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Tetrahedron Letters 45 (2004) 6173–6177
Tetrahedron Letters

A water-soluble non-aggregating fluorescent octa-carboxylic acid derived from tetraphenylmethane: synthesis and optical properties ☆

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Received 7 April 2004; revised 22 May 2004; accepted 3 June 2004
Available online 2 July 2004

Abstract—The synthesis and optical properties of an octa-substituted dendritic fluorescent compound having tetraphenylmethane as the core and bithiophene as the chromophoric arms, and its water-soluble octa-carboxylic acid derivative are reported.

During the last decade, branched and dendritic organic materials based on several tetrahedral core compounds such as tetraphenylmethane,[1] tetraphenylsilane,[2] and adamantane[3] have attracted increasing interest in chemistry and materials science. They have shown many unusual properties including optical, electronic and thermal properties, and have been investigated as light-emitting materials,[1–4] electronically active materials,[5] and molecular caltrops in scanning probe microscopy,[6] etc. Such materials also represent an important class of diagnostic and sensoring agents.[7] It has been well established that good water solubility, minimal self-aggregation in aqueous media, and preferably, multiple chromophores are important properties for a fluorescent agent to be used for biomedical applications.[8] As such, water-soluble dendritic fluorescent materials based on the above-mentioned cores are interesting candidates for these applications. However, such dendritic materials have not been used for clinical applications, mainly due to the difficulties in their syntheses.[9] We have previously reported a novel class of water-soluble fluorescent polymers comprising hydrophobic tetraphenylmethane–oligothiophene chromophoric cores and hydrophilic poly(ethyleneglycol) arms.[10] We found that the self-aggregation of the polymers in aqueous media was minimized efficiently due to their branched structures.[10] In continuation of our studies on water-soluble non-aggregating multi-chromophoric fluorescent probes, we herein report the synthesis and optical properties of an eight-armed tetrahedral fluorescent compound and its water-soluble octa-carboxylic acid derivative. These compounds have dendrimer-like highly hindered structures yet were much more easily synthesized. The octa-carboxylic acid exhibited absorption and PL pH-sensitivity and did not show obvious aggregation in aqueous media.

The synthesis of the eight-armed tetraphenylmethane–bithiophene adduct **2** and its octa-carboxylic acid derivative **3** is shown in Scheme 1.† Nitration of tetraphenylmethane with fuming nitric acid and subsequent Pd/C-catalyzed hydrazine reduction gave C(p-$C_6H_4NH_2$)$_4$.[11] Bromination of C(p-$C_6H_4NH_2$)$_4$ with neat Br_2 gave the octa-brominated **1** in 75% yield.[5a] The ^{1}H NMR spectrum of **1** in DMF-d_7 exhibited a broad peak at δ 5.60 (NH_2) and a singlet at δ 7.85 (Ar-H). Compound **1** underwent Suzuki coupling with 2,2′-bithiophene-5-boronic acid to give **2** in 20% yield. Although **2** has a highly hindered structure, unlike other similar tetrahedral molecular glass materials,[2] it only exhibited a T_m at 210 °C and a T_c at 185 °C. The ^{1}H NMR spectrum of **2** in $CDCl_3$ showed one doublet of doublets (dd) signal at δ 7.02 (dd, 8H, $^3J_{H-H} = {}^3J_{H-H'} = 3.6$ Hz), which is typical for the β-H of bithienyl moieties. In addition, three well-separated doublets at δ 7.06, 7.18 and 7.22 (bithienyl-H) and one singlet at δ

Keywords: Tetrahedral material; Tetraphenylmethane; Oligothiophenes; Water-soluble fluorescent probe; Non-aggregating luminescent material; pH-indicator.

