

Cyclometalated Ir(III) Complexes Involving Functionalized **Terpyridine-Based Ligands Exhibiting Aggregation-Induced** Emission and Their Potential Applications in CO₂ Detection

Vishwa Deepak Singh, Rajendra Prasad Paitandi, Bhupendra Kumar Dwivedi, Roop Shikha Singh, and Daya Shankar Pandey*®

Department of Chemistry, Institute of Science, Banaras Hindu University, Varanasi 221 005, U.P., India

Supporting Information

ABSTRACT: Synthesis of three novel terpyridine-based donor-acceptor (D-A) ligands (TP1, TP2, TP3) and cyclometalated iridium complexes $[Ir(ppy)_2TP1]^+PF_6^-$ (C1), $[Ir(ppy)_2TP2]^+PF_6^-$ (C2), and $[Ir(ppy)_2TP3]^+PF_6^-$ (C3) [ppy = 2-phenyl pyridine] involving these were described. The ligands and complexes were characterized by spectroscopic studies (¹H, ¹³C, ¹⁹F, ³¹P, ESI-MS, UV-vis, and fluorescence). Crucial role of intermolecular interactions in aggregation-caused quenching (ACQ; C2) and aggregation-induced emission (AIE; C3) was rationalized by X-ray single-crystal analyses. Vital role of restricted intramolecular rotation (RIR) in inducing AIE upon aggregation via $\pi - \pi$ interactions in these complexes was scrutinized by various studies. Because of strong intramolecular charge transfer these D-A based AIEgens exhibited solvatochromism. Further, AIE property of the complexes C1 and C3 was exploited toward detection of CO₂.

INTRODUCTION

Luminescent cyclometalated Ir(III) complexes have fascinated the scientific community due to their potential applications in diverse areas including solar energy conversion, sensing, phosphorescent organic-light emitting diode (OLEDs), and light-emitting electrochemical cells.¹ Presence of the heavy atom Ir(III) in phosphorescent materials induces strong spinorbit coupling and facilitates fast intersystem crossing (ISC). Therefore, numerous Ir(III) complexes exhibiting long luminescence lifetime,^{2,3} large Stokes shifts,^{4,5} and high quantum yield^{6,7} coupled with good photostability^{8,9} have been developed, and their applicability has been extensively investigated in various areas.¹⁰⁻¹² On the one hand, it has been illustrated that these properties can be easily tuned by varying cyclometalated (C^N) and ancillary (N^N) ligands about the metal center.^{13,14} On the other hand, the scope of Ir(III) complexes in many applications is restricted due to strong interaction between closely packed molecules; however, it can be circumvented via the use of sterically hindered bulky ligands.^{15–18}

Furthermore, intriguing properties of the aggregationinduced emission (AIE) luminophores have opened new avenues in chemical research.¹⁹⁻²⁴ AIE is largely controlled by the processes like restriction of intramolecular motion (RIM), twisted intramolecular charge transfer (TICT), E/Z isomerization, excited-state intramolecular proton transfer (ESIPT), conformational planarization, excimer and J-aggregate formation.²⁵ Several solid-state emitting materials based on these



processes have been developed and have categorically shown that blue emitters dominate over red ones. Further, deep red/ near-infrared (DR/NIR) solid-state emitters are a must in the fabrication of full-color OLEDs, optical probes for bioimaging, and biomedical applications.²⁶ In this direction, donoracceptor (D-A) molecules have attracted attention of many research groups due to their excellent photophysical and photochemical properties.^{27,28} In such systems the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are well-separated and cause facile intramolecular charge transfer, which plays a vital role in the design of D-A based AIE-active luminogens.²⁹

Although a variety of AIE-active organic luminogens have been reported in the literature, metal-based AIE active luminogens are rather scarce. Recently some metal complexes, particularly those based on heavy metals, have been reported to display excellent AIE activity.³⁰⁻³² The metal-based AIEactive luminogens are highly emissive in the solid state and play a decisive role in construction of advanced optically active materials and OLEDs. As well, detection of CO₂ is a challenging task for the scientific community. Some of the methods usually employed for its detection are based on electrochemical (EC), nondispersive infrared (NDIR), gas chromatographic, mass spectrometric, Severinghaus potenti-ometry, etc. $^{33-35}$ These require extensive instrumental setup

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and maintenance, and they are time-consuming. Besides, some of these (EC and IR) are sensitive toward water vapor and carbon monoxide (CO), too. To overcome the problems associated with traditional methods CO_2 sensors based on fluorescence changes have shown great promise because of their advantages like high tolerance toward interfering agents (H₂O and CO) and ability to show efficient visibility to naked eyes. In this direction, AIE-active fluorescent sensors are being developed for quantitative detection of CO_2 .

Considering these points through this work three terpyridine-based D–A type ligands 4'-(anthracen-9-yl)-2,2':6',2''terpyridine (**TP1**), 3-([2,2':6',2''-terpyridin]-4'-yl)-9-methyl-9*H*-carbazole (**TP2**), and 3-([2,2':6',2''-terpyridin]-4'-yl)-10methyl-10*H*-phenothiazine (**TP3**) and three novel Ir(III) complexes $[Ir(ppy)_2$ **TP1** $]^+PF_6^-$ (**C1**), $[Ir(ppy)_2$ **TP2** $]^+PF_6^-$ (**C2**), and $[Ir(ppy)_2$ **TP3** $]^+PF_6^-$ (**C3**) containing aforesaid ligands were designed and synthesized. Donor moiety in these systems were purposefully incorporated to enhance electron cloud on the N^N chelating site. Because of charge separation between donor and acceptor units these ligands and complexes display excellent photophysical properties with large Stokes shift. Through this contribution we describe photophysical properties and aggregation behavior of the cyclometalated Ir(III) complexes (**C1–C3**) along with their promising applications in detection of CO₂.

