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Fluorescent Conjugated Dendrimers with Fluorinated Terminal Groups: Nanofiber Formation and Electroluminescence Properties

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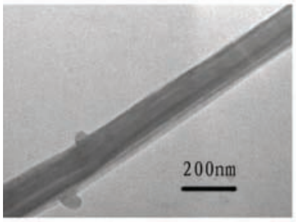
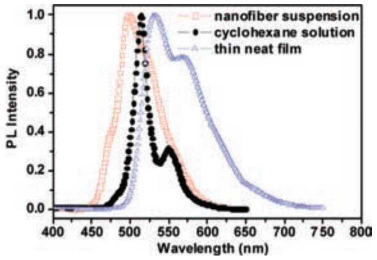
ABSTRACT





Two conjugated dendrimers with fluorinated terminal groups have been designed and synthesized. Dendrimer TP1 exhibits nanofibrous self-assembly ability accompanied by an unusual blue-shifted emission from nanofibers, and TP2 shows efficient electroluminescence property in single-layer organic light-emitting diodes (OLEDs).

Light-emitting dendrimers have attracted intense interest currently due to their potential use in full color displays.[1] Generally, dendrimers are hyperbranched macromolecules composed of a core, dendrons, and surface groups. It is envisioned that dendrimers possess many merits such as well-defined structures, super chemical purity, simple solution-processable film formation, efficient photon-harvesting, energy transduction capability, and controllable optical and electrical characteristics through core, dendron, and surface group selection. Moreover, the dendritic architecture provides a way to modulate intermolecular interaction and suppress excimer formation by controlling dendrimer generations.[2] There are several classes of well-studied fluorescent dendrimers, such as dendrimers extended by "stiff dendrons" (stilbene)[2a,b,3] and "soft dendrons" (poly(benzyl ether)).[1g,h,4]

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However, the performance of the electroluminescence (EL) devices utilizing these dendrimers is far from satisfactory. There are relatively few reports on the synthesis of dendrimers with acetylene linkages because they are considered as unpromising light-emitting materials for organic light-emitting diodes (OLEDs). The facile formation of excimer quenches the photoluminescence (PL) and EL, which has significantly lowered their performances.[1a,j,k,5]

On the other hand, one-dimensional self-assembly of functional materials has attracted increasing interest in the fabrication of nanoscale optoelectronic devices.[6] Recently, some reports suggest that the aromatic organic molecules and large macrocyclic aromatic molecules are prone to one-dimensional self-assembly through strong $\pi-\pi$ interaction.[7] There are also reports on the self-assembly of stiff polyphenylene dendrimers with pentafluorophenyl units.[8] The driving force for nanofiber formation is attributed to the increase in intermolecular $\pi-\pi$ stacking and van der Waals interactions among dendrons by pentafluorophenyl units. In acetylene-linked dendrimers, their stretched and planar structures may enable facile $\pi-\pi$ stacking, resulting in efficient intermolecular electronic coupling. Thus, it is expected that acetylene-linked dendrimers with the proper modification of dendrons can self-assemble into high-order structures under suitable conditions.

In this communication, we wish to report two novel solution-processable, acetylene-linked dendrimers composed of a pyrene core and carbazole/fluorene dendrons based on our previous work.[9] The fluorine atoms are introduced at the peripheries of the dendrimers. Their strong electron-withdrawing property may enhance electron transportation,[10] thus balancing the number of holes and electrons in LEDs. The structures of the dendrimers, **TP1** and **TP2**, and their synthetic routes are illustrated in Scheme 1. The syntheses of intermediates **1**[11] and **5**[9] have been submitted. Compounds **2**−**4**, **TP1**, and **TP2** are prepared following the reference methods[12] involving a Sonogashira coupling reaction. The structures of intermediates and products are verified by ^{1}H and ^{13}C NMR spectroscopy, MALDI-TOF MS measurement, and elemental analysis. Both dendrimers are highly soluble in common organic solvents, such as CH_2Cl_2, $CHCl_3$, THF, and toluene. Their thermal stability is investigated by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) in N_2 at a heating rate of 20 °C/min. Dendrimers **TP1** and **TP2** exhibit high glass-transition temperatures (T_g's) at 142 and 130 °C, respectively, and decomposition temperatures (T_d's, corresponding to a 5% weight loss) at 456 and 444 °C, respectively.

