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Synthesis and Photophysical Properties of Carbazole-Based Blue Light-Emitting Dendrimers

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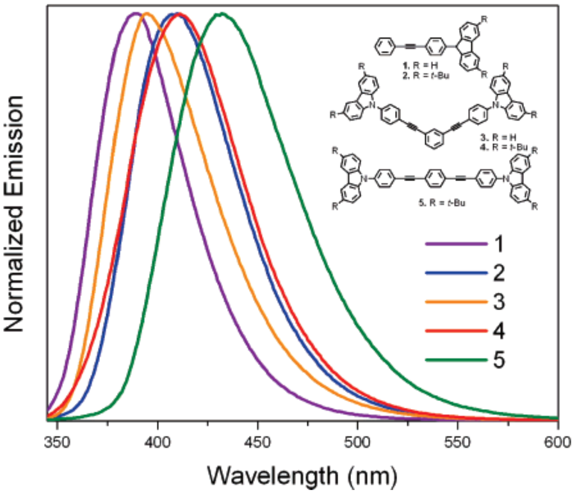

A new class of highly fluorescent and stable carbazole-based dendrimers (**1**−**5**) that contain the ethynylbenzene and diethynylbenzene cores has been synthesized and characterized. They show very high extinction coefficients of absorption ($A_{\max} \approx 328-353$ nm) and high quantum yields of fluorescence ($\lambda_{\max} \approx 386-437$ nm; $\Phi_F \approx 0.72-0.89$; $\tau_F \approx 2.09-3.91$ ns) in dichloromethane. The quantum yields of fluorescence of **1**−**5** in the solid state are equally high ($\lambda_{\max} \approx 385-422$ nm; $\Phi_F \approx 0.40-0.85$). These data indicate their potential use as blue-emitting materials in organic light-emitting diodes (OLEDs).

Introduction

Ever since Tang and Vanslyke constructed electroluminescent (EL) devices using organic materials as emitters, development of new EL materials has become an active area of research because of their potential use in displays.[2] A large effort to make organic light-emitting diode (OLED)-based technology a possible alternative to liquid crystal-based displays and to develop OLED displays for other niche lighting applications has also been underway. Red, green, and blue emitters are required for the fabrication of a full-color display. The stability and efficiency of green and red emitters have approached commercially viable levels.[3] But the design and synthesis of blue emitters suitable for fabrication of stable OLED devices remains a major challenge.[4] The performance of blue emitters is not as efficient as that of red and green emitters.[5]

Carbazole-based compounds are known for their intense luminescence[6,7] and widely used in OLEDs as blue emitters,[8−12]

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[1] Contribution No. 633 from the Center for Photochemical Sciences.

[2] (a) Tang, C. W.; Vanslyke, S. A. *Appl. Phys. Lett.* **1987**, *51*, 913. (b) Shinar, J. *Organic Light-Emitting Devices*; Springer-Verlag: New York, 2003. (c) Müllen, K.; Scherf, U. *Organic Light-Emitting Devices. Synthesis, Properties and Applications*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2006.

[3] Mondal, R.; Shah, B. K.; Neckers, D. C. *J. Org. Chem.* **2006**, *71*, 4085.

[4] Shah, B. K.; Neckers, D. C.; Shi, J.; Forsythe, E. W.; Morton, D. *J. Phys. Chem. A* **2005**, *109*, 7677.

[5] Chan, L.; Lee, R.; Hsieh, C.; Yeh, H.; Chen, C. *J. Am. Chem. Soc*. **2002**, *124*, 6469.

[6] Yu, H.; Zain, S. M.; Eigenbrot, I. V.; Phillips, D. *Chem. Phys. Lett.* **1993**, *202*, 141.

[7] Howell, R.; Taylor, A. G.; Phillips, D. *Chem. Phys. Lett.* **1992**, *188*, 119.

[8] Almeida, K. D.; Bernede, J. C.; Marsillac, S.; Godoy, A.; Diaz, F. R. *Synth. Met.* **2001**, *122*, 127.

[9] Lee, J.; Woo, H.; Kim, T.; Park, W. *Opt. Mater.* **2002**, *21*, 225.

