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Solution processible distyrylarylene-based fluorescent dendrimers: Tuning of carbazole-dendron generation leads to nondoped deep-blue electroluminescence

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ABSTRACT

A series of solution processible fluorescent dendrimers named PVCt1, PVCt2 and PVCt3 have been designed and synthesized by using 4,4′-distyryl-1,1′-biphenylene as the core and oligocarbazole as the dendron. When the dendron generation grows, the conjugation extension is limited due to the enhanced torsion between core and dendron, and simultaneously the intermolecular interactions can be weakened owing to the dendron encapsulation. As a result, a considerable hypsochromic shift is observed for both the photoluminescence and electroluminescence spectra in nondoped solid states, and the corresponding CIE coordinates move from (0.16, 0.21) of PVCt1 to (0.16, 0.15) of PVCt2 and (0.16, 0.10) of PVCt3. Moreover, compared with the sky-blue PVCt1 (0.82%), the nondoped device based on PVCt3 emits a deep-blue light with an improved external quantum efficiency of 2.81%. These results indicate that the tuning of carbazole-dendron generation can lead to deep-blue distyrylarylene-based fluorescent dendrimers used for efficient nondoped OLEDs.

1. Introduction

Besides small molecules and polymers, dendrimers that are composed of core, dendrons and surface substituents have also attracted much interest in organic light-emitting diodes (OLEDs) [1,2]. They possess not only the well-defined structures of small molecules for ease purification to favor the synthesis and device reproducibility, but also the good solution processibility of polymers to ensure the cost-effective fabrication via wet methods [3–6]. According to the used core, they can be generally divided into phosphorescent and fluorescent dendrimers. On one hand, phosphorescent dendrimers containing triplet emitter as the core have been widely and extensively investigated by many groups [7–23]. For example, by tuning the central core (e.g. Ir [7–19], Pt [20] and Au complexes [21]) or the peripheral dendron (e.g. Müllen- [7,8], Fréchet- [9], phenylene- [10,11], carbazole- [12–18], and arylamine-based dendrons [19] as well as hybridized [22] and bipolar dendrons [23]), highly efficient solution-processed phosphorescent OLEDs with emissions in the whole visible region have been successfully reported, whose performance could well compete with those of vacuum-deposited small molecules. On the other hand, the singlet-based fluorescent dendrimers [24–29], especially blue-emitting ones, remain less attention even though the dendritic blue fluorescent emitters are believed to show better device lifetime than the blue phosphorescent counterparts.

In this article, we demonstrate a series of solution processible fluorescent dendrimers named PVCt1, PVCt2 and PVCt3 by using 4,4′-distyryl-1,1′-biphenylene as the core and oligocarbazole as the dendron (Scheme 1). With the increasing dendron generation, the conjugation extension is limited due to the enhanced torsion between core and dendron, and the intermolecular interactions can be effectively prevented at the same time due to the dendron encapsulation. Consequently, the photoluminescence (PL) in solid states is found to be blue-shifted from 461/484 nm of PVCt1 to 439/452 nm of PVCt3 accompanied by the gradually enhanced PL quantum yields (PLQYs) from 40% to 59%. The corresponding solution-processed device based on PVCt3 as the nondoped emitting layer obtains a deep-blue electroluminescence (EL) with Commission International De L'Eclairge (CIE) coordinates of (0.16, 0.10) and a peak external quantum efficiency (EQE) of 2.81%. Compared to the sky-blue emissive PVCt1 (CIE: (0.16, 0.21); EQE: 0.82%), the improved blue color purity and device efficiency clearly indicate that the tuning of the carbazole-dendron generation is a promising strategy to realize efficient nondoped deep-blue EL in fluorescent dendrimers.

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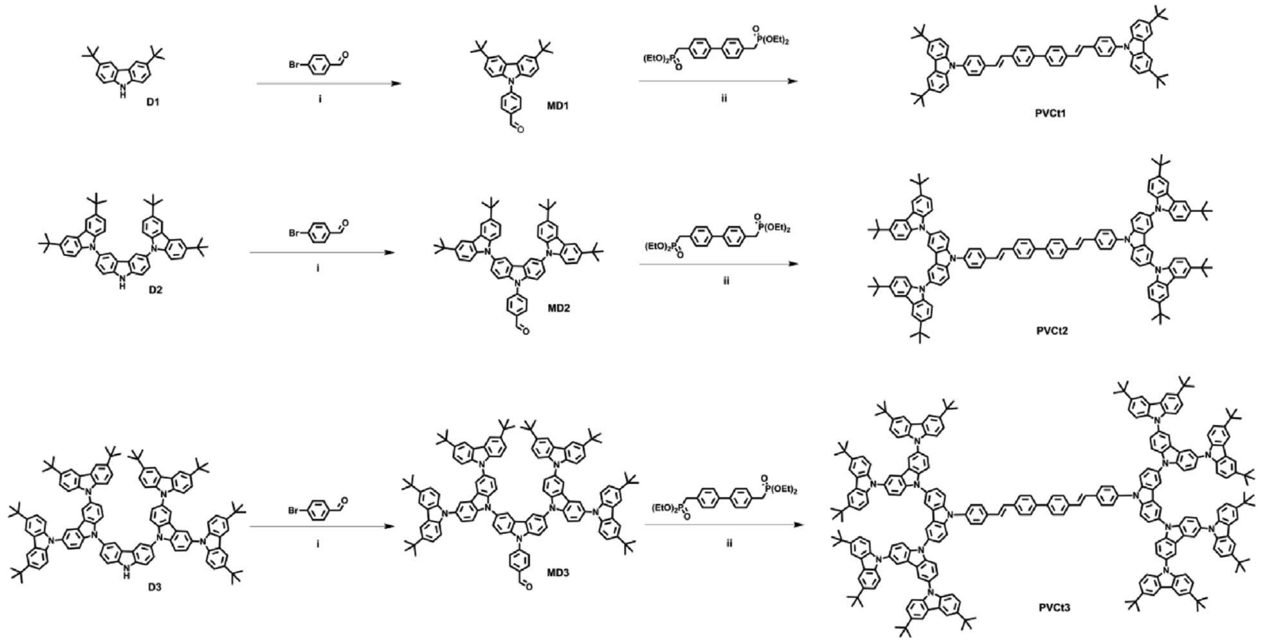