☆ Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.tetlet.2004.06.019

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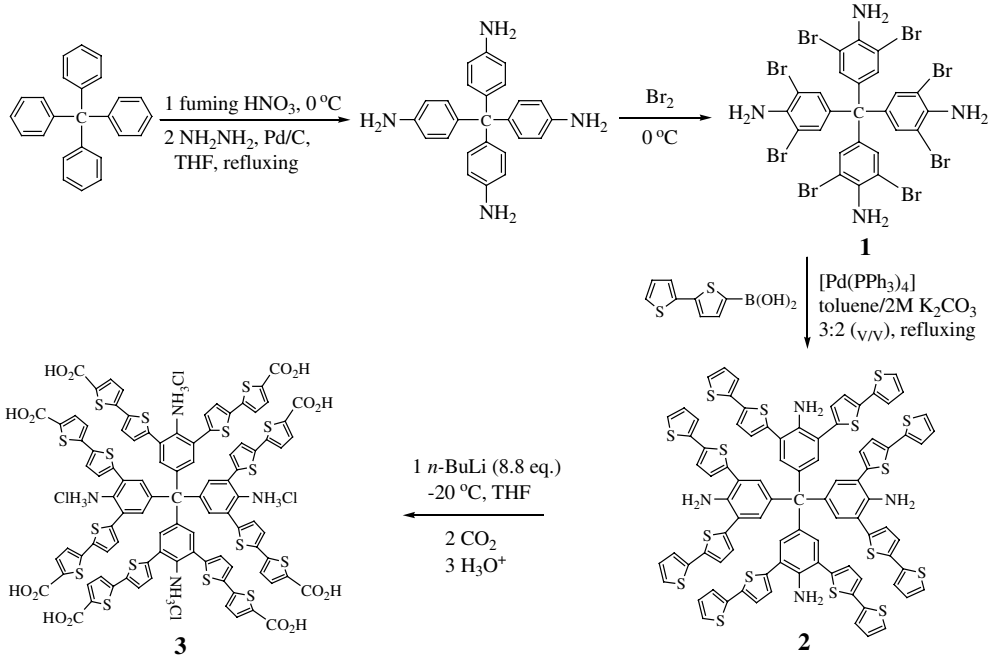
doi:10.1016/j.tetlet.2004.06.019



Scheme 1. Synthesis of the eight-armed fluorescent compounds **2** and **3**.

7.08 (Ar-*H*) were observed (Fig. 1). The ^{13}C NMR spectrum of **2** showed 12 aromatic-*C* atoms. The MALDI-TOF MS of **2** showed a molecular ion peak at 1695.1 (M^+). These data prove unambiguously the complete substitution of the bromo groups in **1** with bithienyl moieties. Finally, deprotonation and subsequent reaction of **2** with CO_2 gave **3**, quantitatively, as a yellow solid. Compound **3** was soluble in both organic solvents (THF and DMF) and dilute aqueous alkaline solutions. The full substitution of the acidic α-*H* atoms in the bithienyl moieties of **2** by eight carboxyl groups was proved by ^1H NMR and MALDI-TOF MS spectroscopic studies. For example, the ^1H NMR spectrum of **3** in DMF-d_7 exhibited three well resolved doublets at δ 7.45, 7.57 and 7.77, and one singlet at δ 7.50, due to protons from the bithienyl moieties and the aryl groups, respectively (Fig. 2). The characteristic dd signal of the β protons of the bithienyl groups was not observed, indicating complete carboxylation of the α-*C* positions of the bithienyl groups. The MS spectrum of **3** showed a molecular ion peak at 2052.4 (M^++6). The IR spectra of **1**–**3** exhibited strong absorptions at 3431–3439 (major) and 3350–3358 cm^{-1} (shoulders), due to the N–H stretching of primary amino groups. In addition, the IR spectrum of **3** also exhibited strong absorptions at 1657 and 1104 cm^{-1}, due to C=O and O–H stretches of the carboxylic acid groups.

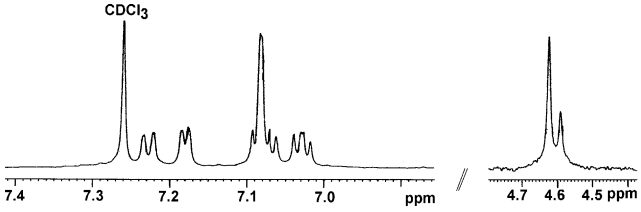


Figure 1. The ^1H NMR spectrum of **2** in $CDCl_3$.

