Photoresponsive dendrimers

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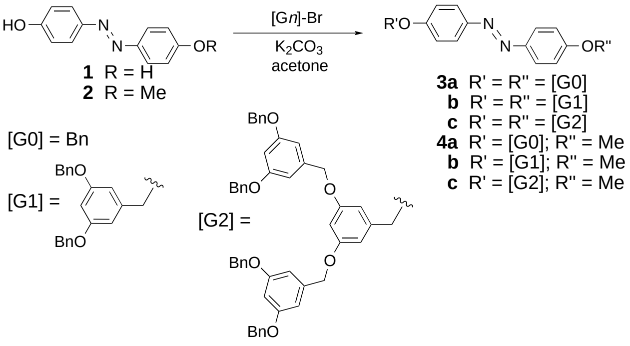
Benzyl aryl ether dendrimers with azobenzene central linkers undergo reversible *cis*/*trans* isomerization of the azobenzene moiety upon exposure to ultraviolet light.

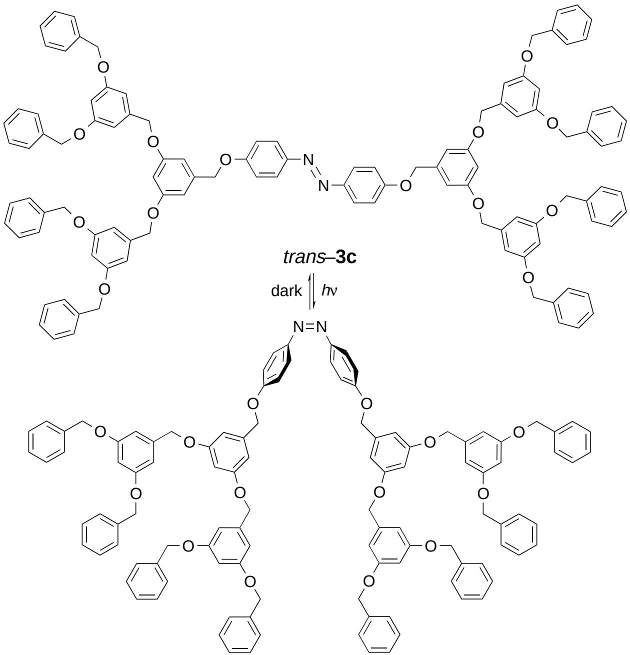
The elegance with which nature uses light energy to alter function in photoresponsive systems has led chemists to engage in much mimicry.[1] Progress has been made in designing systems containing photoresponsive moieties in small molecules,[2–4] polymers[5–8] and peptides[9–11] for the photocontrol of ion recognition and transport,[12] membrane permeability[13] and structure,[14] enzyme activity[2] and materials properties.[5,8,15] Typically, small molecule systems are well-understood. Their responsiveness is predictable and easily controlled. Macromolecular systems, however, while abundant and widely studied, are typically ill-defined and the photoresponsive effect is difficult to predict *a priori* or to control in a precise manner. Dendrimers, a new class of macromolecule in which the structure of the material is well-defined, are prepared in a way which would allow precise placement of a photoactive moiety within the dendrimer interior. More predictable control of photoinduced configurational changes should be possible, allowing potential reversible alteration of function. By placing a single photoactive moiety in the centre, rather than on the exterior,[16] of a dendrimer a small configurational change will effect a large conformational change throughout the dendrimer structure. Here we report the synthesis of dendrimers with azobenzene central linkers which undergo reversible configurational changes in response to light energy. This represents the first reversible topological change induced in a dendrimer through configurational change of the central linker.

Photoresponsive dendrimers of the zeroth, first and second generations were prepared by reaction of azobenzene-derivative central linkers **1**[17] and **2**‡ with the appropriate dendritic bromides[18] in the presence of K_2CO_3 in acetone (Scheme 1).§ Zeroth and first generation materials **3a** and **b** and **4a** and **b** are pale orange crystalline solids, while second generation materials **3c** and **4c** are orange glasses.¶

Dendrimers **3a**–**c** and **4a**–**c** all exhibited the expected photoresponsive behaviour. For example, dark incubation of a dichloromethane solution (40 μm) of second generation dendrimer **3c** served to maximize the absorbtion at 360 nm (ε_{max} = 32 500) corresponding to the *trans*-azobenzene chromophore. Irradiation of this solution with 350 nm light resulted in clean photoisomerization to *cis*-**3c** (Scheme 2), as evidenced by a decrease in the absorbance at 360 nm and an increase in absorbances 314 and 450 nm (Fig. 1). A photostationary state was reached within approximately 60 s. Thermal reversion to the original dark-incubated spectrum was observed over the



