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# Ligand-Mediated Photophysics Adjustability in Bis-tridentate Ir(III) Complexes and Their Application in Efficient Optical Limiting Materials

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attentively and characterized scientifically. The crystalline structures of **Ir1**, **Ir3** and **Ir4** were resoundingly confirmed by XRD. With the aid of experimental and theoretical methods, their photophysical properties at transient and steady states were scientifically investigated. The broadband charge-transfer absorption for these aforementioned Ir(III) complexes is up to 600 nm as shown in the UV-visible absorption spectrum. The emission lifetimes of their excited states are good. Between the visible and



near-infrared regions, Ir1–Ir5 possessed powerful excited-state absorption. Hence, a remarkably robust reverse saturable absorption (RSA) process can occur once the complexes are irradiated by a 532 nm laser. The RSA effect follows the descending order: Ir3 > Ir5 > Ir4  $\approx$  Ir1 > Ir2. To sum up, modifying electron-donating units (–OCH<sub>3</sub>) and large  $\pi$ -conjugated units to the pyridyl N<sup>C</sup>N-type ligands is a systematic way to markedly raise the RSA effect. Therefore, these octahedral bis-tridentate Ir(III) complexes are potentially state-of-the-art optical limiting (OPL) materials.

# INTRODUCTION

Organometallic complexes, especially transition metal Ir(III) complexes, are widely used to fabricate nonlinear optical materials as a result of their distinctive optoelectronic properties as well as broadband ground-state absorption (GSA), powerfully engrossing excited-state absorption (ESA), and high triplet quantum yields.<sup>1-4</sup> RSA process (with the enhancement of incident light intensity, the absorptivity of the materials heightens due to the stronger ESA than GSA) is one in all the nonlinear absorption phenomena.<sup>5-9</sup> In this regard, numerous octahedral tris-bidentate Ir(III) complexes have been reportable as efficient RSA materials.<sup>10-12</sup>

Tris-bidentate Ir(III) complexes are a kind of classic nonlinear optical absorbers based on the RSA mechanism due to the  $d-\pi$  interactions between the metal and the chelating ligands. This interaction spontaneously causes charge transfers (CT) between the coordinate metal and ligands.<sup>13,14</sup> These CT processes are efficaciously tuned by induced and conjugated effects on the logically modified cyclometalating ligands.<sup>15</sup> The nonlinear absorption (NLA) response of organometallic  $\pi$ -conjugated molecules is also influenced subtly in this process.<sup>16–18</sup> Although these complexes possessed broadband NLA response at 532 nm laser pulses, the event of Ir(III) complexes with efficient RSA remains in its infancy because of the extreme synthetic versatility of ligands.<sup>19–21</sup> One of the most immediate problems for scientists to deal with is how to effectively simplify complex structures and adjust the optical limiting ability at ease so that researchers can explore the structure-property relationship explicitly as a result.

It is gratifying that Ir(III) complexes concurrently coordinated with two tridentate ligands, also known as bistridentate Ir(III) complexes, show concise geometric structure, are easily adjustable electron transition characteristics, and stabilize a metal-centered d-d excited state according to the previous research results.<sup>17,18,22</sup> Faced with satisfying results, bis-tridentate Ir(III) complexes as newly fashioned optical absorbents deserve to be explored in depth. In 2017, Chi and co-workers reported bis-tridentate Ir(III) complexes with nanosecond lifetime bearing pyrazolyl tridentate ligands (pzpyph) show the weak  ${}^{3}\pi - \pi^{*}/{}^{3}MLCT$  absorption band within the region of  $\geq$ 470 nm.<sup>23</sup> Ir(III) complexes bearing tridentate ligands (bis(imidazolylidene)-benzene and 6-pyrazolyl-2-phenoxylpyridine) have shown weak  ${}^{1,3}MLCT$  absorption bands between 350 and 430 nm.<sup>22</sup> This feeble and spin-

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**Figure 1.** (a) N<sup>A</sup>C-type coordination mode for unmodified tridentate ligand; (b) N<sup>A</sup>C<sup>A</sup>N-type bonding modes for functionalized tridentate ligands ( $R = -CH_3$ , -F,  $-CF_3$ , etc.).

Scheme 1. Schematic Diagram of Electron Transition and Chemical Structures for Ir1-Ir5



forbidden <sup>3</sup>MLCT and  ${}^{3}\pi-\pi^{*}$  absorption bands after 400 nm is essential to broaden GSA to the near-infrared region and improve nonlinear absorption performance.<sup>5,24</sup> Hence, what would be a meaningful strategy for constructing potential reverse saturable absorbers is the employment of modified tridentate ligands to coordinate with iridium center.

A cationic Ir(III) complex bearing N<sup>^</sup>C<sup>^</sup>N-type ligands (1,3di(2-pyridinyl)-benzene and its derivatives) and N<sup>^</sup>N<sup>^</sup>C-type ligand (6-phenyl-2,2'-bipyridine) were selected as the basic models. These targeted octahedral Ir(III) complexes exhibit <sup>3</sup>MLCT/<sup>3</sup>LLCT states in the region of over 450 nm. This character endows Ir(III) complexes with weak but quite broad GSA.<sup>25–28</sup> Unfortunately, there are few reports about the properties of triple-excited states. This limits its application as photoelectric materials to a considerable extend. Interestingly, but notably, Williams and Chi's groups mentioned that the dominant construction of Ir(III) coordination with an unmodified N<sup>^</sup>C<sup>^</sup>N-type pyridyl ligand is bidentate N<sup>^</sup>Ccoordination (Figure 1a).<sup>18,29</sup> To entirely refrain from severe defects, introducing substituents ( $-CH_3$ , -F, and  $-CF_3$ ) at the fourth and sixth positions and  $\pi$ -conjugated pyridine units (isoquinolyl) are both admirable measures (Figure 1b).<sup>28,30</sup>

Bearing this in mind, five cationic bis-tridentate Ir(III) complexes, Ir1–Ir5, were designed and synthesized (Scheme 1.). These complexes all consist of a N^N^C-type ligand (6-phenyl-2,2'-bipyridine, L0) and a N^C^N-type ligand (L1–L5): 1,3-dimethyl-4,6-dipyridylbenzene (L1), 1,3-difluoro-4,6-dipyridylbenzene (L2), 1,3-dimethoxy-4,6-diisoquinolylbenzene (L3), 1,3-difluoro-4,6-diisoquinolylbenzene (L4), and 1,3-diisoquinolylbenzene (L5). A pair of substituents with different electronic properties were concurrently placed at the fourth and sixth sites of the central benzene unit for N^C^N-type ligand. These mated groups can not only prevent the C^N combination but also adjust the photophysics of expectant bis-

tridentate Ir(III) complexes. Such a study would play an important role when scientists clearly understand the relationship between structure and property. Meanwhile, it is more likely to serve as a modified version in terms of the rational style of bis-tridentate Ir(III) complexes for specific nonlinear optical absorbers.

