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A new 2-phenylpyridine-type (ppy-type) ligand with dithieno[3,2-*b*:2',3'-*d*]phosphole oxide (DTPO) group has been successfully synthesized. Based on this novel ligand, three cyclometalated iridium(III) complexes (**P-Ir-P**, **P-Ir-T** and **P-Ir-C**) are synthesized with symmetrical and unsymmetrical structures. Photophysical results reveal that these cyclometalated iridium(III) complexes can show weak near-infrared (NIR) phosphorescence emission with 739 nm for **P-Ir-P**, 750 nm for **P-Ir-T** and 746 nm for **P-Ir-C**, respectively. Importantly, transient absorption characterization shows that these cyclometalated iridium(III) complexes can exhibit strong excited state absorption in the range from *ca*. 520 to 700 nm, indicating their optical power limiting (OPL) potential in this wavelength range. Open-aperture *Z*-scan against 532 nm laser shows their OPL ability in the order of **P-Ir-P** > **P-Ir-C** > **P-Ir-T**. The complex **P-Ir-P** even show better OPL ability than the state-of-the-art OPL material C₆₀, indicating important potential of these cyclometalated iridium(III) complexes as new OPL materials.

Introduction

Among all the phosphorescent transition-metal complexes, 2phenylpyridine(ppy)-type iridium(III) complexes have attracted numerous research efforts both in academic and industry for their high phosphorescent quantum yield, tunable emission color and easy purification.¹⁻⁶ So, ppy-type cyclometalated iridium(III) complexes can show great potential in organic light-emitting diodes (OLEDs),7-10 photodynamic therapy,^{11,12} solar cells,^{13,14} photovoltaics,15 bioimaging¹⁶⁻¹⁸ and photocatalysis^{19,20} etc. Attributed to the spinorbital coupling effect of Ir(III) ions, these complexes can show efficient intersystem crossing from singlet states to triplet states, endowing these novel iridium complexes excellent phosphorescent ability even at room temperature.²¹⁻²⁴ Importantly, the photophysical and functional properties of these ppy-type cyclometalated iridium(III) complexes can be effectively tuned by the functionalization of their major and/or the auxiliary ligands around the Ir(III) coordination spheres.^{23,25} Hence, ppy-type cyclometalated iridium(III) complexes can show diverse properties to meet the requirements in various fields aforementioned.

Recently, inspired by the success of other type transition-metal complexes, such as Pt(II) acetylides,²⁶⁻³⁰ as promising optical power limiting (OPL) materials for protecting both human eyes and optical

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phosphorescent or triplet emission ability. 24,35 If the triplet states possess high absorption ability, the high triplet quantum should benefit their OPL behavior based on reverse saturable absorption (RSA) mechanism for nano-second laser.^{33,36} In recent years, Sun's group have employed several ppy-type cyclometalated iridium(III) complexes to explore their OPL potential.^{11,33,37} It has been found that these complexes can exhibit obvious triplet state absorption and induce obvious OPL effect,^{32,37} indicating their potential as new OPL materials. To the best of our knowledge, all the reported OPL materials based on the ppy-type cyclometalated iridium(III) complexes adopt the symmetric structure with two identical ppytype major ligands.^{37,34} Hence, developing ppy-type cyclometalated iridium(III) complexes with new structures should be very necessary for obtaining novel OPL materials. As aforementioned, photophysical properties of the ppy-type cyclometalated iridium(III) complexes can be tuned by the chemical

sensors in the occasion of suddenly exposed to laser beams, ppy-type

cyclometalated iridium(III) complexes have been employed to investigate OPL ability as well. $^{31-34}$ Due to the strong spin-orbit

coupling (SOC) effect induced by the Ir(III) center, ppy-type

cyclometalated iridium(III) complexes can show high triplet or

phosphorescent quantum yield indicated by their high

cyclometalated iridium(III) complexes can be tuned by the chemical structures of their ppy-type ligands. Our recent results have indicated that new unsymmetrical ppy-type cyclometalated iridium(III) complexes bearing two different ppy-type major ligands and one acetylacetone (acac) auxiliary ligand can possess excited states with different feature from those of their symmetric counterparts.^{1,23,38} According to the OPL mechanisms, OPL effect is typically induced by the strong absorption ability of the excited states.^{12,31,36} Hence, adopting unsymmetrical structure should represent a new outlet to tune the OPL performance of the ppy-type cyclometalated iridium(III) complexes.

Dithieno[3,2-b:2',3'-d]phosphole oxide (DTPO) represents a kind of conjugated organic system formed by fusing both two electron-

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ARTICLE

Page 2 of 11

rich thiophene segments and one electron-deficient phosphole oxide unit. Hence, many organic DTPO-based derivatives had been developed to show unique photophysical properties.³⁹⁻⁴¹ However, to the best of our knowledge, DTPO unit has not been introduced into ppy-type iridium(III) complexes. So, in this research, DTPO unit has been employed to develop new ppy-type ligand. With the DTPObased ligand, new ppy-type cyclometalated iridium(III) complexes adopting symmetric and unsymmetrical structures have been developed. Through the diverse structures, donor (D) and acceptor (A) have been introduced into the cyclometalated iridium(III) complexes to investigate their effect on OPL behavior and get structure-activity information. Critically, these novel cyclometalated iridium(III) complexes with DTPO group can outperform the state-ofthe-art OPL material C₆₀, indicating their potential in the field of OPL.

