

Photoswitchable Flexible and Shape-Persistent Dendrimers: Comparison of the Interplay between a Photochromic Azobenzene Core and Dendrimer Structure

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Abstract: Two analogous classes of dendrimers with a single azobenzene moiety at the core have been prepared. Flexible benzyl aryl ether dendrimers **1a–e** were obtained in good yields by direct alkylation of diphenolic azobenzene **3** with benzyl aryl ether dendrons [G-*n*]-Br (*n* = 0–4). In rigid dendrimers **2a–e**, the azobenzene configurational switch was linked to phenylacetylene dendrons through acetylenic linkages to maintain the shape-persistent nature of these dendrimers. A comparison of these two different classes of dendrimers with azobenzene cores reveals a difference in the properties of the photochromic moiety upon dendritic incorporation as well as a significant difference in the photomodulation of dendrimer properties. The *E* → *Z* photoisomerization quantum yield decreased markedly with increasing generation for dendrimers **1a–e** but only slightly for dendrimers **2a–e**. However, increasing generation did not significantly alter thermal isomerization kinetics or activation barriers. The hydrodynamic volumes of azobenzene-containing dendrimers **2b–e** were significantly modulated when the azobenzene unit is subjected to irradiation, while those of dendrimers **1b–e** were only slightly affected.

Introduction

The manipulation of the shape and conformation of globular macromolecules remains an important goal into the 21st century. Dendrimers have played an important role in nanotechnology systems as inherently globular building blocks.¹ Manipulation of dendrimer size, shape, and properties promises to provide a wide range of materials with different potential functions.² Wishing to probe the nature of azobenzene-based photomodulation of dendrimer properties, we have previously synthesized azobenzene-containing benzyl aryl ether dendrimers that undergo reversible configurational changes—and concomitant changes in physical properties such as polarity and hydrodynamic volume—in response to light energy.^{3,4} Herein we report

the design and synthesis of shape-persistent dendrimers with photochromic linkages⁵ and the first direct comparison of the effect of photochromic incorporation at the core of two fundamentally different classes of dendrimers: one with a flexible benzyl aryl ether framework and another with a shape-persistent framework of phenylacetylene subunits.⁶ While the photochromic behavior of the azobenzene core exhibits varying sensitivity to the nature of the dendrimer architecture, photoisomerization effects discrete dendrimer size changes that differ dramatically depending on the rigidity of the dendrimer framework.

Results and Discussion

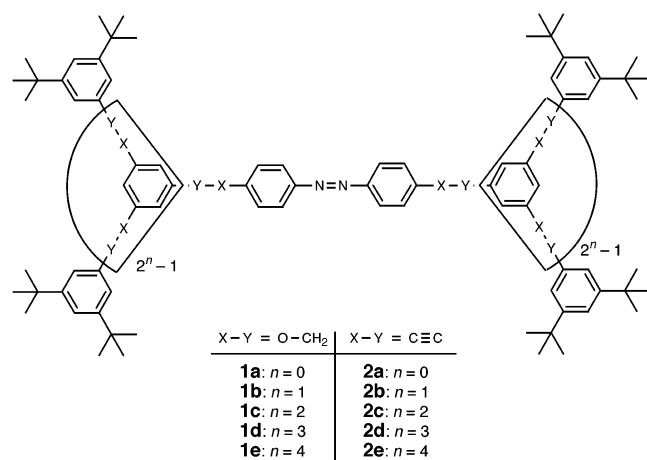
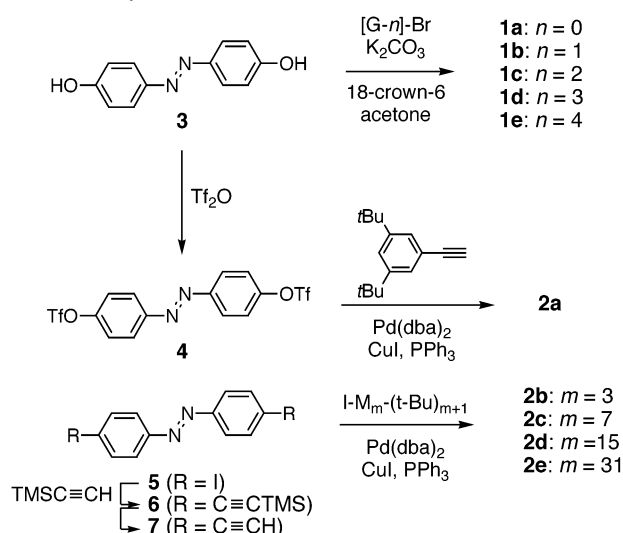
To explore the effect of dendrimer subunit structure on the behavior of photochromic dendrimers, we prepared two different classes of mono(azobenzene)-containing dendrimers (Chart 1). Flexible^{3c,7} benzyl aryl ether dendrimers **1a–e** were obtained in good yields by direct alkylation of diphenolic azobenzene **3**⁸ with benzyl aryl ether dendrons [G-*n*]-Br (*n* = 0–4).⁹ In rigid² dendrimers **2a–e**, the azobenzene configurational switch was

