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Synthesis, Photophysics, and Reverse Saturable Absorption of *trans*-Bis-cyclometalated Iridium(III) Complexes (C^N^C)Ir(R-tpy)⁺ (tpy = 2,2':6',2"-Terpyridine) with Broadband Excited-State Absorption

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ABSTRACT: Extending the bandwidth of triplet excited-state absorption in transition-metal complexes is appealing for developing broadband reverse saturable absorbers. Targeting this goal, five bis-terdentate iridium(III) complexes (**Ir1-Ir5**) bearing *trans*-bis-cyclometalating (C^N^C) and 4'-R-2,2':6',2"-terpyridine (4'-R-tpy) ligands were synthesized. The effects of the structural variation in cyclometalating ligands and substituents at the tpy ligand on the photophysics of these complexes have been systematically explored using spectroscopic methods (i.e., UV–vis absorption, emission, and transient absorption spectroscopy) and time-dependent density functional theory (TDDFT) calculations. All complexes exhibited intensely structured ${}^{1}\pi,\pi^{*}$ absorption bands at <400 nm and broad charge transfer (${}^{1}CT$)/ ${}^{1}\pi,\pi^{*}$ transitions at 400–600 nm. Ligand structural variations; however, they had a significant effect on the molar extinction coefficients of these



absorption bands. All complexes emitted featureless deep red phosphorescence in solutions at room temperature and gave broadband and strong triplet excited-state absorption ranging from the visible to the near-infrared (NIR) spectral regions, with both originating from the ${}^{3}\pi,\pi^{*}/{}^{3}$ CT states. Although alteration of the ligand structures influenced the emission energies slightly, these changes significantly affected the emission lifetimes and quantum yields, transient absorption spectral features, and the triplet excited-state quantum yields of the complexes. Except for Ir3, the other four complexes all manifested reverse saturable absorption (RSA) upon nanosecond laser pulse excitation at 532 nm, with the decreasing trend of RSA following Ir2 \approx Ir4 > Ir1 > Ir5 > Ir3. The RSA trend corresponded well with the strength of the excited-state and ground-state absorption differences (Δ OD) at 532 nm for these complexes.

INTRODUCTION

In the past 20 years, octahedral d⁶ iridium(III) complexes have gained intense interest because of their rich photophysical properties, such as long-lived triplet excited states, high phosphorescence quantum yields, excellent emission color tunability, and good chemical and thermal stability.^{1–4} Various Ir(III) complexes have been explored for a wide range of applications, including luminescent bioimaging,^{5–11} photodynamic therapy (PDT),^{8–17} low-power upconversion,^{18,19} organic light-emitting diodes (OLED),^{20,21} light-emitting electrochemical cells (LEECs),^{22,23} nonlinear optics,^{24–27} etc. Efficient tuning of the photophysical properties of the Ir(III) complexes for specific applications can be realized via structural modifications of the coordinating/cyclometalating ligands,^{26–28} while understanding the structure–property correlations holds the key for developing Ir(III) complexes with predetermined properties.

Among the various Ir(III) complexes, tris-bidentate Ir(III) complexes bearing cyclometalating ligands, such as $Ir(C^N)_3$ and $(C^N)_2Ir(N^N)^+$ (where C^N denotes the cyclometalating ligands and N^N represents the diimine ligands), are the

most widely studied prototypes.^{3,25,26} 2-Phenylpyridine (ppy) and its derivatives have been the most utilized cyclometalating ligands owing to their ease of synthesis and determinable photophysical properties for the resultant Ir(III) complexes. Optimization of the absorption and emission characteristics of these complexes can be realized through introducing electron-donating/-withdrawing substituents or fusing aromatic rings on the C^N and/or N^N ligands.^{17,21–28}

In contrast to the tris-bidentate cyclometalated Ir(III) complexes, bis-terdentate Ir(III) complexes endow important advantages due to their axial symmetry that precludes geometrical isomers and facile tuning of intramolecular charge transfer.²⁹ However, most of the reported bis-terdentate Ir(III) complexes are the bis-terpyridine (tpy) complexes Ir-

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Scheme 1. Structures and Synthetic Route for (C^N^C)Ir(tpy)⁺ Complexes Ir1-Ir5



 $(tpy)_{2}^{3+}$.^{16,30–34} Studies on other types of bis-terdentate Ir(III) complexes, especially those with trans-bis-cyclometalating ligands, have been quite limited.^{29,30,34-37} The challenges probably arise from the harsh reaction conditions in synthesizing these complexes, including high reaction temperature (>180 °C), restrictions to light and oxygen, and low product yield. The groundbreaking work on using 2,6-diphenylpyridine (dppy) derivatives as the trans-bis-cyclometalating ligand (C^N^C) was reported by Scandola and co-workers.35,36 It was revealed that the heteroleptic linearly arranged (C^N^C)- $Ir(tpy)^+$ complexes exhibited bathochromically shifted charge transfer absorption and emission in comparison to their bisterpyridine counterparts Ir(tpy)₂^{3+,35-37} These changes were rationalized by the stronger σ -donating ability of the C^N^C ligand, which raised the C^N^C- and metal-based highest occupied molecular orbital (HOMO) and the lowest singly occupied molecular orbital (1-SOMO), consequently lowering the ligand-to-ligand charge transfer (LLCT)/metal-to-ligand charge transfer (MLCT) absorption and emitting states.³⁵ The substituents $(CH_3 \text{ or } Br)$ on the 4'-phenyl group of the tpy ligand manifest some effects on the emission energies, while substitution on the 4-phenyl ring of the C^N^C ligand had a negligible effect on the emission energies of the complexes. Nonetheless, the types of substituents investigated have been quite limited, and exploration of the potential applications of this type of complexes is scarce.^{35–37} To the extent of our knowledge, the only reported work on utilizing a $(C^N^C)Ir(tpy)^+$ type complex is the selective photooxidation of DNA purine base.³

