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Aggregation-Induced Emission Activity in Iridium(III) **Diimine Complexes: Investigations of Their Vapochromic Properties**

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Two iridium(III) diimine complexes [mono(1,10-phenanthroline)bis(triphenylphosphine)(dihydrido)iridium(III) hexafluorophosphate (1) and mono(1,10-phenanthroline)bis(triphenylphosphine)(hydrido)(chloro)iridium(III) hexafluorophosphate (2)] have been synthesized from a single two-step reaction. The structures of 1 and 2 both adopt distorted octahedral geometries, as established by single-crystal X-ray diffraction. The complexes, upon irradiation with UV light at 365 nm, emit faint light in solution and bright light in the solid state. The ground- and excited-state properties of these complexes were investigated through density functional theory (DFT) and time-dependent DFT calculations. The calculated energies for the transitions from the ground state to the singlet and triplet excited states were close to those de-

Introduction

Luminescent materials are widely used as vapoluminescent materials to detect volatile organic compounds (VOCs) in the environment or workplace.^[1-13] These materials usually show changes in emission intensity or wavelength when exposed to specific VOCs. This variation in luminescence properties triggered by the presence of VOCs results in changes in, for example, metallophilic interactions,^[14] hydrogen bonding,^[15] solvent-metal bonds,^[16] and aromatic

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termined from the experimental absorption and emission. Their molecular orbitals were also exploited to compute the ground-state dipole moments and redox potentials. Several experiments were performed to demonstrate the "aggregation-induced emission" (AIE) activity of these complexes. AIE was triggered by the restricted intramolecular rotation of the rotating units (phenyls in triphenyphosphines) in these molecules in the solid state. The solid thin films of 1 and 2exhibit solvent-polarity-dependent vapour-responsive emission properties (vapoluminescent). The rationale for the different emission behavior in the solid state has been thoroughly investigated. The packing diagrams of 1 and 2 show that there is enough space available to accommodate small organic solvent molecules inside the crystal lattices.

 π - π stacking interactions.^[17] There have been many reports of organometallic and coordination complexes of Ru,[18] Sn,^[19] Pt/Pd,^[20] Cu,^[21] Zn,^[22] Au,^[23] Ag,^[24] and Re/Co^[25] that have been used in vapor-responsive luminescent materials. However, the most extensive studies have been carried out with platinum(II) and gold(I). Metallophilic interactions between Pt^{II} or Au^I are either disrupted or enhanced upon interaction with VOCs, thereby altering the gap between the highest-occupied molecular orbital (HOMO) and the lowest-unoccupied molecular orbital (LUMO), thus leading to distinct changes in the emission or absorption spectra. In comparison with other luminescent metallic complexes, several distinct advantages have been observed with cyclometalated iridium(III) complexes, for example, superior quantum efficiencies, easy tunability of light emission wavelength, higher thermal and electrochemical stability, and straightforward synthetic routes in comparison with other analogues.^[26] Notwithstanding, reports on emitting iridium(III) complexes as vapoluminescent materials are very limited.^[12]

Recently we reported^[27] a one-pot synthetic route to aggregation-induced-emission (AIE)-active monocyclometalated iridium(III) complexes and their easy tunability throughout the visible range within the common framework of an iridium(III) complex.^[28] AIE^[29-32] is an anomalistic



phenomenon and the most efficient process for tackling the aggregation-caused quenching (ACQ)^[30] effect. AIE activity mainly arises from the restricted rotation of a freely rotating part of the molecular system either in concentrated solution/or in the solid state. This restricted rotation blocks non-radiative pathways and opens up radiative channels, thereby facilitating very bright emission in the solid state.

Herein we report the synthesis of an AIE-active diiminebased chromophore ligated to iridium(III) complexes and their vapor-responsive luminescence properties. The excited-state properties of these complexes have been characterized through DFT chemical quantum calculations.

Results and Discussion

Syntheses

The strategy for the synthesis of a diimine complex with iridium(III) originated from our previous report^[27] in which we had synthesized a monocyclometalated iridium(III) complex in a one-pot reaction. On addition of 1,10-phenanthroline to the reaction mixture (in place of 2-phenylpyridine in the same reaction protocol^[27]), two spots were observed very close on a TLC plate. These two species were difficult to separate by using traditional purification techniques, for example, column chromatography and recrystallization. Therefore these impure products were mixed with potassium hexafluorophosphate in methanol and the reaction mixture was treated with microwave irradiation leading to an exchange of counter ions, with Cl⁻ being replaced by PF₆⁻. A solid residue corresponding to complex 2 separated from solution. Thus, this process facilitates the separation and subsequent purification of complexes 1 and 2. In this case, the diimine iridium(III) complex resulted in dihydride (1) and chlorohydride (2) complexes, in contrast to the reaction with the cyclometalated ligand in which the chlorohydride was the sole product obtained (Scheme 1, D). The formation of the dihydride complex in the case of the cyclometalated ligand was prevented probably to avoid the presence of strong *trans*-influencing substituents (hydride and C of the cyclometalated ligand) *trans* to each other.

