

Cyclometalated Ir(III) complexes containing ancillary pyrazole-based ligands

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A series of neutral mononuclear cyclometalated Ir(III) complexes, [Ir(ppy)₂(Me₂pzh)Cl] (1), [Ir(ppy)₂(Mepzh)Cl] (2), [Ir(ppy)₂(Mepz)(Mepzh)] (3), [Ir(ppy)₂(Phpz)(PhpzH)] (4), [Ir(ppy)₂(NPpz)(NPpzH)] (5) and [Ir(ppy)₂(NP-2-pz)(NP-2-pzh)] (6) [where ppyH = 2-phenylpyridine; Me₂pzh = 3,5-dimethylpyrazole; Mepzh = 3-methylpyrazole; PhpzH = 3-phenylpyrazole; NPpzH = 3-(1-naphthyl)pyrazole; NP-2-pzh = 3-(2-naphthyl)pyrazole] have been synthesised and structurally characterised. While (1) and (2) contain neutral pyrazole ligands which binds in a κ' manner, in compounds (3)–(6), one of the pyrazole ligands is anionic while the other is neutral. In the latter also the pyrazole ligands bind to the metal in a κ' manner. Further, the two types of pyrazoles interact with each other by H-bonded interaction. The photophysical and electrochemical properties of all of these compounds have been studied which reveal that the absorption/emission behaviour of these compounds is dependent on the Ir(ppy)₂ unit of the complexes; the ancillary pyrazole ligands do not influence the photophysical behavior in any significant manner.

Keywords: Coordination chemistry, Cyclometallated complexes, Pyrazoles, Iridium, Photophysical properties, Colour tuning, Luminescence

Tuning the colour of luminescence is an important endeavor in display technology research.¹ In this regard, the use of organic/organometallic compounds in display devices has been an area that is being pursued vigorously, both because of the opportunities they present as well as the challenges that need to be overcome. Among organometallic complexes, those that contain heavy metal ions such as Pt(II),² Ir(III),³ Os(III)⁴ or Rh(III)⁵ show highly efficient room temperature phosphorescence, because of strong spin-orbit coupling. Among these compounds, the family that has received the greatest attention thus far has been the cyclometalated complexes of Ir(III). The favorable and strong spin-orbit coupling provided by Ir(III) as well as the scope for significant electronic interaction between Ir(III) and its immediate ligand manifold are largely responsible for the excellent photophysical properties exhibited by these compounds.⁶ In addition, the emission colour of cyclometalated Ir(III) complexes, can be modulated by a careful variation of both, the cyclometalating as well as the ancillary ligand.⁷

Though there have been several reports involving compounds that exhibit red and green emission, achieving pure blue colour is still a difficult challenge. One of the approaches is to use a cyclometalating ligand that contains electron

withdrawing substituents, thereby lowering the HOMO energy and increasing the HOMO-LUMO gap.⁸ Another strategy is to use ancillary ligands such as cyanide⁹ or isocyanide¹⁰ which also facilitate the tuning of the HOMO-LUMO gap. A third approach involving the use of *N*-containing ancillary ligands such as pyrazoles,¹¹ triazole¹² or tetrazoles¹³ is in vogue with varying extent of success.

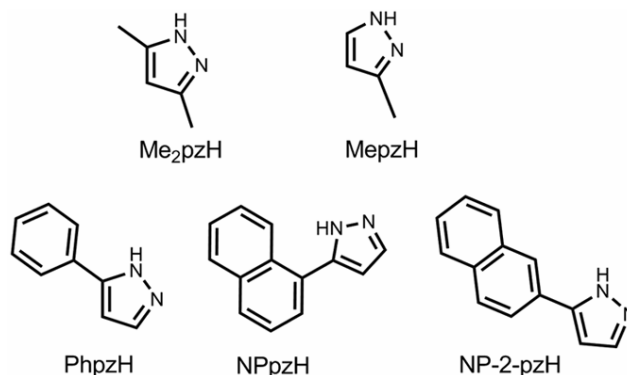
Pyrazole-containing ligands have been used both as a cyclometalating as well as an ancillary ligand.¹⁴ Thus, Thompson and coworkers^{14d,14e} have reported a series of cyclometalated iridium complexes that contained pyrazolyl and bis-(pyrazolyl)borates as ancillary ligands. DFT calculations reveal that the lowest energy excited state for these complexes is an admixture of ³LC and ³MLCT. Any change in the nitrogen ancillary ligand can alter the HOMO energy, which in turn can change the energy of the MLCT. As mentioned above, some pyrazole ligands have already been investigated as ancillary ligands in Ir(III) complexes. However, keeping in view the vast structural modifications that can be achieved on the pyrazole ligands, we felt that their full potential has not been completely exploited. Further, beside the question of colour tuning, from a fundamental point of view, we were interested in knowing the type of coordination interactions that would ensue upon

