

*Electronic Supporting information (ESI)*

**Small molecular neutral microcrystalline iridium(III)  
complexes as promising molecular oxygen sensors**

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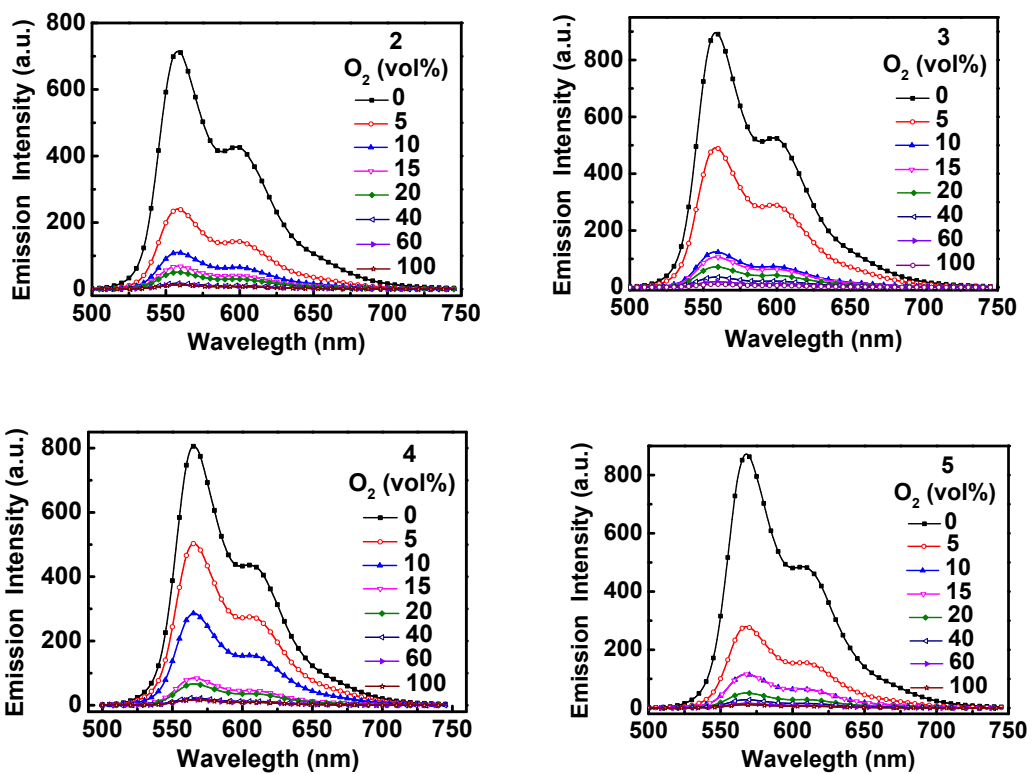
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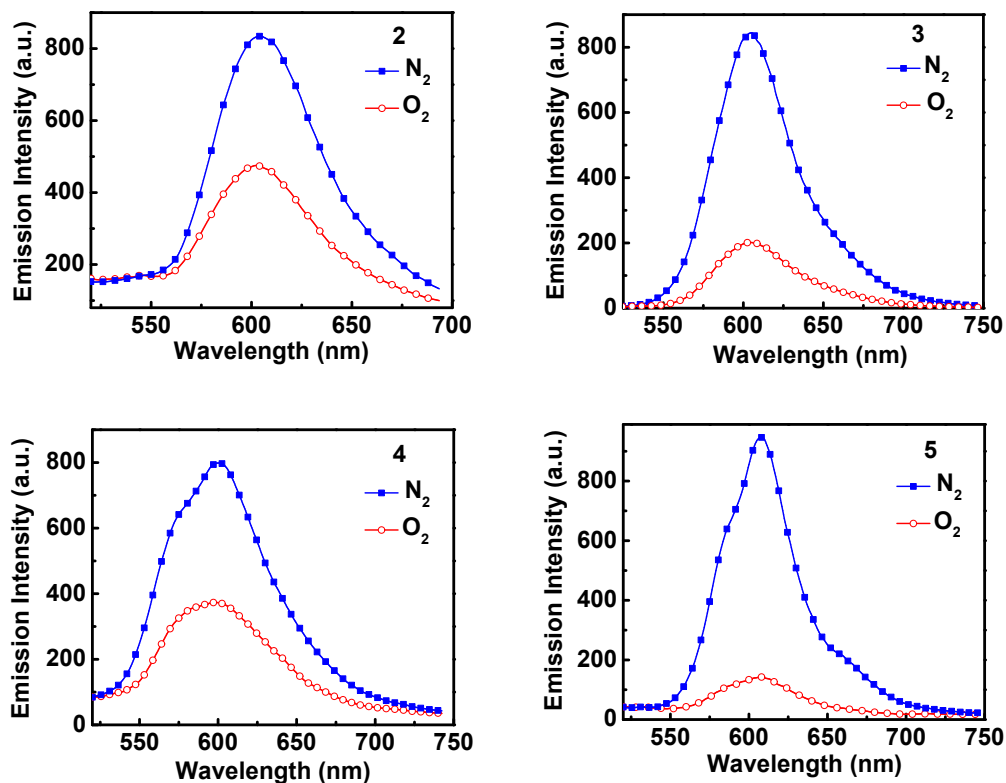
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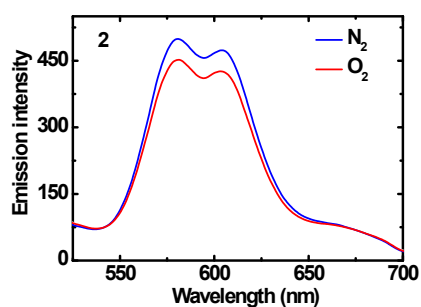
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**Fig. S1** PL emission spectra of dilute toluene solutions of **2-5** at varied concentrations of O<sub>2</sub> in N<sub>2</sub> ( $10^{-5}$  M,  $\lambda_{\text{ex}} = 480$  nm).



**Fig. S2** PL emission spectra of microcrystalline powder samples of **2-5** in pure  $N_2$  and pure  $O_2$ . ( $\lambda_{ex} = 385$  nm for **2**,  $\lambda_{ex} = 400$  nm for **3**, and  $\lambda_{ex} = 480$  nm for **4** and **5**)



**Fig. S3** PL emission spectra of the microcrystalline thin-film sample of **2** in  $N_2$  and  $O_2$  atmosphere ( $\lambda_{ex} = 385$  nm).

**Table S1** The relevant X-ray crystallographic analysis results as well as oxygen sensing properties of the four neutral Ir(III) complexes

Compd.	$(I_0 - I_{100})/I_0^a$	$K_{SV}^b$	$R^2$	$t_{\downarrow, \uparrow, 95\%}$ (s) <sup>c</sup>	Void fraction <sup>d</sup>
<b>2</b>	9.2%	-	-	-, -	1.2% (2.7%)
<b>3<sup>e</sup></b>	70.3%	2.380	0.9996	126, 285	1.5% (1.5%)
<b>4</b>	86.7%	6.409	0.9979	46, 130	0.8% (19.9%)
<b>5</b>	50.2%	1.057	0.9954	92, 108	3.5% (16.3%)

