

View Article Online View Journal

RSC Advances

This article can be cited before page numbers have been issued, to do this please use: Y. Liu, Q. Bai, J. Li, S. Zhang, C. Zhang, F. Lu, B. Yang and P. Lu, *RSC Adv.*, 2016, DOI: 10.1039/C5RA25424H.



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. This Accepted Manuscript will be replaced by the edited, formatted and paginated article as soon as this is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the <u>Ethical guidelines</u> still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



www.rsc.org/advances

COYAL SOCIETY

Journal Name

ARTICLE

Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Efficient Pyrene-Imidazole Derivatives for Organic Light-emitting Diodes

Yulong Liu,^a Qing Bai,^a Jinyu Li,^a Shitong Zhang,^a Chen Zhang,^a Fang Lu,^b Bing Yang,^a and Ping Lu^{*a}

Two light emitting materials, 9-phenyl-10-(4-(1,2,2-triphenylvinyl)phenyl)-9H-pyreno[4,5-d]imidazole (PyTPEI) and 9phenyl-10-(4'-(1,2,2-triphenylvinyl)-[1,1'-biphenyl]-4-yl)-9H-pyreno[4,5-d]imidazolepyreneimidazole (PyPTPEI), containing pyrene, imidazole and tetraphenylethene units are synthesized with high yields. Both of them exhibit good thermal stability with decomposition temperature of 458 °C and 474 °C, respectively. The fluorescent quantum efficiency in amorphous film are as high as 70% for PyTPEI and 63% for PyPTPEI, respectively. In particular, PyPTPEI shows the blueshifted emission due to the more twisted conformation and reduced intermolecular interaction as compared with PyTPEI. The maximum current efficiency and maximum brightness of non-doped OLED device using PyTPEI as active layer reaches 8.73 cd/A and 27419 cd/m², which is better than that of PyPTPEI (7.68 cd/A and 19419 cd/m²).

Introduction

Published on 02 February 2016. Downloaded by Gazi Universitesi on 02/02/2016 15:30:35.

Over the past decades, organic light-emitting diodes (OLEDs) have been one of the mostly developed field due to their potential applications in large-area, high-resolution flat panel displays and full-color lighting sources.1 Creation of the luminogens with high solid-state efficiency is very important to facilitate the applications in OLEDs.² Pyrene represents one of the mostly investigated small organic molecule which is best known for its high photoluminescence efficiency, good thermal stability, and promising carrier mobility.³ However, pyrene π system suffers heavily from the aggregation-caused-quenching (ACQ) effect originating from the strong π - π interaction of pyrene, which would limit its solid-state emission to some extent.⁴ So far, some chemical modifications have been introduced with the aim of inhibiting molecular aggregation including the attachment of branched alkyl,⁵ blending with transparent polymers, etc.^{6,7} These processes, however, are often accompanied by severe side effects. For example, the steric effects of bulky alicyclics can twist the conformations of the chromophoric units and jeopardize the electronic conjugation in the luminophores.⁵ And non-conjugated polymers can dilute the luminophore density and subsequently obstruct the charge transport in electroluminescence (EL) devices.⁷ Alternative strategy is of great interest.

In recent year, the attachment of aggregation-induced emission (AIE) group, such as tetraphenylethylene (TPE), into the ACQ units has proved to be a promising way to provide the

^bPharmacy Department, Changchun Medical College, China.

+Electronic Supplementary Information (ESI) available: See DOI: 10.1039/x0xx00000x



^aState Key Laboratory of Supramolecular Structure and Materials, Jilin University, Street No.2699, Changchun, 130012, China.E-mail: <u>lup@ilu.edu.cn</u>.



Scheme 1 Synthetic routes to PyTPEI and PyPTPEI.

Field.

Published on 02 February 2016. Downloaded by Gazi Universitesi on 02/02/2016 15:30:35.

Results and discussion

Synthesis and Characterization

The synthesis process for PvTPEI and PvPTPEI were shown in Scheme 1. The synthetic formulation strategy is based on the heterocyclization of imidazole and pyrene,¹⁶ whereby pyrene-4, 5-tetraone and 4-bromobenzaldehyde were applied as the starting materials to afford compound 1.15(a) Compounds 2a and 2b could be obtained through the boronation of (2bromoethene-1,1,2-triyl)tribenzene and (2-(4respectively.17 bromophenyl)ethene-1,1,2-triyl)tribenzene, And then, the targeted products were achieved by the Pdcatalyzed Suzuki cross-coupling reaction with high yields. The compounds were thoroughly characterized by NMR (¹H and ¹³C) spectroscopy, mass spectrometry and elemental analysis. The analytical data of PyTPEI and PyPTPEI were consistent well with their proposed structure.

