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Electroluminescence from a new distyrylbenzene based triazine dendrimer

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We have synthesised a new distyrylbenzene cored dendrimer which utilises triazine rings to link the surface groups. It was found that methoxy surface groups were sufficient to give the dendrimer good solubility and good quality thin films could be prepared by spin-coating from solution. The dendrimer was luminescent both in solution and the solid state with the emission occurring from the core. The photoluminescence quantum yield was determined to be 31 ± 3% in the solid state. The dendrimer was incorporated into a single layer light-emitting diode (ITO/dendrimer/Ca) and was found to emit blue light with an external quantum efficiency of 0.003%.

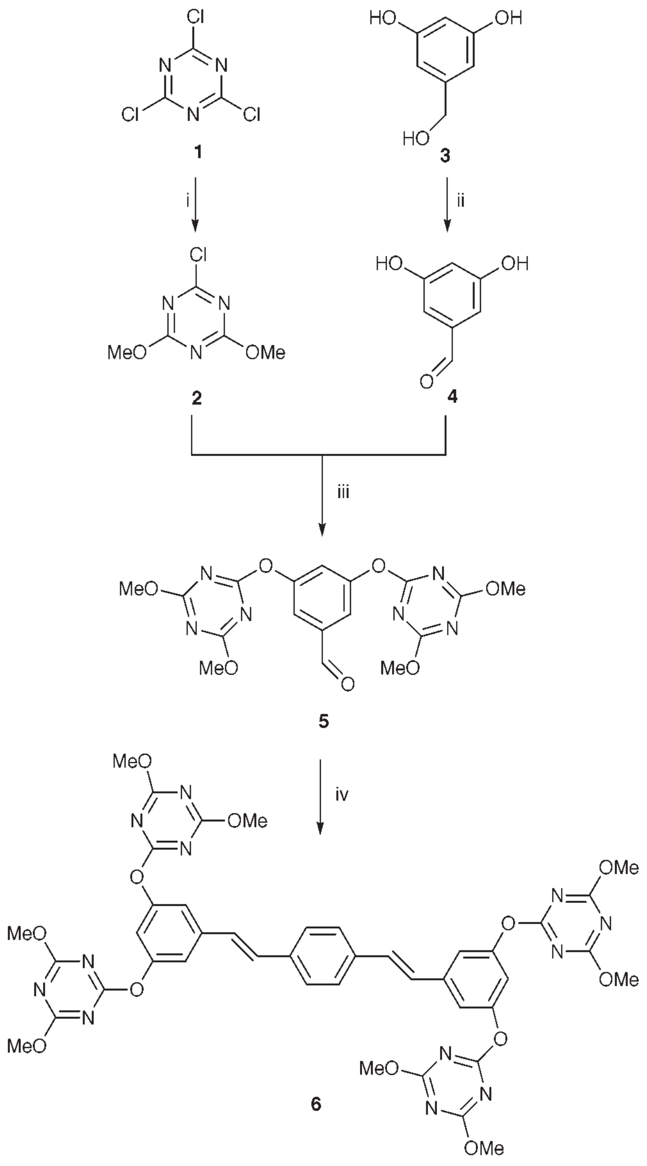
Introduction

Since the discovery of efficient electroluminescence (EL) in small organic molecules[1] and conjugated polymers[2] there has been a great deal of interest in synthesising new materials to increase efficiency and stability of organic light-emitting diodes (LEDs). One of the issues which affects both molecular and polymeric materials is that changes in the structure to effect a variation in the electronic properties can often change the processing properties. Light-emitting materials based on conjugated dendrimers offer a potential solution to this problem due to the fact that in higher generations it is only the surface groups which come in contact with the environment. This means that changes to the electronic properties should have little effect on the processing of the materials. Although there have been a number of reports on the synthesis and study of electroactive dendrimers,[3] including dendrimers as hole and electron transport layers for LEDs,[3c,d] there have only been a couple of publications where the dendrimer is used as the light-emitting layer.[3e,g] The two families of light-emitting dendrimers have contained either *meta*-linked stilbene[3e] or diphenylacetylene dendrons[3g] with luminescent cores. A further reason for an interest in dendrimers for use in LEDs is that they can potentially contain both electron and hole transport components without the concern of aggregation which could occur if the two components were put down in a single layer. This is important as many organic materials used for EL applications exhibit much greater hole than electron mobilities, which can be detrimental to the device EL efficiency. In this paper we present the synthesis, physical and electronic properties, and LED device characteristics of a new triazine containing first generation dendrimer. The triazine unit can play two important roles; first it can act as the branch point of a dendrimer;[4] and second, it has good electron affinity,[5] akin to the oxadiazole unit, and hence may act as an electron transport component. The core chosen for this study was the distyrylbenzene moiety which is of interest as a blue light-emitting material.

Results and discussion

Synthesis

