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Pyrene-Based Blue Emitters with Aggregation-Induced Emission Features for High-Performance Organic Light-Emitting Diodes

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Pyrene is a representative aggregation-caused quenching (ACQ) chromophore. Herein, by introducing tetraphenylethylene or triphenylethylene with a typical aggregation-induced emission (AIE) characteristic at the 2,7-positions, we have succeeded in converting it into AIE type luminogens (AIEgens). The new compounds, namely **Py-TPE** and **Py-TriPE**,exhibit strong sky-blue emission (<490 nm) with high quantum yield in both the aggregated state and solid state. Non-doped organic light-emitting diodes (OLEDs) using **Py-TPE** and **Py-TriPE** as emitters were fabricated. Among them, the device with a configuration of ITO/HATCN (5nm)/TAPC (40nm)/TCTA (5nm) /**Py-TPE** (20nm)/Bepp2 (45 nm)/Liq (2nm)/Al afforded sky-blue light at 493 nm at low turn-on voltage (3.1 V) with a maximum luminance of 15750 cd m-2, a current efficiency of 7.34 cd A-1, a powder efficiency of 6.40 lm W-1 and an external quantum efficiency of 3.19%). The electron-transporting material (Bepp2) and the symmetry of the present AIEgens play significant roles in improving the luminance of the devices with low efficiency roll-off. This work thus opens up new avenues for the design of new pyrene-based AIEgens for fabricating blue high-performance OLEDs.

Introduction

Organic light emitting diodes (OLEDs) have shown great commercial application in full-colour displays and solid-state lighting,[1-3] due to their many advantages, such as low power consumption, high efficiency and good colour purity.[4-6] In terms of full-colour displays, blue emitting materials show unique superiority for optical properties *versus* red and green emitters.[7-10] The blue materials can be further functionalized to green, red, as well as white emitters by facile synthetic strategies and doping methods.[3,5] However, it is challenging to access the blue emitter and blue OLED devices due to their large energy gaps (>2.75 eV) and stability drive voltages, etc.[8] Recently, emerging topics have focused on the construction of high-efficiency blue emitting materials with high external quantum efficiencies (EQE) by using phosphorescent[11-13] or thermally activated delayed fluorescence (TADF) materials.[14-17] However, the development of such materials remains elusive thus far. Therefore, fundamental and technological interest in deep-blue/ blue fluorescent materials remains and a great deal of effort has been devoted to the topic of preparing high-efficiency blue emitters for potential OLED applications.[18,19]

The large π-conjugated polycyclic aromatic hydrocarbon (PAH) pyrene possesses high electron mobility and good light-emitting properties.[20-21] However, pyrene exhibits fluorescence quenching with low quantum yield in the condensed state due to the large planar structure, and this is an example of an aggregation-caused quenching (ACQ) chromophore.[22] To take full advantage of pyrene as an organic optical material, efficient approaches to overcome its ACQ phenomenon need to be developed.[23] Functionalization of pyrene is sometimes a deliberate choice/strategy.[20,23,25,26] Indeed, our group has shown that pyrene derivatives can also exhibit AIE characteristics by integrating suitable motifs.[27-33] For example, the pyrene-functionalized tetraphenylethene (TPE) TTPEPy emits a weak emission in solution, but shows strong sky-blue light both in the frozen solution (77K) and the solid state with high solid PL (Φ*f* = 0.7). The resulting AIE-active pyrene-based multilayered OLED devices displayed a maximum luminance (*L*max) of 18000 cd m-2.[34] The problem with such systems is the difficulty balancing the relationship between the emission colour and the drive voltage. In practice, it is essential for fabrication of blue high-performance OLEDs to have low voltage and excellent electroluminescence (EL) properties.