Since 2013, our group has systematically investigated the reverse saturable absorption (RSA, a nonlinear absorption in which the stronger excited-state absorption over the groundstate absorption enhances the absorptivity of a material when the incident light fluence increases) of cyclometalated trisbidentate Ir(III) complexes.^{17,24–27,38–50} Our ultimate goal has been to develop reverse saturable absorbers with broadband absorption in the visible to the NIR regions for optical limiting applications.⁵¹ It is known that the predominant parameter determining the RSA strength is the ratio of the excited-state absorption (ESA) cross section (σ_{ev}) with respect to that of the ground state (σ_0) at the defined wavelength; a broadband reverse saturable absorber is anticipated to possess a very weak ground-state absorption but much stronger ESA at 400-900 nm. Although many of our studied tris-bidentate Ir(III) complexes display very strong RSA at 532 nm, the lack of ground-state absorption at the longer visible to NIR regions and the insufficient ESA intensity in the NIR regions hamper their potential as broadband reverse saturable absorbers. To date, the RSA of bis-terdentate Ir(III) complexes has not been investigated. Because the broad and strong ESA in the red spectral regions in some of the reported $Ir(tpy)_2^{3+}$ and $(C^N^C)Ir(tpy)^+$ complexes^{16,34–36} (in some cases extending to the NIR regions) and their red-shifted ground-state absorption via appropriate substitution on the terpyridine ligand¹⁶ are desirable features for RSA, the bis-terdentate Ir(III) complexes could exhibit a strong RSA in the long visible spectral regions. Moreover, the stronger σ -donating ability of the C^N^C ligand could further bathochromically shift the charge-transfer ground-state absorption bands in the $(C^N^C)Ir(tpy)^+$ type of complexes with respect to their corresponding $Ir(tpy)_{2}^{3+}$ types,³⁷ which would further broaden the RSA spectral region.

To verify this prediction, we have designed and synthesized a series of $(C^N^C)Ir(tpy)^+$ complexes bearing the transcyclometalating ligand dppy (or its derivative) and tpy ligand with different substituents: i.e., [(2-phenylbenzo[*h*]quinoline)-Ir(4'-phenyl-tpy)]⁺ (Ir1), [(2,6-diphenylpyridine)Ir(4'-phenyl-tpy)]⁺ (Ir2), [(2,6-diphenylpyridine)Ir(4'-(4-dimethylaminophenyl)-tpy)]⁺ (Ir3), [(2,6-diphenylpyridine)Ir(4'-dimethylamino-tpy)]⁺ (Ir4), [(2,6-diphenylpyridine)Ir(4'-(4- $HOCH_2CH_2OOC$ -phenyl)-tpy)]⁺ (Ir5) (the structures are shown in Scheme 1). A series of spectroscopic techniques and theoretical simulations were utilized to systematically study their photophysical properties. Their ESAs and RSAs at 532 nm were manifested as well. In comparison to Ir2, Ir1 containing a C^N^C ligand with a fused additional phenyl ring allows for demonstration of the effects of expansive π conjugation in the C^N^C ligand. Ir3-Ir5 have either strongly electron donating or withdrawing substituents on the tpy ligand to tune the photophysical properties and RSAs of these complexes.

EXPERIMENTAL SECTION

Synthesis and Characterization. All solvents and reagents were obtained from VWR Scientific and used as received unless otherwise mentioned. Silica gels (230–400 mesh) and Al_2O_3 gels (activated, neutral, Brockmann I) for column chromatography were purchased from Sorbent Technology. The ligand 2,6-diphenylpyridine (dppy) was obtained from Alfa Aesar, while 2-phenylbenzo[h]quinoline was synthesized according to the literature procedure.⁵² The N^N^N ligands 4'-phenyl-2,2':6',2"-terpyridine,⁵³ 4'-(4-dimethylaminophen-

yl)-2,2':6',2"-terpyridine,⁵⁴ 4'-dimethylamino-2,2':6',2"-terpyridine,⁵⁵ 4'-(4-COOH-phenyl)-2,2':6',2"-terpyridine,⁵⁶ (4'-phenyl-tpy)IrCl₃,⁵⁷ and (4'-(4-COOH-phenyl)-tpy)IrCl₃/(4'-(4-HOCH₂CH₂OOC-phenyl)-tpy)IrCl₃⁵⁸ were prepared according to the procedures reported in the literature. The synthesis and characterization of (4'-(4dimethylaminophenyl)-tpy)IrCl₃, (4'-dimethylamino-tpy)IrCl₃, and Ir1–Ir5 are reported below. ¹H NMR spectroscopy, electrospray ionization high-resolution mass spectrometry (ESI-MS), and elemental analysis were used to characterize the structures of Ir1– Ir5. The NMR spectra were collected on a Bruker-400 spectrometer. ESI-MS data were obtained on a Waters Synapt G2-Si mass spectrometer. Elemental analyses were carried out by NuMega Resonance Laboratories, Inc. (San Diego, CA).

General Synthetic Procedure for (4'-R-tpy)lrCl₃. The ligand 4'-R-tpy (0.1 mmol, R = phenyl, 4-dimethylaminophenyl, dimethylamino, 4-COOH-phenyl) and IrCl₃·3H₂O (0.1 mmol) were added to 10 mL of ethylene glycol. The suspension was purged with N₂ and heated to 160 °C for 15 min in dark. After the mixture was cooled to room temperature, the precipitate was collected, washed with water (2 × 10 mL) and ethanol (2 × 10 mL), and then dried under vacuum to yield the target complex, which was used for the following reaction step without further purification.

It should be noted that when 4'-(4-COOH-phenyl)-tpy reacted with IrCl₃·3H₂O, the resultant complex was presumed to be a mixture of (4'-(4-COOH-phenyl)-tpy)IrCl₃ and its ester (4'-(4-HOCH₂CH₂OOC-phenyl)-tpy)IrCl₃ due to the possible reaction between the carboxyl group and ethylene glycol at a high reaction temperature, as reported previously in the literature.⁵⁸ However, because of the poor solubility of the complexes, they were not separated and were used directly for the following reaction step, in which the higher reaction temperature (196 °C) and longer reaction time (24 h) could convert the remaining COOH group into an ester group and thus the pure complex (4'-(4-HOCH₂CH₂OOC-phenyl)-tpy)Ir(dppy)PF₆ (IrS) was separated.

