

# Chemical Science

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## ARTICLE

### High-efficiency and Low Efficiency Roll-Off Near-Infrared Fluorescent OLEDs through Triplet Fusion

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Though urgently needed, high-performance near-infrared organic light-emitting diodes (NIR-OLEDs) are still rare. NIR-OLEDs based on conventional NIR fluorescent materials usually suffer from low external quantum efficiencies (EQEs) because of the intrinsic obstacles according to the spin-statistics limit and energy-gap law. Herein, we realized high-efficiency and low efficiency roll-off fluorescent NIR-OLEDs through efficient triplet fusion of a bipolar host doped with a special naphthoselenadiazole emitter (4,9-bis(4-(2,2-diphenylvinyl)phenyl)naphtho[2,3-c][1,2,5]selenadiazole, NSeD). Unlike typical NIR organic donor-acceptor (D-A) chromophores, NSeD features a non-D-A structure and very large HOMO/LUMO overlap and displays strong deep-red to NIR fluorescence and unique ambipolar character. The corresponding photoluminescence quantum efficiency of NSeD reaches 52% in solution and remains 17% in the blend film. The optimized NIR-OLEDs demonstrated a strong emission at 700 nm, a high maximum EQE of 2.1% (vs. the predicted theoretical maximum efficiency 1.3%) and the EQE remained around 2% over a wide range of current densities from 18 to 200 mA cm<sup>-2</sup>, which is amongst the highest performance of NIR-OLEDs based on organic fluorescent materials.

#### Introduction

After decades of effort, organic light-emitting diodes (OLEDs) have gained great breakthrough in flat-panel displays, solid-state lighting and other applications especially in visible region.<sup>1-4</sup> Recently, as the extension of visible light, near-infrared OLEDs (NIR-OLEDs) have aroused growing interest due to their potential application in night-vision and information-secured displays, optical telecommunication, phototherapy, etc.<sup>5-9</sup> To date, several types of organic or metal-complex materials have been used as emitters in NIR-OLEDs, including fluorescent organic dyes with donor-acceptor (D-A) structures,<sup>10, 11</sup> transition-metal complexes,<sup>12</sup> lanthanide complexes,<sup>6, 13</sup> conjugated polymers.<sup>14-16</sup> Amongst these materials, transition-metal complexes (*e.g.*, containing Pt<sup>2+</sup>, Os<sup>3+</sup>, Ir<sup>3+</sup>) can exploit the normally non-radiative triplet excitons and so help realize high external quantum efficiencies (EQEs) for NIR-OLEDs.<sup>12, 17-23</sup> However, such high EQE values usually suffered from noticeable efficiency roll-offs with increasing current density, which could be mainly ascribed to the long lifetime of triplet excitons.<sup>12, 17-25</sup> In addition, the price and rarity of these noble metals would limit their mass production and future application.

Conventional organic fluorescent materials with cost

advantage show easy tunable emission by finely combining D-A chromophores;<sup>11</sup> however, these D-A compounds usually exhibit low quantum efficiency in NIR spectral range mainly because of the intrinsic limitation according to the energy-gap law, which describes an exponential increase in the non-radiative rate with a decrease of the energy gap.<sup>26, 27</sup> In addition, the limited overlap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in such D-A compounds results in a much lower radiative-transition rate.<sup>26, 28</sup> Further coupled with the upper limit of radiative singlet exciton ratio of 25% in the conventional fluorescent OLEDs (FOLEDs), the corresponding NIR-OLEDs virtually give very low EQEs (below 1%). Thus it is still highly challenging to realize highly efficient NIR-OLEDs based on conventional fluorescent materials, which would require innovative approaches to enhance not only the radiative-transition rate of NIR-emitting organic compounds but also the radiative exciton ratio of the corresponding OLEDs.

Approaches to harvest the 75% triplet excitons of organic fluorescent materials are highly desired to enhance radiative exciton ratio and thus enable highly efficient NIR-OLEDs with cost advantage. In 2014, Ma et al. proposed hybridized local and charge-transfer (HLCT) state to employ high-lying triplet excitons and reported efficient NIR-OLEDs with a maximum EQE of 1.54% around 700 nm and a high radiative exciton ratio of 48%.<sup>29</sup> Recently, Wang et al. employed a thermally activated delayed fluorescence (TADF) emitter for efficient nondoped NIR-OLEDs with a maximum EQE of 2.1% and an emission at 710 nm.<sup>30</sup> An alternative strategy to harness the triplet excitons of organic fluorescent materials involves triplet

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†Electronic Supplementary Information (ESI) available: Compound characterisation data, crystallographic data, UPS spectra, EL spectra of device E, emission spectra of NSeD in toluene, Phosphorescence spectra of Ga<sub>2</sub>(saph)<sub>2</sub>q<sub>2</sub>. See DOI: 10.1039/x0xx00000x

