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# Introduction

In the past two decades, OLEDs have been regarded as the "third generation of flat panel displays" and the "next generation of lighting technology", and have attracted much attention in both scientific and industrial communities.<sup>1–4</sup> According to the electroluminescence (EL) mechanism, OLEDs could be classified into two main categories, namely fluorescent (FOLEDs) and phosphorescent ones (PhOLEDs). Although high reliability has

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 $\dagger$  Electronic supplementary information (ESI) available: Synthesis procedures, characterization data, photophysical and electrochemical properties, electroluminescence properties, and <sup>1</sup>H NMR, <sup>13</sup>C NMR, FT-IR, and HRMS spectra. See DOI: 10.1039/c5tc00779h

# Simultaneous harvesting of triplet excitons in OLEDs by both guest and host materials with an intramolecular charge-transfer feature *via* triplet-triplet annihilation<sup>†</sup>

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A red naphthalimide derivative with an intramolecular charge-transfer (ICT) feature, namely (*E*)-2-(4-(*t*-butyl)-phenyl)-6-(2-(6-(diphenylamino)naphthalen-2-yl)vinyl)-1*H*-benzo[*d*e]isoquinoline-1,3(2*H*)-dione (**NA-TNA**), was designed and synthesized. Photophysical and magneto-electroluminescence (MEL) characterization results revealed that **NA-TNA** could harvest triplet excitons *via* a triplet–triplet annihilation (TTA) process in organic light-emitting diodes (OLEDs) due to the presence of a lower-lying triplet excited state with  ${}^{3}\pi\pi^{*}$  character. Consequently, using **NA-TNA** as a guest compound and **CzPhONI**, another ICT-featured naphthalimide derivative with triplet fusion delayed fluorescence (TFDF) character as host material, a high-performance orange OLED with 6 wt% **NA-TNA** doped **CzPhONI** film as the emitting layer was acquired. The maximum current efficiency (LE<sub>max</sub>), brightness ( $L_{max}$ ), and external quantum yield (EQE<sub>max</sub>) of this device should not exceed 3.34%. On the contrary, the reference device with a **NA-TNA** doping level of 1.4 wt% showed much inferior performance, with a LE<sub>max</sub>, a  $L_{max}$ , and an EQE<sub>max</sub> of 3.19 cd A<sup>-1</sup>, 24900 cd m<sup>-2</sup> and 2.49%, respectively. The high performance of the 6 wt% **NA-TNA** doped device was attributed to the efficient harvesting of triplet excitons by both the guest and host materials.

been achieved in FOLEDs, the maximum internal quantum efficiency (IQE<sub>max</sub>) of FOLEDs is generally limited to 25% according to spin statistics.<sup>5</sup> While for PhOLEDs, although a high IQE<sub>max</sub> of 100% could be achieved,<sup>6</sup> their disadvantage lies in the relatively high cost of the rare metal complexes.<sup>4,7</sup>

Recently, FOLEDs capable of harvesting both singlet and triplet excitons have aroused great research interest due to their combined high efficiency and low cost.<sup>3,4,8</sup> So far, three possible mechanisms have been reported for such FOLEDs, namely thermally activated delayed fluorescence (TADF), hybridized local and charge-transfer excited states (HLCT), and triplet-fusion delayed fluorescence (TFDF). For TADF-OLEDs, although their potential IQE<sub>max</sub> could reach 100%,<sup>7,9–11</sup> the conflict between the small singlet-triplet energy gap ( $\Delta E_{ST}$ ) and the high radiative rate within TADF luminogens makes it difficult to design highperformance TADF materials rationally.4,11 While for HLCT materials,<sup>4,12-14</sup> although high photoluminescence (PL) efficiency could be achieved, these compounds should disobey Kasha's rule, so that the internal conversion from  $T_n$  to  $T_m$ states (m < n) could be blocked effectively.<sup>14,15</sup> Therefore, the rational molecular design of HLCT materials is still a great challenge.3 However, for OLEDs based on TFDF materials, their IQEmax could reach 62.5% if triplet excitons could be up-converted

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efficiently into singlet ones through the triplet–triplet annihilation (TTA) process.<sup>8,16–24</sup> More importantly, the harvesting of triplet excitons could be realized not only by the non-doped emitters<sup>21,22</sup> and doping guests at relative high doping levels,<sup>17,23</sup> but also by the host compounds with TFDF character.<sup>24</sup> Because the prerequisite for TFDF materials is  $2E_{\rm T} \ge E_{\rm S}$ , which could be fulfilled by many conjugated systems whose S<sub>1</sub> and T<sub>1</sub> states are both of  $\pi\pi^*$  character,<sup>25–29</sup> the rational molecular design of TFDF materials should be easier than that of TADF and HLCT compounds.

Currently, most of the research studies related to TFDF-OLEDs are focused on the elucidation of the role the TTA process plays in the enhancement of EL efficiency;<sup>19,20</sup> while the TFDF compounds used are generally limited to those with  $\pi\pi^*$  character.<sup>25–29</sup> However, our recent study has revealed that ICT-featured compounds could also act as promising TFDF materials if they possess a lowest triplet excited state with  ${}^{3}\pi\pi^{*}$  character.<sup>30</sup> Because most of the lower-bandgap fluorophores like orange and red ones are D- $\pi$ -A compounds with ICT feature,<sup>31-33</sup> and the harvesting of triplet excitons could be actualized by TFDF-guests if their doping levels are relatively high,17,23 the development of novel lowerbandgap ICT-TFDF guest fluorophores with alleviated concentration quenching may give access to high-performance OLEDs with desirable batch-to-batch reproducibility for massive production. Moreover, if the host compound also displays TFDF character, triplet excitons might be utilized not only by the TFDF guest dopant, but also by the TFDF-host compound through the TTA process followed by efficient energy transfer (ET) from host to guest materials.<sup>30</sup> Yet to the best of our knowledge, so far no reports could be found using TFDF-characterised hosts and guests to harvest triplet excitons simultaneously in OLEDs.