For pyrene, vastly different electron affinities are exhibited at the different positions around the rings. In particular, differing electrophilic substitution activity is observed at the 1-, 3-, 6-, and 8-positions (active sites), *versus* the 4-, 5-, 9-, 10-positions (K-region) and the 2,7-positions.[20,21] Furthermore, the turn-on voltage for OLED devices is tunable over the range 3.1 V to 7.9 V, which is achieved via modification of the substituents at pyrene.[35] For example, the 2-substituted pyrene-based AIEgen exhibits a low turn-on voltage (3.4 V) with blue EL emission (496 nm) and a *L*max of 16264 cd m-2. Recently, we have explored an efficient approach to tunable light-emitting devices by incorporating TPE units at the 2,7-positions of pyrene. The TPE moieties were found not only to play a crucial role in tuning the emission wavelength, but were also capable of switching the pyrene-based material from ACQ to AIE.[22] Herein, we employ tetraphenylethylene (TPE) or triphenylethylene (TriPE) substituents at the 2,7-positions of pyrene.[36,37] The two new pyrenes, **Py-TPE** and **Py-TriPE** were synthesized by a Pd-catalyzed Suzuki-Miyaura cross-coupling reaction in good yield, and are not only just excellent blue emitters with novel AIE features, but provide a high-performance sky-blue OLED with maximum luminance, current efficiency, powder efficiency and external quantum efficiencies of 15750 cd m-2, 7.34 cd A-1 6.40 lm W-1 and 3.19% at low turn-on voltages (3.1 V), respectively.

Results and discussion

Synthesis

As shown in Scheme 1, the Suzuki-Miyaura cross-coupling reaction of pyrene-2,7-diboronic acid bis(pinacol) ester[38] with the respective bromo derivatives afforded **Py-TPE** and **Py-TriPE** in high yield. All compounds were characterized by 1H/13C NMR spectroscopy and high resolution mass spectrometry (HRMS). Both compounds exhibited good thermal stability with decomposition temperatures of 500oC for **Py-TPE**and 405oC for **Py-TriPE**, respectively.



**Scheme 1.** The synthetic route to the pyrene-based compounds **Py-TPE** and **Py-TriPE.**

Photophysical Properties

Both pyrene-based compounds **Py-TPE** and **Py-TriPE** exhibit good solubility in common organic solvents, such as chloroform, dichloromethane (CH2Cl2), tetrahydrofuran (THF), dimethyl sulfoxide (DMSO), but were insoluble in water. Given this, the UV-vis absorption and photoluminescence (PL) spectra of **Py-TPE** and **Py-TriPE** were investigated in dilute THF and in different mixtures of THF/water. The key optical data are listed in Table 1 and in the supporting information. As shown in Figure 1, the compound **Py-TPE** emitted weak fluorescence with a maximum peak at 450 nm, whilst on increasing the fraction of H2O up to 60%, the emission intensity was enhanced by ~60-fold compared to that observed in pure THF, In addition, the vibronic peak was observed in *f*w= 60% due to the formation of large size nanoparticles. On continuing to increase the percentage water content, the PL intensity slightly decreases (see Fig, 1 top right) but then subsequently rises to afford a 200-fold increase and a large red-shifted emission peak at 491nm in the fraction of water *f*w= 99%. Under same experimental conditions, **Py-TriPE** exhibited similar PL behaviour, and the PL spectra was enhanced *ca*. 16-fold with the observation of a 34 nm red-shifted emission peak on increasing the fraction of H2O. Clearly, both compounds are AIE active compounds. In particular, during the process of increasing the fraction of water from 0% to 99%, the emission of **Py-TPE** and **Py-TriPE** were tuned from deep blue through blue to sky blue simply by adjusting the volume ratio of THF and water. This is attributed to different conformations and molecular packing adopted in the respective aggregates.[39]

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**Figure. 1.** (A) PL spectra of **Py-TPE** in THF/water mixtures with different water fractions (*f*w), (B) Plot of relative PL intensity (*I*/*I*0) *versus* the composition of THF/water mixture of **Py-TPE**, where *I*0 is the PL intensity in pure THF solution. Inset: fluorescent photographs of **Py-TPE** in THF/ water mixtures (*f*w = 0, 60% and 99%) taken under UV illumination λmax ex = 365nm, (C) Normalized PL spectra of **Py-TPE** and (D) **Py-TriPE** recorded in THF solutions at various concentration from 10−5 -10−2 M and in film at 25 °C.

