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Synthesis and electrochemical characterization of donor–acceptor phenylazomethine dendrimers

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Abstract—The synthesis of the first donor–acceptor phenylazomethine dendrimers (**4** and **5**) is described. A convergent method is used via the condensation of aromatic ketones with an appropriately functionalized tri(aminophenyl)-*s*-triazine promoted by titanium (IV) chloride. Cyclic voltammetry investigations show a donor–acceptor behaviour due to the presence of the electron acceptor *s*-triazine core and the donor ability of the conjugated peripheral butoxybenzene units.

Synthetic macromolecules containing π-conjugated systems[1] have attracted a great interest owing to their potential as photosynthetic antennas, molecular wires for electron and energy transfer and also as materials for optoelectronic devices. In this context, monodisperse dendritic materials emerge as an attractive alternative to conjugated polymers in optoelectronic applications, as they combine a well-defined architecture and conjugation length with good processability.[2] For instance, dendritic macromolecules have been incorporated into organic light emitting diodes (OLEDs) as hole transport components, electron transporting components or even as single component emitters.[3]

So far, dendritic analogues of the most important conjugated polymeric materials, namely poly(phenyleneethynylene) (**1**),[4] poly(phenylenevinylene) (**2**)[5] and poly(phenylene) (**3**),[6] derivatives (Fig. 1) have been already proposed as monodisperse macromolecular alternatives to the parent polymers.

Although poly(azomethine)s have attracted growing attention during the last few years as advanced electronics materials, owing to their semiconductive and photoconductive properties,[7] the dendrimeric analogues of poly(azomethine)s have received much less attention from the materials point of view and only recently have been used as metal complexing systems for sensors.[8]

In this communication we report a straightforward synthesis for the first donor–acceptor dendrimeric analogues of poly(azomethine)s **4** and **5** (Fig. 2), in which electron donating butoxybenzene units are linked to a *s*-triazine acceptor core through phenylazomethine spacers.

Compounds containing *s*-triazine units have been the subject of extensive research owing to their ability to form mesophases[9] and as NLO[10] and two photon absorption materials,[11] among others. More interestingly, its high electron affinity and structural symmetry has enabled its use as electron injection and transport materials in macromolecular systems.[12]

Since poly(azomethines)s can be synthesized from diamines and dialdehydes by solid-state or solution polycondensation,[7b] we have selected the 2,4,6-tri-(*p*-aminophenyl)-*s*-triazine (**12**) as the core for the attachment of electron donor conjugated dendrons in the convergent syntheses of dendrimers **4** and **5**. Thus, generation of *p*-nitrobenzilimidate by heating *p*-nitrobenzonitrile (**10**) in the presence of sodium methoxide followed by acid catalyzed cyclotrimerization affords in a 'one pot' procedure, the corresponding symmetrically substituted tri(*p*-nitrophenyl)-*s*-triazine (**11**),[13] which was finally reduced to yield the target tri(*p*-aminophenyl)-*s*-triazine (**12**) in a 94% yield (Scheme 1).

Dendritic polyphenylazomethines **4** and **5** were synthesized by following the convergent method depicted in Scheme 1. 4,4′-Dibutoxybenzophenone (**6**)[14] was allowed to react with tri(*p*-aminophenyl)-*s*-triazine (**12**)

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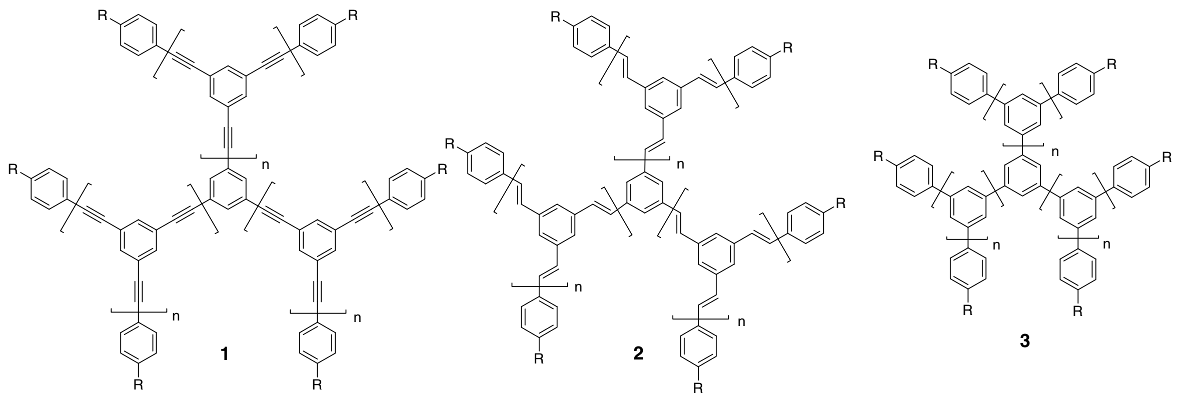


Figure 1. Polyphenyleneethynylene (**1**), polyphenylenevinylene (**2**) and polyphenylene (**3**) type dendrimers.

