



Soluble dipolar dendrimers with peripheral sulfone groups

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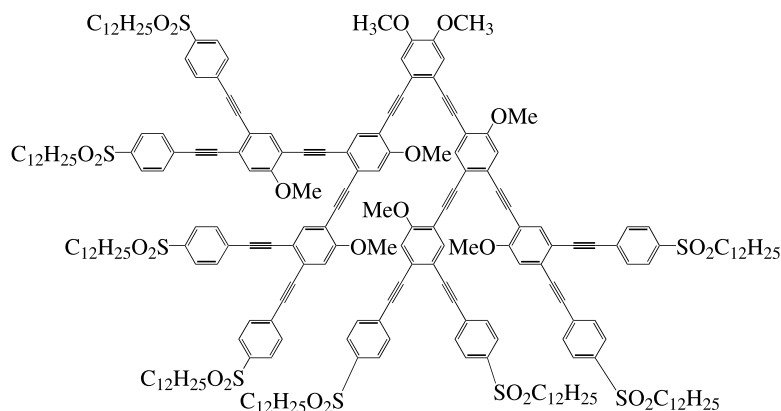
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Abstract—A dipolar dendron based on *meta* and *para* linked poly(phenyl acetylene)s with eight electron donor–acceptor pairs in direct conjugations is synthesized through a convergent approach. © 2002 Published by Elsevier Science Ltd.

Organic conjugated molecules and polymers are electrically active materials that have found increasing applications as active components in a number of electronic devices,¹ such as light emitting diodes (LEDs),² field-effect transistors (FETs),³ solid state lasers,⁴ and other electro-optic devices.⁵ As a fundamentally new macromolecular architecture, dendritic conjugated macromolecules have also been developed in recent years.⁶ The π -conjugated segments in these dendrimers impart interesting photophysical properties⁷ and applications in, for example, LEDs have been demonstrated.⁸ However, application of conjugated dendrimers as nonlinear optical (NLO) materials has received less attention.⁹ This is not surprising as the π -conjugations of the majority of the conjugated dendrimers, due to the interruption by the commonly applied *meta*-branching scheme, are rather limited. It is also synthetically challenging to introduce multiple electron donor–acceptor pairs into the dendritic structure in a way so that they

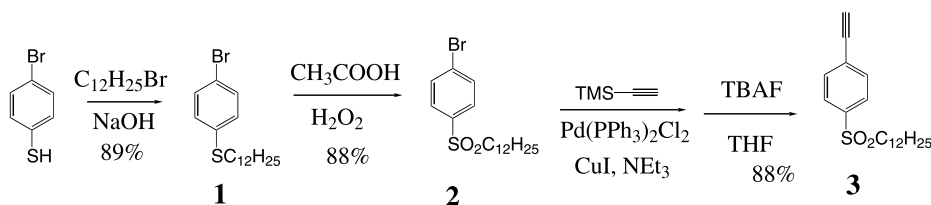
all contribute to the overall nonlinearity. In this paper, we report the synthesis of a third generation dendron, shown as **G3**, which is based on asymmetrically branched phenyl acetylene.¹⁰ Sulfone, as the electron-withdrawing group, is introduced to the *para* position of each peripheral phenyl ring. To improve the solubility, a long alkyl chain is attached to the sulfone group. There are eight methoxy groups as the electron donors, distributed at the core and the center-layer phenyl rings. Each methoxy group forms a conjugated pair with one sulfone group, which constitutes a traditional linear organic NLO active chromophore.¹¹ The **G3** dendron thus contains eight chromophores in one molecule. Due to steric interactions, the dendron likely adopts a three-dimensional (3D) conformation, thus representing a unique 3D chromophore where both the diagonal and off-diagonal β -components (β is the first hyperpolarizability) will contribute to the overall nonlinearity.¹²



G3

Keywords: dendrimers; electronic spectra; dipole moments.

