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Naphthalimide-arylamine derivatives with aggregation induced delayed fluorescence for realizing efficient green to red electroluminescence;

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Aggregation-induced emission (AIE) can enhance luminescent intensity in the solid-state by suppressing concentration quenching and exciton annihilation, while thermally activated delayed fluorescence (TADF) can offer highly efficient luminescence by harvesting singlet and triplet excitons. High performance organic light-emitting diode (OLED) materials with simultaneous TADF and AIE features are in high demand. Herein, we proposed a rational molecular design that exhibits both features, *i.e.*, aggregation-induced emissiondelayed fluorescence (AIDF), and green to red fluorescence with high photoluminescence guantum yield (up to 87.4% in doped films). Two D-A type emitters NAI-BiFA and NAI-PhBiFA are developed based on a central naphthalimide acceptor core and arylamine donor units. In comparison with NAI-BiFA, NAI-PhBiFA inserts the phenyl linker between the D and A units, forming a spatially twisted structure and resulting in a blue shift emission. While a non-doped OLED employing NAI-PhBiFA as an orange emitter exhibited an external quantum efficiency (EQE) of only 1.39%, a doped OLED based on NAI-PhBiFA demonstrated a remarkable improvement including a maximum EQE of 7.59%, a maximum current efficiency (CE) of 27.95 cd A^{-1} and a maximum power efficiency (PE) of 20.97 lm W^{-1} . In addition, a host-free device employing NAI-BiFA as an emitter achieved CIE (0.65, 0.34), which is very close to the National Television Standards Committee's (NTSC) standard red (0.67, 0.33). The high efficiencies and low roll-offs in both the doped or non-doped devices demonstrate that our molecular design strategy is highly promising for a variety of OLED applications.

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1. Introduction

Inspired by the promise of nearly 100% internal quantum efficiency (IQE) for organic light-emitting diodes (OLEDs), thermally activated delayed fluorescence (TADF) from donor–acceptor type organic molecules without the use of any precious metals have drawn much attention owing to its ability to harvest all electrogenerated excitons.^{1–3} Generally, triplet excitons are lost by the non-radiative transition in conventional fluorescent emitters, but can

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^b Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Institute of Functional Nano & Soft Materials (FUNSOM) & Collaborative, Innovation Center of Suzhou Nano Science and Technology, Soochow University, Suzhou, Jiangsu, 215123, P. R. China be converted into singlet excitons by means of small singlet-triplet splitting energy ($\Delta E_{\rm ST}$) driven up-conversion (TADF, Eosin-type) or triplet-triplet fusion (TTF, pyrene-type) induced reverse intersystem crossing (RISC).⁴ In contrast to the maximum IQE of 62.5% based on the annihilated triplet OLEDs,⁵ complete triplet to singlet up-conversion followed by singlet transition could possibly result in 100% IQE in TADF devices.⁶⁻⁸ Another factor restricting luminescence efficiency is the serious intermolecular π - π stacking in the aggregated state, which often weakens or even quenches the light emission.^{9–11} This is a common phenomenon widely known as "aggregation-caused quenching" (ACQ). Actually, the ACQ effect is a quite thorny obstacle for the fabrication of efficient optoelectronic devices such as OLEDs,¹² in which the emitting layers are commonly used in the aggregated state as thin solid films. In order to alleviate or hinder the notorious ACQ, Tang et al. proposed a diametrically opposite concept of aggregation-induced emission (AIE),¹³ whose mechanism can be rationalized as the restriction of intramolecular rotations (RIR) and restriction of intramolecular vibrations (RIV) in the solid state.14,15 Engineering applications of luminophores usually use them as a

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whole (aggregate) rather than individual molecules (solution). Therefore, a molecular design possessing AIE characteristics is of importance for real-world utilization. Most AIE molecules are still traditional fluorescent materials, whose maximum exciton utilization in OLEDs is only 25%,^{16–19} which greatly limits further improvement of device efficiency. AIE molecules are expected to achieve greater breakthroughs by introducing new photophysical mechanisms such as TADF. That is, designing a molecule featuring TADF in combination with AIE properties can greatly improve the efficiency of OLEDs. Therefore, the utilization of aggregation-induced emission-delayed fluorescence²⁰ (AIDF) materials has become significant in improving the external quantum efficiencies (EQE) of OLEDs.²¹⁻²³

In the case of TADF emitters, RISC from a triplet excited state to a singlet excited state activated by small ΔE_{ST} dominates the light-emitting performance of the devices. A feasible way to decrease $\Delta E_{\rm ST}$ of emitters is by separating the wave function of the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO).²⁴ In most cases, the HOMO and LUMO separation was achieved by proper selection of the donor and acceptor moieties in the donor-acceptor type molecular structure.^{25,26} However, a small overlap of frontier molecular orbitals normally leads to low oscillator strength (f)of luminophores, leading to reduction in the photoluminescence quantum yield (PLQY).²⁷ A phenyl linker inserted between the donor and acceptor is viable to tackle this problem. The phenyl linker can not only induce a HOMO-LUMO overlap in the local segment, but also dramatically increase the PLOY. Therefore, most TADF emitters were designed with a donor-linker-acceptor style building block.^{28–30} In the case of AIE emitters, the working mechanism is prone to the restriction of intramolecular motions (RIM), including rotation and vibration. Therefore, the principle of designing a vibratile core and rotatable peripheries applies to most AIEgens. Highly twisted conformation resulting from the large torsion angles between the peripheries and the central plane may cause intermolecular steric repulsion, which hampers the dense face-to-face packing structure and π – π stacking interaction in the solid state.

