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Published in:
Scientific Reports

Published: 21/10/2015

Document Version:
Final Published version, also known as Publisher's PDF, Publisher's Final version or Version of Record

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Publication record in CityU Scholars:
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Published version (DOI):
[10.1038/srep15394](https://doi.org/10.1038/srep15394)

Publication details:
Chung, L.-H., Lo, H.-S., Ng, S.-W., Ma, D.-L., Leung, C.-H., & Wong, C.-Y. (2015). Luminescent Iridium(III) Complexes Supported by N-Heterocyclic Carbene-based C[∧]C[∧]C-Pincer Ligands and Aromatic Diimines. *Scientific Reports*, 5, Article 15394. <https://doi.org/10.1038/srep15394>

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SCIENTIFIC REPORTS

OPEN

Luminescent Iridium(III) Complexes Supported by N-Heterocyclic Carbene-based C¹C¹C¹-Pincer Ligands and Aromatic Diimines

Received: 22 June 2015
Accepted: 16 September 2015
Published: 21 October 2015

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Iridium(III) hydrido complexes containing N-heterocyclic carbene (NHC)-based pincer ligand 1,3-bis(1-butylimidazolin-2-ylidene)phenyl anion (C¹C¹C¹) or 1,3-bis(3-butylbenzimidazolin-2-ylidene)phenyl anion (C²C²C²) and aromatic diimine (2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), 4,4'-dimethyl-2,2'-bipyridine (Me₂bpy), or dipyrido-[3,2-f:2',3'-h]-quinoxaline (dpq)) in the form of [Ir(C¹C¹C¹)(N¹N)(H)]⁺ have been prepared. Crystal structures for these complexes show that the Ir–C_{NHC} distances are 2.043(5)–2.056(5) Å. The hydride chemical shifts for complexes bearing C¹C¹C¹ (–20.6 to –20.3 ppm) are more upfield than those with C²C²C² (–19.5 and –19.2 ppm), revealing that C¹C¹C¹ is a better electron donor than C²C²C². Spectroscopic comparisons and time-dependent density functional theory (TD-DFT) calculations suggest that the lowest-energy electronic transition associated with these complexes ($\lambda = 340\text{--}530\text{ nm}$ ($\epsilon \leq 10^3\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$)) originate from a $d_{\pi}(\text{Ir}^{\text{III}}) \rightarrow \pi^*(\text{N}^1\text{N})$ metal-to-ligand charge transfer transition, where the $d_{\pi}(\text{Ir}^{\text{III}})$ level contain significant contribution from the C¹C¹C¹ ligands. All these complexes are emissive in the yellow-spectral region (553–604 nm in CH₃CN and CH₂Cl₂) upon photo-excitation with quantum yields of 10^{–3}–10^{–1}.

Polypyridyl ruthenium(II) or other d⁶-transition metal complexes represent an important class of emissive molecular material^{1–14}. Their triplet [$d_{\pi}(\text{M}) \rightarrow \pi^*(\text{polypyridyl})$] metal-to-ligand charge transfer (³MLCT) excited-states are known to derive rich photophysical and photochemical properties, and their applications in solar energy conversion^{11,15}, organic light emitting devices (OLEDs)¹⁶, photochemistry^{11,12}, and bio-labelling reagents¹⁷ have received considerable interest. Regarding the design of transition metal-containing luminophores, iridium(III) center has received great attention on the basis that it is a heavier analogue of ruthenium(II) center^{18,19}.

After the isolation of stable NHCs by Arduengo and co-workers in 1991²⁰, intensive investigations on NHCs and the derived metal complexes have been centralized on the development of catalytic reagents for organic transformations^{21–25}. On the other hand, employment of N-heterocyclic carbenes (NHCs)-derived ligands as an alternative of polypyridines in the design of transition metal-based luminophores is growing to be an important research topic recently. For example, emissive Ru(II)²⁶, Ir(III)^{18,19}, and Pt(II)²⁷ complexes supported by NHCs have been reported. Several emissive NHC-containing

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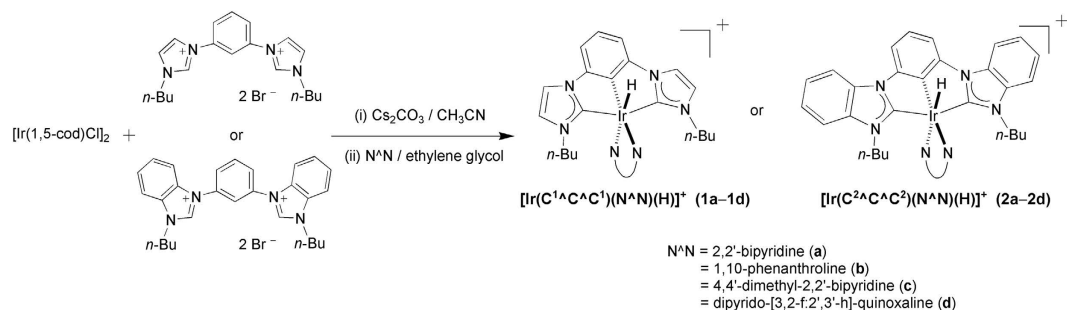


Figure 1. Synthetic route of 1–2

multinuclear Cu, Ag, and Au complexes have also been prepared, in which the NHCs facilitate the metal-metal interaction-induced emissions^{28,29}.

We have initiated a program to develop organometallic Ru(II)/Os(II)–diimine and related luminophores^{30–33}, and very recently we have reported emissive osmium(II) carbonyl complexes bearing 1,3-bis(1-methylimidazolium-2-ylidene)phenyl anion (${}^{\text{Me}}\text{C}^1\wedge\text{C}^1\wedge\text{C}^1\text{Me}$) or 1,3-bis(3-methylbenzimidazolium-2-ylidene)phenyl anion (${}^{\text{Me}}\text{C}^2\wedge\text{C}^2\wedge\text{C}^2\text{Me}$) and aromatic diimine in the form of $[\text{Os}(\text{C}^1\wedge\text{C}^1\wedge\text{C}^1)(\text{N}^{\wedge}\text{N})(\text{CO})]^+$ ³⁰. Spectroscopic and theoretical investigations on $[\text{Os}(\text{C}^1\wedge\text{C}^1\wedge\text{C}^1)(\text{N}^{\wedge}\text{N})(\text{CO})]^+$ have revealed that the emissive state for $[\text{Os}(\text{C}^1\wedge\text{C}^1\wedge\text{C}^1)(\text{N}^{\wedge}\text{N})(\text{CO})]^+$ originates from a $d_{\pi}(\text{Os}^{\text{II}}) \rightarrow \pi^*(\text{N}^{\wedge}\text{N})$ MLCT transition, where the $\text{C}^1\wedge\text{C}^1\wedge\text{C}^1$ ligands contribute significantly to both the $d_{\pi}(\text{Os}^{\text{II}})$ and $\pi^*(\text{N}^{\wedge}\text{N})$ levels. This suggests that the NHC-derived ligands would not only act as point charge/spectator ligands, but can also be involved in the emissive excited-state to modify the photophysical properties of a metal–diimine luminophore. As an extension to scrutinize the effect of $\text{C}^1\wedge\text{C}^1\wedge\text{C}^1$ pincer ligands on the photophysical properties of a $[\text{M}(\text{N}^{\wedge}\text{N})]$ moiety, we now present the preparation, spectroelectrochemical, photophysical, and theoretical investigations of a class of emissive hydrido iridium(III) complexes bearing $\text{C}^1\wedge\text{C}^1\wedge\text{C}^1$ pincer ligands and aromatic diimines, $[\text{Ir}(\text{C}^1\wedge\text{C}^1\wedge\text{C}^1)(\text{N}^{\wedge}\text{N})(\text{H})]^+$.