Thermal Properties

The thermal stability of PyTPEI and PyPTPEI was characterized by thermal gravimetric analysis (TGA) and differential scanning calorimetry (DSC) under a nitrogen atmosphere. As shown in Fig. 1, PyTPEI and PyPTPEI exhibited excellent thermal stability with decomposition temperature (5% weight loss) at 458 °C and 474 °C, respectively. In DSC heating cycles, no T_g was detected for PyTPEI due to its rigid polycyclic skeleton, and T_m appeared at 315 °C. While T_g and T_m for PyPTPEI were at 162 °C and 283 °C respectively, which was much lower than PyTPEI demonstrating a more flexible molecular feature in PyPTPEI



Fig. 1 DSC and TGA thermograms of PyTPEI and PyPTPEI under nitrogen at a heating rate of 10 $^{\circ}$ C min⁻¹.

resulting from the additional phenyl ring between pyreneimidazole and TPE. The rigid pyrene-imidazole moiety was responsible for their high thermostability. In addition, the exothermic peak was at 243 °C for PyTPEI and 235 °C for PyPTPEI during the thermal scanning indicating the crystalline state. (Fig. 1 and Fig. S9, ESI⁺). The good thermal stability is very important for their applications in OLEDs.

Photophysical Properties

The absorption spectra and PL emission spectra of TPE and intermediate 1 were measured in Fig. 2A and Fig. 2B. As can be seen from Fig. 2A, TPE show absorption at 315 nm corresponding to its π - π * transitions. However, intermediate 1 exhibits complex absorption profiles, owing to multiple localized $\pi-\pi^*$ transitions, which originated from the combination of pyrene and imidazole segment. Thus the absorption profiles of PyTPEI and PyPTPEI are similar to that of intermediate 1 which are dominated by multiple localized π - π^* transitions originating from pyrene, imidazole and the TPE chromophores. The observed peak in the longer-wavelength region of 386 nm with vibrational fine structure is attributed to pyrene-imidazole-localized π - π * electronic excitation (Fig. 2C). The absorption spectra for each compound in amorphous film were very similar to that of solution, except that the absorption edges were both red-shifted about 5 nm (Fig. 2D). The optical energy gaps for PyTPEI and PyPTPEI were thus calculated to be 2.90 and 2.88 eV (Table 1), respectively. Both of them showed AIE-activity, that is, they were non-emissive in THF but exhibited intense emission in their aggregate state (Fig. S10 and Fig. S11, ESI^{\dagger}). Interestingly, PyTPEI showed a green emission peaking at 488 nm, whereas PyPTPEI displayed blueshifted emission peaking at 473 nm in film although it possessed one more phenyl ring. This might be derived from the reduced intermolecular interactions in PyPTPEI because the newly formed biphenyl unit between pyrene-imidazole and TPE could rotate freely and increase the steric hindrance in solid state. The quantum efficiencies in films measured by integral sphere were as high as 70% for PyTPEI and 63% for PyPTPEI, respectively. However PLQY of intermediate 1 in film was only 9.6% with considerable bathochromic-shift (69nm) of emission compared to that of intermediate 1 in dilute solution (Fig. 2B). In addition, the emission spectra of intermediate 1 became broad and structureless, which is typical for excimer

DOI: 10.1039/C5RA25424H

Journal Name



Fig. 2 Normalized absorption and emission spectra of intermediate 1, TPE, PyTPEI and PyPTPEI in 2-methyltetrahydrofuran (A, B, C 10^{-5} M) and in film (B, D thickness: 30 nm).

 Table 1. Optical and electrochemical properties of PyTPEI and PyPTPEI.