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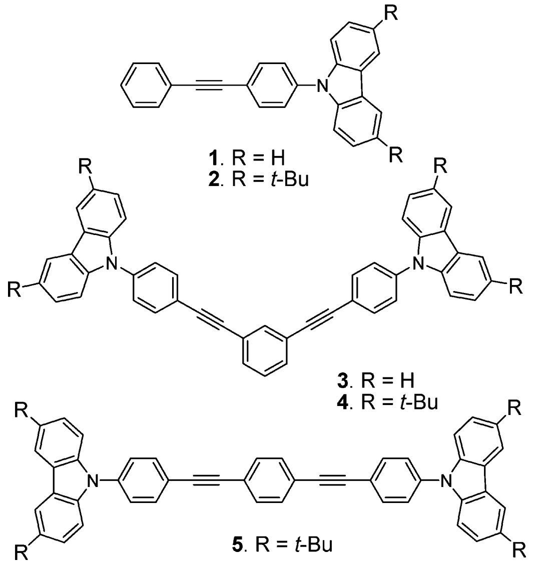
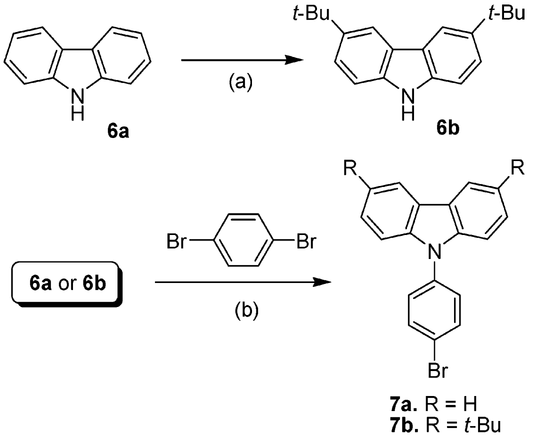
CHART 1



white emitters,[13] green emitters[14] and red emitters.[15] They also undergo reversible oxidation processes, making them suitable hole carriers.[16] We have synthesized a new class of carbazole-based stable dendrimers that contain the ethynylphenyl core (**1**−**5**, Chart 1) in order to develop stable blue emitters which also have hole transporting properties. While 9-(4-(2-phenylethynyl)-phenyl)-9*H*-carbazole (**1**) and 3,6-di-*tert*-butyl-9-(4-(2-phenylethynyl)phenyl)-9*H*-carbazole (**2**) are monodenderons, 9-(4-(2-(3-(2-(4-(9*H*-carbazol-9-yl)phenyl)ethynyl)phenyl)ethyny) phenyl)-9*H*-carbazole (**3**), 3,6-di-*tert*-butyl-9-(4-(2-(3-(2-(4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)ethynyl)phenyl)ethynyl)phenyl)-9*H*-carbazole (**4**), and 3,6-di-*tert*-butyl-9-(4-(2-(4-(2-(4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)ethynyl)phenyl)ethynyl)phenyl)-9*H*-carbazole (**5**) are *meta*- and *para*-substituted didendrons.

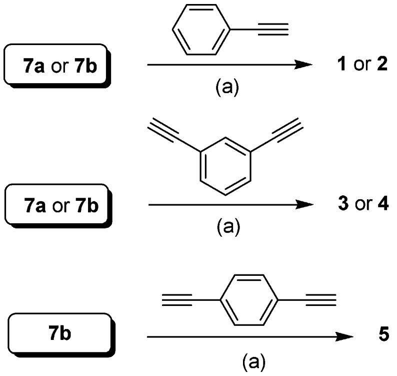
In designing these dendrimers, the ethynylphenyl group was preferred as the core because of its linearity, generally high fluorescence quantum yield, emission in the violet-blue region, and synthetic advantage.[17] A number of compounds containing the ethynylphenyl group as a conventional core have been synthesized and studied for their applications in electrooptical devices.[18] The carbazole group has another advantage: it is easier to modify the 3- and 6-positions and tune the molecular properties.[19] In this report, we present an easy synthesis and discuss the interesting photophysical properties of **1**−**5**. Not only do they exhibit intense luminescence both in solution and in the solid state, but they also show excellent stability. The solvatochromism exhibited by these dendrimers is also discussed.

SCHEME 1[a]



[a] Reagents and conditions: (a) *tert*-butyl chloride, zinc chloride, nitromethane, 40−50 °C, 5 h; (b) Cu, potassium carbonate, 18-crown-6, *o*-dichlorobenzene, reflux, 12 h.

SCHEME 2[a]



[a] Reagents and conditions: (a) CuI, $Pd(PPh_3)_2Cl_2$, PPh_3, triethylamine, tetrahydrofuran, reflux, 12 h (for **1** and **2**), 72 h (for **3** and **4**), and 7 days (for **5**).

Results and Discussions

Synthesis. Following literature[13] methods, carbazole (**6a**) and 3,6-di-*tert*-butyl-9*H*-carbazole (**6b**) were converted into 9-(4-bromophenyl)carbazole (**7a**) and 9-(4-bromophenyl)-3,6-di-*tert*-butylcarbazole (**7b**), respectively (Scheme 1). The latter compounds are the main intermediates in the synthesis of **1**−**5**. Compounds **1** and **2** were synthesized by Sonogashira coupling of 1-ethynylbenzene with **7a** and **7b**, respectively (Scheme 2). Similar Sonogashira coupling of **7a** and **7b** with 1,3-diethynylbenzene yielded **3** and **4**, respectively. Finally, **5** was prepared by coupling 1,4-diethynylbenzene with **7b** (Scheme 2). The coupling of **7a** with 1,4-diethynylbenzene was not successful probably due to lower solubility of the final product (dendrimer similar to **5** without *tert*-butyl groups) in common solvents.