Results

Synthesis. Emissive Ir(III) complexes $[\text{Ir}(\text{C}^1\wedge\text{C}^1\wedge\text{C}^1)(\text{N}^{\wedge}\text{N})(\text{H})]^+$ (**1–2**) were prepared by refluxing $[\text{Ir}(\text{C}^1\wedge\text{C}^1\wedge\text{C}^1)(\text{CH}_3\text{CN})(\text{Br})(\text{H})]$ with $\text{N}^{\wedge}\text{N}$ in ethylene glycol (Figure 1). $[\text{Ir}(\text{C}^1\wedge\text{C}^1\wedge\text{C}^1)(\text{CH}_3\text{CN})(\text{Br})(\text{H})]$ were synthesized analogously to the corresponding known complexes $[\text{Ir}(\text{Ar}^{\text{C}}\wedge\text{C}^1\wedge\text{C}^1\wedge\text{Ar}^{\text{C}})(\text{CH}_3\text{CN})(\text{Cl})(\text{H})]$ and $[\text{Ir}(\text{Me}^{\text{C}}\wedge\text{C}^1\wedge\text{C}^1\wedge\text{C}^1\text{Me})(\text{CH}_3\text{CN})(\text{I})(\text{H})]$ ($\text{Ar}^{\text{C}}\wedge\text{C}^1\wedge\text{C}^1\wedge\text{Ar}^{\text{C}} = 1,3\text{-bis}(1\text{-arylimidazolium-2-ylidene})\text{phenyl anion}$)^{23,24}. The presence of the hydride ligands in **1–2** was confirmed by the ¹H NMR signals at -20.6 to -19.2 ppm and $\nu_{\text{Ir-H}}$ at 2126 to 2189 cm^{-1} . Both the ¹H and ¹³C NMR spectra signify that **1–2** possess a pseudo-plane of symmetry in solution on the NMR time scale at room temperature. For instances, there are 17 and 19 sets of aromatic ¹³C signal for **1a** and **1b**, respectively. The ¹³C NMR signals at 167.8–180.6 ppm for **1–2** are typical for metalated NHC. It is noted that the hydride chemical shifts for **1a–1d** (-20.55 to -20.27 ppm) are nearly 1 ppm more upfield than those for **2a–2d** (-19.50 to -19.21 ppm). Since the hydride chemical shifts indicate that the electronic shielding effect of the hydrido group results from the metal core's electron cloud, they can be used as probes for the donating ability of the $\text{C}^1\wedge\text{C}^1\wedge\text{C}^1$ ligands³⁴. Therefore, the more upfield hydride chemical shifts for **1a–1d** when compared with **2a–2d** reveals that $\text{C}^1\wedge\text{C}^1\wedge\text{C}^1$ is a stronger electron donor than $\text{C}^2\wedge\text{C}^2\wedge\text{C}^2$. The same conclusion has recently been made in the comparison of the ν_{CO} between $[\text{Os}(\text{Me}^{\text{C}}\wedge\text{C}^1\wedge\text{C}^1\wedge\text{C}^1\text{Me})(\text{N}^{\wedge}\text{N})(\text{CO})]^+$ and $[\text{Os}(\text{Me}^{\text{C}}\wedge\text{C}^2\wedge\text{C}^2\wedge\text{C}^2\text{Me})(\text{N}^{\wedge}\text{N})(\text{CO})]^+$ ³¹. These findings are also consistent with the NHC donor strengths determined by Huynh *et al.*, where benzimidazolium-2-ylidene is suggested to have a weaker donor strength compared with imidazolium-2-ylidene³⁵. Complex $[\text{Ir}(\text{C}^1\wedge\text{C}^1\wedge\text{C}^1)_2]^+$ has also been synthesized according to the method reported in literature²³ for spectroscopic comparisons.

The molecular structures of **1a**(ClO₄), **2a**(ClO₄), and **2b**(ClO₄)₃·CH₃CN have been determined by X-ray crystallography. Perspective views of the cations **1a** and **2b** are depicted in Figure 2; selected bond distances and angles are summarized in Table 1. In each case, the Ir atom adopts a distorted octahedral geometry, with the $\text{C}^1\wedge\text{C}^1\wedge\text{C}^1$ -pincer coordinating in a meridional mode. The ring systems on $\text{C}^1\wedge\text{C}^1\wedge\text{C}^1$ are not perfectly co-planar: the NHC moieties (i.e. imidazolium-2-ylidene or benzimidazolium-2-ylidene units) are tilted towards the hydride ligands, and the angles between the NHC planes are 12.36–22.54°. These angles are larger than those found in $[\text{Ir}(\text{Me}^{\text{C}}\wedge\text{C}^1\wedge\text{C}^1\wedge\text{C}^1\text{Me})(\text{CH}_3\text{CN})(\text{I})(\text{H})]$, $[\text{Ir}(\text{C}^{\text{Me}}\wedge\text{C}^{\text{Me}}\wedge\text{C}^{\text{Me}})(\text{CH}_3\text{CN})(\text{I})_2]$ ($\text{C}^{\text{Me}}\wedge\text{C}^{\text{Me}}\wedge\text{C}^{\text{Me}} = 1,3\text{-bis}(1\text{-butylimidazolium-4,6-dimethylbenzene})$) and $[\text{Ir}(\text{Ar}^{\text{C}}\wedge\text{C}^1\wedge\text{C}^1\wedge\text{Ar}^{\text{C}})(\text{CH}_3\text{CN})(\text{Cl})(\text{H})]$ in which the angles between the NHC planes are 2.73°, 3.63° and 5.60–15.58° respectively^{23,24}. As a comparison, the ring systems on $\text{C}^1\wedge\text{C}^1\wedge\text{C}^1$ for $[\text{Os}(\text{Me}^{\text{C}}\wedge\text{C}^1\wedge\text{C}^1\wedge\text{C}^1\text{Me})(\text{N}^{\wedge}\text{N})(\text{CO})]^+$ and $[\text{Os}(\text{Me}^{\text{C}}\wedge\text{C}^2\wedge\text{C}^2\wedge\text{C}^2\text{Me})(\text{N}^{\wedge}\text{N})(\text{CO})]^+$ ($\text{N}^{\wedge}\text{N} = \text{bpy}$ or phen) are more close to a co-planar configuration (angles between the NHC planes are 2.30–13.00°)³¹. The $\text{C}_{\text{NHC}}\text{-Ir-C}_{\text{Ph}}$ angles for these complexes are 77.22(11)–78.74(15)°, which are only slightly larger than the $\text{C}_{\text{NHC}}\text{-Os-C}_{\text{Ph}}$ angles in $[\text{Os}(\text{Me}^{\text{C}}\wedge\text{C}^1\wedge\text{C}^1\wedge\text{C}^1\text{Me})(\text{N}^{\wedge}\text{N})(\text{CO})]^+$ and $[\text{Os}(\text{Me}^{\text{C}}\wedge\text{C}^2\wedge\text{C}^2\wedge\text{C}^2\text{Me})(\text{N}^{\wedge}\text{N})(\text{CO})]^+$ (75.6(3)–76.8(3)°)³¹. The Ir– C_{NHC} distances (2.043(5)–2.056(5) Å) are notably longer than the Ir– C_{Ph} distances (1.959(4)–1.986(5) Å). Similar findings have been observed

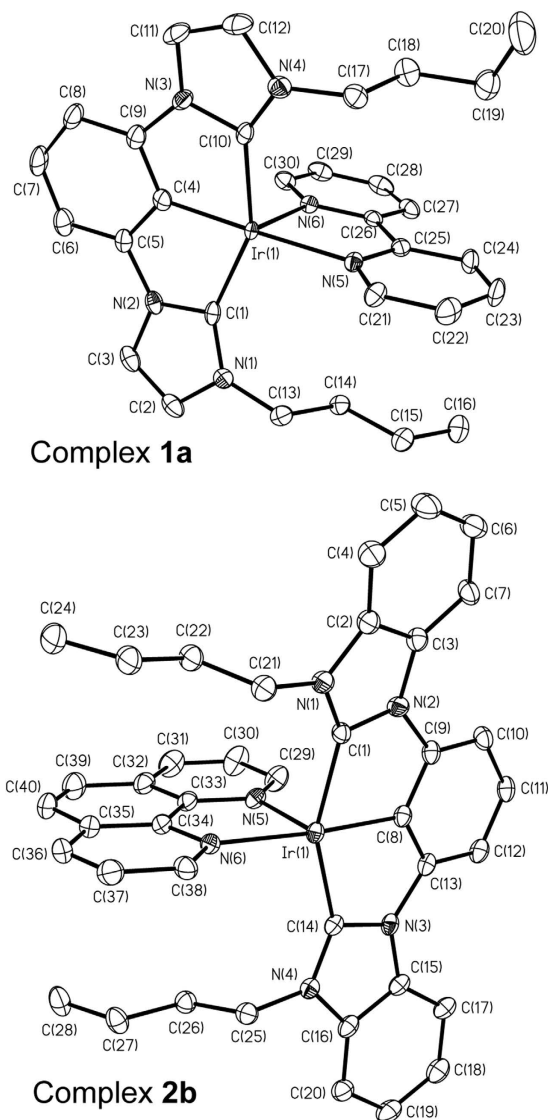


Figure 2. Perspective views of **1a** (top) and **2b** (bottom); thermal ellipsoids are at the 50% and 30% probability level, respectively. Hydrogen atoms are omitted for clarity.

complex	1a	2a	2b
Ir–C _{NHC}	2.049(3), 2.055(3)	2.044(4), 2.046(4)	[2.052(5), 2.056(5)]; [2.045(5), 2.049(5)]; [2.043(5), 2.044(5)]
Ir–C _{Ph}	1.975(3)	1.959(4)	1.986(5); 1.982(5); 1.980(5)
Ir–N _N N (trans to Ph)	2.130(2)	2.134(3)	2.140(4); 2.134(4); 2.149(4)
Ir–N _N N (trans to H)	2.144(2)	2.154(3)	2.135(5); 2.148(4); 2.141(5),
C _{NHC} –Ir–C _{Ph}	77.22(11), 77.86(11)	78.30(15), 78.74(15)	[77.7(2), 77.8(2)]; [77.8(2), 77.9(2)]; [77.7(2), 78.7(2)]
∠Ph/NHC	7.90, 16.96	5.06, 7.35	[4.86, 10.71]; [8.21, 8.35]; [3.35, 10.50]
∠NHC/NHC	22.54	12.36	14.83; 16.41; 13.85

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **1a**, **2a**, and **2b**. The angle between the rings (∠Ph/NHC or ∠NHC/NHC) are calculated from all non-hydrogen atoms on the ring moiety). For **2b**, the crystal contains three crystallographically independent Ir complexes in an asymmetric unit; structural data from each complex are grouped in brackets and listed in the order of Ir(1), Ir(2), and Ir(3).