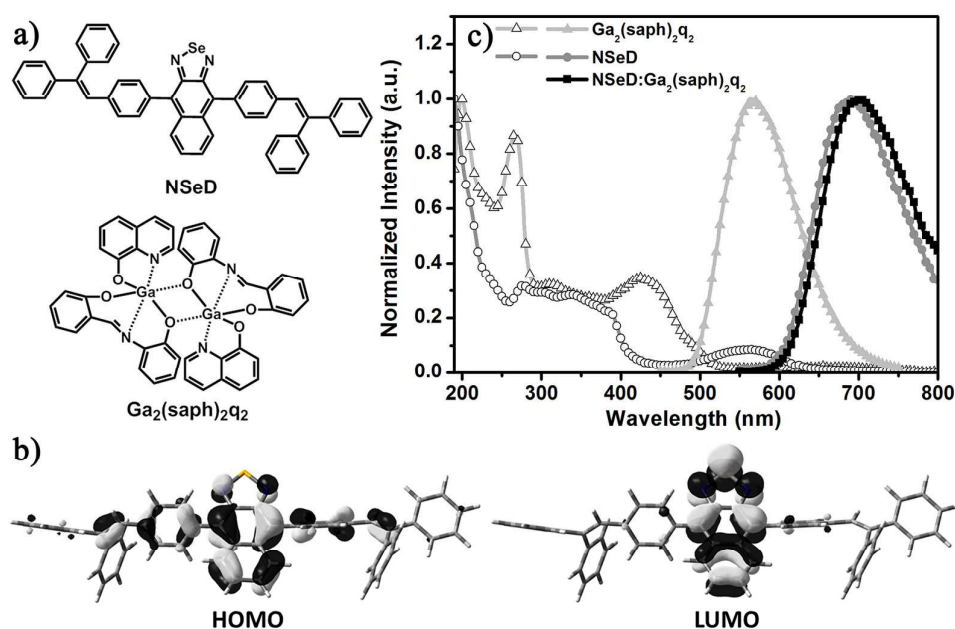
fusion (TF).<sup>31, 32</sup> The theoretical maximum singlet excitation production yield through TF is 50%, which would contribute the maximum radiative excitation ratio up to 62.5%.<sup>33</sup> In 2009, Kondakov et al. reported high-efficiency red FOLEDs through the TF of host material achieving a high EQE of 11.3%.<sup>33</sup> In 2013, Monkman et al. reported highly efficient green FOLEDs via ultrahigh-efficiency TF of a special anthracene/tribenzenamine emitter achieving a 6% EQE, which is far exceeding the theoretical maximum EQE of 3.55%.<sup>34</sup> Recently, Lu et al. reported a charge-transfer-featured naphthalimide derivative, which could harvest triplet excitons through TF and act as an efficient host for orange-red FOLEDs.<sup>35</sup> To our best knowledge, there are no reports on efficient NIR-OLEDs through TF. Herein, we considered TF could likewise provide an alternative strategy to realize highly efficient NIR-FOLEDs.

To enable highly efficient NIR-OLEDs through TF, the more feasible approach is via efficient TF of the host rather than the direct TF from the emitter, since the triplet excitons of the NIR emitter may decay dominantly via non-radiative transition in accord to the energy gap law. In this work, we realized high-performance NIR-OLEDs via high-efficiency TF of a bipolar host doped with a special naphthoselenadiazole emitter. The bipolar host material is bis(salicylidene-*o*-aminophenolato)-bis(8-quinolinoato)-bis-gallium(III) [Ga<sub>2</sub>(saph)<sub>2</sub>q<sub>2</sub>], which was found to harvest triplet efficiently through TF and then transfer its singlet excitons to the dopant 4,9-bis(4-(2,2-diphenylvinyl)phenyl)-naphtho[2,3-*c*][1,2,5]selenadiazole (NSeD). Unlike typical D-A compounds, NSeD has very large HOMO/LUMO overlap and displays strong deep-red to NIR fluorescence and the corresponding quantum efficiency

