A New Carbazole-based Conjugated Multibranched Molecule and Its Tetramer as Hole Transporting Materials

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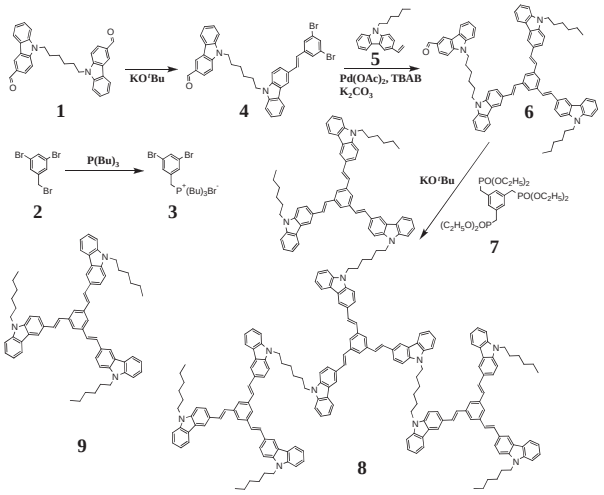
A conjugated multibranched molecule, 1,3,5-tris{(*E*)-2-[9-hexyl-9*H*-carbazol-3-yl]vinyl}benzene (THCEB) and its tetramer, 1,3,5-tris((*E*)-2-{9-[6-(3-{(*E*)-3,5-bis[(*E*)-2-(9-hexyl-9*H*-carbazol-3-yl)vinyl]styryl}-9*H*-carbazol-9-yl)hexyl]-9*H*-carbazol-3-yl}vinyl)benzene (4(THCEB)), have been synthesized through Heck coupling and Horner–Emmons reactions in moderately good yields. These compounds exhibited good self-film-forming properties by spin coating. These two large molecules showed an absorption maxima at around 346–348 nm in their solution states. The maximum PL intensities of THCEB and 4(THCEB) films were commonly observed at around 450 nm, except for a strong emission band at 535 nm in THCEB. In the tetramer, the emission at 535 nm was highly suppressed. This observation was explained in terms of the time-resolved photophysical properties of these molecules with the help of a possible mechanism.

Efficient hole transport is a prerequisite for achieving high-performance EL devices with well-balanced hole and electron injections. In a multilayer device, the individual layers should be optimized in order to achieve energy levels for the suitable highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO).[1,2]

Carbazole derivatives are well adopted to act as hole-transport molecules or as host molecules in a light-harvesting system.[3] Recently, Li et al. reported the interesting properties of carbazole-based multibranched molecules. 1,3,5-Tris[2-(9-ethylcarbazol-3-yl)ethylene]benzene (TECEB) was prepared as a hole-transporting material for organic light-emitting devices (OLEDs).[4] Li et al. claimed that TECEB is comparable to 1,4-bis(1-naphthylphenylamino)biphenyl (NPB) in terms of the HOMO/LUMO energy levels and carrier mobility. Hence, the performance of a standard multilayer EL device, in which a TECEB layer is used, is enhanced owing to improved luminance properties. Since it is poorly soluble in many common organic solvents, we must explore a new class of carbazole-based materials that are easily soluble in organic solvents for solution processing. In this study, we report THCEB and its tetramer and illustrate their thermal and photophysical properties.

THCEB was synthesized by following the literature method (Scheme 1).[5] The convergent synthesis of the multibranched molecule, 4(THCEB), was carried out on the basis of a typical Horner–Emmons reaction using an aromatic core. **1** was reacted with tributyl(3,5-dibromobenzyl)phosphonium bromide (**3**) to yield **4**. Through the Heck coupling reaction, **4** and **5** were condensed to yield **6**. Hexaethyl benzene-1,3,5-triyltris(methylene)-triphosphonate **7** was used as the core moiety in the Horner–Emmons reaction to yield **8**, which is the tetramer of **9**. The yield of this coupling reaction is fairly high: around 60%.[6]



Scheme 1. Structures of 4(THCEB) (**8**) and THCEB (**9**).