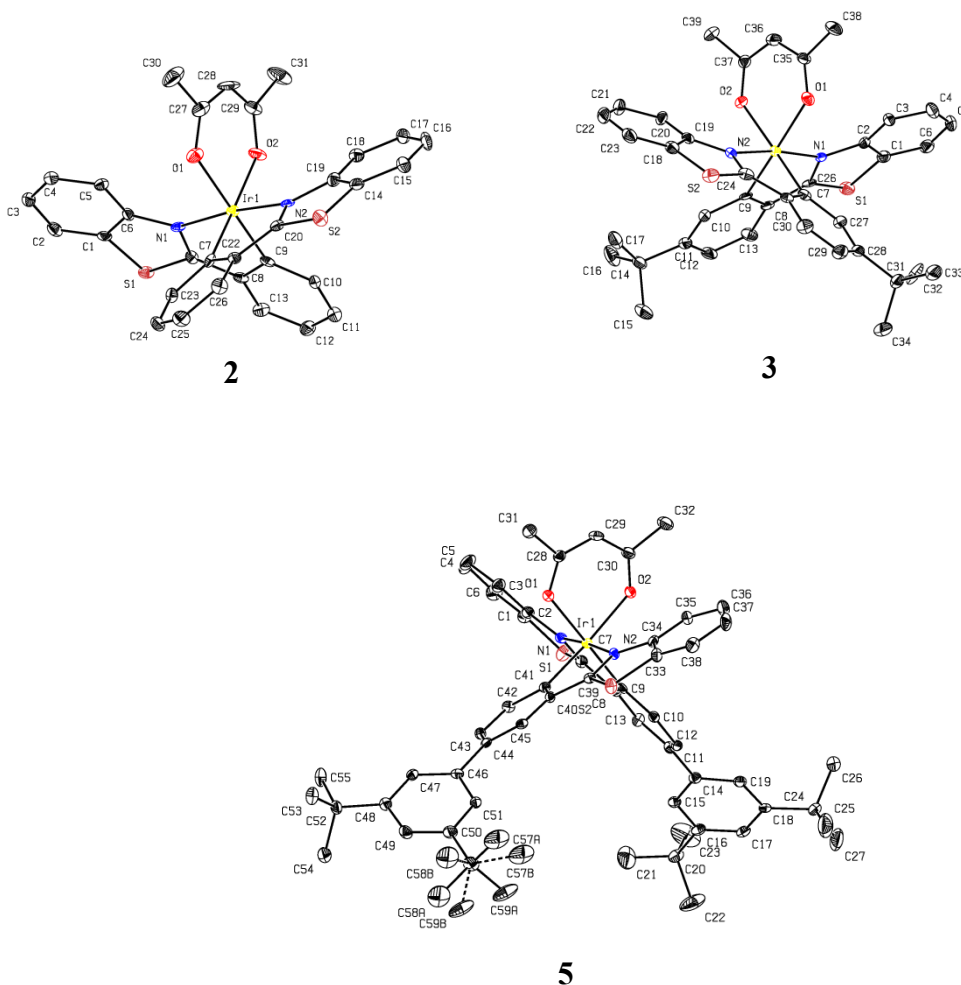
<sup>a</sup>  $I_0$  and  $I_{100}$  represent the PL intensity at  $\lambda_{PL,max}$  in nitrogen with oxygen concentration of 0 and 100 vol%, respectively;

<sup>b</sup>  $K_{SV}$  is the associated Stern-Volmer quenching constant;

<sup>c</sup>  $t_{\downarrow, \uparrow, 95\%}$  is the 95% response ( $N_2 \rightarrow O_2$ ) or recovery ( $O_2 \rightarrow N_2$ ) time;

<sup>d</sup> The fraction of free volume in the unit-cell; data listed in parentheses are those calculated from the desolvated crystal structures;

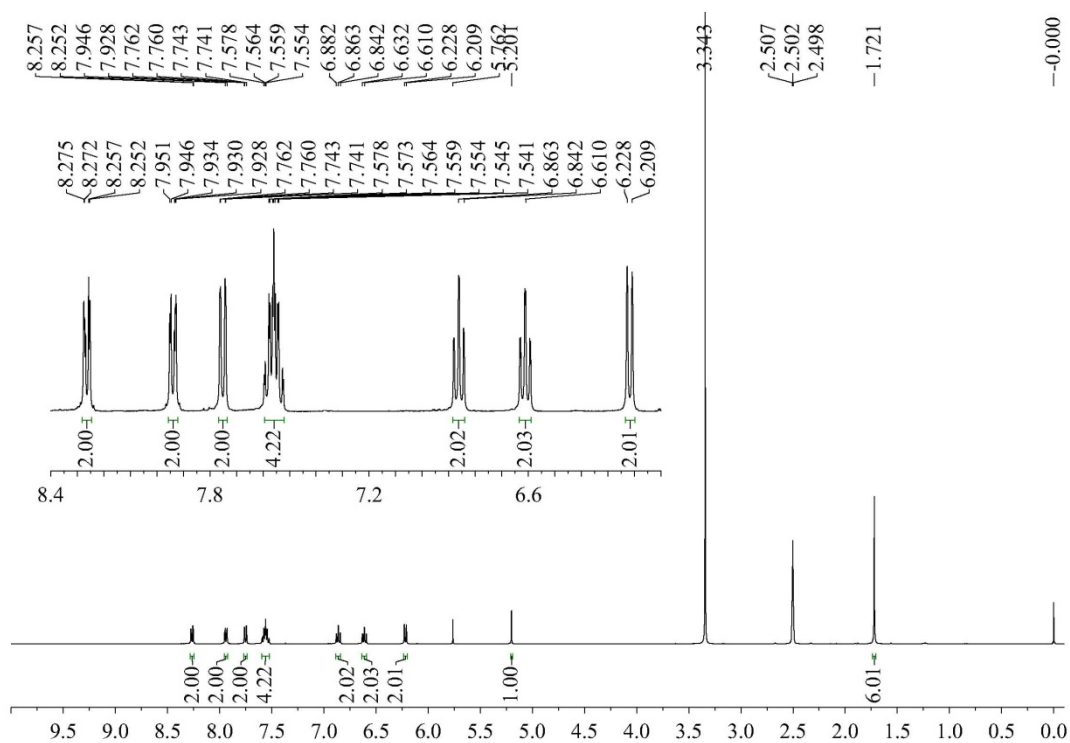
<sup>e</sup> Without any cocrystallized solvent molecules in the crystal structure.



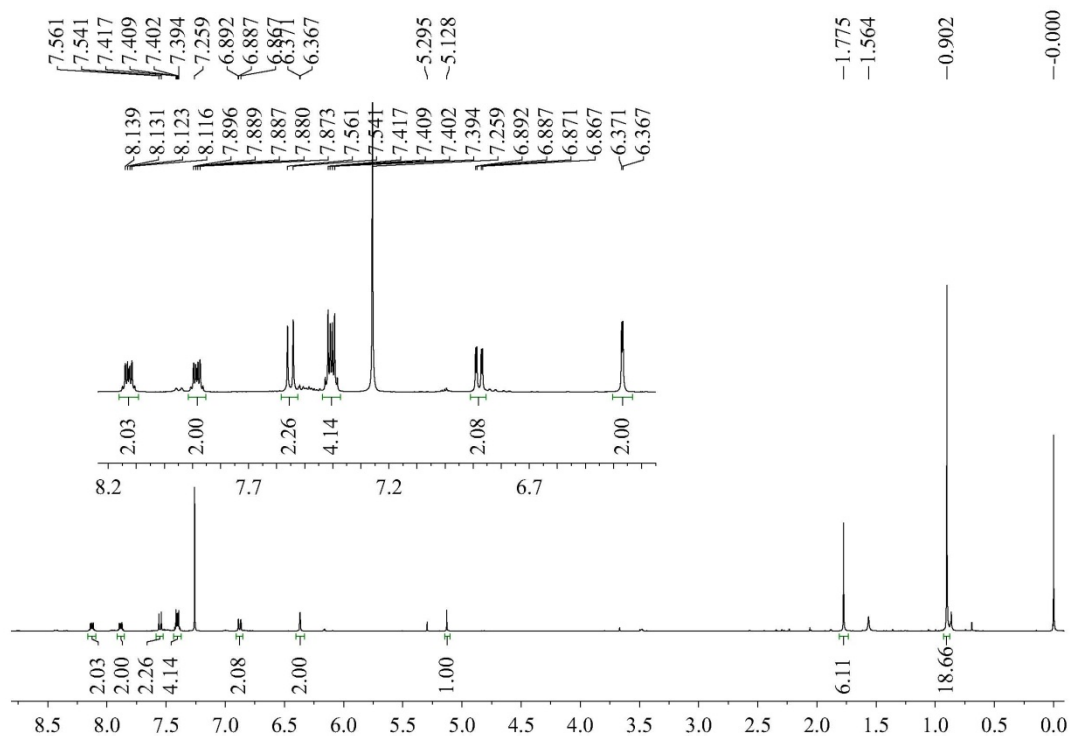
**Fig. S4** ORTEP plot of the structures of **2**, **3** and **5** (with their solvent molecule and hydrogen atoms removed for clarity, ellipsoids at 30% probability).

