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High-efficiency deep-blue luminophores, especially those satisfying the National Television Standards Committee (NTSC) blue standard Commission Internationale de l'Éclairage (CIE) coordinates of (0.14, 0.08), are vital to full-color displays and solid-state illumination. However, deep-blue luminescent materials with efficient photoluminescent quantum yields (φ_{PLS}) and high external quantum efficiencies (EQEs) over 5% remain very limited. Imidazole has shown great potential in optoelectronic fields owing to its ambipolar nature. Combining imidazole with rigid aromatic rings, such as naphthalene, phenanthrene and pyrene, could effectively enlarge the π -electronic delocalization, reduce non-radiative transitions of molecules and ensure high φ_{PL} s in solid-state. Herein, two symmetrically twisted pyreno[4,5-d]imidazole-anthracene structural isomers, 9,10-bis(4-(10-phenyl-9H-pyreno[4,5-d]imidazol-9-yl)phenyl)anthracene (N-BPyIA) and 9,10-bis(4-(9phenyl-9H-pyreno[4,5-d]imidazol-10-yl)phenyl)anthracene (C-BPyIA) have been designed and synthesized by connecting one anthracene group with two pyreno[4,5-d]imidazole groups at N1 and C2 position, respectively. They both show high φ_{PL} s in neat films (46% for N-BPyIA and 54% for C-BPyIA), good thermal stabilities (T_d > 541 °C), and appropriate energy levels for carrier injections. N-BPyIA shows better performance than C-BPyIA when applied in OLEDs. The non-doped device based on N-BPyIA shows sky blue emission with CIE coordinates of (0.22, 0.31), achieving a high EQE of 5.63% with a low efficiency roll-off. In particular, doped device with better performance is further realized, providing an EQE of 7.67% and the deepblue emission (CIE (0.15, 0.10)), which is very close to the NTSC standard. Such high OLED efficiency maybe be ascribed to the triplet energy harvesting by triplet-triplet annihilation. And to our best knowledge, this is one of the best outcomes of deep-blue imidazole-based fluorescent OLEDs. The results also pave the way to a new type of high-efficiency deep-blue organic luminescent materials regulated by structural isomerization.

Introduction

Organic light-emitting diodes (OLEDs) have been widely researched and applied in flat-panel display applications owing to their distinct superiorities such as flexibility, light weight, low energy cost and so forth.¹ Blue light-emitting materials is indispensable in OLEDs because they furnish one of the three primary colors (red, green, and blue), lower the power loss in full-color displays, and can be applied as excitation source to generate green, red and white lightings by energy transfer to emissive dopants.² Nevertheless, The device performance of blue OLEDs falls behind the green and red ones on account of the intrinsically wider energy gaps of blue emitters.³ During the past decades, blue phosphorescent materials based on transition metal complexes have already achieved satisfying device performance with external quantum efficiency (EQE) over 20%.⁴ However, it is hard to acquire efficient pure or deepblue phosphors due to the serious non-radiative process via metal d-orbitals when lifting the radiative metal-ligand charge transfer (MLCT) band into the higher energy region.⁵ In addition, blue phosphorescent materials are not circumstancefriendly and cost-effective, which hampers their large-scale applications. Recent developments in blue OLEDs mainly focus on the thermally activated delayed fluorescence (TADF) materials, which in principle could achieve 100% internal efficiency through reversed intersystem crossing between the lowest singlet (S1) and triplet (T1) excited states via directly connecting donor (D)-acceptor (A) groups with a big torsion angel.⁶ However, on account of strong charge transfer (CT) effect, most of high-efficiency TADF blue materials emit the sky blue or bluish-green lighting and only a few chromophore systems could achieve satisfactory device performance in deepblue region but with severe efficiency roll-off.⁷ Therefore, deepblue emitters based on pure aromatic structures still remain an urgent concern.

1,3-Imidazole is a flat asymmetric aromatic heterocycle, which contains two nitrogen atoms with different bonding modes and thus intrinsic ambipolar property.⁸ The idea that combining imidazole with rigid aromatic rings, such as naphthalene, phenanthrene and pyrene, to construct highly