Experimental

General information

All the reactions were conducted under a nitrogen atmosphere and no special precautions were required during the workup. The solvents were purified by routine procedures and distilled under dry nitrogen before use. Commercially available reagents were used without further purification unless otherwise stated. The reactions were monitored by thin-layer chromatography (TLC) purchased from Merck & Co, Inc. Flash column chromatography and preparative TLC were carried out using silica gel from Shenghai Qingdao (200–300 mesh).

Physical characterization

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UV/vis spectra were measured on a Perkin-Elmer UV-vis NIR Spectrometer Lambda 950. The photoluminescent (PL) properties and the phosphorescent lifetimes of the iridium(III) complexes were obtained using a spectrophotometer from Edinburgh Instruments (FLS920). Cyclic voltammetry was performed using a Princeton Applied Research model 2273A potentiostat with a glassy carbon working electrode, a platinum sheet counter electrode, and a platinum-wire reference electrode with the scan rate of 50 mV s⁻¹. The supporting electrolyte used was 0.1 M [nBu₄N]BF₄ solution in degassed CH₂Cl₂ with ferrocene (Fc) as the calibrant. ¹H, ¹³C and ³¹P NMR spectra were recorded in CDCl₃ on a Bruker Avance 400 or 600 MHz spectrometer and chemical shifts were referenced to the solvent residual peak at d 7.26 ppm for ¹H and 77.0 ppm for ¹³C, respectively. Elemental analyses were performed on a Flash EA 1112 elemental analyzer. Mass spectra (MS) were recorded on a Finnigan MAT SSQ710 spectrometer. The thermal gravimetric analysis (TGA) was conducted on a METTLER TOLEDO TGA2 star system under nitrogen with a heating rate of 20 K min⁻¹. Transient absorption (TA) behaviors were characterized by femtosecond (fs) time-resolved pump-probe technique with pump pulses centered at 400 nm with energies of 3.2 mJ cm⁻². In the TA measurements, the output of the laser was split into two beams: the stronger beam was used as the excitation light and the other beam was focused into a sapphire plate with 1 mm thickness to generate the broad band white-light probe pulses of 1k Hz from 450 to 750 nm. The transmitted probe pulses from the sample were collected by a fibre-coupled spectrometer connected to a computer. The TA data were recorded as a function of the delay time between the pump and $pr\partial De \partial Msesson DODTOO102C$

Computational details

Geometrical optimizations were conducted using the popular B3LYP density functional theory (DFT). The effective core potentials with the LanL2dz basis set were employed for the Ir atom,^{50,51} whereas the basis set used for C, H, O, N, S and P atoms was 6-31G (d, p). The energies of the excited states of the complexes were computed by TD-DFT (time-dependent density functional theory) based on the ground-state geometries. All the calculations were carried out by using the Gaussian 09 program.⁴³

Synthesis

Synthetic procedures for 3,3',5,5'-tetrabromo-2,2'-bithiophene,⁴⁴ 3,3'-dibromo-2,2'-bithiophene,⁴⁵ dithieno[3,2-b:2',3'-d]phosphole oxide⁴¹ and 2-bromodithieno[3,2-b:2',3'-d]phosphole oxide⁴⁶ follow the literature methods. Hence, their synthetic details have been provided in the ESI.[†]

L-P

To the solution of 2-bromodithieno[3,2-b:2',3'-d]phosphole oxide (0.37 g, 1.0 mmol), 2-(tri-nbutylstannyl)pyridine (0.41 g, 1.1 mmol) and $Pd(PPh_3)_4$ (64 mg) as catalyst in toluene (15 mL) under N_2 atmosphere was heated to 110 °C overnight. Upon cooling to room temperature, the resulting solution was removed under reduced pressure. The crude product was purified on a silica gel column using ethyl acetate and CH_2Cl_2 (1:1, v/v) as eluent to give the product as yellow solid (0.26 g, 71%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.55 (d, J = 4.8 Hz, 1H), 7.80-7.48 (m, 2H), 7.69 (td, J = 8.0, 2.0 Hz, 1H), 7.58-7.53 (m, 3H), 7.47-7.42 (m, 2H), 7.34 (dd, J = 3.2, 4.8 Hz, 1H), 7.19-7.18 (m, 2H); ^{13}C NMR (150 MHz, CDCl_3): δ (ppm) 151.56, 149.64, 149.09 (d, J = 13.2 Hz), 146.85 (d, J = 22.05 Hz), 146.18 (d, J = 23.85 Hz), 139.68 (d, J = 111.0 Hz, 1H), 138.85 (d, J = 111.75 Hz), 136.84, 132.55 (d, J = 30.0 Hz), 130.92 (d, J = 11.1 Hz), 129.90, 129.11(d, J = 15.06 Hz), 128.99 (d, J = 13.05 Hz), 126.12 (d, J = 15.0 Hz), 122.60, 122.44 (d, J = 15.0 Hz), 118.52; ³¹P NMR (162 MHz, CDCl₃): δ (ppm) 18.61; FAB-MS (m/z): 365 [M]⁺; Elemental analysis calcd (%) for C₁₉H₁₂NOPS₂: C 62.45, H 3.83; found: C 62.36, H 3.75.