EXPERIMENTAL SECTION

Reagents. Anthracene aldehyde, phenothiazine, carbazole, and 2acetylpyridine were procured from Sigma-Aldrich, India. Common reagents, KOH/NaOH, and solvents dimethyl sulfoxide (DMSO), dichloromethane (DCM), acetonitrile, dimethylformamide (DMF), and methanol, etc., were procured from Avra Chemicals and dried and distilled following standard literature procedures prior to their use.³⁶ All the synthetic manipulations were performed under oxygen-free nitrogen atmosphere, and photophysical studies were made using spectroscopic-grade solvents.

General Information. Electronic absorption and fluorescence spectra were acquired on a Shimadzu UV-1800 and PerkinElmer LS 55 fluorescence spectrometer, respectively, at room temperature. ¹H (500 MHz) and ¹³C (125 MHz) NMR spectra were acquired at room temperature on a JEOL AL 500 FT-NMR spectrometer using tetramethylsilane [Si(CH₃)₄] as an internal reference. Electrospray ionization mass spectrometric (ESI-MS) measurements were made on a Bruker-Daltonics, Micro-TOF-Q II mass spectrometer. Scanning electron microscopic images were captured on JEOL JSM 840A using silicon wafer. The lifetime measurements were made using a TCSPC system from Horiba Yovin (model: Delta Flex). Samples were excited at 368 nm using a picosecond diode laser (model: Delta Diode). The data analysis software. Dynamic light scattering (DLS) studies were performed on a HORIBA particle size analyzer SZ-100.

Syntheses. Synthesis of C1. The precursor complex $[(ppy)_2 Ir(\mu -$ Cl)]₂ (108 mg, 0.1 mmol) was added to a stirring solution of TP1 (103 mg, 0.25 mmol) in 1:1 CH₂Cl₂/CH₃OH (50 mL), and the resulting solution was further stirred for an additional 12 h at room temperature. Subsequently, a solution of NH₄PF₆ (40 mg, 0.25 mmol) dissolved in methanol was added to it and stirred for 1 h to afford a reddish-brown precipitate. The solvent was removed under reduced pressure, and residue was purified by silica gel column chromatography using dichloromethane. Yield: 63.2% (167 mg). ¹H NMR (DMSO- d_{6i} 500 MHz, δ ppm): 5.37 (d, 1H, J = 8.0 Hz), 5.88 (t, 2H, J = 6.5 Hz), 6.20 (t, 1H), 6.53 (t, 1H), 6.71 (t, 1H), 6.80 (dd, 2H, J = 9.5 Hz), 6.86–6.91 (p, 2H, J = 7.5 Hz), 6.95–7.01 (p, 2H, J = 7.5 Hz), 7.17 (t, 1H), 7.27 (t, 1H), 7.40 (t, 1H), 7.46-7.59 (m, 4H), 7.67 (br., 2H), 7.71 (s, 1H), 7.85 (dd, 2H, J = 5.0 Hz), 8.10 (m, 2H), 8.23 (m, 3H), 8.35 (d, 2H, J = 7.5 Hz), 8.68 (s, 1H), 8.78 (s, 1H), 8.84 (d, 1H, J = 8.5 Hz), 8.89 (s, 1H), 9.45 (d, 1H, J = 6.0 Hz). ¹³C

NMR (DMSO- d_{6i} 125 MHz, δ ppm): 120.0, 120.5, 123.3, 124.3, 125.1, 125.3, 125.9, 126.0, 126.2, 126.3, 127.4, 127.5, 129.1, 129.3, 129.5, 129.8, 130.4, 130.6, 131.2, 131.6, 132.5, 139.2, 143.0, 143.7, 149.5, 150.3, 152.6, 166.8, 168.0. ³¹P NMR (DMSO- d_{6i} 202 MHz, δ ppm): -132.7, -136.2, 139.8, -143.3, -146.8, -150.3, and -153.8. ¹⁹F NMR (DMSO- d_{6i} 470 MHz, δ ppm): -69.2 and -70.7. ESI-MS. (Calc., found, m/z):[M - PF₆]⁺ 910.2522, 910.2527. Anal. Calcd (%) for C₅₁H₃₅F₆IrN₅P: C, 58.06; H, 3.34; N, 6.64; found: C, 58.95; H, 3.38; N, 4.78.