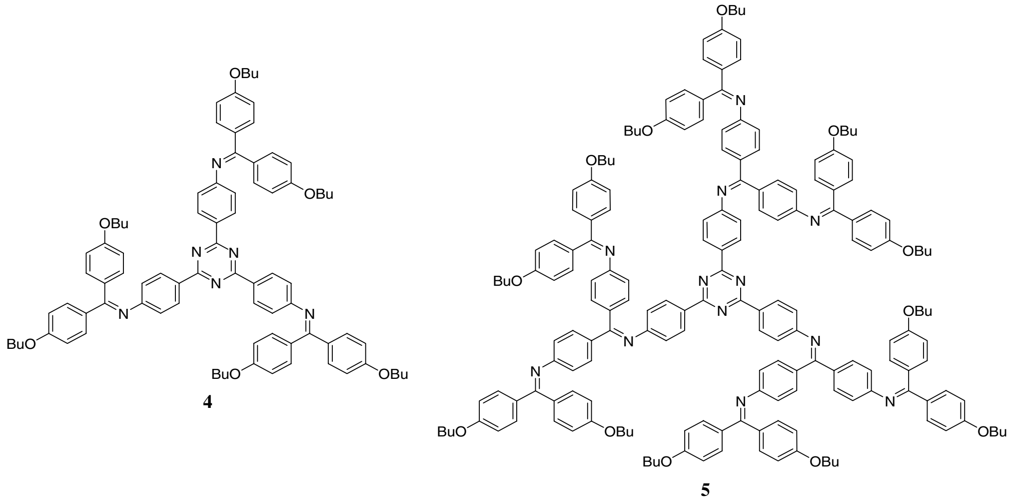
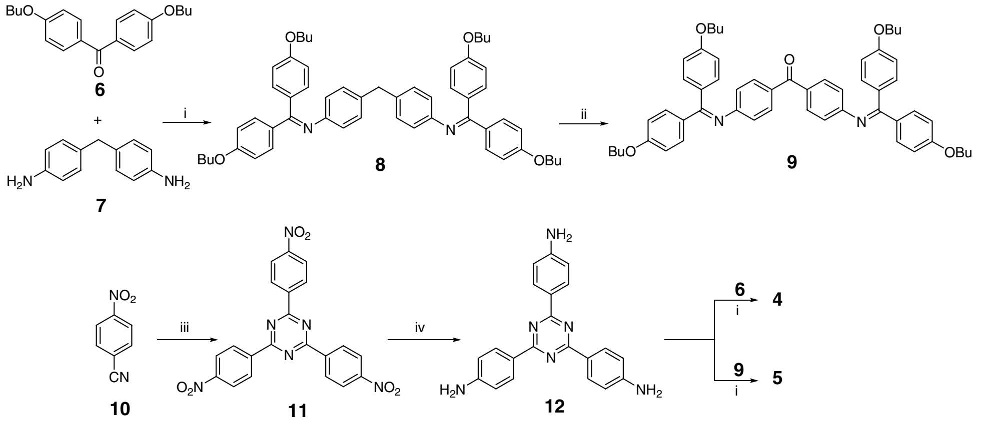


Figure 2. Donor–acceptor dendritic polyphenylazomethines **4** and **5**.



Scheme 1. Reagents and conditions: (i) DABCO, $TiCl_4$, toluene, Ar, 110 °C; (ii) $KMnO_4$, Bu_4PBr, benzene, reflux; (iii) (1) NaOMe, MeOH, 25 °C, (2) AcOH, 90 °C; (iv) Fe, $FeSO_4$ ($7\,H_2O$), H_2O, DME, reflux.

in the presence of titanium (IV) chloride as dehydrating agent and DABCO to yield the first generation dendrimer **4**. The synthesis of the imino-containing dendron **9** to form the second generation dendrimer started with a similar condensation between 4,4′-dibutoxybenzophenone (**6**) and the commercially available 4,4′-methylenedianiline (**7**) under analogous conditions to afford **8** in 75% yield. In our hands, the direct condensation of **6** with 4,4′-diaminobenzophenone to give directly **9** tends to be difficult to control and yields complex mixtures of self-condensation products. In order to circumvent self-condensation, an advantageous strategy to obtain **9** involves the condensation of 4,4′-methylene-dianiline with **6**, followed by selective oxidation of **8** with potassium permanganate in the presence of tetrabutylphosphonium bromide. This procedure allows the obtention of the suitably functionalized dendron **9** in a 48% yield.

