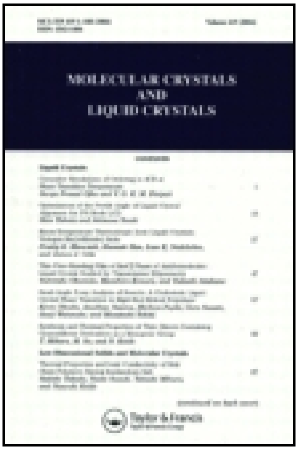

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Synthesis and Characterization of π-Conjugated Multi-branched Molecules Bearing Carbazole and Phenothiazine Peripheral Groups

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Synthesis and Characterization of π-Conjugated Multi-branched Molecules Bearing Carbazole and Phenothiazine Peripheral Groups

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A novel class of conjugated multi-branched molecules bearing N*-hexyl substituted carbazoles and phenothiazine as peripheral groups and [2,4,5-Tris-(diethoxyphosphorylmethyl)benzyl]phosphonic acid diethyl ester core has been synthesized through Horner-Emmons reaction in moderate to good yield. 8HCz-Den and 8HPTz-Den molecules have absorption maxima at 349 and 381 nm in solution states and maximum PL intensities were observed at 434 and 506 nm, respectively. They exhibited good self-film forming properties by solution casting and spin coating. In particular, by doping [2,6-bis(2-(5-(dibutylamino)phenyl)vinyl)-4H-pyran-4-ylidene]propanedinitrile, red emission could be achieved through complete Förster energy transfer process from the light harvesting host to the guest molecule.*

Keywords: absorption; electroluminescence; energy transfer; multi-branched molecule; photoluminescence

INTRODUCTION

Multi-branched and conjugated polymers have attracted considerable attention because of their various applications in electronics and optoelectronics such as organic light-emitting diodes(OLEDs) [1–4]

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and photovoltaic cells [5]. However, it is difficult to control their molecular weight and purify these polymers. Dendrimers, which are perfect monodispersed macromolecules with a regular and highly branched three-dimensional architecture, represent a key stage in the ongoing evolution of polymer chemistry [6–9]. Along with flexible backbone dendrimers, conjugated dendrimers with rigid structures, such as phenylacetylene [10–12], phenylene vinylene [13–15], and polyphenylene [16] dendrimers have also been developed in recent years.

Carbazole and phenothiazine based multi-branched molecules can also be employed for carrier transporting materials and as luminescent host materials in EL devices [17–19]. We herein report the synthesis and photophysical characterization of a novel class of conjugated multi-branched molecules bearing carbazoles and phenothiazines as peripheral groups. In addition, we fabricate the composite film after doping [2,6-bis(2-(5-(dibutylamino)phenyl)vinyl)-*4H*-pyran-4-ylidene]propanedinitrile (DADB) into two multi-branched molecules with the concentration. We investigated the possibility to show red emission through complete or partial Förster resonance energy transfer process.

EXPERIMENTAL

Instrumental Analysis

^{1}H NMR spectra were recorded on a Varian Mercury NMR 300 Hz spectrometer using deuterated chloroform ($CDCl_3$-*d*) purchased from Cambridge Isotope Laboratories, Inc. Elemental analysis was performed by using an EA1112 (Thermo Electron Corp.) elemental analyzer. Time-of flight mass spectrometry (MALDI-TOF) was performed using a Voyager-DE STR MADI-TOF (matrix; DHB) mass spectrometer.

Thermal properties were studied under a nitrogen atmosphere on a Mettler DSC 821^e instrument. Thermal gravimetric analysis (TGA) was conducted on a Mettler TGA50 thermal analysis system under a heating rate of 10°C/min.

Absorption and Photoluminescence Spectroscopy

Studying absorption and PL spectral behavior, thin films of multi-branched molecules were fabricated on quartz substrates as follows. The solution (2 wt%) of each molecule in monochlorobenzene was filtered through an acrodisc syringe filter (Millipore 0.2 μm) and subsequently spin-cast on the quartz glass. The films were dried overnight at 80°C for 24 hours under vacuum. Absorption spectra of film samples and chloroform solution (conc. 1.5×10^{-6} mole/L) were obtained using a UV-vis spectrometer (HP 8453, PDA type) in the wavelength range of 190–1100 nm. PL spectra were recorded with an AMINCO-Bowman series-2 luminescence spectrometer.

Synthesis

We synthesized the intermediate compounds, **2**, **3** by the literature method [20,21].

