

Luminescent Dendrons with Oligo(phenylenevinylene) Core Branches and Oligo(ethylene oxide) Terminal Chains

Liming Ding, Dongwook Chang, and Liming Dai*

Department of Chemical and Materials Engineering, School of Engineering, University of Dayton, Dayton, Ohio 45469

Tao Ji and Sinan Li

Department of Polymer Engineering, University of Akron, Akron, Ohio 44325

Jianping Lu and Ye Tao

Institute for Microstructural Sciences, National Research Council, Ottawa, Canada

Donavon Delozier and John Connell

NASA Langley Research Center, Hampton, Virginia 23681

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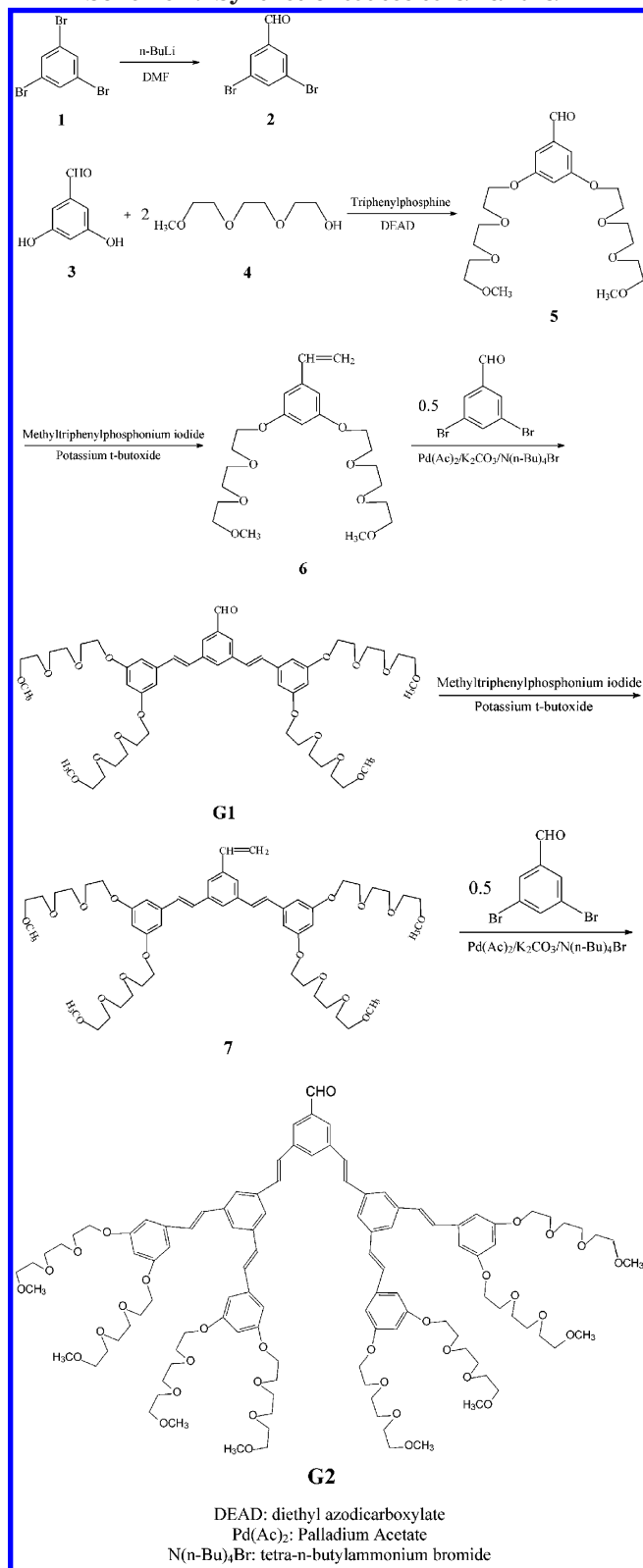
Introduction