#### EXPERIMENTAL SECTION

**Synthesis and Characterization.** All reagents are commercially available and without further purification. They were purchased from the Bidepharm and Energy Chemical Regent Co., Ltd. Silica gels (200–300 mesh) were used for separation and purification in column chromatography. NMR spectra systematically characterized all interrelated intermediates and fancy ligands. The desired bistridentate Ir(III) complexes were scrupulously characterized by NMR technology and HRMS. <sup>1</sup>H NMR and <sup>19</sup>F NMR were carried out on a Bruker-400 spectrometer. HRMS was carried out on an AB Sciex X-500B QTOF-mass spectrometer. Single-crystal X-ray diffraction (XRD) for the partially targeted complexes was collected on a BRUKER D8 VENTURE PHOTON100.

X-ray Crystallographic Analysis. Fortunately, with the help of the solvent diffusion method, single crystals of complexes Ir1, Ir3, and Ir4 were acquired in air and at room temperature. The cell parameters were collected by XRD. The crystal structures of Ir1 (CCDC 1847634), Ir3 (CCDC 1846057), and Ir4 (CCDC 1846058) were submitted to the CCDC. The single crystals of Ir1 formed in the methyl *tert*-butyl ether and acetonitrile system and were scrupulously characterized at 296 K. Likewise, Ir3 and Ir4 formed in the methyl *tert*-butyl ether and methylene chloride system and were characterized at 153 K. The circumstantial data were enumerated in Table S1.

**Photophysical Measurements.** In this work, Persee-TU-1900 UV and Hitachi-F4600 fluorescence are respectively accepted to measure UV–visible absorption and emission spectrum of title complexes Ir1–Ir5. The photoluminescence quantum yields of these desired Ir(III) complexes are evaluated in a scientifically relative actinometry method.<sup>31,32</sup> Under the circumstances, tris(2,2'-

bipyridine)dichlororuthenium(II) in the deoxy CH<sub>3</sub>CN is an extremely adaptive reference ( $\Phi_{em} = 0.097$ ,  $\lambda_{ex} = 436$  nm). The triplet properties were measured with an LP980 laser flash photolysis spectrometer. All samples prepared from Ir1–Ir5 were deoxy at full steam and excited by 355 nm third-harmonic Nd:YAG laser (Quantel Brilliant, 4.1 ns, 1 Hz). A singlet depletion method is a scientific tool to estimate the triplet molar extinction coefficients ( $\varepsilon_T$ )<sup>33</sup> and quantum yield ( $\Phi_T$ ).<sup>34</sup> Under this situation, silicon 2,3-naphthalocyanine bis(trihexylsilyloxide) (SiNc) in the degassed benzene is the most recognized reference ( $\varepsilon_{S90} = 70\,000 \text{ M}^{-1}\cdot\text{cm}^{-1}$ ,  $\Phi_T = 0.20$ ).<sup>35</sup>

Computational Methods. To predict the electronic properties of complexes Ir1-Ir5 in the ground and excited states, the DFT and time-dependent DFT methods were used. When this occurs, PBE1PBE was adopted to simulate the excited electronic states, 6-31G(d) for C, H, O, N, P, and F atoms, and effective core potential (ECP) of LANL2DZ basis set for Ir<sup>3+</sup> were accepted simultaneously. Under the conductor-like polarizable continuum model (PCM),<sup>37</sup> the effect induced by CH<sub>2</sub>Cl<sub>2</sub> was evaluated. The electrons in the ground state were carried out by full equilibrium geometry optimizations. The electronic properties of excited states were completely optimized deeply explored based on the ground-state molecular geometry. All theoretical calculations are carried out in the Gaussian 16 software package.<sup>39</sup> To approximately simulate the absorption spectrum, the Gaussian function acceptably consistent with the thermal broadening at the actual absorption spectra (0.10 eV was set as the line-broadening parameter) was adopted. To describe the excited states (Figure 5),<sup>40</sup> the natural transition orbitals (NTOs) are simulated by the TD-DFT method<sup>41</sup> and visualized by VMD software packages (the isovalue was set as 0.02).<sup>42</sup>

**Nonlinear Transmission Experiment.** The desired Ir(III) complexes were irradiated by a 532 nm Nd:YAG laser (Quantel Brilliant, 4.1 ns, 10 Hz) to evaluate their nonlinear absorption property. At 532 nm, the linear transmission of these samples in CH<sub>3</sub>CN was limited to 80%. The detailed experimental procedures have been described previously.<sup>43,44</sup> In this work, the measured beam radius of the focal point was approximately 97  $\mu$ m.

Synthesis of N^C^N-Type Ligands. Precursors 1–4 have recently been reported.<sup>28,45–48</sup> The fancy N^C^N-type ligands (structure shown in Scheme 1) 1,3-dimethyl-4,6-di(2-pyridinyl)-benzene (L1),<sup>28</sup> 1,3-difluoro-4,6-di(2-pyridinyl)-benzene (L2),<sup>28,49</sup> 1,3-difluoro-4,6-di(1-isoquinolyl)-benzene (L4),<sup>49</sup> and 1,3-di(1-isoquinolyl)-benzene (L5)<sup>30,49</sup> were synthesized according to the literature procedures.

1,3-Dimethoxy-4,6-phenyldiboronic Acid Bis(pinacol ester) **2**. A mixture of 1,3-dibromo-4,6-dimethoxybenzene (3.5 g, 11.83 mmol), bispinacolatodiboron (6.61 g, 26.02 mmol), AcOK (6.97 g, 70.96 mmol), and Pd(dppf)Cl<sub>2</sub> (0.44 g, 0.60 mmol) was degassed in 40 mL of dry DMF by bubbling N<sub>2</sub> for 15 min. Then, the mixture was tenderly stirred at 96 °C for 24 h. Once the ingredients have been completely consumed, the mixture was filtered promptly. The filtrate was gingerly extracted by EA and repeatedly washed with water. With the aid of anhydrous MgSO<sub>4</sub>, the black organic phase was dried, and the solvent was removed. White solid **2** (3.33 g, yield: 72.1%) was gained by silica-gel column chromatography ( $V_{Petroleum-ether}/V_{Ethyl-acetate} = 8/1$ ). <sup>1</sup>H NMR (400 MHz, chloroform-d)  $\delta$  7.83 (s, 1H), 6.42 (s, 1H), 3.89 (d, J = 25.1 Hz, 6H), 1.34 (s, 24H).

