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1. Introduction

Driven by the promising applications of near-infrared (NIR) organic/ polymer light-emitting diodes (NIR-OLEDs/PLEDs) in night-vision and information-security displays,¹ telecommunications² and photodynamic therapies,³ concerted efforts have been devoted to the development of new and efficient NIR-emitters. In this context, owing to the harvesting of both singlet and triplet excitons towards a theoretical η_{IQE} (internal quantum efficiency) of 100%, NIR-emissive transition-metal (Pt(II), Ir(III) or Os(II), *etc.*) complex phosphors⁴ together with TADF (thermal activated delayed fluorescence) molecules⁵ capable of the facilitated reverse intersystem crossing (RISC) are highly attractive. Importantly, the octahedral Ir(III)-complexes with rather short triplet lifetimes and high efficiency which is competitive to those of

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High-performance near-infrared (NIR) polymer light-emitting diodes (PLEDs) based on bipolar Ir(III)-complex-grafted polymers†

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Despite the cost-effective and large-area scalable advantages of NIR-PLEDs based on iridium(III)complex-doped polymers, the intrinsic phase-separation issue leading to inferior device performance is difficult to address. In this study, taking the vinyl-functionalized **[Ir(igbt)₂(vb-ppy)]** (Hqibt = 1-(benzo[*b*]thiophen-2-yl)-isoquinoline; **vb-Hppy** = 2-(4'-vinylbiphenyl-4-yl)pyridine) as the polymerized complex monomer, two series of Ir(III)-complex-grafted polymers **Poly(NVK-co-[Ir(iqbt)₂(vb-ppy)]**) and **Poly((vinyl-PBD)-co-NVK-co-[Ir(iqbt)₂(vb-ppy)]**) (NVK = *N*-vinyl-carbazole; **vinyl-PBD** = 2-(4-(*tert*-butyl)phenyl)-5-(4'-vinyl-[1,1'-biphenyl]-4-yl)-2,5-dihydro-1,3,4-oxadiazole) are obtained, respectively. Moreover, by using the bipolar Ir(III)-complex-grafted polymer further doped or grafted with an electron-transport unit as the emitting layer (EML), reliable NIR-PLEDs are realized. In particular based on the concurrent covalentlinkages of both the Ir(III)-complex and the **vinyl-PBD** towards the carrier-balanced **NIR-PLED-III**, the achievement of an almost negligible (<5%) efficiency roll-off does not sacrifice the attractive efficiency (η_{EOE}^{max} = 3.6%). This finding makes bipolar Ir(III)-complex-grafted polymers a good platform to achieve high-performance NIR-PLEDs.

> other triplet-utilized counterparts, together with the superiority of a significantly alleviated efficiency roll-off, have particular appeal for application in NIR-OLEDs/PLEDs.

> Until now, concrete C^N-cyclometalated Ir(III)-complexes possessing neutral $[Ir(C^N)_3]$ -homoleptic⁶ or $[Ir(C^N)_2(L^X)]$ heteroleptic ($L^X = O^O^7$ or N^O^8) and cationic $[Ir(C^N)_2(N^N)]^+$ forms9 have been demonstrated for developing reliable NIR-OLEDs/PLEDs, and the wavelength- η_{EOE} (external quantum efficiency) relationship is summarized in Fig. 1 and Table S1 (ESI⁺). Nonetheless, as constrained by the so-called "energy gap law",¹⁰ it remains a real challenge to develop new Ir(III)-complex-based NIR-emitters to achieve high efficiency. On the other hand, to suppress the detrimental triplet-triplet annihilation (TTA)¹¹ of the Ir(m)-complex-based phosphors with narrow HOMO-LUMO band-gaps for the NIR emissions, it is necessary and also challenging to dope one specific Ir(m)-complex into an appropriate small-molecule host for the vacuum-deposited/solutionprocessed NIR-OLED (NIR-OLEDs-V/S) or polymeric matrix for the NIR-PLEDs (Table S1, ESI⁺ and Fig. 1), respectively. In comparison, although cost-effective solution-processed NIR-PLEDs with Ir(m)-complex-doped polymers as the EMLs are more advantageous for the large-area scalability, the simple doping suffers from an inevitable phase-separation issue,¹² thereby leading to inferior device efficiency and serious efficiency roll-off. Noticeably, despite the certain efficiency progress

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Fig. 1 The λ_{em} -relative η_{EQE} comparison between the NIR-PLEDs-I-III in this work with those from Ir^{3+} -complexes doping in small-molecular or polymer host with vacuum-deposition (NIR-OLEDs-V) or solution-processing (NIR-OLEDs-S/PLEDs).

appreciable from the supplementation of one electron-transport layer (ETL) towards the facilitated carriers' balance for some multilayer NIR-PLEDs,¹² the issues of device instability and undesirable efficiency-roll-off caused by the heterogeneity of the Ir(m)-complexdoping polymer systems are still difficult to address.