The use of polymeric light-emitting diodes (LEDs) for flat panel displays offers many advantages, including large-area fabrication, light weight, flexibility, low operating voltage, and ease of color tuning.^{1,2} Since the discovery of electroluminescence from poly(*p*-phenylenevinylene) (PPV) in 1990,³ many light-emitting polymers have been developed,⁴ and polymer light-emitting devices of novel features (e.g., patterned multicolor emissions) attractive for practical applications have been made through intriguing molecule/device designs and constructions.^{1,4,5} Chemical modification can often adjust the band gap of light-emitting polymers, leading to effective color tuning of the devices.⁶ Continued interest in the exploration of new chromophore structures, and hence new emission properties, has spurred considerable attention on the design and synthesis of novel light-emitting materials. Dendritic macromolecules provide unique molecular architectures for various use in LEDs.⁷ They can be designed to possess conjugated core branches for an efficient emission and/or charge transportation with appropriate terminal groups/chains for good processability. For instance, Jenekhe et al.⁸ have developed n-type light-emitting conjugated dendrimers based on a benzene core and diphenylquinoline peripheral groups. LEDs based on these dendrimers as electron-transport layers showed good performance.

We have previously demonstrated that PPV derivatives with oligo(ethylene oxide) side chains show properties characteristic of two components with synergetic effects.⁵ The covalent linkages between PPV and oligo(ethylene oxide) constituents can effectively minimize the phase separation problem often associated with conventional light-emitting electrochemical cells (LECs).⁹ The oligo(ethylene oxide) side chains have also been demonstrated to facilitate the construction of light-emitting micropatterns by region-selective deposition of the chromophores through the oligo(ethylene oxide) polar groups.⁵

* Corresponding author. E-mail: ldai@udayton.edu.

Scheme 1. Synthetic Routes to G1 and G2



In this work, novel amphiphilic light-emitting dendrons with oligo(phenylenevinylene) core branches and oligo(ethylene oxide) terminal chains (OPV-*d*-OEO) were prepared. These dendrons combine the stiff and insoluble conjugated core branches with the highly flexible and soluble oligo(ethylene oxide) terminal chains

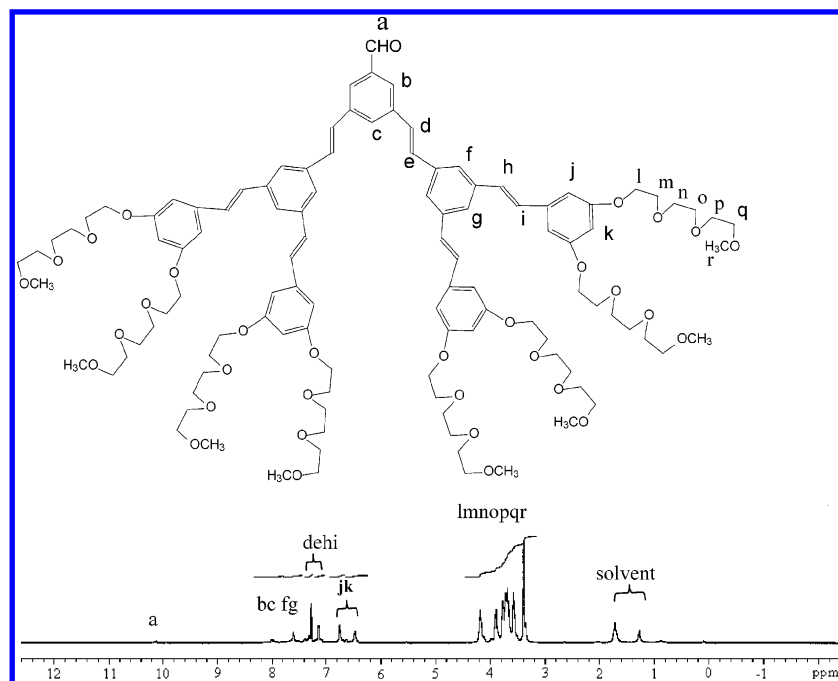


Figure 1. ^1H NMR spectrum of G2 in CDCl_3 .

into one macromolecule. Because of the amphiphilic properties arising from the large difference in solubility between the two constituent components, unique concentration-dependent photoluminescence (PL) was observed for aqueous solutions of these dendrons. The PL emission depends also strongly on solvent polarity. This paper presents the synthesis and characterization of OPV-*d*-OEO with a generation number of 1 (G1) and 2 (G2), along with their fluorescence properties in various solvents of different polarities.

