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# Understanding Mechanochromic Luminescence on Account of Molecular Level Based on Phosphorescent Iridium(III) Complex Isomers

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ABSTRACT: Mechanochromic luminescent (MCL) materials are promising in pressure sensors, security papers, photoelectric devices and optical data recording. Although some kinds of MCL-active iridium(III) complexes with various soft substituent functional ligands (e.g., dendritic carbazole, flexible chains, and Schiff base ligands) were reported, the MCL mechanism is still not clear and mainly ascribes to the physical phase transformations from crystalline state to amorphous state in response to force stimulus at present stage, and deserves further study in order to obtain more intelligent MCL materials. Herein, two new iridium(III) complex isomers are tactfully constructed and show distinctly opposite MCL



properties in spite of the same physical phase transformations happening on them. The absolutely out of the ordinary MCL mechanism has been presented on account of molecular level for the first time via the comparative study of photophysical properties based on isomers 1 and 2 with the help of crystal structure analysis, room/low temperature emission spectra, NMR, PXRD, and TD-DFT calculations. All of these results suggest that the emitting state dominated by the triplet charge transfer excited state ( ${}^{3}CT$ ) plays a key role in achieving mechanochromic luminescence in iridium(III) complex systems.

# 1. INTRODUCTION

Mechanochromic luminescent (MCL) materials are a class of "smart" materials whose emission properties can be changed upon external force stimulus (e.g., grinding, heating, and vapor fuming), and have attracted significant interest and attention due to their widespread applications, including pressure sensors, security papers, photoelectric devices, and optical data recording. $^{1-5}$  In recent years, various kinds of organic MCL materials including small organic molecules, organic cocrystal molecules, organic polymers, macrocyclic molecules, and transition metal complexes have been reported.<sup>6-14</sup> The MCL mechanisms are now mainly attributed to the physical phase transformations from crystalline state to crystalline state, or from crystalline state to amorphous state in response to force stimulus.<sup>15–18</sup> These transformations are accompanied by a change in the molecular conformations, molecular packing modes, and metal-metal distances, which changes the HOMO-LUMO energy levels and consequently results in the photophysical properties.

In our previous work, a series of iridium(III) complexes via smart ligand design strategies, such as dendritic carbazole, flexible chains, and Schiff based ligands, has been proven to be an alternative way to achieve mechanochromic luminescence (Figure S1).<sup>19-33</sup> The design strategy is that the relatively flexible functional ligands possess strong twisting skeletons or relatively loose intermolecular stacking modes that can be easily modified or their intermolecular interactions can be destroyed by the external mechanical perturbation, then resulting in the MCL phenomenon.

In the past few years, some kinds of MCL-active iridium(III) complexes have been developed. However, the MCL mechanism is less well studied.<sup>34</sup> Therefore, it is very important to further reveal the MCL mechanism especially on account of molecular level and provide more accurate design discipline for effectively achieving MCL materials. In this work, two new iridium(III) complex isomers with extremely rigid ligands are subtly designed and synthesized. Interestingly, isomer 1 exhibits an MCL phenomenon, whereas isomer 2 does not show any mechanochromic luminescence although both isomers undergo a similar physical phase transformation process (crystal to amorphous phase transition) in response to external force stimulus. This is completely

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different from the previously reported mechanism of MCL materials. Therefore, it is believed that the comparative study of photophysical properties of these two isomers is significant to further understand the MCL mechanism for the future development of MCL-active materials. The detailed single crystal structure analysis, luminescence behavior study at both 298 and 77 K, <sup>1</sup>H and <sup>13</sup>C NMR measurements, powder X-ray diffraction (PXRD), and time-dependent density functional theory (TD-DFT) calculation results indicate that the physical phase transformations from crystalline state to amorphous state originating from the destruction of intermolecular stacking modes is not the primary cause for the MCL property. It is worthy of attention that the emitting state dominated by the triplet charge transfer excited state (<sup>3</sup>CT) plays a key role in obtaining MCL properties in the iridium(III) complex system. This work represents a new MCL mechanism on account of molecular level which might provide a new platform for the future design of highly efficient MCL materials.