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Chart 1

Scheme 1. Synthesis of Dendrimers **1a–e** and **2a–e**

linked to phenylacetylene dendrons through acetylenic linkages to maintain the shape-persistent nature of these dendrimers (Scheme 1).^{5a} Zeroth-generation dendrimer **2a** was prepared through the direct coupling of 3,5-di-*tert*-butylphenylacetylene¹³ and 4,4'-dihydroxyazobenzene ditriflate (**4**). First- through fourth-generation dendrimers **2b–e** were prepared from diacetylenic azobenzene core **7** in moderate yields by Pd(0)-catalyzed coupling with the iodo-functionalized phenylacetylene dendrons.¹⁰ All compounds were characterized by a combination of ¹H and ¹³C NMR, mass spectrometry, and UV–visible absorption spectroscopy.

The absorption spectra of dendrimers **1a–e** and **2a–e** exhibit both dendron and azobenzene $\pi-\pi^*$ bands as expected. Generational growth of benzyl aryl ether dendrimers **1a–e** was confirmed by the increase in absorbance of the 280 nm band that corresponds to the dioxygenated aromatic chromophores of these dendrons relative to the azobenzene chromophore at ca. 360 nm. A similar increase in absorbance of the phenylacetylene dendron chromophore at 295 nm relative to the red-shifted azobenzene $\pi-\pi^*$ band at ca. 380 nm was observed for dendrimers **2a–e** (Figure 1).

The relative effects of the two different dendrimer classes on the photochromic behavior of the azobenzene central linkers

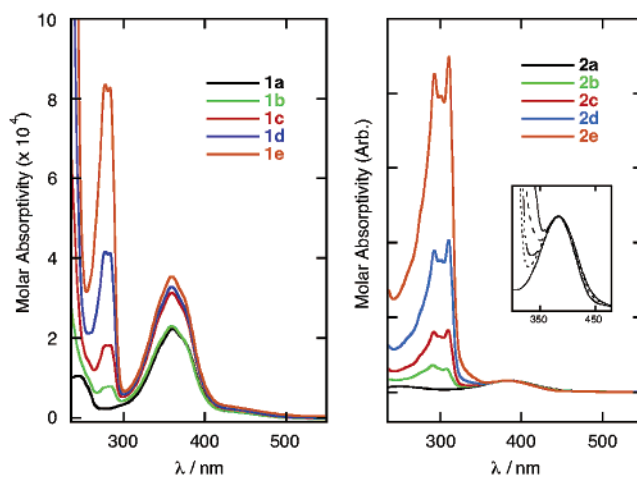


Figure 1. (Left) Absorbance spectra of solutions (CH₂Cl₂) of zeroth through fourth-generation dendrimers **1a–e**. (Right) Absorbance spectra of solutions (CHCl₃) of zeroth through fourth-generation dendrimers **2a–e** (normalized at 382 nm).

Table 1. Selected Physical Data for Dendrimers **1a–e** and **2a–e**

compd	ϕ_{E-Z}^a	$k_{21} (\times 10^5 \text{ s}^{-1})$	$k_{40} (\times 10^4 \text{ s}^{-1})$	$k_{60} (\times 10^3 \text{ s}^{-1})$	E_a (kcal/mol)
1a	0.30	0.938	0.834	0.736	21.8
1b	0.25	1.11	1.12	0.690	20.6
1c	0.18	0.954	0.932	0.756	21.8
1d	0.18	1.11	1.27	0.833	21.6
1e	0.14	1.81	2.16	1.31	21.4
2a	0.041	6.82	4.17	2.35	17.7
2b	0.037	6.28	4.56	3.03	19.4
2c	0.029	6.73	4.93	3.25	19.3
2d	0.023	11.7	8.23	4.71	18.5
2e	0.023	17.8	12.9	8.03	19.0

^a Measured at 350 nm for **1a–e** and at 380 nm for **2a–e**. See Experimental Section for details.

