

# $\pi$ -Conjugated Dendrimers Based on Bis(enediynyl)benzene Units

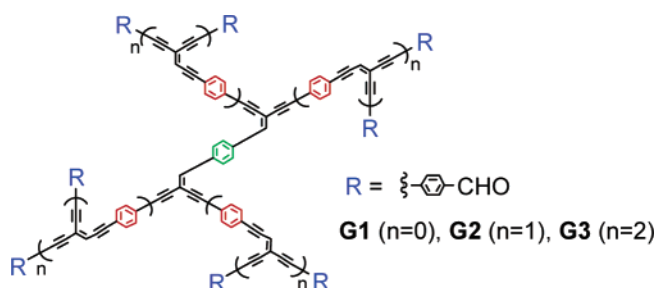
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## ABSTRACT

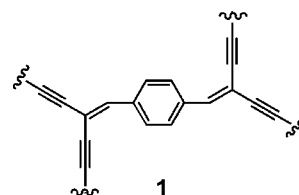


We have synthesized a new family of  $\pi$ -conjugated dendrimers that are based on bis(enediynyl)benzene units by using both divergent and convergent approaches. The compounds at all three generations have strong bluish-green fluorescence, especially the third-generation dendrimer, which has the highest extinction coefficient and quantum efficiency in this series.

The past several decades have been witness to dramatic developments in the field of organic and polymer light-emitting diodes (LEDs).<sup>1</sup> Whereas low-molecular-weight organic materials can be processed into device structures by thermal evaporation under high vacuum, polymers can be deposited simply by spin-coating or even printing.<sup>2</sup> Excellent progress has been made in the efficiencies and lifetimes of devices and in the tuning of colors using both low-molecular-weight organic materials and polymers. Dendrimers are organic macromolecules that have a regular array of highly branched units surrounding a central core.<sup>3</sup> A wide range of synthetic methodologies have been applied to the efficient synthesis of dendrimers. Two general approaches are used commonly to synthesize these molecules, namely the divergent growth approach and the convergent approach.<sup>3</sup> Along

with flexible backbone dendrimers,  $\pi$ -conjugated dendritic molecules have received considerable attention as a new class of LED materials.<sup>4</sup> These shape-persistent macromolecules, which have well-defined nanometer sizes and intrinsic rigidity, exhibit interesting physical and chemical properties.

Curiously, there have been few examples of  $\pi$ -conjugated dendrimers based on bis(enediynyl)benzene (Figure 1).