General procedure for the synthesis of iridium(III) complexes

Under N₂ atmosphere, **L-P** (1.1 equiv), **L-P/L-T/L-C** (1.1 equiv) and IrCl₃. nH₂O (60 wt%, 1.0 equiv) were heated to 110 °C in the mixture of THF and H₂O (3:1, v/v) for 16 h. The reaction mixture was then cooled to room temperature and water was added. After extracted with CH₂Cl₂, the organic phase was dried over anhydrous Na₂SO₄ and solvent was removed under reduce pressure. The μ -chloro-bridged dimer was obtained as colored residue. After stirring the reaction mixture of acetylacetone and tBuOk in CH₂Cl₂ for half an hour under N₂ atmosphere. The μ -chloro-bridged dimer was added, then the reaction mixture was stirred for 2 h. The resulting solution was removed under vacuum to obtain the crude solid production which was purified with thin layer chromatography on silica gel with appropriate eluents to obtain the complex.

P-Ir-P. Yield: 50%. ¹H NMR (600 MHz, CDCl₃): δ (ppm) 8.58 (d, *J* = 3.6 Hz, 1H), 8.24 (d, *J* = 3.7 Hz, 1H), 8.06 (d, *J* = 5.16 Hz, 2H), 7.58 (td, *J* = 7.8, 1.2 Hz, 1H), 7.45 (m, 2H), 7.35-7.32 (m, 2H), 7.23-7.21 (m, 2H), 7.17-7.14 (m, 2H), 7.10-7.08 (m, 1H), 6.97-6.87 (m, 5H), 6.82-6.85

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(m, 2H), 6.32 (d, J = 1.8 Hz, 1H), 5.22 (s, 1H), 1.87 (s, 3H), 1.73 (s, 3H); ¹³C NMR (150 MHz, CDCl₃) δ (ppm) 185.57, 184.09, 166.42, 163.26, 150.84, 148.16, 145.18, 144.08, 140.27, 137.69, 136.94, 136.43, 131.12, 130.14, 129.92 (d, J = 11.1 Hz), 128.85, 128.16 (d, J = 13.5 Hz), 125.62, 125.35 (d, J = 13.5 Hz), 125.12, 125.44, 124.53, 123.27, 121.45, 120.04, 119.59, 119.10, 118.20 (d, J = 12.0 Hz), 118.16, 117.22, 110.35, 100.62, 28.56, 28.42; ³¹P NMR (162 MHz, CDCl₃): δ (ppm) 18.33; FAB-MS (m/z): 1020 [M]⁺; Elemental analysis calcd (%) for C₄₃H₂₉IrN₂O₄P₂S₄: C 50.63, H 2.87, N 2.75; found: C 50.53, H 2.79, N, 2.66.

P-Ir-T. Yield: 22%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.18 (d, *J* = 5.6 Hz, 1H), 7.74 (dd, *J* = 9.2, 7.2 Hz, 2H), 7.65 (d, *J* = 8.0 Hz, 1H), 7.54-7.48 (m, 2H), 7.40-7.26 (m, 5H), 7.21-7.14 (m, 5H), 7.08 (dd, *J* = 4.8, 3.2 Hz 1H), 6.97-6.93 (m, 7H), 6.74 (td, *J* = 6.4, 1.0 Hz, 1H), 6.48 (dd, *J* = 8.4, 2.4 Hz 1H), 6.34 (t, *J* = 6.4 Hz, 1H), 5.57 (d, *J* = 2.4 Hz, 1H), 5.17 (s, 1H), 1.78 (s, 3H), 1.73 (s, 3H); ¹³C NMR (100MHz, CDCl₃): δ (ppm) 184.23, 184.02, 168.76, 163.21, 150.32 (d, *J* = 19.5 Hz), 148.71 (d, *J* = 28.85 Hz), 148.01 (d, *J* = 29.85 Hz), 147.49, 147.36, 144.54, 144.00, 143.84, 143.77, 143.28, 141.53 (d, *J* = 107.7 Hz), 140.43 (d, *J* = 20.25 Hz), 139.13, 136.74, 132.00, 131.81 (d, *J* = 11.10 Hz), 131.73, 131.29, 128.77, 128.34, 128.12 (d, *J* = 27.3 Hz), 127.8 (d, *J* = 14.1 Hz), 125.44,

125.35, 124.76, 124.16, 122.56, 119.52, 118.99, 118.29, 118.29, 118.29, 118.29, 118.29, 115.05, 100.29, 28.76, 28.55; ³¹P NMR (162 MH2, COCB) (6), 17.78; FAB-MS (m/z): 977 [M]⁺; Elemental analysis calcd (%) for $C_{47}H_{35}IrN_{3}O_{3}PS_{2}$: C 57.77, H 3.61, N 4.30; found: C 57.66, H 3.56, N 4.19.