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(10) Ding, J.; Gao, J.; Cheng, Y.; Xie, Z.; Wang, L.; Ma, D.; Jing, X.; Wang, F. *Adv. Funct. Mater.* **2006**, *16*, 575.

(11) Morin, J.; Boudreault, P.; Leclerc, M. *Macromol. Rapid Commun*. **2002**, *23*, 1032.

(12) Grigalevicius, S.; Ma, L.; Xie, Z.; Scheri, U. *J. Polym. Sci., Part A*: *Polym. Chem.* **2006**, *44*, 5987.

(13) Liu, Y.; Nishiura, M.; Wang, Y.; Hou, Z. *J. Am. Chem. Soc*. **2006**, *128*, 5592.

(14) Thomas, K. R.; Lin, J. T.; Tao, Y. T.; Ko, C. *J. Am. Chem. Soc*. **2001**, *123*, 9404.

(15) Guan, M.; Chen, Z.; Bian, Z.; Liu, Z.; Gong, G.; Baik, W.; Lee, H.; Huang, C. *Org. Electron.* **2006**, *7*, 330.

(16) Loiseau, F.; Campagna, S.; Hameurlaine, A.; Dehaen, W. *J. Am. Chem. Soc*. **2005**, *127*, 11352 and references therein.

(17) (a) Rodríguez, J. G.; Esquivias, J.; Lafuente, A.; Díaz, C. *J. Org. Chem.* **2003**, *68*, 8120. (b) Yamaguchi, Y.; Kobayashi, S.; Wakamiya, T.; Matsubara, Y.; Yoshida, Z. *Angew. Chem., Int. Ed.* **2005**, *44*, 7040. (c) Yamaguchi, Y.; Ochi, T.; Miyamura, S.; Tanaka, T.; Kobayashi, S.; Wakamiya, T.; Matsubara, Y.; Yoshida, Z. *J. Am. Chem. Soc.* **2006**, *128*, 4504.

(18) (a) Schumm, J. S.; Pearson, D. L.; Tour, J. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1360. (b) Meier, H.; Ickenroth, D.; Stalmach, U.; Koynov, K.; Bahtiar, A.; Bubeck, C. *Eur. J. Org. Chem.* **2001**, 4431. (c) Anderson, S. *Chem. Eur. J.* **2001**, *7*, 4706.

(19) Joule, J. A. *Adv. Heterocycl. Chem.* **1984**, *35*, 83.

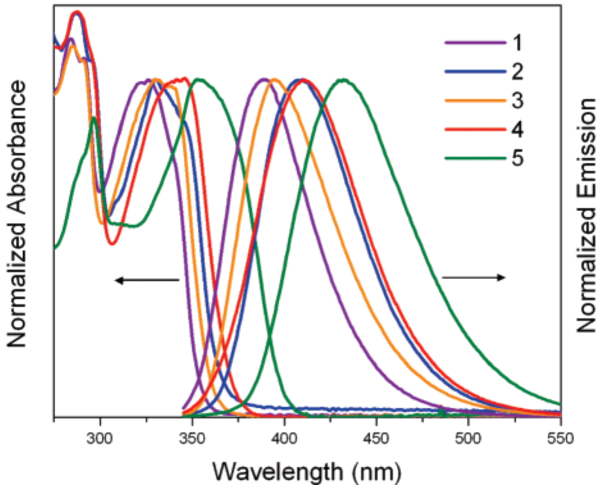

FIGURE 1. Normalized absorption and emission spectra of **1**−**5** recorded in dichloromethane.

TABLE 1. Photophysical Data of 1−5[a] Recorded in Dichloromethane

compd	A_{max} (nm)	ϵ (dm^3 cm^{-} mol^{-1})	λ_{max} (nm)	Φ_F	τ_F (ns)	k^o_R (s^{-1})	k^o_{NR} (s^{-1})
1	326	30125	390	0.72	2.53	2.80×10^8	1.15×10^8
2	334	32808	410	0.80	3.91	2.04×10^8	5.10×10^7
3	329	54712	394	0.80	2.44	3.27×10^8	8.28×10^7
4	337	48525	411	0.83	3.62	2.29×10^8	4.70×10^7
5	353	66750	432	0.89	2.09	4.26×10^8	5.24×10^7

[a] Excitation wavelength = 340 nm for Φ_F and τ_F. TheΦ_F values (±0.01−0.03) are relative to that of diphenyanthracene (0.90 in cyclohexane). The τ_F values were measured from argon-saturated solutions and decay was monitored at the corresponding λ_{max}.