To circumvent such problems, to some extent, we can rely on a conceptual approach to use Ir(m)-complex-grafted polymers in solution-processed multi-layer NIR-PLEDs. On one hand, benefiting from the covalent-bonding linkage, the NIR-emitting Ir(m)complexes are molecularly dispersed into a hole-transporting polymer host with a uniform phase. Meanwhile, further through the doping or grafting of the electron-transport molecule, the resultant Ir(m)-complex-grafted polymers could exhibit a bipolar (electron/hole-transport ability) nature. In particular, through the smooth feeding ratio tuning of both the Ir(m)-complex and electron-transport molecule into the hole-transport polymer matrix, much room can be achieved to facilely reform the carrier's balance within the bipolar polymer towards an optimized optoelectronic feature. Noticeably, although bipolar Ir(m)-complexgrafted polymers capable of showing monochromatic¹³ or panchromatic¹⁴ emission in the visible-light range are achieved, no examples of their fabrication for NIR-PLEDs, to our knowledge, have been reported. Herein, taking the NIR-emitting [Ir(igbt)2(vbppy)] with one vinyl group as the polymerizable complex monomer, as shown in Scheme 1, two series of Ir(m)-complex-grafted polymers Poly(NVK-co-[Ir(igbt)₂(vb-ppy)]) (100:1, 150:1 or 200:1) and Poly((vinyl-PBD)-co-NVK-co-[Ir(iqbt)₂(vb-ppy)]) (15:150:1) are obtained from its copolymerization with NVK and/or monomer vinyl-PBD with the facilitated electron-transport, respectively. Moreover, using the Ir(m)-complex-grafted polymer doped or grafted with an electron-transport molecule as the EML, respectively, the first-examples of bipolar Ir(m)-complex-grafted NIR-PLEDs are also pursued.

2. Experimental section

The information on starting materials and general characterization methods is provided in the ESI.^{\dagger} The HC^{N1} main ligand **Hiqbt** was synthesized by the Suzuki coupling of 2-Cl-isoquinoline with benzo[*b*]thien-2-yl boronic acid as reported in our recent literature.^{8e} As to the μ -chloro-bridged dimeric intermediate [**Ir(iqbt**)₂(μ -Cl)]₂, it was prepared according to the typical Nonoyama procedure.¹⁵ For the vinyl-functionalized HC^N² ancillary ligand **vb-Hppy**, it was synthesized from the improved Suzuki coupling reaction of 4-vinylphenyl-boronic acid with 2-(4-bromophenyl)-pyridine as in the literature.¹⁶ The vinyl-modified electron-transport monomer **vinyl-PBD** was obtained through the dehydration cyclization¹⁷ and the subsequent Suzuki coupling reaction.¹⁸

Synthesis of the vinyl-functionalized complex monomer [Ir(iqbt)₂(vb-ppy)]

To a solution of the µ-chloro-bridged dimeric intermediate [Ir(iqbt)₂(µ-Cl)]₂ (270 mg, 0.18 mmol) in mixed solvents of CH₂Cl₂ (8 mL) and MeOH (4 mL), the synthesized vb-Hppy (139 mg, 0.54 mmol) and AgCF₃SO₃ (138 mg, 0.54 mmol) were added, and the mixture was heated at 45 °C under a dry N₂ atmosphere for 24 h. After cooling to room temperature, the white solid was removed and the residue was purified by column chromatography on silica gel using CH2Cl2/acetonitrile (v/v = 2:1) as the eluent. Yield: 35 mg (20%). Calc. for C₅₃H₃₄IrN₃S₂: C, 65.68; H, 3.54; N, 4.34%. Found: C, 65.63; H, 3.58; N, 4.30%. FT-IR (KBr, cm⁻¹): 3051 (w), 2953 (m), 2918 (m), 2851 (m), 2359 (w), 1618 (w), 1601 (w), 1582 (w), 1558 (w), 1541 (w), 1501 (w), 1468 (w), 1452 (w), 1435 (m), 1412 (s), 1375 (w), 1360 (w), 1335 (m), 1306 (w), 1288 (w), 1273 (w), 1231 (m), 1157 (w), 1148 (w), 1124 (w), 1067 (w), 1040 (w), 1020 (w), 988 (w), 962 (w), 910 (m), 862 (w), 845 (w), 806 (m), 779 (w), 760 (m), 727 (vs), 706 (w), 687 (s), 662 (m), 633 (w), 598 (w), 565 (w), 528 (w), 500 (w). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.27 (d, 1H, -Py), 8.80 (d, 1H, -Py), 8.51 (d, 1H, -Py), 8.06 (d, 1H, -Py), 8.02 (d, 1H, -Py), 7.95 (m, 7H, -Ph), 7.84 (t, 2H, -Ph), 7.69 (t, 2H, -Ph), 7.64 (d, 1H, -Py), 7.61 (d, 2H, -Ph), 7.58 (d, 1H, -Py), 7.53 (t, 2H, -Ph), 7.49 (d, 1H, -Ph), 7.39 (d, 1H, -Ph), 7.23 (d, 1H, -Ph), 7.17 (m, 2H, -Ph), 7.11 (t, 1H, -Ph), 6.88 (t, 2H, -Ph), 6.82 (t, 1H, -Ph), 6.66 (t, 1H, -CH=), 5.65 (d, 1H, =CH₂), 5.15 $(d_1H) = CH_2$. ESI-MS (in CH_2Cl_2) m/z: 970.21 (100%), $[M + H]^+$.

