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Novel 1,8-naphthalimide derivatives for standard-red organic light-emitting device applications

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Three red-emissive D-π-A-structured fluorophores with aromatic amine as donor, ethene-1,2-diyl as π-bridge, and 1,8-naphthalimide as acceptor subunits, namely (E)-6-(4-(dimethylamino)styryl)-2-hexyl-1H-benzo[de]isoquinoline-1,3(2H)-dione (Nap1), (E)-2-(2,6-di(isopropyl)phenyl)-6-(4-(dimethylamino)styryl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (Nap2) and (E)-2-(2,6-di(isopropyl)phenyl)-6-(2-(1,1,7,7-tetramethyl-2,3,6,7-tetrahydro-1H,5H-pyrido[3,2,1-ij]quinolin-9-yl)vinyl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (Nap3), were designed and synthesized. In-depth investigations on the correlations between their molecular structures and photophysical characteristics revealed that the presence of an electron-rich 4-dimethylaminophenyl donor moiety in compound Nap1 could endow it with red emission (e.g., λPLmax = 641 nm in the host/guest blend film with 14 wt% guest composition); the replacement of the n-phenyl group of Nap1 bonding to the imide nitrogen atom into a more bulky 2,6-di(isopropyl)phenyl one would result in compound Nap2 with more alleviated concentration quenching; while the alteration of the 4-(dimethylaminophenyl) donor subunit of Nap2 into a more electron-donating 1,1,7,7-tetramethyljulolidin-9-yl substituent would render compound Nap3 with more improved chromaticity (e.g., λPLmax = 663 nm in 14 wt% guest-doped film). Consequently, Nap3 could not only emit standard-red fluorescence with satisfactory chromaticity, but also show suppressed intermolecular interactions. Using Nap3 as the dopant, a heavily-doped standard-red organic light-emitting diode (OLED) with device configuration of ITO/MoO3 (1 nm)/TCTA (40 nm)/CzPhONI:Nap3 (14 wt%) (20 nm)/TPBI (45 nm)/LiF (1 nm)/Al (80 nm) was fabricated, and the Commission Internationale de L’Eclairage coordinates, maximum external quantum efficiency and maximum current efficiency of this OLED are (0.67, 0.32), 1.8% and 0.7 cd A-1, respectively. All these preliminary results indicated that 1,8-naphthalimide derivatives could act as quite promising standard-red light-emitting materials for OLED applications.

1. Instruction

Owing to their merits like solid-state self-emission, wide viewing angle, facile color tunability and processability, organic light-emitting devices (OLEDs) have been considered as quite competitive candidates for flat-panel display applications.1 In comparison with phosphorescent OLEDs, fluorescent ones are more suitable with respect to display applications due to their faster response as well as lower efficiency roll-off.2 For full-color display applications, it is necessary to develop red, green, and blue fluorescent OLEDs with high efficiency and appropriate chromaticity, yet compared with that of blue3b and green3b devices, the performance of red fluorescent OLEDs with good chromaticity is unsatisfactory. For example, although the current efficiency (CE) of red OLEDs with Commission Internationale de L’Eclairage (CIE) coordinates of (0.63, 0.37) could reach 11.5 cd A-1,4 their chromaticity is far from standard-red whose CIE coordinates should be close to (0.67, 0.33) according to the stipulation from the National Television Standards Committee. As far as standard-red OLEDs are concerned, although according to a technical report from Idemitsu Kosan Co., high performance devices with CE of 11.0 cd A-1 could be achieved,5b no detailed information about the molecular structures of the emitting materials and the device structures could be found; while in scientific literature reports, the performance of standard-red OLEDs was rather poor, with their maximum CE lower than 3.0 cd A-1, and external quantum efficiencies (EQEs) less than 4.0%.6 In addition, due to the notorious concentration quenching of the guest fluorophores, the best standard-red OLED bearing guest/host doping structure (CEmax: 1.6 cd A-1) has just a low doping-level of 2 wt%,6d hence the manufacturing process should be precisely controlled to acquire good device reproducibility.7 Consequently, it is highly demanded to exploit novel high performance standard-red fluorophores with suppressed concentration quenching,6c,8 so that OLEDs with relatively high doping-levels or even self-hosted device structure could be achieved.