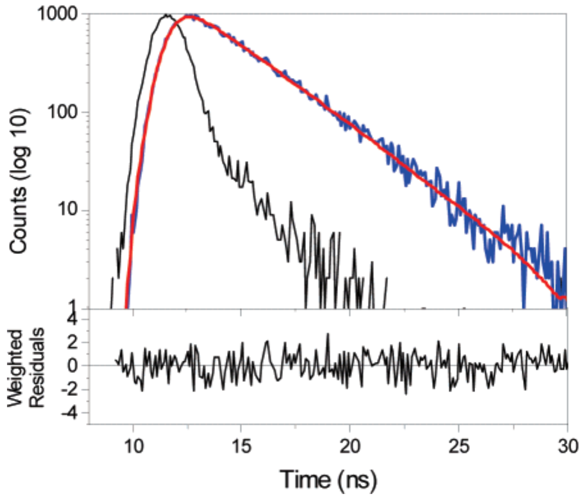

FIGURE 2. Fluorescence decay of **1** monitored at λ_{max} = 390 nm in dichloromethane (τ_F = 2.53 ns, χ^2 = 1.08); excitation wavelength = 340 nm.

TABLE 2. Photophysical Data of 4 and 5 Measured in Different Solvents[a]

	4				**5**			
solvent	A_{max} (nm)	λ_{max} (nm)	Φ_F	τ_F (ns)	A_{max} (nm)	λ_{max} (nm)	Φ_F	τ_F (ns)
pentane	340	359	0.76	1.38	356	385	0.89	0.72
toluene	345	379	0.82	1.65	359	400	0.86	0.85
chloroform	344	400	0.84	2.51	356	419	0.69	1.34
dichloromethane	345	416	0.88	3.62	355	437	0.89	2.09
methanol	338	426	0.81	4.88	354	453	0.41	3.21
acetonitrile	340	435	0.87	5.51	353	470	0.67	4.22

[a] Excitation wavelength = 340 nm for measuring Φ_F and τ_F. The Φ_F values (±0.01−0.03) are relative to that of diphenyanthracene (0.90 in cyclohexane). The τ_F values were measured from argon-saturated solutions and decay was monitored at the corresponding λ_{max}.

Photoluminescence in Solution. Absorption spectra of **1**−**5** recorded in dichloromethane show a $\pi-\pi^*$ band at ~325−353 nm (Figure 1). The absorption maxima of **3** (329 nm) and **4** (337 nm) are not significantly red-shifted from that of **1** (326 nm) and **2** (334 nm), respectively. This indicates that there is only a slight conjugation between the carbazole arms when they are linked at the *meta*-positions of the central phenyl ring.[20] Compound **5** having arms at the *para*-positions of the central phenyl ring expectedly showed a larger red-shifted absorption relative to that of **1**−**4**, indicating a significant conjugation in **5**.

When excited at 340 nm, dilute solutions of **1**−**5** in dichloromethane showed violet to blue emission (Figure 1). It is interesting that the dendrimers that have *tert*-butyl groups (**2** and **4**) show significantly red-shifted fluorescence relative to those that have no *tert*-butyl groups (**1** and **3**). On the other hand, the emission maxima of **3** (394 nm) and **4** (411 nm) are similar to those of **1** (390 nm) and **2** (410 nm), respectively. This indicates that the density of chromophores in a molecule can be enhanced through a *meta* linkage without significantly perturbing the purity of the emission. That there is a larger extension of conjugation in **5** than in **3** and **4** is reflected in its emission; the fluorescence spectrum of **5** (λ_{max} = 437 nm) was the most red-shifted among all the compounds studied.

The fluorescence quantum yields (Φ_F) and lifetimes (τ_F) of **1**−**5** recorded in dichloromethane are presented in Table 1 along with their absorption (A_{max}) and emission (λ_{max}) maxima. The Φ_F values of **1**−**5** were found in the range of 0.72−0.89 relative to that of 9,10-diphenylanthracene (0.90 in cyclohexane).[21] Fluorescence decays of **1**−**5** were fitted with monoexponential functions indicating emission from the singlet excited state in each case. The nonradiative decay of the singlet state was calculated to be about 2 to 4 times lower than the radiative decay for **1**−**5**.

Φ_F values of **4** and **5** measured in various solvents are presented in Table 2. The Φ_F values of **4** were found in the range of 0.76−0.88 irrespective of the solvent polarity, while those of **5** were comparatively lower in polar solvents than in nonpolar solvents. For example, the Φ_F value of **5** in methanol (0.41) was almost half that observed in pentane (0.89) or toluene (0.86). In each solvent, the fluorescence decay of **4** and **5** could be fit monoexponentially, indicating the singlet states are formed exclusively. Interestingly, the τ_F values of both **4** and **5** showed strong solvent dependence and gradually increased with an increase in the solvent polarity. The τ_F value of **4**, for example, was lowest in pentane (0.72 ns) and highest in acetonitrile (4.22 ns). Similarly, the τ_F value of **5** gradually increases from 1.38 ns in pentane to as high as 5.51 ns in acetonitrile.