Ligand 1,3-Dimethoxy-4,6-di(1-isoquinolyl)-benzene (L3). 4,6-Dimethoxy-1,3-phenyldiboronic acid bis(pinacol ester) (1.7 g, 1.0 mmol), 1-chloroquinoline (1.5 g, 2.5 mmol), and Pd(pph<sub>3</sub>)<sub>4</sub> (0.25 g, 0.22 mmol) were placed in 48 mL of toluene and 16 mL of 2 M K<sub>2</sub>CO<sub>3</sub> aqueous solution by bubbling N<sub>2</sub> for 15 min. The intricate mixture was refluxed for 16 h. Once the ingredients have been completely consumed, the mixture was filtered promptly. The filtrate was gingerly extracted by DCM and repeatedly washed with water. With the aid of anhydrous MgSO<sub>4</sub>, the black organic phase was dried, and the solvent was removed. White solid L3 (1.27 g, yield: 74.5%) was gained by silica-gel column chromatography ( $V_{Petroleum-ether}/V_{Ethyl-acetate} = 1/1$ ). <sup>1</sup>H NMR (400 MHz, chloroform-d)  $\delta$  8.57 (d, J = 5.7 Hz, 2H), 7.89 (d, J = 8.5 Hz, 2H), 7.83 (d, J = 8.1 Hz, 2H), 7.65 (dd, J = 15.5, 6.7 Hz, 4H), 7.55–7.46 (m, 3H), 6.77 (s, 1H), 3.82 (s, 6H).

Ligand 6-Phenyl-2,2'-bipyridine Ligand (LO). 6-Bromo-2,2'bipyridine (4.0 g, 16.48 mmol), phenylboronic acid (2.47 g, 20.28 mmol), and Pd(pph<sub>3</sub>)<sub>4</sub> (0.95 g, 0.85 mmol) were placed in 90 mL of toluene and 30 mL of 2 M K<sub>2</sub>CO<sub>3</sub> aqueous solution by bubbling N<sub>2</sub> for 15 min. The refluxed mixture was gently stirred for 12 h. Once the ingredients have been completely consumed, the mixture was filtered promptly. The filtrate was gingerly extracted by DCM and repeatedly washed with water. With the aid of anhydrous MgSO4, the black organic phase was dried, and the solvent was removed. White solid L0 (3.15 g, yield: 82.3%) was gained by silica-gel column chromatography ( $V_{\text{Petroleum-ether}}/V_{\text{Ethyl-acetate}} = 1/1$ ). <sup>1</sup>H NMR (400 MHz, chloroform-d)  $\delta$  8.73–8.68 (m, 1H), 8.65 (d, J = 8.0 Hz, 1H), 8.38 (dd, J = 7.8, 0.8 Hz, 1H), 8.16 (dd, J = 5.3, 3.3 Hz, 2H), 7.90 (t, J =7.8 Hz, 1H), 7.88-7.83 (m, 1H), 7.78 (dd, J = 7.8, 0.9 Hz, 1H), 7.55-7.49 (m, 2H), 7.45 (ddd, J = 7.3, 3.7, 1.3 Hz, 1H), 7.33 (ddd, J = 7.5, 4.8, 1.2 Hz, 1H).

General Synthesis Route for the Desired Ir(III) Complexes. Combining the previous work by Williams et al., N<sup>A</sup>C<sup>A</sup>N-type ligands L1-L5 (1.0 mmol) and IrCl<sub>3</sub>·3H<sub>2</sub>O (1.02 mmol) were placed in 90 mL of 2-methoxy ethanol and 30 mL of deionized water. The mixture was degassed continuously by N<sub>2</sub> and tenderly refluxed for 24 h. Once the ingredients have been completely consumed, the mixture is filtered promptly. A mass of precipitated solid was gathered, rinsed by EtOH, and dried systematically. Chloro-bridged iridium dimeric complexes D1-D5 were obtained and directly used without further purification.<sup>19,26</sup> The chloro-bridged Ir(III) dimeric complex (1.0 mmol), ligand L0 (2.20 mmol), and silver trifluoromethanesulfonate (4.8 mmol) were placed in 100 mL of degassed ethylene glycol under N2. The assortments were blended seamlessly at 30 °C for 1 h and then refluxed overnight. Once the ingredients have been completely consumed, the isopyknic KPF<sub>6</sub> aqueous solution was blended seamlessly for 11 h under ambient temperatures. The assortments were gingerly extracted by DCM and repeatedly washed by deionized water. With the aid of anhydrous MgSO<sub>4</sub>, the chromatic organic phase was dried, and the solvent was removed. Desired complexes Ir1-Ir5 were purified from silica-gel column chromatography  $(V_{
m Dichloromethane}/$  $V_{\text{Methanol}} = 100/1$ ).

Complex *Ir1*. Orange solid (yield: 56.3%). <sup>1</sup>H NMR (400 MHz, dimethyl sulfoxide- $d_6$ )  $\delta$  8.85–8.74 (m, 2H), 8.59 (d, J = 8.2 Hz, 1H), 8.39 (t, J = 8.1 Hz, 1H), 8.23 (d, J = 8.4 Hz, 2H), 8.10 (t, J = 7.9 Hz, 1H), 7.91 (d, J = 7.1 Hz, 1H), 7.87–7.77 (m, 2H), 7.48 (dd, J = 10.1, 5.1 Hz, 3H), 7.39–7.33 (m, 1H), 7.18 (s, 1H), 6.98 (t, J = 6.1 Hz, 2H), 6.83 (t, J = 8.0 Hz, 1H), 6.62 (td, J = 7.4, 1.1 Hz, 1H), 5.78 (d, J = 7.5 Hz, 1H), 2.92 (s, 6H). ESI-HRMS (m/z): calcd for [C<sub>34</sub>H<sub>26</sub>N<sub>4</sub>Ir]<sup>+</sup>, 683.17812. Found 683.17883.

*Complex Ir2.* Yellow solid (yield: 52.1%). <sup>1</sup>H NMR (400 MHz, dimethyl sulfoxide- $d_6$ )  $\delta$  8.88–8.75 (m, 2H), 8.60 (d, J = 8.0 Hz, 1H), 8.42 (t, J = 8.0 Hz, 1H), 8.19 (d, J = 8.2 Hz, 2H), 8.12 (t, J = 7.9 Hz, 1H), 7.91 (t, J = 8.0 Hz, 3H), 7.67 (d, J = 5.2 Hz, 1H), 7.56 (d, J = 5.5 Hz, 2H), 7.39 (dt, J = 12.9, 9.4 Hz, 2H), 7.07 (t, J = 6.6 Hz, 2H), 6.87 (t, J = 7.5 Hz, 1H), 6.67 (t, J = 7.3 Hz, 1H), 5.82 (d, J = 7.4 Hz, 1H). <sup>19</sup>F NMR (377 MHz, dimethyl sulfoxide- $d_6$ ):  $\delta$  68.99 (s, 1F), 70.88 (s, 1F). ESI-HRMS (m/z): calcd for [ $C_{32}H_{20}F_2N_4Ir$ ]<sup>+</sup>, 691.12798. Found, 691.12799.