Generally, red electrofluorescent materials could be classified into two main categories, namely compounds bearing polycyclic...
aromatic hydrocarbon (PAHs) structures and compounds showing intramolecular charge-transfer (ICT) character with D-π-A molecular structures (where D denotes electron-donor and A denotes electron-acceptor).\textsuperscript{5-10} To acquire standard-red fluorescence, PAHs compounds should possess relatively large conjugation systems, e.g., polyacenes\textsuperscript{11a} and porphyrins\textsuperscript{11b,c}. Yet to prepare these compounds, delicate synthetic and purifying procedures have to be involved.\textsuperscript{12} Additionally, serious concentration quenching is often observed in these PAHs due to their intense intramolecular interactions.\textsuperscript{16} On the other hand, ICT-featured red fluorophores bearing D-π-A molecular skeletons have attracted much attention due to their more facile molecular tailoring.\textsuperscript{13} Currently, the reported red electrofluorescent ICT-compounds could be assorted, according to their acceptor constructive units, as maleimide derivatives,\textsuperscript{14} benzothiadiazole derivatives,\textsuperscript{15} fumaronitrile derivatives,\textsuperscript{6,16} and 4-dicyanomethylene-4H-pyran derivatives\textsuperscript{17} etc. However, despite the fact that 1,8-naphthalimide is a widely-used acceptor subunit for constructing high performance green\textsuperscript{18} and yellow\textsuperscript{19} ICT-featured electroluminescent (EL) materials, quite limited success has been achieved in terms of high performance orange and red ones. In 2003, using 1,8-naphthalimide and quinoline as the acceptor segments, Lee \textit{et al.}\textsuperscript{20} reported an naphthalimide luminogen, but the OLED based on it could only emit orange-red EL with $\lambda_{EL,max}$ of 608 nm. Subsequently, Tian \textit{et al.}\textsuperscript{21} reported that D-A fluorophores with 1,8-naphthalimide as the acceptor subunit could act as red EL materials, yet both the chromaticity and the performance of the OLED are unsatisfactory ($\lambda_{EL,max} = 620$ nm, $L_{max}$ (maximum brightness) is 15 cd m$^{-2}$). Although in 2005, Cheng \textit{et al.}\textsuperscript{22} have fabricated red OLEDs with CIE coordinates of (0.63, 0.36) using 1,8-naphthalic anhydride derivatives as light-emitting materials, the $CE_{max}$ of these devices is as low as 0.6 cd A$^{-1}$. Nevertheless, our recent work has revealed that 1,8-naphthalimide derivative could act as high performance orange EL guest material, and the corresponding OLED shows $CE_{max}$ of 7.2 cd A$^{-1}$, $EQE_{max}$ of 3.6%, and $L_{max}$ of 16800 cd m$^{-2}$\textsuperscript{23}. Despite the fact that the CIE coordinates of this device are just (0.56, 0.44), its high performance has triggered our speculation that through rational molecular design, 1,8-naphthalimide derivatives may also act as quite promising standard-red EL materials.

Recently, it has been reported that the D-π-A-structured 1,8-naphthalimide derivative NIM (structure shown in Figure 1) could emit intense orange fluorescence in solid state ($\lambda_{PL,max} = 597$ nm).\textsuperscript{24} To construct fluorophores with more red-shifted photoluminescence (PL) emission bands than that of NIM, herein, we altered the 4-(diphenylamino)phenyl (DPAP) donor segment of NIM into a more electron-rich 4-(dimethylamino)phenyl (DMAP) or 1,1,7,7-tetramethyljulolidin-9-y1 (TMJ) donor segment, and constructed three objective compounds (Nap1–3, structures shown in Figure 1). Additionally, to alleviate the intermolecular interactions, a bulky 2,6-di(isopropyl)phenyl substituent was bonded to the imide nitrogen atom of Nap2 and Nap3. As expected, Nap1–3 all could emit standard-red fluorescence in thin solid film state, and Nap2 and Nap3 show more suppressed concentration quenching than Nap1. Using Nap3 as the guest dopant, a high performance standard-red OLED with a relatively heavy doping-level of 14 wt% was achieved. The device shows CIE coordinates of (0.67, 0.32), $EQE_{max}$ of 1.8%, and $CE_{max}$ of 0.7 cd A$^{-1}$, indicating that 1,8-naphthalimide derivatives should be promising candidates as high performance standard-red EL materials.

