

Supporting Information

Supramolecular Architectures, Photophysics and Electroluminescence of 1, 3, 4-Oxadiazole-based Iridium (III) Complexes: from μ -Dichloro Bridged Dimer to Mononuclear Complexes

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1. General information and details of characterization.

¹H NMR, ¹³C NMR and ³¹P NMR spectra were recorded on Varian Mercury VX-300 MHz spectrometer. Elemental

analysis of carbon, hydrogen, and nitrogen was performed on a Carlorerba-1106 microanalyzer. Mass Spectra (FAB-MS) was determined by VJ-ZAB-3F Mass Spectrometer. Thermo gravimetric analysis (TGA) was performed with a Shimadzu-DT 40 instrument at a heating rate of 10 °C/min under static air and argon with gas flow of 50 ml/min. Cyclic voltammetry (CV) were recorded on CHI voltammetric analyzer. Anhydrous CH₂Cl₂ and THF were used as the solvent under nitrogen atmosphere, respectively. Tetra (*n*-butyl)-ammonium hexafluorophosphate (TBAPF₆) (0.1 M) was used as supporting electrolyte. The conventional three-electrode configuration consists of platinum working electrode, a platinum wire auxiliary electrode and an Ag wire quasi-reference electrode. The redox potentials were calibrated versus a ferrocenium/ferrocene (Fc⁺/Fc) redox couple used as an internal reference. UV-Vis absorption spectra were recorded on Shimadzu 160A UV-Vis recording spectrophotometer. PL spectra were performed on Perkin-Elmer LS 55 luminescence spectrophotometer.

Materials and Methods. All reactions and manipulations were carried out under argon atmosphere. All silica gel column chromatography was performed with use of silica gel (200~300 mesh). 2, 5-di-*p*-tolyl-1, 3, 4-oxadiazole, 2, 5-bis (4-methoxyphenyl)-1, 3, 4-oxadiazole, potassium *O*, *O'*-diethyldithiophosphate (KEt₂dtp) and sodium *N*, *N'*-diethyl-dithiocarbamate (NaEt₂dtc) were prepared according to the literature, respectively. Iridium trichloride hydrate and other chemicals were commercially available and used as received unless otherwise stated.

Synthesis of dinuclear Ir(III) complexes. Iridium trichloride hydrate (0.352 g, 1.0 mmol), combined with 2.5 equiv of 1, 3, 4-oxadiazole derivatives, was dissolved in a mixture of 2-ethoxyethanol (30 ml) and water (10 ml), and then refluxed for 24h. The solution was cooled to room temperature, and the resulting yellow precipitate was collected by filtration and washed with water, ethanol and hexane. After dried under vacuum, the crude product was recrystallized from dichloromethane/hexane (1:1, v/v).

Tetrakis[2,5-bis(4-methoxyphenyl)-1,3,4-oxadiazolyl-C²,N](μ-dichloro)diiridium(III) dichloromethane solvate [Ir(mox)₂Cl]₂·2CH₂Cl₂ 1: Yield: 65 %. ¹H NMR (CDCl₃, ppm) δ: 7.84 (d, *J* = 8.4 Hz, 8H), 7.43 (d, *J* = 8.4 Hz, 4H), 6.64 (d, *J* = 8.4 Hz, 8H), 6.42 (d, *J* = 8.1 Hz, 4H), 6.02 (s, 4H), 3.84 (s, 12H), 3.50 (s, 12H). Calcd for C₆₄H₅₂O₁₂N₈Cl₂Ir₂·2CH₂Cl₂: C, 45.29; H, 3.22; N, 6.40, Found: C, 45.23; H, 3.10; N, 6.21 %.

Tetrakis[2, 5-di-*p*-tolyl-1, 3, 4-oxadiazolyl-C²,N](μ-dichloro)diiridium(III) [Ir(tox)₂Cl]₂: Yield: 70 %. ¹H NMR (CDCl₃, ppm) δ: 7.85 (d, *J* = 8.1 Hz, 8H), 7.41 (d, *J* = 8.1 Hz, 4H), 6.96 (d, *J* = 7.8 Hz, 8H), 6.66 (d, *J* = 7.5 Hz, 4H), 6.31(s, 4H), 2.33 (s, 12H), 2.04 (s, 12H).

