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Ethynylphenyl-Linked Carbazoles as a Single-Emitting Component for White Organic Light-Emitting Diodes

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A comparative photophysical study of several new dendrimers consisting of the ethynylphenyl core and carbazole dendrons (**1**−**5**) is presented. Dilute solutions of **1**−**5** show intense blue emission in dichloromethane (λ_{max} = 410−438 nm, Φ_F = 0.53−0.91, τ_F = 2.09−3.91 ns). The solvatochromic and solid-state emission behavior of **1**−**5** (λ_{max} = 426−443 nm, Φ_F = 0.30−0.90) is discussed. The geometry of **5** allows formation of a strong electromeric state, which was not the case with **1**, indicating that the ethynylphenyl group can be used to tune dendrimer electroluminescence (EL) properties. An organic light-emitting diode (OLED) consisting of **1** as the emitting layer showed blue emission (CIE: 0.28, 0.20), whereas the EL of **5** (CIE: 0.34, 0.36) was found to be close to ideal white light. White OLEDs consisting of **5** as the emitting layer showed a maximum brightness of 450 cd/m^2 and a maximum efficiency of 0.11 cd/A at 11 V.

Introduction

Solid-state lighting technologies have received increased attention because of their potential to be an efficient replacement for conventional lighting sources. For example, it has been predicted that over a 20 year period, solid-state lighting could reduce global electricity use by 50% and power consumption by 760 GW in the United States alone.[1,2] Organic, inorganic, and organic−inorganic hybrid materials have been tried in next-generation solid-state lightings that are based on light-emitting diode (LED) technologies.[3−13] Because organic materials are easily synthesized and processed, white organic light-emitting diodes (WOLEDs) have received particular attention.[13−17] A combination of three organic components emitting three colors (blue, green, and red) is often used in WOLEDs.[16−19] Another widely employed approach is to use a single chromophore that emits white light, resulting from the combination of its monomeric (blue) and excimeric or electromeric (orange) emission.[4,8,13] The latter emission results from a stacking of molecules that is usually induced by $\pi-\pi$ interactions.

Research on organic electroluminescence (EL) has focused on both low (small molecule) and extremely high molecular weight (polymer) materials. Recently, however, light-emitting dendrimers have received increased attention because they combine the merits of well-defined structures and the chemical purity of small molecules and the simple solution-processing advantage of polymers.[20−25] By

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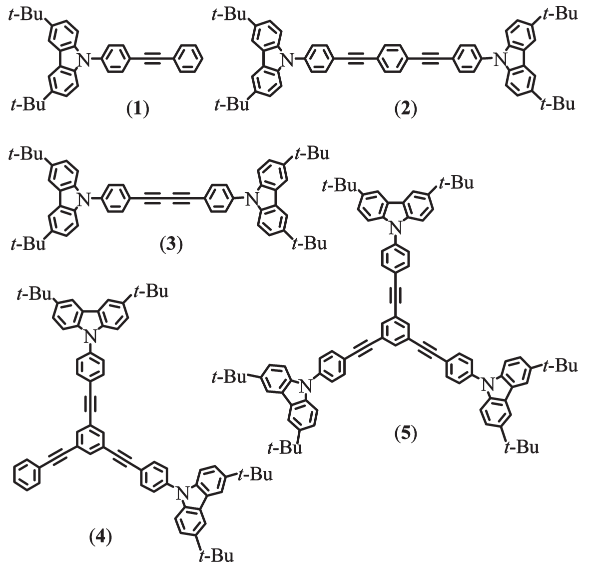
(1) Solid-State Lighting, http://lighting.sandia.gov/.
(2) *The Promise of Solid State Lighting for General Illumination*; Optoelectronics Industry Development Association: Washington, D. C., 2001.
(3) Bowers, M. J.II; McBride, J. R.; Rosenthal, S. J. *J. Am. Chem. Soc.* **2005**, *127*, 15378.
(4) Zhao, Z.; Xu, B.; Yang, Z.; Wang, H.; Wang, X.; Lu, P.; Tian, W. *J. Phys. Chem. C* **2008**, *112*, 8511.
(5) Kulkarni, A. P.; Kong, X.; Jenekhe, S. A. *Macromolecules* **2006**, *39*, 8699.
(6) Kulkarni, A. P.; Jenekhe, S. A. *J. Phys. Chem. C* **2008**, *112*, 5174.
(7) Wang, L.; Wong, W.-Y.; Lin, M.-F.; Wong, W.-K.; Cheah, K.-W.; Tam, H.-L.; Chen, C. H. *J. Mater. Chem.* **2008**, *18*, 4529.
(8) Li, J. -Y.; Liu, D.; Ma, C.; Lengyel, O.; Lee, C.-S.; Tung, C. −H.; Lee, S.-T. *Adv. Mater.* **2004**, *16*, 1538.
(9) Ki, W.; Li, J. *J. Am. Chem. Soc.* **2008**, *130*, 8114.
(10) Peng, Z.; Bao, Z.; Galvin, M. E. *Chem. Mater.* **1998**, *10*, 2086.
(11) Shah, B. K.; Neckers, D. C.; Shi, J.; Forsythe, E. W.; Morton, D. J. *Chem. Mater.* **2006**, *18*, 603.
(12) Shah, B. K.; Neckers, D. C.; Shi, J.; Forsythe, E. W.; Morton, D. J. *J. Phys. Chem. A* **2005**, *109*, 7677.
(13) Liu, Y.; Nishiura, M.; Wang, Y.; Hou, Z. *J. Am. Chem. Soc.* **2006**, *128*, 5592.
(14) Chuen, C. H.; Tao, Y. T. *Appl. Phys. Lett.* **2002**, *81*, 4499.
(15) D'Andrade, B. W.; Holmes, R. J.; Forrest, S. R. *Adv. Mater.* **2004**, *16*, 624.
(16) D'Andrade, B. W.; Forrest, S. R. *Adv. Mater.* **2004**, *16*, 1585.
(17) Yeh, S.; Chen, H.; Wu, M.; Chan, L.; Yeh, H.; Chen, C.; Lee, J. *Org. Electron.* **2006**, *7*, 137.
(18) Abbel, R.; Grenier, C.; Pouderoijen, M. J.; Stouwdam, J. W.; Leclere, P. E. L. G.; Sijbesma, R. P.; Meijer, E. W.; Schenning, A. P. H. J. *J. Am. Chem. Soc.* **2009**, *131*, 833.
(19) Qi, X.; Slootsky, M.; Forrest, S. *Appl. Phys. Lett.* **2008**, *93*, 193306/1–3.
(20) Zhao, Z.; Li, J.-H.; Chen, X.; Wang, X.; Lu, P.; Yang, Y. *J. Org. Chem.* **2009**, *74*, 383.
(21) Burn, P. L.; Lo, S.-C.; Samuel, I. D. W. *Adv. Mater.* **2007**, *19*, 1675.
(22) Anthopoulos, T. D.; Frampton, M. J.; Namdas, E. B.; Burn, P. L.; Samuel, I. D. W. *Adv. Mater.* **2004**, *16*, 557.
(23) Halim, M.; Pillow, J. N. G.; Samuel, I. D. W.; Burn, P. L. *Adv. Mater.* **1999**, *11*, 371.
(24) Lai, W.; Zhu, R.; Fan, Q.; Hou, L.; Cao, Y.; Huang, W. *Macromolecules* **2006**, *39*, 3707.
(25) Kwon, T. W.; Alam, M. M.; Jenekhe, S. A. *Chem. Mater.* **2004**, *16*, 4657.