Inspired by our recent discovery that the ICT compound CzPhONI (structure shown in Fig. 1) is a promising TFDF-host material for high-performance OLEDs,<sup>30</sup> and fluorophores with good structural similarity could form efficient ET pairs,<sup>34</sup> herein, we report the design and synthesis of an ICT-featured red D– $\pi$ –A fluorophore NA-TNA (Fig. 1), in which diphenylamine, vinylnaphthalene and 1,8-naphthalimide act as an electron donor (D), a  $\pi$ -bridge and an electron acceptor (A), respectively. As both CzPhONI and NA-TNA are 1,8-naphthalimide derivatives, they could form an efficient host/guest ET pair; and the presence of a bulky diphenylamine D segment in NA-TNA could endow it with suppressed intermolecular interactions. In addition, similar to CzPhONI, NA-TNA also shows TFDF properties. Using NA-TNA as guest and CzPhONI as host materials, a 6 wt% **NA-TNA** doped OLED with a  $LE_{max}$  of 7.73 cd  $A^{-1}$ , a  $L_{max}$  of 31 940 cd m<sup>-2</sup>, and an EQE<sub>max</sub> of 5.83% was achieved, and the high performance of this device was attributed to the concurrent



Fig. 1 Molecular structure of NA-TNA and CzPhONI

harvesting of triplet excitons by the host and guest materials *via* the TTA process.

# **Experimental section**

#### General information

All the commercially available chemicals were directly used without further purification unless otherwise stated. All the solvents were of analytical grade and were freshly distilled prior to use. <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra were recorded using a Bruker Avance AV II-400 MHz spectrometer, and the chemical shifts were recorded in units of ppm with TMS as the internal standard. Coupling constants (J) were reported in Hertz. FT-IR spectra were recorded on a Perkin-Elmer 2000 infrared spectrometer with KBr pellets under an ambient atmosphere. High resolution MS spectra were recorded using a Q-TOF Premier ESI mass spectrometer (Micromass, Manchester, UK). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on TGA Q500 and DSC Q100 instruments under a nitrogen atmosphere at a heating rate of 10  $^{\circ}$ C min<sup>-1</sup>. PL emission spectra of both solution and thin-film samples were recorded on a Perkin-Elmer LS55 fluorescence spectrophotometer at 298 K. Phosphorescence spectra were determined on a Horiba Jobin Yvon Fluoromax-4 spectrometer at 77 K. The transient photoluminescence decay characteristics of the predegassed solution samples were recorded using a single photon counting controller FluoroHub-B (Horiba Jobin Yvon). The solution samples of NA-TNA in toluene and dimethylsulfoxide  $(5 \times 10^{-6} \text{ mol L}^{-1})$  at room temperature were excited at 450 nm using a NanoLED-450 as the excitation light source, and the sample of NA-TNA in dimethylsulfoxide  $(5 \times 10^{-6} \text{ mol L}^{-1})$  at 77 K was excited at 460 nm using a xenon flashlamp as the excitation light source, and the emitted photons were detected using a TBX detector connected to a TBX-PS power supply. Photoluminescence quantum yields (PLQYs) of the dilute solution samples were determined using Rhodamine B (75% C<sub>2</sub>H<sub>5</sub>OH solution,  $\varphi_{PL} = 0.69$ ) as the standard under an excitation of 460 nm; while the absolute PLQYs of the film samples were determined using a FLS 980 fluorometer (Edinburgh Instruments Ltd) equipped with an integrating sphere and a digital photometer. The UV-Vis absorption spectra were recorded on a Perkin-Elmer Lambda 950 scanning spectrophotometer. The NA-TNA-PMMA composite thin film samples were spin-coated from their corresponding chloroform solutions with a concentration of 25 mg mL<sup>-1</sup> at a speed of 2000 rpm on quartz substrates; while the NA-TNA-CzPhONI composite thin film samples were fabricated via thermo-evaporation in a vacuum, and the film thickness is 50 nm. The PL emission spectrum comprising both the fluorescence and phosphorescence bands of NA-TNA (77 K, after 2 µs delay) was deconvoluted on the basis of the assumption that both the two emission bands are Gaussian. Cyclic voltammetry (CV) measurement was carried out using a PARSTAT 2273 electrochemical workstation at room temperature in anhydrous dichloromethane solution using tetrabutylammonium perchlorate (0.1 mol  $L^{-1}$ ) as the supporting electrolyte at a scanning rate of 50 mV s<sup>-1</sup>. The CV system was constructed using

a three-electrode electrochemical cell consisted of a Pt-wire working electrode, a Pt-wire counter electrode, and a Ag/AgNO<sub>3</sub> reference electrode (0.1 mol L<sup>-1</sup> in acetonitrile) under protection of nitrogen, and each measurement was calibrated with a ferrocene/ferrocenium (Fc/Fc<sup>+</sup>) redox system as the internal standard. Melting points were determined using a X-6 microscopic melting point apparatus.