The second generation dendrimer **5** was obtained in 19% yield by condensation of tri(*p*-aminophenyl)-*s*-triazine (**12**) with dendron **9** under similar conditions to the synthesis of the first generation dendrimer **4**.[15]

In contrast to the characteristic low solubility of poly(phenylazomethines) and also of some *s*-triazine derivatives, dendrimers **4** and **5** show high solubility in common organic solvents due to the presence of the alkoxy chains. This enhanced solubility has made the purification of the dendrons and dendrimers possible by column chromatography and has allowed its full spectroscopical characterization.[16]

Thus, the FT-IR spectra of the dendrimers show the disappearance of the typical absorption bands of the NH_2 and CO groups in the precursors **12** and **6** and **9**, respectively, in favour of the appearance of the characteristic absorption band of the imine group around 1604 cm^{-1}.

The ^{13}C NMR spectra of **4** and **5** displays the signal corresponding to the *s*-triazine carbons at 171 ppm. Whereas a single signal is observed for the equivalent imino groups in the first generation dendrimer **4**, two signals can be observed for the second generation dendrimer **5** corresponding to the two different types of imine groups.

UV–vis absorption spectra were recorded in dichloromethane solutions (Fig. 3 and Table 1) and show maxima at 298 and 341 nm for the first generation dendrimer **4** and 287 and 354 nm for the second generation dendrimer **5** (Fig. 3). Higher molar absorption coefficients can be observed for **5** as corresponds to the higher number of chromophores per molecule in comparison with **4**. In contrast to the conjugated dendrimers **1**–**3**, in which *meta* linkages prevent the extension of the conjugation, in dendrimers **4** and **5** long *para*-conjugated fragments can be observed. This is in agreement with the red shift of the absorption maxima of dendrimers **4** and **5** with respect to triaryl-*s*-triazines such as tri(*m*-xylyl)-*s*-triazine (**13**).

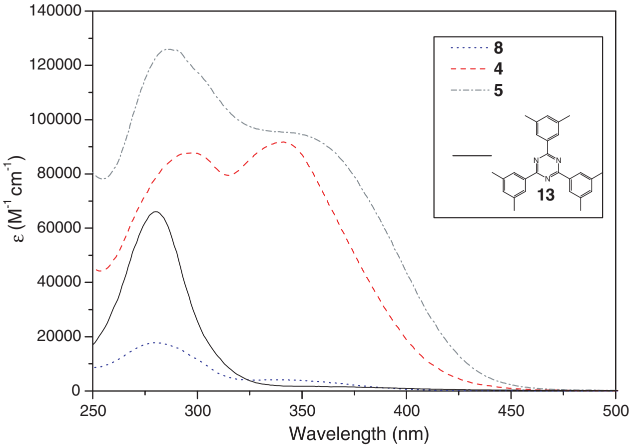


Figure 3. UV–vis absorption spectra of dendrimers **4** and **5**, dendron **8** and triazine reference **13** in dichloromethane.

However, although in **5** longer *para*-conjugated fragments than in **4** can be observed, both dendrimers show similar absorption maxima. This is probably due to distortion from planarity of the higher generation dendrimer,[8a] which restrains the extension of the conjugated chromophore.

The redox behaviour of dendrimers **4** and **5** was investigated by cyclic voltammetry. The reduction waves corresponding to the triaryl-*s*-triazine moieties[17] can be observed at ca. −2.1 V. This value is cathodically shifted in comparison with that of *s*-triazine (−2.59 V) due to the extension of the conjugated system (Fig. 4).

Further conjugation with phenylazomethine moieties stands for the second reduction process observed for the dendrimers at ca. −2.6 V, which is not observed neither in the triaryl-*s*-triazine (**13**) nor in the dendron **8** used as references. Oxidation waves corresponding to the conjugated butoxybenzene fragments can also be observed in the cyclic voltammograms. Similar oxidation values are observed for dendrimer **4** and reference **8**, whereas more positive values are observed for the second generation dendrimer **5**. This is in agreement with a stronger distortion of the peripheral part of the dendrimer in the second generation one, which causes a decrease in the effective conjugation, the other consequence of which is the small red-shift observed in the absorption spectra.

Table 1. Electrochemical and optical properties of dendrimer **4** and **5** and reference compounds **8**, *s*-triazine and tri(*m*-xylyl)-*s*-triazine

Entry	$E^1_{1/2,red}$ (V)[a]	$E^2_{1/2,red}$ (V)[a]	E^1_{OX} (V)[b]	E^2_{OX} (V)[b]	λ_{max} (nm) [ε (M^{-1} cm^{-1})][c]
s-Triazine	−2.59	—	—	—	269 [855]
Tri(*m*-xylyl)-*s*-triazine	−2.14	—	—	—	280 [66,090]
8	—	—	0.87	1.07	338 [4413], 281 [17,753]
4	−2.11	−2.55	0.75	1.07	341 [91,704], 298 [87,713]
5	−2.12	−2.61	1.06	1.26	354 [93,623], 287 [125,873]

Values recorded using TBAHFP (0.1 M) as supporting electrolyte and platinum as counter and working electrodes versus FC/FC$^+$ at 100 mV/s in $c = 5 \times 10^{-3}$ M.

