ChemComm

COMMUNICATION

View Article Online
View Journal | View Issue

Cite this: *Chem. Commun.*, 2014, **50**, 6174

Received 3rd March 2014,
Accepted 15th April 2014

DOI: 10.1039/c4cc01590h

www.rsc.org/chemcomm

Highly efficient exciplex organic light-emitting diodes incorporating a heptazine derivative as an electron acceptor†

Jie Li,[a] Hiroko Nomura,[a] Hiroshi Miyazaki[ab] and Chihaya Adachi*[ac]

Highly efficient exciplex systems incorporating a heptazine derivative (HAP-3MF) as an electron acceptor and 1,3-di(9*H*-carbazol-9-yl)-benzene (mCP) as an electron donor are developed. An organic light-emitting diode containing 8 wt% HAP-3MF:mCP as an emitting layer exhibits a maximum external quantum efficiency of 11.3%.

Organic light-emitting diodes (OLEDs) have attracted tremendous interest because of their promise in optoelectronic devices, especially flat-panel displays and general lighting.[1] Phosphorescent OLEDs containing transition metal complexes can exhibit very high external quantum efficiencies (EQEs) as a result of effective use of both singlet and triplet excitons.[2] Although OLEDs based on conventional fluorescent materials typically show a limited EQE of 5% because only singlet excitons can be harvested under electrical excitation,[3] two new tactics to harvest triplet excitons through triplet–triplet annihilation (TTA)[4] and thermally activated delayed fluorescence (TADF)[5] have been exploited to markedly enhance the EQE of fluorescent OLEDs. In particular, TADF molecules have attracted much more interest because almost 100% internal quantum efficiencies can be achieved. The crucial design strategy of TADF molecules is to possess a small energy gap (ΔE_{st}) between the lowest singlet (S_1) and triplet (T_1) excited states to allow efficient intersystem crossing (ISC). An elaborate molecular design is necessary to obtain a small ΔE_{st} because it is proportional to the exchange energy between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of electron donating and accepting moieties, respectively. Alternatively, small ΔE_{st} can be readily realized by exciplex formation *via* intermolecular charge transfer between electron donors and acceptors.[6] Over the past two decades, interest in exciplexes formed at solid interfaces and in physically blended structures has expanded.[7] With judicious molecule selection, exciplex-based organic light-emitting diodes (ExOLEDs) with EQEs as high as 10.0% have been obtained.[8] However, it is still challenging to explore highly efficient exciplex systems because exciplex formation is usually accompanied with a large red-shift of emission spectra, which tends to decrease photoluminescence (PL) quantum efficiency (PLQE) as well as electroluminescence (EL) performance.

In this communication, we report an exciplex system with a blended structure containing 1,3-di(9*H*-carbazol-9-yl)benzene (**mCP**) as an electron donor, and 2,5,8-tris(4-fluoro-3-methylphenyl)-1,3,4,6,7,9,9*b*-heptaazaphenalene (**HAP-3MF**) as an electron acceptor. The molecular structures of **mCP** and **HAP-3MF** are depicted in Fig. 1. **mCP** is a widely used host molecule possessing two electron-donating carbazole moieties.[9] **HAP-3MF**, which is composed of a heptazine core and three 2-fluorotoluene groups, was designed and synthesized as an electron acceptor. 2-Fluorotoluene groups were introduced to increase the solubility and maintain the electron-withdrawing ability of **HAP-3MF**. The synthesis of **HAP-3MF** is described in the ESI.† We chose a heptazine derivative as an electron acceptor in the exciplex system because it exhibits a number of intriguing thermal,[10] optical,[5g,11] and electronic[12] properties. Although heptazine derivatives are promising candidates for OLEDs, no exciplex system containing a heptazine derivative has been reported. Herein, we examine the photophysical characteristics and EL performance of an **HAP-3MF:mCP** exciplex system.

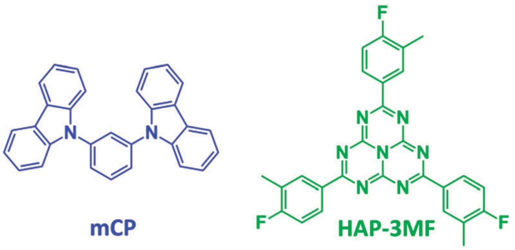

Fig. 1 Molecular structures of **mCP** and **HAP-3MF**.