**Table S2** The crystallographic data and refinement parameters of **2**, **3** and **5**

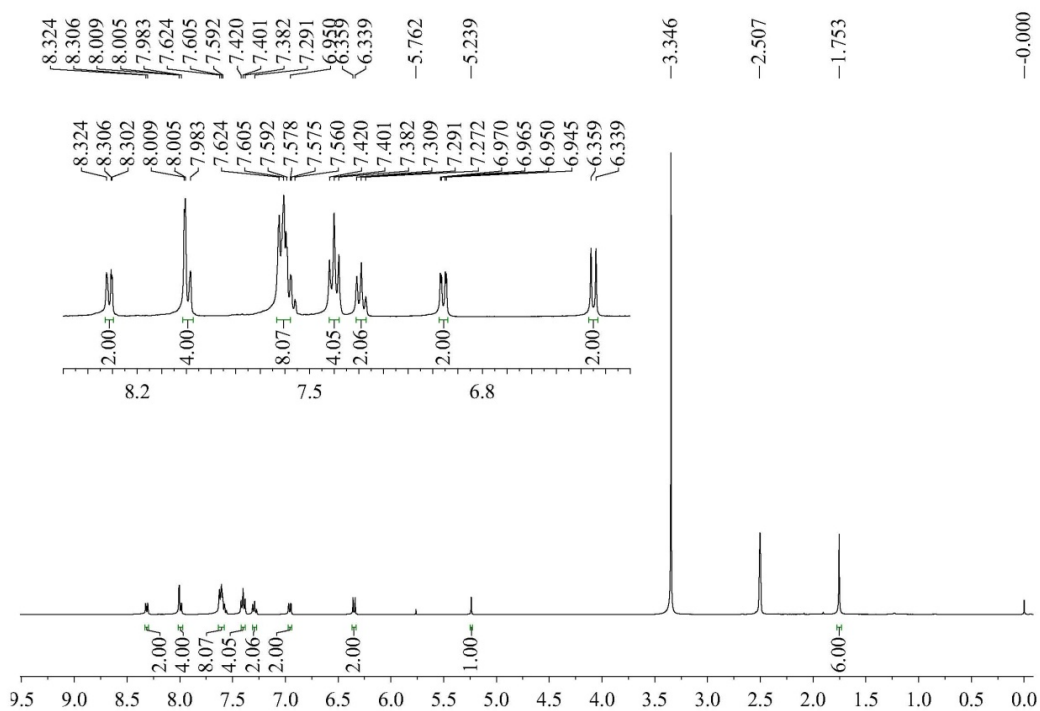
Compound	<b>(2)<sub>4</sub>·CH<sub>3</sub>OH</b>	<b>3</b>	<b>5·CH<sub>2</sub>Cl<sub>2</sub></b>
Empirical formula	C <sub>125</sub> H <sub>95</sub> Ir <sub>4</sub> N <sub>8</sub> O <sub>9</sub> S <sub>8</sub>	C <sub>39</sub> H <sub>39</sub> IrN <sub>2</sub> O <sub>2</sub> S <sub>2</sub>	C <sub>60</sub> H <sub>65</sub> IrN <sub>2</sub> O <sub>2</sub> S <sub>2</sub> Cl <sub>2</sub>
Formula weight	2878.36	824.04	1173.36
Temperature	142.95 (10) K	142.95 (10) K	143.0 (10) K
Crystal system	Triclinic	Orthorhombic	Triclinic
Space group	P-1	Pbca	P-1
a	18.4383 (5) Å	13.4876 (4) Å	12.8835 (3) Å
b	18.6855 (6) Å	18.3802 (6) Å	14.7285 (4) Å
c	19.9281 (6) Å	27.8072 (9) Å	16.0114 (4) Å
$\alpha$	107.775 (3) deg	90.00 deg	103.949 (2) deg
$\beta$	99.052 (2) deg	90.00 deg	93.493 (2) deg
$\gamma$	117.763 (3) deg	90.00 deg	103.298 (2) deg
Volume	5407.5 (3) Å <sup>3</sup>	6893.5 (4) Å <sup>3</sup>	2847.72 (13) Å <sup>3</sup>
Z	2	8	2
Calculated density	1.768 mg·mm <sup>-3</sup>	1.588 mg·mm <sup>-3</sup>	1.368 mg·mm <sup>-3</sup>
Absorption coefficient	5.126 mm <sup>-1</sup>	4.032 mm <sup>-1</sup>	2.553 mm <sup>-1</sup>
F(000)	2818	3296	1196
Crystal size	0.35 × 0.3 × 0.3 mm	0.4 × 0.4 × 0.25 mm	0.35 × 0.30 × 0.25 mm
Reflections collected	44827	39733	25244
Independent reflections	22073 [R(int) = 0.0374]	7034 [R(int) = 0.0827]	11636 [R(int) = 0.0417]
$\theta$ -range for data collection	3.04 to 26.372°	2.93 to 26.371°	2.894 to 26.371°
Goodness-of-fit on F <sup>2</sup>	1.090	1.150	1.032
Final R indices [I > 2 $\sigma$ (I)]	R <sub>1</sub> = 0.0444, wR <sub>2</sub> = 0.0962	R <sub>1</sub> = 0.0598, wR <sub>2</sub> = 0.1123	R <sub>1</sub> = 0.0387, wR <sub>2</sub> = 0.0877
R indices (all data)	R <sub>1</sub> = 0.0631, wR <sub>2</sub> = 0.1056	R <sub>1</sub> = 0.0804, wR <sub>2</sub> = 0.1230	R <sub>1</sub> = 0.0464, wR <sub>2</sub> = 0.0913
Largest diff. peak and hole	3.40 and -2.20 e·Å <sup>-3</sup>	2.18 and -3.02 e·Å <sup>-3</sup>	1.56 and -0.95 e·Å <sup>-3</sup>



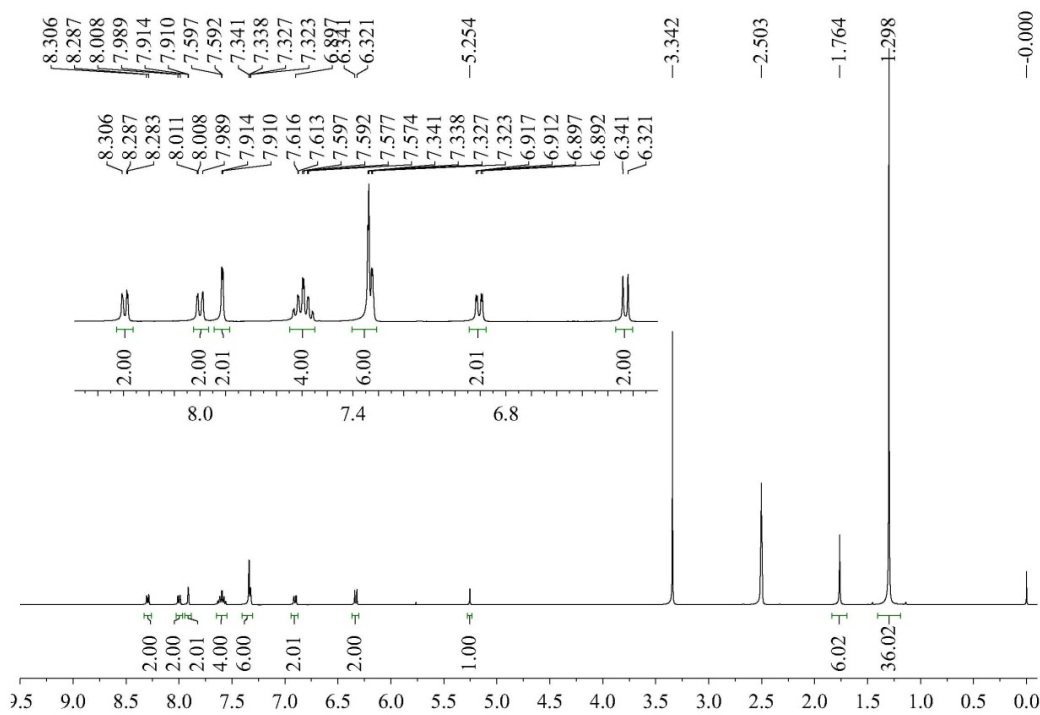
**Fig. S5** The  $^1\text{H}$ NMR spectrum of the microcrystalline powder sample of complex **2** after the oxygen quenching experiments.