#### **Computational method**

Quantum chemical optimizations on the energy levels of NA-TNA in the ground state and the lowest singlet and triplet excited states were performed using the Gaussian 09 package.35 The ground state and the lowest triplet excited state were optimized using the density functional theory (DFT) with restricted BP86 and unrestricted BP86 (UBP86) at the basis set level of 6-31G(d,p), respectively, while the lowest singlet state geometry optimization was done by means of time dependent DFT (TDDFT) at the BP86/6-31G(d,p) level. Full geometry optimizations were performed without any symmetry constraint. Also, all geometries were confirmed as stationary structures by the presence of only real frequencies at the same level of theory. Transition energies, oscillator strength and natural transition orbitals (NTOs)36 were evaluated using TDDFT calculations at the levels of M06-2X/6-311G(d,p) for the S<sub>0</sub> and T<sub>1</sub> states, and B3LYP/6-311G(d,p) for the S<sub>1</sub> state, based on their corresponding optimized geometries. Considering the solvent effects, all the above calculations were carried out in DMSO media within the framework of the polarized continuum model.37,38

#### **OLED** fabrication and measurements

Indium-tin oxide (ITO) coated glass substrates were cleaned with alcohol, acetone, and deionized water sequentially before being used and then treated by oxygen plasma for 2 min. Organic functional layers were thermo-evaporated in a vacuum  $(3 \times 10^{-4} \text{ Pa})$  with a deposition rate of 2–3 Å s<sup>-1</sup>, then the metallic cathode was deposited with a rate of 2–3 Å s<sup>-1</sup> at 3 ×  $10^{-3}$  Pa. The active area of the OLEDs was 1 × 1 mm<sup>2</sup>. Immediately after the sample preparation, the current densityvoltage–luminance (*I–V–L*) characteristics of the OLEDs were measured using a Keithley 2611 Source Meter and a PR705 Spectra Colorimeter, which can also record EL spectra and Commission Internationale de l'Eclairage (CIE) coordinates accurately. All of the measurements were conducted in air at room temperature. The EQE<sub>max</sub> of the OLEDs was calculated using a computer program on the basis of the previously reported literature.<sup>39</sup>

#### Transient electroluminescence decay measurement

For the transient EL experiments, a pulse generator (Agilent 8114A, 100 V/2 A) was used to apply a rectangular pulse voltage of 9 V to our devices. The pulse repetition rate was 500 Hz with a width of 20  $\mu$ s. The emission of the OLEDs was collected using an optic fiber connected to a Hamamatsu photomultiplier (PMT) (H10721-20) with the time resolution of 0.57 ns. The PMT was connected to one of the channels of a digital oscilloscope (Tektronix DPO7104, sampling rate: 5 GS per s; resolution: 100  $\mu$ V) with 50  $\Omega$  input resistance. In order to extract the remnant

and trapped carriers in the OLEDs (which would recombine and produce delayed fluorescence), an offset voltage of -4 V was applied between the voltage pulses.

#### Magneto-electroluminescence (MEL) measurements

For the MEL measurements, the magnetic field with a maximum strength of 200 mT was applied parallel to the device surface (perpendicular to the current direction). A Keithley 2612 Source Meter was used to provide the voltage bias from one channel and simultaneously recorded the current signals. Another channel of the Keithley 2612 was used to record the EL intensity of the OLEDs collected using an optic fiber connected to a highly sensitive Hamamatsu photomultiplier (H10721-20). During the test, the photomultiplier was placed far away from the electromagnet to make sure that there is no magnetic field dependence on its output. The resolution of MEL response has been found to be 0.01%. In this method, the EL signals before and after the subjection to the magnetic field were recorded to calculate the average value of the zero-field signals. The magnetic field effects in EL were obtained by MEL =  $\Delta$ EL/EL = (EL(B) - EL(aver,0))/EL(aver,0). All the measurements were carried out in an ambient atmosphere without encapsulation.

### Results and discussion

#### Excited-state properties of NA-TNA

To validate the ICT character of **NA-TNA**, UV-Vis absorption and PL emission spectra of **NA-TNA** in solvents with different polarities were recorded ( $10^{-6}$  mol L<sup>-1</sup>). As shown in Fig. 2 and Table 1, although no significant solvent effect could be observed in its absorption spectra, the PL emission spectra of **NA-TNA** display distinct positive solvatochromism. In nonpolar cyclohexane (CHX), **NA-TNA** shows a fluorescence band with vibrational structure ( $\lambda_{PLmax} = 505$  nm), which could be chiefly assigned to the  ${}^{1}\pi\pi^{*}$  transition of **NA-TNA**; with increasing solvent polarity, the emission spectrum of **NA-TNA** becomes broadened and bathochromically shifted (*e.g.*,  $\lambda_{PLmax} = 540$  nm in Tol;  $\lambda_{PLmax} = 608$  nm in THF;  $\lambda_{PLmax} = 634$  nm in DCM; and  $\lambda_{PLmax} = 687$  nm in DMSO), indicative of the strong ICT character of its lowest singlet excited state. Additionally, according to the Lippert–Mataga plot of **NA-TNA** (Fig. 3), a good linear correlation



Fig. 2 (a) Normalized absorption and (b) normalized fluorescence spectra of **NA-TNA** in solvents with different polarities under an excitation of 460 nm. Here, CHX denotes cyclohexane; Tol denotes toluene; EA denotes ethyl acetate; THF denotes tetrahydrofuran; DCM denotes dichloromethane; and DMSO denotes dimethylsulfoxide.

