High-efficiency dual-dopant polymer light-emitting diodes with ultrafast inter-fluorophore energy transfer

Le Yang[1,2], *Vincent Kim*[1], *Yaxiao Lian*[3], *Baodan Zhao*[1], *Dawei Di*[1,3*]

Summary

The integration of organic light-emitting diodes (OLEDs) into modern electronics has affirmed their role in next-generation display technologies, presenting advantages in energy efficiency, flexibility, large-area fabrication and low-cost solution-processability. Maintaining high luminance and colour purity in OLEDs is an important goal, particularly for high-efficiency devices utilising triplet excitons. Here we report solution-processed dual-dopant polymer LEDs, where highly-efficient electroluminescence occurs via an intermolecular energy transfer from carbene-metal-amides (CMAs) (which exhibit rapid singlet-triplet interconversion) to a fluorescent rubrene-derivative. This design enables solution-processed OLEDs with external quantum efficiencies of >20% (corresponding to near-100% internal quantum efficiencies), and a peak luminance of 75000 cd m^{-2}. We show the emission originates from the singlet state of the rubrene-derivative. Ultrafast optical measurements indicate the inter-fluorophore energy transfer occurs within 0.3 ps, at an efficiency of >96%. Such devices preserve the relatively narrow emission bandwidth of conventional fluorophores for colour purity, showing potential in energy-efficient printable electronics.

Keywords

Solution processing; organic light-emitting diodes; carbene-metal-amides; fluorescence; energy transfer

[1] Cavendish Laboratory, University of Cambridge, J J Thomson Avenue, Cambridge CB3 0HE, UK.

[2] Institute of Materials Research and Engineering (IMRE), Agency for Science, Technology and Research (A*STAR), 2 Fusionopolis Way, Singapore 138634, Singapore.

[3] State Key Laboratory of Modern Optical Instrumentation, College of Optical Science and Engineering, Zhejiang University, Hangzhou 310027, China.

*Lead Contact, Email: daweidi@zju.edu.cn; dd403@cam.ac.uk

Introduction

The successful demonstration of small-molecule and polymer thin-film organic light-emitting diodes (OLEDs) in the 1980s marked milestone establishments in the field of organic electronics.[1,2] In recent years, OLEDs have increasingly been incorporated into commercial display and lighting applications, driven by the need for high visual quality and energy efficiency. In conventional fluorescent emitters in OLEDs, bound electron-hole pairs or excitons are formed spontaneously upon charge injection, following a spin statistical ratio of 25% (emissive) spin-singlet to 75% (dark) spin-triplet states. It therefore introduces a 25% internal quantum efficiency (IQE) threshold for emission via the radiative recombination of singlets. Extensive effort has been spent into harnessing the 75% dark states for more efficient electroluminescence (EL), and some representative photoemission mechanisms and materials designs exploiting triplets include phosphorescence from heavy-metal complexes,[3-6] thermally-activated delayed fluorescence (TADF) from organic molecules with reduced exchange energies,[7-10] triplet fusion in organic fluorophores,[11-13] and rotationally-accessed spin-state interconversion in CMA molecules.[14,15] Indeed, utilising triplet excitons is also an important area of research for organic and hybrid solar cells,[16-19] and spectral conversion.[20-21]

For high-efficiency OLEDs, phosphorescence, TADF and CMA materials enable one-for-one triplet-to-photon conversion, and have achieved close-to-100% IQE in devices.[4,8,14] Triplet fusion harvests triplets in a two-for-one fashion, imposing a theoretical IQE limit of 62.5%.[12,13,22] Though less efficient than the other emission mechanisms, triplet fusion is nonetheless a very critical design targeting simple fluorescent emitters (with otherwise a 25% IQE ceiling), which take an important role in practical OLED applications for their relative stability, narrower emission bandwidth (and hence higher colour purity), and the ability to achieve colour-saturated pixels for full-colour displays. Recognising the necessity to enhance efficiencies in these fluorescent OLEDs, phosphorescent and TADF sensitizers have been introduced to achieve more efficient triplet exciton utilisation and emission via Förster resonance energy transfer (FRET).[23-26] Here, we explore an alternative solution, by incorporating CMA-based sensitizers as an energy transfer medium into solution-processed molecularly-doped polymer LEDs. CMA complexes serve as the site of exciton generation, where nearly all triplets formed on the CMA molecules rapidly convert to (and intermixes with) singlets due to singlet-triplet energy degeneracy (close-to-zero exchange energy).[14,27] The singlet excitons on CMA complexes are efficiently transferred to the fluorescent emitter and subsequently radiatively decay. We have been able to achieve more than 20% external quantum efficiency (EQE, η_{ext}) in EL from a simple yellow fluorophor, corresponding to near-100% IQE (η_{int}) (assuming an outcoupling factor of 0.2-0.3),[28,29] indicating an efficient one-for-one exciton-to-photon utilisation of all injected charges.