altering the steric and electronic nature of the pyrazole ligand. Keeping this in view, we have chosen a series of alkyl- and aryl substituted pyrazoles as ancillary ligands (Scheme 1). This study reports the synthesis, X-ray crystal structures, electrochemical behaviour and photophysical studies of [Ir(ppy)₂(Me₂pzh)Cl] (**1**), [Ir(ppy)₂(Mepzh)Cl] (**2**), [Ir(ppy)₂(Mepzh)(Mepzh)] (**3**), [Ir(ppy)₂(Phpz)-(PhpzH)] (**4**), [Ir(ppy)₂(NPpz)(NPpzH)] (**5**), [Ir(ppy)₂-(NP-2-pz)(NP-2-pzH)] (**6**).

Materials and Methods

All manipulations were carried out under an inert atmosphere with the use of standard Schlenk-line techniques. Glassware were dried prior to use. Solvents were dried by conventional methods and deoxygenated prior to use. IrCl₃·3H₂O was purchased from Arora Matthey, India. Triflic acid, silver carbonate, 2-phenyl pyridine, *N,N'*-dimethyl-formamide-dimethylacetal and 3-methyl pyrazole were purchased from Aldrich and used as received. Acetophenone, 1-acetylnaphthalene, 2-acetyl-naphthalene and hydrazine hydrate were purchased from Spectrochem, India. Me₂pzh,¹⁵ PhpzH,¹⁶ NPpzH,¹⁵ NP-2-pzh¹⁵ were synthesised according to literature procedures.

Elemental analyses were carried out by using a Thermo quest CE instrument (model EA1110) CHNSO elemental analyzer. ¹H NMR spectra were obtained on a JEOL-JNM LAMBDA (400 model) spectrometer. ¹H NMR chemical shifts were referenced to the residual hydrogen signal of the deuterated solvents. ESI-MS analyses were performed on a Waters Micromass Quattro Micro triple quadrupole mass spectrometer. UV-visible spectra were recorded using a Perkin-Elmer Lambda-20 UV/vis absorption spectrophotometer. Emission spectra and corresponding life times were measured by time-correlated single photon counting method using a Fluorolog FL3-21 (Horiba Jobin Yvon) spectrofluorometer equipped with a xenon flash lamp. Emission quantum yields were determined by comparison with the emission of a solution of quinine sulfate ($\Phi = 0.545$) in 1 *N* of H₂SO₄, employed as a standard.¹⁷ The excitation wavelength used was 350 nm. The quantum yields were then calculated using the expression, $\Phi_S = \Phi_R (A_S/A_R) (n_S^2/n_R^2)$. Here, the subscripts S and R denote sample and reference respectively, Φ is the fluorescence quantum yield, *A* is the integrated area under the corrected fluorescence spectra, and *n* is the refractive index of the solvent.



Scheme 1

Cyclic voltammetric studies were performed on a BAS Epsilon electrochemical workstation in DCM with 0.1 *M* tetra-*n*-butylammonium hexafluorophosphate (TBAPF₆) as the supporting electrolyte. The working electrode was a BAS Pt disk electrode, the reference electrode was Ag/AgCl and the auxiliary electrode was a Pt wire. The ferrocene/ferrocenium couple occurs at $E_{1/2} = +0.51$ (70) V versus Ag/AgCl under the same experimental conditions. The potentials are reported in volts (V) and the ΔE ($E_{p,a} - E_{p,c}$) values are in millivolts (mV) at a scan rate 100 mVs⁻¹.

X-ray data collection and refinement

Single-crystal X-ray studies were performed on a CCD Bruker Smart Apex diffractometer equipped with an Oxford Instruments low-temperature attachment. All data were collected at 100(2) K using graphite monochromated Mo-K_α radiation (λ_{α} 0.71073 Å). The frames were indexed, integrated, and scaled using the SMART and SAINT software packages,¹⁸ and the data were corrected for absorption using the SADABS programs.¹⁹ Structures were solved and refined with the SHELX suite of programs²⁰ as implemented in X-seed²¹. The “SQUEEZE” option in PLATON program²² was used to remove a disordered solvent molecule from the overall intensity data of compounds (**4**) and (**6**). The figures were drawn using ORTEP.²³ All hydrogen atoms, except pyrazole NH hydrogens, were included at geometrically calculated positions in the final stages of the refinement and were refined according to the “riding model”. The NH hydrogen was not located for (**1**). In all other cases, it was located in the difference Fourier map and refined with restraint. All non-hydrogen atoms were refined with anisotropic thermal parameters except C43 and C51 in compounds (**2**) and (**5**), respectively. Compound (**1**) crystallizes in chiral space group

$P2_12_12_1$ with Flack parameter 0.00(1). Pertinent crystallographic data for compounds (1) – (6) are summarized in Table 1.

