

Design and Synthesis of Photoresponsive Poly(benzyl ester) Dendrimers with *all*-Azobenzene Repeating Units

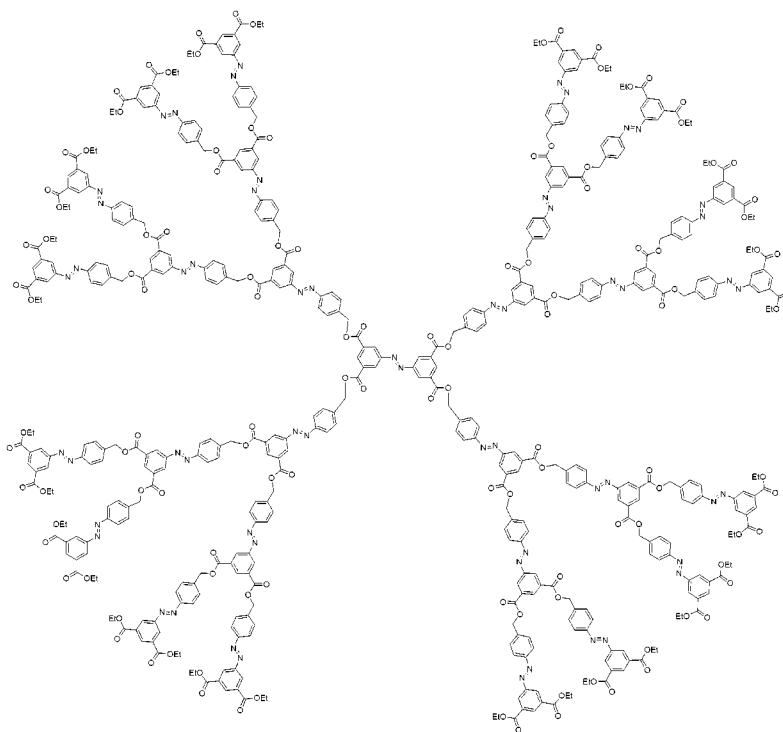
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ABSTRACT



A novel class of dendrons and dendrimers containing *all*-azobenzene units (up to 29 azobenzene groups) was designed and synthesized by the convergent method using a protected orthogonal AB₂ monomer (10) and tetra-functionalized core (11) as building blocks. The preparation of the key monomer (10) involved condensation of a protected nitroso compound (9) and 5-aminoisophthalic acid. These are the first examples of photoresponsive dendrimers with *all*-azobenzene repeating units.

Azobenzene dyes have long been investigated because of their interesting *cis*–*trans* photoisomerization phenomena. Ultrathin films containing azo dyes are of interest for optical

applications such as inducing control in LC molecules (command layer effects), holographic surface relief gratings, optical storage media, nanoscale applications, etc.¹ For

example, Gibbons and co-workers² have shown the potential for anisotropic optical display control by photoinduced alignment of azo dyes on a spin-coated polymer matrix.

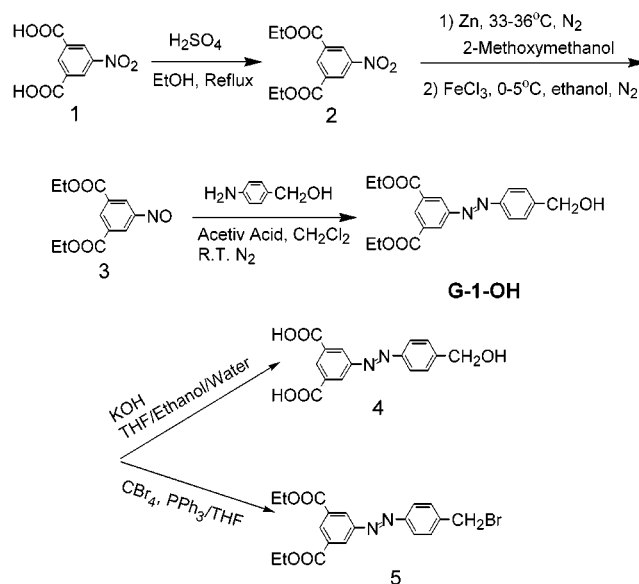
Dendrimers have been the subject of intensive investigation as a result of both their unique physical properties and structures.³ Outstanding features of dendrimers are a highly branched structure, a monodispersed molecular weight, a globular and symmetrical conformation, and a high density of peripheral functionalities. As macromolecules, they can incorporate photoactive,⁴ electroactive,⁵ and recognition elements⁶ into their architectures at different positions with properties very different from those of linear polymers or small molecules. The incorporation of a photochromic moiety in dendritic architectures is very attractive because of the possibility of creating new optical materials⁷ and optical devices.⁸ McGrath⁹ and others¹⁰ have prepared dendritic macromolecules with photochromic azobenzene units in dendrimer exterior and interior architectures to obtain photo-switchable systems. However, only two examples of dendrons with the azobenzene groups *in* and *throughout* the architecture are known.¹¹ Their primary focus was on obtaining organic nonlinear optical materials.