---

[a] *Department of Chemistry and Biochemistry, and Center for Organic Photonics and Electronics Research (OPERA), Kyushu University, 744 Motooka, Nishi, Fukuoka 819-0395, Japan. E-mail: adachi@cstf.kyushu-u.ac.jp*

[b] *Functional Materials Laboratory, Nippon Steel and Sumikin Chemical Co., Ltd, 46–80 Nakabaru, Sakinohama, Tobata, Kitakyushu, Fukuoka 804-8503, Japan*

[c] *International Institute for Carbon Neutral Energy Research (WPI-I^{2}CNER), Kyushu University, 744 Motooka, Nishi, Fukuoka 819-0395, Japan*

† Electronic supplementary information (ESI) available: Synthesis scheme, experimental details and additional photophysical data. See DOI: 10.1039/c4cc01590h

The HOMO and LUMO levels of **HAP-3MF** are −6.0 and −3.4 eV, which were estimated by ultraviolet photoelectron spectroscopy and subtracting the energy gap from the HOMO level, respectively (Fig. S1, ESI†). The thermal stability of **HAP-3MF** was measured by thermogravimetric-differential thermal analysis; it exhibited fairly high thermal stability with an initial decomposition temperature of 413.5 °C (Fig. S2, ESI†). The ultraviolet-visible (UV-vis) absorption and PL spectra of **mCP**, **HAP-3MF**, and 25 wt% **HAP-3MF:mCP** films are presented in Fig. 2a. Absorption peaks at 329 and 342 nm originate from **mCP**, and the dominant absorption peak of **HAP-3MF** is centered at 334 nm. The UV-vis absorption spectrum of a 25 wt% **HAP-3MF:mCP** blend film is similar to that of an **mCP** one. No new absorption band appeared at longer wavelengths, indicating the absence of charge transfer between **mCP** and **HAP-3MF**. Both **mCP** and **HAP-3MF** solid films show well-resolved PL spectra resulting from π–π^* or n–π^* emissions.[13] In contrast, the PL of the blend film exhibits typical exciplex characteristics with a peak at around 550 nm, which is red-shifted compared with those of **mCP** and **HAP-3MF** films. Interestingly, the exciplex system shows a rather high PLQE of 55.7%, which is much higher than that of a **HAP-3MF** film with a PLQE of 12.7%. This is unusual behavior compared with conventional exciplex systems, which usually possess PLQEs lower than that of each single layer. Furthermore, the red-shift between the PL peaks of **HAP-3MF** (526 nm) and a 25 wt% **HAP-3MF:mCP** blend film (550 nm) is just 24 nm. The photon energy of the exciplex is therefore only slightly lower than that of **HAP-3MF**. The similar HOMO levels of **mCP** and **HAP-3MF** suppress the red-shift of exciplex emission. Moreover, the half width at half maximum (HWHM) of the exciplex emission is narrow compared with those observed for other conventional exciplex systems.[6–8] The HWHM of 83 nm of the blend film is only slightly larger than that of **HAP-3MF** alone (66 nm). These unique PL characteristics could be ascribed to the rigid and relatively planar geometries of **HAP-3MF** and **mCP** molecules, which tend to result in tight molecular packing of π-conjugated moieties and very strong intermolecular interactions.[7]

To obtain an optimized exciplex system, **HAP-3MF:mCP** blend films with various weight ratios were fabricated and characterized. The UV-vis absorption and PL spectra of these films are depicted in Fig. 2b, and the PLQEs of **HAP-3MF:mCP** exciplex systems with various weight ratios in air and nitrogen are summarized in Table S1, ESI.† We found that the 8 wt% **HAP-3MF:mCP** exciplex system exhibits a remarkably high PLQE of 66.1% and a rather small PL spectral red-shift of 12 nm compared with that of an **HAP-3MF** film.

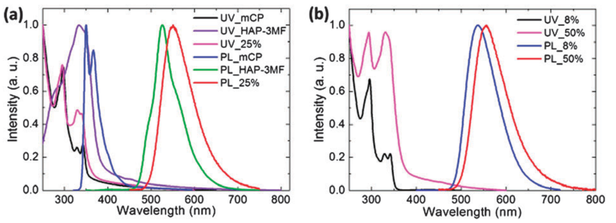

Fig. 2 (a) UV-vis absorption and PL spectra of **mCP**, **HAP-3MF**, and 25 wt% **HAP-3MF**:**mCP** in solid films at 300 K. (b) UV-vis absorption and PL spectra of **HAP-3MF**:**mCP** blend films with various weight ratios at 300 K.