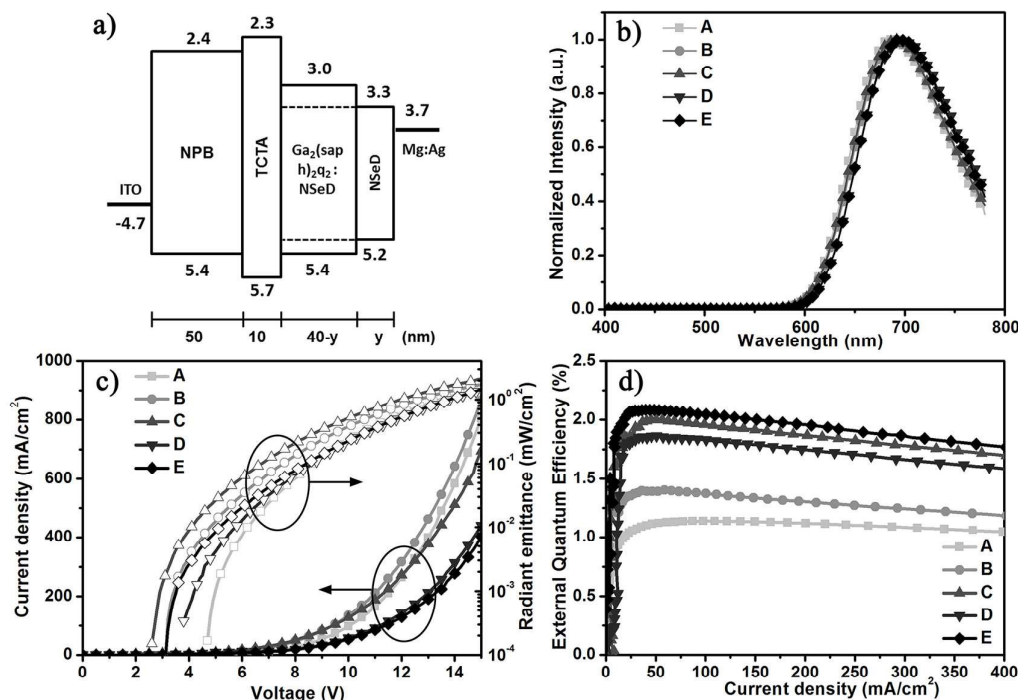
reaches 52% in solution and remains 17% in the Ga<sub>2</sub>(saph)<sub>2</sub>q<sub>2</sub>:NSeD blend film. The optimized NIR-OLEDs without outcoupling enhancements achieved a strong NIR emission at 700 nm and a high EQE of up to 2.1% at 42 mA cm<sup>-2</sup>, which is far beyond the predicted theoretical maximum value of 1.3%. In particular, the EQEs remained around 2% over a wide range of current densities from 18 to 200 mA cm<sup>-2</sup>.

## Results and Discussions

Fig. 1 shows the molecular structures and their photophysical properties of the compounds used. The host material Ga<sub>2</sub>(saph)<sub>2</sub>q<sub>2</sub> is a homemade binuclear gallium complex with an emission peak at 563 nm and bipolar character.<sup>36, 37</sup> Recently, it has proven an excellent host for NIR-emitting iridium complex.<sup>38</sup> In previous work, our group reported a series of naphtho[2,3-*c*][1,2,5]thiadiazole derivatives which possess both ambipolar transporting property and high fluorescence quantum yield.<sup>39, 40</sup> Among these materials, 4,9-bis(4-(2,2-diphenylvinyl)phenyl)naphtho[2,3-*c*][1,2,5]thiadiazole (NTD) exhibits highly efficient red emission. To tune the emission energy into NIR region, NSeD was synthesized by replacing the sulfur atom of NTD with selenium.<sup>41-43</sup> As depicted in the single crystal structure (Fig. S3†), NSeD is a nonplanar molecule based on naphtho[2,3-*c*][1,2,5]selenadiazole connected with bulky aryl substituents on both sides in the *trans* configuration. There are two sets of orientations for naphthoselenadiazole core and each set of orientation possesses 50% occupancy. The crystal packing diagram (Fig. S4†) reveals that the weak C-H...N interactions (*D*



**Fig. 1** a) Molecular structures of the NSeD and Ga<sub>2</sub>(saph)<sub>2</sub>q<sub>2</sub>. b) Isocontour plots of frontier orbitals of NSeD. The isocontour value  $|\psi|$  is 0.03. c) The absorption (open symbol) and emission spectra (solid symbol) of Ga<sub>2</sub>(saph)<sub>2</sub>q<sub>2</sub>, NSeD and the 50 wt% Ga<sub>2</sub>(saph)<sub>2</sub>q<sub>2</sub>:NSeD films at 298K.



**Fig. 2** a) The energy level diagram of devices. b) Electroluminescent spectra (at 8 V) of devices with the architecture of ITO/NPB (50 nm)/TCTA (10 nm)/Ga<sub>2</sub>(saph)<sub>2</sub>q<sub>2</sub>:NSeD (x wt %, 40-y nm)/NSeD (y nm)/Mg:Ag (150 nm) (device A: x = 100, y = 0, device B: x = 25, y = 0, device C: x = 50, y = 0, device D: x = 75, y = 0, device E: x = 50, y = 10). c) Current density (*J*)-voltage (*V*)-radiant emittance (*R*) characteristics of devices. d) External quantum efficiency-current density characteristics of devices.

= 2.847 Å,  $\theta = 165.4^\circ$ ) are the main force maintaining molecular order; face-to-face  $\pi$ - $\pi$  stacking interactions are negligible, which is beneficial to hinder the undesired photoluminescence self-quenching.

