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Introduction

Phosphorescent ionic transition-metal complexes (iTMCs) are receiving numerous interests due to their great potential in numerous fields, such as organic optical devices,¹ chemosensors,² biological probes³ and photosensitizers for photoinduced hydrogen production.⁴ Among the reported iTMCs, cationic Ir(m) complexes have especially attracted a great deal of interest because they exhibit high phosphorescence efficiencies close to unity endowed by the strong spin–orbit coupling effect of the Ir(m) atom.⁵ In addition, they also show good photo- and thermal stabilities, relatively short excitedstate lifetimes, as well as easy tunability of the emission color, which makes them an attractive alternative for optoelectronic applications, in particular in solid-state light-emitting

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Enhancing the luminescence properties and stability of cationic iridium(III) complexes based on phenylbenzoimidazole ligand: a combined experimental and theoretical study[†]

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Herein we designed and synthesized a series of cationic iridium(III) complexes with a phenylbenzoimidazole-based cyclometalated ligand, containing different numbers of carbazole moieties from zero to three (complexes **1–4**). The photophysical and electrochemical properties of this series have been systematically investigated. The complexes exhibit strong luminescence in both solution and in neat films, as well as excellent redox reversibility. Introducing carbazole groups into the complexes is found to lead to substantially enhanced photoluminescence quantum efficiency in the neat film, but has little effect on the emitting color and excited-state characteristics as supported by density functional theory (DFT) results. DFT calculations also suggest that functionalized complexes **2–4** reveal better hole-transporting properties than **1**. More importantly, all complexes effectively reduce the degradation reaction to some extent in metal-centered (³MC) excited-states, demonstrating their stability. Further studies indicate that restriction of opening of the structures in the ³MC state is caused by the unique molecular conformation of the phenylbenzoimidazole ligand, which is first demonstrated here in cationic iridium(III) complexes without intramolecular π - π stacking. These results presented here would provide valuable information for designing and synthesizing highly efficient and stable cationic iridium(III) complexes suitable for the optical devices.

> electrochemical cells (LECs).⁶ As a new type of organic electroluminescent devices, LECs offer several advantages (*e.g.*, simple device architecture, low turn-on voltage and independence of the work function) over conventional multilayered organic light-emitting diodes (OLEDs). Since the first report of Ir(m)-based LECs,⁷ extensive research has been conducted on the design of cationic Ir(m) complexes and the fabrication of devices.⁸ Up to now, green, yellow, orange and red emitting devices have been developed through ingenious ligand control. Besides, white LECs are realized by combining bluegreen and red emitting cationic Ir(m) complexes in a hostguest system.^{6a,b,9} All these promising characteristics and developments make cationic Ir(m) complexes highly appealing as candidates for potential flat-panel displays and low-cost solid-state lighting sources.

> Despite these advances, the intrinsic excited-state selfquenching associated with triplet-triplet annihilation always occurs because of the strong interactions between closely packed molecules, which remarkably hampers their applications in highly efficient and stable devices. Ir(m)-based LECs as single-layered electroluminescent devices, only consist of cationic Ir(m) complexes as the active component.

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The performance of the devices in principle is determined by the photophysical and excited-state properties of the Ir(III) complexes.¹⁰ Therefore, the exploitation of novel cationic Ir(III) complexes for efficient LECs is attracting significant interest in recent years. From the molecular-design point of view, introducing steric hindrance or bulky side groups into ligands of the complexes is an effective strategy to suppress the emission quenching and enhance the device performance.¹¹ In addition, such functional groups can make the complexes more hydrophobic, which reduces the possibility of ligandexchange reaction caused by nucleophiles, leading to more stable complexes.¹² In this regard, several cationic Ir(III) complexes with functionalized ancillary ligands have been synthesized, which exhibit enhanced photophysical and electroluminescent properties.9,13 However, to our best of knowledge, only few examples of cationic Ir(III) complexes that are functionalized via modifying cyclometalated ligands, have been reported up to now. Moreover, the effect of functional groups on the intrinsic properties of the complexes, such as photophysical, electrochemical and charge transporting properties, has not been well addressed. Further development of multifunctional cationic Ir(m) complexes and investigation of the structure-property relationship is an important issue for achieving highly efficient optical devices. In addition to the experimental studies, theoretical investigations have been proven to be a very useful approach to describe the ground and excited-state electronic structures of phosphorescent complexes and to predict the intrinsic properties of unsynthesized ones.14 In particular, density functional theory (DFT) and time dependent DFT (TD-DFT) calculations have been successfully applied to investigate the nature of the emitting excited state and to analyze the charge transporting properties of organic luminescent materials.15

