Cyclometalated Ir(III) Complex as a Metalloligand and a Selective Cu(II) Sensor: Synthesis and Structural Characterization of a Heterometallic Tetranuclear Ir(III)/Cu(II) Complex

Vadapalli Chandrasekhar,*†‡ Mrituanjay D. Pandey,*§ and R. Suriya Narayanan‡

1Department of Chemistry, Indian Institute of Technology Kanpur, Kanpur 208 016, India
2Tata Institute of Fundamental Research, Hyderabad 500107, India
3Department of Chemistry, Institute of Science, Banaras Hindu University, Varanasi, Uttar Pradesh 221005, India

ABSTRACT: A cyclometalated Ir(III) complex, [Ir(ppy)2(LH)] (2) [LH2 = 1,2-bis(pyridine-2-carboxamido)benzene; ppyH = 2-phenylpyridine] was synthesized and structurally characterized. [Ir(ppy)2(LH)] contains free donor sites and functions as a metalloligand. Accordingly, it interacts with a Cu(II) salt to afford the heterometallic tetranuclear complex, [{Ir(ppy)2(L)}2{Cu2Cl2}] (3). In the latter, a CuCl2 dimer bridges the two cyclometalated Ir(III) units, resulting in a IrIII–CuII–CuII–IrIII motif. 2 also functions as a selective and reversible sensor for Cu2+, as revealed by quenching of its emission and subsequent revival of the luminescence signal upon addition of EDTA.

INTRODUCTION

In recent years, the research on the design of polynuclear transition metal complexes has been on the forefront owing to their intriguing structural organization which offers scope for diverse applications.1−7 The synthesis of such complexes can be accomplished by several ways. One of these is by the use of multifunctional ligands and relies on the so-called serendipity-based approach.8−10 Although the latter methodology has been tremendously successful, its drawback is that the nature and structure of the product cannot be designed a priori. On the other hand, preformed transition metal complexes that themselves have coordination functionalities can be utilized to obtain polynuclear assemblies based on a complex-as-ligand approach.11−14 Previously, research from our group has focused on the synthesis, structural characterization, and photophysical studies of cyclometalated Ir(III) complexes,12−14 where by utilizing various types of ancillary ligands we successfully achieved the assembly of mono-, di- and tri-nuclear Ir(III) complexes. Our group has also been involved in the assembly of heterometallic 3d/4f complexes that possess interesting magnetic properties.15−18 In this connection, we envisioned the possibility of synthesizing heterometallic complexes that contain cyclometalated Ir(III) motifs. There have been literature precedents for this idea.19−22 For example, Collin, Flamigni, and co-workers have reported the synthesis of Ir(III)−Cu(I) pseudo rotaxane, the Cu(I) center in this complex was found to quench the emission of the Ir(ppy)2 unit.23 De Cola and co-workers have shown the use of Ir(III) complexes for the assembly of Ir(III)−Ln(II) complexes.24−25 Lin and co-workers have reported coordination polymers bearing Ir(ppy)3 motifs. The porous coordination polymers so obtained could sense dioxygen by luminescence quenching.26 In another study, Ir(III)−Pt(II)-based phosphorescent oligometallaynes were designed utilizing iridium(III) metalloligands possessing bifunctional pendant acetylene groups.27 Keeping these developments in mind, we have designed a cyclometalated Ir(III) metalloligand, Ir(ppy)2(LH) (2) [LH2 = 1,2-bis(pyridine-2-carboxamido)benzene; ppyH = 2-phenylpyridine] and assembled a novel tetranuclear heterometallic complex, [{Ir(ppy)2(L)}2{Cu2Cl2}] (3) containing a IrIII–CuII–CuII–IrIII sequence. We also demonstrate the utility of 2 as a selective turn-off sensor for Cu2+. These results are discussed here in.