Synthesis of C2. It was prepared following the above procedure for C1 using TP2 (104 mg, 0.25 mmol) in place of TP1. Further, the solvent was removed under vacuum pressure and purified by silica gel column chromatography using dichloromethane and methanol (9:1). Red crystals of the desired product were obtained by slow evaporation of acetonitrile over dichloromethane solution of the complex. Yield: 75.5% (200 mg). ¹H NMR (DMSO- d_{6} , 500 MHz, δ ppm): 3.91 (s, 3H), 5.34 (d, 1H), 5.76 (d, 1H, J = 7.5 Hz), 6.23 (t, 1H, J = 7.5 Hz), 6.54 (t, 1H, J = 8.0 Hz), 6.72 (t, 2H, J = 7.5 Hz), 6.85 (t, 1H, J = 8.5 Hz), 6.96 (1H, t, J = 4.5 Hz), 7.07 (t, 1H, J = 7.5 Hz), 7.18 (t, 1H), 7.25-7.28 (m, 2H), 7.45 (d, 1H, J = 10.0 Hz), 7.49 (1H, t), 7.54 (1H, d), 7.61 (m, 3H), 7.71 (t, 2H, J = 9.5 Hz), 7.85 (t, 1H, J = 8.5 Hz), 7.91 (t, 1H, J = 12.5 Hz), 8.01 (s, 1H), 8.08 (d, 1H), 8.13 (d, 1H), 8.16 (d, 1H, J = 10 Hz), 8.28 (m, 3H), 8.86 (s, 1H), 9.04 (m, 2H),9.22 (m, 2H). ¹³C NMR (DMSO- d_6 , 125 MHz, δ ppm): 29.8, 110.2, 120.1, 120.5, 120.8, 121.0, 121.2, 122.7, 123.3, 123.4, 123.5, 124.2, 124.3, 125.1, 125.2, 125.3, 125.9, 127.0, 128.4, 129.6, 130.5, 130.6, 132.1, 136.3, 139.0, 139.1, 141.8, 142.7, 143.7, 148.4, 151.3, 157.3, 157.6, 163.0, 166.4, 168.1. ³¹P NMR (DMSO- d_{6} , 202 MHz, δ ppm): -133.0, -136.5, -140.0, -143.5, -147.0, -150.5, and -154.1. ¹⁹F NMR (DMSO- d_6 , 470 MHz, δ ppm): -69.2 and -70.7. ESI-MS. (Calc., found, m/z): $[M - PF_6]^+$ 913.2631, 913.2740. Anal. Calcd (%) for C₅₀H₃₆F₆IrN₆P: C, 56.76; H, 3.43; N, 7.94; found: C, 55.68; H. 2.46: N. 7.16.

Synthesis of C3. This complex was prepared following the above procedure for C1 using TP3 (111 mg, 0.25 mmol) in place of TP1. The reaction mixture was removed in vacuo and purified by silica gel column chromatography using dichloromethane and methanol (9:1). Dark red crystals of the desired product were obtained by slow evaporation of acetonitrile over dichloromethane solution of the complex. Yield: 67.5% (184.5 mg). ¹H NMR (DMSO- d_6 , 500 MHz, δ ppm): 3.46 (s, 3H), 5.33 (d, 1H, J = 8 Hz), 5.75 (d, 1H, J = 7.5 Hz), 6.24 (t, 1H), 6.54 (t, 1H), 6.73 (t, 2H, J = 7.5 Hz), 6.90 (t, 1H, J = 7.5 Hz), 6.95 (t, 1H, J = 5.0 Hz) 7.02 (dd, 2H), 7.07 (2H, t), 7.18 (d, 2H, J = 7.5 Hz), 7.26 (t, 1H, J = 7.0 Hz), 7.29 (t, 1H, J = 8 Hz), 7.47 (d, 1H, J = 8.0 Hz), 7.52 (d, 1H, J = 6.0 Hz), 7.64–7.61 (m, 2H), 7.78 (d, 1H, J = 8.0 Hz), 7.87 (t, 2H, J = 9.0 Hz), 7.94 (t, 1H), 8.04 (t, 2H), 8.12 (d, 1H, J = 8.0 Hz), 8.09 (d, 1H, J = 8.0 Hz), 8.18 (d, 1H, J = 8.5 Hz,), 8.29 (t, 1H), 8.83 (br. 1H), 9.08 (s, 1H), 9.19 (d,1H, J = 8.0 Hz). ¹³C NMR (DMSO-*d*₆, 125 MHz, δ ppm): 35.4, 114.8, 115.1, 119.5, 120.0, 120.1, 121.3, 122.3, 122.8, 122.9, 123.0, 123.2, 123.8, 124.3, 124.8, 125.8, 126.1, 126.9, 127.6, 127.9, 128.1, 129.1, 130.0, 131.6, 135.8, 138.5, 138.6, 139.3, 143.2, 144.2, 147.6, 147.9, 148.1, 148.6, 149.0, 156.7, 162.5, 165.9, 167.5. ³¹P NMR (DMSO-d₆, 202 MHz, δ ppm): -133.0, -136.5, -140.0, -143.5, -147.0, -150.5, and -154.1. ¹⁹F NMR (DMSO- d_{6} , 470 MHz, δ ppm): -69.2 and -70.7. ESI-MS. (Calc., found, m/z): $[M - PF_6]^+$ 910.2522, 910.2527. Anal. Calcd (%) for C₅₀H₃₆F₆IrN₆PS: C, 55.09; H, 3.33; N, 7.71; S, 2.94; found: C, 53.99; H, 2.46; N, 6.59; S, 2.58.

X-ray Structure Determination. Crystals suitable for X-ray singlecrystal analyses for C2 and C3 were obtained by slow diffusion of acetonitrile over a dichloromethane solution of the respective complex. X-ray data were collected on a Bruker APEX-II CCD diffractometer at 296 K (C2) and 273 K (C3) equipped with a graphite monochromator and Mo K α (l = 0.71073 Å) radiation. Data collections were made using ϕ and ω scan mode. Structures were solved by direct methods (SHELXS 97) and refined using full-matrix least-squares on F^2 (SHELX 14).^{37,38} All the non-H atoms were treated anisotropically. The H atoms attached to carbon were included as fixed contribution, calculated geometrically, and refined using SHELX riding model. Computer program PLATON was used Scheme 1. Scheme Showing Synthesis of Ligands TP1-TP3 and Complexes C1-C3



Figure 1. Absorption spectra of TP1, TP2, TP3 (a) and C1, C2, C3 (b) in CH₃CN (c, 50 μ M).

for analyzing the interaction and stacking distances.³⁹ CCDC deposition Nos. 1824607 (C2) and 1819368 (C3) contain supplementary crystallographic data for this paper.