in dendrimers **1a–e** and **2a–e** were investigated by optical spectroscopy. Photoisomerization of the central linkers from the *E* to *Z* configuration in all dendrimers was confirmed by the decrease in absorbance of the respective $\pi-\pi^*$ bands upon irradiation with the appropriate wavelength (350 nm for **1a–e**; 380 nm for **2a–e**) of dichloromethane solution of the dendrimers. The photochromic behavior of the two series of dendrimers is markedly different. First, the order of magnitude difference in quantum yield (ϕ_{E-Z}), already present in **1a** and **2a**, indicates that the *p*-phenylacetylenic substitution affects the electronic structure of the central azobenzene (Table 1). Moreover, different behaviors are observed within the series as a function of generation. While the rigid dendrimers **2a–e** show just a slight decrease in ϕ_{E-Z} , presumably due to an increase in the gyration radius, with increasing generation, a larger decrease in ϕ_{E-Z} is observed in the flexible dendrimers. This decrease is accompanied by an increase in the extinction coefficient of the central azobenzene (Figure 1). A similar decrease in ϕ_{E-Z} , as well as an increase in extinction coefficient, can also be seen when compound **1a** is dissolved in a nonpolar solvent (e.g., in hexane $\phi_{E-Z} = 0.17$ and $\epsilon = 2.9 \times 10^4$). This suggests that the dendrons influence the solvation of the central azobenzene with increasing generation.¹¹ Further studies are underway.

The kinetics of the thermal *Z* \rightarrow *E* isomerization provide a quantitative measure of the effect of dendrimer incorporation

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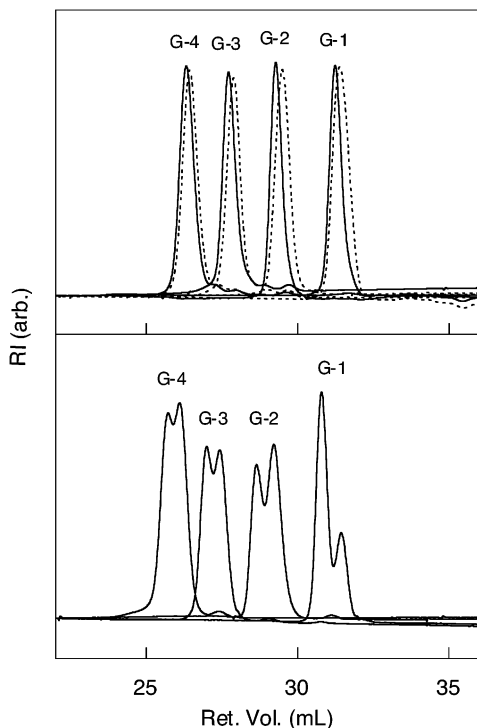


Figure 2. GPC traces for dendrimers (top) **1b–e** before (—) and after (---) irradiation with 350 nm light and (bottom) **2b–e** after irradiation with 380 nm light.

on azobenzene thermochromism. The thermal $Z \rightarrow E$ isomerization was monitored at three different temperatures for both the benzyl aryl ether-based dendrimers **1a–e** and rigid phenylacetylene dendrimers **2a–e**. Interestingly, despite the apparent rigidity of the dendritic architecture in **2a–e**, the thermal isomerization process is relatively unaffected by increasing generation under these dilute solution conditions. As observed previously in azobenzene-containing benzyl aryl ether dendrimers,³ the first-order rate constants for the thermal process in *all dendrimers studied* is $\sim 10^{-5}$ at ambient temperature and increases approximately an order of magnitude every 20 K, and the activation energy (E_a) for this process is invariant with respect to increasing dendrimer size (Table 1).^{3,4} Note that the rate constants for $Z \rightarrow E$ thermal isomerization of *both* series of dendrimers increases by a factor of 2–3-fold on going from the second to fourth generation. However, this rate increase is consistent over the temperature range studied and likely results from a deviation in the preexponential factor.¹² Hence, the activation energy is essentially constant over the generation range studied here and is consistent with typical azobenzenes.

However, we did observe that while a spin-coated film of second-generation benzyl aryl ether dendrimer **1c** underwent $E \rightarrow Z$, a corresponding film of dendrimer **2c** was unaffected by extensive irradiation. This lack of photoisomerization activity could be due to restriction imposed by the rigid matrix.¹³ It is probable that the extremely low quantum yield for photoisomerization (vide supra) coupled with an increase in nonradiative decay processes in the condensed state contributes to this lack of photoisomerization activity for **2c**.

(12) Curiously, the rigid polyphenylene azobenzene-containing dendrimers of ref 5b exhibit an even more modest variance in their thermal isomerization rate constants with increasing generation, yet the authors claim structure-dependent photoresponsive behavior.

