

Article pubs.acs.org/IC

Multifunctional Cationic Iridium(III) Complexes Bearing 2-Aryloxazolo[4,5-f][1,10]phenanthroline (N^N) Ligand: Synthesis, Crystal Structure, Photophysics, Mechanochromic/Vapochromic Effects, and Reverse Saturable Absorption

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Supporting Information

ABSTRACT: A series of 2-aryloxazolo[4,5-f][1,10]phenanthroline ligands (N^N ligands) and their cationic iridium-(III) complexes $(1-11, aryl = 4-NO_2$ -phenyl (1), 4-Br-phenyl (2),Ph (3), 4-NPh₂-phenyl (4), 4-NH₂-phenyl (5), pyridin-4-yl (6), naphthalen-1-yl (7), naphthalen-2-yl (8), phenanthren-9-yl (9), anthracen-9-yl (10), and pyren-1-yl (11)) were synthesized and characterized. By introducing different electron-donating or electron-withdrawing substituents at the 4-position of the 2phenyl ring (1-5), or different aromatic substituents with varied degrees of π -conjugation (6–11) on oxazolo[4,5-f][1,10]phenanthroline ligand, we aim to understand the effects of terminal substituents at the N^N ligands on the photophysics of cationic Ir(III) complexes using both spectroscopic methods and quantum chemistry calculations. Complexes with the 4-R-phenyl



substituents adopted an almost coplanar structure with the oxazolo[4,5-f][1,10]phenanthroline motif, while the polycyclic aryl substituents (except for naphthalen-2-yl) were twisted away from the 0xazolo[4,5-f][1,10] phenanthroline motif. All complexes possessed strong absorption bands below 350 nm that emanated from the ligand-localized ${}^{1}\pi,\pi^{*}/{}^{1}$ LCT (intraligand charge transfer) transitions, mixed with ¹LLCT (ligand-to-ligand charge transfer)/¹MLCT (metal-to-ligand charge transfer) transitions. At the range of 350-570 nm, all complexes exhibited moderately strong ¹ILCT/¹LLCT/¹MLCT transitions at 350-450 nm, and broad but very weak ³LLCT/³MLCT absorption at 450–570 nm. Most of the complexes demonstrated moderate to strong room temperature phosphorescence both in solution and in the solid state. Among them, complex 7 also manifested a drastic mechanochromic and vapochromic luminescence effect. Except for complexes 1 and 4 that contain NO₂ or NPh₂ substituent at the phenyl ring, respectively, all other complexes exhibited moderate to strong triplet excited-state absorption in the spectral region of 440-750 nm. Moderate to very strong reverse saturable absorption (RSA) of these complexes appeared at 532 nm for 4.1 ns laser pulses. The RSA strength followed the trend of $7 > 11 > 9 > 3 > 2 \approx 4 > 5 \approx 10 \approx 6 \approx 8 > 1$. The photophysical studies revealed that the different 2-aryl substituents on the oxazole ring impacted the singlet and triplet excited-state characteristics dramatically, which in turn notably influenced the RSA of these complexes.

INTRODUCTION

Luminescent octahedral d⁶ Ir(III) complexes have been extensively explored due to the efficient intersystem crossing induced by the heavy Ir(III) ion, which results in strong room temperature phosphorescence in solutions. In addition, the Ir(III) complexes possess broad charge transfer absorption in the visible spectral region, intriguing electrochemical properties, and high chemical, thermal, and optical stabilities. These unique properties make Ir(III) complexes promising candidates for a variety of optoelectronic and biomedical applications, such as variety of optoelectronic and biomedical applications, such as organic light-emitting devices (OLEDs),¹⁻³ light-emitting electrochemical cells (LEECs),⁴⁻⁶ photocatalysis,⁷ upconversion,⁸ nonlinear optics,⁹⁻²⁵ biosensing and bioimaging,²⁶⁻³¹ and photodynamic therapy.^{25,32-36} To meet the specific requirements for each application, structural modifications are needed for fine-tuning of the chemical, electronic, or optical properties of the Ir(III) complexes.

Cationic heteroleptic Ir(III) complexes are interesting candidates for the aforementioned applications because the ground-state and excited-state properties of these complexes can be readily tuned by substituents on the cyclometalating (C^N) ligands or the diimine (N^N) ligand,^{9,10,21,37-40} or by variation of the π -conjugation of the C^N or N^N ligands.^{8,11,12,15-25,41} One class of frequently used π -conjugated N^N ligand is the 2-arylimidazole [4,5-f] [1,10] phenanthroline.

Received: June 12, 2017

Scheme 1. Synthetic Routes of Complexes 1-11



Due to the ease of preparation, and facile tuning of the photophysical and electronic properties via substitution at the 2-aryl ring or the imidazole ring, or via variations of pH value or cation/anion, this type of ligand has been widely used in developing Ir(III) complexes for biomolecular targeting or labeling, chemosensing, photocatalysis, and photosensitization applications.^{8,42–50} Although the photophysical properties of these complexes are very promising, the presence of acidic N– H hydrogen on the imidazole ring makes the formed complexes

sensitive to the polarity and nature of the solvent, the pH values of the solution, and the counterion in the case of cationic Ir(III) complexes. While such sensitivity to environmental changes can be beneficial for sensing applications, it would cause potential stability issues for optoelectronic device fabrication and application. In addition, the N–H hydrogen would expel the 2-H on the 2-aryl ring, making the 2-aryl substituent noncoplanar with the imidazole[4,5-f][1,10]phenanthroline motif and thus reducing the impact of the substituent at the aryl ring on the photophysics and electrochemical properties of the Ir(III) complexes. It has been reported that the dihedral angle between the 2-(4-trifluoromethyl)phenyl ring and the imidazole[4,5-f][1,10]phenanthroline motif was $\sim 11^{\circ}$.⁴²

To overcome these drawbacks, we focus our investigations on replacing the imidazole ring by its isoelectronic oxazole ring, which substitutes the N-H unit by one O atom on the ring and consequently makes the 2-aryl substituent more coplanar with the oxazolo [4,5-f] [1,10] phenanthroline. Unfortunately, due to the challenge in synthesizing 2-aryloxazolo[4,5-f][1,10]phenanthroline, the studies on 2-aryloxazolo[4,5-f][1,10]phenanthrolines and their corresponding transition-metal complexes are quite limited. $^{51-61}$ To date, the only method reported for the synthesis of 2-aryloxazolo[4,5-f][1,10]phenanthrolines was the cyclization reaction between 1,10phenanthroline-5,6-dione and arylaldehyde in the presence of NH_4OAc in refluxing acetic acid.^{62,63} This method is the same method used for the synthesis of 2-arylimidazole [4,5-f] [1,10]phenanthrolines, during which 2-aryloxazolo [4,5-f] [1,10]phenanthrolines were formed as the byproducts in some cases, and thus the yield was very low (ca. 10%).^{62,63} In addition, only limited types of 2-aryl substituents were introduced to the oxazolo [4,5-f][1,10] phenanthroline motif as reported in the literature.⁵¹⁻⁶³ In view of the potentially better coplanarity between the 2-aryl substituent and the oxazolo[4,5-f][1,10]phenanthroline motif, we anticipate a more pronounced impact of the substituents on the 2-aryl motif. Therefore, the photophysical properties of the resulting Ir(III) complexes could be rationally tuned via π -conjugation or different substituents on the 2-aryl group. Moreover, better coplanarity could potentially improve the emission efficiency and may cause red-shifts of the charge transfer absorption band(s) in the UV-vis absorption spectra of the Ir(III) complexes, which could benefit the applications of OLEDs, photosensitization, or broadband reverse saturable absorption (RSA, a nonlinear optical phenomenon responsible for increasing the absorptivity of a material with increased incident fluence, which has potential applications in optical switching,⁶⁴ laser mode locking,⁶⁵ optical pulse shaping,⁶⁶ spatial light modulation,⁶⁷ laser beam compression and limiting,^{68,69} etc.)

In this work, we developed a new synthetic route that can be used for synthesis of oxazolo [4,5-f] [1,10] phenanthroline with different aryl substituents at the 2-position of the oxazole ring. Eleven 2-aryloxazolo[4,5-f][1,10]phenanthrolines, i.e., 2-(4nitrophenyl) (L1), 2-(4-bromophenyl) (L2), 2-phenyl (L3), 2-(4-diphenylaminophenyl) (L4), 2-(4-aminophenyl) (L5), 2-(pyridin-4-yl) (L6), 2-(naphthalen-1-yl) (L7), 2-(naphthalen-2yl) (L8), 2-(phenanthren-9-yl) (L9), 2-(anthracen-9-yl) (L10), and 2-(pyren-4-yl) (L11), were synthesized and used as the N^N ligand for preparation of biscyclometalated monocationic Ir(III) complexes 1-11 (structures of the complexes are shown in Scheme 1). By introducing different electron-donating or electron-withdrawing substituents at the 4-position of the 2phenyl ring (1-5), and different aromatic substituents with varied degrees of π -conjugation (6–11) on oxazolo[4,5f [1,10] phenanthroline, we aim to understand the effects of terminal substituents at the N^N ligands on the photophysics of cationic Ir(III) complexes. We also intend to demonstrate the feasibility of these Ir(III) complexes as reverse saturable absorbers, which require weak ground-state absorption but strong excited-state absorption in the visible to the near-IR region, high quantum yield of the triplet excited-state formation, and long-lived triplet excited state. In addition to

the photophysical and RSA studies, we found that complex 7 exhibited interesting mechanochromic and vapochromic luminescence effects, which showed the potential of these complexes as smart pressure or organic vapor sensing materials.

EXPERIMENTAL SECTION

Synthesis and Characterizations. All reagents including pbromonitrobenzene, p-dibromobenzene, bromobenzene, 4-bromopyridine, 1-bromonaphthalene, 2-bromonaphthalene, 4-diphenylaminobenzaldehyde (DABA) were purchased from Sigma-Aldrich or Alfa Aesar Co. Ltd. Tetrahydrofuran (THF) was distilled under N2 over sodium benzophenoneketyl. All other reagents were used as received. Silica gels (230-400 mesh) used for chromatography were purchased from Sorbent Technology. The intermediate compounds and ligands were characterized by ¹H NMR spectroscopy, while the Ir(III) complexes were characterized by ¹H NMR, HRMS, and elemental analysis. ¹H NMR spectra were measured on a Bruker 400 MHz spectrometer using CDCl₃ as the solvent, with tetramethylsilane (TMS) as internal standard. ESI-HRMS analyses were performed on a Waters Synapt G2-Si mass spectrometer. Elemental analyses were carried out by NuMega Resonance Laboratories, Inc., in San Diego, California. Powder X-ray diffraction (XRD) patterns of the samples were collected on a Phillips X'Pert MPD powder X-ray diffractometer.

