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π-Conjugated Aromatic Enynes as a Single-Emitting Component for White Electroluminescence

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White organic light-emitting devices (WOLEDs) have attracted much current interest because of their good potential for various lighting applications, such as low-cost, large-area flat-panel displays. An ideal white emission should be composed of the three primary colors (blue, green, and red) and cover the whole visible range from 400 to 700 nm. Most of the WOLEDs reported so far have relied on the use of a combination of several organic components that emit different colors of light to fully span the entire visible spectrum.[1] Compared to the multi-emitting-component WOLEDs, a single-emitting-component WOLED could show many advantages, such as better stability, better reproducibility, and a simpler fabrication process. However, few materials are known to show white-light emission as a single-emitting component, and none have been reported to emit "pure" white light.[2] Therefore, the search for new organic light-emitting materials with new structures for use in single-emitting-component WOLEDs is of obvious interest and importance.

We report here the synthesis and photo- and electroluminescence properties of carbazole-substituted aromatic (*E*)- and (*Z*)-enynes.[3] These new π-conjugated compounds, in particular, the (*E*)-enyne isomer, can serve as an excellent single-emitting component for WOLEDs, emitting almost "pure" white light with stable CIE (Commission Internationale de l'Eclairage) coordinates under different driving voltages.

Catalytic dimerization of terminal alkynes by organolanthanide complexes to give conjugated enynes has been reported previously by our group and others.[4] By use of the organolanthanide catalysts **1** and **2**, the carbazole-substituted phenyl enynes (*Z*)-CPEY and (*E*)-CPEY could be easily prepared, respectively, with excellent regio- and stereoselectivity, as shown in Scheme 1.[5] On irradiation at 365 nm in CH_2Cl_2, both (*E*)-CPEY and (*Z*)-CPEY showed intense blue fluorescence, with an emission peak centered at $\lambda_{max} = 455$ nm and a quantum yield of ca. 0.75 for (*E*)-CPEY and 0.70 for (*Z*)-CPEY (Figure 1). In the thin films, however, the photoluminescence (PL) spectra showed extra broad emissions at 510−520 nm and tailed to 600 nm in addition to the strong emission at 455 nm, probably because of formation of excimers (vide infra).

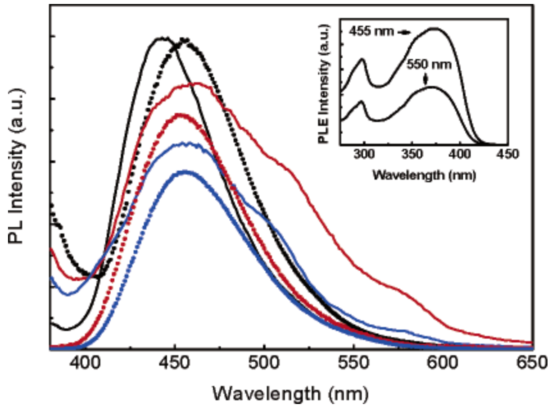
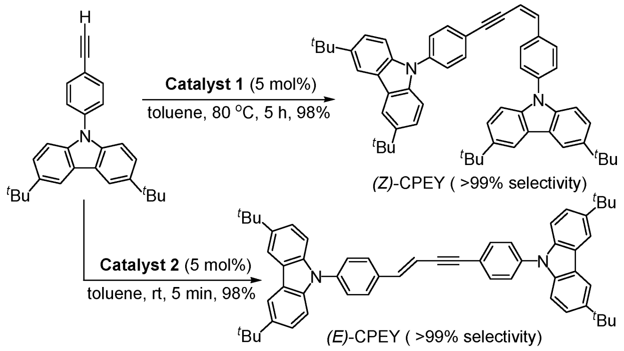


Figure 1. Photoluminescence (PL) spectra of (*E*)-CPEY (red dotted line, in CH_2Cl_2; red solid line, in a vacuum-deposited film), (*Z*)-CPEY (blue dotted line, in CH_2Cl_2; blue solid line, in a vacuum-deposited film), NPB in a vacuum-deposited film (black solid line), and (*E*)-CPEY doped in NPB (ca. 1:1 w/w) in a vacuum-deposited film (black dotted line). Inset: Excitation spectra of (*E*)-CPEY monitored at 455 and 550 nm in a vacuum-deposited film.