Complexes 1 and 2 were characterized by ¹H, ¹³C, and ³¹P NMR spectroscopy (see Figures S1 and S2 in the Supporting Information). The ³¹P NMR spectra each show a single resonance peak for both complexes 1 and 2 at δ = 20.88 and 29.49 ppm, respectively. ¹H NMR peaks for the hydrides can be observed at $\delta = -19.24$ and -17.56 ppm for complexes 1 and 2, respectively. The hydride peaks appear as triplets due to P–H coupling ($J_{P-H} \approx 15$ Hz). The value of J_{P-H} indicates the hydride to be *cis* to the phosphorus in both complexes.^[33] The ¹H NMR spectrum of 1 (Figure S1a) clearly exhibits seven sets of protons: Four generated from the resonances of 1,10-phenanthroline, two from the triphenylphosphines, and one from the hydride. These observations, along with a single hydride NMR peak, substantiate the symmetrical geometry of 1 (see Figure S1a). In the case of 2, more than four sets of protons were observed from 1,10-phenanthroline, which clearly indicates the unsymmetrical geometry of 2 (see Figure S2a). The presence of the Ir-H bond in 1 and 2 was confirmed from the corresponding stretching frequency at 2179 and 2152 cm^{-1} (see Figures S1d and S2d), respectively.

Structural Characterization Based on X-ray Crystallography

The structures of complexes **1** and **2** were established by a single-crystal X-ray diffraction study at 100 K. The ORTEP diagrams (Figure 1 and Figure S3) show the structures to be distorted octahedrals, and selected bond lengths and bond angles are presented in Table S1 and Table S2 in the Supporting Information. The packing diagrams for the two complexes (Figure 2 and Figure S3) show that each of these complexes contains eight dichloromethane (dcm) molecules per unit cell (both complexes were recrystallized from dcm). The void space for **1** was calculated to be



Scheme 1. Protocol for the synthesis of complexes 1 and 2.



980.1 Å³, compared with a cell volume of 4837.5 Å³. For **2**, the void space and cell volume are 906.2 and 4964.8 Å³, respectively. The ratios of total cell volume to the void volume, occupied by solvent molecules, are 4.9 and 5.3 for complexes **1** and **2**, respectively. These similar ratios for **1** and **2** suggest similar occupancy values of the dcm molecules, namely eight dcm molecules per unit cell of **1** and **2** (Figure 2). These dcm molecules in the crystal lattices presumably substitute other volatile solvent molecules upon exposure.



Figure 1. ORTEP structures of 1 and 2. Ellipsoids are drawn at the 50% probability level. All the H atoms (except hydrides), solvent molecules, and the counter ion have been omitted for clarity.

UV/Vis Absorption Spectra

Complexes 1 and 2 exhibit intense absorption bands in the range 240–320 nm at a concentration of 10^{-5} M in dcm. The molar extinction coefficients (ε) corresponding to the absorption maxima were found to be higher than 4.5×10^4 M⁻¹ cm⁻¹ (Table 1). Thus, the absorption bands can be attributed to ligand-centered transitions. The spectra show a long absorption tail starting at 320 nm and extending to 450 nm ($\lambda_{max} = 364$ and 410 nm for 1, and 358 and 400 nm for 2; Figure 3). Close scrutiny reveals that this long tail consists of two partially resolved broad absorption bands.



Figure 3. Solution absorption spectra for 1 and 2 at a concentration of 10^{-5} M in dcm (inset: enlarged absorption spectra in the region 290–450 nm). The calculated wavelengths are given in spectra (364 and 410 nm for 1, and 358 and 400 nm for 2).

Results from TDDFT Calculations

The molecular orbitals in complexes 1 and 2 that have a significant involvement in low-lying excitation are shown in Figure 4 and Figure S4 in the Supporting Information. All the pertinent energy gaps and the assignments of each transition are listed in Table 1.