Emission spectra of **1** were recorded at different concentrations in dichloromethane (see the Supporting Information) to asses the extent of possible dimer formation. We could see sharp

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(20) Yamaguchi, Y.; Ochi, T.; Miyamura, S.; Tanaka, T.; Kobayashi, S.; Wakamiya, T.; Matsubara, Y.; Yoshida, Z. *J. Am. Chem. Soc.* **2006**, *128*, 4504.

(21) Sciano, J. C. *Handbook of Organic Photochemistry*; CRC Press: Boca Raton, FL, 1989; Vol. 1, p 231.

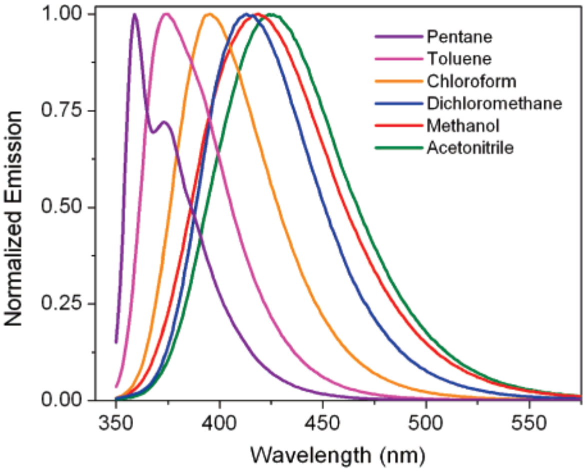

FIGURE 3. Normalized emission spectra of **2** recorded in different solvents.

concentration quenching at very high concentration only but no red shift in its emission spectra indicating no aggregation up to concentrations as high as 10 mmol.

Each dendrimer shows significant solvatochromism. The emission spectra exhibit a more significant red shift in polar solvents than in nonpolar solvents (see the Supporting Information). For example, the emission maximum of **2** in acetonitrile (434 nm) is about 75 nm red-shifted from that in pentane (359 nm) (Figure 3). Similarly the emission maxima of **5** gradually increases going from pentane (385 nm) to acetonitrile (470 nm). This solvatochromic effect can be attributed to a decrease in the energy of the singlet excited states as a function of an increase in the polarity of the solvents.

Typically, a fluorophore has a larger dipole moment in the excited state than in the ground state. Following excitation, solvent dipoles can reorient or relax lowering the energy of the excited state.[21] The solvent dependency of emission of **1**−**5** can be described by plotting the Stokes shift against orientation polarizability (Δ×c4).[22] Mataga−Lippert plots of **1** and **2** are shown in Figure 4. The slope gives the variation of dipole moment upon excitation. The linear relationship suggests the presence of just one excited state. This was also revealed from the monoexponential decay of the florescence of the dendrimers.[16] The solvatochromic effect indicates the dendrimers possess intramolecular charge transfer from the donor (carbazole) to the acceptor (ethynyl) units.[23] Compounds **3** and **4** have higher solvatochromic displacements than **2** because the former compounds have an additional donor acceptor unit. On the other hand, although **5** also has an additional donor acceptor unit, it shows less solvatochromic shift. This may be due to **5** being more symmetrical than **3** and **4**, which results in lower excited state dipole of **5** getting less stabilization by the solvent dipole.[24]

Solid-State Photoluminiscence. Solid-state emissions of **1**−**5** as recorded in poly(methyl methacrylate) (PMMA) matrix (Figure 5) are structured and similar to those obtained in solution. However, the emission spectra recorded from thin films of the dendrimers (Figure 6) are less structured and broader.

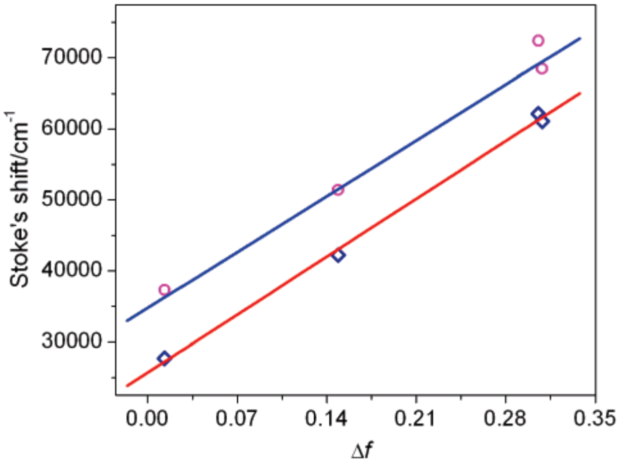

FIGURE 4. Mataga−Lippert plot of **1** (red) and **2** (blue) (solvents: toluene, chloroform, methanol, and acetonitrile in the order of increasing Stokes shifts).

