Contents lists available at ScienceDirect

Organic Electronics

journal homepage: <http://www.elsevier.com/locate/orgel>

Pyrene-based hyperbranched porous polymers with doped Ir(piq) (acac)₂ red emitter for highly efficient white polymer light-emitting diodes

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ARTICLE INFO

Keywords:

Hyperbranched porous polymers
White light
Polymer light-emitting diodes Electroluminescence spectra

ABSTRACT

Here, we designed and prepared a series of hyperbranched porous polymers constructed using fluorene branches and pyrene core, and all hyperbranched porous polymers exhibit intense blue fluorescence, good morphological stability, and high thermal stability. Further, it is found that the aperture sizes for hyperbranched porous polymers can be adjusted by simply changing the content of pyrene and fluorene in the synthesis process. When the feed ratios of pyrene in the total polymers is 15 mol%, the optimized aperture size was obtained, which is slightly larger than the wavelength of complementary red emitter Bis(1-phenylisoquinoline)(acetylacetonate) iridium (III) (Ir(piq)₂acac), indicating the Ir(piq)₂acac can well distributed in the apertures of hyperbranched porous polymers in co-doped film of Ir(piq)₂acac and hyperbranched porous polymers. The fabricated polymer- light-emitting diode (PLED) with such co-doped film as light-emitting layer realizes good white emission with almost equal blue and red emission intensity from hyperbranched porous polymers and Ir(piq)₂acac. The balanced electroluminescent (EL) spectra contribute to ideal Commission Internationale de l'Eclairage (CIE) coordinate of (0.326, 0.374) located at white light zone. In addition, the device also achieves high device performance with maximum luminance and current efficiency reaching 5369 cd/m² and 8.35 cd/A, respectively. We believe that such porous-structure polymers have huge potential applications in the development of highly efficient white PLEDs with reducing production cost.

1. Introduction

In the past decades, white polymer light-emitting diodes (WPLEDs) have been widely recognized owing to their potential applications in large-area full-color and flexible displays, backlights and solid lighting sources, and their great advantages such as high stability, low price, as well as easy fabrication process, etc [1–6]. A general approach to obtain white-light emission from a single molecule or polymer is to simultaneously implant complementary blue-light emitting and orange-light emitting units [7–10] or blue-, green- and red-light emitting units in the same molecule or polymer. But in order to achieve ideal white light-emitting polymer, one person has to repeatedly carry out lots of

experiments though adjusting the proportion of complementary units, which lead to a colossal waste of materials, energy, and time. For facilitating the commercialization of WPLEDs, it is very urgent to achieve white light-emitting polymers with simple preparation process and low cost.

Porous organic polymers have gained a lot of attentions for their amorphous and crystalline materials with versatile applications in biomedical, gas storage and separation, construction materials catalyst, lithium ion batteries, membrane filters sensors, and electro-optical displays, because of their low density, high surface areas, and good thermal stability [11–19]. Ordered and tunable pores porous organic frameworks can be obtained by changing building blocks or their contents. In

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Scheme 1. Synthesis of the hyperbranched porous polymers.

particular, owing to the extended π -conjugation and suitable highest occupied molecular orbital (HOMO) to lowest unoccupied molecular orbital (LUMO) energy orientations, the semiconducting POPs have recently drawn a surging interest in organic photovoltaics, optoelectronics, and photo-induced organic transformations [20–23]. Among various blue emitting materials, pyrene employed as hole-transporting or host materials for a potentially high performance organic light-emitting diodes (OLED) applications due to its native deep blue fluorescence and high photoluminescence quantum yield, excellent thermal stability, good carrier mobility and emission properties [24–33].

In this work, we designed and prepared a series of hyperbranched porous polymers with different aperture sizes by changing the content of 1,3,6,8-tetrasubstituted pyrene core and 2,7-bisubstituted 9,9-dioctylfluorene building blocks, and all hyperbranched porous polymers exhibit intense blue fluorescence, good morphological stability, and high thermal stability. The hyperbranched porous polymer, with a 15 mol% feed ratio for pyrene in the total polymers, shows a optimized aperture size, which is slightly larger than the maxlength of complementary red emitter Ir(piq)₂acac, indicating the Ir(piq)₂acac can well distributed in the apertures of hyperbranched porous polymers in co-doped film of Ir(piq)₂acac and hyperbranched porous polymers. The fabricated PLED with such co-doped film as light-emitting layer realizes good white emission, where the EL spectra contain almost equal blue and red emission intensity from hyperbranched porous polymers and Ir(piq)₂acac. The balanced EL spectra also contribute to ideal CIE coordinate of (0.326, 0.374) located at white light zone. Moreover, the device also achieves high device

performance with maximum luminance and current efficiency reaching 5369 cd/m² and 8.35 cd/A, respectively.