Chart 1



regulating dendrimer synthesis, one could expect predictable tuning of photophysical and electrochemical properties.[26−28] Although dendrimers consisting of different types of dendrons and chromophores have been the subject of a number of EL studies, few reports discuss the EL behavior of dendrimers consisting of ethyne linkages.[20,21,29,30] Ethyne linkages allow the compounds to adopt a planar structure, which induces stronger intermolecular interactions between chromophores. We proposed that ethyne linkages could be effectively used to control the degree of intermolecular interaction in dendrimers to achieve white emission from a single component.

Herein, we report synthesis and a comparative photophysical study of several ethnynylphenyl-dendron-based compound/dendrimers consisting of a different number of the carbazole moieties (**1**−**5**, Chart 1). The ethynylphenyl group was chosen as the dendrimer core because of its linearity, generally high fluorescence quantum yield, emission in the violet-blue region, and ease of synthesis.[31−33] Carbazoles are efficient blue emitters and hole-transporters[34−37] and both carbazole-based small molecules and polymers have been extensively investigated for applications in optoelectronic devices such as photovoltaics and OLEDs.[38−42] Li et al. achieved broad white emission from 1,3,5-tris(2-(9-ethylcarbazyl-3)-ethylene)benzene utilizing both monomer and electromer emissions.[8] Liu et al. obtained white EL from carbazoles linked through an enyne bond.[11] Very recently, Zhao et al. demonstrated efficient yellow EL from acetylene-linked dendrimers consisting of carbazole/fluorene dendrons and a pyrene core.[20] We have shown that ethynylphenyl-based carbazole derivatives emit efficiently both in solution and in the solid state.[34] Recently, we have found that the emission of carbazole can be red-shifted as much as 120 nm by *N*-substitution.[43] In fact, our work demonstrates that carbazoles can be appropriately substituted to achieve blue, green, and red emissions.[43] Suitably substituted carbazoles can be precipitated into nanoparticles exhibiting highly red-shifted and reversible emissions.[44] We now demonstrate that the geometry of carbazole-based dendrimers, and thus the $\pi-\pi$ interactions, can be controlled through ethyne linkages such that white EL can be obtained from a single emitter. A device containing **5** as the emitting layer exhibits white EL with a maximum brightness of 450 cd/m^2 and a maximum current efficiency of 0.11 cd/A at 11 V. Commission Internationale d'Enclaorage (CIE) chromaticity coordinates (0.35, 0.36) of the device was found to be close to those of ideal white light.

Results and Discussion

Synthesis. The syntheses of **1** and **2** are described elsewhere.[34] Compound **3** was obtained by self-coupling of 3,6-di-*tert*-butyl-9-(4-ethynylphenyl)-*9H*-carbazole (**8**) and the latter subjected to Sonogashira coupling with 1,3-dibromo-5-(2-phenylethynyl)benzene (**9**) to obtain **4** (Scheme 1). Compound **8** was synthesized by ethynylation of 3,6-di-*tert*-9-(4-iodophenyl)-*9H*-carbazole (**6**). The latter was prepared following our previously described methods.[44] Compound **9**, required for the synthesis of **4**, was obtained by reaction of 1,3-dibromo-5-iodobenzene with phenylacetylene under Sonogashira conditions. Dendrimer **5** was prepared by an alternate route, i.e., coupling **6** with 1,3,5-triethynylbenzene. The latter was obtained by standard ethynylation of 1,3,5-triiodobenzene.[45] These reactions are facile, easy to perform, and produce acceptable overall yields of **3**−**5**.