Figure 3 shows the UV and PL spectra of **2** in THF. The UV spectrum of **2** exhibits two bands at 248 nm (ε 6.8×10^4 M^{-1} cm^{-1}) and 396 nm (ε 9.0×10^4 M^{-1} cm^{-1}) with red tailing to 450 nm. The long wavelength maximum of **2** is substantially red shifted relative to bithiophene (302 nm), indicating the formation of an extended π-delocalized system among the two bithienyl groups and the aryl ring. The excitation spectrum of **2**, however, is not identical to its UV spectrum; it exhibits two peaks at 343 and 440 nm. The emission spectra of **2**

† Physical data for compounds **1**–**3**. Tetra(4-amino-3,5-dibromo)phenylmethane (**1**). Mp 310 °C. Anal. Calcd for $C_{25}H_{16}Br_8N_4$: C, 29.7; H, 1.6; N, 5.5. Found: C, 30.1; H, 1.4; N, 5.2. ^1H NMR (DMF-d_7): δ 5.60 (br, 8H, suppressed by D_2O, NH_2), 7.85 (s, 8H, Ph-*H*). IR (KBr, cm^{-1}): 3439, 3358, 1609, 1469, 738. MS (EI), *m/z*: 1011.7 (M^+, 22%). Tetra(4-amino-3,5-di(2,2′-bithiophene-5-yl))phenylmethane (**2**). Mp 210 °C. Anal. Calcd for $C_{89}H_{56}N_4S_{16}$: C, 63.1; H, 3.3; N, 3.3. Found: C, 62.8; H, 3.2; N, 3.0. ^1H NMR ($CDCl_3$): δ 4.61 (br, 8H, suppressed by D_2O, NH_2), 7.02 (dd, 8H, $^3J_{H-H} = {}^3J_{H-H'} = 3.6$ Hz, H_β of bithienyl), 7.06 (d, 8H, $^3J_{H-H} = 3.2$ Hz, bithienyl-*H*), 7.08 (s, 8H, Ph-*H*), 7.08–7.09 (m, 8H, bithienyl-*H*), 7.18 (d, 8H, $^3J_{H-H} = 3.6$ Hz, bithienyl-*H*), 7.22 (d, 8H, $^3J_{H-H} = 5.2$ Hz, bithienyl-*H*). ^{13}C NMR ($CDCl_3$): δ 64.4, 123.7, 124.2, 124.6, 124.8, 125.0, 128.3, 129.0, 133.8, 136.3, 136.7, 137.5, 141.4. IR (KBr, cm^{-1}): 3439, 3351, 1609, 1465, 791, 699. MS (MALDI-TOF, matrix: 4-hydroxyazobenzene-2-carboxylic acid), *m/z*: 1695.1 (M^+, 10%). Tetra[4-amino-3,5-di(5′-carboxyl-2,2′-bithiophene-5-yl)]phenylmethane (**3**). Mp >300 °C (dec). Anal. Calcd for $C_{97}H_{56}N_4O_{16}S_{16}$·4HCl: C, 52.8; H, 2.7; N, 2.6. Found: C, 52.4; H, 2.8; N, 2.4. ^1H NMR (DMF-d_7): δ 7.45 (d, $^3J_{H-H} = 3.6$ Hz, 8H, bithienyl-*H*), 7.50 (s, 8H, Ph-*H*), 7.48–7.52 (m, 8H, bithienyl-*H*), 7.57 (d, $^3J_{H-H} = 3.6$ Hz, 8H, bithienyl-*H*), 7.77 (d, 8H, $^3J_{H-H} = 3.6$ Hz, bithienyl-*H*). IR (KBr, cm^{-1}): 3432, 1657, 1506, 1447, 1300, 1104, 1019, 791. MS (MALDI-TOF, matrix: dithranol+silver trifluoroacetate), 2052.4 (M^++6, 25%); GPC, M_w 2220, M_n 2210.