Compound	$\lambda_{abs}^{a,b}$ (nm)	$\lambda_{PL}^{a,b}$ (nm)	Φ_{f}^{c}	E_g^d	E_{g}^{e}
	solu/film	solu/film		[eV]	[eV]
PyTPEI	290,350,386/	433/488	0.70	2.90	2.99
	295,353,388				
PyPTPEI	290,348,386/	436/473	0.63	2.88	2.92
	296,354,390				

^a Measured in 2-methyltetrahydrofuran. ^b Measured in solid thin film on quartz plates. ^c Determined in evaporated film by the measurement in integrating sphere system. ^d Optical energy bandgap (E_g^{opt}) estimated from the absorption edge in solution. ^e Electrochemical bandgap determined from cyclic voltammetry.

emission.^{4,14a} Obviously, aggregation in intermediate 1 redshifts emission and decreases emission efficiency dramatically with notorious ACQ effect. In consequence, attaching TPE units to a pyrene-imidazole as ornaments endows the resultant products with typical AIE activity and efficient solid-state photoluminescence.

X-ray Molecular Structure and Crystal Packing

The single crystal of PyTPEI was obtained by the solvent evaporation method in dichloromethane. As depicted in Fig. 3, the crystal belonged to triclinic space group *P-1*. The whole molecule formed an anti-parallel arrangement, pyrene-imidazole and TPE units alternately stacked together based on head-to-tail intermolecular interactions.¹⁸ There was no overlap between the adjacent pyrene unit which suggested that the generally obseved excimer formation via π - π stackings in pyrene π -system could be avoided and accordingly eliminated the ACQ effect. It is found that there were four C-H••• π (I, II, III, IV) interactions between hydrogen atom on phenyl rings of TPE and the π clouds of pyrene in adjacent molecules with distances of 2.73-2.99 Å, and one C-H•••N (V)



DOI: 10.1039/C5RA25424H

Fig. 3 (A) Molecular structure of PyTPEI in one unit cell. (B) Top view. (C) Molecular arrangement along a axis, side view.



Fig. 4 The HOMOs and LUMOs for PyTPEI and PyPTPEI obtained at the B3LYP/6-31G level.

interaction between N-3 atom of imiazole and hydrogen atom on phenyl ring attaching to the N-1 atom of imidazole in adjacent molecule along b axis with a distance of 2.97 Å (Fig. S12, ESI^{\dagger}). The abundant intermolecular interactions helped to lock the molecular rotations of TPE in the solid state and suppress the non-radiative pathway of consuming the exciton energy to further increase the photoluminescence efficiency. **Theoretical Calculations**

To evaluate their frontier molecular orbitals and energy bandgaps, density functional theory (DFT) calculations were performed with a B3LYP/6–31G(d,p) basis set using the Gaussian 03W program (Fig. 4). The distribution of the lowest unoccupied molecular orbitals (LUMOs) and the highest occupied molecular orbitals (HOMOs) were very similar for PyTPEI and PyPTPEI. The HOMOs of the two objective compounds were mainly delocalized over the pyreneimidazole segment, while their LUMOs were mainly located on imidazole and TPE groups. In addition, the calculated bandgaps of the compounds were nearly same which is consistent with their comparison of experimental bandgap based on optical energy bandgap and electrochemical bandgap. **Electrochemical Properties**

The electrochemical properties of these compounds were examined by cyclic voltammetry (CV). Both of them underwent irreversible oxidation and reduction process in dry dichloromethane and DMF using $(Bu_4N)PF_6$ as electrolytes under N₂ atmosphere. According to the onset potentials, the HOMO levels of PyTPEI and PyPTPEI were calculated to be - 5.30 and -5.36 eV, while the LUMO levels of PyTPEI and PyPTPEI were calculated to be -2.31 eV and -2.44 eV,



Fig. 5 Cyclic voltammogram of PyTPEI and PyPTPEI in CH₂Cl₂ (oxidation) and DMF (reduction), measured with 0.1 M (Bu_4N)PF₆ as supporting electrolyte at a scan rate of 100 mV s⁻¹.



Fig. 6 (A) Electroluminescence (EL) spectra for PyTPEI and PyPTPEI measured at 9 V. (B) Current density-voltage-brightness (J-V-L) characteristics. (C) Current efficiency versus brightness curves. (D) Current efficiency and power efficiency versus current density curves.

respectively, by comparison to ferrocene (Fig. 5). The HOMO-LUMO energy gaps obtained from CV measurement concided well with the optical energy gaps got from UV-vis measurements (Table 1).

