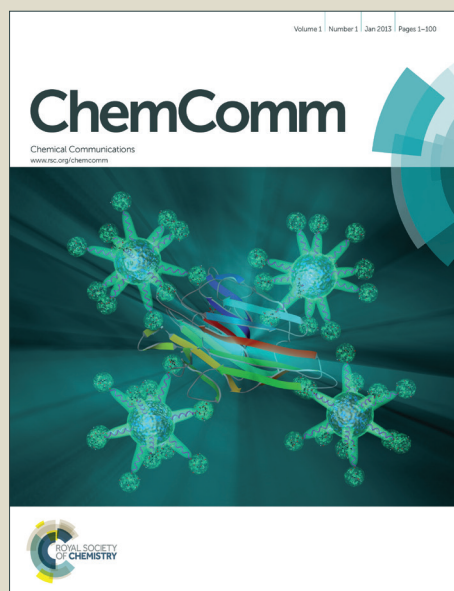


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Small molecular neutral microcrystalline iridium(III) complexes as promising molecular oxygen sensors

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Small molecular neutral Ir(III) complexes have been demonstrated to be promising self-inclusive microcrystalline thin-film oxygen sensors with relatively high sensitivity ($K_{sv} = 6.41$), good stability, and linear Stern-Volmer behavior ($R^2 = 0.9979$).

Owing to their advantages including high selectivity, high sensitivity, fast response, good reversibility, real-time and non-destructive detection, solid-state optical sensors capable of detecting molecular oxygen content in gaseous and aqueous media have attracted much attention.¹ In comparison with fluorescent dyes, phosphorescent complexes are more preferred oxygen-sensing materials since their long-lived highly efficient phosphorescence could be drastically quenched by molecular oxygen.² In addition, as small molecular complexes have better solubility than porous coordination polymers, membrane devices based on them could be more easily fabricated via solution-processing.³ However, in self-inclusive condensed state, most of the small molecular complexes suffer from poor optical response toward gaseous oxygen due to their limited oxygen "solubility" and permeability for the lack of sufficient void space and channels, accordingly, they generally need to be dispersed into porous matrices to acquire better oxygen quenching sensitivity.⁴ Nonetheless, sensors based on composite systems will incur non-uniform emitting sites, hence show unsatisfactory reproducibility and nonlinear Stern-Volmer (SV) behavior,⁵ which restrict their practical applications.

Consequently, it is highly demanded to exploit small molecular phosphorescent complexes with porous structure in their solid states.⁵⁻⁷ In 2007, Mann *et al* reported that some porous microcrystalline small molecular cationic Ru(II) complexes could act as self-inclusive oxygen sensors.^{5a} According to X-ray crystallographic characterization results, they found that the presence of bulky counter anions in these Ru(II) salts could promote the formation of void space and channels; and the oxygen quenching efficiencies of these complexes correlate highly not only with the void space fraction, but also with the channel quality (isolated "pockets" or continuous ones) and the lifetime of the complexes.^{6,7} Thanks to Mann *et al* for their enthusiastic efforts, high performance

self-inclusive small molecular oxygen-sensing chelates with SV constant (K_{sv}) of as high as 96 have been developed.^{7b} However, so far all the reported small molecular self-inclusive oxygen-sensing complexes are cationic ones, which are easily affected by nucleophilic reagents including environmental counter-anions, hence may show reduced sensitivity and complicated response toward oxygen, especially in dissolved oxygen sensing applications.⁸ Although neutral complexes should be more promising in this regard, to our knowledge, there have been no reports on them as crystalline oxygen sensors.

In 2011, we found that in its microcrystalline powder state, the neutral Ir(III) complex **1** bearing bulky *t*-butyl-modified phenyls shows photoluminescence (PL) quenching toward gaseous oxygen; while the reference compound **2** just displays relatively poor oxygen quenching property.⁹ X-ray crystallographic analysis revealed that in the single crystal structure of **1**, only isolated void space with low void fraction of 2.4% could be observed, but spacious cavities with high quality channels could be obtained after the cocrystallized solvent molecules were removed. Therefore, we tentatively attributed the efficient oxygen sensing capability of **1** to the presence of void space and channels in its microcrystalline state.

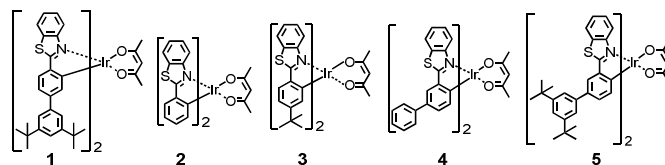


Fig. 1 Molecular structures of the Ir(III) complexes 1-5.