Complex	$E_{1/2}/V$ vs $Cp_2Fe^{+/0}$	
	reduction	oxidation
1a	−1.93	$E_{pa} = 0.7$
1b	−1.95	$E_{pa} = 0.71$
1c	−2.00	$E_{pa} = 0.69$
1d	−1.83	$E_{pa} = 0.70$
2a	−1.87	$E_{pa} = 0.76$
2b	−1.87	$E_{pa} = 0.76$
2c	−1.95	$E_{pa} = 0.73$
2d	−1.73	$E_{pa} = 0.77$
$Ir(C^1\wedge C^1)_2^+$	—	0.71

Table 2. Electrochemical Data. Supporting electrolyte: 0.1 M $[Bu_4N]PF_6$ in CH_3CN . $E_{1/2} = (E_{pc} + E_{pa})/2$ at 298 K for reversible couples. Anodic peak potential (E_{pa}) at scan rate of 100 mV s^{-1} are recorded for irreversible oxidation wave.

in $[Ir^{(Me)C^1\wedge C^1(Me)}(CH_3CN)(I)_2]^{23}$, $[Ir^{(Me)C^1\wedge C^1(Me)}(CH_3CN)(I)(H)]^{24}$, $[Ir(C^{\wedge Me}C^{Me\wedge})(CH_3CN)(I)_2]$ ($C^{\wedge Me}C^{Me\wedge} = 1,3\text{-bis}(1\text{-butylimidazolium})\text{-}4,6\text{-dimethylbenzene}$)²³, $[Ir^{(Ar)C^1\wedge C^1(Ar)}(CH_3CN)(Cl)(H)]^{24}$, and Zr, Rh, and Os complexes bearing similar $C^1\wedge C^1$ -pincer ligands^{31,36}. Since the Ir–C_{ph} distances in *fac*- $[Ir(C^1\wedge C^1)_3]$ and *mer*- $[Ir(C^1\wedge C^1)_3]$ ($C^1\wedge C^1 = 1\text{-phenyl-}3\text{-methylbenzimidazol-}2\text{-ylidene-C,}C^2$) are in the range of $2.071(7)\text{--}2.099(4)\text{ \AA}^{18}$, the significantly shorter Ir–C_{ph} distances in this work most likely arise from the strain intrinsic to the metal– $C^1\wedge C^1$ moieties.

Electrochemistry. Cyclic voltammetry has been used to examine the electrochemistry of the complexes (Table 2; all values vs $Cp_2Fe^{+/0}$). **1–2** show irreversible first oxidation waves at $E_{pa} = 0.69$ to 0.77 V (scan rate = 100 mV s^{-1}), and reversible first reduction couples at $E_{1/2} = -2.00$ to -1.73 V . It is noted that both the first oxidation waves and the first reduction couples are sensitive to the change of $C^1\wedge C^1$ and N^N. For example, the first reduction potentials for **1a–1d** (-2.00 to -1.83 V) are slightly more negative than those for **2a–2d** (-1.95 to -1.73 V), and the ease of reduction follows the order: **d** > **b** ≈ **a** > **c**. These findings suggest that both the highest occupied molecular orbitals (HOMOs) and the lowest unoccupied molecule orbitals (LUMOs) for **1–2** contain contributions from the $C^1\wedge C^1$ and N^N, in agreement with our DFT calculations (see discussion below). Moreover, the contribution of N^N to the LUMOs of **1–2** is apparent as $[Ir(C^1\wedge C^1)_2]^+$ does not feature any reduction wave within the solvent window.

UV–Visible Absorption and Spectroelectrochemistry. The UV–visible spectral data for **1**, **2**, and $[Ir(C^1\wedge C^1)_2]^+$ are summarized in Table 3, and their absorption spectra are depicted in Figure 3. **1–2** exhibit intense, high-energy absorptions at $\lambda \leq 340\text{ nm}$ ($\epsilon \geq 10^4\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$), and moderately intense bands at $\lambda > 340\text{ nm}$ ($\epsilon \approx 10^3\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$) with tailing up to 530 nm . In the literature, Ir(III) complexes bearing aromatic diimine ligands such as $[Ir(bpy)_3]^{3+}$ and $[Ir(phen)_3]^{3+}$ feature highly intense absorptions at $\lambda \leq 320\text{ nm}$ ($\epsilon \geq 10^4\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$), and these are ascribed to $\pi \rightarrow \pi^*(N^N)$ intraligand (IL) transitions^{37–39}. In addition, $[Ir(C^1\wedge C^1)_2]^+$ exhibits intense absorptions at $\lambda \leq 330\text{ nm}$ ($\epsilon \geq 10^4\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$), which are expected to be a mixture of $d_{\pi}(Ir^{III}) \rightarrow \pi^*(C^1\wedge C^1)$ metal-to-ligand charge transfer (MLCT) and $\pi \rightarrow \pi^*(C^1\wedge C^1)$ IL transition. With the origin of absorptions for $[Ir(N^N)_3]^{3+}$ and $[Ir(C^1\wedge C^1)_2]^+$ as references, the high-energy absorptions at $\lambda \leq 340\text{ nm}$ for complexes **1–2** are assigned to be a mixing of $\pi \rightarrow \pi^*(C^1\wedge C^1)$ IL, $\pi \rightarrow \pi^*(N^N)$ IL, and $d_{\pi}(Ir^{III}) \rightarrow \pi^*(C^1\wedge C^1)$ MLCT transitions.

On the other hand, the electronic transitions at $\lambda = 340\text{--}530\text{ nm}$ ($\epsilon \leq 10^3\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$) for **1–2** should contain some $d_{\pi}(Ir^{III}) \rightarrow \pi^*(N^N)$ MLCT character, reasons are as follows: (1) $[Ir(bpy)_3]^{3+}$, $[Ir(phen)_3]^{3+}$, and $[Ir(ppy)_2(bpy)]^+$ ($ppy = 2\text{-phenylpyridine}$) feature $d_{\pi}(Ir^{III}) \rightarrow \pi^*(N^N)$ MLCT transitions in similar energy region ($\lambda_{max} = 370\text{--}520\text{ nm}$, $\epsilon \leq 10^3\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$),^{38–43} (2) a red-shift in absorption energy is observed when N^N is changed from Me_2bpy to bpy , and from $phen$ to dpq ; (3) **1–2** display solvatochromic effect in the spectral region concerned. For example, the λ_{max} for **1a** within this spectral region is 374 nm in CH_3CN , and is 384 nm in CH_2Cl_2 ; (4) there are no corresponding absorption bands for $[Ir(C^1\wedge C^1)_2]^+$. This assignment is consistent with the TD-DFT calculations on complexes **1a** and **2a**, which suggest that the nature of electronic transitions in the spectral region concerned to be mainly attributed to the HOMO–1 \rightarrow LUMO and HOMO–2 \rightarrow LUMO transitions, where the HOMO–1 and HOMO–2 have higher Ir contribution (27–59%) than that in LUMO (3–4%), and LUMO has higher N^N contribution (93%) than those in HOMO–1 and HOMO–2 (3–15%) (see discussion below). The contribution of N^N to the LUMOs for **1** and **2** is further confirmed by spectroelectrochemistry. Thin-layer UV–visible spectroelectrochemistry has been employed to acquire the absorption spectra for **1a**[−] and **2a**[−], the reduced forms of **1a** and **2a** respectively (Figure 4). The isosbestic spectral