Scheme 1. Regio- and Stereoselective Synthesis of Conjugated Enynes



Catalyst 1: $Me_2Si(C_5Me_4)(N(C_6H_3Me_2\text{-}2,6))Lu(CH_2SiMe_3)(THF)$
Catalyst 2: $(C_5Me_5)_2LaCH(SiMe_3)_2$

To investigate the electroluminescence (EL) properties of these compounds, a single-layer device with a structure of ITO/(*E*)-CPEY(60 nm)/LiF/Al (ITO = indium−tin−oxide) (device 1) was fabricated by vacuum deposition of (*E*)-CPEY. Compared to the PL spectrum of the (*E*)-CPEY film, the EL spectrum of the (*E*)-CPEY-based device became significantly broader, with the long-wavelength emissions around 510 and 590 nm being much stronger (Figure 2). The whole device emitted white light with CIE coordinates of (0.29, 0.30), as a result of the combination of the blue emission around 455 nm with the longer-wavelength green (510 nm) and orange-red (590 nm) emissions. The analogous (*Z*)-CPEY-based device ITO/(*Z*)-CPEY(60 nm)/LiF/Al (device 2) showed a similar EL spectrum, although its CIE coordinates (0.23, 0.26) were not as close to those of pure white light (0.33, 0.33) under the same conditions (Figure 2). To facilitate the hole injection from the anode and increase the efficiency of the EL device 1, a thin layer of 4,4′-bis(1-naphthylphenylamino)biphenyl (NPB) (HOMO = −5.5 eV, LUMO = −2.4 eV)[1k,l] was added by vacuum deposition between the (*E*)-CPEY layer (HOMO = −5.96 eV, LUMO = −3.01 eV) and ITO (work function, −4.7 eV). As shown in Figure 2, such a double-layer device ITO/NPB(30 nm)/(*E*)-CPEY(40 nm)/LiF/Al (device 3) showed much better performance as a WOLED which

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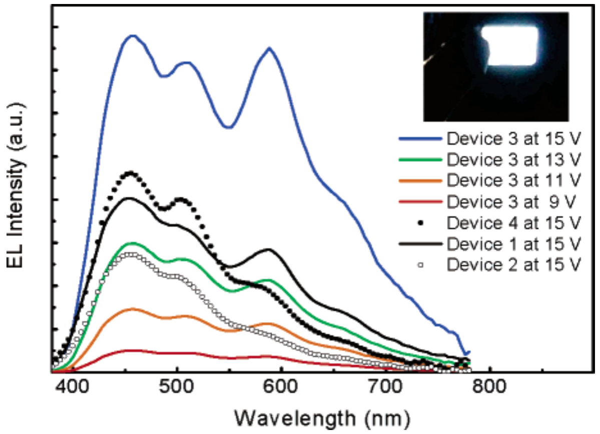

Figure 2. Electroluminescence (EL) spectra of single-emitting-component (*E*)-CPEY- or (*Z*)-CPEY-based devices: device 1, ITO/(*E*)-CPEY(60 nm)/LiF/Al; device 2, ITO/(*Z*)-CPEY(60 nm)/LiF/Al; device 3, ITO/NPB(30 nm)/(*E*)-CPEY(40 nm)/LiF/Al; device 4, ITO/NPB(30 nm)/(*Z*)-CPEY(40 nm)/LiF/Al. NPB = 4,4′-bis(1-naphthylphenylamino)biphenyl. Inset: Photograph of device 3 at a driving voltage of 15 V.

emitted white EL with the spectrum covering the whole visible range from 400 to 700 nm. Under a driving voltage of 16 V, an almost pure white emission was achieved with CIE coordinates of (0.32, 0.33), maximum brightness of 1395 cd m^{-2}, and maximum current efficiency of 2.07 cd A^{-1}. As far as we are aware, this is the purest white emission ever reported for a single-emitting-component WOLED. The quality of the white emission remained almost unchanged in the driving voltage range of 9−16 V, as shown by the little variations in the CIE coordinates (0.30, 0.32)−(0.32, 0.33). A true photograph of device 3 under 15 V is shown in the inset of Figure 2.