(4'-(4-Dimethylaminophenyl)-tpy)lrCl₃. With 4'-(4-dimethylaminophenyl)-tpy (35.2 mg, 0.1 mmol) and IrCl₃·3H₂O (35.2 mg, 0.1 mmol) as the starting materials, a dark red powder was obtained as the product (41 mg, 63%). ¹H NMR (400 MHz, d_6 -DMSO): δ 9.21 (dd, J = 5.6, 1.0 Hz, 2H), 8.97 (s, 2H), 8.89 (d, J = 8.1 Hz, 2H), 8.27 (td, J = 7.9, 1.5 Hz, 2H), 8.13 (d, J = 9.0 Hz, 2H), 7.97–7.89 (m, 2H), 6.93 (d, J = 9.1 Hz, 2H), 3.10 (s, 6H).

(4'-Dimethylamino-tpy)IrCl₃. With 4'-dimethylamino-tpy (27.6 mg, 0.1 mmol) and IrCl₃·3H₂O (35.2 mg, 0.1 mmol) as the starting materials, a dark red powder was obtained as the product (45 mg, 78%). ¹H NMR (400 MHz, d_c -DMSO): δ 9.19 (d, J = 5.7 Hz, 2H), 8.72 (d, J = 7.4 Hz, 2H), 8.21 (t, J = 7.1 Hz, 2H), 7.90 (s, 2H), 7.89–7.83 (m, 2H), 3.46 (s, 6H).

General Procedure for the Synthesis of Ir1–Ir5. (4'-R-tpy)IrCl₃ (0.2 mmol), the C^N^C ligand (0.2 mmol), and AgOTf (154 mg, 0.6 mmol) in ethylene glycol (10 mL) were heated to reflux under an N₂ atmosphere at 196 °C for 24 h in the dark. After the mixture was cooled to rt, NH₄PF₆ (163 mg, 1.0 mmol) was added to the mixture and then stirring was continued at rt for 2 h. The formed AgCl precipitate and other black byproducts were removed using a flash silica gel column with methanol as eluent. After removal of methanol, deionized water was added to precipitate the crude product. The pure product was isolated by silica gel chromatography with CH₂Cl₂/acetonitrile as eluent (from 1/0 to 50/1, v/v). The orange or orange-red band was collected and dried under vacuum to afford the target complex.

Ir1. With (4'-phenyl-tpy)IrCl₃ (121 mg, 0.2 mmol) and 2phenylbenzo[*h*]quinoline (51 mg, 0.2 mmol) as the starting materials, an orange powder was obtained as the product (11 mg, 6%). ¹H NMR (400 MHz, CDCl₃): δ 8.89 (s, 2H), 8.65 (d, *J* = 7.9 Hz, 2H), 8.40 (d, *J* = 8.6 Hz, 1H), 8.18 (dd, *J* = 8.0, 3.5 Hz, 3H), 7.87 (dd, *J* = 14.0, 7.8 Hz, 4H), 7.77 (d, *J* = 8.8 Hz, 1H), 7.71 (t, *J* = 7.8 Hz, 2H), 7.57 (t, *J* = 7.5 Hz, 1H), 7.47 (t, *J* = 7.1 Hz, 3H), 7.17–7.11 (m, 1H), 7.04 (dd, *J* = 11.6, 5.7 Hz, 3H), 6.83 (t, *J* = 6.8 Hz, 1H), 6.52 (d, *J* = 6.4 Hz, 1H), 6.36 (d, *J* = 6.7 Hz, 1H). ESI-HRMS (*m*/*z*): calcd for [C₄₀H₂₆F₆IrN₄P. $1.2 CH_2 Cl_2 \cdot 0.8 CH_3 CN:$ C, 49.69; H, 3.00; N, 6.50. Found: 49.65; H, 3.24; N, 6.77.

Ir2. With (4'-phenyl-tpy)IrCl₃ (121 mg, 0.2 mmol) and 2,6diphenylpyridine (46 mg, 0.2 mmol) as the starting materials, an orange powder was obtained as the product (10 mg, 6%). ¹H NMR (400 MHz, CD₃OD): δ 9.19 (s, 2H), 8.84 (d, *J* = 7.8 Hz, 2H), 8.28– 8.22 (m, 2H), 8.09 (s, 3H), 8.04–7.97 (m, 2H), 7.87 (d, *J* = 7.3 Hz, 2H), 7.80 (d, *J* = 5.2 Hz, 2H), 7.75 (t, *J* = 7.5 Hz, 2H), 7.66 (t, *J* = 7.4 Hz, 1H), 7.32 (ddd, *J* = 7.3, 5.8, 1.3 Hz, 2H), 6.96 (td, *J* = 7.8, 1.2 Hz, 2H), 6.74 (td, *J* = 7.3, 1.1 Hz, 2H), 6.23 (d, *J* = 6.6 Hz, 2H). ESI-HRMS (*m*/*z*): calcd for [C₃₈H₂₆IrN₄]⁺, 731.1789; found, 731.1795. Anal. Calcd for C₃₈H₂₆F₆IrN₄P·0.2CH₂Cl₂: C, 51.39; H, 2.98; N, 6.28. Found: C, 51.05; H, 3.26; N, 6.25.