To date, the development of efficient long-wavelength emitters has long been hampered by their much lower emission efficiency compared with their blue and green counterparts. The external quantum efficiencies of state-of-the-art TADF-OLEDs have reached 37% for blue,³¹ 30% for green³² and 20% for red.³³ Generally, longwavelength emitters suffer from the increasingly nonradiative internal conversion process governed by the energy gap law,³⁴ hence it's very difficult to achieve a high photoluminescence quantum yield. The aforementioned empirical design methods were used by many researchers to improve the efficiency of orange-to-red OLEDs.35-37 However, the structures of reported molecules are mainly based on dicyanopyrazino phenanthrene, which has a relatively hard to modify structure.^{38,39} Herein, naphthalimide (NAI) is selected as the chromophore because appropriate electron-donating or electron-withdrawing substituents bonded to NAI may facilitate the bathochromic shift of the emission color. In this context, two D-A type orange to red compounds NAI-BiFA and NAI-PhBiFA were designed and prepared (Fig. 1a). In order to design long-wavelength emitters, rigid π -conjugated electron-withdrawing cores with deep LUMOs are desired. NAI is



Fig. 1 (a) Molecular structure of NAI–BiFA and NAI–PhBiFA. (b) The optimized geometrical configuration and (c) calculated frontier molecular orbital (FMO) electron density distribution of emitters NAI–BiFA and NAI–PhBiFA.

selected as the acceptor skeleton on the basis of the strong electronwithdrawing ability and a planar rigid architecture. Furthermore, NAI derivatives have proved to be promising because NAI could be further modified as orange or red chromophore. The C4 position and the anhydride O position of the NAI core could connect a wide range of aromatic substituents to extend the conjugated system of the molecules. Meanwhile, the introduction of 2,6-diphenyl-4toluene and N-([1,1'-biphenyl]-4-yl)-9,9-dimethyl-9H-fluoren-2amine featuring huge steric-hindrance can not only improve the quantum yield but also inhibit strong π - π stacking and molecular interactions in the aggregated state, which directly leads to the AIE effect. For NAI-PhBiFA, we demonstrate that the introduction of the π -bridge has a positive effect on the increase of the fluorescence rate (k_f) constant and PLQY. The HOMO and LUMO of NAI-PhBiFA were almost completely separated, which is beneficial to give a relatively smaller ΔE_{ST} , thus ensuring distinct TADF characteristics with a higher RISC rate (k_{ISC}) and an efficient fluorescent radiation transition. High performance green to red doped and non-doped devices based on the CBP (4,4'-bis(Ncarbazolyl)-1,1'-biphenyl) host were fabricated, and high efficiencies of 27.95 cd A⁻¹ (7.59%) for NAI-PhBiFA with CIE coordinates of (0.35, 0.60) were realized. Host-free OLEDs employing the compound NAI-BiFA as the emitter were fabricated with the CIE of (0.65, 0.34), which is very close to the National Television Standards Committee's (NTSC) standard red (0.67, 0.33). Our work confirms that the designing approach of NAI derivatives is valuable for highly efficient green to red AIDF emitters.

2. Results and discussion

2.1 Synthesis and characterization

The synthesis routes of NAI-BiFA and NAI-PhBiFA are outlined in Scheme S1 (ESI[†]). Firstly, the precursor DPMNA was synthesized by a typical Suzuki cross-coupling reaction and reduction reaction. Followed by treatment with 4-bromo-1,8-naphthalic anhydride under reflux for two days, the key intermediate NAIBr-DPM was obtained in about 68% yield. Finally, the target compounds NAI-BiFA and NAI-PhBiFA were prepared in over 80% yield. Herein, this synthesis method could conveniently construct NAI derivatives with various structures.⁴⁰ An NAI bromide intermediate was prepared in a facile approach between arylamine and anhydride sites of NAI. Then, the target products are afforded through the typical Suzuki cross-coupling reactions, Buchwald-Hartwig reaction or Ullmann reaction between the NAI bromide intermediate and boric acid derivatives, boric acid ester derivatives or secondary amine derivatives. ¹H NMR and high-resolution mass (MALDI-TOF MS) characterization reveal that the intermediates and the final products have the right structure and high purity. Both of the molecules have good solubility in common organic solvents such as THF, dichloromethane, chloroform and toluene. The detailed synthetic procedure and analysis are depicted in the Experimental section.

2.2 Photo-physical properties

To analyze the optical properties, nine kinds of solutions of both emitters were examined by steady-state UV-Vis absorption and PL emission at the ambient temperature. As shown in Fig. 2a, the absorption spectra of both emitters in various solvents are similar. For **NAI–BiFA**, the maximum absorption of 330 nm is attributed to the π – π * transition of the locally excited (LE) state of the NAI backbone.⁴¹ Besides, the relatively weak band at 473 nm belongs to the intramolecular charge transfer (ICT) from the donor arylamine unit to the acceptor NAI moiety.^{38,42} In contrast to **NAI–BiFA**, the weak band of **NAI–PhBiFA** blue shifts from 473 nm to 431 nm, which indicated that the molecular conjugation could be influenced by insertion of the phenyl moieties between NAI and arylamine. Moreover, the absorption thresholds of **NAI–PhBiFA** and **NAI–PhBiFA** were extended to a longer wavelength of 569 nm and 522 nm, respectively. The corresponding optical band gaps were estimated to be 2.18 eV and 2.38 eV on the basis of absorption edge, respectively.

The solvatochromism of both NAI-based luminogens was further confirmed by measuring PL emission in various organic solvents with different polarities. As mentioned above, absorption profiles changed scarcely and were almost independent of solvent polarity. Oppositely, the peak position of the emission is remarkably affected by the solvent polarity. As shown in Fig. 2b, the emission spectra of both emitters exhibit bathochromic shift accompanied by an increase of solvent polarity. NAI-BiFA exhibits an obvious bathochromic shift from 526 nm in low polarity n-hexane to 595 nm in highly polar acetonitrile. A similar phenomenon for NAI-PhBiFA is also observed with the change of solvent polarity from low-polarity n-hexane (481 nm) to high-polarity acetonitrile (602 nm). The large solvatochromic shift suggests that the emissions of both compounds exhibit a typical ICT character. The influence of solvent polarity was quantitatively investigated through the Lippert-Mataga model:43

$$\Delta \nu \equiv \nu_{ab} - \nu_{em} = \frac{2\Delta f}{hca^3} (\mu_e - \mu_g)^2 + \text{const.}$$
$$\Delta f = \frac{\varepsilon - 1}{2\varepsilon + 2} - \frac{n^2 - 1}{2n^2 + 1}$$

where Δv is the Stokes shift, Δf is the solvent polarity parameter, *h* is the Planck constant, *c* is the speed of light, *a* is the radius of the chromophore, μ_e and μ_g are the dipole moments in the excited (e) and ground (g) states, and ε and *n* are the constant and refractive index of the solvent, respectively. According to the plots of $\Delta v vs$. Δf , **NAI–BiFA** and **NAI–PhBiFA** exhibit notable positive slopes after linear fitting, with their values calculated to be 8290 and 13177 (Fig. 2c), respectively. The dipole moment changes between the excited state and the ground state, which can serve as an empirical scale to evaluate the ICT. These observations clearly illustrate that **NAI–BiFA** and **NAI–PhBiFA** in the excited state possess the ICT character.⁴⁴