Theoretical Studies. The Gaussian 09 program package⁴⁰ was employed for the density functional theory (DFT) calculations^{41,42} at Becke's three-parameter functional and Lee-Yang-Parr hybrid functional (B3LYP)^{43,44} level of calculations. Molecular structures of TP1-TP3 and C1 were designed using ChemBioDraw Ultra software, and their three-dimensional (3D) views were optimized by minimizing energy of the molecules using MM2 mode with the same software, while initial geometry for the compound C2 and C3 was taken from the single-crystal X-ray data and subjected to optimization. For nonmetal atoms (C, H, N, S, P, F), $6-31G^{**^{45-48}}$ was used as basis set for ground-state geometry optimization and conformational stability in gaseous state of the ligands (TP1-TP3), while metal center (Ir) was described by LANL2DZ⁴⁹ effective core potential (ECP) basis set for C1-C3. The UV-vis spectra of TP1-TP3 and C1-C3 were investigated by performing time-dependent DFT (TD-DFT) using B3LYP method in acetonitrile solvent considered within self-consistent reaction field (SCRF) theory with Polarizable Continuum Model (C-PCM) of Gaussian 09 software.⁵⁰⁻

RESULT AND DISCUSSION

Synthesis and Characterization. The ligands TP1–TP3 were prepared following literature procedures.^{53–55} These reacted with chloro-bridged dimeric complex $[(ppy)_2Ir(\mu-Cl)]_2$ in dichloromethane/methanol (1:1) under stirring conditions (12 h, room temperature) to afford cationic complexes C1–C3 in moderate to good yield (60–80%).

The complexes (C1-C3) were isolated as their hexafluorophosphate salts. A simple synthetic strategy adopted for preparation of the ligand TP1-TP3 and complexes C1-C3 is shown in Scheme 1.

The ligands and complexes under investigation are air-stable, non-hygroscopic solids, soluble in common organic solvents like acetonitrile, methanol, ethanol, acetone, dichlo-romethane, chloroform, dimethylformamide, and dimethyl sulfoxide and insoluble in diethyl ether, petroleum ether, and hexane. These were characterized by satisfactory elemental analyses, ESI-MS, ¹H and ¹³C NMR, and UV–vis spectral studies. The molecular structures of C2 and C3 were determined crystallographically.

NMR Spectral Studies. ¹H, ¹³C, ¹⁹F, and ³¹P NMR spectral data for TP1–TP3 and C1–C3 are summarized in the Experimental Section, and resulting spectra are depicted in Supporting Information (Figures S1–S9). The –NCH₃ protons of ligands resonated as a singlet at δ 3.90 (TP2) and 3.43 (TP3) ppm, while signals due to aromatic protons appeared as a broad multiplet (δ 7.20–8.86 ppm). Upon complexation with the metal center –NCH₃ protons shifted downfield and appeared at δ 3.91 and 3.46 ppm, respectively, for C2 and C3, while aromatic protons due to C1–C3 resonated in the range of δ 5.25–9.45 ppm. The occurrence and chemical shifts for various signals in the ¹H NMR spectra strongly suggested formation of the compounds.⁵⁶ ¹³C, ¹⁹F, and ³¹P NMR spectral data (summarized in Experimental

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Figure 2. Emission spectra of TP1-TP3 (a) and C1-C3 (b) in CH₃CN (c, 50 μ M).



Figure 3. Emission spectra of TP2 (a), TP3 (b), C2 (c), and C3 (d) in different solvents (c, 50 μ M).

Section) also corroborated well with formation of respective ligands (TP1-TP3) and complexes (C1-C3).

Mass Spectral Studies. ESI-MS strongly supported formation of these compounds. In their spectra the ligands displayed molecular ion peaks due to $[M + H]^+$ at m/z 410.2 (calcd. 409.1579), **TP1**; 413.1768 (calcd. 412.1688), **TP2**; and 445.1467 (calcd. 444.1409), **TP3**, respectively (Figure S10). Similarly, complexes containing these ligands (**C1–C3**) exhibited molecular ion peaks due to $[M - PF_6]^+$ at m/z 910.2527 (calcd. 910.2522), **C1**; 913.2470 (calcd. 913.2631), **C2**; and 945.2695 (calcd m/z; 945.2351), **C3**, respectively,

arising due to loss of the counteranion hexafluorophosphate (Figure S11).

Photophysical Studies. UV–Vis absorption and emission spectra of **TP1–TP3** and **C1–C3** were acquired in CH₃CN (c, 50 μ M) at room temperature; the resulting data are summarized in Table S1, and corresponding spectra are shown in Figures 1 and 2.