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efficient blue emitters is proven to be successful in optoelectronic fields.⁹ Bipolar electronic structure of 1,3imidazole derived from two distinct sp² hybrid nitrogen atoms also meets well with the requirement of balanced charge transport in OLEDs. Rigid planar π conjugation could reduce non-radiative transitions of molecules and ensure high φ_{PL} s in solid-state. Phenanthro[9,10-d]imidazole (PI) has been extensively studied to build numerous efficient blue fluorescent emitters with notable device performances in recent years.¹⁰ Pyreno[4,5-d]imidazole (Pyl), as another important type derivative of 1,3-imidazole with a more extended acene structure, has also attracted more and more attentions recently.¹¹ Benefited from the expansive π -electronic delocalization as well as rigidity of molecular plane, Pyl group possesses high φ_{PL} s, enhanced thermal stability, and promising carrier mobility, which endows it to be a promising unit for lightemitting materials with pure aromatic structure. However, pyrene itself tends to form excimers in solid state due to extensive π conjugation, resulting in red-shifted emission and reduced solid-state $\varphi_{\mathsf{PL}}\mathsf{s},$ high-efficiency deep-blue luminophores containing PyI moiety remain rather rare.¹²

In this work, we attempt to achieve new deep-blue emitters with pure aromatic structure by constructing PyI-based 9,10-Bis(4-(9-phenyl-9H-pyreno[4,5structural isomers. d]imidazole)-10-phenyl) anthracene (C-BPyIA) and 9,10-bis(4-(10-phenyl-9H-pyreno[4,5-d]imidazole)-9-phenyl) anthracene (N-BPyIA) are designed and synthesized, in which the 9,10diphenylanthracene (PAnP) moiety is coupled with two PyI groups at C2 or N1 position to form two structural isomers with symmetrically twisted skeletons. In this way, the steric hindrance between anthracene (An), adjacent benzene as well as Pyl would render C-BPylA and N-BPylA with different distorted configuration to reduce the intermolecular interactions, suppress the red-shifted emission and acquire high φ_{PL} s in blue spectral range. An is also a frequently-used organic group to generate efficient blue emitter with triplet-triplet annihilation (TTA) characteristics.¹³ By combining Pyl with An, it is anticipated that C-BPyIA and N-BPyIA could exhibit good device performance if the non-emissive triplet excitons could be effectively utilized by triplet up-conversion. C-BPyIA and N-BPyIA both exhibit excellent thermal stabilities and blue emission with high φ_{PL} s of 46% and 54%, and appropriate energy levels for carrier injections, respectively. The non-doped OLEDs using C-BPyIA and N-BPyIA as the emitting layers display efficient sky-blue emission with an EQE of 4.78% and 5.63% and CIE coordinates of (0.21 0.32) and (0.22, 0.31), respectively. Notably, better device performances with deeper blue emissions are achieved when C-BPyIA and N-BPyIA are used as dopant emitters. As compared with C-BPyIA which gives an EQE_{max} of 5.90%, the EQE_{max} of N-BPyIA could reach 7.67%. Especially, the device based on N-BPyIA displays CIE coordinates of (0.15, 0.10), which is very close to the NTSC blue standard (0.14, 0.08). TTA mechanism may be assumed to be the major reason for such high efficiency. To the best of our knowledge, this is one of the best results of deep-blue imidazol-based fluorescent OLEDs.

Results and Discussion

Synthesis and Characterization

The molecular structures and synthetic routes of C-BPyIA and N-BPyIA are shown in Scheme 1. The precursors of C-PyIBr and N-PyIBr were attained by one-pot reactions according to our previous report.^{12b} And then, BAnB which was obtained by the boronation of BAnBr, were coupled with C-PyIBr and N-PyIBr, respectively, via Suzuki reactions to obtain the end-products of C-BPyIA and N-BPyIA with high yields. The purity and chemical structures of C-BPyIA and N-BPyIA were detailly characterized by NMR, elemental analysis, FTIR, and MS. The synthetic details are offered in the Supporting Information.

Thermal Properties

Thermodynamic properties were studied by means of thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) under nitrogen atmosphere, and the results are given in Fig. 1 and Table 1. C-BPyIA and N-BPyIA both exhibited the same high decomposition temperature (T_{ds} , corresponding to 5% weight loss) of 541 °C owing to their similar molecular weight, indicating that they could remain stable at high temperature and would not decompose during device evaporation process. C-BPyIA and N-BPyIA did not show any glass transition temperatures (T_{g} s) or melting points during the second heating cycle in DSC, revealing that they tended to form an amorphous morphology. This was further proved by XRD measurement which gave the similar result that no diffraction peak appeared in the XRD patterns (Fig. S2). The good thermal stabilities of C-BPyIA and N-BPyIA are significant to get fine device performances. compounds could endure high temperatures and would not go through decomposition in the device fabrication process by vacuum thermal deposition. Such high T_{ds} and no T_{g} implied that they could keep amorphous morphology in a wide range of temperature, which is highly important to obtain the appreciable device performance.