The electronic structures of NSeD were calculated using DFT calculations based on its single-crystal structure. Unlike typical organic D-A compounds, the HOMO of NSeD is mostly located on naphthoselenadiazole core and has a small contribution from the aryl substituents directly connected with naphthoselenadiazole core, while the LUMO is highly located on naphthoselenadiazole core (Fig. 1b). Such large overlap between HOMO and LUMO suggests NSeD would possess desirable ambipolar character and enhanced fluorescence efficiency.<sup>40, 44</sup> In toluene solution, NSeD exhibits a strong deep-red emission at 670 nm (Fig. S5†) with a high photoluminescence quantum yield (PLQY) of 0.52. The net film of NSeD shows a marked bathochromic shift to 689 nm (Fig. 1c), while the PLQY falls to 0.13 because of aggregation-caused quenching (ACQ).<sup>45</sup> When doped in Ga<sub>2</sub>(saph)<sub>2</sub>q<sub>2</sub> at 50 wt%, the Ga<sub>2</sub>(saph)<sub>2</sub>q<sub>2</sub>:NSeD blend film gives a further bathochromic shift to 700 nm and a markedly improved PLQY of 0.17 due to the suppression of ACQ.

Using Ga<sub>2</sub>(saph)<sub>2</sub>q<sub>2</sub> as host and NSeD as dopant, we fabricated NIR-OLEDs with the device configurations of ITO/NPB (50 nm)/TCTA (10 nm)/Ga<sub>2</sub>(saph)<sub>2</sub>q<sub>2</sub>:NSeD (x wt %, 40-y nm)/NSeD (y nm)/Mg:Ag (150 nm) (device A: x = 100, y =

0, device B: x = 25, y = 0, device C: x = 50, y = 0, device D: x = 75, y = 0, device E: x = 50, y = 10), where ITO is indium tin oxide, NPB is *N,N'*-di(naphthalen-1-yl)-*N,N'*-diphenylbenzidine used as the hole transporting material, TCTA is tris(4-carbazoyl-9-ylphenyl)amine to lower hole transport and balance charge carrier, and Mg:Ag is the cathode. The device architecture and the energy level diagram are depicted in Fig. 2a. The HOMO and LUMO levels of Ga<sub>2</sub>(saph)<sub>2</sub>q<sub>2</sub> and NSeD were estimated from ultraviolet photoelectron spectroscopy (Fig. S6†) and by subtracting the optical energy gaps from the HOMO energies, respectively. The characteristics of these

**Table 1** Electroluminescence Characteristics of the Devices

| Device | NSeD ratio [wt %] | <i>V</i> <sub>on</sub> <sup>a)</sup> [V] | $\lambda_{EL,max}$ <sup>b)</sup> [nm] | EQE <sup>c)</sup> [%] | <i>R</i> <sup>d)</sup> [ $\mu$ W cm <sup>-2</sup> ] |
|--------|-------------------|--|---------------------------------------|-----------------------|---|
| A      | 100               | 4.7                                      | 688                                   | 1.1, 1.1, 1.1         | 1477  |
| B      | 25                | 3.2                                      | 692                                   | 1.4, 1.4, 1.3         | 1720  |
| C      | 50                | 2.6                                      | 692                                   | 2.0, 2.0, 1.7         | 2127  |
| D      | 75                | 3.8                                      | 700                                   | 1.9, 1.8, 1.7         | 1404  |
| E      | 50                | 3.2                                      | 700                                   | 2.1, 2.1, 2.0         | 1451  |

<sup>a)</sup> *V*<sub>on</sub> is the onset voltage obtained at 1 mW m<sup>-2</sup>; <sup>b)</sup> Recorded at 8 V; <sup>c)</sup> Maximum external quantum efficiency, then data at a current density of 100 mA cm<sup>-2</sup> and then at 200 mA cm<sup>-2</sup>; <sup>d)</sup> Recorded at 15 V.

devices are listed in Table 1. Device A with pure NSeD showed an emission at 688 nm and a maximum EQE of 1.1% (Fig. 2d). Device B with 25 wt% NSeD gained an improved EQE up to 1.4%. As the increase of NSeD concentration in emitting layer (EML), device C with 50 wt% NSeD exhibited a much better EQE up to 2.0% with the emission red-shifted to 700 nm. However, the EQE of device D with 75 wt% NSeD decreased slightly to 1.9%, which is in accord with the relatively lower PLQY (0.14) of the 75 wt%  $\text{Ga}_2(\text{saph})_2\text{q}_2$ :NSeD blend film. Thus, device C with 50 wt% NSeD exhibited the best device performance. It is worth noting that device C showed the lowest operation voltage (Fig. 2c) with a low turn-on voltage of 2.6 V (at radiant emittance of  $1 \text{ mW m}^{-2}$ ) and a maximum radiant emittance ( $R_{\text{max}}$ ) of  $2127 \mu\text{W cm}^{-2}$  (at 15 V), which is among the highest values reported in NIR-FOLEDs peaking around 700 nm.<sup>10, 46-48</sup>