2. Experimental section

2.1. Materials and characterization

The detailed descriptions about materials and measurements are displayed in Section S1 in Supporting Information. And the detailed process about OLEDs fabrication and testing can also be found in Section S2 in Supporting Information.

2.2. Syntheses of polymers MOPs-FP1- MOPs-FP20

To a solution of predetermined amount of the monomers 9,9-Dioctyl- 2,7-dibromofluorene (**M1**), 9,9-Dioctylfluorene-2,7- bis(trimethylboronate) (**M2**) and 1,3,6,8-tetrabromopyrene (**M3**) in toluene (30 mL) was added an aqueous solution (5 mL) of Na₂CO₃ (2 M) and a catalytic amount of Pd(PPh₃)₄ (2.0 mol%). Aliquat 336 (1 mL) in toluene (5 mL) was added as the phase transfer catalyst. The mixture was vigorously stirred at 90 °C for 72 h. When cooled to room temperature, the reaction mixture was washed with 2 M HCl and water. The organic layer was separated, and the solution was added dropwise into excess methanol.

Table 1

Polymerization and characterization results for all polymers.

Polymers	η_{M1}	η_{M2}	η_{M3}	Yield(%)	GPC		
					M_n	M_w	PDI
MOPs-FP1	0.48	0.51	0.01	79.8	7932	25248	3.18
MOPs-FP5	0.42	0.53	0.05	75.3	9105	45027	4.95
MOPs-FP10	0.35	0.55	0.10	76.7	9545	38742	4.06
MOPs-FP15	0.27	0.58	0.15	72.9	16572	48969	3.27
MOPs-FP20	0.20	0.60	0.20	61.5	22199	59891	2.70

The precipitates were collected by filtration, and dried under vacuum. The solid was Soxhlet extracted with acetone for 72 h and then passed through a short chromatographic column using toluene as the eluent to afford the hyperbranched porous polymers.

MOPs-FP1:M1 (0.266 g, 0.48 mmol), **M2** (0.325 g, 0.51 mmol) and **M3** (0.005 g, 0.01 mmol). Green powder, yield: 79.8%. ^1H NMR (CDCl_3) δ (ppm): 7.85–7.83 (–ArH–), 7.71–7.67 (–ArH–), 7.49–7.43 (–ArH–), 5.34–5.30 (–ArH–), 2.23–2.00 (–C–CH₂–), 1.26–1.10 (–CH₂–), 0.89–0.79 (–CH₃). EA: N:2.18, C:63.24, H:9.152, S:0.313, C/H ratio:6.9101. **MOPs-FP5:M1** (0.233

g, 0.42 mmol), **M2** (0.338 g, 0.53 mmol) and **M3** (0.026 g, 0.05 mmol). Green powder, yield: 75.3%. ^1H NMR (CDCl_3) δ (ppm): 7.84–7.82 (–ArH–), 7.70–7.64 (–ArH–), 7.48–7.43 (–ArH–),

5.34–5.30 (–ArH–), 2.23–2.00 (–C–CH₂–), 1.26–1.09 (–CH₂–), 0.89–0.75 (–CH₃). EA: N:2.16, C:51.67, H:5.977, S:0.215, C/H ratio:8.6447. **MOPs-FP10:M1** (0.192 g, 0.35 mmol), **M2** (0.354 g, 0.55 mmol) and

M3 (0.052 g, 0.1 mmol). Green powder, yield: 76.7%. ^1H NMR (CDCl_3) δ (ppm): 7.85–7.81 (–ArH–), 7.70–7.67 (–ArH–), 7.48–7.43 (–ArH–),