Synthetic routes for the synthesis of complexes 1-11 are provided in Scheme 1. Compound 1,10-phenanthroline-5,6-dione (PhenDO) was synthesized according to the literature procedure.⁷⁰ The synthetic scheme, experimental details, and ¹H NMR data for the other precursors, i.e., 9-bromomethylphenanthrene, 9-bromomethylanthracene, and 1-bromomethylpyrene, are given in Scheme S1. The Ir(III) dimer [Ir(ppy)₂]₂Cl₂ (ppy refers to 2-phenylpyridine (C^N) ligand) was synthesized following the Nonoyama method.⁷¹ The synthetic details and characterization data for 1,10-phenanthroline-5,6-dione-6oxime (PhenNO), ligands L1–L4 and L6–L11, and complexes 1–11 are provided below.

PhenNO. Compounds 1,10-phenanthroline-5,6-dione (PhenDO) (1.89 g, 9.0 mmol), NH₂OH·HCl (657 mg, 9.45 mmol), and 45 mL of EtOH were added to a flask. The mixture was heated to reflux for 3 h. After cooling to rt, the solid was collected by filtration. The crude product was purified by recrystallization in ethanol to obtain yellow powder (1.46 g, yield: 73%). ¹H NMR (400 MHz, *d*₆-DMSO): δ 9.51 (d, *J* = 8.0 Hz, 1H), 9.12 (dd, *J*₁ = 4.8 Hz, *J*₂ = 1.6 Hz, 1H), 8.92 (dd, *J*₁ = 4.8 Hz, *J*₂ = 1.6 Hz, 1H), 7.92–7.88 (m, 2H).

General Procedure for the Synthesis of L1–L3 and L6–L11. To a Schlenk tube were added PhenNO (135 mg, 0.6 mmol), ArCH₂Br (1.0 mmol), triethylamine (TEA) (182 mg, 1.8 mmol), dry THF (6 mL), and dry DMF (3 mL), and the mixture was degassed with N₂ for 30 min. Then the reaction mixture was stirred at 50 °C for 24 h. The mixture was poured into water and extracted with ether. The organic layer was dried over Na₂SO₄. After removal of the solvent, the residue was purified by column chromatography (silica gel, CH₂Cl₂/MeOH = 100/1, v/v) twice to obtain the crude product. The crude product.

Ligand L1 (crude): light yellow solid (82 mg, 40% yield). Because of the poor solubility of the crude product, the light yellow solid obtained was washed with CH_2Cl_2 and ether and used for the next step reaction without further purification

Ligand L2: white solid (79 mg, 35% yield). ¹H NMR (400 MHz, CDCl₃): δ 9.23–9.21 (m, 2H), 8.92 (d, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 8.66 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 8.24–8.21 (m, 2H), 7.78–7.70 (m, 4H).

Ligand L3: white solid (70 mg, 39% yield). ¹H NMR (400 MHz, CDCl₃): δ 9.22–9.20 (m, 2H), 8.92 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 8.66 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 8.36–8.33 (m, 2H), 7.76–7.72 (m, 2H), 7.58–7.55 (m, 3H).

Ligand **L6**: white solid (57 mg, 32% yield). ¹H NMR (400 MHz, CDCl₃): δ 9.31–9.28 (m, 2H), 8.96 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H),

8.91 (dd, $J_1 = 4.4$ Hz, $J_2 = 1.6$ Hz, 2H), 8.74 (dd, $J_1 = 8.0$ Hz, $J_2 = 1.6$ Hz, 1H), 8.23 (dd, $J_1 = 4.4$ Hz, $J_2 = 1.6$ Hz, 2H), 7.85–7.81 (m, 2H).

Ligand **L7**: white solid (68 mg, 33% yield). ¹H NMR (400 MHz, CDCl₃): δ 9.65 (d, J = 8.4 Hz, 1H), 9.31–9.29 (m, 2H), 9.11 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 8.78 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 8.60 (dd, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 8.12 (d, J = 8.4 Hz, 1H), 8.02 (d, J = 8.4 Hz, 1H), 7.87–7.79 (m, 3H), 7.73–7.66 (m, 2H).

Ligand L8: white solid (73 mg, 35% yield). ¹H NMR (400 MHz, CDCl₃): δ 9.29–9.27 (m, 2H), 9.03 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 8.92 (s, 1H), 8.80 (dd, J_1 = 8.0 Hz, J_2 = 1.6 Hz, 1H), 8.47 (dd, J_1 = 8.8 Hz, J_2 = 2.0 Hz, 1H), 8.10–8.07 (m, 2H), 7.98–7.96 (m, 1H), 7.85–7.81 (m, 2H), 7.66–7.63 (m, 2H).

Ligand L9: white solid (62 mg, 26% isolated yield). ¹H NMR (400 MHz, CDCl₃): δ 9.65 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 9.26–9.23 (m, 2H), 9.04 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 8.81–8.72 (m, 4H), 8.07 (d, J = 8.4 Hz, 1H), 7.82–7.68 (m, 6H).

Ligand **L10**: light yellow solid (31 mg, 13% yield). ¹H NMR (400 MHz, CDCl₃): δ 9.30–9.26 (m, 2H), 9.03 (dd, 1H), 8.71 (s, 1H), 8.66 (dd, 1H), 8.15–8.10 (m, 4H), 7.82–7.73 (m, 2H), 7.55–7.51 (m, 4H).

Ligand L11: greenish-yellow solid (56 mg, 22% yield). ¹H NMR (400 MHz, CDCl_3): δ 9.94 (d, J = 9.6 Hz, 1H), 9.28–9.25 (m, 2H), 9.12 (d, J = 9.6 Hz, 1H), 9.01 (d, J = 8.4 Hz, 1H), 8.82–8.79 (m, 1H), 8.36 (d, J = 8.4 Hz, 1H), 8.35–8.28 (m, 3H), 8.21–8.08 (m, 3H), 7.85–7.81 (m, 2H).

Synthesis of Ligand L4. Compounds 4-diphenylaminobenzaldehyde (164 mg, 0.6 mmol), phenanthrolinedione (126 mg, 0.6 mmol), ammonium acetate (462 mg, 6 mmol), and glacial acetic acid (15 mL) were added to a Schlenk tube. The mixture was degassed with nitrogen for 30 min and then reacted at 110 °C overnight. After cooling to rt, the mixture was poured into water and neutralized with NH₃·H₂O. The mixture was extracted with CH₂Cl₂, and the organic layer was dried over MgSO₄. The crude product was purified by column chromatography (silica gel, CH₂Cl₂/MeOH = 50:1, v/v) twice to afford orange solid 27 mg, yield: 10%. ¹H NMR (400 MHz, CDCl₃): δ 9.28–9.21 (m, 2H), 8.93–8.90 (d, *J* = 8.4 Hz, 1H), 8.63 (d, *J* = 8.4 Hz, 1H), 8.17–8.13 (m, 2H), 7.76–7.70 (m, 2H), 7.34–7.30 (m, 4H), 7.20–7.11 (m, 8H).

General Procedure for the Synthesis of Complexes 1–4 and 6–11. To a stirred solution of L1–L11 (except for L5) (0.1 mmol) and $[Ir(ppy)_2]_2Cl_2$ (54 mg, 0.05 mmol) in degassed CH_2Cl_2 (30 mL) and methanol (15 mL) was added AgSO₃CF₃ (26 mg, 0.1 mmol). The mixture was refluxed overnight under nitrogen. After cooling to rt, NH₄PF₆ (163 mg, 1.0 mmol) was added. The mixture was stirred for another 2 h. After removal of the solvent, the residue was purified by column chromatography (silica gel, CH₂Cl₂/MeOH = 100:1–50:1, v/ v) twice to afford the pure product.

Complex 1: orange solid (34 mg, 35% yield). ¹H NMR (400 MHz, CDCl₃): δ 9.18 (dd, J_1 = 8.3 Hz, J_2 = 1.4 Hz, 1H), 9.12 (dd, J_1 = 8.3 Hz, J_2 = 1.4 Hz, 1H), 8.65–8.55 (m, 2H), 8.48–8.30 (m, 4H), 8.01–7.91 (m, 4H), 7.81–7.69 (m, 4H), 7.52 (d, J = 5.2 Hz, 1H), 7.43 (d, J = 5.2 Hz, 1H), 7.17–7.08 (m, 2H), 7.08–6.98 (m, 3H), 6.96–6.88 (m, 1H), 6.43 (dd, J_1 = 8.2 Hz, J_2 = 1.6 Hz, 2H). ESI-HRMS (m/z): calcd for [C₄₁H₂₆IrN₆O₃]⁺, 843.1698; found, 843.1699. Elemental analysis calcd (%) for C₄₁H₂₆IrN₆O₃PF₆: C, 49.85; H, 2.65; N, 8.51. Found: C, 49.88; H, 3.00; N, 8.56.

Complex **2**: orange solid (58 mg, 57% yield). ¹H NMR (400 MHz, CDCl₃): δ 9.17 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 9.06 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 8.36–8.28 (m, 4H), 8.01–7.90 (m, 4H), 7.78–7.71 (m, 6H), 7.51 (d, J = 5.6 Hz, 1H), 7.40 (d, J = 5.6 Hz, 1H), 7.12 (t, J = 7.6 Hz, 2H), 7.04–6.98 (m, 3H), 6.89 (t, J = 7.6 Hz, 1H), 6.43 (d, J = 8.0 Hz, 2H). ESI-HRMS (m/z): calcd for [C₄₁H₂₆BrIrN₅O]⁺, 876.0936; found, 876.0939. Elemental analysis calcd (%) for C₄₁H₂₆BrIrN₅OPF₆: C, 48.20; H, 2.56; N, 6.85. Found: C, 48.32; H, 2.43; N, 6.62.