 Table 1
 Photophysical properties of NA-TNA in solvents with different polarities

	NA-TNA								
Solvent	$f(\varepsilon) - 1/2f(n^2)$	$\lambda_{\rm abs,max}^{a}$ (nm)	$\lambda_{\text{PLmax}}^{b}$ (nm)	$\tilde{ u}_{f}^{\max}\left(\mathrm{cm}^{-1} ight)$	$\varphi_{\mathrm{PL}}{}^{c}$				
CHX	0.110	442	505	19802	0.46				
Tol	0.127	443	540	18 519	0.34				
EA	0.282	445	605	16 529	0.28				
THF	0.308	446	608	16447	0.26				
DCM	0.319	453	634	15773	0.06				
DMSO	0.374	455	687	14556	0.00				
<sup>a</sup> λ <sub>abs</sub> : 460 nm	absorption mathematically absorption mathematically $c^{\circ} \varphi_{PI}$ : PL quark	ximum. <sup><i>b</i></sup> $\lambda_{em}$ : ntum yield.	fluorescence	maximum (	$\lambda_{ex} =$				

between the solvent polarity parameter and emission maxima  $(\tilde{\nu}_f^{\max})$  could be achieved, confirming the ICT nature of its S<sub>1</sub> state in more polar environments.

In Tol solution, **NA-TNA** displays a biexponential decay  $(\lambda_{em} = 540 \text{ nm}, \tau_1 = 0.22 \text{ ns}, 25.0\%; \tau_2 = 2.26 \text{ ns}, 75.0\%)$ ; while in DMSO solution, its fluorescence decay could only be well-fitted by a tri-exponential function  $(\lambda_{em} = 687 \text{ nm}, \tau_1 = 0.08 \text{ ns}, 97.9\%; \tau_2 = 0.45 \text{ ns}, 2.0\%; \tau_3 = 1.82 \text{ ns}, 0.1\%)$  (Fig. 4a and Table S1, ESI†). Taking into account that **NA-TNA** shows a more red-shifted emission band in DMSO  $(\lambda_{PLmax} = 687 \text{ nm})$ , its ultra-low PLQY in DMSO ( $\varphi_{PL} \sim 0$ ) and much shortened lifetime could be ascribed to its much lowered energy gap that favors the non-radiative internal conversion process.<sup>41</sup> Nevertheless, after being cooled to 77 K, the PL intensity of **NA-TNA** was observed to increase significantly, together with drastically increased decay lifetime ( $\lambda_{em} = 620 \text{ nm}, \tau_1 = 0.530 \text{ µs}, 62.0\%; \tau_2 = 1.554 \text{ µs}, 24.0\%; \tau_3 = 6.369 \text{ µs}, 14.0\%$ ) (Fig. 4b and Table S1, ESI†).



**Fig. 3** Lippert–Mataga plot of the wave number of the emission maxima  $\tilde{\nu}_{f}^{\text{max}}$  of **NA-TNA** versus solvent polarity parameter  $f(\varepsilon - n) = f(\varepsilon) - 1/2f(n^2).^{40}$ 



Fig. 4 (a) Fluorescence decay curves of **NA-TNA** in N<sub>2</sub>-saturated Tol solution (monitored at 540 nm) and DMSO solution (monitored at 687 nm) at room temperature (RT) ( $\lambda_{ex}$  = 450 nm); and (b) the PL decay curve of **NA-TNA** in DMSO solution (monitored at 620 nm) at 77 K ( $\lambda_{ex}$  = 460 nm). Concentration: 5 × 10<sup>-6</sup> M.



Fig. 5 Transient PL characteristics of NA-TNA in DMSO solution (5  $\times$  10  $^{-6}$  M) at 77 K ( $\lambda_{ex}$  = 460 nm).

After being delayed for 2 µs, a newly emerged emission band at longer wavelength with  $\lambda_{PLmax} = 775$  nm was observed (Fig. 5), which could be safely assigned to the phosphorescence of **NA-TNA**. It is noteworthy that with a prolonged delay time of 30 µs, although the phosphorescence band disappeared, the emission band with a  $\lambda_{PLmax}$  of 640 nm still could be observed, indicative of its delayed fluorescence (DF) feature. Taking into consideration that the concentration of **NA-TNA** is as low as  $5 \times 10^{-6}$  M, the TTA process of **NA-TNA** in this frozen sample should be inefficient, hence DF should not be of P-type, *i.e.*, TFDF.

Accordingly, the energy levels of the  ${}^{1}\pi\pi^{*}$  (2.55 eV) and  ${}^{1}\text{CT}^{*}$  (2.20 eV) states of **NA-TNA** were determined from the onset of its fluorescence bands in nonpolar CHX and polar DMSO, respectively;<sup>42</sup> while the T<sub>1</sub> energy level of **NA-TNA** was estimated to be 1.96 eV from the onset of its phosphorescence spectrum<sup>42</sup> through spectral deconvolution (Fig. S1, ESI†). Consequently, the  $\Delta E_{st}$  of **NA-TNA** was calculated to be 0.24 eV.