Ir3. With (4'-(4-dimethylaminophenyl)-tpy)IrCl₃ (130 mg, 0.2 mmol) and 2,6-diphenylpyridine (46 mg, 0.2 mmol) as the starting materials, a red powder was obtained as the product (18 mg, 10%). ¹H NMR (400 MHz, *d*₆-DMSO): δ 9.28 (s, 2H), 9.00 (d, *J* = 8.1 Hz, 2H), 8.26 (d, *J* = 9.1 Hz, 2H), 8.16 (d, *J* = 7.6 Hz, 2H), 8.08 (d, *J* = 7.1 Hz, 1H), 8.06-8.00 (m, 2H), 7.89 (d, *J* = 7.3 Hz, 2H), 7.67 (d, *J* = 5.7 Hz, 2H), 6.67 (t, *J* = 7.3 Hz, 2H), 6.17 (d, *J* = 6.2 Hz, 2H), 3.08 (s, 6H). ESI-HRMS (*m*/*z*): calcd for [C₄₀H₃₁IrN₅]⁺, 774.2211; found, 774.2201. Anal. Calcd for C₄₀H₃₁F₆IrN₅P·1.5H₂O: C, 50.79; H, 3.62; N, 7.40. Found: C, 50.78; H, 3.99; N, 7.24.

Ir4. With (4'-dimethylamino-tpy)IrCl₃ (115 mg, 0.2 mmol) and 2,6-diphenylpyridine (46 mg, 0.2 mmol) as the starting materials, a red powder was obtained as the product (6.7 mg, 4%). ¹H NMR (400 MHz, d_6 -DMSO): δ 8.84 (d, J = 8.1 Hz, 2H), 8.26 (s, 2H), 8.16 (d, J = 7.8 Hz, 2H), 8.08–7.97 (m, 3H), 7.91 (d, J = 7.7 Hz, 2H), 7.60 (d, J = 5.9 Hz, 2H), 7.28 (t, J = 6.0 Hz, 2H), 6.92 (t, J = 6.9 Hz, 2H), 6.73 (t, J = 6.7 Hz, 2H), 6.28 (d, J = 6.5 Hz, 2H), 3.48 (s, 6H). ESI-HRMS (m/z): calcd for [C₃₄H₂₇IrN₅]⁺, 698.1898; found, 698.1898. Anal. Calcd for C₃₄H₂₇F₆IrN₅P·2H₂O: C, 46.47; H, 3.56; N, 7.79. Found: C, 46.23; H, 3.61; N, 7.62.

Ir5. With the mixed (4'-(4-COOH-phenyl)-tpy)IrCl₃/(4'-(4-HOCH₂CH₂OOC-phenyl)-tpy)IrCl₃ (139 mg, 0.2 mmol if it was pure (4'-(4-HOCH₂CH₂OOC-phenyl)-tpy)IrCl₃) and 2,6-diphenyl-pyridine (46 mg, 0.2 mmol) as the starting materials, an orange powder was obtained as the product (11 mg, 6%). ¹H NMR (400 MHz, *d*₆-DMSO): δ 9.49 (s, 2H), 9.09 (d, *J* = 6.9 Hz, 2H), 8.55 (d, *J* = 8.3 Hz, 2H), 8.33 (d, *J* = 8.8 Hz, 2H), 8.23 (d, *J* = 8.4 Hz, 2H), 8.13 (ddd, *J* = 16.5, 9.3, 3.0 Hz, 3H), 7.95 (d, *J* = 7.5 Hz, 2H), 7.77 (d, *J* = 4.9 Hz, 2H), 7.46–7.38 (m, 2H), 6.98–6.90 (m, 2H), 6.76–6.68 (m, 2H), 6.18 (d, *J* = 7.6 Hz, 2H), 5.05 (s, 1H), 4.44–4.37 (m, 2H), 3.83–3.76 (m, 2H). ESI-HRMS (*m*/*z*): calcd for $[C_{41}H_{30}IrN_4O_3]^+$, 819.1949; found, 819.1953. Anal. Calcd for $C_{41}H_{30}F_6IrN_4O_3P$: C, 51.09; H, 3.14; N, 5.81. Found: C, 51.46; H, 3.33; N, 6.12.

Photophysical Study. The solvents used for the photophysical studies were spectroscopic grade and were obtained from Alfa Aesar. A Varian Cary 50 spectrophotometer was used for UV-vis spectral measurements. The emission spectra were recorded on a HORIBA FluoroMax-4 fluorometer/phosphorometer. The emission quantum yields of Ir1-Ir5 in deaerated solutions were determined by the relative actinometry method,⁵⁹ in which a deaerated acetonitrile solution of $[Ru(bpy)_3]Cl_2$ ($\Phi_{em} = 0.097$ in, $\lambda_{ex} = 436$ nm)⁶⁰ was utilized as the reference for all complexes. The nanosecond transient difference absorption (TA) spectra and triplet lifetimes of Ir1-Ir5 in degassed acetonitrile solutions were studied on an Edinburgh LP920 laser flash photolysis spectrometer using the third-harmonic output (355 nm) of a Nd:YAG laser (Quantel Brilliant, 4.1 ns, 1 Hz) as the excitation light. The triplet excited-state molar extinction coefficients at the TA band maxima were estimated using the singlet depletion method.⁶¹ To determine the triplet excited-state quantum yields of Ir1-Ir5, the relative actinometry method⁶² was applied and SiNc $(\varepsilon_{590} = 70000 \text{ M}^{-1} \text{ cm}^{-1}, \Phi_{\text{T}} = 0.20)$ in benzene was used as the standard.⁶³

Nonlinear Transmission Measurements. The RSA strengths of **Ir1–Ir5** were evaluated by nonlinear transmission measurements using a Quantel Brilliant 4.1 ns laser (the repetition rate was set to 10 Hz) as the light source. The concentrations of the acetonitrile

solutions were adjusted to reach a linear transmission of 80% at 532 nm in the cuvette with a 2 mm path length. The experimental setup and details resembled those reported by our group previously.⁶⁴ With an f = 40 cm plano-convex lens, the beam radius was ~96 μ m at the focal point.

Computational Methodology. All complexes of this series were optimized at the singlet ground state at the level of density functional theory (DFT)⁶⁵ using the B3LYP functional.⁶⁶ Ir was treated with the LANL2DZ⁶⁷ basis set that includes the effective core potential. All other atoms were treated with the 6-31G* basis set.^{65,69} Dichloromethane was used as the solvent within the conductor-like polarizable continuum model (CPCM)⁷⁰ reaction field method.