To form highly branched dendrimers rapidly it is advantageous to have two or more branches at every iteration. In addition, if the branching point is to have two or more different moieties attached then there needs to be good control over the order in which each of the groups is added. 1,3,5-Trichloro-2,4,6-triazine fulfils both these criteria as it has three chloro groups which can be sequentially substituted.[6] The convergent synthetic route for the formation of **6** is illustrated in Scheme 1. The first step in the sequence involved the preparation of 2-chloro-4,6-dimethoxy-1,3,5-triazine **2**.[7] Following the reported method we found that the best conditions for the formation of **2** required a slow addition of a methanolic solution of sodium methoxide into a toluene solution of 2,4,6-trichloro-1,3,5-triazine at 0 °C. In contrast to the literature procedure we found that in addition to the desired **2** we also formed the mono-methoxy substituted triazine, 2,4-dichloro-6-methoxy-1,3,5-triazine.[6a] It was therefore important to follow the reaction by GC–MS and so it could be terminated when **2** predominated and under these conditions **2** could be isolated in an 82% yield. If the reaction was carried out at higher temperatures control over the substitution process was, as expected, lost and the trisubstituted product, 2,4,6-trimethoxy-1,3,5-triazine, was formed. The next step in the sequence was the coupling of two equivalents of **2** with 3,5-dihydroxybenzaldehyde[8] **4** to give dendron **5** with an aldehyde focus. This was achieved by reacting the bis-hydroxy anion of **4** in tetrahydrofuran at room temperature and gave dendron **5** in an excellent 94% isolated yield. The final step in the synthesis of **6** required the coupling of two equivalents of **5** with the dianion of tetramethyl 1,4-phenylenedimethylenediphosphonate.[9] However, this reaction proved somewhat capricious, giving at best a 28% yield of the desired dendrimer **6**. The optimum conditions required addition of **5** to an *N*,*N*-dimethylformamide solution of the dianion of the bis-phosphonate at room temperature. The use of *N*,*N*-dimethylformamide as solvent was necessary as the aldehyde **5** had very low solubility in other solvents compatible with the reaction conditions such as tetrahydrofuran and 1,4-dioxane. The low yield is in contrast to the recently reported distyrylbenzene dendrimers which were formed using the same bis-phosphonate but with stilbene based dendrons which gave yields in the region of 55%.[3f] We believe that the dendrimer's instability is due to the lability of the phenoxy–triazine bond which is susceptible to substitution reactions with the phenoxy moieties acting as leaving groups. Part of the reason for the low yield of **6** was that it showed poor



Scheme 1 *Reagents and Conditions*: i, CH_3ONa, CH_3OH, $PhCH_3$, 0 °C; ii, CrO_3, H_2SO_4, acetone, 0 °C; iii, NaH, THF; iv, Tetramethyl 1,4-phenylenedimethylenediphosphonate, NaH, DMF.

stability to chromatography on silica. Dendrimer **6** could be spin-coated to form optical quality thin films from chloroform.