5.34–5.30 (–ArH–), 2.23–2.00 (–C–CH₂–), 1.30–1.07 (–CH₂–), 0.89–0.74 (–CH₃). EA: N:2.23, C:59.80, H:6.723, S:0.259, C/H ratio:8.949. **MOPs-FP15:M1** (0.148 g, 0.27 mmol), **M2** (0.373 g, 0.58 mmol), **M3** (0.078 g, 0.15 mmol). Dark green powder, yield: 72.9%. ^1H NMR (CDCl_3) δ (ppm): 7.85–7.81 (–ArH–), 7.70–7.67 (–ArH–), 7.48–7.43

(–ArH–), 5.36–5.30 (–ArH–), 2.23–2.00 (–C–CH₂–), 1.33–1.24 (–CH₂–), 0.89–0.87 (–CH₃). EA: N:2.26, C:60.91, H:5.734, S:0.197, C/H ratio:10.6226.

MOPs-FP20:M1 (0.110 g, 0.20 mmol), **M2** (0.386 g, 0.60 mmol) and **M3** (0.104 g, 0.20 mmol). Dark green powder, yield: 61.5%. ^1H NMR (CDCl_3) δ (ppm): 7.85–7.81 (–ArH–), 7.70–7.67 (–ArH–), 7.48–7.43

(–ArH–), 5.36–5.30 (–ArH–), 2.23–2.00 (–C–CH₂–), 1.33–1.25 (–CH₂–), 0.89–0.86 (–CH₃). EA: N:2.06, C:47.13, H:3.384, S:0.335, C/H ratio:13.9628.

Fig. 1. Simulation calculation of the porous polymer **MOPs-PF15** (a) and red light unit **Ir(piq)₂acac** (b). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 2. SEM images of the linear polymer film (a) PFs and the hyperbranched porous polymers films: (b) for **MOPs-FP1**, (c) for **MOPs-FP5**, (d) for **MOPs-FP10**, (e) for **MOPs-FP15**, and (f) for **MOPs-FP20**.

Fig. 3. Nitrogen adsorption and desorption curves (a) and pore size distribution curves (b) of the hyperbranched porous polymers.

3. Results and discussion

3.1. Synthesis and characterization

As shown in Scheme 1, a series of the hyperbranched porous polymers based on symmetric building block pyrene and symmetric linker 9- C-alkyl substituted fluorene were synthesized by one-pot Suzuki coupling polycondensation in relatively high yields. To obtain the more suitable aperture matched well with small molecule phosphorescent materials, the proportion of 1,3,6,8-tetrasubstituted pyrene in the total polymers framework was adjusted with the feed ratios of 1 mol%, 5 mol %, 10 mol%, 15 mol%, and 20 mol%, and the corresponding hyperbranched porous polymers are named as **MOPs-FP1**, **MOPs-FP5**, **MOPs-FP10**, **MOPs-FP15**, and **MOPs-FP20**, respectively. The synthetic and structural parameters for **MOPs-FP1** to **MOPs-FP20** are summarized in Table 1. The structural simulation (in Fig. 1) and characterizations reveal that **MOPs-FP15** possesses an interesting 2D plane structure (planar construction). The ^1H NMR was displayed in supporting information Figure S1. As can be seen from Figure S1, the peak integral intensities of the proton signals at the four substitution position of **1,3,6,8-substitutions pyrene** (δ 5.36–5.30) compared with the aromatic ring of fluorene (δ 7.43–7.85) of the polymer is gradually enhanced from **MOPs-FP1** to **MOPs-FP20**, which was consistent with the increasing trend of pyrene content.

3.2. Density functional theory (DFT) calculation

The molecular structure and the energy-minimized conformer of **MOPs-FP15** and **Ir(piq)₂acac** obtained by DFT calculation are shown in Fig. 1. The **MOPs-FP15** molecule presents two-dimensional conformation because of the planar group pyrene. The maximum and minimum value aperture distances of **MOPs-FP15** are 52.24 Å and 16.92 Å, respectively, which are smaller than Forster R_0 radius ($R_0 \approx 65$ Å). The maximum molecular size of **Ir(piq)₂acac** is 15.67 Å. Thus, the **Ir(piq)₂acac** can be well filled in the aperture of the

hyperbranched porous polymer **MOPs-15**, and the formed such structure theoretically can avoid phase separation phenomenon between polymers and **Ir(piq)₂acac** occurred in traditional co-doped layer, and expects efficient interchain Forster ϵ Resonant Energy Transfer (FRET) from host **MOPs-FP15** to **Ir(piq)₂acac** unit could be occurred.