RESULTS AND DISCUSSION

Synthetic and Structural Aspects. The heteroleptic Ir(III) complex, Ir(ppy)2(LH) (2), was obtained in the form of a yellow solid following a sequential two-step synthesis protocol (Scheme 1). In the first step, cyclometalated chloro-bridged iridium(III) dimer, [(ppy)2Ir(μ-Cl)]2 (1), was synthesized following the Nonoyama protocol.28 Subsequently, on reaction of this chloro-bridged iridium(III) dimer with sodium methoxide followed by reaction with the ancillary...
Scheme 1. Synthesis of 2 and Formation of the Tetranuclear Complex 3

Figure 1. ORTEP diagrams of 2 and 3 with the thermal ellipsoids at 40% probability limit (solvent molecules and hydrogen atoms are omitted for clarity).

**Table 1. Crystallographic Data of 2 and 3**

|          | 2       | 3       |
|----------|---------|---------|
| formula  | IrC₆₀H₃₂N₆O₂ | IrC₆₀H₃₈Cl₂Cu₄N₁₃O₄ |
| Fw       | 817.89  | 1831.74 |
| crystal system | monoclinic | triclinic |
| space group | P2₁/c   | P1     |
| a/Å      | 13.305(3) | 12.147(2) |
| b/Å      | 21.832(4) | 12.958(2) |
| c/Å      | 12.476(3) | 14.044(3) |
| α (deg)  | 90      | 75.832(3) |
| β (deg)  | 101.87(3) | 67.388(3) |
| γ (deg)  | 90      | 74.135(3) |
| V/Å³     | 3546.6(12) | 1938.5(6) |
| Z        | 4       | 1       |
| calculated density (g/cm³) | 1.532 | 1.569 |
| absorption coefficient (mm⁻¹) | 3.808 | 4.087 |
| F(000)   | 1616    | 898    |
| theta range for data collection (deg) | 1.91−25.50 | 1.98−25.99 |
| reflections collected | 18688 | 10640 |
| independent reflections | 6574 | 7376 |
| parameters | 442 | 460 |
| goodness-of-fit on F² | 0.951 | 1.084 |
| final R indices | 0.0799 | 0.0392 |
| R indices (all data) | 0.1407 | 0.0455 |

**Table 2. Selected Bond Parameters of 2**

| bond lengths (Å)        |       |
|-------------------------|-------|
| Ir(1)−N(1)              | 2.037(10) |
| Ir(1)−N(3)              | 2.125(10) |
| Ir(1)−C(1)              | 2.005(13) |
| N(4)−C(28)              | 1.183(14) |
| N(5)−C(35)              | 1.357(14) |

| bond angles (°)          |       |
|-------------------------|-------|
| N(1)−Ir(1)−N(2)         | 173.4(4) |
| N(1)−Ir(1)−N(4)         | 80.0(5) |
| N(3)−Ir(1)−N(4)         | 73.3(4) |

**Table 3. Crystallographic Data of 2 and 3**

|          | 2       | 3       |
|----------|---------|---------|
| formula  | IrC₆₀H₃₂N₆O₂ | IrC₆₀H₃₈Cl₂Cu₄N₁₃O₄ |
| Fw       | 817.89  | 1831.74 |
| crystal system | monoclinic | triclinic |
| space group | P2₁/c   | P1     |
| a/Å      | 13.305(3) | 12.147(2) |
| b/Å      | 21.832(4) | 12.958(2) |
| c/Å      | 12.476(3) | 14.044(3) |
| α (deg)  | 90      | 75.832(3) |
| β (deg)  | 101.87(3) | 67.388(3) |
| γ (deg)  | 90      | 74.135(3) |
| V/Å³     | 3546.6(12) | 1938.5(6) |
| Z        | 4       | 1       |
| calculated density (g/cm³) | 1.532 | 1.569 |
| absorption coefficient (mm⁻¹) | 3.808 | 4.087 |
| F(000)   | 1616    | 898    |
| theta range for data collection (deg) | 1.91−25.50 | 1.98−25.99 |
| reflections collected | 18688 | 10640 |
| independent reflections | 6574 | 7376 |
| parameters | 442 | 460 |
| goodness-of-fit on F² | 0.951 | 1.084 |
| final R indices | 0.0799 | 0.0392 |
| R indices (all data) | 0.1407 | 0.0455 |