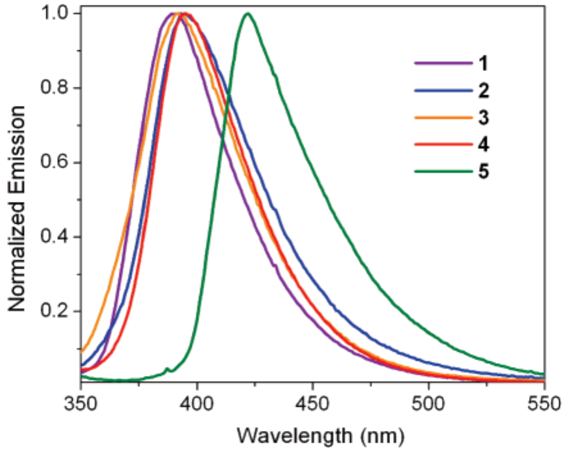

FIGURE 5. Normalized solid-state fluorescence spectra of **1**−**5** recorded in thin films of poly(methyl methacrylate).

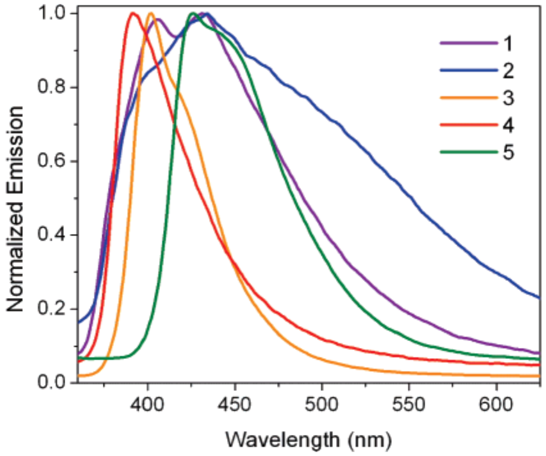

FIGURE 6. Normalized solid-state fluorescence spectra of the thin films of **1**−**5**.

For example, thin films of **1** and **2** show emission from ∼350 nm to more than 550 nm. Interestingly, these broad solid-state emissions were observed mainly from **1** and **2**. Thin films of **3**−**5** showed more structured and narrower emissions like that observed in the PMMA matrix. A head-to-tail compact packing

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[22] Lakowich, J. R. *Principles of Fluorescence Spectroscopy*; Kluwer Academic/Plenum: New York, 1999; p 187.

[23] Fu, H.; Wu, H.; Hou, X.; Xiao, F.; Shao, B. *Synth. Met.* **2006**, *156*, 809.

[24] Thomas, K. R.; Lin, J. T.; Velusamy, M.; Tao, Y.; Chuen, C. *Adv. Funct. Mater.* **2004**, *14*, 83.

TABLE 3. Emission Maxima (λ_{max}) and Quantum Yields of Fluorescence (Φ_F) of 1−5 Recorded in the Solid State

compd	λ_{max} (nm)[a]	λ_{max} (nm)[b]	Φ_F[b]
1	392	406, 431	0.40
2	393	434	0.65
3	392	402	0.85
4	395	392	0.62
5	422	426	0.68

[a] Thin films of PMMA were used as matrices. [b] Data obtained from thin films of **1**−**5**; thin films were prepared by the spin casting method, excitation wavelength = 340 nm; the Φ_F values were measured by using an integrating sphere (errors within 15% range).

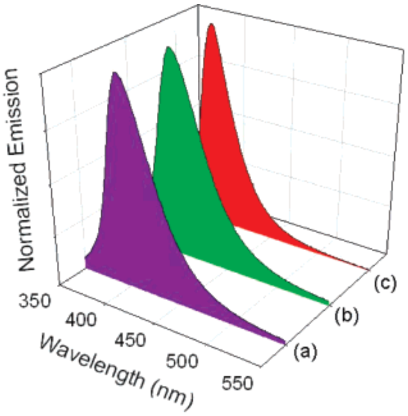

FIGURE 7. Fluorescence spectra recorded from thin films of PMMA containing **1**: (a) pristine, (b) after exposing the film for more than 15 days at ambient conditions, and (c) after heating at 150 °C for 24 h and cooling to room temperature.

may be responsible for excimer formation in the case of **1** and **2**. Thus, in these cases, the emission can be considered to be the combination of the monomeric and excimer emission. Prohibition of compact packing in the case of **3**−**5** due to two bulkier carbazole groups may be the reason why these compounds did not show broader emission.

The quantum yields of fluorescence (Φ_F) in the solid state were measured by using an integrating sphere[25] and are presented in Table 3 along with the emission maxima (λ_{max}). The solid-state emission maxima of **1** and **2** were substantially red-shifted compared to those measured in the matrix PMMA, while such a shift was not observed for **3**−**5**. The solid-state Φ_F values of **1**−**5** ranged from 0.40 to 0.85 with **1** showing the lowest and **3** showing the highest.