complex	λ_{\max}/nm ($\epsilon_{\max}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)
Solvent = CH ₃ CN	
1a	241 (sh, 36670), 283 (26380), 308 (sh, 14980), 319 (sh, 11720), 374 (4240), 439 (sh, 1620)
1b	246 (33910), 260 (30980), 281 (sh, 21780), 308 (10680), 320 (11250), 370 (5460), 455 (sh, 1720)
1c	242 (sh, 37920), 281 (27830), 304 (sh, 16760), 321 (sh, 13090), 371 (4640), 430 (sh, 1950)
1d	250 (sh, 57990), 256 (58720), 288 (37050), 319 (14630), 374 (7180), 459 (sh, 2210)
2a	247 (63480), 271 (44590), 285 (sh, 35650), 309 (25000), 321 (22070), 370 (sh, 5240), 422 (sh, 1710)
2b	248 (57050), 269 (46670), 286 (sh, 30100), 312 (sh, 17530), 321 (19930), 376 (sh, 5090), 430 (sh, 1720)
2c	247 (64180), 270 (48540), 307 (26390), 322 (23220), 369 (sh, 5520), 425 (sh, 1650)
2d	248 (77070), 256 (74100), 285 (47240), 320 (23660), 365 (sh, 7060), 453 (sh, 1660)
[Ir(C ¹ ^C^C ¹) ₂] ⁺	279 (18810), 305 (15410), 318 (15270)
Solvent = CH ₂ Cl ₂	
1a	240 (sh, 40380), 285 (30500), 308 (sh, 15420), 318 (sh, 12550), 351 (4400), 384 (4510), 447 (sh, 1770)
1b	247 (sh, 34120), 262 (33960), 280 (sh, 22810), 309 (10810), 321 (11075), 375 (5690), 472 (sh, 1750)
1c	242 (sh, 40650), 283 (30940), 306 (sh, 16480), 322 (13600), 378 (4670), 422 (sh, 1980)
1d	252 (sh, 60080), 257 (61150), 289 (36820), 320 (14480), 381 (7310), 467 (sh, 2280)
2a	248 (67690), 272 (48350), 282 (sh, 45580), 309 (25340), 321 (23470), 375 (sh, 5460), 441 (sh, 1560)
2b	249 (65520), 269 (56000), 282 (sh, 40080), 311 (sh, 19100), 322 (22270), 385 (sh, 5890), 448 (sh, 1680)
2c	249 (63520), 272 (49670), 308 (25150), 323 (23440), 372 (sh, 5490), 431 (sh, 1820)
2d	249 (80990), 257 (76520), 286 (49670), 321 (23940), 379 (7330), 465 (sh, 1940)
[Ir(C ¹ ^C^C ¹) ₂] ⁺	281 (19600), 305 (15680), 319 (15680)

Table 3. UV-Visible Absorption Data.

changes suggest that the electrochemical reductions of **1a** and **2a** are clean conversions. Notably, reductions of **1a** and **2a** result in enhancement of absorption at ~380 nm and new absorption doublet band near 500 nm. These absorption features were observed in the reduction of [Ir(bpy)₃]³⁺ and are characteristic absorptions for anionic bpy radical (bpy^{•-})⁴⁴.

Emission Spectroscopy. The emission properties of the complexes in fluid solution (CH₃CN and CH₂Cl₂) at 298 K have been investigated (Table 4). Figure 5 depicts the emission spectra for **2a**, **2c**, **2d**, and [Ir(C¹^C^C¹)₂]⁺ in CH₃CN and CH₂Cl₂ which are significantly blue shifted when compared with [Os(C^C^C)(N^N)(CO)]⁺ ($\lambda_{\text{em}} = 676\text{--}731$ nm, solvents = CH₃CN and CH₂Cl₂)³⁰. Quantum yields (Φ) and emission lifetimes (τ) of **1–2** are around $10^{-3}\text{--}10^{-1}$ and $10^2\text{--}10^1$ ns respectively, while those parameters for [Os(C^C^C)(N^N)(CO)]⁺ are around $10^{-4}\text{--}10^{-2}$ and 1–6 μs respectively³⁰. Similar to Os(C^C^C)(N^N)(CO)]⁺, these photophysical parameters for **1–2** are sensitive to the change of C^C^C and N^N, revealing that the emissive state involve both the C^C^C and N^N moieties. For example, in both **1–2** and [Os(C^C^C)(N^N)(CO)]⁺, blue-shift on emission maxima, higher emission quantum yield, and longer excited state lifetime are observed when changing the N^N from 2,2-bipyridine to 1,10-phenanthroline³⁰. The resemblance of the excitation profiles to the absorption spectra signifies that the emissions originate from the energy dissipation of the $d_{\pi}(\text{Ir}^{\text{III}}) \rightarrow \pi^*(\text{N}^{\wedge}\text{N})$ MLCT transitions. Interestingly, similar conclusion has been made on the nature of the emissive excited states in [Os(C^C^C)(N^N)(CO)]⁺³⁰. The emission profile for [Ir(C¹^C^C¹)₂]⁺ is highly structured and the emission maxima (378 and 398 nm) are not sensitive to the change of solvent, therefore these emissions are assigned as $\pi \rightarrow \pi^*$ (C^C^C) ³IL emissions.

Theoretical Calculations. Time-dependent density functional theory (TD-DFT) calculations have been performed on modeling complexes [Ir^(Me)C¹^C^C¹(Me)(bpy)(H)]⁺ (**1a'**) and [Ir^(Me)C²^C^C²(Me)(bpy)(H)]⁺ (**2a'**), in which their metal cores are the same as **1a** and **2a** but the butyl chains on the C^C^C are replaced by methyl groups to reduce computational cost. The ground-state structures of **1a'** and **2a'** have been optimized at the DFT level (functional = PBE0)^{45,46} without symmetry constrain. The conductor-like screening model (COSMO)⁴⁷ has been applied to account for solvent effects upon the electronic transition. All the optimized geometries are in satisfactory agreement with their crystal structures. For example, the Ir–C_{NHC} and Ir–C_{Ph} bond distances calculated for **1a'** (2.05–2.06 and 1.97 Å respectively) are similar to those for **1a** determined by X-ray crystallography (Ir–C_{NHC}: 2.049(3) and 2.055(3) Å; Ir–C_{Ph}: 1.975(3) Å).

The excitation energies and oscillator strengths for the calculated vertical transitions with $\lambda > 360$ nm are summarized in Table 5. Table 6 summarized the compositions of the molecular orbitals (MOs) which

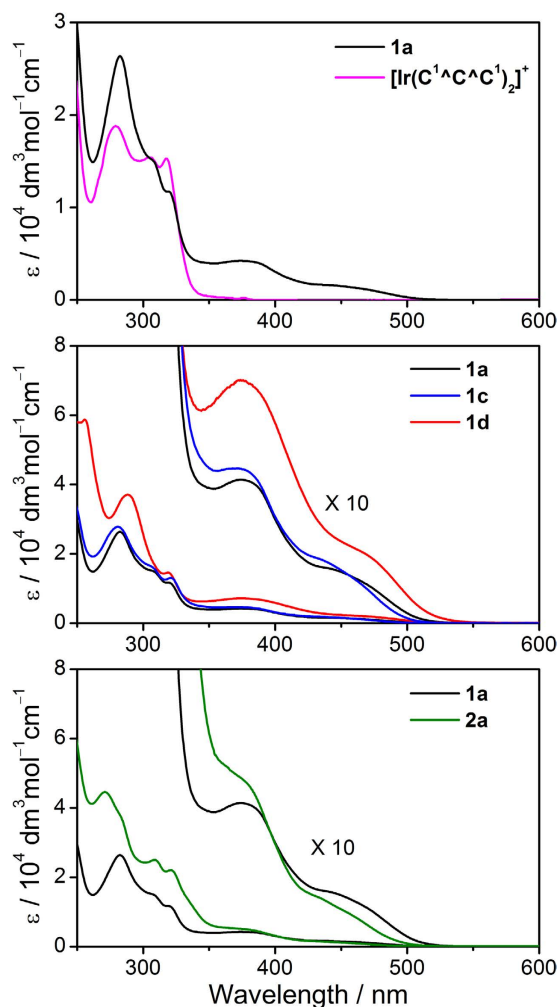


Figure 3. UV-visible absorption spectra of selected complexes in CH₃CN at 298 K.

are involved in the lowest-energy electronic transitions in these complexes. Figure 6 depicts the simulated absorption spectra. It is noted that the calculated lowest-energy dipole allowed transitions ($\lambda > 360$ nm) mainly originate from the HOMO-1 \rightarrow LUMO and HOMO-2 \rightarrow LUMO transitions. The HOMOs-1 and HOMOs-2 have higher Ir contribution (27–59%) than that in LUMOs (3–4%), whereas the LUMOs have higher N^{^N} contribution (93%) than those in HOMOs-1 and HOMOs-2 (3–15%), therefore the transitions contain some Ir \rightarrow $\pi^*(\text{N}^{\wedge}\text{N})$ MLCT character. This finding is consistent with the spectroscopic observation that a red-shift in absorption energy is observed when N^{^N} is changed from Me₂bpy to bpy, and from phen to dpq. Besides, the contribution of C^{^C}C to both the HOMOs-1 and HOMOs-2 are not low (27–69%), suggesting that the C^{^C}C ligands contribute significantly to the $d_{\pi}(\text{Ir}^{\text{III}})$ levels. The electronic difference density plots for **1a'** and **2a'** in their lowest-energy excited state (Figure 6, generated by taking the difference in the excited-state electron density and ground-state electron density) clearly show that electronic charge is depleted from the Ir center and accumulated at the N^{^N} moiety. The emissions from complexes **1–2** are thus believed to be originated from the triplet $d_{\pi}(\text{Ir}^{\text{III}}) \rightarrow \pi^*(\text{N}^{\wedge}\text{N})$ MLCT states.