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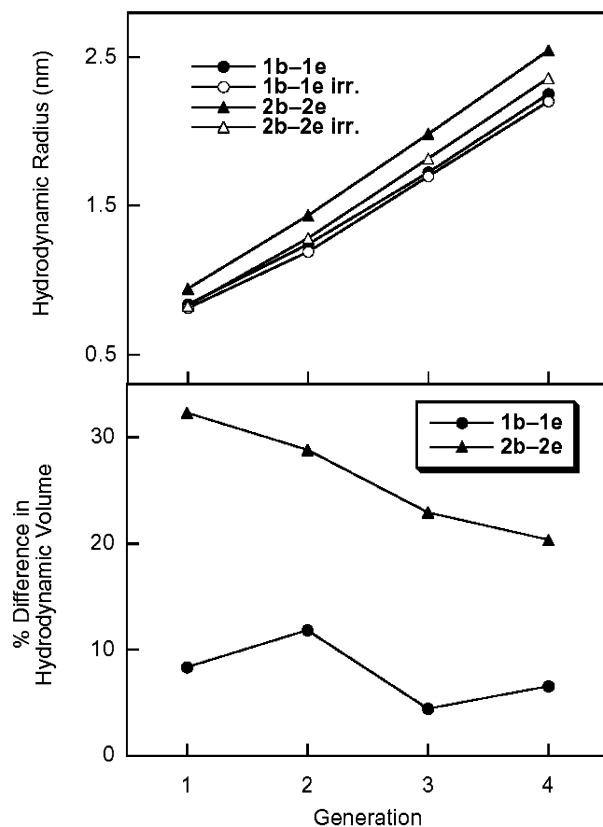


Figure 3. (Top) Calculated hydrodynamic radii¹⁴ of **1b–e** (●, ○) and **2b–e** (▲, △) before (solid symbols) and after (open symbols) irradiation. (Bottom) Percent difference in calculated hydrodynamic volume as a result of irradiation for **1b–e** (●) and **2b–e** (▲).

The effect of azobenzene isomerism on the three-dimensional molecular size of dendrimers **1b–e** and **2b–e** was studied by gel-permeation chromatography (GPC). All dendrimers exhibited a reproducible increase in GPC retention volume, indicating a discrete decrease in hydrodynamic size, following irradiation of the sample (Figure 2). From the observed elution volumes we calculated hydrodynamic radii of dendrimers **1b–e** and **2b–e** before and after irradiation as well as the percent difference in hydrodynamic volume as a result of irradiation.¹⁴ When these two series of values are plotted versus generation (Figure 3), several conclusions can be drawn. First, a consistent decrease in hydrodynamic size is seen after irradiation for each dendrimer architectural class. Second, within the same architectural class of dendrimers, the percent change in hydrodynamic volume caused by azobenzene isomerism generally decreases with increasing generation. Third, comparison of the percent difference in hydrodynamic volume as a result of irradiation between **1b–e** and **2b–e** reveals a much larger size difference for the latter dendrimers. For example, for second-generation dendrimers **1c** and **2c**, the percent difference in hydrodynamic volume between the *E* and *Z* forms was 12% and 29%, respectively. Clearly, the shape-persistent dendrimers consisting of rigid phenylacetylene dendrimer subunits reflect the configuration of a central azobenzene more efficiently than those with

(14) GPC elution volumes were converted to hydrodynamic volume values by use of the relationship $V_h = 0.4(KM^{a+1})$, where K and a are the Mark–Houwink constants for polystyrene in 1,2-dichloroethane and M is the coeluting polystyrene molecular weight. Hydrodynamic radius was calculated from the volume with the assumption of a spherical shape and by use of the formula for the volume of a sphere, $V = (4/3)\pi r^3$.

flexible benzyl aryl ether subunits, a most interesting consequence of the flexible versus rigid nature of these two classes of structures in responding to the covalently incorporated photochromic switch. Indeed, irradiation of a single azobenzene in the core of a rigid dendritic structure is as effective at size modulation as three azobenzenes in a flexible benzyl aryl ether dendrimer.^{3c}

Summary

A comparison of two different classes of dendrimers with azobenzene cores reveals a difference in the properties of the photochromic moiety upon dendritic incorporation as well as a significant difference on the photomodulation of dendrimer properties. The hydrodynamic volume of azobenzene-containing dendrimers can be significantly modulated when the azobenzene unit is subjected to irradiation, depending on dendrimer construction.