Synthesis of mononuclear Ir(III) complexes. [Ir(tox)₂Cl]₂ (120 mg, 0.0827 mmol), 0.25 mmol ancillary ligands, such as acetylacetone for **2**, KEt₂dtp for **3** and NaEt₂dtc for **4**, and Na₂CO₃ (106 mg, 1.0 mmol) were dissolved in 2-ethoxyethanol (10 ml). The mixture was refluxed under argon for 15 ~ 18 h. After cooling to room temperature, small quantity water was added. The resulting yellow precipitate was collected by filtration and washed with water, ethanol and hexane. After dried under vacuum, the crude product was purified by column chromatography on silica gel with CH₂Cl₂/petroleum ether (1:1~1:3) as eluent.

Bis(2, 5-di-*p*-tolyl-1, 3, 4-oxadiazolyl-C²,N)iridium(acetylacetonate) [Ir(tox)₂(acac)] 2: Yield (based on the dimer): 86 %. ¹H NMR (CDCl₃, 300MHz) δ: 8.12 (d, *J* = 8.1 Hz, 4H), 7.48 (d, *J* = 8.1 Hz, 2H), 7.37 (d, *J* = 8.1 Hz, 4H), 6.72 (d, *J* = 7.5, 2H), 6.51 (s, 2H), 5.27 (s, 1H), 2.46 (s, 6H), 2.16 (s, 6H), 1.90 (s, 6H). Anal. Calcd for C₃₇H₃₃O₄N₄Ir: C, 56.26; H, 4.21; N, 7.09. Found: C, 56.01; H, 4.28; N, 6.94 %. MS (FAB): *m/e*, 790 (M⁺).

Bis(2, 5-di-*p*-tolyl-1, 3, 4-oxadiazolyl-C²,N) iridium (*O*,*O'*-diethyldithiophosphate) [Ir(tox)₂(Et₂dtp)] 3: Yield

(based on the dimer): 82 %. ^1H NMR (CDCl_3 , 300MHz) δ : 8.02(d, $J = 7.5$ Hz, 4H), 7.40 (d, $J = 7.8$ Hz, 2H), 7.321 (d, $J = 7.8$ Hz, 4H), 6.65 (d, $J = 7.8$ Hz, 2H), 6.52 (s, 2H), 4.45 (m, 2H), 4.15 (m, 2H), 2.41 (s, 6H), 2.09 (s, 6H), 1.26 (t, $J = 7.2$ Hz, 6H). ^{13}C NMR (CDCl_3 , 300 MHz): 175.9, 163.3, 150.8, 143.0, 142.2, 134.4, 130.2, 126.8, 124.9, 123.2, 122.8, 120.9, 63.4, 22.2, 21.9, 16.5, 16.4. ^{31}P NMR (CDCl_3 , 300MHz): 106.5; Anal.Calcd for $\text{C}_{36}\text{H}_{36}\text{O}_4\text{N}_4\text{S}_2\text{PIr}$: C, 49.36; H, 4.14; N, 6.40. Found: C, 49.30; H, 4.01; N, 6.68 %. MS (FAB): m/e, 876 (M^+).

Bis(2, 5-di-*p*-tolyl-1, 3,4-oxadiazolyl- C^2 ,N) iridium (*N,N'*-diethyldithiocarbamate) [$\text{Ir}(\text{tox})_2(\text{Et}_2\text{dtc})$] **4:** Yield (based on the dimer): 85 %. ^1H NMR (CDCl_3 , 300MHz) δ : 8.14 (d, $J = 7.5$ Hz, 2H), 7.48 (d, $J = 7.2$ Hz, 2H), 7.36 (d, $J = 8.1$ Hz, 2H), 7.24 (s, 2H), 6.69 (d, $J = 7.8$ Hz, 2H), 6.54 (s, 2H), 3.88 (m, 2H), 3.48 (m, 2H), 2.47 (s, 6H), 2.15 (s, 6H), 1.28 (t, $J = 6.9$ Hz, 6H). ^{13}C NMR (CDCl_3 , 300MHz): 174.6, 162.1, 154.1, 141.3, 140.2, 133.6, 128.8, 125.9, 123.4, 121.8, 121.5, 120.2, 42.3, 30.9, 28.7, 28.3, 21.7, 20.9, 20.7, 13.1, 11.4. Anal.Calcd for $\text{C}_{37}\text{H}_{36}\text{O}_2\text{N}_5\text{S}_2\text{Ir}$: C, 52.96; H, 4.32; N, 8.55. Found: C, 52.57; H, 3.90; N, 8.89 %. MS (FAB): m/e, 839 (M^+).

