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Synthesis and phosphorescent properties of the copolymers of N-vinylcarbazole, methyl methacrylate and iridium complex

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The copolymers containing carbazole unit and iridium complexes, such as $(Ir(bpy)_2Cl$, $Ir(mbpy)_2Cl$ and $Ir(Brbpy)_2Cl$, were synthesized via radical copolymerization of *N*-vinylcarbazole, methyl methacrylate and iridium complex. The synthesized copolymers were characterized by FT-IR, UV-Vis absorption spectroscopy and photoluminescence (PL) spectroscopy, respectively. According to the results, the copolymers $(Ir(Brbpy)_2Cl/PVK$ and $Ir(mbpy)_2Cl/PVK)$ exhibit yellow phosphorescence with an emission peak at around 553 nm under UV-visible light in the solid state. The results also reveal almost complete energy transfer from the host carbazole segments to the guest Ir complex in the copolymer film when the Ir content reaches 1.0 wt.%. The synthesized copolymers are good candidates as blue or yellow phosphorescent materials for PLED applications.

Keywords: *iridium complexes; phosphorescent material; carbazole; copolymer; energy transfer*

1. Introduction

Phosphorescent transition metal complexes, in particular iridium (Ir) complexes [1–4], have attracted great attention due to their capability to harvest both singlet and triplet excitons to realize theoretical 100 % internal quantum efficiency. The high-efficiency organic light-emitting diodes (OLEDs) based on small molecular phosphors have been successfully fabricated via vacuum deposition technology [5].

In comparison to the small molecular iridium complexes, the phosphorescent polymer is believed to be suitable for low-cost solution processing, such as spin-coating, ink-jet printing, etc. [6]. Up to now, there are generally two strategies to realize phosphorescent PLEDs. One strategy is physical blending of the phosphor with a polymer host. However, the device based on the blending material has some disadvantages, such as triplet annihilation arising from dopant aggregation or phase separation. As a result of triplet annihilation, the device exhibits fast efficiency decay at high current density. The other strategy is chemical bonding of the phosphor to the main-chain or side-chain of a poly-

mer. Various phosphorescent polymers have been developed recently by this strategy [7–10]. Phosphorescent dendrimers or hyperbranched polymers are also employed for their inherent topological features. In these dendrimers or hyperbranched polymers, an iridium complex is surrounded by a branched shell to avoid the phenomenon of self-aggregation in the solid state. However, these materials are usually prepared by Suzuki coupling reaction or Diels-Alder cycloaddition reaction which require more complicated conditions and more expensive iridium complexes [11–14].

In this paper, three iridium complexes with different dipyridyl substituents were synthesized. They were further incorporated to the polymer backbones by radical copolymerization of vinylcarbazole, methyl methacrylate and iridium complex. Compared to the Suzuki coupling reaction or Diels-Alder cycloaddition reaction, this method is simple and raw material is cheap. In these copolymers, the carbazole acts as the host, the methyl methacrylate acts as the ligand and the iridium complex acts as the guest. All the copolymers can emit blue, yellow or blue-yellow light, characterized as the metal-based phosphorescence. The photophysical properties, energy transfer in the host-guest system and electrochemical properties were also studied.

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Preliminary results indicate that these materials are promising in optoelectronic applications.

2. Experimental

2.1. Measurements

The FT-IR spectra were measured on Nicolet FTS spectrometer by dispersing the samples in KBr pellets. Elemental microanalyses (for C, H and N) were performed on an Elementar Vario EL III elemental analyser. The GPC analysis of the polymers was conducted on a Waters 1515 with THF as the eluent and poly (styrene) as a standard. Iridium content was measured with the Jobin Yvon Ultima 2 inductively coupled plasma OES spectrometer (ICP). ^{1}HNMR was conducted on Bruker Ascend 400 MHz nuclear magnetic resonance spectrometer. Thermogravimetric analysis (TGA) was conducted on a Mettler Toledo TGA/SDTA851e analyzer at a heating rate of 20 °C/min and under an air flow rate of 75 ml/min. Differential scanning calorimetry (DSC) measurements were carried out on the Mettler Toledo DSC 822e system under N_2 and at a heating rate of 10 °C/min. UV-visible absorption and fluorescence spectra were measured on a Shimadzu UV-NIR 1601 spectrophotometer and on an Edinburgh F900 luminescence spectrophotometer. Fluorescence lifetimes were recorded on a single-photon-counting spectrometer from Edinburgh Instruments (F900) with a hydrogen-filled pulse lamp as the excitation source. Cyclic voltammetry (CV) measurements were conducted using a three-electrode cell under an argon atmosphere. The polymer films on a glassy carbon electrode (working electrode) were scanned anodically and cathodically in a solution of tetrabutylammonium hexafluorophosphate (n-Bu$_4$NPF$_6$) in acetonitrile (0.1 M) with Ag/AgCl and a platinum wire as the reference and counter electrode, respectively.