Scheme 1. Synthetic route of the distyrylarylene-based fluorescent dendrimers PVCt1 ~ PVCt3. Reagents and conditions: (i) CuI, (+/−)-trans-1,2-diaminocyclohexane, K_3PO_4, toluene, 110 °C; (ii) t-BuOK, THF, 0 °C.

2. Results and discussion

2.1. Synthesis and characterization

Scheme 1 outlines the synthetic route for the distyrylarylene-based fluorescent dendrimers PVCt1 ~ PVCt3. With the first, second and third generation carbazole dendrons D1 ~ D3 in hand, at first, they were treated with 4-bromobenzaldehyde via a CuI-catalyzed Ullmann reaction to afford the key intermediates MD1 ~ MD3. Finally, a Horner-Wadsworth-Emmons reaction between MD1 ~ MD3 and 4,4′-Bis(diethylphosphonomethyl)biphenyl was carried out to give the desired dendrimers PVCt1 ~ PVCt3 in an acceptable moderate yield of 62–71%. All the dendrimers could be easily and satisfactorily purified by column chromatography, and their molecular structures were fully characterized and confirmed by ^{1}H NMR spectra, MALDI-TOF mass spectroscopy and elemental analysis. Moreover, they were readily soluble in common organic solvents including chloroform, toluene, chlorobenzene, *o*-dichlorobenzene and mesitylene, ensuring the formation of high-quality films prepared via spin-coating.

2.2. Thermal properties

The thermal properties of the dendrimers PVCt1 ~ PVCt3 were investigated by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) at a scanning rate of 10 °C $\min^{-1}$ under a nitrogen atmosphere. As shown in Fig. 1, the decomposition temperature (T_d) corresponding to a 5% weight loss is considerably up from 484 °C of PVCt1 to 503 °C of PVCt2 and 537 °C of PVCt3. Meanwhile, a distinct endothermic peak related to the glass transition (T_g) appears at 293, 338 and 371 °C for PVCt1, PVCt2 and PVCt3, respectively. The obtained high T_d and T_g for PVCt1 ~ PVCt3 imply that these distyrylarylene-based fluorescent dendrimers may have excellent thermal and morphological stability, a favorable feature for the realization of long-term OLEDs.

2.3. Photophysical properties

Fig. 2 presents the UV–Vis and PL spectra both in solutions and films for the dendrimers PVCt1 ~ PVCt3, and the data are summarized in Table 1. As can be clearly seen in Fig. 2a, the low-energy absorption bands in the range of 310–425 nm can be safely ascribed to the π-π* transitions of the distyrylarylene-based core, while the high-energy absorption located at about 298 nm are from the peripheral carbazole dendrons. Moreover, an obvious hypsochromic shift is observed for the absorption onset from PVCt1 to PVCt3, corresponding to the elevated optical bandgap from −2.95 eV to 3.02 eV. Accordingly, their maximum emissions in toluene solutions also show a small blue-shift of 8 nm. These observations suggest that the conjugation length turns out to be shorter after the introduction of the large-size oligocarbazole. To further study this point, we performed density functional theory (DFT) simulations for the geometrical structures of PVCt1 ~ PVCt3. As depicted in Fig. 3, the torsion angle θ_1 between two diphenylethylene moieties in the core keeps nearly unchanged. However, the torsion angle θ_2 between core and dendron is gradually up from 52.2° of PVCt1 to 55.6° of PVCt2 and 57.8° of PVCt3, which may be responsible for the limitation of the conjugation extension and thus the gentle blue-shifted absorption and PL spectra observed in solutions.

On going from solutions to films, the PL spectra become structureless and red-shifted (Fig. 2b), indicative of aggregation to some extent. Despite such a bathochromic trend, the PL does moved from 461/484 nm of PVCt1 to 439/452 nm of PVCt3. Compared with the solution counterparts, a larger blue-shift of 22 nm is found in the film PL spectra. Besides the above-mentioned torsion between core and dendron, the weakened intermolecular interactions also contribute to the difference for the long-axis distance is up from 32 Å to 52 Å with the increasing generation number (Fig. 3). This is further verified by the film PLQYs, which show a significant enhancement from 40% of PVCt1 to 59% of PVCt3.

2.4. Electrochemical properties

Cyclic voltammetry (CV) was performed to probe the electrochemical properties of PVCt1 ~ PVCt3. During the anodic sweeping in dichloromethane, they all exhibit multiple reversible oxidation processes, whereas no reduction signals are detected upon the cathodic scan (Fig. 4). When the dendron generation grows, the first oxidation wave is found to be down-shifted to a negative potential resulting from the much richer electron-cloud density of the high-generation