Conclusion

In this work a series of emissive Ir(III) hydrido complexes bearing the NHC-derived tridentate C^{^C}C pincer ligands and aromatic diimines have been prepared. This joint experimental and theoretical study reveals that the lowest-energy absorptions associated with these complexes arise from a $d_{\pi}(\text{Ir}^{\text{III}}) \rightarrow \pi^*(\text{N}^{\wedge}\text{N})$ MLCT transition, where the C^{^C}C ligands contribute significantly to the $d_{\pi}(\text{Ir}^{\text{III}})$ level. It is therefore evident that the C^{^C}C ligands can modulate the photophysical properties via the formation of the hybrid [Ir + C^{^C}C] molecular orbitals, and this work highlights the opportunities of using NHC-derived ligands to modulate the photophysics of a [M(N^{^N})] core.

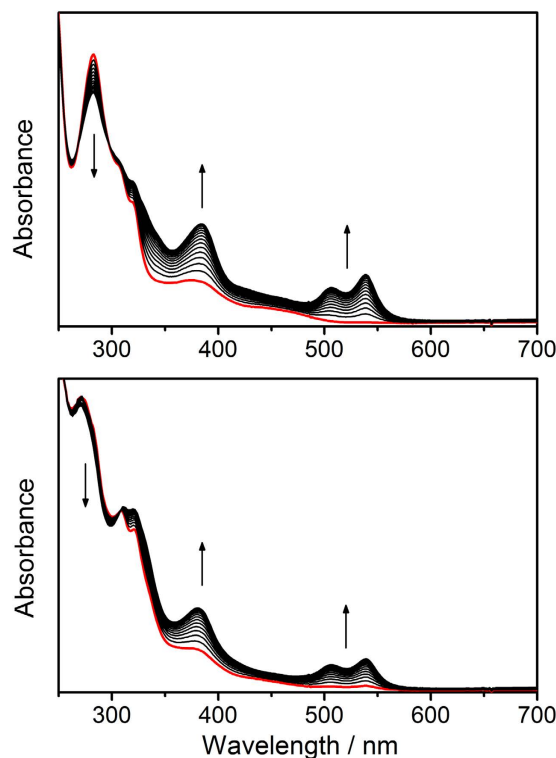


Figure 4. UV-visible absorption spectra for **1a** (top) and **2a** (bottom) in CH₃CN at 298 K during electrochemical reduction at -1.95 V vs Cp₂Fe⁺⁰ (10 s traces; initial trace is shown in red).

Methods

General Procedure. All reactions were performed under an argon atmosphere using standard Schlenk techniques unless otherwise stated. All reagents and solvents were used as received. The C[^]C[^]C ligand precursors, i.e. benzene-bridged bisimidazolium bromide⁴⁸, and [Ir(1,5-cod)Cl]₂ (cod = 1,5-cyclooctadiene)⁴⁹, were prepared according to literature methods. [Ir(C[^]C[^]C)(CH₃CN)(Br)(H)] were synthesized analogously to the corresponding known complexes [Ir(Ar[^]C[^]C[^]C(Ar[^])(CH₃CN)(Cl)(H)] and [Ir(Me[^]C[^]C[^]C(Me[^])(CH₃CN)(I)(H)]^{23,24}. ¹H, ¹³C{¹H}, DEPT-135, ¹H-¹H COSY, and ¹H-¹³C HSQC NMR spectra were recorded on Bruker 400 DRX FT-NMR spectrometer. Figure 7 depicts the labeling scheme for the H and C atoms. Peak positions were calibrated with solvent residue peaks as internal standard. Electrospray mass spectrometry was performed on a PE-SCIEX API 3000 triple quadrupole mass spectrometer. Infrared spectra were recorded as KBr plates on an Avatar 360 FTIR spectrometer. UV-visible spectra were recorded on a Shimadzu UV-1700 spectrophotometer. Elemental analyses were done on an Elementar Vario Micro Cube carbon-hydrogen-nitrogen elemental micro-analyzer. Cyclic voltammetry was performed with a CH Instrument model 600C series electrochemical analyzer/workstation. All the electrochemical measurements were performed in CH₃CN solution with [n-Bu₄N]PF₆ (0.1 M) as supporting electrolyte at room temperature. The glassy-carbon working electrode was polished with 0.05 μm alumina on a microcloth, sonicated for 5 min in deionized water, and rinsed with CH₃CN before use. An Ag/AgNO₃ (0.1 M in CH₃CN) electrode was used as reference electrode, with a platinum wire as the counter electrode. All solutions were degassed with nitrogen before experiments. The E_{1/2} value of the ferrocenium/ferrocene couple (Cp₂Fe⁺⁰) measured in the same solution was used as an internal reference. Steady-state emission spectra were obtained on a Jobin Yvon Fluorolog-3-TCSPC spectrophotometer. Sample and standard solutions were degassed with at least three freeze-pump-thaw cycles. The emission quantum yields for complexes **1-2** were measured by the method of Demas and Crosby⁵⁰ with [Ru(bpy)₃](PF₆)₂ in degassed CH₃CN as standard (Φ_r = 0.062), whereas that for [Ir(C[^]C[^]C[^]C[^])₂]⁺ was measured with quinine sulphate in 0.1M H₂SO₄ as standard (Φ_r = 0.58)⁵¹. The emission quantum yields were calculated by Φ_s = Φ_r(B_r/B_s)(n_s/n_r)²(D_s/D_r), where the subscripts s and r refer to sample and reference standard solution, respectively, n is the refractive index of the solvents, D is the integrated intensity, and Φ is the luminescence quantum yield. The quantity B is calculated by B = 1 - 10^{-AL}, where A is the absorbance at the excitation wavelength and L is the optical path length⁵².

[Ir(C[^]C[^]C)(N[^]N[^]H)](ClO₄), **1-2(ClO₄).** A mixture of [Ir(1,5-cod)Cl]₂ (0.10 mmol), benzene bridged bisimidazolium or bisbenzimidazolium bromide (0.20 mmol), and Cs₂CO₃ (0.43 mmol) was refluxed in CH₃CN (30 ml) for 16 h. Upon cooling to room temperature, the solvent was removed by reduced pressure and the residue was extracted with CH₂Cl₂. The [Ir(C[^]C[^]C)(CH₃CN)(Br)(H)] obtained from this

complex	λ_{em}/nm	Quantum yield (Φ)	Lifetime (τ)/ns
Solvent = CH ₃ CN			
1a	577	4.53×10^{-3}	21
1b	563	3.50×10^{-2}	244
1c	565	1.09×10^{-2}	38
1d	580	7.97×10^{-3}	30
2a	588	2.00×10^{-3}	10
2b	575	8.99×10^{-3}	51
2c	575	4.18×10^{-3}	15
2d	604	2.45×10^{-3}	11
[Ir(C ¹ ^A^C^A^C ¹) ₂] ⁺	378	4.22×10^{-1b}	4663
	398		4802
	sh, 416		5001
Solvent = CH ₂ Cl ₂			
1a	568	1.34×10^{-2}	47
1b	553	1.19×10^{-1}	790
1c	555	3.31×10^{-2}	91
1d	567	3.82×10^{-2}	121
2a	578	6.03×10^{-3}	26
2b	560	4.92×10^{-2}	181
2c	566	1.35×10^{-2}	43
2d	584	1.16×10^{-2}	51
[Ir(C ¹ ^A^C^A^C ¹) ₂] ⁺	378	6.07×10^{-1b}	4906
	398		5094
	sh, 416		5298

Table 4. Emission Data for Complexes 1, 2, and [Ir(C¹^A^C^A^C¹)₂]⁺ in solution at 298 K. Measurement conditions: Concentration = 3.0×10^{-5} M; λ_{ex} = 420 nm for 1–2, 340 nm for [Ir(C¹^A^C^A^C¹)₂]⁺. Quantum yields for complexes 1–2 and [Ir(C¹^A^C^A^C¹)₂]⁺ were determined using [Ru(bpy)₃]²⁺ and quinine sulphate as references, respectively.