#### Theoretical calculations

To better understand the properties of the excited states of **NA-TNA**, quantum chemical calculations on the ground state, and the lowest singlet and triplet excited states of **NA-TNA** were performed using the Gaussian 09 package. As depicted in Fig. 6, for the  $S_0 \rightarrow S_1$  transition in the ground state of **NA-TNA**, the hole is mainly delocalized on the whole D- $\pi$ -A molecular skeleton of **NA-TNA**, while the particle is mainly localized on the  $\pi$ -A moiety. Hence the  $S_0 \rightarrow S_1$  excitation of **NA-TNA** should contain a major part of  $\pi\pi^*$ -featured transition with some contribution of CT transition from D to A subunits. While in



Fig. 6 The natural transition orbitals (isovalue surface 0.02 a.u.) for  $S_0 \rightarrow S_1$ ,  $S_0 \leftarrow S_1$  and  $S_0 \leftarrow T_1$  transitions for **NA-TNA** in DMSO, derived from TDDFT calculations.

the case of the lowest singlet state  $(S_1)$ , the hole and the particle are predominantly localized on the D- $\pi$  and A moieties of NA-TNA, respectively, implying that the radiation process from S<sub>1</sub> to S<sub>0</sub> should be prevailed with CT character. Being differed from the S1 state, the hole and the particle NTOs of the lowest triplet state were both found to be localized mainly on the  $\pi$ -A moiety, indicating that the radiation process of NA-TNA from T<sub>1</sub> to  $S_0$  should be predominated with  $\pi\pi^*$  character. The calculated transition energies of both the absorption and fluorescence emission bands of NA-TNA (2.79 eV and 1.87 eV, respectively, vide Table S2, ESI<sup>†</sup>) well reproduce their corresponding experimental values (2.73 eV and 1.80 eV), suggesting that these computational results are reliable.

Consequently, according to these calculation results, the T<sub>1</sub> state of **NA-TNA** is of  ${}^{3}\pi\pi^{*}$  character, while the HOMO and the LUMO of NA-TNA in its S1 state still have some overlap, indicative of the presence of a <sup>3</sup>CT\* energy level between the  ${}^{3}\pi\pi^{*}$  and  ${}^{1}\text{CT}^{*}$  energy levels. Because the  $\Delta E_{\text{ST}}$  of **NA-TNA** is as low as 0.24 eV, the  ${}^3\pi\pi^*$  excitons of NA-TNA may undergo a reverse internal conversion to its <sup>3</sup>CT\* state, followed by a reverse intersystem crossing process from the <sup>3</sup>CT\* state to the <sup>1</sup>CT\* state.<sup>43</sup> Hence the DF of NA-TNA in DMSO solution at 77 K might be assigned to TADF. Yet at room temperature, the T1 state of NA-TNA should suffer from serious non-radiative relaxation due to the relative low bandgap of NA-TNA, hence no DF was observed.

#### Energy transfer between NA-TNA and CzPhONI

According to these photophysical and theoretical studies, NA-TNA should be an ICT-featured compound possessing a  $T_1$  state with  ${}^3\pi\pi^*$  character, hence analogous to CzPhONI,  ${}^{30}$ NA-TNA may be a TFDF compound capable of utilizing triplet excitons through the TTA process. However, the ultra-low PLQY of NA-TNA in its thin solid film state (0.068, vide Table 2) would limit its potential application as a high-performance nondoped OLED light-emitter. As CzPhONI has been demonstrated to be a promising TFDF host material,<sup>30</sup> to evaluate whether CzPhONI and NA-TNA could act as an efficient host-guest ET pair, so that triplet excitons could be utilized concurrently by the host and guest materials in OLEDs, the absorption spectrum of NA-TNA and the PL emission spectrum of CzPhONI in solid film states were recorded. As illustrated in Fig. 7, a good spectral overlap between the emission band of CzPhONI and the absorption band of NA-TNA could be observed, implying that effective ET may take place between them. Further PL characterization on NA-TNA doped PMMA films (Fig. S2, ESI<sup>+</sup>)



Fig. 7 Normalized fluorescence spectrum of CzPhONI, absorption spectrum of NA-TNA, and fluorescence spectra of NA-TNA in CzPhONI at different doping levels in the solid film state ( $\lambda_{ex}$  = 380 nm).

and NA-TNA doped CzPhONI films at different doping levels (Fig. 7) indicated that even in the 1.4 wt% NA-TNA doped CzPhONI film, no emission from CzPhONI could be observed, implying that the ET between NA-TNA and CzPhONI is quite efficient. The 1.4 wt% NA-TNA doped CzPhONI film displays a high PLQY of 0.802; but with increasing NA-TNA composition (6.0 wt%, 10.0 wt% and 15.0 wt%), the PLQY of the blending films drops gradually (0.668, 0.605, and 0.336 in sequence), which may be ascribed to the concentration quenching of NA-TNA. Yet even at a high doping level of 10 wt%, a satisfactory PLQY of 0.605 could be achieved, indicating that the molecular interactions in NA-TNA are not much serious, and high-performance heavily doped OLEDs may be achieved using NA-TNA as a guest compound.

It should be pointed out that at relatively low doping levels  $(\leq 10 \text{ wt\%})$ , the PLQYs of NA-TNA doped CzPhONI films are even higher than those of the NA-TNA solution ( $\sim$  46%), which should be an abnormal phenomenon. After careful structural analysis, we conjectured that in the solution state, the presence of a diphenylamino group in NA-TNA may trigger intramolecular rotation that exhausts the energy of the excited states,<sup>44</sup> *i.e.*, NA-TNA might be an aggregation-induced-emissionenhancement (AIEE) luminogen. Consequently, the PL behavior of NA-TNA in CH3CN-water mixtures with different water fractions  $(f_w)$  was investigated (Fig. S3, ESI<sup>†</sup>). The results indicated that NA-TNA is AIEE-active in CH3CN, hence the more enhanced PLOYs of NA-TNA:CzPhONI film samples may arise from the restriction of intramolecular rotation of NA-TNA in the condensed state.