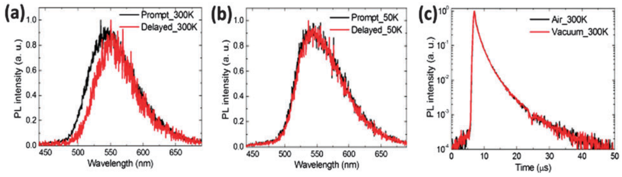

Fig. 3 Transient PL decay properties of an 8 wt% **HAP-3MF**:**mCP** exciplex system. (a) Prompt and delayed PL spectra under vacuum conditions at 300 K. (b) Prompt and delayed PL spectra under vacuum conditions at 50 K. (c) Transient PL decay in air and under vacuum conditions at 300 K.

Considering the exciplex mechanism, the transient PL decay properties of an 8 wt% **HAP-3MF:mCP** exciplex system were characterized (Fig. 3). The well-overlapped prompt and delayed emission spectra at 300 K confirm that all photons are generated from the same excited state (Fig. 3a). A considerable overlap was also observed between the prompt and delayed spectra at 50 K (Fig. 3b), indicating that the exciplex system possesses a fairly small ΔE_{st}. Fig. 3c shows the transient PL decay of an 8 wt% **HAP-3MF:mCP** film in air and under vacuum conditions at 300 K. The transient decay can be divided into prompt and delayed components. The prompt component with a transient lifetime of 184 ns can be ascribed to conventional fluorescence-based exciplex emission, while the delayed ones with transient lifetimes of 1.7 and 5.7 μs are generated from the delayed exciplex emission after up-conversion of triplet exciplex excitons into the singlet excited state as discussed in a previous report.[6] While we cannot fully characterize the origin of the multiple decay components, it should be caused by the inhomogeneous distribution of **HAP-3MF** molecules in the **mCP** host matrix. Here, we note that the transient PL decay curves in air and under vacuum conditions overlap well, suggesting that oxygen has almost no influence on the PL characteristics, probably because of the rigid and tightly packed environment of an **mCP** host layer. As a consequence, the PLQE of an 8 wt% **HAP-3MF:mCP** exciplex system in air is 65.8%, which is nearly equal to that in nitrogen (66.1%). We can approximately estimate the PLQE of the prompt component, $\Phi_{\mathrm{prompt}} = 18.6\%$, while that of the delayed component, $\Phi_{\mathrm{delayed}} = 47.5\%$ in nitrogen. The transient PL properties of 25 wt% and 50 wt% **HAP-3MF:mCP** exciplex systems are analogous to that of 8 wt% **HAP-3MF:mCP** (Fig. S3 and S4, ESI†).

Using the exciplex-based TADF characteristics, ExOLEDs containing **HAP-3MF:mCP** with various weight ratios were fabricated. The device structure was ITO/α-NPD (30 nm)/TCTA (10 nm)/**HAP-3MF:mCP** (20 nm)/DPEPO (10 nm)/TPBI (40 nm)/LiF (0.8 nm)/Al (100 nm), where ITO is indium tin oxide, α-NPD is *N*,*N*′-di(naphthalen-1-yl)-*N*,*N*′-diphenylbenzidine used as a hole transport layer, TPBI is 1,3,5-tris(*N*-phenylbenzimidazole-2-yl)benzene used as an electron transport layer, and LiF and Al act as the cathode. Thin tris(4-(9*H*-carbazol-9-yl)phenyl)amine (TCTA) and bis(2-(diphenylphosphino)phenyl) ether oxide (DPEPO) layers were inserted to block electrons coming from the cathode and holes from the anode, respectively, and simultaneously confine the excitons in the emitting layer. The device structure and the energy diagram are presented in Fig. 4a. In accordance with PLQE trends, the ExOLED containing 8 wt% **HAP-3MF:mCP** exhibited the best EL performance.

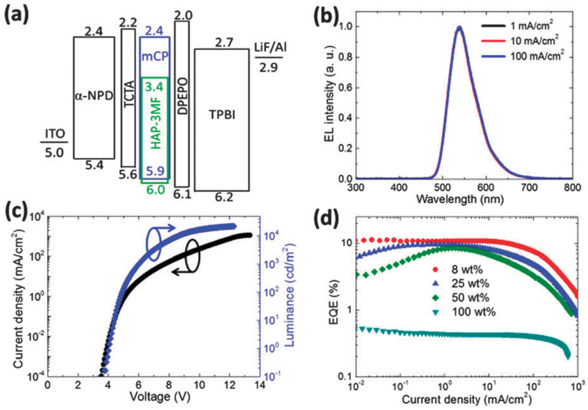

Fig. 4 EL characteristics of an ExOLED containing an 8 wt% **HAP-3MF**:**mCP** blend film as an emitting layer. (a) Device structure and energy level diagrams (values are in eV). (b) EL spectra recorded at various current densities. (c) Current density–voltage–luminance (*J*–*V*–*L*) characteristics. (d) EQE as a function of current density.