# 2. RESULTS AND DISCUSSION

**2.1. Syntheses and Characterization.** Ligand 1 (dptzpy 1) with an sp<sup>3</sup>-hybridized nitrogen (N) atom in the  $\beta$  position was synthesized following a previous method.<sup>25</sup> The corresponding isomeric ligand 2 (dptzpy 2) with  $\alpha$  position sp<sup>3</sup> hybridized N atom is designed and synthesized in this work for the first time (Scheme 1). Finally, two new iridium(III) complexes isomers 1 and 2 were synthesized according to the standard procedure (Scheme 1) in high yield.<sup>35</sup>

2.2. Photophysical Properties. The UV/vis absorption and emission properties study of isomers 1 and 2 were measured in the degassed acetonitrile solution. As shown in Figure 1a, two main absorption bands were observed in both isomers 1 and 2. The strong absorption band from 200 to 350 nm is attributed to spin-allowed  ${}^{1}\pi - \pi^{*}$  transitions of the ligands. The relatively weak absorption peaks at 363 and 420 nm can be assigned to spin-allowed metal-to-ligand chargetransfer (<sup>1</sup>MLCT), ligand-to-ligand charge-transfer (<sup>1</sup>LLCT) and spin-forbidden <sup>3</sup>MLCT and <sup>3</sup>LLCT, respectively.<sup>36</sup> Upon photoexcitation, isomer 1 showed green emission with the peak at 535 nm in acetonitrile solution. In comparison with isomer 1, isomer 2 showed faint emission with two peaks of 488 and 516 nm, respectively. This result indicates that the emission properties were influenced by the positional isomerism of the ancillary ligand, in which the sp<sup>3</sup>-hybridized N atoms in the triazole ring locate separately in the  $\alpha/\beta$ substitution positions of pyridine. The nonradiative transition



Figure 1. (a) UV/vis absorption and emission spectra of isomers 1 and 2 in acetonitrile solution  $(1 \times 10^{-5} \text{ M})$ . Inset: amplified UV absorption spectra of isomers 1 and 2. (b, c) Emission spectra of isomers 1 and 2 in water-acetonitrile mixtures with different water fractions  $(1 \times 10^{-5} \text{ M})$ . Inset: emission intensity changes of isomers 1 and 2 in different water-acetonitrile mixture ratios.

rate  $(k_{\rm nr})$  is 3 orders higher than the radiative transition rate  $(k_{\rm r})$  (Table 1), leading to the emission quenching of isomer 2. In the solid powder state, isomers 1 and 2 show stronger emission in comparison with that in the solution state, and the photoluminescence quantum yields (PLQYs) were measured as 0.96% and 0.25%, which are 10- and 25-fold greater than those in the degassed acetonitrile solution (Table 1). In addition, the  $k_{\rm nr}$  values of both isomers are 0.02 × 10<sup>6</sup> and 1.09 × 10<sup>6</sup> s<sup>-1</sup> in the solid powder state, which are 3 orders lower

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# Table 1. Photophysical Characteristics of Iridium(III) Complexes

isomers	$\lambda_{abs}^{\ a}(nm) \ (\varepsilon \ (10^4 \ M^{-1} \ cm^{-1}))$	$\lambda_{\rm em}~({\rm nm})$	$\lambda_{\rm em}^{\ c}$ (nm)	$\Phi_{\rm em}$ (%)	$\tau$ ( $\mu$ s)	$k_{\rm r}^{\ d} \ (10^6 \ {\rm s}^{-1})$	$k_{\rm nr}^{\ d} \ (10^6 \ {\rm s}^{-1})$
1	242 (0.99), 296 (0.53), 363 (0.11), 420 (0.02)	535, <sup>a</sup> 491 <sup>b</sup>	454, 484, 504	0.093, <sup>a</sup> 0.964 <sup>b</sup>	0.108, <sup>a</sup> 1.546 <sup>b</sup>	0.86, <sup>a</sup> 0.62 <sup>b</sup>	8.40, <sup><i>a</i></sup> 0.02 <sup><i>b</i></sup>
2	245 (0.99), 300 (0.48), 363 (0.10), 420 (0.01)	488, <sup>a</sup> (460, 486, 516) <sup>b</sup>	454, 488, 516	0.010, <sup>a</sup> 0.253 <sup>b</sup>	0.003, <sup>a</sup> 0.684 <sup>b</sup>	3.03, <sup><i>a</i></sup> 0.37 <sup><i>b</i></sup>	300, <sup>a</sup> 1.09 <sup>b</sup>

