



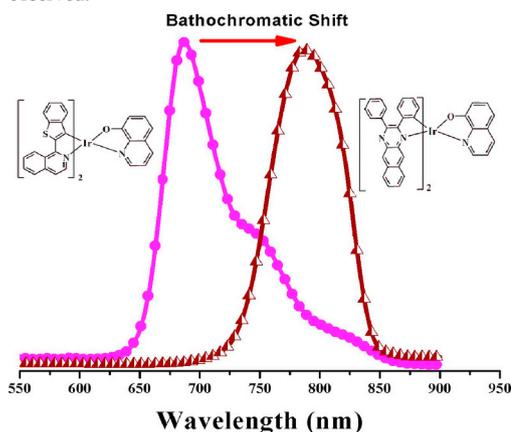
## Short communication

Two efficient near-infrared (NIR) luminescent  $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{O})]$ -characteristic complexes with 8-hydroxyquinoline (8-Hq) as the ancillary ligandJiahao Guo<sup>1</sup>, Jin Zhou<sup>1</sup>, Guorui Fu, Yani He, Wentao Li, Xingqiang Lü\*

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## GRAPHICAL ABSTRACT

Replaced by the large  $\pi$ -conjugation-induced  $\text{C}^{\wedge}\text{N}$  ligand **Hdpbq**, the distinctive bathochromatic shift into a typical NIR region ( $\lambda_{\text{em}} = 786 \text{ nm}$ ) for  $[\text{Ir}(\text{dpbq})_2(8\text{-q})]$  (**2**) relative to that ( $\lambda_{\text{em}} = 687 \text{ nm}$  with a shoulder at  $756 \text{ nm}$ ) of  $[\text{Ir}(\text{iqbt})_2(8\text{-q})]$  (**1**) while relatively lower quantum efficiency  $\Phi_{\text{em}} = 0.16$  versus  $\Phi_{\text{em}} = 0.05$  are observed.



## ARTICLE INFO

## Keywords:

$[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{O})]$ -characteristic Ir(III)-complex  
NIR luminescence  
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Ligands-perturbed effect

## ABSTRACT

Through the utilization of **Hiqbt** (1-(benzo[b]-thiophen-2-yl)-isoquinoline) or **Hdpbq** (2,3-diphenyl benzo[g]quinoxaline) as the  $\text{C}^{\wedge}\text{N}$  main ligand and **8-Hq** (8-hydroxyquinoline) as the  $\text{N}^{\wedge}\text{O}$  ancillary ligand, two  $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\wedge}\text{O})]$ -characterized heteroleptic complexes  $[\text{Ir}(\text{iqbt})_2(8\text{-q})]$  (**1**) and  $[\text{Ir}(\text{dpbq})_2(8\text{-q})]$  (**2**) with desirable soluble and NIR-phosphorescent properties ( $\lambda_{\text{em}} = 687 \text{ nm}$  with a shoulder at  $756 \text{ nm}$ , lifetime  $\tau = 0.73 \mu\text{s}$  and quantum efficiency  $\Phi_{\text{em}} = 0.16$  for complex **1** versus  $\lambda_{\text{em}} = 786 \text{ nm}$ , lifetime  $\tau = 0.47 \mu\text{s}$  and quantum efficiency  $\Phi_{\text{em}} = 0.05$  for complex **2**) are obtained, respectively. In comparison, the distinctive bathochromatic shift into a typical NIR region of complex **2**, arisen from the large-molecule-conjugation-induced narrow energy gap, gives rise to its relatively lower quantum efficiency than that of complex **1**.