2.2. Materials

All manipulations involving air-sensitive reagents were performed in an atmosphere of pure dry N_2 gas. Xylene was purified by routine procedures and distilled under dry N_2 before use. Bipyridine, vinyl carbazole (Aldrich company); 2,5-dibromopyridine, 4,4'-dimethyl-2,2'-dipyridyl, 2,2'-azobisisobutyronitrile (AIBN), methyl methacrylate (MMA), N,N-dimethylformamide (DMF) and other reagents were purchased from J&K Scientific or Shanghai Jingchun Limited Company.

2.3. Synthesis of the complexes

5,5'-dibromo-2,2'-bipyridine (Brbpy) was synthesized according to reference [15]. To the mixture of 2,5-dibromopyridine (1.0 g, 4.2 mmol) and tetrakis (triphenylphosphine) palladium (0.1 g, 0.1 mmol) in a flask, anhydrous and degassed xylene (40 ml) was added from a syringe, followed by hexa-n-butyldistannane (1.5 ml) under N_2 atmosphere. The mixture was heated at 120 °C for several days until all starting materials were consumed. Then the mixture was poured into aqueous EDTA. After the mixture had been stirred, the phase was separated. The aqueous phase was extracted with chloroform and the combined organic phase was dried. After evaporation of the solvents, the crude product was recrystallized from dichloromethane to give white crystals (0.5 g, 38 %). Elemental analysis cacld (%) for $C_{10}N_2H_6Br_2$: C, 38.22 %, H, 1.91 %, N, 8.92 %; found: C, 37.81 %, H, 1.75 %, N, 9.24 %.

Ir(bpy)$_2$Cl: IrCl$_3$.2H$_2$O (1.0 g, 3.0 mmol) and bipyridine (0.93 g, 6.0 mmol) were heated at 120 °C for 12 h in a 2:1 mixture of 2-ethoxyethanol and water under Ar atmosphere. After the mixture had been cooled to 25 °C, the precipitate was filtered off and washed with water and ethanol. The solid was recrystallized from the solution to obtain the orange-red crystals Ir(bpy)$_2$Cl (0.6 g, 37 %). Elemental analysis calcd for Ir(bpy)$_2$Cl: C, 44.48 %, H, 2.96 %, N, 10.38 %; found: C, 44.23 %, H, 3.13 % , N, 10.59 %.

Ir(mbpy)$_2$Cl: The synthesis method is similar to that for Ir(bpy)$_2$Cl; bipyridine was used instead of 4,4'-dimethyl-2,2'-dipyridyl. Elemental analysis calcd (%) for Ir(mbpy)$_2$Cl: C, 48.34 %, H, 4.03 %, N, 9.40 %; found: C, 48.05 %, H, 4.23 %, N, 9.23 %.

Ir(Brbpy)$_2$Cl: The synthesis method was similar to that for Ir(bpy)$_2$Cl; bipyridine was used in-

stead of 5,5'-dibromo-2,2'- bipyridine. Elemental analysis calcd for Ir(Brbpy)$_2$Cl: C, 28.06 %, H, 1.40 %, N, 6.55 %; found: C, 28.31 %, H, 1.68 %, N, 6.79 %.