Synthesis of the Ir³⁺-complex-grafted polymers Poly(NVK-co-[Ir(iqbt)₂(vb-ppy)]) (100:1, 150:1 or 200:1)

A mixture of NVK and the complex monomer $[Ir(iqbt)_2(vb-ppy)]$ at a stipulated feed molar ratio (100:1, 150:1 or 200:1) in the presence of AIBN (azobis(isobutyronitrile); 1.5 mol% of NVK) was dissolved in toluene (30 mL), and the resultant homogeneous solution was purged with N₂ for 10 min and sealed under a reduced N₂ atmosphere. The reaction mixture was heated to 80 °C with continuous stirring for 48 h. The viscous mixture was diluted with toluene (15 mL) and precipitated with *n*-hexane (50 mL) three times. The resulting solid products were collected by filtration and dried at 45 °C under vacuum to constant weight, respectively. For **Poly(NVK-co-Ir(iqbt)_2(vb-ppy))** (150:1): yield: 92%. FT-IR (KBr, cm⁻¹): 3059 (w), 2968 (w), 2934 (w), 2359 (w), 1597 (w), 1483 (m), 1450 (s), 1325 (m), 1223 (m), 1157 (w), 1124 (w), 1028 (w), 1003 (w), 926 (w), 829 (w), 745 (vs), 721 (s),



Scheme 1 Synthetic scheme of the ligands Hiqbt, vb-Hppy, and vinyl-PBD, the complex monomer [Ir(iqbt)₂(vb-ppy)] and their two series of Ir³⁺- complex-grafted polymers Poly(NVK-co-[Ir(iqbt)₂(vb-ppy)]) and Poly((vinyl-PBD)-co-NVK-co-[Ir(iqbt)₂(vb-ppy)]).

617 (w), 567 (w), 528 (w). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 9.24 (m, 3H, -Ph), 8.10–6.04 (br, 1100H + 26H), 5.52–2.75 (br, 138H), 2.38 (b, 1H), 1.65 (b, 2H), 1.30–0.88 (b, 276H). XPS result: 0.80 mol% *versus* NVK. The characterization of the other Ir³⁺-complex-grafted polymers **Poly**(**NVK-co-[Ir(iqbt)₂(vb-ppy)]**) (100:1 or 200:1) is provided in the ESI.†

Synthesis of the bipolar Ir³⁺-polymer Poly((vinyl-PBD)-co-NVKco-[Ir(iqbt)₂(vb-ppy)]) (15:150:1)

The bipolar Ir^{3+} -polymer Poly((vinyl-PBD)-co-NVK-co-[Ir(iqbt)₂(vb-ppy)]) (15:150:1) was synthesized in the same way as the Poly(NVK-co-[Ir(iqbt)₂(vb-ppy)]) (150:1) except that the mixture of the organic monomer vinyl-PBD, NVK and the complex monomer [Ir(iqbt)₂(vb-ppy)] at a stipulated feed molar ratio of 15:150:1 (1.5 mol% of AIBN relative to NVK) instead of the mixture of NVK and the complex monomer [Ir(iqbt)₂(vb-ppy)] at a feeding ratio of 150:1 (1.5 mol% of AIBN relative to NVK) was adopted. For Poly((vinyl-PBD)-co-NVK-co-[Ir(iqbt)₂(vb-ppy)]) (15:150:1): yield: 91%. FT-IR (KBr, cm⁻¹): 3051 (w), 2963 (w), 2932 (w), 2354 (w), 1598 (w), 1483 (m), 1452 (s), 1333 (m), 1225 (m), 1157 (w), 1124 (w), 1027 (w), 1003 (w), 924 (w), 829 (w), 742 (vs), 723 (s), 616 (w), 568 (w), 529 (w). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.13–5.93 (br, 1135H), 4.92–2.39 (b, 135H), 1.59 (s, 135H), 1.28–0.91 (b, 270H). XPS result: 0.78 mol% *versus* NVK.

Device designs of the doping-type NIR-PLED-I based on the Ir³⁺-complex monomer and the grafting-type NIR-PLEDs-II–III based on the Ir³⁺-polymers

Using a mixture of the complex monomer [Ir(iqbt)₂(vb-ppy)] (5 wt%) and the co-host PVK : PBD (65 : 30, wt%; PVK = poly(*N*vinyl-carbazole), PBD = (2-(4-*tert*-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole)) as the EML, the doping-type **NIR-PLED-I** was fabricated with the configuration of ITO/PEDOT:PSS (40 nm)/ PVK:PBD:[Ir(iqbt)₂(vb-ppy)] (120 nm)/TmPyPB (15 nm)/LiF (1 nm)/Al (100 nm) for comparison. As to the grafting-type **NIR-PLEDs-II-III**, they were fabricated with the configurations of ITO/PEDOT:PSS (40 nm)/**Poly(NVK-co-[Ir(iqbt)₂(vb-ppy)]**) (150:1):PBD (30 wt%) (120 nm)/TmPyPB (15 nm)/LiF (1 nm)/ Al (100 nm) and ITO/PEDOT:PSS (40 nm)/**Poly((vinyl-PBD)-co-NVK-co-[Ir(iqbt)₂(vinyl-ppy)])** (15:150:1) (120 nm)/TmPyPB (15 nm)/LiF (1 nm)/Al (100 nm), respectively. Their difference lies in the usage of PVK:PBD:[**Ir(iqbt)₂(vb-ppy)**] for the **NIR-PLED-I, Poly(NVK-co-[Ir(iqbt)₂(vb-ppy)])** (150:1):PBD for the **NIR-PLED-II** or **Poly((vinyl-PBD)-co-NVK-co-[Ir(iqbt)₂(vb-ppy)])** (15:150:1) for the **NIR-PLED-III**, respectively. TmPyPB (1,3,5tri[(3-pyridyl)-phen-3-yl]benzene) was used to further promote the electron-transport ability in the **NIR-PLEDs-I-III**. Details of the series of NIR-PLED fabrication and their testing are presented in the ESI.[†]

3. Results and discussion

Synthesis, characterization and photo-physical properties of the Ir³⁺-complex monomer [Ir(iqbt)₂(vb-ppy)]

Through the improved Suzuki coupling reaction^{8e} of 2-Cl-isoquinoline (instead of 2-Br-isoquinoline^{7g}) with benzo[*b*]thien-2-yl boronic acid, the synthesized HC^N¹ main ligand **Hiqbt** was cyclometalated with IrCl₃·*n*H₂O to give the μ -chloro-bridged dimeric intermediate [**Ir(iqbt**)₂(μ -Cl)]₂ as specified in the literature.¹⁵ Also as shown in Scheme 1, further based on the cyclometalation of the intermediate [**Ir(iqbt**)₂(μ -Cl)]₂ with another vinyl-functionalized HC^N² ancillary **vb**-Hppy by AgCF₃SO₃, the chloride-free, vinyl-functionalized [Ir(C^N¹)₂(C^N²)] complex monomer [**Ir(iqbt**)₂(**vb**-ppy)] was obtained.