Effect of Aging and Annealing on the Solid-State Emission. To evaluate the effect of aging and annealing on the solid-state emission of **1**−**5**, thin films of PMMA containing the dendrimers were exposed to ambient light for several weeks as well as heated to 150 °C for 24 h. The emission spectra of **1** recorded immediately after forming the PMMA thin film, exposing the film to ambient conditions for two weeks, and annealing the film at 150 °C for more than 24 h are shown in Figure 7. There was no change in the emission spectra before and after such treatment. This indicates that **1** maintains its color purity under the conditions we used for aging and annealing. Similar results were obtained for **2**−**5**. This suggests that they are reasonably stable compounds and suitable for use in OLED devices.

Conclusions

Carbazole-based monomeric and dimeric dedrimers (**1**−**5**) were synthesized. Photophysical studies of **1**−**5** indicate that chromophoric density may be increased in these dendrimers through a *meta*-linkage of the dendrons to the central ethnylphenyl core without perturbing the purity of the emission. However, a *para*-linkage of dendrons results in a significant red shift in the emission. Compounds **1**−**5** showed intense luminescence both in solution ($\Phi_F \approx 0.72-0.89$) and in the solid state ($\Phi_F \approx 0.40-0.85$). The solvatochromic effects observed in **1**−**5** can be explained on the basis of charge-transfer complex formation in the excited singlet state. These dendrimers were found to retain their color purity even when they were exposed to 150 °C for more than 24 h. The assessment of OLED device performance of some dendrimers is underway.

Experimental Section

Instrumentation. Mass spectra were recorded on a Shimadzu GCMS-QP5050A instrument equipped with a direct probe (ionization 70 eV). Matrix assisted laser desorption ionization (MALDI) spectra were obtained on a Bruker Daltonic Omniflex instrument (N_2 laser, 337 nm). Melting points are uncorrected. A Bruker spectrometer (working frequency 300.0 MHz for ^{1}H) was used to record the NMR spectra. $CDCl_3$ was the solvent for NMR, and chemical shifts relative to tetramethylsilane at 0.00 ppm are reported in parts per million (ppm) on the δ-scale. Absorption and fluorescence spectra were recorded on a Shimadzu UV-2401 spectrophotometer and a Fluorolog-3 spectrometer, respectively. All measurements were carried out at room temperature unless otherwise specified.

Synthesis. 9-(4-Bromophenyl)carbazole (**7a**) and 9-(4-bromophenyl)-3,6-di-*tert*-butylcarbazole (**7b**) were synthesized following a literature method[13] starting from carbazole (**6a**).

9-(4-(2-Phenylethynyl)phenyl)-9*H*-carbazole (1). Compound **7a** (2.405 g, 7.5 mmol), *trans*-dichlorobis(triphenylphosphine)palladium(II) (0.265 g, 0.375 mmol), triphenylphosphine (0.0975 g, 0.375 mmol), CuI (0.07 g, 0.375 mmol), and anhydrous triethylamine were mixed in a degassed round-bottom flask. The mixture was heated to reflux. A solution of phenylacetylene (0.765 g, 7.6 mmol) in 10 mL of tetrahydrofuran (THF) was added to the above mixture. The mixture was refluxed overnight with stirring. After the reaction mixture was allowed to cool to room temperature, the solvent was evaporated under vacuum. The residue was mixed with dichloromethane and washed with water and then with brine. The organic layer was collected and dried under $MgSO_4$. After filtration, the solvent was removed under vacuum. The crude product was purified by chromatography (silica gel, 80% hexane in dichloromethane) to obtain pure **1** (0.75 g, 31%) as a yellowish white shining solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.30 (m, 2 H), 7.35−7.38 (m, 3 H), 7.41−7.45 (m, 4H), 7.54−7.6 (m, 4H), 7.75 (m, 2H), 8.14 (d, J = 10 Hz, 2H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 89, 91, 110, 120, 122, 122.5, 123, 124, 124, 126, 128, 132, 137, 140; mass spectrum (DIP-MS) m/z M$^+$ 343 (100%); HRMS (EI+) m/z 343.1362, calcd m/z 343.1361; mp 134−136 °C.

3,6-Di-*tert*-butyl-9-(4-(2-phenylethynyl)phenyl)-9*H*-carbazole (2). This compound was obtained in 25% yield as a white shiny solid, following the same procedure described for the synthesis of **1** with **7b** instead of **7a**. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45 (s, 18H), 7.3−7.39 (m, 4H), 7.44−7.5 (m, 1H), 7.52−7.6 (m, 6H), 7.73−7.78 (m, 2H), 8.15 (s, 2H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 32, 35, 88.5, 90,109, 116.5, 122, 123.5, 124, 126.5, 128, 129, 132, 132.5, 133.5, 138, 139, 143.5; mass spectrum (DIP) m/e M$^+$ 455 (60%), 440 (80%), 185 (100%); HRMS (EI+) m/z 455.2621, calcd m/z 455.2613; mp 217−220 °C.

