

Amphiphilic light-emitting dendrons with oligo(phenylene vinylene) branches and oligo(ethylene oxide) terminal chains

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Abstract

We have recently synthesized new amphiphilic light-emitting dendrons with oligo(phenylene vinylene) core–branches and oligo(ethylene oxide) terminal chains (designated as: OPPV-*d*-OPEO). Due to the amphiphilic properties arising from the large difference in solubility between the two components, unique concentration- and temperature-dependent photoluminescence emissions were observed for aqueous solutions of the amphiphilic conjugated dendrons. The synthesis and amphiphilic behaviour of the OPPV-*d*-OPEO in solution are reported in this paper. Effects of the amphiphilic behavior on fluorescence emissions of the dendrons are discussed.

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1. Introduction

The use of polymeric electroluminescent diodes for flat panel displays offers many advantages, including their versatility for fabrication (especially over a large area), lightweight, flexibility, low operating voltage and the ease with which color tuning of light-emission can be achieved [1]. Since the discovery of the electroluminescent light-emission from conjugated poly(*p*-phenylene vinylene), PPV, reported by Friend's group in Cavendish Laboratory at Cambridge in 1990 [2], various other electroluminescent conjugated polymers have been synthesized [3] and many polymer light-emitting devices of novel features (e.g. patterned multi-color emissions) attractive for practical applications have been made through various intriguing device designs and constructions [1]. It is well known now that chemical modification can change the band gap energy of most light-emitting polymers, leading to color tuning for the emitted light. Continued interest in the exploration of new

luminescent structures, and hence novel light-emitting properties, has spurred considerable attention on the design and synthesis of novel conjugate light-emitting materials. In this context, dendritic macromolecules could provide unique molecular architectures for constructing functional conjugated structures of desirable light-emitting properties. For instance, they can be constructed to possess conjugated core/branches for an efficient light-emission and/or charge transportation and appropriate terminal groups/chains for good processability.

We have previously demonstrated that PPV derivatives with oligo(ethylene oxide) side chains show properties characteristic of both constituent components with synergetic effects [4]. It was found, for example, that the covalent linkages between the PPV and oligo(ethylene oxide) constituents could effectively minimize the phase separation problem often associated with conventional LEC devices [1], and that the oligo(ethylene oxide) side chains facilitated the construction of micropatterned light-emitting diodes by region-selective deposition of the light-emitting polymers through the oligo(ethylene oxide) polar groups [5]. In our further investigation on the design and synthesis of new light-emitting conjugated materials, we have recently prepared novel amphiphilic light-emitting dendrons with oligo(phenylene vinylene) core–branches and oligo(ethylene oxide) terminal chains (OPPV-*d*-OPEO). These newly-synthesized dendrons present an unusual situation where

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the stiffness characteristic of insoluble conjugated branches and the high flexibility and solubility associated with the oligo(ethylene oxide) terminal chains are combined into one macromolecule. Due to the amphiphilic properties arising from the large difference in solubility between the two constituent components, unique concentration-/temperature-dependent photoluminescence emissions were observed for aqueous solutions of the conjugated OPPV-*d*-OPEO dendrons. In this paper, we present the synthesis and amphiphilic behaviour of OPPV-*d*-OPEO in solution.

2. Experimental

2.1. Materials

1,3,5-Tribromobenzene, *n*-BuLi and triethylene glycol monomethyl ether were purchased from Aldrich. All of them were used as received. All catalysts and solvents were reagent grade and purchased from commercial sources. Experimental details for the synthesis and characterization of the conjugated dendrons and their intermediates are discussed below.