Linear response time-dependent density functional theory (TD-DFT)⁷¹ was used to calculate the singlet excited-state energy and oscillation strength of the transitions. For calculations of the excited states, the same functional, basis sets, and CPCM solvation method were used as those used for the ground-state calculations. Absorption spectra were plotted using the Gaussian function with the linebroadening parameter of 0.10 eV, which produced an acceptable agreement to the thermal broadening of experimental absorption spectra.

To calculate the emission energies, the analytical gradient TDDFT method was applied to optimize the lowest triplet state,⁷² with the same functional and basis sets as in the ground-state calculations. A qualitative description of excited states was presented using natural transition orbitals (NTOs),⁷³ which represent special distribution of the excited electron/hole wave function. The Gaussian16 software package was used for all calculations.⁷⁴ The VMD software packages⁷⁵ were used to visualize the NTOs with 0.02 isovalue.

RESULTS AND DISCUSSION

Electronic Absorption. The absorption spectra of Ir1-Ir5 in CH_2Cl_2 and in other solvents (acetonitrile, THF, toluene) are presented in Figure 1 and in Figure S1 in the Supporting



Figure 1. Experimental UV–vis absorption spectra of Ir1-Ir5 at room temperature in CH_2Cl_2 . The expanded spectra in the 450–650 nm regions are displayed as inset.

Information, respectively. The associated absorption parameters, i.e. band maxima and molar extinction coefficients, are given in Table 1. In the studied concentration range between 1 $\times 10^{-6}$ and 1 $\times 10^{-4}$ mol L⁻¹, the absorption of Ir1–Ir5 followed Beer's law, indicating the absence of ground-state aggregation below the concentration of 1 $\times 10^{-4}$ mol L⁻¹. The absorption spectra of all complexes shared similar features, with strong absorption bands below 400 nm and broad, moderately strong bands between 400 and 600 nm. Considering the large molar extinction coefficients, the intense absorption bands below 400 nm can be attributed to ligandlocalized spin-allowed ${}^{1}\pi,\pi^{*}$ transitions, while the moderate absorption bands at 400–600 nm are tentatively assigned to charge-transfer (¹CT) transitions mixed with ${}^{1}\pi,\pi^{*}$ characters.

The assignment of the optical transitions making contributions to the absorption bands can be confirmed by the TDDFT calculations. As shown in Figure S2 in the Supporting Information, the calculated spectra matched well with the experimental spectra. The natural transition orbitals (NTOs) in Table 2 indicate that the lowest-energy absorption bands at 490-600 nm are dominated by the ligand-to-ligand charge transfer (¹LLCT)/metal-to-ligand charge transfer (¹MLCT) transitions in Ir1, Ir2, and Ir5, while the corresponding bands in Ir3 and Ir4 that bear the strongly electron donating dimethylaminophenyl or dimethylamino substituents have predominant R-tpy ligand localized ¹ILCT (intraligand charge transfer)/ 1 MLCT/ $^{1}\pi,\pi^{*}$ characters. In contrast, the absorption bands at 400-490 nm in Ir1, Ir2, and Ir5 are dominated by the R-tpy-based ${}^{1}\pi, \pi^{*}/{}^{1}$ ILCT transitions admixing with some ¹MLCT/¹LLCT contributions, whereas these bands in Ir3 and Ir4 have predominant ¹LLCT/¹MLCT characters. For the absorption bands at <400 nm, the NTOs in Tables S1-S5 in the Supporting Information manifest the predominant ${}^{1}\pi,\pi^{*}$ nature, admixing with some charge transfer configurations.

Similar to those reported for $(C^N^C)Ir(tpy)^+$ complexes,^{29,35-37} Ir1-Ir5 exhibited greatly red-shifted and distinguishable ¹LLCT/¹MLCT absorption bands in the regions of 400–600 nm in comparison to that of the $Ir(tpy)_2^{3+}$ prototype^{16,33} because of the stronger σ -donating capability of the trans-bis-cyclometalating C^N^C ligand. Fusing an additional phenyl ring in the C^N^C ligand in Ir1 slightly increased the molar extinction coefficient of the $\pi_{\pi}\pi^{*}/^{1}LLCT/^{1}MLCT$ absorption band at 434 nm owing to the extended π conjugation of the C^N^C ligand in comparison to that in Ir2. However, the intensity of the lowest-energy absorption band at 517 nm in Ir1 is the lowest among these five complexes. A careful examination of the NTOs corresponding to the S1 transitions in these complexes (see Table 2) revealed that the S_1 transition in Ir1 had the least contribution from the tpy-localized ${}^{1}\pi,\pi^{*}$ configuration, which accounted for the lower absorptivity of this absorption band in Ir1 with respect to those in Ir2-Ir4. Considering the effect of the 4'-R substituents at the tpy ligand on the low-energy absorption bands, we can clearly see that the strongly electron donating 4-dimethylaminophenyl substituent drastically increased the molar extinction coefficients of these bands at 400-600 nm in Ir3; however, it did not change the transition energies of these bands. In contrast, the electron-withdrawing ester substituent evoked minor effects on either the energies or the molar extinction coefficients of the absorption bands in Ir5 in comparison to those in Ir2. A comparison of the spectra of Ir3 and Ir4 found that the 4'-phenyl group at the tpy ligand played a distinct role in enhancing both the ${}^{1}\pi,\pi^{*}$ and ${}^{1}CT$ transitions associated with the tpy ligand but did not alter the transition energies.