Electroluminescence Properties

Owing to their high solid-state efficiencies and good thermal stability, non-doped OLEDs based on PyTPEI and PyPTPEI were fabricated with a typical configuration of ITO/PEDOT: PSS (40 nm)/NPB (50 nm)/EML (20 nm)/TPBi (40 nm)/LiF (0.5 nm)/AI (120 nm), where TPBi was used as electron-transport layer and NPB was used as the hole-transport layer. The device performance was summarized in Table 2. Both devices gave green electroluminescence (EL) peaking at 500 nm with Commission Internationale de L'E' clairage (CIE) chromaticity



Fig. 7 The electron and hole current density versus electric field intensity curves of the single carrier devices based on PyTPEI and PyPTPEI.



Fig. 8 AFM images (5 μm \times 5 $\mu m)$ of evaporated films on the quartz plate before and after annealing at 120 °C for 1 h under ambient atmosphere.

coordinate of (0.209, 0.401) for PyTPEI and (0.202, 0.336) for PyPTPEI, respectively, where the initial band of EL spectra in PyPTPEI was blue-shifted about 20 nm compared with PyTPEI (Fig. 6A). The electroluminescent spectra were in consistent with the emission profiles of their amorphous films.

Fig. 6B plots the current density–luminescence–voltage (J– L–V) curves of both devices. The turn-on voltages (V_{on}) of devices were both at 2.8 V suggesting that the dissipation of energy associated with carrier injection or transportation is quite low. The LE curves (Fig. 6D) showed a relatively stable light output, even when the current density approached 300 mA cm⁻², their EL spectrum did not change in operating conditions. The PyTPEI-based device had the highest LE and external quantum efficiency (EQE) of 8.73 cd A⁻¹ and 3.46%, respectively, yielding a maximum luminance of 27419 cd m⁻² at 8.3 V. As compared, the device using PyPTPEI as the active layer showed moderate performance with a $\eta_{c.max}$ of 7.68 cd A

Journal Name

Journal Name

Table 2. Electroluminescence properties of the devices.

Device	V _{on} (V) ^a	CE (cd A ⁻¹) ^b	EQE (%) ^b	Brightness (cd m ⁻²) ^b	EL (nm) ^c	CIE (x,y) ^d
PyTPEI	2.8	8.73	3.46	27419	500	(0.209,
						0.401)
PyPTPEI	2.8	7.68	3.35	19419	500	(0.202,
						0.336)

^a Driving voltage at 1 cd m⁻². ^b Maximum value of current efficiency (CE), external quantum efficiency (EQE) and brightness. ^c Peak wavelength of electroluminescence (EL) spectra. ^d CIE coordinates measured at 1000 cd m⁻².

⁻¹, an EQE of 3.35% and a maximum luminance of 19419 cd m⁻². To further investigate the merits towards fusion of pyrene, imidazole and TPE subunits at molecular level and better understand the effect of 1, 3-imidazole on the energy levels and the carrier injection and transport property in devices, the hole-only device with the configuration of ITO/PEDOT-PSS (40 nm)/NPB (10 nm)/EML (70 nm)/NPB (20 nm)/AI (120 nm) and the electron-only device with the configuration of ITO/TPBi (20 nm)/EML (70 nm)/TPBi (10 nm)/LiF (1 nm)/Al (120 nm) for PyTPE and PyPTPEI were fabricated. The results (Fig. 7) indicated that both PyTPEI and PyPTPEI showed high carrier injection and transport ability which confirmed that 1,3imidazole can act as a bipolar type building block. Their hole current values of PyTPEI and PyPTPEI were very similar and both higher than their corresponding electron current values. Furthermore, electron current values of PyTPEI was much higher than PyPTPEI, indicating that more carriers could be transported to the emitting layer of PyTPEI in OLED, which is crucial to obtain higher efficiency in PyTPEI than PyPTPEI owing to the dual-injection/transportation procedure of OLEDs.

The devices based on PyTPEI and PyPTPEI will stably assemble during the device fabrication process. The amorphous films of PyTPEI and PyPTPEI were obtained through vacuum deposition method as proved by X-ray diffraction (Fig. S15, ESI⁺). Morphology of these films were investigated by atomic force microscopy (AFM). The images are given in Fig. 8. The PyTPEI film exhibits a quite smooth surface morphology with a roughness of 1.40 nm. After annealing at 120 °C for 1 h under ambient atmosphere, the film morphology became more smooth with a roughness of 0.74 nm. In the case of PyPTPEI, it also shows a fairly smooth surface morphology with a roughness of 0.97 nm. After annealing at 120 °C for 1 h under ambient atmosphere, the film morphology is basically unchanged. Both of them provide a homogeneous morphology of amorphous evaporated film indicating the possibility to keep uniform films throughout the device fabrication process.