To further improve the efficiency of NIR-OLEDs, a thin layer (10 nm) of NSeD adjacent to the cathode was added as the electron transporting layer (ETL) to suppress the exciton quenching by cathode while maintaining the total thickness of the OLEDs at 100 nm. The optimized device E ( $x = 50$ ,  $y = 10$ ) achieved a maximum EQE up to 2.1% ( $J = 42 \text{ mA cm}^{-2}$ ) (Fig. 2d) with an emission at 700 nm. The EL spectra are independent of the driving voltage (Fig. S7†). Most notably, the EQE remained almost constant with increasing current densities. At  $J = 100 \text{ mA cm}^{-2}$ , the value of EQE stayed as high as 2.05%. Even at a higher current density of  $J = 200 \text{ mA cm}^{-2}$ , the EQE was still

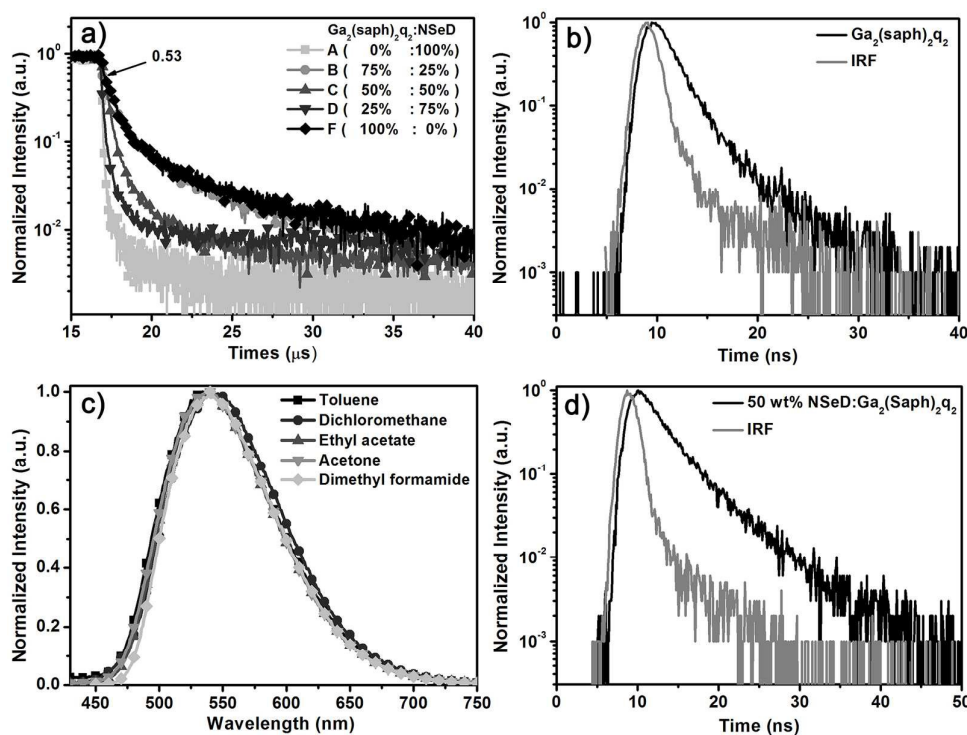
1.96%, which is very desirable for practical application. This indicated that the current-induced exciton quenching was effectively suppressed. On the one hand, as shown in Fig. 2a, the HOMO and LUMO energy level of NSeD locate right inside the host's. Such host/guest heterostructures can efficiently suppress the electric field induced quenching and thus minimize the efficiency roll-off in devices.<sup>38, 49</sup> On the other hand, both  $\text{Ga}_2(\text{saph})_2\text{q}_2$  and NSeD have a bipolar character and thus provides a wide charge recombination region.<sup>50</sup> Overall, the well matched host/guest energy levels and their bipolar characters substantially contribute to the negligible efficiency roll-off of such NIR OLEDs.

In general, the theoretical maximum EQE of OLEDs can be calculated according to the following equation:

$$\text{EQE} = \gamma \times \eta_r \times \text{PLQY} \times \eta_{\text{out}} \quad (1)$$

where  $\gamma$  is the electron/hole recombination ratio,  $\eta_r$  is the exciton formation ratio for radiative transitions ( $\eta_r = 0.25$  for conventional fluorescent emitters) and  $\eta_{\text{out}}$  is the light outcoupling efficiency. Given the PLQY of 50 wt%  $\text{Ga}_2(\text{saph})_2\text{q}_2$ :NSeD films of 0.17, the theoretical maximum EQE of device E should be 0.9-1.3 %, assuming that  $\gamma = 1.0$ ,  $\eta_r = 0.25$ , and  $\eta_{\text{out}} = 0.2-0.3$ .<sup>51-53</sup> However, the achieved EQE (2.1%) of device E is about 1.62 times as high as the theoretical maximum EQE (1.3%). In fact, all the other devices with  $\text{Ga}_2(\text{saph})_2\text{q}_2$ :NSeD blend emitter demonstrated much higher EQEs than their theoretical maximum values.