2.4. Synthesis of copolymers

The copolymerization was carried out in N,N-dimethylformamide with 1 wt.% of 2,2'-azobis-isobutylronitrile (AIBN) as the inititor. A mixture of iridium complex, vinyl-carbazole and methyl methacrylate in a pre-determined molar ratio was allowed to copolymerize under argon atmosphere at 60 °C for 48 h. The resulting solution was poured into an excess volume of methanol under stirring. The precipitate was dissolved in DMF, re-precipitated in methanol twice, and finally dried under reduced pressure. The copolymer products were further purified by Soxhlet extraction with boiling acetone for 24 h, and finally dried in a vacuum oven at 50 °C for 24 h. ^{1}HNMR(CDCl$_3$, 400 MHz) for Ir(mbpy)$_2$Cl/PVK: δ (ppm) 1.40 (3H, CH$_3$), 1.64 (2H, CH$_2$), 2.14 (2H, CH$_2$), 3.70 (1H, –NCH–), 4.20 (3H, COOCH$_3 \rightarrow$ Ir), 7.37, 7.54, 7.65, 7.70, 8.01, 8.18 (carbazole ring-H). The iridium content in the copolymers has been listed in Table 1.

3. Results and discussion

The copolymers were prepared by in-situ copolymerization of vinyl-carbazole, methyl methacrylate and iridium complex. The synthetic route is listed in Fig. 1. The ratio of monomers and yields are listed in Table 1.

Table 1 shows that the M$_n$ (number-average molecular weight) of copolymers are in the range of 8600 – 12000 Da, which is easy to spin the film. The Tg (glass transition temperature) is in the range of 102 – 105 °C and the Td (temperature of 5 % weigh loss) is in the range of 405 – 421 °C, which indicates that the copolymers have high thermal stability for PLED. Fig. 2 shows the IR spectra of the PVK0 and the copolymers with the iridium content of 0.51 wt.%. Compared to the spectrum of PVK0, the characteristic absorption peaks in copolymers containing iridium are similar to those in PVK0. The peaks associated to the vibration of
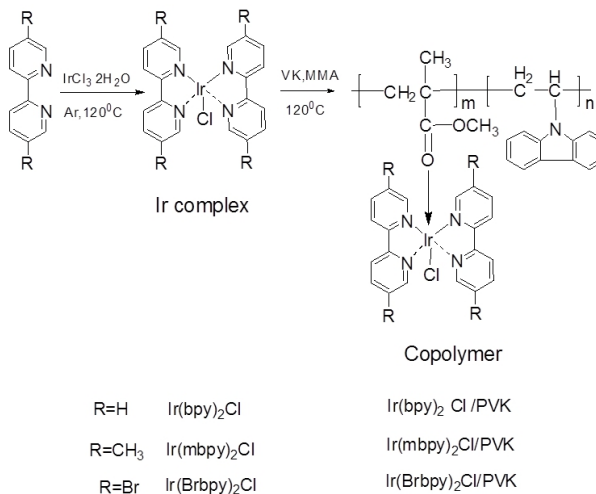

Fig. 1. Synthetic routes of the copolymers.

–COO– in the copolymers containing iridium shift from 1733 to 1724 cm^{-1}, due to the coordination between Ir and C=O. The peaks associated to the vibration of iridium complex do not appear in the copolymers containing iridium because of the low iridium content.
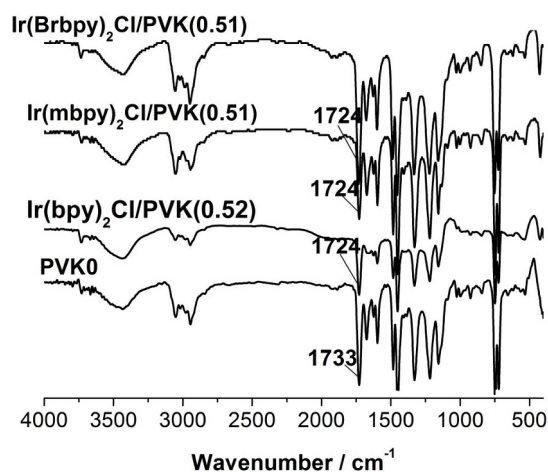

Fig. 2. IR spectra of the copolymers.