#### Thermal and electrochemical properties

The thermal stability of NA-TNA was investigated by thermogravimetric analysis (TGA) and differential scanning calorimetry

Table 2	EL performa	EL performance of devices I, II, III, and IV, and PL maximum and PLQY of the corresponding active films									
Device	$V_{\rm on}$ (V)	$L_{\rm max}  ({\rm cd}  {\rm m}^{-2})$	$\operatorname{LE_{max}}^{a}(\operatorname{cd}\operatorname{A}^{-1})$	$\lambda_{\text{ELmax}}^{b}$ (nm)	EQE <sub>max</sub> <sup>c</sup>	CIE $(x, y)^d$	PLQY <sup>e</sup>	$\lambda_{\text{PLmax}}^{f}(\text{nm})$			
I	4.2	5100	0.53 (124, 5.6)	639 (6)	0.59% (124)	(0.64, 0.36)(6)	0.068	635			
II	2.6	24 900	3.19 (5, 3.2)	570 (10)	2.49% (5)	(0.47, 0.50) $(10)$	0.802	566			
III	2.8	31 940	7.73 (12, 3.2)	583 (10)	5.83% (12)	(0.51, 0.48) $(10)$	0.668	575			
IV	3.2	27 640	5.41(8, 3.2)	608 (10)	4.14% (8)	(0.57, 0.43) $(10)$	0.336	592			

<sup>*a*</sup> Data in parentheses are the corresponding EL brightness (cd m<sup>-2</sup>) and driving voltages (V). <sup>*b*</sup> Data in parentheses are the corresponding driving voltages. <sup>*c*</sup> Data in parentheses are the corresponding EL brightness (cd m<sup>-2</sup>). <sup>*d*</sup> Data in parentheses are the corresponding driving voltages (V). <sup>e</sup> PLQY data of the corresponding active films. <sup>f</sup> PL maximum of the corresponding active films.

(DSC) (diagrams shown in Fig. S4 and S5, ESI<sup>†</sup>). **NA-TNA** has a high decomposition temperature of 423 °C ( $T_d$  corresponds to the temperature at 5 wt% loss). According to DSC measurements, although no distinct  $T_g$  could be identified, **NA-TNA** shows a high melting point of 278 °C. Thus **NA-TNA** displays good thermostability, which is highly desirable for OLED applications.

To estimate the energy levels of the frontier orbitals of NA-TNA, the electrochemical properties of NA-TNA have been investigated by cyclic voltammetry in degassed DCM solution  $(5 \times 10^{-4} \text{ mol } \text{L}^{-1})$  with a Fc/Fc<sup>+</sup> redox couple as the internal standard. As shown in Fig. S6 (ESI<sup>+</sup>), during the anodic scan from 0 to 0.7 V, a reversible oxidation process could be observed in NA-TNA, and its  $E_{1/2}^{\text{ox}}$  was determined to be 0.52 V relative to Fc/Fc<sup>+</sup>. Hence by comparison with the Fc/Fc<sup>+</sup> redox couple whose energy level is -4.80 eV in a vacuum, the highest occupied molecular orbital (HOMO) energy level of NA-TNA was calculated to be -5.32 eV. As no reduction wave could be detected due to the limited range available in DCM, the lowest unoccupied molecular orbital (LUMO) energy level of -3.00 eVwas deduced from the HOMO energy level and the optical bandgap of NA-TNA according to the equation of LUMO = HOMO +  $E_{g}$ . As the HOMO and LUMO energy levels of CzPhONI are -5.64 eV and -3.14 eV, respectively,<sup>30</sup> CzPhONI could act as a suitable host for NA-TNA.

#### **Electroluminescence properties**

To evaluate whether **NA-TNA** is a TFDF material capable of harvesting triplet excitons *via* the TTA process, firstly, we fabricated device I with **NA-TNA** as a non-doped light-emitting material, and the device structure is ITO/MoO<sub>3</sub> (1 nm)/TCTA (40 nm)/CBP (2 nm)/**NA-TNA** (20 nm)/ TPBI (45 nm)/ LiF (1 nm)/Al (80 nm), where TCTA (4,4',4''-tri(*N*-carbazolyl)triphenylamine) acts as a hole-transporting material, and TPBI (1,3,5-tris(1-phenyl-1*H*-benzo[*d*]imidazol-2-yl)benzene) acts as a electron-transporting material (energy level diagram shown in Fig. 8).

The current density-voltage-luminance (J-V-L) and the current efficiency-current density characteristics of device I are shown in Fig. 9a and Fig. S7 (ESI<sup>†</sup>), respectively. The EL spectra of device I under different driving voltages are shown in Fig. S8 (ESI<sup>†</sup>), and some representative data are summarized in Table 2. At a positive bias of 6 V, device I could emit red EL with a  $\lambda_{\rm ELmax}$  of 639 nm and CIE coordinates of (0.64, 0.36). The maximum brightness ( $L_{\rm max}$ ) and current efficiency (LE<sub>max</sub>) of device I are 5100 cd m<sup>-2</sup> and 0.53 cd A<sup>-1</sup>, respectively. Since the PLQY of the neat film of **NA-TNA** is as low as 0.068, the EL



Fig. 8 Device configuration and energy level diagram of devices I-IV.