Near-infrared (NIR) emitting materials have aroused particular interest in electroluminescent diodes promising for military optoelectronics [1], telecommunications [2] and wound healing [3]. In this

perspective, although significant efforts have been devoted to inorganic NIR-emitting materials (nano-crystal [4], halide perovskite [5] or quantum dot [6], etc) for practical NIR-light-emitting diodes (NIR-

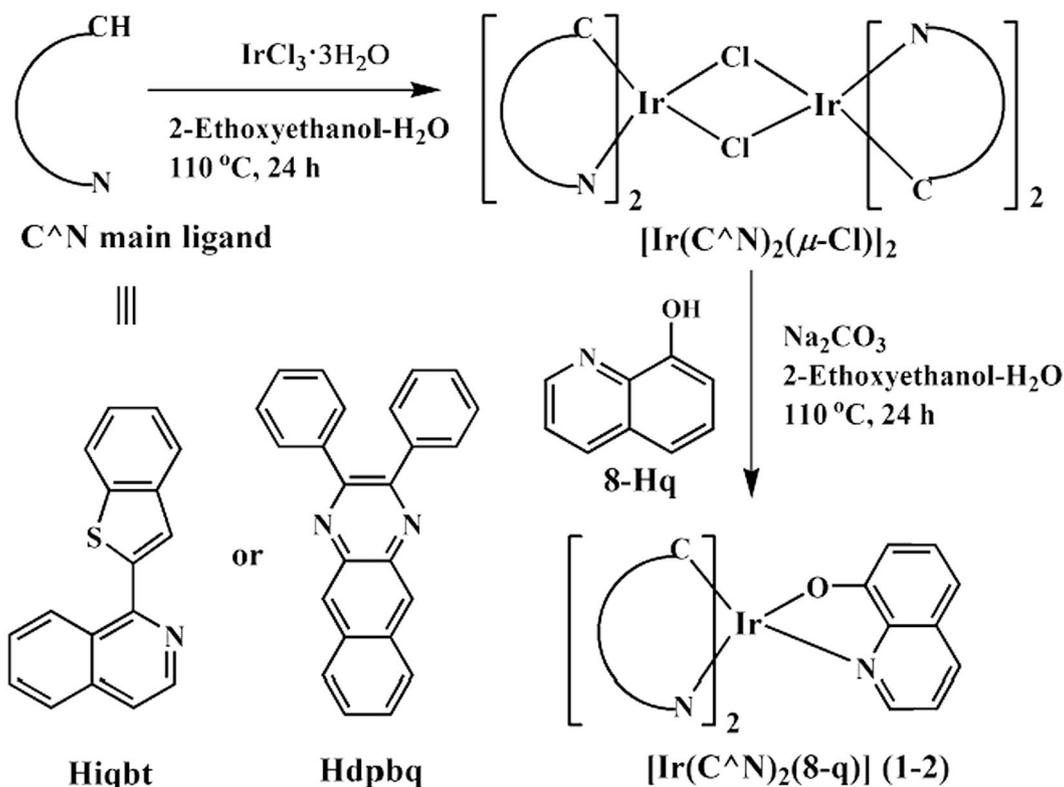
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Scheme 1. Reaction scheme for the synthesis of complexes  $[\text{Ir}(\text{iqbt})_2(8\text{-q})]$  (1) and  $[\text{Ir}(\text{dpbq})_2(8\text{-q})]$  (2).

LEDs), organic-counterparts [7] for NIR organic or polymer light-emitting diodes (NIR-OLEDs or NIR-PLEDs) still dominate in the academic community, which should be arisen from their more versatile and advanced properties in terms of broadened photo- and electro-luminescent spectra as well as endless structure modifications. Moreover, compared with fluorescent small-molecule dyes [8] and conjugated polymers [9] with  $^1\pi\text{-}\pi^*$ -transitions for NIR luminescence, transition-metal-complex- (Pt(II) or Ir(III)-complex etc) [7] and  $\text{Ln}^{3+}$ -complex-resourced (Ln = Nd, Yb or Er) [10] phosphors are worthy of a particular interest because of their harvesting of both singlet and triplet excitons toward a theoretic 100% internal emission efficiency. Noticeably, in contrast to the narrow-energy-gap-confined [11] rather low NIR quantum efficiency for  $\text{Ln}^{3+}$ -complex-based (Ln = Nd, Yb or Er) with the emissive wavelength above 900 nm and the notorious efficiency-roll-off [12] inherently contributed from facile aggregation of Pt (II)-centered square-planar system, the compromise of both desirable high-efficiency and low-efficiency-roll-off, to the best of our knowledge, should be expected for iridium(III)-complexes characteristic of typical octahedral configuration and rather short phosphorescent lifetime.