Photophysical properties

The solution and solid state photoluminescence (PL) and absorption spectra of **6** are shown in Fig. 1. The film absorption peaks at 365 nm and appears slightly broadened and red-shifted with respect to the solution absorption, which peaks at 360 nm. This is probably due to some of the molecules adopting a more planar conformation in the film. In contrast, there is a large red shift in the PL spectrum of **6** in the film (peak at 462 nm) with respect to the solution (peaks at 395 nm and 417 nm, and shoulder at 440 nm) and the emission of the film is also broadened and lacking strong vibrational structure. The energy shift between absorption and PL maxima of 0.72 eV for the film is larger than the corresponding value of 0.49 eV for the solution. Photoluminescence excitation measurements were carried out on the solution with detection at the peaks of the emission spectrum. The spectra closely followed the absorption spectra suggesting that the PL spectra are due to a single light-emitting species which can be excited efficiently across the entire absorption spectrum.

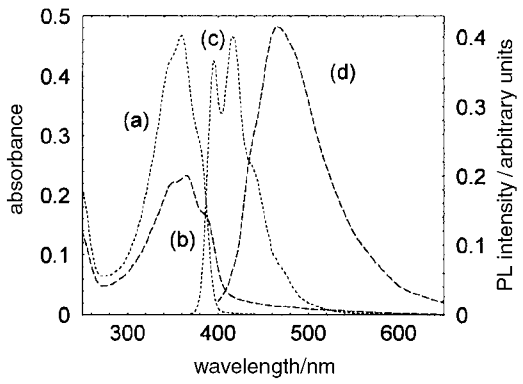


Fig. 1 Absorption and photoluminescence (PL) of **6** as a film on quartz and in chloroform. (a) Solution absorption, (b) Film absorption, (c) Solution PL, (d) Film PL.

Fig. 2 compares the solution absorption and PL spectra of **6** with those of its constituent parts—distyrylbenzene and trimethoxytriazine. Triazine absorbs strongly below 270 nm, but a clear peak is not resolved due to the strong absorption of chloroform below 240 nm. The absorption spectrum (b) is the best-fit weighted sum of triazine absorption and distyrylbenzene absorption (a). As the triazine does not absorb above 300 nm, curves (a) and (b) are identical for longer wavelengths. The spectra for the dendrimer and the core are very similar both for absorption and PL, indicating that the distyrylbenzene core is responsible for the observed spectra. The slight red shift of the PL spectra of **6** with respect to 1,4-bis(3′,5′-di-*tert*-butylstyryl)benzene is due to oxygen atoms. Due to the similarity between the compound studied here and the distyrylbenzene dendrimer with stilbene dendrons reported by Halim *et al.* in ref. 3(*e*) a direct comparison of the photophysical properties of the two materials is valuable. We find that the solution PL of the dendrimer in ref. 3(*e*) is shifted to the red by 15 nm with respect to that of **6**. This indicates that the *meta*-linked conjugated stilbene groups used in the reported material allow a greater electron delocalisation than the oxygen linkages in **6**. The film absorption of the two dendrimers is very similar, whereas the film PL of **6** is shifted to the red by 20 nm with respect to that of the dendrimer previously published.

Given the broad PL emission of **6** in the solid state the possibility of aggregation of **6** in solution was investigated by studying the PL and absorption spectra of solutions over a range of concentrations (5.5×10^{-8} M to 5.5×10^{-4} M). The absorbance was found to scale linearly with concentration. No shift in the absorption spectra was observed and the PL merely displayed a reduction of the high energy vibronic due to increasing self-absorption with increasing concentration. The photoluminescence quantum yield of films of **6** was determined