Scheme 1



Scheme 2

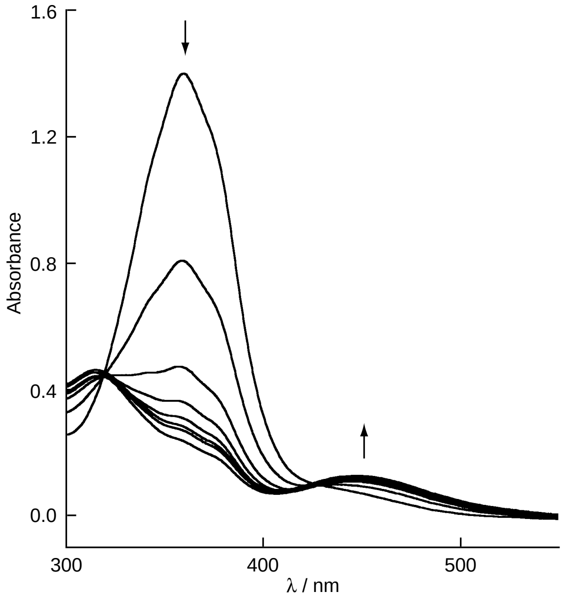


Fig. 1 UV Absorption spectra of second generation photoresponsive dendrimer **4c** (40 μm in CH_2Cl_2) under irradiation conditions (350 nm; 0, 5, 10, 15, 20, 25, 30 and 60 s)

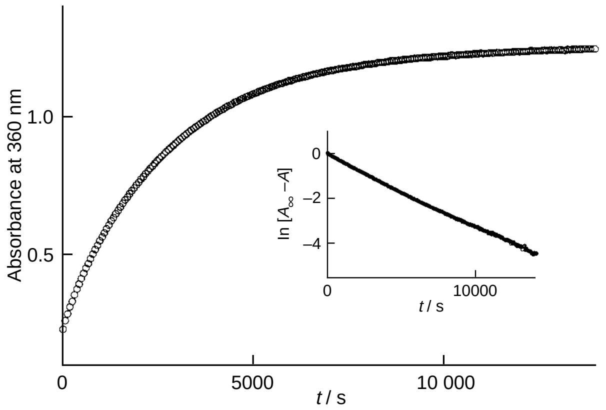


Fig. 2 Plot of absorbance at 360 nm of a sample of **4c** kept in the dark at 293 K after irradiation (10 min at 350 nm). Inset: first order rate constant plot of In[$A_\infty - A$] *vs*. time.

course of approximately 3 h at 293 K in the dark (Fig. 2). The first-order rate constant for this process ($k = 3 \times 10^{-4}$ s^{-1}; $t_{1/2}$ = 40 min) is similar in magnitude to that of other azobenzenes.[19] Exposure to bright sunlight for a period of only several seconds also effected almost complete reversion to the *trans* isomer. Second generation compound **4c** serves as a steric control for **3c**. After isomerization to *cis*-**4c** (350 nm, 10 min), thermal isomerization to *trans*-**4c** occurs with an identical first-order rate constant ($k = 3 \times 10^{-4}$ s^{-1}; $t_{1/2}$ = 40 min). This indicates that there is no strong steric influence on the thermal isomerization of *cis*- to *trans*-**3c**.

The photoinduced conversion of *trans*- to *cis*-dendrimer was also observed by ^{1}H NMR spectroscopy. For example, the methoxy groups in *trans*- and *cis*-**4c** appear as singlets at δ 3.87 and 3.74, respectively, in $CDCl_3$. Irradiation of an NMR sample ($CDCl_3$) of **4c** resulted in a dramatic change in the ratio of these peaks, from 87 : 13 to 8 : 92. Similar changes were observed in the aromatic and benzylic regions of the spectrum.‖

We have demonstrated the photoresponsive properties of a series of simple dendrimers with azobenzene central linkers. We anticipate that switchable dendrimers of this type will have applications in transport systems based on the reversible perturbation of their ability to encapsulate small molecules. We hope to demonstrate these applications in our future studies.

