This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the Information for Authors.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal’s standard Terms & Conditions and the Ethical guidelines still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.
COMMUNICATION

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

Jie Li, Hiroko Nomura, Hiroshi Miyazaki and Chihaya Adachi

Highly efficient exciplex systems incorporating a heptazine derivative (HAP-3MF) as an electron acceptor and 1,3-di(9H-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. 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. Although OLEDs based on conventional fluorescent materials typically show a limited EQE of 5% because only singlet excitons can be harvested under electrical excitation, two new tactics to harvest triplet excitons through triplet-triplet annihilation (TTA) and thermally activated delayed fluorescence (TADF) 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 ($\Delta E_a$) between the lowest singlet ($S_1$) and triplet ($T_1$) excited states to allow efficient intersystem crossing (ISC). Elaborate molecular design is necessary to obtain a small $\Delta E_a$ 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 $\Delta E_a$ can be readily realized by exciplex formation via intermolecular charge transfer between electron donors and acceptors. Over the past two decades, interest in exciplexes formed at solid interfaces and in physically blended structures has expanded. With judicious molecule selection, exciplex-based organic light-emitting diodes (ExOLEDs) with EQEs as high as 10.0% have been obtained. 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(9H-carbazol-9-yl)benzene (mCP) as an electron donor, and 2,5,8-tris(4-fluoro-3-methylphenyl)-1,3,4,6,7,9,9b-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. 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 ESI.† We chose a heptazine derivative as an electron acceptor in the exciplex system because it exhibits a number of intriguing thermal, optical, and electronic 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.

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:mCP centered at 379 nm. The PL spectra of mCP, HAP-3MF, and mCP:HAP-3MF are presented in Fig. 2b. A broad PL peak from mCP centered at 427 nm decreases dramatically upon adding HAP-3MF, and the largest red-shift to 445 nm is observed for HAP-3MF:mCP. Comparable with the UV-vis absorption results, the PL peak of HAP-3MF:mCP centered at 445 nm is contributed to the HAP-3MF component. The photophysical characteristics of HAP-3MF:mCP films are listed in Table 1. The average quantum yield of HAP-3MF:mCP was estimated as 9.7% by comparison with a 10% solution of 9,10-anthracene dicarboxylic acid in dichloromethane.

Fig. 1 Molecular structures of mCP and HAP-3MF.
exhibits a remarkably high PLQE of 66.1% for various weight ratios in air and nitrogen are summarized in Table S1, Fig. 2b, and the PLQEs of the blend film with various weight ratios were fabricated and characterized. To obtain an optimized exciplex system, 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 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 that observed for other conventional exciplex systems. 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.

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 rather small PL spectral red-shift of 12 nm compared with that of an HAP-3MF film. 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). Considerable overlap was also observed between the prompt and delayed spectra at 50 K (Fig. 3b), indicating the exciplex system possesses a fairly small ΔEg. Figure 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 4.7 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, Φprompt = 18.6%, while that of the delayed component is Φdelayed = 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 as a hole transport layer, TPBI is 1,3,5-tris(N-phenylbenzimidazole-2-yl)benzene as an electron transport layer, and LiF and Al act as the cathode. Thin tris(4-(9H-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 energy diagram are presented in Fig. 4a. In accordance with PLQE trends, the ExOLED containing 8 wt% HAP-3MF:mCP exhibited best EL performance. 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 spectral red-shift of 12 nm 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 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 that observed for other conventional exciplex systems. 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.

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 rather small PL spectral red-shift of 12 nm compared with that of an HAP-3MF film. 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). Considerable overlap was also observed between the prompt and delayed spectra at 50 K (Fig. 3b), indicating the exciplex system possesses a fairly small ΔEg. Figure 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 4.7 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, Φprompt = 18.6%, while that of the delayed component is Φdelayed = 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 as a hole transport layer, TPBI is 1,3,5-tris(N-phenylbenzimidazole-2-yl)benzene as an electron transport layer, and LiF and Al act as the cathode. Thin tris(4-(9H-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 energy diagram are presented in Fig. 4a. In accordance with PLQE trends, the ExOLED containing 8 wt% HAP-3MF:mCP exhibited best EL performance. 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 high peak luminance of 22000 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 S5). 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, \[ \text{EQE} = \gamma \times \eta_i \times \text{PLQE} \times \eta_{\text{out}}, \] where \( \gamma \) is the electron/hole recombination ratio, \( \eta_i \) is the excitation formation ratio for radiative transitions (\( \eta_i = 0.25 \) for conventional fluorescent emitters), and \( \eta_{\text{out}} \) is the light out-coupling efficiency. Therefore, the theoretical maximum EQE should be limited to 3.3–5.0% when \( \gamma = 1.0, \eta_i = 0.25, \text{PLQE} = 66.1\% \) and \( \eta_{\text{out}} = 0.2–0.3 \). However, based on the excitation formation mechanism of TADF, we estimate the theoretical maximum EQE is 12.1–18.1% based on \( \Phi_{\text{longe}} \) and \( \Phi_{\text{delayed}} \) values, which results from efficient harvest of triplet exciplex excitons through reverse ISC from \( T_1 \) to \( S_0 \). Because our device structure was not fully optimized, higher EQE would be expected through 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 exciplex system of 8 wt\% HAP-3MF:mCP with a very small \( \Delta E_g \), 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-FCN) at Kyushu University, and the Funding Program for World-Leading Innovative R&D on Science and Technology (FIRST) and the International Institute for Carbon Neutral Energy Research (WPI-FCN). The authors are grateful for the financial support received from the Japan Society for the Promotion of Science. The authors also thank Dr. Yasuyuki Takahara and Dr. Hisashi Tsuchiya for their help and support in the experiments. The authors are grateful to Dr. Akihiko Inoue for his helpful discussions.

Notes and references