3.3. Structural properties

Scanning electron microscope (SEM) images (Fig. 2) shows the micro-structure of the linear polymer polyfluorenes (**PFs**) film and hyperbranched porous polymers films prepared through wet-spinning coating method. From Fig. 2, it can be seen that the resultant pore structures show enormous differences, which are only dependent on the ratios of construction unit pyrene. The linear polymer **PFs** film exhibits severe aggregation phenomenon due to interchain interactions. For **MOPs-FP1** film in Fig. 2b, few varisized holes were formed by interspersing and tight stacking between polymer chains, which is because the relatively low pyrene content results in the larger pore size formed for polymer itself. Compared with the SEM image of **MOPs-FP5** film in Fig. 2c, the pore sizes of hyperbranched porous polymers **MOPs-FP10** and **MOPs-FP15** films show a decreasing trend, accordingly, their surface porosity presents increasing trend with the gradual increased content of pyrene. The pore sizes are approximately 2–3 μm , 1–2 μm and 0.5–1.5 μm for **MOPs-FP5**, **MOPs-FP10**, and **MOPs-FP15**-based films, respectively. The uniformly distributed microspheres can clearly been seen from the micro-structure of polymer **MOPs-FP20** film (Fig. 2f) with the particle size of about 60–100 nm. This may be because the higher content of the branched center based in the polymer **MOPs-FP20** up to 20 mol% generated the relatively large degree of polymerization and its rigid and twisted molecular configuration resulted in inferior solubility. In the low aggregation stage, liquid-liquid phase separation occurs and then the droplets rich in oligomers continue to further polymerize with the construction monomer to obtain the polymer microspheres. The

Fig. 4. UV-vis absorption and PL spectra of the hyperbranched porous polymers: (a) in CHCl_3 solution (10^{-5} M) and (b) in solid film.

Table 2
Thermal and photophysical properties of the copolymers.

Copolymer	T_d (°C)	T_g (°C)	Dilute Solution		Solid Film	
			λ	λ_{PL} (nm)	λ	λ
			abs (nm)		abs (nm)	PL (nm)
MOPs-FP1	410	145	385	419, 442,468	391	460
MOPs-FP5	411	189	379	466	384	468
MOPs-FP10	412	196	376	466	378	471
MOPs-FP15	413	200	371	469	373	473
MOPs-FP20	416	215	369	466	372	484

results show that the pore size of the porous polymer gradually decreases with the increase of the branched center content, and we successfully adjust the pore size of the polymers by changing the branched center content and found the optimized ratio of the porous polymer to dope with phosphorescent material $\text{Ir}(\text{pic})_2\text{acac}$ such as **MOPs-FP15**.

3.4. Nitrogen adsorption

A more accurate pore size statistic was performed as shown in Fig. 3 by nitrogen adsorption test. Fig. 3a and b shows nitrogen adsorption and desorption curves and pore size distribution curves of the five hyperbranched porous polymers synthesized above, respectively. The results reveal that all the five hyperbranched porous polymers show mesoporous properties and the average pore size present a decreasing tendency with the increasing pyrene content, which are consistent with SEM investigation. Especially for **MOPs-FP15**, its average pore diameter (D_{avg}) is located at 3.876 nm (in Supporting information Table S1), and the minimum available aperture shrunk to 1.490 nm.

3.5. Photophysical properties

The normalized UV-vis absorption and PL spectra of the hyperbranched porous polymers in dilute solution are shown in Fig. 4a. The absorption bands of from **MOPs-FP1** to **MOPs-FP20**, located at 385 nm, 379 nm, 376 nm, 371 nm, and 369 nm, respectively, are ascribed to the $\pi-\pi^*$ transitions of poly(fluorene-*alt*-pyrene) backbones [34,35]. Clearly, with the increasing of the content of branched center pyrene, the absorption peaks for corresponding hyperbranched porous polymers exhibit a blue shifted trend, which is attributed to the interruption of the conjugation of the polymer backbone by the introduction of the 1,3,6, 8-tetrabromopyrene linkage. In addition, the hyperbranched porous polymer, synthesized using planar pyrene as the branched center, shows a large steric hindrance, which leads to the distortion of molecular chain and reduced the effective conjugate chain length of polymers. This is another reason for blue shifted absorption peak.