<sup>*a*</sup>Measured in the degassed CH<sub>3</sub>CN solution (10<sup>-5</sup> M) at 298 K. <sup>*b*</sup>Measured in the solid powder state at 298 K. <sup>*c*</sup>Measured in the degassed CH<sub>3</sub>CN solution (10<sup>-5</sup> M) at 77 K. <sup>*d*</sup> $k_r$  and  $k_{nr}$  were calculated according to the equations:  $k_r = \Phi_{em}/\tau$  and  $k_{nr} = (1 - \Phi_{em})/\tau$ .

than those in the solution state. These results indicate that both isomers are potential aggregation-induced emission/ aggregation-induced emission enhancement (AIE/AIEE) materials. Thus, the potential AIE properties of isomers 1 and 2 were further studied. As shown in Figures 1b and 1c, both isomers 1 and 2 both exhibit weak emission in pure acetonitrile solutions. However, when the water fraction exceeds ca. 70%, the emission intensity is dramatically increased for both isomers 1 and 2 (Figure 1c), demonstrating that both isomers 1 and 2 display AIE/AIEE behavior. The UV-visible absorption spectral profiles showed a Mie scattering effect that is evidence for aggregates of isomers 1 and 2 (Figure S4).<sup>37</sup> Furthermore, electron diffraction (ED) and transmission electron microscopy (TEM) experimental results revealed that the amorphous molecular aggregates were formed for both isomers (Figure S5).<sup>38</sup>

2.3. Mechanochromic Luminescent Properties. Recently, AIE-active materials were considered to be potential candidates for highly efficient MCL materials.<sup>17,39-41</sup> Therefore, we investigated the potential MCL properties of isomers 1 and 2 benefiting from their excellent AIE properties. Under ultraviolet light irradiation, the as-prepared powders isomers 1 and 2 exhibit sky blue phosphorescence with emission peaks of 491 and 486 nm, respectively (Figures 2a and 2b). The unground samples of isomers 1 and 2 are hereafter referred to as P1 and P2. Upon grinding treatment of both isomers solid powders on quartz plates with an agate mortar (referred to as G1 and G2, respectively), a red shift of the emission by ca. 36 nm to  $\lambda_{max}$  527 nm was observed for G1. This MCL behavior is reversible such that the emission color can be recovered to the original emission color when heated G1 at 180 °C within 2 min or fumed G1 by dichloromethane (DCM) solvent (Figure 2e). Surprisingly, in contrast, no MCL phenomenon was observed for the corresponding isomer G2 (Figure 2f). The distinctly opposite MCL phenomena based on these two isomers is worthy of attention to further investigate the mechanism of the MCL materials.

2.4. Mechanochromic Luminescent Mechanism Investigations. It is believed that the comparative study of isomers with opposite MCL properties may provide a new way to understand the MCL mechanism. Thus, NMR experiments were first performed to investigate the MCL mechanism of the two isomers. As shown in Figure 3, both isomers showed similar <sup>1</sup>H NMR spectra after the grinding process, and tiny peak splitting changes at 8.1, 7.3, and 7.1 ppm for G1 can be attributed to the different concentrations of sample solutions before and after the grinding process. Therefore, this result implies that the MCL mechanism is not coming from a chemical reaction. To further explore the MCL mechanism, the PXRD patterns of the P1, P2, G1, and G2 were obtained. Both P1 and P2 displayed intense and sharp reflection peaks, which are similar to the simulated XRD results using singlecrystal data of complexes 1 and 2. This result indicated their well-ordered crystalline nature (Figures 2c and 2d). In



Figure 2. Emission spectra of unground P1, ground sample G1, and heated ground sample Heated G1, respectively (a) and P2 and G2 (b). Powder X-ray diffraction patterns of P1, G1, and Heated G1 (c) and P2 and G2 (d). Emission color upon irradiation with 365 nm UV light of P1 and G1 (e) and P2 and G2 (f).