Complex 3: orange solid (64 mg, 68% yield). ¹H NMR (400 MHz, CDCl₃): δ 9.19 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 9.05 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 8.43–8.41 (m, 2H), 8.36–8.32 (m, 2H), 8.02–7.90 (m, 4H), 7.76–7.73 (m, 4H), 7.64–7.62 (m, 3H), 7.52 (d, J = 5.2 Hz, 1H), 7.40 (d, J = 5.2 Hz, 1H), 7.12 (t, J = 7.6 Hz, 2H), 7.02–7.00

(m, 3H), 6.90 (t, J = 7.6 Hz, 1H), 6.43 (d, J = 8.0 Hz, 2H). ESI-HRMS (m/z): calcd for $[C_{41}H_{27}IrN_5O]^+$, 798.1847; found, 798.1847. Elemental analysis calcd (%) for $C_{41}H_{27}IrN_5OPF_6 \cdot 0.2CH_2Cl_2$: C, 51.55; H, 2.88; N, 7.30. Found: C, 51.25; H, 2.54; N, 7.00.

Complex **4**: orange-red solid (57 mg, 51% yield). ¹H NMR (400 MHz, CDCl₃): δ 9.16 (d, J = 8.0 Hz, 1H), 8.99 (d, J = 8.0 Hz, 1H), 8.31 (dd, J_1 = 13.6 Hz, J_2 = 4.0 Hz, 2H), 8.19 (d, J = 8.8 Hz, 2H), 7.98–7.87 (m, 4H), 7.75–7.71 (m, 4H), 7.51 (d, J = 5.6 Hz, 1H), 7.38 (t, J = 7.6 Hz, 5H), 7.25–6.98 (m, 13H), 6.90 (t, J = 6.0 Hz, 1H), 6.43 (d, J = 7.6 Hz, 2H). ESI-HRMS (m/z): calcd for [C₅₃H₃₆IrN₆O]⁺, 965.2584; found, 965.2579. Elemental analysis calcd (%) for C₅₃H₃₆IrN₆OPF₆·2.5H₂O·0.5C₆H₁₄: C, 56.13; H, 4.04; N, 7.01. Found: C, 56.25; H, 4.41; N, 7.14.

Complex **6**: orange solid (56 mg, 59% yield). ¹H NMR (400 MHz, CDCl₃): δ 9.20 (d, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 9.09 (d, J = 8.0 Hz, 1H), 8.93 (d, J = 6.4 Hz, 2H), 8.38 (t, J = 6.0 Hz, 2H), 8.26 (d, J = 6.0 Hz, 2H), 8.02–7.92 (m, 4H), 7.76–7.71 (m, 4H), 7.52 (d, J = 6.0 Hz, 1H), 7.41 (d, J = 6.0 Hz, 1H), 7.12 (t, J = 7.2 Hz, 2H), 7.04–7.00 (m, 3H), 6.91 (t, J = 7.2 Hz, 1H), 6.42 (dd, J_1 = 7.6 Hz, J_2 = 3.6 Hz, 2H). ESI-HRMS (*m*/*z*): calcd for [C₄₀H₂₆IrN₆O]⁺, 799.1799; found, 799.1815. Elemental analysis calcd (%) for C₄₀H₂₆IrN₆OPF₆: C, 50.90; H, 2.78; N, 8.90. Found: C, 50.73; H, 2.90; N, 8.79.

Complex **7**: light yellow solid (52 mg, 52% yield). ¹H NMR (400 MHz, CDCl₃): δ 9.56 (d, J = 8.4 Hz, 1H), 9.32 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 9.11 (dd, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 8.65 (dd, J_1 = 7.2 Hz, J_2 = 1.2 Hz, 1H), 8.39–8.35 (m, 2H), 8.15 (d, J = 8.0 Hz, 1H), 8.04–7.93 (m, 5H), 7.82–7.65 (m, 7H), 7.54 (d, J = 4.8 Hz, 1H), 7.43 (d, J = 4.8 Hz, 1H), 7.13 (t, J = 7.6 Hz, 2H), 7.05–7.70 (m, 3H), 6.91 (td, J_1 = 7.6 Hz, J_2 = 1.2 Hz, 1H), 6.45 (d, J = 7.6 Hz, 2H). ESI-HRMS (*m*/*z*): calcd for [C₄₅H₂₉IrN₅O]⁺, 848.2004; found, 848.2000. Elemental analysis calcd (%) for C₄₅H₂₉IrN₅OPF₆: C, 54.43; H, 2.94; N, 7.05. Found: C, 54.04; H, 2.81; N, 7.06.

Complex **8**: light yellow solid (57 mg, 57% yield). ¹H NMR (400 MHz, CDCl₃): δ 9.17 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 9.09 (dd, J_1 = 8.4 Hz, J_2 = 1.2 Hz, 1H), 8.93 (s, 1H), 8.40 (dd, J_1 = 8.4 Hz, J_2 = 1.6 Hz, 1H), 8.33–8.29 (m, 2H), 8.07–7.96 (m, 3H), 7.92–7.86 (m, 4H), 7.72–7.67 (m, 4H), 7.61–7.57 (m, 2H), 7.50–7.49 (m, 1H), 7.37–7.35 (m, 1H), 7.10–7.06 (m, 2H), 7.00–6.94 (m, 3H), 6.86 (td, J_1 = 8.0 Hz, J_2 = 1.2 Hz, 1H), 6.39 (d, J = 7.6 Hz, 2H). ESI-HRMS (m/z): calcd for [$C_{45}H_{29}IrN_5O$]⁺, 848.2004; found, 848.1999. Elemental analysis calcd (%) for $C_{45}H_{29}IrN_5OPF_6$ ·0.5H₂O: C, 53.94; H, 3.02; N, 6.99. Found: C, 53.79; H, 3.08; N, 7.04.

Complex **9**: light yellow solid (51 mg, 49% yield). ¹H NMR (400 MHz, CDCl₃): δ 9.63 (d, *J* = 8.0 Hz, 1H), 9.33 (d, *J* = 8.4 Hz, 1H), 9.21 (d, *J* = 8.4 Hz, 1H), 8.98 (s, 1H), 8.85 (d, *J* = 8.0 Hz, 1H), 8.77 (d, *J* = 8.0 Hz, 1H), 8.38 (t, *J* = 6.0 Hz, 2H), 8.19 (d, *J* = 8.0 Hz, 1H), 8.07–8.04 (m, 1H), 7.98–7.93 (m, 3H), 7.86–7.70 (m, 8H), 7.57 (d, *J* = 5.6 Hz, 1H), 7.44 (d, *J* = 5.6 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 2H), 7.06–7.00 (m, 3H), 6.92 (t, *J* = 6.8 Hz, 1H), 6.45 (d, *J* = 7.2 Hz, 2H). ESI-HRMS (*m*/*z*): calcd for [C₄₉H₃₁IrN₅O]⁺, 898.2161; found, 898.2180. Elemental analysis calcd (%) for C₄₉H₃₁IrN₅OPF₆· 1.8H₂O: C, 54.73; H, 3.24; N, 6.51. Found: C, 54.60; H, 3.10; N, 6.90.

Complex **10**: light yellow solid (44 mg, 42% yield). ¹H NMR (400 MHz, *d*₆-DMSO): δ 9.35 (d, *J* = 8.8 Hz, 1H), 9.19 (d, *J* = 8.0 Hz, 1H), 9.09 (s, 1H), 8.36-8.31 (m, 5H), 8.25-8.16 (m, 2H), 8.10 (d, *J* = 8.0 Hz, 2H), 8.02-7.92 (m, 5H), 7.70-7.59 (m, 6H), 7.12-6.98 (m, 6H), 6.34 (d, *J* = 5.6 Hz, 2H). ESI-HRMS (*m*/*z*): calcd for [C₄₉H₃₁IrN₅O]⁺, 898.2161; found, 898.2182. Elemental analysis calcd (%) for C₄₉H₃₁IrN₅OPF₆·0.45CH₂Cl₂·1.5H₂O: C, 53.59; H, 3.17; N, 6.32. Found: C, 53.92; H, 3.57; N, 6.65.

Complex 11: yellow solid (49 mg, 45% yield). ¹H NMR (400 MHz, CDCl₃): δ 9.87 (d, *J* = 9.2 Hz, 1H), 9.35 (d, *J* = 8.4 Hz, 1H), 9.14 (d, *J* = 8.0 Hz, 1H), 9.03 (d, *J* = 8.4 Hz, 1H), 8.43−7.95 (m, 13H), 7.78−7.73 (m, 4H), 7.57 (d, *J* = 5.6 Hz, 1H), 7.46 (d, *J* = 5.6 Hz, 1H), 7.14 (t, *J* = 7.6 Hz, 2H), 7.06−7.01 (m, 3H), 6.94 (t, *J* = 7.6 Hz, 1H), 6.46 (d, *J* = 7.6 Hz, 2H). ESI-HRMS (*m*/*z*): calcd for [C₅₁H₃₁IrN₅O]⁺, 922.2161; found, 922.2183. Elemental analysis calcd (%) for C₅₁H₃₁IrN₅OPF₆·0.2CH₂Cl₂: C, 56.73; H, 2.92; N, 6.46. Found: C, 56.64; H, 2.85; N, 6.31.

Complex 5. To a Schlenk tube were added complex 1 (39 mg, 0.039 mmol), Pd/C (10%, 10 mg), and absolute ethanol (6 mL)under N₂ atmosphere. Then hydrazine monohydrate (1 mL) was added dropwise and the mixture was refluxed overnight under N₂ atmosphere. After cooling to rt, the solvent was removed and the residue was purified by column chromatography (Al₂O₃, EtOAc) to afford pale yellow solid (17 mg, yield: 45%). ¹H NMR (400 MHz, $CDCl_3$: δ 9.14 (dd, $J_1 = 8.3$ Hz, $J_2 = 1.5$ Hz, 1H), 8.97 (dd, $J_1 = 8.4$ Hz, $J_2 = 1.4$ Hz, 1H), 8.30 (ddd, $J_1 = 15.1$ Hz, $J_2 = 5.0$ Hz, $J_3 = 1.4$ Hz, 2H), 8.17 (d, J = 8.7 Hz, 2H), 7.95–7.87 (m, 4H), 7.74–7.71 (m, 4H), 7.49 (d, J = 4.8 Hz, 1H), 7.38 (d, J = 6.0 Hz, 1H), 7.11 (t, J = 7.6 Hz, 2H), 7.00-6.91 (m, 3H), 6.89 (t, J = 6.6 Hz, 1H), 6.81 (d, J = 8.8 Hz, 2H), 6.41 (d, J = 6.7 Hz, 2H), 4.20 (s, 2H). ESI-HRMS (m/z): calcd for $[C_{41}H_{28}IrN_6O]^+$, 813.1956; found, 813.1954. Elemental analysis calcd (%) for C₄₁H₂₈IrN₆OPF₆·0.5CH₂Cl₂: C, 49.83; H, 2.92; N, 8.40. Found: C, 49.92; H, 2.73; N, 8.46.