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Footnotes

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‡ Preparation of **2**: a solution of $NaNO_2$ (0.52 g, 7.5 mmol) in H_2O (minimum to dissolve) was added dropwise to a cold (5 °C) solution of 4-methoxyaniline (0.89 g, 7.2 mmol) and 9 m H_2SO_4 (4 ml). The resulting solution was added dropwise to a cold (5 °C) solution of phenol (0.70 g, 7.4 mmol) and 2 m NaOH (10 ml). After stirring for an additional 1.5 h, the solution was neutralized (2 m NaOH), extracted with CH_2Cl_2 (3 × 50 ml) and the combined organic extracts were dried (Na_2SO_4) and concentrated. Chromatography (SiO_2, 1 : 3 ethyl acetate–light petroleum) gave **2** (1.06 g, 65%) as a yellow crystalline solid, mp 141.5–142.5 °C (lit.,[20] 142 °C); ^{1}H NMR [400 MHz, $(CD_3)_2CO$]: δ 8.98 (s, 1 H), 7.85 (d, *J* 9.0 Hz, 2 H), 7.80 (d, *J* 8.9 Hz, 2 H), 7.07 (d, *J* 9.0 Hz, 2 H), 6.99 (d, *J* 8.9 Hz, 2 H), 3.88 (s, 3 H).

§ Representative dendrimer preparation (**3c**): a solution of **1** (54 mg, 0.25 mmol), [G2]-Br (ref. 18) (0.45 g, 0.55 mmol), K_2CO_3 (89 mg, 0.65 mmol) and dry acetone (10 ml) was kept at reflux for 24 h. After removal of the solvent by rotary evaporation, the resulting solid residue was partitioned between H_2O (20 ml) and CH_2Cl_2 (20 ml). The organic layer was separated, the aqueous layer was further extracted with CH_2Cl_2 (3 × 20 ml) and the combined organic layers were dried (Na_2SO_4) and concentrated. Flash chromatography of the residue (SiO_2, 1 : 1 CH_2Cl_2–light petroleum gradient to CH_2Cl_2) gave dendrimer **3c** (0.34 g, 80%) as an orange glassy solid.

¶ Satisfactory elemental analyses and spectroscopic data were obtained for all new compounds reported. *Selected data* for **3c**: glassy solid; ^{1}H NMR [400 MHz, $(CD_3)_2CO$]: δ 7.83 (d, *J* 9.1 Hz, 4 H), 7.46–7.30 (m, 40 H), 7.13 (d, *J* 9.1 Hz, 4 H), 6.76 (d, *J* 2.3 Hz, 4 H), 6.74 (d, *J* 2.3 Hz, 8 H), 6.61 (t, *J* 2.3 Hz, 6 H), 5.17 (s, 4 H), 5.09 (s, 16 H), 5.07 (s, 8 H); ^{13}C NMR [100 MHz, $(CD_3)_2CO$]: δ 160.6, 160.2, 160.1, 147.2, 139.2, 139.1, 139.0, 136.8, 128.6, 128.0, 127.5, 124.4, 115.1, 106.4, 101.6, 70.13, 70.11, 70.0 (Calc. for $C_{110}H_{94}N_2O_{14}$: C, 79.20; H, 5.68; N, 1.68. Found: C, 78.83; H, 5.78; N, 1.54%). For **4c**: glassy solid; ^{1}H NMR [400 MHz, $(CD_3)_2CO$]: δ 7.87 (d, *J* 9.1 Hz, 2 H), 7.84 (d, *J* 9.1 Hz, 2 H), 7.46–7.30 (m, 20 H), 7.14 (d, *J* 9.0 Hz, 2 H), 7.08 (d, *J* 9.0 Hz, 2 H) 6.80 (d, *J* 2.3 Hz, 2 H), 6.76 (d, *J* 2.3 Hz, 4 H), 6.62 (t, *J* 2.4 Hz, 3 H), 5.17 (s, 2 H), 5.09 (s, 8 H), 5.07 (s, 4 H), 3.89 (s, 3 H); ^{13}C NMR [100 MHz, $(CD_3)_2CO$]: 161.6, 160.6, 160.2, 160.1, 147.2, 147.1, 139.2, 139.0, 136.8, 128.6, 128.0, 127.6, 124.4, 124.3, 115.1, 114.2, 106.4, 106.3, 101.7, 101.6, 70.1, 70.084, 70.0, 55.5 (Calc. for $C_{62}H_{54}N_2O_8$: C, 77.96; H, 5.70; N, 2.93. Found: C, 78.01; H, 5.89; N, 2.92%).

‖ *Selected data* for *cis*-**3c**: ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.40–7.29 (m, 20 H), 6.78–6.74 (m, 8 H), 6.64 (d, *J* 2.3 Hz, 4 H), 6.60 (d, *J* 2.0 Hz, 2 H), 6.55 (t, *J* 2.8 Hz, 2 H), 6.52 (t, *J* 2.4 Hz, 1 H), 5.01 (s, 8 H), 4.945 (s, 4 H), 4.938 (s, 2 H), 3.74 (s, 3 H).

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