2. Experimental section

2.1 General information

All the reagents involved in the synthetic procedures were commercially available and used without purification unless otherwise stated. Cyclohexane (CHX), tetrachloromethane, toluene (Tol), chloroform, tetrahydrofuran (THF), dichloromethane (DCM), acetonitrile, N,N-dimethyl formamide (DMF) were of analytical grade and were distilled freshly prior to use. $^1$H NMR and $^{13}$C NMR spectra were recorded on a BRUKER AVANCE AV II-400 MHz spectrometer in DMSO-$d_6$ or CDCl$_3$ using TMS as the internal standard. High resolution MS spectra were recorded on a Shimadzu LCMS-IT-TOF. FT-IR spectra were recorded on a Perkin-Elmer 2000 infrared spectrometer with KBr pellets under ambient atmosphere. UV-Vis absorption spectra were measured on a Perkin-Elmer Lambda 950 scanning spectrophotometer. PL spectra were recorded on a Perkin-Elmer LS55 fluorescence spectrophotometer at 298 K. The absolute PL quantum yields (QYs) of both solution and film samples were determined on a FluoroMax-4 spectrofluorometer (Horiba Jobin Yvon) equipped with an integrating sphere and digital photometer. Both the two fluorimeters have been corrected for the wavelength dependence of the sensitivity of the detectors and throughput of the monochromators. The Nap/CzPhONI composite as well as the Nap neat thin film samples were spin-coated from their corresponding chloroform solutions with concentration of 10 mg/mL at a speed of 1500 rpm/min on quartz substrates for 40 s. Cyclic voltammetry measurements were performed in anhydrous acetonitrile (5 × 10$^{-4}$ mol L$^{-1}$) solutions of Nap1–3, using 0.10 mol L$^{-1}$ Bu$_4$NClO$_4$ as the supporting electrolyte under N$_2$ atmosphere on a LK 2010A electrochemical work station at room temperature, and the three-electrode cell comprised a Pt working electrode, a Pt wire counter electrode, and a Ag/AgNO$_3$ (0.1 M in acetonitrile) reference electrode. A ferrocene/ferrocenium redox couple was employed as the external standard.
2.2 OLED fabrication and measurements

Indium–tin oxide (ITO) coated glass substrate was cleaned by sonication successively in alcohol, acetone, methanol, and deionized water, followed by UV-ozone oxygen plasma treatment for 2 min before use. Organic functional layers were thermo-evaporated in vacuum (3 × 10⁻⁴ Pa) with a deposition rate of 0.1 nm s⁻¹. After deposition of the organic layers, the LiF-Al cathode was prepared first by thermal deposition of a LiF thin film (1 nm) followed by the deposition of an Al layer (80 nm). The active area of the OLEDs was 1 × 1 mm². The thicknesses of the organic layers and the cathode were controlled using a quartz crystal thickness monitor. The thicknesses were measured accurately. All the measurements on the devices were carried out in ambient atmosphere without further encapsulation.

2.3 Synthesis

The synthetic routes to Nap1–3 are outlined in Scheme 1. Intermediates 2, 3, 5, 6 were synthesised according to literature reports.