contrast, these diffraction peaks became weaker and broader after the grinding process for both G1 and G2, suggesting that physical phase transformations from crystalline state to amorphous state happen in response to force stimulus. However, isomer 2 is not an MCL-active material although its physical phase transformations from crystalline state to amorphous state happened upon grinding, as shown in Figure 2f. Furthermore, upon heating treatment of G1, the amorphous state was reverted to the crystalline state with intense and sharp reflection peaks (Figure 2c). However, the partially different PXRD patterns between P1 and heated G1 indicated that the crystal packing mode was not converted to the original crystal packing mode upon heat treatment. Therefore, the different crystal packing modes may lead to the heated G1 showing wider peak width in comparison with **P1** in the emission spectra (Figure 2a).

To further search valuable clues to explain the opposite MCL phenomena observed in isomers 1 and 2, we successfully obtained single-crystal structures of both isomers by the



Figure 3. <sup>1</sup>H NMR spectra of isomers 1 (a) and 2 (b) before and after the grinding process in DMSO- $d_6$ .

solvent diffusion method (from *n*-pentane to dichloromethane). As shown in Figure 4 and Table S1, both isomers exhibit a slightly distorted octahedral geometry around the iridium center. Interestingly, the single-crystal structures of the two isomers exhibit identical crystal systems and space groups, and the spatial arrangements including complex cations, the anions  $PF_6^-$ , the solvent molecule dichloromethane, and even the inter- or intramolecular interactions are very similar in their single-crystal structures. The overlay crystal structures of the two isomers show only tiny differences (Figure 4i). These results indicate that both isomers 1 and 2 might possess similar changes in molecular packing, molecular conformation, and metal-metal distance upon the grinding process, which means both of them should exhibit similar MCL properties as previously reported.

It is worth noting that isomer 2 exhibits a shoulder emission peak no matter whether in solution or in aggregate state in comparison with isomer 1 (Figures 1 and 2a,b). The shoulder emission peaks in iridium complex system were usually ascribed to the triplet ligand-centered (<sup>3</sup>LC) excited state.<sup>4</sup> Therefore, we speculate that the opposite MCL mechanism may be related to the different excited-state properties of the isomers. Thus, to further study the excited-state properties of both isomers, the emission properties of both isomers in various organic solvents were studied. As shown in Figures 5a and 5b, isomer 1 exhibited a solvation effect, indicating that the <sup>3</sup>CT excited state dominates the emitting excited state of isomer 1. However, in contrast to isomer 1, no emission shift was observed in isomer 2, demonstrating that the <sup>3</sup>LC excited state is the dominant emitting excited state of isomer 2. In addition, 298 and 77 K emission spectra of both isomers in the degassed CH<sub>3</sub>CN solution have also been studied, as shown in Figures 5c and 5d. At 77 K, both isomers show similar emission features with peaks at 454, 484, 504 nm and 454, 488, 516 nm, respectively (Table 1) along with classical phosphorescent emission features with lifetimes of 1.546 and 0.684  $\mu$ s, respectively. With a decrease in temperature from



Figure 4. Crystal packing modes of isomers 1 (a) and 2 (b). Intermolecular H–F interactions between two molecules of isomers 1 (c) and 2 (d) in the X-ray crystal structure. Intermolecular CH… $\pi$  interactions between two molecules of isomers 1 (e) and 2 (f) in the X-ray crystal structure. Intramolecular  $\pi$ - $\pi$  interactions of isomers 1 (g) and 2 (h) in the X-ray crystal structure. (i) Overlay image of the molecular conformations of isomers 1 and 2.



Figure 5. Emission spectra of isomers 1 (a) and 2 (b) in various kinds of organic solvents  $(1 \times 10^{-5} \text{ M})$ . Emission spectra of isomers 1 (c) and 2 (d) measured at 77 and 298 K. Electron density distribution calculated for the lowest lying triplet states  $(T_1)$  of isomers 1 (e) and 2 (f).