2.2. Characterization

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker AC-200 NMR spectrometer. Ultraviolet–visible (UV–vis) measurements were made on a Lamda 9 UV/vis spectrophotometer while photoluminescent (PL) emission measurements were performed on a Perkin-Elmer LS55 luminescence

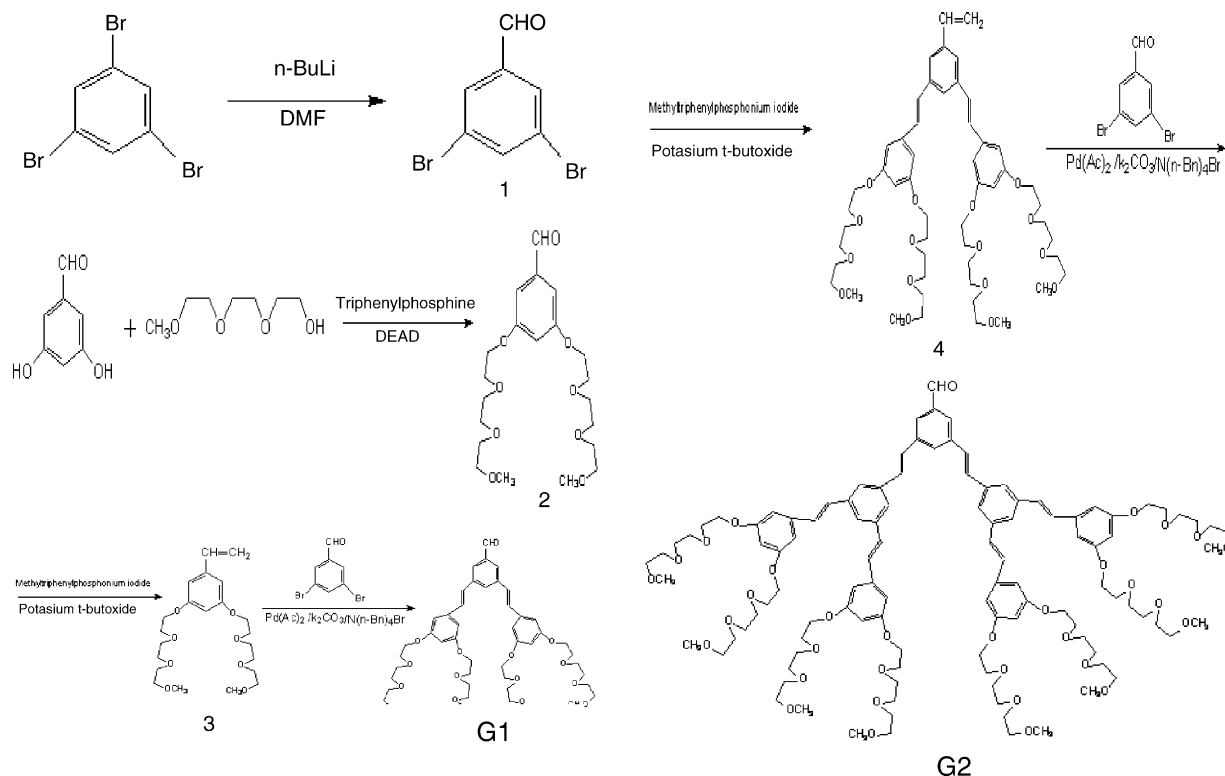
spectrometer. The surface tension of the dendron (both G1 and G2) solutions were measured on a dynamic surface contact angle unit. The concentration-dependent measurements of the surface tension were used to obtain the critical micelle concentration (CMC).

3. Results and discussion

3.1. Dendron synthesis and spectroscopic studies

The amphiphilic dendrons are composed of an aldehyde focal point, conjugated stilbene branch and multiple triethyleneglycolmonomethyl ether groups at the periphery. The synthetic strategy for the formation of dendron G1 and G2 was shown in Scheme 1. As can be seen, 3,5-dibromobenzaldehyde (**1**) was prepared by reacting 1,3,5-tribromobenzene with DMF in the presence of *n*-BuLi, while 3,5-triethyleneglycobenzaldehyde (**2**) was synthesized by the Mitsunobu reaction of phenol and alcohol. Compound **2** was then converted to compound **3** by Wittig reaction. Dendron G1 was then prepared in a high yield (80%) by the Heck reaction of **3** and 3,5-dibromobenzaldehyde.