Pyrene is known to be a deep blue emitter in dilute solution, however it readily forms π-aggregates/excimers and displays an excimer emission at high concentration. When the phenyl ring of TPE was replaced by pyrene unit, an aggregation-enhanced excimer emission in this system was observed.[40] On the other hand, pyrenes prefer to exhibit multiple photoluminescence, included monomer emission, excimer emission, and charge-transfer emission processes[40] due to their different molecular packing, When the concentration of **Py-TPE** was increased, even in the film, the excimer emission peak was not observed either in solution, the aggregated state or in the film, which is due to the bulky TPE suppressing the π-stacking. Thus, the PL spectrum of **Py-TPE** in dilute THF exhibits two weak emission peaks at 450nm and 483 nm, may originate from the monomer emission and charge-transfer emission.

**Table 1**. The photophysical and electrochemical properties of **Py-TPE** and **Py-TriPE**

|  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Compd | λmaxabs(nm)  solns*a* | λmaxPL (nm)  solns*a*/ films*b* | | *Φf* | ι(ns) | LUMO  (eV) | HOMO  (eV) | △Eg  (eV) | *T*g*g/Tdh*  (oC) |
| **Py-TPE** | 325, 342 | 450 (0%)  482 (99%) | 462 | 0.57 (99%)  0.62 (film) | 4.17 (99%)  4.66 (film) | -1.50c/1.91d | -5.20c/5.14e | 3.70c/3.23f | 167/500 |
| **Py-TriPE** | 327, 346 | 441 (0%)  490 (99%) | 453 | 0.02 (99%)  0.03 (film) | 1.63 (99%)  1.94 (film) | -1.44/1.94 | -5.17/5.12 | 3.73/3.18 | 147/405 |
| *a*Maximum absorption wavelength measured in THF at room temperature. *b*Measured in thin neat films. *c*Calculated by DFT/B3LYP/6-31G\* using Gaussian 03 software, dLUMO=HOMO+Eg, edetermined by CV using the ferrocene HOMO level, calculated from the empirical formulae HOMO = −(4.8 + Eonsetox − Eonsetox(Fc)) f estimated from UV/Vis absorption spectra, g Melting temperature (*T*m) obtained from differential scanning calorimetry (DSC) measurement. *h*Decomposition temperature (*T*d) obtained from thermogravimetric analysis (TGA). | | | | | | | | | |

However, for **Py-TriPE,** as the concentration increased from 10-5 to 10-2 M, the PL spectrum exhibited a large red-shifted emission peak from 443 to 523 nm, which corresponds to monomer emission (443nm) and excimer emission (523nm), respectively. This concentration-dependent PL behaviour may be attributed to strong intermolecular C–H···π interactions which cause a J-aggregate at high concentration.[37] The emission peak undergoes a large hypsochromic shift to 453 nm in the film compared to its position when in 10-2 M solution.

To investigate the solvatochromic effect on the photophysical behaviour of both the 2,7-substituted pyrenes, their photophysical properties in six different solvents were measured and the experimental data is summarized in Table S2. As shown in figure S11, as the solvent polarity varies from hexane to DMF, the emission behaviour changes greatly. For example, the maximum emission peak of **Py-TPE** is located at λ max em = 510 nm in hexane and λ max em = 427 in acetonitrile, respectively. We infer that the **Py-TPE** exhibits an aggregation emission peak in hexane while due to theirs solubility in low polar solvents, which would lead to a different molecular packing morphology. Similarly, the emission of compound **Py-TriPE** did not exhibited a obvious large shift (Table S2).

In addition, the fluorescence quantum yield (*Φf*) and lifetime has been estimated in film and in solid state. As listed in Table 1, the blue emitter **Py-TPE** showed high quantum yield and longer fluorescence lifetime than **Py-TriPE**. Although both compounds have a similar molecular structure, the different photophysical properties may be attributed to the C=C bond located at the 2,7-position, which leads to a significant rearrangement of the electronic charge over the molecular framework,[41]and electron excitation could then be tranferred though the extra deactivation pathways. Therefore, the **Py-TPE** is an excellent candidate for use in high-performance blue-emitting materials in OLEDs.