Also, the bond parameters, around Ir(III), are not affected upon binding to Cu(II) (Table 3). The two Ir(III) centers in 3 are connected by a Cu₂Cl₂ dimer. Each Cu(II) is bound to the metalloligand through a N, N, O coordination involving the carboxamide arm. As a result, each Cu(II) is part of three ring systems which vary in size (7, 5, and 4, Figure 1). The Cu(II) centers are in a distorted square pyramidal geometry (τ (index of trigonality) = 0.41; for a perfect square pyramid, τ = 0 and...
for a perfect trigonal bipyramid, \( r = 1 \). Each Cu(II) contains a 2N, 2Cl, O coordination environment where the square plane is formed by two nitrogen atoms \([N(5), N(6)]\) and one oxygen atom \([O(1)]\) of the carboxamide ligand along with a chloride ion. The apical site is occupied by another chloride ion. The apical \( \text{Cu}−\text{Cl} \) distance is longer, which is 2.582 Å in comparison to the basal \( \text{Cu}−\text{Cu} \) distance, 2.314 Å (Figure S1, Supporting Information). The Cu(II) lies above the mean basal plane by \( \sim 0.3 \) Å. The \( \text{Cu}_2\text{Cl}_2 \) bridging unit is nearly a square with the two \( \text{Cu}−\text{Cl} \) distances being 2.314 and 2.582 Å, whereas the \( \text{Cu}−\text{Cl}−\text{Cu} \) and the \( \text{Cl}−\text{Cu}−\text{Cl} \) bond angles are 91.6° and 88.4° respectively. Interestingly, apart from one example, in many \( \text{Cu}_2\text{Cl}_2 \) dimers, the bond angles deviate from 90.0°. The overall molecular structure of 3 has a crystallographic center of inversion which is located between the two central copper(II) ions. Finally, the Ir(III) and Cu(II) atoms are coplanar, the Ir(1)−Cu(1)−Cu(1′)−Ir(1′) dihedral angle is 180°.

**Photophysical Properties.** The neutral mononuclear complex, \( \text{Ir}(\text{ppy})_2(\text{LH}) \) (2), exhibits an intense absorption at around 250–300 nm \((\epsilon > 10^4 \text{ M}^{-1} \text{ cm}^{-1})\) in the ultraviolet region which is attributed to the \( \pi−\pi^* \) transitions associated with the coordinated ligands (Figure 2 and Table 4). The low-energy bands in the wavelength ranging from 350 to 400 nm \((\epsilon \approx 6000−5000 \text{ M}^{-1} \text{ cm}^{-1})\) extending up to the visible region could be assigned to spin-allowed \( 1\text{MLCT}, 1\text{LCT}, \) and \( 3\text{ILCT} \) spin transitions. On the other hand, the spin-forbidden transitions \( (3\text{MLCT}, 3\text{LLCT}, \) and \( 3\text{ILCT}) \) are associated with the low extinction coefficient \((\epsilon \approx 400 \text{ M}^{-1} \text{ cm}^{-1})\), as expected for this family of complexes, which could be located at around 448 nm. Strong spin−orbit coupling effects associated with the Ir(III) metal center facilitate the spin-forbidden transitions. On the basis of the time-dependent density functional theory (TDDFT) calculations performed on 2 considering the ground-state geometry-optimized parameters (Tables S1−S3: Supporting Information), we have assigned the bands (Tables S1-S3: Supporting Information). These absorption features are similar in nature as observed in previous literature reports.

![Figure 2](image)

**Figure 2.** Absorption spectra of 2 (10.0 \( \mu \text{M} \)) in acetonitrile upon addition of increasing concentrations of \( \text{Cu}^{2+} \).