As a matter of fact, from the viewpoint of lowering the emissive energy of iridium(III)-complexes to a restrictive NIR region (700–2500 nm), several approaches have been reported. Utilizing the large  $\pi$ -conjugation porphyrin- [13] or corrole-based [14] macrocycles as the ligands is highly praised at first, since their substantial NIR phosphorescence is commonly originated from the intraligand charge transfer ( $^3\text{ILCT}$ ) in the Ir(III)-complexes. However, despite the desirable emission wavelength extended to 800 nm or above for these Ir(III)-complexes, distinctively low NIR quantum efficiencies regulated by energy-gap law [11] actually limit their use for NIR-OLEDs. In contrast, one of the most successful approaches relies on the  $\pi$ -conjugated expansion of the main  $\text{C}^{\wedge}\text{N}$ -cyclometalated ligand especially incorporated with electron-rich substituents to afford the *fac*- $[\text{Ir}(\text{C}^{\wedge}\text{N})_3]$ -characteristic homoleptic complex [15] with the expected NIR luminescence ranging at 700–800 nm. Nonetheless, severe aggregation-induced quenching effect from the large  $\pi$ -conjugation of the  $\text{C}^{\wedge}\text{N}$  main ligand,

also makes the molecular design of the *fac*- $[\text{Ir}(\text{C}^{\wedge}\text{N})_3]$ -complex much challenging in the obtainment of its efficient NIR-OLED or NIR-PLED. Convincingly, significant electronic perturbation can be achieved by modification of the  $\text{L}^{\wedge}\text{X}$  ancillary ligands [16], from which, the energy gap of its typical  $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{L}^{\wedge}\text{X})]$ -complex is actually adjusted, while bathochromic-shift to effectively narrow the energy gap for NIR luminescence does not have a universal effect. For example, within the typical  $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\circ}\text{O})]$ -complexes with pic as the ancillary ligand, contrast to the rational blue-shift for the well-known Flpic complex ( $\text{Flpic} = \text{bis}[2\text{-}(4,6\text{-difluorophenyl})\text{pyridinato-}\text{C}^2, \text{N}](\text{pic})\text{-iridium(III)}$ ) [17], a slight red-shifting [18] at 698 nm for  $[\text{Ir}(\text{iqbt})_2(\text{pic})]$  is realized in relative to that (690 nm) of the *fac*- $[\text{Ir}(\text{iqbt})_3]$  [19]. Moreover, in consideration of the resolution to  $[\text{Ir}(\text{iqbt})_2(\text{pic})]$  insolubility for solution-processed OLEDs, the success of our reported two  $[\text{Ir}(\text{iqbt})_2(\text{N}^{\circ}\text{O})]$ -complexes [20] with pic-derived hpa or  $\text{BF}_2\text{-hpa}$  as the  $\text{N}^{\circ}\text{O}$  ancillary ligand, motivates us a particular concern on the evolution of some other  $\text{N}^{\circ}\text{O}$  ancillary ligands. Herein, with 8-hydroxyquinoline (8-Hq) as the  $\text{N}^{\circ}\text{O}$  ancillary ligand, its two new  $[\text{Ir}(\text{C}^{\wedge}\text{N})_2(\text{N}^{\circ}\text{O})]$ -heteroleptic complexes with different  $\pi$ -conjugation  $\text{C}^{\wedge}\text{N}$  main ligands of **Hiqbt** or **Hdpbq** are rationally designed, from which, the desirable red-shifted emission within the NIR regime affected by the electronic perturbations of the  $\text{C}^{\wedge}\text{N}$  main ligand and the  $\text{N}^{\circ}\text{O}$  ancillary ligand are also explored.

