Synthesis and spectral properties of triazine-based dendritic dithienylethenes

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Two novel triazine-based dendrimers comprising a dithienylethene core and eight and 16 ethyl groups around the periphery were synthesised in high yields in a convergent way, without using tedious protection and chromatographic separation steps. Their optical properties such as photochromism, fluorescence emission and film-forming behaviour were investigated. The new symmetrical dendritic dithienylethenes showed typical photochromic behaviour in solution and good film-forming performance in a poly(methyl methacrylate) (PMMA) matrix. Moreover, the dendrimers have demonstrated remarkable fluorescence enhancement and good solubility in common organic solvents, compared with the corresponding small molecule diarylethene. Thus, the new dendrimers as optoelectronic materials, have potential applications in optical storage, photo-switches, and so on.

Keywords: dendritic diarylethene, dendrimer, photochromism, fluorescence

Among the various types of photochromic compounds,[1] diarylethenes, especially dithienylethenes, are one of the most promising candidates as optical memory and photo-switch materials due to their good thermal stability and impressive feature of fatigue-resistance.[2–7] Diarylethenes can undergo cyclisation/cycloreversion (photochromic) reactions via interconversion of both the open-ring and closed-ring isomers. Great efforts have been made to synthesise new diarylethene derivatives by altering the heteroaryl moieties or the substituents on the heteroaryl rings.[8–10] So far, several research groups have reported substituent effects on the photochromic performance of diarylethenes.[11–15] Compared with small molecules, polymers are more advantageous as materials because of the ease with which they form films, flakes, and/or beads. Therefore, polymerisation techniques have been widely exploited in the modification of diarylethenes.[16] Applications have been developed for optoelectronic devices such as optical storage and photoswitches.[7]

In comparison with conventional polymers, dendrimers are special synthetic macromolecules with the characteristics of regular branches, high symmetry, and rigidity, which always exhibit special properties such as good solubility and flexibility, low viscosity, and so on.[17] In recent years, the potential applications of dendrimers have been widely studied in many fields such as photochemistry and/or photophysics,[18] pharmacology,[19] catalysis,[20] materials,[21] and nanoscience.[22]

Based on these advantages, we deduced that dendron-modified diarylethenes would have good physical, chemical and/or optical properties. For example, rigid and globular dendron-modified fluorescent diarylethenes are expected to reduce or eliminate the aggregation-induced fluorescence quenching, and enhance fluorescence emission.[23–26] Also, the coupling of dendrons with a diarylethene core is thought to improve its solubility as there are an abundance of solublising peripheral groups on the dendrons.[27] Photochromic dendrimers such as dendritic spiropyrans have been studied in recent years with encouraging results.[28] To the best of our knowledge, there have been no reports on dendritic diarylethenes except Shimomura's publications a decade ago.[29,30] However, Shimomura's work did not overcome the general difficulties of preparing dendrimers. Tedious preparative thin layer chromatographic separation processes were needed, and low yields of higher generation dendrimers were obtained (*e.g.* the third generation dendrimer in 28% yield.), a problem usually encountered during dendrimer preparations. Moreover, no photochromic behaviour nor fluorescent properties of the diarylethene-containing dendrimers were described in Shimomura's work.

Herein, we have rationally designed a new type of triazine-based dendritic dithienylethenes. Our new dendrimers can be efficiently prepared in high yields under mild conditions by using a convergent method,[31] and no protection/deprotection protocols nor chromatographic separation steps were involved in the whole synthesis. Moreover, the new symmetrical dendritic dithienylethenes are easily soluble in most common organic solvents, and show a remarkable fluorescence enhancement, unlike the single dithienylethene core **5** that has low solubility and weak fluorescence.

Results and discussion

The synthetic route to the dendrimers is illustrated in Scheme 1. First, the triazine-based dendrons **2** and **4** were synthesised in a convergent way according to the literature.[32] A portion of 2.2 equiv of diethylamine was treated with cyanuric chloride in CH_2Cl_2 containing an excess of diisopropylethylamine (DIPEA) at 0 °C to give compound **1** in 95% yield, which was allowed to further react with 5 equiv of piperazine in THF at reflux to afford compound **2** in 91% yield. Compound **3** was also obtained from triazine **2** in 92% yield by reaction with cyanuric chloride. Similarly, compound **4** was prepared in 90% yield. Compounds **7** and **8** were synthesised from the dibromo-derivative of the diarylethene chromophore **6**, which was coupled to the corresponding of triazine-based dendrons (2.0 equiv.) in the presence of K_2CO_3 (2.5 equiv.).