Ligands displayed absorptions (λ_{abs} , nm) at 256, 385 (TP1); 297, 324 (TP2); and 255, 362 (TP3). The band at lower wavelength was assigned to $\pi - \pi^*$, and the higher one was assigned to the intraligand charge transfer (ILCT) transition. Similarly, the absorption band for complexes (C1-C3) red-



Figure 4. Emission spectra of C1 (a) and C3 (b) in CH₃CN/water mixture with different water fraction (c, 50 μ M).

shifted with respect to corresponding ligands due to increased electron-accepting properties of the terpyridine π^* orbitals upon coordination with Ir(III) ion.^{57,58} Main absorption bands appeared at 256, 387 (C1); 287, 385 (C2); and 258, 413 (C3) nm. Upon excitation, ligands showed single emission band, while complexes dispalyed structured emission peaks. A solution of **TP1** showed emission at 425 nm, and C1 appeared at 440 nm. On the one hand, similarly, upon excitation at 324 and 362 nm, **TP2** and **TP3** displayed single strong emission at 438 and 528 nm with a Stokes shift of 114 and 166 nm, respectively. On the other hand, complexes C2 and C3 displayed bathochromic shifted emissions at 558 and 538 nm with a large Stokes shift of 173 and 125 nm, respectively. The emission bands of C1–C3 are ascribed to ¹LC excited states, and a mixture of ¹MLCT character was also contributed.^{59,60}

Further, luminophores (TP1-TP3 and C1-C3) displayed strong ICT due to D-A structure and are very sensitive to solvent polarity. Broad solubility range of TP1-TP3 and C1-C3 in common organic solvents, specifically, benzene, toluene, 1,4-dioxane, CHCl₃, tetrahydrofuran (THF), CH₂Cl₂, DMF, CH₃CN, and CH₃OH prompted us to examine their solvatochromic behavior. Figure 3 clearly shows that an increase in solvent polarity from nonpolar (benzene, f = 0.030) to polar (methanol, f = 0.309) led the emission maxima for TP1-TP3 and C1-C3 to display red shift along with broadening, which suggested the involvement of ICT. To have better understanding of the effect of solvent polarity on emission behavior and effect of change in the dipole moment between the ground- and excited-state relationship between the Stokes shift and orientation polarizability (Δf) (Lippert-Mataga plot) as well as $E_{\rm T}$ 30 parameter were examined (Figure S13).

$$\Delta f = f(\varepsilon) - f(n^2) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

where Δf represents orientation polarizability, ε is the static dielectric constant of the solvent, and *n* is the refractive index.

The solvatochromism is attributed to dipole–dipole interaction between the solute and solvent molecules.⁶¹ Further, the excited state stabilizes to greater extent in solvents of high dipole moment and cause lowering of the energy of system leading to a bathochromic shift. On the one hand, the Lippert–Mataga plot between Stokes shift and orientation polarizability (Δf) showed linear relation indicating greater

polarization of the excited relative to ground state (Figure S13). On the other hand, linear relationship between the Stokes shift versus $E_{\rm T}$ (30) with positive slope showed that solute-solvent interactions are responsible for the observed solvatochromism (Figure S13).⁶² An examination of emission spectra for TP2, TP3 and C2, C3 revealed prominent red shift $(\Delta \lambda)$ of ~69, 61, 131, and 72 nm with increasing solvent polarity. The excited state of luminogens in nonpolar solvent (benzene) is in equilibrium with surrounding solvent molecules, and its planar conformation is stabilized by the electronic conjugation resulting in a sharp locally excited (LE) emission. On the other hand, broad and structureless emission bands observed in polar solvent (methanol) were attributed to an ICT state, whose energy is stabilized in polar solvents.⁶³ Sharp emission maxima for TP2 and TP3 appeared at 389 and 475 nm in benzene, while in methanol, dual emission peak is observable at 458 and 536 nm (ICT state) with large red shift $(\Delta \lambda \approx 69 \text{ and } 61 \text{ nm}, \text{ respectively})$. At the same time shoulder emerged at 370 and 463 nm due to remnant of LE emission state. Similarly, C3 showed sharp emission band at 495 nm due to LE emission state in benzene, while in methanol a dual emission band was observed at 567 nm (ICT state) with a shoulder at 506 nm (LE state). Noticeably, C2 shows dual emission in most of the polar solvents due to existence of a mixture of LE and ICT emission states.⁶⁴ The LE emission state was observed at ~440 nm, while the ICT state was at \sim 560 nm. On the one hand, both complexes showed a remarkable bathochromic shift (~130 nm, C2 and ~72 nm, C3) after changing solvent polarity from nonpolar to polar. On the other hand, emission spectra of TP1 and C1 showed small (~13 and 3 nm, respectively) shift with increasing solvent polarity (Figure S12). TP1 showed sharp emission maxima at 424 nm in benzene and red-shifted to 437 nm in methanol, while emission spectra of C1 exhibited dual emission. The emission spectra of C1 in benzene showed a dual band at 419 and 438 nm. Further on changing the solvent polarity to methanol, very small red shift observed in both maxima (420 and 441 nm).

AIE Behavior. The AIE behavior of ligands and complexes was investigated in CH₃CN/water system by varying water percentage. Ligands (**TP1–TP3**) do not show any major changes up to $f_w = 60\%$, but as f_w reaches 70%, bathochromic shift occurred with prominent level off tail in the absorbance indicating aggregate formation (Figure S14 and Table S3).



Figure 5. Emission spectra of C1 (a) and C3 (b) in methanol/glycerol mixture with different glycerol volume fractions (c, 50 μ M).



Figure 6. A logarithmic view of the time-resolved fluorescence of C1 (a) and C3 (b) in CH₃CN ($f_w = 0\%$) and water ($f_w = 100\%$) (c, 50 μ M).