In PL spectra, **MOPs-FP1** has three emission peaks at 419 nm, 442 nm, and 468 nm, where the main emission peak at 419 nm and a slight vibronic shoulder at 442 nm can be attributed to the emissions of fluorene units, and the emission bands at 468 nm originates from the pyrene group. Since the content of branched center in **MOPs-FP1** is only 1 mol %, its emission peak is almost overlapping with that of polyfluorene, where a weak emission peak at 468 nm is only observed. The main emission peaks of **MOPs-FP5**, **MOPs-FP10**, and **MOPs-FP20** are located at 419 nm and 468 nm, in which the emission peak at 419 nm are decreased significantly and emission peak at 468 nm are stronger. This indicates the enhanced incomplete energy transfer from fluorene to pyrene unit with the increase of the branched content of hyperbranched porous polymer in dilute solution.

In films, the hyperbranched porous polymers exhibit UV-vis absorption bands at around 380 nm owing to the $\pi-\pi^*$ transitions of the poly(fluorene-*alt*-pyrene) backbones (Fig. 4b and Table 2). The trend is the same as it was in the solution that the maximum absorption bands of all hyperbranched porous polymers gradually shifted to low band with the increasing content of branched center pyrene. The absorption peak

Fig. 5. Transient decay spectra of the all hyperbranched porous polymers (a) and **MOPs-FP1**, **MOPs-FP5**, **MOPs-FP10**, **MOPs-FP15**, and **MOPs-FP20** (b-f) in the solid state at 300 K.

Fig. 6. AFM images (5 × 5 μm) of the hyperbranched porous polymer films: (a) for **MOPs-FP1**, (b) for **MOPs-FP5**, (c) for **MOPs-FP10**, (d) for **MOPs-FP15**, and (e) for **MOPs-FP20**.

of polymer film is slightly red-shift with respect to those in dilute solution. In PL spectra, the maximum emission bands of polymers all shift reddish with the increase of the branched center pyrene, which are located at 460 nm, 468 nm, 471 nm, 473 nm, and 484 nm for **MOPs-FP1** to **MOPs-FP20**, respectively, which is because the increase in molecular rigidity results in red shift. The PL spectrum of **MOPs-FP1** has only emission peak at 460 nm different from which in a dilute solution, indicating the hyperbranched porous polymers **MOPs-FP1** tends to intermolecular aggregate in solid state due to existing bits of branched center pyrene. Moreover, the PL spectra shape of the hyperbranched porous polymers **MOPs-FP5** to **MOPs-FP20** are almost the same in dilute solution, but there's a slight red shift. Obviously, four-arm structure pyrene with certain amount in the hyperbranched porous polymers could effectively inhibit the molecules accumulation and intermolecular interactions. However, the PL spectra of **MOPs-FP20** in films was observed red shift for 22 nm compared to in dilute solution, being attributed to the formation of π stacked based planate pyrene units, which the effect stronger than inhibition based hyperbranched structure. **3.6. Fluorescence lifetime**

Fig. 5 shows the room-temperature transient decay curve of the hyperbranched porous polymers in solid state. The prompt fluorescence of five hyperbranched porous polymers all displayed second-order double exponential decay with longer lifetimes in the range 3.7–5.9 ns, manifesting the lifetimes of the hyperbranched porous polymers gradually increased with the aggrandizing of branched center pyrene. It is owing to the π - π^* accumulation and intermolecular aggregation and interactions were effectively inhibited with the aggrandizing of branched center pyrene, which could cause fluorescence quenching and fluorescence efficiency decreasing.

Besides, the fluorescence lifetime increase in the enlargement of the rigidity of the hyperbranched porous polymers indicates less dynamical quenching as a consequence of the reduced mobility of the Py molecule. Hence, the fluorescence lifetimes of the hyperbranched porous polymers gradually increased with the increasing of pyrene content.