The ^{1}H NMR and ^{13}C NMR spectra of the dendrimer **8** are illustrated in Fig. 1. Typical protons on **8** have been labelled with *a–i* (Fig. 1a). The triplet signal *a* at the chemical shift of 1.15 ppm and the quartet peak *b* at 3.64 ppm corresponds to the CH_3 and CH_2 units, respectively of 16 ethyl groups. Protons labelled with *c*, *d* and *e* on piperisine groups are located within the multiplet signals at 3.7–3.8 ppm. However, the *f* protons on piperisine groups shifted to about 2.46 ppm, which may be ascribed to the influence of the dithienylethene core. The singlet peaks of *g* and *i* at 3.65 and 1.88 ppm are the CH_2 and CH_3 groups bonded to the thienyl groups, respectively. Protons labelled with *h* are located at low field and correspond to the aryl protons on the thienyl groups.

Typical carbons on **8** have been labelled with *a–p* (Fig. 1b). Carbons *a* and *b* at 13.5 and 41.1 ppm are the CH_3 and CH_2 units respectively from the 16 ethyl groups. Carbons labelled with *c*, *d* and *g*, *h* at about 165 ppm correspond to the carbons of six triazine rings. At the chemical shift of around 43 ppm are the *e*, *f* and *i* carbons from the piperazine rings; however,