In this paper, we describe the preparation and theoretical investigation of a series of cationic Ir(m) complexes by attaching different numbers of carbazole groups into cyclometalated and/or ancillary ligands (see Scheme 1). The carbazole moiety is chosen as a functional unit. Not only is carbazole a good charge-transporting group, which is beneficial for the improvement of device performance, but it is also considered as an efficient hydrophobic group to decrease nucleophilic attack, leading to more stable iTMCs.¹⁶ Complex 1 is used as a reference to compare with the other three cationic Ir(III) complexes. Their synthesis, photophysical and electrochemical properties have been investigated in detail. In addition, their photophysical and charge-transporting properties are evaluated with the help of theoretical calculations. The obtained results reveal that the introduction of the rigid carbazole group into cationic Ir(III) complexes peripheries lead to much higher quantum efficiency in neat films as well as a significant increase in the charge-transporting ability, but have little effect on emission color. Furthermore, our theoretical calculations indicate that the unique molecular structure is conducive to restricting the opening of the structure of the complexes in metalcentered (³MC) states, demonstrating their stability when used in LECs.



Scheme 1 Chemical structures of cationic Ir(III) complexes 1-4

Experimental section

Materials and measurements

All reagents and solvents employed were commercially available and used as received without further purification. The solvents for syntheses were freshly distilled over appropriate drying reagents. All experiments were performed under a nitrogen atmosphere by using standard Schlenk techniques. ¹H NMR spectra were measured on a Bruker Avance 500 MHz instrument with tetramethylsilane as the internal standard. The molecular weights of ligands and complexes were tested by using electrospray-ionization mass spectroscopy and matrix-assisted laser desorption-ionization time-of-flight (MALDI-TOF) mass spectrometry, respectively. UV-vis absorption spectra were recorded on a Hitachi U3030 spectrometer. The emission spectra were recorded using an F-7000 FL spectrophotometer. The excited-state lifetime were measured on a transient spectrofluorimeter (Edinburgh FLS920) with time-correlated single-photon counting technique. The photoluminescence quantum yields (PLQYs) of the neat film were measured in an integrating sphere. Cyclic voltammetry was performed on a BAS 100 W instrument with a scan rate of 100 mV s⁻¹ in CH₃CN solutions with the three-electrode configuration: a glassy-carbon electrode as the working electrode, an aqueous saturated calomel electrode as the pseudo-reference electrode, and a platinum wire as the counter electrode, respectively. A 0.1 M solution of tetrabutylammonium perchlorate (TBAP) in CH₃CN was used as the supporting electrolyte, and the ferrocene-ferrocenium (Fc⁺/Fc) potential was measured and selected as the internal standard.

Synthesis

Synthesis of the cyclometalated and ancillary ligands. Synthesis of the cyclometalated ligands and ancillary ligands as



Scheme 2 Chemical structures of the cyclometalated and ancillary ligands used in this work.

shown in Scheme 2 (**Phbd**, **Crbd**, **L1** and **L2**) were prepared using the previously reported procedures.¹⁷ The detailed synthetic procedures and corresponding ¹H NMR data for all ligands can be found in the ESI.[†]

Synthesis of $[Ir(Phbd)_2Cl]_2$. The organometallated dimer $[Ir(Phbd)_2Cl]_2$ was synthesized from reaction of $IrCl_3 \cdot 3H_2O$ (0.81 g, 2.32 mmol) with 1,2-diphenyl-1*H*-benzo[*d*]imidazole (Phbd, 1.39 g, 5.13 mmol) in 2-ethoxyethanol–water (3 : 1 v/v, 40 mL) for 24 h. The mixture was treated with water (30 mL) to induce precipitation of a yellow solid. The product was filtered out and washed with diethyl ether, followed by ethanol, and dried (1.12 g. 0.92 mmol, 79%). Mass spectrometry and ¹H NMR were performed to verify the resulting produces containing the corresponding chloro-bridged dimers (ESI, Fig. S1 and S2[†]). Other chloride-bridged complexes, $[Ir(Crbd)_2Cl]_2$, was synthesized using a method similar to that for $[Ir(Phbd)_2Cl]_2$. The chloro-bridged dimers were used in the subsequent reactions without further purification.