Dendron G2 was synthesized by first converting G1 into compound **4** via Wittig reaction and then reacting **4** with 3,5-dibromobenzaldehyde through the Heck reaction. The yield of G2 by Heck reaction is low (30%), partially due to the difficulties in the purification for the following reasons. 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, with respect to G1, makes



Scheme 1. Reactions towards the first (G1) and second (G2) generation of dendrons.

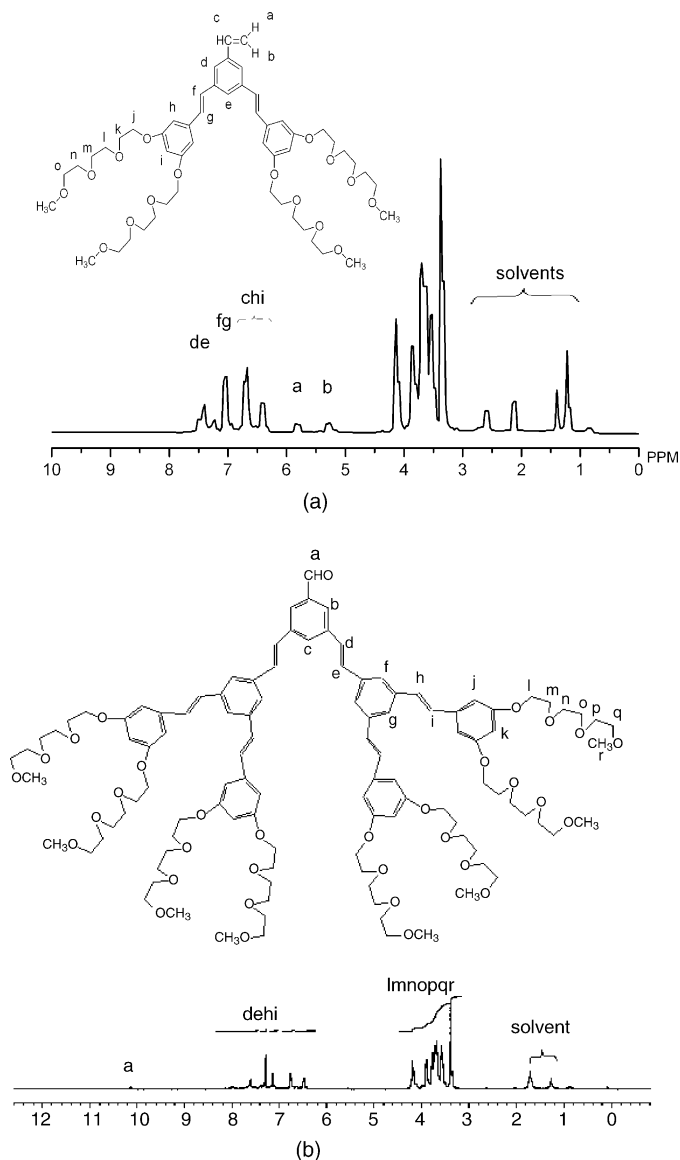


Fig. 1. ¹H NMR (CDCl₃) of (a) G1-(CH=CH₂) and (b) G2-CHO.

the column chromatography of G2 very difficult, if not impossible. We found that both compound **4** and G2 have very strong interactions with silica gel matrix in the column so that highly polar solvents are required for the elution. However, highly polar

solvents could also elute the side products together with G2 and **4**. Consequently, suitable eluents for an effective separation of the desired product from the side products have to be those solvents of 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 by the eluent of low polarity.

As expected, both dendrons G1 and G2 are soluble in most common organic solvents, including chloroform, methylene dichloride, THF, methanol, and acetone. The good solubility facilitates their characterization by various solution methods. Fig. 1a and b shows ¹H NMR spectra for G1 and G2, respectively, which have been fully assigned according to the structures given in the insets.