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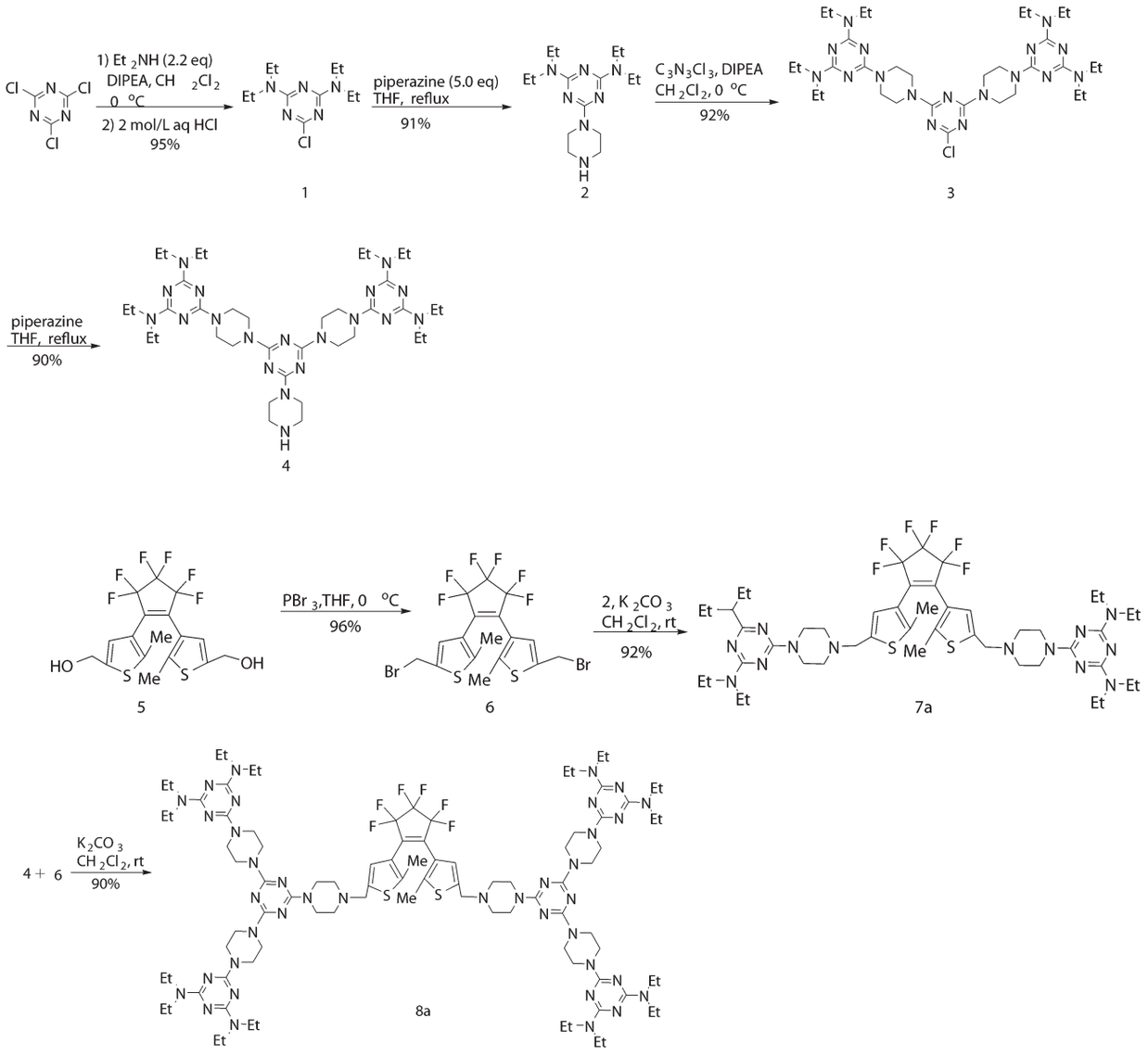
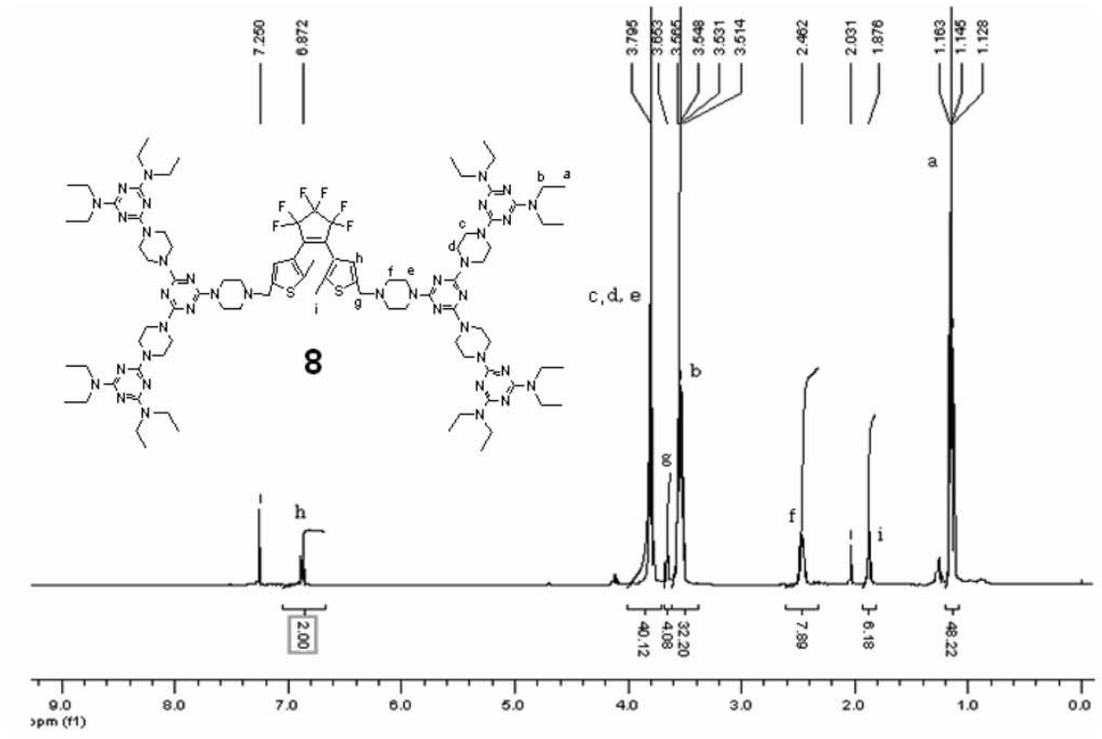


Scheme 1 Synthesis of dendritic dithienylethenes **7a** and **8a**.