*Complex Ir3.* Red solid (yield: 62.3%). <sup>1</sup>H NMR (400 MHz, dimethyl sulfoxide- $d_6$ )  $\delta$  8.81 (dd, J = 8.0, 4.5 Hz, 2H), 8.64 (t, J = 7.8 Hz, 3H), 8.42 (t, J = 8.1 Hz, 1H), 8.06 (t, J = 7.9 Hz, 1H), 7.92 (d, J = 7.7 Hz, 1H), 7.84 (d, J = 7.6 Hz, 2H), 7.75 (td, J = 13.7, 6.4 Hz, 4H), 7.52 (d, J = 5.1 Hz, 1H), 7.35 (d, J = 6.4 Hz, 2H), 7.32–7.28 (m, 1H), 7.16 (d, J = 6.3 Hz, 2H), 6.93 (s, 1H), 6.82 (t, J = 7.5 Hz, 1H), 6.59 (t, J = 7.4 Hz, 1H), 5.79 (d, J = 7.5 Hz, 1H), 4.22 (s, 6H). ESI-HRMS (m/z): calcd [ $C_{42}H_{30}IrN_4O_2$ ]<sup>+</sup>, 815.19925. Found, 815.19910.

Complex Ir4. Orange solid (yield: 63.4%). <sup>1</sup>H NMR (400 MHz, dimethyl sulfoxide- $d_6$ )  $\delta$  8.86 (dd, J = 11.0, 8.1 Hz, 2H), 8.68 (d, J = 8.1 Hz, 3H), 8.50 (t, J = 8.1 Hz, 1H), 8.09 (td, J = 8.0, 1.5 Hz, 1H), 8.04–7.98 (m, 2H), 7.96 (d, J = 6.9 Hz, 1H), 7.94–7.84 (m, 4H), 7.66–7.52 (m, 4H), 7.42 (d, J = 6.4 Hz, 2H), 7.32–7.25 (m, 1H), 6.84 (t, J = 7.1 Hz, 1H), 6.61 (t, J = 7.4 Hz, 1H), 5.57 (d, J = 6.8 Hz,

#### Scheme 2. Synthesis Routes for Complexes Ir1-Ir5



1H). <sup>19</sup>F NMR (377 MHz, dimethyl sulfoxide- $d_6$ ):  $\delta$  69.05 (s, 1F), 70.93 (s, 1F). ESI-HRMS (m/z): calcd for  $[C_{40}H_{24}F_2N_4Ir]^+$ , 791.15928. Found, 791.15912.

*Complex Ir5.* Orange solid (yield: 64.2%). <sup>1</sup>H NMR (400 MHz, dimethyl sulfoxide- $d_6$ )  $\delta$  9.34 (d, J = 8.6 Hz, 2H), 9.00 (d, J = 8.1 Hz, 2H), 8.86 (dd, J = 12.9, 8.1 Hz, 2H), 8.68 (d, J = 8.2 Hz, 1H), 8.48 (t, J = 8.1 Hz, 1H), 8.07 (td, J = 8.0, 1.5 Hz, 1H), 8.01 (d, J = 8.1 Hz, 2H), 7.99–7.85 (m, 5H), 7.79 (t, J = 8.0 Hz, 1H), 7.51 (d, J = 6.5 Hz, 2H), 7.42 (t, J = 6.1 Hz, 3H), 7.28–7.23 (m, 1H), 6.83–6.77 (m, 1H), 6.52 (td, J = 7.5, 1.2 Hz, 1H), 5.50 (d, J = 6.7 Hz, 1H). ESI-HRMS (m/z): calcd for [ $C_{40}H_{26}N_4Ir$ ]<sup>+</sup>, 755.17812. Found, 755.17816.

# RESULTS AND DISCUSSION

Synthesis and Characterization. The precise synthesis pathways for N<sup>^</sup>C<sup>^</sup>N-types ligands L1-L5, N<sup>^</sup>N<sup>^</sup>C-type ligand L0, and bis-tridentate Ir(III) complexes Ir1-Ir5 are presented in Scheme 2. The synthesis method of ligands L1 and L2 is a representative Still cross-coupling reaction catalyzed by palladium.<sup>28</sup> Ligands L3-L5 and L0 are successfully synthesized supported by the mechanism of the Suzuki reaction.<sup>49</sup> Corresponding octahedral Ir(III) complexes Ir1-Ir5 are precisely prepared with a typical two-step synthesis strategy. Cyclometalating tridentate N^C^N-type ligands L1-L5 were treated with IrCl<sub>3</sub>·3H<sub>2</sub>O to form highly purified  $[Ir(N^{C^{N}}N)Cl(\mu-Cl)]_{2}$  D1–D5. Without purification of preceding chloro-bridged complexes, the intermediates with L0 ligand in refluxing ethylene glycol coordinate to get the heteroleptic product (Ir1-Ir5). This two-step methodology is often distributed below gentle conditions, and the yields are also moderate. All complexes show good solubility in THF, CH<sub>2</sub>Cl<sub>2</sub>, CH<sub>3</sub>CN, toluene, and DMSO. <sup>1</sup>H NMR, <sup>19</sup>F NMR, and HRMS determined the geometrical structures of obtained Ir(III) complexes.

**Crystallography.** The crystal structures of complexes **Ir1**, **Ir3**, and **Ir4** ensure the existence of two tridentate chelates organized within the orthometric bonding mode (Figure 2a). The crystallographic data are summarized in detail in Table S1. The pivotal bond lengths and angles are compiled in Tables S2–S4. They correspond with those of other related bistridentate Ir(III) complexes.<sup>50–53</sup>

Figure 2a clearly indicates that  $Ir^{3+}$  is octahedrally surrounded by one N<sup>C</sup>C<sup>N</sup>-type ligand and one N<sup>A</sup>N<sup>C</sup>-type ligand (L0). Ligands L0 of complexes Ir1, Ir3, and Ir4 were approximately coplanar (a dihedral angle of 175.484, 175.540, and 177.213°, respectively) with the central iridium ion. However, the N<sup>C</sup>A<sup>N</sup>-type ligands of complexes Ir1, Ir3, and Ir4 were twisted out of the central Ir ion with a dihedral angle of 156.307, 159.822, and 160.635°, respectively. The cyclometalating tridentate ligands of both complexes exhibit short Ir–C distances for the central phenyl of N<sup>C</sup>A<sup>N</sup>-type ligand and terminal phenyl of N<sup>A</sup>C-type ligand (cf. Ir1–C(13\_2) = 1.9826 Å and Ir1–C(34\_2) = 2.0556 Å for Ir1, Ir–C(5) = 1.9409 Å and Ir–C(42) = 2.0210 Å for Ir3; Ir–C(15) = 1.9251 Å and Ir–C(25) = 2.0310 Å for Ir4).