Its EL spectra measured at 1, 10, and 100 mA cm^{-2} are shown in Fig. 4b. The photon energy of the exciplex obtained from the onset of the EL spectra (490 nm) is determined to be 2.5 eV, which is consistent with the difference between the LUMO of **HAP-3MF** (−3.4 eV) and HOMO of **mCP** (−5.9 eV). Current density–voltage–luminance (*J*–*V*–*L*) characteristics of the ExOLED are depicted in Fig. 4c. A low turn-on voltage of 4.0 V and quite a high peak luminance of 22 000 cd m^{-2} at 12.2 V were observed. More importantly, the ExOLED incorporating 8 wt% **HAP-3MF:mCP** as an emitting layer showed a rather high maximum EQE of 11.3% along with rather low roll-off characteristics, which is higher than those of 25 wt% (9.6%), 50 wt% (8.5%) and 100 wt% (0.53%) **HAP-3MF:mCP** systems (Fig. 4d and Fig. S5, ESI†). Consequently, the EQE decreased as the weight ratio of **HAP-3MF** was increased. We believe that it should be due to concentration quenching in consideration of relatively planar molecular geometry of **HAP-3MF**. The EQE substantially exceeds the theoretical maximum if the emitter is assumed to be a conventional fluorescent molecule. The theoretical maximum EQE can be calculated from the following equation, EQE = $\gamma \times \eta_r \times$ PLQE $\times \eta_{out}$, where γ is the electron/hole recombination ratio, η_r is the exciton formation ratio for radiative transitions ($\eta_r = 0.25$ for conventional fluorescent emitters), and η_{out} is the light out-coupling efficiency. Therefore, the theoretical maximum EQE should be limited to 3.3–5.0% when $\gamma = 1.0$, $\eta_r = 0.25$, PLQE = 66.1% and $\eta_{out} = 0.2$–0.3. However, based on the exciton formation mechanism of TADF, we estimate that the theoretical maximum EQE is 12.1–18.1% based on Φ_{prompt} and $\Phi_{delayed}$ values, which results from efficient harvest of triplet exciplex excitons through reverse ISC from T_1 to S_1.[5d] Because our device structure was not fully optimized, higher EQE would be expected through a careful device structure design. Thus, the extraordinarily high EQE of this ExOLED should be ascribed to efficient up-conversion of triplet exciplex excitons under electrical excitation.

In summary, we designed a highly efficient 8 wt% **HAP-3MF:mCP** exciplex system with a very small ΔE_{st}, resulting in efficient exciton up-conversion and a high PLQE of 66.1%. Using this exciplex system as an emitting layer in an ExOLED, a rather high EQE of 11.3% was obtained. These findings are of fundamental interest for the development of highly efficient OLEDs based on exciplex systems. Through elaborate molecular design and careful selection of electron donors and acceptors, we believe that ExOLEDs with enhanced efficiencies can be expected.

This work was supported in part by the Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST) and the International Institute for Carbon Neutral Energy Research (WPI-I^{2}CNER) sponsored by MEXT.