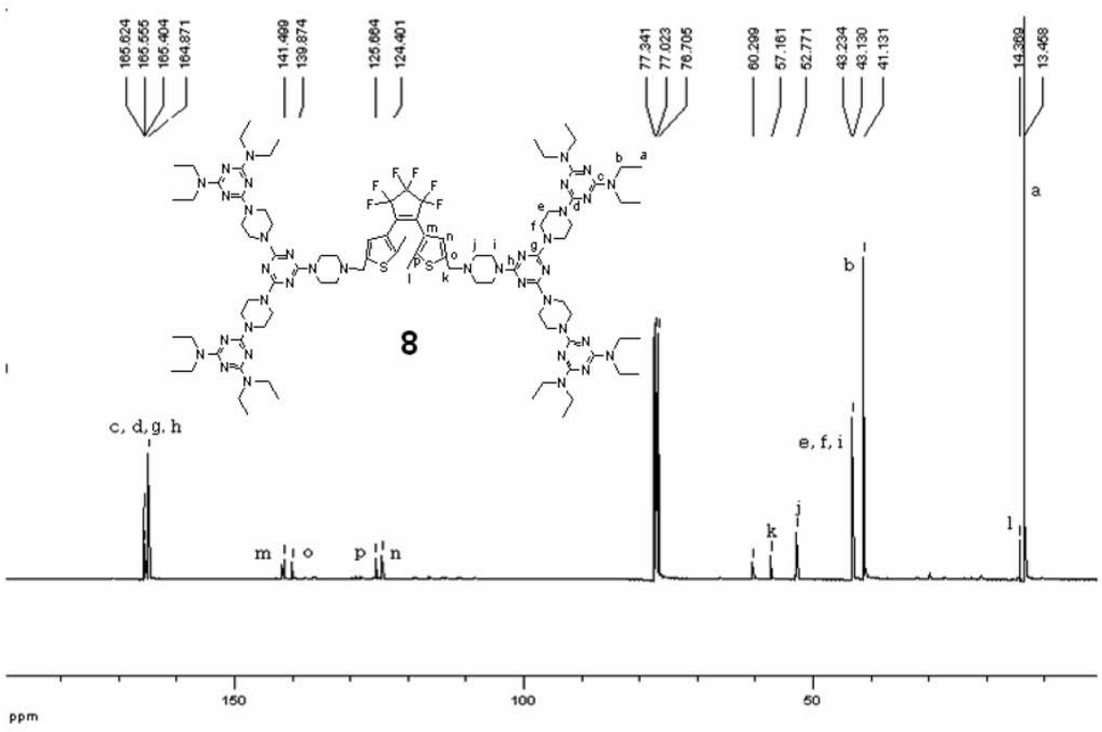
the chemical shift of the *j* carbons from the piperazines was deshielded and resonated at 62.8 ppm, which may be attributed to the effect of the dithienylethene core. The signals *k* and *l* at 57.2 and 14.3 ppm are due to the CH_2 and CH_3 groups bonded to the thienyl moieties, respectively. Carbons of the thienyl rings labelled with *m*, *n*, *o* and *p* are located in the range 124–141 ppm. The carbons of the hexafluorocyclopentene ring have no peaks in the ^{13}C NMR spectrum. Characterisation and ^{1}H NMR and ^{13}C NMR spectra of compounds **1**–**4** and **6**–**8** are available as Electronic Supplementary Information.

The photochromic reactions of dendritic dithienylethenes **7** and **8** were illustrated in Scheme 2. The colourless open-ring isomers **7a** and **8a** will be converted to their purple closed-ring isomers **7b** and **8b** upon irradiation with an appropriate UV light, and a visible light irradiation will make the closed-ring isomers return to their previous open-ring states. Details of the absorption spectra of compounds **7** and **8** induced by photo-irradiation at room temperature in dichloromethane ($c = 1.0 \times 10^{-4}$ mol L^{-1}) are shown in Fig. 2. The absorption maximum of **7a** was observed at 236 nm, while that of **8a** appeared at 249 nm. Upon irradiation with 297 nm light, the colourless solution of **7a** turned purple due to the appearance of a new visible absorption band centred at 526 nm. This colour change was attributed to the formation of closed-ring isomer **7b** from its open-ring counterpart. The purple solution reverted to colourless state upon irradiation with visible light ($\lambda >$ 450 nm), which indicated that **7b** returned to the initial structure **7a**. Similarly, upon irradiation with 297 nm light, the colourless solution of **8a** turned purple and the absorption maximum was observed at 526 nm, as the closed-ring isomer **8b** was generated. The purple colour disappeared upon irradiation with visible light ($\lambda > 450$ nm). These facts indicate that the dendron-modified compounds **7a** and **8a** retain the good photochromic properties associated with diarylethenes.