Figure 2. Unit cell packing diagrams of 1 and 2 showing the locations of the CH₂Cl₂ solvent molecules.

Table 1. Calculated excitation wavelengths (λ_{cal}), oscillator strengths (*f*), MLCT, and transition energies (*E*) determined at the TDDFT/ B3LYP level in dcm for a few transitions. All the excitations reported herein initiate from the singlet ground state (S_o). The corresponding experimental wavelengths (λ_{expl}) are shown in separate columns (**1** in above and **2** in below).

States	$\lambda_{cal} [nm]$	λ_{expt} [nm]	E [eV]	f	Assignments	MLCT [%]
S ₁	379	410	3.27	0.06	HOMO→LUMO (97%)	33.17
S_2	369	_	3.36	0.0003	HOMO–1 \rightarrow LUMO (98.5%)	90.6
S ₃	361	364	3.43	0.02	HOMO \rightarrow LUMO+1 (95%)	32.3
T ₁	524	542	2.36	0	HOMO \rightarrow LUMO+1 (25.3%)	8.65
					HOMO-3 \rightarrow LUMO+1 (25%)	5.58
S_1	386	400	3.21	0.000023	HOMO–1 \rightarrow LUMO (81%)	38.5
					$HOMO \rightarrow LUMO + 1 (15\%)$	2.25
S_2	374	_	3.31	0.00004	HOMO→LUMO (79%)	11.58
_					HOMO–1 \rightarrow LUMO (15%)	7.12
S ₃	358	358	3.46	0.036000	HOMO–2→LUMO (75.5%)	18.0
2					HOMO \rightarrow LUMO+1 (16%)	2.4
T_1	528	531	2.35	0	HOMO-3 \rightarrow LUMO+1 (20%)	1.0
					HOMO-2 \rightarrow LUMO+1 (17%)	4.0
					HOMO-2 \rightarrow LUMO (13%)	3.1
					HOMO \rightarrow LUMO (4%)	0.6



Figure 4. Selected frontier molecular orbitals for 2.

The calculated energy gaps between the S_0 and S_1 states are 3.27 eV (379 nm) and 3.36 eV (386 nm) for complexes 1 and 2, respectively, and are consistent with the experimentally observed absorption wavelengths (Table 1). Similarly, the $S_0 \rightarrow T_1$ transition energies for complexes 1 (524 nm) and 2 (528 nm) are consistent with the experimental emission spectra at the blue edge (Table 1). This consistency between the experimental and calculated transition frequencies prove the accuracy of the molecular orbital diagrams. Complexes 1 and 2 differ in their metal-to-ligand charge-transfer (MLCT) transition character due to different extents of orbital contributions from different ligands (see Table S3).

The redox potentials were measured by cyclic voltammetry relative to an internal ferrocene reference (Cp₂Fe/ Cp₂Fe⁺ = 0.62 V vs. SCE in dcm). Complexes **1** and **2** show metal-centered irreversible oxidation potentials at 1.331 and 1.329 V, respectively. The reduction potentials observed for 1 and 2 at -0.700 and -0.740 V, respectively, correspond to the LUMO state of the phenanthroline ligand^[34] in both the complexes.

Vapoluminescence

Complex 1 was recrystallized from dcm. It emits greenish yellow light on exposure to UV radiation (shown as a thin film in Figure 5, a). The emission color of this complex in a thin film changes from greenish yellow to yellow upon exposure to solvents with a higher polarity than dcm [dielectric constant (ε) = 8.93], for example, acetone (ε = 20.7) and acetonitrile (ε = 37.5). Upon exposure to solvents with a lower polarity than dcm, for example, chloroform (ε = 4.81), benzene (ε = 2.27), or 1,4-dioxane (ε = 2.25), the solid thin films (recrystallized from dcm) emit yellowish green and bluish green light (Figure 5, a).

Complex 2 recrystallized from dcm emits green light. The thin film of 2 analogously emits blue emission upon exposure to nonpolar solvents (benzene, 1,4-dioxane) and green light in polar solvents (chloroform, acetone, acetonitrile; see Figure S5a in the Supporting Information). A distinct difference was observed in the emission spectra of thin films in polar and nonpolar solvents. The thin films exposed to nonpolar solvents show structured emission, whereas broad emission was observed from thin films exposed to polar solvents (Figure 5, b). Two peaks separated by approximately 1408 cm⁻¹ are observed in the structured emission spectra recorded in nonpolar solvents (1,4-doxane, benzene), which correspond to the stretching of double bonds in the aromatic ligands.^[35] The maximum emission wavelength gradually shifts towards a longer wavelength with increasing solvent polarity (Figure 5, b). In the absorption spectra, different band-edge absorptions can be observed for a thin film of 1 exposed to polar and nonpolar solvents. In the