298 to 77 K, isomer 1 shows blue-shifted emission (ca. 51 nm) of the main peak from 535 to 484 nm, and two weak shoulder peaks at  $45\hat{4}$  and 504 nm can be attributed to the vibronic progressions.<sup>43</sup> This result suggests that the emitting state of isomer 1 is dominated by the predominant <sup>3</sup>CT excited state at room temperature. In contrast to isomer 1, no blue-shifted emission was observed for isomer 2, and similar emission features with three peaks at 454, 488, and 516 nm were observed at both 298 and 77 K, respectively, which certifies that the emitting state of isomer 2 is dominated by the predominant <sup>3</sup>LC excited state at both room and low temperature. These results indicate that the two isomers possess essentially different emitting excited state characters at room temperature: predominant <sup>3</sup>CT for isomer 1 and predominant <sup>3</sup>LC for isomer 2. These results are consistent with the emission properties of two isomers measured in various organic solvents.

**2.5. Theoretical Investigations.** Time-dependent density functional theory (TD-DFT) was performed to further investigate the excited-state properties of two isomers. As shown in Figure 5e and 5f and Table S2, the largest contribution for  $T_1$  state of isomer 1 comes from the HOMO to LUMO transition (61%) with <sup>3</sup>MLCT/<sup>3</sup>LLCT characteristics. In addition, a relatively large contribution comes from the HOMO-3 to LUMO transition (17%) with <sup>3</sup>MLCT/<sup>3</sup>LLCT/<sup>3</sup>LC characteristics. However, for isomer 2, the largest contribution for  $T_1$  state comes from a HOMO-1 to LUMO transition (71%) with <sup>3</sup>LC characteristic. And the

partial contribution comes from a HOMO to LUMO transition (10%) with <sup>3</sup>MLCT/<sup>3</sup>LLCT characteristics. The detailed excited state transition components of isomers 1 and 2 are shown in Table S2. All of these TD-DFT results indicate that the emitting excited state of isomers 1 and 2 should originate from a mixture of <sup>3</sup>MLCT, <sup>3</sup>LLCT, and <sup>3</sup>LC characters. The main difference is that the emitting triplet states of isomers 1 and 2 are dominated by <sup>3</sup>CT and <sup>3</sup>LC, respectively, which is consistent with the experimental results obtained in the low temperature emission (77 K) spectra and solvation effect experiments. Therefore, all of the above mentioned results suggest that the MCL behavior of isomer 1 stems from the <sup>3</sup>CT dominant emitting excited state along with the force stimulus-induced change in intermolecular stacking modes. Thus, we try to find the reason why <sup>3</sup>CT state promotes MCL behaviors through calculating the transition dipole moment from  $T_1$  to ground state  $(S_0)$ . According to Kasha's exciton model, the molecular transition dipole moments from ground state (S<sub>0</sub>) to excited state (or from excited state to ground state) determine the excited-state energy distributions of dimers, and thus influence the absorption and emission wavelengths.<sup>44</sup> Therefore, the molecule with a larger transition dipole moment should exhibit larger variations in the photoluminescent spectra by force stimulus. Here, we calculated the transition dipole moments from the first triplet state  $(T_1)$  to  $S_0$  for both isomers with a zero-order regular approximation (ZORA) Hamiltonian in scalar approximation in the ADF code,<sup>45,46'</sup> which shows 0.266 and 0.0454 Debye for isomers 1 and 2 (Table S2), respectively. This indicates that the isomer 1 with CT characterization and a larger transition dipole moment is more sensitive to the force stimulus than isomer 2, which guarantees that isomer 1 possesses the MCL phenomenon.

The structures and excited-state properties of previously reported representative MCL-active iridium(III) complexes have been summarized to further verify the universality of this MCL mechanism (Figure S1), including dendritic ligand type, flexible chain ligand type, rigid ligand type, and bridged dinuclear iridium(III) complexes. The emitting excited state for all kinds of MCL-active iridium(III) complexes are indeed dominated by <sup>3</sup>CT excited states, such as <sup>3</sup>MLCT, <sup>3</sup>LLCT, and <sup>3</sup>ILCT. This summary is consistent with the conclusion presented in this work and further elucidates the main mechanism of MCL phenomena on account of molecular level.