Synthesis of [Ir(Phbd)₂(L1)]PF₆ (1). A solution of ligand L1 (0.30 g, 1.1 mmol) and the dichloro-bridged [Ir(Phbd)₂Cl]₂ (0.77 g, 0.5 mmol) in dichloromethane (20 mL) and methanol (10 mL) was heated to reflux for 24 h in the dark. After cooling to room temperature, the mixture was filtered, and then an excess of solid KPF₆ was added and stirred for another 0.5 h at room temperature. The solvent was removed under reduced pressure and the residue was purified by silica gel column chromatography to yield 1 as an orange powder (71%). ¹H NMR (500 MHz, DMSO-d₆, ppm): δ 8.26 (d, *J* = 6 Hz, 1H), 8.13 (t, J = 8 Hz, 1H), 7.72–7.75 (m, 12H), 7.67–7.69 (m, 1H), 7.61 (d, J = 8 Hz, 1H), 7.57 (d, J = 7.5 Hz, 1H), 7.51 (t, J = 8 Hz, 1H), 7.42–7.44 (m, 1H), 7.20–7.30 (m, 4H), 7.16 (d, J = 8 Hz, 1H), 7.06-7.13 (m, 3H), 7.03 (t, J = 7.5 Hz, 1H), 6.83-6.91 (m, 3H), 6.78 (t, J = 7.5 Hz, 1H), 6.60-6.65 (m, 3H), 6.48 (d, J = 7.5 Hz, 1H)1H), 6.39 (d, *J* = 8.5 Hz, 1H), 5.93 (d, *J* = 8.5 Hz, 1H), 5.78 (d, *J* = 8.5 Hz, 1H). ESI-MS: m/z 1002.30 (M - PF₆). The related complexes (2, 3 and 4) were prepared using similar procedures.

Synthesis of $[Ir(Phbd)_2(L2)]PF_6$ (2). Yield 65%. ¹H NMR (500 MHz, DMSO-d₆, δ [ppm]]: 8.30–8.32 (m, 3H), 8.23–8.24

(m, 1H), 8.12 (d, J = 8.5 Hz, 2H), 7.94 (t, J = 7.5 Hz, 1H), 7.70–7.84 (m, 13H), 7.51–7.57 (m, 5H), 7.45 (d, J = 3 Hz, 1H), 7.36–7.39 (m, 2H), 7.25–7.29 (m, 3H), 7.03–7.13 (m, 4H), 6.85–6.91 (m, 3H), 6.80 (t, J = 2.5 Hz, 1H), 6.62–6.67 (m, 3H), 6.50 (d, J = 7.5 Hz, 1H), 6.43 (d, J = 8.5 Hz, 1H), 5.99 (d, J = 8.0 Hz, 1H), 5.82 (d, J = 8 Hz, 1H). ESI-MS: m/z 1167.37 (M – PF₆).

Synthesis of [Ir(Crbd)₂(L1)]**P**₆ (3). Yield 62%. ¹H NMR (500 MHz, DMSO-d₆, δ [ppm]]: 8.31–8.32 (m, 5H), 8.05–8.17 (m, 7H), 7.91–8.01 (m, 1H), 7.78–7.86 (m, 5H), 7.65–7.67 (m, 5H), 7.59 (d, J = 6.5 Hz, 1H), 7.51–7.56 (m, 5H), 7.32–7.41 (m, 9H), 7.28 (t, J = 8.5 Hz, 1H), 7.21 (d, J = 8.5 Hz, 1H), 7.16 (t, J = 8.5 Hz, 1H), 7.10 (t, J = 7.5 Hz, 1H), 6.92–7.01 (m, 6H), 6.76 (d, J = 7.5 Hz, 1H), 6.57 (d, J = 8.5 Hz, 1H), 6.47 (d, J = 8 Hz, 1H), 5.98 (d, J = 8 Hz, 1H), 5.83 (d, J = 8.5 Hz, 1H). ESI-MS: m/z 1332.42 (M – PF₆).

Synthesis of $[Ir(Crbd)_2(L2)]PF_6$ (4). Yield 51%. ¹H NMR (500 MHz, CDCl₃, δ [ppm]): 8.33 (d, J = 5.5 Hz, 1H), 8.22 (d, J = 3 Hz, 2H), 8.21 (d, J = 3 Hz, 2H), 8.14–8.17 (m, 3H), 8.01–8.06 (m, 3H), 7.92–7.97 (m, 4H), 7.82–7.86 (m, 2H), 7.73–7.75 (m, 1H), 7.58–7.69 (m, 10H), 7.50–7.55 (m, 7H), 7.44 (d, J = 8.5 Hz, 1H), 7.30–7.40 (m, 9H), 7.26–7.27(m, 1H), 7.19–7.25 (m, 2H), 7.00–7.03 (m, 1H), 6.88–6.97 (m, 6H), 6.79–6.80 (m, 1H), 6.66 (d, J = 7 Hz, 1H), 6.59 (d, J = 8.5 Hz, 1H), 6.17 (d, J = 8.5 Hz, 1H), 5.91 (d, J = 8.5 Hz, 1H). ESI-MS: m/z 1497.48 (M – PF₆).