The  $\text{C}^{\wedge}\text{N}$  main ligand **Hiqbt** was synthesized by an improved Suzuki coupling reaction [19] between cost-effective 2-Cl-isoquinoline while not 2-Br-isoquinoline and benzo[*b*]-thien-2-yl boronic acid in 73% yield. As to the  $\text{C}^{\wedge}\text{N}$  main ligand **Hdpbq**, it was obtained from the equimolar condensation of 2,3-naphthalenediamine with benzyl in the presence of oxalic acid according to the well-established procedure from the literature [21]. As shown in Scheme 1, each of the  $\mu$ -chloro-bridged dimer intermediates  $[\text{Ir}(\text{iqbt})_2(\mu\text{-Cl})]_2$  and  $[\text{Ir}(\text{dpbq})_2(\mu\text{-Cl})]_2$  were rationally prepared from the reaction of  $\text{IrCl}_3 \cdot 3\text{H}_2\text{O}$  with the corresponding  $\text{C}^{\wedge}\text{N}$  main ligand of **Hiqbt** or **Hdpbq**, and used directly for the next step without further purification. Further through the reaction of the  $\text{N}^{\circ}\text{O}$  ancillary ligand 8-Hq with the corresponding  $\mu$ -chloro-bridged dimer intermediate  $[\text{Ir}(\text{iqbt})_2(\mu\text{-Cl})]_2$  or  $[\text{Ir}(\text{dpbq})_2(\mu\text{-Cl})]_2$ , two

**Table 1**  
Photo-physical and electrochemical properties of complexes 1–2 in solution at room temperature.

Complex	Absorption		Emission				Energy level		
	$\lambda_{\text{abs}}^{\text{a}}$		$\lambda_{\text{em}}^{\text{a}}$	$\tau^{\text{a}}$	$\Phi_{\text{em}}^{\text{a}}$	$k_{\text{r}}^{\text{a}}$	$k_{\text{nr}}^{\text{a}}$	HOMO <sup>b</sup>	LUMO <sup>b</sup>
	(nm)		(nm)	( $\mu\text{s}$ )		( $\times 10^5 \text{ s}^{-1}$ )	( $\times 10^5 \text{ s}^{-1}$ )	(eV)	(eV)
[Ir(iqbt) <sub>2</sub> (8-q)] (1)	229, 284, 367, 443, 500, 654		687, 756(sh)	0.73	0.16	2.19	1.15	-5.172	-2.662
[Ir(dpbq) <sub>2</sub> (8-q)] (2)	238, 285, 325, 411, 541, 689		786	0.47	0.05	1.06	2.02	-5.148	-3.140

Rate constant  $k_{\text{r}}$  and  $k_{\text{nr}}$  are calculated using the equations  $k_{\text{r}} = \Phi_{\text{em}}/\tau$  and  $k_{\text{nr}} = (1-\Phi_{\text{em}})/\tau$  on the assumption that  $\Phi_{\text{ISC}} = 1$  (ISC = intersystem crossing).

<sup>a</sup> In degassed CH<sub>2</sub>Cl<sub>2</sub> solution.

<sup>b</sup> HOMO and LUMO levels are obtained from electrochemical determination, respectively.

new Ir(III)-complexes [Ir(iqbt)<sub>2</sub>(8-q)] (1) and [Ir(dpbq)<sub>2</sub>(8-q)] (2) are isolated, respectively.