Synthesis of Compound 1

The same procedure was employed to prepare the compound **2**: Instead of phenothiazine, we used carbazole. ^{1}H NMR (400 MHz, $CDCl_3$) δ 10.10 (s, 1H), 8.29 (s, 2H), 8.18 (d, $J = 8.0$ Hz, 2H), 7.93 (s, 3H), 7.74 (d, $J = 8.0$ Hz, 2H), 7.51 (t, $J = 8.0$ Hz, 2H), 7.50 (d, $J = 16.0$ Hz, 2H), 7.45 (d, $J = 8.0$ Hz, 2H), 7.44 (d, $J = 8.0$ Hz, 2H), 7.29 (t, $J = 8.0$ Hz, 2H), 7.24 (d, $J = 16.0$ Hz, 2H), 4.31 (t, 4H), 1.86–1.94 (m, 4H), 1.39–1.46 (m, 4H), 1.29–1.37 (m, 8H), 0.90 (t, 6H).

Anal. Calcd for $C_{47}H_{48}N_2O$ C, 85.93; H, 7.37; N, 4.26. Found: C, 85.90; H, 7.53; N, 4.07.

Synthesis of 8HCz-Den

Compound **1** (820 mg, 1.25 mmol) and **3** (212 mg, 0.312 mmol) were dissolved in 30 ml of dry THF. The resulting solution was added dropwise slowly to THF solution (20 mL) of potassium *tert*-butoxide (140 mg, 1.25 mmol) under N_2 for 12 h at room temperature. The reaction was quenched by adding a small amount of HCl solution and extracted with dichloromethane. The organic phase was dried over $MgSO_4$. Chromatography on silica gel (hexane/chloroform 1:4) gave 612 mg (yield: 73%) of green powder. T_g 96°C. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.12 (s, 8H), 8.02 (d, $J = 8.4$ Hz, 8H), 8.00 (s, 2H), 7.77 (d, $J = 15.3$ Hz, 4H), 7.75 (s, 8H), 7.71 (s, 4H), 7.57 (d, $J = 8.4$ Hz, 8H), 7.44 (t, $J = 8.4$ Hz, 8H), 7.41 (d, $J = 15.3$ Hz, 8H), 7.34 (d, $J = 15.3$ Hz, 4H), 7.30 (d, $J = 8.4$ Hz, 8H), 7.16 ~ 7.22 (m, 16H), 7.11 (d, $J = 8.4$ Hz, 8H), 4.00 (t, 16H), 1.66 ~ 1.75 (m, 16H), 1.18 ~ 1.29 (m, 48H), 0.84 (t, 24H); MALDI-TOF MS m/z calcd $C_{198}H_{198}N_8$ $(M + H)^+$ 2688.5812, Found 2689.8746.

Synthesis of 8HPTz-Den

Compound **2** (1.12 mg, 1.55 mmol) and **3** (263 mg, 0.387 mmol) were dissolved in 30 ml of dry THF. The resulting solution was added dropwise slowly to THF solution (20 mL) of potassium *tert*-butoxide (174 mg, 1.55 mmol) under N_2 for 12 h at room temperature. The reaction was quenched by adding a small amount of HCl solution and extracted with dichloromethane. The organic phase was dried over $MgSO_4$. Chromatography on silica gel (hexane/chloroform 1:4) gave 810 mg (yield: 71%) of orange powder. T_g 80°C; ^1H NMR (300 MHz, $CDCl_3$) δ 7.76 (s, 2H), 7.57 (d, $J = 15.3$ Hz, 4H), 7.50 (s, 8H), 7.46 (s, 4H), 7.10 ~ 7.19 (m, 40H), 6.81 ~ 6.97 (m, 20H), 6.78 (d, $J = 8.4$ Hz 8H), 6.61 (m, $J = 8.4$ Hz 8H), 3.71 (t, 16H), 1.69 ~ 1.78 (m, 16H), 1.34 ~ 1.42 (m, 16H), 1.25 ~ 1.33 (m, 32H), 0.87 (t, 24H); MALDI-TOF MS m/z calcd $C_{198}H_{199}N_8\ S_8\ (M+H)^+$ 2944.3578, Found 2945.3600.