P-Ir-C. Yield: 25%. ¹H NMR (400 MHz, CDCl₃): δ (ppm) 8.30 (d, *J* = 5.6 Hz, 1H), 8.04 (d, *J* = 7.6 Hz, 2H), 7.88 (d, *J* = 8.4 Hz, 1H), 7.79-7.72 (m, 3H), 7.65 (td, *J* = 7.4, 1.2 Hz, 1H), 7.54 (t, *J* = 7.2 Hz, 1H), 7.48-7.31 (m, 9H), 7.20 (t, *J* = 3.8 Hz, 2H), 7.09-7.06 (m, 2H), 6.93 (dd, *J* = 2.4, 4.8 Hz, 1H), 6.84 (td, *J* = 4.8, 1.3 Hz, 1H), 6.47 (t, *J* = 6.6 Hz, 1H), 6.29 (d, *J* = 1.6 Hz, 1H), 5.23 (s, 1H), 1.84 (s, 3H), 1.76 (s, 3H); ¹³C NMR (100 MHz, CDCl₃): δ (ppm) 184.44, 184.27, 168.52, 163.46, 150.34 (d, *J* = 4.5 Hz), 149.24, 148.25 (d, *J* = 10.5 Hz), 144.57, 144.37, 144.34, 143.87 (d, *J* = 23.50 Hz), 141.85, 141.13, 140.43 (d, *J* = 19.5 Hz), 140.25, 137.66, 137.20, 131.99, 131.90, 131.79 (d, *J* = 19.5 Hz), 131.28, 129.59, 128.27, 128.18, 128.08, 125.46, 125.38, 124.63, 123.23, 120.86, 119.84, 119.44, 119.26, 119.16, 117.30, 110.73, 100.46, 29.34, 28.6; ³¹P NMR (162 MHz, CDCl₃): δ (ppm) 17.96; FAB-MS (m/z): 975 [M]⁺; Elemental analysis calcd (%) for C₄₇H₃₅IrN₃O₃PS₂: C 57.89, H 3.41, N 4.31; found: C 57.81, H 3.46, N 4.22.



Scheme 1. Synthetic pathway of ligand L-P.

Results and discussion

Synthetic strategies and structural characterization

Chemical structures and detailed synthetic method of the ppy-type ligand **L-P** with DTPO group are shown in Scheme 1. In order to obtain the designed complexes, the synthesis of **L-P** is crucial. The synthesis of **L-P** was started with bromination of 2,2'-bithiophene to obtain 3,3',5,5'-tetrabromo-2,2'-bithiophene, which was converted into 3,3'-dibromo-2,2'-bithiophene through selective debromination with Zn/CH₃COOH-HCl in a yield of *ca.* 80%. Through lithiation in anhydrous THF at -78 °C, subsequent treatment with dichlorophenylphosphine and finally adding H₂O₂, 3,3'-dibromo-2,2'-bithiophene [3,2-b:2',3'-d]phosphole oxide. Finally, through Stille coupling reaction, **L-P** could be obtained in a yield of 71%. In the ¹H NMR spectrum of **L-P**, the doublet peak at *ca.* 8.55 ppm can be assigned to the proton attaced to the carbon atom

adjacent to the nitrogen atom in the pyridine ring. The td peak at *ca.* 7.69 ppm is induced by the proton on the carbon atom at the *para*-position phosphine atom in the pendent phenyl ring of the phosphole oxide unit. The peak with δ at 18.61 ppm is induced by the phosphole oxide unit of DTPO group in the ³¹P NMR spectrum of **L-P**.

After obtaining L-P, the designed symmetric complex P-Ir-P had been prepared according to the reported two-step pathway (Scheme 2). The unsymmetrical counterparts P-Ir-T and P-Ir-C were prepared by similar synthetic strategy by adding two kinds of ppy-type ligand L-P and L-T/L-C in the first step for synthesis of Ir(III) µ-chloro-bridged dimers. Then, the dimers were treated with the mixture of acetylacetone and *t*BuOK to obtain the unsymmetrical complexes P-Ir-T and P-Ir-C. Clearly, in the synthesis of unsymmetrical complexes, the symmetrical complexes can be formed as well. Fortunately, they can be separated easily through either column or TLC chromatography due to the difference in molecular polarity. In their