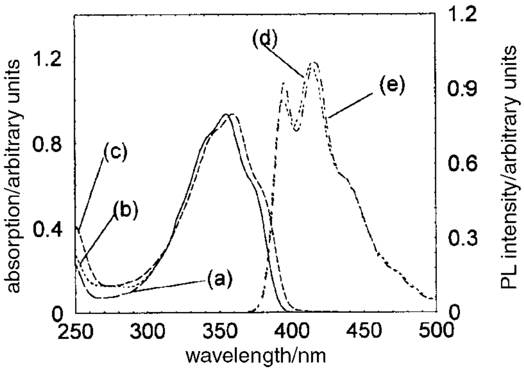


Fig. 2 Comparison of solution absorption and PL of **6** with the distyrylbenzene (DSB) core. (a) DSB core absorption, (b) Best fit of the sum of triazine and DSB absorption, (c) Absorption of **6**, (d) DSB PL, (e) PL of **6**.

to be 31±3%. This value is comparable to quantum yields reported for distyrylbenzene dendrimers with stilbene dendrons.[3e]

Electroluminescence

Single layer LEDs were fabricated by spin-coating **6** from chloroform solution onto etched ITO substrates followed by evaporation of calcium cathodes to complete the device. A typical current and light-output against voltage measurement is shown in Fig. 3 for a device with a 50 nm thick film of **6** and an active area of 2 mm^2. It can be seen that the current turn-on occurs before any light is emitted and that the current flow is very noisy. This may be due to poor stability, and related to the poor chemical stability observed during the synthesis and purification of **6**. The later onset of the light output with respect to the current flow is indicative of a strong imbalance between the charge carriers which is likely to arise from both unbalanced mobilities and a difference in barrier heights to injection. The external quantum efficiency of the device is correspondingly low and was measured to be in the order of 0.003%. This efficiency is similar to that reported by Halim *et al.* for a first generation distyrylbenzene dendrimer with stilbene dendrons[3e] in the same device configuration, which is comparable to that of a PPV single layer device with aluminium contacts. The luminance was found to be at best 1 Cd m^{-2} at 10 mA cm^{-2}. The colour of the emitted light was light blue to white and the EL spectrum is shown in Fig. 4. Comparison of the EL and PL spectra (Fig. 4) shows that the EL emission peak (506 nm) is shifted to the red by 44 nm with respect to the PL spectrum (462 nm). Also, the EL spectrum appears broadened with respect to the PL spectrum. We found that the EL intensity decreased within a few minutes of operation of the device and the emitted light was observed to change irreversibly from blue-white to white, which could be due to a change in morphology of the material.

The device characteristics changed as the device was run repeatedly and current–voltage characteristics displayed symmetrical ohmic behaviour in the low forward and reverse bias region, which could be due to the formation of conductive metal pins or chains through the film. A possible explanation for this is the diffusion of calcium through the material. It is also conceivable that the low workfunction electrode reacts directly with the material after deposition, forming an insulating interfacial layer which impedes electron injection. This instability could well be related to the chemical reactivity of the triazine centre observed during the synthesis of **6**.

Conclusions

We have prepared a new triazine branched distyrylbenzene dendrimer for applications in organic LEDs. It was shown that the triazine dendrons with simple surface groups lend high solubility of the distyrylbenzene core without affecting the photophysical properties of the chromophore. Good quality luminescent films were made from the material and blue emitting devices with external quantum efficiencies of 0.003% were fabricated using calcium electrodes. We have demonstrated that triazine is indeed a useful route in the synthesis of electroactive dendrimers. However, the poor stability of the material under investigation in this report during both synthesis and device operation suggests that the phenoxy link of the dendrons to the core is a poor choice. Future work will explore different linkages to improve the stability of triazine dendrimers.

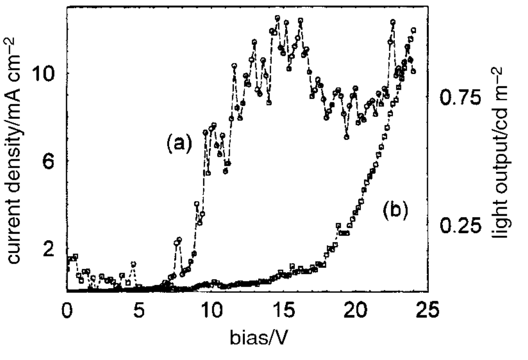


Fig. 3 Current (a) and light output (b) against voltage for a single layer ITO/**6**/Ca device.