Results and Discussion

As shown in Scheme 1, the amphiphilic dendrons are composed of an aldehyde focal point, conjugated stilbene core branch, and multiple triethylene glycol monomethyl ether groups at the periphery. To synthesize dendrons G1 and G2, 3,5-dibromobenzaldehyde (**2**) was prepared by reacting 1,3,5-tribromobenzene (**1**) with DMF in the presence of *n*-BuLi (*n*-butyllithium), followed by hydrolysis in 2 N HCl and purification via recrystallization. In the meantime, 3,5-triethyleneglycobenzaldehyde (**5**) was prepared via the Mitsunobu reaction¹⁰ of phenol with alcohol, which was then converted to compound **6** by the Wittig reaction.¹¹ Dendron G1 was then prepared in a high yield (80%) by Heck reaction¹² of **6** and 3,5-dibromobenzaldehyde. Dendron G2 was synthesized by first converting G1 into compound **7** via the Wittig reaction and then reacting **7** with 3,5-dibromobenzaldehyde through the Heck reaction. The yield of G2 by the Heck reaction is low (30%), partially due to the difficulties in the purification. Since crystallization is not applicable to the viscous liquid of G2, the most effective purification method for G2 is column chromatography. However, the much higher polarity of G2 relative to G1 makes the column chromatography of G2 very difficult. Both compound **7** and G2 have very strong interactions with silica gel matrix in the column, so high polar solvents are required for the elution. However, high polar solvents could also elute the side products together with G2 and **7**. Therefore, the suitable eluents for an effective separation of the desired product from

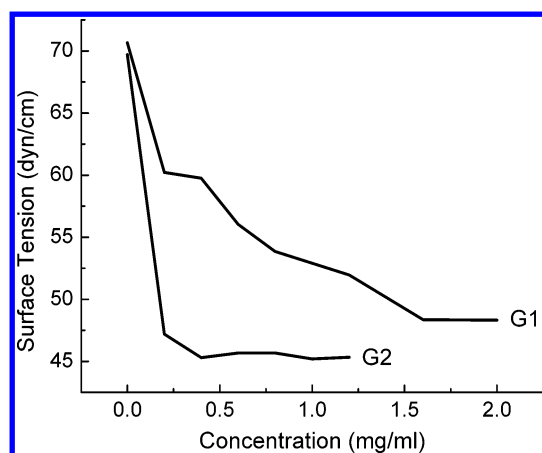


Figure 2. Concentration dependence of surface tension for G1 and G2 water solution at 20 °C.

the side products have to be those solvents of a relatively low polarity, though some loss of the product is inevitable due to the failure of completely eluting the product out from the silica gel column.

As expected, both dendrons G1 and G2 are soluble in most common organic solvents, such as chloroform, methylene dichloride, THF, methanol, and acetone. The good solubility facilitates their characterization by various solution methods. Figure 1 shows the ^1H NMR spectrum of G2 in CDCl_3 , which has been fully assigned. Since G1 and G2 contain hydrophobic and hydrophilic parts in one molecule, typical amphiphilic behavior can be expected in their solutions. Indeed, Figure 2 shows a decrease in the surface tension with increasing dendron concentration to a certain value (ca. 48.4 and 45.7 dyn/cm for G1 and G2, respectively) before leveling off with further increase in concentration due to the dendron aggregation. The critical aggregation concentration (CAC—a concentration above which aggregation occurs) for G1 and G2 was estimated to be 1.60 and 0.40 mg/mL, respectively. The much slower decrease of the surface tension with increasing concentration and the significantly higher CAC value observed for G1 with