Results & Discussion

The active materials used in this work are 2,8-di-tert-butyl-5,11-bis(4-tert-butylphenyl)-6,12-diphenyltetracene (TBRb), a simple yellow fluorescent rubrene-derivative, and CMA1, a representative molecule in the CMA family (Fig. 1A),[14,15,27] selected based on their optical properties. There is strong spectral overlap between the donor CMA1 PL spectrum and the emitter TBRb absorption spectrum, as highlighted by the turquoise box in Fig. 1B, implying the possibility of efficient FRET from CMA1 to TBRb. The Forster radius is estimated to be 5.4 nm, from the spectral overlap of the CMA1 emission spectrum and the TBRb absorption spectrum. The grey box in Fig. 1B represents the spectral window for selective optical excitation of CMA1 in the CMA1:TBRb system. To achieve a device-like materials composition, the mixed dopants are incorporated in a spin-coated poly(9-vinylcarbazole) (PVK) film, at CMA1 20 wt%:TBRb 2 wt% (herein denoted as PVK:CMA1:TBRb), and excited at 370 nm. Its PL peak coincides very well with that of a PVK film doped with TBRb 5 wt% (herein referred to as PVK:TBRb), with supressed CMA1 emission (Fig. S1), indicating effective energy transfer from CMA1 to TBRb in the PVK film.

To investigate the effectiveness of inter-fluorophore energy transfer in working devices, we fabricated OLEDs based on the dual-dopant system and characterised their EL properties. The solution-processed OLED device architecture (Fig. 2A) is adapted from our previous work,[12,14] with the emissive layer consisting of a thin PVK:CMA1 20 wt%:TBRb 2 wt% film ("dual-dopant device"). The two control devices have emissive layers of PVK:CMA1 20 wt% ("CMA1 device") and PVK:TBRb 10-20 wt% ("TBRb device") respectively. Starting from patterned indium tin oxide (ITO) on glass, all four organic layers were simply spin-coated from solutions or inks: poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT:PSS) from an aqueous suspension (~30 nm layer); the hole-transporting/electron-blocking poly[9,9-dioctylfluorene-co-N-(4-butylphenyl) diphenylamine] (TFB) from a toluene solution (~200 nm); the emissive layer from N,N-dimethylformamide (DMF) (~30 nm); and the electron-transporting/hole-blocking bathophenanthroline (Bphen) from methanol (~70 nm).

Similar to the PL observation, it is evident that the steady-state EL emission in the dual-dopant device originates from TBRb only (Fig. 2B). Fig. 2C shows the EQEs of some of the best OLEDs we fabricated in this work and a statistical distribution of the peak EQEs across 436 dual-dopant devices, with further performance parameters listed in Table 1. We note that the statistical distribution of the device EQEs is likely due to the low boiling-point solvent (methanol) currently used for the deposition of the electron-transport layer (Bphen), and hence can be improved in future work. A histogram of peak EQEs from TBRb-only control devices can be found in Fig. S2A. It is possible that a stereotypical two-for-one triplet fusion enhancement is present in the dual-dopant device. However, in the most ideal case a triplet fusion-enhanced OLED should encompass an IQE upper limit of 62.5%, which translates to an EQE ceiling of 12.5-18.7% (outcoupling factor of 0.2-0.3).[12] Having a peak EQE of more