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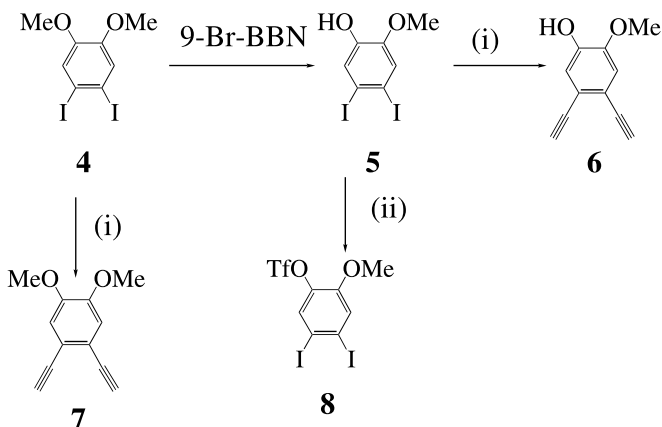


Scheme 1.

G3 was synthesized through a convergent approach, which starts from the exterior of the eventual dendron.⁶ The peripheral unit (compound **3**) was synthesized according to Scheme 1. Starting from 4-bromobenzene-1-thiol, alkylation of thiol with 1-bromododecane gives compound **1** in 89% yield. Subsequent oxidation of sulfide to sulfone yields **2**. Palladium-catalyzed coupling between aryl bromide with trimethylsilylacetylene, followed by desilylation gives compound **3** in 88% overall yield (from **2**).

Except for the peripheral phenyl rings, all other phenyl groups in **G3** have a 1,2,4,5 substitution pattern. Five compounds (**4–8**) with such a substitution scheme were synthesized as the building blocks for the construction of the dendron series (**G1**, **G2**, **G3**). The syntheses for such compounds are shown in Scheme 2.

The syntheses of **4**, **5** and **6** have previously been reported.¹⁰ Compound **7** was prepared from **4** by the Sonogashira coupling reaction.¹³ Compound **8** was synthesized from **5** in excellent yields.



Scheme 2. (i) (a) Trimethylsilylacetylene, Pd(PPh₃)₂Cl₂, CuI, NEt₃, DMF; (b) Bu₄NF, THF; (ii) (CF₃SO₂)₂O/pyridine.

The iterative synthesis to **G3** as well as the synthesis to lower-generation dendrons **G1** and **G2**, is shown in Scheme 3. Direct coupling between **3** (2 equiv.) and **4** gives **G1** in 67% yield. To prepare higher-generation dendrons, a first generation dendron with a triflate group at the core, **G1-OTf**, was synthesized by the coupling of **3** with **8**, taking advantage of the higher reactivity of iodo over triflate in the Sonogashira coupling reaction.¹⁴ The cross-coupling of triflate with acetylene could be carried out between **G1-OTf** and **7** to give **G2** in 74% yield or between **G1-OTf** and **6** to give **G2-OH** in 67% yield. Conversion of **G2-OH** to **G2-OTf** is trivial and efficient. Similar to the synthesis of **G2**, **G3** was prepared from the coupling of triflate with acetylene.¹⁵ The yield is 58%. It should be noted that the procedures from **G1-OTf** to **G3**, namely **G1-OTf**→**G2-OH**→**G2-OTf**→**G3**, could be repeated on