Photoluminescence. The emission of Ir1-Ir5 was investigated in CH₃CN, THF, CH₂Cl₂, and toluene + 5% CH₂Cl₂ at rt. The normalized emission spectra in CH₂Cl₂ are displayed in Figure 2, and the emission parameters are given in Table 1. The emission spectra and parameters in the other solvents are presented in Figure S3 and Table S6 in the Supporting Information. Upon excitation at the corresponding charge transfer bands, all complexes exhibited deep red emission, with the emission energies varying from 661 nm in Ir1 to 688 nm in Ir5 and the emission lifetimes falling into the pubs.acs.org/IC

Table 1. Photophysical Properties of Complexes Ir1-Ir5

	$\lambda_{\rm abs}/{\rm nm} (\log \varepsilon)^a$	$\lambda_{\rm em}/{\rm nm}$ $(\tau_{\rm em}/\mu s); \Phi_{\rm em}^{\ \ b}$	$k_{\rm r}/{ m s}^{-1}$ ^c	$k_{\rm nr}/{\rm s}^{-1} d$	$\lambda_{\text{T1-Tn}}/\text{nm} \ (\tau_{\text{TA}}/\mu s; \log \epsilon_{\text{T1-Tn}}); \ \Phi_{\text{T}}^{\ e}$
Ir1	286 (4.86), 434 (4.05), 517 (3.57)	661 (2.08); 0.072	5.17×10^{4}	6.66×10^{5}	375 (2.11; -), 625 (2.15; 4.34); 0.67
Ir2	280 (4.77), 308 (4.61), 445 (4.01), 527 (3.82)	678 (2.05); 0.033	2.06×10^{4}	6.05×10^{5}	360 (1.61; -), 612 (1.64; 4.64); 0.78
Ir3	280 (4.80), 311 (4.76), 461 (4.36), 528 (4.26)	679 (3.12); 0.049	3.27×10^{4}	6.35×10^{5}	399 (2.39; -), 768 (2.46; 4.52); 0.48
Ir4	280 (4.73), 324 (4.23), 437 (3.85), 528 (3.74)	676 (1.46); 0.015	6.04×10^{4}	3.97×10^{6}	366 (1.12; -), 550 (1.16; -), 750 (1.14; 4.54); 0.17
Ir5	283 (4.81), 309 (4.65), 450 (4.08), 529 (3.87)	688 (1.66); 0.022	5.30×10^{4}	2.36×10^{6}	360 (1.88; -), 639 (1.84; 4.88); 0.25

^{*a*}Electronic absorption band maxima (λ_{abs}) and molar extinction coefficients (log ε) in CH₂Cl₂ at room temperature. ^{*b*}Room-temperature emission band maxima (λ_{em}) and lifetimes (τ_{em}) for Ir1–Ir5 measured in CH₂Cl₂ ($c = 1 \times 10^{-5} \text{ mol L}^{-1}$). The emission quantum yields were obtained using [Ru(bpy)₃]Cl₂ ($\Phi_{em} = 0.097$, $\lambda_{ex} = 436 \text{ m}$) in a deaerated acetonitrile solution as the reference. ^{*c*}Radiative decay rates (k_r) calculated by $k_r = \Phi_{em}/(\Phi_T \tau_{em})$. ^{*d*}Nonradiative decay rates (k_{nr}) calculated by $k_{nr} = (1 - \Phi_{em})/(\Phi_T \tau_{em})$. ^{*c*}Nanosecond TA band maxima (λ_{T1-Tn}), triplet excited-state lifetimes (τ_{TA}), and quantum yield (Φ_T) measured in CH₃CN at room temperature.

Table 2. Natural Transition Orbitals (NTOs) for the Major Transitions Making Contributions to the Low-Energy Absorption Bands of Ir1–Ir5 in CH₂Cl₂



range of 1.46–3.12 μ s in degassed CH₂Cl₂ solutions. The emission was subject to oxygen quenching, exhibited large red shifts in comparison to the excitation wavelengths, and possessed long-lived lifetimes. All of these features suggest a phosphorescent nature of the emission, which is in line with that reported for the other (C^N^C)Ir(tpy)⁺ complexes in the literature.^{29,35–37} In addition, the markedly red shifted but

poorly resolved emission spectra are also in accordance with those observed for the other reported $(C^N^C)Ir(tpy)^+$ complexes,^{29,35–37} while they are quite distinct from those reported for the $Ir(tpy)_2^{3+}$ complexes.^{16,33,37}

The featureless emission bands and the 1.46–3.12 μ s lifetimes of **Ir1–Ir5** imply a charge transfer character of the emitting state, which has been reported for the other



Figure 2. Normalized emission spectra of **Ir1** ($\lambda_{ex} = 500 \text{ nm}$), **Ir2** ($\lambda_{ex} = 460 \text{ nm}$), **Ir3** ($\lambda_{ex} = 460 \text{ nm}$), **Ir4** ($\lambda_{ex} = 460 \text{ nm}$), and **Ir5** ($\lambda_{ex} = 450 \text{ nm}$) in the N₂-purged CH₂Cl₂ solution at room temperature ($c = 1 \times 10^{-5} \text{ mol } \text{L}^{-1}$). The sticks indicate the emission energies calculated by TDDFT using the B3LYP functional in CH₂Cl₂.

 $(C^N^C)Ir(tpy)^+$ complexes in the literature.^{29,35,36} However, in view of the very minor solvatochromic effects in different solvents with varied polarities (see Figure S3 in the Supporting Information), the emitting states should have significant ligand-centered ${}^3\pi,\pi^*$ configurations. This attribution is consistent with the recent report on the (CH₃OPh-C^N^C)-Ir(HO₂CPh-tpy)⁺ complex.³⁷

Further evidence supporting this assignment comes from the TDDFT calculation results via optimizing the lowest triplet excited states (T_1) of Ir1–Ir5. As shown in Table 3 and Figure 2, except for Ir4, the trend in the calculated emission energies for the other four complexes qualitatively matches the experimental emission energy trend. The off-trend of Ir4 could arise from the underestimated lowest triplet-state energy