Experimental Section

Materials and Methods. NMR spectroscopy and mass spectrometry (MS) were performed on commercially available instrumentation. Gel-permeation chromatography (GPC) was performed on a system consisting of a Shimadzu LC-10AD pump, a Shimadzu RID-6 RI detector, and a Rheodyne 7725I injector running CH₂Cl₂ at 1 mL/min through three columns (Jordi Gel 500 Å, 1000 Å, and 10 000 Å DVB, 250 × 10 mm) in series at ambient temperature. Tetrahydrofuran (THF) was distilled under N₂ from sodium benzophenone ketyl. Acetone was dried over crushed 3 Å molecular sieves. Potassium carbonate (granular, J. T. Baker) was dried at 100 °C at reduced pressure and stored in a vacuum oven. Fréchet-type bromides⁹ ([G-1]Br, [G-2]Br, [G-3]Br), 3,5-di-*tert*-butylbenzyl bromide, phenylacetylene dendrons [I-M₃-(t-Bu)₄, I-M₇-(t-Bu)₈, I-M₁₅-(t-Bu)₁₆, and I-M₃₁-(t-Bu)₃₂],¹⁰ 3,5-di-*tert*-butylphenylacetylene,¹⁰ and compounds **3**¹⁵ and **5**¹⁶ were prepared according to the literature. All other reagents were purchased from commercial suppliers and used as received. Flash chromatography was performed by the method of Still et al.¹⁷ using silica gel (32–63 μm, Scientific Adsorbants, Inc., Atlanta GA). Thin-layer chromatography (TLC) was performed on precoated plates (Silica Gel HLO, F-254, Scientific Adsorbants, Inc.). All quantum yields were calculated relative to potassium ferrioxalate.¹⁸ The concentrations of the dendrimer solution were adjusted so that their absorbance at the π–π* peak was between 0.006 and 0.008. Every measurement was repeated 3 times.

1a. A solution of 3,5-di-*tert*-butylbenzyl bromide (0.10 g, 0.35 mmol), THF (10 mL), 4,4'-hydroxyazobenzene (36 mg, 0.17 mmol), potassium carbonate (49 mg, 0.35 mmol), and 18-crown-6 (9 mg, 0.035 mmol) was maintained at reflux overnight. After the reaction was complete by TLC (SiO₂, 9:1 hexanes–ethyl acetate), the mixture was filtered and the solvent was concentrated. The residue was purified by flash column chromatography (SiO₂, 9:1 hexanes–ethyl acetate) to afford **1a** as a yellow solid (73 mg, 70%): ¹H NMR (500 MHz, CDCl₃) δ 7.91 (d, 4H, *J* = 9.0 Hz), 7.41 (d, 2H, *J* = 2.0 Hz), 7.28 (t, 4H, *J* = 2.0 Hz), 7.10 (d, 4H, *J* = 9.0 Hz), 5.09 (s, 4H), 1.32 (s, 36H); ¹³C NMR (62.9 MHz, CDCl₃) δ 31.5, 34.9, 71.1, 115.0, 122.2, 122.4, 124.3, 135.4, 147.1, 151.2, 161.0; MS (MALDI) *m/z* 618.3332.

1b. Following the procedure for **1a**, [G-1]-Br (0.20 g, 0.33 mmol), THF (10 mL), 4,4'-dihydroxyazobenzene (32.0 mg, 0.16 mmol), 18-crown-6 (10 mg), and potassium carbonate (21 mg, 0.15 mmol) yielded, after purification by flash column chromatography (SiO₂, 9:1 hexanes–ethyl acetate), **1b** as a yellow solid (0.13 g, 71%): ¹H NMR (250 MHz,

CDCl₃) δ 7.92 (d, *J* = 8.5 Hz, 4H), 7.39 (t, *J* = 1.7 Hz, 4H), 7.26 (t, *J* = 1.7 Hz, 8H), 6.72 (d, *J* = 2.0 Hz, 4H), 6.64 (d, *J* = 2.0 Hz, 2H), 5.09 (s, 4H), 4.99 (s, 8H), 1.32 (s, 72H); ¹³C NMR (62.9 MHz, CDCl₃) δ 31.5, 34.8, 70.3, 71.0, 101.6, 102.0, 106.3, 107.1, 115.1, 122.3, 124.4, 135.6, 138.8, 147.0, 151.0; MS (MALDI) *m/z* 1268.2015 (M + H).