Since the overall emission pattern of the EL spectrum of the (*E*)-CPEY-based double-layer device 3 was similar to that of the single-layer device 1 (Figure 2), the longer-wavelength EL emissions (510 and 590 nm) of these two devices should have similar origins, which thus ruled out the possibility of formation of a new species such as an exciplex at the NPB/(*E*)-CPEY interface in the case of device 3.[6] To probe the origins of the longer-wavelength emissions, photoluminescence excitation (PLE) spectra of a (*E*)-CPEY thin film were measured for emissions at 455 and 550 nm. As shown in the inset of Figure 1, the PLE spectra for both emissions were similar to each other, suggesting that these two PLE spectra should have a common excitation pathway, thus excluding the possibility of formation of a new fluorophore in the film.[7a,b] Accordingly, the long-wavelength emissions in the PL spectra of the (*E*)-CPEY film should result from excimers. Since the long-wavelength broad peaks at 510 and 590 nm in the EL spectra of devices 1 and 3 (Figure 2) are very close to the location of the longer-wavelength shoulders in the PL spectra of the (*E*)-CPEY film (Figure 1), the longer-wavelength emissions in the EL spectra should also result from excimers. The difference in line shape (or emission intensity) between the EL spectra and the PL spectra might be because electron injection can sometimes generate excitons that cannot be induced by optical excitation.[7c]

In summary, carbazole-substituted aromatic enynes, such as (*E*)-CPEY, which are easily prepared by catalytic dimerization of a terminal alkyne, can act as an excellent single-emitting component for WOLEDs, as a result of combination of the blue emission from an isolated molecule with the longer-wavelength emissions (green and orange-red) from eximers. The (*E*)-CPEY-based double-layer device (device 3) emitted almost pure white light with CIE coordinates of (0.32, 0.33), maximum brightness of 1395 cd m^{-2}, and maximum current efficiency of 2.07 cd A^{-1}. To the best of our knowledge, this is the purest white emission with high luminescence and high efficiency ever reported for a single-emitting-component WOLED. The quality of the white emission remained almost unchanged under varying driving voltages, demonstrating an advantageous potential of single-emitting-component WOLEDs.

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Supporting Information Available: Experimental details and spectral data for all new compounds and OLED structure, characterization, and performance data for all devices. This material is available free of charge via the Internet at http://pubs.acs.org.

References

(1) For examples, see: (a) Kido, J.; Shionoya, H.; Nagai, K. *Appl. Phys. Lett.* **1995**, *67*, 2281−2283. (b) Tasch, S.; List, E. J. W.; Ekström, O.; Graupner, W.; Leising, G.; Schlichting, P.; Rohr, U.; Geerts, Y.; Scherf, U.; Müllen, K. *Appl. Phys. Lett.* **1997**, *71*, 2883−2885. (c) Xie, Z. Y.; Huang, J. S.; Li, C. N.; Wang, Y.; Li, Y. Q.; Shen, J. C. *Appl. Phys. Lett.* **1999**, *74*, 641−643. (d) Deshpande, R. S.; Bulović, V.; Forrest, S. R. *Appl. Phys. Lett.* **1999**, *75*, 888−890. (e) Feng, J.; Li, F.; Gao, W. B.; Liu, S. Y.; Liu, Y.; Wang, Y. *Appl. Phys. Lett.* **2001**, *78*, 3947−3949. (f) Liu, Y.; Guo, J. H.; Zhang, H. D.; Wang, Y. *Angew. Chem., Int. Ed.* **2002**, *41*, 182−184. (g) D’Andrade, B. W.; Thompson, M. E.; Forrest, S. R. *Adv. Mater.* **2002**, *14*, 147−151. (h) Adamovich, V.; Brooks, J.; Tamayo, A.; Alexander, A. M.; Djurovich, P. I.; D’Andrade, B. W.; Adachi, C.; Forrest, S. R.; Thompson, M. E. *New J. Chem.* **2002**, *26*, 1171−1178. (i) Mazzeo, M.; Pisignano, D.; Della Sala, F.; Thompson, J.; Blyth, R. I. R.; Gigli, G.; Cingolani, R.; Sotgiu, G.; Barbarella, G. *Appl. Phys. Lett.* **2003**, *82*, 334−336. (j) D’Andrade, B. W.; Brooks, J.; Adamovich, V.; Thompson, M. E.; Forrest, S. R. *Adv. Mater.* **2002**, *14*, 1032−1036. (k) D’Andrade, B. W.; Holmes, R. J.; Forrest, S. R. *Adv. Mater.* **2004**, *16*, 624−628. (l) Kanno, H.; Sun, Y.; Forrest, S. R. *Appl. Phys. Lett.* **2005**, *86*, 263502.