Figure 5. (a) Thin-film emission color of 1 (bluish-green to yellow) with systematic increase of solvent polarity (polarity increases in the order 1,4-dioxane < benzene < chloroform < dcm < acetone < acetonitrile) on exposure to UV radiation ($\lambda_{max} = 365$ nm). (b) Emission spectra of the corresponding thin films moistened with the solvents.

case of nonpolar solvents, the observed absorption wavelength is less than 350 nm and for polar solvents is greater than 400 nm (see Figure S6a). In addition, a long tail followed by a band-edge absorption is observed for the latter case only (see Figure S6b). These spectroscopic observations suggest that the nature of the lowest excited states of the thin-film samples exposed to nonpolar solvents predominantly consist of ligand-centered states. The nature of the lowest excited states changes to a MLCT state on exposure of the thin films to polar solvents. In other words, switching of the excited state occurs due to a change in the dielectric medium around the thin-film samples (Figure 6). The ground-state dipole moments (DMs) for both 1 and 2 were calculated by DFT calculations. The excited-state dipole moments for both complexes were calculated by using Equation (1)^[36,37]

$$\Delta \mu = \mu_e - \mu_g = \sqrt{\frac{m \times 81}{\left(\frac{6.2}{a}\right)^3 11307.6}}$$
(1)

in which μ_e is the excited-state dipole moment, μ_g is the ground-state dipole moment, *a* is Onsager's cavity radii, and *m* is the slope of the linear plot of E_T^N versus the Stokes shift.



Figure 6. Solvent-polarity-dependent tuning of metal-to-ligand charge transfer (MLCT) states lead to different emission colors of **1** and **2** in the solid state (dcm, acetone etc. stabilize the MLCT states more than 1,4-dioxane, benzene etc.).^[20e]

The calculated excited-state dipole moment (μ_e) is greater than the ground-state DM (μ_g ; DMs for 1: μ_g = 45.9 D, μ_e = 60.7 D; DM for 2: μ_g = 31.0 D, μ_e = 36.4 D; see Tables S4 and S5 and Figures S7 and S8 in the Supporting Information). Higher DM values in the excited states support the lowering in energy of the MLCT state with increasing solvent polarity. This fact, in combination with the spectroscopic observations of the thin films described earlier, support the switching of the lowest excited state to MLCT from a ligand-centered (LC) state with increasing polarity of slovents (Figure 6). In this case, the nature of the excited state is predominantly of MLCT character. The observed maximum emission wavelength in chloroform (λ_{max} = 512 nm) shifts to a longer wavelength when the thin film is exposed to solvents of higher polarity. The thin films of 1 exposed to dcm, acetone, and acetonitrile, respectively, have λ_{max} values of 518, 524, and 540 nm.

Similarly, thin films of **2** recrystallized from dcm emit blue light when exposed to relatively low-polar solvents (1,4-dioxane, benzene), which changes to green in relatively high-polar solvents [chloroform ($\lambda_{max} = 507 \text{ nm}$), dcm ($\lambda_{max} = 513 \text{ nm}$), acetone ($\lambda_{max} = 516 \text{ nm}$), acetonitrile ($\lambda_{max} = 518 \text{ nm}$)]. The vapor-responsive color and data from dipole moment calculations, and emission and absorption spectra are shown in Figure S5a,b and Figure 6b in the Supporting Information.

The original green emission of 2 in dcm changes to blue on exposure of the film to 1,4-dioxane. This thin film reemits green light after heating at 70 °C for 15 min followed by exposure to dcm vapor (Figure 7). It is observed that the emission color of the thin film of 2 turns to green on exposure to dcm, and the blue emission reappears when the thin film is exposed to 1,4-dioxane. These observations support the switching of the emission color of 2 on reversibly changing the volatile organic solvent. Similar switching of the emission color of 1 is also observed (see Figure S9 in the Supporting Information). We recrystallized 1.2 dcm from 1,4-dioxane and the resulting 1 showed the same VOC property as was observed in the thin film of 1.2 dcm on



exposure to 1,4-dioxane after heating (as discussed earlier, see Figure S10). We recorded the ¹H NMR spectrum of the resulting complex. The presence of the proton peak of 1,4-dioxane at around 3.7 ppm is clearly observed in the NMR spectrum (see Figure S11), whereas the proton peak of dichloromethane (ca. 5.3 ppm) was not observed. The observation of a proton peak from dioxane supports the replacement of dcm molecules with 1,4-dioxane prior to occupying the crystal sites by dcm molecules.