Photoluminescence in Solution and in the Solid State. Absorption spectra of **1-5** recorded in dichloromethane

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(26) Burn, P. L.; Samuel, I. D. W. *Mater. Today* **1998**, *1*, 3.
(27) Goodson, T. *Annu. Rev. Phys. Chem.* **2005**, *56*, 581.
(28) Fréchet, J. M. J.; Tomalia, D. A.; Eds., *Dendrimers and Other Dendritic Polymers*; Wiley−VCH: Chichester, U.K., 2001.
(29) Wang, P. W.; Liu, Y. J.; Decadoss, C.; Bharathi, P.; Moore, J. S. *Adv. Mater.* **1996**, *8*, 237.
(30) Cha, S. W.; Choi, S.-H.; Kim, K.; Jim, J.-I. *J. Mater. Chem.* **2003**, *13*, 1900.
(31) Rodríguez, J. G.; Esquivias, J.; Lafuente, A.; Díaz, C. *J. Org. Chem.* **2003**, *68*, 8120.
(32) Yamaguchi, Y.; Kobayashi, S.; Wakamiya, T.; Matsubara, Y.; Yoshida, Z. *Angew. Chem., Int. Ed.* **2005**, *44*, 7040.
(33) Yamaguchi, Y.; Ochi, T.; Miyamura, S.; Tanaka, T.; Kobayashi, S.; Wakamiya, T.; Matsubara, Y.; Yoshida, Z. *J. Am. Chem. Soc.* **2006**, *128*, 4504.
(34) Adhikari, R. M.; Mondal, R.; Shah, B. K.; Neckers, D. C. *J. Org. Chem.* **2007**, *72*, 4727.
(35) Zhao, Z.; Li, J.-H.; Chen, X.; Lu, P.; Yang, Y. *Org. Lett.* **2008**, *10*, 3041.
(36) Zhu, Z.; Moore, J. S. *J. Org. Chem.* **2000**, *65*, 116.
(37) Zhu, Z.; Moore, J. S. *Macromolecules* **2000**, *33*, 801.
(38) Sigwalt, P.; Wegner, G.; Morin, J.-F.; Leclerc, M.; Ades, D.; Siove, A. *Macromol. Rapid Commun.* **2005**, *26*, 761.
(39) Morin, J.; Boudreault, P.; Leclerc, M. *Macromol. Rapid Commun.* **2002**, *23*, 1032.
(40) Jiang, X.; Register, R. A.; Richard, A.; Killeen, K. A.; Thompson, M. E.; Pschenitzka, F.; Sturm, J. C. *Chem. Mater.* **2000**, *12*, 2542.
(41) Boudreault, P.-L. T.; Blouin, N.; Leclerc, M. *Adv. Polym. Sci.* **2008**, *212*, 99.
(42) Blouin, N.; Leclerc, M. Acc. Chem. Res. **2008**, *41*, 1110 and references there in.
(43) Adhikari, R. M.; Neckers, D. C.; Shah, B. K. *J. Org. Chem.* **2009**, *74*, 3341.
(44) Adhikari, R. M.; Shah, B. K.; Palayangoda, S. S.; Neckers, D. C. *Langmuir* **2009**, *25*, 2402.
(45) Suresh, P.; Srimurugan, S.; Babu, B.; Pati, H. N. *Tetrahdedron: Assym.* **2007**, *18*, 2820.

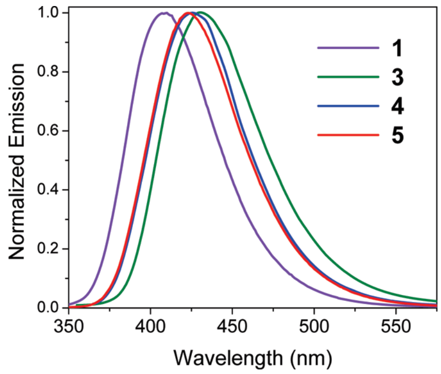
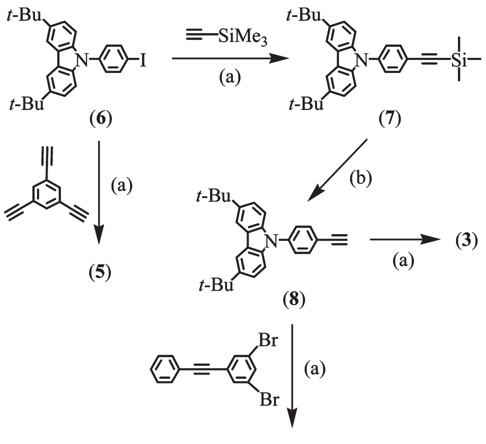


Figure 1. Normalized emission spectra of **1** and **3**−**5** recorded in dichloromethane (λ_{exc}, 340 nm).

Scheme 1. [a]



[a] Reagents and conditions: (a) $Pd(PPh_3)_2Cl_2$, PPh_3, CuI (stirring at room temperature in triethylamine for 12 h for **7**, refluxing for 2 days in *N*,*N*-diisopropylethylamine for **3** and **4**, and refluxing for 4 days in *N*,*N*-diisopropylethylamine for **5**); (b) aqueous NaOH, methanol, dichloromethane, room temperature, overnight stirring.

Table 1. Absorption Maximum (A_{max}), Emission Maximum (λ_{max}), Fluorescence Quantum Yield (Φ_F), and Fluorescence Lifetime (τ_F) of 1−5 Recorded in Dichloromethane and in the Thin Film[a]

	solution				solid	
compd	A_{max} (nm)	λ_{max} (nm)	Φ_F	τ_F (ns)	λ_{max} (nm)	Φ_F
1[b]	334	410	0.80	3.91	434	0.65
2[b]	353	432	0.89	2.09	426	0.68
3	355	438	0.53	2.43	437	0.30
4	348	431	0.90	3.21	443	0.72
5	347	428	0.91	3.68	430	0.90

[a] Excitation wavelength = 340 nm for measurements of Φ_F and τ_F. The Φ_F values recorded in dichloromethane (±0.01−0.04) are relative to that of 9,10-diphenylanthracene (0.90 in cyclohexane), whereas the Φ_F values from thin films were measured using an integrating sphere (errors within 15% range). The τ_F values were measured from argon-saturated solutions and decay was monitored at the corresponding λ_{max}. [b] The photophysical data of **1** and **2** are reproduced from ref 34.

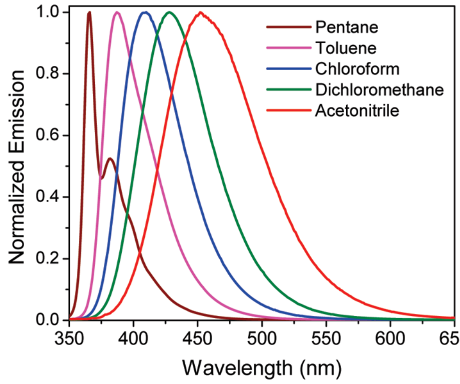


Figure 2. Normalized emission spectra of **5** recorded in different solvents (λ_{exc}, 340−350 nm).