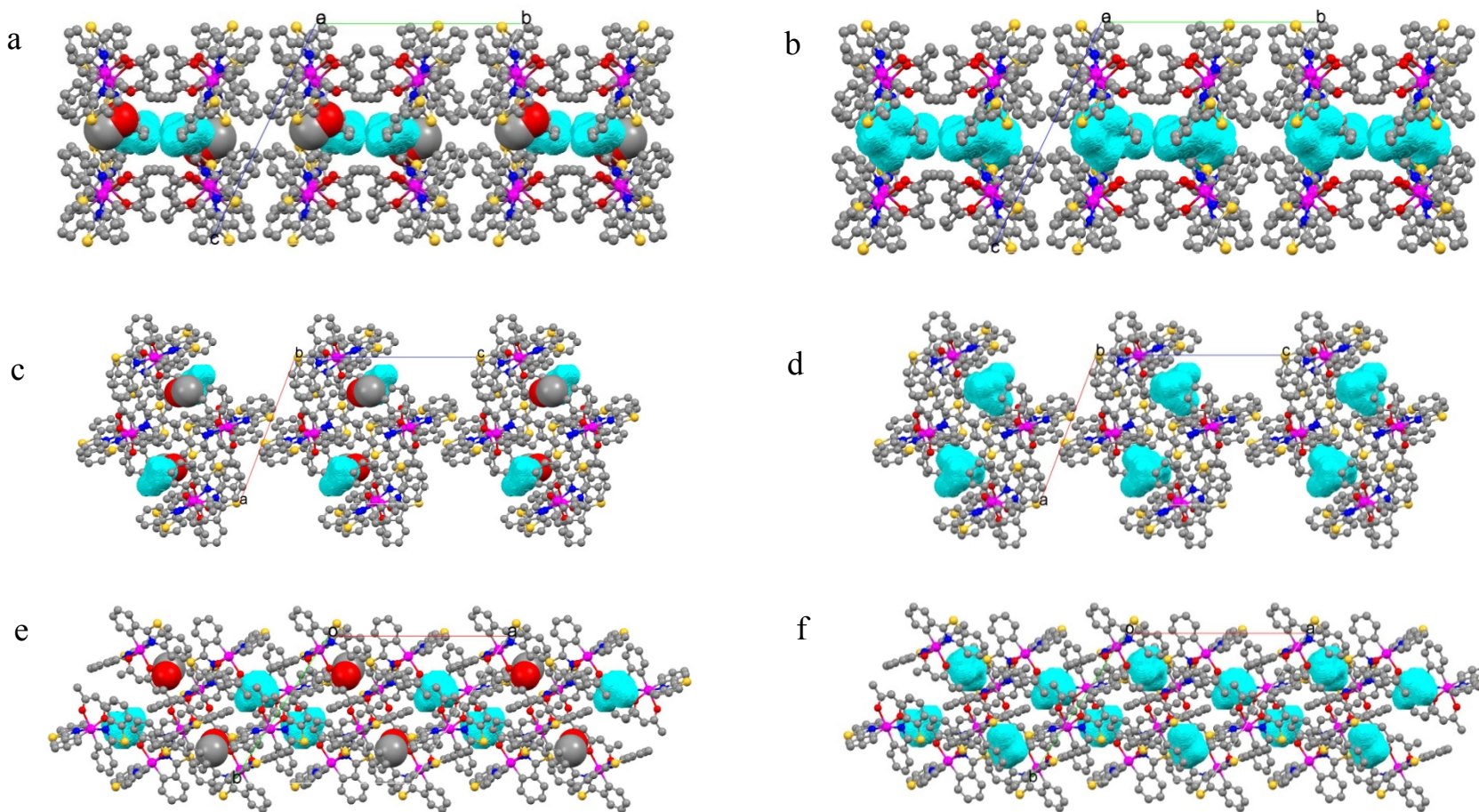
**Fig. S6** The  $^1\text{H}$ NMR spectrum of the microcrystalline powder sample of complex **3** after the oxygen quenching experiments.



**Fig. S7** The  $^1\text{H}$ NMR spectrum of the microcrystalline powder sample of complex **4** after the oxygen quenching experiments.

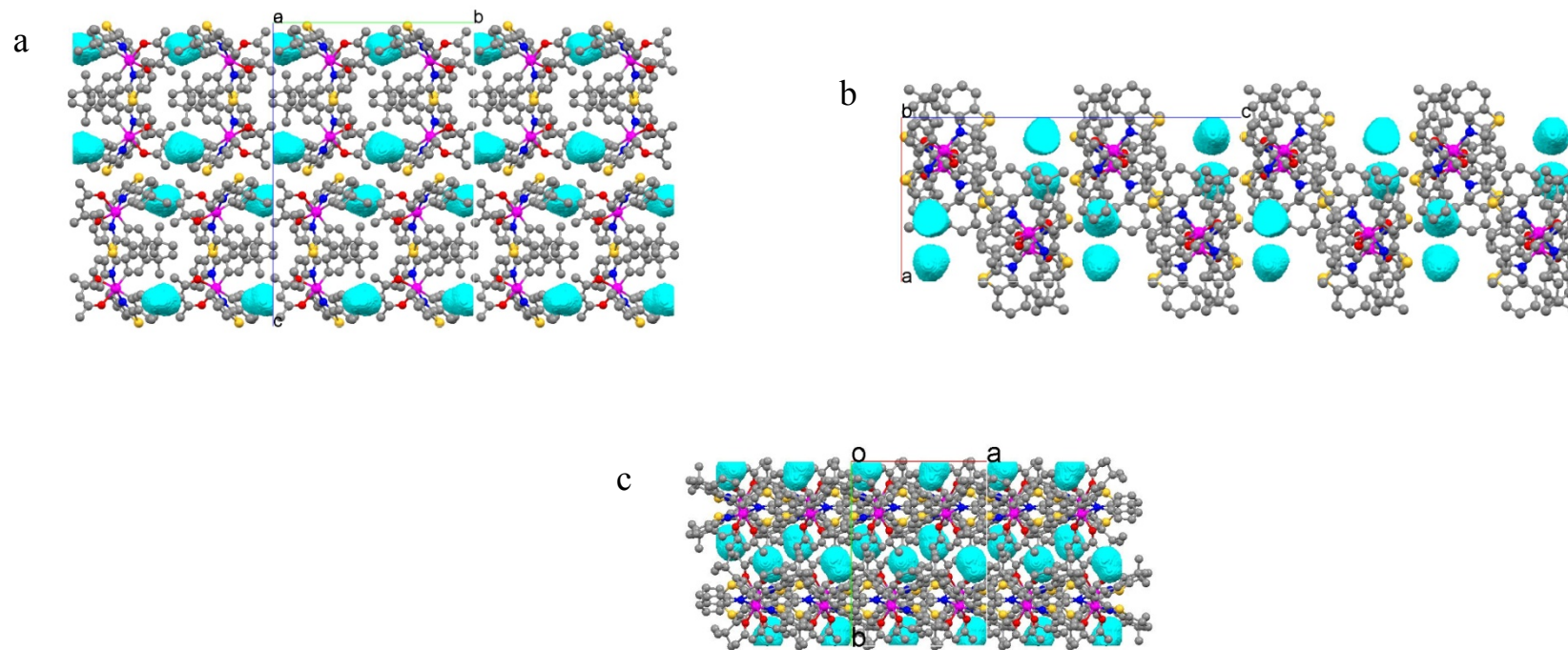


**Fig. S8** The  $^1\text{H}$ NMR spectrum of the microcrystalline powder sample of complex **5** after the oxygen quenching experiments.