**Fig. 9** (a) Current density-voltage-luminance (J-V-L) characteristics of device I (inset: the EL spectrum of device I at 6 V); and (b) the MEL of device I as a function of external magnetic field (MEL = (EL(B) - EL(0))/EL(0)).

performance of this non-doped OLED is quite satisfactory. In fact, the  $EQE_{max}$  of device I is 0.59%, which is much higher than that predicted from the 25% singlet production limit (0.34%), indicative of the effective utilization of triplet excitons in this device. Because magneto-electroluminescence (MEL) measurement has been verified to be an effective method to identify the TTA process,45,46 here, we employed MEL measurements to testify if the triplet excitons were harvested through the TTA process in device I. As shown in Fig. 9b, at a low driving voltage of 4 V (around the turn-on voltage), the MEL of device I increases sharply within the low-field hyperfine regime (<20 mT), then becomes saturated with increasing magnetic field, suggesting that there is no significant TTA process in device I. Yet with increasing applied bias hence increasing current density, the MEL of device I shows a rapid increase within the low-field regime (<20 mT) and a down trend in the high-field regime (>20 mT).<sup>45,46</sup> Taking into consideration that the charge injection within device I is ambipolar and balanced, this negative MEL effect could be safely assigned to TTA rather than triplet-polaron interactions (TPIs).47-49 Accordingly, the TTA process becomes more remarkable in this device at higher bias, and NA-TNA should be a TFDF-featured light-emitting material.

Although the low  $\varphi_{PL}$  of **NA-TNA** in neat film limits its application as a non-doped OLED fluorophore, the high PLQYs of its heavily doped films and the TFDF character of **NA-TNA** make it a quite promising guest candidate. More importantly, as **NA-TNA** and **CzPhONI** could form an efficient ET pair, triplet excitons could be harvested by both **NA-TNA** and **CzPhONI** *via* the TTA process in OLEDs if heavily doped **NA-TNA–CzPhONI** films are used as the light-emissive layer. To validate this hypothesis, we fabricated two OLEDs with the device configuration of ITO/MoO<sub>3</sub> (1 nm)/TCTA (40 nm)/CBP (2 nm)/**CzPhONI**: **NA-TNA** (20 nm, *x* wt%)/TPBI (45 nm)/LiF (1 nm)/Al (80 nm), where the composition of **NA-TNA** is 1.4 wt% (device II) or 6.0 wt% (device III).

As shown in Fig. 10, Fig. S7 (ESI<sup>†</sup>), and Table 2, at a positive bias of 10 V, 1.4 wt% **NA-TNA-**doped device II exhibits yellow emission with a  $\lambda_{ELmax}$  of 570 nm and CIE coordinates of (0.47, 0.50), and the  $L_{max}$ , LE<sub>max</sub> and EQE<sub>max</sub> of this device are 24 900 cd m<sup>-2</sup>, 3.19 cd A<sup>-1</sup> and 2.49%, respectively. While for device III with a higher **NA-TNA** doping level of 6.0 wt%, its  $\lambda_{ELmax}$  is redshifted to 583 nm with CIE coordinates of (0.51, 0.48) at 10 V, which is consistent with the PL spectral characteristics of the



Fig. 10 (a) Current density–voltage–luminance (J-V-L) characteristics of devices II–IV; and (b) EL spectra of devices II–IV (at 10 V).

active layers (Fig. 7). Moreover, in comparison with that of device II, the EL performance of device III is drastically enhanced, with a  $L_{\text{max}}$ , a LE<sub>max</sub> and an EQE<sub>max</sub> of 31 940 cd m<sup>-2</sup>, 7.73 cd A<sup>-1</sup> and 5.83%, respectively. It is noteworthy that although the PLQY of 1.4 wt% **NA-TNA-CzPhONI** doped film is higher than that of the 6.0 wt% doped one ( $\varphi_{\text{PL}}$ : 0.802 vs. 0.668), the EQE<sub>max</sub> of device II is much inferior to that of device III (2.49% vs. 5.83%). In fact, the EQE<sub>max</sub> of 5.83% has broken through the 25% singlet production limit of device III (3.34%), hence more efficient triplet exciton harvesting should occur in device III than in device II.

Further MEL characterization results indicated that although analogous to device I, devices II and III also show distinct TTAfeatured MEL response, they both exhibit a more apparent downward trend in MEL relative to device I at higher driving voltage, and device III shows the highest TTA portion value among the three devices (Fig. 9b and 11). For non-doped device I, the TTA process of the NA-TNA triplet excitons should be a competitive process with the radiative and non-radiative decay processes. Since the relative low bandgap of NA-TNA favors the nonradiative decay process, the TTA process in device I might be less efficient. For device II, as the composition of NA-TNA is as low as 1.4 wt%, most of the triplet excitons should be formed on CzPhONI upon charge injection, which might undergo radiative/non-radiative decay, TTA, and Dexter ET processes to NA-TNA. Taking into consideration that the Dexter ET process should be inefficient in this low doping-level device,50 and the higher bandgap of CzPhONI relative to NA-TNA should be adverse to the non-radiative decay of triplet excitons, the TTA process for CzPhONI excitons may be more efficient, hence a higher TTA portion value was observed in device II than in device I. Yet it should be pointed out that the triplet excitons of NA-TNA formed through direct charge injection or Dexter ET in device II could not be utilized effectively due to the low

composition of **NA-TNA**. In the case of device III, however, as the guest composition is as high as 6 wt%, although the triplet excitons should be formed mainly on **CzPhONI** upon direct charge injection, some triplet excitons could also be formed on **NA-TNA** through charge trapping or efficient Dexter ET.<sup>51,52</sup> Since the composition of **CzPhONI** is still as high as 94 wt%, similar to device II, **CzPhONI** should also contribute to the harvesting of triplet excitons *via* the TTA process in device III; but the triplet excitons of **NA-TNA** could also be utilized *via* the TTA process owing to the relatively high doping level of **NA-TNA**. Consequently, in device III, both the host and the guest compounds could contribute to the harvesting of triplet excitons, which may account for the higher TTA portion value in this device.