We found the AIE-activity of **NAI–BiFA** and **NAI–PhBiFA** from the photo-luminescence (PL) spectra in THF/water mixtures with different water fractions (Fig. S13, ESI†). As shown in Fig. S13b (ESI†), **NAI–BiFA** and **NAI–PhBiFA** have similar tendencies of AIE feature (relative intensity of fluorescence I/I_0 vs the water fraction f_w). Take **NAI–BiFA** as an example, **NAI–BiFA** emits at 592 nm in dilute THF solution. In the initial stage of addition of



Fig. 2 UV-vis spectra (a) and normalized PL spectra (b) of NAI–BiFA and NAI–PhBiFA in solvents with various polar parameters. (c) Plot of Stokes shift $(\Delta \nu)$ of NAI–BiFA and NAI–PhBiFA versus Δf of their solutions.

a poor solvent (water), the PL intensities abruptly weakened accompanied by the blue shift of emission peaks. Specifically, more than 40% fluorescence intensity was quenched and a blue shift of about 51 nm could be discerned at f_w of 40%. The phenomenon at this stage is mainly due to the twisted intramolecular charge-transfer (TICT) effect of NAI-BiFA in the gradually strengthened polar mixed solvent of THF/water with a higher fraction of polar water.45 Afterwards, a prominent fluorescence enhancement together with a bathochromic shift of peaks was observed as the water ratio reached 50%, which is attributed to aggregate formation due to the worsened solvating power of the aqueous mixture and a lower impact of polarity of the solvent on NAI-BiFA.46 Simultaneously, intramolecular motions and the rotation of the aryl rings are restricted, and thus the nonradiative decay channel of the excited state is blocked, which leads to the unique aggregation-enhanced emission (AEE). It is worth noting that the weaker emission of NAI-PhBiFA in the THF/ water mixtures with a f_w of 70% compared to that with a f_w of 60% is probably due to the difference in aggregate morphology. To investigate whether NAI-BiFA and NAI-PhBiFA still are AIE active after eliminating the interaction between the polar solvent and both emitters, the emission spectra of both emitters in CH₂Cl₂ and CH₂Cl₂/hexane solutions were recorded (Fig. 3). Because of nonradiative decay via the active intramolecular rotations of its phenyl and arylamine moieties, NAI-BiFA and NAI-PhBiFA are weakly emissive in CH₂Cl₂. When the hexane content in the solution of NAI-BiFA or NAI-PhBiFA was increased gradually, its emission maximum blue shifts moderately. The emission intensities were almost unchanged while the hexane content was below 40%, however, the fluorescence intensity increased abruptly while the hexane content was greater than 60%. On continuing to increase the hexane content, the fluorescence intensity keeps increasing



Fig. 3 (a) PL spectra of NAI–BiFA and NAI–PhBiFA in CH_2Cl_2 /hexane mixtures with different hexane fractions (f_w) and (b) changes in the emission intensity of NAI–BiFA and NAI–PhBiFA in CH_2Cl_2 /hexane mixtures with various volume fractions of hexane (0–90%).

until it reaches a maximum at 90% hexane content, demonstrating a typical AIE activity. The absolute PLQY values measured using an integrating sphere under an N₂ atmosphere for the neat films are 26% and 55% for **NAI–BiFA** and **NAI–PhBiFA**, respectively. While, the PLQY values of co-doped films (5 wt% emitters: CBP) are 62% and 87% for **NAI–BiFA** and **NAI–PhBiFA**, respectively. Small ΔE_{ST} of the emitters is one of the most important factors which dominate the light-emitting performance of the devices. We estimated the S₁ and T₁ energy levels of **NAI–BiFA** and **NAI–PhBiFA** to be 2.26/2.11 eV and 2.34/2.22 eV according to the onsets of the fluorescence and phosphorescence spectra of 5 wt% **NAI–BiFA** and **NAI–PhBiFA** doped on CBP film (Fig. 4a), and thus ΔE_{ST} is calculated to be 0.15 and 0.12 eV, respectively. Herein, the $\Delta E_{\rm ST}$ value of **NAI–PhBiFA** is smaller than that of **NAI–BiFA**, which is attributed to the inserted phenyl linker induced better separation of HOMO–LUMO. Therefore, the more effective RISC process of **NAI–PhBiFA** can be expected and will result in highly efficient triplet exciton utilization. Then, the transient photoluminescence decay characteristics of **NAI–BiFA** and **NAI–PhBiFA** in doped films were investigated and are depicted in Fig. S18 (ESI†). With the temperature increasing from 77 K to 300 K, the delayed lifetime of **NAI–BiFA** and **NAI–PhBiFA** is gradually increased, which is consistent with its TADF characteristics.⁴⁷ As shown in Fig. 4b and c, at room temperature, a prompt decay exhibited a lifetime



Fig. 4 (a) Fluorescence spectra at 300 K and phosphorescence spectra at 77 K for 5 wt%-doped thin films of NAI–BiFA and NAI–PhBiFA in a CBP host. Transient decay spectra of NAI–BiFA (b) and NAI–PhBiFA (c) at 300 K. Inset: Decay measured over a time range of 500 ns.

 (τ_p) of 12.45 ns and 8.3 ns for **NAI–BiFA** and **NAI–PhBiFA** in the range of 200 ns, which is attributed to the direct fluorescence process from S₁ to S₀. Meanwhile, in a nitrogen atmosphere, a double-component emission decay profile was obtained in the time range of 100 µs with a delayed lifetime (τ_d) of 7.68 µs and 9.09 µs, respectively. To further understand the radiative and nonradiative decay processes for both emitters, their rate constants of radiative decay (k_r) from S₁ to S₀ are estimated to be 1.62 and 0.49 × 10⁷ s⁻¹, respectively. The relatively higher RISC rate constants (k_r) of **NAI–PhBiFA** (3.56 × 10⁵ s⁻¹) compared to that of **NAI–PhBiFA** (2.45 × 10⁵ s⁻¹) may afford better efficiency of the device. The photophysical rate constants are summarized in Table 2.

2.3 Thermal properties

The thermal properties of the materials were estimated using differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA). In merit of the NAI core, both **NAI–BiFA** and **NAI–PhBiFA** showed a high glass transition temperature (T_g) of over 160 °C and a high decomposition temperature (T_d) of over 440 °C. As shown in Fig. S14 and S15 (ESI†), **NAI–PhBiFA** exhibited a higher thermal stability at the T_d of 480 °C and T_g of 166 °C than that of **NAI–BiFA** (T_d of 440 °C and T_g of 163 °C), which was ascribed to the high rigidity of the inserted phenyl groups. These parameters indicated the excellent thermal stability of the materials.