Scheme 1

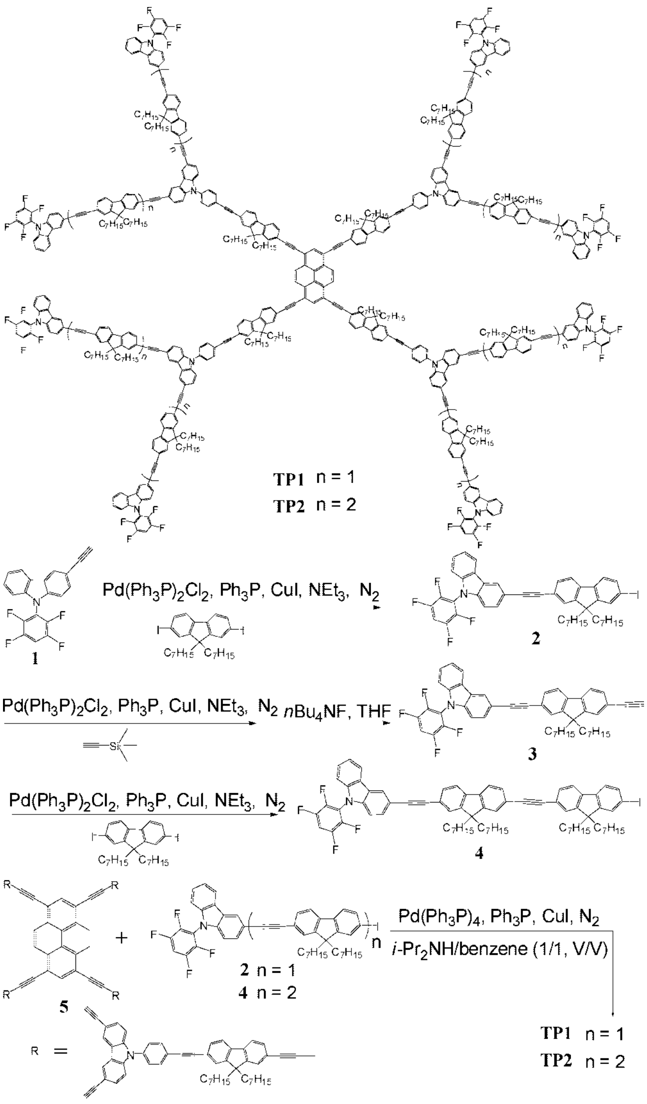

Figure 1 shows the UV−vis absorption and PL emission spectra of **TP1** and **TP2** in CH_2Cl_2 solutions (~10^{-6} M) and in thin neat films. The absorption spectra are normalized using the core absorption bands as references. The absorption spectra of the dendrimers exhibit two prominent absorption bands. The first band is attributed to the $\pi-\pi^*$ transition of the core (pyrene with a certain extension) with a maximum absorption peak at ~501 nm. The $\pi-\pi^*$ transition of an unsubstituted pyrene ring is generally located at 337 nm, while that of a tetrasubstituted conjugated pyrene (for

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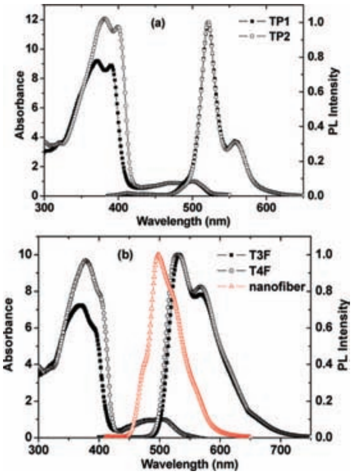

Figure 1. UV−vis absorption and PL spectra of dendrimers in dilute CH_2Cl_2 solutions (a) and in solid states (b).

instance with phenyl groups) appears in the visible region (~395 nm). The much redder core absorption in **TP1** and **TP2** reveals that the dendrimers are highly conjugated. The second band is assigned to the absorption of the dendrons with a maximum absorption peak at ~390 nm for **TP1** and ~399 nm for **TP2**. Dendrimers **TP1** and **TP2** show comparable mole absorption coefficients (ε) of the first band (0.96×10^5 and 1.04×10^5 M^{-1} cm^{-1}, respectively), while **TP2** shows a larger ε value (11.4×10^5 M^{-1} cm^{-1}) for the second band than **TP1** (8.59×10^5 M^{-1} cm^{-1}) due to its larger dendrons. Similar absorption spectra for both dendrimers are observed in thin neat films, except for a slight red shift and a loss of fine structures.