As the N<sup>C</sup>/N-type ligand of complex Ir1 (coordinated with 1,3-di(2-pyridinyl)-benzene) is different from that of the other two complexes (Ir3 and Ir4, coordinated with 1,3-di(1-isoquinolyl)-benzene), this results in the unique crystal system of complex Ir1 (triclinic, the crystal system of Ir3 and Ir4 is monoclinic). On account of the differences in the way molecules are stacked, this chemical phenomenon appears. For complex Ir1, packing between two molecules is achieved



Figure 2. (a) Crystal structures of Ir1, Ir3, and Ir4. (b-d) Crystal packing modes of Ir1, Ir3, and Ir4, respectively. For clarity, the solvent and hydrogens are omitted.

by the interaction of a pyridine ring on the N^C^N-type ligand of one molecule with a benzene ring on the N^N^C-type ligand of the other (Figure 2b). In contrast, the accumulation of complexes Ir3 and Ir4 is caused by the interaction of isoquinoline rings on the N^C^N-type ligand between two molecules (Figure 2c,d). All complexes have adequate  $\pi-\pi$ stacking distances (Ir1: 3.3501 Å; Ir3: 3.3251 Å; Ir4: 3.5515 Å). According to the value of the stacking distance, bistridentate Ir (III) complexes modified by electron-donating groups show shorter distances (Ir1 with  $-CH_3$  and Ir3 with  $-OCH_3$ ). The different  $\pi$ -conjugation and the electronic properties of substituents of the N^C^N-type ligands in the Ir(III) complexes lead to the different stacking modes and distances.

Electronic Absorption. Figure 3a,b visually includes the theoretical simulated and experimental UV-vis absorption spectra of complexes Ir1-Ir5 in dichloromethane. The related parameters were summarized in Table 1. Although there are differences between the calculated absorption bands and the experimental results, the overall trend is consistent. In the 220-330 nm range, the most vital absorption should be put down to  $\pi - \pi^*$  transitions induced by  $\pi$ -conjugated ligands. It is also compatible with the largest  $\varepsilon$  values and the feeble solvatochromic effect presented in Figure S11. The spectra of all complexes vary significantly due to the different functional N<sup>^</sup>C<sup>^</sup>N-type ligands. A notable difference between complexes Ir1, Ir2, and complexes Ir3, Ir4 is the change of molar extinction coefficients at ≤330 nm, which must be associated with introducing isoquinoline units in place of the pyridine ring.<sup>27</sup> In terms of the moderate absorption around 330–450 nm, it belonged to the representative spin-allowed CT (<sup>1</sup>LLCT/<sup>1</sup>MLCT) transitions mixed with sectional  $\pi - \pi^*$  state.<sup>27,17,18,22,23,54,55</sup> The relatively weak bands over 450 nm come down to typical <sup>3</sup>MLCT and partial  ${}^{3}\pi-\pi^{*}$  state regarding the other reported Ir(III) complexes.<sup>18,22,32,54</sup> The assignment for the absorption band is supported by the NTOs listed in Figure 5 and Table S5. Compared with complex Ir1 bearing a methylated N<sup>^</sup>C<sup>^</sup>N-type ligand (L1 with the electron-donating  $-CH_3$  groups), it is indicated that the blue-shifted <sup>1</sup>MLCT transition emerges in fluorinated complex Ir2. This result is also confirmed by complexes Ir3  $(-OCH_3)$ and Ir4 (-F) bearing the opposite electronegative groups. At the same time, complex Ir5 bearing a larger  $\pi$ -conjugated N<sup>^</sup>C<sup>^</sup>N-type isoquinolinated ligand (L5) displays the most red-shifted <sup>1</sup>MLCT band due to the smallest energy gap ( $\Delta E_{\sigma}$ ) between HOMO and LUMO.

**Photoluminescence.** Figure 3c is the normalized emission spectra for Ir1–Ir5, which are powerfully plagued by the modificatory N<sup>C</sup>N-type ligands. The degassed solvents with different polarities influence the excited-state characteristics (Figure S12). The corresponding parameters turn up in Tables 1 and 2. The emission bands presented in Figures 3b and S12 are wide and structureless. Given the minor solvatochromic effects in Figure S12, the prevailing  ${}^{3}\pi - \pi^{*}$  states induced by  $\pi$ -conjugated ligands with lesser  ${}^{3}MLCT/{}^{3}LLCT$  characters were ascribed to the root of the emitting-states for Ir1–Ir5.



Figure 3. (a) Calculated and (b) experimental ( $c = 1.0 \times 10^{-5}$  M) UV-vis absorption spectra for Ir1-Ir5 at ambient temperature in methylene chloride. The interposed spectra in (b) represent the magnifying absorption at 550-800 nm. (c) Normalized emission spectrum ( $c = 1.0 \times 10^{-5}$  M) for Ir1-Ir5 at ambient temperature in deoxy methylene chloride.

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# Table 1. Experimental Photophysical Parameters of Ground and Excited State for Ir1-Ir5

	abs $\lambda$ [nm] ( $\varepsilon \times 10^4$ L mol <sup>-1</sup> cm <sup>-1</sup> ) <sup><i>a</i></sup>	em $\lambda_{\max}$ [nm] $(\tau/ns; \Phi)^b$	$\lambda_{\text{T1-T}n}/\text{nm} (\tau_{\text{T}}/\text{ns}; \epsilon_{\text{T}} \times 0^4 \cdot \text{L} \cdot \text{mol}^{-1} \text{ cm}^{-1}; \Phi_{\text{T}})^c$
Ir1	231 (5.16), 269 (4.17), 288 (3.65), 368 (1.14), 413 (1.16), 481 (0.09)	608 (72; 0.25)	455(76, -, -), 555(69, -, -) <sup>d</sup>
Ir2	235 (6.14), 269(4.50), 311 (2.28), 333 (1.62), 390 (1.33), 459 (0.13)	557 (191; 0.31)	$420(185, -, -), 530(177, -, -)^d$
Ir3	229 (9.96), 267 (6.14), 317 (4.63), 427 (2.04)	603 (367; 0.22)	500(324, 2.80, 0.35)
Ir4	230 (8.07), 265 (7.56), 305 (3.62), 330 (2.72), 387 (1.28), 438 (1.94)	585 (425; 0.38)	495(392, 3.23, 0.28)
Ir5	228 (5.32), 262 (4.24), 307 (2.10), 465 (1.09)	584 (341; 0.44)	520(300, 1.69, 0.17)

"Absorption spectra were recorded in dichloromethane at indoor temperature. <sup>b</sup>Emission spectra were recorded in deoxy methylene chloride at ambient temperature. <sup>c</sup>TA spectra were recorded in deoxy acetonitrile at ambient temperature. <sup>d</sup>The  $\varepsilon_{T}$  values can be reckoned due to the lack of bleaching bands in the TA spectrum.