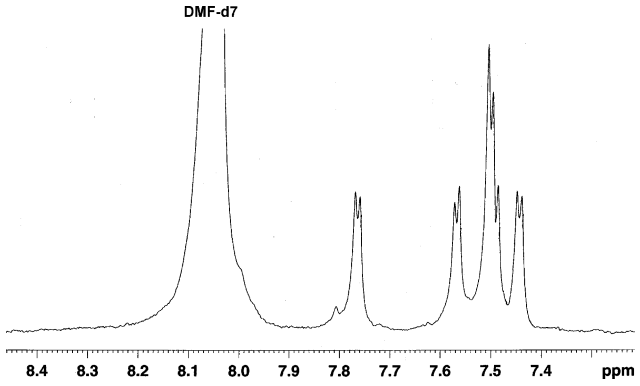


Figure 2. The ^{1}H NMR spectrum of **3** in DMF-d_7.

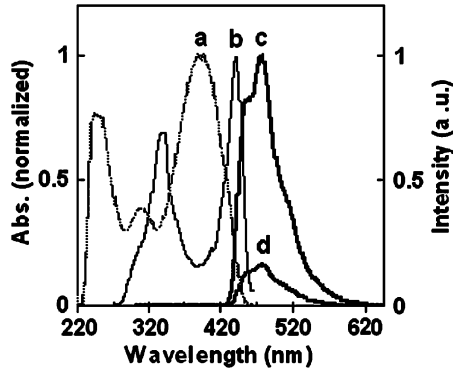


Figure 3. The UV and PL spectra of **2** in THF (concentration at ca. 1×10^{-7} M): (a) the UV spectrum; (b) the excitation spectrum ($\lambda_{em}=478$ nm); (c) and (d) the emission spectra with λ_{ex} at 440 and 396 nm, respectively. The intensity of spectrum d is normalized relative to that of c.

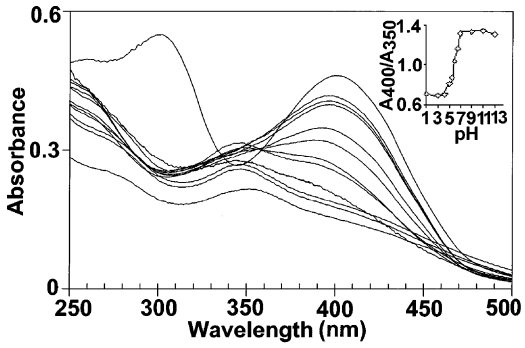


Figure 4. The UV spectral changes of **3** (1×10^{-5} M) in different aqueous pH buffer and THF solutions. From bottom to top: pH = 1.0, 3.0, 4.0, 4.5, 5.0, 5.5, 6.0, 7.0, 9.0, 11.0, 13.0 and THF. Insert: The absorbance ratio of λ_{400} and λ_{350} as a function of pH.

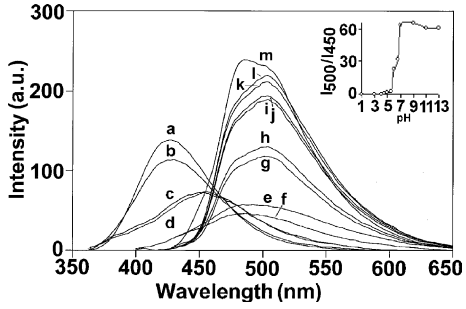


Figure 5. The PL spectral changes of **3** (1×10^{-5} M) in different aqueous pH buffer and THF solutions. From a to m: pH = 1.0, 3.0, 4.0, 4.5, 5.0, 5.5, 6.0, 6.5, 7.0, 13.0, 11.0, 9.0 and THF. Insert: The intensity ratio of 500 and 450 nm as a function of solution pH. The potassium salt of **3** was used for UV and PL determinations in THF.

obtained by excitation at 440 and 396 nm, respectively, show a similar spectral pattern with a similar emission maximum at 478 nm and a shoulder peak at 460 nm. However, the former emission is much stronger than the latter (quantum yields: 11.2% vs 0.4%). It should be noted that the PL spectra were recorded with a dilute sample (abs. <0.05) to avoid absorption saturation. The significant red shift of the excitation maximum relative to absorption maximum indicates that the aromatic rings of **2** adopt a more nearly planar conformation, thus a higher degree of conjugation in the excited state. Such differences are due to the highly hindered and multi-chromophoric structure of **2**, in which conformation and complex intramolecular electron delocalizations and π–π interactions influence its PL properties.[12]