(Nap1) A schlenk flask was charged with a mixture of 2 (0.13 g, 0.9 mmol), 5 (0.30 g, 0.9 mmol), Pd(OAc)₂ (3.5 mg, 0.02 mmol), P(o-tolyl)₃ (8.3 mg, 0.03 mmol), triethylamine (6.0 mL) and N,N-dimethylformamide (DMF) (7.0 mL). The reaction mixture was heated at 90 °C for 24 h under argon. After being cooled to room temperature, the mixture was poured into water (100 mL), extracted by dichloromethane (4 × 20 mL), and the organic phase was combined and washed by brine, then dried over anhydrous Na₂SO₄. After the solvent was removed under vacuum, the crude product was purified by column chromatography over silica gel (eluent: petroleum ether/dichloromethane=15/1, v/v), followed by recrystallization from a mixture of cyclohexane and dichloromethane to afford pure Nap1 as a red solid (0.1 g, 30%). δ values (400 MHz; DMSO-d₆; MeSi) 9.00 (1H, d, J = 9.2 Hz, ArH), 8.53 (1H, d, J = 7.2 Hz, ArH), 8.45 (1H, d, J = 8.0 Hz, ArH), 8.21 (1H, d, J = 8.4 Hz, ArH), 7.96 (1H, d, J = 16.0 Hz, =CH), 7.89 (1H, t, J = 7.6 Hz, J = 8.0 Hz, ArH), 7.71 (2H, d, J = 8.4 Hz, ArH), 7.55 (1H, d, J = 16.0 Hz, =CH), 6.89 (2H, d, J = 8.4 Hz, ArH), 4.05 (2H, t, J = 7.2 Hz, =CH₂), 3.00 (6H, s, -NMe₂), 1.64 (m, 2H, -CH₂, -CH₂), 1.31 (m, 6H, -CH₂), 0.87 (m, 3H, -CH₃).

Compound Nap2 was prepared as a red solid with a yield of 50% using the similar procedure for the synthesis of Nap1, but with 5 rather than 6 as the reactant. δ values (400 MHz; DMSO-d₆; MeSi) 9.11 (1H, d, J = 8.8 Hz, ArH), 8.59 (1H, d, J = 6.8 Hz, ArH), 8.50 (1H, d, J = 8.0 Hz, ArH), 8.25 (1H, d, J = 8.0 Hz, ArH), 8.01 (1H, d, J = 16.0 Hz, =CH), 7.93 (1H, t, J = 6.4 Hz, J = 8.0 Hz, ArH), 7.73 (2H, d, J = 8.8 Hz, ArH), 7.60 (1H, d, J = 15.6 Hz, =CH), 7.45 (1H, t, J = 7.6 Hz, ArH), 7.33 (2H, d, J = 7.6 Hz, ArH), 6.78 (2H, d, J = 8.8 Hz, ArH), 3.00 (6H, s, -NMe₂), 2.66 (2H, m, Ar-CH) 1.05 (12H, d, J = 6.8 Hz, =CH₂), δ values (100 MHz; CDCl₃; MeSi) 164.4, 164.2, 150.9, 142.4, 135.6, 131.2, 131.0, 130.1, 129.4, 128.9, 128.5, 126.3, 124.8, 123.1, 122.9, 118.4, 112.2, 40.5, 40.3, 31.6, 28.1, 26.8, 22.6, 14.1. FT-IR νmax/cm⁻¹ 1655(C=O), 1358(C₁₋N). HRMS (ESI) m/z: calcd. for [M + H⁺]: C₂₄H₂₁N₄O₂⁺, 427.2380; found, 427.2365.