than 20% in the dual-dopant device here clearly surpasses the triplet fusion limit. And since it corresponds to a near-unity IQE, it implies that the EL is dominated by a one-for-one exciton-to-photon conversion and nearly all excitons, regardless of their initial spin, are being utilised for emission. This is supported by the transient EL kinetics (Fig. 2D), where the dual-dopant EL decays via an initial faster relaxation pathway followed by a slower channel with µs lifetime. The slower EL kinetics cannot be described by a bimolecular decay function, a fingerprint of triplet-triplet annihilation (triplet exciton fusion).[12,13] Furthermore, the intensity of PL from similarly prepared dual-dopant films shows a linear (rather than quadratic) dependence on the excitation power (Fig. S3). Therefore, triplet fusion following triplet-triplet energy transfer is less likely to be the dominant channel towards emission in the dual-dopant OLED, though we cannot completely rule out its contribution to the EL process. Note that the faster and slower EL spectra are nearly identical (Fig. S2B), suggesting that they originate from the same emissive species.

The presence of the CMA1 dopant significantly enhances the performance of electro-fluorescence from TBRb, as evident in the following ways. 1) The dual-dopant devices can withstand operation at a higher applied voltage than the TBRb-only devices, even though all three types of devices turn on at ~2.8-3 V (Fig. 2E). 2) The maximum luminance from the dual-dopant OLEDs reaches 75 000 cd m^{-2}, much higher than the TBRb-only devices at 12 000 cd m^{-2}, and even higher than that achieved for the highly-efficient green CMA1-only devices at 61 000 cd m^{-2} (Fig. 2E, Table 1). 3) The EQE roll-off at higher current densities is drastically reduced for the dual-dopant compared to TBRb-only devices (Fig. 2C).

Based on the EL characteristics, we consider a mechanism present in these working dual-dopant devices illustrated in Fig. 2F. The majority of excitons are initially formed on CMA1 complexes due to the dilute concentration of TBRb, according to the usual spin-statistical ratio of 25% singlets to 75% triplets. The majority of the singlets on CMA1 undergo FRET efficiently to S_1 of TBRb and recombine radiatively spontaneously. The triplets (T_1) on CMA1 can undergo reverse intersystem crossing (RISC) competently (at an estimated rate of 1.5×10^6 s^{-1} at 300K, Fig. 3E, vide infra) to S_1, and then go through FRET to the emissive S_1 of TBRb. In competition with the FRET process, intersystem crossing (ISC) converts S_1 on CMA1 to T_1, which can undergo RISC back to the singlet manifold and then FRET to TBRb in an energetically favourable manner. Hence, all excitons regardless of their initial spin, can be transferred onto S_1 of TBRb and emit, resulting in a yellow polymer LED with efficiency significantly above the conventional fluorescence efficiency limit.

Meanwhile, to corroborate the suggested mechanism, further photophysical measurements were conducted (Fig. 3). From ns-µs time-resolved PL spectra of a PVK:CMA1:TBRb blend film, we observe an appearance of the 480 nm emission from the CMA1 at t = 0 ns (i.e. immediately after the laser pulse), which completely disappears and is followed by PL from TBRb (~550 nm) within the first 2 ns, the temporal resolution of the measurement