Consequently, to seek for high performance oxygen sensing self-inclusive microcrystalline neutral complexes, we screened Ir(III) complexes **3-5** bearing bulky substituents like *t*-butyl and/or phenyl on their cyclometallate ligands; while **2** was used as the reference compound to investigate the relationship between the oxygen sensing and packing properties. Because the oxygen-sensing performance of phosphorescent dyes often differs significantly in solution, bulk-solid and thin-film states,¹⁰ the oxygen quenching behavior of **2-5** in solution and

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microcrystalline powder states were investigated first. As shown in Fig. S1 and S2, the toluene solutions of **2-5** all display significant PL quenching toward oxygen, with quenching fractions $[(I_0 - I_{100})/I_0]$, where I_0 and I_{100} represent the PL intensity at $\lambda_{\text{PL,max}}$ in N_2 with O_2 concentration of 0 and 100 vol%, respectively] of 37.5–67.4% and 91.8–93.9% at O_2 vol% of 5% and 20%, respectively; while in crystalline powder state, although their oxygen quenching is not as efficient as that in solution, PL quenching fractions of 43.0%, 76.0%, 54.0% and 90.9% still could be achieved for **2-5** in sequence in pure oxygen. However, since the loose powders are difficult to handle in sensor applications, microcrystalline thin-film samples were prepared for **2-5**, and their oxygen quenching properties were studied. As shown in Fig. S3, **2** shows poor PL response toward oxygen with quenching fraction of 9.2%; but **3-5** show distinct optical response toward molecular oxygen, with PL quenching fractions of 70.3%, 86.7% and 50.6% in sequence (Fig. 2a-c and Table 1).

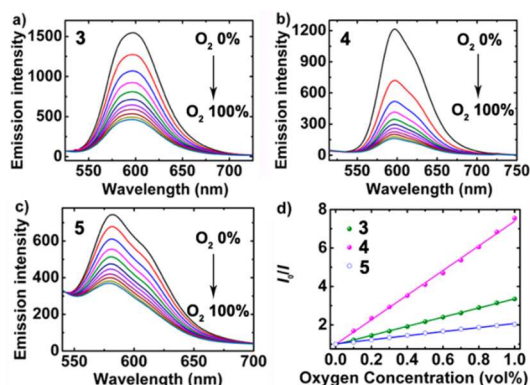


Fig. 2 (a-c) The PL emission spectra of microcrystalline thin-film samples of **3-5** at varied concentrations of O_2 in N_2 ($\lambda_{\text{ex}} = 480 \text{ nm}$); and (d) the corresponding linear regression fitting results of the Stern-Volmer plots of **3-5**.

In addition to their relatively high PL quenching fractions, the thin film samples of **3-5** display strictly linear SV behavior in the full oxygen concentration range from 0 to 100 vol% (Fig. 2d) with R^2 of 0.9954–0.9996, implying the microenvironments within the crystalline sensing films are uniform, hence they might act as oxygen sensors with desirable single-point calibration.^{7a} According to these SV plots, the K_{sv} values of **3**, **4** and **5** are calculated to be 2.38, 6.41 and 1.06, respectively, thus both **3** and **4** show good sensitivity that meets with the requirement for practical applications.^{1b} In fact, the K_{sv} of **4** is also much higher than that of the crystalline cationic Ir(III) complex oxygen sensor reported recently ($K_{\text{sv}} = 2.82$).^{2b}

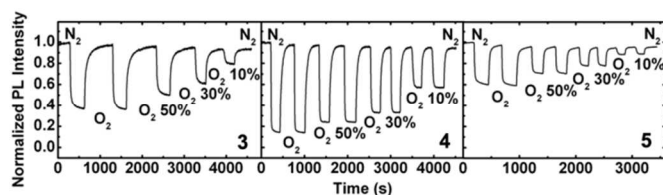


Fig. 3 The PL response/recovery curves of **3** ($\lambda_{\text{em}} = 598 \text{ nm}$), **4** ($\lambda_{\text{em}} = 597 \text{ nm}$) and **5** ($\lambda_{\text{em}} = 581 \text{ nm}$) at different concentrations of O_2 (vol%) in N_2 .