Theoretical Calculations

To understand the electronic properties and geometrical structures of C-BPyIA and N-BPyIA, density functional theory



Scheme 1 Synthesis routes of C-BPyIA and N-BPyIA. a) Suzuki coupling reaction: $Pd(PPh_3)_4$, K_2CO_3 , toluene, 85 °C, 48 h under N_2 protection.

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(DFT) calculations were performed with the ground state geometry optimized at the B3LYP/6-31G(d,p) level. The optimized molecular geometry, the lowest unoccupied molecular orbital (LUMO) and the highest occupied molecular orbital (HOMO) density maps are shown in Fig. 2. C-BPyIA and N-BPyIA both possessed nearly orthogonal geometries between the An and adjacent phenyl with similar torsion angel of 76.2° and 78.1°, respectively, which was attributed to the steric repulsion effect of the neighbouring hydrogens at the 2,6position of phenyl group and 1,4,5,8-position of An.¹⁴ Whereas the dihedral angles between the phenyl and Pyl group were much different, which were found to be 25.3° for C-BPyIA and 79.4° for N-BPyIA, respectively. This is derived from the various linking fashion of Pyl and PAnP in these two structural isomers. It could be inferred that stronger steric hindrance and repulsion effect between hydrogen atoms on phenyl and pyrene ring manifested relatively bigger torsion angle when the PAnP moiety was coupled with Pyl groups at N1 position in N-BPyIA. The twisted molecular conformation can efficiently limit the π conjugation and lead to bluer emission. C-BPyIA and N- BPyIA had similar LUMOs distributions, mainly located on the electron-deficient An unit. However, the HOMO distributions were significantly different, where the HOMO were mainly delocalized over the backbone in C-BPyIA, but for C-BPyIA, HOMO and LUMO

exhibited large degree orbital overlap and spatial separation, while HOMO and LUMO of N-BPyIA almost complete separation on account of the twisted almost conformations and ineffective electronic communications. In addition, these distributions of HOMO and LUMO indicated that C-BPyIA and N-BPyIA possessed some CT property. This orbital-distribution characteristic originating from PyI orientation effect in N-BPyIA was beneficial to the transportation of holes and electrons and thus the enhancement of device performance.¹⁵

Photophysical Properties

Fig. 3 shows the UV-vis absorption and PL spectra measured in tetrahydrofuran (THF) dilute solution and thin films on quartz substrates of C-BPyIA and N-BPyIA. Detailed photophysical data are summarized in Table 1. The absorption profiles of C-BPyIA and N-BPyIA in THF and thin films were nearly the same. Compared to the absorption spectra of PAnP and Pyl (Fig. S3-S4), the well-resolved 394 nm absorption peaks were π - π * characteristic transitions of An moiety.¹⁶ The absorption band centred at 380 nm in THF belonged to the π - π * transitions of Pyl group. However, because the absorption profiles of PAnP and PyI at short wavelength below 450 nm showed a big overlap, the absorption peaks at 355 nm might belong to overlapped peak of PAnP and PyI. Both compounds showed blue emissions in THF and solid-state films. In THF, PL emission peak of the C-BPyIA was located at 443 nm, whereas N-BPyIA showed a little blue-shifted PL emission peak owing to more distorted molecular structure. When deposited on quartz substrates, the emission peaks were red-shifted to 463 and 461 nm for C-BPyIA and N-BPyIA, respectively, due to the enhanced intermolecular interactions in film state. No excimer emission was observed in film state. The solvation effect on PL properties was investigated in several solvents with different polarities. As displayed in Fig. S7-S8, the emission peak of C-BPyIA shifted from 435 nm in n-hexane to 465 nm in acetone with a 30 nm variation and the emission peak of N-BPyIA shifted from 433 nm in n-hexane to 461 nm in acetone with 29 nm variation accompanied by the gradually broadening of emission spectra, indicating C-BPyIA and N-BPyIA possessed some CT property. The φ_{PL} s of N-BPyIA in dilute THF solution, neat films, and doped PMMA films (5 wt%) were 65%,46%, and 61%, respectively. By contrast,



Fig. 3 Absorption and PL spectra of A) C-BPyIA and N-BPyIA in THF dilute solution (Concentration: 10^{-5} mol L⁻¹) and B) evaporated films.



Fig. 2 Optimized molecular geometries and LUMO and HOMO distributions of the molecular C-BPyIA and N-BPyIA.