Conclusions

In summary, we have designed and synthesized two efficient light emitting materials, PyTPEI and PyPTPEI, and determined their difference and relationship upon their molecular structure. A comparative study of these two compounds through spectroscopic, electrochemical, crystallographic,

quantum calculations and OLEDs are performed. Both of them – show high thermal stability. The attachment of TPE group to pyrene-imidazole endows PyTPEI and PyPTPEI with AIE-activity and high efficiencies in solid state. A blue-shifted fluorescence of PyPTPEI in the solid state is observed due to the reduced intermolecular interactions. In OLEDs, PyTPEI shows a better device performance with the maximum current efficiency of 8.73 cd A⁻¹. Even when the brightness reached 10000 cd m⁻², the device still exhibits a very low efficiency roll-off. These molecules provides a design strategy to prevent the aggregation-induced fluorescence quenching of pyrene π system and facilitates their applications in OLEDs.

Experimental Section

All of the reagents and solvents used for the syntheses were purchased from Aldrich or Acros and were used as received. All of the reactions were performed under a dry-nitrogen atmosphere. The ¹H NMR spectra were recorded on an AVANCZ 500 spectrometers at 298 K by utilizing deuterated dimethyl sulfoxide (DMSO) as solvents and tetramethylsilane (TMS) as a standard. The ¹³C-NMR spectra were recorded on an AVANCZ 500 spectrometers at 298 K by utilizing deuterated trichloromethane as solvents and tetramethylsilane (TMS) as a standard. The final compounds were characterized by Flash EA 1112, CHNS-O elemental analysis instrument. The MALDI-TOF mass spectra were recorded using an AXIMA-CFRTM plus instrument. Diffraction data were collected on a Rigaku RAXIS-PRID diffractometer using the ω -scan mode with graphitemonochromator Mo•Ka radiation. UV-vis absorption spectra were recorded on UV-3100 spectrophotometer. Fluorescence measurements were carried out with RF-5301PC. The film PL efficiencies were measured on a Gliden Fluorescence Systemusing an integrating sphere, with a 366.8 nm Edinburgh Instruments Ltd light emitting diode as the excitation source. Instrument model (FLS920). Thermal gravimetric analysis (TGA) was measured on a Perkin-Elmer thermal analysis system from 30 °C to 900 °C at a heating rate of 10 K/min under nitrogen flow rate of 80 ml/min. Differential scanning calorimetry (DSC) was performed on a NETZSCH (DSC-204) unit from 30 °C to 400 °C at a heating rate of 10 K/min under nitrogen atmosphere. The electrochemical properties (oxidation and reduction potentials) were carried out via cyclic voltammetry (CV) measurements by using a standard one-compartment, three-electrode electrochemical cell given by a BAS 100B/W electrochemical analyzer.

Tetrabutylammoniumhexafluorophosphate (TBAPF6) in anhydrous dimethyl formamide (DMF) or anhydrous dichloromethane (0.1 M) were used as the electrolyte for negative or positive scan. The ground-state geometries were optimized at the B3LYP/6-31G(d, p) level, which is a common method to provide molecular geometries. The HOMO/LUMO distributions are calculated on the basis of optimized groundstate.

Device Fabrication: The EL devices were fabricated by vacuum deposition of the materials at 10^{-6} Torr onto ITO glass with a sheet resistance of 25 Ω square⁻¹. All of the organic

RSC Advances Accepted Manuscrip

DOI: 10.1039/C5RA25424H Journal Name

ARTICLE

layers were deposited at a rate of 1.0 Å s⁻¹. The cathode was deposited with LiF (0.5 nm) at a deposition rate of 0.1 Å s⁻¹ and then capping with Al metal (120 nm) through thermal evaporation at a rate of 4.0 Å s⁻¹. The electroluminescent (EL) spectra and Commission Internationale De L'Eclairage (CIE) coordination of these devices were measured by a PR650 spectroscan spectrometer. The luminance-current and densityvoltage characteristics were recorded simultaneously with the measurement of the EL spectra by combining the spectrometer with a Keithley model 2400 programmable voltage-current source. All measurements were carried out at room temperature under ambient conditions.