Theoretical calculations

All calculations on the ground and excited electronic state of the complexes were carried out at B3LYP level¹⁸ within the Gaussian 09 software package¹⁹ together with 6-31G* basis sets for C, H, N atoms and the LANL2DZ for Ir atom. An effective core potential (ECP) replaces the inner core electrons of iridium leaving the outer core $(5s)^2(5p)^6$ electrons and the $(5d)^6$ valence electrons of Ir(m). The geometry of the metalcentered triplet (³MC) was fully optimized and was calculated at the spin-unrestricted UB3LYP level with a spin multiplicity of 3. All expectation values calculated for S^2 were smaller than 2.05. The geometry optimization for all complexes in the different states was carried out without the counterions. The ionization potentials and the electron affinities were obtained using B3LYP/6-31G*/LANL2DZ method with charge of 2 and 0, respectively.

Results and discussion

Photophysical properties

The UV-visible absorption and photoluminescent (PL) spectra for all complexes in CH_2Cl_2 solution are depicted in Fig. 1 and detailed photophysical characteristics are summarized in Table 1. All complexes exhibit similar absorption patterns. The dominant absorption bands in the ultraviolet region below 350 nm are mainly attributed to spin-allowed π - π * transitions from the ligands. These results are confirmed by the spectral profile of the π - π * transitions for the corresponding free ligands (see Fig. S3, ESI[†]). The relatively weak absorption 250000

200000

150000

100000

50000

0

300

ε (M⁻¹cm⁻¹)

bands from 350 nm extending to the visible region are ascribed to both spin-allowed, spin-forbidden metal-to-ligand charge transfer (MLCT) and ligand-to-ligand charge transfer (LLCT) characters mixed with some ligand-centered (LC) content, by reference to reported Ir(III) complexes.²⁰

To assist in assigning the nature of the excited states involved in the experimental absorption spectra, 40 singlet excited-states have been calculated based on TD-DFT calculations (vide supra). The results shown in Fig. S4-S7, ESI⁺ reveal that the simulated absorption spectra agree well with the experiment. The calculated excited energies, configurations, oscillator strength, along with corresponding orbital distributions of the four complexes, are summarized in Tables S1-S4, ESI[†] and shown in Fig. S8-S11 (ESI[†]). Here, taking complex 1 as an example, as shown in Fig. S8, ESI⁺ the occupied molecular orbitals involved in main excitations, HOMO -1, HOMO-3 and HOMO-4, mainly reside on the cyclometalated ligands, while HOMO-7 locates on the ancillary ligand with no distribution on the cyclometalated ligands. Except for the lowest-unoccupied molecular orbital (LUMO) of complex 1 that resides on ancillary ligand, LUMO+1 and LUMO+2 still delocalize over the cyclometalated ligands. Based on TD-DFT



500

600

400

results (Table S1, ESI[†]), the absorption bands in the region of 270–350 nm originate predominantly from the excitation of HOMO–4 \rightarrow LUMO+1, HOMO–3 \rightarrow LUMO+2 and HOMO–7 \rightarrow LUMO. Accordingly, the high-energy absorption bands ($\lambda_{abs} < 350$ nm) are mainly attributed to the π – π * transitions of the free ligands. For 1, the calculated absorption bands from 380 nm extending to the visible region result from the excitation of HOMO \rightarrow LUMO, HOMO–1 \rightarrow LUMO and HOMO \rightarrow LUMO+1. The HOMO of 1 localizes on Ir atom with some distribution on cyclometalated ligands. Thus, these absorption bands are assigned to the mixture of MLCT and LLCT, with additional LC excited-state characters, which is in line with our experimental data and previous reports.^{6a,8g,20} The corresponding assignments for the absorption bands of complexes 2–4 are achieved according to the TD-DFT results.

