-labeling agents.

In summary, we have synthesized a novel class of tetrahedral fluorescent compounds from tetrakis(4-bromophenyl)methane and oligothiophenes, and synthesized water-soluble fluorescent PEG polymers. Such water-soluble fluorescent materials showed minimal self-aggregation in aqueous media and are potential bio-sensoring agents.

## Acknowledgements

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7. Physical data for compounds **1**–**9**. **1**. M.p. 236.2 °C. Anal. calcd for $C_{41}H_{28}S_4$: C, 75.9; H, 4.3; Found: C, 76.2; H, 3.9. $^1$H NMR ($CDCl_3$): $\delta$ 7.07 (dd, 4H, $^3J_{HHa} = {}^3J_{HHb} = 3.6$ Hz, $H_\beta$ of thienyl), 7.22–7.31 (m, 16H, *aromatics*), 7.54 (d, $^3J_{HH} = 8.4$ Hz, 8H, Ph-*H*). MS (EI): 648.2 ($M^+$). **2**. M.p. 346.7 °C. Anal. calcd for $C_{57}H_{36}S_8$: C, 70.0; H, 3.7; Found: C, 69.5; H, 3.5. $^1$H NMR ($CDCl_3$): $\delta$ 7.03 (dd, 4H, $^3J_{HHa} = 3.6$ Hz, $^3J_{HHb} = 5.2$ Hz, $H_\beta$ of bithienyl), 7.14 (d, 4H, $^3J_{HH} = 3.6$ Hz, bithienyl-*H*); 7.18–7.25 (m, 12H, *aromatics*), 7.32 (d, 8H, $^3J_{HH} = 7.6$ Hz, Ph-*H*), 7.60 (d, 8H, $^3J_{HH} = 7.6$ Hz, Ph-*H*). MS (EI): 977.4 ($M^+$). **3**. M.p. 202.9 °C. Anal. calcd for $C_{73}H_{44}S_{12}$: C, 67.1; H, 3.4; Found: C, 66.5; H, 3.7. $^1$H NMR ($CDCl_3$): $\delta$ 7.03 (dd, 4H, $^3J_{HHa} = 3.6$ Hz, $^3J_{HHb} = 5.2$ Hz, $H_\beta$ of terthienyl), 7.10 (m, 8H, terthienyl-*H*), 7.15 (d, 4H, $^3J_{HH} = 4.0$ Hz, terthienyl-*H*), 7.19 (d, 4H, $^3J_{HH} = 3.6$ Hz, terthienyl-*H*), 7.22–7.38 (m, 8H, terthienyl-*H*), 7.39 (d, 8H, $^3J_{HH} = 7.6$ Hz, Ph-*H*), 7.60 (d, 8H, $^3J_{HH} = 7.6$ Hz, Ph-*H*). MS (FAB): 1306.0 ($M^+$). **4**. M.p. > 350 °C (dec.). $^1$H NMR (DMF-$d_7$): $\delta$ 7.2–7.6 (m, 24H, *aromatics*), 7.67 (d, 8H, $^3J_{HH} = 8.8$ Hz, Ph-*H*). IR (KBr, $cm^{-1}$): 3417.0 (s), 1664.5 (s), 1458.1 (s),

1435.9 (m), 632.3 (s). MS (FAB): 1153.5 ($M^+$). **5**. M.p. 244.5 °C. $^{1}$H NMR (acetone-$d_6$): $\delta$ 7.35 (d, 4H, $^{3}J_{\mathrm{HH}} = 3.6$ Hz, terthienyl-*H*), 7.38 (d, 4H, $^{3}J_{\mathrm{HH}} = 3.6$ Hz, terthienyl-*H*), 7.40–7.50 (m, 24H, *aromatics*), 7.70 (d, 8H, $^{3}J_{\mathrm{HH}} = 8.0$ Hz, Ph-*H*), 7.74 (d, 4H, $^{3}J_{\mathrm{HH}} = 3.2$ Hz, terthienyl-*H*). IR (KBr, cm$^{-1}$): 3431.7 (s), 1660.8 (s), 1447.0 (m), 1259.0 (m), 794.5 (s). MS (FAB): 1482.2 ($M^+$). **6**. $M_{\mathrm{w}}$, 5800; $M_{\mathrm{n}}$, 5160. $^{1}$H NMR (acetone-$d_6$): 3.60 (s, PEG-*H*), 7.2–7.6 (m, *aromatics*), 7.70 (d, $^{3}J_{\mathrm{HH}} = 7.8$ Hz, Ph-*H*). IR (KBr, cm$^{-1}$): 3431.7, 1642.4, 1458.1, 1351.2, 1247.9, 1096.8. **7**. $M_{\mathrm{w}}$, 5880; $M_{\mathrm{n}}$, 5260. $^{1}$H NMR (acetone-$d_6$): 3.7 (s, PEG-*H*), 7.3–7.6 (m, *aromatics*), 7.71 (d, $^{3}J_{\mathrm{HH}} = 8.0$ Hz, Ph-*H*), 7.75 (d, $^{3}J_{\mathrm{HH}} = 3.6$ Hz, terthienyl-*H*). IR (KBr, cm$^{-1}$): 3432.8, 1648.4, 1460.0, 1351.0, 1249.9, 1098.8. **8**. M.p. 215.0 °C. Anal. calcd for $C_{33}H_{22}Br_2S_2$: C, 61.7; H, 3.5; Found: C, 60.9; H, 3.5. $^{1}$H NMR ($CDCl_3$): $\delta$ 7.05 (dd, 2H, $^{3}J_{\mathrm{HHa}} = {}^{3}J_{\mathrm{HHb}} = 3.6$ Hz, $H_\beta$ of thienyl), 7.10 (d, 4H, $^{3}J_{\mathrm{HH}} = 8.8$ Hz, Ph-*H*), 7.19 (d, 4H, $^{3}J_{\mathrm{HH}} = 8.8$ Hz, Ph-*H*), 7.28 (d, 2H, $^{3}J_{\mathrm{HH}} = 3.6$ Hz, thienyl-*H*), 7.31 (d, 2H, $^{3}J_{\mathrm{HH}} = 3.6$ Hz, thienyl-*H*), 7.40 (d, 4H, $^{3}J_{\mathrm{HH}} = 8.4$ Hz, Ph-*H*), 7.52 (d, 4H, $^{3}J_{\mathrm{HH}} = 8.4$ Hz, Ph-*H*). MS (EI): 642.5 ($M^+$). **9**. M.p. 180.0 °C. Anal. calcd for $C_{49}H_{31}BrS_6$: C, 66.0; H, 3.5; Found: C, 67.0; H, 4.0. $^{1}$H NMR (acetone-$d_6$): $\delta$ 6.70 (m, 4H, $H_\beta$ of bithienyl), 7.02 (d, 8H, $^{3}J_{\mathrm{HH}} = 8.8$ Hz, Ph-*H*), 7.08–7.17 (m, 11H, bithienyl-*H*), 7.34 (d, 6H, $^{3}J_{\mathrm{HH}} = 8.8$ Hz, Ph-*H*), 7.44 (d, 2H, $^{3}J_{\mathrm{HH}} = 8.4$ Hz, Ph-*H*). MS (EI): 892.0 ($M^+$).

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