DFT calculations

In order to obtain an understanding of the geometric and electronic structure of the **Py-TPE** and **Py-TriPE** at a molecular level, density functional theoretical (DFT) calculations (B3LYP/6-31G\*basis set) were carried out using the Gaussian 09 program.[42] The calculated highest occupied molecular orbital (HOMO), the lowest unoccupied molecular orbital (LUMO) level of the pyrene-based molecules and the electronic density are all illustrated in Figure 2.

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**Figure 2.** Molecular orbital plots of **Py-TPE** and **Py-TriPE** calculated at B3LYP/6-31G level.

Given the nodal plane of the pyrene passes through the C2 and C7 carbon atoms, the TPE moieties at the 2,7-positions show a weak electron interaction with the pyrene core. As shown in Figure 2, the HOMOs of the **Py-TPE** and **Py-TriPE** were delocalized over the entire molecular frameworks along the Z-axis of the pyrene core, whilst the electron cloud of the LUMO of the **Py-TPE** is mainly located on the pyrene core. We note though that the LUMO of **Py-TriPE** is almost spread across the entire molecule via the C=C bonds. The different electron distributions arise from the expanding π-conjugation, which we propose significantly affects the intrinsic intramolecular charge transfer. The HOMO-LUMO gaps were calculated at 3.70 eV for **Py-TPE** and 3.73eV for **Py-TriPE**, respectively. Furthermore, experimental HOMO values of **Py-TPE** and **Py-TriPE** were evaluated by cyclic voltammetry in 0.1 M CH2Cl2/ TBAP (tetrabutylammonium perchlorate) at room temperature under N2 atmosphere, using Fc/Fc+ as the internal reference. Both compounds showed an irreversible oxidation process with a similar onset oxidation potential (Eonsetox) of 0.77 and 0.75 V. Therefore, the HOMO levels are estimated from the Eonsetox by using the empirical formula HOMO = -(4.8 + *E*oxonset - *E*ox fconset). and the LUMO values could be determined according to equation LUMO = HOMO + Eg (eV), where Eg was estimated from UV-vis absorption. The electrocdata are summarized in Table S1. The results indicated the experimental data is in good agreement with the DFT calculations.

OLED Device fabrication and characterization

Considering the excellent thermal stability and high PL properties of **Py-TPE** and **Py-TriPE**, four multilayer non-doped OLEDs devices were fabricated with the following structures: ITO/HATCN (5 nm) /TAPC (40 nm) /TCTA (5 nm) /EML (20nm)/ETL (45 nm)/ Liq (2 nm)/Al (Figure 3). where the 1,4,5,8,9,11-hexaazatriphenylenehexacarbonitrile (HATCN), 4,4’-cyclohexylidenebis[N,N-bis(4-methylphenyl)benzenamine] (TAPC) and tris(4-carbazoyl-9-ylphenyl)amine (TCTA) were adopted as hole-transporting layers (HTL), and the pyrene-based AIEgen as the light-emitting layer. Furthermore, to improve the efficiency of these OLEDs, 1,3-bis[3,5-di(pyridin-3-yl)phenyl]benzene (BmPyPB) and bis[2-(2-hydroxyphenyl)pyridinato]beryllium (Bepp2) were used as the electron-transporting layer (ETL) in devices 1-3 and devices 2- 4, respectively. Figures 4a-d display the EL spectra, the voltate-current density-Luminance (V-I-L), the external quantum efficiency *versus* current density and the current density *versus* current efficiency curve, and the EL properties of devices 1-4 are summarized in table 2.

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**Figure 3.** A) The schematic energy level diagram of the materials used in the fabrication of the OLED devices, B) and C) the optimized devices **2** and **4** using **Py-TPE** and **Py-TriPE** as emitter and Bepp2 as ETL.

The four non-doped devices **1**-**4** emitted a sky blue EL peak at 484 nm, 492 nm, 480 nm and 483 nm, respectively with low turn-on voltage over the range 3.1-3.6 V. The **Py-TPE** exhibited an EL peak at 484nm in device **1**, which is similar to the singlet emission in the aggregation state or as the film. When the ETL of BmPyPB was replaced by Bepp2 in device 2, the EL emission of **Py-TPE** in device **2** exhibited a slight red-shift of 8 nm compared to device **1**, which is thought to be due to the strong electron-withdrawing ability of Bepp2.