**Figure 1.** Bis(enediynyl)benzene.

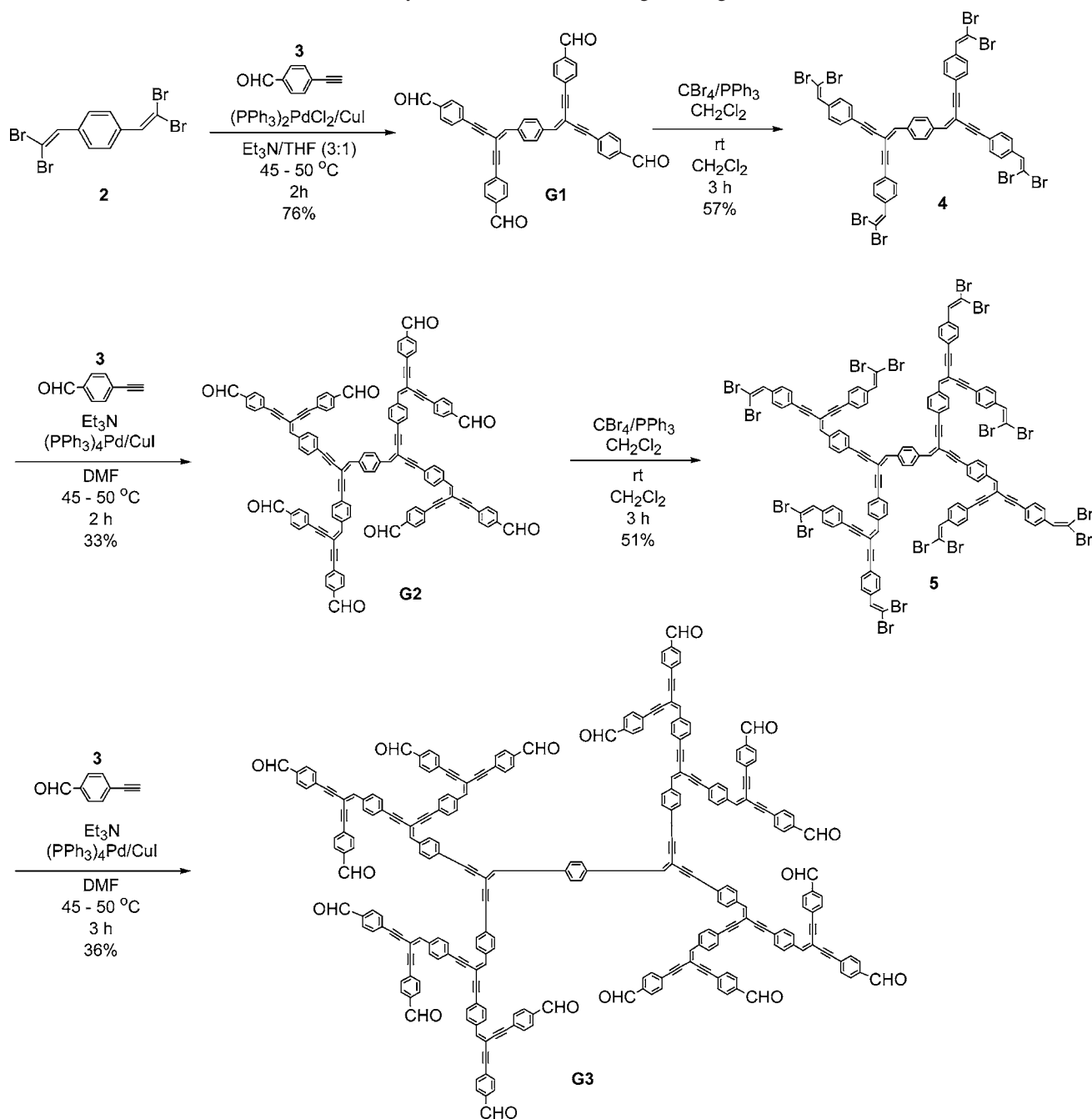
Recently, we and Neckers' group reported that bis(enediynyl)aryl compounds possess photophysical and photochemical properties that are appropriate for various applications as materials.<sup>5,6</sup> In this paper, we present our design, synthesis, and photophysical studies of bis(enediynyl)benzene-based

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**Scheme 1.** Synthesis of Dendrimers Using a Divergent Method



dendrimers that we prepared using both divergent and convergent synthetic methodologies.

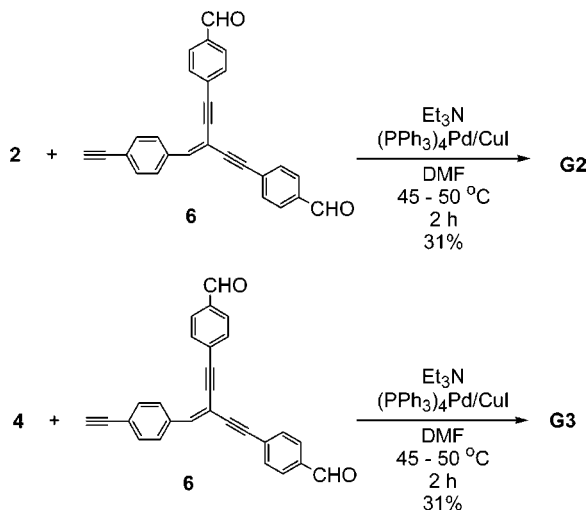
The divergent approach we followed to prepare our dendrimers is illustrated in Scheme 1. The synthetic strategy we used to construct the bis-enediynes involved alternating Sonogashira reactions<sup>7</sup> and Corey–Fuchs dibromoolefinations<sup>8</sup> and began with 1,4-bis(2,2-dibromoethenyl)benzene **2**. The Sonogashira reactions between aryl bromides (**2**, **4**, and **5**) and 4-ethynylbenzaldehyde<sup>9</sup> (**3**) proceeded smoothly to afford dendrimers **G1**, **G2**, and **G3**, respectively, in moderate yields (33–76%). Considering the rigidity and steric hindrance in **G3**, the yield of 36% is quite remarkable. The dibromoolefinations were relatively clean and

only a few side products were formed in the Sonogashira reactions in addition to the desired products.