(E)-2-(2,6-diisopropylphenyl)-6-(4-(dimethylamino)styryl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (Nap3). Compound Nap3 was prepared as a dark red solid with a yield of 24% using the similar procedure for the synthesis of Nap1, but with 4 and 6 rather than 2 and 5 as the reactants. The crude product was purified by column chromatography over silica gel (eluent: petroleum ether/dichloromethane=15/1, v/v), followed by recrystallization from a mixture of n-hexane and dichloromethane for three times. δ values (400 MHz; DMSO-d₆; MeSi) 9.16 (1H, d, J = 8.4 Hz, ArH), 8.60 (1H, d, J = 7.2 Hz,
bonding to the imide nitrogen atom into a 2,6-dipropylphenyl group would just bring a little effect on the conjugation bathochromic shift (~30 nm) than that of =CH), 7.52 (2H, s, ArH), 7.45 (1H, t, ArH), 8.49 (1H, d, ArH), 3.23 (4H, t, =CH), 7.34 (2H, d, J = 7.6 Hz, ArH), 3.23 (4H, t, J1 = 6.4 Hz, J2 = 6.0 Hz, -NCH2), 2.67 (2H, m, Ar-CH), 1.73 (4H, t, J1 = 5.6 Hz, J2 = 6.0 Hz, Ar-CH2), 1.32 (12H, s, -CH2), 1.06 (12H, d, J = 4.0 Hz, -CH3), δC (100 MHz; CDCl3; Me2Si) 164.5, 164.2, 145.7, 143.2, 137.0, 131.8, 131.6, 131.1, 130.5, 129.6, 129.4, 126.3, 123.9, 123.3, 123.1, 122.8, 119.9, 117.0, 46.8, 36.4, 32.3, 30.8, 29.1, 24.0. FT-IR v/cm−1 1661 (C=O), 1576 (C=N). HRMS (ESI) m/z: calcd. for [M + H]+ 611.3618, 611.3632; found, 611.3632.

3. Results and discussion

3.1 Photophysical properties in dilute solutions

The UV-Vis absorption spectra of Nap1–3 in dilute solutions with different polarities are illustrated in Figure 2, and the corresponding data are summarized in Table 1. In similar solvent, the absorption maximum (λabsmax) of Nap2 is slightly red-shifted (~7 nm) compared with that of Nap1; but the λabsmax of Nap3 is considerably red-shifted (>30 nm) than those of Nap1 and Nap2. Therefore, the replacement of the n-hexyl bonding to the imide nitrogen atom into a 2,6-di(isopropyl) phenyl group would just bring a little effect on the conjugation length of these compounds; but the presence of a TMJ rather than a DMAP donor subunit in Nap3 would endow it with such extended π-conjugation system. As expected, in every solvent, the absorption bands of all the three objective compounds are red-shifted than that of NIM, which should be chiefly attributed to the more electron-donating capability of DMAP and TMJ groups than that of DPAP. With an increase in solvent polarity from cyclohexane (CHX) to dichloromethane (DCM), the absorption bands of Nap1–3 show 20–30 nm red-shifts, indicative of the ICT character of the three compounds in their ground states.20,29

Consistent with the absorption characteristics of NIM and Nap1–3, the PL emission maximum (λPLmax) of Nap3 is more bathochromic-shifted (~30 nm) than that of Nap2 or Nap1 in every solvent; the λPLmax of Nap2 is just slightly (3–5 nm) red-shifted than that of Nap1; and the λPLmax of Nap1–3 are significantly red-shifted than that of NIM (Figure 3 and Table 1). In comparison with their absorption spectra, the fluorescent spectra of Nap1–3 were observed to show more significant positive solvatochromism (e.g., for Nap3: λPLmax = 553 nm in CHX; λPLmax = 622 nm in toluene; λPLmax = 680 nm in Acetone).
chloroform; $\lambda_{\text{PL}} = 722$ nm in DCM; and $\lambda_{\text{PL}} = 750$ nm in acetone), indicative of the strong ICT character of the lowest singlet excited states of Nap1–3. This deduction was further confirmed by the Lippert-Mataga plots of Nap1–3 (see Figure S1, ESI), since good linear correlations between solvent polarity parameter and Stokes shifts could be achieved in all these Naps. It should be pointed out that in solvents with moderate polarity like chloroform and tetrahydrofuran (THF), Nap1–3 could emit red fluorescence with high PL quantum yields (PLQY, $\Phi_{\text{PL}}$). For example, in THF solution, both Nap1 and Nap2 show $\lambda_{\text{PL}}$ of $> 650$ nm and $\Phi_{\text{PL}} > 0.5$; and the chloroform solution of Nap3 displays $\lambda_{\text{PL}}$ of 680 nm and a $\Phi_{\text{PL}}$ of 0.45. With further increased solvent polarity to acetone, the PL emission spectra of Nap1–3 were all observed to shift to near infrared region approaching $\sim 750$ nm; but their $\Phi_{\text{PL}}$ were found to decrease drastically, which might arise from the much intensified non-radiative internal conversion processes in these compounds due to their much lowered energy gaps.\(^9\) Nevertheless, taking into consideration that Nap1–3 could emit highly efficient red fluorescence in solvents with medium polarity, they might act as promising red EL materials.