2. OLED fabrication and measurements.

Organic layers were fabricated by high-vacuum thermal evaporation onto a pre-cleaned indium tin oxide (ITO, 30 Ω /square). The glass substrates were sequentially cleaned by detergent, deionized, water, ethanol, acetone and chloroform in ultrasonic bath and heated in an ultra-infrared dry oven. In a vacuum chamber with a pressure of <10⁻⁴ Pa, 40 nm of (4, 4'-bis{*N*-(1-naphthyl-*N*-phenyl- amino)biphenyl})(NPB) as the hole transorting layer(HTL), 30 nm of Ir complexes doped 4, 4'-biscarbazolybiphenyl (CBP) as the emitting layer, 10 nm of 2, 9-dimethyl-4, 7-diphenyl-1, 10-phenanthroline (BCP) as a hole and exciton blocking layer, 30 nm of AlQ₃ as the electron trans porting layer (ETL), and a cathode composed of 1 nm of lithium fluoride and 100 nm of aluminum were sequentially deposited onto the substrate to construct the device. The *J-V-B* of EL devices was measured at ambient condition with a Keithley 2400 Source meter and a Keithley 2000 Source multimeter equipped with a calibrated silicon photodiode. The EL spectra were measured by JY SPEX CCD3000 spectrometer.

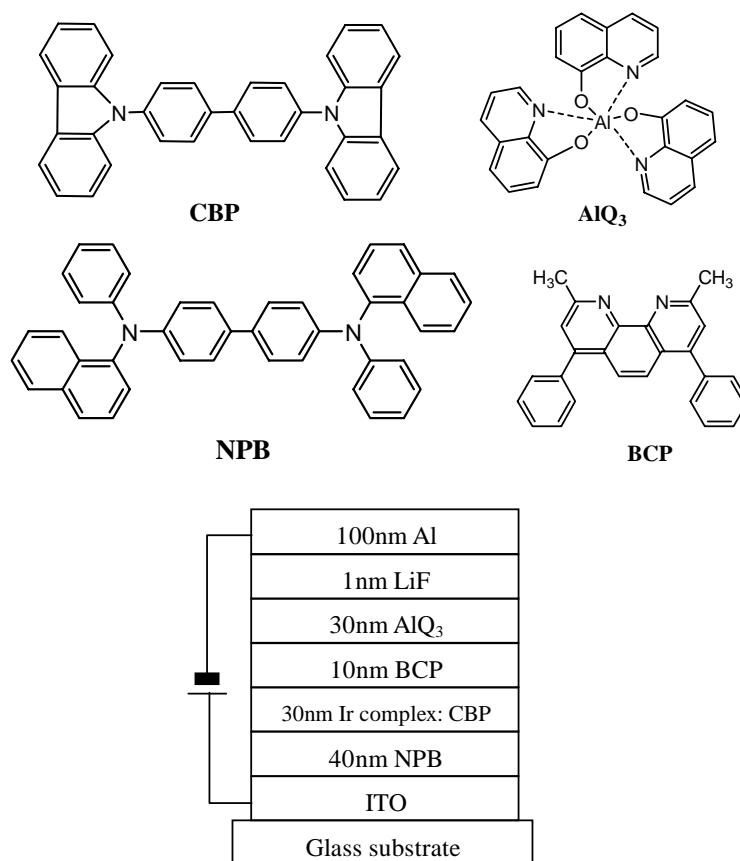


Figure S1. The configuration of device and the molecular structures of the compounds used in the devices.