3.2. Amphiphilic properties

The newly-synthesized dendrons with an oligo(phenylene vinylene) core-branch and oligo(ethylene oxide) terminal chains (both G1 and G2) present an unusual situation where the insoluble conjugated branches are combined with the water-soluble oligo(ethylene oxide) terminal chains into one macromolecule. By analogy with other block copolymers dissolved in a selective solvent [6], amphiphilic behavior can be expected in solutions of these dendrons. Fig. 2a and b shows the concentration-dependence of the surface tension in water at 20 °C for the G1 and G2, respectively, indicating a typical micellization behavior. As seen in Fig. 2, the surface tension decreases with increasing dendron concentration to a limiting value (ca. 50 and 45 Dynes/cm for the G1 and G2, respectively) and then remains unchanged despite further increase in the dendron concentration due to the micelle formation. From Fig. 2a and b, we can, therefore, obtain the critical micellization concentrations (CMCs) of 2.5×10^{-4} and 2.0×10^{-4} g/ml for G1 and G2, respectively.

3.3. Photoluminescent properties

The UV-visible absorption spectra of the dendrons in chloroform are given in Fig. 3a, which shows an absorption peak shift from 308 nm for dendron G1 to 318 nm for dendron G2. The longer absorption wavelength of dendron G2 than that of dendron G1 is due to the longer conjugation length associated with the stilbene part in G2 molecule. The fluorescence behaviors of these two dendrons in solution were also studied (Fig. 3b and c).

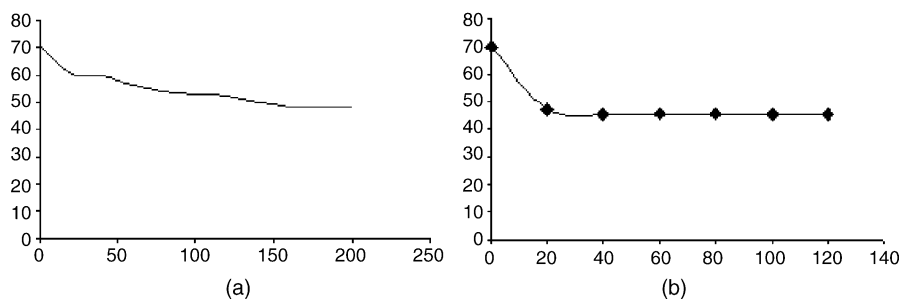


Fig. 2. The surface tension (Dynes/cm) vs. the concentration (10^{-5} g/ml) for (a) G1 and (b) G2 in water at 20 °C.