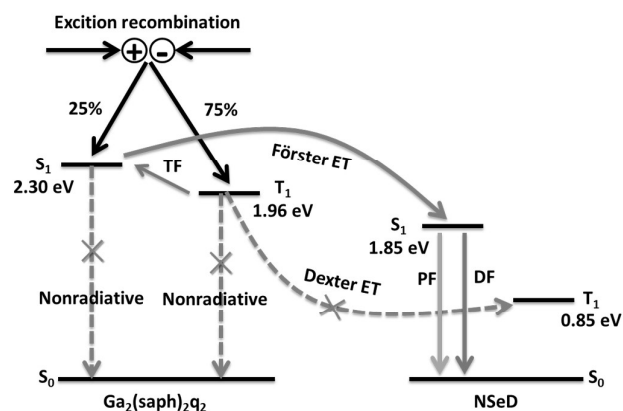
To unravel the electroluminescent (EL) mechanism in these



**Fig. 3** a) The transient EL decay curves of devices A-D with different  $\text{Ga}_2(\text{saph})_2\text{q}_2$  concentration observed at 700nm with a voltage of 5 V. And the transient EL decay curves of device F (pure  $\text{Ga}_2(\text{saph})_2\text{q}_2$ ) observed at 580nm with a voltage of 5.5 V. b) The PL transient decay curves of the  $\text{Ga}_2(\text{Saph})_2\text{q}_2$  film observed at 560 nm. c) Emission spectra of  $\text{Ga}_2(\text{Saph})_2\text{q}_2$  in different solvents. d) The PL transient decay curves of the 50 wt%  $\text{Ga}_2(\text{saph})_2\text{q}_2$ :NSeD film observed at 680 nm ( $\lambda_{\text{ex}} = 380 \text{ nm}$ ).

devices, the transient EL measurements were carried out on these devices. To note, devices A-D have the same device structure, but different ratio of  $\text{Ga}_2(\text{saph})_2\text{q}_2$  in the EML. Device A with pure NSeD showed very sharp EL decay curve (Fig. 3a), indicating that almost all of the radiative excitons are short-lived. In contrast, devices B-D with  $\text{Ga}_2(\text{saph})_2\text{q}_2$ :NSeD blend EML all demonstrated the existence of delayed fluorescence. Interestingly, the intensity of the delayed component increased with increasing  $\text{Ga}_2(\text{saph})_2\text{q}_2$  concentration, which suggests the delayed fluorescence could be correlated with  $\text{Ga}_2(\text{saph})_2\text{q}_2$ . To further identify the origin of the delayed fluorescence, device F with the pure  $\text{Ga}_2(\text{saph})_2\text{q}_2$  as EML was fabricated with a configuration of ITO/NPB (50 nm)/TCTA (10 nm)/ $\text{Ga}_2(\text{saph})_2\text{q}_2$  (40 nm)/Mg:Ag (150 nm). As expected, device F gave prominent delayed fluorescence (Fig. 3a) and the delayed fluorescence component contributed about 53% of the total EL signal. However, the transient PL decay of pure  $\text{Ga}_2(\text{saph})_2\text{q}_2$  film exhibited a very short lifetime of 1.9 ns (Fig. 3b). And  $\text{Ga}_2(\text{saph})_2\text{q}_2$  had no solvatochromic effects in different solvents with an emission at 540 nm (Fig. 3c), indicating that the excited singlet state of  $\text{Ga}_2(\text{saph})_2\text{q}_2$  is not charge-transfer-featured. In addition, the  $T_1$  energy of  $\text{Ga}_2(\text{saph})_2\text{q}_2$  was found to be 1.96 eV (Fig. S8<sup>†</sup>), which is about 0.34 eV lower than  $S_1$  energy (2.30 eV). Accordingly, it could be ruled out that the delayed fluorescence comes TADF of  $\text{Ga}_2(\text{saph})_2\text{q}_2$ . On the other hand, the 50 wt%  $\text{Ga}_2(\text{saph})_2\text{q}_2$ :NSeD blend film actually gave very similar PL spectrum to that of pure NSeD film and very short lifetime of 3.4 ns (Fig. 3d). Given the embedded HOMO and LUMO of NSeD in that of  $\text{Ga}_2(\text{saph})_2\text{q}_2$ , there is no considerable driving force to allow the possible exciplex between  $\text{Ga}_2(\text{saph})_2\text{q}_2$  and NSeD.<sup>54, 55</sup> Hence it also could be ruled out that the delayed fluorescence comes from the possible exciplex formed between  $\text{Ga}_2(\text{saph})_2\text{q}_2$  and NSeD. Therefore, the strong delayed EL could be unambiguously ascribed to extra radiative singlet excitons generated via the efficient TF of  $\text{Ga}_2(\text{saph})_2\text{q}_2$  and then transferred into the singlet state of NSeD, which help bring about the breakthrough of the theoretical maximum EQE in device E.