Figure 7. (a) Solid-state reversal of the emission color of **2** from blue to green (on exposure to dcm) and green to blue (on exposure to 1,4-dioxane). The photograph was taken under excitation at 364 nm. (b1) Reversibility of the solid-state emission spectrum of **2** with repeated VOC exposure: a. **2** Recrystallized from dcm, b. after exposure to 1,4-dioxane, c. after exposure to dcm after heating the film at 70 °C for 15 min, and d. after exposure to 1,4-dioxane. (b2) Switching of the emission wavelength (ca. 515 nm to ca. 465 nm and back) on repeated alternating exposure to dcm and 1,4-dioxane, respectively.

As described above, the void space available for potentially occupying solvent molecules in 1 and 2 are 980.1 and 906.2 Å³, respectively, per unit cell of the crystal lattice (vide supra). The crystal packing diagrams for 1 and 2 (crystals recrystallized from dcm) demonstrate that the interstitial positions are occupied by dcm molecules (eight dcm molecules per unit cell of the crystals in each case; Figure 2). Powder X-ray diffraction patterns of thin-film samples of 1 exposed to dcm exactly match the structure determined by single-crystal X-ray diffraction. On the basis of this similarity, the thin-film structure has been identified as $1\cdot 2CH_2Cl_2$ (see Figure S12 in the Supporting Information). The powder X-ray patterns for the thin films of 1 in other solvents (1@1,4-dioxane, 1@acetonitrile) are similar to that of 1.2CH₂Cl₂ (the structure obtained from single-crystal X-ray diffraction; see Figure S12a). The above experiment was performed with 2 and gave a similar result (see Figure S12b). Note that 1 (or 2) exhibits a broad and featureless emission spectrum (with faint yellow emission color) after dissolving it in dcm. This observation remains true irrespective of the polarity of the solvent (see Figure S13a,b). The solution absorption spectra of 1 and 2 in different solvents barely show any difference (see Figure S13c,d) in contrast to solid thin films (Figure 5, b). Similar findings^[20e] were found for the (4,4'-tert-butyl-2,2'-bipyridine)(p-dimesitylborylphenylacetylene)platinum-(II) complex, in which the vapoluminescent properties of the solid thin film depend on the polarity of the solvent, but the same was not observed in solution. This anomalous observation can presumably be explained by localized dipole-dipole interactions in the thin films with guest solvents occupying the void space, rather than the interactions between 1 (or 2) and the continuously changing dipoles in bulk solution.[20e]

Aggregation-Induced Emission Activity

A number of controlled experiments were performed to investigate the cause of the strong solid-state emission behavior exhibited by 1 and 2 with yellow and green luminescence at $\lambda_{\text{max}} = 518$ and 513 nm, respectively (Table 2). Complexes 1 and 2 were both found to be almost nonemissive after dissolution in thf. However, the intensity of the emission increased significantly in 90:10 water/thf (Figure 8 and Figure S14 in the Supporting Information). As these complexes are insoluble in water, the observed increase in PL intensity with increasing concentration of water (visible as suspended particles) proves that these complexes show aggregation-induced emission (AIE) activity. The emission intensities of 1 and 2 in 90:10 water/thf were found to be 30 and 74 times higher, respectively, than their PL intensities in thf. Note that, unlike the analogous iridium(III) complexes with cyclometalated ligands published by our group,^[27] the PL intensities of these diimine complexes remain unchanged up to 60:40 water/thf (Figure 8 and Figure S14). This disparity is evident from the ionic nature of these species (1 and 2), which renders them more soluble than their neutral cyclometalated analogues (Scheme 1, D). In another experiment, a slow enhancement of PL emission intensity was observed with a gradual increase in the concentration of viscous poly(ethylene glycol) (PEG) at a fixed concentration of 1 (or 2) in thf (see Figure S15). The luminescence intensity increased by factors of 2.7 and 2.9 for 1 and 2, respectively, in 90:10 PEG/thf, which suggests that the complexes possess some rotationally active moiety. Hindrance of the rotationally active group with increasing viscosity of the solution may be responsible for the increasing luminescence intensity. Based on these experiments, it is proposed that rotation of the rotationally active group is restricted in the solid state. The particle sizes of the aggregated forms of 1 and 2 obtained in 90:10 water/thf determined by dynamic light scattering experiments were found to be 146 and



Table 2. Photophysical properties of 1 and 2.