The thermal properties of the products were studied under a nitrogen atmosphere on a Mettler DSC821e instrument. The glass-transition temperatures (T_gs) of THCEB and 4(THCEB) were 50 and 106 °C, respectively (Table 1). THCEB melted at around 181 °C, indicating that it is a semicrystalline material. No discernible melting behavior up to 290 °C was observed in the DSC thermogram of 4(THCEB). It should be noted that 4(THCEB) exhibits an amorphous morphology in a solid film, due to which it can be applied to hole-transport layers (HTL) or can be used as a host material in an OLED.

Figure 1 displays the absorption and PL spectra of THCEB and 4(THCEB) in dilute chloroform solutions and in films. The results show that the absorption and emission maxima of all the molecules appeared at almost identical wavelengths. The absorption spectra in solutions reveal the characteristic absorption peaks of carbazole between 346 and 348 nm. Generally, the red shift of λ_{max} in a film relative to that in a solution is observed because of intermolecular interactions between the molecules existing in the ground state. 4(THCEB) exhibited a 6-nm red

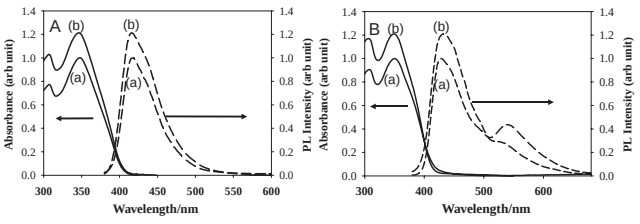


Figure 1. UV–vis absorption (solid lines) and PL spectra (dotted lines) of THCEB (a) and 4(THCEB) (b). A: solution state, B: film state.

Table 1. Measured and calculated parameters for THCEB and 4(THCEB)

	T_g /°C	T_m /°C	T_d /°C	Absorption/nm		Emission/nm		λ_{cutoff} /nm	E_{HOMO}[a] /eV	E_{LUMO}[b] /eV	ΔE_g^{opt} [c] /eV
				Solution	Film	Solution	Film				
THCEB	50	181	430	348	349	419	450 (530)	414	−5.49	−2.49	2.99
4(THCEB)	106	—	408	346	352	424	451	421	−5.45	−2.50	2.94

[a]HOMO = (4.40 + E_{ox}^{onset}) from cyclic voltametry. [b]LUMO = HOMO − E_g^{opt}. [c]Estimated from the onset of absorption edge ($E_g^{opt} = 1240/\lambda_{onset}$).

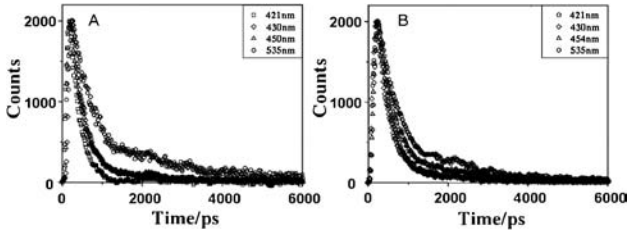


Figure 2. Time-resolved PL signal profiles of the two molecules in film states. A: THCEB; B: 4(THCEB). Excitation at 380 nm and PL decay monitored at the corresponding maximum PL wavelengths.

shift due to the presence of flexible spacers between the THCEB molecules.

The PL spectra of the synthesized molecules in films exhibited a red shift by 27–31 nm; further, these peaks were broader than those of the spectra in chloroform. The emission intensity of THCEB at around 535 nm in its PL spectrum was higher in the film state than that of 4(THCEB). This increase in the intensity is attributed to a large population of the excimers or high degree of intermolecular interactions in the solution state (See Figure 1B).

For the time-resolved PL analysis, all the samples were excited by 400-nm pulses generated by frequency doubling of the 800-nm, 100-fs pulse from a mode-locked Ti/sapphire laser oscillator (Coherent, Chameleon). The PL kinetic profiles were recorded using a time-correlated single photon counting (TCSPC, EG&G Ortec) setup equipped with a photon-counting MCP-PMT (Hamamatsu) detector.