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| Table 1 Key thermal and photophysical properties of C-BPyIA and N-BPyIA DOI: 10.1039/C9TC02990 | | | | | | | | | | | |
|--|----------------------|-------------------|------------------------|---|------------------------|-------------|-----------|--|--|--|--|
| Compound | λ_{abs} (nm) | | λ _{PL} (nm) | $oldsymbol{arphi}_{PL}S^{c}$ | HOMO/LUMO ^f | E_{g}^{g} | T_d/T_g | | | | |
| | Solª | Film ^b | solª/film ^b | solª/film ^b /dfilm ^d / dfilm ^e | (eV) | (eV) | [°C] | | | | |
| C-BPyIA | 355,383,395 | 353,385 | 443/463 | 74/54/70/67 | -5.42/-2.64 | 2.78 | 541/- | | | | |
| N-BPyIA. | 355,383, 395 | 359, 384 | 440/461 | 65/46/61/56 | -5.41/-2.57 | 2.84 | 541/- | | | | |
| | | | | | | | | | | | |

^a Measured in dilute THF solution (10⁻⁵ mol L⁻¹) at room temperature. ^b Thin films on quartz. ^c Absolute PL quantum yield evaluated using an integrating sphere. ^d Doped PMMA films (5 wt%). ^e Doped CBP films (15 wt%). ^f Measured by cyclic voltammetry and calculated by comparing with ferrocene (Fc). ^g Bandgap calculated from $E_g = LUMO - HOMO$.

C-BPyIA had even better $\varphi_{\rm PL}$ s, 74%, 54%, and 70% in the above states, which confirmed that partly degree orbital overlap of HOMO and LUMO expressed a more powerful radiative transition rate and thus higher $\varphi_{PL}s$. In addition, C-BPyIA and N-BPyIA still remained decent φ_{PL} s in neat films, manifesting that twisted molecular conformation could suppress intermolecular interactions and keep the high φ_{PL} s in solid-state. As displayed in Fig. S9, the PL of C-BPyIA and N-BPyIA in nondoped films exhibited monoexponential attenuation with nanosecond time scale. No delayed constituent could be viewed, demonstrating the emission merely originated from transient decay of S₁ state and excluding the possibility of TADF. According to the PL emission in n-hexane, the S1 state energy was calculated as 2.80 eV for C-BPyIA (443 nm) and 2.82 eV (440 nm) for N-BPyIA. In both 2-methyltetrahydrofuran solution and neat film at 77 K, phosphorescence spectra of N-BPyIA and C-BPyIA could not be detected due to the low population and high non-radiative transition rate of T₁ exciton. As shown in Fig. S5, the phosphorescence spectrum of Pyl in 77 K after 50 ms delayed emission exhibited fine vibrational structure and the corresponding energy value of T_1 was thus confirmed to be 2.17 eV according to the first vibrational peak of phosphorescence at 572 nm. According to literatures, the T_1 value of anthracene derivatives is approximately 1.8 eV on account of the long $\boldsymbol{\pi}$ conjugation of anthracene, which is lower than the T₁ of PyI.¹⁴ Thus, T₁ energies of N-BPyIA and C-BPyIA should be equal to or lower than the T_1 of An (1.8 eV) according to the Kasha's rule. Apparently, TADF cannot take place because of such large energy gap between S₁ and T₁. However, TTA process is energypermitting because of $2T_1 > S_1$. Therefore, we deem that TTA is likely to happen to benefit the enhancement of the device efficiency.

Electrochemical Properties.

Cyclic voltammetry (CV) was employed to calculate the HOMO/LUMO energy levels of the target materials. The onset oxidation potentials of C-BPyIA and N-BPyIA were at 0.82 and 0.79 V, respectively, and the HOMO energy values were calculated to be - 5.42 and -5.39 eV. The LUMO energy levels could be obtained in the same way of -2.64 and -2.60 eV, respectively, which are higher than the classical electron-transporting material TPBi (-2.70 eV),

benefiting to the electron injection in devices. The energy gaps between the HOMO and LUMO energy levels of the two compounds were calculated to be 2.78 and 2.79 eV, respectively, indicating that two pyreno[4,5-d]imidazole groups substituted either at C2 or N1 position barely changed the emission colour, which was also in accordance with the photophysical results.