3.1. Optical properties

Fig. 3a shows the UV absorption spectra of the copolymers in N,N-dimethylformamide solvent (the concentration is 10^{-4} mol/l). Fig. 3b displays the UV absorption spectra of Ir(mbpy)$_2$Cl/PVK with a different iridium content. In the UV ab-

Table 1. The ratio and the data of monomers and copolymers[a].

Copolymers(Ir content)[b] (wt.%)		Ir complex (mg)	VK (g)	AIBN (mg)	MMA (ml)	Conv.[c] (%)	Tg[d] (°C)	Td[e] (°C)	Mn[f] (Da)	τ[g] (μs)	PDI[f]
	0.26	4.0	0.20	0.41	0.02	73	105	405	9000		1.71
Ir(Brbpy)$_2$Cl /PVK	0.51	7.9	0.20	0.42	0.02	72	103	408	8600		1.82
	0.73	12.0	0.20	0.53	0.02	72	105	407	9100	1.21	1.80
	0.26	3.2	0.20	0.31	0.02	65	106	409	8900		2.01
Ir(mbpy)$_2$Cl /PVK	0.51	6.4	0.20	0.52	0.02	66	102	408	11000		1.89
	0.74	9.6	0.20	0.62	0.02	65	104	410	12000	1.30	1.80
	1.0	12.8	0.20	0.50	0.02	63	105	413	11500		1.91
	0.25	3.0	0.20	0.36	0.02	67	103	412	10050		2.12
Ir(bpy)$_2$ Cl /PVK	0.52	6.0	0.20	0.40	0.02	67	106	415	11200		1.90
	0.73	9.0				67	105	416	9700		1.87
PVK0			0.20	0.34	0.02	60	104	421	8600		2.15

[a]: Copolymerization of N-vinylcarbazole (VC) and methyl metacrylate (MMA) in the presence of iridium complexes carried out in N,N'-dimethylformamide

[b]: Ir content estimated from ICP.

[c]: Conversion rate Conv. is the ratio of the mass of the monomer and polymer.

[d]: Glass transition temperature Tg estimated from DSC.

[e]: Temperature of 5 % weigh loss, Td, measured by TGA

[f]: Number-average molecular weight Mn [Da] and polydispersity index PDI estimated by GPC using poly (styrene) as a standard.

[g]: The luminescence decay time τ monitored at 553 nm.

sorption spectrum of PVK0, the strong absorption band at 295 nm is attributed to $^1A \rightarrow {}^1B_a$ of the carbazole rings, while the two peaks at 328 and 342 nm correspond to the $^1A \rightarrow {}^1L_b$ transition of the carbazole rings [16]. The absorption spectra of the copolymers containing iridium are quite similar to that of PVK0. The absorbance intensity of the copolymers containing iridium is higher than that of PVK0 due to the induction of iridium complex. The absorbance intensity increases with increasing the iridium content. No distinct absorption belonging to the Ir complex is observed because of its low content.