# Table 2. Emission Data in Different Solvents at Room Temperature for Bis-tridentate Ir(III) Complexes Ir1–Ir5

$\lambda_{ m em}/ m nm~(\Phi_{ m em})^a$						
	toluene	THF	DCM	CH <sub>3</sub> CN		
Ir1	608 (0.27)	604 (0.32)	599 (0.37)	608 (0.25)		
Ir2	554 (0.31)	559 (0.35)	551 (0.41)	557 (0.31)		
Ir3	603 (0.26)	602 (0.36)	601 (0.37)	603 (0.22)		
Ir4	587 (0.34)	585 (0.49)	582 (0.52)	585 (0.38)		
Ir5	588 (0.24)	584 (0.66)	583 (0.61)	584 (0.44)		
0	orr . 1. m	1 ()	( )			

<sup>*a*</sup>The QY in different solvents ( $\lambda_{ex} = 436$  nm) was evaluated in a scientifically relative actinometry method.

On the basis of what happens on the emission spectrum, the emissive characters of Ir1-Ir5 were deeply affected by the different electronegative groups at the fourth and sixth position of fluorinated Ir(III) complex Ir2 demonstrated the vast majority blue-shifted emanation. Replacement of the fluorinated N^C^N-type ligands (L2 in Ir2, L4 in Ir4) with methylated and methoxy-based ligands (L1 in Ir1 and L3 in Ir3, severally) red-shifts the maximum emission peaks in a breeze. Furthermore, the complexes Ir1 and Ir3 respectively bearing an electron-donating substituent ( $-CH_3$ ,  $-OCH_3$ ) exhibit a faintly bathochromic-shifted emission compared to those of fluorinated complexes Ir2 and Ir4. As vividly shown in Figure S12, the emission of all complexes exhibits a slight negative solvatochromic effect due to the stronger MLCT

transition mingled with  $\pi - \pi^*$ . Isoquinolinated Ir(III) complexes Ir3–Ir5 portrayed the generation of the prevailing  $\pi - \pi^*$  emissive state. The large  $\pi$ -conjugated N<sup>C</sup>N-type ligands decrease the  $\pi - \pi^*$  transition energies and red-shift the emission peaks.<sup>54</sup> Compared with Ir2, the emission of Ir4 was bathochromically shifted and with an apparent charge-transfer process. Such an effect in extending the  $\pi$ -conjugation has been observed for many luminescent Ir(III), <sup>17,18,49,54,59</sup> and Pt(II)<sup>49</sup> metal complexes.

**Theoretical Calculation.** To intuitively perceive the photophysical properties of complexes Ir1–Ir5, DFT and TD-DFT calculations were accomplished in dichloromethane. Remarkably, the geometries of Ir1, Ir3, and Ir4 were described in the light of their X-ray structural data, while Ir2 and Ir5 were optimized based on the closely related Ir(III) complexes Ir1 and Ir3, respectively. The computational methods were described in the Experimental Section.

Figure 4 demonstrated that the lowest unoccupied molecular orbitals (LUMOs) are nearly distributed in L0 (N^N^C-type ligand) for all the complexes. The highest occupied molecular orbitals (HOMOs) are primarily delocalized on the 1,3-di(2-pyridinyl)-benzene or 1,3-di(1-isoquinolyl)-benzene ligand (N^C^N-type ligands) admixed with orbitals from the metallic element. Compared with Ir2, introducing the electron-donating groups and extending the  $\pi$ -conjugation can obviously reduce the value of energy gap ( $\Delta E_g$ ) and increase the value of HOMO. Unlike complexes Ir1 and Ir2 modified



Figure 4. Calculated molecular structures, orbits, and HOMO-LUMO energy levels of titled Ir(III) complexes Ir1-Ir5 (Figures S13-S17 list all orbitals that were calculated).

Table 3. Excitation Energies (eV), Wavelengths (nm), Oscillator Strengths (f), and Dominant Contributing Configurations of the Lowest Singlet and Triplet Excited States for the Optimized Ground-State Geometries of Ir(III) Complexes Ir1–Ir5 in Methylene Dichloride<sup>a</sup>

	state	excitation energies (eV)	$\lambda$ (nm)	f	orbital contribution (>20%)	prominent assignment
T <sub>m</sub> 1	$S_1$	2.177	569	0.0041	HOMO to LUMO (98%)	MLCT, LLCT, ILCT, MC
111	$T_1$	2.029	611	0	HOMO to LUMO (83%)	MLCT, LLCT, ILCT, MC
1.0	$S_1$	2.325	533	0.0089	HOMO to LUMO (98%)	MLCT, LLCT, ILCT, MC
Ir2	$T_1$	2.054	604	0	HOMO to LUMO (81%)	MLCT, LLCT, ILCT, MC
I2	$S_1$	1.737	714	0.0084	HOMO to LUMO (93%)	MLCT, LLCT, ILCT, MC
Ir3	$T_1$	1.551	799	0	HOMO to LUMO (85%)	MLCT, LLCT, ILCT, MC
T=4	$S_1$	2.335	531	0.0083	HOMO to LUMO (97%)	MLCT, LLCT, ILCT, MC
114	$T_1$	2.057	603	0	HOMO to LUMO (78%)	MLCT, LLCT, ILCT, MC
Tť	$S_1$	2.252	551	0.0069	HOMO to LUMO (97%)	MLCT, LLCT, ILCT, MC
Irs	$T_1$	2.046	606	0	HOMO to LUMO (79%)	MLCT, LLCT, ILCT, MC
$^{a}$ Table S5 lists all charge characters and MO transition that were calculated.						