2.4 Theoretical calculations

To further gain insight into the molecular structures and electronic properties of the NAI-based luminogens, computational simulations are employed by utilizing density functional theory (DFT) and time-dependent density functional theory (TD-DFT) performed at a level of Lee-Yang-Parr functional (B3LYP)/6-31G(d). The distributions of frontier molecular orbital (FMO), electron exchange energy (ΔE_{st}) and the energy gap (E_{s}) between the HOMO and LUMO levels are depicted in Fig. 1c. Evidently, NAI-BiFA and NAI-PhBiFA exhibited a clear pattern of electron density-distribution separation between the HOMO and LUMO. For both emitters, the LUMO is located predominantly on the central NAI acceptor, while the HOMO of NAI-PhBiFA was mainly distributed over the entire arylamine donor and extended to the bridged benzene ring with little residue on the NAI part, the HOMO of NAI-BiFA was mainly distributed over the entire arylamine donor and extended to the NAI part. Due to the similar LUMO distribution, a relatively more efficiently separated FMO distribution of NAI-PhBiFA is observed. Therefore, NAI-PhBiFA could induce a reduced ΔE_{st} value compared to that of NAI-BiFA, suggesting that excitons may be readily harvested by efficient RISC between the T_1 and S_1 states. As shown in Fig. 1b, the conformation of two molecules is similar with the dihedral angels of 69° between the NAI and 2,6-diphenyltoluene units, whereas the dihedral angels between NAI and arylamine of NAI-**BiPhFA** were found to be 75° and 81°, respectively. The dihedral angle of NAI-PhBiFA between bridged phenyl and NAI was 51°. Closer inspection reveals the dihedral angles between bridged phenyl and arylamine of NAI-PhBiFA were 67° and 69°, respectively.

The changes of dihedral angles are compressed compared to that of **NAI–BiFA** resulting from the insertion of the phenyl group. Multiple twisted configurations could effectively suppress the formation of a coplanar aggregation and prevent the formation of excimers and exciplexes in the solid state.

2.5 Electrochemical properties

The electrochemical properties of both emitters were investigated by cyclic voltammetry (CV) based on the classical three electrode system. The CV curves of NAI-BiFA and NAI-PhBiFA are shown in Fig. S16 (ESI[†]). Both emitters show reversible oxidation processes, indicating their good electrochemical stability. The HOMO energy level can be calculated by the empirical equation HOMO = $(E_{ox} + 4.40)$ eV, where E_{ox} is the onset potential of oxidation. The oxidative onset potentials of NAI-BiFA and NAI-PhBiFA are 0.84 eV and 0.65 eV with respect to ferrocene, respectively. The oxidation potential threshold decreases with the insertion of the phenyl linker. The LUMO levels are calculated through subtraction of the optical energy gap (E_g) from the HOMO energy levels. Pertinent energy level data are also listed in Table 1. The HOMO energies of NAI-BiFA and NAI-PhBiFA were -5.24 eV and -5.05 eV, respectively. By subtracting the optical energy band gaps from the HOMO energy levels, the LUMO energy levels of NAI-BiFA and NAI-PhBiFA were calculated to be -2.18 eV and -2.38 eV, respectively.

2.6 Electroluminescence properties

To confirm the AIDF properties of the newly synthesized emitters, multilayered OLEDs were fabricated using the following configuration (Fig. 5): indium tin oxide (ITO)|HAT-CN (15 nm)|TAPC (40 nm)|TCTA (5 nm)|x wt%-emitter:CBP (20 nm)|TmPyPB (40 nm)|LiF (1 nm)|Al (100 nm). In this device architecture, HAT-CN (2,3,6,7,10,11-hexacyano-1,4,5,8,9,12-hexaazatriphenylene) and LiF were used as the hole-injection layer (HIL) and the electron-injection layer (EIL), respectively. TAPC (1,1-bis(4-di-ptolylaminophenyl)cyclohexane) and TmPyPB (3,3'-[5'-[3-(3-pyridinyl)phenyl][1,1':3',1"-terphenyl]-3,3"-diyl]bispyridine) served as the hole-transporting layer (HTL) and the electron-transporting layer (ETL), respectively. To reduce the hole-injection barrier between TAPC and the CBP-hosted emission layer (EML), a thin layer of 4,4',4''-tris(carbazol-9-yl)triphenylamine (TCTA) was inserted at the HTL/EML interface. Owing to the larger energy bandgap of CBP compared to that of the dopant molecules, a sequential charge trapping is expected. Moreover, TmPyPB as an ETL with a low-lying HOMO energy level can prevent hole leakage and allow a better confinement of charge carriers and excitons within the EML.

As shown in Fig. 5b and c, the corresponding nondoped devices using **NAI-BiFA** and **NAI-PhBiFA** as the EML exhibit orange and red emission with CIE coordinates of (0.65, 0.34) for **NAI-BiFA** and (0.53, 0.46) for **NAI-PhBiFA**, respectively. Although both of the nondoped devices possess low efficiencies, a maximum EQE of 1.53 and 1.39%, maximum current efficiency (CE) of 2.44 and 3.71 cd A^{-1} and maximum power efficiency (PE) of 1.85 and 2.39 lm W^{-1} are achieved (Fig. 6). It is worth noting that a **NAI-BiFA** based device exhibits red emission with a peak at 628 nm

Table 1 Phc	tophysic	al and t	hermal dat	ta of the I	NAI-base	¢d emitt€	ers NAI	-BiFA an	d NAI-P	hBiFA								
		Fluoi	rescence									- ·	ОМОН		LUMO		$E_{ m g}$	
Compound	λ _{max,abs} ' [nm]	a λ_{\max}^{ℓ}	^a FWHM ^b [nm]	$\gamma_{\max}^{c} F$ [nm] [1	WHM ^b [mn	PLQY ^c	λ_{\max}^{d}	FWHM ^b	PLQY ^d	$E_{ m S}/E_{ m T}/\Delta E_{ m ST}{}^e$	$T_g^{f/\circ \mathbf{C}}$	$\Gamma_{d}^{g/\circ C}$	Calculated ^h eV]	Measured ⁱ [eV]	Calculated ^h [eV]	Measured ^j [eV]	Calculated M [eV] [e	Meas eV]
NAI-BiFA NAI-PhBiFA	332, 48 [,] 343, 44 ⁷	4 588 7 592	82 93	636 1 601 1	13 05	0.26 0.55	593 555	103 89	$0.62 \\ 0.87$	2.26/2.11/0.15 2.34/2.22/0.12	163 4 166 4	140 180	-5.20 -5.04	-5.24 -5.05	-2.30 -2.29	-3.06 -2.67	2.90 2. 2.75 2.	2.18 2.38