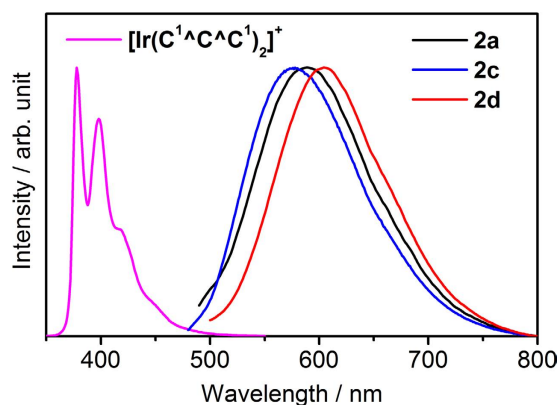


Figure 5. Emission spectra for 2a, 2c, 2d, and [Ir(C¹^A^C^A^C¹)₂]⁺ (λ_{ex} = 420 nm for 1–2, 340 nm for [Ir(C¹^A^C^A^C¹)₂]⁺).

extract was used for the synthesis of 1–2 without further purification. A mixture of [Ir(C¹^A^C^A^C¹)(CH₃CN)(Br)(H)] (0.15 mmol) and diimine (0.5 mmol) was refluxed in ethylene glycol for 3 h. Upon cooling to room temperature, the resultant solution was added to a saturated NaClO₄ solution to give brown solids. The crude product was eluted by column chromatography (neutral alumina, 9:1 (v/v) CH₂Cl₂/CH₃CN as

complex	experimental $\lambda_{\max}/\text{cm}^{-1}$ ($\epsilon_{\max}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)	TD-DFT calculations	
		excitation energy/ cm^{-1} (oscillator strength)	contribution
1a'	22780 (sh, 1620)	21540 (0.0086)	88.8% HOMO-1 \rightarrow LUMO
			7.41% HOMO-2 \rightarrow LUMO
			1.30% HOMO \rightarrow LUMO
	26740 (4240)	25100 (0.1077)	87% HOMO-2 \rightarrow LUMO
			7.07% HOMO-1 \rightarrow LUMO
2a'	23700 (sh, 1710)	23260 (0.0121)	89.6% HOMO-1 \rightarrow LUMO
			5.12% HOMO-2 \rightarrow LUMO
			3.02% HOMO-3 \rightarrow LUMO
	27030 (sh, 5240)	25920 (0.1109)	1.13% HOMO-8 \rightarrow LUMO
			86.6% HOMO-2 \rightarrow LUMO
		6.11% HOMO-1 \rightarrow LUMO	
		2.09% HOMO-3 \rightarrow LUMO	

Table 5. Calculated Vertical Transition Energies ($\lambda > 360 \text{ nm}$) for 1a' and 2a' at the TD-DFT/COSMO level (Solvent = CH₃CN). Excitations with oscillator strength $< 5 \times 10^{-3}$ are omitted; solvent = CH₃CN.

complex	MO	% composition			
		Ir	N^N	C^A^C	H _{hydride}
1a'	HOMO-2	58.93	14.51	26.56	0.00
	HOMO-1	34.22	3.77	61.99	0.02
	HOMO	33.74	4.45	61.53	0.28
	LUMO	3.50	92.93	3.57	0.00
2a'	HOMO-3	10.46	1.13	88.41	0.00
	HOMO-2	56.27	13.54	30.19	0.00
	HOMO-1	27.45	3.35	69.20	0.01
	HOMO	27.81	3.80	68.07	0.32
	LUMO	3.41	92.87	3.72	0.00

Table 6. Selected Molecular Orbital Compositions (%) for 1a' and 2a'.

eluent) as a yellow band. After removal of solvent, the yellow solid was recrystallized by slow diffusion of Et₂O into CH₃CN solution to give yellow crystals.

Complex 1a. Yield: 0.06 g, 50%. Anal. Calcd for C₃₀H₃₄N₆Ir(ClO₄): C, 46.78; H, 4.45; N, 10.91. Found: C, 46.70; H, 4.51; N, 10.88. ¹H NMR (400 MHz, CD₃CN): δ -20.46 (s, 1H, Ir-H), 0.58–0.99, 1.18–1.32 (m, 14H, C₃H₇ of *n*-Bu); 3.17–3.22 (m, 4H, CH₂ of *n*-Bu); 7.05 (d, 2H, $J = 2.1 \text{ Hz}$, H_l); 7.16–7.16 (m, 1H, H_g); 7.22–7.29 (m, 3H, H_i + H_j); 7.41 (d, 1H, $J = 5.2 \text{ Hz}$, H_h); 7.65–7.69 (m, 1H, H_b); 7.74 (d, 2H, $J = 2.1 \text{ Hz}$, H_k); 7.88 (td, 1H, $J = 8.0, 1.6 \text{ Hz}$, H_f); 8.21 (td, 1H, $J = 8.0, 1.6 \text{ Hz}$, H_c); 8.38 (d, 1H, $J = 8.0 \text{ Hz}$, H_e); 8.55 (d, 1H, $J = 8.0 \text{ Hz}$, H_d); 9.67 (d, 1H, $J = 5.2 \text{ Hz}$, H_a). ¹³C NMR (100 MHz, CD₃CN): δ 13.7, 20.2, 34.5, 50.1 (*n*-Bu); 108.3 (C_j); 117.0 (C_k); 121.6 (C_l); 122.9 (C_i); 124.6 (C_e); 125.3 (C_d); 127.7 (C_g); 129.0 (C_b); 138.2 (C_c); 138.3 (C_f); 142.9 (Ir-C_{ph}); 146.1 (Quaternary C in C¹^A^C^1); 151.7 (C_h); 156.9, 157.0 (Quaternary C in bpy); 157.2 (C_a); 167.9 (Ir-C_{carbene}). IR (KBr, cm⁻¹): $\nu_{\text{Ir-H}} = 2189$, $\nu_{\text{Cl-O}} = 1086$. ESI-MS: m/z 670 [M⁺].

Complex 1b. Yield: 0.06 g, 50%. Anal. Calcd for C₃₂H₃₄N₆Ir(ClO₄): C, 48.39; H, 4.31; N, 10.58. Found: C, 48.08; H, 4.36; N, 10.40. ¹H NMR (400 MHz, CD₃CN): δ -20.27 (s, 1H, Ir-H), 0.14–0.51, 0.89–1.06 (m, 14H, C₃H₇ of *n*-Bu); 2.92–3.15 (m, 4H, CH₂ of *n*-Bu); 6.98 (d, 2H, $J = 2.0 \text{ Hz}$, H_l); 7.21–7.37 (m, 3H, H_i + H_j); 7.51 (dd, 1H, $J = 8.0, 5.0 \text{ Hz}$, H_g); 7.74 (d, 2H, $J = 2.0 \text{ Hz}$, H_k); 7.77 (d, 1H, $J = 5.0 \text{ Hz}$, H_h); 8.04 (dd, 1H, $J = 8.0, 5.0 \text{ Hz}$, H_b); 8.12 (d, 1H, $J = 8.8 \text{ Hz}$, H_e); 8.22 (d, 1H, $J = 8.8 \text{ Hz}$, H_d); 8.44 (d, 1H, $J = 8.0 \text{ Hz}$, H_f); 8.78 (d, 1H, $J = 8.0 \text{ Hz}$, H_c); 9.97 (d, 1H, $J = 5.0 \text{ Hz}$, H_a). ¹³C NMR (100 MHz, CD₃CN): δ 13.6, 20.0, 34.4, 50.1 (*n*-Bu); 108.4 (C_j); 117.1 (C_k); 121.6 (C_l); 123.2 (C_i); 126.4 (C_e); 127.8 (C_b); 128.8 (C_d); 128.9 (C_c); 132.1, 132.6 (Quaternary C in phen); 137.4 (C_c); 137.6 (C_f); 142.6 (Ir-C_{ph});

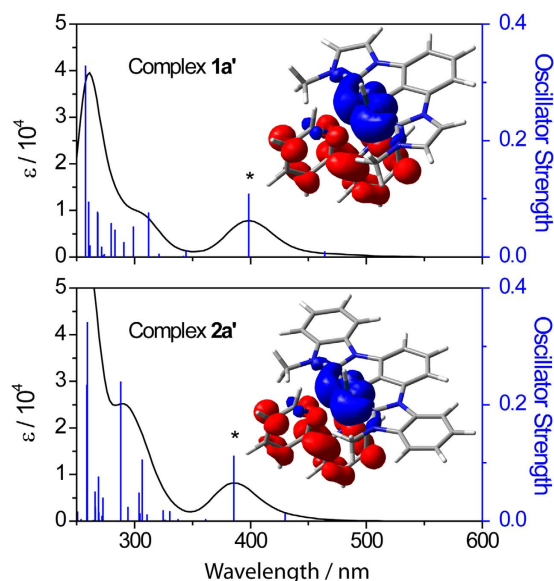


Figure 6. TD-DFT calculated absorption spectrum for model complexes **1a'** and **2a'** in CH_3CN .

Excitation energies and oscillator strengths are shown by the blue vertical lines; spectrum (in black) is convoluted with a Gaussian function having a full width at half-maximum of 3000 cm^{-1} . Inserts show the electronic difference density plots for **1a'** and **2a'** at the vertical transitions marked with * (isodensity value = 0.002 au ; charge accumulation and depletion are represented in red and blue respectively).

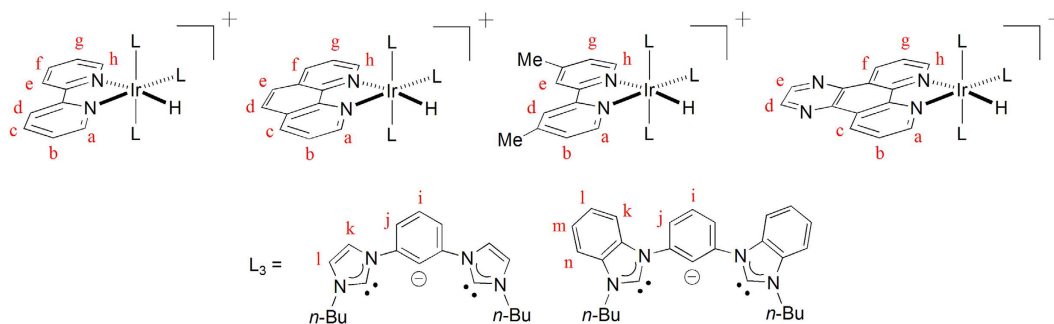


Figure 7. Labeling scheme for H and C atoms in **1-2**.