Figure 2 displays the PL decay profiles of the films monitored at 421, 430, 450, and 535 nm. The observed decay profiles fitted well with the single- or double-exponential decay functions for calculating the time constants (τ_1 and τ_2) time (see Table 2). Figure 2A clearly shows that the PL decay rate at 535 nm is slower than that at other wavelengths. On close examination, it was revealed that the PL intensity at 535 nm shows two decay components. This is likely to occur owing to the minor simultaneous excitation of the excimer at 535 nm, in addition to the major emission from the singlet excited state of carbazole.

The HOMO and LUMO levels were determined to be in the range of −5.45 to −5.49 and −2.49 to −2.50 eV, respectively (see Table 1). Since these values are comparable to the energy levels suitable for a HTL in a multilayer EL device, it is stated that these compounds can be used as HTLs for efficient carrier transport and also as electron blocking layers.

In conclusion, THCEB is inherently semicrystalline, due to which it is not suitable for use as a functional layer in multilayer EL devices. We have synthesized a new compound, 4(THCEB), which is highly soluble in most organic solvents, due to which the crystallinity and intermolecular interactions are diminished. Thus, 4(THCEB) is expected to be a potential candidate for hole transportation in future EL devices.

Table 2. Fitted parameters for THCEB and 4(THCEB)[a]

Sample	λ_{det} /nm[b]	A_1	τ_1/ps	A_2	τ_2/ps
THCEB	421	100	305		
	430	100	307		
	450	100	301		
	535	69	446	31	2635
4(THCEB)	421	100	314		
	430	100	303		
	450	100	318		
	535	83	432	17	2137

[a]Uncertainty is ±1% of the measured value. [b]λ_{det}/nm = detecting wavelength, λ_{ex} = 380 nm.

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References and Notes

1 H. Yan, B. J. Scott, Q. Huang, T. Marks, *Adv. Mater.* **2004**, *16*, 1948.
2 Y.-H. Niu, B. Chen, S. Liu, H. Yip, J. Bardecker, A. K.-Y. Jen, J. Kavitha, Y. Chi, C.-F. Shu, Y.-H. Tseng, C.-H. Chien, *Appl. Phys. Lett.* **2004**, *85*, 1619.
3 Y. Agata, H. Shimizu, J. Kido, *Chem. Lett.* **2007**, *36*, 316.
4 J. Li, D. Liu, Y. Li, C.-S. Lee, H.-L. Kwong, S. Lee, *Chem. Mater.* **2005**, *17*, 1208.
5 M. J. Cho, H. S. Kim, T. W. Lee, J.-I. Jin, D. H. Choi, Y. M. Kim, B.-K. Ju, *Macromol. Res.* **2007**, *15*, 595.
6 THCEB: ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.87 (t, 9H), 1.25–1.42 (m, 18H), 1.84–1.91 (m, 6H), 4.28 (t, 6H), 7.23 (d, J = 16.0 Hz, 3H), 7.26 (t, J = 8.0 Hz, 3H), 7.39–7.42 (m, 6H), 7.45 (d, J = 16.0 Hz, 3H), 7.48 (t, J = 8.0 Hz, 3H), 7.64 (s, 3H), 7.73 (d, J = 8.0 Hz, 3H), 8.15 (d, J = 8.0 Hz, 3H), 8.29 (s, 3H). Anal. Calcd for $C_{66}H_{69}N_3$: C, 87.66; H, 7.69; N, 4.65%. Found: C, 87.24; H, 7.60; N, 4.45%. MALDI-TOF MS m/z: calcd $C_{66}H_{69}N_3$ (M^+) 904.5564; found 904.0753. 4(THCEB): ^{1}H NMR (400 MHz, $CDCl_3$): δ 0.84–0.88 (m, 18H), 1.17–1.41 (m, 48H), 1.66–1.89 (m, 24H), 4.03–4.28 (m, 24H), 7.11–7.24 (m, 24H), 7.27–7.50 (m, 48H), 7.51–7.61 (m, 12H), 7.62–7.78 (m, 12H), 8.07–8.16 (m, 12H), 8.18–8.28 (m, 12H). Anal. Calcd for $C_{246}H_{234}N_{12}$: C, 87.97; H, 7.02; N, 5.00%. Found: C, 87.85; H, 7.11; N, 5.05%. MALDI-TOF MS m/z: calcd for $C_{246}H_{234}N_{12}$ (M^+) 3355.8679; found 3355.7195.

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