Fig. 4 shows the emission spectra of PVK0 excited at 350 nm and UV-Vis spectra of the Ir complexes. There are two weak broad peaks at around 390 nm and 430 nm appearing in the absorption spectra of the iridium complexes. The absorption peak at around 390 nm can be assigned to the spin-allowed singlet metal-to-ligand charge-transfer (^{1}MLCT)(dπ(Ir)-π*(bpy)) and the peak at 430 nm can be assigned to spin-forbidden triplet metal-to-ligand charge-transfer (^{3}MLCT)(dπ(Ir)-π*(bpy)) transitions owing to the large spin-orbit-coupling induced by the heavy-metal iridium center [17]. It can be seen from Fig. 4 that there is a good spectral overlap between the PL emission spectrum of the host polymer PVK0 and the absorption spectrum of the guest Ir(mbpy)$_2$Cl. The spectral overlap between emission spectrum of PVK0 and the absorption spectrum of Ir(bpy)$_2$Cl is small. According to the Föster mechanism, the dipole-dipole interaction results in efficient transfer of the singlet-excited-state energy from the host to the guest. The efficiency of the Föster energy transfer is dependent on the spectral overlap between the host emission spectrum and the guest absorption spectrum [18]. Therefore, the good overlap ensures efficient Föster energy transfer from the host PVK0 to the guest Ir complex in Ir(mbpy)$_2$Cl/PVK. Fig. 5
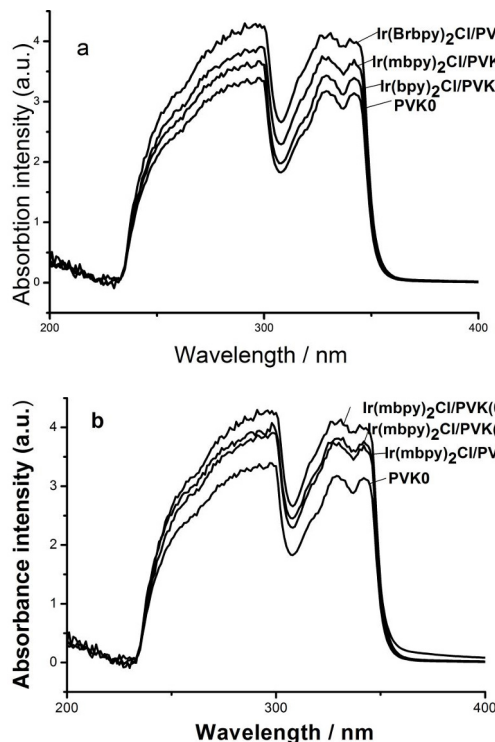
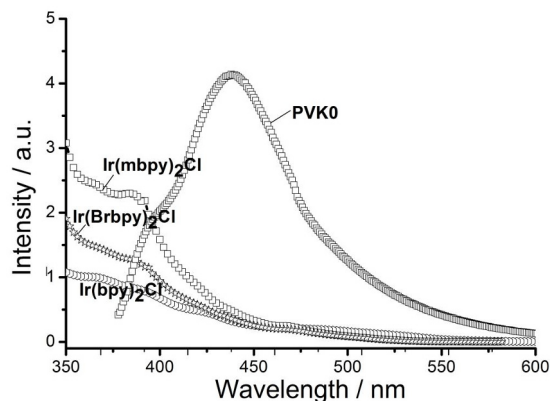Fig. 3. UV absorption spectra of (a) copolymers (b) Ir(mbpy)$_2$Cl/PVK with different iridium content.

Fig. 4. Emission spectra of PVK0 excited at 350 nm and UV-Vis spectra of the Ir complexes.

Fig. 5. Emission spectra of Ir complexes in solvent excited at 370 nm.

shows the emission spectra of Ir complexes in dilute DMF solvent excited at 370 nm. Two of the iridium complexes, Ir(mbpy)$_2$Cl and Ir(Brbpy)$_2$Cl, can emit yellow light with maximum peak at about 563 nm, whereas Ir(bpy)$_2$Cl emits orange light with a maximum peak at 590 nm. These emissions are assigned to Ir-centered ^{3}MLCT emissions [19]. The smaller Stokes shift between emission band (at about 563 nm or 590 nm)) and the lowest energy absorption band (at about 500 nm) in the iridium complexes, suggest that the phosphorescence originates primarily from the ^{3}MLCT state, together perhaps with a less contribution from the $^3\pi$-π^* excited states.

Fig. 6a and 6b show the excitation and the emission spectra of the PVK0 and the copolymers with the iridium content of 0.51 wt.% in the films, respectively. It is shown that the copolymers (Ir(Brbpy)$_2$Cl/PVK and Ir(mbpy)$_2$Cl/PVK) can be excited in the range of 300 – 450 nm. The emission peak at about 429 nm, which is attributed

to the host emission of carbazole rings, appears in the spectra of the copolymers. Compared to the spectra of PVK0, the phosphorescence emission peak at about 553 nm, which is attributed to the characteristic emission of iridium ion only, appears in the spectra of Ir(Brbpy)$_2$Cl/PVK and Ir(mbpy)$_2$Cl/PVK. However, the relative emission intensity at 553 nm of Ir(mbpy)$_2$Cl/PVK is stronger than that of Ir(Brbpy)$_2$Cl/PVK in the film because of the existence of efficient energy transfer from the host PVK0 to the guest Ir(mbpy)$_2$Cl. The emission peak at 553 nm does not appear in the spectra of Ir(bpy)$_2$Cl/PVK. These results are consistent with the spectral overlap between the host emission spectrum and the guest absorption spectrum.