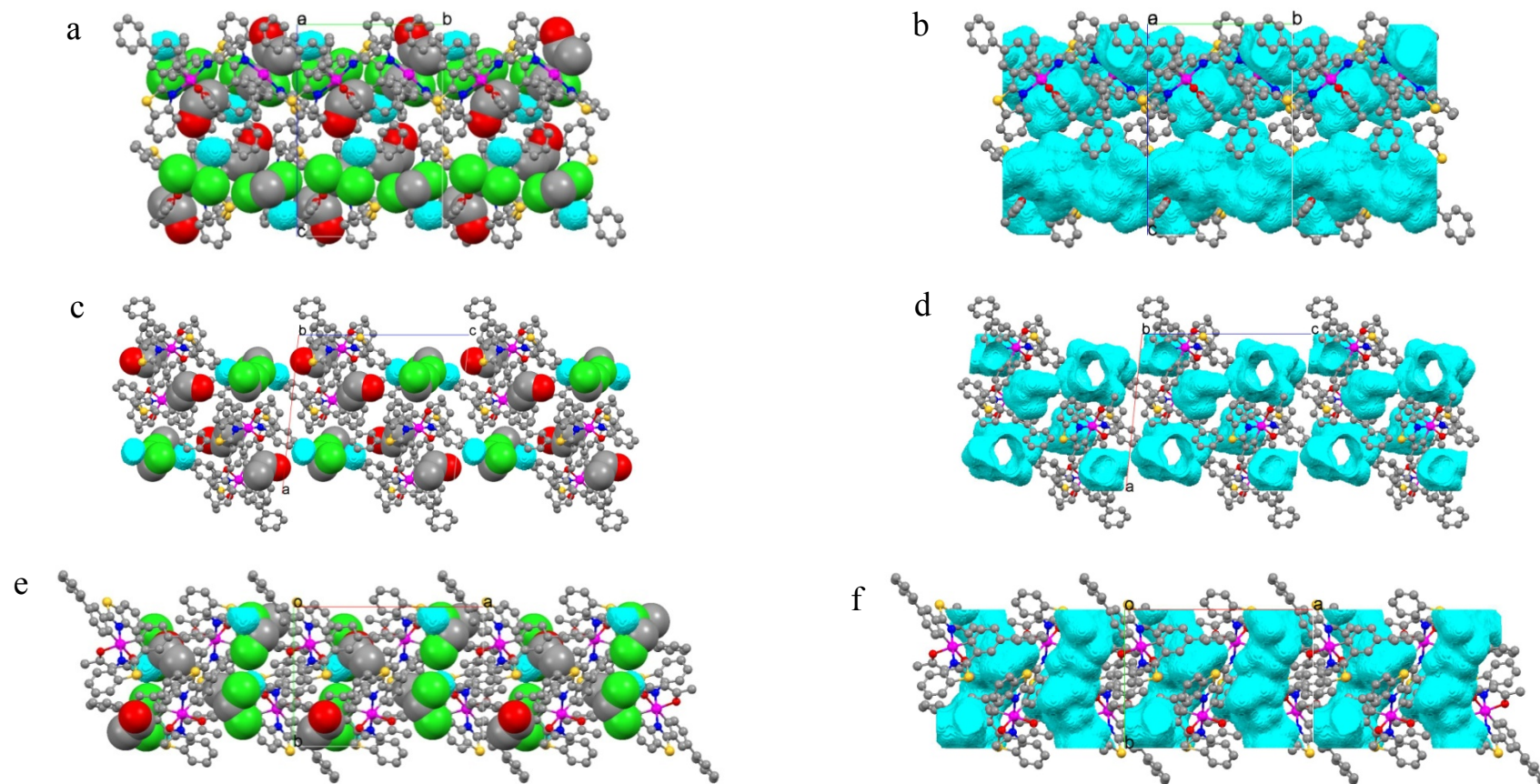


**Fig S9** Pictorial representations of the open voids and channels of complex **2** with its cocrystallized solvent molecules retained (left) or removed (right) using MERCURY/Voids (filled with cyan sphere probes whose radius is 1.2 Å; the solvent molecules are shown in space-filling model). (a) and (b): viewing down the *a*-axis; (c) and (d): viewing down the *b*-axis; (e) and (f): viewing down the *c*-axis.