The effect of concentration upon the fluorescence emission of **7a** and **8a** was examined in CH_2Cl_2 solution at room temperature (Fig. 3). When the concentration of dendritic diarylethene **7a** ranged from 1×10^{-6} to 1×10^{-4} mol L^{-1}, the maximum emission revealed a red shift, and the relative intensity rose dramatically, especially from 5×10^{-5} to 1×10^{-4} mol L^{-1}. However, change of the concentration from 1×10^{-4} to 1×10^{-3} mol L^{-1} caused the relative fluorescence intensity to

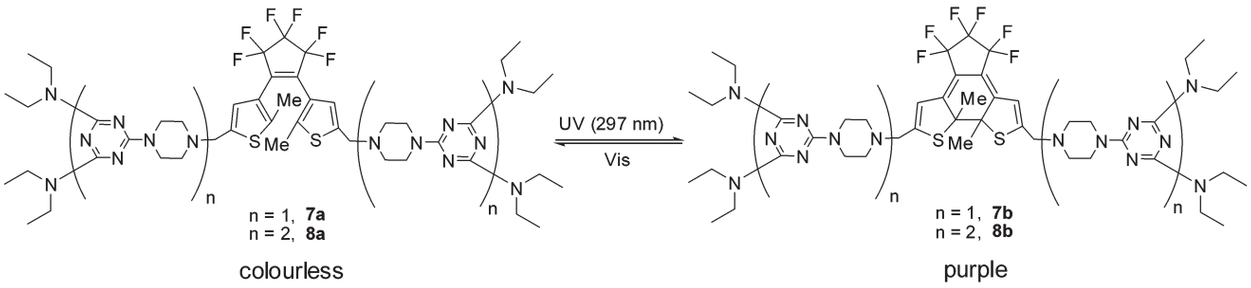


(**a**)



(**b**)

Fig. 1 (**a**) The ^{1}H NMR spectrum of the dendrimer **8**; (**b**) The ^{13}C NMR spectrum of the dendrimer **8**.



Scheme 2 Photochromism of dendritic dithienylethenes **7** and **8**.

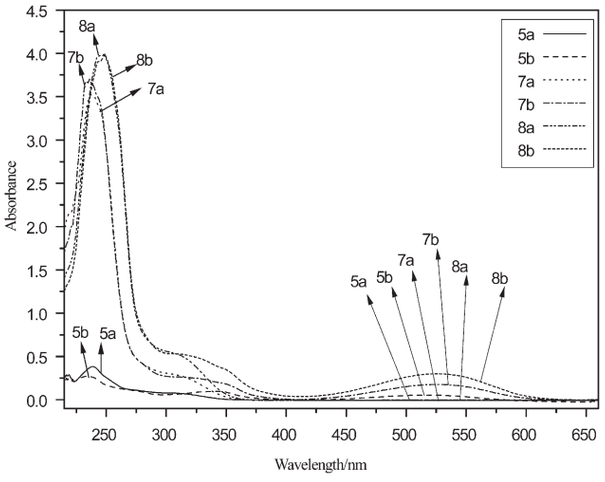


Fig. 2 Absorption spectral changes of dendrimers **7** and **8** in dichloromethane at room temperature (1.0×10^{-4} mol L^{-1}; **7a** and **8a**: the open-ring isomers; **7b** and **8b**: the closed-ring isomers).