Syntheses of the complexes

$[\text{Ir}(\text{ppy})_2(\text{Me}_2\text{pzH})\text{Cl}]$ (1)

A mixture containing $[(\text{ppy})_2\text{Ir}(\mu\text{-Cl})]_2$ (120 mg, 0.11 mmol) and Me_2pzH (22 mg, 0.23 mmol) was heated to reflux for 12 hours under a N_2 atmosphere. Subsequently, the volume of the bright yellow coloured solution was reduced to ~2 mL and diethyl ether was added to induce precipitation. The solid obtained was filtered, washed with diethyl ether (5 mL, 3 times) and dried in vacuum. This compound was identified as (1). The analytically pure compound was obtained by crystallisation from dichloromethane/hexane mixture. Yield: 114 mg (81 %). Anal. (%): Calcd for $\text{C}_{27}\text{H}_{24}\text{IrN}_4\text{Cl}$: C, 51.29; H, 3.82; N, 8.86; Found: C, 51.01; H, 3.65; N, 8.90. ^1H NMR (CDCl_3 , 400 MHz, δ): 12.80 (s, 1H), 9.72 (d, 1H, 5.8 Hz), 7.96 (d, 1H, 5.8 Hz), 7.83 (d, 1H, 7.5 Hz), 7.7 - 7.62 (m, 2H), 7.49 (m, 1H), 7.08 - 6.96 (m, 2H), 6.77 - 6.72 (m, 3H), 6.65 - 6.59

(m, 3H), 6.22 (d, 1H, 7.6 Hz), 6.08 (d, 1H, 7.5 Hz), 5.61 (s, 1H), 3.04 (s, 6H). ESI-MS: m/z 633 $[\text{M} + \text{H}]^+$, m/z 598 $[\text{M} - \text{Cl}]^+$.

$[\text{Ir}(\text{ppy})_2(\text{MepzH})\text{Cl}]$ (2)

The reaction of $[(\text{ppy})_2\text{Ir}(\mu\text{-Cl})]_2$ (100 mg, 0.09 mmol) and MepzH (17 mg, 0.20 mmol) was carried out following a procedure similar to that described for the synthesis of (1). Yield: 91 mg (79 %). Anal. (%): Calcd for $\text{C}_{26}\text{H}_{22}\text{IrN}_4\text{Cl}$: C, 50.51; H, 3.58; N, 9.06; Found: C, 50.39; H, 3.59; N, 8.98. ^1H NMR (CDCl_3 , 400 MHz, δ): 13.01 (s, 1H), 9.75 (d, 1H), 8.01 (d, 1H), 7.97 (d, 1H), 7.81 (d, 1H), 7.72 - 7.68 (m, 2H), 7.50 - 7.25 (m, 4H), 7.03 - 6.80 (m, 4H), 6.61 (m, 2H), 6.29 (d, 1H), 6.01 (d, 1H), 3.01 (s, 3H). ESI-MS: m/z 619 $[\text{M} + \text{H}]^+$, m/z 584 $[\text{M} - \text{Cl}]^+$.

$[\text{Ir}(\text{ppy})_2(\text{Mepz})(\text{MepzH})]$ (3)

A mixture containing $[\text{Ir}(\text{ppy})_2\text{Cl}]_2$ (108 mg, 0.10 mmol) and AgOTf (50 mg, 0.20 mmol) in 20 mL of acetone was refluxed under N_2 for 2 hours. The yellow slurry was allowed to cool and AgCl was removed by filtration. To this filtrate was added MepzH

Table 1 — Crystallographic data and pertinent refinement parameters for (1) – (6)