Notes and references

1 (*a*) C. W. Tang and S. A. VanSlyke, *Appl. Phys. Lett.*, 1987, **51**, 913; (*b*) J. H. Burroughes, D. D. C. Bradley, A. R. Brown, R. N. Marks, K. Mackay, R. H. Friend, P. L. Burns and A. B. Holmes, *Nature*, 1990, **347**, 539; (*c*) M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson and S. R. Forrest, *Nature*, 1998, **395**, 151; (*d*) S. Reineke, F. Lindner, G. Schwartz, N. Seidler, K. Walzer, B. Lussem and K. Leo, *Nature*, 2009, **459**, 234.
2 (*a*) M. Cocchi, D. Virgili, V. Fattori, D. L. Rochester and J. A. G. Williams, *Adv. Funct. Mater.*, 2007, **17**, 285; (*b*) Y.-C. Chiu, J.-Y. Hung, Y. Chi, C.-C. Chen, C.-H. Chang, C.-C. Wu, Y.-M. Cheng, Y.-C. Yu, G.-H. Lee and P.-T. Chou, *Adv. Mater.*, 2009, **21**, 2221; (*c*) Y.-S. Park, S. Lee, K.-H. Kim, S.-Y. Kim, J.-H. Lee and J.-J. Kim, *Adv. Funct. Mater.*, 2013, **23**, 4914.
3 (*a*) M. A. Baldo, M. E. Thompson and S. R. Forrest, *Nature*, 2000, **403**, 750; (*b*) W. C. Wu, H.-C. Yeh, L.-H. Chan and C.-T. Chen, *Adv. Mater.*, 2002, **14**, 1072.
4 (*a*) D. Y. Kondakov, T. D. Pawlik, T. K. Hatwar and J. P. Spindler, *J. Appl. Phys.*, 2009, **106**, 124510; (*b*) S. M. King, M. Cass, M. Pintani, C. Coward, F. B. Dias, A. P. Monkman and M. Roberts, *J. Appl. Phys.*, 2011, **109**, 074502.
5 (*a*) A. Endo, K. Sato, K. Yoshimura, T. Kai, A. Kawada, H. Miyazaki and C. Adachi, *Appl. Phys. Lett.*, 2011, **98**, 083302; (*b*) T. Nakagawa, S.-Y. Ku, K.-T. Wong and C. Adachi, *Chem. Commun.*, 2012, **48**, 9580; (*c*) G. Méhes, H. Nomura, Q. Zhang, T. Nakagawa and C. Adachi, *Angew. Chem., Int. Ed.*, 2012, **51**, 11311; (*d*) H. Tanaka, K. Shizu, H. Miyazaki and C. Adachi, *Chem. Commun.*, 2012, **48**, 11392; (*e*) Q. Zhang, J. Li, K. Shizu, S. Huang, S. Hirata, H. Miyazaki and C. Adachi, *J. Am. Chem. Soc.*, 2012, **134**, 14706; (*f*) H. Uoyama, K. Goushi, K. Shizu, H. Nomura and C. Adachi, *Nature*, 2012, **492**, 234; (*g*) J. Li, T. Nakagawa, J. MacDonald, Q. Zhang, H. Nomura, H. Miyazaki and C. Adachi, *Adv. Mater.*, 2013, **25**, 3319.
6 (*a*) S. Iwata, J. Tanaka and S. Nagakura, *J. Chem. Phys.*, 1967, **47**, 2203; (*b*) K. Goushi, K. Yoshida, K. Sato and C. Adachi, *Nat. Photonics*, 2012, **6**, 253.
7 (*a*) S. A. Jenekhe and J. A. Osaheni, *Science*, 1994, **265**, 765; (*b*) T. Noda, H. Ogawa and Y. Shirota, *Adv. Mater.*, 1999, **11**, 283; (*c*) Y. Shirota and H. Kageyama, *Chem. Rev.*, 2007, **107**, 953; (*d*) S. L. Lai, M. Y. Chan, Q. X. Tong, M. K. Fung, P. F. Wang, C. S. Lee and S. T. Lee, *Appl. Phys. Lett.*, 2008, **93**, 143301; (*e*) W.-Y. Hung, G.-C. Fang, Y.-C. Chang, T.-Y. Kuo, P.-T. Chou, S.-W. Lin and K.-T. Wong, *ACS Appl. Mater. Interfaces*, 2013, **5**, 6826; (*f*) D. Graves, V. Jankus, F. B. Dias and A. Monkman, *Adv. Funct. Mater.*, 2014, **24**, 2343.
8 K. Goushi and C. Adachi, *Appl. Phys. Lett.*, 2012, **101**, 023306.
9 Q. Wang, J. Ding, D. Ma, Y. Cheng, L. Wang, X. Jing and F. Wang, *Adv. Funct. Mater.*, 2009, **19**, 84.
10 B. Jürgens, E. Irran, J. Senker, P. Kroll, H. Müller and W. Schnick, *J. Am. Chem. Soc.*, 2003, **125**, 10288.
11 (*a*) R. S. Hosmane, M. A. Rossman and N. J. Leonard, *J. Am. Chem. Soc.*, 1982, **104**, 5497; (*b*) E. Kroke, M. Schwarz, E. Horath-Bordon, P. Kroll, B. Noll and A. D. Norman, *New J. Chem.*, 2002, **26**, 508.
12 W. Zheng, N.-B. Wong, W. Wang, G. Zhou and A. Tian, *J. Phys. Chem. A*, 2004, **108**, 97.
13 D. R. Miller, D. C. Swenson and E. G. Gillan, *J. Am. Chem. Soc.*, 2004, **126**, 5372.