Compared to Ir(Brbpy)$_2$Cl and Ir(mbpy)$_2$Cl with emission wavelength at 563 nm, the emissions
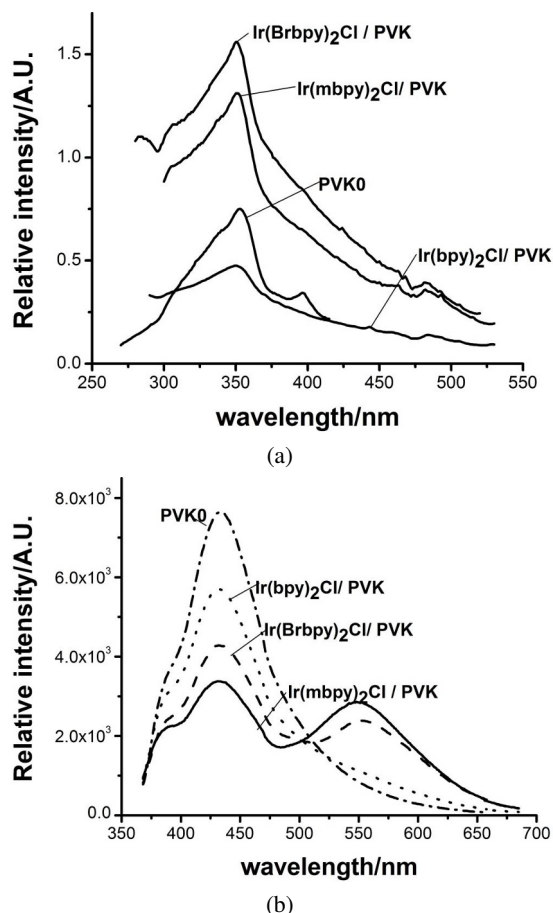
Fig. 6. PL spectra of the copolymers in the film (a) excitation spectra of copolymers recorded by monitoring the emission at the wavelength of 553 nm (b) emission spectra of copolymers recorded at the excitation by the wavelength of 370 nm.

of ^{3}MLCT based on the interaction of copolymers (Ir(Brbpy)$_2$Cl/PVK and Ir(mbpy)$_2$Cl/PVK) are observed and blue-shifted significantly. This is correlated with the coordination of iridium and carbonyl of MMA during copolymerization and the different states.

Fig. 7 shows the emission spectra of Ir(mbpy)$_2$Cl/PVK with a different iridium content in the film. There is a strong blue emission peak (at around 429 nm) in the spectrum when the iridium content is only 0.26 wt.%. With the iridium content increased to 0.51 wt.%, the blue emission peak becomes less-intense and the yellow phosphorescence emission peak (at around 553 nm) becomes dominant. When the content increases to 1.0 wt.%,

the blue emission peak almost disappears, only the yellow emission appears. These observations suggest that efficient energy transfer from the host to the guest takes place and the intensity increases with increasing Ir content. Thus, the emission color of copolymers can be adjusted by choosing the proper Ir complex and changing its content. Because the yellow emission and blue emission are the complementary lights, these copolymers can be the candidate materials applied in the white polymer light-emitting diodes. Moreover, the observed lifetimes of these copolymers recorded at around 553 nm are in the range of 1.21 – 1.35 μs in the films, indicating the triplet nature of the emission peak. The luminescence decay times are summarized in Table 1.
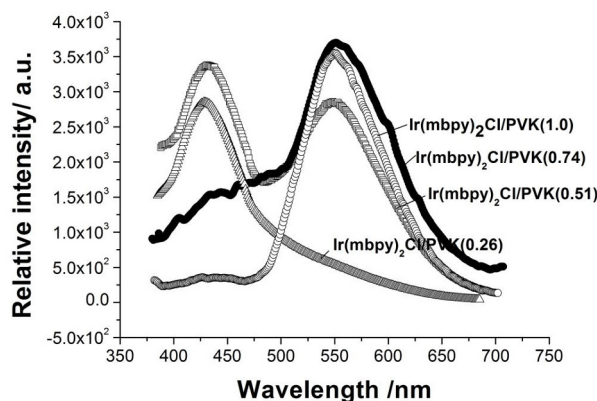

Fig. 7. Emission spectra of Ir(mbpy)$_2$Cl/PVK with different iridium content in the film, excited at 370 nm.