It is also known that the frontier molecular orbitals are very important since they are directly linked to the photophysical properties, such as absorption and emission. Herein, further insight into their photophysical properties are gained via the DFT approach. The frontier molecular orbitals of them, *i.e.* the highest-occupied molecular orbital (HOMO) and the lowestunoccupied molecular orbital (LUMO), and the energy evolution for complexes 1-4 are illustrated in Fig. 2. Similar to reported cationic Ir(III) complexes,^{6a,8e,21} the HOMOs of them reside on the cyclometalated ligands (mainly on π orbitals of the benzimidazole group) and the iridium ions, while the LUMOs mainly delocalize over the pyridinylbenzoimidazole moieties of the ancillary ligands. Clearly, the peripheral carbazole groups in complexes 2-4 do not contribute to both the HOMOs and LUMOs. In addition, the calculated HOMO energy levels (-5.68 eV for 1, -5.69 eV for 2, -5.71 eV for 3 and -5.70 eV for 4) and LUMO energy levels (-2.52 eV for 1, -2.55 eV for 2, -2.54 eV for 3 and -2.56 eV for 4) are similar. As a result, the calculated HOMO-LUMO gap for complex 1 is 3.16 eV. Complexes 2-4 also show almost identical HOMO-LUMO gaps as calculated for 1, with the values of 3.14, 3.17 and 3.16 eV for complexes 2, 3 and 4, respectively. The theoretical calculation results suggest that attaching the carbazole groups to the cyclometalated and/or the ancillary ligands of complexes 2-4 does not significantly influence the HOMO and

Complex	Emission at room ter	Electrochemical data ^c				
	λ_{\max}^{a}/nm	$\Phi^{b}\left(au/\mu \mathrm{s} ight)$	$10^{-5} \kappa_{\rm r} / {\rm s}^{-1}$	$10^{-5}\kappa_{ m nr}/{ m s}^{-1}$	$E_{ m ox}^{1/2}/ m V$	$E_{\rm red}^{1/2}/{ m V}$
1	$569 (CH_2Cl_2)$	0.60 (0.70)	8.7	5.7	0.86	-1.82
	571 (neat film)	0.18(0.25)				
2	$572 (CH_2Cl_2)$	0.43 (0.70)	6.1	8.1	$0.85, 1.02^d$	-1.81
	574 (neat film)	0.25(0.62)				
3	$569 (CH_2Cl_2)$	0.46 (0.75)	6.1	7.2	$0.85, 1.00^d$	-1.81
	575 (neat film)	0.23 (0.63)				
4	$570 (CH_2Cl_2)$	0.44 (0.63)	7.0	8.8	$0.79, 1.06^d$	-1.81
	577 (neat film)	0.31 (0.66)				

1.0

0.0

700

 Table 1
 Photophysical and electrochemical properties of complexes 1–4

^{*a*} Emission spectra of complexes **1–4** were measured in CH₂Cl₂ solution. ^{*b*} Quantum yields were measured in an integrating sphere system. ^{*c*} Collected in CH₃CN solutions; *vs.* Fc⁺/Fc (Fc is ferrocene). ^{*d*} Irreversible.



Fig. 2 Schematic diagram showing the electron density distribution and the energy values calculated for the HOMO and LUMO of complexes **1–4**.

LUMO energy levels as well as HOMO–LUMO energy gaps compared with those of **1**. Similar electrochemical gaps and emission energies are thus expected for these complexes.

Upon photoexcitation, each complex displays broad, almost featureless and strong emission spectra in both CH₂Cl₂ solutions and neat films at room temperature. In solution, the emission peaks maxima of complexes 1-4 are at 569, 572, 569, 570 nm, with quantum efficiency (Φ) of 0.60, 0.43, 0.46 and 0.44 for 1, 2, 3 and 4 respectively. Compared with complex 1, the decrease in Φ in CH₂Cl₂ solution for complexes 2-4 is presumably attributed to more efficient non-radiative decay caused by intramolecular rotation of the carbazole group.²² The calculated nonradiative rates (κ_{nr}) in solution also exhibit the same trend. Compared with 1, complexes 2-4 show relatively large κ_{nr} values as presented in Table 1. In sharp contrast, functionalized complexes 2-4 show much higher Φ in neat films than that of complex 1 (see Table 1), indicating that the incorporation of a carbazole group at the periphery of the complexes can effectively reduce the self-quenching. The excited-state lifetimes for them in neat films have also been measured and the results show that excited-state lifetime increases with increasing the number of carbazole groups (Table 1). This results further support that the bulky moieties attached into the Ir(III) complexes decrease the intermolecular interaction, leading to much higher Φ in neat films.^{11a} Moreover, upon cooling the CH₂Cl₂ solution to 77 K, the emission spectra of complexes 1-4 are largely blue-shifted, but the shape of peaks remains broad and featureless (Fig. S12, ESI⁺). The broad and unstructured shapes of emission spectra in both the solution and films as well as the rigid-chromism indicate that their excited-states show predominant ³MLCT character.8f,23