[a] *N*,*N*-Dimethylformamide.

[b] Dichloromethane.

[c] In dichloromethane.

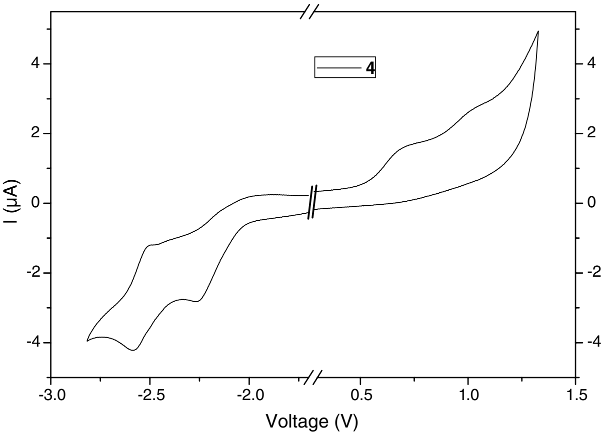


Figure 4. Cyclic voltammogram of **4** in dichloromethane (oxidation) and dimethylformamide (reduction). TBAHPF (0.1 M) solutions, 20 °C, scan rate of 100 mV/s, Pt disk working electrode, potentials versus FC/FC$^+$.

In conclusion, two novel donor–acceptor phenylazomethine dendrimers with a *s*-triazine core and bearing peripheral butoxybenzene moieties have been synthesized. These materials show an amphoteric redox behaviour due to the acceptor ability of the *s*-triazine moiety and the donor ability of the conjugated butoxybenzene systems. The synthetic strategy employed paves the way for the incorporation of stronger donors at peripheral positions and the syntheses of higher generation dendrimers. Work is in progress in order to conduct the photophysical study of these donor–acceptor dendrimers to determine the existence of energy and/or photoinduced electron transfer processes.

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15. Synthesis of dendrons. General procedure: to a solution under argon atmosphere of **12** (0.42 mmol), **6** or **9** (1.35 mmol) and DABCO (3.78 mmol) in 10 ml of dry toluene, $TiCl_4$ (1.45 mmol) is added dropwise and the crude is heated at reflux. After 3 h, the mixture is filtered, vacuum-evaporated and the remaining material is purified by column chromatography over silica gel.
16. Selected spectroscopic data for **4**: ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 8.55$ (m, 6H), 7.73 (m, 6H), 7.10–6.73 (m, 24H), 4.02 (m, 6H), 3.90 (m, 6H), 1.86–1.70 (m, 12H), 1.54–1.45 (m, 12H), 1.03–0.92 (m, 18H). ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 171.1$, 168.6, 162.1, 160.0, 156.1, 132.6, 131.9, 131.6, 131.2, 131.0, 130.0, 128.2, 121.8, 114.7, 114.4, 114.2, 68.3, 68.0, 31.6, 19.6, 14.2. FT-IR (KBr): ν (cm^{-1}): 3052, 2956, 2931, 1591, 1569, 1506. MS (FAB: NBA): $m/z = 1279.7$ $[M+H]^+$. Elem. Anal. Calcd for $C_{84}H_{90}N_6O_6$: C: 78.84%, H: 7.09%, N: 6.57%. Found C: 78.97%, H: 6.95%, N: 6.31%. Mp: 186 °C. Compound **5**: ^1H NMR ($CDCl_3$, 300 MHz): $\delta = 7.85$–7.43 (m, 24H), 7.15–6.48 (m, 60H), 4.13–3.75 (m, 24H), 1.85–1.66 (m, 24H), 1.55–1.37 (m, 24H), 1.08–0.80 (m, 36H). ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 171.2$, 168.2, 168.1, 162.8, 161.6, 159.8, 156.1, 134.1, 132.6, 131.9, 131.5, 131.4, 130.6, 121.8, 121.3, 68.3, 68.1, 31.6, 19.6, 14.2. FT-IR (KBr): ν (cm^{-1}): 3037, 2958, 2933, 2871, 1604, 1587, 1569, 1508, 1247. MS (ESI): $m/z = 2788.1$ $[M+H]^+$. Elem. Anal. Calcd for $C_{186}H_{192}N_{12}O_{12}$: C: 80.14%, H: 6.94%, N: 6.03%. Found: C: 79.64%, H: 6.83%, N: 5.89%. Mp: 109 °C.
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