with 1,3-di(2-pyridinyl)-benzene ligand, the HOMO levels of Ir3, Ir4, and Ir5 (modified with larger  $\pi$ -conjugated N<sup>A</sup>C<sup>A</sup>N-type ligand) are mainly distributed on one of the isoquinolines, the central benzene ring, and the metal. Upon enlarging  $\pi$ -conjugation by replacing pyridinyl units with isoquinolinyl units in N<sup>A</sup>C<sup>A</sup>N-type ligands (L1 and L2 vs L3–L5), the results significantly indicate a less contribution to HOMO by the isoquinoline moieties of L3–L5 chelate. As we all tend to acknowledge, this phenomenon suggested that the energy of  $\pi$ -bonding orbital increase and  $\pi^*$  antibonding orbital energy decrease, due to the extending of  $\pi$ -conjugation by introducing isoquinolinyl unit. Consequently, the energy gap of  $\pi$ – $\pi^*$  and MLCT transition, and the absorption/emission band, considerably red-shift (compared Ir4 with Ir2).<sup>54</sup>

The essential parameters for Ir1-Ir5 are presented in Tables 2 and S5. The important frontier MOs (11 HOMOs and 11 LUMOs) of Ir1-Ir5 are illustrated in Figures S13-S17. The results showed that  $S_0 \rightarrow S_1$  and  $S_0 \rightarrow T_1$  transitions (HOMO  $\rightarrow$  LUMO) made dominant contributions to the excited states (Table 3). The calculated excitation energies are closely related to the experimental values. This indicates that the TD-DFT methodology in this work is suitable for predicting the lowest Franck-Condon transition based on the optimized geometry structures of desired complexes Ir1-Ir5 in the S<sub>0</sub> and T<sub>1</sub> states.<sup>50,55,57</sup> What should be paid attention to is that the excitation energy's unique localization/ delocalization properties of the exciting wave function will affect the measuring precision.<sup>14</sup> The dramatic difference of the absorption wavelength might be related to the  $\pi$ -electronaccepting ability of the modified groups at the fourth and sixth positions of the central ring in N<sup>^</sup>C<sup>^</sup>N-type ligand, thereby leading to the unique absorption behavior of the abovementioned Ir(III) complex.<sup>60</sup> Given the electron cloud distributions of the HOMOs and LUMOs for these complexes, the electronic excitation between the  $S_0$  and  $T_1$  states is primarily from HOMO to LUMO. All the complexes in the T<sub>1</sub> state presented a mixed MLCT  $(d\pi(Ir) \rightarrow \pi^*(N^N^C)/$  $(N^{\wedge}C^{\wedge}N))$ , LLCT  $(\pi(N^{\wedge}C^{\wedge}N) \rightarrow \pi^{*}(N^{\wedge}N^{\wedge}C))$ , ILCT, and slightly MC transition characters.

In Figure 5, the NTOs at the T<sub>1</sub> states for Ir1 and Ir2 revealed that the electrons and holes have predominantly emerged in the N<sup>^</sup>N<sup>^</sup>C-type ligands and d-orbitals of Ir<sup>3+</sup>. Interestingly, the electrons and holes for Ir3–Ir5 are mainly found in the N<sup>^</sup>N<sup>^</sup>C-type ligands and d-orbitals of Ir<sup>3+</sup>. As a whole, the emissive states for Ir1 and Ir2 can be ascribed to a  ${}^{3}\pi-\pi^{*}$  state derived from the N<sup>^</sup>N<sup>^</sup>C-type ligand (L0) with



**Figure 5.** Natural transition orbitals (NTOs) of  $S_1-S_3$  and  $T_1-T_3$  states for the titled Ir(III) complexes Ir1–Ir5. (Green represents electrons, blue represents holes.)

partial <sup>3</sup>MLCT  $(d\pi(Ir) \rightarrow \pi^*(N^{\Lambda}N^{\Lambda}C))/{}^{3}LLCT$  characters. The emissive characters for Ir3–Ir5 are  ${}^{3}\pi-\pi^*$  state, coming from the N^C^N-type ligands (L3–L5) with <sup>3</sup>MLCT  $(d\pi(Ir) \rightarrow \pi^*(N^{\Lambda}C^{\Lambda}N))/{}^{3}LLCT$  character.<sup>14</sup>

**Transient Absorption (TA).** In Figure 6a-e, nanosecond TA spectra for desired complexes Ir1-Ir5 bearing functionalized N<sup>C</sup>N-type ligands were carried out in degassed acetonitrile to meticulously explore the characters at triplet excited-state. The related parameters are compiled in Table 1.

The character of TA spectra for the titled complexes can be identified without difficulty. Between the visible and near-IR regions, **Ir1–Ir5** show relatively broad and positive absorption bands (i.e., 380–800 nm for **Ir1** and **Ir2**, 455–800 nm for **Ir3** and **Ir4**, and 480–800 nm for **Ir5**). The spectra of **Ir3–Ir5** feature a bleaching band at 425 nm for **Ir3**, 430 nm for **Ir4**, and 460 nm for **Ir5**. These bleaching bands are essentially related to the <sup>1</sup>CT absorption bands in the respective GSA



**Figure 6.** (a–e) Time-dependent and (f) zero-time TA spectrum and of Ir1–Ir5 in deoxy acetonitrile, respectively.  $\lambda_{ex} = 355$  nm;  $A_{355} = 0.4$  in a 1 cm cuvette.



Figure 7. (a) Output versus incident energy density for Ir1-Ir5 in deoxy acetonitrile for 4.1 ns laser pulses at 532 nm. (b) Schematic diagrams for OPL effect of bis-tridentate Ir(III) complexes based on RSA mechanism.

(Figure 3a). Ir1,Ir2 and Ir5,Ir3/4 show similar absorption peak shapes and triplet lifetimes according to the TA spectra. Therefore, the excited states concluded in this part and the emissive state were of the same ancestry. Considering these features, the origin of the observed TA excited state for Ir1–Ir5 can be resolved into  ${}^{3}\pi - \pi^{*}/{}^{3}$ CT state.

In contrast, the intensity and maximum absorption peak of TA and related parameters ( $\tau_{\rm T}$ ,  $\varepsilon_{\rm T}$ , and  $\Phi_{\rm T}$ ) for Ir(III) complexes in question are dramatically influenced by the attached substituents on the N<sup>A</sup>C<sup>A</sup>N-type ligands. In contrast

to Ir5 (515 nm), the TA peak of Ir4 (i.e., 495 nm) showed a blue-shifting trend. Under the influence of the charge-transfer character at  $T_1$  states, -F substituents attached in the N<sup>C</sup>Ntype ligands (compared Ir2 with Ir1, Ir4 with Ir3 and Ir5) can efficaciously prolong the triplet lifetime. In the same way, the characters as mentioned earlier, are also affected deeply by the inductive effect and conjugated effect that occurred in the modified N<sup>C</sup>N-type ligands. Ir1 and Ir2 lack the groundstate bleach at 440 nm, which dramatically differs from Ir3– Ir5. Moreover, the lifetimes measured by the time-resolved TA spectrum are about half as long as Ir3–Ir5 as that with the larger  $\pi$ -conjugation. These characteristics support that the absorbing excited state of Ir3–Ir5 partly originates from a  ${}^{3}\pi-\pi^{*}$  state, likely localized on isoquinoline units.