instrument. We discuss later that the dominant inter-fluorophore energy transfer process occurs on ultrafast (fs) timescales. There is very minor red-shifting thereafter, from 580 nm (at 2 ns) to 590 nm (stabilising ~50-100 ns) (Fig. 3A), agreeing with the PVK:TBRb sample that also sees minor spectral shifts within the first ~50 ns before stabilising at 590 nm (Fig. S4A). This behaviour contrasts with the PVK:CMA1 20 wt% control sample (herein referred to as PVK:CMA1), where a continuous red-shifting of spectra is observed from 480 nm (at 0 ns) to 535 nm (at ~2-5 μs range), over 260 meV lower in energy (Fig. S4B). From the ns-μs PL kinetics (Fig. 3B), the long exciton decay lifetime of CMA1 in PVK:CMA1 film (~800 ns) agrees with prompt fluorescence from CMA1 being outcompeted by ISC (followed by RISC). In contrast, the main emission process of PVK:CMA1:TBRb follows a much faster decay profile (35 ns lifetime), similar to the PVK:TBRb trace (20 ns lifetime) (Fig. 3B), signifying emission in PVK:CMA1:TBRb is dominated by TBRb. A minor tail of delayed fluorescence is observed in the PVK:CMA1:TBRb film, due to a small proportion of excitons undergoing rapid ISC and RISC on CMA1 before transferring via FRET to the TBRb. We performed additional transient PL studies on the PVK:CMA1:TBRb sample under cryogenic conditions. The delayed component has a temperature-dependent lifetime, decreasing from ~1 μs at 4K to ~210 ns at 300K (Fig. S4C), following a similar trend to the PVK:CMA1 control film whose lifetime decreases from 5.5 μs at 4K to 700 ns at 300K (Fig. S4D). Above 100K, a temperature-dependent activation energy (E_A) likely associated with the energy required for partial intramolecular rotation in CMA1 can be extracted from the lifetimes of the delayed component at 100K-300K, yielding a value of 29 meV for PVK:CMA1:TBRb (Fig. S4E) and 72 meV for PVK:CMA1 control (Fig. S4F). We speculate that the much smaller E_A needed in the dual-dopant system could be due to the following factors. The addition of TBRb dopant makes the polymer matrix less rigid, introducing an increased rotational flexibility for the CMA1; or it could be that the rapid FRET process establishes a new equilibrium of the singlet-triplet interconversion, resulting in a smaller activation energy required for efficient emission. The PVK:CMA1 behaviour complies with CMA1 neat film observation previously reported: the PVK matrix here reduces geometrical or rotational freedom for the CMA dopants, hence the longer timescales and higher E_A obtained here than the CMA1 neat-film measurements.[14]

We illustrate the photoemission pathways under optical excitation in Fig. 3C. Intramolecular rotation (of both static and dynamic types) in CMA1 brings about a continuum of its S_1 energy, where higher S_1 energies correspond to stronger oscillator strength. Optical excitation would pump the ground state S_0 on CMA1 to the highest S_1 state present (process 1). Rapid ISC (process 4), RISC (process 3) and FRET to TBRb S_1 state (process 5) would depopulate S_1 efficiently, resulting in minimal direct emission from the CMA1 S_1 excitons (process 2). The energy transfer process from CMA1 to TBRb is highly efficient, and emission occurs predominantly from the S_1 of TBRb. Due to the dilute concentration of TBRb, it is assumed that the initial exciton formation occurs mainly on CMA1. The majority of the emission is nearly identical to the fluorescence from TBRb, as the direct singlet exciton formation on CMA1 upon optical excitation can undergo immediate FRET to TBRb S_1 state and emit. A minor delayed component would arise from the ISC and RISC between the S_1 and T_1 states of

the CMA1 before undergoing FRET to TBRb. As discussed previously, we did not find evidence for triplet fusion-based fluorescence in the dual-dopant system (Fig. S3).

The singlet absorption features of PVK:CMA1 and PVK:CMA1:TbRb samples on fast timescales (ps-ns) overlap considerably, so a direct estimate of the energy transfer rate is difficult using singlet absorption alone. As shown in Fig. 4A, the significantly slowed relaxation of the 670-675 nm singlet absorption feature[14] (with characteristic decay times increased from ~10 ps to ~1 ns) agrees with our hypothesis that the energy transfer from S_1 of CMA1 to the S_1 of TbRb (process 5 of Fig. 3C) is considerably faster than the $S_1 \rightarrow T_1$ ISC time (~ 10 ps) of CMA1 (process 4 of Fig. 3C). From Fig 4B, the triplet T_1 state on the CMA1 (with an absorption peak at around 635-640 nm)[14] is found to be depopulated much more quickly in the presence of TBRb, with a decay lifetime reduced from ~320 ns to ~11 ns. This is most likely driven by the very fast energy transfer onto the S_1 of the TBRb (process 5 of Fig. 3C) in combination with the relatively slower $T_1 \rightarrow S_1$ RISC in CMA1 (process 3), effectively outcompeting the $S_1 \rightarrow T_1$ ISC process (process 4 of Fig. 3C). From these decay lifetimes, the energy transfer efficiency is estimated to be >96% (Supplemental Information), agreeing with the spectral evidence of complete energy transfer in Fig. 2B and S1. The effective timescale of the energy transfer process is estimated to be ~0.3 ps, significantly faster than the typical values (ranging from 1 ns to tens of ns) for FRET in organic LEDs.[30]