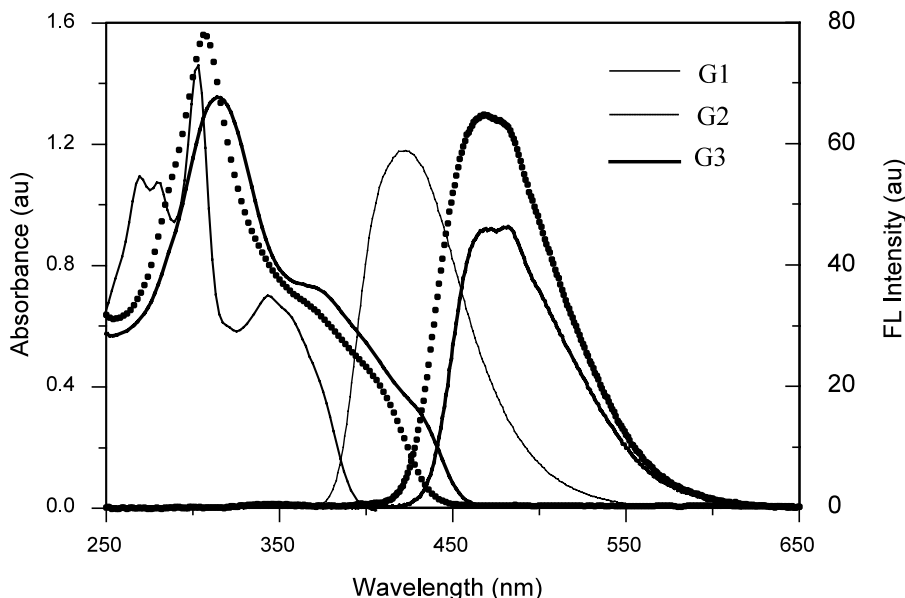
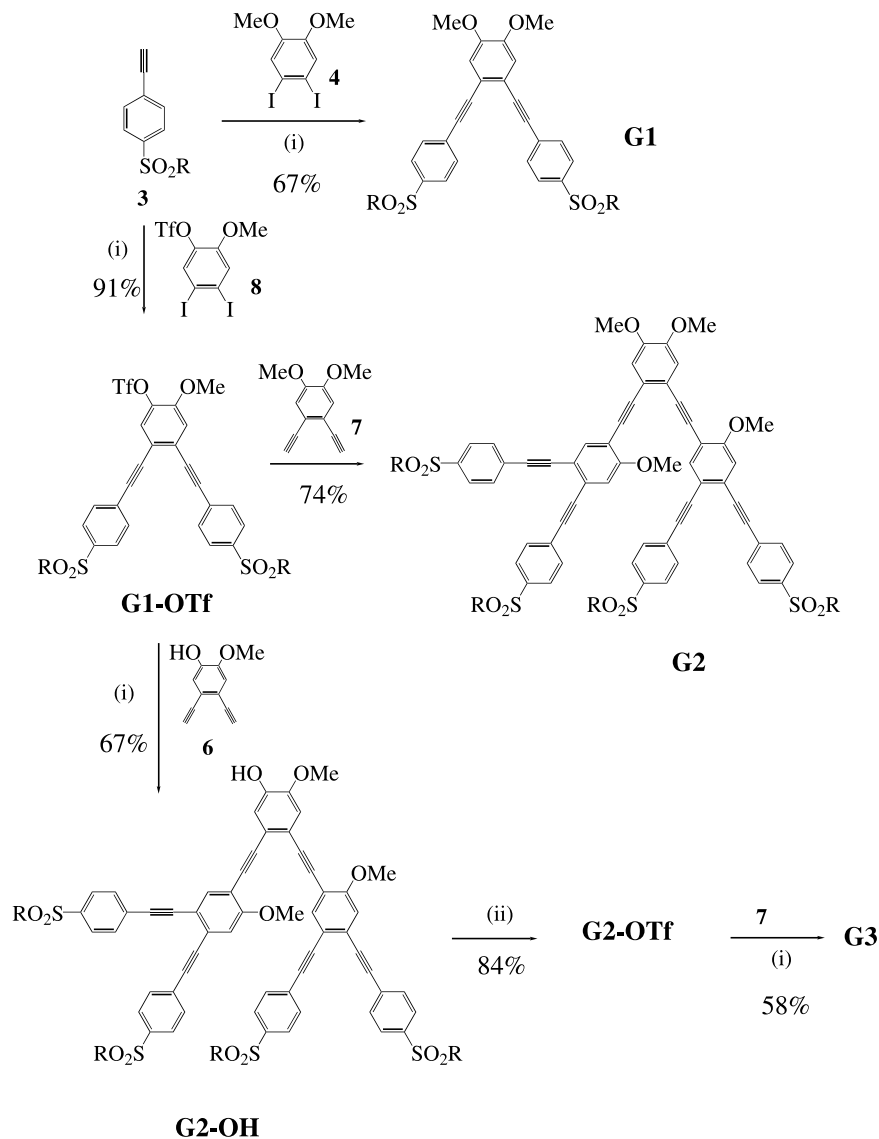


Figure 1. UV-vis absorption and fluorescence emission spectra of **G1–G3**.