The single-carrier devices

To evaluate the hole and electron injection/transport abilities, single carrier devices were fabricated with the structures of indium tin oxide (ITO)/ hexaazatriphenylenehexacarbonitrile (HATCN) (6 nm)/ N,NO-bis(naphthalen-1-yl)-N,N,O-bis(phenyl)-benzidine (NPB) (10 nm)/ C-BPyIA or N-BPyIA (80 nm)/NPB (20 nm)/Al (100 nm) for holeonly device and ITO/ (1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi) (20 nm)/ C-BPyIA or N-BPyIA (80 nm)/TPBi (10 nm)/LiF (1 nm)/AI (100 nm) for electron-only device. For hole-only device, NPB neighboring to the cathode AI was employed to block electrons, which guaranteed the hole-only characteristic of the devices. Likewise, TPBi in the electron-only device near the anode ITO was applied to prevent hole injection. The current densityvoltage (J-V) curves are shown in Fig. S10 and C-BPyIA and N-BPyIA all showed decent transmitting capacity of holes and electrons. In addition, N-BPyIA possessed better transmitting capacity of holes and electrons, which was benefited to the enhancement of device performance.



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| Table 2 Key Performance Parameters of the EL performances of OLEDs based on C-BPyIA and N-BPyIA DOI: 10.1003/05/05/002500 | | | | | | | | | | |
|---|--------------|-------------------------------|-----------------------|-----------------------|---------------------------------|-------------------------|------------------|--|--|--|
| device | V_{on}^{a} | L _{max} ^b | CE_{max}^{c} | PE_{max}^{d} | EQE ^e (%) | $EL\lambda_{max}{}^{f}$ | CIE ^g | | | |
| | (V) | (cd m ⁻²) | (cd A ⁻¹) | (Im W ⁻¹) | max/100/1000 cd m ⁻² | (nm) | (x, y) | | | |
| А | 3.0 | 43127 | 10.12 | 8.53 | 4.78/4.70/4.60 | 476 | (0.21,0.32 | | | |
| В | 3.0 | 46509 | 12.64 | 10.66 | 5.63/5.63/4.93 | 472 | (0.22,0.31) | | | |
| С | 3.6 | 18027 | 6.69 | 5.83 | 5.90/4.12/3.10 | 450 | (0.15,0.12) | | | |
| D | 3.6 | 15674 | 7.98 | 6.78 | 7.67/6.60/5.13 | 448 | (0.15,0.10) | | | |
| | | | | | | | | | | |

^a Turn-on voltage at 1 cd m⁻². ^b Maximum luminance. ^c Maximum current efficiency. ^d Maximum power efficiency. ^e Maximum external quantum efficiency/100/1000 cd m⁻². ^f EL emission peak of EL spectrum at 5V. ^g Commission International de l'Éclairage (CIE) coordinates at 5 V.



Fig. 5 Characteristics of nondoped multilayer devices A and B:A) Current density (J–V) and luminance (L–V) plots;B) Luminance efficiency–voltage and EQE–voltage characteristics; Inset: EL spectra of the devices).

Electroluminescence Properties.

To verify the potential application of C-BPyIA and N-BPyIA as blue luminophores in electroluminescence (EL) devices, we first fabricated the nondoped multilayer devices with the configuration of ITO/HATCN (6 nm)/NPB (25 nm)/tris(4-(9Hcarbazol-9-yl)phenyl)amine (TCTA) (15 nm)/C-BPyIA or N-BPyIA (20 nm)/TPBi (40 nm)/LiF (0.5 nm)/Al (120 nm) (devices A or B), where ITO was the anode, HATCN was the hole injecting layer, NPB was the hole transporting layer (HTL), TCTA was the exciton blocking layer. C-BPyIA or N-BPyIA was the emitting layer (EML), TPBi was the electron transporting layer and holeblocking layers owing to its deep HOMO level (-6.30 eV). LiF was the electron injecting layer and Al was the cathode. The characteristic curves and device data are shown in Fig. 5 and Table 2, respectively. Non-doped devices showed blue electroluminescence peaking at 476 nm for C-BPyIA and 472 nm for N-BPyIA. The EL emission coincided with the corresponding thin-film PL spectra of emitters (Fig. S12), suggesting that the EL emission was from the EML and no excimer emission existed in device. The EL spectra of devices A and B remained stable over various driving voltages (Fig. S14), ensuring good colour stability. The turn-on voltage (Von) was only 3.0 V, disclosing effective charge injections. The maximum luminescence (Lmax) was over 40000 cd m⁻². The C-BPyIA-based devices exhibited moderate performance with a maximum current efficiency (LE_{max}) of 10.12 cd A⁻¹, a maximum power efficiency (PE_{max}) of 8.53 lm W⁻¹, and a maximum EQE_{max} of 4.78%. By contrast, the N-BPyIA-based devices showed better performance with LE_{max}, PE_{max} and EQE_{max} values of 12.64 cd $A^{\text{-1}},$ 10.66 lm $W^{\text{-1}},$ 5.63%, respectively. In addition, the both of the non-doped devices showed quite small efficiency roll-offs.