The vinyl-functionalized complex monomer $[Ir(iqbt)_2(vb-ppy)]$ was well characterized *via* EA, FT-IR, ¹H NMR and ESI-MS, despite the failure to produce its single-crystals. Evidently, in the ¹H NMR spectrum (Fig. S1, ESI†) of the complex monomer $[Ir(iqbt)_2(vb-ppy)]$, the stipulated molar ratio of 2:1 between the C^N¹ (iqbt)⁻ and the C^N² (vb-ppy)⁻ proton resonances confirms its desirable $[Ir(C^N^1)_2(C^N^2)]$ component. Meanwhile, attributed to the incorporation of the asymmetric vinyl-functionalized HC^N² ancillary vb-Hppy, the point group of its complex monomer $[Ir(iqbt)_2(vb-ppy)]$ is C_1 , from which the two sets of doublet peaks at $\delta = 8.80$ and

Paper

8.51 ppm can be safely assigned to the two protons on the C atoms adjacent to N atoms in the pyridyl rings of the two $(iqbt)^{-}$ -C^N¹ ligands, respectively. Moreover, upon the Ir(m)-coordination, besides the double signal ($\delta = 9.27$ ppm) of the proton on the C atom adjacent to N atoms in the pyridyl ring of the (vb-ppy)⁻-C^N² ligand being significantly down-field shifted compared to that ($\delta = 8.70$ ppm) for the free vb-Hppy, the slightly high-field shifts ($\delta = 6.66, 5.65$ and 5.15 ppm) of the vinyl-terminal proton resonances for the complex monomer [Ir(iqbt)₂(vb-ppy)] relative to those ($\delta = 6.78, 5.82$ and 5.30 ppm) of the free vb-Hppy further verify the successful vinyl-modification. Furthermore, the ESI-MS result of the complex monomer [Ir(iqbt)₂(vb-ppy)] exhibits the strongest mass peak at m/z 970.21 assigned to the major species [M + H]⁺, indicating that its [Ir(C^N¹)₂(C^N²)]-characteristic unit can remain stable in solution.

The photo-physical properties of the complex monomer [Ir(iqbt)2(vb-ppy)] were examined in degassed solution at RT or 77 K, and the results are summarized in Table S2 (ESI⁺) and Fig. 2. As shown in Fig. 2, in contrast to the limited ($\lambda_{ab} < 400$ nm; Fig. S2, ESI†) absorptions of the two kinds of C^N ligands, the complex monomer [Ir(igbt)₂(vb-ppy)] exhibits significantly broadened UV-visible-NIR absorption: intense absorption bands below 420 nm from the intraligand π - π * transitions, moderate absorption bands (λ_{ab} = 456, 487 (sh), 518 and 557 (sh) nm) assigned to the $^{1,3}LLCT/^{1,3}MLCT$ -admixed (LLCT = ligand-to-ligand charge transfer; MLCT = metal-to-ligand charge transfer) transitions, and weak bands extending over 600 nm probably from the $S_0 \rightarrow T_1$ excitation. Upon photoexcitation at λ_{ex} = 463 nm, the complex monomer [Ir(iqbt)₂(vb**ppy**)] displays a strong NIR emission (58% of the $\lambda_{\rm em} \geq$ 700 nm proportion) peaking at 693 nm with a shoulder at 754 nm (Fig. 2). In contrast to the non-emissive character $(\lambda_{em} = 415 \text{ nm for the HC}^{N^1} \text{ ligand Hight and } \lambda_{em} = 403 \text{ nm}$ for the HC^N² ligand **vb-Hppy**; Fig. S2, ESI^{\dagger}) of the two C^N ligands in the NIR range, the NIR emission of the complex monomer [Ir(iqbt)₂(vb-ppy)] should originate from the Ir³⁺induced T1 state. Moreover, the time-decayed monoexponential lifetime of 0.25 µs (Fig. S3, ESI†) was obtained at $\lambda_{em} = 693$ nm for the complex monomer [Ir(iqbt)₂(vb-ppy)] species, confirming the intrinsic NIR-phosphorescent nature.