Compound	(1)	(2)	(3)·CH ₃ CN	(4)·CH ₂ Cl ₂	(5)	(6)·CH ₂ Cl ₂
Emp. formula	$\text{C}_{27}\text{H}_{23.5}\text{ClIrN}_4$	$\text{C}_{26}\text{H}_{22}\text{ClIrN}_4$	$\text{C}_{32}\text{H}_{30}\text{IrN}_7$	$\text{C}_{41}\text{H}_{32}\text{Cl}_2\text{IrN}_6$	$\text{C}_{48}\text{H}_{35}\text{IrN}_6$	$\text{C}_{49}\text{H}_{36}\text{Cl}_2\text{IrN}_6$
Formula wt	631.65	618.13	704.83	871.83	888.02	971.94
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2_12_12_1$	$P2_1/c$	$C2/c$	$P-1$	$P-1$	$P2_1/n$
<i>a</i> (Å)	11.6049(8)	9.786(2)	36.447(5)	9.6716(7)	9.8476(9)	19.387(5)
<i>b</i> (Å)	17.1101(12)	9.2614(19)	10.562(5)	13.6783(10)	13.6875(12)	9.231(5)
<i>c</i> (Å)	22.9387(16)	24.705(5)	15.031(5)	14.1533(10)	14.8383(13)	22.651(5)
α (°)	90.00	90.00	90.00	79.5990(10)	73.1270(10)	90.000(5)
β (°)	90.00	91.80(3)	99.935(5)	87.9120(10)	72.1600(10)	98.024(5)
γ (°)	90.00	90.00	90.00	80.3420(10)	82.549(2)	90.000(5)
<i>V</i> (Å ³)	4554.7(5)	2238.0(8)	5699(3)	1815.5(2)	1820.1(3)	4014(3)
<i>Z</i>	8	4	8	2	2	4
ρ_{calcd} (g cm ⁻³)	1.842	1.835	1.643	1.595	1.620	1.608
μ (mm ⁻¹)	6.004	6.107	4.720	3.863	3.713	3.504
<i>F</i> (000)	2460	1200	2784	862	884	1932
Collected	29299	19659	19205	10517	10171	22548
Independent	10900	5519	4858	7214	7157	8206
Obs. [$I > 2\sigma(I)$]	9946	4029	4303	6770	6612	6791
No. of variables	598	294	328	435	491	527
Goodness-of-fit	1.026	1.070	1.073	1.124	1.041	1.032
Final <i>R</i> indices [$I > 2\sigma(I)$] ^a						
<i>R</i> 1	0.0405	0.0412	0.0305	0.0331	0.0342	0.0435
<i>wR</i> 2	0.0929	0.0931	0.0708	0.0871	0.0814	0.0989
<i>R</i> indices (all data) ^a						
<i>R</i> 1	0.0465	0.0671	0.0357	0.0360	0.0385	0.0549
<i>wR</i> 2	0.0963	0.1097	0.0739	0.0964	0.0849	0.1045

^a $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ with $F_o^2 > 2\sigma(F_o^2)$. $wR_2 = [\sum w(|F_o|^2 - |F_c|^2)^2 / \sum |F_o|^4]^{1/2}$.

(34 mg, 0.41 mmol) and triethyl amine (0.05 ml). The solution was refluxed under nitrogen for 12 h. The solution was allowed to cool to room temperature when a yellow solid separated out. The solid was separated, washed with diethylether and dried under vacuum. Analytically pure compound was obtained by crystallization from dichloromethane/hexane mixture. Yield: 141 mg (62 %). Anal. (%): Calcd for $C_{30}H_{27}IrN_6$: C, 54.28; H, 4.09; N, 12.66; Found: C, 54.12; H, 3.99; N, 12.51. 1H NMR ($CDCl_3$, 400 MHz, δ): 10.01 (s, 1H), 8.75 (d, 1H), 8.08 (d, 2H), 7.77 (d, 2H), 7.81 (d, 2H), 7.70 - 7.65 (m, 4H), 7.56 - 7.25 (m, 4H), 6.99 - 6.80 (m, 2H), 6.50 (m, 2H), 6.32 (d, 1H), 3.10 (s, 3H), 3.01 (s, 3H). ESI-MS: m/z 665 $[M+H]^+$, m/z 584 $[M-Mepz]^+$.

[Ir(ppy)₂(Phpz)(PhpzH)] (4)

The reaction of $[Ir(ppy)_2Cl]_2$ (108 mg, 0.10 mmol), AgOTf (50 mg, 0.20 mmol), PhpzH (59 mg, 0.41 mmol) and triethylamine (0.05 ml) was carried out following a procedure similar to that described for the synthesis of (3). Analytically pure compound was obtained by crystallization by slow diffusion of hexane into a concentrated dichloromethane solution. Yield: 107 mg (68 %). Anal. (%): Calcd for $C_{40}H_{31}IrN_6$: C, 60.97; H, 3.96; N, 10.66; Found: C, 60.50; H, 4.05; N, 10.90. 1H NMR ($CDCl_3$, 400 MHz, δ): 12.51 (s, 1H), 8.01 (d, 2H), 7.77 (d, 2H), 7.60 - 7.53 (m, 8H), 7.19 - 7.15 (m, 6H), 6.88 - 6.83 (m, 2H), 6.77 - 6.73 (m, 2H), 6.63 (d, 4H), 6.29 - 6.26 (m, 4H). ESI-MS: m/z 789 $[M+H]^+$, m/z 646 $[M-Phpz]^+$.