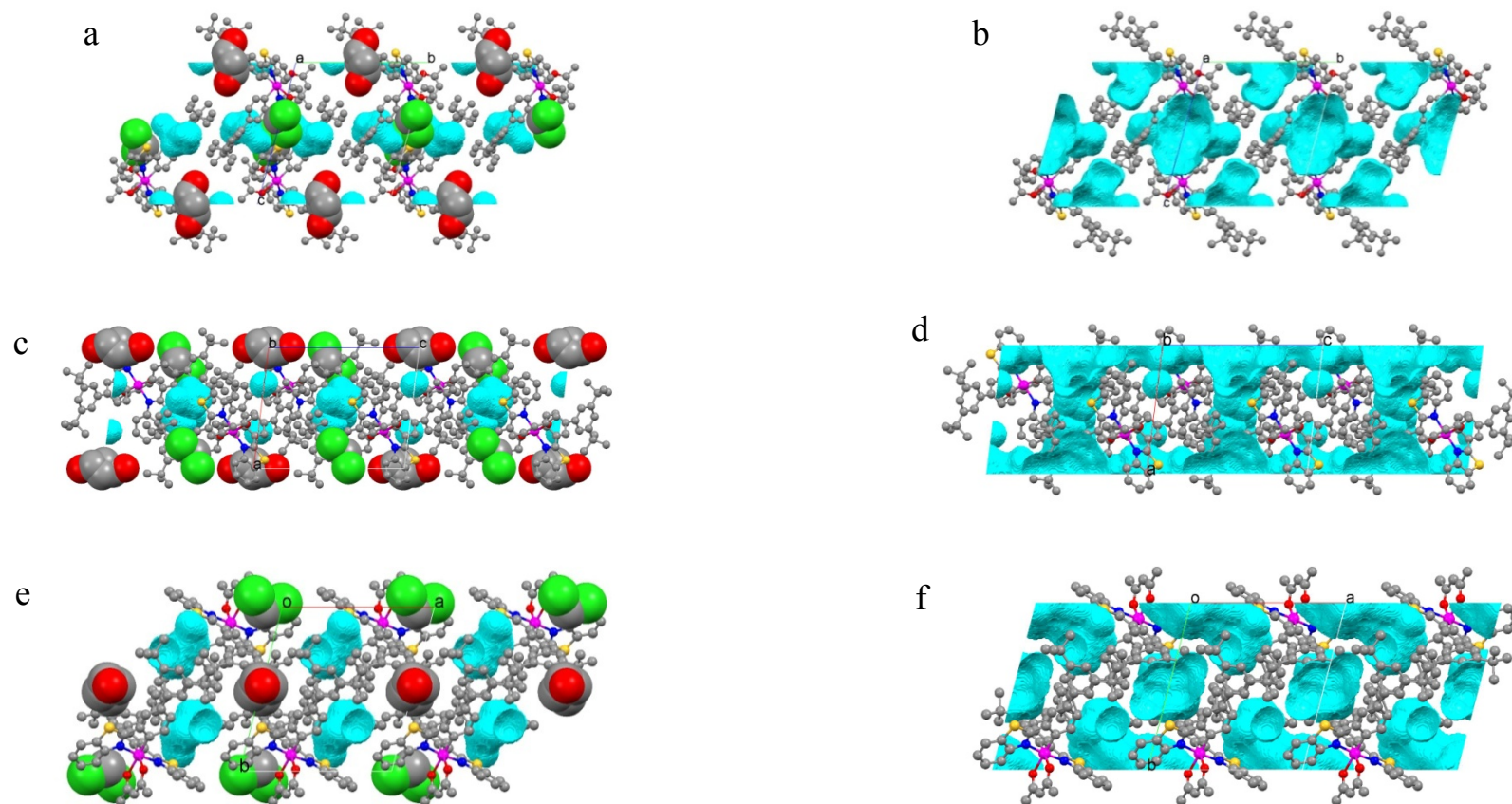




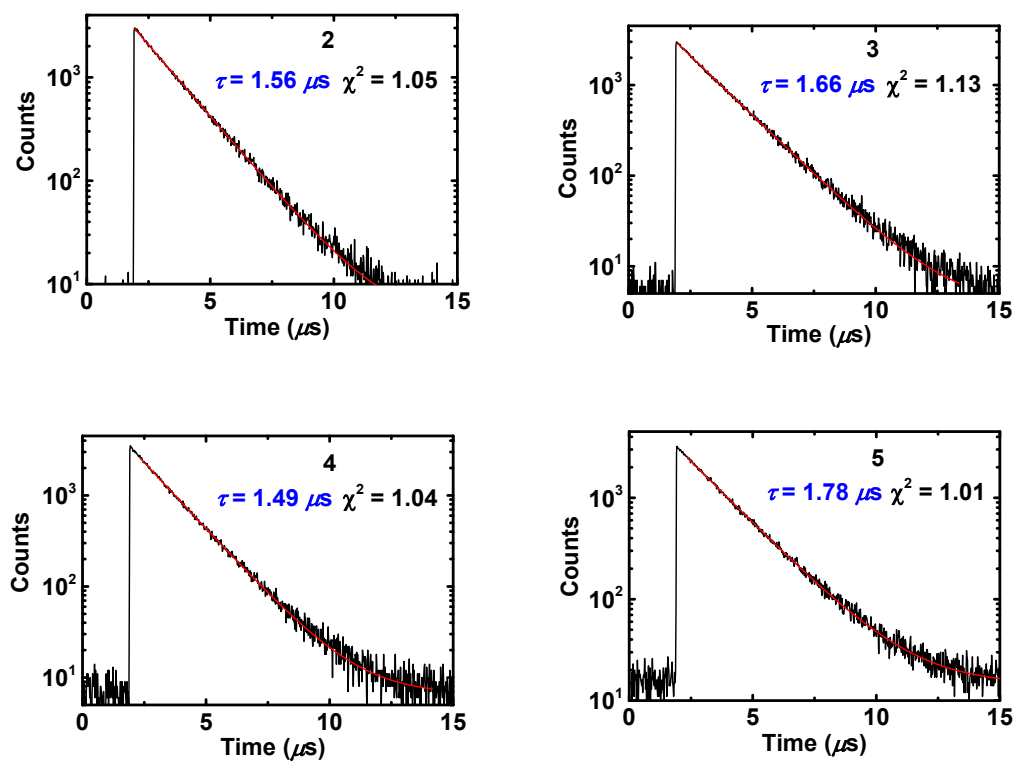
**Fig S10** Pictorial representations of the open voids and channels of complex **3** (without cocrystallized solvent molecules in its single crystal structure) using MERCURY/Voids (filled with cyan sphere probes whose radius is 1.2 Å). (a) viewing down the *a*-axis; (b) viewing down the *b*-axis; (c) viewing down the *c*-axis.



**Fig S11** Pictorial representations of the open voids and channels of complex **4** with its cocrystallized solvent molecules retained (left) or removed (right) using MERCURY/Voids (filled with cyan sphere probes whose radius is 1.2 Å; the solvent molecules are shown in space-filling model). (a) and (b): viewing down the *a*-axis; (c) and (d): viewing down the *b*-axis; (e) and (f): viewing down the *c*-axis.



**Fig S12** Pictorial representations of the open voids and channels of complex **5** with its cocrystallized solvent molecules retained (left) or removed (right) using MERCURY/Voids (filled with cyan sphere probes whose radius is 1.2 Å, the solvent molecules are shown in space-filling model). (a) and (b): viewing down the *a*-axis; (c) and (d): viewing down the *b*-axis; (e) and (f): viewing down the *c*-axis.



**Fig. S13** Phosphorescence decay curves of 2-5 in 2-MeTHF solution ( $10^{-5}$  M).



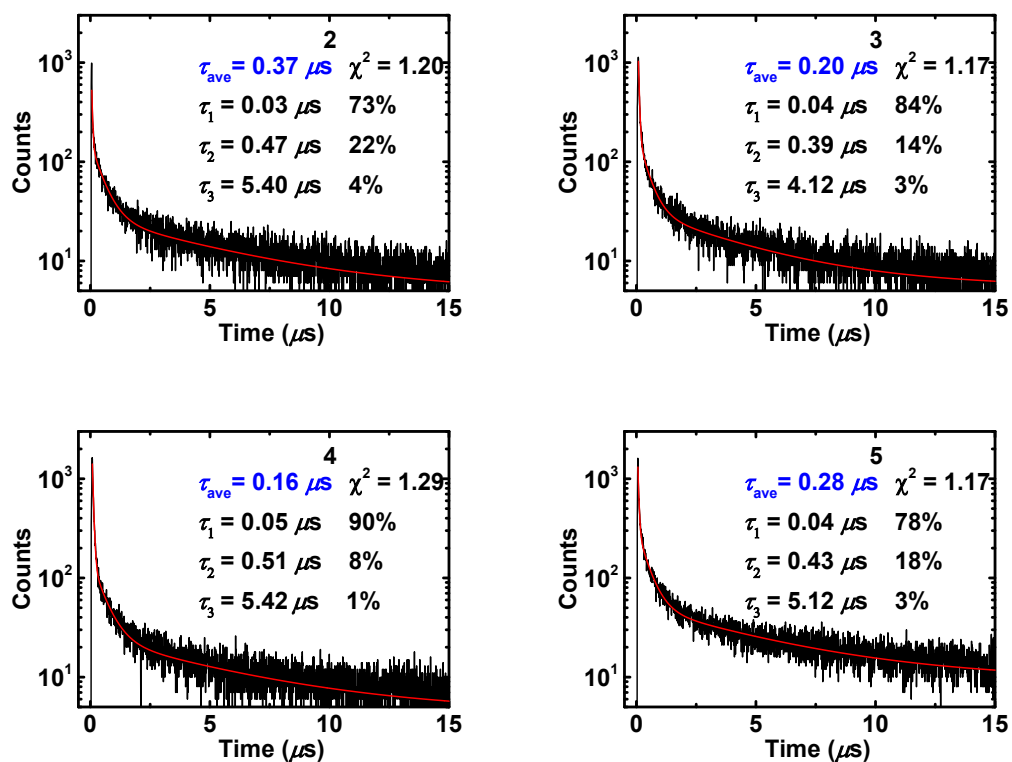


Fig. S14 Phosphorescence decay curves of 2-5 in microcrystalline thin-film samples under  $N_2$ .

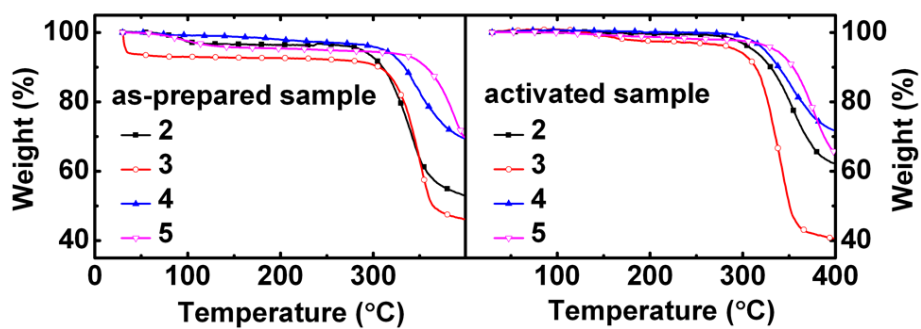


Fig. S15 TGA thermograms of the as-prepared and activated microcrystalline samples of 2-5.

## Experimental details

### 1) The details for the preparation of microcrystalline samples and oxygen sensing measurements

The crystalline samples used in oxygen sensing were prepared by dissolving the iridium complexes in a mixture of methanol and dichloromethane (1/1, v/v), then the solutions were dropped onto a 4 cm × 1 cm glass substrate, followed by allowing the solvent to slowly evaporate to afford tightly adhered microcrystalline as-prepared films. The films were dried in an oven under 30 °C for 36 h to remove the potential cocrystallized solvent molecules (activated ones) before oxygen sensing experiments.

The glass substrates coated with the microcrystalline films were placed into a quartz cuvette. In order to minimize the scattering effect, the substrate was angled at 135° towards the excitation beam so that the direct reflections would travel in the opposite direction of the detector. The mixed gas (N<sub>2</sub> and O<sub>2</sub>) was introduced into the sample cell by a soft plastic tube and the oxygen sensing experiments were carried out under ambient conditions. The specific concentrations of oxygen in nitrogen at atmospheric pressure (from 0~100% in volume fraction) were generated with two mass flow controllers (Brooks Instrument BV, Veenendaal, Netherlands). The solid-state PL spectra and response/recovery curves of these samples under different atmosphere were collected with a HITACHI F-7000 fluorescence spectrophotometer. Emission intensity data for microcrystalline samples were collected and displayed as a Stern-Volmer (SV) plot ( $I_0/I$  vs volume fraction of oxygen in nitrogen,  $I_0$  represents the PL emission intensity at oxygen concentration of 0%).