Meanwhile, to further improve the device efficiency and color purity, we also constructed the doped EL device. CBP was selected as the host because of the good overlap between the absorption spectrum of C-BPyIA and N-BPyIA and the emission band of CBP (Fig. S13). The doped devices consisted of ITO/HATCN (6 nm)/NPB (25nm)/TCTA (15 nm)/emitting layer (C-BPyIA or N- or N-BPyIA/CBP-15 wt%, 20 nm)/TPBi (40 nm)/LiF (0.5 nm)/Al (120 nm) (Device C or D). The performance of device C (C-BPyIA:15%) and device D (N-BPyIA:15%) are provided in Fig. 6 and summarized in Table 2. Both the doped OLEDs showed significantly improved blue colour purities and blue-shifted EL emission, with the maximum peak of 450 nm for C-BPyIA and 448 nm for N-BPyIA. It is worth noting that the CIE (0.15, 0.10) of device D based on N-BPyIA was very close to the NTSC blue standard (0.14, 0.08). The EL spectra barely changed under different voltages (Fig. S14), illustrating the good stability of device. The Von increased from 3 to 3.6 V for C-BPyIA and N-BPyIA because of the larger Eg of the host. The doped OLEDs all showed improved device efficiencies compared with that of nondoped devices. Device C achieved good LEmax and EQEmax of 5.83 cd A⁻¹ and 5.90%, respectively. Moreover, device D possessed an even better performance with the LE_{max} up to 7.98 cd A^{-1} and the EQE_{max} of 7.67%.

The transient EL decay of N-BPyIA-based device was measured to explore the origin of its high efficiency in OLED. As displayed in Fig. 7, given a fleet electric excitation pulse, nondoped and doped devices of N-BPyIA both showed a fleet EL response with the lifetime (τ_s) of nanosecond scale originating from the transient fluorescence of emitters and a delayed EL decay with microsecond scale. In addition, the percentage of delayed



Fig. 6 Characteristics of doped multilayer devices C and D: A) Current density (J–V) and luminance (L–V) plots; B) Luminance efficiency–voltage and EQE–voltage characteristics; Inset: EL spectra of the devices.

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Fig. 7 Transient EL decay of non-doped and doped devices based on N-BPyIA emitter at the same current density.

attenuation gradually decreased from 5 V to 10 V (Fig. S17). At low voltage, enough triplet excitons were converted by TTA process and lead to a great part of delayed constituent which could benefit to the enhancement of device performance. As the voltage increased, the triplet excitons may be consumed by charges or undergo other consumption processes which would result in the decrease of delayed constituent and thus the decline of the EQE. The variation tendency about the delayed component along with the driving voltage was in consistent with the driving voltage-EQE curves (Fig. S16). Considering the large energy gap difference between S_1 and T_1 , the delayed component could not be caused by TADF process. In addition, as TADF materials tend to show more distinct delayed curve and much slower EL attenuation,10c we could infer that TADF mechanism could not explain the delayed constituent of device. TTA probably may be the pathway to utilize the non-emissive triplet excitons which contributed to such a high device efficiency.

Conclusions

In summary, two blue light-emitting symmetrically structural isomers, C-BPyIA and N-BPyIA, by coupling two PyI groups with one 9,10-diphenylanthracene moiety at C2 and N1 positions, respectively, have been successfully synthesized and well characterized. The design strategy has induced highly twisted torsion angels between Pyl and An, especially in N-BPylA, which entitles N-BPyIA with a bluer emission as compared with C-BPyIA. Both C-BPyIA and N-BPyIA exhibit excellent thermal stabilities, high φ_{PL} s and suitable HOMO and LUMO energy levels for applications in OLEDs. Their non-doped devices show blue electroluminescence, high EQE and small efficiency rolloffs. When doped with CBP host, much improved device efficiencies and better blue colour purities are all achieved. In particular, utilizing N-BPyIA as emitter, the doped device exhibits a LE_{max} up to 7.98 cd A⁻¹ and a maximum EQE of 7.67% with CIE coordinates of (0.15, 0.10), which is close to the NTSC blue standard (0.14, 0.08) and comparable to state-of-the-art deep-blue emitters. These encouraging results would contribute to the development of highly efficient deep-blue Pylbased luminophores. The work also provides a novel design

strategy to obtain the deep-blue material by conveniently adjusting the substituent positions on ArPskeletors/C9TC02990G

Experimental

General information

All the reagents and solvents used for the syntheses were purchased from Aldrich and Acros and used as received. Synthetic procedures

9,10-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl) anthracene (BAnB)