respectively. $\Delta E_{ST} = E_S - E_T$, $T_{g:}$ glass transition temperature, Calculated from DFT at the B3LYP/6-31G(d) level. ¹ HOMO was $^{k}E_{g}$; the optical band gap was calculated from the absorption c Measured in the vacuum evaporated film at room temperature. d Measured in 5 wt%-doped thin film at measured from the onset value of the oxidation potential. J LUMO was measured from the HOMO and the optical band gap E_{g} . room temperature. ^c Singlet and triplet energy level are estimated from the onset of fluorescence and phosphorescence spectra, $T_{\rm d}$: decomposition temperature at weight loss of 5%, obtained from TGA measurements. a Measured in CH₂Cl₂ solution at room temperature. ^b Full-width at half-maximum. measurements. obtained from DSC spectra.

Table 2 Summary of photophysical rate constants for $\ensuremath{\mathsf{NAI-BiFA}}$ and $\ensuremath{\mathsf{NAI-PhBiFA}}$

Emitter	$k_{\rm r}^{\ a} \left[10^7 \ {\rm s}^{-1} \right]$	$k_{\rm nr}^{\ \ b} \left[10^7 \ {\rm s}^{-1} \right]$	$k_{\rm ISC}{}^c \left[10^7 \ {\rm s}^{-1}\right]$	$k_{\mathrm{RISC}}^{d} \left[10^5 \mathrm{~s}^{-1} \right]$
NAI-BiFA	2.65	1.62	1.78	2.45
NAI-PhBiFA	3.25	0.49	2.37	3.56

^{*a*} Rate constant for fluorescence radiative decay. ^{*b*} Rate constant for nonradiative internal conversion. ^{*c*} Rate constant for intersystem crossing (ISC). ^{*d*} Rate constant for reverse intersystem crossing (RISC).

and CIE coordinates of (0.65, 0.34), which not only meets the general requirements for red emission ($\lambda_{\text{max}} > 600$ nm) and the CIE coordinates of ($x \ge 0.60$, $y \le 0.40$) but is also close to the National Television Standards Committee's (NTSC) standard red (0.67, 0.33). The low performance of a non-doped device may be ascribed to the low PLQY and exciton utilization efficiency, especially for the utilization of the triplet excitons. Neither of the EL spectra has a vibronic feature and coincides with the PL spectra of the thin film (Fig. S17, ESI†), which implies an effective charge injection and recombination in the EML. The turn-on voltages (V_{ons}) of the nondoped devices employing **NAI-BiFA** and **NAI-PhBiFA** are as low as 2.9 V, which is mainly attributed to the nature of small energy gap and excellent charge transport.

For comparison, doped OLEDs are also fabricated by using co-deposited films of NAI-BiFA and NAI-PhBiFA and the common host material (CBP) with a high triplet energy that can effectively forbid back energy transfer from the guest to the host, and thus the triplet excitons can be confined within the guest emitters. In a host-guest system, where emitter molecules can be diluted in the host matrix, device efficiency can be further improved via an efficient Förster energy transfer.48,49 As shown in Fig. 6 and Table 3, NAI-BiFA and NAI-PhBiFA were doped into the CBP host with an optimized doping concentration of 5 wt% as the emitting layer. In favor of the examined OLEDs, the nonradiative decay pathways were found to be further reduced in CBP films doped at 5.0 wt%, giving rise to the PLQY values of 62% for NAI-BiFA and 87% for NAI-PhBiFA, respectively. Obviously, the CIE color of the doped devices based on NAI-BiFA ranged from orange to red with $\lambda_{\rm EL}$ lying between 570 nm and 615 nm due to the increased concentration. Moreover, the CIE color of the doped devices based on NAI-PhBiFA ranged from green to orange with $\lambda_{\rm FL}$ lying between 529 nm and 575 nm due to the increased concentration. Compared to the host-free device, it is evident that the doped devices display blue shifted and narrow EL spectra. It should be understood from two perspectives on blue shift. Generally, CBP as a nonpolar host material can decrease medium polarity. Moreover, dopants dispersed in the host may eliminate the effect of intermolecular close stacking. Upon increasing the doping concentration of NAI-BiFA and NAI-PhBiFA, the maximum luminance decreases as doping concentration increases. Meanwhile, the EL emissions constantly shift to the longer wavelength region with the CIE value variation from 2 wt% (0.46, 0.51) to nondoped (0.65, 0.34) for NAI-BiFA and 2 wt% (0.31, 0.60) to nondoped (0.531, 0.463) for NAI-PhBiFA, respectively.

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Fig. 5 (a) Energy level diagrams of devices based on NAI–BiFA and NAI–PhBiFA as the EML, respectively. (b) EL spectra in OLEDs based on an emitting layer containing a CBP host blended with NAI–BiFA and NAI–PhBiFA at different doping concentrations. (c) Color coordinates in the CIE 1931 chromaticity diagram at different doping concentrations. (d) Current density–voltage–luminance plots.



Fig. 6 Current efficiency-luminance characteristics of OLEDs based on NAI-BiFA (a) and NAI-PhBiFA (b). External quantum efficiency-luminance characteristics of OLEDs based on NAI-BiFA (c) and NAI-PhBiFA (d).

Table 3 EL performances of the fabricated OLEDs

Emitter	Conc. (wt%)	$V_{\rm on}{}^a$	$L_{\rm max} \left({\rm cd} \ {\rm m}^{-2} \right)$	$\lambda_{\rm EL} ({\rm nm})$	FWHM (nm)	$\operatorname{CE}_{\max}{}^{b}$ (cd A^{-1})	$PE_{max}^{b} (lm W^{-1})$	EQE^{b} (%)	$\operatorname{CIE}^{c}(x,y)$
NAI-BiFA	2	3.3	27 040	570	81	21.30	17.59	6.60	(0.460, 0.513)
	5	3.3	59 490	575	83	14.69	10.98	4.80	(0.496, 0.494)
	10	3.2	22 050	584	72	13.07	9.78	4.72	(0.528, 0.467)
	20	3.3	12 110	594	88	13.75	10.79	5.86	(0.562, 0.435)
	30	3.1	15 210	602	77	15.25	13.30	7.21	(0.586, 0.411)
	50	3.2	15 700	608	84	9.97	8.69	5.17	(0.599, 0.399)
	70	3.2	16 030	615	85	7.93	7.32	4.41	(0.606, 0.392)
	Neat	2.9	10 200	628	98	2.44	1.85	1.53	(0.654, 0.344)
NAI-PhBiFA	2	3.6	41 040	529	75	26.71	19.95	7.56	(0.311, 0.599)
	5	3.4	51 220	538	77	27.95	20.97	7.59	(0.349, 0.599)
	10	3.2	52 180	547	76	27.21	19.42	7.41	(0.387, 0.582)
	20	3.4	34 940	556	77	26.73	19.08	7.34	(0.420, 0.563)
	30	3.1	47 480	565	85	25.14	20.77	7.35	(0.459, 0.531)
	50	3.0	65 690	571	99	19.87	18.35	6.25	(0.486, 0.508)
	70	3.2	65 150	575	83	14.31	13.22	4.63	(0.501, 0.494)
	Neat	2.9	14 310	583	82	3.71	2.39	1.39	(0.531, 0.463)