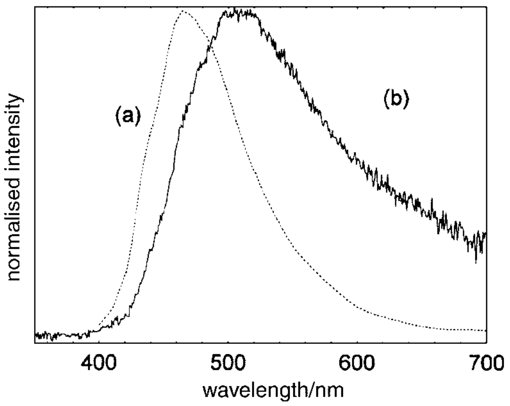


Fig. 4 PL (a) and EL (b) spectra of a thin film of **6**.

Experimental

^{1}H NMR spectra were recorded on Varian Gemini 200 (200 MHz) and Bruker AM-500 (500 MHz) spectrometers. Infrared spectra were recorded using KBr disks with a Perkin Elmer Paragon 1000 infrared spectrometer. UV–visible spectra were recorded on a Perkin Elmer Lambda 14P UV–visible spectrophotometer or a Perkin Elmer Lambda 19 spectrophotometer. Mass spectra were recorded on a Hewlett Packard series 1050 atmospheric pressure chemical ionisation spectrometer (APCI MS) or a Micromass BIO-Q Mass Spectrometer. GC–MS analysis was carried out using a Hewlett Packard 5890 GC using an SGE PPX 5 12m column and TRIO 1 mass spectrometer. Melting points were determined on a Gallenkamp melting point apparatus and are uncorrected. All solvents for recrystallisation were distilled before use. Tetrahydrofuran was dried over sodium wire and freshly distilled before use. Toluene was azeotropically distilled before use. Methanol was dried over calcium sulfate and freshly distilled before use. Column chromatography was performed using either the flash chromatography technique or gravity feed chromatography, with Acros Organics silica gel, 0.035–0.07 mm. Where solvent mixtures are used the proportions are given by volume.

Dendrimer **6** was readily soluble in chloroform, which was used as the solvent for spin-coating and solution measurements. Photoluminescence spectra were obtained with a Perkin Elmer 50B luminescence spectrometer. The excitation was at the absorption maximum. The absolute photoluminescence quantum yield under excitation at 360 nm was measured in air using an integrating sphere to collect the light emitted in all directions.[10] LEDs were made by spin-coating the dendrimer onto an ITO coated glass substrate. The substrates were carefully cleaned with acetone and propan-2-ol in an ultrasonic bath before being dried with nitrogen. Spin speeds were typically between 1000 and 2000 rpm resulting in device thicknesses between 50 and 100 nm at spinning solution concentrations of 20 mg ml^{-1}. The resulting films appeared uniform. Calcium electrodes were evaporated at a rate of 0.1 nm s^{-1} onto the dendrimer film at a pressure of

1×10^{-5} mbar and capped with aluminium to prevent oxidation. LEDs were tested under vacuum using a Keithley source measure unit and a calibrated photodiode. Typical device areas were 2 mm^2. Current–voltage measurements were made in steps of 0.1 V at intervals of 300 ms. Device efficiencies were deduced from measurements of the light emitted in the forward direction following Greenham *et al.*[11] The electroluminescence spectrum was measured with a CCD spectrometer.