More importantly, the devices **1** and **2** exhibited excellent EL properties, for example, in device **1**, the **Py-TPE** exhibited the best performance with a maximum brightness (Lmax) of 5453 cd m-2, a maximum current efficiency (ηc,max) of 7.82 cd A-1 and a maximum powder efficiency (ηp,max) of 6.40 lm W-1. Interestingly, the brightness of device **2** was enhanced to 15750 cd m-2 with equal ηc,max and ηp,max of 7.34 cd A-1 and 6.03 lm W-1 at a CIE coordinate of (0.234, 0.389). This EL efficiency is higher than previously reported.[28] On the other hand, the EL peak of **Py-TriPE** exhibited a large red shift emission at 480 nm and 483 nm in devices **3** and **4**, respectively compared to those in their respective films, which is ascribed to their different molecular morphology.[43]



**Figure 4.** (A) EL spectra, plot of (B) luminance and current density with the applied voltage, (C) and the current density *versus* external quantum efficiency and (D) current density *versus* current efficiency curve; using **Py-TPE** as the emitter in EL devices **1**-**2** and the **Py-TriPE** in devices **3**-**4**.

However, due to the delocalized π-electrons over the entire molecular frameworks, the use of **Py-TriPE** as the emitter in device **3** led to low EL efficiencies compared to devices **1**-**2**: the Lmax, ηp,max and ηc,max are 1287 cd m-2, 2.08 cd A-1 and 1.76 lm W-1 at a CIE coordinate of (0.203, 0.310). It should be noted that the EL property exhibited a near 3-fold improvement in brightness for device **4** compared to device **3**. In addition, the maximum EQE of devices **1** and **2** increased to 3.19%; the corresponding values in devices **3** and **4** are 0.98% and 1.07%, respectively. Additionally, the applied voltage had a limited effect on the EL emission when increased from 4 to 10V in the four devices (Figure S14). Evidently, using the strong electron-transporting layer Bepp2 in devices **2** and **4**, enables the brightness of the blue OLED device to show a large improvement in this pyrene system. Although the efficient ETL materials BmPyPB or Bepp2 show a similar mobility of ~10-4 cm2 V-1 s-1,[44-46] the Bepp2 in devices **2** and **4** exhibits a lower efficiency roll-off (4.1% for device **2** and 7.5 for device **4** at 1000 cd m-2) compared to BmPyPB in devices **1** and **3** (Table 2), which may be ascribed to the increased stability of the interface of EML|Bepp2, which is beneficial to the transportation of electrons/current density compared with EML|BmPyPB. (Figure 4B) More importantly, the symmetrically 2,7-substituted pyrene-based AIE proved to be an excellent emitting material for high-performance blue OLEDs with lower turn-on voltage and higher EL efficiency. In addition, the efficiency roll-off for devices **1** and **3** is higher than that of devices **2** and **4**, which may be due to the interface between the organic dyes and ETL which can impact on the charge transport and EL properties.[47]

Charge Transport Properties

To better understand the EL properties, the electron/hole motilities of **Py-TPE** and **Py-TriPE** were measured via the space-charge-limited current (SCLC) method.[48,49,50] The electron- and hole-only devices with configuration of ITO/TmPyPB(10 nm)/ EML (80 nm)/LiF (1 nm)/Al and ITO/TmPyPB(10 nm)/ EML (80 nm)/LiF (1 nm)/Al , respectively, were fabricated. Figure S19 illustrates the current density-applied voltages (*J-V*) of the four devices, and indicates the presence of *J-V* behaviour/ohmic characteristics at low voltages. As the applied voltage is raised, the current correlates with the applied voltage, which is space-charge limited?. Furthermore, the SCLC characteristics could be described through the Mott−Gurney equation.[48,49,50]