Noticeably, the NIR-emissive lifetime ($\tau = 0.25 \ \mu s$) is remarkably shorter than those of the heteroleptic Ir³⁺-complexes $[Ir(iqbt)_2(O^O)]^{7d,g}$ or $[Ir(iqbt)_2(N^O)]^{8e}$ which should be originated from the stronger π -backbonding effect¹⁹ due to the asymmetric C^{N²}-(**vb-ppy**) ancillary π -donor in the complex monomer [Ir(iqbt)₂(vb-ppy)] with a restricted vibronic motion to the NIR-emitting excited-state. Accordingly, owing to the large radiative rate constant ($k_r = 7.6 \times 10^5 \text{ s}^{-1}$), its NIRemissive efficiency of Φ_{PL} = 0.19 is realized. Furthermore, as illustrated for the emission (85% of the $\lambda_{\rm em} \geq$ 700 nm proportion; Fig. 2) with a well-resolved vibronic structure at 77 K, the 0-0 transition at 704 nm and the 0-1 transition at 764 nm with small bathochromic shifts compared to the RT one (Fig. 2) give a Huang–Rhys factor (S_M) of 0.98, suggesting that the complex monomer [Ir(iqbt)₂(vb-ppy)] has a weak geometry distortion²⁰ of the T₁ state relative to the ground state. As a result, the thermal gravimetric (TG; Fig. S4, ESI[†]) analysis reveals that the complex monomer [Ir(iqbt)2(vb-ppy)] exhibits a desirably good thermal stability with a comparable decomposition temperature (T_d , with 5 wt% weight loss) of 384 °C to those of typical $[Ir(C^N)_3]$ -homoleptic⁶ complexes.

Electronic structure calculations of the complex monomer [Ir(iqbt)₂(vb-ppy)]

To explore the absorption nature of the complex monomer [Ir(iqbt)₂(vb-ppy)], DFT/TD-DFT (time-dependent density functional theory) calculations based on its optimized S₀ geometry were performed, and the results are summarized in Table S3 (ESI[†]) and Fig. 3. As shown in Fig. 3, in contrast to the almost entire contribution (92.76%) from one C^N^1 -(igbt)⁻ main ligand to the LUMO, the HOMO is mainly (51.01% and 23.06%) localized at the two C^N¹-(igbt)⁻ main ligands and accompanied by the substantial (23.73%) contribution from the Ir(III)-centre and less (2.20%) contribution from the C^N^2 -(vb-ppy)⁻ ancillary ligand. However, different from the dominant (84.71%) contribution from one C^N¹-(iqbt)⁻ main ligand and the more substantial (10.22%) contribution from the C^N^2 -(vb-ppy)⁻ ancillary ligand to the LUMO+1, the LUMO+2 is predominantly (86.93%) located at the C^N^2 -(vb-ppy)⁻ ancillary ligand. Meanwhile, besides the prevalent (74.44%) contribution from the two C^N¹-(iqbt)⁻ main



Fig. 2 Normalized UV-visible-NIR absorption and emission spectra for [lr(iqbt)₂(vb-ppy)] (λ_{ex} = 463 nm) in degassed CH₂Cl₂ solution and PVK-PBD (65:30, weight ratio; λ_{ex} = 273 nm) in film at RT or 77 K.



Fig. 3 The HOMO and LUMO patterns for the complex monomer $[lr(iqbt)_2(vb-ppy)]$ based on its optimized S0 geometry.

ligands to the HOMO-2 like the HOMO-1 (97.79%), some substantial contributions from the Ir(III)-centre (14.59%) and the C^N²-(vb-ppy)⁻ ancillary ligand (10.97%) are observed. Further checking from Table S3 (ESI^{\dagger}), the calculated S₀ \rightarrow S_n (n = 1-4) transition absorption wavelengths of the complex monomer [Ir(iqbt)₂(vb-ppy)] are predicted at 558, 512, 489 and 445 nm, respectively. For the S_0 \rightarrow S_1 transition absorption at 558 nm, the population analysis of the HOMO \rightarrow LUMO (97.64%) transition verifies the partial (22.7%) ¹MLCT, the substantial (21.6%) ¹ILCT (intraligand charge transfer) and the dominant (51.4%) ¹LLCT feature from the π orbitals of one C^N^1 -(iqbt)⁻ main ligand to the π^* orbitals of the other one. The calculated absorption peak at 512 nm, 489 nm or 445 nm mainly results from the corresponding HOMO \rightarrow LUMO+1 (95.32%), HOMO \rightarrow LUMO+2 (97.26%) or HOMO-1 \rightarrow LUMO (76.73%) transition, respectively, also exhibiting the ¹LLCT/¹MLCTadmixed character. Hence, all the calculated absorptions featuring ¹LLCT/¹MLCT-admixed transitions are in good agreement with the experimental data (λ_{ab} = 557, 518, 487 and 456 nm) of the complex monomer [Ir(iqbt)₂(vb-ppy)] in solution. Interestingly, due to the large contribution combined from the HOMO \rightarrow LUMO (59.94%) and the HOMO-1 \rightarrow LUMO (30.32%) transitions to the T₁ state, the experimental $S_0 \rightarrow T_1$ absorption (over 600 nm) transition can be reasonably assigned to the ³ILCT/³MLCT/³LLCT-admixed transitions.

In order to definitely elucidate the NIR-emissive behaviour of the complex monomer [**Ir**(**iqbt**)₂(**vb-ppy**)], natural transition orbital (NTO; Table S4 (ESI[†]) and Fig. 4) calculations were further performed on its optimized T₁ geometry, where based on the entire (100%) hole \rightarrow particle transition, the ³ILCT dominated (73.8%) and the less prevalent (13.9%) ³MLCT transitions are responsible for its NIR-emitting phosphorescence.