1c. Following the procedure for **1a**, [G-2]-Br (0.34 g, 0.27 mmol), THF (20 mL), 4,4'-hydroxyazobenzene (28 mg, 0.13 mmol), potassium carbonate (40 mg, 0.28 mmol), and 18-crown-6 (7 mg, 0.026 mmol) yielded, after purification by flash column chromatography (SiO₂, 9:1 hexanes–ethyl acetate), **1c** as a yellow solid (0.27 g, 78%): ¹H NMR (500 MHz, CDCl₃) δ 7.88 (d, 4H, *J* = 8.5 Hz), 7.43 (t, 8H, *J* = 2.0 Hz), 7.30 (d, 16H, *J* = 2.0 Hz), 7.08 (d, 4H, *J* = 8.5 Hz), 6.76 (d, 8H, *J* = 2.0 Hz), 6.74 (t, 4H, *J* = 2.0 Hz), 6.67 (t, 4H, *J* = 2.0 Hz), 6.64 (t, 2H, *J* = 2.0 Hz), 5.10 (s, 4H), 5.03 (d, 24H, *J* = 8.0 Hz), 1.31 (s, 144H); ¹³C NMR (62.9 MHz, CDCl₃) δ 31.5, 34.8, 70.1, 71.0, 101.5, 101.7, 103.1, 106.3, 115.1, 122.3, 124.4, 135.7, 139.0, 139.2, 147.2, 151.0, 160.2, 160.4, 160.6; MS (MALDI) *m/z* 2565.509, 2588.581 (M + Na), 2604.560 (M + K).

1d. A solution of [G-3]-Br (0.30 g, 0.12 mmol), acetone (10 mL), 4,4'-hydroxyazobenzene (12 mg, 0.059 mmol), potassium carbonate (16 mg, 0.12 mmol), and 18-crown-6 (3 mg, 0.012 mmol) was maintained at reflux overnight. After the reaction was complete by TLC (SiO₂, 9:1 hexanes–ethyl acetate), the mixture was filtered and the solvent was concentrated. The residue was purified by flash column chromatography (SiO₂, 9:1 hexanes–ethyl acetate) to afford **1d** as a yellow solid (0.17 g, 59%): ¹H NMR (500 MHz, CDCl₃) δ 7.86 (d, 4H, *J* = 9.0 Hz), 7.37 (t, 16H, *J* = 2.0 Hz), 7.25 (d, 32H, *J* = 2.0 Hz), 7.03 (d, 4H, *J* = 9.0 Hz), 6.71 (d, 16H, *J* = 2.0 Hz), 6.70 (t, 8H, *J* = 2.0 Hz), 6.69 (d, 4H, *J* = 2.0 Hz), 6.63 (t, 8H, *J* = 2.0 Hz), 6.61 (t, 4H, *J* = 2.0 Hz), 6.59 (t, 2H, *J* = 2.0 Hz), 5.28 (s, 4H), 5.01 (s, 56H), 1.29 (s, 288H); ¹³C NMR (62.9 MHz, CDCl₃) δ 31.4, 34.8, 70.1, 71.0, 101.6, 106.5, 122.5, 135.7, 139.0, 151.0, 160.2, 160.4; MS (MALDI) *m/z* 5183.338 (M + Na).

1e. Following the procedure for **1d**, [G-4]-Br (0.38 g, 0.074 mmol), acetone (10 mL), 4,4'-hydroxyazobenzene (8 mg, 0.037 mmol), potassium carbonate (10 mg, 0.074 mmol), and 18-crown-6 (2 mg, 0.001 mmol) yielded, after purification by flash column chromatography (SiO₂, 9:1 hexanes–ethyl acetate), **1e** as a yellow solid (0.17 g, 59%): ¹H NMR (500 MHz, CDCl₃) δ 7.85 (d, 4H, *J* = 8.0 Hz), 7.36 (t, 32H, *J* = 2.0 Hz), 7.24 (d, 64H, *J* = 2.0 Hz), 6.89 (d, 4H, *J* = 8.0 Hz), 6.70 (m, 120H), 6.61–6.58 (m, 30H), 4.97 (s, 124H), 1.30 (s, 576H). ¹³C NMR (62.9 MHz, CDCl₃) δ 31.4, 34.8, 70.1, 71.0, 101.6, 106.5, 106.6, 122.227, 122.3, 135.7, 139.0, 151.0, 160.2, 160.4; MS (MALDI) *m/z* 10386.144 (M + Na).

2a. A heavy-walled glass tube joined to a Teflon screw valve was charged with **4** (0.956 g, 2.0 mmol), 3,5-di-*tert*-butylphenylacetylene (0.856 g, 4 mmol), Pd(dba)₂ (46 mg, 0.08 mmol), CuI (15 mg, 0.08 mmol), PPh₃ (105 mg, 0.4 mmol), LiCl (504 mg, 12 mmol), and Et₃N (20 mL). The mixture was freeze–pump–thaw degassed three times at –78 °C, sealed, and heated at 80 °C for 4 days. The mixture was filtered and the solvent was evaporated under reduced pressure. Purification of the residue by flash chromatography (SiO₂, hexane increasing to 8:1 hexane–CH₂Cl₂) gave **2a** as a red solid (0.47 g, 64%): ¹H NMR (500 MHz, C₆D₆) δ 7.90 (d, *J* = 6.5 Hz, 4H), 7.72 (m, 4H), 7.60 (d, *J* = 6.5 Hz, 4H), 7.53 (m, 2H), 1.23 (s, 36H); ¹³C NMR (62.9 MHz, C₆D₆) δ 31.3, 35.4, 89.0, 94.2, 122.2, 123.32, 123.6, 123.6, 124.8, 124.6, 132.8, 151.4; MS (MALDI) *m/z* 606.3180.