Page 4 of 11

ARTICLE

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Journal Name

¹H NMR spectra (Figure S1 in Electronic supplementary information, ESI), the signals at 8.58 and 8.24 ppm for P-Ir-P, 8.18 and 7.74 ppm for P-Ir-T and 8.30 and 8.04 ppm for P-Ir-C can be assigned to the protons attached to the carbon atoms adjacent to the nitrogen atom in the pyridyl ring of the two ppy-type ligands. The acetylacetone auxiliary ligand (acac) has been indicated by the three singlet peaks at *ca*. 5.2, 1.8 and 1.7 ppm, respectively. In their ³¹P NMR spectra (Figure S1), all the complexes can exhibit resonance peak with δ *ca*. 18 ppm which can be attributed to the P atom in phosphole oxide

unit of DTPO group. As shown in Figure 1, the single crystal Strate crystallography further confirms the absolute thermical structure of the complex **P-Ir-C**. Clearly, two different ppy-type ligands and one acetylacetone anion centering on Ir(III) atom adopt a distorted octahedral chelating skeleton with *cis*-C,C, *cis*-O,O and *trans*-N,N disposition. The DTPO group adopts rigid planar geometry with phenyl ring and P=O bond sticking out of its molecular planar. The detail of related crystal data and selected bond angles and lengths of **P-Ir-C** are summarized in Table S1 and S2.



Scheme 2. Synthetic pathway of the cyclometalated iridium(III) complexes with DTPO group.

Thermal and photophysical properties

Both thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) have been employed to characterize thermal properties of these cyclometalated iridium(III) complexes under a nitrogen follow. The TGA results show that these complexes possess high thermal stability with decomposition temperature > 300 °C, indicating their good thermal stability.

UV-vis absorption spectra of these cyclometalated iridium(III) complexes can be seen in Figure 2. There are two kinds of obvious absorption bands in their absorption spectra. According to the analogues in literature references,^{47,48} the intense absorption bands before 450 nm can be assigned reasonably to the spin-allowed π – π * transitions of the ppy-type organic ligands, which can also be ascertained by their high extinction coefficients (loge *ca.* 4.0) (Table 1). On the contrary, the weaker low-energy absorption bands after

450 nm extended to the visible region should be induced by the charge-transfer (CT) transition process.



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Figure 1. ORTEP drawing of **P-Ir-C** with thermal ellipsoids drawn at the 25% probability level (H atoms are omitted for clarity).

The UV-vis absorption and photoluminescence (PL) spectra of these complexes are shown in Figure 2 and 3, respectively. In order to illustrate the absorption behavior of these cyclometalated iridium(III) complexes, TD-DFT calculations have been carried out. The pattern of key molecular orbitals (MO) and detailed calculation results for these iridium(III) complexes are shown in Figure 4 and Table 2, respectively. Due to their large coefficient in CI expansion (> 0.9) with the corresponding lowest excited states, the HOMO \rightarrow LUMO (H \rightarrow L) transition can show the feature of the lowenergy absorption bands of these iridium(III) complexes. From the MO pattern shown in Figure 4, the $H \rightarrow L$ transition in **P-Ir-P** mainly show intraligand charge transfer (ILCT) feature (Figure 4). In addition, due to the different contributions to HOMO (ca. 15.07%) and LUMO (ca. 1.39%) from the d_{π} orbital of the Ir(III) center (Table 2), some metal-to-ligand charge transfer (MLCT) feature can be associated with the $H \rightarrow L$ transition in **P-Ir-P** as well. So, the low-energy absorption bands of P-Ir-P can exhibit ILCT feature with some MLCT character. Differently, for both P-Ir-T and P-Ir-C, their HOMOs mainly locate on the π orbitals of L-T for P-Ir-T and L-C for P-Ir-C, while their LUMOs are contributed by the π^* orbitals of **L-P**, showing obvious ligand-to-ligand charge transfer (LLCT) features. Accordingly, the low-energy absorption bands in the UV-vis spectra of P-Ir-T and P-Ir-C should mainly show LLCT character. Due to the strong electrondonating ability associated with carbazole and diphenylamine units, the lowest energy transition in **P-Ir-T** and **P-Ir-C** is mainly from π orbitals of carbazole and diphenylamine units to the π^* orbitals of L-P containing electron-accepting moiety, restraining the involvement of d_{π} orbital from Ir(III) center. As a result, LLCT character can associate with the low-energy absorption bands in the UV-vis spectra of P-Ir-T and P-Ir-C.

Under UV light irradiation at 450 nm, two emission bands can be observed in the PL spectra of these complexes (Figure 3). Their highenergy emission bands at *ca*. 530 nm should be the metal-disturbed singlet emission of ligand **L-P** due to the nanosecond lifetime and their great resemblance. Clearly, the low-energy emission band should be phosphorescent emission indicated by their remarkably large Stokes shifts (Table 1). The phosphorescent wavelengths for these complexes are 739 nm for **P-Ir-P**, 750 nm for **P-Ir-T** and 746 nm for **P-Ir-C**, respectively (Table 1). Hence, these complexes can show near-infrared (NIR) phosphorescence emission. Obviously, the broad structure-less spectral line-shape has indicated charge transfer (CT) feature of the NIR phosphorescent band (Figure 3).1039/D0DT00102C