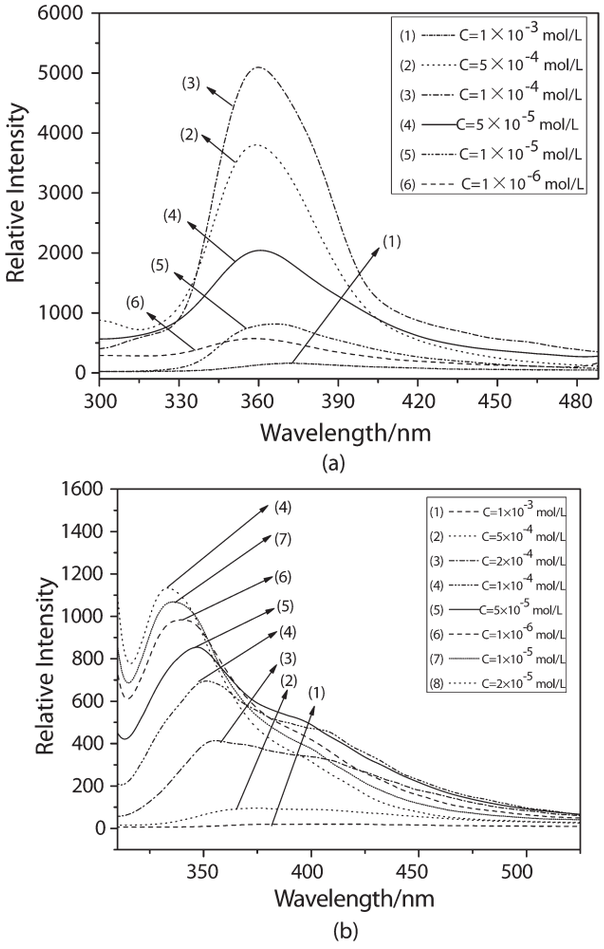


Fig. 3 (a) Concentration effect on the fluorescent emission of **7a** in CH_2Cl_2 at room temperature; (b) Concentration effect on the fluorescent emission of **8a** in CH_2Cl_2 at room temperature.

decrease abruptly. The intensity at the concentration of 1×10^{-3} mol L^{-1} was even lower than that of 1×10^{-6} mol L^{-1} (Fig. 3a). Compound **8a** showed similar dependence on the concentration, but the relative fluorescence intensity was lower than that of **7a** (Fig. 3b). At higher concentration, for example, 10^{-3} mol L^{-1}, quite low intensity may result from molecular aggregation and fluorescence quenching.[33] Figure 4 illustrates the fluorescence comparison of **7a**, **8a** and small molecule **5** in dichloromethane at room temperature. Without dendritic modification, the intermediate dithienylethene **5** has very weak fluorescence upon excitation at 290 nm and gives maximal fluorescent emission at about 420 nm; when dendritic moieties were coupled with **5,** both **7a** and **8a** showed good fluorescence under the same conditions. Excited at 290 nm, the fluorescence emissions of **7a** and **8a** were observed at 362 nm and 349 nm. Therefore, compared with the simple dithienylethene **5**, introduction of a dendritic moiety into the diarylethene core has a positive effect on the emission of fluorescence. Further comparison shows that compound **5** has a very different fluorescence maximum to **7a** and **8a**, *i.e.*, **5** has a different Stoke's shift to **7a** and **8a**, which may be ascribed to the influence of triazinyl dendrons on the diarylethene core. Unfortunately, a higher generation dendrimer would decrease the fluorescence intensity of dendritic diarylethenes. This undesired phenomenon might be explained by the higher generation dendrimer making the conjugated structure of the dendrons twist, thus causing lower energy transfer efficiency or increased photoelectron transfer (PET) fluorescence quenching resulting from the larger number of amino groups in **8a**.[34]

Good solubility of materials is often required in the case of easy processing and manipulation. Dendrimers can be used to enhance solubility due to their regular and tunable structures.[35,36] The new dendrimer demonstrated good solubility in common solvents such as CH_2Cl_2, $CHCl_3$, THF, EtOAc, CH_3CN and DMF, in contrast to the small molecular dithienylethene **5**. Moreover, the dendritic dithienylethene **8** had good compatibility with PMMA polymer, resulting in its good film-forming performance. In fact, a uniform thin film of compound **8** in a PMMA matrix has been prepared easily by a spin-coating technique.

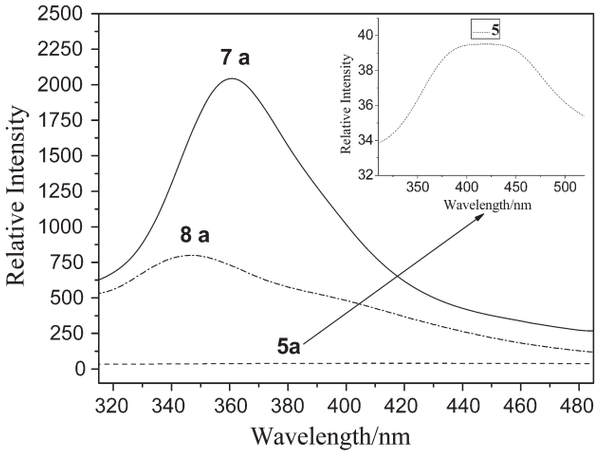


Fig. 4 Fluorescence spectra of dendrimers **7a** and **8a** as well as **5** in CH_2Cl_2 (5.0×10^{-5} mol L^{-1}) at room temperature, excited at 290 nm.