The absorption and emission spectra of **3** in different pH buffer and THF solutions are shown in Figures 4 and 5, respectively. A summary of the optical data of **3** is given in Table 1. In pH 1.0–5.5 solutions, the UV spectra exhibit long wavelength maxima around 348 nm, and weaker shoulder bands around 400 nm. With an increase in pH, the band around 400 nm becomes stronger and finally it becomes the major band at pH 6.0. The absorbance ratio of 400 and 350 nm becomes constant at pH 7.0–13.0 solutions (Fig. 4, insert). The evolution of emission spectra of **3** with the increase of pH follows a similar tendency to that of the UV spectra. In pH 1.0–3.0 acidic solutions, **3** emits indigo light with the

Table 1. The optical data of **3** in different pH buffer and THF solutions

Solvent	pH	λ_{max} (nm)		Φ_{PL} (%)
		Absorption ($\varepsilon\times10^4$, $M^{-1}cm^{-1}$)	Emission (fwhm/nm)	
Aqueous pH buffer solutions	1.0	348 (2.1)	428 (70)[a]	5.7
	3.0	347 (2.6)	430 (75)[a]	4.2
	4.0	347 (2.7)	444 (94)[a]	3.5
	4.5	347 (2.8)	450 (95)[a]	3.1
	5.0	347 (3.2)	480 (102)[a]	2.2
	5.5	350 (3.1)	486 (100)[a]	2.9
	6.0	388 (3.2)	504 (88)[b]	5.0
	6.5	393 (3.5)	503 (87)[b]	4.1
	7.0	397 (4.0)	504 (85)[b]	5.4
	9.0	397 (4.2)	503 (85)[b]	6.1
	11.0	398 (4.2)	503 (85)[b]	5.9
	13.0	398 (4.1)	503 (86)[b]	5.3
THF	—	400 (4.0)	485 (78)[b]	5.4

[a] Excited at 350 nm.
[b] Excited at 406.5 nm.

emission maxima centered around 430 nm. With increased pH, the emission maximum is red shifted gradually and reaches 504 nm with a shoulder band around 486 nm in the pH 6.0 solution. The PL intensity increases significantly with an increase of pH from 5.5 to 9, whereas it decreases slightly when the pH is increased further from 11 to 13. The spectral patterns and emission maxima are the same in pH 6.0–13.0 buffer solutions. An analysis of I_{500}/I_{450} versus pH shows a similar trend to that of A_{400}/A_{350} (Fig. 5, insert). In THF solution, **3** exhibits an emission maximum at 486 nm and a shoulder band around 503 nm. It is important to note that, however, the quantum yield and fwhm (full width at half-maximum) values of **3** in THF and aqueous buffer solutions are similar. This is in contrast to similar poly(ethyleneglycol) linked four-armed water-soluble tetrahedral fluorescent derivatives of tetraphenylmethane, which showed significant red shift and broadening in the emission spectrum, and a decrease in quantum efficiency due to self-aggregation of the compounds in aqueous media.[10] The similarities of the emission spectra and quantum yields of **3** in aqueous solution and THF suggest that, as expected, self-aggregation of **3** in aqueous solution is not obvious due to its highly hindered structure.

The UV and PL pH-sensitivity of **3** is apparently due to its carboxyl and amino groups. Furthermore, it is likely that the two distinct absorption and emission bands are due to two species (Scheme 2), since the evolution of the emission and absorption spectra versus pH exhibit similar trends.[13] To further confirm this, we examined the PL spectra of **3** in pH solutions at excitation wavelengths of 350 and 406.5 nm, respectively. The excitation of the pH 4.5 solution of **3** at these wavelengths gave two different emission spectra indicating that two different species were present at this pH. Similar experiments showed that the pH 1.0–3.0 solutions were not emissive in nature when excited at 406.5 nm, whereas excitation of a pH 7.0 solution at the two wavelengths gave almost identical emission spectra, indicating that the fully protonated or fully deprotonated form is present predominately in these pH solutions, respectively (Fig. 6). In pH 4.0–6.0 buffer solutions, the gradual change in the UV and PL spectra of **3** indicate that complex ionization processes and multiple species are present. The CO_2H and NH_3^+ are electron-withdrawing groups whereas CO_2^- and NH_2 are electron-donating groups, which account for the significant difference in the absorption and emission maxima of their respective species.