146.4 (Quaternary C in $\text{C}^1\wedge\text{C}\wedge\text{C}^1$); 148.4, 148.8 (Quaternary C in phen); 152.6 (C_h); 157.3 (C_a); 168.1 ($\text{Ir}-\text{C}_{\text{carbene}}$). IR (KBr, cm^{-1}): $\nu_{\text{Ir}-\text{H}} = 2179$, $\nu_{\text{Cl}-\text{O}} = 1094$. ESI-MS: m/z 695 [M^+].

Complex 1c. Yield: 0.05 g, 40%. Anal. Calcd for $\text{C}_{32}\text{H}_{38}\text{N}_6\text{Ir}(\text{ClO}_4)$: C, 48.14; H, 4.80; N, 10.53. Found: C, 48.44; H, 5.08; N, 10.45. ^1H NMR (400 MHz, CD_3CN): δ -20.55 (s, 1H, Ir-H), 0.58–0.98, 1.19–1.38 (m, 14H, C_3H_7 of $n\text{-Bu}$); 2.39 (s, 3H, CH_3 of Me_2bpy); 2.61 (s, 3H, CH_3 of Me_2bpy); 3.26 (t, 4H, $J = 7.8\text{ Hz}$, CH_2 of $n\text{-Bu}$); 6.96 (d, 1H, $J = 5.6\text{ Hz}$, H_g); 7.05 (d, 2H, $J = 2.1\text{ Hz}$, H_i); 7.20 (d, 1H, $J = 5.6\text{ Hz}$, H_h); 7.21–7.29 (m, 3H, $\text{H}_i + \text{H}_j$); 7.50 (d, 1H, $J = 5.6\text{ Hz}$, H_b); 7.73 (d, 2H, $J = 2.1\text{ Hz}$, H_k); 8.23 (s, 1H, H_e); 8.39 (s, 1H, H_d); 9.46 (d, 1H, $J = 5.6\text{ Hz}$, H_a). ^{13}C NMR (100 MHz, CD_3CN): δ 13.7, 20.3, 34.5, 50.1 ($n\text{-Bu}$); 21.1, 21.3 (CH_3 of Me_2bpy); 108.2 (C_j); 117.0 (C_k); 121.5 (C_l); 122.7 (C_i); 125.2 (C_e); 125.8 (C_d); 128.4 (C_g); 129.6 (C_b); 143.4 ($\text{Ir}-\text{C}_{\text{phen}}$); 146.1 (Quaternary C in $\text{C}^1\wedge\text{C}\wedge\text{C}^1$); 150.5, 150.7 (Quaternary C in Me_2bpy); 150.9 (C_h); 156.6 (C_a); 156.8, 156.9 (Quaternary C in Me_2bpy); 168.4 ($\text{Ir}-\text{C}_{\text{carbene}}$). IR (KBr, cm^{-1}): $\nu_{\text{Ir}-\text{H}} = 2159$, $\nu_{\text{Cl}-\text{O}} = 1107$. ESI-MS: m/z 699 [M^+].

Complex 1d. Yield: 0.06 g, 45%. Anal. Calcd for $\text{C}_{34}\text{H}_{34}\text{N}_8\text{Ir}(\text{ClO}_4)$: C, 48.25; H, 4.05; N, 13.24. Found: C, 48.47; H, 4.28; N, 13.06. ^1H NMR (400 MHz, CD_3CN): δ -20.29 (s, 1H, Ir-H), 0.27–0.75, 1.08–1.21 (m, 14H, C_3H_7 of $n\text{-Bu}$); 2.91–3.22 (m, 4H, CH_2 of $n\text{-Bu}$); 7.00 (d, 2H, $J = 2.1\text{ Hz}$, H_i); 7.24–7.37 (m, 3H, $\text{H}_i + \text{H}_j$); 7.65 (dd, 1H, $J = 8.2, 5.2\text{ Hz}$, H_g); 7.76 (d, 2H, $J = 2.0\text{ Hz}$, H_k); 7.87–7.88 (m, 1H, H_h); 8.18 (dd, 1H, $J = 8.2, 5.2\text{ Hz}$, H_b); 9.18 (d, 1H, $J = 2.1\text{ Hz}$, H_l); 9.22 (d, 1H, $J = 2.1\text{ Hz}$, H_d); 9.41 (dd, 1H, $J = 8.2, 1.2\text{ Hz}$, H_f); 9.75 (dd, 1H, $J = 8.2, 1.2\text{ Hz}$, H_c); 10.09 (dd, 1H, $J = 5.2, 1.2\text{ Hz}$, H_a). ^{13}C NMR (100 MHz, CD_3CN): δ 13.5, 20.1, 34.3, 50.2 ($n\text{-Bu}$); 108.5 (C_j); 117.2 (C_k); 121.7 (C_l); 123.3 (C_i); 127.6 (C_g); 128.9

(C_b); 130.8, 131.5 (Quaternary C in dpq); 134.0 (C_c); 134.2 (C_f); 140.5, 140.5 (Quaternary C in dpq); 142.2 (Ir–C_{ph}); 146.3 (Quaternary C in C¹^C^C¹); 147.7, 147.8 (C_d + C_e); 149.7, 150.0 (Quaternary C in dpq); 153.9 (C_h); 158.5 (C_a); 167.8 (Ir–C_{carbene}). IR (KBr, cm⁻¹): ν_{Ir–H} = 2131, ν_{Cl–O} = 1108. ESI-MS: *m/z* 747 [M⁺].

Complex 2a. Yield: 0.07 g, 50%. Anal. Calcd for C₃₈H₃₈N₆Ir(ClO₄): C, 52.44; H, 4.40; N, 9.66. Found: C, 52.45; H, 4.38; N, 9.46. ¹H NMR (400 MHz, CD₃CN): δ -19.50 (s, 1H, Ir–H), 0.40–1.07, 1.23–1.47 (m, 14H, C₃H₇ of *n*-Bu); 3.30–3.59 (m, 4H, CH₂ of *n*-Bu); 7.07 (t, 1H, *J* = 6.4 Hz, H_g); 7.28–7.35 (m, 2H, H_m); 7.37–7.50 (m, 6H, H_h + H_i + H_j + H_n); 7.71–7.74 (m, 1H, H_b); 7.77–7.87 (m, 3H, H_j + H_f); 8.21 (d, 2H, *J* = 8.0 Hz, H_k); 8.27–8.31 (m, 1H, H_c); 8.38 (d, 1H, *J* = 8.2 Hz, H_e); 8.60 (d, 1H, *J* = 8.2 Hz, H_d); 9.51 (d, 1H, *J* = 5.3 Hz, H_a). ¹³C NMR (100 MHz, CD₃CN): δ 13.8, 20.4, 33.3, 47.5 (*n*-Bu); 109.7 (C_j); 111.9 (C_l/C_n); 112.2 (C_k); 123.6 (C_f); 123.9 (C_m); 124.6 (C_c); 124.7 (C_l/C_n); 125.5 (C_d); 127.9 (C_g); 129.3 (C_b); 133.0, 135.6 (Quaternary C in C²^C^C²); 138.7 (C_f); 138.8 (C_c); 142.9 (Ir–C_{ph}); 146.6 (Quaternary C in C²^C^C²); 152.2 (C_h); 156.6 (Quaternary C in bpy); 157.2 (C_a); 157.3 (Quaternary C in bpy); 180.1 (Ir–C_{carbene}). IR (KBr, cm⁻¹): ν_{Ir–H} = 2126, ν_{Cl–O} = 1075. ESI-MS: *m/z* 771 [M⁺].