	Medium	UV/Vis ^[a] λ_{max} [nm] (ϵ [10 ⁴ M ⁻¹ cm ⁻¹])	$PL^{[b]}\lambda_{max}$ [nm]	QE ^[c] [%]	τ [μs]
1	solution solid state	269 (5.0), 364 (0.50), 410 (0.40)	538 518	0.75 2.95 ^[e]	0.00125 ^[d]
2	solution solid state	269 (5.2), 358 (0.40), 400 (0.20)	531 513	0.93 1.43 ^[e]	0. 00630 ^[d]

[a] Spectra were recorded in degassed dichloromethane (dcm) at room temperature at a concentration of 10^{-5} M. [b] Spectra were recorded in dcm. [c] The quantum yields were measured in degassed dcm using Coumarin 153 (QY = 0.38 in ethanol) as reference. [d] Life-times were measured in dry thf. [e] Aggregated form of the complexes in 9:1 water/thf (v/v).

186 nm, respectively (see Figure S16). The packing diagrams of 1 and 2 show that several intermolecular interactions exist between the phenyls in the triphenylphosphine units and neighboring molecules, the PF_6^- counter ions, and the interstitially accommodated dcm solvent molecules (see Figure S17). Thus, the rotation of the phenyl groups in triphenylphosphine is hindered in the solid state due to these interactions. This hindered rotation of the phenyl rotors will block the nonradiative channels, lose energy, and open up new radiative pathways leading to significantly improved solid-state quantum efficiency.^[38] Both complexes in dichloromethane exhibit very weak PL intensity in comparison with their corresponding solid/aggregated forms (see Figure S18). We have demonstrated this effect in a different



Figure 8. (a) Variation of PL intensity of 2 with increasing concentration of water in a solution of 2 in thf (concd. of 0% water: 1 mg 2 in 10 mL thf; concd. of 30% water: 1 mg 2 in 7 mL thf and 3 mL water; concd. of 60% water: 1 mg 2 in 4 mL thf and 6 mL water; concd. of 90% water: 1 mg 2 in 1 mL thf and 9 mL water). (b) Corresponding emission spectrum with increasing concentration of water.

manner, as described below. The ratios of the total integrated area under the solid-state photoluminescence (PL) spectrum (I_s) to its absorption $(A_s; absorbance values corre$ spond to their excitation wavelengths), $Q_s = I_s/A_s$, were calculated for **1** and **2** and found to be 8.2×10^9 and 1.4×10^{10} , respectively. Similarly, values of $Q_{\rm sol}$ for 1 and 2 (sol represents solution state; $Q_{sol} = I_{sol}/A_{sol}$, 1 and 2 dissolved in pure thf) were calculated to be 8.9×10^8 and 7.2×10^8 , respectively. The ratios of $Q_s/Q_{sol}^{[39]}$ for 1 and 2 are thus 9.2 and 19.7, respectively, which are in support of the strong emission observed for 1 and 2 in the solid state compared with their solutions. Time-resolved photoluminescence spectra for 1 and 2 were measured in pure thf and the lifetimes determined were 1.25 and 6.3 ns, respectively. The life-times of the complexes 1 and 2 in 90:10 (v/v) water/ thf are significantly longer at 2.95 and 1.63 µs, respectively (Table 2 and Figure S19). These increased life-times in 90:10 water/thf evidence the improved luminescence yield aggregated in comparison with in pure thf.^[40] The solution quantum efficiencies (in pure thf) of 1 and 2 were determined to be 0.75 and 0.93%, respectively (Coumarin 153 with quantum yield = 0.38 in ethanol was used as reference).^[41]

Conclusion

Two new mono(diimine)-based complexes of iridium(III) have been synthesized. In general, diimine complexes of iridium(III) emit weak light in both solid and solution states. However, these synthesized diimine complexes emit strong light in the solid state due to aggregation-induced emission activity. This approach has led to improved solid-state light emission properties in the diimine iridium(III) system. These complexes are useful as vapor-responsive luminescent materials. To the best of our knowledge, these are the first examples of iridium complexes that are AIE-active molecules for sensing VOCs.

Experimental Section

Materials: Iridium(III) chloride hydrate, 1,10-phenanthroline, 2ethoxyethanol, potassium hexafluorophosphate, and triphenylphosphine were purchased from Sigma–Aldrich Chemical Company Ltd. Sodium carbonate and the UV/Vis-grade solvents (dcm, hexane, ethyl acetate) were procured from Merck.