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### Table 3. Selected Bond Parameters of 3

| bond lengths (Å) | Ir(1)−N(1) | Ir(1)−N(2) | Ir(1)−N(3) | Ir(1)−N(4) | Ir(1)−N(5) | Ir(1)−N(6) |
|------------------|------------|------------|------------|------------|------------|------------|
|                  | 2.035(5)   | 2.037(5)   | 2.137(5)   | 2.181(5)   | 2.095(5)   | 2.019(5)   |

### Table 4. Photophysical Data of 2 in Acetonitrile Solution

| complex | absorption \( \lambda_{\text{max}, \text{nm}} \) (\( \epsilon; 10^3 \)) | emission \( \lambda_{\text{em}}, \Phi \) |
|---------|---------------------------------------------|--------|
| 2       | 254 (5.2), 334 (1.8), 378 (1.5), 434 (0.5), 448 (0.4) | 520     | 0.11    |

The formation of the heterometallic complex 3, whose molecular structure has been described above, prompted us to examine the changes in the optical spectra of 2 upon the addition of increased concentrations of various metal ions (Figure 2). Except for \( \text{Cu}^{2+} \), \( \text{Pb}^{2+} \), and \( \text{Hg}^{2+} \) other metal ions \((\text{Ca}^{2+}, \text{Cd}^{2+}, \text{Mn}^{2+}, \text{Ni}^{2+}, \text{and Zn}^{2+})\) exerted very little influence on the absorption features (Figure S2). Upon the addition of increasing amounts of \( \text{Cu}^{2+} \) to an acetonitrile solution of 2, a gradual decrease in the molar absorptivity of the broad band at \( \sim 370 \text{ nm} \) with a concomitant increase in the higher energy absorption band was observed (Figure 2). A well-defined isobestic point could be located at 327 nm, indicating strong ground state interactions between 2 and \( \text{Cu}^{2+} \). The stoichiometry of the complex was determined by Job’s method by maintaining the sum of the initial concentration of \( \text{Cu}^{2+} \) and 2 constant at 20 \( \mu \text{M} \) and the mole fraction of \( \text{Cu}^{2+} \) ion varied from 0 to 1. The absorbance of 2 at 312 nm in the absence \((A_0)\) and presence \((A)\) of \( \text{Cu}^{2+} \) was determined. A plot of \((A - A_0)/A_0\) vs the mole fraction of \( \text{Cu}^{2+} \) showed an inflection point at 0.5, indicating a 1:1 stoichiometry of the \( \text{Cu}^{2+}:2 \) in the complex (Figure S3). As already noted above, the complex formation with a molar ratio of 1:1 has been established by the single X-ray crystal structure of 3.
Addition of Hg$^{2+}$ and Pb$^{2+}$ to 2 at high concentrations (100 μM) also results in an increase of the molar absorptivity of the high-energy bands of 2 and a decrease in absorptivity of the low-energy bands (Figure S4, Supporting Information). However, in contrast to the situation with Cu$^{2+}$, isosbestic points could not be located for the interaction of Hg$^{2+}$ and Pb$^{2+}$ with 2 (Figure S4, Supporting Information).

The emission spectrum of 2 is characterized by a single structure-less band at ~520 nm upon excitation at 360 nm (Figure 3). The influence of the addition of various metal ions upon the emission spectrum of 2 is shown in Figure 3a, which clearly reveals that while Cu$^{2+}$ completely quenches the emission intensity, the other ions do not have any effect. A study on the effect of concentration of Cu$^{2+}$ on the emission intensity of 2 revealed that at 20 μM concentration (vis-à-vis 10 μM of 2) complete quenching of emission intensity was observed (Figure 3b). Thus, 2 can be considered as a turn-off sensor for Cu$^{2+}$ with a detection limit of 1 ppm. The quenching of emission intensity affected by the addition of Cu$^{2+}$ is not affected in the presence of other metal ions, such as Cd$^{2+}$, Hg$^{2+}$, Pb$^{2+}$, and Zn$^{2+}$ (Figure SS, Supporting Information). Interestingly, the quenching of emission intensity of 2 by Cu$^{2+}$ can be completely reversed by the addition of an aqueous solution of EDTA to a solution of 2 and Cu$^{2+}$ in acetonitrile; the emission at 520 nm was completely recovered (Figure SS, Supporting Information). The stability constant ($K_s$) for the binding of 2 with Cu$^{2+}$ was calculated to be 4.5 x 10$^8$ L mol$^{-1}$ from the change of the emission intensity data at 520 nm as a function of the concentration of Cu$^{2+}$ ion added using a nonlinear least square fit (Supporting Information, Figure S6). In an air-equilibrated solution, the quantum yield of 2 (reference, quinine sulfate) was found to be 0.11, which decreases to 0.01 upon interaction with Cu$^{2+}$. The emission spectrum of 3 is presented in the Supporting Information (Figure S7). This quenching of emission by Cu$^{2+}$ may be due to the paramagnetic nature of Cu$^{2+}$.