As shown in Fig. 3, **3-5** all display reversible PL quenching response toward oxygen, with >90% recovery of initial PL intensity during the ~3 h measurement, indicating that all these samples possess stable porous structures as well as excellent

photostability. Further ^1H NMR characterization on the samples after oxygen quenching experiments confirmed that all these complexes have not been decomposed after contact with oxygen under irradiation (Fig. S5–S8). The 95% response time ($t_{195\%}$, by the 95% decrement of PL intensity after switching from pure N_2 to pure O_2) for **3**, **4** and **5** is determined to be 126, 46 and 92 s in sequence; while the 95% recovery time ($t_{195\%}$, by the 95% increase of PL intensity after switching from pure O_2 to pure N_2) is 285, 130 and 108 s for **3**, **4** and **5**, respectively. Owing to their relatively rapid response/recovery, excellent reproducibility and high sensitivity, these neutral complexes should be promising oxygen sensors for practical applications, and **4** is more perspective due to its concurrent rapid response (46 s) and recovery (130 s) as well as high sensitivity.

Table 1 Void fraction, lifetime and oxygen quenching efficiency data of **2-5**

Compd	$(I_0 - I_{100})/I_0$	K_{sv}	void fraction ^a	τ (μs) ^b	τ (μs) ^c
2	9.2%	-	2.7%	1.56	0.37
3	70.3%	2.38	1.5%	1.66	0.20
4	86.7%	6.41	19.9%	1.49	0.16
5	50.6%	1.06	16.3%	1.78	0.28

^a Calculated from desolvated crystal structures;

^b Lifetime measured in N_2 degassed dilute 2-methyltetrahydrofuran solution (10^{-5} M);

^c Lifetime measured in N_2 purged microcrystalline thin-solid film states.

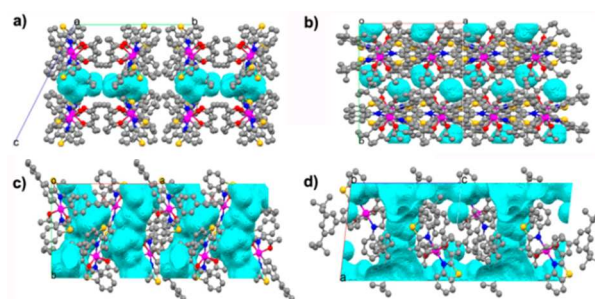


Fig. 4 Pictorial representations of the open voids and channels of complexes **2-5** with their cocrystallized solvent molecules removed using MERCURY/VOID (filled with cyan sphere probes whose radius is ~1.2 Å). (a) Viewing down the a -axis of **2**; (b) viewing down the c -axis of **3**; (c) viewing down the c -axis of **4**; and (d) viewing down the b -axis of **5**.

Since according to Mann's report, the oxygen sensing properties of porous cationic chelates could be rationally predicted through their crystal structures, single crystal structures of **2-5** were determined through X-ray crystallography (single crystal samples were grown exclusively from $\text{CH}_3\text{OH}/\text{CH}_2\text{Cl}_2$, the identical solvent system used in preparing the film samples for oxygen sensing experiments). The calculated void fractions of the four complexes after the cocrystallized solvent molecules (if present) were removed from the lattice were summarized in Table 1. Among the four compounds, **4** has the highest void fraction of 19.9%; while **3** owns the lowest void fraction of 1.5%. However, **5** and **4** showed the most efficient oxygen quenching in powder and thin solid film states, respectively; yet the oxygen quenching efficiency of **3** was found to be much higher than that of **2** despite of its lower void fraction. As the quality of the void spaces in the crystal structure should also be another important factor determining the oxygen sensing ability of the compounds, we calculated the open voids which are big enough to hold a spherical probe with radius of 1.2 Å in **2-5**. As shown in Fig. 4 and Fig. S9–12, in both **4** and **5**, spacious channels of open space running through the structures could be found; but the

voids in **2** and **3** were found to be isolated pockets. Consequently, there should be negligible correlation between oxygen sensing capability and the void fraction/quality in the single crystal structures of these complexes, since complex **3** with low void fraction and poor channels still displays a high oxygen quenching fraction of 70.3%. Moreover, the quite analogous lifetimes of these Ir(III) complexes under N₂ (1.49–1.78 μs in dilute solution, 0.16–0.37 μs in microcrystalline thin-solid film states, vide Table 1 and Fig. S13, S14) suggest that the dissimilar sensing properties of **2–5** should not originate from their different excited state lifetimes. It is noteworthy that the emission decay data of all these thin film samples were satisfactorily fitted using three weighted exponentials, which seems to be contradictory to their linear SV behavior. However, similar phenomena have also been observed by Mann *et al* in porous oxygen-sensing Cu(I) salts,^{6,7b} which need further in-depth investigations.