2-Chloro-4,6-dimethoxy-1,3,5-triazine (2)

A freshly prepared solution of sodium methoxide in methanol (1 M, 100 cm^3) was added dropwise to an ice cold solution of 2,4,6-trichloro-1,3,5-triazine (9.20 g, 50.0 mmol) in toluene (100 cm^3) under argon whilst maintaining the reaction temperature at 0 °C. The reaction mixture was stirred at 0 °C for 2 h with the progress of the reaction being monitored by GC–MS. The cold reaction mixture was filtered, and the residue washed well with cold dichloromethane. The filtrate was collected and the solvent completely removed to yield a white crystalline solid (8.49 g). The residue was purified by column chromatography over silica using ethyl acetate–light petroleum (1 : 3) as eluent and two bands were collected and the solvent completely removed. The front running band contained 2,4-dichloro-6-methoxy-1,3,5-triazine[6a] which was isolated as a white solid (0.89 g, 10%) δ_H(CDCl$_3$; 200 MHz) 4.14 (3H, s, OCH$_3$); *m*/*z* (GC–MS) 181.0 (MH$^+$ 100%). The second eluting band contained **2** which was isolated as a white solid (7.20 g, 82%) mp 75–76 °C (lit.,[7] 75–76 °C) (Found: C, 34.50; H, 3.36; N, 24.12. $C_5H_6ClN_3O_2$ requires C, 34.21; H, 3.44; N, 23.93%); λ_{max}(CH$_2$Cl$_2$)/nm (log ε) 236 (4.63); δ_H(CDCl$_3$, 200 MHz) 4.09 (3H, s, OCH$_3$); *m*/*z* (GC–MS) 176 (MH$^+$ 100%).

3,5-Dihydroxybenzaldehyde (4)

Freshly prepared Jones' reagent was added dropwise to an ice cold solution of 3,5-dihydroxybenzyl alcohol (**3**) (4.00 g, 28.5 mmol) in distilled acetone (178 cm^3) over 6 min. The reaction temperature was maintained at 0 °C during the addition. The mixture was stirred for a further 7 min at 0 °C and then poured into diethyl ether (1500 cm^3). The organic layer was washed with saturated sodium bicarbonate solution (6×100 cm^3), brine (5×120 cm^3), dried over anhydrous sodium sulfate, filtered, and the solvent completely removed to give **4** as a pale brown solid (3.11 g, 79%) mp 161–162 °C (lit.,[8] 162–163 °C); δ_H(CD$_3$COCD$_3$; 200 MHz) 6.65 (1 H, dd, $J_{2,4}=J_{6,4}=3$ Hz, C(4)H), 6.88 (2 H, d, $J_{4,2}=J_{4,6}=3$ Hz, C(2)H and C(6)H), 8.77 (2 H, s, ArOH), and 9.84 (1 H, s, CHO).

3,5-Bis(4′,6′-dimethoxy-1′,3′,5′-triazin-2-yloxy)benzaldehyde (5)

Sodium hydride (60% dispersion in mineral oil; 1.22 g, 30.4 mmol) was added to a stirred solution of 2-chloro-4,6-dimethoxy-1,3,5-triazine (5.21 g, 29.7 mmol) and 3,5-dihydroxybenzaldehyde (2.00 g, 14.5 mmol) in anhydrous tetrahydrofuran (280 cm^3) at room temperature under argon. The reaction mixture was stirred at room temperature for 20 h and then water (120 cm^3) and dichloromethane (400 cm^3) were added. The organic layer was separated, and the aqueous layer was extracted with dichloromethane (4×100 cm^3). The combined organic layers were dried over anhydrous sodium sulfate, filtered, and the solvent completely removed to give a cream solid. The residue was purified by precipitation from chloroform by the addition of five-fold excess of ether to give **5** as a white powder (5.66 g, 94%) mp 181–183 °C (Found: C, 49.25; H, 3.79; N, 20.26. $C_{17}H_{16}N_6O_7$ requires C, 49.04; H, 3.87; N, 20.19%); ν_{max}(KBr disc)/cm^{-1} 1712 (CHO); λ_{max}(CH$_2$Cl$_2$)/nm (log ε) 248 (5.43) and 297 (3.35); δ_H(CDCl$_3$; 500 MHz) 3.99 (12 H, s, OCH$_3$), 7.27 (1 H, dd, $J_{2,4}=J_{6,4}=2$ Hz, C(4)H), 7.66 (2 H, d, $J_{4,2}=J_{4,6}=2$ Hz, C(2)H and C(6)H), and 10.0 (1 H, s, CHO); δ_C(CDCl$_3$; 250 MHz) 56, 120, 122, 138, 153, 173, 174, and 190; *m*/*z* (APCI$^+$) 417.4 (MH$^+$ 100%).