RESULTS AND DISCUSSION

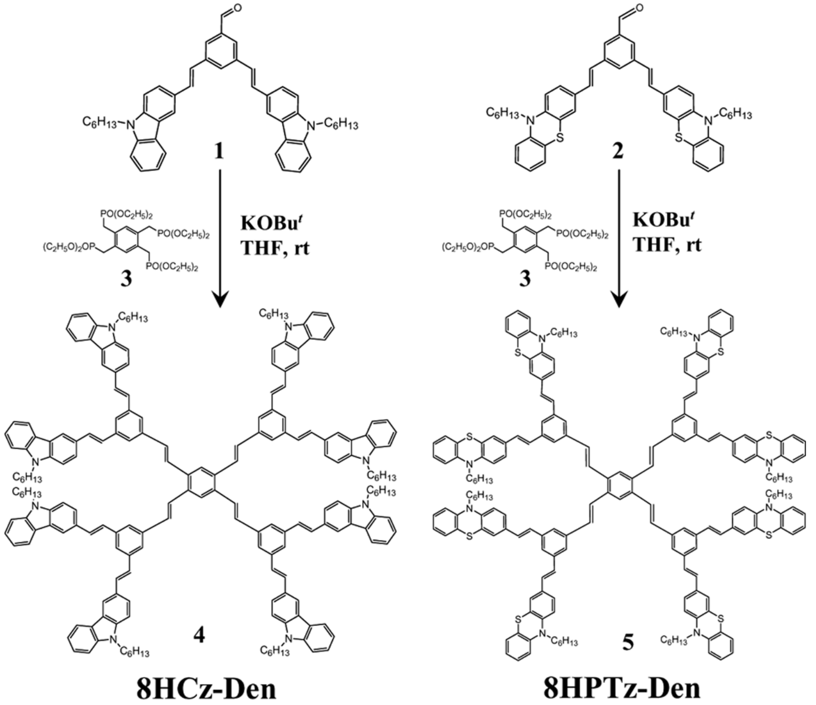
We herein report the synthesis and photophysical characterization of two new π-conjugated multi-branched molecules bearing carbazoles and phenothiazines as peripheral groups.

In order to prepare 8HCz-Den and 8HPTz-Den, compounds **1** and **2** were prepared by the Heck coupling reaction of 3-vinyl-9*H*-hexylcarbazole/3-vinyl-10*H*-hexylphenothiazine and 3,5-dibromobenzaldehyde [20].

The convergent syntheses of the multi-branched molecules were conducted based on the typical Horner-Emmons condensation of 1/**2** and [2,4,5-tris(diethoxy-phosphorylmethyl)benzyl]phosphonic acid diethyl ester core (Scheme 1). The reaction yield of this coupling reaction is fairly high to be around 71–73%.

The identity and purity of the synthetic materials were confirmed by ^1H NMR, MALDI-TOF mass spectrometry, and elemental analysis. These synthetic materials were found to have a good self-film-forming property and showed good solubility in various organic solvents such as chloroform, xylene, chlorobenzene, and tetrahydrofuran (THF).

The thermal properties of the multi-branched molecules were characterized by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). **8HCz-Den** and **8HPTz-Den** exhibit no discernible crystalline-isotropic transitions observed in DSC thermograms (see Table 1). The glass transition temperatures (T_gs) of the two molecules are 96 and 80°C for **8HCz-Den** and **8HPTz-Den**, respectively. This indicates that all molecules can exhibit an amorphous morphology in solid films. When comapring two glass transition temperatures, we found the fact that they are strongly dependent on the molecular planarity of carbazole units. It implies that a carbazole moiety has more planar than the phenothiazine moiety. Non-polar van



SCHEME 1 Synthetic route for the 8HCz-Den and 8PTz-Den.

der Waals interaction between carbazole moieties is a important molecular specific interaction which can affect the physical properties significantly. TGA measurements at a heating rate of 10°C/min under nitrogen revealed good thermal stability. Two multi-branched molecules are thermally stable up to 392–445°C. (see Table 1) Higher thermal stability of 8HCz-Den can be attributed to the reason we described above.

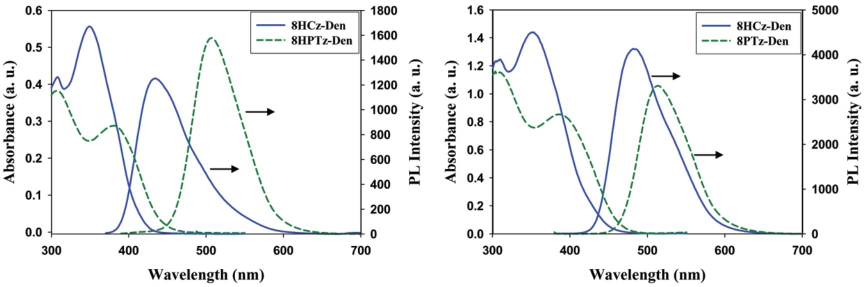
TABLE 1 Thermal and Photophysical Properties of 8HCz-Den and 8HPTz-Den

				λ_{max} (nm)		λ_{ex} (nm)		λ_{em} (nm)	
Compound	T_g (°C)	T_d (°C)	ε ($M^{-1}cm^{-1}$)	Solution	Film	Solution	Film	Solution	Film
8HCz-Den	96	445	356,000	349	350	345	370	434	485
8HPTz-Den	80	392	175,000	381	384	370	365	506	513

Figure 1 displays the absorption and PL spectra of the synthesized compounds such as **4** and **5** in dilute chloroform solutions and films. The absorption $\lambda_{\max}$ of 8HCz-Den and 8HPTz-Den appeared 349 and 381 nm in solution, respectively. In the ground state, two branched large molecules do not exhibit high molecular interaction.