3.2 PL emission properties in crystalline powder and thin film states

To investigate their potentials as red light-emitting materials in OLEDs, PL emission spectra of Nap1–3 in crystalline powder and thin film states were recorded. As shown in Figure 4 and Table 2, in both powder and film states, all the three compounds could emit standard-red fluorescence with $\lambda_{\text{PL}}$ of 660–700 nm, and Nap3 shows the most red-shifted emission band. In each case, the PL spectrum of the film sample of Nap is slightly broader and red-shifted than that of the crystalline powder sample, which should be attributed to their different molecular conformations in crystalline and amorphous states.\(^30\)

Despite the fact that in dilute solutions, the fluorescence band of Nap2 is slightly red-shifted than that of Nap1, its $\lambda_{\text{PL}}$ was observed to be even 6 nm blue-shifted than that of Nap1 in neat film state (669 nm vs 675 nm), and its $\Phi_{\text{PL}}$ is also higher than that of Nap1 (0.02 vs 0.01). Hence we could infer that the presence of a more bulky 2,6-di(isopropyl)phenyl rather than a n-hexyl group in Nap2 should be propitious to the suppression of intermolecular interactions of these fluorophores, and hence...
could promote less concentration quenching. Although the $\Phi_{PL}$s of these neat film samples are rather low ($< 0.02$), which would limit their potentials as high-performance non-doped red EL dopants, the relatively high $\Phi_{PL}$s of Nap1–3 in medium-polarity solvents spur us to prepare guest/host composite films using Nap1–3 as dopants. As the compound CzPhONI (structure shown in Figure 5) we have developed recently is a high performance host material for an orange naphthalimide guest compound,23 herein we chose it as the host material to fabricate Nap/CzPhONI guest/host composite films with different doping-levels.

As shown in Figure 4 and Table 2, for all the three compounds, with increasing concentration of Nap from 2 wt% to 14 wt%, the $\lambda_{PL_{\text{max}}}$ of the corresponding Nap/CzPhONI composite film red-shifts gradually. Excitingly, at a relatively high doping-level of 14 wt%, the film samples with Nap1 and Nap2 as guests could emit red fluorescence with $\lambda_{PL_{\text{max}}}$ of 630–640 nm; and the 14 wt% Nap3 composite film could emit standard-red fluorescence with satisfactory chromaticity ($\lambda_{PL_{\text{max}}}$ = 663 nm). Analogous to the PL emission property of their neat films, in every doping-level, the $\lambda_{PL_{\text{max}}}$ of Nap2 was observed to be blue-shifted for 5–10 nm than that of Nap1, validating the more suppressed intermolecular interactions in Nap2 than Nap1. In composite films with Nap1 and Nap2 as guests, no emission from the CzPhONI host ($\lambda_{PL_{\text{max}}} \sim 500$ nm)23 could be discerned at each doping-level, indicative of the efficient energy transfer between the host and guest compounds. While for CzPhONI/Nap3 composite films, the emission band from CzPhONI is discernible at relative low doping-level of 2 wt%, hence the energy transfer efficiency between CzPhONI and Nap3 should not be as high as that between CzPhONI and Nap1/Nap2.

In comparison with those of the neat films, the $\Phi_{PL}$s of the guest/host blend film samples are much improved (Table 2). For all the three compounds, the highest PLQYs of the blend films are obtained at the lowest doping-level of 2 wt%. With increasing guest doping ratios from 2 wt% to 14 wt%, the $\Phi_{PL}$ of Nap1-based film drops considerably from 0.37 to 0.16; while the $\Phi_{PL}$s of Nap2- and Nap3-based samples are lowered from 0.46 to 0.27 and from 0.23 to 0.15, respectively, both are less significant than that of the Nap1-based one, indicating that Nap2 and Nap3 show more alleviated self-quenching relative to Nap1. Consequently, owing to the concurrent presence of a strong electron-donating TMJ group and a bulky 2,6-di(isopropyl)phenyl substituent, Nap3 possesses not only an extended π-conjugation system, but also alleviated concentration quenching, hence is a perspective candidate as standard-red EL material.