Because amides are also well-known receptors for anions, the absorption and emission titration of 2 with various common anions was carried out. We were unable to detect any major changes in such titrations except that the molar absorption of 2 (~250 nm) increases slightly upon binding with iodide ions (Figures S8 and S9, Supporting Information).

**DFT and TDDFT Studies of 2.** Computational calculations (density functional theory (DFT)) on 2 shed light on its electronic structure and supplement in the understanding of its optical response. Isosurfaces of few relevant molecular orbitals of 2 are presented in Figure S10, while the corresponding orbital compositions are given in Table S1. From our results, we clearly see that some of the orbitals viz. highest occupied molecular orbital (HOMO), HOMO-1, and HOMO-2 are primarily centered on the Ir atom (21–40%); varying percentages are present on both the cyclometalating and the ancillary ligand. On the contrary, orbitals such as lowest unoccupied molecular orbital (LUMO), LUMO+1, and LUMO +2 are all composed of ligand orbitals with appreciably small contributions of Ir orbitals (<4%). These results are in good agreement with what has been reported for this family of complexes. The results of the TDDFT calculations using PBE0 functional and LANL2DZ/6-31G(d) basis sets with polarizable continuum model (PCM), taking into account the solvation effects, are given in Tables S2–S3 (Supporting Information). On the basis of these calculations, the lowest energy absorptions (singlet and triplet) can be assigned to possess mixed metal-to-ligand charge transfer (MLCT), ligand to ligand charge transfer (LLCT), and intraligand charge transfer (ILCT) characteristics. A comparison of the experimental and DFT simulated spectra by considering only the singlet transitions is displayed with the help of vertical bars in Figure S11.

**CONCLUSIONS**

In summary, we report here the synthesis and structural characterization of a Ir(III)-Ca(II)-based tetranuclear complex (3) using a cyclometalated Ir(III) complex (2) as a metalloligand. To the best of our knowledge, 3 represents the first example of a structurally characterized heterometallic Ir(III)–Cu(II) complex. The cyclometalated Ir(III) complex, 2, functions as a selective Cu$^{2+}$ sensor with a detection limit of 1 ppm. Our results provide further insights into the expanding field of cyclometalated Ir(III) complexes other than their well-explored role as phosphorescent emitters.

**EXPERIMENTAL SECTION**

**General.** We procured iridium chloride from Arora Matthey, Kolkata, India. 2-Phenyl pyridine, o-phenylenediamine, and Cu(ClO$_4$)$_2$·6H$_2$O were obtained from the Aldrich Chemical Company, USA, and used as it is without any further purification. Perchlorate salts, namely, Pb(ClO$_4$)$_2$·6H$_2$O, Hg(ClO$_4$)$_2$·6H$_2$O, Ca(ClO$_4$)$_2$·6H$_2$O, Zn(ClO$_4$)$_2$·6H$_2$O, Cd(ClO$_4$)$_2$·6H$_2$O, Ni(ClO$_4$)$_2$·6H$_2$O, and Mg(ClO$_4$)$_2$·6H$_2$O, were made from their carbonate salts on reaction with perchloric acid. All other useful chemicals were obtained from S. D. Fine-Chemicals, Mumbai, India. Solvents used in the reactions were freshly distilled according to the standard...
procedures under inert atmosphere.® Freely prepared sodium methoxide was used for the reaction.