X-ray Crystallographic Analysis. Single crystals of complexes **3** and 7 were obtained by slow diffusion of diethyl ether into their dilute dichloromethane solutions. Single crystal X-ray diffraction data of **3** (CCDC 1457721) and 7 (CCDC 1509624) were collected on a Bruker Apex Duo diffractometer with an Apex 2 CCD area detector at T = 296 and 101 K, respectively. Mo radiation was used. All structures were processed with an Apex 2 v2010.9-1 software package (SAINT v.7.68A, XSHELL v.6.3.1).^{72–74} A direct method was used to solve the structure after multiscan absorption corrections. Details of data collection and refinement are given in Table S1.

Photophysical Measurements. All the solvents used for photophysical studies were spectrophotometric grade and purchased from Alfa Aesar Co. Ltd. A Cary 50 spectrophotometer and an HORIBA Fluoro-Max 4 fluorescence spectrophotometer were used to measure the UV–vis absorption and emission spectra, respectively. The emission quantum yields were determined by the relative actinometry method⁷⁵ in degassed solutions, in which a degassed CH₃CN solution of $[Ru(bpy)_3]Cl_2 (\Phi_{em} = 0.097, \lambda_{ex} = 436 \text{ nm})^{76}$ was used as the reference for 1–11. The nanosecond transient difference absorption (TA) spectra and decays were measured in degassed CH₃CN solutions on an Edinburgh LP920 laser flash photolysis spectrometer. The third harmonic output (355 nm) of a Nd:YAG laser (Quantel Brilliant, pulse width = 4.1 ns, repetition rate = 1 Hz) was used as the excitation source. Each sample was purged with argon for 45 min prior to measurement.

Singlet depletion method⁷⁷ was used to determine the triplet excited-state molar extinction coefficients (ε_{T1-Tn}) at the TA band maximum. After the ε_{T1-Tn} value was obtained, the triplet excited-state quantum yield was calculated by the relative actinometry,⁷⁸ in which SiNc in benzene was used as the reference ($\varepsilon_{590} = 70\ 000\ M^{-1}\ cm^{-1}$, $\Phi_T = 0.20$).⁷⁹

Computational Methods. The ground-state geometry optimization and absorption spectra calculations were performed using the Gaussian09 software package.⁸⁰ The ideal octahedral geometries of complexes 1–11 were optimized in their singlet and triplet spin configurations by density functional theory (DFT) using the hybrid Perdew, Burke, and Ernzerhof functional (PBE1PBE)^{81–83} and the LANL2DZ basis set^{84–86} assigned for Ir and Br atoms and 6-31G* basis set^{87–91} for all the remaining atoms. The absorption spectra were calculated using linear-response time dependent DFT (TDDFT)^{92,93} by iteratively solving the eigenvalue equation using the Davidson algorithm.^{94–97} For excited-state calculations, the density functional and basis sets were chosen being the same as those for the groundstate calculations. A total of 80 excited states were calculated with their corresponding transition energies and oscillator strengths. The profile of absorption spectra was plotted based on inhomogeneous Gaussian line broadening of 0.1 eV to fit the profile of the experimental spectra at room temperature.

The phosphorescence energies were calculated using the Δ SCF approach,⁹⁸ where the lowest triplet ground-state geometry was optimized using an unrestricted DFT method, and then the lowest triplet excitation energy was calculated through a combined scalar relativistic ZORA⁹⁹ and TDDFT approach using NWChem software.¹⁰⁰

Both DFT and TDDFT calculations were performed in solvent utilizing the conductor-like polarizable continuum model $(CPCM)^{101-103}$ implemented in Gaussian09. Phosphorescence calculations were performed using the COSMO continuum solvation model^{104,105} applying two-time-scale model of solvent polarization,¹⁰⁶ which accounts for the nonequilibrium effect of slow component of reaction field of solvent, as implemented in the NWChem software package. Acetonitrile (CH₃CN, $\varepsilon_r = 37.5$) was chosen as the solvent medium for consistency with the experiments. A considerable agreement was observed in the profiles of simulated spectra and the experimental UV–vis spectra, especially at the low-energy absorption region, indicating the validity of our computational approach for simulating optical spectra of the considered complexes.

Natural transition orbital (NTO)¹⁰⁷ analysis was performed using Gaussian09 software to obtain the hole–electron pairs that correspond to each absorption frequency, where a hole–electron transition from a ground state to an excited state could be realized through unitary transformation of transition density matrix of a specific excited state.¹⁰⁷ For visualizing the lowest-energy emitting state, we plotted the dominant molecular orbitals by performing the eigenvector analysis on the lowest excited state. Chemcraft-1.7 software¹⁰⁸ was used for plotting the ground- and excited-state charge densities by setting the isovalue as 0.02.

Nonlinear Transmission Experiment. The nonlinear transmission experiments at 532 nm for complexes 1-11 were carried out in acetonitrile solutions in a 2 mm cuvette using 4.1 ns laser pulses. The linear transmission of 1-11 in acetonitrile was adjusted to 90% in the 2 mm cuvette at 532 nm. A Quantel Brilliant ns laser with a repetition rate of 10 Hz was used as the light source. The experimental setup and details were described previously.¹⁰⁹ The beam radius at the focal point was approximately 96 μ m.

RESULTS AND DISCUSSION

Synthesis and Characterization. Although many methods have been developed for synthesizing 2-arylbenzoxazoles, the synthetic methods for 2-aryloxazolo[4,5-f][1,10]phenanthrolines are extremely rare due to the difficulties in synthesizing the required phenanthroline precursors.¹¹⁰ The classical methods utilized for the synthesis of benzoxazoles are the condensation of 2-aminophenol with either aldehyde or carboxylic acid followed by oxidative cyclization.¹¹¹ Thus, obtaining 6-amino-1,10-phenanthrolin-5-ol becomes the key for the synthesis of 2-aryloxazolo [4,5-f] [1,10] phenanthrolines based on these methods. Unfortunately, despite many attempts, it has not proven possible to obtain 6-amino-1,10-phenanthrolin-5-ol via any of the methods depicted in Scheme S2. Therefore, considerable efforts had been switched to synthesize the 2-aryloxazolo[4,5-f][1,10]phenanthrolines via cross-coupling reaction between 5,6-dibromophenanthroline and benzamide, followed by intramolecular cyclization (see route 5 in Scheme S2) in the presence of transition metal catalysts, such as Pd(OAc)₂, Pd₂(dba)₃, CuI, CuCl₂, and CuO. However, none of these efforts led to the desired compound after dozens of experiments. Finally, by modification of the procedure reported by Katritzky for synthesizing 2-substituted benzoxazoles via cyclization of α -oxo-oximes,¹¹² we succeeded in obtaining 2phenyloxazolo[4,5-f][1,10]phenanthroline (ligand L3) via a condensation reaction between 1,10-phenanthroline-5-oxo-6oxime and phenylmethyl bromide in dry THF/DMF in the presence of triethylamine under N₂ atmosphere. The same procedure was then followed to synthesize the other 2aryloxazolo[4,5-f][1,10]phenanthroline ligands (except for L5) with the corresponding arylmethyl bromides and 1,10phenanthroline-5-oxo-6-oxime. The yields of the reactions were in the range of 13-39%, due to the formation of probable ring-opening byproducts 6-(arylmethyl)imino-1,10-phenan-



Figure 1. (a) Perspective view of **3a** with the thermal ellipsoids drawn at the 50% probability level and the H atoms omitted for clarity. (b) Schematic diagram of the asymmetric unit for **3**. (c) Molecular stacking in crystals of **3**: green dotted lines, $\pi \cdots \pi$ interactions; red dotted lines, intermolecular C-H \cdots F interactions.



Figure 2. (a) Schematic diagram of the overlay of the two diastereomers of 7 in the unit cell. PF_6 anions are omitted for clarity. (b) Perspective view of 7 with the thermal ellipsoids drawn at the 50% probability level and the H atoms removed for clarity. (c) Molecular stacking in crystals of 7: green dotted lines indicate the $\pi \cdots \pi$ interactions.

throlin-5-ones. The structures of L2–L4 and L6–L11 were characterized by ¹H NMR. Because of the poor solubility of L1, it was unable to be purified via column chromatography or recrystallization. Therefore, the crude product of L1 was washed with CH_2Cl_2 and ether and used for the complexation reaction without further purification.

Complexes 1–4 and 6–11 were obtained via reaction of the corresponding 2-aryloxazolo[4,5-*f*][1,10]phenanthroline ligand with the [Ir(ppy)₂Cl]₂ dimer in refluxing CH₃OH/CH₂Cl₂ as we reported before for the synthesis of other heteroleptic cationic Ir(III) complexes,^{21,24} whereas complex 5 was obtained by reduction of the NO₂ group in complex 1. The structures of 1–11 were characterized by ¹H NMR spectroscopy (see Figures S1–S11), elemental analyses, and high resolution mass spectrometry. The structures of the complexes were further confirmed by X-ray single crystal structural analysis of complexes 3 and 7 (Figures 1 and 2, vide infra).

Geometry Optimization. The geometries of 1-11 were optimized in CH₃CN using DFT (see Figures S12 and S13). The optimized geometries of complexes 1-3, 5, 6, and 8 displayed almost coplanar orientation between the 2-aryl substituents and the oxazolo[4,5-f][1,10]phenanthroline motif. For complex 4, while the 2-phenyl ring was coplanar with the oxazolo[4,5-f][1,10]phenanthroline motif, the propeller shaped diphenylamino substituent was twisted from the 2-phenyl ring with dihedral angles of ca. 47° . In contrast, upon geometry optimization of complexes 7 and 9-11, the 2-aryl substituents (i.e., naphthalen-1-yl, phenanthren-9-yl, anthracen-9-yl, and pyren-1-yl) were twisted from oxazolo[4,5-f][1,10]-phenanthroline by angles of ca. $16-50^{\circ}$. The dihedral angle in

7 (25.2°) is smaller than that obtained from the single crystal structure (50.9°, vide infra). This difference could be attributed to the different temperatures used for the calculation (0 K) and for the crystallography (100 K) and the different forms (i.e., calculation was done in CH₃CN solution while the single crystal structure was obtained in the solid state). Additionally, intermolecular interactions in crystals, which are absent in calculations of an isolated molecule, may also be responsible for this difference in dihedral angle. Overall, calculations show that phenyl and its derivatives adopt an almost coplanar structure with the oxazolo[4,5-*f*][1,10]phenanthroline motif, while the polycyclic arene (except for naphthalen-2-yl) substituents are twisted away from the oxazolo[4,5-*f*][1,10]phenanthroline motif.