^{*a*} Voltage required for 1 cd m⁻². ^{*b*} current efficiency (CE_{max}), power efficiency (PE_{max}), external quantum yield (EQE_{max}). ^{*c*} The CIE are measured at 1000 cd m⁻².

It is a common character that the efficiencies decline to some degree as luminance increases. In contrast, NAI-PhBiFA has a higher k_{RISC} value than that of NAI-BiFA. Therefore, the enhanced RISC process effectively shortens the TADF lifetime, which endows reduced triplet exciton density for suppressed TTA and STA. Consequently, the device based on NAI-PhBiFA could retain rather high EQE values of 7.59%, even when driven at a practical luminance of 100 cd m^{-2} for display applications, the EQE values of the devices using NAI-BiFA and NAI-PhBiFA were reduced to 9.2% and 8.1%, respectively. Hence, the efficiency roll-off was apparently mitigated using NAI-PhBiFA with smaller $\Delta E_{\rm ST}$ as the TADF emitters. At 1000 cd m⁻², the CE and EQE are moderately decreased to 14.12 cd A⁻¹ and 4.43% for NAI-BiFA and 22.29 cd A^{-1} and 6.01% for NAI-PhBiFA, respectively. The current efficiency roll-off is 33.7% for NAI-BiFA and 20.1% for NAI-PhBiFA, respectively, which is among those of most doped OLEDs based on TADF emitters.⁵⁰ The nondoped devices have poor efficiency, which is probably caused by the major triplet-triplet and/or singlet-triplet annihilations in the condensed neat film. However, the roll-off values of nondoped devices are notably smaller than that of doped OLEDs. For instance, external quantum efficiency roll-off of NAI-PhBiFA is nearly zero, calculated from peak values to those at 1000 cd m⁻² (1.38%) and 5000 cd m^{-2} (1.30%), demonstrating a greatly advanced efficiency stability of nondoped OLEDs. The short lifetime, broad recombination zone and weak interactions of excitons in the neat film should be conducive to the decrease of efficiency roll-off.

3. Experimental sections

3.1 Materials and instruments

Unless otherwise noted, commercially available reagents employed for the synthesis were purchased from Aldrich, J&K and TCI companies and used as received. ¹H magnetic resonance (NMR) spectra were recorded on a Bruker AVANCE III 400 MHz spectrometer or a 600 MHz spectrometer, using CDCl₃ or DMSO[d_6] as the solvent and tetramethylsilane (TMS) as the internal standard. High resolution mass spectra were recorded on a AB SCIEX 5800 matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectrometer. Elemental analysis for C, H and N were performed on an Elementar Analysensysteme GmbH. All manipulations involving air-sensitive reagents were performed in an atmosphere of dry Ar. Absorption spectra of the target compounds were recorded on a Perkin Elmer Lambda-750 UV-vis-NIR spectrophotometer. Steady-state and transient-state emission spectra in both solution and solid state were recorded on a LS 55 fluorescence spectrometer. For the solid samples, the quantum yields for the compounds were determined at room temperature through an absolute method using an Edinburgh Instruments integrating sphere coupled to a modular Edinburgh FLS 920 fluorescence spectrophotometer. The absolute quantum yield was calculated using the following equation:

 $\frac{\int L_{\text{emission}}}{\int E_{\text{reference}} - \int E_{\text{sample}}}$. In the equation, L_{emission} is the emission spectrum of the sample, recorded using the sphere, E_{sample} is the spectrum of the incident light used to excite the sample, recorded using the sphere and $E_{reference}$ is the spectrum of light used for excitation with reference to the sphere. The method is accurate to within 10%. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on Perkin Elmer TGA 4000 and DSC 8000 thermal analyzers under a nitrogen atmosphere at a heating rate of 10 °C min⁻¹. Cyclic voltammetric (CV) measurements were carried out in a conventional three electrode cell using a Pt button working electrode 2 mm in diameter, a platinum wire counter electrode and a saturated calomel electrode (SCE) reference electrode on a computer-controlled CHI660d electrochemical workstation at room temperature. Reduction CV of all compounds was performed in CH₂Cl₂ containing teterabutylammonium hexafluorophosphate (Bu₄NPF₆, 0.1 M) as the supporting electrolyte. Ferrocene was used as an external standard. Electrochemistry was performed at a scan rate of 100 mV s⁻¹.

3.2 Computational method

The theoretical investigation of geometry optimization was performed using the Gaussian 09 program package.⁵¹ Density functional theory (DFT) was calculated at Beck's three-parameter hybrid exchange functional⁵² and Lee, Yang and Parr correlation functional⁵³ B3LYP/6-31G(d). The spin density distributions were visualized using Gaussview 5.0.8.

3.3 Device fabrication and measurements

HAT-CN, TAPC, CBP, TmPyPB and LiF were purchased from Lumtec Corp. (Taiwan, China). Prior to the device fabrication, the patterned ITO-coated glass substrates were scrubbed and sonicated consecutively with detergent water, deionized water and acetone, dried in a drying cabinet, and then exposed to a UV-ozone environment for 30 min. After these processes, the substrates were transferred into a vacuum chamber for sequential deposition of all the organic layers by thermal evaporation with a base pressure (\sim 4.0 \times 10⁻⁴ Pa) at a rate of 0.1–0.2 nm s⁻¹ and monitored in situ with the quartz oscillator. LiF covered by Al is used as a cathode without breaking the vacuum. All the samples were measured directly after fabrication without encapsulation at room temperature under the ambient atmosphere. The electroluminescent spectra were recorded on an Ocean Optics spectrometer. The current-voltage-luminance characteristics were measured using a PR655 Spectrascan spectrometer and a Keithley 2400 programmable voltage-current source. The external quantum efficiency (EQE) and luminous efficiency (LE) were calculated assuming the Lambertian distribution, and then calibrated to the efficiencies obtained at 1000 cd m^{-2} in the integrating sphere (Jm-3200).