(DCM) show a π−π* band at ~334−355 nm (spectra provided in the Supporting Information). Absorption maxima (A_{max}) of **2** (353 nm) and **3** (355 nm) are red-shifted relative to **1** (334 nm), owing to an increased conjugation in **2** and **3**. The carbazole arms are at the para-positions of the central phenyl rings in **2** and **3**. On the other hand, meta-linkages of the carbazole moieties to the central phenyl ring in **4** and **5** result in discontinuity of effective conjugation. Consequently, the A_{max} of **4** (338 nm) and **5** (347 nm) are slightly blue-shifted relative to **2** and **3**.

Emission behavior and photophysical properties of **1** and **2** recorded in different solvents were provided earlier.[34] Both emit intensely blue in DCM. However, the emission of **2** (λ_{max} = 432 nm) was observed to be considerably red-shifted to that of **1** (λ_{max} = 410 nm). This can be attributed to an increased conjugation in **2** relative to **1**. Dilute solutions of **3**−**5** in DCM showed intense blue emission when excited at 340 nm (Figure 1), similar to those of **1** and **2**. Emission maxima of **4** (431 nm) and **5** (428 nm) are similar to those of **2** (432 nm) and **3** (438 nm). Given the meta-linkages of the carbazole units to the central phenyl ring in **4** and **5**, one would assume the emission of these dendrimers to be blue-shifted relative to those of **2** and **3**. Nonetheless, it should be noted that although the effective conjugation is broken in **4** and **5**, some electronic communication between the arms can still be expected.[33] This results in the similar emission maxima of **2**−**5**. Fluorescence quantum yields (Φ_F) were found to be quite high for **1**−**5** (~80−90%) in DCM, except for **3** (53%) (Table 1). The fluorescence decay profiles of **1**−**5** (τ_F ≈ 2.09−3.91 ns) could be satisfactorily fitted with monoexponential functions, indicating emission from a single excited state in each case. Thus, the possibility of the ethynylphenyl and carbazole moieties behaving as two separate chromophoric units can be ruled out.

Dendrimers **3**−**5** show significant solvatochromism, similar to **1** and **2**.[34] For example, the emission spectra of **5** show a red-shift of more than 85 nm from nonpolar (pentane) to polar (acetonitrile) (Figure 2). There is no noticeable difference in the A_{max} of these dendrimers in different solvents (see the Supporting Information). Thus, the solvatochromic effect is related to a decrease in the energy of the singlet excited state because of the reorientation or relaxation of the solvent dipoles.[46] Lowering of the energy of the excited state is facilitated by the polar nature of the excited state, which possibly results from intramolecular charge transfer from the donor (carbazole) to the acceptor (ethynyl) units, giving rise to the impact of polar solvents on the emission.[34]

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(46) Lakowich, J. R. *Principles of Fluorescence Spectroscopy*; Kluwer Academic/Plenum: New York, 1999.

Table 2. Photophysical Data of 1 and 5 Recorded in Different Solvents[a]

	1				**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	325	359	0.76	1.68	346,360	366	0.90	1.70
toluene	329	374	0.85	1.77	349	387	0.92	1.72
chloroform	320	395	0.64	2.39	350	410	0.96	2.52
dichloromethane	334	410	0.80	3.91	350	428	0.91	3.68
methanol	325	418	0.53	4.99	348	438	0.72	5.11
acetonitrile	325	424	0.70	4.75	347	452	0.84	6.09

[a] Excitation wavelength = 340 nm for measurements of Φ_F and τ_F. The Φ_F values recorded in dichloromethane (±0.01−0.03) are relative to that of 9,10-diphenylanthracene (0.90 in cyclohexane). The τ_F values were measured from argon-saturated solutions and decay was monitored at the corresponding λ_{max}.

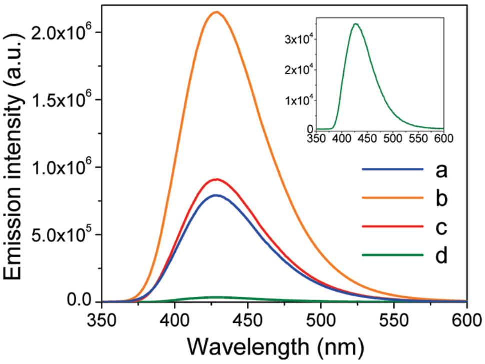

Figure 3. Emission spectra of **5** recorded in dichloromethane at different concentrations: (a) 3.5×10^{-6} M, (b) 3.5×10^{-5} M, (c) 3.5×10^{-4} M, and (d) 3.5×10^{-3} M (inset: the enlarged emission spectrum of **5** recorded at 3.5×10^{-3} M).

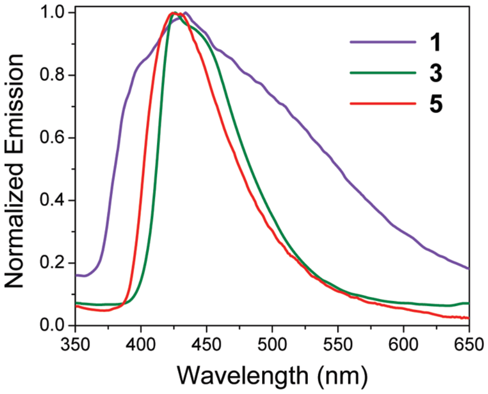

Figure 4. Thin film emission spectra of **1**, **3**, and **5**.