In conclusion, we have demonstrated highly efficient solution-processed dual-dopant fluorescent OLEDs with EQEs of >20%, and a peak brightness of 75 000 cd m^{-2}. Our transient and steady-state optical measurements reveal that ultrafast energy transfer takes place between the low-exchange-energy CMA sensitizer and the fluorescent TBRb emitter, showing an estimated energy transfer time of ~0.3 ps and an energy transfer efficiency of > 96%. The combination of dopants has allowed for significant spectral overlap and ultrafast, highly efficient energy transfer, leading to OLEDs with near-unity IQEs. The design also produces brighter solution-processed OLEDs than its conventional fluorescent counterpart, exhibiting potential for energy-efficient printable display and solid-state lighting applications.

Experimental Procedures

Full details on experimental procedures can be found in the Supplemental Information.

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Author Contributions

L.Y. fabricated and characterised the OLEDs, prepared samples for photophysical measurements, and performed the steady-state measurements. L.Y. and D.D. conducted the temperature-dependent and time-resolved PL measurements. V.K. carried out the transient absorption studies. Y.L. conducted the excitation power-dependant PL intensity measurements. B.Z. performed some steady-state optical measurements. L.Y. and D.D. analysed the data and prepared the manuscript. D.D. conceived and planned the project.

Declaration of Interests

The authors declare no competing financial interests.

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Main figure titles & legends:

Figure 1. Dopants used in the OLED active layer and their basic optical properties. (A) Chemical structures of TBRb and CMA1. **(B)** Steady-state absorption and photoluminescence spectra of neat films of CMA1 and TBRb. The turquoise box highlights the spectral overlap between the emission of the donor (CMA1) and the absorption of the emitter (TBRb). The light grey box shows the spectral window where CMA1 can be selectively excited.

Figure 2. OLED devices and EL characteristics. (A) Multilayer solution-processed OLED device architecture. **(B)** EL spectra of a dual-dopant device ("CMA1:TBRb") compared with the two control devices. **(C)** EQE versus current densities curves for the best dual-dopant device as well as the two control devices. Inset: a histogram of the peak EQEs from 436 dual-dopant devices. **(D)** Transient EL measurements of devices after being held at 0.3 mA cm^{-2} by a pulse generator. At time zero the electrical excitation is turned off, and the EL signal starts to decay with time, measured by an ICCD camera. **(E)** Luminance versus voltage

curves of the OLEDs. **(F)** Proposed mechanism of a dual-dopant device under electrical excitation.

Figure 3. Photophysical processes and measurements of a PVK:CMA1:TBRb blend film. (A) Time-resolved PL spectra at room temperature. The 0-2 ns curve records the co-emission of a higher-lying singlet state of CMA1 (~490 nm) and a TBRb singlet (~550 nm). Subsequently, the TBRb singlet relaxes to a more stable state at ~580-590 nm. **(B)** Total PL intensity decay kinetics, together with control films of PVK:CMA1 and PVK:TBRb (excitation wavelength: 400 nm). **(C)** Schematic illustration of the exciton interconversion processes under optical excitation in a PVK:CMA1:TBRb blend film.

Figure 4. Ultrafast transient absorption measurements of PVK:CMA1:TBRb and PVK:CMA1 films. (A) Transient absorption kinetics of 670-675 nm. The film was excited by 400 nm, 80 fs laser pulses at a fluence of 190 μJ cm^{-2} per pulse. **(B)** Transient absorption kinetics of 635-640 nm. The film was excited by 355 nm, 1 ns laser pulses at a fluence of 13 μJ cm^{-2} per pulse.

Main tables & titles:

Table 1. OLED device performance parameters.

Emissive layer dopants	**EQE (%)** **(max. / 100 cd m^{-2} / 1000 cd m^{-2})**	**Current Efficiency (cd A^{-1})** **(max. / 100 cd m^{-2} / 1000 cd m^{-2})**	**Max. Luminance (cd m^{-2})**
CMA1: TBRb	20.4 / 16.5 / 14.0	71.0 / 57.0 / 48.7	75 000
TBRb	6.6 / 3.4 / 1.9	17.0 / 10.9 / 6.4	12 000