3.4 Synthesis

Synthesis of 2,6-diphenyl-4-nitrotoluene (DPNT). 1,3-Dibromo-2-methyl-5-nitrobenzene (1.76 g, 6 mmol), sodium tetraphenylboron (1.76 g, 5 mmol), and tetrabutylammonium bromide (0.39 g, 1.2 mmol) were taken in a round-bottomed flask. After argon was bubbled through the mixture for 30 min, palladium chloride (26.9 mg, 0.12 mmol) and potassium carbonate (7.63 g, 72 mmol) were added and the resultant mixture was stirred overnight at 65 °C under an argon flow. The precipitate was filtered off, and the filtrate was washed with brine, dried over anhydrous MgSO₄, filtered and concentrated to dryness. The resulting solid was purified by chromatography on silica gel (eluent: EtOAc/hexanes, 1:5) to afford DPNT (1.56 g, 90%) as a white solid. ¹H NMR (TMS, CDCl₃, 400 MHz): ppm δ = 8.11 (s, 2H), 7.42-7.50 (m, 6H), 7.36 (d, J = 6.8 Hz, 4H), 2.19 (s, 3H); MALDI-TOF: *m*/*z* calcd for C₄₃H₃₃N₃O: 259.14; found: 259.11; elemental analysis calcd (%) for C₁₉H₁₅NO₂: C 78.87, H 5.23, N 4.84; found: C 78.96, H 5.19, N 4.85.

Synthesis of 3,5-diphenyl-4-methylbenzenamine (DPMNA). DPNT (2.89 g, 10 mmol) was combined with zinc powder (3.27 g, 50 mmol) and calcium chloride (1.10 g, 5 mmol) in 80 mL ethanol and 20 mL water. The mixture was refluxed for 10 h and was then removed by filtration. The filtrate was poured into cold water. After removal of the solvent, the crude product was purified by recrystallization with ethanol to yield the white needle-like crystals (2.38 g, 92%). ¹H NMR (TMS, CDCl₃, 400 MHz): ppm δ = 7.32–7.43 (m, 10H), 6.64 (s, 2H), 3.39 (s, 2H), 1.99 (s, 3H); elemental analysis calcd (%) for C₁₉H₁₇N: C 87.99, H 6.61, N 5.40; found: C 88.10, H 5.57, N 5.44.

Synthesis of 6-bromo-2-(2'-methyl-[1,1':3',1"-terphenyl]-5'yl)-1*H*-benzo[*de*]isoquinoline-1,3-dione (NAIBr-DPM). A flask was charged with 4-bromo-1,8-naphthalic anhydride (3.11 g, 12 mmol), 4-methyl-3,5-diphenylaniline (2.76 g, 12 mmol) and 80 mL EtOH. The reaction was refluxed for 3 days under argon. After cooling down to room temperature, the solvent was removed in vacuum to afford the crude product, which was further purified by column chromatography on silica gel to yield a yellow product (3.52 g, 68%). ¹H NMR (TMS, CDCl₃, 400 MHz): ppm δ = 8.62–8.72 (m, 2H), 8.45–8.48 (dd, *J* = 2.4, 7.6 Hz, 1H), 8.07–8.13 (d, *J* = 8.0 Hz, 1H), 7.86–7.95 (m, 1H), 7.33–7.46 (m, 11H), 7.21 (s, 1H), 2.20 (s, 3H); MS: *m/z* calcd for C₃₁H₂₀BrNO₂: C 71.82, H 3.89, N 2.70; found: C 71.89, H 3.87, N 2.78.

Synthesis of N-(4-phenylboronic acid pinacol ester)-N-([1,1'biphenyl]-4-yl)-9,9-dimethyl-9H-fluoren-2-amine (BPFB). PdCl₂(dppf)₂ (1,1-bis(diphenylphosphino)ferrocene-palladium(II)dichloride) (109.8 mg, 0.15 mmol) was added to a suspension of N-([1,1'biphenyl]-4-yl)-N-(4-bromophenyl)-9,9-dimethyl-9H-fluoren-2-amine (1549.4 mg, 3.0 mmol), bis(pinacolato)diboron (990.4 mg, 3.9 mmol) and potassium acetate (588.8 mg, 6.0 mmol) in dioxane (20 mL) at room temperature. After stirring at room temperature for 20 min, the mixture was heated to 80 °C and stirred for 24 hours. The reaction mixture was extracted with DCM and further purified by column chromatography on silica gel (petroleum ether/ethyl acetate = 20:1, v/v) to obtain BPFB as a white solid (1183.4 mg, 70%). ¹H NMR (500 MHz, CDCl₃, δ) 7.76–7.80 (dd, J = 5.5 Hz, 2H), 7.66–7.67 (t, J = 7.0, 4H), 7.58–7.59 (d, J = 8.5 Hz, 2H), 7.51– 7.53 (d, J = 7.0 Hz, 1H), 7.43-7.46 (t, J = 7.5, 2H), 7.27-7.35 (m, 4H), 7.15–7.16 (d, J = 8.5 Hz, 2H), 7.00–7.06 (m, 3H), 1.39 (s, 6H), 1.28 (s, 12H). EI-MS (m/z): calcd for C₃₉H₃₈BNO₂ 563.299011; found, 563.299440 [M⁺].