The two Ir(III)-complexes 1–2 are much soluble in common organic solvents except water, which significantly different from the relative insolubility [Ir(iqbt)<sub>2</sub>(pic)] [18] while comparable to that of our reported two [Ir(iqbt)<sub>2</sub>(N<sup>ˆ</sup>O)]-complexes [20] with pic-derived hpa or BF<sub>2</sub>-hpa as the N<sup>ˆ</sup>O ancillary ligand, renders the incorporation of the 8-Hq N<sup>ˆ</sup>O ancillary ligand for its new [Ir(C<sup>ˆ</sup>N)<sub>2</sub>(8-q)] complexes (HC<sup>ˆ</sup>N = **Hiqbt** or **Hdpbq**) an opportunity to solution-processed electro-luminescent devices. Moreover, Ir(III)-complexes 1–2 were well-characterized by EA, FT-IR, <sup>1</sup>H NMR and ESI-MS. In the <sup>1</sup>H NMR spectrum (Fig. 1S) of complex 1, the iridium(III)-induced significantly spread shifts of the (iqbt)<sup>-</sup> or (dpbq)<sup>-</sup> and (L<sup>n</sup>)<sup>-</sup> combined proton resonances ( $\delta = 9.13$ –6.39 ppm) relative to those ( $\delta = 8.65$ –7.43 ppm) of the free **Hiqbt** ligand are observed. Moreover, the proton signals of the (iqbt)<sup>-</sup> and (8-q)<sup>-</sup> ligands with a stipulated molar ratio of 2:1 could further confirm the [Ir(iqbt)<sub>2</sub>(8-q)] (1) characteristic of the typical [Ir(C<sup>ˆ</sup>N)<sub>2</sub>(N<sup>ˆ</sup>O)]-heteroleptic complexes [22]. For comparison, despite the similar combination of both the (dpbq)<sup>-</sup> and (8-q)<sup>-</sup> proton resonances (also in Fig. 1S) in a 2:1 M ratio for complex 2, its evident converge ( $\delta = 8.72$ –6.25 ppm) of the proton signals relative to those ( $\delta = 9.13$ –6.39 ppm) of complex 1, should be arisen from the strong current-circular effect with the large  $\pi$ -conjugated (dpbq)<sup>-</sup> C<sup>ˆ</sup>N ligand for complex 2 as compared to the (iqbt)<sup>-</sup> C<sup>ˆ</sup>N ligand in complex 1. Furthermore, the ESI-MS spectra of the two iridium(III)-complexes 1–2 exhibit a similar pattern, where a strongest mass peak at  $m/z$  858.10 (1) or 1000.15 (2) assigned to the major species [M + H]<sup>+</sup>, respectively, indicates that each of the respective heteroleptic [Ir(C<sup>ˆ</sup>N)<sub>2</sub>(N<sup>ˆ</sup>O)] unit retains stable in solution. The thermal stability of the two iridium(III)-

complexes 1–2 investigated by thermogravimetric analysis (TGA; Fig. 2S) shows that their decomposition temperatures ( $T_{\text{d}}$ , corresponding to 5% weight loss) can be up to 300 °C.