When the water fraction was varied from f_w 70 to 100%, the absorption spectra of these compounds exhibited red shifts (386 to 397, TP1; 323 to 353, TP2; 361 to 399 nm, TP3) with enhanced absorbance. Variation in the emission intensity for aggregates was also investigated using similar solvent system. With variation in water fraction TP1-TP3 displayed analogous emission features. At f_w 0% TP1 displayed emission maxima (λ_{max}) at 424 nm, which shifted to 441 nm at f_w 100% with quenched emission. Similarly, TP2 and TP3 at f_w 0% showed emission maxima at 438 and 529 nm, which showed quenching with increasing water fraction; further, at f_w 100% it significantly red-shifted (λ_{max} = 481 and 565 nm, respectively; Figure S15). From the available data it was concluded that these luminogens show typical aggregation-caused quenching (ACQ) behavior with obvious red shift. Likewise, complexes C1–C3 do not show any major change in absorption behavior up to f_w 80%, but at f_w 90% these displayed leveling off tail indicating formation of aggregates (Figure S16). Furthermore, at f_w 100% the complexes C1-C3 display the red shift with small increase in absorbance also suggesting the formation of aggregates.65,66

Effect of aggregation on excited-state emission for the complexes was monitored under analogous conditions using similar solvent system. With increasing water content (up to f_w 50%) fluorescence intensity of the band at 437 nm quenched for complex **C1**. Further, increase in water content (f_w 60% to

90%) enhanced the fluorescence intensity with a small red shift (λ , 441 nm), and at f_w 100% it showed a quenched emission due to precipitation (Figure 4a). Likewise, emissiondue to C3 at 516 nm (f_w 0%) showed quenching with increasing water content (up to f_w 70%). It is noteworthy to mention that at f_w 80% a new band emerged at 608 nm with a shoulder at 547 nm. Further, at f_w 90% emission intensity enhanced with bathochromic shift (λ , 610 nm), and the shoulder peak shifted at 550 nm (Figure 4b). A dramatic fluorescence enhancement for the band at 611 nm was observed at f_w 100%, with diminished intensity for the original band at 516 nm. On the one hand, as both C1 and C3 displayed fluorescence enhancement upon aggregation, these can be treated as AIE luminogens. On the other hand, at f_w 0% complex C2 showed emission band at 556 nm, and its intensity diminished with continual increase of water content up to $f_w 100\%$ (Figure S17) and Table S3).

AlE Mechanism. After optical properties of C1 and C3 were examined, an attempt was made to investigate the mechanism of AIE. It is well-known that emission enhancement for AIE-active luminogens arises mainly due to RIR, which strongly depends on viscosity of the solution. In this regard, to have detailed information, emission spectra of C1 and C3 were acquired in a mixture of methanol/glycerol (c, 50 μ M) with varying glycerol fraction. As shown in Figure 5 emission intensity for C1 (\sim 2 times) and C3 (\sim 5 times)



Figure 7. SEM images of aggregates of C1 (a), C2 (b), and C3 (c) formed in mixture of CH₃CN/water (c, 50 μ M).

enhanced with increasing glycerol fraction without any apparent change in position of the emission maxima (446 nm; C1, and 506 nm; C3). It indicated that increasing solvent viscosity augmented emission intensity, probably due to restriction of intramolecular motion, and advocated the involvement of RIR in AIE.

Further, time-resolved emission decay profiles for C1 and C3 were acquired in CH₃CN and CH₃CN/water mixture. Diverse decay dynamics shown by the complexes suggested dissimilar emission behavior in the aforesaid solvent systems. Average fluorescence lifetime (τ_{av}) for these compounds in CH₃CN (f_{wr} 0%) was ~0.23 (C1) and ~1.58 ns (C3), while in 100% water it came out to be ~3.87 (C1) and ~2.68 ns (C3), respectively (Figure 6). Enhanced fluorescence lifetime observed at high water fraction may be related to formation of aggregates. In aggregated state, intramolecular motion gets restricted causing lowering of nonradiative decay, thereby enhancing emission with longer lifetime. From the above results it was concluded that RIR process is responsible for AIE.⁶⁷

Morphological Studies. To have deep insight into morphology of the aggregates formed in CH_3CN /water mixture scanning electron microscopic (SEM) studies were performed (Figure 7). C1 and C3 showed spherical nanoballs of average size 40–50 nm, whereas C2 exhibited discrete nanoball aggregates of the average size (90 nm).

Crystal Structures. Structures of C2 and C3 were determined by X-ray single-crystal analyses. These crystallize in monoclinic system with $P2_1/n$ (C2) and Cc (C3) space groups. Details about data collection, solution, and refinement are gathered in Table 1. Selected geometrical parameters are given in Table S2, while pertinent views along with atom numbering scheme are depicted in Figure 8. From the structure it is evident that in these complexes N5 and N6 from 2-phenylpyridine are *trans*-disposed⁶⁸⁻⁷¹ (Figure 8). Crystal structure further revealed that $[(ppy)_2Ir]$ unit in theses complexes is coordinated with N^N-chelating site of the terpyridine moiety creating a slightly distorted octahedral environment about Ir(III) center. On the one hand, in C2, the C28-Ir1-N6, C39-Ir1-N5, and N3-Ir-N4 bite angles are $80.8(6)^{\circ}$, $80.2(5)^{\circ}$, and $75.7(4)^{\circ}$, respectively. On the other hand, for C3 the bite angles C39-Ir1-N6, C33-Ir1-N5, and N2-Ir1-N3 are 80.8(6)°, 81.4(6)°, and 75.5(4)°, respectively. Average Ir1-C [Ir-C 1.991 Å; C2 and Ir-C 2.012 Å; C3] and Ir1–N bond lengths [Ir–N 2.109 Å; C2 and 2.108 Å; C3] and C-Ir-C, C-Ir-N, and N-Ir-N bond angles are close to those reported in other cyclometalated Ir(III) complexes.^{72,73}