Based on the above results and discussions, we proposed the possible energy transfer processes in these NIR-OLEDs. As shown in Fig. 4, the desirable processes are indicated by solid arrows while the undesirable ones resulting in a loss in efficiency by dotted arrows with a cross. After charge recombination, the generated singlet excitons of  $\text{Ga}_2(\text{saph})_2\text{q}_2$  are directly transferred into the singlet state of NSeD via Förster energy transfer and then decay as the prompt fluorescence of NSeD. The triplet excitons of  $\text{Ga}_2(\text{saph})_2\text{q}_2$  can be up-converted into its singlet states through TF and then transfer into the singlet state of NSeD and decay as the delayed fluorescence of NSeD or, they may Dexter transfer to the triplet state of NSeD, which is a source of loss. To note, Dexter energy transfer is a short-range coherent transfer of an exciton from a donor to an acceptor site at a rate proportional to the orbital overlap of the donor and acceptor molecules, attenuating exponentially with distance.<sup>26</sup> In our case, the HOMO and LUMO of NSeD are mainly located on the central



**Fig. 4** Schematic illustration of the energy transfer processes in NIR-OLEDs. TF stands for triplet fusion, PF for prompt fluorescence, DF for delayed fluorescence and ET for energy transfer. The energy levels given are for  $\text{Ga}_2(\text{saph})_2\text{q}_2$  and NSeD.

naphthoselenadiazole core, which is well protected by the lateral bulky and twisted aryl substituents. These bulky aryl substituents result in a large distance of 9.88–11.30 Å between neighboring naphthoselenadiazole cores in single crystals (Fig. S9<sup>†</sup>), which would effectively separate  $\text{Ga}_2(\text{saph})_2\text{q}_2$  and NSeD molecules in the mixed films and limit their frontier orbital overlap. In addition, the Dexter transfer rate is also proportional to the spectral overlap of the two species because the donor exciton energy must closely match that of the acceptor.<sup>26</sup> For NSeD, the  $T_1$  was calculated to be 0.85 eV, which is much lower than that of  $\text{Ga}_2(\text{saph})_2\text{q}_2$  (1.96 eV). Such large energy mismatch (1.11 eV) would inhibit the Dexter energy transfer between the  $T_1$  of  $\text{Ga}_2(\text{saph})_2\text{q}_2$  and NSeD. Therefore, fortunately, the undesirable Dexter energy transfer between  $\text{Ga}_2(\text{saph})_2\text{q}_2$  and NSeD can be significantly suppressed. On the other hand, the emission of  $\text{Ga}_2(\text{saph})_2\text{q}_2$  shows good overlap with the absorption of NSeD (Fig. 1c), which helps provide highly efficient Förster energy transfer between the  $S_1$  of  $\text{Ga}_2(\text{saph})_2\text{q}_2$  and NSeD. Such efficient Förster energy transfer as well as the efficient TF of  $\text{Ga}_2(\text{saph})_2\text{q}_2$  contribute to the unexpectedly high EQEs in these NIR-OLEDs with  $\text{Ga}_2(\text{saph})_2\text{q}_2$ :NSeD blend emitter.

## Conclusions

In summary, high-performance NIR-FOLEDs via TF have been achieved with a  $R_{\text{max}}$  of 2127  $\mu\text{W cm}^{-2}$ , a maximum EQE up to 2.1% and the EQE staying around 2% over a wide range of current densities from 18 to 200  $\text{mA cm}^{-2}$ , which is amongst the highest performance of NIR-OLEDs based on organic fluorescent materials.<sup>10, 29, 46–48</sup> The transient PL and EL studies revealed that such high EQE (vs. the predicted theoretical maximum efficiency 1.3%) could be attributed to the effective TF from the bipolar host  $\text{Ga}_2(\text{saph})_2\text{q}_2$ . The NIR emitter, NSeD featuring a non-D-A structure and very large HOMO/LUMO overlap, displays strong deep-red to NIR fluorescence and

unique ambipolar character, thus contributing to such unexpectedly high EQEs and negligible efficiency roll-off. It is anticipated that this work provides a promising strategy to realize high-efficiency and low efficiency roll-off NIR-FOLEDs via TF.

## Experimental section

### General Methods:

All commercially available reagents and chemicals were used without further purification. All reactions involving air-sensitive reagents were carried out under an atmosphere of nitrogen.  $\text{Ga}_2(\text{saph})_2\text{Q}_2$ , 4,9-Dibromonaphtho[2,3-c][1,2,5]selenadiazole and [4-(2,2-diphenylvinyl)phenyl]boronic acid was synthesized as according to literatures.<sup>36, 56, 57</sup>  $^1\text{H}$  NMR spectra were measured on a JEOLAL-600 MHz spectrometer at ambient temperature. High resolution mass spectra were recorded using a waters GCT Premier time-of-flight mass spectrometer in electron-impact (EI) mode. Elemental analyses were performed on a flash EA 1112 spectrometer. Absorption spectra were recorded using a UV-vis spectrophotometer (Agilent 8453). The emission spectra and the transient photoluminescence measurements were carried out using a transient spectrometer (Edinburg FL920P). The photoluminescence quantum efficiencies were measured using an absolute photoluminescence quantum yield measurement system (Hamamatsu C11347). The time-resolved PL spectra were measured on a laser flash photolysis spectrometer (Edinburg LP-920). The  $1 \times 10^{-5}$  M solution was used for photoluminescence spectra measurement. And small-molecule organic films for optical measurements were fabricated by thermal evaporation under high vacuum ( $10^{-4}$  Pa) onto clean quartz substrates. The organic film used for the measurement of phosphorescence spectra was fabricated by dropping the mixed solution (2%wt  $\text{Ga}_2(\text{saph})_2\text{Q}_2$ :10%wt Flrpic: PMMA) onto clean quartz substrates. The ultraviolet photoelectron spectroscopy measurements were performed using photoelectron spectrometer (Thermo Fisher ESCALAB 250Xi) equipped a He-discharge lamp providing He-I photons of 21.22 eV with a bias of -5.0 V and the position of Fermi edge was calibrated using a clean Ag film.