2b. A heavy-walled glass tube joined to a Teflon screw valve was charged with **7** (0.13 g, 0.56 mmol), I-M₃-(t-Bu)₄ (0.74 g, 1.2 mmol), Pd(dba)₂ (13 mg, 0.023 mmol), CuI (4 mg, 0.023 mmol), PPh₃ (30 mg, 0.11 mmol), and Et₃N (20 mL). The mixture was degassed three times at –78 °C, sealed, and heated at 60 °C for 17 h. The mixture was filtered and the solvent was evaporated under reduced pressure to give the crude product, which was purified by flash chromatography (SiO₂, hexane increasing to 4:1 hexane–CH₂Cl₂) to give **2b** as a red solid (0.34 g, 49%): ¹H NMR (500 MHz, C₆D₆) δ 7.94 (d, *J* = 5 Hz, 4H),

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7.84 (t, $J = 1.5$ Hz, 4H), 7.78 (d, $J = 1.5$ Hz, 4H), 7.71 (m, 8H), 7.51 (d, $J = 5$ Hz, 4H), 1.23 (s, 72H); ^{13}C NMR (62.9 MHz, C_6D_6) δ 31.4, 34.9, 87.4, 91.0, 91.3, 92.8, 122.8, 123.3, 123.6, 124.4, 125.1, 126.3, 126.6, 132.9, 134.4, 151.4; MS (MALDI) m/z 1232.0717 (M + H).

2c. Following the procedure for **2b**, **7** (100 mg, 0.435 mmol), I-M₇-(t-Bu)₈ (1.20 g, 0.956 mmol), Pd(dba)₂ (10 mg, 0.017 mmol), CuI (3.3 mg, 0.017 mmol), PPh₃ (23 mg, 0.087 mmol), and Et₃N (40 mL) yielded, after purification by flash chromatography (SiO₂, hexane increasing to 4:1 hexane-CH₂Cl₂), **2c** as a red solid (0.67 g, 62%): ^1H NMR (500 MHz, C_6D_6) δ 7.96 (d, $J = 8.5$ Hz, 4H), 7.86 (t, $J = 1.5$ Hz, 4H), 7.81 (d, $J = 1.5$ Hz, 8H), 7.72–7.69 (m, 24H), 7.68–7.67 (m, 2H), 7.60 (d, $J = 8.5$ Hz, 4H), 7.53 (t, $J = 1.5$ Hz, 4H), 1.24 (s, 144H); ^{13}C NMR (62.9 MHz, C_6D_6) δ 31.4, 34.9, 87.4, 90.0, 91.0, 91.2, 92.8, 122.8, 123.4, 123.7, 124.2, 125.2, 126.6, 132.9, 134.4, 151.4; MS (MALDI) m/z 2481.572.

2d. Following the procedure for **2b**, **7** (60 mg, 0.26 mmol) and I-M₁₅-(t-Bu)₁₆ (1.30 g, 0.52 mmol), Pd(dba)₂ (6 mg, 0.01 mmol), CuI (2 mg, 0.01 mmol), PPh₃ (14 mg, 0.052 mmol), and Et₃N (20 mL) yielded, after purification by flash chromatography (SiO₂, hexane increasing to 4:1 hexane-CH₂Cl₂), **2d** as a red solid (0.82 g, 63%): ^1H NMR (500 MHz, C_6D_6) δ 7.96 (d, $J = 8.0$ Hz, 4H), 7.84 (s, 8H), 7.82 (s, 16H), 7.81 (s, 4H), 7.73 (d, $J = 1.5$ Hz, 8H), 7.68 (m, 38H), 7.61 (d, $J = 8.0$ Hz, 4H), 7.51 (s, 16H), 1.24 (s, 288H); ^{13}C NMR (62.9 MHz, C_6D_6) δ 31.36, 34.86, 87.40, 89.24, 89.92, 90.14, 92.84, 122.81, 123.33, 123.66, 124.13, 124.50, 125.19, 126.58, 132.91, 134.39, 135.03, 151.30; MS (MALDI) m/z 4983.610.