(1)

where ε0 is the free-space permittivity (8.85 × 10-14 C V-1 cm-1); εr is the relative dielectric constant (can be assumed to be 3.0 for organic semiconductors); μ is the charge mobility, L is the thickness of the organic layer, and E is the electric field. Normally, the charge mobility (μ) and depends on the electric field, which can be determined by the Poole−Frenkel formula:

(2)

where γ is the Poole−Frenkel factor and μ0 is the zero-field mobility. Based on equations (1) and (2), the current density (J) of SCLC can be determined by following formula:

(3)

Via fitting the J-V curves in the SCLC regime to equation 3, the values of μ0 and γ were obtained, and thus the field-dependent electron mobility and the hole mobility could be calculated according to equation 2. The electron mobilities of **Py-TPE** and **Py-TriPE** are 2.51×10-7 and 3.65×10-8 cm2 V‒1 s‒1, whilst the hole mobilities are 2.46×10-8 and 7.96×10-8 cm2 V‒1 s‒1 at 3.6 × 105 V cm−1 electric field. The related low electron/hole mobilities of both 2,7-substituted pyrene-based AIEgen may be ascribed to the pure polycyclic aromatic hydrocarbon frameworks.

A summary of the EL parameters for the OLEDs devices is given in Table 2. Use of the AIEgens as emitter materials, such as TPE-cored or alike[39,51] allows for the facile fabrication of green OLED devices with impressive EL properties, however this cannot be achieved for blue emission. As an example, the pyrene-1-substituted ethene (DPDPyE) based device emits at 516 nm (EL peak) at a low turn-on voltage of 3.2 V and with maximum luminance of ηc,max, ηp,maxand the EQEs are 49830 cd cm-2, 10.2 cd A-1, 9.2 lm W-1 and 3.3%;[40] respectively. In contrast, use of the pyrene derivative (ACQ compound) as the emitting-light layer, allowed access to a blue/deep blue OLED device with high voltage (>7 eV) and low ηp,max.[52-56] Moreover, position-dependence pyrenes have the potential to play a significant role in affecting the EL parameters, e.g. 1,3,6,8- tetra- substituted pyrenes exhibit higher brightness and external EQE and lower turn-on voltage *versus* related mono- and di-substituted pyrenes. This may contribute to the molecular symmetry, which has been shown to improve the charge carrier mobility for both holes and electrons.[28,54,55] Thus, to balance the key factors of emission colour, hole mobility and the brightness efficiency of OLED devices, the TPE moieties where employed as substituents to decorate the pyrene core at the 1-,3-, 6- and 8-positions or the 2,7-positions. The result was impressive blue sky EL emission with brightness (>10000 cd m-2) and low efficiency roll-off.[34,56]

**Table 2**. Summary of the electroluminescent performance of the sky-blue devices.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
| Device | Von  (V) | Lmax  (cd/m2) | CEa  (cd/A) | PEa  (lm/W) | EQEa  (%) | λmaxb  (nm) | Roll-off b  (%) | CIE (x, y)b |
| **1** | 3.2 | 5453 | 7.82/6.92 | 6.40/3.73 | 3.66/3.25 | 484 | 11.2 | (0.22, 0.34) |
| **2** | 3.1 | 15750 | 7.34/7.01 | 6.03/3.90 | 3.19/3.06 | 492 | 4.1 | (0.23, 0.39) |
| **3** | 3.5 | 1287 | 2.08/1.01 | 1.76/0.34 | 0.98/0.52 | 480 | 46.9 | (0.20, 0.31) |
| **4** | 3.4 | 5797 | 2.19/1.95 | 1.82/0.75 | 1.07/0.99 | 483 | 7.5 | (0.20, 0.31) |
| **a**Order of maximum, then values at 1000 cd m-2;b measured at 1000 cd m-2. | | | | | | | | |