In dilute CH_2Cl_2 solutions, when excited with a wavelength within the range of the dendron absorption band, both dendrimers exhibit narrow PL emission spectra with a full width at half-emission maximum (fwhm) of about 23 nm and emission peaks located at 522 nm with a shoulder peak at about 558 nm, which is attributed to the emission of the core. There is only a trace emission from dendrons in the range of 400 ~ 450 nm, which indicates efficient photon harvesting and energy transfer from dendrons to the core. In thin neat films, **TP1** and **TP2** exhibit strong yellow emission with peaks at 532 and 530 nm and relatively weak peaks at 568 nm, respectively. The emission spectra are broad with fwhm's of 90 and 85 nm, respectively, which are ~10 nm red-shifted with respect to those in CH_2Cl_2 solutions. These are ascribed to aggregate formation in the solid states. Both dendrimers are highly fluorescent in solutions and neat films. The PL quantum yields of **TP1** and **TP2** are calculated to be 0.52 and 0.55, respectively, using 9,10-bis(phenylethynyl)anthrecene ($\phi = 1.0$ in degassed cyclohexane)[13] as a standard.

Dendrimer **TP1** exhibits a facile one-dimensional self-assembling property. The procedure of the fabrication of **TP1** nanofiber is very simple. A certain amount of **TP1** is dissolved in a mixture solvent of CH_2Cl_2/cyclohexane (1/10 v/v). Since CH_2Cl_2, a "good" solvent for **TP1**, evaporates faster than the "poor" solvent cyclohexane, the solubility of **TP1** in the mixed solvent becomes lower as the solvent evaporates, which induces the **TP1** molecules to aggregate. After deposition for several days, green floc aggregates appear in solution. After shaking, the floc aggregates are dispersed, resulting in a nanofibrous suspension. No aggregates are formed in **TP2** under the same fabrication condition. Figure 2 displays the TEM micrographs of **TP1** nanofibers drop-casted and dried on 200-mesh copper grids covered with carbon films. It can be seen that floc aggregates are composed of entangled nanofibers and bundles. The diameter of the fiber varies greatly. Some of them show a diameter of about 6.3 nm or less, which is smaller than the calculated molecular diameter of **TP1** (about 9 nm), while the diameter of others can be as large as about 200 nm or more. Interestingly, the nanofiber suspension exhibits a green emission with a peak at 498 nm, which is blue-shifted by 34 nm with respect to that in thin neat film. This emission differs from the single molecule emission in dilute CH_2Cl_2 (521 nm) or in cyclohexane (514 nm) solutions. This blue-shifted emission is somewhat abnormal because, generally, aggregation of molecules through intermolecular $\pi-\pi$ interaction should result in a red-shifted emission.[7b,14] These findings suggest that the self-assembly process occurs in a nonhomocentric way in which the adjacent dendrimer molecules stack face-to-face because this will lead to a close packing of the pyrene cores and thereafter a broad, redder emission from the pyrene aggregates.[15] This is further substantiated by the diameter of some fibers, whose value is

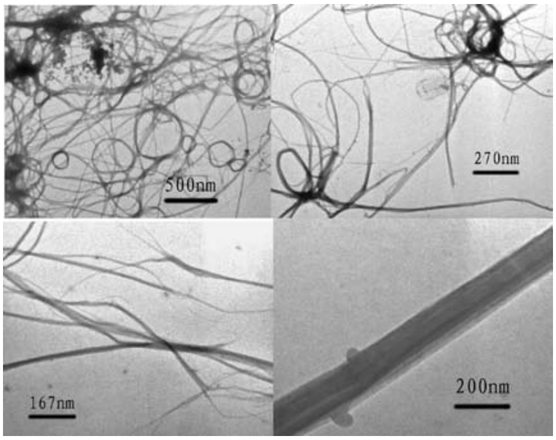

Figure 2. TEM micrographs of **TP1** nanofiber suspension drop-casted and dried on a 200-mesh copper grid covered with a carbon film.

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smaller than that of a single molecule. In this stage, we have not been able to confirm the exact assembling pattern.