3. Coordination geometries around Ir(III) ions for 1-4.

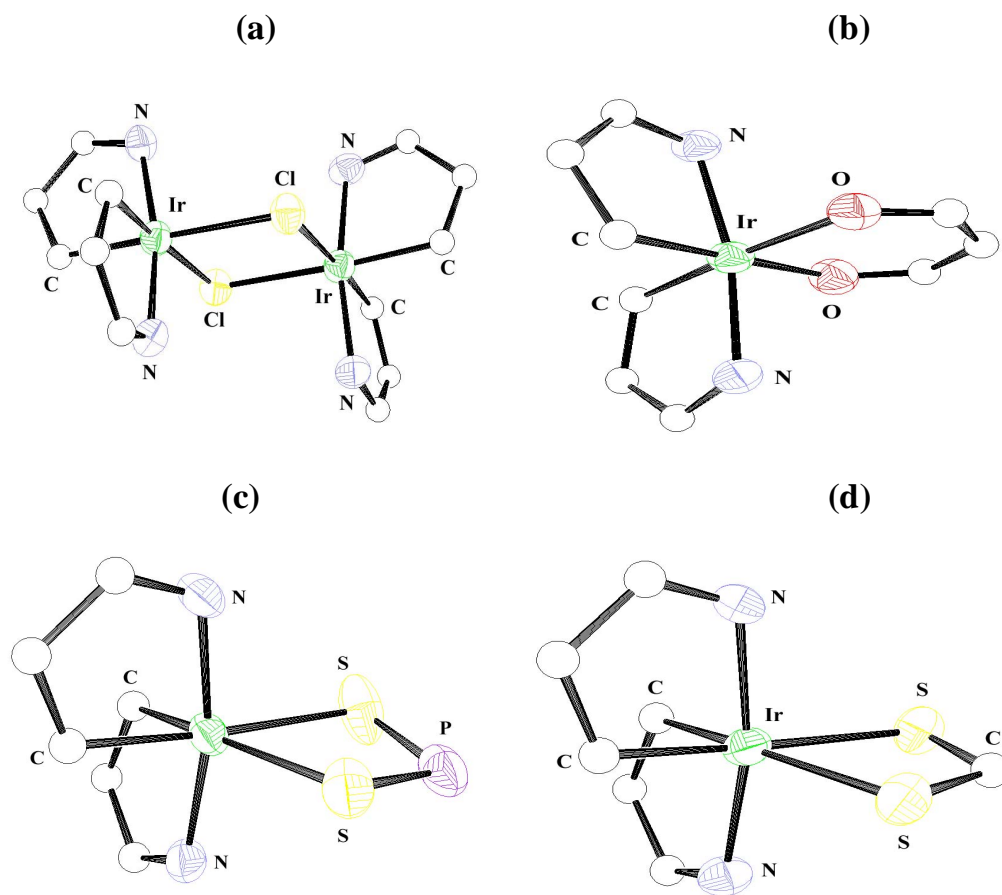


Figure S2. Coordination Geometries around Ir (III) ions in 1 (a), 2 (b), 3 (c) and 4 (d).

4. Crystal packing views of 1-4.

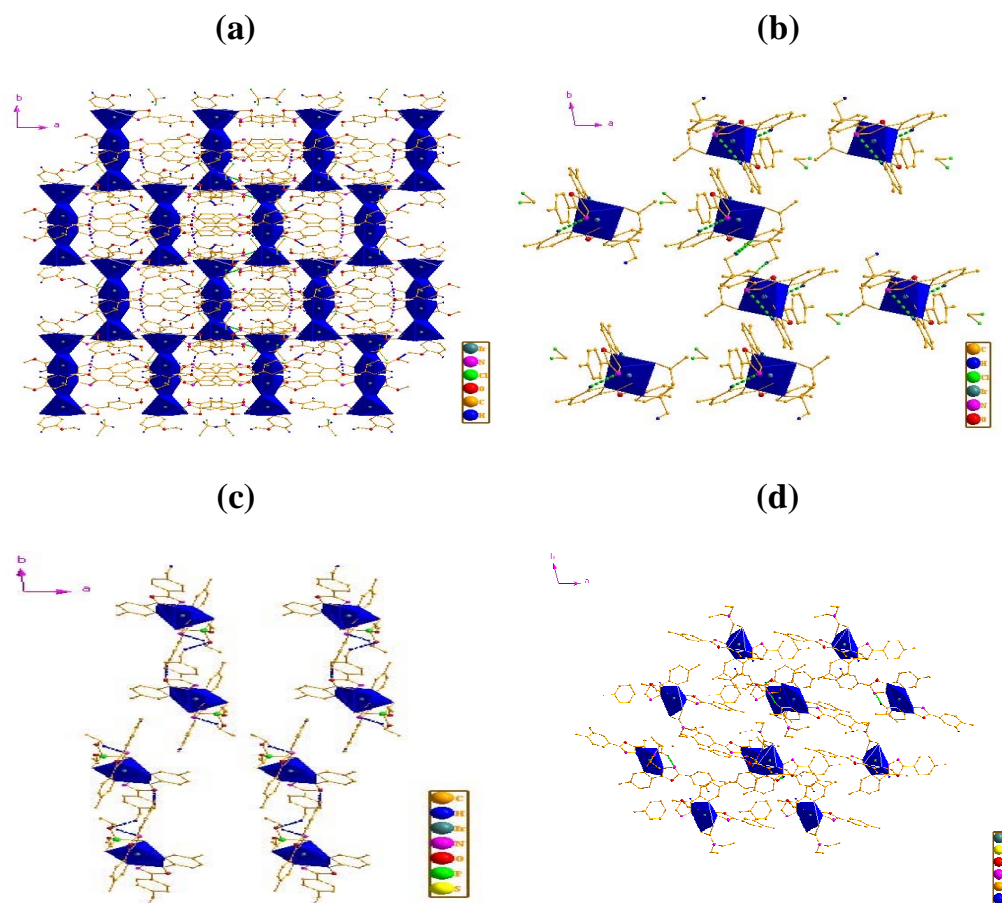


Figure S3. Crystal packing viewed along the *c*-axis of 1 (a), 2 (b), 3 (c) and 4 (d).