All these microcrystalline samples display brilliant long-term stability with just slight changes in emission intensity (< 10%) under continuous illumination in the presence or absence of oxygen over a ~3 h period. It is noteworthy that the Stern-Volmer plots of all these complexes were found to be identical to those initially measured after storage for four weeks in air; while compound 4 was found to display quite identical oxygen sensing capability after storage in air for five months.

For oxygen quenching experiments of microcrystalline powder samples of these

complexes, the microcrystalline powders were exclusively prepared by recrystallization from dichloromethane/methanol, followed by drying under vacuum at 80 °C for 24 h. Then the crystals were crushed and mounted on glass substrates by double-sided adhesive. The substrates were put into a quartz cuvette and angled at 135° towards the excitation beam in a HITACHI F-7000 fluorescence spectrophotometer, followed by introducing pure N<sub>2</sub> or O<sub>2</sub> into the cuvette, and recording the PL excitation and emission spectra.

## 2) X-ray crystallographic analysis

The crystallographic data of **2**, **3** and **5** reported here had been deposited in the Cambridge Database (CCDC 1006719 for **2**, 1006717 for **3**, and 1006718 for **5**); while the crystallographic data of **4** had been deposited in the Cambridge Database with reference No of 857631 before.<sup>2</sup> The determination of the unit cell and data collection for the crystals were performed on a Xcalibur Eos X-ray single crystal diffractometer equipped with graphite monochromator Mo-K $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation. The data collection was executed using CrysAlis Program. Structures were solved by direct method and successive Fourier difference syntheses (SHELXS-97),<sup>3</sup> and were refined by full-matrix least-squares procedure on  $F^2$  with anisotropic thermal parameters for all non-hydrogen atoms (SHELXL-97), and all of the hydrogen atoms were placed in idealized positions and refined as riding atoms with relative isotropic displacement parameters. The disordered methanol and/or dichloromethane solvent in **4** and **5**, which were unable to model, was removed with the PLATON/SQUEEZE<sup>4</sup> programs to improve the refinement.

Packing analysis of the crystal cells was carried out using PLATON, and the free volume as well as void fractions were calculated using PLATON/VOID<sup>5</sup>. Pictorial representations of the solvent accessible channels were obtained using Mercury/Voids<sup>6</sup> with the probe radius set as 1.2  $\text{\AA}$  and the approximate grid spacing set as 0.1  $\text{\AA}$ .

## 4) Phosphorescence life time measurements

Phosphorescence lifetimes were determined on a steady and transient state fluorometer (FLS980, Edinburgh Instruments Ltd.) with time-correlated single photon counting

(TCSPC) system using a nanosecond flash lamp at 375 nm as light source. The typical response time of this laser system was < 1 ns. The phosphorescence lifetime of the complexes was obtained by fitting the corresponding decay curves using FAST-Advanced Fluorescence lifetime software.

### **5) Powder X-ray diffraction (PXRD) measurements**

The PXRD measurement of the microcrystalline film samples were carried on a Philips DX-100 sealed-tube X-ray generator (Cu target;  $\lambda = 0.2$  nm) with power of 40 kV and 35 mA. The corresponding XRD data of these samples in single crystal were simulated with .cif file by Mercury/Powder pattern.

### **6) Thermogravimetric analysis**

Thermogravimetric analysis (TGA) was performed on a TGA Q500 instruments. The solid samples of the complexes were freshly scratched from the glass substrates of the as-prepared and activated thin film samples, stored at 30 °C for ten minutes, then heated at a heating rate of 10 °C/min under nitrogen atmosphere.

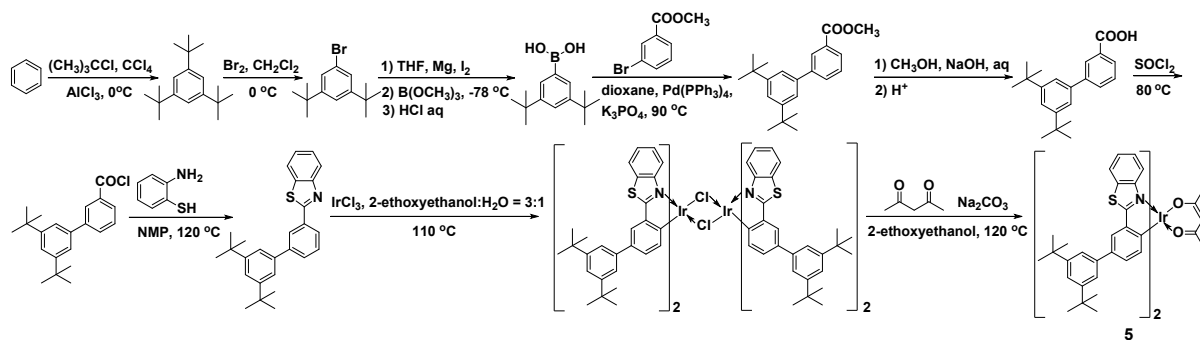
### **7) Synthesis and characterization**

All the chemicals and reagents involved in the synthetic procedure were commercially available, and were used without purification unless otherwise stated. All the solvents used were of analytical grade and distilled freshly prior to use according to the standard procedures.

The  $^1\text{H}$  NMR and  $^{13}\text{C}$  NMR spectra of the intermediates and objective compounds were measured on a Bruker AVII-400 spectrometer in  $\text{DMSO-}d_6$  or  $\text{CDCl}_3$  using TMS as internal standard. High resolution MS spectra were recorded on a Water Q-TOF-Premier instrument.

The iridium complexes **1**<sup>7</sup>, **3**<sup>8</sup> and **4**<sup>2</sup> were prepared according to our previous work; **2** was synthesized according to literature;<sup>9</sup> while compound **5** was synthesized according to the following synthetic route as well as procedures.





Intermediates 1,3,5-tri-*t*-butylbenzene and 1-bromo-3,5-di-*t*-butylbenzene were synthesized according to literature reports.<sup>10</sup>

### Synthesis of (3,5-di-*t*-butylphenyl)boronic acid

1-Bromo-3,5-di-*t*-butylbenzene (0.60 g, 2.2 mmol), magnesium (0.058 g, 2.4 mmol) were added into 10 mL anhydrous THF. After the reaction was initiated by iodine granule, the mixture was stirred at 70 °C for 2 h. Then reaction mixture was cooled to room temperature and added dropwise into a solution of trimethylborate (0.34 g, 3.3 mmol) dissolved in 10 mL of anhydrous THF at -78 °C. The reactant was stirred for 12 h at room temperature, and then 10 mL of aqueous hydrochloric acid (1 mol·L<sup>-1</sup>) was added into the reaction mixture and stirred for 3 h, followed by extraction with diethyl ether (3 × 20 mL). The organic layer was washed with brine, dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>, then the solvent was removed in vacuum to yield the crude product. The crude product was purified by recrystallization from hexane to yield white solid (0.29 g, 56%).

### Synthesis of methyl 3',5'-di-*t*-butylbiphenyl-3-carboxylate

Methyl 3-bromobenzoate (0.21 g, 1.0 mmol), (3,5-di-*t*-butylphenyl)boronic acid (0.26 g, 1.1 mmol), K<sub>3</sub>PO<sub>4</sub>·3H<sub>2</sub>O (0.55 g, 3 e.q.) and Pd(PPh<sub>3</sub>)<sub>4</sub> (5.8 mg, 0.005 eq.) were mixed in 20 mL of argon pre-degassed dioxane. After stirring at 90 °C for 7 h under argon, the mixture was cooled to room temperature and poured into 100 mL of water followed by extraction with ethyl acetate (3 × 20 mL). The organic layer was washed with water and brine, then dried over anhydrous Na<sub>2</sub>SO<sub>4</sub>. After the removal of solvent in vacuum, the crude product was purified through column chromatograph over silica using petroleum

ether : dichloromethane (5:1) as eluent to yield the pure product as white solid (0.28 g, 85.6%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ(ppm): 8.25 (s, 1H, ArH), 8.10 (d, *J* = 7.6 Hz, 1H, ArH), 7.77 (d, *J* = 8.0 Hz, 1H, ArH), 7.51 (t, *J* = 8.0, 1H, ArH), 7.47 (s, 1H, ArH), 7.42 (s, 2H, ArH), 1.39 (s, 18H, -C(CH<sub>3</sub>)<sub>3</sub>).