The chloro-bridged precursor [(ppy)2Ir(µ-Cl)]2 (1) was synthesized following the literature report employing the Nonoyama protocol,® by the reaction of IrCl3·nH2O with 2.5 equiv of the cyclometalating ligand 2-phenyl pyridine in a 3:1 solvent mixture of 2-ethoxyethanol and water. The ancillary picolinamide ligand 1,2-bis(pyridine-2-carboxamido) benzene (LH2) was synthesized following a reported method.®

**Caution:** Although we have encountered no complications, perchlorate salts should be handled with care because they are potentially explosive.

**Instrumentation.** With the help of a Waters Micromass Quatro Micro triple quadrupole mass spectrometer, all ESI-MS analyses were recorded. Methanol (2) or acetonitrile (3) was used as the solvent, whereas nitrogen gas has been used for desolvation for the electrospray ionization (positive ion, in full scan mode). The 1H NMR spectra were recorded on a JEOL-DELTA2 500 model spectrometer by employing CDCl3 as the solvent and TMS as the reference. The infrared (IR) spectra were recorded on a Bruker FT-IR Vector 22 model (as KBr pellets in the range 4000–400 cm−1). The ThermoQuest CE instruments CHNS-O, EA/110 model was used for the elemental analyses. A PerkinElmer-LAMDA 20 UV–visible spectrometer was employed for recording the UV–visible spectra. A PerkinElmer spectrophotometer (LS-55 model) was used to record the steady state emission spectra. Quantum yield measurements were done considering quinine sulfate in 1.0 N sulfuric acid solution as the reference (Φ = 0.54 ± 0.2 where λexc = 350 nm). The following equation was used for the calculation of the quantum yield

\[
\Phi = \Phi_R (A_R / A_S) (I_S / I_R) (n_R^2 / n_S^2)
\]

In the above expression, \( \Phi \) is the fluorescence quantum yield, where the subscripts S and R represent the sample and reference, respectively. \( A_R \) and \( A_S \) are the solution absorbances at the excitation wavelength, \( I_S \) and \( I_R \) are the integrated emission intensities, and \( n_R \) and \( n_S \) are the refractive indices of the solvent used for measurement.

**X-ray Structural Analysis.** A CCD Bruker SMART APEX diffractometer was used for X-ray diffraction data collection at 100K that uses graphite monochromated Mo Kα radiation (λ = 0.71073 Å). For collecting frames of data, indexing reflections, and determining lattice parameters, the program SMART® was used. In addition, other programs that have been used for our analysis are SAINT (for the integration of the reflection data), SHELXTL,® (for determining the space group and structure), SHELXL-2016 (for least-squares refinements on F2), and Olex2/mask® (for treating the disordered solvent molecules in compounds 2 and 3; Supporting Information, Table S5). The refinement of all nonhydrogen atoms was done with anisotropic displacement parameters. All hydrogen atoms were refined isotropically, and by using a riding model, these were fixed at geometrically calculated positions. With the aid of the ORTEP program, all molecular graphics have been generated.

**Computational Details.** Gaussian 03 was employed for all computational (DFT) calculations.® The geometrical parameters of 2 as obtained from the crystal structure analysis were subjected to further optimization using the PBE0 density functional.® In addition, double zeta LANL2DZ basis sets along with quasirelativistic pseudopotentials for Ir atoms considering 17 valence electrons were used.® For all other atoms, 6-31G(d) basis sets were chosen. With the optimized geometry from the above DFT procedure (PBE0/LANL2DZ/6-31G(d) level), subsequent TDDFT calculations were performed, taking account of the solvation effect by means of the PCM solvation model® in acetonitrile solution. With the help of GaussSum® software, the electronic spectrum simulation (with fwhm = 0.4 eV) was done. GaussView was used for the visualization of the orbitals, and Vmdzes® was used to calculate the percentage contributions of respective orbitals on the metal and ligands.