3.7. Film morphology

The morphology of the spin-coated films of the hyperbranched porous polymers was measured using atomic force microscopy (AFM) at a tapping mode and presented in Fig. 6. It shows the average surface roughness were 1.927 nm, 1.170 nm, 4.971 nm, 0.903 nm, and 0.290 nm, respectively, corresponding to the variation of content for branched center pyrene from 1 mol%, 5 mol%, 10 mol%, 15 mol%, to 20 mol%. All the films show flat and smooth surface without any defects. The results imply that hyperbranched porous materials can help to form homogeneous films with good quality. But the surface of the **MOPs-FP20** film appears to be rougher and thinner compared to that for other polymers, which should be attributed to its poor solubility determined by the rigid and twisted molecular configuration. Porous polymer **MOPs-FP15** has the lowest surface roughness and the best surface topography, which is favorable for PLEDs fabrication.

3.8. Electroluminescent properties

Based on excellent optical and thermal performance, we elect **MOPs-FP15** as emitter to evaluate the feasibility of the prepared hyperbranched porous polymers above applied in PLEDs. The devices with the

Table 3

Electrochemical properties of all hyperbranched porous polymers.

Polymers	λ_{onset} (nm)	E_g (eV)	$E_{\text{onset/Ox}}$ (V)	HOMO (eV)	LUMO (eV)
MOPs-FP1	460	2.70	0.67	5.17	2.47
MOPs-FP5	468	2.65	0.63	5.13	2.48
MOPs-FP10	471	2.63	0.63	5.13	2.50
MOPs-FP15	473	2.62	0.76	5.26	2.64
MOPs-FP20	484	2.56	0.63	5.13	2.57

configuration of ITO(180 nm)/PEDOT:PSS(40 nm)/**MOPs-FP15** or **MOPs-FP15: Ir(piq)₂(acac)** (35 nm)/1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBi) (45 nm)/LiF(1 nm)/Al(120 nm) were fabricated, and the device structure and

Fig. 7. Device structure (a) and energy-level (b) diagrams of PLEDs fabricated in this work.

energy level diagrams of the fabricated devices is shown in Fig. 7a and b, respectively. In these devices, ITO and Al served as anode and cathode, respectively; 40 nm-thick PEDOT:PSS layer is used as hole injection and transport layer; 35 nm-thick **MOPs-FP15** or **MOPs-FP15: Ir(piq)₂(acac)** layer is used as light-emitting layer, 40 nm-thick TPBi layer is used as electron-transfer layer; and 1 nm-thick LiF layer is used as electron-injection layer [36–40]. From Fig. 7b, clearly, due to the incorporation of the group pyrene into the backbone, the LUMO level of polymers is effectively reduced to 2.64 eV (Table 3), well matched to that (2.7 eV) of TPBi, as well as very close HOMO level between PEDOT:PSS and polymers, which effectively facilitate the injection of hole and electron carriers into light-emitting layer in fabricated PLEDs [41,42].

Fig. 8a shows the electroluminescence spectra of **MOPs-FP15**-based nondoped device at 9 V. It can be seen that the emission spectrum of **MOPs-FP15**-based non-doped device is located at blue light bands with the emission

peak at 473 nm, which is well consistent to the PL spectrum of **MOPs-FP15** in thin film. Further, we doped red phosphor of **Ir(piq)₂(acac)** in **MOPs-FP15** as light-emitting layer to fabricate the doped devices, where the variations of doping concentration (0.05 mol %, 0.08 mol%, 0.1 mol%, 0.5 mol%, and 1 mol%) are corresponding to the doped devices A, B, C, D, and E, respectively. The EL performances for doped devices A, B, C, D, and E are summarized in Table 4. Clearly, except for an intrinsic blue emission from **MOPs-FP15**, an obvious red emission stemmed from **Ir(piq)₂(acac)** is observed for all doped devices A-D due to the incomplete energy transfer from **MOPs-FP15** to **Ir(piq)₂(acac)**. And with the doping concentration increase of **Ir(piq)₂(acac)** in **MOPs-FP15**, the corresponding device shows an increasing intensity of red emission because of an increased energy transfer from **MOPs-FP15** to **Ir(piq)₂(acac)**. When the doping concentration are 0.08 mol% and 0.1 mol%, the corresponding devices B and C realize ideal white emission with the balanced emissions of blue and red light bands. For example, the CIE coordinates for device B and C are (0.327, 0.358) and (0.326, 0.374), well falling in the white light zone. From Fig. 9a, all doped devices A-D also achieve high luminance, 3819 cd/m² for device A, 3938 cd/m² for device B, 5369 cd/m² for device C, 5216 cd/m² for device D, and 5104 cd/m² for device E,