To understand the nature of the emissive excited state involved in the emission process, quantum chemical calculations have been performed. The electronic and molecular structures of the lowest triplet state (T_1) for complexes **1–4** were optimized at the unrestricted UB3LYP level with a spin



Fig. 3 Spin density and electron density distribution calculated for the optimized lowest lying triplet states (T_1) of complexes 1 and 4. The energy difference E computed between the S_0 and T_1 states of complexes 1 and 4 is 2.23 and 2.23 eV, respectively.

multiplicity of 3. The energy difference between T_1 and S_0 is calculated to be similar for 1 (2.23 eV, 556 nm), 2 (2.23 eV, 556 nm), 3 (2.24 eV, 554 nm) and 4 (2.23 eV, 556 nm), respectively, which is consistent with the trends of their emission energy. Fig. 3 depicts the HOMO and LUMO orbitals of complexes 1 and 4 that are mainly involved in the S_0-T_1 transitions along with the spin density contour for the T₁ excited states. The corresponding data for complexes 2 and 3 can be found in Fig. S13 (see ESI[†]). The four complexes exhibit a similar spin density distribution in the T₁ state, that is, Ir: 0.43, cyclometalated ligand (C^N): 1.37, ancillary ligand (N^N): 0.20 for 1; Ir: 0.41, C^N: 1.39, N^N: 0.20 for 2; Ir: 0.43, C^N: 1.37, N^N: 0.20 for 3; Ir: 0.43, C^N: 1.39, N^N: 0.20 for 4, respectively. It is noted that the unpaired-electron spin density distribution for complexes 1–4 perfectly matches the topology of the HOMO \rightarrow LUMO excitation from which the T_1 excited-states originate (see Fig. 3 and Fig. S13, ESI⁺). These results further confirmed that the mixed ³MLCT and ³LLCT excited-state characters are attributed to their lowest triplet states. The introduction of carbazole groups to both ligands has little effect on the excitedstate characters as well as emission color, which is in good agreement with our experimental data (see emission spectra, Fig. 1).

Electrochemical properties

The electrochemical behaviors of complexes **1–4** have been determined by cyclic voltammetry (CV) and the redox potentials are listed in Table 1. According to previous reports, the reduction of cationic Ir(m) complexes usually occurs on the ancillary ligands.^{11*b*,24} It is proposed that all complexes exhibit similar reduction processes in CV curves. As expected, the electrochemical data show that each complex exhibits a reversible reduction process in CH₃CN solution at ~–1.81 V *vs.* Fc/Fc⁺. The almost identical reduction potentials for all complexes also suggest that the carbazole group introduced into both ligands exerts little influence on the LUMO level of the complexes. For oxidation processes, all complexes show one reversible oxidation peak at ~+0.79–0.86 V *vs.* Fc/Fc⁺. Moreover, an additional oxidation peak at ~+1.00–1.06 V has been observed

in complexes 2–4, which might be attributed to the attachment of the carbazole groups. Their redox reversibility indicates that both the holes (upon oxidation) and electrons (upon reduction) can be easily transported and is beneficial for the application of the complexes in LECs. The electrochemical gap for complexes 1–4 is 2.68, 2.64, 2.66, 2.60 eV, respectively, further indicating that the attachment of carbazole group does not significantly affect their emission energy as well as electrochemical properties. The trends are in good agreement with their photophysical data (see Section 2.1) and the theoretical values calculated for HOMO–LUMO energy gaps (3.16 for 1, 3.14 for 2, 3.17 for 3, 3.16 eV for 4, respectively).

Metal-centered states (³MC)

Cationic Ir(III) complexes as emitter layer in LECs exhibit several advantages compared with OLEDs, and much effort has been devoted to the development of novel charged Ir(III) complexes and optimization of LECs recently. However, the relatively short lifetime of devices is observed in iTMC-based LECs and mainly originates from the degradation process of iTMC in metal-centered (³MC) states during the device operation;²⁵ the ³MC state is essentially defined as the excitation of an electron from the occupied $t_{2g}(d\pi)$ HOMO to the unoccupied $e_{2g}(d\sigma^*)$. The rupture of metal-ligand bonds would open the structures of the complexes and enhance the reactivity of complexes in the ³MC state, resulting in detrimental degradation processes and unstable LECs.^{6d,26} To evaluate the stability of the complexes, the ³MC states of them have been studied following the methodology illustrated in the reported works.^{8e,25,27} The metal-centered characters of the triplet state for complexes 1-4 were confirmed by the spin densities calculated for the optimized ³MC state geometries. The spin densities are mainly concentrated on the iridium atom, and have 1.53, 1.54, 1.54 and 1.54 unpaired electrons for complexes 1, 2, 3 and 4 in ${}^{3}MC$ excited-states, respectively (ESI, Fig. S14^{\dagger}). In addition, ³MC states are calculated to lie 0.63 eV (1), 0.66 eV (2), 0.64 eV (3) and 0.66 eV (4), respectively, above the lowest triplet states. The similar energy difference between the ³MC excited-state and T1 state indicates that the probability of populating the ³MC states should be approximately similar for the four complexes.