Tetramethyl 1,4-phenylenedimethylenediphosphonate[9]

A solution of 1,4-bis(chloromethyl)benzene (10.00 g, 57.1 mmol) in trimethyl phosphite (37.5 cm^3, 35.65 g, 287.30 mmol) was heated at reflux for 15 h. Excess trimethyl phosphite was removed by distillation and the crude product was distilled under reduced pressure to give a clear colourless oil of tetramethyl 1,4-phenylenedimethylenediphosphonate which solidified on cooling (11.95 g, 65%) bp 217–220 °C at 0.15 mmHg (Found: C, 44.67; H, 6.08. $C_{12}H_{20}P_2O_6$ requires C, 44.73; H, 6.26%); ν_{max}(KBr disc)/cm^{-1} 1037, 1044 (POCH$_3$), and 1259 (P=O); λ_{max}(CH$_2$Cl$_2$)/nm (log ε) 213sh (2.33), 258 (2.40), 265 (2.45), 270 (2.34), and 273sh (2.25); δ_H(CDCl$_3$; 200 MHz) 3.16 (4 H, d, $^2J_{PCH_2}=20$ Hz, CH$_2$) 3.68 (6 H, d, $^3J_{POCH}=11$ Hz, OCH$_3$), and 7.27 (4 H, s, ArH); δ_C(CDCl$_3$; 250 MHz) 32 (d, $J=9$ Hz), 53 (t, $J=3$ Hz), and 130; *m*/*z* (ETOF CI$^+$) 323.1 (MH$^+$ 100%).

(*E*),(*E*)-3′,3″,5′,5″-Tetrakis(4,6-dimethoxy-1,3,5-triazin-2-yloxy)distyrylbenzene (6)

Sodium hydride (60% dispersion in oil; 30 mg, 0.74 mmol) was added to a solution of tetramethyl 1,4-phenylenedimethylenediphosphonate (100 mg, 0.31 mmol) in dry *N*,*N*-dimethylformamide (0.6 cm^3) at room temperature under nitrogen. The mixture was stirred at room temperature for 1 h. Compound **5** (260 mg, 0.62 mmol) was added to the solution and the reaction mixture was stirred at room temperature for 3 h. Ether (5 cm^3) was added to the reaction mixture which caused precipitation of a yellow gum. The supernatant was removed and the residue was repeatedly triturated with ether until the crude product was a free flowing solid. The residue was purified by chromatotron chromatography using light petroleum–dichloromethane–triethylamine (50 : 49 : 1) as eluent. The first band was collected and the solvent completely removed to give **6** as a pale yellow powder (39.1 mg, 28%) mp 220–221 °C (Found C, 55.53; H, 4.15; N, 18.23. $C_{42}H_{38}N_{12}O_{12}$ requires C, 55.88; H, 4.24; N, 18.61%); ν_{max}(KBr disc)/cm^{-1} 1366 and 1570; λ_{max}(CH$_2$Cl$_2$)/nm (log ε) 347sh (4.79), 360 (4.79), and 380sh (4.58); δ_H(CDCl$_3$, 200 MHz) 4.01 (24 H, s, OCH$_3$, 6.97 (2 H, dd, $J_{2',4'}=J_{6',4'}=2$ Hz, C(4′)H), 7.08 (4 H, s, vinyl H), 7.25 (4 H, d, $J_{4',2'}=J_{4',6'}=2$ Hz, C(2′)H and C(6′)H), and 7.49 (4 H, s, C(4)H); *m*/*z* (APCI$^+$) 903 (M$^+$) and 904 (MH$^+$).

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