Complex 2b. Yield: 0.05 g, 40%. Anal. Calcd for C₄₀H₃₈N₆Ir(ClO₄): C, 53.71; H, 4.28; N, 9.40. Found: C, 53.75; H, 4.30; N, 9.45. ¹H NMR (400 MHz, CD₃CN): δ -19.21 (s, 1H, Ir–H), 0.19–0.35, 0.38–0.45, 0.52–0.67 (m, 14H, C₃H₇ of *n*-Bu); 3.26–3.46 (m, 4H, CH₂ of *n*-Bu); 7.26–7.39 (m, 4H, H_l/H_m + H_n); 7.39–7.48 (m, 3H, H_g + H_m/H_l); 7.52 (t, 1H, *J* = 8.0 Hz, H_i); 7.81 (d, 2H, *J* = 5.1 Hz, H_f); 7.87 (d, 2H, *J* = 8.0 Hz, H_j); 8.08–8.18 (m, 2H, H_b + H_e); 8.21–8.29 (m, 3H, H_d + H_k); 8.41 (d, 1H, *J* = 8.2 Hz, H_n); 8.88 (d, 1H, *J* = 8.2 Hz, H_c); 9.96 (d, 1H, *J* = 8.2 Hz, H_a). ¹³C NMR (100 MHz, CD₃CN): δ 13.8, 20.3, 33.3, 47.6 (*n*-Bu); 109.8 (C_j); 111.9 (C_l/C_m/C_n); 112.3 (C_k); 123.9 (C_i); 124.0 (C_l/C_m/C_n); 124.8 (C_l/C_m/C_n); 126.7 (C_g); 128.1 (C_b); 128.8 (C_d); 129.1 (C_e); 132.2, 132.7 (Quaternary C in phen); 133.1, 135.7 (Quaternary C in C²^C^C²); 137.9 (C_h); 138.1 (C_c); 142.6 (Ir–C_{ph}); 146.9 (Quaternary C in C²^C^C²); 148.3, 148.9 (Quaternary C in phen); 153.2 (C_f); 157.4 (C_a); 180.4 (Ir–C_{carbene}). IR (KBr, cm⁻¹): ν_{Ir–H} = 2129, ν_{Cl–O} = 1090. ESI-MS: *m/z* 795 [M⁺].

Complex 2c. Yield: 0.05 g, 40%. Anal. Calcd for C₄₀H₄₂N₆Ir(ClO₄): C, 53.47; H, 4.71; N, 9.35. Found: C, 53.53; H, 4.77; N, 9.57. ¹H NMR (400 MHz, CD₃CN): δ -19.48 (s, 1H, Ir–H), 0.60–0.97, 1.34–1.47 (m, 14H, C₃H₇ of *n*-Bu); 2.33 (s, 3H, CH₃ of Me₂bpy); 2.67 (s, 3H, CH₃ of Me₂bpy); 3.39–3.67 (m, 4H, CH₂ of *n*-Bu); 6.90 (d, 1H, *J* = 5.7 Hz, H_g); 7.25 (d, 1H, *J* = 5.7 Hz, H_n); 7.28–7.38 (m, 2H, H_m); 7.40–7.50 (m, 5H, H_l + H_i + H_j); 7.54–7.65 (m, 1H, H_b); 7.81 (d, 2H, *J* = 8.0 Hz, H_j); 8.17–8.35 (m, 3H, H_e + H_k); 8.46 (s, 1H, H_d); 9.42 (d, 1H, *J* = 5.6 Hz, H_a). ¹³C NMR (100 MHz, CD₃CN): δ 13.8, 20.5, 33.4, 47.6 (*n*-Bu); 21.1, 21.3 (CH₃ of Me₂bpy); 109.6 (C_j); 111.9 (C_l/C_n); 112.2 (C_k); 123.5 (C_i); 123.9 (C_m); 124.7 (C_l/C_n); 125.3 (C_e); 126.0 (C_d); 128.6 (C_g); 130.0 (C_b); 133.0, 135.7 (Quaternary C in C²^C^C²); 143.4 (Ir–C_{ph}); 146.7 (Quaternary C in C²^C^C²); 151.1, 151.3 (Quaternary C in Me₂bpy); 151.3 (C_h); 156.6 (Quaternary C in Me₂bpy); 156.7 (C_a); 157.1 (Quaternary C in Me₂bpy); 180.6 (Ir–C_{carbene}). IR (KBr, cm⁻¹): ν_{Ir–H} = 2133, ν_{Cl–O} = 1094. ESI-MS: *m/z* 799 [M⁺].

Complex 2d. Yield: 0.06 g, 40%. Anal. Calcd for C₄₂H₃₈N₈Ir(ClO₄): C, 53.30; H, 4.05; N, 11.84. Found: C, 53.41; H, 4.25; N, 11.94. ¹H NMR (400 MHz, CD₃CN): δ -19.22 (s, 1H, Ir–H), 0.23–0.79, 1.18–1.48 (m, 14H, C₃H₇ of *n*-Bu); 3.17–3.61 (m, 4H, CH₂ of *n*-Bu); 7.28–7.46 (m, 6H, H_l + H_m + H_n); 7.54 (t, 1H, *J* = 8.0 Hz, H_j); 7.59 (dd, 1H, *J* = 8.2, 5.2 Hz, H_g); 7.89 (d, 2H, *J* = 8.0 Hz, H_f); 7.91–7.93 (m, 1H, H_h); 8.16–8.35 (m, 3H, H_b + H_k); 9.18 (d, 1H, *J* = 2.1 Hz, H_e); 9.24 (d, 1H, *J* = 2.1 Hz, H_d); 9.37 (dd, 1H, *J* = 8.2, 1.4 Hz, H_i); 9.85 (dd, 1H, *J* = 8.2, 1.3 Hz, H_c); 10.11 (dd, 1H, *J* = 5.2, 1.3 Hz, H_a). ¹³C NMR (100 MHz, CD₃CN): δ 13.7, 20.4, 33.3, 47.7 (*n*-Bu); 109.9 (C_j); 112.0 (C_l/C_m/C_n); 112.3 (C_k); 124.1 (C_i); 124.1, 124.9 (C_l/C_m/C_n); 127.8 (C_g); 129.2 (C_b); 130.9, 131.6 (Quaternary C in dpq); 133.1 (Quaternary C in C²^C^C²); 134.5 (C_c); 134.6 (C_f); 135.7 (Quaternary C in C²^C^C²); 140.4, 140.5 (Quaternary C in dpq); 142.3 (Ir–C_{ph}); 146.9 (Quaternary C in C²^C^C²); 147.8 (C_e); 147.9 (C_d); 149.5, 150.2 (Quaternary C in dpq); 154.5 (C_h); 158.6 (C_a); 180.1 (Ir–C_{carbene}). IR (KBr, cm⁻¹): ν_{Ir–H} = 2130, ν_{Cl–O} = 1097. ESI-MS: *m/z* 847 [M⁺].

X-ray Crystallography. X-ray diffraction data for **1a**(ClO₄), **2a**(ClO₄), and [**2b**(ClO₄)]₃·CH₃CN were collected on an Oxford Diffraction Gemini S Ultra X-ray single crystal diffractometer with Cu Kα radiation (λ = 1.54178 Å) at 133 K. The data were processed using CrysAlis⁵³. The structures were solved by Patterson and Fourier methods and refined by full-matrix least-squares based on *F*² with program SHELXS-97 and SHELXL-97⁵⁴ within WinGX⁵⁵. All non-hydrogen atoms were refined anisotropically in the final stage of least-squares refinement. The positions of H atoms were calculated based on riding mode with thermal parameters equal to 1.2 times that of the associated C atoms. CCDC 1416088–1416090 contain the supplementary crystallographic data for this paper, which can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational Methodology. DFT calculations were performed on model complexes [Ir^{(MeC¹^C^C¹Me)(bpy)(H)}]⁺ (**1a'**) and [Ir^{(MeC²^C^C²Me)(bpy)(H)}]⁺ (**2a'**). Their electronic ground states

were optimized without symmetry constrain using the density functional PBE^{45,46}. The def2-SVP basis sets were used for the H, C, and N atoms, while the def2-TZVP(-f) basis sets were used for the Ir atoms⁵⁶. Zero-order regular approximation (ZORA) was employed to account for relativistic effects. Tight SCF convergence (10^{-8} au) was used for all calculations. The vertical transition energies for these model complexes in CH₃CN were computed at their respective gas-phase optimized ground-state geometries using time-dependent-DFT (TD-DFT) method with the same density functional and basis sets in the geometry optimizations. The combination of the resolution of the identity and the “chain of spheres exchange” algorithms (RIJCOSX)⁵⁷ was used to accelerate all DFT and TD-DFT calculations with the use of appropriate auxiliary basis sets. The conductor-like screening model (COSMO)⁴⁷ was used to account for solvent effects upon the electronic transition. All the calculations were performed using the ORCA software package (version 3.0.2)⁵⁸.

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Acknowledgements

The work described in this paper was supported by the Hong Kong Research Grants Council (Project No. CityU 103911), and the Special Equipment Grant from the Hong Kong University Grants Committee (SEG_CityU02). We are grateful to Dr. Shek-Man Yiu for X-ray diffraction data collection and Mr. Pak-Kei Pat for technical support.

Author Contributions

L.H.C., H.S.L. and S.W.N. carried out all the experiments and performed the data analysis; D.L.M., C.H.L. and C.Y.W. designed the experiments, analyzed the results and wrote the manuscript. All authors reviewed the manuscript.

Additional Information

Competing financial interests: The authors declare no competing financial interests.

How to cite this article: Chung, L.-H. *et al.* Luminescent Iridium(III) Complexes Supported by N-Heterocyclic Carbene-based C[∧]C[∧]C-Pincer Ligands and Aromatic Diimines. *Sci. Rep.* **5**, 15394; doi: 10.1038/srep15394 (2015).



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