In light of the experimental and theoretical results, Bolink *et al.* have demonstrated that the metal–ligand bond length in the ³MC state played a key role for the stability of the Ir(m)-based LECs. The selected key bond lengths for complexes 1–4 in ³MC states have been determined and are shown in Fig. 4. As found in previous studies, construction of intramolecular π - π interactions in cationic Ir(m) complexes is an effective approach to reduce the opening of structures in the ³MC state.^{11e,26,28} Interestingly, the opening of the structure of the complexes in the ³MC state for complexes 1–4 is effectively restricted, leading to the virtual decoordination of only one of the N_{cyclometalated ligand} atoms, although they do not possess intramolecular π -stacking. For example, the Ir–N bonds (BL2) of the cyclometalated ligands in complex 1 close to the benzo-imidazole moiety of the ancillary ligand only lengthen from



Fig. 4 Selected bond lengths at optimized ${}^{3}MC$ excited-states of complexes 1–4.

2.08 Å in the ground state (S_0) to 2.25 Å in the 3MC state. In contrast, electron promotion results in the elongation of another Ir-N_{cyclometalated ligand} length (BL1), from 2.08 Å in the S_0 state to 2.74 Å in ³MC state for 1. Similar trends for the changes in bond lengths are also observed in complexes 2-4. As a consequence, relative high stability of complexes 1-4 in LECs might be expected. Herein, the question remains as to what results in restriction of the rupture of metal-ligand bond in ³MC states for these complexes. Is it caused by the cyclometalated ligand or by the ancillary ligand? To address this question, detailed analysis of ³MC states for another two cationic Ir(III) complexes as shown in Fig. 5, have been performed. Two complexes, C1 and C2, contain the same cyclometalated ligand and ancillary ligand as our studied complexes 1-4, respectively, but a different third ligand. The geometry optimization of ³MC state for C1 and C2 were carried out using the same method as complexes 1-4 (Fig. S15, ESI⁺).

As shown in Fig. 5, it is clear that both bond lengths of Ir-N_{cyclometalated ligand} in C1 are lengthened from 2.08 and 2.08 Å in S₀ to 2.50 and 2.51 Å in ³MC state, respectively, indicating that the cationic Ir(m) complexes with pyridinylbenzoimidazole-based ancillary ligands cannot effectively restrict the opening of the structure. However, we find that the bond length (BL2) of C2 only lengthens from 2.08 Å in S_0 to 2.25 Å in the ³MC state, which is very similar to those found in complexes 1-4. Based on these results, it is suggested that the cationic Ir(m) complexes with phenylbenzoimidazole-based cyclometalated ligand would aid in reducing the degradation reaction in ³MC in some extent and precluding the attack by nucleophiles.^{6d,11e} This finding would be helpful to further designing stable cationic Ir(III) complexes for use in LECs through carefully functionalizing phenylbenzoimidazole ligand.



Fig. 5 (a) Chemical structures of complexes C1 and C2. (b) Minimum-energy structures calculated for the ${}^{3}MC$ states of C1 and C2; BL1 and BL2 represent the bond lengths of Ir–N_{cyclometalated ligand} of both complexes.

Charge carrier injection and transporting properties

It is well known that IP and EA are usually the main factors in evaluating the efficiency of holes and electrons injection; lower IP and higher EA are beneficial to injection of holes and electrons, respectively.²⁹ To investigate the effects of the functional group (carbazole moiety) on the charge-injection and transport properties of complexes, some parameters such as ionization potentials (IP), electron affinities (EA) and the reorganization energy (λ) have been calculated through theoretical calculations. For clarity, a schematic diagram of the calculated parameters is presented in Fig. S16, ESI.[†] The values of the IP and EA together with hole extraction potential (HEP) and electron extraction potential (EEP) for complexes 1-4, which are obtained by using reported methods, are listed in Table 2. Compared with complexes 1-3, complex 4 that contains much more carbazole moieties shows a significant decrease in IP, indicating that the introduction of carbazole group endows corresponding complexes with better hole-injection ability. Note that, all complexes exhibit nearly identical EA potential, thus implying that they have comparable electron-injection abilities.