A convenient method for dendrimer synthesis is the assembly of dendrons to a core unit (i.e., the convergent approach), which is used widely to form functional dendrimers or simply to enlarge a compound.<sup>10</sup> We adopted this method to synthesize **G2** and **G3**, as indicated in Scheme 2, using the readily available ethynyldibenzaldehyde<sup>11</sup> **6** as a dendron. Pd/Cu-catalyzed cross-coupling of **2** and **4** with dendron **6** afforded the dendritic molecules **G2** and **G3**, respectively, which bear peripheral aldehyde units.

All of these dendritic molecules are quite stable toward air and commonly used organic solvents; they are slightly

**Scheme 2.** Synthesis of Dendrimers Using a Convergent Method



soluble in  $\text{CHCl}_3$ , THF, DMF, and DMSO. We confirmed the structures of all these dendrimers by  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy, mass spectrometry, and elemental analysis.<sup>12</sup> The observed chemical shifts in the  $^1\text{H}$  NMR spectra are very similar within this series of compounds. All dendrimers **G1–G3** possess proton chemical shifts at ca. 10 ppm that are due to their formyl groups. We confirmed the structures of the dendrimers clearly by mass spectrometry. The mo-

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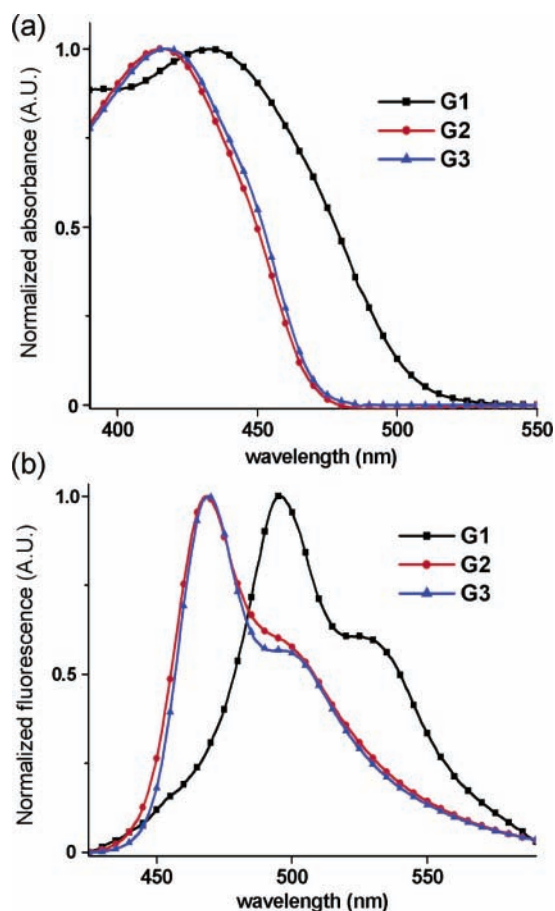
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(12) See the Supporting Information.

lecular ions in the FAB mass of **G1** and **G2** were found at  $m/z$  643.3 and 1659.1, which are consistent with the calculated values of  $m/z$  643.2 and 1659.5, respectively. MALDI-TOF analysis verified the monodisperse nature of **G3**; the mass of its molecular ion,  $m/z$  3691.2, is consistent with the calculated value of  $m/z$  3691.1. The values of  $M_n$  of **G1–G3** obtained by gel permeation chromatography (GPC) measurements using polystyrene standards—540, 860, and 1500, respectively—were lower than the mass spectrometry-derived molecular weights.<sup>12</sup> These significant deviations between GPC and MS results, especially for **G3**, may reflect the dissimilar shapes of these dendrimers, which are compact and spherical in solution, and the polystyrene standards.<sup>4f,13</sup>