A gradual increase in fluorescence lifetimes was observed for **1** from pentane (τ_F = 1.68 ns) to acetonitrile (τ_F = 4.75 ns). Dendrimer **5** showed similar behavior. Its τ_F gradually increased as solvent polarity increased (Table 2). Stabilization of the relatively polar singlet excited state of **1** and **5** in a polar solvent appears to be the reason for this.[46] However, no order was observed in the Φ_F values of either **1** or **5**. The Φ_F value of **1** was the highest in toluene (85%), whereas that of **5** was highest in chloroform (96%). The Φ_F values of both **1** (53%) and **5** (72%) were lowest in methanol.

Significant fluorescence quenching of **5** was observed in DCM at higher concentrations (Figure 3). Though the fluorescence intensity almost doubles when the concentration of **5** is increased from 3.5×10^{-6} M to 3.5×10^{-5} M, it decreases by almost the same amount when the concentration is increased to 3.5×10^{-4} M and is almost completely quenched at a concentration as high as 3.5×10^{-3} M. Even though the fluorescence intensity is significantly decreased at a higher concentration ($> 1 \times 10^{-3}$ M), the λ_{max} remains unchanged (Table 2). Similar behavior is observed with **1**.[34] However, little quenching of fluorescence was observed for **3** and **4** up to a concentration as high as 1×10^{-3}M, although in these cases, the λ_{max} values were found to be slightly red-shifted (see the Supporting Information). Because the ethynylphenyl moieties of **1** can stack together in a tail to tail fashion without any steric hindrance, aggregation may be induced even at a lower concentration (~1×10^{-4} M) in **1**. Such aggregation is minimized in **3** and **4** because of the presence of the *tert*-butyl groups at both dendrons, and, thus, these dendrimers do not undergo aggregation even at relatively higher concentrations (~1×10^{-3} M). The case of **5** is interesting. Apparently, the effect in **5** is not similar to that observed in **3** and **4**, although it has three *tert*-butyl groups that could prevent aggregation. Weak aggregation in which the carbazole dendron of a dendrimer is aligned between the two arms of another dendrimer may be a possibility.

The thin-film emission of **1** was red-shifted by more than 20 nm than the corresponding emission in DCM. In fact, a broad emission ranging from 340 to 650 nm was observed from the thin film of **1**, which is considerably different than that observed in solution.[34] On the other hand, the thin film spectra of **2**−**5** were similar to the corresponding spectra recorded in dilute solutions, the difference being that the thin film spectra were a little broader. It is evident that because of the dendrimeric structure of **2**−**5**, stacking of the carbazole groups and therefore the formation of excimers was largely hindered. For example, the solid-state emission of **5** (λ_{max} = 430 nm, Figure 4) is similar to the emission observed in DCM (λ_{max} = 428 nm). The Φ_F values recorded of the thin films of **1**−**4** were noticeably lower than those observed in DCM. Nonetheless, the Φ_F values observed in both DCM (91%) and the solid state (90%) were almost the same for **5**.

It should be noted that these dendrimers are robust fluorescent materials. For example, the emission spectra of **5** remain unchanged when its thin film was left at ambient condition for several months or heated at 150 °C for about 48 h. Similar behaviors were observed for **1**.[34] This indicates that both **1** and **5** show no decomposition

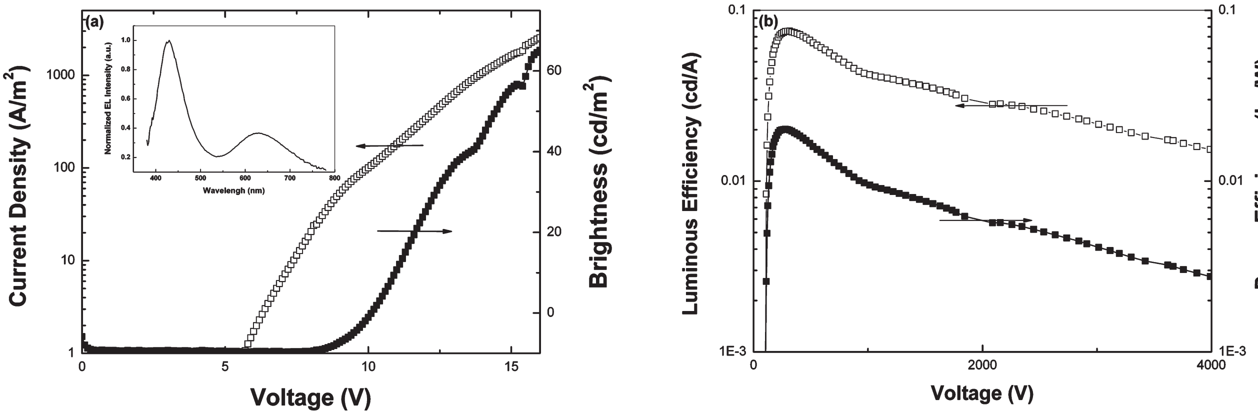

Figure 5. (a) *J*−*V*−*L* characteristics (inset: electroluminescence spectrum) and (b) current efficiency curves of a device consisting of **1** as the emitting layer (device configuration: ITO/NPB (40 nm)/**1** (vacuum deposited, 30 nm)/Bphen (20 nm)/Mg:Ag/Ag).

and maintain the color purity under the conditions mentioned above.

Electroluminescence. Films of **1** fabricated by either vacuum deposition or spin coating tend to crystallize and good quality films suitable for device fabrication could not be obtained from **2**−**4**. Nevertheless, **5** formed good quality amorphous film with fairly smooth surface and devices consisting of **1** and **5** as the emitting layer could be fabricated and characterized.[47] A device with a configuration of ITO/NPB (40 nm)/**1** (vacuum deposited, 0 nm)/Bphen (20 nm)/Mg:Ag/Ag showed an EL spectrum consisting of a blue emission peak (430 nm) and a small shoulder at 630 nm (Figure 5).[48]

The EL spectrum of **1** was similar to the thin film photoluminescence (PL) emission, except that the former is structured and has two distinct peaks. The blue part of both EL and PL spectra originate from the same radiative-decay process of singlet excitons. The 630 nm shoulder of EL spectrum corresponds to the emission from an electromer,[4,8] the latter corresponding to an excimeric state formed upon electric excitation. The turn on voltage of the device was 10.3 V and it exhibited blue EL (CIE: 0.28, 0.20) with a maximum brightness of 66 cd/m^2 at 16.3 V and a maximum efficiency of 0.075 cd/A at 11.9 V. A device containing spin-coated **1** showed even poorer characteristics with the turn on voltage of 18.2 V, a maximum brightness of 14 cd/m^2 at 21.0 V, and a maximum efficiency of 0.017 cd/A. The poor performance of these devices is probably because of the poor quality of films of **1** resulting from its tendency to crystallize.