In this paper, we present the first convergent synthesis of a novel photoresponsive *all*-azobenzene dendrimer from monodendrons with orthogonal azobenzene groups. Our goal is to create an "intelligent" macromolecule whose molecular

shape and size can be changed upon irradiation with UV light. We are interested in the formation of well-defined domain structures of azobenzene dyes with unique photoisomerization and photoalignment properties compared to those of individual dyes, side chain polymers, and domain aggregates.^{1,8} It will be interesting to observe how chromophoric groups on the dendrimer can be influenced by cooperative motion to change the "global" shape of the individual dendrimers to anisotropic configurations, e.g., spherical to ellipsoidal, etc.¹²

Our synthesis starts with the photochromic **G-1-OH** and AB₂ monomer **4**, designed and synthesized as shown in Scheme 1. **G-1-OH** was derived from the nitroso compound

Scheme 1. Synthetic Route for **G-1-OH** and the AB₂ Monomer **4**



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3, which was made from the diethyl ester nitro compound **2**. The nitro compound was prepared by esterification of 5-nitroisophthalic acid, **1**. This esterification with ethanol in the presence of catalytic concentrated H₂SO₄ under reflux afforded the diethyl ester **2** at 88% yield. Reduction of **2** was accomplished using Zn dust at 33–35 °C to form a hydroxylamine intermediate. This was followed by oxidation of the hydroxylamine intermediate with FeCl₃ in one pot to give the nitroso compound **3** with an overall 47% yield. Condensation of **3** with 4-aminobenzyl alcohol in CH₂Cl₂ catalyzed by acetic acid gave the first generation azo-dendron **G-1-OH** in a good yield of 86%. Saponification of the **G-1-OH** with aqueous KOH in refluxing mixture of EtOH afforded the AB₂ monomer **4** in 84% yield. Bromination of the **G-1-OH** with CBr₄/Ph₃P gave the bromomethyl compound **5**. The crystal structure of **G-1-OH** was determined by X-ray diffraction (Figure 1).

The Generation 2 dendron (**G-2-OH**) was obtained by refluxing of the AB₂ monomer **4** and benzyl bromide **5** in

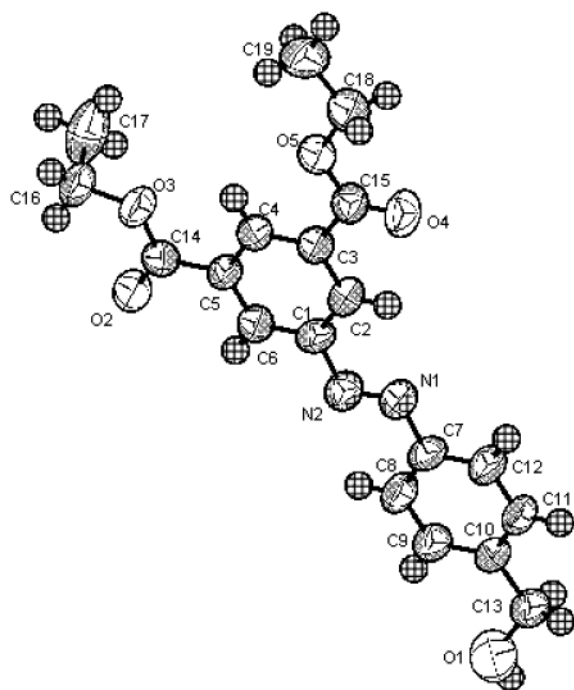
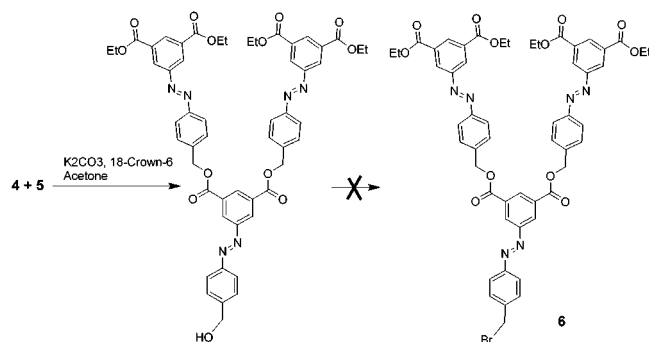