To gain further insights into the origin of the high efficiency of device III, we measured the transient EL of devices I-III. As shown in Fig. 12, although all these three devices show microsecond-scaled DF, the relative DF intensity in device III is much higher than that in device I or II, confirming the more efficient TTA process in device III.

In principle, at a higher guest doping-level, the triplet excitons of NA-TNA formed through Dexter ET and charge trapping processes could be utilized more efficiently via the TTA process, yet the dropped PLQY stemming from the concentration quenching of NA-TNA should be adverse to the device efficiency. To confirm this conjecture, we fabricated device IV with a NA-TNA doping-level of 15 wt%. Despite the fact that the PLQY of the active layer is as low as 0.336, device IV shows a relatively high EQE<sub>max</sub> of 4.14%, note that the 25% singlet production limit of device IV should just be 1.68%. Hence the triplet exciton harvesting efficiency is indeed higher in device IV than that in device III. Nevertheless, the EQE<sub>max</sub> of device IV is still inferior to that of device III (4.14% vs. 5.83%), which should be attributed to the much lower PLQY of the active layer of device IV (0.336 vs. 0.668). Therefore, to get OLEDs with high EQE, a trade-off between triplet exciton harvesting efficiency and concentration quenching should be achieved.

According to the energy level diagram, a possible mechanism of the TTA and ET processes within device III is tentatively proposed (Fig. 13). Upon charge injection, most of the singlet and triplet excitons are formed on **CzPhONI** with <sup>1</sup>CT\* and <sup>3</sup>CT\* character, respectively. As efficient ET could take place between **CzPhONI** and **NA-TNA**, most of the <sup>1</sup>CT\* excitons of the host could be transformed into the <sup>1</sup>CT\* excitons of **NA-TNA** through



Fig. 11 The MEL of devices II(a) and III(b) as a function of external magnetic field (MEL = (EL(B) – EL(0))/EL(0)).



Fig. 12 Transient EL response of devices I–III (driven under rectangular pulsed voltages of 9 V with an offset of -4 V).



Fig. 13 Schematic diagram for the proposed TTA and energy transfer processes in device III.

the Förster ET process. But the majority of <sup>3</sup>CT\* triplets of **CzPhONI** would be quenched by its lower-lying <sup>3</sup> $\pi\pi\pi^*$  state.<sup>30</sup> Taking into consideration that the concentration of **NA-TNA** in device III is 6 wt%, some <sup>3</sup> $\pi\pi^*$  excitons of **CzPhONI** could be transformed into the triplet excitons of **NA-TNA** *via* the Dexter ET process, <sup>51,52</sup> which could be converted into <sup>1</sup> $\pi\pi^*$  excitons of **NA-TNA** through the TTA process. While the rest <sup>3</sup> $\pi\pi^*$  excitons of **CzPhONI** could undergo a TTA process to generate <sup>1</sup> $\pi\pi^*$  excitons of **CzPhONI**, which could be converted to <sup>1</sup>CT\* *via* internal conversion. Consequently, in device III with relatively high guest concentration, the triplet excitons could be effectively harvested not only by the host compound, but also by the guest compound, resulting in high EL performance.

# Conclusions

A red naphthalimide derivative with D- $\pi$ -A molecular structure, namely NA-TNA, was designed and synthesized. Photophysical characterization revealed that NA-TNA is an ICT-featured compound: while theoretical calculation and MEL characterization indicated that NA-TNA is a promising TFDF material because its lowest triplet energy level possesses  ${}^{3}\pi\pi^{*}$  character. In addition, NA-TNA could form an efficient ET pair with the TFDFcharacterised host compound CzPhONI due to their structural similarity, and the presence of a bulky diphenylamine D subunit in NA-TNA endows it with suppressed intermolecular interactions, thereupon high PLQY could be achieved in NA-TNA-CzPhONI blending films at relatively high guest doping levels. Taking advantages of the TFDF characters of both NA-TNA and CzPhONI and the relatively high PLQY of the heavily doped guest/host active-layer, in OLEDs with 6 wt% doped NA-TNA-CzPhONI film as the emissive layer, triplet excitons could be harvested efficiently not only by the host, but also by the guest materials through the TTA process, hence the device displays high performance with a  $L_{\text{max}}$  of 31 940 cd m<sup>-2</sup> and a LE<sub>max</sub> of 7.73 cd  $A^{-1}$ , and the EQE<sub>max</sub> is 5.83%, which break through the 25% singlet production limit of this device. Our results indicated that ICT-featured TFDF compounds should be quite promising OLED light-emitting materials, and may shed light on the molecular design strategy for the guest fluorophores to achieve high-performance OLEDs by way of TFDF.

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