Single-layer devices consisting of **5** as the emitting layer, on the other hand, exhibited white EL. For example, the EL (CIE: 0.35, 0.36 at 12 V) of a device with a configuration of ITO/PEDOT:PSS/**5** (spin-coated)/Cs_2CO_3/Al was observed to closely approach CIE coordinates of pure white with color rendering index (CRI) as high as 87 (spectra and current-density-luminescence (*J*−*V*−*L*) as well as current-efficiency profiles provided in the Supporting Information).[49] The maximum brightness and efficiency were, respectively, 115 cd/m^2 at 13 V and 0.022 cd/A. A device with a configuration of ITO/PEDOT:PSS/**5** (spin-coated)/Bphen/Mg:Ag showed a much better performance (Figure 6). The EL of the device (CIE: 0.34, 0.36) at 11 V was close to ideal white light with a CRI value as high as 89. The turn on voltage (~6.6 V) was much lower than that observed for **1**. With this device, a maximum brightness of 450 cd/m^2 at 13 V and a maximum efficiency of 0.11 were achieved.

The EL of **5** is clearly a combination of emissions corresponding to monomeric units (blue) as well as electromers (orange). Interestingly, the blue component of the emission was found dependent upon the voltage applied. It initially increases with an increase in the electric field, but decreases at the higher voltages (Figure 5a). Similar behaviors have been observed with other blue and green emitters.[5] The phenomenon is related to charge-trapping and the radiative recombination efficiency of the electron−hole (e−h) pairs, which depend on the electric field.[50,51] At the lower electric strength, charge-trapping and recombination of e−h pairs occurs both at the monomeric and excimeric manifolds. The probability of the trapped electrons recombining with mobile holes on the monomeric manifold is facilitated initially with an increase in the electric strength until a saturation point is reached. The recombination of e−h pairs on the excimeric manifold dominates at the higher electric strength. Although both monomeric and electromeric emissions were observed from **1**, the intensity of the electromeric emission was too low to produce white EL. On the other hand, the orange component of the EL of **5** remains strong, probably because of an optimal intramolecular distance in the film of **5**, which allows formation of a strong electromeric state.

Conclusions

Several dendrimers consisting of the ethynylphenyl core and carbazole dendrons (**1**−**5**) were easily synthesized

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(47) Hou, L. D.; Duan, L.; Qiao, J.; Li, W.; Zhang, D. Q.; Qiu, Y. *Appl. Phys. Lett.* **2008**, *92*, 263301.

(48) ITO = Indium tin oxide; NPB = 4,4′-bis[*N*-(1-naphthyl)-*N*-phenylamino] biphenyl; Bphen = 4,7-diphenyl-1,10-phenanthroline.

(49) PEDOT:PSS = poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate).

(50) Lupton, J. M.; Klein, J. *Phys. Rev. B* **2002**, *65*, 193202/1–4.

(51) Nikitenko, V. R.; Lupton, J. M. *J. Appl. Phys.* **2003**, *93*, 5973.