**Synthesis.** Synthesis of [(ppy)LH/2] (2). Freshly prepared solid sodium methoxide (0.025 g, 0.466 mmol) was added to a 30 ml dichloromethane solution of [(ppy)2Ir(µ-Cl)] (0.10 g, 0.093 mmol), and the reaction mixture was stirred for 2 h till the solution changed color from yellow to orange. To this solution, the ancillary ligand 1,2-bis(pyridine-2-carboxamido)-benzene (LH2) (0.065 g, 0.205 mmol) was added at once. The reaction mixture was further stirred for 12 h at room temperature followed by filtration and removal of the solvent in vacuo to afford a yellow oil. A yellowish solid compound was obtained upon the addition of diethyl ether (10 mL) followed by trituration. The solution was filtered to afford the solid compound which was further washed with cold methanol and dried. Single crystals for X-ray diffraction were grown by dissolving the yellow solid in dichloromethane and layering with a few drops of methanol. (Yield: 0.112g, 74%).

Characterization data: ESI-HRMS (100% methanol) m/z: 819.2055 ([M + H]+). 1H NMR (500 MHz, CDCl3; δ 6.24 (d, J = 7.3 Hz, 1H), 6.40 (d, J = 7.3 Hz, 1H), 6.79–6.84 (m, 2H), 6.88–6.94 (m, 4H), 6.98 (t, J = 7.0 Hz, 1H), 7.06 (t, J = 6.1 Hz, 1H), 7.44–7.46 (m, 2H), 7.57–7.68 (m, 4H), 7.76 (d, J = 4.9 Hz, 1H), 7.82 (d, J = 7.9 Hz, 1H), 7.86–7.92 (m, 4H), 8.34 (d, J = 7.9 Hz, 1H), 8.39 (d, J = 6.7 Hz, 1H), 8.59 (d, J = 6.7 Hz, 1H), 8.70 (d, J = 4.5 Hz, 1H), 8.75 (d, J = 5.5 Hz, 1H), 9.22 (d, J = 7.9 Hz, 1H), 12.35 (s, 1H). IR (KBr, cm−1): 3247 (w), 3053 (w), 1671 (m), 1604 (s), 1571 (vs), 1509 (vs), 1473 (vs), 1450 (s), 1420 (m), 1346 (m), 1289 (m), 1266 (w), 1225 (w), 1197 (w), 1158 (w), 1086 (w), 1060 (w), 1030 (w), 997 (w), 897 (w), 846 (w), 793 (w), 753 (s), 689 (m), 629 (m), 582 (w), 585 (w), 487 (w). Anal. Calcd for C40H29IrN6O2: C, 58.74; H, 3.57; N, 9.18; Found: C, 52.68; H, 3.12; N, 9.26.

Characterization data: ESI-HRMS (100% methanol) m/z: 898.1347 ([M/2 + H + CH3CN]+), 880.1180 ([M/2 + CH3CN]+), 585.0932 ([M/2 + Cl]+). IR (KBr, cm−1): 3160 (s), 3053 (s), 2922 (m), 1582 (vs), 1537 (vs), 1237 (s), 1158 (s), 1066 (m), 1028 (w), 958 (w), 902 (w), 796 (w), 757 (vs), 734 (m), 688 (w), 598 (w). Anal. Calcd for C80H56Cl2Cu2Ir4N12O4: C, 52.45; H, 3.08; N, 9.18; Found: C, 52.68; H, 3.12; N, 9.26.
Additional crystallographic data, absorption, emission spectra, and computational data details (PDF)
CCDC—1497274 (for 2) and CCDC—1497275 (for 3), contains crystallographic supplementary data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (CIF)

■ AUTHOR INFORMATION

Corresponding Author
*E-mail: vc@iitk.ac.in, vc@tifrh.res.in. Phone: (+91) 512-259-7259. Fax: (+91) 521-259-0007/7436.

ORCID
Vadapalli Chandrasekhar: 0000-0003-1968-2980

Author Contributions
V.C., B.M. and M.D.P. designed and performed the study and wrote the manuscript. R.S.N. contributed to the X-ray crystallography. All authors commented on the manuscript. The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes
The authors declare no competing financial interest.

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■ ABBREVIATIONS

ppyH, 2-phenylpyridine; EDTA, ethylenediaminetetraacetic acid; MLCT, metal-to-ligand charge transfer; LLCT, ligand to ligand charge transfer; ILCT, intraligand charge transfer; TDDFT, time dependent density functional theory

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