**Table 3** Summary of representative performances of OLED using AIEgen and pyrene as emitters

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| emitter | Von  (V) | Lmax  (cd m-2) | ηC,max  (cd A-1) | ηp,max  (lm W-1) | λEL  (nm) | CIE (x, y) | EQE(%) |
|  | 4.6 | 13700 | 11 | 6.4 | 520 | (0.27, 0.50) | 3.5 |
|  | 3.2 | 49830 | 10.2 | 9.2 | 516 |  | 3.3 |
|  | 7.77 | -- | 3.34 | 1.46 | 460 | (0.17, 0.20) | -- |
|  | 3.5 | 300 | 0.3 | ~0.06 | 456 | (0.15, 0.32) | -- |
|  | 4.0 | 2058 | 2.7 | 1.03 | 450 | (0.14, 0.09) | 3.26 |
|  | 3.6 | 13400 | 7.3 | 5.6 | 484 | -- | 3.0 |
|  | 3.6 | 36300 | 12.3 | 7.0 | 488 | -- | 4.95 |
|  | 4.2 | 18287 | 2.94 | 1.79 | 448 | (0.15, 0.09) | 3.46 |
| Configuration of the OLED devices:  Ref.[40] ITO/NPB (60 nm)/emitter (20 nm)/TPBi (10 nm)/Alq3 (30 nm)/LiF (1 nm)/Al (100 nm)  Ref.[28] ITO/PEDOT:PSS /NPB (40 nm)/emitter (10-20 nm)/TPBI (35 nm)/Ca:Ag  Ref.[51, 34,57] ITO/NPB (60 nm)/emitter (20 nm)/TPBi (40 nm)/LiF (1 nm)/Al (100 nm)  Ref.[52] ITO/2-TNATA(60 nm)/NPB (15 nm)/emitter(35 nm)/Alq3(20 nm)/LiF:Al  Ref.[53] ITO/PEDOT:PSS/emitter/CsF/Al | | | | | | | |

Experimental

General: 1H and13C NMR spectra (400 MHz) were recorded on a Bruker AV 400 spectrometer using chloroform-d solvent and tetramethylsilane as internal reference. J-values are given in Hz. High-resolution mass spectra (HRMS) were taken on a GCT premier CAB048 mass spectrometer operating in a MALDI-TOF mode. PL spectra were recorded on a Hitachi 4500 spectrofluorometer. UV-vis absorption spectra were obtained on a Milton Ray Spectrofluorometer. PL quantum yields were measured using absolute methods. The cyclic voltammetry was carried out in 0.10 M tetrabutylammonium perchlorate in anhydrous dichloromethane and THF at a scan rate of 100 mV s−1 at room temperature. Thermogravimetric analysis was carried on a TA TGA Q5500 under dry nitrogen at a heating rate of 10oC/min. Thermal transitions were investigated by differential scanning calorimetry using a TA DSC Q1000 under dry nitrogen at a heating rate of 10 oC/min. The quantum chemistry calculation was performed on the Gaussian 09W (B3LYP/6–31G\* basis set) software package.[42]

**Synthesis of Py-TPE (1).** A mixture of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene **1** (0.51 mmol, 1.0 eq), 1-(4-bromophenyl)-1,2,2-triphenylethylene (1.12 mmol, 2.2 eq) in toluene (15 mL) and ethanol (4 mL) at room temperature was stirred under nitrogen. Then, potassium carbonate (2.04 mmol, 4.0 eq) and tetrakis(triphenylphosphine)palladium(0.051 mmol, 0.1 eq) were added. After the mixture was stirred for 30 min at room temperature under nitrogen, the mixture was heated to 90 °C for 48 h with stirring. After cooling to room temperature, the mixture was quenched with water, extracted with CH2Cl2 (3 × 100 mL), and washed with water and brine. The organic extracts were dried with MgSO4 and evaporated. The residue was purified by column chromatography using CH2Cl2/hexane mixture (VCH2Cl2:Vhexane = 1:1) as eluent to give compound **Py-TPE** as a light yellow powder (286 mg, yield 60%). 1H NMR (400 MHz, CDCl3): δ = 7.08 (m, 4 H), 7.15 (m, 26 H), 7.21 (d,*J* = 8.3 Hz, 4 H), 7.65 (d, *J* = 8.3 Hz, 4 H), 8.08 (s, 4 H), 8.34 (s, 4H) ppm; 13C NMR (100 MHz, CDCl3) 13C NMR (101 MHz, CDCl3) *δ* = 143.14, 140.63, 139.90, 138.51, 137.72, 131.42, 130.85, 130.79, 130.76, 127.22, 127.12, 127.05, 126.48, 125.95, 125.91, 125.85, 122.96, 76.71, 76.40, 76.08, 0.36; HRMS FABS (M + H+) calcd for C68H48 864.3756, found 862.3588.