#### 3. CONCLUSION

In conclusion, we design and synthesize two new phosphorescent iridium(III) complex isomers with rigid substituent ligands. Interestingly, the emission properties of these two isomers were greatly affected by the positional isomerism of the ancillary ligand. When the sp<sup>3</sup>-hybridized N in the triazole ring locates in the  $\beta$  substitution position of the pyridine ring in the ancillary ligand, isomer 1 exhibits <sup>3</sup>CT emitting characteristics. However, isomer 2 possesses <sup>3</sup>LC emitting characteristics in which sp<sup>3</sup>-hybridized N in the triazole ring locates in the  $\alpha$  substitution position of the pyridine ring in the ancillary ligand. More importantly, these two isomers along with the same physical phase transformations from crystalline state to amorphous state possess extremely opposite MCL properties. Single-crystal structure analysis, low temperature emission experiments, NMR, PXRD, and TD-DFT calculations have been carried out to provide new insights into the nature of MCL phenomena of iridium(III) complexes on account of molecular level. All experimental and TD-DFT calculations results proposed that the phase transition resulting from the destruction of intermolecular stacking modes is not the only reason for the MCL property, and the <sup>3</sup>CT dominant emitting excited state plays a key role in achieving MCL in iridium(III) complexes. Isomer 1 with CT characterization and a larger transition dipole moment is more sensitive to force stimulus than isomer 2, since force stimulus could lead to larger intermolecular packing changes. This work might provide particularly valuable information for the further understanding of the MCL mechanism and supply new guidelines to the design and preparation of MCL-active iridium(III) complexes.

# 4. EXPERIMENTAL SECTION

4.1. General Information and Materials. All chemicals were purchased from commercial suppliers without further purification unless otherwise stated. All syringes, glassware, needles, and magnetic stirring bars were dried thoroughly in a vacuum oven. Thin-layer chromatography (TLC) was used for monitoring reactions. <sup>1</sup>H NMR spectra were recorded at 25 °C on a Varian 600 MHz spectrometer, and TMS was used as the internal standard. The chemical shifts ( $\delta$ ) are given in parts per million relative to the internal standard TMS (0 ppm for 1H). UV-vis absorption spectra were recorded on a Shimadzu UV-3100 spectrophotometer. Photoluminescence spectra, excited-state lifetimes, and photoluminescence quantum yields (PLQYs) were determined using an Edinburgh FLSP920 spectrofluorimeter with an integrating sphere. Powder X-ray diffraction patterns of isomers were collected on a Rigaku Dmax 2000 instrument on solid powders. Differential scanning calorimetry (DSC) curves were measured with a PerkinElmer DSC-7 thermal analyzer under nitrogen with a heating rate 10 °C min<sup>-1</sup>. Transmission electron microscopy (TEM) was performed using a TECNAI F20 microscope.

**4.2.** Preparation of Ligand dptzpy 1 (Ligand 1). A suspension of 3-phenyl-5-(pyridin-2-yl)-1,2,4-triazole (3.38 g, 15.2 mmol), iodobenzene (4.9 g, 24 mmol), cuprous iodide (0.96 g, 5.0 mmol), 1,10-phenanthroline (1.92 g, 9.6 mmol), and cesium carbonate (7.44 g, 22 mmol) in a 200 mL round flask with 80 mL of dry DMF, under nitrogen protection reflux for 24 h. After the mixture was cooled to room temperature, DMF was concentrated under reduced pressure, and the residue was extracted with ethyl acetate and water. The organic phase was dried over anhydrous sodium sulfate, and ethyl acetate was removed under reduced pressure. The crude product was separated and purified by column chromatography with dichloromethane/petroleum ether (3/1 v/v) to give a white solid in a yield of 58%.

Spectral data of ligand dptzpy **1** are as follows. <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  8.51 (dt, *J* = 4.8, 1.3 Hz, 1H), 8.29–8.24 (m, 2H), 7.95 (dt, *J* = 7.9, 1.1 Hz, 1H), 7.78 (td, *J* = 7.7, 1.8 Hz, 1H), 7.50–7.40 (m, 8H), 7.30 (ddd, *J* = 7.6, 4.8, 1.2 Hz, 1H).