5. Thermogravimetric analysis (TGA) plots of 1-4.

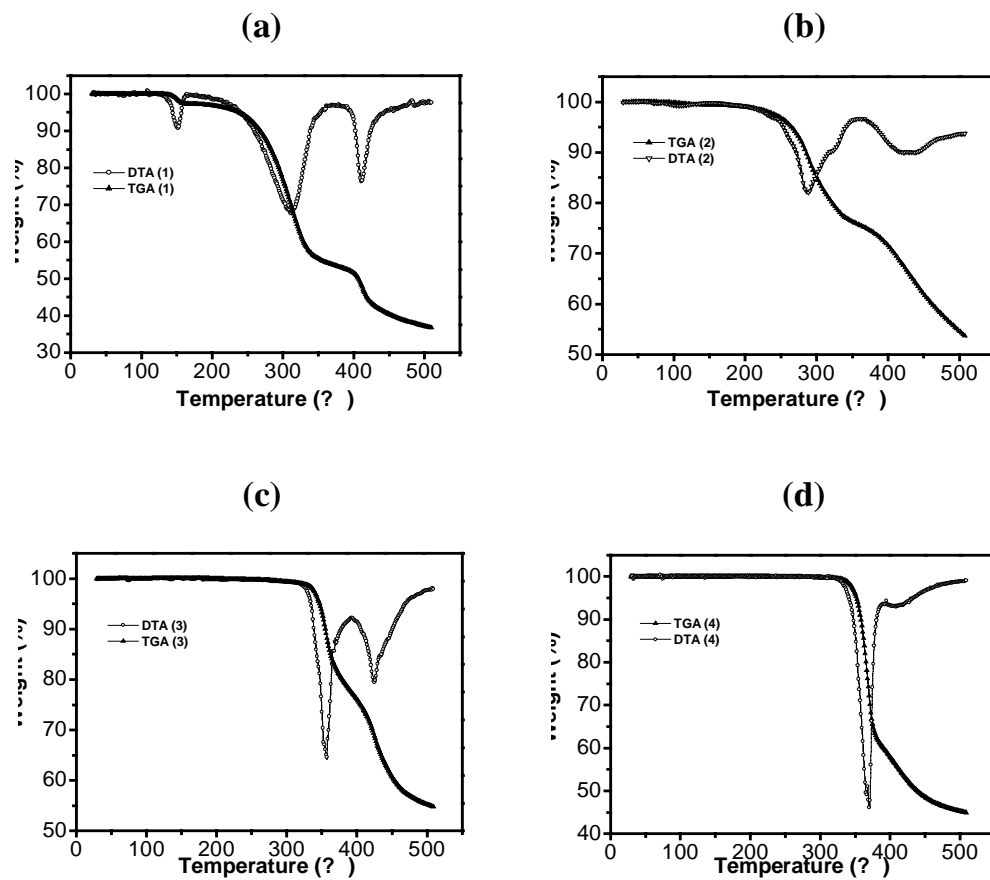


Figure S4. TGA/DTA curves for complex 1 (a), 2 (b), 3 (c) and 4 (d).

6. Photophysical data of Ir(III) Complexes.

Table S1. Photophysical data for the iridium complexes.

Complex	UV-Vis ^a	PL λ_{max} nm		Φ_f^d
	λ_{abs} (log ϵ) nm	solution ^a	Film ^b	⌊ % ⌋
1	243(3.9), 296(4.0), 358(3.4), 417(3.1), 448(2.7)	535 565	541 570	2.6
2	251(3.9), 296(4.0), 367(3.3), 422(3.1), 454(2.8)	519 547	526 557	32.6
3	248(3.9), 296(4.0), 365(3.4), 410(3.2), 443(2.7)	501 536	511 547	13.2
4	250(4.0), 300(3.9), 373(3.4), 412(3.1), 445(2.7)	506 538	517 550	19.5

^a in CH₂Cl₂ solution at 298K. ^b in PMMA film (7 % weight ratio). ^cQuantum yield was measured in CH₂Cl₂ solution relative to quinine bisulfate (10⁻⁵ M in 1.0 N H₂SO₄).