### Synthesis of 2-(3',5'-di-*t*-butylbiphenyl-3-yl)benzo[*d*]thiazole

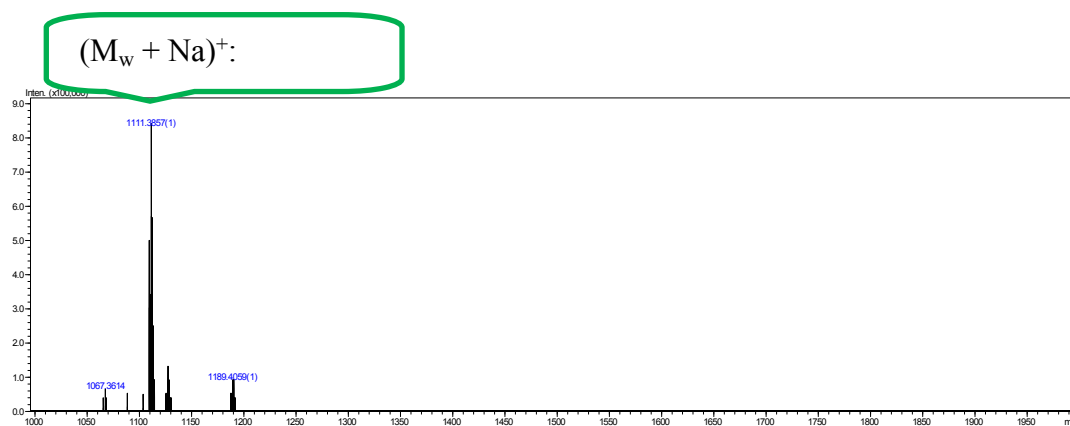
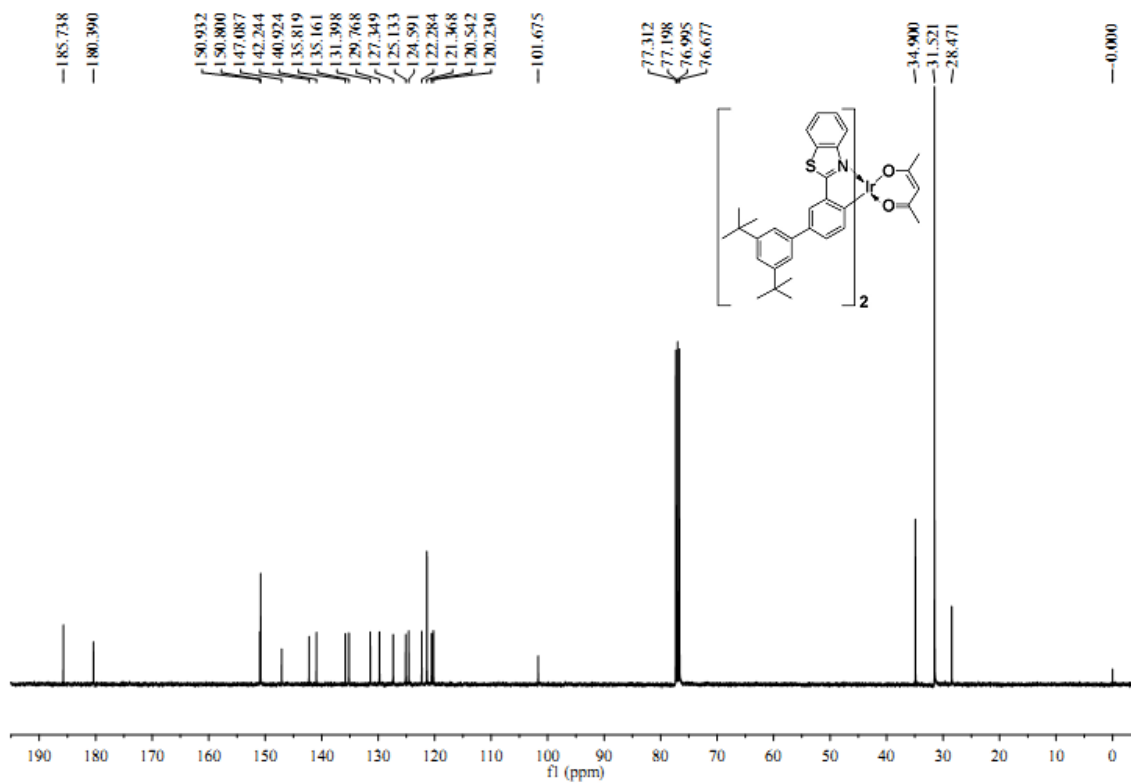
The intermediate 3',5'-di-*t*-butyl-biphenyl-3-carboxylic acid was prepared by hydrolysis of methyl 3',5'-di-*t*-butylbiphenyl-3-carboxylate with a high yield of 96%. Then 2.0 g (6.45 mmol) 3',5'-di-*t*-butyl-biphenyl-3-carboxylic acid was refluxed with 20 mL thionyl chloride for 1 h. After the removal of excessive thionyl chloride in vacuum, the residue was dissolved in 20 mL of *N*-methylpyrrolidinone (NMP), then added dropwise into a solution of 0.89 g (7.1 mmol) of *o*-aminothiophenol in 20 mL NMP under argon atmosphere. After stirring at 100 °C for 1 h, the reactant was cooled down to room temperature, poured into water, then neutralized with 7 mol·L<sup>-1</sup> aqueous ammonia to pH = 8~9. The precipitate was filtered and recrystallized from alcohol to afford the pure product (1.8 g, 69.9%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ(ppm): 8.26 (s, 1H, ArH), 8.09 (t, *J* = 8.8 Hz, 2H, ArH), 7.92 (d, *J* = 8.0 Hz, 1H, ArH), 7.70 (d, *J* = 8.0 Hz, 1H, ArH), 7.57 (t, *J* = 7.6 Hz, 1H, ArH), 7.53-7.48 (m, 4H, ArH), 7.40 (t, *J* = 7.6 Hz, 1H, ArH), 1.41 (s, 18H, -C(CH<sub>3</sub>)<sub>3</sub>).

### Synthesis of bis[2-(3',5'-di-*t*-butylbiphenyl-3-yl)benzothiazole-*N,C*']iridium(III) (acetylacetonate) (5)

2-(3',5'-Di-*t*-butylbiphenyl-3-yl)benzo[*d*]thiazole (2.4 mmol) and IrCl<sub>3</sub>·*n*H<sub>2</sub>O (1 mmol) were added in 20 mL of mixing solvents of 2-ethoxyethanol and water (3:1). The reactant was refluxed under argon for 24 h, then the precipitate was filtered and washed with 10 mL of hydrochloric acid (1 mol·L<sup>-1</sup>) and methanol (3 × 15 mL) in sequence. The filter cake was dried in vacuum to afford the dichloro-bridged iridium(III) complexes.<sup>9</sup> The iridium dimer (0.1 mmol), acetylacetonate (0.3 mmol) and sodium carbonate (1 mmol) were added in 10 mL of 2-ethoxyethanol and refluxed under argon for 12 h. After cooled down, the precipitate was collected and purified by column chromatography using CHCl<sub>3</sub>

as eluent, followed by more than three times recrystallization procedure to afford the objective complex with satisfactory purity. Yield : 98 mg (55%). <sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>) δ(ppm): 8.15 (m, 2H, ArH), 7.92 (m, 2H, ArH), 7.81 (d, *J* = 1.2 Hz, 2H, ArH), 7.46 (m, 4H, ArH), 7.33 (m, 6H, ArH), 6.91-6.88 (m, 2H, ArH), 6.52 (d, *J* = 8.0 Hz, 2H, ArH), 5.17 (s, 1H, -CH), 1.81 (s, 6H, -CH<sub>3</sub>), 1.33 (s, 36H, -C(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>) δ(ppm): 185.74, 180.39, 150.93, 150.80, 147.09, 142.24, 140.92, 135.82, 135.16, 131.40, 129.77, 127.35, 125.13, 124.59, 122.28, 121.37, 120.54, 120.23, 101.68, 34.90, 31.52, 28.47. ESI-MS: *m/z* 1111.3857 (M + Na)<sup>+</sup>; Calcd. For (M<sub>w</sub> + Na)<sup>+</sup>: 1111.3858.

# <sup>13</sup>C NMR and HRMS spectra of complex 5



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