2e. Following the procedure for **2b**, **7** (48 mg, 0.21 mmol), I-M₃₁-(t-Bu)₃₂ (2.1 g, 0.42 mmol), Pd(dba)₂ (4.8 mg, 0.008 mmol), CuI (1.6 mg, 0.008 mmol), PPh₃ (11 mg, 0.04 mmol), and Et₃N (20 mL) yielded, after purification by flash chromatography (SiO₂, hexane increasing to 4:1 hexane-CH₂Cl₂), **2e** as a red solid (1.05 g, 51%): ^1H NMR (500 MHz, C_6D_6) δ 7.96 (d, $J = 8.0$ Hz, 4H), 7.84 (d, $J = 1.5$ Hz, 16H), 7.82 (d, $J = 1.5$ Hz, 8H), 7.81 (d, $J = 1.5$ Hz, 32H), 7.80 (d, $J = 1.5$ Hz, 4H), 7.76 (d, $J = 1.5$ Hz, 16H), 7.71–7.65 (m, 78H), 7.59 (d, $J = 8.0$ Hz, 4H), 7.51 (d, $J = 1.5$ Hz, 32H), 1.24 (s, 576H); ^{13}C NMR (62.9 MHz, C_6D_6) δ 31.36, 34.85, 87.40, 89.48, 89.92, 90.14, 92.84, 122.81, 123.33, 123.66, 124.13, 124.50, 125.19, 126.58, 132.91, 134.39, 135.03, 151.30; MS (MALDI) m/z 10 037 (M + Cu).

4,4'-Dihydroxyazobenzene Ditriflate (4). To a solution of **3** (1.0 g, 4.67 mmol) in 10 mL of pyridine under nitrogen was added Tf₂O

(1.73 mL, 10.28 mmol) at 0 °C over 10 min. After the addition completed, the mixture was stirred at room temperature for another 2 h. Then 20 mL of water was added to quench the reaction. The mixture was extracted with hexane (2 × 100 mL) and dried (MgSO₄) and the solvent was evaporated under reduced pressure to give the crude product, which was purified by flash column chromatography (SiO₂, 10:1 hexane-ether) to afford the solid **4** (1.37 g, 61%): ^1H NMR (250 MHz, CDCl₃) δ 8.04 and 7.94 (AA'BB' pattern, $J = 8.7$ Hz, 4H); ^{13}C NMR (62.9 MHz, CDCl₃) δ 151.3, 151.2, 124.9, 122.3, 121.3.

4,4'-Bis(trimethylsilylethynyl)azobenzene (6).¹⁹ A heavy-walled glass tube joined to a Teflon screw valve was charged with azobenzene **5**¹⁵ (2.8 g, 6.45 mmol), trimethylsilylacetylene (2.53 g, 25.8 mmol), Pd(dba)₂ (148 mg, 0.258 mmol), CuI (49 mg, 0.258 mmol), PPh₃ (338 mg, 1.29 mmol), and Et₃N (50 mL). The mixture was freeze-pump-thaw degassed three times at -78 °C, sealed, and heated at 60 °C for 17 h. The mixture was filtered and the solvent was evaporated under reduced pressure to give the crude product, which was purified by flash chromatography (SiO₂, hexane) to give **6** as a red solid (92%, 2.2 g): ^1H NMR (500 MHz, C_6D_6) δ 7.85 and 7.59 (AA'BB' pattern, $J = 5.0$ Hz, 4H), 0.24 (s, 18H); ^{13}C NMR (62.9 MHz, CDCl₃) δ 151.8, 132.8, 126.0, 122.9, 104.6, 97.3, -0.1.

4,4'-Bis(ethynyl)azobenzene (7).¹⁹ To a solution of **6** (1.5 g, 4.0 mmol) in 60 mL of THF/H₂O (5:1) at room temperature was added ⁿBu₄N⁺F⁻ (2.3 g, 8.8 mmol). The mixture was stirred overnight. The solvent was evaporated under reduced pressure, the residue was dissolved in ethyl acetate (50 mL), and the organic layer was dried over MgSO₄ and evaporated to give the crude product, which was purified by flash column chromatography (SiO₂, 4:1 hexane-CH₂Cl₂) to give **7** as a solid (0.82 g, 89%): ^1H NMR (500 MHz, C_6D_6) δ 7.88 and 7.64 (AA'BB' pattern, $J = 8.6$ Hz, 4H), 3.22 (s, 2H); ^{13}C NMR (62.9 MHz, CDCl₃) δ 138.4, 133.0, 125.0, 122.9, 83.2, 79.7.

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