Table 2 Vertical ionization potential (IP), vertical electron affinity (EA), extraction potential (HEP and EEP) and intramolecular reorganization energy (λ_{hole} and $\lambda_{electron}$). All units in eV

Complex	IP/V	HEP	EA/V	EEP	$\lambda_{ m hole}$	$\lambda_{ m electron}$
1	8.35	8.11	3.21	3.67	0.24	0.46
3	8.12 7.79	8.03 7.72	3.23	3.74 3.72	0.09	0.51
4	7.70	7.65	3.28	3.79	0.05	0.51

According to the Marcus electron transfer regime,³⁰ two important parameters, *i.e.* reorganization energy (λ) and electronic coupling (t) are considered to evaluate the chargetransfer rate and balance. However, the electronic coupling cannot be determined accurately without the packing structure. Thus, only the reorganization energy for all complexes was calculated to preliminarily evaluate the charge-transfer rate in this work. According to the semiclassical Marcus–Hush model,³⁰ the charge transfer rate k can be calculated as following eqn (1), in which λ is the reorganization energy, $k_{\rm B}$ is the Boltzmann constant, A is a factor related to the electronic coupling between adjacent molecules and T is the temperature.

$$k = A \exp\left(-\frac{\lambda}{4k_{\rm B}T}\right) \tag{1}$$

As seen in eqn (1), it can be found that the charge transport rate strongly depends on the reorganization energy λ . It is accepted that λ is determined by fast changes in molecular geometry when a charge is added or removed and slow variations in the surrounding medium, *i.e.* the inner reorganization energy (λ_i) and the external reorganization energy (λ_e). As presented in the previous report, λ_e is very small and λ_i is dominant in λ . Hence, we only discuss λ_i to investigate their charge-transfer rate in this work. From Fig. S16, the reorganization energy for the hole and electron transfer can be evaluated according to the following expressions (eqn (2) and (3)), respectively.³¹

$$\lambda_{\text{hole}} = \lambda^{+} + \lambda^{0}$$

= $[E^{+}(\mathbf{M}^{0}) - E^{+}(\mathbf{M}^{+})] + [E^{0}(\mathbf{M}^{+}) - E^{0}(\mathbf{M}^{0})]$
= $\mathbf{IP} - \mathbf{HEP}$ (2)

$$\begin{aligned} h_{\text{electron}} &= \lambda^{-} + \lambda^{0} \\ &= [E^{-}(\mathbf{M}^{0}) - E^{-}(\mathbf{M}^{-})] + [E^{0}(\mathbf{M}^{-}) - E^{0}(\mathbf{M}^{0})] \\ &= \text{EEP} - \mathbf{EA} \end{aligned}$$
(3)

The calculated λ_{hole} and $\lambda_{\text{electron}}$ values are summarized in Table 2. Clearly, the λ_{hole} values for complexes 2–4 are obviously smaller than that of complex 1, indicating that complexes 2–4 reveal better hole-transporting properties with respect to 1. In contrast to the obvious changes in λ_{hole} , the $\lambda_{\text{electron}}$ for all complexes is almost the same. The obtained results suggest that the attachment of the carbazole moiety to the complexes slightly affects the electron-transporting properties, but effectively improve the hole-transporting properties of the complexes.²⁹ The enhanced quantum efficiency, excellent redox reversibility, better stability and hole-transporting of functionalized complexes 2, 3 and 4 make them good candidates for optical devices.

Conclusion

In summary, a new family of cationic Ir(III) complexes using phenylbenzoimidazole-based ligand as main ligands has been

designed and prepared. Different numbers of carbazole moieties are attached into complexes with a focus on investigating their structure-property relationship. The photophysical and electrochemical results suggest that they exhibit strong luminescent with main ³MLCT/³LLCT excited-state characters and good redox reversibility. Importantly, attaching carbazole moiety at the peripheral of the complexes leads to much higher quantum efficiency in neat films due to increase in intermolecular separation, but has neglectable influence on emission spectra as well as excited-state properties. Compared with 1, significant increase in the charge-transporting ability has been shown for complexes 2-4, as demonstrated by DFT calculation. Furthermore, the unique molecular structure of the phenylbenzoimidazole ligands can restrict the opening of the structure of them in ³MC states effectively, demonstrating their stability when used in LECs, which is first found in cationic Ir(m) complexes without intramolecular π -stacking. It is believed that the results obtained in this work would provide useful information for the design and preparation of highly efficient and stable cationic Ir(m) complexes as well as LECs. Work on these aspects are underway in our laboratory.

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