**Nonlinear Absorption and Mechanism.** When it comes to the broad and positive TA absorption bands, Ir1–Ir5 all exhibit stronger ESA for the GSA (Figure 6f). For these welldesigned complexes, the RSA process can occur in this region. Considering the prerequisites for triggering RSA effects, optical power limiting (OPL) response for Ir1–Ir5 can occur. The desired bis-tridentate Ir(III) complexes were irradiated by a S32 nm Nd:YAG laser through the normative nonlinear transmission experiment to evaluate the OPL response.<sup>1,43,44,61</sup> Figure 7a demonstrated that all complexes could exhibit a remarkable NLA-response-based RSA process. With the increasing energy of the incident laser, the output energy density has a nonlinear decline. The strength of the OPL response follows the trend Ir3 > Ir5 > Ir4 ≈ Ir1 > Ir2, with Ir3 exhibiting the most potent RSA effect.

Complexes Ir3, Ir4, and Ir5 with larger  $\pi$ -conjugated N<sup>C</sup>/N-type ligands displayed a more robust OPL responses than those of Ir1 and Ir2. Ir2 with strongly electron-withdrawing -F groups exhibited the worst NLA response. Influenced by intramolecular charge-transfer transition, the GSA of Ir4 and Ir5 at 532 nm is drastically increased. Hence, compared with Ir4 and Ir5, Ir3 presented the best NLA response in this work. As we know, the quantitative relation of the ESA cross section with the GSA cross section ( $\sigma_{ex}/\sigma_0$ ) is the most important factor to verdict the strength of RSA. In Table 4, complexes Ir3-Ir5 possess larger  $\sigma_{ex}$  values at 532

Table 4. GSA ( $\sigma_0$ ) and ESA ( $\sigma_{ex}$ ) Cross Sections of Complexes Ir1–Ir5 in Deoxy Acetonitrile at 532 nm<sup>*a*</sup>

	Ir1	Ir2	Ir3	Ir4	Ir5
$\sigma_0/10^{-19}~{ m cm}^2$	7.64	3.82	26.74	15.28	38.20
$\sigma_{\mathrm{ex}}/10^{-19}~\mathrm{cm}^2$	Ь	Ь	78.27	33.78	110.78
$\sigma_{ m ex}/\sigma_0$	ь	Ь	2.93	2.21	2.90
$\Phi_{ m T}\sigma_{ m ex}/\sigma_0$	Ь	Ь	1.02	0.63	0.49

<sup>*a*</sup>σ = 2303ε/N<sub>A</sub>. In the equation, N<sub>A</sub> represents Avogadro's constant. For σ<sub>0</sub>, ε is from UV–vis absorption spectra. For σ<sub>ev</sub> ε is ε<sub>T</sub> from the TA spectrum. <sup>*b*</sup>Cannot be calculated due to lack of bleaching bands in the TA spectrum.

nm. Although the  $\sigma_{\rm ex}$  value of Ir5 is the largest, the enormous  $\sigma_0$  value counteracts the strong ESA. Therefore, the RSA effect of Ir5 is significantly suppressed. Fortunately, large  $\pi$ -conjugated bis-tridentate Ir(III) complexes exhibit better RSA, which Ir2 and Ir4 elucidate. However, the RSA effects for  $-{\rm CH}_3$  and  $-{\rm OCH}_3$  modified bis-tridentate Ir(III) complexes is much stronger than those for  $-{\rm F}$  modified complexes (compared Ir1 with Ir2, compared Ir3 with Ir4). This means that attaching electron-donating units in these titled Ir(III) complexes can efficiently enhance the RSA effect. In this work, Ir3 and Ir5 are good candidates for nonlinear optical absorbers due to the ideal RSA effect and long-lived lifetimes.

On the basis of the above analysis and discussion, a possible mechanism for RSA processes has schemed provisionally in Figure 7b. Under 532 nm laser excitation, the above-mentioned Ir(III) complexes, Ir1-Ir5, at the  $S_0$  state took in optical energy and was excited to the  $S_1$  state. Then, the molecules absorbed optical energy energetically and were

excited to a higher singlet state  $(S_n)$  to induce the OPL effect or undergo heavy-atom-effect-induced ISC to the first triplet state  $(T_1)$ . As Ir (III) complexes accumulate in a certain amount in the  $T_1$  state, the more optical energy they absorb, and the higher the triplet state  $(T_n)$  they reach. An efficient NLA response was produced based on the RSA process that depends on strong ESA.

# CONCLUSIONS

Five bis-tridentate Ir(III) complexes with NLA properties were investigated profoundly by chromatographic and crystallographic methods. The differences in photophysical characteristics induced by introducing electron-donating/-withdrawing substituents and expanding  $\pi$ -conjugated systems at the N<sup>^</sup>C<sup>^</sup>N-type ligands were discussed. These obtained bistridentate Ir(III) complexes show weak and broadband GSA to the NIR region and the broadly strong triplet ESA. Notably, the large  $\pi$ -conjugated N<sup>A</sup>C<sup>A</sup>N-type ligands can endow complexes with a significant redshift of  $^{1,3}MLCT/^3\pi-\pi^*$ bands of complexes Ir3-Ir5 between 430 and 600 nm in comparison to those of complexes Ir1 and Ir2 without the larger  $\pi$ -conjugated ligands. The result of theoretical calculation demonstrated that the emitting state of all titled Ir(III) complexes show mixed MLCT, LLCT ( $\pi$ (N<sup> $\wedge$ </sup>C<sup> $\wedge$ </sup>N)  $\rightarrow$  $\pi^*(N^N^C)$ , ILCT, and slightly MC transition character. The experimental results agree well with the calculated results. All complexes possess broadband  ${}^{3}\pi - \pi^{*/3}$ MLCT ESA. On account of the strong ESA, all complexes exhibit a strong NLA response, which follows the descending order Ir3 > Ir5 >Ir4  $\approx$  Ir1 > Ir2. In consideration of their much broader GSA and stronger ESA at 532 nm, larger  $\pi$ -conjugated Ir3 and Ir5 manifested a much stronger RSA. Therefore, these Ir(III) complexes with neoteric bis-tridentate configuration are stateof-the-art and potentially broadband OPL materials with more exciting work to come.

#### ASSOCIATED CONTENT

#### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.1c01142.

<sup>1</sup>H NMR spectra; HRMS; crystallographic data; Absorption and emission spectrum in differentiated polar solvents; DFT and TD-DFT results (PDF)

# **Accession Codes**

CCDC 1846057, 1846058, and 1847634 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.

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