Synthesis, characterization and photo-physical properties of the two series of Ir³⁺-complex-grafted polymers

Considering the excellent physical properties (high thermal stability, good mechanical intensity and excellent spin-coated film-formability, *etc.*) of the semi-conducting PVK as a popular polymer host,²¹ the grafting-type Ir^{3+} -polymers **Poly(NVK-co-**[**Ir(iqbt)**₂(**vb-ppy**)]) with different feeding ratios (100:1, 150:1 or 200:1) were synthesized from the AIBN-initiated copolymerization (Scheme 1) of NVK and the complex monomer [**Ir(iqbt)**₂(**vb-ppy**)]. As a matter of fact, not only does the PVK host function as a hole-transport matrix, it with the significantly higher T₁ level also acts as an effective energy donor to



Fig. 4 The NTO pattern for the $T_1 \rightarrow S_0$ emission of the complex monomer $[lr(iqbt)_2(vb-ppy)]$ based on its optimized T_1 geometry.

transfer energy *via* the Förster mechanism²² to the low energystate Ir³⁺-complex-acceptor. Moreover, to further overcome the electron-transport deficiency of the Ir³⁺-polymer **Poly(NVK-co-**[Ir(iqbt)₂(vb-ppy)]), another grafting-type Ir³⁺-polymer **Poly((vinyl-PBD)-co-NVK-co-**[Ir(iqbt)₂(vb-ppy)]) (also Scheme 1) was designed, where through the AIBN-assisted ternary copolymerization of NVK, the complex monomer [Ir(iqbt)₂(vb-ppy)] and the electron-transport monomer vinyl-PBD, the bipolar (electron/ hole-transport) Ir³⁺-polymer **Poly((vinyl-PBD)-co-NVK-co-**[Ir(iqbt)₂(vb-ppy)]) (15:150:1) was obtained.

To verify the AIBN-assisted radical copolymerization,²³ both series of grafting-type Ir³⁺-polymers were characterized by FT-IR, ¹H NMR and GPC (gel permeation chromatography) methods. On one hand, in the ¹H NMR spectrum (Fig. S1, ESI⁺) of the representative $Poly(NVK-co-[Ir(iqbt)_2(vb-ppy)]) (150:1)$ or Poly((vinyl-PBD)-co-NVK-co-[Ir(iqbt)₂(vb-ppy)]) (15:150:1), the presence of the broadened proton resonances of the polymerized [Ir(iqbt)₂(vb-ppy)], NVK and/or vinyl-PBD, together with the disappearance of their original vinyl-characteristic proton resonances, indicate that the complex monomer [Ir(iqbt)₂(vb-ppy)] and/or the vinyl-PBD are actually covalent-bonded into the corresponding PVK backbone. On the other hand, GPC results (Table S5, ESI⁺) show that all the PDIs (PDI = M_w/M_n) with different feed molar ratios for the two kinds of the grafting-type Ir^{3+} -polymers are in a relatively narrow range (<1.30) due to the AIBN-initiated radical copolymerization.²³ Moreover, with regard to the actual Ir³⁺-complex-grafting content, the XPS (X-ray photoelectron spectroscopy) quantitative analyses reveal that every Ir³⁺-complex-grafting content is found to be slightly higher than the corresponding initial feeding ratio, which probably arises from the loss of oligomeric PVK during the isolation of one specific Ir³⁺polymer.²⁴ Furthermore, the PXRD (powder X-ray diffraction) pattern (Fig. S5, ESI⁺) of either Poly(NVK-co-[Ir(iqbt)₂(vb-ppy)]) or Poly((vinyl-PBD)-co-NVK-co-[Ir(iqbt)2(vb-ppy)]) just exhibits the PVK-based amorphous peaks, suggesting the low-concentration homogeneous dispersion of the monomers [Ir(iqbt)2(vb-ppy)] and/or vinyl-PBD into the PVK backbone. TG and DSC (differential scanning calorimetry; Fig. S4, ESI[†]) results of these grafting-type Ir³⁺-polymers show that an improved $(T_d; > 400 \,^{\circ}\text{C})$ thermal stability over that (384 $\,^{\circ}\text{C})$ of the complex monomer $[Ir(iqbt)_2(vb-ppy)]$ and a desirable T_g (glass transition temperature) above 160 °C are observed.

The photo-physical properties of the two series of graftingtype Ir³⁺-polymers **Poly(NVK-co-[Ir(iqbt)₂(vb-ppy)])** (100:1, 150:1 or 200:1) and **Poly((vinyl-PBD)-co-NVK-co-[Ir(iqbt)₂(vb-ppy)])** (15:150:1) were investigated in solid-state or solution at RT, and the data are summarized in Table S2 (ESI†) and Fig. 5 and Fig. S6 (ESI†). As shown in Fig. S6 (ESI†), both the DR (diffuse reflection) and the solution absorption spectra of all the graftingtype Ir³⁺-polymers show significantly broader absorption bands than that of the PVK, in which, besides the strong absorptions below 400 nm attributed to the π - π * transitions from the organic portions of PVK and the ligands, the absorptions across the whole visible range should be assigned to the ^{1,3}LC/^{1,3}MLCT and S₀ \rightarrow T₁ admixed transitions of the grafted complex monomer [**Ir(iqbt)₂(vb-ppy)**]. Noticeably, owing to the significant spectral overlap (also Fig. 2) between the absorption of the complex



Fig. 5 Normalized emission spectra of the Ir^{3+} -polymers Poly(NVK-co-[Ir(iqbt)₂(vb-ppy)]) (100:1, 150:1 or 200:1) and Poly((vinyl-PBD)-co-NVK-co-[Ir(iqbt)₂(vb-ppy)]) (15:150:1) in solid-state at RT.