The photo-physical properties of the C<sup>ˆ</sup>N main ligand **Hiqbt** or **Hdpbq**, the N<sup>ˆ</sup>O ancillary ligand **8-Hq** and their two Ir(III)-complexes 1–2 in solution were explored using absorption and photo-luminescence spectrometers, and the results are summarized in Table 1 and Figs. 1–2 and 3–5S. In contrast to the strong absorption bands limited to the  $\lambda_{\text{abs}} < 400$  nm range for the ligands **Hiqbt**, **Hdpbq**, and **8-Hq**, as shown in Fig. 1, both complexes 1–2 exhibit significantly broadened UV–visible–NIR absorption spectra: the intense absorption bands below 400 nm assigned to the spin-allowed intra-ligand  $\pi$ - $\pi^*$  transitions; the moderate absorption bands in the 400–600 nm region probably arisen from the mixed <sup>3</sup>LC/<sup>1,3</sup>MLCT (LC = ligand-centered; MLCT = metal-to-ligand charge transfer, d- $\pi^*$ ) transitions [20]; and the weak absorption bands (654 nm for complex 1 or 689 nm for complex 2) extending over 600 nm possibly attributed to the ground-state excitation into the lowest triplet state ( $S_0 - T_1$ ). Worthy of notice, the low-energy <sup>3</sup>LC/<sup>1,3</sup>MLCT absorption of complex 1 locates at  $\lambda_{\text{abs}} = 500$  nm, which is distinctively blue-shifted by 39 nm relative to that ( $\lambda_{\text{abs}} = 539$  nm) of the parent *fac*-[Ir(iqbt)<sub>3</sub>] complex [19]. Similarly, an evident blue-shift by 25 nm as compared with the low-energy <sup>3</sup>LC/<sup>1,3</sup>MLCT absorption ( $\lambda_{\text{abs}} = 525$  nm) of complex [Ir(iqbt)<sub>2</sub>(pic)] [18], should result from the change in N<sup>ˆ</sup>O-chelate ancillary ligand field strength. As to complex 2 based on the larger  $\pi$ -conjugation C<sup>ˆ</sup>N ligand **Hdpbq**, besides the decreased Ir(III)-centered d-(t<sub>2g</sub>) orbital energy (541 nm) relative to that (500 nm) of complex 1, the lowest-energy absorption edge almost extends to ca. 700 nm, indicating that the molecular conjugation is significantly increased for the formation of [Ir(dpbq)<sub>2</sub>(8-q)] (2) in a delocalized state. Upon photo-excitation ( $\lambda_{\text{ex}} = 387$  nm, Fig. 3S), as

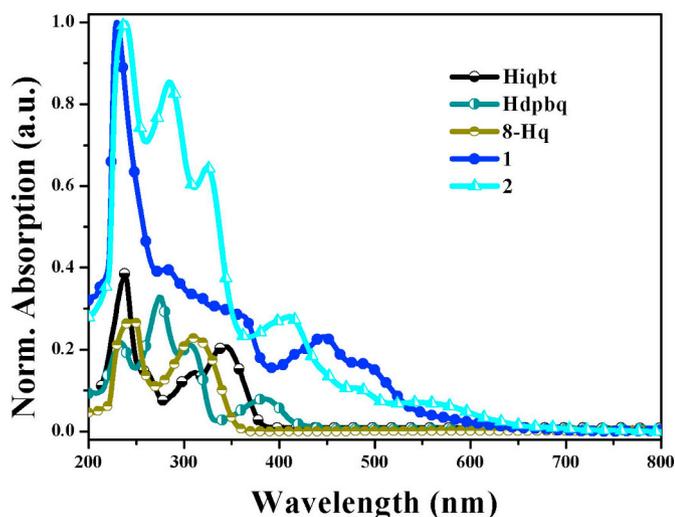


Fig. 1. Normalized UV–Visible–NIR absorption for the Ir(III)-complexes 1–2 in contrast to those of the three ligands **Hiqbt**, **Hdpbq**, **8-Hq** in degassed CH<sub>2</sub>Cl<sub>2</sub> solution at RT.

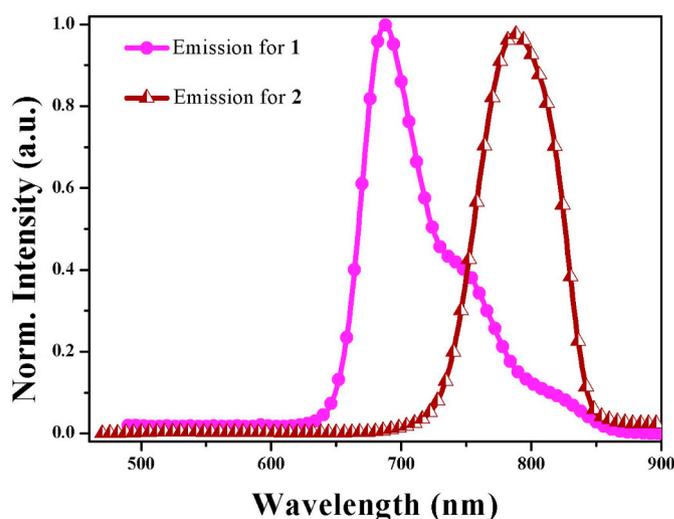


Fig. 2. Normalized NIR photo-luminescence spectra for complexes 1–2 in degassed CH<sub>2</sub>Cl<sub>2</sub> solution at RT.