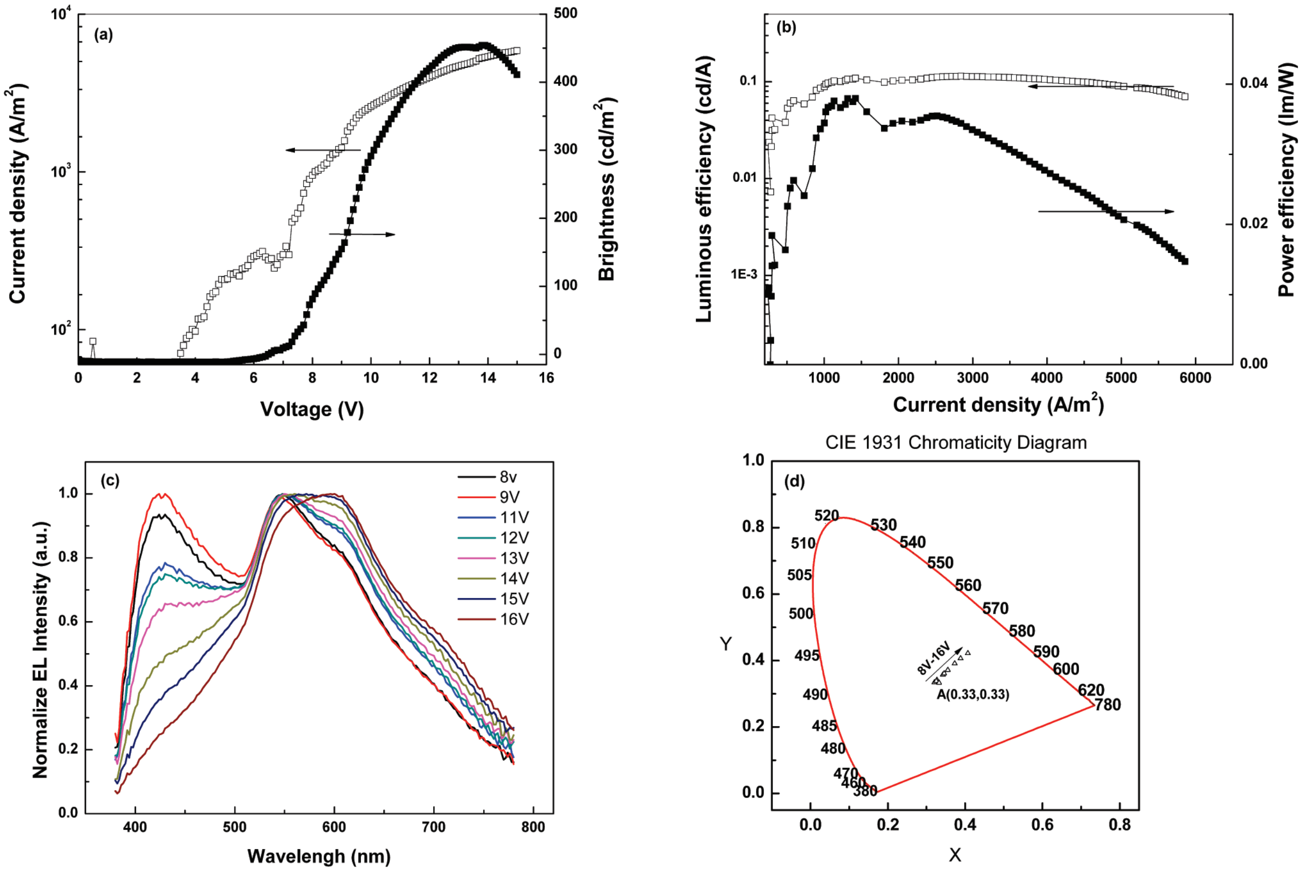

Figure 6. (a) $J-V-L$ characteristics, (b) current efficiency curves, (c) electroluminescence spectrum, and (d) CIE coordinates observed at different electric fields of a device consisting of **5** as the emitting layer (device configuration: ITO/PEDOT:PSS/**5** (spin-coated)/Bphen/Mg:Ag).

by Sonogashira coupling. Dilute solutions of **1**−**5** show intense blue emission in DCM (λ_{max} = 410−438 nm, Φ_F = 0.53−0.91). They show significant solvatochromism because of the intramolecular charge transfer from donor (carbazole) to acceptor (ethynyl) resulting in a polar singlet excited state. A systematic increase in the fluorescence lifetime of **1** (τ_F = 1.68−4.75 ns) and **5** (τ_F = 1.70−6.09 ns) was observed when the solvent was changed from nonpolar (pentane) to polar (acetonitrile). The solid state emissions of **1**−**5** (λ_{max} = 426−443 nm, Φ_F = 0.30−0.90) were slightly red-shifted but similar to the corresponding emission recorded in DCM, except for **1**. A thin film of the latter showed a broad emission (340−650 nm). The EL spectrum of **1** was more structured with a strong band in the blue region (λ_{max} = 430 nm) and a small shoulder at 630 nm. A single-layer OLED consisting of **1** as the emitting layer showed blue emission (CIE: 0.28, 0.20) with a maximum brightness of 66 cd/m^2 at 16.3 V and a maximum efficiency of 0.075 cd/A at 11.9 V. On the other hand, the EL of **5** (CIE: 0.34, 0.36) was found close to ideal white light. WOLEDs consisting of **5** as the emitting layer showed a maximum brightness of 450 cd/m^2 at 13 V and a maximum efficiency of 0.11. The white EL from **5** is a combination of monomeric (blue) and electromeric (orange) emissions. The geometry of **5** allows for formation of a strong electromeric state; such was not the case with **1**, indicating that the ethynylphenyl group can be employed to tune the EL properties of dendrimers.

Experimental Section

Instrumentation. Mass spectra were recorded on a GCMS instrument equipped with a direct probe (ionization 70 eV). The NMR spectra were recorded at a working frequency of 300.0 MHz for ^{1}H. $CDCl_3$ 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 appropriate spectrophotometers. All measurements were carried out at room temperature unless otherwise specified.

Synthesis. The syntheses of **1** and **2** are provided in our previous publication.[34] The syntheses of **3**−**5** mainly involved standard Sonogashira coupling.

3,6-Di-*tert*-butyl-9-(4-ethynylphenyl)-*9H*-carbazole (8). It was prepared by subjecting **6** to a standard ethynylation procedure. Compound **6** (10 mmol), *trans*-dichlorobis(triphenylphosphine)-palladium(II) (0.5 mmol), triphenylphosphine (0.5 mmol), CuI (0.5 mmol), trimethylsilylacetylene (11 mmol), and anhydrous triethylamine (60 mL) were mixed in a degassed round-bottom flask. The mixture was refluxed overnight with stirring. After the reaction mixture was allowed to cool to room temperature, and the solvent was evaporated under a vacuum. The residue was mixed with DCM and washed with water and then brine. The organic layer was collected and dried under $MgSO_4$. After filtration, the solvent was removed under a vacuum. The crude product (**7**) was purified by chromatography (alumina gel, 90% hexane in DCM). Compound **7** was then stirred at room temperature with DCM, methanol, and excess of aqueous sodium hydroxide overnight. The mixture was dried and extracted with DCM to obtain pure **8** (Yield 81%) as a yellowish white shining solid. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.5 (s, 18 H), 3.15 (s, 1 H), 7.36 (d, 2H), 7.45 (d, 2H), 7.55 (d, 2H), 7.69 (d, 2H), 8.15 (s, 2H). ^{13}C NMR (300 MHz, CDCl$_3$): δ 31.5, 34.6, 83, 109, 116, 120, 124, 126.8, 130, 134, 139,143. HRMS (EI+) measured, m/z 379.234; calcd, m/z 379.230.