With regard to feature of the NIR phosphorescent emission, natural transition orbital (NTO) analysis was carried out for the $S_0 \rightarrow T_1$ excitation based on the optimized T_1 geometries of these iridium(III) complexes (Figure 5 and Table 3). We will focus on the NTO results to elucidate the phosphorescent behaviors of these iridium(III) complexes. From the NTO pattern in Figure 5, it is obvious that $S_0 \rightarrow T_1$ excitation of these iridium(III) complexes can have rendered the broad structure-less spectral line-shape for the NIR phosphorescence (Figure 3). Reasonably, electron-donating ability of carbazole and diphenylamine units the will promote the Hole \rightarrow Particle transition (*i.e.* $S_0 \rightarrow T_1$ transition) to lead lower T_1 energy-level of **P-Ir-T** and **P-Ir-C** than **P-Ir-P**. Hence, **P-Ir-T** (*ca.* 750 nm) and **P-Ir-C** (*ca.* 746 nm) should exhibit longer phosphorescent wavelength that **P-Ir-P** (*ca.* 739 nm), which has been indicated by the experimental result (Table 1).



Figure 2. UV-vis spectra for cyclometalated iridium(III) complexes in CH_2Cl_2 solution at 298 K.



Figure 3. PL spectra for cyclometalated iridium(III) complexes in CH_2Cl_2 solution at 298 K.

Table 1 Photophysical and thermal data of the cyclometalated iridium(III) complexes.

Compound	Absorption λ_{abs} (nm) ^{<i>a</i>} 298 K	Emission λ _{em} (nm) ^a 298 K	τ (ns) ^ь 298 K	PLQY 298 K	Τ _d (°C)
P-Ir-P	252 (4.11), 288 (4.02), 315 (3.94), 384 (4.01) 429 (3.80), 490 (3.34), 502 (3.34)	519/739	5.15/N.A.	0.09	345
P-Ir-T	254 (4.31), 288 (4.23),383 (4.23), 427 (4.02), 492 (3.54), 506 (3.55)	517/750	7.02/N.A.	0.06	306
P-Ir-C	258(4.33), 287 (4.11), 331 (3.99), 346 (3.99) 400 (3.80), 426 (3.75), 484 (3.46), 500(3.47)	523/746	5.16/N.A.	0.09	331

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^aMeasured in CH₂Cl₂ at a concentration of 10⁻⁵ M, loge values are shown in parentheses. ^bMeasured in CH₂Cl₂ with the excitation source was a 405 View Article Online nm picosecond LED (The τ for the NIR phosphorescence could not be determined due to their very weak intensities). DOI: 10.1039/D0DT00102C



Figure 4. Molecular orbital (MO) patterns for these cyclometalated iridium(III) complexes based on their optimized S₀ geometries.

Table 2 TD-DFT results for these cyclometalated iridium(III) complexes based on their optimized S₀ geometries.

Complex	МО	Contribut	tion percentag orbitals of lig	es of metal d_{π} (gand to MOs (9)	orbitals and π 6) a	Main configuration of $S_0 \rightarrow S_1$ excitation/ λ_{cal} (nm) / E_{cal}/f^b	Main configuration of $S_0 \rightarrow T_1$ excitation/ E_{cal}/λ_{cal} (nm) ^b
		lr	L-P	L-P	асас		
	L+1	2.26	1.33	95.89	0.49	H→L (95.88%)	H→L +1 (81.07%)
P-Ir-P	L	1.39	97.36	1.07	0.18	2.5054 eV	1.7326 eV
	н	15.07	9.99	72.74	2.19	494.87	715.6
	H-1	11.31	74.21	12.74	1.70	0.0191	0
		Ir	L-P	L-T	acac		
P-Ir-T	L+1	4.31	0.63	94.36	0.69	H→L (94.83%)	H→L+1 (64.07%)
	L	1.29	98.37	0.17	0.16	2.187 eV	1.7388 eV
	н	1.77	0.89	97.15	0.17	566.90	713.04
	H-1	26.23	57.09	13.74	14.23	0.0034	0
		Ir	L-P	L-C	acac		
P-Ir-C	L+1	4.50	0.46	94.30	0.72	H→L (97.61%)	H→L+1 (76.11%)
	L	1.37	98.25	0.20	1.75	2.4662eV	1.7494 eV
	н	1.40	0.84	97.63	0.12	502.73	708.7
	H-1	21.18	67.60	9.39	1.74	0.0063	0

 a H \rightarrow L denotes transition from HOMO to LUMO, while H \rightarrow L+1 represents transition from HOMO to LUMO+1. $^{b}E_{cal}$, λ_{cal} and f denote calculated excitation energy, calculated emission wavelength and oscillator strength, respectively. The oscillator strength of $S_0 \rightarrow T_1$ is zero owing to the spin-forbidden character of singlet-triplet transition under TD-DFT calculation in the Gaussian program with no consideration of spin-orbital coupling.