Table 1 summarizes the photophysical properties of dendritic molecules **G1–G3**, **4**, and **5** in  $\text{CHCl}_3$  solutions. We determined the fluorescence quantum yields ( $\phi_F$ ) of the fluorophores in  $\text{CHCl}_3$ , using a 0.1 N aqueous NaOH solution of fluorescein as a standard.<sup>14</sup>

The UV–vis absorption spectrum of the **G1** dendrimer displays an absorption maximum at 433 nm. The relative blue shifts observed for **G2** and **G3** probably are due to the substitution effect of the aldehyde group: As the generations increase, the formyl groups are located further from the core (Figure 2a). The emission maxima of the dendrimers are



**Figure 2.** Normalized (a) absorbance and (b) fluorescence spectra of dendrimers **G1–G3** recorded in  $\text{CHCl}_3$  at 20 °C. Emission spectra were obtained upon excitation at the absorption maxima.

**Table 1.** Photophysical Data of the Dendrimers in CHCl<sub>3</sub>

compd	$\lambda_{\text{abs}}/\text{nm}^a$	$\epsilon/\text{mol}^{-1} \text{ cm}^{-1}$	$\lambda_{\text{em}}/\text{nm}^{b,c}$	$\phi_{\text{F}}^d$
<b>G1</b>	433	22 500	497	0.38
<b>4</b>	411	45 300	497	0.35
<b>G2</b>	415	61 500	468	0.79
<b>5</b>	415	57 300	465	0.52
<b>G3</b>	418	86 000	469	0.80

<sup>a</sup> Only the largest absorption maximum is listed in each case. <sup>b</sup> Wavelength of emission maximum when excited at the absorption maximum. <sup>c</sup> Peaks contain a shoulder having a longer wavelength. <sup>d</sup> Quantum efficiencies were measured using fluorescein in 0.1 N NaOH as a standard,  $\lambda_{\text{ex}} = 436 \text{ nm}$ .

affected by this shift pattern in the absorption spectra. The fluorescence spectra of all these dendritic molecules show two strong emission bands in the visible region, which results in their bluish-green colors (Figure 2b). Although dendrimer **G3** has a longer conjugation length than **G2**, its absorbance and emission maxima are not red-shifted significantly, which presumably arises because of the torsion between the benzene rings that is caused by the increased steric hindrance as the number of generations increases. Interestingly, of this series of dendrimers, **G2** and **G3** possess the highest quantum efficiencies ( $\phi_{\text{F}} = 0.79$  and  $0.80$ , respectively).

There are two important points worth emphasizing. First, the synthetic approach—consecutive dibromoolefination and Sonogashira coupling—that we have developed here is very efficient for preparing the conjugated dendrimers via either

divergent or convergent methods. This approach is also very versatile for the syntheses of the dendrimers that possess different photophysical properties, which can be achieved through variations in the nature of the building molecules and the functional groups presented at the peripheries. The second point is that this synthetic approach, which is based on bis(enediynyl)benzene units, can be utilized in the design of functional materials because of their excellent quantum efficiencies.

We have prepared a new family of  $\pi$ -conjugated dendrimers, which are based on bis(enediynyl)benzene units, as potential candidates for materials applications by applying two synthetic approaches: a divergent method using alternating dibromoolefination and Pd/Cu-catalyzed cross-coupling and a convergent method using Pd/Cu-catalyzed cross-coupling between bromoaryl compounds and ethynyldibenzaldehyde as a dendron. The resulting dendrimers maintain uniform structures in terms of the linking units involved between the generations. All three generations of dendrimers exhibit strong bluish-green fluorescence, especially the third-generation one, **G3**, which has the highest extinction coefficient and quantum efficiency in the whole series of compounds. Hence, we believe that this approach will be applicable for the construction of other structurally uniform and well-defined  $\pi$ -conjugated functional dendrimers.

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**Supporting Information Available:** Complete experimental details (including <sup>1</sup>H and <sup>13</sup>C NMR spectroscopic, MS, GPC, and elemental analysis data). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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