Synthesis of compound 1: A mixture of aniline (2.3 ml, 25.0 mmol), pyrene-4,5-dione (1.2 g, 5.0 mmol), 4bromobenzaldehyde (1.2 g, 6.0 mmol), ammonium acetate (1.5 g, 20.0 mmol), and acetic acid (15 ml) was refluxed under nitrogen in an 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. Yield: 86.0%. MS: 472.5 (M (H⁺)). ¹H NMR (500 MHz, DMSO-d₆, 25°C): δ 8.95 (d, J = 7.0 Hz, 1H), 8.33 (d, J = 7.4 Hz, 1H), 8.27-8.17 (m, 4H), 7.86-7.72 (m, 6H), 7.63-7.58 (m, 4H), 7.32 (d, J = 7.9 Hz, 1H).

PyTPEI: 4,4,5,5-tetramethyl-2-(1,2,2-**Synthesis** of triphenylvinyl)-1,3,2-dioxaborolane (2a) (0.92 g, 2.4 mmol), 10-(4-bromophenyl)-9-phenyl-9H-pyreno[4,5-d]imidazole (1) (0.95 g, 2.0 mmol), dry toluene (24 mL), and 16 mL aqueous of K₂CO₃ solution (2.0 mol L⁻¹) were placed in a round-bottom flask. Pd(PPh₃)₄ (0.14 g, 0.12 mmol) was then added and the mixture was vigorously stirred at 90 °C for 48h. After cooling to room temperature, the resulting mixture was extracted with dichloromethane followed by purification by column chromatography on silica gel. Yield: 80%. MS: 649.2 (M (H^{+})). ¹H NMR (500 MHz, DMSO-*d*₆, 25°C): δ 8.91 (d, *J* = 7.6 Hz, 1H), 8.31 (d, J = 7.3 Hz, 1H), 8.25-8.17 (m, 4H), 7.78-7.71 (m, 6H), 7.41 (d, J = 8.5 Hz, 2H), 7.30 (d, J = 8.3 Hz, 1H), 7.18-7.12 (m, 9H), 7.02-6.94 (m, 8H). 13 C NMR (125 MHz, CDCl₃, 25°C): δ 143.5, 143.4, 143.3, 132.2, 131.7, 131.4, 131.33, 131.29, 130.1, 129.2, 128.8, 128.0, 127.8, 127.69, 127.67, 127.5, 126.59, 126.56, 126.42, 125.3, 124.4, 124.3, 123.6, 122.9, 117.97. Elemental analysis: calculated for C₄₉H₃₂N₂: C, 90.71; H, 4.97; N, 4.32; found: C, 90.87; H, 4.74; N, 4.39.

Synthesis of PyPTPEI: 4,4,5,5-tetramethyl-2-(4-(1,2,2triphenylvinyl)phenyl)-1,3,2-dioxaborolane (2b) (1.10 g, 2.4 mmol). 10-(4-bromophenyl)-9-phenyl-9H-pyreno[4,5d]imidazole (1) (0.95 g, 2.0 mmol), dry toluene (24 ml), and 16 mL aqueous of K_2CO_3 solution (2.0 mol L⁻¹) were placed in a round-bottom flask. Pd(PPh₃)₄ (0.14 g, 0.12 mmol) was then added and the mixture was vigorously stirred at 90 °C for 48h. After cooling to room temperature, the resulting mixture was extracted with dichloromethane followed by purification by column chromatography on silica gel. Yield: 85%. MS: 726.0 (M (H^{+})), ¹H NMR (500 MHz, DMSO- d_{6} , 25°C): δ 8.96 (d, J = 7.6 Hz, 1H), 8.32 (d, J = 7.2 Hz, 1H), 8.23 (t, J = 8.6 Hz, 1H), 8.21-8.16 (m, 3H), 7.85-7.80 (m, 2H), 7.76 (dt, J = 7.9, 6.8 Hz, 4H), 7.68 (dd, J = 21.5, 8.5 Hz, 4H), 7.53 (d, J = 8.3 Hz, 2H), 7.31 (d, J = 7.8 Hz, 1H), 7.20-7.08 (m, 9H), 7.07-6.96 (m, 8H). ¹³C NMR (125

MHz, CDCl₃, 25°C): δ^{13} C NMR (126 MHz, CDCl₃) δ 143.72, 143.69, 143.66, 143.3, 141.3, 140.4, 137.8, 132.2, 131.9, 131.7, 131.4, 131.34, 130.26, 130.0, 129.7, 129.2, 128.0, 127.8, 127.71, 127.65, 127.57, 126.58, 126.56, 126.52, 126.47, 126.1, 125.3, 124.6, 124.3, 123.6, 122.9, 118.0. Elemental analysis: calculated for C55H36N2: C, 91.13; H, 5.01; N, 3.86; found: C, 91.27; H, 5.14; N, 3.59.