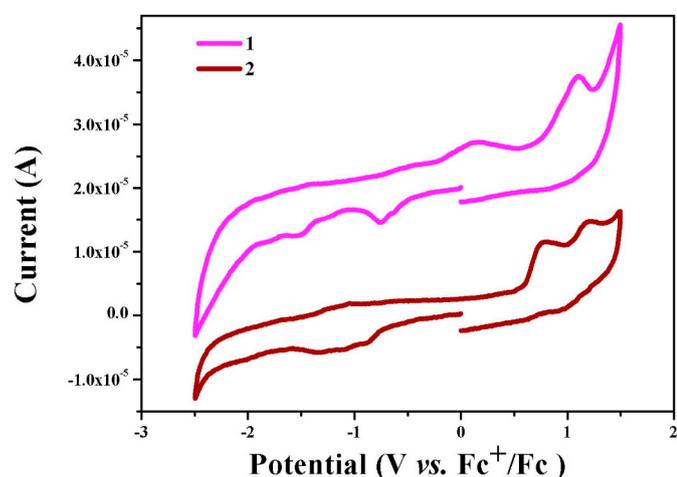


Fig. 3. Cyclic voltammograms of complexes 1–2 recorded versus  $\text{Fc}^+/\text{Fc}$  in solution at RT under a  $\text{N}_2$  atmosphere (scan rate =  $100 \text{ mV s}^{-1}$ ).

shown in Fig. 2, the strong emission peak (687 nm) of complex 1 lies at the edge of the NIR region besides a shoulder peak at 756 nm. By contrast, complex 2 exhibits a typical NIR luminescence with the emissive wavelength up to 786 nm. Due to the non-emissive character (Fig. 4S) of both the C'N main ligand **Hiqbt** or **Hdppq** and the N'O ancillary ligand **8-Hq** in that NIR region, the NIR emissions of complexes 1–2 should originate from the ligands-perturbed  $^3\text{LC}/^{1,3}\text{MLCT}$ -excited state. Moreover, the NIR emissive nature of the two complexes is characteristic of typical phosphorescence (Fig. 5S), confirming from the substantial  $\tau = 0.73 \mu\text{s}$  for complex 1 and  $\tau = 0.47 \mu\text{s}$  for complex 2, respectively. Worthy of notice, although the desirable bathochromic shifts of complex 1 at 687 nm relative to those (682–683 nm) [18] of complexes  $[\text{Ir}(\text{iqbt})_2(\text{N}^{\text{N}})]^+$  while the slight blue-shifts relative to those of complexes *fac*- $[\text{Ir}(\text{iqbt})_3]$  (690 nm) [19], *pic*-derived  $[\text{Ir}(\text{iqbt})_2(\text{N}^{\text{O}})]$  (692–700 nm) [18,20] and  $[\text{Ir}(\text{iqbt})_2(\text{O}^{\text{O}})]$  (707–710 nm) [23] are observed, its attractive quantum yield of  $\Phi_{\text{em}} = 0.16$  endowed by strong ligands-perturbed effect, can be further validated from the considerably high radiative rate constant ( $k_r = 2.19 \times 10^5 \text{ s}^{-1}$ ) and the relatively low non-radiative rate constant ( $k_{\text{nr}} = 1.15 \times 10^5 \text{ s}^{-1}$ ). For comparison, the distinctively low quantum efficiency ( $\Phi_{\text{em}} = 0.05$ ) for complex 2 advantageous of a typical NIR (786 nm) phosphorescence, should be regulated from the energy-gap law [11] and also confirmed by its two times smaller  $k_r$  of  $1.06 \times 10^5 \text{ s}^{-1}$  while two times larger  $k_{\text{nr}}$  of  $2.02 \times 10^5 \text{ s}^{-1}$  as compared to complex 1.