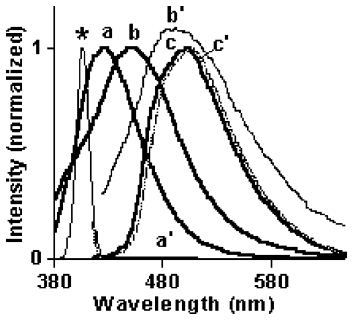


Figure 6. Emission spectra of **3** in pH 1.0 (a and a′), pH 4.5 (b and b′), and pH 7.0 (c and c′) with excitation at 350 nm (a, b, and c) and 406.5 nm (a′, b′, and c′), respectively. (*) From the excitation light.

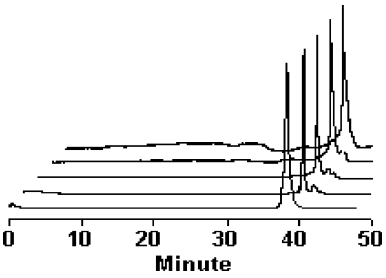
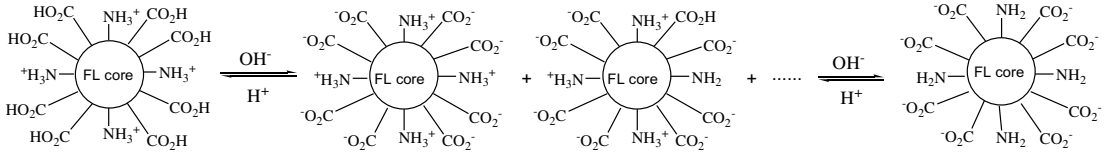


Figure 7. The aqueous GPC traces of **3** (1×10^{-5} M in buffer solutions). From bottom to top: pH 1.0, 3.0, 5.0, 7.0, and 9.0, respectively. The UV detector was set at 400 nm.

Finally, we investigated the self-aggregation behavior of **3** in aqueous media by aqueous gel permeation chromatography (GPC), which has been developed as a useful method to determine molecular weights and aggregation numbers of aggregates of amphiphilic polymers in aqueous media.[14] In view of the strong absorption of **3** at long wavelengths, we chose a UV detector setting of 400 nm to monitor the GPC elute. Figure 7 shows aqueous GPC traces of **3** in various pH solutions. In all the pH solutions, only one species, which is the parent compound, was detected (retention time: 38.0 ± 0.1 min, $M_w \sim 1850$ with polydispersity of 1.01). Therefore **3** was not prone to self-aggregation in aqueous media probably due to its highly hindered structure and static repulsion from COO^- or NH_3^+ groups present in the outer sphere.

In conclusion, we have developed a facile method for the synthesis of an octa-carboxylic acid from an eight-armed tetraphenylmethane–bithiophene adduct. The



Scheme 2. The acid–base equilibrium of **3** in aqueous media.

compound is water-soluble and showed no obvious self-aggregation in aqueous media. Compound **3** emits indigo light in strongly acidic solution and emits blue-green light in neutral and alkaline solutions, whereas its UV and PL spectra are highly sensitive in pH 4.0–6.0 solutions. To our best knowledge, compounds **2** and **3** are the first examples of eight-armed tetrahedral luminescent compounds derived from tetraphenylmethane.[1–4] It has been well established that an 'ideal' fluorescent probe should bear a large but distinct number of chromophores as well as a single biologically active group.[8,15] By using the eight reactive α-carbon sites of bithienyl moieties in **2**, it would be easy to introduce a selective binding ligand to one arm and several hydrophilic segments to other arms in a stepwise way. Studies on the synthesis of such fluorescent probes and detailed studies on the photophysical behavior of **3** are in progress.

Acknowledgements

We are grateful to the Agency for Science, Technology and Research (A*Star), Singapore for financial support.

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