[Ir(ppy)₂(NPpz)(NPpzH)] (5)

The reaction of $[Ir(ppy)_2Cl]_2$ (100 mg, 0.09 mmol), AgOTf (50 mg, 0.20 mmol), NPpzH (80.4 mg, 0.414 mmol) and triethylamine (0.05 ml) was carried out following a procedure similar to that described for the synthesis of (3). Yield: 119 mg (72 %). Anal. (%): Calcd for $C_{48}H_{35}IrN_6$: C, 64.91; H, 3.97; N, 9.46; Found: C, 64.85; H, 3.81; N, 9.04. 1H NMR ($CDCl_3$, 400 MHz, δ): 11.98 (s, 1H), 8.08 (d, 1H), 7.98 (d, 1H), 7.80 (d, 1H), 7.75 (d, 1H), 7.68 - 7.55 (m, 8H), 7.51 (d, 2H), 7.30 - 7.15 (m, 6H), 7.00 - 6.83 (m, 10H), 6.73 (d, 2H), 6.53 (d, 2H), 6.35 (d, 1H). ESI-MS: m/z 889 $[M+H]^+$, m/z 696 $[M-NPpz]^+$.

[Ir(ppy)₂(NP-2-pz)(NP-2-pzH)] (6)

The reaction of $[Ir(ppy)_2Cl]_2$ (100 mg, 0.09 mmol), AgOTf (50 mg, 0.20 mmol), NP-2-pzH (80 mg, 0.41 mmol) and triethyl amine (0.05 ml) was carried out following a procedure similar to that described for

the synthesis of (3). Yield: 125 mg (76 %). Anal. (%): Calcd for $C_{48}H_{35}IrN_6$: C, 64.91; H, 3.97; N, 9.46; Found: C, 64.72; H, 3.51; N, 9.32. 1H NMR ($CDCl_3$, 400 MHz, δ): 12.01 (s, 1H), 8.06 (d, 1H), 7.98 (s, 2H), 7.80 (d, 1H), 7.74 (d, 1H), 7.58 - 7.55 (m, 6H), 7.48 (d, 2H), 7.25 - 7.19 (m, 6H), 6.97 - 6.86 (m, 8H), 6.80 (t, 2H), 6.70 (d, 2H), 6.43 (d, 2H), 6.32 (d, 1H). ESI-MS: m/z 889 $[M+H]^+$, m/z 696 $[M-NP-2-pz]^+$.

Results and Discussion

Synthetic aspects

Direct reaction of the chloro-bridged dimer $[(ppy)_2Ir]_2(\mu-Cl)_2$ with the corresponding pyrazole ligands under refluxing conditions afforded $[Ir(ppy)_2(Me_2pzH)Cl]$ (1) and $[Ir(ppy)_2(MepzH)Cl]$ (2), both of which contain a chloride and a pyrazole ligand. On the other hand, the initial reaction of $[(ppy)_2Ir]_2(\mu-Cl)_2$ with AgOTf (OTf = CF_3SO_3), followed by reaction with the pyrazole ligands afforded chloride-free neutral compounds $[Ir(ppy)_2(Mepz)(MepzH)]$ (3), $[Ir(ppy)_2(Phpz)(PhpzH)]$ (4), $[Ir(ppy)_2(NPpz)(NPpzH)]$ (5), and $[Ir(ppy)_2(NP-2-pz)(NP-2-pzH)]$ (6). In (3)–(6), while one of the pyrazole ligands is deprotonated and anionic the other is neutral and retains the NH hydrogen. All the compounds have been characterised by analytical and spectroscopic techniques (see experimental section). ESI-MS spectra of each of these six complexes reveal the molecular ion signal $[M+H]^+$. The unambiguous structural characterisation of these complexes was carried out by X-ray crystallography as described below.

Molecular structures of (1) – (6)

The molecular structures of (1) – (6) were determined by X-ray crystallography. All the complexes are neutral. Details of the data collection and refinement procedures are presented in the experimental section. Tables S1 – S6 (Supplementary Data) summarise the bond parameters for these compounds. A comparison of relevant bond distances for these compounds is given in Table 2.