### Single-Crystal Structure:

The single crystal of NSeD was obtained in the process of vacuum sublimation. The low temperature (104.6K) single-crystals X-ray experiments were performed on a Rigaku RAXIS-SPIDER IP diffractometer with graphite-monochromatized  $\text{MoK}\alpha$  radiation ( $\lambda=0.71073$  Å). Data collection and reduction, cell refinement, and experiential absorption correction for all compounds were performed with the Rigaku RAPID AUTO software package (Rigaku, 1998, Version 2.30). The structure was solved by direct methods and refined against F2 by full-matrix least-squares techniques. CCDC 1402824 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge

Crystallographic Data Centre via [www.ccdc.cam.ac.uk/data\\_request/cif](http://www.ccdc.cam.ac.uk/data_request/cif).

### Synthesis of NSeD:

4,9-Dibromonaphtho[2,3-c][1,2,5]selenadiazole (0.98 g, 2.5 mmol), [4-(2,2-diphenylvinyl)phenyl]boronic acid (1.88 g, 6.25 mmol), tetrakis(triphenylphosphine)palladium(0) (0.29 g, 0.25 mmol), potassium carbonate (1.73 g, 12.5 mmol), toluene (50mL), ethanol (38mL) and distilled water (25mL) were first mixed. The mixture was heated to reflux under a nitrogen atmosphere for 24h. After cooling to room temperature, the mixture was filtered off and washed by hot water, hot petroleum ether and hot ethanol subsequently and dried in vacuum. The crude product was then purified by vacuum train sublimation to afford a red solid (0.87 g, 1.17 mmol, 47%).  $^1\text{H}$  NMR (600 MHz,  $\text{CD}_2\text{Cl}_2$ ,  $\delta$ ): 7.731 (m, 2H), 7.449-7.296 (m, 24H), 7.247 (d,  $J = 8.1\text{Hz}$ , 4H), 7.186 (m, 2H), 7.139 (s, 2H). HRMS-EI ( $m/z$ ): calcd for  $\text{C}_{50}\text{H}_{34}\text{N}_2\text{Se}$ , 742.1887; found: 742.1871. Elemental analysis calcd for  $\text{C}_{50}\text{H}_{34}\text{N}_2\text{Se}$ : C, 80.96; H, 4.62; N, 3.78; found: C, 81.10; H, 4.65; N, 3.90.

### Theoretical Calculations, Computational Details:

All of the calculations were performed using the Gaussian 09 program package.<sup>58</sup> The ground state geometries of and NSeD were optimized based on the single-crystal structure. The triplet energy of NSeD was calculated based on the optimized ground-state geometry. Calculations on the ground and excited electronic states of NSeD were performed with density functional theory (DFT) and time-dependent DFT (TDDFT) using the B3LYP functional with 6-31G(d) basis set in vacuum.<sup>59, 60</sup>

### Device fabrication and measurements:

The devices were fabricated by thermal evaporation under high vacuum (ca.  $7 \times 10^{-4}$  Pa) onto ITO-coated glass substrates. The substrates were carefully cleaned and treated with UV ozone for 10 min before vacuum thermal deposition. All OLED devices were encapsulated in a standard dry nitrogen glove box after fabrication and then measured in ambient. The measurements of the transient electroluminescence were carried out using a transient spectrometer (Edinburg FL920P) and the Agilent 8114A Programmable Pulse Generator was used to generate appropriate excitation waveforms with a pulse width of 15  $\mu\text{s}$ . The amplitude of the pulse was 8 V or 8.5V, and the baseline was -3 V. The period was 50  $\mu\text{s}$ , delayed time 25  $\mu\text{s}$ , and duty cycle 30%. The current-voltage characteristics were measured with a Keithley 4200 semiconductor characterization system and optical power was determined using a Newport 1936-C power meter coupled to a calibrated Newport 918D-UV-OD3 detector with a spectral response range from 200 to 1100 nm. The electroluminescence spectra of the OLEDs were obtained using a multichannel spectrometer (PR 705). The EQE of the NIR EL was determined according to the literature method, by measuring the light intensity in the forward direction and assuming the external emission profile to be Lambertian.<sup>61, 62</sup>

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