### 3.3 Electrochemical properties

To estimate the energy levels of the frontier orbitals of Nap1–3, their electrochemical property were investigated by cyclic voltammetry (CV) in degassed 5 × 10^{-4} mol L\(^{-1}\) anhydrous acetonitrile solutions with Fe/Fe\(^+\) redox couple as the external standard, and the cyclic voltammograms are shown in Figure S2 (in ESI). During the anodic scan from 0 V to 0.50 V, both Nap1 and Nap2 show reversible oxidation waves with half wave potentials ($E_{1/2}$) of 0.24 V vs Fe/Fe\(^+\); but Nap3 shows a reversible oxidation wave with $E_{1/2} = 0.05$ V vs Fe/Fe\(^+\). Upon cathodic scan from 0 V to −1.95 V, Nap1 shows a reversible reduction wave with $E_{1/2} = −1.70$ V vs Fe/Fe\(^+\); while both Nap2 and Nap3 show reversible reduction waves with $E_{1/2} = −1.66$ V vs Fe/Fe\(^+\). Hence the calculated electrochemical band-gaps of Nap1–3 are 1.94 eV, 1.90 eV and 1.71 eV in sequence, which are consistent with their optical bandgaps (2.19 eV, 2.17 eV and 1.85 eV for Nap1–3 in sequence) deduced from the onset of their UV-Vis absorption spectra in dilute acetonitrile solutions (Figure S3 in ESI).

In comparison with the Fe/Fe\(^+\) redox couple whose energy level is −4.88 eV in vacuum,24 the HOMO energy levels of Nap1–3 are calculated to be −5.12 eV, −5.12 eV and −4.93 eV in turn; and their LUMO energy levels are calculated to be −3.18 eV, −3.22 eV and −3.22 eV in sequence. As the HOMO and LUMO energy levels of CzPhONI are −5.60 eV and −3.10 eV, respectively,25 the HOMO energy difference between CzPhONI and Nap1–2 is 0.48 eV, but that between the HOMOs of CzPhONI and Nap3 is as large as 0.67 eV. Hence CzPhONI should be a more ideal host material for Nap1–2 than Nap3, which may account for the more efficient energy transfer process between CzPhONI and Nap1–2 than Nap3.

### 3.4 Electroluminescent properties

Based on these photophysical and electrochemical experimental results, thermo-evaporated OLEDs with Nap3/CzPhONI composite film as light-emitting layer (EML) were fabricated. As the device structure is ITO/MoO\(_3\) (1 nm)/Ta (40 nm)/CzPhONI/Nap3 (x wt%) (20 nm)/TPBI (45 nm)/LiF (1 nm)/Al (80 nm), where Ta (4.4′,4′-tri(N-carbazolyl) triphenylamine) serves as the hole-transporting material (HTM), TPBI (1,3,5-tris(1-phenyl-1H-benzol[d]imidazol-2-yl)benzene) serves as the electron-transporting material (ETM). The energy level diagram of the devices is shown in Figure 5. According to the device characterization results, device I, II and III with Nap3 concentration of 2 wt%, 4 wt% and 14 wt%, respectively were prepared. The EL spectra and the luminance-voltage-current density ($L-I-V$) characteristics of devices I–III are shown in Figure 6, and some representative EL performance data are summarized in Table 3.
Devices I–III all display bias-independent EL spectra, with $\lambda_{\text{EL max}}$ of 636 nm, 644 nm and 657 nm (vide Figure 6a and Figure S4 in ESI), and CIE coordinates of (0.62, 0.37), (0.65, 0.34) and (0.67, 0.32) in sequence. Hence devices I and II can emit red EL, but device III shows standard-red EL with satisfactory chromaticity. Compared with the corresponding PL spectra of their EML, the EL spectra of all the devices are much broadened and slightly blue-shifted. Because the emission band of Nap3 correlates highly with environment polarity, and the EML of the OLEDs is as thin as 20 nm, carrier recombination may occur not only within the EML, but also at the TcTa/EML or EML/TPBI interfaces, these may account for the broadened and blue-shifted EL spectra of these devices. In addition, although the emission from CzPhONI is discernible in the PL spectrum of 2 wt% Nap3/CzPhONI composite film, it could not be observed in the EL spectrum of device I, indicative of the more efficient energy transfer and/or charge carrier trapping on Nap3 in the EL process. As shown in Figure 6b, under similar driving voltages, the current density of device II is lower than that of device I; but that of the more heavily-doped device III is comparable with that of device I. Consequently, it should be the energy transfer mechanism that dominates the EL emission process in device I and II whose guest doping-levels are relatively low; but it should be the direct charge carrier trapping mechanism that governs the EL process in device III. In fact, according to the energy level diagram of the devices (Figure 5), Nap3 should act as efficient hole-carrier traps due to its much higher HOMO energy level than those of the host and HTM.