Scheme 3. (i) Pd(PPh₃)₂Cl₂, CuI, NEt₃, DMF; (ii) (CF₃SO₂)₂O/pyridine.

G2-OTf (\rightarrow **G3OH** \rightarrow **G3-OTf** \rightarrow **G4**) to prepare even higher generation dendrons.

UV–vis absorption and fluorescence emission spectra of these dendrons are shown in Fig. 1. From **G1** to **G2**, significant red shift (~ 50 nm) is observed for both the absorption and emission spectra. Compared to **G2**, however, **G3** has only a slightly red-shifted (~ 5 nm) absorption spectra. Both dendrons have nearly identical fluorescence emission except that the emission edge of **G3** is slightly red-shifted. These results are different from those obtained on unsymmetrical dendrimers without electron-withdrawing groups, where significant red shifts (~ 30 nm) are observed for both absorption and emission spectra of **G3** over **G2**.¹⁰

In summary, we report the synthesis of soluble dipolar dendrons based on conjugated dendrimers. The outlined synthetic approach can be applied to prepare similar dendrons with other electron-withdrawing groups.¹⁶ Studies on the dipole moments and hyperpolarizabilities of these NLO dendrons are in progress.

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15. **G1**: Mp: 96–98°C. ¹H NMR (CDCl₃, 400 MHz) δ 0.88 (t, *J*=6.0 Hz, 6H, CH₂CH₃), 1.2–1.4 (m, 36H, (CH₂)₉), 1.74 (m, 4H, CH₂), 3.11 (t, *J*=7.6 Hz, 4H, SCH₂), 3.97 (s, 6H, OCH₃), 7.07 (s, 4H, Ar-H), 7.70 (d, *J*=6.8 Hz, 4H, Ar-H), 7.90 (d, *J*=6.8 Hz, 4H, Ar-H). LR-FAB for C₄₈H₆₆O₆S₂ calcd 802.43. Found: 803. **G2**: Mp: 181–184°C. ¹H NMR (CDCl₃, 250 MHz): δ 0.88 (m, 12H, CH₂CH₃), 1.2–1.8 (m, 80H, CH₂), 3.03 (t, *J*=7.9 Hz, 4H, SCH₂), 3.13 (t, *J*=7.9 Hz, 4H, SCH₂), 3.97 (m, 12H, OCH₃), 7.11 (d, 4H, *J*=8.5 Hz, Ar-H), 7.58 (d, 4H, *J*=8.5 Hz, Ar-H), 7.70 (d, 4H, *J*=8.5 Hz, Ar-H), 7.80 (s, 2H, Ar-H), 7.83 (s, 4H, Ar-H), 7.94 (d, *J*=8.5 Hz, 4H, Ar-H). LR-FAB for C₁₀₆H₁₃₄O₁₂S₄ calcd 1726.88. Found: 1727.2. **G3**: Mp: 202–205°C. ¹H NMR (CDCl₃, 250 MHz): δ 0.88 (m, 6H, CH₂CH₃), 1.2–1.8 (m, 160H, CH₂), 3.10 (m, 16H, SCH₂), 3.95 (m, 24H, OCH₃), 7.10 (m, 8H, Ar-H), 7.52 (m, 8H, Ar-H), 7.62 (d, 4H, *J*=8.5 Hz, Ar-H), 7.68 (d, 4H, *J*=8.5 Hz, Ar-H), 7.76 (d, 4H, *J*=8.5 Hz, Ar-H), 7.76 (s, 4H, Ar-H), 7.79 (s, 4H, Ar-H), 7.85 (s, 2H, Ar-H), 7.88 (s, 4H, Ar-H), 7.95 (d, *J*=8.5 Hz, 4H, Ar-H). MALDI-TOF for C₂₂₂H₂₇₀O₂₄S₈ calcd 3575.77. Found: 3578.31.
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