Figure 1. The crystal structure of **G-1-OH**.

the presence of potassium carbonate and 18-crown-6 with an 84% yield, forming an organic solid (Scheme 2). Unlike

Scheme 2. Synthesis of Dendron G-2-OH

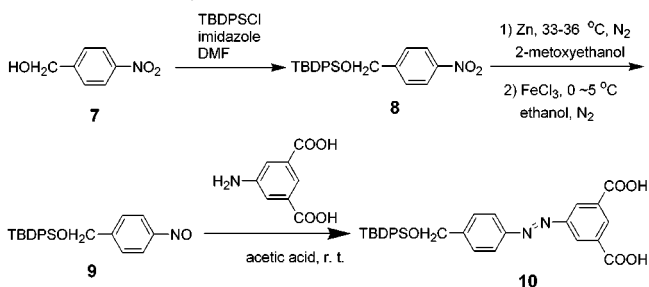


the preparation of **5**, the **G-2-OH** could not be brominated by $\text{CBr}_4/\text{PPh}_3$, even when using an excess of $\text{CBr}_4/\text{PPh}_3$ at higher temperature. Also, an array of brominating agents¹³ (PBr_3 ,^{13a} PPh_3/NBS ,^{13b} $\text{NBS}/\text{Me}_2\text{S}$,^{13c} Me_3SiBr ,^{13d} and $\text{Me}_3\text{SiBr}/2,6\text{-di-}t\text{-butylpyridine}$) consistently gave unsatisfactory results. It is unclear why these reactions do not work. A similar phenomenon has been observed in other literature.^{13c} So we turned to design and synthesize the AB_2 monomer

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10, which contained two activated carboxylic groups for generation growth and a hydroxymethyl group protected by *tert*-butyldiphenylsilane chloride (TBDPSCI) for next generational growth as outlined in Scheme 3. 4-Nitrobenzyl

Scheme 3. Synthesis of a Protected AB_2 Monomer (10)

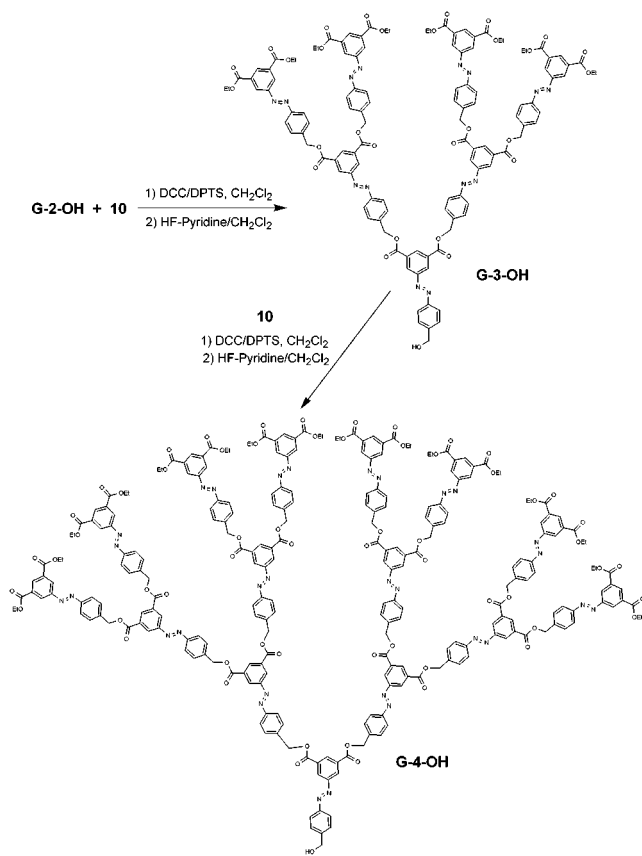


alcohol **7** was treated with *tert*-butyldiphenylsilane chloride in the presence of imidazole in DMF to afford the protected silyl ether compound **8** in an excellent 96% yield. Reduction of **8** was similar to the preparation of nitroso compound **3** and followed by oxidation yielded nitroso compound **9** in a good 82% yield.