X-ray Crystallography. Single crystals suitable for X-ray crystallographic analysis of complexes 3 and 7 were obtained by diffusing diethyl ether into dilute CH_2Cl_2 solutions of the complexes, and their crystal structures were determined at 100 K. Complexes 3 and 7 crystallized in the triclinic *P*-1 and monoclinic C1 2/c 1 space group, respectively. The details of the crystallographic data are summarized in Table S1. The obtained crystal structures and packing modes of 3 and 7 are shown in Figures 1 and 2, respectively. The selected bond lengths and angles are compiled in Tables S2–S4.

Crystal structural analysis of complex 3 revealed that the unit cell contained two independent host molecules with distinct conformations (referred to as 3a and 3b, see Figures 1b and 1c and Table S2). Each of the iridium ions is octahedrally coordinated by one N^N ligand and two C^N ligands, with dihedral angles of ca. 77.6–97.3°. However, in conformer 3a,



Figure 3. Experimental UV-vis absorption spectra of 1-6 (a) and 7-11 (b) in CH₃CN. The insets in panels a and b show the expanded experimental spectra beyond 500 nm.

Table 1. Experimental Photophysical Data for 1–

	$\lambda_{ m abs}/ m nm^{a}~(arepsilon/10^4~ m L~mol^{-1}~cm^{-1})$	$\lambda_{\rm em}/{\rm nm}^b$ $(au_{\rm em}/\mu s);$ $\Phi_{\rm em},$ rt	$k_{\rm r}/{ m s}^{-1c}$	$k_{\rm nr}/{ m s}^{-1d}$	$\lambda_{\rm em}/{\rm nm}^e$ $(au_{\rm em}/\mu { m s}),$ 77 K	$\lambda_{\rm em}/ nm^{f},$ rt	$\lambda_{T1-Tn}/nm^g (\varepsilon_{T1-Tn}/10^4 L mol^{-1}cm^{-1}, \tau_T/\mu s); \Phi_T$
1	280 (5.66, sh), 334 (3.76), 387 (1.97, sh), 432 (0.26, sh)	530 $(-)^h$; $-^h$	<i>i</i>	_i	522 (306), 566 (250)	_h	_h
2	272 (5.25), 280 (5.19), 340 (2.00, sh), 374 (0.80), 390 (7.86), 438 (0.15, sh)	600 (0.36); 0.16	4.4×10^{5}	2.3×10^{6}	531 (5.59)	598	425 (- ^{<i>j</i>} , 0.34), 590 (1.64, 0.34); 0.59
3	270 (4.59), 336 (1.43, sh), 377 (0.60), 392 (0.57), 432 (0.12, sh)	600 (0.37); 0.21	5.7×10^{5}	2.1×10^{6}	524 (6.37)	584	425 (-, 0.35), 600 (1.45, 0.36); 0.79
4	285 (3.88, sh), 390 (3.18), 460 (0.25, sh)	$597 (-)^{h};$ 0.005	_i	_ ⁱ	535 (220), 574 (188)	605	_j
5	289 (4.61), 335 (3.89), 363 (3.24, sh), 450 (0.26, sh)	590 (0.03); 0.008	2.7×10^{5}	3.3×10^{7}	526 (94), 564 (74)	574	457 (2.94, 0.03); 0.23
6	270 (6.82), 331 (2.31, sh), 368 (0.94), 384 (1.00), 441 (0.14, sh)	602 (0.30), 0.15	5.0×10^{5}	2.8×10^{6}	527 (5.13)	608	420 (- ^{<i>j</i>} , 0.34), 609 (2.95, 0.34); 0.45
7	285 (3.34), 336 (2.37), 349 (2.28), 394 (0.88), 432 (0.18, sh)	600 (2.47); 0.19	7.7×10^{4}	3.3×10^{5}	550 (362), 594 (280)	568	539 (4.40, 2.59); 0.39
8	267 (8.26), 281 (6.25, sh), 316 (3.84), 334 (3.56), 352 (2.69, sh), 369 (1.33, sh), 395 (1.09), 426 (0.30, sh)	600 (0.37); 0.18	4.9×10^{5}	2.2×10^{6}	520 (334), 560 (235)	598	432 (- ^{<i>j</i>} , 0.39), 590 (2.61, 0.39); 0.31
9	261 (8.45), 286 (4.58, sh), 336 (2.85), 372 (1.94, sh), 395 (1.07, sh), 430 (0.18, sh)	600 (2.47); 0.20	8.1×10^{4}	3.2×10^{5}	550 (2580), 597 (2110)	601	435 (5.09, 2.38), 531 (4.37, 2.38); 0.37
10	253 (10.38), 368 (1.15), 387 (1.27), 464 (0.18, sh)	590 (0.39); 0.007	1.8×10^{4}	2.5×10^{6}	555 (4.62), 600 (3.89)	_h	432 (- ^{<i>j</i>} , 24.4), 513 (3.57, 25.0); 0.58
11	283 (6.80, sh), 382 (4.68), 398 (4.49), 415 (4.02), 448 (0.30, sh)	$548_{h}(0.60);$	i	_i	$ \begin{array}{c} 658 (-^{h}), \\ 721 (-^{h}) \end{array} $	_h	483 (3.39, 28.5); 0.68

^{*a*}Room temperature electronic absorption band maxima and molar extinction coefficients in CH₃CN. ^{*b*}Room temperature emission energy, lifetime, and quantum yield in CH₃CN. ^{*c*}Radiative decay rate in CH₃CN at room temperature. ^{*d*}Nonradiative decay rate in CH₃CN at room temperature. ^{*e*}Emission energies and lifetimes at 77 K measured in 2-methyltetrahydrofuran glassy matrix, $c = 1 \times 10^{-5}$ mol/L. ^{*f*}Room temperature emission energy in the solid state. ^{*g*}IN TA band maxima, triplet extinction coefficients, triplet excited-state lifetimes and quantum yield in toluene. The reference used was SiNc in C₆H₆ ($\varepsilon_{590} = 70,000 \text{ L mol}^{-1} \text{ cm}^{-1}, \Phi_T = 0.20$). ^{*h*}Signal was too weak to be detected. ^{*i*}Cannot be calculated. ^{*j*}The ground-state absorption at these wavelengths could not be neglected; thus the singlet depletion method could not be used to estimate the ε_{T1-Tn} values at these wavelengths.

the 2-phenyl ring was almost coplanar (with a dihedral angle of 0.81°) with the oxazolo [4,5-f][1,10] phenanthroline motif, which is much smaller than the 11° dihedral angle reported for the Ir(III) complex with 2-(4-trifluoromethyl)phenylimidazole[4,5-f][1,10]phenanthroline ligand.⁴² The length of the bridging C-C bond (C61-C67) between the 2-phenyl substituent and the oxazolo [4,5-f] [1,10] phenanthroline motif was 1.465 Å. However, in conformer 3b, the 2-phenyloxazolo part was slightly bent from the phenanthroline (the dihedral angle is ca. 10.1°), with a shorter bond length of 1.430 Å for the bridging C–C bond (C31–C32). The interactions between the adjacent 3a and 3b molecules led to the formation of crossstacked dimers with C···O distance of 3.089 Å, C···N distance of 3.205 Å, $\pi \cdots \pi$ distance of 3.290 Å, and C...C distance of 3.265 Å. Meanwhile, the relatively strong intermolecular C-H…F interactions (3.060-3.350 Å) between the cationic

complex and its PF_6 counteranion also played a very important role in the crystal formation, especially for the formation of the distorted conformer **3b**. It is relatively rare that an organometallic complex possesses two distinct conformations in one crystal structure.

Figure 2a presents the cocrystal (1:1) of two diastereomers of complex 7 in one unit cell. The coordination core $Ir(phen)(ppy)_2^+$ was the same in both diastereomers. However, the 2-(naphthalen-1-yl)oxazolo parts were mirror image to each other in the diastereomers. In both isomers, the 2-(naphthalen-1-yl) rings were twisted out of the oxazolo[4,5-f][1,10]phenanthroline plane with a dihedral angle of 50.9°. The planar oxazolo[4,5-f][1,10]phenanthroline motifs in two adjacent complexes were packed by $\pi \cdots \pi$ (3.400 Å) and C–H···O interactions in a head-to-head fashion, while the PF₆ anion connected two face-to-face complexes by C–H···F interactions.

Table 2. Natural Transition Orbitals (NTOs) Representing the Lowest Energy Transitions



All these interactions led to a tight diamond array along the b axis. To the best of our knowledge, cocrystallization of two diastereomers in one lattice is also rare in organometallic complexes.

Electronic Absorption. The UV–vis absorption characteristics of complexes 1–11 were studied in CH₃CN at different concentrations (5×10^{-6} to 1×10^{-4} mol L⁻¹). The absorption obeyed the Beer's law in the studied concentration range, suggesting the absence of ground-state aggregation in this concentration range. This phenomenon is consistent with that reported for other Ir(III) complexes^{15–25} and is attributed to the octahedral geometry around the Ir(III) ion, which reduces the intermolecular interactions. The experimental UV–vis absorption spectra of 1–11 in CH₃CN are presented in Figure 3, and the absorption band maxima and extinction coefficients are compiled in Table 1. The simulated UV–vis absorption spectra via TDDFT calculations and the comparison to those of the experimental spectra are provided in Figure S14. The theoretical spectra overall reproduced the experimental spectral features very well.