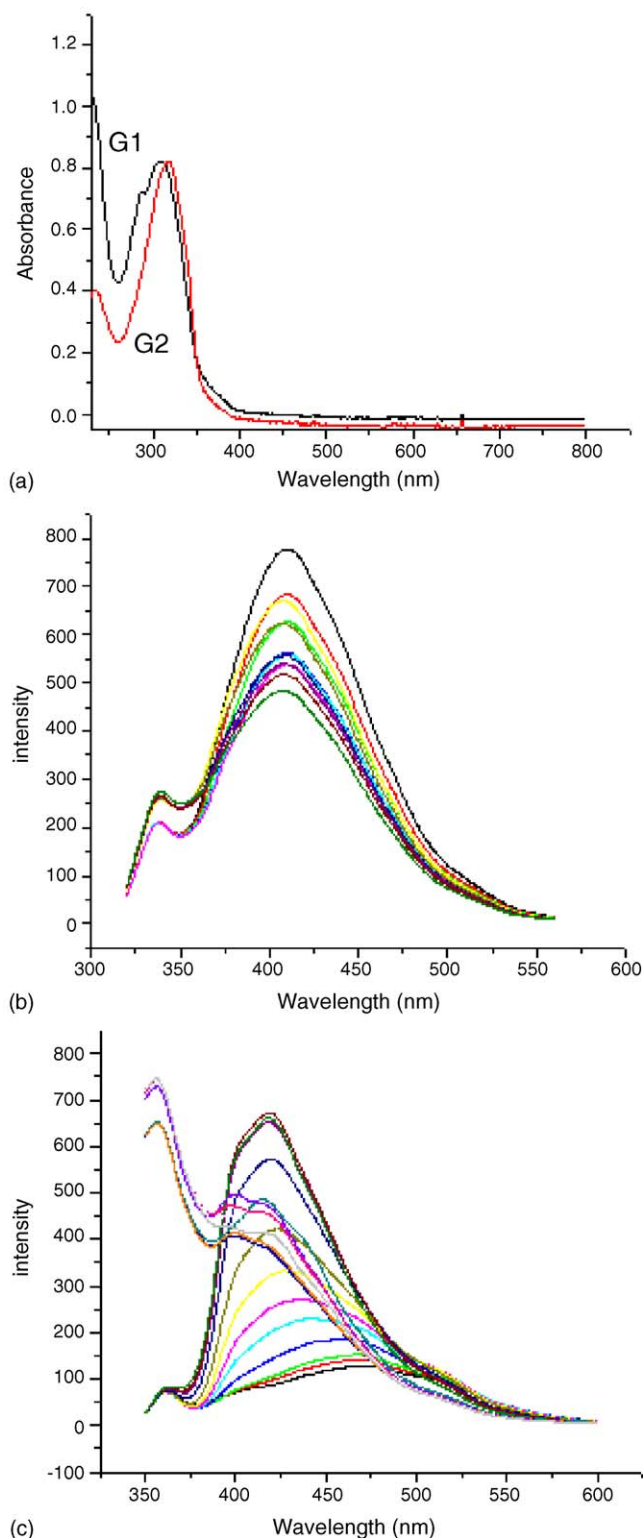


Fig. 3. (a) UV/vis spectra for G1 and G2 in chloroform and fluorescence spectra of (b) G1 and (c) G2.

At a concentration below CMC, dendron G1 showed a maximum emission at around 410 nm in water. The peak intensity (~ 750) decreased with time and gradually came to a stable state (~ 500). When the solution was heated, the intensity increased

up to a value even higher than that at the stable state, which, however, decreased again by cooling the solution down back to room temperature (Fig. 3b). It was suspected that the dendron G1 molecules aggregated more or less with time even at an overall concentration lower than the CMC due to their amphiphilic behavior, leading to the observed decrease in emission intensity with time. Heating could cause dissociation of the aggregated structure to increase the emission intensity.

On the other hand, a maximum emission wavelength shifted from around 480 to 425 nm was observed when a G2 solution (concentration above CMC) was added into the solvent (final concentration below CMC). This was accompanied by an increase in the emission peak intensity from about 100 to 700 (Fig. 3c). Based on the above observation, we assumed that a dilution-induced dissociation occurred when a solution of G2 with its concentration above CMC was added into the pure solvent, leading to a blue shift in the emission wavelength with a concomitant increase in the emission intensity.

4. Conclusion

We have synthesized a class of new amphiphilic conjugated dendrons consisting of an oligo(phenylene vinylene) core–branch and oligo(ethylene oxide) terminal chains (OPPV-*d*-OPEO) and investigated their amphiphilic and optoelectronic properties in solution. It was demonstrated that micellization occurs in solutions of the OPPV-*d*-OPEO due to counterbalance between the oligo(phenylene vinylene) core–core attraction interaction and oligo(ethylene oxide) solvation forces. The surface tension data and spectroscopic results presented in this paper indicate that the OPPV-*d*-OPEO dendrons are amphiphilic with a critical micellization concentration (CMC) of ca. 2×10^{-4} g/ml. The amphiphilic behavior causes interesting concentration/time/temperature-dependent photoluminescence emissions in solutions.

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