(2) For examples of single-emitting-component WOLEDs, most of which were based on polymers, see: (a) Lee, Y.-Z.; Chen, X.; Chen, M.-C.; Chen, S.-A.; Hsu, J.-H.; Fann, W. *Appl. Phys. Lett.* **2001**, *79*, 308−310. (b) Tsai, M.-L.; Liu, C.-Y.; Hsu, M.-A.; Chow, T. *J. Appl. Phys. Lett.* **2003**, *82*, 550−552. (c) Li, J. Y.; Liu, D.; Ma, C.; Lengyel, O.; Lee, C.-S.; Tung, C.-H.; Lee, S. *Adv. Mater.* **2004**, *16*, 1538−1541. (d) Furuta, P. T.; Deng, L.; Garon, S.; Thompson, M. E.; Fréchet, J. M. J. *J. Am. Chem. Soc.* **2004**, *126*, 15388−15389. (e) Liu, J.; Zhou, Q.; Cheng, Y.; Geng, Y.; Wang, L.; Ma, D.; Jing, X.; Wang, F. *Adv. Mater.* **2005**, *17*, 2974−2978. (f) Tu, G.; Mei, C.; Zhou, Q.; Geng, Y.; Wang, L.; Ma, D.; Jing, X.; Wang, F. *Adv. Funct. Mater.* **2006**, *16*, 101−106.

(3) Carbazolyl was chosen as a subsituent, because it is well known to show high charge mobility and interesting optical and electronic properties.[7a,b]

(4) (a) Nishiura, M.; Hou, Z. *J. Mol. Catal. A: Chem.* **2004**, *213*, 101−106 and references therein. (b) Nishiura, M.; Hou, Z.; Wakatsuki, Y.; Yamaki, T.; Miyamoto, T. *J. Am. Chem. Soc.* **2003**, *125*, 1184−1185. (c) Heeres, H. J.; Teuben, J. H. *Organometallics* **1991**, *10*, 1980−1986.

(5) For mechanistic aspects of such alkyne dimerization, see ref 4.

(6) In fact, the PL spectrum of (*E*)-CPEY doped in NPB (ca. 1:1 w/w) in a vacuum-deposited film showed a sharp emission around 455 nm without tailing to long wavelength (Figure 1). This strongly suggests that (*E*)-CPEY excimer formation was hindered even by NPB in the doped film and thus excludes again the possibility of exciplex formation between (*E*)-CPEY and NPB.

(7) (a) Zhang, Z.-B.; Fujiki, M.; Tang, H.-Z.; Motonaga, M.; Torimitsu, K. *Macromolecules* **2002**, *35*, 1988−1990. (b) Takihana, Y.; Shiotsuki, M.; Sanda, F.; Masuda, T. *Macromolecules* **2004**, *37*, 7578−7583. (c) Berggren, M.; Gustafsson, G.; Inganäs, O.; Andersson, M. R.; Hjertberg, T.; Wennerström, O. *J. Appl. Phys.* **1994**, *76*, 7530−7534.

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