As shown in Figure 3, the spectra of all complexes possessed intense absorption bands below 350 nm, moderately strong absorption bands between 350 and 450 nm, and broad but weak tails at ca. 450-570 nm. Based on the molar extinction coefficients, the minor solvatochromic effect in different solvents (Figure S15), and the calculated natural transition orbitals (NTOs, Table 2 and Tables S5 and S6), we attribute the highest-energy absorption bands at <300 nm to the ppy ligand localized ${}^{1}\pi,\pi^{*}$ transitions, and the strong absorption bands between 300 and 350 nm predominantly to the N^N and/or ppy ligand localized ${}^{1}\pi,\pi^{*}$ transitions mixed with significant contributions from the ¹LLCT (π (ppy) \rightarrow $\pi^{*}(\text{phen}))/^{1}\text{MLCT} (d(\text{Ir}) \rightarrow \pi^{*}(\text{phen}))/^{1}\text{ILCT} (\pi(\text{Ar}) \rightarrow$ $\pi^*(\text{phen})$) transitions. For the absorption bands between 350 and 450 nm, ¹ILCT/¹LLCT/¹MLCT transitions played the major role, admixing with contributions from the ppy ligand localized ${}^{1}\pi,\pi^{*}$ transitions. The ¹ILCT transition became the dominant contributor in complexes 3, 4, 5, and 7-11 that either bear strongly electron-donating substituents at the 4position of the 2-aryl group or have the aromatic rings with



Figure 4. Normalized emission spectra of (a) 1-11 in CH₃CN solutions and (b) 2-9 in the solid state at rt.

good π -donating ability. On the contrary, complexes 1, 2, and 6 containing electron-withdrawing substituents/group (NO2, Br, and pyridyl) had the ¹LLCT/¹MLCT as the major contributors to their 350-450 nm bands. It should be noted that, for all complexes, the lowest-energy singlet transition (S_1) is exclusively ¹LLCT/¹MLCT (see NTOs in Table 2) in nature. Both electron-donating substituents (NPh₂ and NH₂ in 4 and 5, respectively) and electron-withdrawing substituents (NO₂ and Br in 1 and 2, respectively) at the 4-position of the 2-aryl group significantly increased the molar extinction coefficients of the absorption bands compared to those in 3. Comparison of the spectra of 3 to 6 revealed that the spectra of these two complexes had similar shapes; however, the electron-deficient pyridyl ring caused a slight blue-shift of the absorption bands in 6 but increased the extinction coefficients of the corresponding bands.

In addition to the aforementioned absorption bands, all complexes possessed very weak absorption tails at ca. 450-570 nm. In view of the small molar extinction coefficients and with reference to the other reported Ir(III) complexes,^{20,22,24,25,41,113} this tail can be ascribed to the spin-forbidden transitions from ³LLCT/³MLCT.

Photoluminescence. The emission spectra of 1-11 were investigated in different solvents and in the solid state at rt, and in MTHF glassy matrix at 77 K. Their normalized emission spectra in CH₃CN at rt are presented in Figure 4, and the emission data are summarized in Table 1. As shown in Figure 4a and Table 1, complexes 2-10 exhibited red emission with the band maxima at ca. 600 nm in degassed CH₃CN at rt, along with lifetimes spanning from tens of nanoseconds to several microseconds (see Table 1). In contrast, the emission of complexes 1 and 11 is blue-shifted. Considering the proneness of emission toward oxygen quenching, the large Stokes shifts, and the relatively long emission lifetimes, we assign the emission of these complexes to phosphorescence. The emission quantum yields of these complexes show that strongly electronwithdrawing or -donating substituents in complexes 1, 4, and 5 and more π -expansive aryl substituents in complexes 10 and 11 either significantly decreased the radiative decay rates (k_r) , such as in 10, or increased the nonradiative decay rates (k_{nr}) , such as in 5, which consequently decreased the emission quantum yields in these complexes. The different solvents also influenced the emission characteristics pronouncedly (Table 3 and Figure S16). The data presented in Table 3 clearly demonstrated that the emission was much stronger in less polar solvents such as toluene, CH₂Cl₂, and THF compared to that in more polar solvents, such as acetone and acetonitrile. Especially the

Table 3. Emission Data for Complexes 1-11 in Different Solvents at Room Temperature^{*a*}

	$\lambda_{ m em}/ m nm~(au_{ m em}/ m ns,~\Phi_{ m em}{}^{b})$							
	toluene/ 10% CH ₂ Cl ₂	THF	CH ₂ Cl ₂	acetone	acetonitrile			
1	601 (310, 0.16)	604 (290, 0.097)	595 (150, 0.084)	$532 (-, -)^{c}$	$530 (-, -)^c$			
2	600 (370, 0.22)	600 (380, 0.22)	587 (670, 0.45)	600 (340, 0.17)	600 (360, 0.16)			
3	600 (400, 0.30)	600 (410, 0.24)	584 (700, 0.62)	600 (360, 0.21)	600 (370, 0.21)			
4	597 (100, 0.054)	592 (180, 0.088)	582 (820, 0.47)	595 (50, 0.008)	597 (-, 0.005) ^c			
5	581 (10, 0.019)	589 (40, 0.016)	579 (780, 0.77)	593 (10, 0.007)	590 (30, 0.008)			
6	601 (330, 0.19)	605 (330, 0.16)	592 (600, 0.34)	605 (290, 0.11)	602 (300, 0.15)			
7	600 (3770, 0.32)	600 (1330, 0.25)	585 (2900, 0.50)	600 (1540, 0.18)	600 (2470, 0.19)			
8	600 (410, 0.24)	600 (420, 0.21)	586 (720, 0.48)	600 (367, 0.17)	600 (370, 0.18)			
9	589 (4090, 0.24)	596 (1590, 0.32)	584 (3000, 0.55)	600 (1570, 0.17)	600 (2470, 0.20)			
10	588 (390, 0.004)	589 (600, 0.13)	580 (690, 0.015)	590 (390, 0.008)	590 (390, 0.007)			
11	541 (-, -), 664 (-, -) ^c	585, (-, -), 665 (-, -), 730 (-, -) ^c	577 (-, -), 664 (-, -) ^c	548 (-, -), 659 (-, -) ^c	548 (600, -) ^c			

^aThe excitation wavelength was 436 nm. ^bThe reference used for the quantum yield measurement was $[Ru(bpy)_3]Cl_2$ in degassed CH₃CN solution ($\Phi_{em} = 0.097$, $\lambda_{ex} = 436$ nm). ^cThe emission signals were too weak to allow for the lifetimes and quantum yields to be accurately measured.

emission became the strongest in CH_2Cl_2 . Similar to their very weak emission in solutions, the emission of complexes 1, 10, and 11 in the solid state (Figure 2b) was nondetectable, while the other complexes exhibited bright yellow to orange emission.

It is worth noting that, in comparison to the reported Ir(III) complex bearing the 2-phenylimidazole [4,5-f][1,10]-phenanthroline (N^N) ligand (i.e., complex 1 in ref 43), the corresponding oxazole based complex 3 in this work possessed a similar emission lifetime (ca. 700 ns in CH₂Cl₂) but much stronger emission intensity, which is reflected by the much larger emission quantum yield of 0.62 for complex 3 in this work vs 0.24 for complex 1 in ref 43 in CH₂Cl₂ solutions. In addition, the emission energy of 3 (584 nm in CH₂Cl₂ and 598 nm in CH₃CN) in this work is lower than that of 1 in ref 43



Figure 5. (a) Normalized emission spectra of complex 7 in the solid state, after grinding, and after fuming with CH_2Cl_2 . The inset shows the emission photograph of the initial sample and ground sample of 7 under irradiation of 365 nm UV light. (b) XRD patterns of the corresponding samples.

(568 nm in CH₂Cl₂ and 587 nm in CH₃CN). The almost identical emission lifetime for these two complexes suggests that the emission of 3 likely emanates from the same emitting state for 1 in ref 43, i.e., the ³MLCT/³LLCT state, which will be discussed further in the following paragraphs. The red-shifted emission band and enhanced emission of complex 3 in this work should be attributed to the almost coplanar structure of the phenyl ring with respect to the oxazolo [4,5-f] [1,10]phenanthroline motif in complex 3, which increased the k_r in 3 (i.e., $8.9 \times 10^5 \text{ s}^{-1}$ for 3 vs $3.4 \times 10^5 \text{ s}^{-1}$ for 1 in ref 43) while decreasing the $k_{\rm nr}$ (5.4 × 10⁵ s⁻¹ for 3 vs 1.1 × 10⁶ s⁻¹ for 1 in ref 43). Complexes 1 and 11 exhibited anomalous solventdependent emission energy compared to the minor solvatochromic effects observed in complexes 2-10 (Figure S16). The emission energies were drastically blue-shifted in more polar solvents, such as CH₃CN and acetone, compared to those in THF, CH₂Cl₂, and toluene. The excitation spectra of 1 in CH₃CN and THF were different (Figure S17). Thus, we speculate that the emitting state of 1 in high polarity solvents is different from that in low to medium polarity solvents. This speculation is partially confirmed by the low temperature study at 77 K (vide infra, Figures S18 and S19) and is fully supported by the NTOs of the emitting states. Differing from 1, which has the emitting state switched in different solvents, 11 appeared to show dual emission in all of the solvents tested except for CH₃CN, in which the emission was too weak to observe the longer wavelength emission bands. The high-energy emission band at <600 nm was structureless, while the low-energy emission possessed somewhat vibronic structures with a clear progression of 1340 cm⁻¹ in THF. The long-wavelength emission band(s) became the dominant one in THF. In view of the different features for these bands, we tentatively ascribe the origin of the high-energy emission to a charge transfer excited state and the low-energy emission to the ligand-localized ${}^{3}\pi,\pi^{*}$ state. The dual emission phenomenon has been reported for Ru(II) complexes that contain the pyrenyl substituent on the diimine ligand.¹¹⁴ This notion is also supported by the 77 K emission study discussed in the following paragraph.