For insight into the electronic structures of the two NIR-emissive complexes 1–2, their electrochemical properties in anhydride MeCN solution were investigated, and the results were summarized in Table 1 and Fig. 3. During the anodic scan shown in Fig. 3, a reversible oxidation process is detected at half-wave potentials of +0.372 and +0.348 V versus  $\text{Fc}^+/\text{Fc}$  for complexes 1–2, respectively, which should originate from the one-electron oxidation [12] of the Ir(III)-center and the cyclometalated benzo[*b*]thiophene or benzo[*g*]quinoxaline moieties. As compared with complex 1, the **Hdppq**-based complex 2 starts to be oxidized at the more positive potential with the shift of 0.024 V, which should reasonably ascribed to its more difficult oxidation due to the stronger  $\pi$ -back-bonding effect from the Ir(III)-center to the C'N main ligands. Considering no distinctive reduction waving for each of the two Ir(III)-complexes and basing on the reasonable  $E_{\text{g}}^{\text{OPT}}$  value of 2.07 eV for complex 1 or 1.90 eV for complex 2 estimated from the low-energy absorbance edge (599 nm for complex 1 versus 653 nm for complex 2), the determined HOMO and LUMO levels of  $-5.172$  and  $-2.662$  eV for complex 1 or  $-5.148$  and  $-3.140$  eV for complex 2 are obtained, respectively. In agreement with the  $E_{\text{g}}^{\text{OPT}}$ -sized trend [20] and the actual bathochromic shift of complex 2 in comparison

with complex 1, complex 2 exhibits a slightly narrower HOMO-LUMO gap of 2.008 eV than that (2.662 eV) of complex 1.

In summary, through **Hiqbt** or **Hdppq** as the C'N main ligand and **8-Hq** as the N'O ancillary ligand, two new soluble Ir(III)-complexes  $[\text{Ir}(\text{iqbt})_2(\text{8-q})]$  (1) and  $[\text{Ir}(\text{dppq})_2(\text{8-q})]$  (2) characteristic of a similar  $[\text{Ir}(\text{C}'\text{N})_2(\text{N}'\text{O})]$ -heteroleptic configuration are obtained, respectively. In comparison with the photo-physical property ( $\lambda_{\text{em}} = 687 \text{ nm}$  with a shoulder at 756 nm, lifetime  $\tau = 0.73 \mu\text{s}$  and quantum efficiency  $\Phi_{\text{em}} = 0.16$ ) for complex 1, complex 2 with large-molecule-conjugation exhibits the distinctive bathochromic shift into a typical NIR region ( $\lambda_{\text{em}} = 786 \text{ nm}$ ), endowing a particular opportunity to future NIR-OLED.

## Acknowledgements

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## Appendix A. Supplementary data

The information of raw materials and methods, and the synthesis and characterization of the two C'N ligands **Hiqbt** and **Hdppq**, the two  $\mu$ -chloro-bridged dimmer intermediates  $[\text{Ir}(\text{iqbt})_2(\mu\text{-Cl})_2]$  and  $[\text{Ir}(\text{dppq})_2(\mu\text{-Cl})_2]$  and their two Ir(III)-complexes  $[\text{Ir}(\text{iqbt})_2(\text{8-q})]$  (1) and  $[\text{Ir}(\text{dppq})_2(\text{8-q})]$  (2) depicted in the Supporting information. The  $^1\text{H}$  NMR spectra, the TG spectra, the solution visible emission and/or excitation spectra of the ligands **Hiqbt**, **Hdppq** and **8-Hq** and the two Ir(III)-complexes 1–2 and the time-decayed curves deposited in Figs. 1–4S, respectively. Supplementary data to this article can be found online at <https://doi.org/10.1016/j.inoche.2019.01.019>.

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