Table 3. NTOs Representing the Transitions That Contribute to the T_1 States of Ir1–Ir5 in CH₂Cl₂ Calculated by the TDDFT Δ SCF Method, Which Are Optimized with the B3LYP Functional and LANL2DZ/6-31G* Basis



that can be understood in terms of the ground-state triplet instability problem.⁷⁶ It has been reported that, in cases where the Hartree-Fock (HF) stability is less than ~ 2 eV, the inclusion of exact HF exchange in the functional (e.g., 25% in B3LYP) leads to an artificial decrease in excitation energy of the triplet state. The lower degree of HF stability in Ir4 in comparison to that in the other complexes is presumably rationalized by the lack of a phenyl ring in the substituent on the tpy ligand, which places the electron-donating $N(CH_3)_2$ group closer to the tpy ligand, resulting in a higher order of electron density redistribution between the substituent and the tpy ligand. However, this discrepancy in the excitation energy is expected to negligibly affect the special localization/ delocalization properties of the excited wave function. The NTOs corresponding to the T₁ states of Ir1-Ir5 illustrate that both the electrons and holes are predominantly distributed on the N^N^N ligands and the metal d orbitals, with the holes also containing slightly more distribution on the C^N^C ligand. Therefore, the nature of the emitting states in these complexes can be ascribed to the 4'-R-tpy ligand localized ${}^{3}\pi,\pi^{*}$ states admixing with some ${}^{3}MLCT/{}^{3}LLCT$ characters. For Ir3, the electron distribution of the holes is mainly on the 4'-(4-dimethylaminophenyl)pyridine motif and the metal d orbital, while the electron density is delocalized on the entire N^N^N ligand. Thus, the emitting state of Ir3 has a significant ³ILCT configuration in addition to the aforementioned ${}^{3}\pi,\pi^{*}/{}^{3}MLCT/{}^{3}LLCT$ characters.

In comparison to the emission of Ir2, the emission energy of Ir1 is increased, concomitant with a higher emission quantum yield but a similar emission lifetime. The increased emission quantum yield should be attributed to the much higher radiative decay rate (k_r) in Ir1. A closer examination of the holes of the T₁ states revealed an increased ³LLCT character in the emitting state of Ir1 in comparison to that of Ir2 due to the π -extended C^N^C ligand in Ir1, which likely accounted for the increased k_r value and consequently a higher emission quantum yield in Ir1 while the nonradiative decay rates remained similarly. Different from the effect of alteration of the cyclometalating ligand, incorporating a strongly electron donating dimethylamino substituent either on the 4'-phenyl ring or directly on the tpy ligand exerted a minor effect on the emission energies of Ir3 and Ir4. However, these structural variations pronouncedly affected the emission lifetimes and quantum yields in Ir3 and Ir4 in comparison to those in Ir2. Complex Ir3 with the dimethylamino substituent on the phenyl ring exhibited a longer emission lifetime and higher emission quantum yield, with the latter stemming from a 59% higher k_r value and a merely 5.0% higher k_{nr} value with respect to those of Ir2. In contrast, directly attaching the dimethylamino substituent to the tpy ligand in Ir4 resulted in a 2.9-fold increase in k_r but a 6.6-fold increase in k_{nr} in comparison to those of Ir2, which shortened the emission lifetime and lowered the emission quantum yield for Ir4. On consideration of the effects of the electron-withdrawing ester group in Ir5, it caused a 10 nm bathochromic shift of the emission spectrum in comparison to that of Ir2 due to the stabilization of the electron in the T₁ state by the electronwithdrawing substituent. Meanwhile, the k_r value was altered to 2.6-fold and $k_{\rm nr}$ to 3.9-fold increases with respect to those of Ir2. Consequently, the emission lifetime was shortened, and the quantum yield was reduced in Ir5 in comparison to those in Ir2.

Transient Absorption (TA). TA spectroscopy is a powerful technique to provide further information on the triplet excited-state absorption and decay characteristics. To better understand the triplet excited-state properties, especially to figure out the spectral regions where the excited-state absorption is stronger than that of the ground state, the nanosecond TA of Ir1–Ir5 was studied in acetonitrile solutions at room temperature. Figure 3 displays the TA



Figure 3. TA spectra of **Ir1–Ir5** in acetonitrile immediately after laser excitation ($\lambda_{ex} = 355$ nm). $A_{355} = 0.4$ in a 1 cm cuvette.

spectra immediately after 355 nm laser excitation, and the time-resolved TA spectra are provided in Figure S4 in the Supporting Information. The TA parameters such as the band maxima, triplet excited-state lifetimes deduced from the decay profiles of TA, and the T₁ state extinction coefficients and quantum yields are compiled in Table 1. The deduced TA lifetimes for Ir1–Ir5 in acetonitrile are in line with their respective emission lifetimes in the same solution, indicating that the transient absorbing and emitting species originate from the same state. Considering the natures of the emitting states discussed in the section on emission, we can assign the observed TA signals from these complexes to the ${}^{3}\pi, \pi^{*}/{}^{3}MLCT/{}^{3}LLCT$ T₁ states in these complexes, with the T₁ state in Ir3 admixing with a significant ${}^{3}ILCT$ character.

As demonstrated in Figure 3, all complexes exhibited a positive TA band at 350-420 nm and broad and strong positive TA band(s) from the visible region extending to the NIR region (i.e., 496-800 nm for Ir1, 517-800 for Ir2 and Ir5, 550–800 nm for Ir3, and 456–800 nm for Ir4). Bleaching occurred at the wavelengths essentially in accordance with the ¹CT bands in their respective UV-vis absorption spectra. The TA spectral features of Ir1, Ir2, and Ir5 resembled each other; however, the TA signals were much stronger in Ir2 with respect to those in Ir1 and Ir5. This could be related to the highest triplet excited-state formation quantum yield of Ir2 among these complexes. For Ir3, its broad TA band kept increasing in the NIR regions, which could be ascribed to the ³ILCT character in its T₁ state. In contrast, the TA spectrum of Ir4 was guite distinct from those of Ir1–Ir3 and Ir5 in that the positive TA bands were much broader with two band maxima at 550 and 750 nm, respectively. However, the TA intensities of Ir4 were weaker in the entire TA spectrum in comparison to those of the other complexes. This reflects the absence of the phenyl ring in the N^N^N ligand in Ir4, confirming the involvement of the 4'-R-tpy ligand in the transient absorbing T₁ state in these complexes.