To get deep insight into weak interactions involved in the aggregated state, crystal packing in C2 and C3 was carefully examined. Packing in C3 revealed the occurrence of two $\pi-\pi$ interactions (3.31–3.38 Å) between phenothiazine unit of one molecule with ppy of another one (Figure S19). Further, ppy

Table 1. Crystal Data and Structure Refinement Parameters for C2 and C3

crystal parameters	C2	C3
empirical formula	C ₅₀ H ₃₆ F ₆ IrN ₆ P	C50H36F6IrN6PS
formula weight	1058.02	1090.08
crystal system	monoclinic	monoclinic
space group	$P2_1n$	Сс
a (Å)	14.610(7)	18.999(7)
b (Å)	14.736(6)	17.668(7)
c (Å)	19.900(7)	14.379(6)
α (deg)	90.00	90.00
β (deg)	101.456(3)	120.44(10)
γ (deg)	90.00	90.00
V (Å ³)	4199.4(3)	4161.7(3)
color and habit	red, block	red, block
Ζ	4	4
dcal (g/cm ³)	1.673	1.740
temperature (K)	296(2)	273(2)
wavelength (Å)	0.710 73	0.710 73
$\mu \text{ (mm}^{-1})$	3.289	3.370
GOF on F ²	1.050	1.029
R indices (all data)	$\begin{array}{l} R_1 = \ 0.0588 \ wR_2 = \\ 0.0870 \end{array}$	$\begin{array}{l} R_1 = 0.0652 \ wR_2 = \\ 0.1618 \end{array}$
final R indices $[I > 2\sigma(I)]$	$\begin{array}{l} R_1 = \ 0.0399 \ wR_2 = \\ 0.0780 \end{array}$	$\begin{array}{l} R_1 = 0.0606 \ wR_2 = \\ 0.1578 \end{array}$

unit associated with phenothiazine moiety also interacted with another unit of cyclometalated ppy via two $\pi - \pi$ interactions (3.39 Å; Figure S20). Slipped stacking in C3 weakens the $\pi - \pi$ interactions and favors J-aggregation (Figure S20c). These interactions provide a rigid 3D network resulting in aggregates with enhanced emission in aggregated state by blocking nonradiative processes. On the one hand, it also reflected better electronic communication between the molecules promoting red shift upon aggregation. On the other hand, crystal structure of C2 revealed existence in a dimeric form in an antiparallel (head-to-tail) orientation. In this molecule $\pi - \pi$ interactions occur between carbazole moiety of one molecule and pyridine ring (of ppy) of the adjacent one at a interacting distance of 3.31 Å (Figure S19). A closer look at the packing in C2 revealed that existence of dimeric form, which is further strengthened via $\pi - \pi$ interactions (range of 3.2–3.3 Å) of the metal chelated terpyridine units of each other. This strong $\pi - \pi$ interaction can quench fluorescence in the aggregated state.

DENSITY FUNCTION THEORY CALCULATIONS

Further, theoretical studies showed that HOMO of the terpyridine-functionalized ligands **TP1**, **TP2**, and **TP3** are mainly localized on donor units (anthracene, carbazole, and phenothiazine), while LUMO is localized on acceptor unit (terpyridine) of the **TP2** and **TP3**. On the other hand, in **TP1** the LUMO is concentrated on anthracene moiety itself. On the one hand, the band gaps between the HOMO (-5.18, **TP1**;



Figure 8. ORTEP views of C2 (a) and C3 (b) at 50% thermal ellipsoid probability (H atoms are omitted for clarity).



Figure 9. Frontier molecular orbitals of C1, C2, and C3 obtained from DFT calculations.

Scheme 2. Formation of Carbamate Ionic Liquid



-5.35, **TP2**; -5.06 eV, **TP3**) and LUMO (-1.66, **TP1**; -1.28, **TP2**; -1.39 eV, **TP3**) for ligands are 3.52, 4.07, and 3.67 eV, respectively (Figure S21). On the other hand, the HOMOs of the complexes are mainly distributed over donor moieties (i.e., anthracene, carbazole, and phenothiazine), and LUMOs are on the acceptors (i.e., terpyridine; Figure 9). Complexes **C1**-**C3** showed almost the same LUMO level (-4.70, **C1**; - 4.53, **C2**; and -4.59 eV, **C3**), which may be due to similar acceptor unit, whereas HOMO level was at -7.40 = (C1), -7.42 = (C2), and -6.94 eV (**C3**). Theoretical HOMO–LUMO gap for **C1**, **C2**, and **C3** is calculated as 2.70, 2.89, and 2.35 eV, respectively. Thus, spatial distribution between the HOMO

and LUMO suggested possibility of a typical ICT between the donor and acceptor moieties. As observed in the absorption spectra (Figure 1), bathochromic shift in the complexes (C1-C3) as compared to respective ligands (TP1-TP3) can be ascribed as lower band gap between HOMO and LUMO. Further the UV-vis spectra of TP1-TP3 and C1-C3 were obtained from theoretical study (TD-DFT; Figures S22-S27). The details of absorption wavelength, energy, oscillation strength (f), assignment, and transitions are summarized in Table S4. On the one hand, for TP1-TP3 show that the HOMO \rightarrow LUMO as a main transition and contributed 92, 88, and 77%, respectively. On the other hand, for C1 and C2 the major transition band is due to HOMO \rightarrow LUMO(+1), HOMO(-1) \rightarrow LUMO; HOMO(-1) \rightarrow LUMO(+1) and HOMO \rightarrow LUMO transitions. In both the cases LUMO and LUMO(+1) are mainly distributed over terpyridine unit, while HOMO and HOMO(+1) are mainly over donor unit (i.e., anthracene and carbazole, respectively), metal center, and ppy unit. Further, transitions observed in C3 are HOMO(-1) \rightarrow LUMO and HOMO \rightarrow LUMO. In C3 the HOMO is localized



Figure 10. (a)Emission spectra of C1 in DMA/CIL mixture with different fraction of CIL ($f_{CIL} = 0-90\%$). (b) Plot between emission intensity and CIL fraction.