Electrochemical properties

In order to characterize the electrochemical properties of these cyclometalated iridium(III) complexes with DTPO unit, cyclic voltammetry (CV) measurements have been carried out under a nitrogen atmosphere, calibrated with a ferrocene/ferrocenium (Fc/Fc⁺) redox couple as an internal reference. From the date in Table 3, P-Ir-P shows the first oxidation potential E_{ox} at ca. 0.56 V, while

that for **P-Ir-C** is *ca.* 0.54 V (Table 4). Differently, besides E_{ox} at *ca.* 0.52 V, **P-Ir-T** can possess another oxidation possess with lower E_{ox} at ca. 0.43 V, which can be assigned to the oxidation of electron-rich diphenylamine unit. The oxidation possess with Eox at ca. 0.5 V for the three complexes should be induced by the oxidation process of their Ir(III) center. Owing to two electron-withdrawing DTPO moieties coordinated with Ir(III) center, P-Ir-P can exhibit higher Eox

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Journal Name

of Ir(III) center than **P-Ir-T** and **P-Ir-C** (Table 4). In addition, these cyclometalated iridium(III) complexes can show two reduction processes. The first reversible reduction should be assigned to the reduction process of DTPO unit, locating at *ca.* -2.0 V (Table 4). The

second quasi-reversible reduction wave should be induced by the reduction of pyridyl group in the ppy-type1011gands00T0these cyclometalated iridium(III) complexes.

Table 3 NTO results for these cyclometalated iridium(III) complexes based on optimized T1 geometries.

Complexes	NTO ^a	Contribution percentages of metal d_π orbitals and π orbitals of ligand to NTOs (%)				
		lr	L-P	L-P	acac	
P-Ir-P	Н	3.92	95.02	0.84	0.20	
	Р	0.96	98.55	0.27	0.20	
		Ir	L-P	L-T	acac	
P-Ir-T	Н	4.97	93.61	0.11	0.26	
	Р	0.73	97.07	0.27	0.09	
		Ir	L-P	L-C	acac	
P-Ir-C	Н	4.32	94.95	0.61	0.20	
	Р	2.09	97.53	0.23	0.15	

^a H and P represent NTO hole and particle orbital, respectively

Table 4 Redox properties of these cyclometalated iridium(III) complexes.

Compound	E _{pa} (V)	E _{pc} (V)	E _{HOMO} ^c (eV)	E _{LUMO} ^c (eV)	$E_g^{CV}(eV)$
P-Ir-P	0.56 ^a	-1.92 ^b , -2.29 ^a	-5.22	-2.88	2.34
P-Ir-T	0.43 ^{<i>a</i>} , 0.52 ^{<i>a</i>}	-2.05 ^b , -2.40 ^a	-5.11	-2.75	2.36
P-Ir-C	0.54 ^a	-1.91 ^b , -2.41 ^a	-5.16	-2.89	2.27

^{*a*} Irreversible or quasi-reversible. The value was derived from the anodic or cathodic peak potential. ^{*b*} Reversible. The value was set as $E_{1/2}$. ^{*c*} HOMO levels are calculated according to the onset potential of the first irreversible oxidation wave, respectively. ^{*d*} LUMO levels are derived from the $E_{1/2}$ potential of the first reversible reduction wave.



Figure 5. Natural transition orbital (NTO) patterns for $S_0 \rightarrow T_1$ excitation for these cyclometalated iridium(III) complexes based on their optimized T_1 geometries.

Optical power limiting behaviors

Attributing the strong SOC effect to heavy metal centers, these cyclometalated iridium(III) complexes have shown NIR phosphorescent ability, indicating the formation of triplet excited states (T_1). Based on reverse saturable absorption (RSA) mechanism of T_1 states for a nano-second laser, the long-live T_1 states can show the potential of furnishing good OPL ability to these cyclometalated iridium(III) complexes. To the best of our knowledge, OPL properties have not been reported for unsymmetrical cyclometalated

iridium(III) complexes. Therefore, it should be very necessary to investigate their OPL performances in view of both developing new OPL materials and providing valuable structure–activity information for guiding the design of highly efficient OPL materials based on cyclometalated iridium(III) complexes. It is well-known that forming Donor(D)-Acceptor(A) structure is very critical for optimizing NLO properties. DTPO can act as electron acceptor. Obviously, introducing DTPO unit to the iridium(III) complexes should form new D-A structures to furnish improved OPL behaviours. Hence, the OPL

Journal Name

ARTICLE

properties of these cyclometalated iridium(III) complexes have been investigated.

To investigate the potential of these cyclometalated iridium(III) complexes as OPL materials, their transient absorption behavior was studied. The transient absorption difference spectra for these cyclometalated iridium(III) complexes are presented in Figure 6. As shown in Figure 6, these complexes exhibit broad and strong broad positive absorption bands from 520 to 700 nm and obvious bleaching bands from 480 to 520 nm. The bleaching bands are also in agreement with the ground-state absorption spectra, which can be attributed to the depletion of the ground CT states. These results indicate that these cyclometalated iridium(III) complexes can exhibit strong excited state absorption in the range from 520 to 700 nm, since their excited-state absorption (ESA) is stronger than the ground-state absorption. Hence, significant RSA can occur in this spectral region.