3.2. Electrochemical properties

Matching of the valence band (or the highest occupied molecular orbital (HOMO)) and conduction band (or the lowest unoccupied molecular orbital (LUMO)) energy levels of the active material to the work functions of the corresponding cathode and anode is important for the performance of a light emitting device. Cyclic voltammetry (CV) is an effective method for exploring the relative ionization and reduction potentials. Fig. 8 shows the cyclic voltammograms of Ir(mbpy)$_2$Cl/PVK(1.0). In the applied potential range between −2.0 V and 2.0 V, a irreversible peak and a reversible reduction-oxidation peaks appear in the copolymer

Ir(mbpy)$_2$Cl/PVK(1.0). The onset oxidation potential (E_{onset}(ox)) is 1.48 V and onset reduction potential (E_{onset}(red)) is -1.20 V. It is suggested that the copolymer containing iridium has better electron injection and transporting properties due to the incorporation of charged Ir complex into the copolymer.
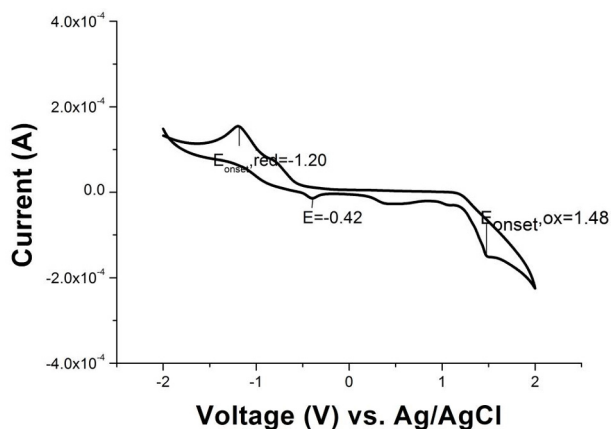

Fig. 8. CV curve of Ir(mbpy)$_2$Cl/PVK(1.0) in 0.1M n-Bu$_4$NPF$_6$/acetonitrile.

The HOMO and LUMO energy levels of the polymer materials can be calculated from the E_{onset}(ox) and E_{onset}(red), based on the reference energy level of ferrocene (4.8 eV below the vacuum level) [20, 21]:

$$HOMO = E_{onset}(ox) + 4.8 - E_{Foc} \qquad (1)$$

$$LUMO = E_{onset}(red) + 4.8 - E_{Foc} \qquad (2)$$

wherein E_{Foc} is the potential of Foc(ferrocene)/Foc$^+$ vs. Ag/AgCl. The value of E_{Foc} is 0.40 V. According to the Eq. 1 and Eq. 2, HOMO level of Ir(mbpy)$_2$Cl/PVK(1.0) is estimated to be about 5.88 eV, and LUMO level to be about 3.2 eV. As a result, it may be a good candidate as a electrophosphorescent material for application in PLED.

4. Conclusions

A series of copolymers containing carbazole unit and iridium complex were synthesized via radical copolymerization of N-vinylcarbazole, methyl methacrylate and iridium complex. The copolymers have the Mn of 8600 – 12000 Da and the Td of 405 – 421 °C. It indicates that the copolymers have the high thermal stability for PLED. The optical properties suggest that efficient energy transfer from the host (PVK0) to the guest (iridium complex) takes place and the emission intensity increases with increasing Ir content. By choosing the proper Ir complex and changing the content of Ir complex, these copolymers can emit yellow, blue or blue-yellow emission under UV-visible light in film. Moreover, the observed lifetimes of the copolymers recorded at around 553 nm are in the range of 1.21 – 1.35 μs in the film indicating the triplet nature of the emission peak. Thus, these copolymers are potential candidates for yellow or blue phosphorescent materials applied in the white polymer light emitting diodes.

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