monomer [Ir(iqbt)₂(vb-ppy)] and the emission of PVK, effective Förster energy transfer²² should occur. Convincingly, upon photoexcitation, the resulting emissions (Fig. 4) of all the grafting-type Ir³⁺polymers do not show the simple addition spectra, but they are highly related to the stipulated feeding ratio. For the Poly(NVK-co-[Ir(iqbt)₂(vb-ppy)]) (100:1 or 150:1), photo-excitation gives rise to the almost entire NIR emission (λ_{em} = 696 nm), resembling that (Fig. 2) of the complex monomer [Ir(iqbt)₂(vb-ppy)] in solution. The absence of the PVK-based blue-light is due to the effective Förster energy transfer²² from the PVK to the Ir³⁺-complex-acceptor, giving rise to the satisfactory $\Phi_{\rm PL}$ of 0.13 (100:1) or 0.16 (150:1). On further increasing the feeding ratio up to 200:1, the dual-emitting ($\Phi_{\rm PL}$ = 0.21) behaviour associated with the PVK-centered emission at 420 nm and the Ir³⁺-complex-based NIR emission ($\lambda_{em} = 690$ nm) is observed, and the 28 ns of the PVK-centered lifetime together with the Ir³⁺-complex-decayed lifetime of 1.29 µs further confirm the dualemitting character (Fig. S7, ESI†). Accordingly, based on the equation²⁵ $\Phi_{\rm ET} = 1 - (\tau_{\rm DA}/\tau_{\rm D}) (\tau_{\rm DA} \text{ or } \tau_{\rm D} \text{ is the donor's amplitude-}$ weighted lifetime with and without acceptor, respectively; $\tau_D = 44$ ns $(\lambda_{em} = 430 \text{ nm})$ for the pure PVK as in the literature²⁶) for **Poly(NVKco-[Ir(iqbt)**₂(**vb-ppy)]**) (200:1), the Förster energy transfer $\Phi_{\rm ET}$ of 36% is qualitatively estimated. For comparison, accompanied by the almost constant and mono-exponential Ir3+-complex-decayed lifetime (1.24 µs) for Poly(NVK-co-[Ir(iqbt)₂(vb-ppy)]) (150:1) and the significantly reduced lifetime of 0.97 µs for Poly(NVK-co-[Ir(iqbt)₂(vbppy]] (100:1), the facilitated separation of the complex monomers [Ir(iqbt)₂(vb-ppy)] within the PVK backbone should occur at the lower Ir³⁺-complex-grafting level (150:1 or 200:1), from which the undesirable aggregation-caused quenching (ACQ)²⁷ effect from the high grafting content (100:1) is effectively suppressed. Interestingly, with an appropriate amount of the electron-transport vinyl-PBD further grafted for the bipolar Poly((vinyl-PBD)-co-NVK-co-[Ir(iqbt)2-(vb-ppy)]) (15:150:1), besides the similar Ir³⁺-complex-based NIR emission (λ_{em} = 693 nm) to that of Poly(NVK-co-[Ir(iqbt)₂(vb-ppy)]) (150:1), its typical and comparable NIR-emitting phosphorescence (τ = 1.25 µs and $\Phi_{\rm PL}$ = 0.17) is also observed.

Device performance of NIR-PLEDs-I-III based on the complex monomer [Ir(iqbt)₂(vb-ppy)] and its Ir³⁺-polymers

Due to the suitability of PVK-PBD (65:30; wt%) with good hole/ electron transport as the co-host,²⁸ it is of interest to use the



Fig. 6 Device structures and energy level diagrams for the doping-type **NIR-PLED-I** (a) and the grafting-type **NIR-PLEDs-II–III** (b and c); normalized EL spectra (d); R-J-V (e) and $\eta_{EQE}-R$ curves (f).

efficient NIR-emitting complex monomer [Ir(iqbt)2(vb-ppy)] as the dopant (5 wt%) for the prototype NIR-PLED-I with the configuration shown in Fig. 6(a). Attributed to the fact that the experimental (Fig. S8, ESI^{\dagger}) HOMO (-5.17 eV) and LUMO (-3.03 eV) levels of the complex monomer [Ir(iqbt)₂(vb-ppy)] aligned well within the band gap (-6.2 to -5.5 eV of HOMO)and -2.6 to -2.0 eV of LUMO) of PVK-PBD, the injected electrons and holes through the PVK-PBD matrix are first trapped, and then direct charge trapping²⁹ should occur within the NIR-emitting Ir(m)-complexes. As expected, as shown in Fig. 6(d), the electroluminescence spectra of the NIR-PLED-I are voltage-independent while just Ir(III)-complex-related NIR (λ_{em} = 696 and 756 (sh) nm; *ca.* 70% of the $\lambda_{em} \ge 700$ nm proportion) emissions well resembled that (also Fig. 2) of the complex monomer [Ir(igbt)₂(vb-ppy)] in solution. The absence of the PVK-PBD residual light indicates that the effective Förster energy transfer²² also takes place within the doping EML upon electrical driving. For the NIR-PLED-I, upon the turn-on voltage (V_{on} , defined as the voltage of the output irradiance $(R) = 5.0 \text{ W sr}^{-1} \text{ cm}^{-2}$) of 9.0 V, as shown in Fig. 6(e), both the R and the current density (J) monotonically increase with the increase of the applied bias voltage (V), exhibiting an R^{\max} of 3772.1 W sr⁻¹ cm⁻² with a J^{max} of 452.8 mA cm⁻² at 21.0 V. Meanwhile, the NIR-PLED-I exhibits the R-regulated waving for the η_{EQE} (Fig. 6(f)), where the $\eta_{\text{EOE}}^{\text{max}}$ of 4.1% with the $R = 65.5 \text{ W sr}^{-1} \text{ cm}^{-2}$ at 12.0 V and about 30% efficiency-rolloff in the higher radiance range of $R = 65.5-3772.1 \text{ W sr}^{-1} \text{ cm}^{-2}$ are observed. It is worthy of note that due to the contribution from more excitons confined within the broadened recombination zone supplemented with the facilitated electron-transport TmPyPB,30

the overall device performance of the **NIR-PLED-I** is at the toplevel (also Fig. 1) and comparable to the best one^{7c} among the previously reported NIR-PLEDs.