The molecular structure of (1) shows octahedral coordination geometry around the central iridium (Fig. 1a). This compound crystallises in the orthorhombic $P2_12_12_1$ space group. The asymmetric unit contains two molecules with similar bond parameters and we restrict our discussion to only one of these molecules. Four of the six coordinating sites around iridium are occupied by the two cyclometallating ppy (C^N) ligands. The remaining

Table 2 — Comparison of selected bond distances (Å) for (1) – (6)

Compd.	Ir – C11	Ir – C22	Ir – N1	Ir – N2	Ir – N3/Cl ^a	Ir – N5
(1)	2.006(6)	2.001(7)	2.045(6)	2.058(6)	2.183(6)	2.506(2)
(2)	2.008(6)	2.009(6)	2.044(5)	2.054(5)	2.168(5)	2.499(2)
(3)	2.016(5)	2.007(5)	2.040(4)	2.037(4)	2.160(4)	2.158(4)
(4)	2.000(5)	2.015(5)	2.036(4)	2.039(4)	2.154(4)	2.146(4)
(5)	2.011(4)	2.019(4)	2.040(4)	2.036(4)	2.148(4)	2.164(4)
(6)	2.027(5)	2.000(5)	2.047(4)	2.026(5)	2.144(4)	2.142(4)

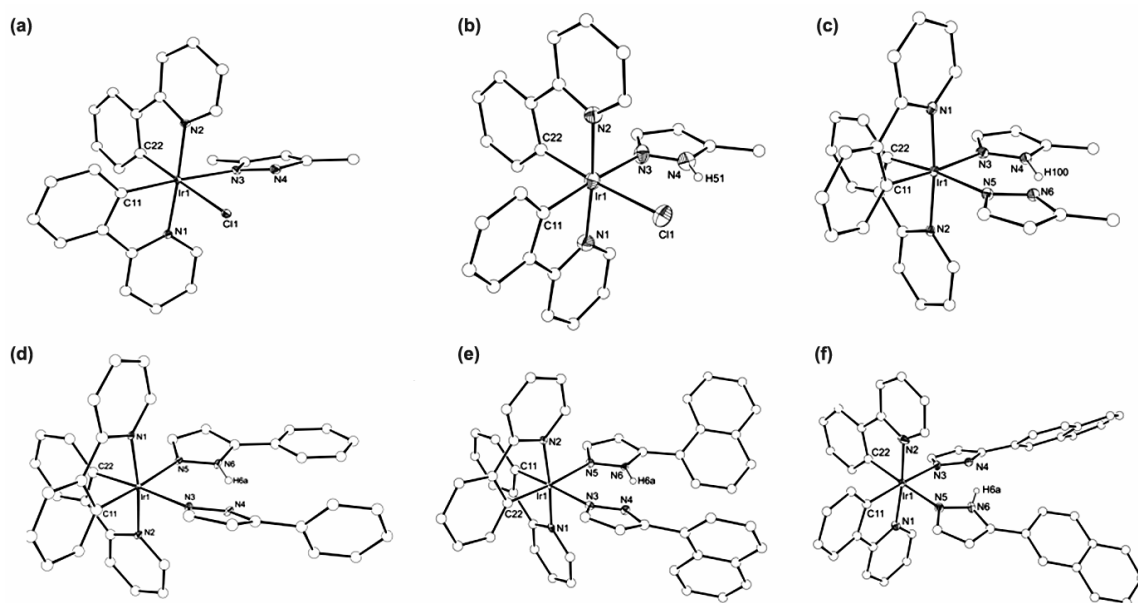
^a For compounds (1) and (2).

Fig. 1 — ORTEP diagrams (30 % probability thermal ellipsoids) of compounds (1) – (6) (a – f). Important atoms have been labeled. Hydrogen atoms, except the NH hydrogens, have been omitted for the sake of clarity.

two sites are coordinated to the nitrogen atom of a Me₂pzH ligand and a Cl ligand. The *cis*-C, C and *trans*-N, N chelate disposition of the ppy ligands of the chloro-bridged precursor complex is retained in the complex. The pyrazolyl N atom coordinated to Ir is positioned *trans* to the metallated C atom of one of the ppy ligands resulting in a longer Ir-N (Me₂pzH) distance (2.183(6) Å) in comparison to Ir-N (ppy) distances (2.045(6), 2.058(6) Å) found in other instances.^{14c} The pyrazole NH hydrogen could not be located with certainty in the difference Fourier map.

The overall structure of (2) is identical to (1) (Fig. 1b). The Ir-N (MepzH) distance (2.168(5) Å) is marginally shorter than the corresponding Ir-N (Me₂pzH) distance (2.183(6) Å) in (1). This is probably due to the relief of steric crowding around the metal. The NH hydrogen of the pyrazole ligands was located in the Fourier difference map and it was found to be projected towards the metal-bound chlorine with H...Cl separation distance 2.296 Å.