All the three devices display comparable turn-on voltages of 3.1 V. Device I exhibits relative high EL performance with $L_{\text{max}}$, $CE_{\text{max}}$ and $EQE_{\text{max}}$ of 10900 cd m$^{-2}$, 1.9 cd A$^{-1}$ and 2.1%, respectively, indicating that Nap3 is a quite promising guest compound for OLED applications. However, the chromaticity of this device is still unsatisfactory. With increasing doping-level to 4 wt%, the resulting device II shows EL that approaches standard-red emission, with $L_{\text{max}}$, $CE_{\text{max}}$ and $EQE_{\text{max}}$ of 6600 cd m$^{-2}$, 1.1 cd A$^{-1}$ and 1.8%, respectively. For device III with further increased doping-level, it could emit standard-red EL with $L_{\text{max}}$ of 2660 cd m$^{-2}$, $CE_{\text{max}}$ of 0.7 cd A$^{-1}$, and $EQE_{\text{max}}$ of 1.8%. It should be pointed out that compared with the state-of-art standard-red electroluminescent OLEDs, the PLQYs of the active layers using Nap3 as guest dopant are unsatisfactory, which may eventually limit the efficiency of the devices. Nevertheless, as the dilute chloroform solution of Nap3 could emit standard-red fluorescence with $\Phi_{\text{PL}}$ of ~ 0.45, the PLQY of the EML with Nap3 as the guest compound might be enhanced drastically if more appreciate host material were used. Moreover, the device structure, doping level and layer thickness used here have not been optimized for either low driving voltage or high efficiency, thus much improved EL performance should be expected after further optimization has been carried out on these issues.

### Conclusions

Using electron-rich arylamino groups as the donor constructive units, three red-emissive naphthalimide derivatives were designed and synthesized, and the correlations between the molecular structures and photophysical properties of these compounds have been investigated. The results indicated that the presence of a more electron-donating compound might be enhanced drastically if more appreciate host material were used. Moreover, the device structure, doping level and layer thickness used here have not been optimized for either low driving voltage or high efficiency, thus much improved EL performance should be expected after further optimization has been carried out on these issues.
not only shows standard-red fluorescence with satisfactory chromaticity, but also shows suppressed concentration quenching. Using Nap3 as the guest dopant, a heavily-doped standard-red OLED was achieved, whose CIE coordinates, EQE_{max} and CE_{max} are (0.67, 0.32), 1.8% and 0.7 cd A^{-1}, respectively. To the best of our knowledge, this is the first example of standard-red-emissive 1,8-naphthalimide derivative for OLED applications. All these preliminary results indicated that through rational molecular design, 1,8-naphthalimide derivatives could act as quite promising standard-red light-emitting materials for OLED applications.

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Notes and references

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A 1,8-naphthalimide derivative has been demonstrated to be a high performance standard-red EL material.