Characterization: ¹H, ¹³C, and ³¹P NMR spectra were recorded with a 400 MHz Bruker spectrometer using CDCl₃ as solvent and tetramethylsilane ($\delta = 0$ ppm for ¹H and ¹³C NMR) and phos-



phoric acid (δ = 0 ppm for ³¹P NMR) as internal standards. IR spectra were recorded with FTIR Shimadzu (IR Prestige-21) and Perkin–Elmer Spectrum 100 FTIR spectrometers. UV/Vis absorption spectra were recorded with Shimadzu UV-1800 and 2550 spectrophotometers. Steady-state photoluminescence spectra were recorded with a FLS920-s Edinburgh spectrofluorimeter. Elemental analyses were carried out by using an Elementar VARIO III instrument. The particle sizes of the nanoaggregates were determined by using a Malvern Zetasizer (MAL1040152) instrument. Microwave reactions were carried out in a CEM Discover (mode 1908010) oven. PXRD patterns were recorded with a Rigaku Miniflex II desktop X-ray diffractometer.

All the reactions were performed under nitrogen and monitored by TLC (TLC plates precoated with 0.20 mm silica gel). Cyclic voltammetry measurements were performed with a Potentiostat/ Galvanostate Model 263 A instrument. The platinum, glassy carbon, and Ag/AgCl electrodes were used as counter, working, and reference electrodes, respectively, and the scan rate was maintained at 50 mVs⁻¹. The complexes and 0.1 M lithium perchlorate (LiClO₄, 100 mg, as supporting electrolyte) were dissolved in acetonitrile (10 mL). The experiments were conducted under an inert atmosphere. The volume occupied by the solvent molecules (void space in the unit cell of the crystal lattice) was calculated by WinGx.^[42]

Synthesis of 1 and 2: Triphenylphosphine (622 mg, 2.348 mmol) was added to iridium(III) chloride (200 mg, 0.6711 mmol) in 2-ethoxyethanol (15 mL) and the reaction mixture was heated at reflux at 135 °C for 4 h. Then 1,10-phenanthroline (241 mg, 1.342 mmol) and sodium carbonate (211 mg, 2.013 mmol) were added and the reaction mixture further heated at reflux for 3 h. The resulting reaction mass was then cooled to room temperature and the crude product was dried under reduced pressure in a rotary evaporator. Potassium hexafluorophosphate (100 mg) was mixed with the crude product in methanol (4 mL) and the solution was heated in a microwave oven (MW) for 10 min at 60 °C (pressure, 100 psi; power, 100 W). The reaction mass was cooled to room temperature and the solid residue was collected by filtration and washed with cold methanol several times to obtain pure complex 2. Then the mother liquor was evaporated under reduced pressure to dryness to collect complex 1 (mixed with a little impurity of 2). Complex 1 was purified by column chromatography eluting with methanol/dcm (1:10; $R_{\rm f}$ = 0.55; Scheme 1). Single crystals of both complexes suitable for X-ray diffraction were grown from dcm/hexane (1:1) at room temperature. Data for 1: Yellow solid; yield: 35.77%. ¹H NMR (400 MHz, CDCl₃): δ = 8.46 (d, J = 5.1 Hz, 2 H), 8.30 (d, J = 8.1 Hz, 2 H), 7.91 (s, 2 H), 7.27-7.17 (m, 19 H), 7.13 (m,10 H), 7.05–6.92 (m, 3 H), -19.24 (t, J = 16.4 Hz, 2 H) ppm. ¹³C NMR (101 MHz, CDCl₃): δ = 133.00, 132.14, 132.04, 131.98, 131.96, 128.58, 128.46 ppm. ³¹P NMR (162 MHz, CDCl₃): δ = 20.88 ppm. IR (KBr): $\tilde{v} = 2179$ (m, v_{Ir-H}) cm⁻¹. C₄₈H₄₀F₆IrN₂P₃ (1043.99): calcd. C 55.22, H 3.86, N 2.68; found C 55.28, H 3.77, N 2.75. Data for 2: Pale-green solid; yield: 11.06% ¹H NMR (400 MHz, $CDCl_3$): $\delta = 9.14$ (d, J = 5.0 Hz, 1 H), 8.49 (d, J = 7.7 Hz, 1 H), 8.35 (d, J = 8.2 Hz, 1 H), 8.13 (q, J = 8.9 Hz, 2 H), 7.71-7.53 (m, 2 H), 7.39–7.26 (m, 6 H), 7.27–7.04 (m, 24 H), 6.61 (dd, J = 8.2, 5.5 Hz, 1 H), -17.56 (t, J = 14.3 Hz, 1 H) ppm. ¹³C NMR $(101 \text{ MHz}, \text{ CDCl}_3)$: $\delta = 133.03, 132.13, 132.04, 131.99, 131.97,$ 128.57, 128.45 ppm. ³¹P NMR (162 MHz, CDCl₃): δ = 29.49 ppm. IR (KBr): 2152 (m, v_{Ir-H}) cm⁻¹. C₄₈H₃₉ClF₆IrN₂P₃ (1078.43): calcd. C 53.46, H 3.62, N 2.60; found C 53.43, H 3.60, N 2.65. (Scheme 1).