1,3-Dibromo-5-(2-phenylethynyl)benzene (9). The same Sonogashira coupling condition and workup methods applied for the preparation of **7** from **6** was used in the synthesis of **9**. A mixture of 1,3-dibromo-5-iodobenzene[52] (5 mmol), *trans*-dichlorobis(triphenylphosphine)palladium(II) (0.25 mmol), triphenylphosphine (0.25 mmol), CuI (0.25 mmol), phenylacetylene (6 mmol), and anhydrous triethylamine (40 mL) was stirred overnight at room temperature. The crude product was purified by chromatography (silica gel, 80% hexane in DCM) to obtain pure **9** (Yield 50%) as a white powder. ^{1}H NMR (300 MHz, CDCl$_3$): δ 7.4 (m, 3H), 7.6 (s, 2H), 7.68 (m, 3H). ^{13}C NMR (300 MHz, CDCl$_3$): δ 90, 93, 123, 128.5, 129, 131.5, 132.5, 133, 134. HRMS (EI+) measured, m/z 333.901; calcd, m/z 333.899.

3,6-Di-*tert*-butyl-9-(4-(4-(4-(3,6-di-*tert*-butyl-*9H*-carbozol-9-yl)-phenyl)buta-1,3-diynyl)phenyl)-9*H*-carbazole (3). It was obtained as a major side product (28%) during the preparation of **4**. ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.5 (s, 36H), 7.39−7.47 (d, 4H), 7.47−7.53 (d, 4H), 7.56−7.67 (d, 4H), 7.75.0−7.81 (d, 4H), 8.16 (s, 4H). ^{13}C NMR (300 MHz, CDCl$_3$) δ 31.5, 34.6, 75, 80, 90, 91, 109, 114, 120, 124, 126, 134, 138.5, 139, 143.5. HRMS (EI+) measured, m/z 756.447; calcd, m/z 756.444.

3,6-Di-*tert*-butyl-9-(4-(2-(3-(2-(4-(3,6-di-*tert*-butyl-*9H*-carbozol-9-yl)phenyl)ethynyl)-5-(2-phenylethynyl)phenyl)ethynyl)phenyl)--*9H*-carbazole (4). The same Sonogashira coupling condition and workup methods applied for **9** was used in the preparation of **4**. A mixture of **8** (2.2 mmol), *trans*-dichlorobis(triphenylphosphine)-palladium(II) (0.02 mmol), triphenylphosphine (0.02 mmol), CuI (0.02 mmol), **4** (1 mmol), and anhydrous *N*,*N*-diisopropylethylamine (20 mL) was refluxed for 2 days with stirring. The crude product was purified by chromatography (alumina gel, 80% hexane in DCM) to obtain pure **4** (25%) as a white shining solid. ^{1}H NMR (300 MHz, CDCl$_3$): δ 1.5 (s, 36H), 7.4−7.45 (m, 7H), 7.49−7.54 (m, 4H), 7.6−7.65 (m, 6H), 7.75−7.8 (m, 7H), 8.2 (s, 4H). ^{13}C NMR (300 MHz, CDCl$_3$): δ 31.5, 34.6, 88, 89, 90, 91, 109, 116, 121, 123, 124, 124.2, 126, 128, 132, 133, 134, 138.5, 139, 144. HRMS (EI+) measured, m/z 932.510; calcd, m/z 932.507.

9-(4-(2-(3,5-bis(2-(4-(3,6-di-*tert*-butyl-*9H*-carbazol-9-yl)phenyl)-ethynyl)phenyl)ethynyl)phenyl)-3,6-di-*tert*-butyl-*9H*-carbazole (5). The same Sonogashira coupling condition and workup methods applied for **9** was used in the preparation of **5**. A mixture of **6** (3 mmol), *trans*-dichlorobis(triphenylphosphine)palladium(II) (0.02 mmol), triphenylphosphine (0.0.02 mmol), CuI (0.0.02 mmol), 1,3,5-triethynylbenzene[45] (1 mmol), and anhydrous *N*, *N*-diisopropylethylamine (30 mL) was refluxed for 4 days with stirring. The crude product was purified by chromatography (alumina gel, 80% hexane in DCM) to obtain pure **5** (45%) as a white shining solid. ^{1}H NMR (300 MHz, CDCl$_3$) δ 1.5 (s, 54H), 7.37−7.43 (d, 6H), 7.43−7.5 (d, 6H), 7.56−7.64 (d, 6H), 7.75 (m, 9H), 8.15 (s, 6H). ^{13}C NMR (300 MHz, CDCl$_3$) δ 31.5, 34.6, 88, 90, 109, 117, 118, 121, 123, 123.5, 126, 133, 134, 138.5, 139, 143. HRMS (EI+) measured, m/z 1209.697; calcd, m/z 1209.690.

Fluorescence Quantum Yields (Φ_F). The Φ_F values in solution were measured following a general method using 9,10-diphenylanthracene (Φ_F = 0.9 in cyclohexane) as the standard.[53] 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 was used for the calculation of Φ_F. The refractive indices of solvents at the sodium D line were used for the calculation of the Φ_F values. The Φ_F values in the solid state were measured following a literature method.[54] 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 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 values.[12]

Fluorescence Lifetime (τ_F) Measurement. Solutions of the samples 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. Inbuilt software allowed the fitting of the decay spectra (χ^2 = 1−1.5) and yielded the fluorescence lifetimes.

Device Fabrication and Characterization. The device fabrication processes followed are described elsewhere.[47] The diode area was 9 mm^2. The thickness of the film was measured using an atomic force microscope (AFM, Seiko, SPA-400). The *J*−*L*−*V* characteristics were recorded with a Keithley 4200 semiconductor characterization system. The EL spectra and CIE coordinators were collected using a spectrophotometer (Photo Research PR705). All measurements were carried out in air at room temperature.

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Supporting Information Available: Absorption and emission spectra, fluorescence decay profiles, and NMR spectra of **1**−**5**, *J*−*V*−*L* characteristics, current efficiency curves, electroluminescence spectra, and CIE coordinates observed at different electric fields of a device consisting of **5** as the emitting layer (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(52) Lustenberger, P.; Diederich, F. *Helv. Chim. Acta* **2000**, *83*, 2875.

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

(54) De Mello, J. C.; Wittman, J. C.; Friend, R. H. *Adv. Mater.* **1997**, *9*, 230.