Acknowledgements

This work was supported by the Ministry of Science and Technology of China (2013CB834801), and the National Science Foundation of China (21374038 and 91233113).

Notes and references

- (a) C. W. Tang, S. A. VanSlyke, Appl. Phys. Lett., 1987, 51, 913; (b) S. R. Forrest, M. E. Thompson, Chem. Rev., 2007, 107, 923; (c) T. P. I. Saragi, T. Spehr, A. Siebert, T. F. Lieker, J. Salbeck, Chem. Rev., 2007, 107, 1011; (d) C. D. Müller, A. Falcou, N. Reckefuss, M. Rojahn, V. Wiederhirn, P. Rudati, H. Frohne, O. Nuyken, H. Becker, K. Meerholz, Nature, 2003, 421, 829; (e) J. U. Park, M. Hardy, S. J. Kang, K. Barton, K. Adair, D. K. Mukhopadhyay, C. Y. Lee, M. S. Strano, A. G. Alleyne, J. G. Georgiadis, P. M. Ferreira, J. A. Rogers, Nat. Mater., 2007, 6, 782.
- (a) D. A. Pardo, G. E. Jabbour, N. Peyghambarian, Adv. Mater., 2 2000, 12, 1249; (b) S. R. Forrest, Nature, 2004, 428, 911.
- З (a) T. M. Figueira-Duarte, K. Müllen, Chem. Rev., 2011, 111, 7260; (b) S. Bailey, D. Visontai, C. J. Lambert, M. R. Lambert, H. Frampton, D. Frampton, J. Chem. Phys., 2014, 140, 054708; (c) S. Q. Zhang, X. L. Qiao, Y. Chen, Y. Y. Wang, R. M. Edkins, Z. Q. Liu, H. X. Li, Q. Fang, Org. Lett., 2014, 16, 342.
- 4 (a) K.-C. Wu, P.-J. Ku, C.-S. Lin, H.-T. Shih, F.-I. Wu, M.-J. Huang, J.-J. Lin, I.-C. Chen, C.-H. Cheng, Adv. Funct. Mater., 2008, 18, 67; (b) J. N. Moorthy, P. Natarajan, P. Venkatakrishnan, D.-F. Huang, T. J. Chow, Org. Lett., 2007, 9, 5215; (c) T. Oyamada, H. Uchiuzou, S. Akiyama, Y. Oku, N. Shimoji, K. Matsushige, H. Sasabe, C. Adachi, J. Appl. Phys., 2005, 98, 074506; (d) I. B. Berlman, J. Phys. Chem., 1970, 74, 3085.
- (a) C.-L. Chiang, S.-M. Tseng, C.-T. Chen, C.-P. Hsu, C.-F. Shu, 5 Adv. Funct. Mater., 2008, 18, 248; (b) J.-S. Yang, J.-L. Yan, Chem. Commun., 2008, 1501; (c) J. Wang, Y. F. Zhao, C. D. Dou, H. Sun, P. Xu, K. Q. Ye, J. Y. Zhang, S. M. Jiang, F. Li, Y. Wang, J. Phys. Chem. B, 2007, 111, 5082; (d) J. N. Moorthy, P. Natarajan, P. Venkatakrishnan, D.-F. Huang, T. J. Chow, Org. Lett., 2007, 9, 5215.
- 6 (a) C. Fan, S. Wang, J. W. Hong, G. C. Bazan, K. W. Plaxco, A. J. Heeger, Proc. Natl. Acad. Sci. USA, 2003, 100, 6297; (b) B. S. Gaylord, S. Wang, A. J. Heeger, G. C. Bazan, J. Am. Chem. Soc., 2001, 123, 6417.
- 7 S. Hecht, J. M. J. Fréchet, Angew. Chem. Int. Ed., 2001, 40, 74.
- 8 (a) Y. N. Hong, J. W. Y. Lam, B. Z. Tang, Chem. Soc. Rev., 2011, 40, 5361; (b) Y. N. Hong, J. W. Y. Lam, B. Z. Tang, Chem. Commun., 2009, 4332; (c) X. F. Ji, P. Wang, H. Wang, F. H. Huang, Chinese J. Polym. Sci., 2015, 33, 890; (d) Y. Liu, X. Feng, J. B. Shi, J. G. Zhi, B. Tong, Y. P. Dong, Chinese J. Polym. Sci., 2012, 30, 443.
- (a) H. Vollmann, H. Becker, M. Corell, H. Streeck, Liebigs Ann., 1937, 531, 1; (b) L. Altschuler, E. Berliner, J. Am. Chem. Soc., 1966, 88, 5837.
- 10 (a) M. J. S. Dewar, R. D. Dennington, J. Am. Chem. Soc., 1989, 111, 3804; (b) R. A. Hites, Calculated Molecular Properties of Polycyclic Aromatic Hydrocarbons, Elsevier, New York, 1987.