The emission of all complexes except for 1 and 11 at 77 K in butyronitrile glassy matrix was blue-shifted in comparison to those in CH₃CN solutions at rt (see Figure S18) due to the rigidochromic effect.^{115,116} The thermally induced Stokes shifts (ΔE_{th}) for 2–6 and 8 are ca. 2200 cm⁻¹, while for 7, 9, and 10 they are around 1300 cm⁻¹. The large ΔE_{th} values for these complexes indicate charge transfer nature of the emitting states for these complexes because charge transfer states are less

stabilized due to the lack of solvent reorganization in the rigid frozen matrix. In contrast to these complexes, the $\Delta E_{\rm th}$ value for complex 1 is only ~320 cm⁻¹, implying the ${}^{3}\pi,\pi^{*}$ nature of the emitting state for this complex in CH₃CN. However, the ΔE_{th} value was approximately 2600 cm⁻¹ in MTHF for 1 (Figure \$19), suggesting a charge transfer nature of the emitting state in MTHF. This finding supports our aforementioned assumption that the dramatically different emission energy of 1 in solvents with different polarities indeed emanates from different emitting states. Such a notion is further confirmed by the molecular orbitals corresponding to the emitting triplet excited states of 1 in CH₃CN and THF (Table S7). For complex 11, the $\Delta E_{\rm th}$ value in MTHF was ~180 cm⁻¹ for the low-energy emission band(s), which is in accordance with our presumed ${}^{3}\pi,\pi^{*}$ nature of this emission band. Interestingly, the emission of 11 in BuCN glassy matrix at 77 K manifested a similar energy and shape to that in MTHF glassy matrix, implying that, at low temperature, only the low-energy ${}^{3}\pi,\pi^{*}$ state emit.

To unambiguously assign the nature of the emitting states in 1-11 and understand the aforementioned different emission characteristics of these complexes, TDDFT calculations of the emission of 1-11 in CH₃CN were conducted, and the obtained emission energies and molecular orbitals (MOs) corresponding to the phosphorescent emitting states are provided in Table S7. The emission of 1 in THF was also calculated to understand the different natures of the emitting state in different solvents. The calculated emission energies reproduced the experimental emission energies very well, with 1 and 11 having higher emission energies and the other complexes possessing similar emission energies. Meanwhile, the MOs in Table S7 clearly show the different natures of the emitting states for these complexes in CH₃CN and for 1 in different solvents. In CH₃CN, the electrons of 1 are delocalized on the ppy ligands, the d-orbitals of the Ir(III) ion, and the 2-phenyloxazolo[4,5f][1,10]phenanthroline, while the holes are exclusively on the 2-(4-NO₂-phenyl)oxazole component. Thus, the emitting state of 1 in CH₃CN has the ${}^{3}\pi,\pi^{*}/{}^{3}ILCT/{}^{3}LLCT/{}^{3}MLCT$ parentage and led to emission at high energy (i.e., 530 nm). In contrast, the emitting state became the ³LLCT/³MLCT state in THF, resulting in emission at ~600 nm. In complexes 2 and 6 that either have a weak electron-withdrawing Br substituent at the phenyl ring or bear the electron deficient pyridyl ring, the emitting states all have the ³LLCT/³MLCT nature mixed with some ${}^{3}\pi,\pi^{*}$ and minor ${}^{3}\text{ILCT}$ (in 6) character. The emitting state of 3 has pure ³LLCT/³MLCT character; while in 4 and 5,

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Figure 6. Nanosecond TA spectra of (a) 2, 3, and 5 and (b) 6-11 in CH₃CN immediately after 355 nm excitation. $A_{355} = 0.4$ in a 1 cm cuvette.

which contain strongly electron-donating NPh₂ or NH₂ substituents, the emitting states are exclusively ³ILCT within the N^N ligands. For complexes 7–11, which contain π -donating polycyclic aromatic rings, their emitting states have predominant ³ILCT/³ π , π^* characters; while the contribution of the pyrene-based ³ π , π^* character increased in 11. In complex 8, ³MLCT state appears to make important contribution to the emission as well. Overall, electron-donating substituents or polycyclic aromatic rings significantly increased the ³ILCT (π (donor) $\rightarrow \pi^*$ (phen)) character in the emitting states; while electron-withdrawing substituents induced more ³ π , $\pi^*/^3$ ILCT (π (phen) $\rightarrow \pi^*$ (acceptor)) character. Variations of the emitting state parentage account for the observed differences in emission characteristics in different solvents and the varied $\Delta E_{\rm th}$ values.

Mechanochromic and Vapochromic Luminescence. The mechanochromic effect is a phenomenon by which the color and/or the luminescence of a solid-state material changes upon applying mechanical forces. The change in luminescence could be energy or intensity. Such a phenomenon has potential applications in mechanosensors, security printing, or optical storage.¹¹⁷⁻¹²⁴ Interestingly, the as-prepared pale yellow powder of complex 7 exhibited bright yellow phosphorescence $(\lambda_{\text{max}} = 568 \text{ nm})$ under UV light irradiation. After grinding, an orange powder with orange emission ($\lambda_{max} = 609$ nm) was obtained (Figure 5a). The ground orange powder was readily converted back to the initial yellow emission by exposure to CH₂Cl₂, acetone, diethyl ether, methanol, or THF vapors for several seconds to minutes, with CH₂Cl₂ vapor giving the fastest change. Evidently, complex 7 manifested a pronounced mechanochromic effect and vapochromic effect, which can be easily observed by naked eyes. Moreover, the convertibility of the emission color change for complex 7 in CH₂Cl₂ can be repeated for many cycles, which is an important feature for applications in sensing and security printing.

To understand the mechanochromic behavior of 7, a powder X-ray diffraction (PXRD) study was carried out. The PXRD patterns (Figure 5b) were consistent with the single-crystal diffraction data of 7. The sharp and intense reflection peaks in the simulated XRD patterns based on the single crystal X-ray data represented the characteristic diffraction peaks of 7 in the crystalline state. In contrast, the ground sample exhibited weaker and broader diffraction signals, indicating an amorphous state. After fuming the ground sample with CH_2Cl_2 vapor, the intense and sharp diffraction peaks were recovered. This implies that the mechanochromic effect of 7 emanates from the

crystallization-amorphization conversion upon external stimuli.

To rationalize the unique mechanochromic behavior that was only observed in complex 7, but not in the other complexes, we compared the crystal packing patterns of 7 and 3. The single crystal packing pattern of 7 shown in Figure 2c revealed that the molecules of 7 adopted a slipped head-to-head arrangement with an intermolecular $\pi - \pi$ distance of 3.40 Å between the two phenanthroline rings on the two closest neighboring molecules, resulting in a relatively weaker packing. Considering the presence of two diastereomers in one unit cell, and the twisted naphthalen-1-yl ring from the oxazolo[4,5-f][1,10]phenanthroline motif, we infer that the molecular packing is relatively loose with low lattice energy. Thus, the packing can be readily modified by external mechanical grinding, resulting in increased coplanarity between the naphthalen-1-yl ring and the oxazolo[4,5-f][1,10] phenanthroline motif. This improves the π -conjugation and intermolecular interactions; both of them can cause a bathochromic shift of the emission. In contrast, complex 3 adopted a face-to-face packing in its single crystal with a closer $\pi - \pi$ distance of 3.29 Å between the two phenanthroline rings on the two adjacent molecules. Consequently, the packing in 3 was more stable due to stronger intermolecular interactions. Therefore, unlike what was observed in 7, the emission of 3 cannot be readily modified upon applying external stimuli.

Transient Absorption. To further understand the influence of the substituent at the oxazolo[4,5-f][1,10]-phenanthroline ligand on the triplet excited-state characteristics, nanosecond transient absorption (TA) studies of complexes 1-11 were carried out. The TA spectra of 2, 3, and 5-11 recorded upon excitation at 355 nm in degassed acetonitrile solutions are shown in Figure 6 and Figure S20. The TA of 1 and 4 were too weak to be detected. The triplet excited-state absorption band maxima, molar extinction coefficients, lifetimes, and quantum yields of 2, 3, and 5-11 in CH₃CN are compiled in Table 1.

Figure 6 shows that the TA spectra of 2, 3, and 5-10 possess broad positive absorption bands from ca. 410 to 800 nm, while the positive absorption band appears at 435–740 nm for 11. The TA spectra of 2, 3, 6, and 8 exhibited similar shape and intensity, and the triplet lifetimes deduced from the decay of TA were similar to those obtained from the decay of emission. These features suggest that the TA of 2, 3, 6, and 8 likely originates from the same excited state that emits. Thus, the transient absorbing excited states for 2, 3, 6, and 8 can be ascribed predominantly to ³MLCT/³LLCT states for these four

complexes. The undetectable TA of complexes 1 and 4 are likely attributed to the rapid decay of the triplet excited states (<10 ns), which exceeds the time resolution of our nanosecond TA Instruments. Complex 5 exhibited positive absorption bands in the same wavelength range of 410-800 nm as those observed in complexes 2, 3, 6, and 8, but with quite different spectral feature(s). The TA decay profile of 5 resembled that of its emission decay profile, implying that the TA of 5 arises from its ³ILCT state. In contrast, the TA features of 7, 9, 10, and 11 are all distinct from each other and differ from those of 2, 3, 5, 6, and 8 with respect to spectral shape, lifetime, and TA intensity. The TA of 7, 9, 10, and 11 are all much stronger and longer-lived than those of 2, 3, 5, 6, and 8. The TA lifetimes of 7 and 9 were similar to those obtained from emission, while the TA lifetimes of 10 and 11 were one order of magnitude longer than their corresponding emission lifetimes. Considering the nature of the emitting states for these complexes, we attribute the transient absorbing species in 7 and 9 to ${}^{3}\text{ILCT}/{}^{3}\pi_{n}\pi^{*}$ and those for complexes 10 and 11 to the respective anthracenyl or pyrenyl substituted N^N ligand based ${}^3\pi,\pi^*$ states due to their much longer TA lifetimes. Assigning the nature of the longlived transient absorbing states in these two complexes to the anthracene and pyrene based ${}^{3}\pi,\pi^{*}$ states was excluded because the observed TA spectra of 10 and 11 are quite different from those reported for anthracene¹²⁵ and pyrene.¹²⁶ The different TA lifetimes and emission lifetimes in 10 and 11 also clearly indicate the different origins of the emitting and TA states. Although this phenomenon is uncommon, it has been reported in Ru(II),^{127–131} Pt(II),^{132,133} and other Ir(III)²⁵ complexes that contain large π -conjugated aromatic substituents like pyrenyl group on the ligand(s), in which the complexes demonstrated a high-lying, short-lived charge transfer emitting state and a low-lying, long-lived nonemissive but strongly absorbing ${}^{3}\pi,\pi^{*}$ state. ${}^{25,127-133}$ This phenomenon suggests that the anthracenyl or pyrenyl substituted N^N ligand based ${}^{3}\pi,\pi^{*}$ states in complexes 10 and 11 are substantially lower than their emitting states, thus thermal equilibration between these two states is impeded, leading to the rapid population of the longlived dark ${}^{3}\pi,\pi^{*}$ state instead.