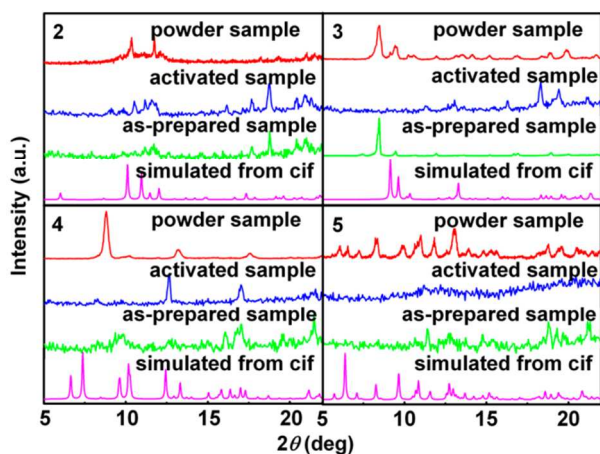


Fig. 5 The powder X-ray diffraction patterns of the microcrystalline thin-film samples (red lines: microcrystalline powder; blue lines: activated film; green lines: as-prepared film;) and single crystal samples (pink lines: simulated from the corresponding .cif files) of **2–5**.

Consequently, differed from those cationic Ru(II) or Cu(I) salts reported by Mann *et al*, the oxygen-sensing capability of the microcrystalline neutral Ir(III) complexes films we reported here could not be rationally predicted through their single crystal structures. Hence we began to conjecture if the packing patterns and the residue solvents of the microcrystalline samples differ from those of the single crystal samples. Thereupon, powder X-ray diffraction (PXRD) patterns of the microcrystalline powder, the as-prepared and the activated thin-film samples of **2–5** were recorded and compared with those simulated from the corresponding .cif files of the single crystals. As shown in Fig. 5, both the powder and the film samples show different diffraction signals with those of their corresponding single crystal samples, confirming that the lattice structures within the microcrystalline film and single crystal samples are not identical. Further thermogravimetric analysis (TGA) indicated that the solvent contents of the activated film samples are also quite different with those of the single crystals as well as the as-prepared ones. In fact, compared to the as-prepared film samples, the activated ones all display less weight loss (Fig. S15), confirming the occurrence of desolvation during the activation procedure. It is noteworthy that although no solvated molecules could be found in the single crystal lattice of **3**, distinct weight loss could be observed in 30–150 °C in both the as-synthesized and activated samples of **3**, confirming the large structural difference between the single crystal and microcrystalline film samples of **3**. Accordingly, these neutral

Ir(III) complexes should possess dissimilar packing structures and different solvent contents in microcrystalline and single crystalline states, hence it should be inappropriate to predict the oxygen sensing properties of these microcrystalline thin-film samples via their corresponding single crystal structures.

Conclusions

In conclusion, we demonstrated that small molecular neutral Ir(III) complexes are quite promising high performance microcrystalline self-inclusive oxygen sensors. Yet differed from those oxygen-sensing cationic Ru(II) and Cu(I) salts, these microcrystalline Ir(III) complexes were found to show negligible relationship between the oxygen quenching efficiency and the amount of void space and quality of void channel in their single crystal structures, because the packing structures and the solvent contents of these two crystalline states are dissimilar. Consequently, oxygen sensing capability of these neutral Ir(III) complexes should be carefully ascertained to avoid the missing of hidden high performance oxygen sensing materials.

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Notes and references

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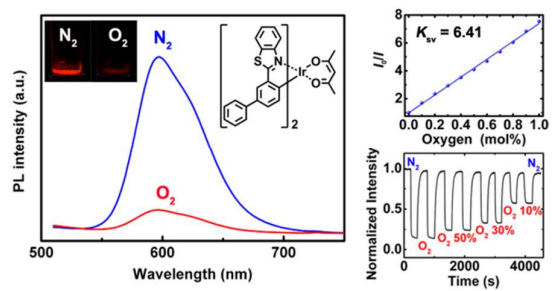
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† Electronic Supplementary Information (ESI) available: Synthetic and oxygen sensing experimental details, additional spectroscopic property and XRD data. CCDC 1006719 for **2**, 1006717 for **3** and 1006718 for **5**. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c000000x/

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Small molecular neutral microcrystalline iridium(III) complexes could act as high performance self-inclusive oxygen sensors