Table 4

EL Performances of the hyperbranched porous polymers doped devices.

polymers	$\eta_{\text{doped-Ir}}$ mol %	L_{max} (cd/ m [2])	CE_{max} (cd/A)	LE_{max} (lm/W)	CIE^b (x,y)
devices A	0.05	3819	5.26	1.79	(0.324, 0.430)
devices B	0.08	3938	5.80	1.97	(0.312, 0.404)
devices C	0.10	5369	8.35	3.09	(0.326, 0.374)
devices D	0.50	5216	7.04	2.61	(0.555, 0.305)
devices E	1.00	5104	3.96	1.28	(0.613, 0.313)

^a Maximum luminance at applied voltage. ^b CIE values measured at a voltage of 11 V for all devices.

Fig. 8. EL spectra of the polymer non-doped devices at 9 V (a) and the polymer doped devices with different content of red group (b-f). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 9. Current density-voltage-brightness (J - V - L) curves characteristics (a) and Current efficiency-current density characteristics (b) of hyperbranched porous polymers doped devices.

respectively. With the increasing doping concentration, the corresponding device show an in turn increasing luminance, which can be ascribed to the more effective emission intensity for $\text{Ir}(\text{piq})_2\text{acac}$ than MOPs-FP15 . From Fig. 9b, all doped devices A-D also obtain current efficiency, reaching 5.26 cd/A for device A, 5.80 cd/A for device B, 8.35 cd/A for device C, 7.04 cd/A for device D, and 3.96 cd/A for device E, respectively. The higher device efficiency for devices B and C than devices A, D, and E is attributed to the good tradeoff for energy transfer from MOPs-FP15 to $\text{Ir}(\text{piq})_2\text{acac}$ because of suitable doping concentration. These results show that the prepared hyperbranched porous polymers is a kind of high performance light-emitting material, and the hyperbranched porous polymers doped with $\text{Ir}(\text{piq})_2\text{acac}$ as light-emitting layer can be employed to realize good white emission by intermolecular incomplete energy transfer, indicating their huge potential applications in PLEDs.

4. Conclusions

In this work, we designed and prepared a series of hyperbranched porous polymers constructed using fluorene branches and pyrene core, and all hyperbranched porous polymers exhibit intense blue fluorescence, good morphological stability, and high thermal stability. The hyperbranched porous polymers based four functionalities pyrene effectively inhibit the molecules accumulation and intermolecular interactions to extended the fluorescence lifetimes. The aperture size for these porous polymers can be adjusted by simply changing the content of the building block pyrene in the synthesis process. Based on this approach, the optimized aperture size was obtained in hyperbranched porous polymers MOPs-FP15 , which is slightly larger than the maxlength of complementary red emitter $\text{Ir}(\text{piq})_2\text{acac}$, indicating the $\text{Ir}(\text{piq})_2\text{acac}$ can well distributed in the aperture of hyperbranched porous polymers. The fabricated PLED with such co-doped film as light-emitting layer realizes good white emission with ideal CIE coordinate of (0.326, 0.374). Moreover, the device also achieves high device performance with maximum luminance and current efficiency reaching 5369 cd/m^2 and 8.35 cd/A , respectively. We believe that such porous-structure polymers have huge potential applications in the development of highly efficient white polymer light-emitting diodes with reducing production cost.

Notes

The authors declare no competing financial interest.

Acknowledgements

The authors are grateful to the “the National Natural Science Foundation of China (61705158, 61605138, 61605137, 61775155, 61705156), Shanxi Province Natural Science Foundation (201601D202030, 201601D021018, 201601D011031, 201801D 221102); and Scientific and Technological

Innovation Programs of Higher Education Institutions in Shanxi (2016134, 2016135, 201802111)”.

Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.orgel.2019.105487>.

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