Based on the UV-vis spectra of these cyclometalated iridium(III) complexes (Figure 2), it can be clearly seen that they display very low ground-state absorption at 532 nm. Hence, their absorption behaviors are adaptable to characterize their OPL properties against 532 nm laser beam. Together with their transient absorption behavior, these cyclometalated iridium(III) complexes should possess strong OPL effect for 532 nm laser beam. On this basis, The OPL performances of these cyclometalated iridium(III) complexes have been carried out in CH_2Cl_2 solution with a high linear transmittance (T_0) of *ca*. 85% through open-aperture *Z*-scan method.

In the Z-scan measurement (Figure S2), the incident irradiance upon the solution samples was changed according to their Z-position (against focal point Z_0). When the sample stays far from the focal point with the weak incident laser irradiance, the transmittance (T) of the iridium(III) complexes solution can remains constant, exhibiting linear optical property (*i.e.* obeying Beer's law) (Figure 7). However, when the sample is gradually moved towards the focus with the incident laser irradiance increase (Figure S1), the T of the sample decreases to show OPL effect (Figure 7).

According to the good fitness between the Z-scan data and RSA mechanism (Figure S3), the OPL behavior of these cyclometalated iridium(III) complexes can be attributed to the reverse RSA of their T_1 states (Figure S3). The molecules in the ground state (S_0) can be excited to the first singlet states (S_1) by weak absorbing energy of laser irradiance. Meanwhile, as a result of strong SOC effect induced by the Ir(III) center. The S_1 states can convert to the first triplet states

(T₁) via intersystem crossing (ISC) process. Undoubtedly, the T₁ states possess much longer lifetime than duration the set of t furnishing enough time to the T₁ states for extensive absorbing energy of laser irradiance to be excited to a higher triplet states (T_n) and induce OPL effect (Figure S4). Clearly, P-Ir-P can outperform the unsymmetrical complexes P-Ir-T and P-Ir-C as OPL materials for 532 nm laser and even show better OPL ability than the state-of-the-art OPL material C₆₀ (Figure 7). Compared with P-Ir-T, the unsymmetrical analog P-Ir-C can possess enhanced OPL performance which is comparable to that of C_{60} . Hence, the OPL ability of these cyclometalated iridium(III) complexes fells in the order of P-Ir-P > P-Ir-C > P-Ir-T, showing excellent consistency with their transient absorption ability at 532 nm (Figure 6). The OPL ability of these cyclometalated iridium(III) complexes based on the RSA mechanism can be characterized by using the figure of merit factor σ_{ex}/σ_{o} = $In \textit{T}_{sat}/In \textit{T}_{o},$ where σ_{o} and σ_{ex} represent the ground-state absorption cross-section and the effective excited-state absorption crosssection, respectively. Accordingly, the σ_{ex}/σ_o values of P-Ir-P, P-Ir-T and P-Ir-C are 7.34, 4.02 and 6.17, respectively. Based on their absorption behavior (Figure 2), P-Ir-T shows stronger ground-state absorption ability to furnish higher σ_0 than that of **P-Ir-P** and **P-Ir-C**. Accordingly, **P-Ir-T** possesses the lowest σ_{ex}/σ_0 among the three complexes. So, it seems that introducing electron-donating group to the ppy-type iridium(III) complexes might not represent a feasible way to optimizing their OPL ability.



Figure 6. Time-resolved nanosecond transient difference absorption spectra of these cyclometalated iridium(III) complexes in CH_2Cl_2 solution. λ_{ex} = 400 nm. (c = 1 × 10 ⁻⁵ M).

ARTICLE



Figure 7. Open-aperture *Z*-scan curves for these unsymmetrical cyclometalated iridium(III) complexes with T₀ of *ca.* 85%.

Conclusions

Three cyclometalated iridium(III) complexes adopting symmetric and unsymmetrical structures have been developed with a new ppy-type ligand bearing dithieno[3,2-*b*:2',3'-*d*]phosphole oxide (DTPO) unit. It has been shown that these ppy-type cyclometalated iridium(III) complexes can show NIR phosphorescent emission beyond 730 nm. The transient absorption difference spectra of these complexes have indicated their potential as broad-band OPL materials from 520 to 700 nm. The *Z*-scan measurement against 532 nm laser has revealed that these ppy-type cyclometalated iridium(III) complexes can even possess comparable or better OPL ability with respect to that of the state-of-the-art OPL material C₆₀. All these results should indicate great potential of these DTPO-based iridium(III) complexes as new OPL materials.

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Iridium(III) complexes with dithieno[3,2b:2',3'-d]phosphole oxide group and their high optical power limiting performances

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New cyclometalated iridium(III) complexes with dithieno[3,2-b:2',3'-d]phosphole oxide group can show higher optical power limiting ability than C₆₀ for 532 nm laser.