Conclusion

In summary, we have rationally designed two new triazine-based dendrimers containing a diarylethene core, with eight and 16 ethyl groups in the periphery, respectively. The products were synthesised in high yields without employing protection/deprotection or chromatographic separation steps. These dendrimers have good solubility in common organic solvents. For optical properties, the two dendritic diarylethenes have demonstrated good photochromic behaviour and strong fluorescence emission compared with the corresponding small diarylethene molecule **5**. The results of this study are helpful to design efficient photoactive diarylethene derivatives.

Experimental

Dichloromethane was refluxed with CaH_2, and distilled. Tetrahydrofuran (THF) was refluxed with sodium and benzophenone, and distilled. All other chemicals, reagents, and solvents were used as received from commercial sources without further purification. ^{1}H NMR and ^{13}C NMR spectra were recorded at 400 MHz and 100 MHz respectively on a Bruker 400 spectrometer for solutions in $CDCl_3$, with tetramethylsilane (TMS) as the internal standard. The FTIR spectra were recorded via the KBr pellet method by using a Bruker V70 FTIR spectrophotometer. The mass spectra were recorded on a ESI-FTICR mass spectrometer (Varian 7.0T). UV–Vis absorption spectra were measured using a Perkin Elmer Lambda-900 spectrophotometer. The photoluminescence were recorded on a Hitachi F-450 fluorescence spectrophotometer.

2,6-Bis(diethylamino)-4-chloro-1,2,4-triazine (**1**): A solution of diethylamine (1.39 g, 19.04 mmol) and diisopropylethylamine (DIPEA) (3.14 mL, 19.04 mmol) in dichloromethane were cooled on an ice bath, followed by the addition of cyanuric chloride (1.60 g, 8.66 mmol). The solution was stirred at 0 °C for 1 h and then at room temperature for 24 h. The mixture was washed with aqueous HCl and water, respectively, and then dried over anhydrous Na_2SO_4. The solvent was removed *in vacuo* to give product **1** (2.12 g, 95%) as a pale yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (t, 12H, J = 7.0 Hz), 3.25 (m, 8H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.7, 13.2, 41.3, 41.6, 164.0, 168.9. IR (KBr) υ 2981, 2942, 1559, 1548, 1465 cm^{-1}.

2,6-Bis(diethylamino)-4-piperazino-1,2,4-triazine (**2**): Compound **1** (2.12 g, 8.22 mmol) and piperazine (3.54 g, 41.09 mmol) in THF were refluxed overnight and then evaporated. The residue was dissolved in dichloromethane, washed with aqueous KOH and water, respectively, and then dried. The solvent was removed to afford product **2** (2.30 g, 91%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14 (t, 12H, J = 7.0 Hz), 1.92 (s, 1H), 2.86 (t, 4H, J = 5.0 Hz), 3.63 (q, 8H, J = 7.0 Hz), 3.74 (t, 4H, J = 5.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 41.0, 44.3, 46.1, 164.8, 165.5. IR (KBr) υ 3316, 2969, 2928, 1532, 1489 cm^{-1}.

2,6-Bis{[2,6-bis(diethylamino)-1,3,5-triazin-4-yl]piperazine-1,4-diyl}-4-chloro-1,3,5-triazine (**3**): A solution of **2** (2.30 g, 7.48 mmol) and DIPEA (1.24 mL, 7.48 mmol) in CH_2Cl_2 (50 mL) was cooled in an salt/ice-bath before cyanuric chloride (0.63 g, 3.40 mmol) was added. The reaction solution was stirred in ice-bath for 1 h and at room temperature for 24 h. The reaction mixture was washed with 5 mol L^{-1} aq HCl (2 × 100 mL), then water (2 × 100 mL) and dried over sodium sulfate. The solvent was removed at reduced pressure to give crude product **3** as a white solid, which was then recrystallised in petroleum ether/CH_2Cl_2 to provide white crystals (2.32 g, 92%). M.p. 220–221 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.14 (t, 24 H, J = 7.0 Hz), 3.54 (q, 16H, J = 7.0 Hz), 3.82 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.5, 41.2, 42.8, 43.1, 43.5, 164.5, 164.7, 165.5, 169.6. IR (KBr) υ 2979, 2928, 1531, 1492 cm^{-1}.