Condensation of the nitroso compound **9** with 5-aminoisophthalic acid using acetic acid as solvent produced the new AB_2 monomer **10** in 90% yield as an orange solid. With the new AB_2 monomer **10**, the third and fourth generation dendrons (**G-3-OH** and **G-4-OH**) based on **G-2-OH** and the monomer **10** were smoothly obtained following the convergent synthetic approach developed by Fréchet and Hawker.¹⁴ This involved an iterative and alternating sequence of DCC (dicyclohexyl carboxycardodiimide)/DPTS (4-dimethylamino pyridinium-4-toluenesulfonate) mediated esterifications¹⁵ and deprotection by HF –pyridine as shown in Scheme 4. The reactions were selected because they are known to be extremely mild and fast and afford high conversions. Thus, the coupling of the **G-2-OH** alcohol with the AB_2 monomer **10** in the presence of DCC and catalytic amount of DPTS, followed by deprotection with HF –pyridine, proceeded cleanly and efficiently. The reaction gave the **G-3-OH** dendron in a good yield of 78% after purification. For deprotection of the alcohol group, initial attempts to desilylate using TBAF (tetrabutylammonium fluoride) proved unsuccessful. This reaction gave complicated mixtures attributable to cleavage of the ester linkages. We also tried to use a THF – HCl (aq) system to desilylate. Under this reaction condition the protecting group could not be completely removed at room temperature and the product tends to decompose at higher temperatures. These two steps were methodically repeated to convert the **G-3-OH** to **G-4-OH** with a 56% overall yield. In addition, perfect *all*-azobenzene dendrimers based on poly(benzyl ester) monodendrons were prepared by coupling different generation monodendrons with a tetra-functionalized azobenzene core, **11**, using the

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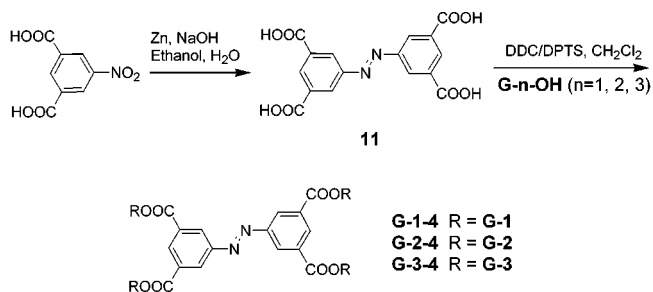
Scheme 4. Synthesis of the Dendrons via a Convergent Approach



same coupling conditions described above, Scheme 5. This compound **11** was obtained from the reductive coupling of 5-nitroisophthalic acid with Zn/NaOH in a refluxing mixture of EtOH and water in 62% yield.

Thus, coupling dendrons **G-1-OH**, **G-2-OH**, and **G-3-OH** with the tetra-functionalized core **11** in the presence of DCC/DPTS afforded the *all*-azobenzene dendrimers **G-1-4**, **G-2-4**, and **G-3-4** in 82%, 54%, and 38% yields, respectively (Scheme 5). The synthetic azobenzene dendrons and dendrimers were characterized by NMR, MALDI-TOF MS, and elemental analysis (Supporting Information). The ^1H NMR shift of the ethyl groups at the peripheries of the dendrons and dendrimers and benzyl methyl groups were useful in the characterization. The chemical shift of benzyl methyl

Scheme 5. Synthesis of the *all*-Azobenzene Dendrimers



groups was consistently around 5.53 ppm, while those of OCH_2- and $-\text{CH}_3$ of ethyl groups were around 4.45 and 1.44 ppm, respectively. The relative integrations for these three areas were a useful diagnostic tool for characterizing the generation of the dendrons and dendrimers. MALDI-TOF mass spectra confirmed that all the dendrons and dendrimers obtained are of high purity and essentially monodispersed. Their m/z values are identical to the correct molecular weights as expected for their structures.

In conclusion, *all*-azobenzene dendrimers bearing up to 29 azobenzene units were first successfully synthesized by coupling synthetic monodendrons in a convergent approach. These dendrons and dendrimers were constructed by using orthogonal azobenzene groups as repeating units and benzyl ester bonds as linkers. Thus, a new class of macrodyes was synthesized. These photoresponsive dendrons and dendrimers will be systematically investigated for their photoisomerization, photoalignment, and photochromic changes both as thin films and in different matrices, e.g. polymers and solution. The progress will be reported in due course.

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Supporting Information Available: Experimental details and characterization data for all the compounds reported. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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