Although both dendrimers have rigid and hyperbranched structures, they exhibit good film-forming ability. Their film morphology is detected by atomic force microscopy (AFM) at a tapping model, and the images of **TP2** are displayed in Figure 3. An essentially smooth and amorphous film can be obtained from the dendrimer solution by a simple spin-coating method, which simplifies the OLED fabrication.

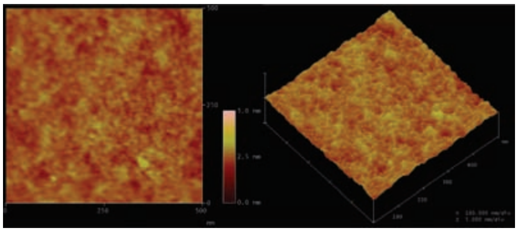

Figure 3. AFM images of **TP2** (left, top view; right, side view) spin-coated on SiO_2/Si substrate at a spin speed of 2000 rpm from 2 wt % *p*-xylene solution.

The EL properties of **TP1** and **TP2** were investigated in single-layer devices with the configuration of ITO (120 nm)/PEDOT (25 nm)/**TP1** or **TP2**/Cs_2CO_3 (1 nm)/Al (100 nm) fabricated by spin-coating with a speed of 1500 rpm from their 2% (wt %) *p*-xylene solutions. The PEDOT (poly(3,4-ethylenedioxythiophene)) layer was used for hole injection, and an ultrathin layer of Cs_2CO_3 was spin coated to effectively enhance electron injection before the Al cathode deposited by thermal evaporation. Details of the device fabrication can be found elsewhere.[16] Figure 4 shows the EL spectra and current density−voltage−luminance (*J*−*V*−*L*) characteristics of the devices. Dendrimers **TP1** and **TP2** exhibit yellowish green (Commission International d'Eclairage (CIE): 0.38, 0.61; and 0.36, 0.62, respectively) EL emissions with main peaks at 532 nm and shoulder peaks at 568 nm, which is almost the same as the emission in films. The device of **TP2** exhibits a maximum efficiency of 2.7 cd/A at 5.8 V and a maximum brightness of 5300 cd/m^2 at 11 V, while that of **TP1** shows relatively inferior performances with a maximum efficiency of 1.2 cd/A at 6.4 V and a maximum brightness of 2530 cd/m^2 at 9 V.

Compared with the performances of LEDs utilizing dendrimers with similar structures but without fluorine atoms,[9] the efficiency of **TP2**-based LED is almost double and the voltages requested to attain a brightness of 100 and 1000 cd/m^2 are almost halved. Moreover, the turn-on voltage decreases obviously. The improvements should be attributed to the introduction of fluorine atoms at the peripheries of the dendrimers which facilitate electron transport and thus balance the number of the hole and electrons. Induction of different molecular packing patterns may also account for such enhancement.

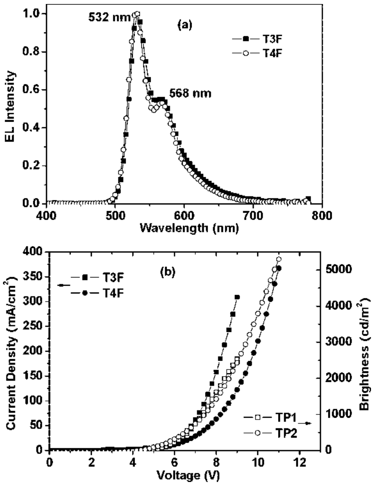

Figure 4. EL spectra (a), and *J*−*V*−*L* characteristics (b) of devices (ITO/PEDOT/**TP1** or **TP2**/Cs_2CO_3/Al).

In summary, we have synthesized and characterized two acetylene-linked dendrimers with a pyrene core. Dendrimer **TP1** easily self-assembles into nanofibers under simple conditions. Dendrimer **TP2** exhibits yellowish green (CIE: 0.38, 0.61) EL emission. When compared with dendrimers with similar structures, **TP2**-based single-layer LED exhibits improved performances with a maximum efficiency of 2.7 cd/A at 5.8 V and a maximum brightness of 5300 cd/m^2 at 11 V. These results indicate that dendrimers with fluorinated terminal groups are promising candidates for optoelectronic materials.

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Supporting Information Available: Experimental, NMR, and mass spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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