2,6-Bis{[2,6-bis(diethylamino)-1,3,5-triazin-4-yl]piperazine-1,4-diyl}-4-piperazino-1,3,5-triazine (**4**): Similar to the synthesis of compound **2**, compound **4** was prepared from intermediate **3** (2.32 g, 3.19 mmol) and piperazine (830 mg, 9.59 mmol). After workup, compound **4** was afforded as a white solid (2.23 g, 90%). M.p. 161–162 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (t, 24H, J = 6.8 Hz), 1.73 (s, 1H), 2.87 (t, 4H, J = 4.8 Hz), 3.64 (q, 16H, J = 7.2 Hz), 3.74–3.75 (m, 4H), 3.75–3.80 (m, 16H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 12.5, 40.2, 42.2, 42.3, 43.6, 45.2, 163.9, 164.57, 164.61, 164.7. IR (KBr) υ 3333, 3010, 2818, 2778, 1696, 1656, 1589, 1442, 1348, 780 cm^{-1}.

1,2-Bis(5-bromomethyl-2-methyl-3-thienyl)-3,3,4,4,5,5-hexafluorocyclopentene (**6**): To a stirred solution of compound **5** (200 mg, 0.466 mmol) in THF (50 mL) at 0 °C, phosphorus tribromide (0.013 mL, 0.338 mmol) was added. After stirring for 18 h and then evaporation under vacuum, the residue was dissolved in dichloromethane, washed with water (2 × 100 mL) and dried over sodium sulfate. The solvent was removed at reduced pressure to give crude **6** as a yellow solid. Careful recrystallisation from petroleum ether/THF afforded white crystals (248 mg, 96%). M.p. 162–163 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.88 (s, 6H), 4.63 (s, 4H), 7.05 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.4, 25.9, 124.6, 127.5, 139.0, 143.7. IR (KBr) υ 3019, 2922, 2853, 1640, 1555, 1438, 1337, 985 cm^{-1}.

$C_{48}H_{69}F_6N_{13}S_2$ (**7**): A solution of intermediate **2** (554 mg, 1.80 mmol), compound **6** (100 mg, 0.180 mmol), K_2CO_3 (64.8 mg, 0.469 mmol) in CH_2Cl_2 (50 mL) was stirred for 18 h at room temperature. The reaction mixture was washed with water (100 mL) and dried over sodium sulfate. The solvent was removed at reduced pressure to give 165 mg (92%) of product **7** as a purple solid. ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.13 (t, 24H, J = 6.8 Hz), 1.88 (s, 6H), 2.45 (m, 8H), 3.53 (q, 16H, J =7.0 Hz), 3.63 (s, 4H), 3.77–3.78 (m, 8H), 6.84 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 13.4, 14.3, 41.1, 43.0, 52.8, 57.2, 124.4, 125.6, 139.9, 141.4, 164.9, 165.5. IR (KBr) υ 3073, 2971, 2930, 2862, 2811, 1706, 1666, 1539, 1491, 1432, 1371, 1330 cm^{-1}. MS m/z (M^+) 1005. Anal Calcd for $C_{48}H_{69}F_6N_{13}S_2$: C, 57.29; H, 6.91; N, 18.10. Found: C, 57.33; H, 6.89; N, 18.12%.

$C_{91}H_{140}F_6N_{38}S_2$ (**8**): Prepared in a similar manner as **7** Reaction of intermediate **4** (800 mg, 1.03 mmol) and compound **6** (100 mg, 0.180 mmol) provided product **8** as a purple solid (313 mg, 90%). ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.15 (t, 48H, J = 7.0 Hz), 1.88 (s, 6H), 2.46 (s, 8H), 3.54 (q, 32H, J = 6.8 Hz), 3.65 (s, 4H), 3.80 (m, 40H), 6.87 (s, 2H). ^{13}C NMR (100 MHz, $CHCl_3$) δ 13.4, 14.4, 29.7, 41.1, 43.1, 43.2, 52.8, 57.2, 60.3, 124.4, 125.7, 139.9, 141.5, 164.9, 165.4, 165.56, 165.62. IR (KBr) υ 3070, 2972, 2929, 2857, 1705, 1666, 1532, 1485, 1431, 1370, 1326 cm^{-1}. MS m/z (M^+) 1943. Anal Calcd for $C_{91}H_{140}F_6N_{38}S_2$: C, 56.21; H, 7.26; N, 27.37. Found: C, 56.24; H, 7.28; N, 27.41%.

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