Similar to the trend observed for emission, both the strongly electron-withdrawing NO₂ group and electron-donating NPh₂ and NH₂ substituents on the oxazolo[4,5-f][1,10]phenanthroline ligand reduced the triplet excited-state lifetime of the complexes, likely due to the stronger charge transfer character in the lowest triplet excited states of these two complexes, i.e., stronger ³LLCT character in 1 and ³ILCT character in 4 and 5 (see the molecular orbitals (MOs) corresponding to the triplet emitting states of 1, 4, and 5 in CH₃CN in Table S7). The reduced triplet lifetime and weak phosphorescent emission are common features for Pt(II) and Ir(III) complexes studied before that bear strongly electron-donating NPh₂ substituent on the ligands.^{21,134,135} On the contrary, extending π -conjugation of the polycyclic aromatic substituents via benzannulation at the 2,3-position of phenyl ring in complexes 7, 9, 10, and 11 increased the triplet lifetimes and the TA intensity. These variations could be related to the increased steric hindrance between the aromatic substituents and the oxazolo [4,5-f] [1,10] phenanthroline motif, which changed the parentage of the lowest triplet excited states from ³MLCT/³LLCT states to the N^N ligand based ³ILCT or $^{3}\pi,\pi^{*}$ state.

Reverse Saturable Absorption (RSA). RSA is one of the nonlinear optical phenomena in which the absorptivity of the

material increases with increased incident fluence. To achieve RSA, the material is required to have a large ratio (>1) of the excited-state absorption cross section (σ_{ex}) relative to that of the ground-state absorption (σ_0) at the interested wavelengths. Meanwhile, the excited-state lifetime needs to be longer than the laser pulse width. For RSA of ns laser pulses, a high quantum yield of triplet excited-state formation is also crucial.

Based on the broad and positive TA signals for these complexes in the region of ca. 425-800 nm as discussed in the TA section, we anticipate that these complexes exhibit RSA in the visible spectral region upon ns laser irradiation. Therefore, nonlinear transmission experiments at 532 nm using 4.1 ns laser pulses were carried out for 1-11 in acetonitrile solutions with a 90% linear transmission in a 2 mm cuvette at 532 nm. Figure 7 displays the nonlinear transmission vs incident energy



Figure 7. Nonlinear transmission curves for complexes 1-11 in acetonitrile at 532 nm in a 2 mm cuvette. The pulse duration was 4.1 ns, and the linear transmission of all solutions was 90% at 532 nm in a 2 mm cuvette. The radius of the beam waist at the linear focal plane was approximately 96 μ m.

curves for complexes 1–11. The transmission of the solutions kept decreasing with the increase of the incident energy, confirming the occurrence of RSA in all complexes. The strength of the RSA for these complexes followed this trend: 7 > 11 > 9 > 3 > 2 \approx 4 > 5 \approx 10 \approx 6 \approx 8 > 1. Complexes 7, 9, and 11 that possess larger π -conjugated aromatic substituents displayed much stronger RSA than the complexes possessing the phenyl substituent; and complex 1 with strongly electron-withdrawing NO₂ substituent exhibited the weakest RSA.

It appears that the RSA trend of 1-11 parallels the intensity of the TA signal at zero decay at 532 nm, but opposes the strength of the ground-state absorption at 532 nm (see the inset in Figure 3). This is in accordance with the key parameter determining the strength of RSA, i.e., the ratio of the excitedstate absorption cross section to that of the ground state (σ_{ex} / σ_0). As presented in Table 4, complexes 7, 9, and 11 possess very much larger excited-state absorption cross sections at 532 nm, but small ground-state absorption cross sections. Thus, the $\sigma_{\rm ex}/\sigma_0$ ratios are much larger in these three complexes in comparison to the other complexes. These ratios are also among the largest values for Ir(III) complexes reported to date.^{15–21,25} In complex 10, although its σ_{ex} value at 532 nm is the third largest, its much stronger ground-state absorption at 532 nm (actually the largest σ_0 value among all complexes) counteracts the strong excited-state absorption. Consequently, the $\sigma_{\rm ex}/\sigma_0$ ratio for 10 is significantly reduced and the RSA became weaker. Among these complexes, complex 1 bearing

	1	2	3	4	5	6	7	8	9	10	11
$\sigma_0/10^{-19}~{ m cm}^2$	3.51	2.79	2.02	3.51	2.52	2.60	1.45	3.55	2.82	8.60	3.32
$\sigma_{\mathrm{ex}}/10^{-17}~\mathrm{cm}^2$	Ь	5.75	5.08	Ь	7.35	7.06	17.3	8.67	16.7	12.5	11.2
$\sigma_{ m ex}/\sigma_0$	Ь	206	250	Ь	292	272	1193	244	590	145	337
$\Phi_{ m T}\sigma_{ m ex}/\sigma_0$	Ь	123	199	Ь	66	122	470	75	218	85	228
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Table 4. Ground-State (σ_0) and Excited-State (σ_{ex}) Absorption Cross Sections of Complexes 1–11 in Acetonitrile at 532 nm^a

 ${}^{a}\sigma = 2303\varepsilon/N_{AV}$ where N_{A} is Avogadro's constant. ε_{0} is obtained from the UV–vis absorption spectra, ε_{ex} is estimated from the Δ OD values at 532 nm and at the bleaching band minimum immediately after the laser excitation using the singlet depletion method.⁷⁷ ^bDue to the undetectable TA signals, these values were unable to be estimated or calculated.

the strongly electron-withdrawing NO₂ substituent exhibited the weakest RSA, likely due to the short triplet lifetime and stronger ground-state absorption. A general trend appeared that the complexes possessing larger π -conjugated aromatic substituents, such as those in 7, 9, and 11, displayed much stronger RSA than the complexes possessing the phenyl substituent. Considering the strong RSA of 7, 9, and 11 at 532 nm and their long triplet lifetimes, they are good candidates for applications that require strong RSA at 532 nm. For complex 10, although its RSA is not the strongest at 532 nm, its broader weak ground-state absorption to 700 nm and broad excited-state absorption in the visible to the near-IR region, and its long-lived triplet excited state, make it a potential good candidate as broadband optical limiting material.

CONCLUSIONS

We have developed a new synthetic route for the synthesis of 2aryl-substituted oxazolo[4,5-f][1,10] phenanthroline. A series of cationic Ir(III) complexes utilizing these 2-aryloxazolo[4,5f [1,10] phenanthrolines (1–11) as the diimine ligands were synthesized and characterized by ¹H NMR, HRMS, elemental analysis, and X-ray crystallography. Single crystal X-ray analysis revealed that the 2-phenyl substituent adopted an almost coplanar orientation with the oxazolo [4,5-f] [1,10]phenanthroline motif in complex 3. However, the polycyclic aryl substituents, such as naphthalen-1-yl (7), phenanthren-9-yl (9), anthracen-9-yl (10), and pyren-1-yl (11), still twisted away from the oxazolo[4,5-f][1,10] phenanthroline plane based on the single crystal structure of 7 and the DFT optimized geometries of 9-11. The increased coplanarity did not exert pronounced impact on the energies of the electronic transitions in their UV-vis absorption spectra in comparison to their corresponding complexes bearing the 2-phenylimidazole[4,5f][1,10]phenanthroline ligand. However, the increased coplanarity significantly improved the emission intensity both in solution and in the solid state. Among all complexes, complex 7 showed not only intense emission in solutions but also drastic mechanochromic and vapochromic effects in the solid state. Both the electron-withdrawing (NO₂) and electron-donating $(NPh_2 \text{ and } NH_2)$ substituents at the 4-position of the phenyl ring dramatically decreased the emission intensity and reduced the emission lifetimes in polar solvents like CH₃CN. In line with this trend, all complexes except for 1 and 4, which contain NO₂ and NPh₂ substituent, respectively, at the 4-position of the phenyl ring, exhibited moderate to strong triplet excited-state absorption in the visible to the near-IR spectral region; and complexes bearing π -expansive substituents at the 2-position of the oxazolo [4,5-f] [1,10] phenanthroline ligand possessed strong excited-state absorption and longer lifetimes. Especially the anthracen-9-yl substituent in 10 and pyren-1-yl substituent in 11 made these two complexes possessing very long-lived transient absorbing T₁ excited states. All complexes exhibited

strong reverse saturable absorption (RSA) at 532 nm for ns laser pulses. The strength of RSA followed this trend: 7 > 11 > $9 > 3 > 2 \approx 4 > 5 \approx 10 \approx 6 \approx 8 > 1$. Again, complexes with π expansive substituents on the oxazolo [4,5-f] [1,10]phenanthroline ligand manifested much stronger RSA compared to the complexes with phenyl or substituted phenyl on the oxazolo [4,5-f] [1,10] phenanthroline ligand mainly due to their much stronger excited-state absorption at 532 nm. Therefore, these complexes could be good candidates for photonic applications that require strong RSA at 532 nm, while complex 10 with weak ground-state absorption extending to 700 nm but broad and strong excited-state absorption in the visible to the near-IR region, and long-lived triplet excited state, has the potential to be developed into a broadband optical limiting material. In addition, the drastic mechanochromic and vapochromic effects revealed in complex 7 make it a promising candidate for security printing or pressure sensing.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b01472.

¹H NMR, UV–vis, emission, excitation, and TA spectra, X-ray crystallographic data, optimized ground-state geometries, NTOs, MOs, and the full author list for ref 80 (PDF)

Accession Codes

CCDC 1457721 and 1509624 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.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

We would like to thank Dr. A. Ugrinov at North Dakota State University for his help in the X-ray crystallographic measurements. We acknowledge the financial support from the National Science Foundation (DMR-1411086 and CNS- 1229316) for materials synthesis, characterization, and computational simulation of the optical spectra. For computational resources and administrative support, authors thank the Center for Computationally Assisted Science and Technology (CCAST) at North Dakota State University. S.K. thanks the National Energy Research Scientific Computing Center (NERSC) allocation award 86678, supported by the Office of Science of the Department of Energy under Contract No. DE-AC02-05CH11231. For partial financial support of the quantum chemistry software, S.K. acknowledges Sloan Research Fellowship BR2014-073.

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