The PL spectra of two molecules in solutions and films are featureless and are almost a mirror-image of the low-energy absorption band. The PL spectra of the synthesized molecules in films exhibit a red-shift and become broader in comparison to the spectra in chloroform. These features are usually observed for organic and polymer conjugated materials mainly due to the different polarity of the environments. When we compare the PL spectra of two compounds in film state, 8HCz-Den showed larger spectral shift ($\Delta\lambda_{\mathrm{emission}} = 51$ nm) than that of 8HPTz-Den ($\Delta\lambda_{\mathrm{emission}} = 7$ nm). Therefore, in an excited state, the carbazole moiety induces higher molecular interaction to induce this effect.

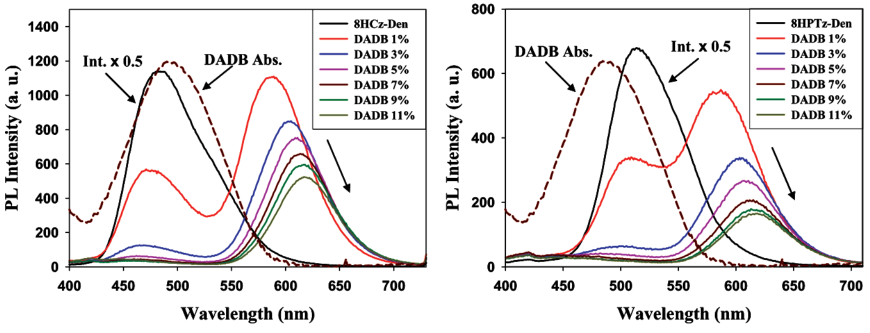
In order to examine the functions of these compounds as host material in OLEDs, [2,6-bis(2-(5-(dibutylamino)phenyl)vinyl)-*4H*-pyran-4-ylidene]propanedinitrile (DADB) [22] was mixed into **8HCz-Den** and **8HPTz-Den** at six different concentrations in monochlorobenzene. Subsequently, thin films were fabricated on a quartz substrate for obtaining the PL spectra with excitation at 370 nm (8HCz-Den) and 365 nm(8HPTz-Den). Figure 2 shows the variation of the PL spectra with the **DADB** concentration (conc. = 1–11 wt%); (dashed line) absorption spectrum of polystyrene doped with DADB. **8HCz-Den** and **8HPTz-Den** exhibited greenish blue and green emission predominantly; the maximum intensity of emission appeared at



(a)

(b)

FIGURE 1 Absorption and PL spectra of the multi-branched molecules. (a) Solution in chloroform (1.5×10^{-6} M), (b) Film (thickness: 80 nm).



(a) (b)

FIGURE 2 PL spectra of the multi-branched molecules doped with DADB in film states. (a) 8HCz-Den doped with DADB, (b) 8HPTz-Den doped with DADB (thickness: 30 nm).

around 485 and 513 nm, respectively. With an increase in the concentration of **DADB**, the intensity at 485 and 513 nm decreases drastically. Further, red emission at around 620 nm increases significantly.

DADB is capable of electronic excitation *via* Förster energy transfer from the host material. Photoluminescence (PL) studies of the doped matrix demonstrated that a significantly high energy transfer from **8HCz-Den** and **8HPTz-Den** to **DADB** is achieved. From Figure 2, it is clearly evident that the emission spectra of **4** and **5** and absorption spectrum of DADB dye overlap favorably, which enables an efficient energy transfer. In particular, we speculated that efficient energy transfer from a singlet and triplet state of the carbazole moiety to the **DCM** derivatives can enhance red emission in the **DADB** doped matrix. When doped with 5 wt% **DADB** into **8HCz-Den**, we were able to obtain the highest PL intensity at 613 nm. The concentration of **DADB** could be optimized to 5 wt% in this experiment. Therefore, if we investigate the optimum concentration for complete or incomplete energy transfer from the host to the dopant, red or white emission behavior can be observed and it can be utilized for white light electroluminescence in our future study.

CONCLUSION

We have synthesized novel multi-branched molecules for host materials for red emitting EL devices. The HOMO and LUMO energies of the synthesized molecules are suitable for hole transporting materials in a multilayer EL device. The absorption and PL spectra indicate that the molecules bearing carbazoles or phenothiazines as peripheral groups can exhibit highly isolated photophysical properties. It can be considered that these carbazole-labeled multi-branched molecules can potentially be used for white organic light-emitting devices optimizing the concentration of DADB.

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