**Synthesis of Py-TriPE (2).** A mixture of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)pyrene **1** (0.51 mmol, 1.0 eq), bromotriphenylethylene (1.53 mmol, 3.0 eq) in toluene (15 mL) and ethanol (4 mL) at room temperature was stirred under nitrogen. Then, potassium carbonate (2.04 mmol, 4.0 eq) and tetrakis(triphenylphosphine)palladium(0.051 mmol, 0.1 eq) were added. After the mixture was stirred for 30 min at room temperature under nitrogen, the mixture was heated to 90 °C for 48 h with stirring. After cooling to room temperature, the mixture was quenched with water, extracted with CH2Cl2 (3 × 100 mL), and washed with water and brine. The organic extracts were dried with MgSO4 and evaporated. The residue was purified by column chromatography using CH2Cl2/hexane mixture (VCH2Cl2:Vhexane = 1:2) as eluent to give compound **Py-TriPE** as a yellow powder (358 mg, yield 63%). 1H NMR (400 MHz, CDCl3) δ = 7.80 (s, 4H), 7.68 (s, 4H), 7.19 – 7.04 (m, 24H), 7.03 – 6.95 (m, 6H) ppm; 13C NMR (100 MHz, CDCl3) δ = 143.51, 143.20, 142.92, 141.25, 140.84, 140.39, 130.94, 130.89, 130.75, 130.05. 127.44, 127.13, 127.10, 127.08, 126.62, 125.91, 125.88, 125.83, 122.56 ppm. HRMS (MALDI−TOF): m/z calcd for C56H40 710.30, found 710.2973.

OLED device fabrication and measurement

Devices with active areas of 16 mm2 were grown on patterned ITO glass substrates with a sheet resistance of 10 Ω sq-1. Before OLED fabrication, the ITO glass substrates were cleaned with detergent and deionized water, dried in an oven at 120 C for 1 hour, then treated with UV-ozone for 15 minutes, and finally loaded into a deposition chamber with a basic pressure of 1×10-4 Pa. The organic layers were fabricated by evaporating organic layers at a rate of 1-2 Ås-1. A layer of Liq with 2 nm thickness was deposited at a rate of 0.1 Ås-1, and finally Al was deposited at a rate of approximately 5.0 Å s-1as the cathode. The current–voltage–brightness characteristics and electroluminescence (EL) spectra were measured with a Keithley 2400 source meter and a Luminance Meter LS110, and electroluminescence (EL) spectra were measured with a Flame-S-VIS-NIR (Serial Number: FLMS03334).

Conclusions

Inspired by the special electronic structure of pyrene, two 2,7-substituted pyrene-based compounds incorporating the AIE features of **Py-TPE** and **Py-TriPE** were prepared and characterized. Given their excellent thermal and photophysical properties, both compounds were used as highly efficient emitters for blue OLED devices. The optimized device **2** with the configuration ITO / HATCN (5 nm) / TAPC(40 nm) / TCTA (5 nm) / Py-TPE (20nm) / ETL (45 nm) / Liq:Al displayed sky-blue emission with maximum luminance (15750 cd m-2), and current efficiency (7.34 cd A-1) at a CIE coordinate of (0.234, 0.389). Importantly, these symmetric 2,7-substituted pyrene-based AIEgens when employed as emitters exhibit excellent properties, typically lowering the turn-on voltage and improving the luminance and external quantum efficiencies in OLED devices. This is attributed to the facile charge carrier mobility of the symmetrically2,7-substituted pyrene-based AIEgens and the balancing of the hole-/electron-transporting ability. In addition, it is necessary to optimize the electron-transporting layer of the OLED to lower the efficiency roll-off exhibited by strong electron-transporting materials in pyrene chemistry. This strategy is valuable for designing new pyrene-based AIEgens for constructing high efficiency blue OLED devices.

Conflicts of interest

There are no conflicts to declare.

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