4.3. Preparation of Ligand dptzpy 2 (Ligand 2). Benzonitrile (10.3 g, 100 mmol) and 70 mL of ethanol were placed in a 250 mL single-neck flask. The mixture was cooled to 0 °C and acetyl chloride (62.8 g, 800 mmol) added dropwise. After the addition, the mixture was warmed to room temperature and allowed to react for 8 h. Then, the reaction solution was concentrated under reduced pressure to remove excess acetyl chloride and ethanol. 100 mL of water was added to the residue, and the solution was neutralized with saturated NaHCO<sub>3</sub> solution and extracted with ether. The organic phase was dried with anhydrous magnesium sulfate, and the ether was removed under reduced pressure to give the intermediate product ethyl benzimidate. Ethyl benzimidate (5.96 g, 40 mmol) was dissolved in 150 mL of dichloromethane. This solution was cooled to 0 °C, and benzoyl chloride (5.62 g, 40 mmol), triethylamine (4.44 g, 44 mmol), and acylation catalyst 4-dimethylaminopyridine (DMAP, 0.49 g, 40 mmol) were added dropwise. After the addition, the temperature was raised to 30 °C and the mixture allowed to react for 6 h. Subsequently, 2-hydrazine pyridine (4.37 g, 40 mmol) was added dropwise to the reaction solution and stirring was continued for 6 h at

room temperature. After the reaction was over, the mixture was extracted with dichloromethane and water. The organic phase was dried over anhydrous sodium sulfate, and dichloromethane was removed under reduced pressure. The crude product was separated and purified by column chromatography with dichloromethane/ petroleum ether (2/1 v/v). The product was colorless transparent crystals in a yield of 17%.

Spectral data of ligand dptzpy **2** are as follows <sup>1</sup>H NMR (600 MHz, CDCl<sub>3</sub>, ppm):  $\delta$  8.45 (dd, J = 4.9, 2.1 Hz, 1H), 8.30–8.25 (m, 2H), 7.83 (ddt, J = 9.6, 7.8, 1.8 Hz, 1H), 7.59 (ddd, J = 8.5, 6.3, 1.5 Hz, 3H), 7.52–7.42 (m, 4H), 7.42–7.35 (m, 2H), 7.32 (ddt, J = 6.3, 4.8, 1.6 Hz, 1H).

**4.4. Preparation of Iridium(III) Complex Isomer 1.** A suspension of ligand dptzpy 1 (1.192 g, 4 mmol, 2.00 equiv) and the dichloro-bridged diiridium(III) complex  $[Ir(N^{C}-dfppy)_{2}CI]_{2}^{2}$  (2.432 g, 2 mmol, 1.00 equiv) in MeOH (50 mL) and CH<sub>2</sub>Cl<sub>2</sub> (50 mL) was refluxed under an inert atmosphere of N<sub>2</sub> in the dark for 6 h. The solution was then cooled to room temperature, and excess solid potassium hexafluorophosphate was added to the solution. The mixture was stirred for 30 min at room temperature, and then the suspension was filtered and the precipitate was purified by column chromatography with dichloromethane/methanol (40/1 v/v) to produce isomer 1 in a yield of 63%.