Figure 11. (a) Emission spectra of C3 in DMA/CIL mixture with different fraction of CIL (f_{CIL} , 0–90%). (b) Plot between emission intensity and CIL fraction.

on electron-rich phenothiazine, and LUMO is on electronwithdrawing terpyridine, while HOMO(-1) is distributed over Ir(III) and ppy moiety. Thus, overall theoretical studies corroborated well with the experimental results.

Detection of CO₂. Highly polar and viscous carbamate ionic liquids (CIL) can be obtained by bubbling CO₂ into a solution of amines (Scheme 2). Thus, an amine solution of AIE-active luminogens upon interaction with CO₂ may turn on light emission due to formation of aggregates and activation of RIR via creation of polar and viscous CIL.⁷⁴

Considering these points we examined the applicability of C1 and C3 in CO₂ detection and thoroughly characterized generated CIL by IR and ¹³C NMR spectroscopies (Figures S28 and S29).^{75–77} In this direction, solubility of AIE-active luminogens C1 and C3 was scrutinized in various amines like piperidine, pyridine, 1,8-diazabi-cyclo-[5,4,0]-undec-7-ene (DBU), and dimethylamine (DMA). It was observed that these complexes are completely soluble in DMA. Further, complexes C1 and C3 weakly fluoresce in DMA; however, gradual bubbling of CO₂ to a solution of complexes in DMA substantially enhanced the fluorescence intensity. An increase of CIL fraction in DMA/CIL solution led to enhancement of the emission intensity up to 3.2 (C1) and 1.5 (C3) times at

 $f_{\rm CIL}$ 90% relative to that in DMA (Figures 9 and 10). It showed a linear relationship between emission intensity and $f_{\rm CIL}$ added to DMA solution. A comparison of viscosity effect on AIE for C1 and C3 in glycerol/methanol relative to DMA/CIL showed similar results. Additionally, DLS studies affirmed the nanoaggregates size (~150 nm, C1 and ~120 nm, C3; Figure S33).

Further, to examine response of C1 and C3 in DMA solution toward CO₂ different fractions of CO₂ were purged through a solution of C1 and C3 in DMA at a fixed rate and time. It was observed that with increasing bubbling volume emission intensity gradually enhanced and gave a linear plot (Figures S30 and S31). It indicated that C1 and C3 serve as promising probes for CO₂. Noticeably, emission spectra of C1 and C3 in DMA (Figure 11) showed no appreciable changes after a long time exposure to air (10-15 min). In addition, it is well-known that CO does not react with amines; therefore, present CIL-based CO₂ sensor is highly insensitive to common interfering agents as well as addition of water droplets exerted negligible effect on the viscosity of CIL system (Figure S32). These observations demonstrated that our sensory system is stable and nonsensitive to atmospheric N_2 , O_2 , low concentration of CO_2 (400 ppm), and CO. The CO_2 sensing mechanism was related to formation of highly polar and

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viscous CIL upon bubbling CO_2 gas through a solution of the complexes in DMA. The generated viscous environment may restrict intramolecular motion of luminogens causing emission enhancement due to restriction of nonradiative processes. On the one hand, additionally, an increase in volume of CO_2 augments viscosity of the CIL; thus, it may offer quantitative detection of CO_2 gas. On the other hand, reversibility of the sensory system was confirmed by heating CIL. After it was heated, CIL breaks in its constituents, and the peak at ~161 ppm diminished in its ¹³C NMR (Figure S28).

CONCLUSION

Summarily, this work deals with synthesis and thorough characterization of three novel D-A based functionalized terpyridine ligands (TP1-TP3) and cyclometalated Ir(III) complexes (C1-C3). Photophysical properties (UV-vis, fluorescence, and solvatochromism) of the complexes suggested intramolecular charge transfer from donor to acceptor moiety. Crystal packing in these systems revealed occurrence of ACQ in C2 and AIE in C3, which has further been supported by UV-vis and fluorescence spectral studies. The viscochromism and time-resolved fluorescence lifetime measurements advocated that RIR is accountable for these intriguing photophysical properties. In addition, a simple method based on applicability of C1 and C3 has been developed for detection of CO2. Thus, through this work a highly ambitious approach has been developed toward fluorescent detection of CO₂ via AIE.

ASSOCIATED CONTENT

S Supporting Information

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¹H, ¹³C, ¹⁹F, ³¹P NMR, ESI-MS, IR, fluorescence spectra, SEM images, theoretical studies, DLS studies, and tabulated data (PDF)

Accession Codes

CCDC 1819368 and 1824607 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*E-mail: dspbhu@bhu.ac.in or dsprewa@yahoo.com.

ORCID 🔍

Daya Shankar Pandey: 0000-0002-6576-4234

Notes

The authors declare no competing financial interest.

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