9-(4-(2-(3-(2-(4-(9*H*-Carbazol-9-yl)phenyl)ethynyl)phenyl)ethyny) phenyl)-9*H*-carbazole (3). Compound **3** was obtained

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[25] De Mello, J. C.; Wittman, J. C.; Friend, R. H. *Adv. Mater.* **1997**, *9*, 230.

following the same procedure described for the synthesis of **1** with 1,3-diethynylbenzene instead of phenylacetylene in a half molar ratio. 1,3-Diethynylbenzene was added to **7a**, and the mixture was refluxed for 3 days. This gave pure **3** in 20% yield as a white shiny solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.3 (m, 4H), 7.4−7.5 (m, 9H), 7.6 (m, 6H), 7.8 (m, 5H), 8.15 (d, $J = 10$ Hz, 4H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 89, 119.5, 120, 122, 123.5, 126, 127, 129, 132, 133.5, 135, 138, 141; mass spectrum (MALDI-TOF) *m*/*z* M^+ 608; HRMS (FAB+) *m*/*z* 608.225, calcd *m*/*z* 608.2252; mp 217−219 °C.

3,6-Di-*tert*-butyl-9-(4-(2-(3-(2-(4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)ethynyl)phenyl)ethynyl)phenyl)-9*H*-carbazole (4). Compound **4** was obtained following the same procedure described for the synthesis of **3**. 1,3-Diethynylbenzene was treated with **7b**, and the reaction mixture was refluxed for 3 days to obtain pure **4** in 20% yield as a white shiny solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45 (s, 36H), 7.38−7.42 (m, 5H), 7.47−7.51 (m, 4H), 7.53−7.62 (m, 7H), 7.75−7.8 (m, 4H), 8.15 (s, 4H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 32, 35, 89.5, 90, 109, 110, 116.5, 120.5, 121, 124, 126, 126.5, 127, 128, 132, 133.5, 135, 138, 138.5, 143.5; mass spectrum (MALDI-TOF) *m*/*z* M^+ 833; HRMS (FAB+) *m*/*z* 832.4756, calcd *m*/*z* 832.4754; mp 202−205 °C.

3,6-Di-*tert*-butyl-9-(4-(2-(4-(2-(4-(3,6-di-*tert*-butyl-9*H*-carbazol-9-yl)phenyl)ethynyl)phenyl)ethynyl)phenyl)-9*H*-carbazole (5). Compound **5** was obtained by reaction of 1,3,5-triethynylbenzene (in one-third molar ratio) with **7b**. The mixture was refluxed for 7 days to obtain pure **5** in 18% yield as a white shiny solid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.45 (s, 36H), 7.38−7.52 (m, 8H), 7.58−7.6 (m, 8H), 7.72−7.78 (m, 4H), 8.15 (s, 4H); ^{13}C NMR (300 MHz, $CDCl_3$) δ 32, 35, 89.5, 90, 109, 117, 123, 127, 132, 133, 139, 143; mass spectrum (MALDI-TOF) *m*/*z* M^+ 833, HRMS (FAB+) *m*/*z* 832.4756, calcd *m*/*z* 832.4754; mp >360 °C.

Fluorescence Quantum Yields (Φ_F). The Φ_F values in solution were measured following a general method with 9,10-diphenylanthracene ($\Phi_F = 0.9$ in cyclohexane) as the standard. Diluted solutions of **1**−**5** in appropriate solvents were used for recording the fluorescence spectra. Sample solutions were taken in quartz cuvettes and degassed for ∼15 min. The degassed solutions had absorbances of 0.05−0.09 at 340 nm. The fluorescence spectra of each were recorded 3−4 times and an average value of integrated areas of fluorescence used for the calculation of Φ_F. The refractive indices of solvents at the sodium D line were used. The Φ_F values in the solid state were measured following a literature method.[25] A concentrated dichloromethane solution of sample was cast as thin films on quartz plates and then was allowed to dry. The plate was inserted into an integrating sphere and the required spectra were recorded. The samples were excited at 340 nm. It is well-known that for compounds showing an overlap of the absorption and the emission spectra (a small Stokes shift), the use of an integrating sphere results in a substantial loss of emission due to reabsorption of the emitted light. A method employed earlier was used to minimize the impact of this on the calculation of the Φ_F.[3]

Fluorescence Lifetime (τ_F) Measurement. Solutions of **1**−**5** that showed absorbances of 0.1−0.25 at 340 nm were placed in quartz cuvettes. Fluorescence decay profiles of argon-degassed (∼15 min) solutions were recorded with use of a single photon counting spectrofluorimeter. Decays were monitored at the corresponding emission maximum of the compounds. In-built software allowed the fitting of the decay spectra ($\chi^2 = 1-1.5$) and yielded the fluorescence lifetimes.

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Supporting Information Available: ^{1}H NMR and ^{13}C NMR spectra of **1**−**5**, UV−vis and fluorescence spectra of **1**−**5** recorded in different solvents, and fluorescence decay profiles of **1**−**5** in dichloromethane. This material is available free of charge via the Internet at http://pubs.acs.org.

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