Spectral data of iridium(III) complex isomer 1 are as follows. <sup>1</sup>H NMR (600 MHz, DMSO- $d_{6}$ , ppm):  $\delta$  8.70 (d, J = 5.6 Hz, 1H), 8.33 (d, J = 8.5 Hz, 1H), 8.13 (dt, J = 18.8, 8.1 Hz, 2H), 8.06 (d, J = 4.6Hz, 2H), 7.97 (d, J = 5.8 Hz, 1H), 7.89 (dd, J = 12.3, 6.2 Hz, 3H), 7.85-7.78 (m, 3H), 7.72-7.67 (m, 1H), 7.45 (t, J = 6.7 Hz, 1H), 7.40 (d, J = 8.2 Hz, 1H), 7.35–7.27 (m, 2H), 7.15–7.05 (m, 4H), 6.99-6.91 (m, 1H), 5.59 (dd, J = 8.4, 2.1 Hz, 1H), 5.36 (dd, J = 8.6, 2.1 Hz, 1H). <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ , ppm):  $\delta$  163.2 (d, J = 6.25 Hz), 162.7 (d, J = 6.25 Hz), 162.0 (d, J = 12.5 Hz), 161.6, 161.4 (q, J = 46.25 Hz), 161.1 (t, J = 11.25 Hz), 160.0 (t, J = 13.75 Hz),156.5, 152.1 (d, J = 6.25 Hz), 151.8, 151.6, 150.6, 144.2, 140.5 (d, J = 13.75 Hz), 136.4, 132.4, 130.9, 130.6, 130.2, 129.4, 128.7, 127.9, 127.2, 126.5, 125.9 (d, J = 6.25 Hz), 125.1, 124.7, 113.8 (q, J = 45.0 Hz), 99.6 (t, J = 53.75 Hz), 98.8 (t, J = 53.75 Hz). MS (MALDI-TOF) [m/z]: 1016.19 (M - PF<sub>6</sub>). Anal. Calcd for C<sub>41</sub>H<sub>26</sub>F<sub>10</sub>IrN<sub>6</sub>P: C, 48.48; H, 2.58; N, 8.27. Found: C, 48.41; H, 2.59; N, 8.29.

**4.5. Preparation of Iridium(III) Complex Isomer 2.** The synthesis of iridium(III) complex isomer 2 was similar to that of iridium complex isomer 1 except that the ligand dptzpy 1 was replaced by dptzpy 2. The yield of as-synthesized isomer 2 was 57%.

Spectral data of iridium(III) complex isomer 2 are as follows. <sup>1</sup>H NMR (400 MHz, DMSO- $d_6$ , ppm):  $\delta$  8.84 (d, J = 5.6 Hz, 1H), 8.40 (dd, *J* = 19.8, 7.1 Hz, 2H), 8.15 (t, *J* = 7.0 Hz, 2H), 8.03 (dt, *J* = 17.2, 8.1 Hz, 2H), 7.89 (d, J = 7.4 Hz, 2H), 7.75 (ddd, J = 27.1, 15.0, 7.5 Hz, 4H), 7.60-7.51 (m, 1H), 7.48-7.38 (m, 2H), 7.32 (q, J = 6.2, 5.4 Hz, 2H), 7.22 (d, J = 7.4 Hz, 2H), 7.10 (t, J = 7.7 Hz, 2H), 7.00 (t, J = 10.2 Hz, 1H), 5.64 (dd, J = 8.3, 2.2 Hz, 1H), 5.41 (dd, J = 8.6, 2.1 Hz, 1H). <sup>13</sup>C NMR (125 MHz, DMSO- $d_{6}$ , ppm):  $\delta$  165.5, 163.2 (d, J = 6.25 Hz), 162.4 (d, J = 7.5 Hz), 161.9 (d, J = 12.5 Hz), 161.6 (d, J = 12.5 Hz), 160.0 (d, J = 13.75 Hz), 158.7, 152.0 (d, J = 7.5 Hz), 151.7, 150.8, 149.8 (d, J = 7.5 Hz), 149.4, 147.8, 142.1, 140.9, 133.1, 131.3, 130.0 (d, J = 17.5 Hz), 128.6, 128.0 (q, J = 52.5 Hz), 127.3, 126.4 (d, J = 11.25 Hz), 125.2, 124.6, 124.1 (d, J = 18.75 Hz), 123.3 (d, J = 20.0 Hz), 117.9, 114.1 (q, J = 67.5 Hz), 99.9 (t, J = 52.5 Hz), 99.0 (t, J = 53.75 Hz). MS (MALDI-TOF) [m/z]: 1016.78 (MPF<sub>6</sub>). Anal. Calcd for C41H26F10IrN6P: C, 48.48; H, 2.58; N 8.27. Found: C, 48.72; H, 2.55; N, 8.05.

#### ASSOCIATED CONTENT

#### **Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.0c03515.

Additional photophysical properties, TEM and ED experiments, TGA and DSC curves, X-ray crystallographic data, and TD-DFT calculations (PDF)

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#### Accession Codes

CCDC 2002958–2002959 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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