Considering the almost identical Ir³⁺-complex-grafted content between Poly(NVK-co-[Ir(iqbt)2(vb-ppy)]) (150:1) and Poly((vinyl-**PBD**)-co-NVK-co-[Ir(igbt)₂(vb-ppy)]) (15:150:1) comparable to that of the doping system (PVK: PBD: [Ir(iqbt)₂(vb-ppy)]; 65:30:5, wt%) for the NIR-PLED-I, the bipolar Ir³⁺-polymers of Poly(NVK-co-[Ir(iqbt)2(vb-ppy)]) (150:1) and Poly((vinyl-PBD)-co-NVK-co-[Ir(iqbt)₂(vb-ppy)]) (15:150:1) further doped with PBD and grafted with vinyl-PBD were used as the EML for the grafting NIR-PLEDs-II-III (Fig. 6(b and c)), respectively. Through the further grafting of the vinyl-PBD for the Poly((vinyl-PBD)-co-NVK-co-[Ir(iqbt)₂(vb-ppy)]) (15:150:1), the electron-transport promotion is reflected from its experimentally (Fig. S9, ESI⁺) stabilized LUMO level (-3.19 eV) in comparison to that (-3.08 eV)of the Poly(NVK-co-[Ir(iqbt)₂(vb-ppy)]) (150:1). Excitingly, for both the NIR-PLED-II with the doping of PBD into Poly(NVK-co-[Ir(iqbt)₂(vb-ppy)]) (150:1) and the NIR-PLED-III based on **Poly((vinyl-PBD)-co-NVK-co-[Ir(iqbt)₂(vb-ppy)])** (15:150:1), Ir(m)complex-exclusive NIR-emissive spectra similar to those of the NIR-PLED-I or their photo-luminescence results (also Fig. 5) in solid-states are observed. As compared with the NIR-PLED-I, due to the deeper LUMO gap between PBD and Poly(NVK-co-[Ir(iqbt)₂(vb-ppy)]) (150:1), the V_{on} of the NIR-PLED-II is up to 11.0 V. Moreover, the decreased $\eta_{\text{EQE}}^{\text{max}}$ of 2.5% and the R^{max} of 1239.2 W sr⁻¹ cm⁻² show a good trade off with the significantly alleviated (ca. 3%) efficiency roll-off within the 12.0-21.0 range, which should be attributed to the lower carrier-trapping probability with the better carrier-balance within Poly(NVK-co-[Ir(iqbt)2(vb-ppy)]) (150:1). By contrast, using Poly((vinyl-PBD)-co-NVK-co-[Ir(iqbt)2(vbppy)]) (15:150:1) as the bipolar EML for the NIR-PLED-III, Förster energy transfer²² and carrier-trapping²⁹ mechanisms also concurrently proceed within the TmPyPB-assisted recombination zone.30 Interestingly, for the NIR-PLED-III, besides the low $V_{\rm on}$ at 7.5 V and the $\eta_{\text{EOE}}^{\text{max}}$ up to 3.6% at 9.0 V, the high R^{Max} of 6559.3 W sr⁻¹ cm⁻² at 21.0 V is at the cost of the highest J^{max} of 647.5 mA cm⁻². Nonetheless, the superior device performance of the NIR-PLED-III is represented by the η_{EQE}^{max} of 3.6% (9.0 V) and the weak (ca. 4%) efficiency roll-off with a preserved η_{EQE} of 3.4% at 21.0 V, which means that the high-efficiency of the NIR-PLED-I and the negligible efficiency roll-off of the NIR-PLED-II are well realized for the NIR-PLED-III. Importantly, this result makes bipolar Ir(III)-complex-grafted polymers a conceptual strategy to achieve high-performance NIR-PLEDs.

4. Conclusions

In summary, through the copolymerization of NVK, the vinylfunctionalized NIR-emitting monomer [Ir(iqbt)₂(vb-ppy)] and/ or the electron-transporting monomer vinyl-PBD, two series of Ir(m)-complex-grafted polymers Poly(NVK-co-[Ir(iqbt)₂(vb-ppy)]) (100:1, 150:1 or 200:1) and Poly((vinyl-PBD)-co-NVK-co-[Ir(iqbt)₂(vb-ppy)]) (15:150:1) are obtained, respectively. Moreover, using the doping system of PVK:PBD:[Ir(iqbt)₂(vb-ppy)] or **Poly(NVK-co-[Ir(iqbt)**₂(**vb-ppy)]**) (150:1) doped with PBD and the grafting system of the bipolar **Poly((vinyl-PBD)-co-NVK-co-**[**Ir(iqbt)**₂(**vb-ppy)**]) (15:150:1) as the EML, reliable **NIR-PLEDs-I-III** are realized, respectively. Excitingly, for the **NIR-PLED-III** based on the bipolar **Poly((vinyl-PBD)-co-NVK-co-[Ir(iqbt)**₂(**vbppy)]**) (15:150:1), the superior device performance (the η_{EQE}^{max} of 3.6% and the negligible (<5%) efficiency roll-off) makes bipolar Ir(m)-complex-grafted polymers a new platform to achieve high-performance NIR-PLEDs.

Conflicts of interest

There are no conflicts to declare.

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