Synthesis of 6-([1,1'-biphenyl]-4-yl(9,9-dimethyl-9H-fluoren-2-yl)amino)-2-(2'-methyl-[1,1':3',1"-terphenyl]-5'-yl)-1H-benzo[de]isoquinoline-1,3(2H)-dione (NAI-BiFA). NAIBr-DPM (1.03 g, 2 mmol), N-([1,1'-biphenyl]-4-yl)-9,9-dimethyl-9H-fluoren-2-amine (0.72 g, 2 mmol), and ^tBuOK (0.58 g, 6 mmol) were taken in a roundbottomed flask. Xylene (40 mL) was added, and argon was bubbled through the mixture for 30 min. Pd(OAc)₂ (22.5 mg, 0.1 mmol) and $P(^{t}Bu)_{3}$ (60.7 mg, 0.3 mmol) were then added and the resultant mixture was stirred overnight at 130 °C under an argon flow. The precipitate was filtered off, and the filtrate was washed with brine, dried over anhydrous Na2SO4, filtered and concentrated to dryness. The resulting solid was purified by chromatography on silica gel (eluent: EtOAc/hexanes, 1:5) to afford NAI-BiFA (1.18 g, 74%) as a red solid. ¹H NMR (600 MHz, CDCl₃): ¹H NMR (600 MHz, CDCl₃) δ 8.59 (t, J = 7.8 Hz, 2H), 8.28 (d, J = 8.4 Hz, 1H), 7.67 (d, J = 7.8 Hz, 1H), 7.63 (d, J = 7.8 Hz, 1H), 7.60 (d, J = 7.2 Hz, 2H), 7.54 (d, *J* = 8.4 Hz, 2H), 7.39–7.51 (m, 13H), 7.34 (dd, *J* = 7.2, 7.2 Hz, 4H), 7.29 (t, J = 6.6 Hz, 1H), 7.24 (s, 2H), 7.16 (d, J = 9.0 Hz, 3H), 7.08 (d, J = 8.4 Hz, 1H), 2.20 (s, 3H), 1.38 (s, 6H); ¹³C NMR (151 MHz, CDCl3) δ 164.53, 163.95, 155.54, 153.55, 151.13, 147.72, 147.59, 143.74, 141.69, 140.20, 138.51, 136.35, 135.39, 133.70, 132.55, 132.47, 131.72, 131.62, 130.74, 129.52, 128.93, 128.84, 128.17, 128.06, 127.92, 127.19, 127.11, 126.99, 126.72, 126.28, 125.39, 123.91, 123.41, 123.18, 122.57, 121.00, 119.67, 118.69, 118.46, 46.92, 27.01, 26.92, 18.70. MALDI-TOF-MS: *m/z* calcd for C₅₈H₄₂N₂O₂:800.33, found: 800.677. Elemental analysis calcd (%) for C₅₈H₄₂N₂O₂: C 87.19, H 5.30, N 3.51; found: C 87.24, H 5.27, N 3.56.

Synthesis of 6-(4-([1,1'-biphenyl]-4-yl(9,9-dimethyl-9H-fluoren-2-yl)amino)phenyl)-2-(2'-methyl-[1,1':3',1"-terphenyl]-5'-yl)-1H-benzo-[de]isoquinoline-1,3(2H)-dione (NAI-PhBiFA). A mixture of NAIBr-DPM (0.52 g, 1 mmol), (biphenyl-4-yl)(9,9-dimethyl-9H-fluoren-2yl)[4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl]amine (0.56 g, 1.1 mmol), tetrakis(triphenylphosphine)palladium (11.6 mg, 0.01 mmol), tetrabutylammonium bromide (32.3 mg, 0.01 mmol) and aqueous solution of sodium hydroxide (2 mol L^{-1} , 6 mmol) in THF (20 mL) was stirred under argon at 80 °C for 24 h. After quenching with aqueous NH₄Cl solution, the mixture was extracted with CH2Cl2. The combined organic extracts were washed with brine and dried over anhydrous MgSO₄. After removing the solvent, the residue was purified by column chromatography on silica gel using ethyl acetate as the eluent to afford NAI-PhBiFA (0.67 g, 77%) as an orange power. ¹H NMR (600 MHz, $CDCl_3$) δ 8.69 (d, J = 7.8 Hz, 2H), 8.50 (d, J = 8.4 Hz, 1H), 7.77 (t, J = 7.8 Hz, 2H), 7.68 (d, J = 8.4 Hz, 2H), 7.62 (d, J = 7.2 Hz, 2H), 7.58 (d, J = 8.4 Hz, 2H), 7.41–7.48 (m, 12H), 7.30–7.35 (m, 11H), 7.24 (s, 2H), 7.21 (d, J = 8.4 Hz, 1H), 2.20 (s, 3H), 1.56 (s, 6H); ¹³C NMR (150 MHz, CDCl₃) δ 164.61, 164.40, 155.38, 153.61, 148.39, 147.07, 146.74, 146.50, 143.83, 141.66, 140.47, 138.75, 136.05, 136.01, 135.27, 133.77, 133.18, 132.45, 132.05, 131.59, 131.34, 130.91, 130.16, 129.52, 129.26, 128.91, 128.82, 128.07, 128.02, 127.80, 127.07, 127.04, 127.00, 126.81, 126.77, 126.72, 124.71, 124.38, 123.06, 122.72, 122.56, 121.38, 120.89, 119.69, 119.62, 46.95, 27.13, 18.70. MALDI-TOF-MS: m/z calcd for C₆₄H₄₆N₂O₂:876.36, found: 876.681. Elemental analysis calcd (%) for C₆₄H₄₆N₂O₂: C 87.84, H 5.30, N 3.66; found: C 87.88, H 5.27, N 3.69.

4. Conclusions

In conclusion, two novel orange to red emitters, **NAI–BiFA** and **NAI–PhBiFA**, are developed by incorporating a central naphthalimide acceptor core and arylamine donor units. Both emitters exhibit obvious AIE nature in THF/water mixtures and solventchromism under solvents of different polarity, due to a solventdependent stabilization of intramolecular charge transfer in the excited state. To illustrate the molecular structure and property relationship, we inserted a phenyl bridge between the D and A units in **NAI–PhBiFA** and compared it with a D–A type molecule **NAI–BiFA**. The introduction of a π -bridge in the D– π –A type molecule **NAI–PhBiFA** positively influenced the PLQY, ΔE_{ST} and k_{RSIC} , due to the large steric hindrance and dihedral angles. The doped film of **NAI–PhBiFA** in a CBP host possesses a higher PLQY (87%) than that of **NAI–BiFA** (62%). The non-doped OLEDs adopting **NAI–BiFA** and **NAI–PhBiFA** as light emitters exhibited a maximum EQE of 1.53% and 1.39% with the CIE coordinate of (0.64, 0.35) and (0.53, 0.46), respectively. The doped OLEDs with a low doping concentration (5 wt%) offered a superb CE of 14.7 cd A^{-1} and 28.0 cd A^{-1} as well as an EQE of 4.81% and 7.59% for **NAI-BiFA** and **NAI-PhBiFA**, respectively. With the increase of doping concentration, the peak efficiency is decreased but the efficiency roll-off becomes apparently smaller. In summary, we believe combining both AIE and TADF features is a very promising molecular design principle to realize ideal light emitters for efficient and stable OLEDs with simple structures.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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