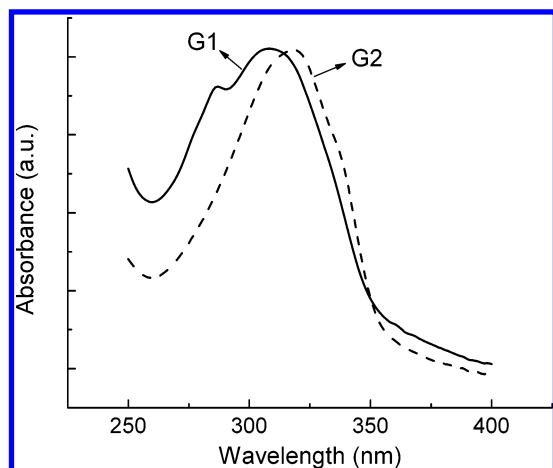


Figure 3. Absorption spectra for G1 and G2 in chloroform.

respect to G2 indicate a weaker tendency toward aggregation for G1 due to its relatively smaller molecular size. The longer stilbene branches and more oligo(ethylene oxide) terminal chains in G2 lead to relatively stronger intermolecular interactions and easier chain entanglements in solution and hence aggregation at a relatively lower concentration.

The absorption spectra of G1 and G2 in chloroform are given in Figure 3 with absorption peaks at 309 and 318 nm, respectively. Compared with G1, the 9 nm red shift in absorption for G2 is attributable to the longer conjugation length of its stilbene core. The fluorescence of G1 and G2 in solution was also investigated. Figure 4a shows a PL peak at 411 nm for an aqueous solution of G1 at concentration below CAC at room temperature. Above CAC, the PL peak red shifts to 418 nm due to the aggregation-induced π - π stacking which enhances π -electron delocalization over the aggregated stilbene cores. Similarly, G2 also shows a red shift in solution PL from 434 nm below CAC to 457 nm above CAC (Figure 4b). The larger red shift in PL for G2 solution (23 nm) compared with G1 solution proves again the stronger aggregation tendency for G2 (vide supra).

As G1 and G2 molecules consist of nonpolar stilbene core branches and highly polar ethylene oxide units, they can be regarded as polar molecules. By analogy to other bipolar molecules, therefore, G1 and G2 could show certain solvent-polarity-dependent molecular interactions and aggregate structures in solution. As expected, we observed a general trend, with some fluctuation, in the red shift of G2 PL with increasing solvent polarity above the CAC (see Table S1, Figure 5). In particular, the PL peak at 457 nm for G2 in water blue-shifted to 407 nm when a less polar solvent such as *p*-xylene was used. Since G2 is more soluble in a more polar solvent and the concentration used for all G2 solutions (0.67 mg/mL) is higher than the CAC in water (0.40 mg/mL), we believe that G2 molecules exist in aggregation form in all studied solutions. In a nonpolar solvent, the stilbene chromophore units are more randomly distributed in the solution due to the relatively strong interaction between the nonpolar solvent and stilbene units. In a polar solvent (e.g., water), however, strong interactions between the solvent molecules and the polar ethylene oxide chains could "stretch" the ethylene oxide chains relatively away from the stilbene chromophore core, facilitating the intermolecular interaction (aggregation) between the "naked" stilbene cores. This could lead to the formation of a 3-D supramolecular