In a 250 mL round flask, a mixture of 9,10-dibromoanthracene (3.36 g, 10 mmol), bis(pinacolato)diboron (4.6 g, 18 mmol), KOAc (5.9 g, 60 mmol), 1,4-dioxane (80 mL), and Pd(dppf)Cl₂ (490 1,1'-bis(mg. 0.6 mmol: dppf = diphenylphosphino)ferrocene) was added and stirred at 85 °C, under N₂ protection for 48 h. The reaction was then quenched by water and the mixture was extracted with dichloromethane for three times. After evaporating the solvent, the crude product was purified by column chromatography to give a yellow solid (petroleum ether/dichloromethane = 4:1 v/v) (2.6 g, yield: 62%). ¹H NMR (500 MHz, DMSO-d₆) δ: 8.22 (dd, J = 6.7, 3.2 Hz, 4H), 7.56 (dd, J = 6.7, 3.2 Hz, 4H), 1.54 (s, 24H). MALDI-TOF (m/z): $[M^+]$ Calcd for $C_{26}H_{32}B_2O_4$: 430.16; Found: 430.3. pyrene-4,5-dione (PyO₂)

NaIO₄ (12.30 g, 57.3 mmol), H₂O (80 mL), and RuCl₃ • xH₂O (0.35 g, 1.7 mmol) were added to the solution of the pyrene (2.80 g, 14.0 mmol) in dichloromethane (60 mL) and acetonitrile (60 mL). The dark brown suspension was stirred at room temperature overnight. The resulting mixture was extracted by chloroform, and the solvent was removed under reduced pressure to afford a dark orange solid. Then column chromatography on silica gel gave red powder (petroleum ether/dichloromethane = 1:1 v/v) (1.21 g, Yield: 36%). ¹H NMR (500 MHz, CDCl₃) δ :8.53 (dd, J = 7.4, 1.1 Hz, 2H), 8.22 (dd, J = 7.9, 1.1 Hz, 2H), 7.89 (s, 2H), 7.79 (t, J = 7.7 Hz, 2H). MALDI-TOF (m/z): [M⁺] Calcd for C₁₆H₈O₂: 232.16; Found: 232.1.

10-(4-bromophenyl)-9-phenyl-9H-pyreno[4,5-d]imidazole (C-PyIBr)

A mixture of aniline (2.3 mL, 25.0 mmol), pyrene-4,5-dione (1.2 g, 5.0 mmol), 4-bromobenzaldehyde (1.2 g, 6.0 mmol), ammonium acetate (1.5 g, 20.0 mmol), and acetic acid (15 mL) was refluxed under nitrogen in oil bath. After 2 h, the mixture was cooled and filtered. The solid product was washed with an acetic acid/water mixture (1:1, 50 mL). And then, it was separated by chromatography (petroleum ether/dichloromethane = 1:1 v/v) to afford a white solid. (1.93 g, yield: 84%). ¹H NMR (500 MHz, DMSO-d₆) δ :8.95 (d, J =7.0 Hz, 1 H), 8.33 (d, J =7.4 Hz, 1 H), 8.27-8.17 (m, 4 H), 7.86-7.72 (m, 6 H), 7.63-7.58 (m, 4 H), 7.32 (d, J =7.9 Hz, 1 H). MALDI-TOF (m/z): [M⁺] Calcd for C₂₉H₁₇BrN₂: 473.37; Found: 472.7.

9-(4-bromophenyl)-10-phenyl-9H-pyreno[4,5-d]imidazole (N-PyIBr)

A mixture of 4-bromoaniline (2.3 mL, 25.0 mmol), pyrene-4,5-dione (1.2 g, 5.0 mmol), benzaldehyde (1.2 g, 6.0 mmol), ammonium

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acetate (1.5 g, 20.0 mmol), and acetic acid (15 mL) was refluxed under nitrogen in oil bath. After 2 h, the mixture was cooled and filtered. The solid product was washed with an acetic acid/water mixture (1:1, 50 mL). And then, it was separated by chromatography (petroleum ether/dichloromethane = 1:1 v/v) to afford a white solid. (1.86 g, yield: 81%). ¹H NMR (500 MHz, CDCl₃) δ :9.14 (d, J = 6.9 Hz, 1H), 8.23 (d, J = 6.9 Hz, 1H), 8.20-8.12 (m, 2H), 8.08 (dd, J = 12.3, 8.2 Hz, 2H), 7.84-7.76 (m, 2H), 7.73 (t, J = 7.8 Hz, 1H), 7.65 (dd, J = 7.4, 2.1 Hz, 2H), 7.53-7.44 (m, 3H), 7.42-7.35 (m, 3H). MALDI-TOF (m/z): [M⁺] Calcd for C₂₉H₁₇BrN₂: 473.37; Found: 471.8.