In contrast to the chloride-containing compounds (1) and (2), compound (3) contains two pyrazole ligands, one of which functions as an anionic ligand while the other is a neutral ligand (Fig. 1c). This compound crystallizes in the monoclinic *C2/c* space group. The two pyrazolyl rings in (3) are nearly coplanar with the angle between the two pyrazolyl planes being 2.9(2)°. The NH hydrogen of the pyrazole ligand was located and refined with restraint. The N4-H4A and N4...N6 distances are 0.909 and 2.570(4) Å and N4-H4A-N6 angle is 155.5(1)°, indicating a hydrogen bonded interaction between H4A and N6. The Ir-C and Ir-N bond lengths follow the same trend as in (2) (Table 1).

Compounds (4) (Fig. 1d), 5 (Fig. 1e) and 6 (Fig. 1f) contain two aryl (phenyl, 1-naphthyl, 2-naphthyl) substituted pyrazoles, one of which is anionic while the other is neutral, a situation that is similar to that found in (3). An important difference is that the pyrazole units deviate considerably from planarity.

The angles between two pyrazolyl planes in compounds (**4**) – (**6**) are 27.9(2)°, 17.9(2)°, 30.4(2)°. The N6...N4 separations are 2.662, 2.649, 2.670 Å and N6-H6A...N4 angles are 158.4(1), 150.0(1) and 156.6(1)° respectively.

Electrochemistry

Cyclic voltammetric studies were performed on compounds (**1**)–(**6**) and the results are summarized in the Table 3. A metal-based irreversible oxidation event is observed for all the compounds. Oxidation potentials are slightly higher for the chloride-containing compounds (**1**) (1.01 V) and (**2**) (1.04 V). For compounds (**3**) – (**6**), the corresponding potential varies between 0.96 – 0.99 V. An irreversible reduction event was observed in all the cases, which is assigned to the reduction of the cyclometalating ppy ligand.²⁴ Evidently the ancillary ligands do not show any redox activity in the potential window of the experiments, or they are merged with the ppy-based reductions. Nevertheless, the CV experiments indicate that the ground state electronic structures of these compounds are very similar.

Table 3 — Electrochemical data for compounds (**1**) – (**6**) in acetonitrile

Comp.	(1)	(2)	(3)	(4)	(5)	(6)
[Ox] ^a	+1.01	+1.04	+0.96	+0.98	+0.99	+0.99
[Red] ^b	–1.67	–1.66	–1.69	–1.64	–1.69	–1.69

^aPeak potentials, $E_{p,c}$ for irreversible processes.

^bPeak potentials, $E_{p,a}$ for irreversible processes.

Photophysical properties

Absorption spectra

The absorption spectra of all the complexes follow the trends found in analogous Ir(III) compounds that have been reported by Thompson and co-workers.^{14d,e} The photophysical data of (**1**)–(**6**) are summarized in Table 4. In dichloromethane, these complexes show intense absorption below 350 nm ($\epsilon \approx 1\text{--}6 \times 10^4 \text{ M}^{-1}\text{cm}^{-1}$) which can be attributed to ligand centered (¹LC) transitions of both ppy and ancillary ligands⁶ (Fig. 2). Broad and comparatively weaker bands in the range 350 – 420 nm ($\epsilon \approx 1000\text{--}8000 \text{ M}^{-1}\text{cm}^{-1}$) are observed in each case which are assigned to spin allowed MLCTs. Very weak (and lowest energy) absorption bands beyond 420 nm ($\epsilon \approx 250\text{--}1000 \text{ M}^{-1}\text{cm}^{-1}$) are also observed which are due to ³LC and ³MLCT states.

Table 4 — Photophysical data for (**1**)–(**6**) in dichloromethane

Comp.	Absorption λ_{max} (nm) ($\epsilon \times 10^{-4}$, ($\text{M}^{-1}\text{cm}^{-1}$))	Emission λ_{max} (nm)	T (μs)	Φ_p
(1)	266 (3.34), 339 (1.08), 396 (0.73), 444 (0.38)	498, 526	13.2	0.31
(2)	264 (5.15), 339 (1.16), 395 (0.64), 445 (0.27)	498, 526	13.3	0.29
(3)	261 (6.18), 336 (1.20), 403 (0.56), 456 (0.36)	501, 526	9.9	0.45
(4)	274 (4.85), 337 (0.81), 394 (0.38), 444 (0.15)	496, 523	10.1	0.41
(5)	258 (3.70), 296sh (2.74), 393 (0.38)	498, 523	9.23	0.49
(6)	255 (5.45), 301sh (2.80), 393 (0.23)	495, 523	9.8	0.52