Journal Name

- 11 A. Miyazawa, T. Yamato, M. Tashiro, *Chem. Express*, 1990, **5**, 381.
- 12 (a) Z. J. Zhao, S. M. Chen, J. W. Y. Lam, P. Lu, Y. C. Zhong, K. S. Wong, H. S. Kwok, B. Z. Tang, *Chem. Commun.*, 2010, 46, 2221; (b) Z. J. Zhao, P. Lu, J. W. Y. Lam, Z. M. Wang, C. Y. K. Chan, H. H. Y. Sung, I. D. Williams, Y. G. Ma, B. Z. Tang, *Chem. Sci.*, 2011, 2, 672; (c) Z. Q. Liang, Z. Z. Chu, D. C. Zou, X. M. Wang, X. T. Tao, *Org. Electron.*, 2012, 13, 2898.
- 13 J. Hu, D. Zhang, F. W. Harris, J. Org. Chem., 2005, 70, 707.
- 14 (a) Y. L. Liu, Z. Gao, Z. M. Wang, C. F. Feng, F. Z. Shen, P. Lu, Y. G. Ma, *Eur. J. Org. Chem.*, 2013, **32**, 7267; (b) W. J. Li, L. Yao, H. C. Liu, Z. M. Wang, S. T. Zhang, R. Xiao, H. H. Zhang, P. Lu, B. Yang, Y. G. Ma, *J. Mater. Chem. C*, 2014, **2**, 4733; (c) Z. M. Wang, P. Lu, S. M. Chen, Z. Gao, F. Z. Shen, W. S. Zhang, Y. X. Xu, H. S. Kwok, Y. G. Ma, *J. Mater. Chem.*, 2011, **21**, 5451.
- 15 (a) J. Thaksen, D. Bhausaheb, M. M. Shaikh, M. Rajneesh, J. Mater. Chem. C, 2015, 3, 9981; (b) D. Kumar, K. R. J. Thomas, C. C. Lin, J. H. Jou, Chem. Asian J., 2013, 8, 2111.
- (a) J. Wang, R. Mason, D. VanDerveer, K. Feng, X. R. Bu, J. Org. Chem., 2003, 68, 5415; (b) J. Wang, L. Dyers, R. Mason, P. Amoyaw, X. R. Bu, J. Org. Chem., 2005, 70, 2353.
- 17 (a) W. Y. Dong, Y. Y. Pan, M. Fritsch, U. Scherf, *J. Polym. Sci.*, *Part A: Polym. Chem.*, 2014, **53**, 1753; (b) R. R. Hu, J. L. Maldonado, M. Rodriguez, C. M. Deng, C. K. W. Jim, J. W. Y. Lam, M. M. F. Yuen, G. R. Ortiz, B. Z. Tang, *J. Mater. Chem.*, 2012, **22**, 232.
- 18 (a) Y. Liao, S. Bhattacharjee, K. A. Firestone, B. E. Eichinger, R. Paranji, C. A. Anderson, B. H. Robinson, P. J. Reid, L. R. Dalton, *J. Am. Chem. Soc.*, 2006, **128**, 6847; (b) L. Chen, L. X. Wang, X. B. Jing, F. S. Wang, *J. Mater. Chem.*, 2011, **21**, 10265; (c) A. Lv, M. Stolte, F. Würthner, *Angew. Chem. Int. Ed.*, 2015, **54**, 10512.

Highly efficient green OLED based on AIE-active pyrene-imidazole derivative PyTPEI achieves the highest LE of 8.73 cd/A with low efficiency roll-off.