9,10-(4-(9-phenyl-9H-pyreno[4,5-d]imidazole)-10-phenyl) anthracene (C-BPyIA)

In a 100 mL round flask, a mixture of C-PyIBr (2.13 g, 4.5 mmol), BAnB (0.79 g, 1.8 mmol), K₂CO₃ (4.43 g, 32 mmol), distilled water (16 mL), toluene (24 mL), and [Pd(PPh₃)₄] (0.62 g, 0.54 mmol) was added and refluxed at 90 °C under N2 atmosphere for 48 h. The reaction was then quenched by water and the mixture was extracted with dichloromethane for three times. The organic phase was collected and dried with anhydrous Na₂SO₄ for 30 min. After evaporation of the solvent, the residue was purified via column chromatography using THF as eluent to afford light yellow solid. (0.88 g, yield: 51%). ¹H NMR (500 MHz, CD₂Cl₂) δ:8.33 (s, 2H), 8.29 – 8.10 (m, 9H), 8.09 – 7.91 (m, 8H), 7.90 - 7.69 (m, 13H), 7.68 - 7.46 (m, 8H), 7.43 (m, 2H). ¹³C NMR (126 MHz, CDCl₃) δ:133.66, 132.94, 132.58, 131.94, 130.65, 130.02, 129.33, 128.72, 128.33, 127.64, 127.01, 126.29, 125.81, 124.25, 123.60, 122.64, 121.58. FTIR (KBr, v, cm⁻¹): 3040, 1921, 1791, 1597, 1496, 1452, 1387, 1297, 1221, 1185, 1149, 1102, 1070, 1019, 976, 944, 893, 828, 766, 720, 698, 665, 615, 550, 485, 420. MALDI-TOF (m/z): [M⁺] Calcd for C₇₂H₄₂N₄: 963.16; Found: 965.4. Anal. Calcd for C₇₂H₄₂N₄: C 89.79, H 4.40, N 5.82; Found: C 89.86, H 4.45, N 5.79. 9,10-(4-(10-phenyl-9H-pyreno[4,5-d]imidazole)-9-phenyl)

anthracene (N-BPyIA)

In a 100 mL round flask, a mixture of N-PyIBr (2.13 g, 4.5 mmol), BAnB (0.79 g, 1.8 mmol), $K_2 \text{CO}_3$ (4.43 g, 32 mmol), distilled water (16 mL), toluene (24 mL), and [Pd(PPh₃)₄] (0.62 g, 0.54 mmol) was added and refluxed at 90 °C under N₂ atmosphere for 48 hours. The reaction was then guenched by water and the mixture was extracted with dichloromethane for three times. The organic phase was collected and dried with anhydrous Na₂SO₄ for half an hour. After evaporation of the solvent, the residue was purified via column chromatography using THF as eluent to afford light yellow solid. (0.97 g, yield: 56%). ¹H NMR (500 MHz, CD₂Cl₂) δ:8.33 (s, 2H), 8.27 – 8.23 (m, 4H), 8.22 – 8.10 (m, 5H), 8.07 - 7.91 (m, 9H), 7.90 - 7.68 (m, 12H), 7.68 - 7.45 (m, 9H), 7.45 - 7.38 (m, 1H). ¹³C NMR (126 MHz, CDCl₃) δ:133.66, 132.67, 132.05, 130.93, 130.31, 129.90, 128.80, 128.36, 127.73, 127.24, 126.33, 125.63, 124.97, 124.16, 123.23, 122.74, 122.08, 121.03, 120.06, 118.38. FTIR (KBr, v, cm⁻¹): 3040, 1921, 1798, 1596, 1513, 1485, 1459, 1441, 1394, 1304, 1275, 1185, 1145, 1102, 1070, 1022, 976, 939, 896, 828, 770, 744, 715, 694, 669, 607, 557, 485, 416. MALDI-TOF (m/z): $[M^+]$ Calcd for $C_{72}H_{42}N_4$: 963.16; Found: 965.2. Anal. Calcd for C72H42N4: C 89.79, H 4.40, N 5.82; Found: C 89.88, H 4.43, N 5.78.

Conflicts of interest

There are no conflicts to declare.

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By integrating PyI with anthracene, two high-efficiency blue emitters C-BPyIA and $M \rightarrow BP / A CO2990G$ are obtained. Especially, N-BPyIA exhibits decent device performance with EQE_{max} of 7.67 % in deep blue region.

TOC figure