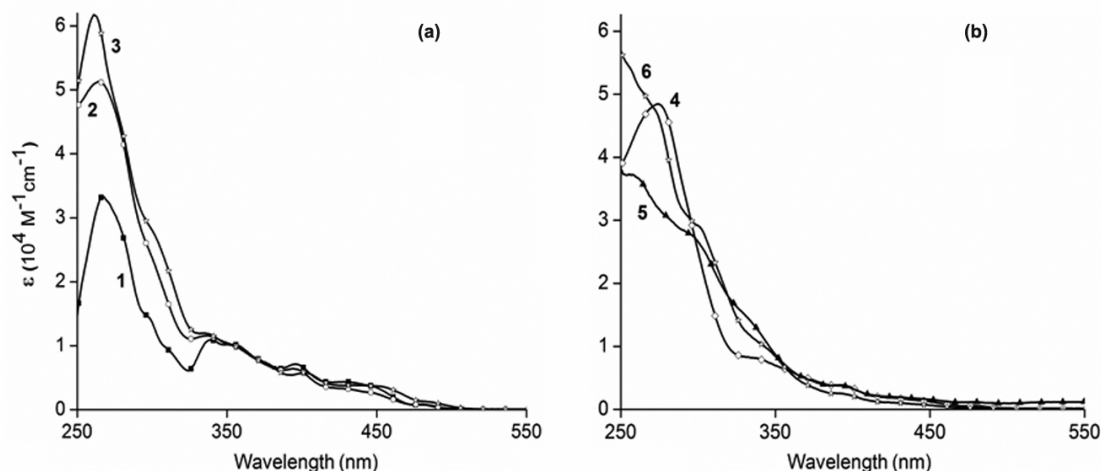


Fig. 2 — Absorption spectra of (a) (**1**) – (**3**) and (b) (**4**) – (**6**) in dichloromethane.

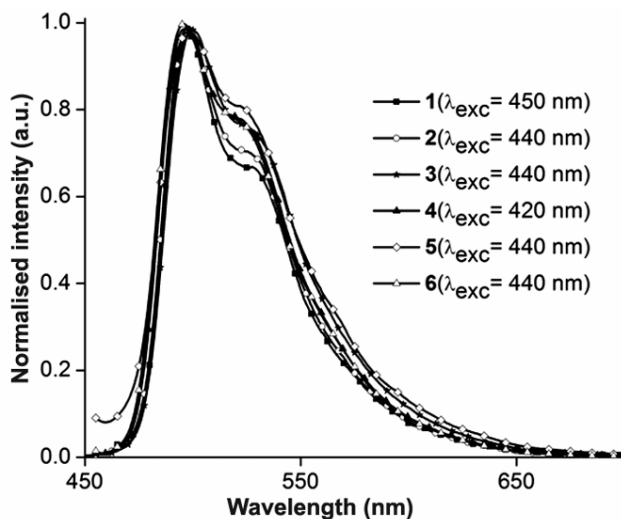


Fig. 3 — Emission spectra of (1) – (6) in dichloromethane. Excitation wavelengths are mentioned in parentheses.

Emission studies

Compounds (1)–(6) synthesized in this work are luminescent at room temperature and the emission data are provided in Table 4. The emission spectra of (1) – (6) are very similar (Fig. 3). All of these compounds show a blue-green emission (λ_{max} in the range 495 – 501 nm with a shoulder around 524 nm). Quantum yields and life-times have been computed in each case and these are in the range reported for analogous Ir(III) cyclometallated compounds.²⁵ It is evident that change of substitution from methyl to phenyl to naphthyl on the pyrazole ligand does not have any significant effect on the nature and the wavelength of emission. In this regard it is important to mention that Thompson and co-workers^{14d} were able to achieve only a minor variation in the emission wavelength (~ 50 nm) by altering substituents in the ancillary bis-pyrazolyl borate (Bpz_2R_2) ligands. This is because the emissive state in all these complexes is largely associated with the cyclometalating ligand. Thus, it may be mentioned that the ancillary ligands used in the present instance are photophysically innocent and varying them in the cyclometalated Ir(III) complexes does not lead to colour tuning.

Conclusions

In conclusion, we have described a series of neutral cyclometalated Ir(III) compounds that contain 2-phenylpyridine as the cyclometalating ligand along with various pyrazole ligands. Both alkyl and aryl substituted pyrazoles have been employed as the

ancillary ligand. All of these complexes are emissive at room temperature with a λ_{max} spanning a narrow range between 495–500 nm. The electrochemical properties of these compounds are also very similar. It is evident that change in substitution in the pyrazole ring does not have any effect on the emission wavelength of these compounds.

Supplementary Data

CCDC 823797 – 823802 respectively contain the supplementary crystallographic data for the complexes (1) – (6) reported herein. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Other supplementary data, viz., the bond parameters for these complexes may be obtained from the authors on request.

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