Reverse Saturable Absorption (RSA). We have manifested that many Ir(III) tris-bidentate complexes exhibited strong RSA and potentially could be utilized as optical limiting materials.^{17,24–27,38–50} Generally, RSA requires a stronger excited-state absorption in comparison to the ground-state absorption at the same wavelength. The TA spectra in Figure 3 illustrated that all complexes, except for Ir3, hold positive signals at 532 nm, implying that the excited-state absorption at this wavelength was stronger than the ground-state absorption. This feature along with their much longer triplet excited-state lifetimes with respect to the pulse width of the laser beams (4.1 ns) indicate that RSA could occur at 532 nm from these complexes upon 532 nm nanosecond laser irradiation. To manifest this assumption, the nonlinear transmission measurements of Ir1-Ir5 in a 2 mm cuvette in acetonitrile solutions were carried out using 4.1 ns laser pulses at 532 nm. The transmittance vs incident energy curves for Ir1-Ir5 are presented in Figure 4. For comparison purposes, solutions with the same linear transmission of 80% at 532 nm in a 2 mm cuvette were employed.



Figure 4. Nonlinear transmission plots of **Ir1–Ir5** in acetonitrile solutions with a linear transmittance of 80% in a 2 mm cuvette at 532 nm. The laser pulse duration was 4.1 ns.

Except for Ir3, the transmission of all the other complexes decreased with an increase in incident energy, suggesting that RSA took place. The strength of the RSA follows the trend Ir2 \approx Ir4 > Ir1 > Ir5 > Ir3, which is essentially in accordance with their corresponding Δ OD values at 532 nm (i.e., 0.012 for Ir1, 0.024 for Ir2, -0.028 for Ir3, 0.026 for Ir4, and 0.008 for Ir5). The stronger RSAs of Ir2 and Ir4 are obviously related to their stronger excited-state absorption at 532 nm with respect to those of the other complexes, whereas the weaker excited-state absorption of Ir3 in comparison to its ground-state absorption (as reflected by the negative ΔOD value) at 532 nm prevents the RSA in Ir3. However, in view of the much stronger TA signals at >585 nm for Ir1-Ir3 and Ir5, the RSA of these complexes could be much stronger than that of Ir4 at wavelengths longer than 585 nm. Nonetheless, Ir4 holds the advantage of a broader excited-state absorption than the other complexes, making it a potential broadband reverse saturable absorber in the visible to the NIR spectral region.

CONCLUSIONS

Five bis-terdentate Ir(III) complexes bearing a *trans*-biscyclometalating ligand and a 4'-R-tpy ligand, i.e. (C^N^C) Ir- $(R-tpy)^+$, were synthesized to explore the effect of C^N^C ligand π conjugation and the 4'-R substituent at the tpy ligand

on the photophysics and excited-state absorption of these complexes to assess the feasibility of these types of complexes as reverse saturable absorbers. In comparison to the $Ir(tpy)_2^{3+}$ complexes, the stronger σ -donating ability of the C^N^C ligand caused a distinct red shift of the ${}^{1}CT/{}^{1}\pi,\pi^{*}$ bands to 400-600 nm. Although structural variations in either the cyclometalating or the tpy ligand exerted a minor effect on the energies of the ${}^{1}CT/{}^{1}\pi,\pi^{*}$ bands, these changes altered the molar extinction coefficients of these absorption bands drastically, especially that with the strongly electron donating 4'-(4-dimethylaminophenyl) substituent (Ir3). All complexes displayed deep red room-temperature phosphorescence (661-693 nm) in a variety of organic solvents (CH₂Cl₂, CH₃CN, THF, and toluene (with 5% CH₂Cl₂)) at room temperature. The emission spectrum of Ir1 with a more π expansive C^N^C ligand was blue-shifted in all solvents in comparison to those of the other complexes bearing the 2,6-diphenylpyridine ligand, concomitant with the highest emission quantum yield. While introducing an electron-withdrawing ester substituent on the 4'-phenyl group of the tpy ligand caused a red shift of the emission spectrum for Ir5 with a reduced emission quantum yield in comparison to those of Ir2, electron-donating 4'-(4dimethylaminophenyl) and 4'-dimethylamino substituents on the tpy ligand had a minor effect on the emission energies of Ir3 and Ir4 with respect to that of Ir2. However, Ir3 possessed a higher emission quantum yield with respect to that of Ir2, whereas the emission quantum yield was lower in Ir4 in comparison to that of Ir2. All complexes exhibited broad and strong nanosecond TA bands in the visible to the NIR region originating from their ${}^{3}\pi_{,}\pi^{*}/{}^{3}CT$ T₁ states. Structural alteration affected the spectral features and the TA signal intensities pronouncedly, with Ir2 giving the strongest TA signals peaking at 612 nm, Ir3 showing the highest TA signals in the NIR, and Ir4 having the broadest TA bands at 456-800 nm. These complexes exhibited varying degrees of RSA at 532

nm, i.e. $Ir2 \approx Ir4 > Ir1 > Ir5 > Ir3$, which primarily corresponded to their ΔOD values at 532 nm. In view of the strongest RSAs of Ir2 and Ir4 at 532 nm and their strong broadband TA signals, these two complexes hold the potential as broadband reverse saturable absorbers for optical limiting of nanosecond laser pulses.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c00961.

Normalized UV-vis absorption and emission spectra of Ir1-Ir5 in different solvents, the time-resolved TA spectra of Ir1-Ir5 in CH₃CN, comparison of the experimental and theoretical UV-vis absorption spectra of Ir1-Ir5 in CH₂Cl₂, Cartesian coordinates of the optimized structures for Ir1-Ir5 in CH₂Cl₂, NTOs for major transitions contributing to the absorption bands at <400 nm, the emission parameters of Ir1-Ir5 in different solvents, and the full author list for refs 56 and 74. (PDF)

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Notes

The authors declare no competing financial interest.

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