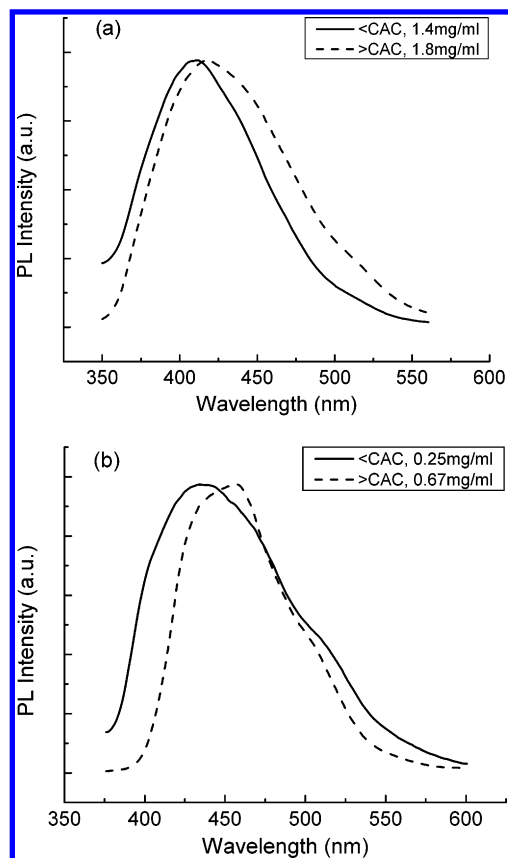


Figure 4. PL spectra for G1 (a) and G2 (b) in water.

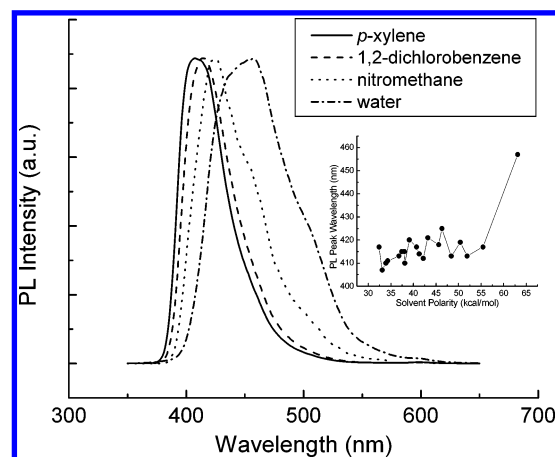


Figure 5. PL spectra of G2 in different solvents (0.67 mg/mL). The inset shows the effect of solvent polarity¹⁴ on PL peak wavelength for the G2 solutions (0.67 mg/mL).

assembly (possibly cylindrical or spherical dendrimer)¹³ with longer effective conjugation lengths and hence the remarkable red shift in PL, though the assembled supramolecular structures are unlikely to be monodispersed. The observed PL spectral broadening for water solution (Figure 5) can be attributable to possible excimer formation. The film PL spectra for G1 and G2 are given in Figure 6, which shows the same peak position at 437 nm with the FWHM values of 55 and 69 nm, respectively. The broader PL spectrum for G2 film suggests, once again, the significance of the excimer formation.

In summary, we have synthesized two novel amphiphilic light-emitting dendrons consisting of hydrophobic oligo(phenylenevinylene) core branches and hydrophilic oligo(ethylene oxide) terminal chains with a

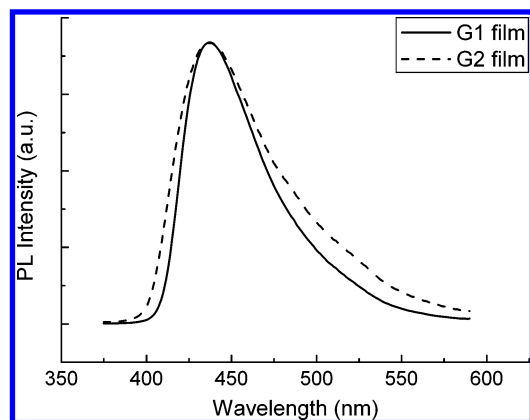


Figure 6. PL spectra for G1 and G2 films.

generation number of 1 (G1) and 2 (G2) and investigated their amphiphilic and fluorescent properties in solution. It was found that dendrons G1 and G2 possess CAC values of 1.60 and 0.40 mg/mL, respectively. The amphiphilic characteristics and the resultant aggregation behaviors led to interesting concentration- and solvent-polarity-dependent fluorescence in solutions. Solution PL spectra for these amphiphilic fluorescent dendrons display red shifts with increasing concentration and/or solvent polarity. The newly discovered solvatochromism in these dendrons could make them very attractive as a new generation of stimuli-responsive materials apart from their potential application in LECs.

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Supporting Information Available: Experimental details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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