Fabrication of Thin Films on Thin Glass Substrates for Photoluminescence Measurements: The 10^{-3} M solutions of 1 and 2 in thf were prepared. Then 2–3 drops of the solution were placed on a thin glass substrate $(2 \times 2 \text{ cm}^2)$ and the solvent allowed to evaporate slowly.

Single-Crystal X-ray Diffraction Study: Single-crystal X-ray diffraction data were collected by using a Bruker AXS Kappa Apex II diffractometer equipped with an Oxford Cryosystem 700Plus liquid nitrogen based cooling device. The data sets were collected at 100 K by using ϕ and ω scans such that the data were completed up to 60° in 2 θ . Data reduction, scaling, merging, and space group determinations were performed by using the APEX2^[43] suite available from Bruker AXS. The crystal structures were solved by direct methods (SHELXS97)^[44] available within Olex 2^[45] suite and the structures were refined by full-matrix least-squares refinement using SHELXL97. All the hydrogen atoms were geometrically fixed at their calculated positions and refined by using the riding model. Geometric calculations were carried out by using PARST97.^[46]

DFT Quantum Chemical Calculations: The ground-state geometries of complexes 1 and 2 were optimized by using density functional theory (DFT) with the B3LYP hybrid functional^[47] starting from their respective crystal structures. A double-zeta basis set (LANL2DZ) and the effective core potential was used on the iridium atom.^[48a-48c] Diffusion functions were added to the chlorine and hydrogen atoms coordinated to iridium by using the 6-311++G(3df,3pd) basis set. The two phosphorus atoms and the two nitrogen atoms coordinated to the iridium were assigned by using the 6-31G** basis set. The remaining carbon and hydrogen atoms were assigned by using the 6-31G* and 3-21G basis sets, respectively. Time-dependent DFT (TDDFT)^[49] calculations were performed on the lowest-energy singlet ground state to probe the absorption and emission properties using the same functional and basis sets. As for the experiment, calculations were performed in dichloromethane solution ($\varepsilon = 8.93$) using the polarizable continuum model.^[50] The 10 lowest singlet and triplet roots of the non-Hermitian eigenvalue equations were obtained to determine the vertical excitation energies. Oscillator strengths were deduced from the dipole transition matrix elements for singlet states only. All the calculations were performed by using the GAMESS-US^[51] software. Canonical molecular orbital analysis (CMO)^[52] was performed to analyze the composition and bonding nature of the molecular orbitals (MOs) by using the NBO 5.0 software.^[53] CMO analysis provided effective information on the bonding nature of MOs such as HOMO-x and LUMO+y and the energies of individual MOs. Partial charge transfer (CT) was characterized for the HOMO-x to LUMO+y transition as shown in Equation (2)

$$CT(M) = [\%(M)HOMO - x] - [\%(M)LUMO + y]$$
 (2)

in which %(M)HOMO–*x* and %(M)LUMO+*y* are the percentages of metal character obtained by CMO analysis. When the contributions to an excited state come from multiple single-electron excitations, the metal CT character is described^[54] by Equation (3)

$$CT_{i}(M) = \sum [Ci(i-j)]^{2}[(M)_{i} - (M)_{i}]$$
(3)

in which Ci(i - j) are coefficients expressed as the excitation amplitudes corresponding to transitions between *i* and *j* states. The dipole moments of the molecules were computed in the optimized ground states by using the dipole moment analysis^[53] module of NBO. In the ground state, the total NBO dipole moment reported includes delocalization correction.

Supporting Information (see footnote on the first page of this article): Additional absorption/emission spectra, DFT results, crystal structural data for 1 and 2.



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