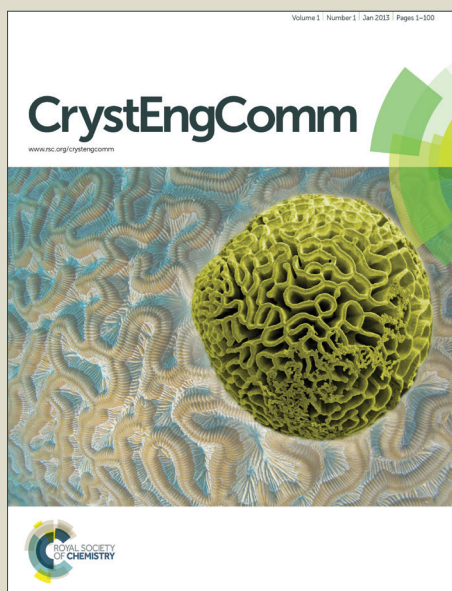


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ARTICLE TYPE

Four New Lead(II)-Iridium(III) Heterobimetallic Coordination Frameworks: Synthesis, Structures, Luminescence and Oxygen-sensing Properties

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Four new lead(II)-iridium(III) heterobimetallic coordination frameworks, i.e., [Pb₂(L)₄(DMF)₂]·ClO₄·2DMF·13H₂O (**1**·DMF), [PbL₂·H₂O]·ClO₄·3C₃H₆O·3H₂O (**1**·Acetone), [PbL₂·H₂O]·3C₃H₆O·3H₂O·CH₃CN (**2**·Acetone), and [Pb₄L₄I₄·(DMF)₂]·10H₂O (**3**·DMF), where L-H₂ = Ir(ppy)₂(H₂dcbpy)PF₆, ppy = 2-phenylpyridine, and H₂dcbpy = 4,4'-dicarboxy-2,2'-bipyridine, have been synthesized and characterized structurally by elemental analyses, IR spectroscopy, optical spectroscopy, and single-crystal X-ray diffraction methods. Heavy atoms, i.e. lead(II) atoms, were introduced to the frameworks and coordinated with the chromophore to promote an efficient intersystem crossing from the singlet to the triplet ³MLCT excited state and further promote sensitivity to oxygen. The emissions of **1**·DMF—**3**·DMF were ascribed to a metal-to-ligand charge transfer transition (MLCT). These four compounds, based on phosphorescence detection, are able to detect oxygen sensitively in real gas, and their noteworthy oxygen-sensing properties were also evaluated. The quenching constants, or *K*_{SV} values, between **1**·DMF—**3**·DMF and oxygen can be deduced to be 1.44, 1.60, 2.85, and 5.11, respectively. The minimum detectable concentrations (LODs) for oxygen of **1**·DMF—**3**·DMF were calculated to be 0.65%, 0.70%, 0.61%, and 0.52%, respectively, from three times signal to noise. Moreover, taking **3**·DMF as an example, the short response time (50 s) and the recovery time (24 s) toward oxygen have been measured. It should be noted that the evaluated recovery time for **3**·DMF is even shorter than those reported for rare-earth MOF films. The gas sensing properties, including sensitivity, sensing linearity, reproducibility, matrix effect, cross-sensitivity effect, temperature effect, and long-term stability, were investigated. Finally, in order to spark a broad spectrum of interest in application aspects, **3**·DMF was mixed with a commercial dye, Coumarin 480 (C480), as a ratiometric oxygen sensor for analysis of real gas in air.

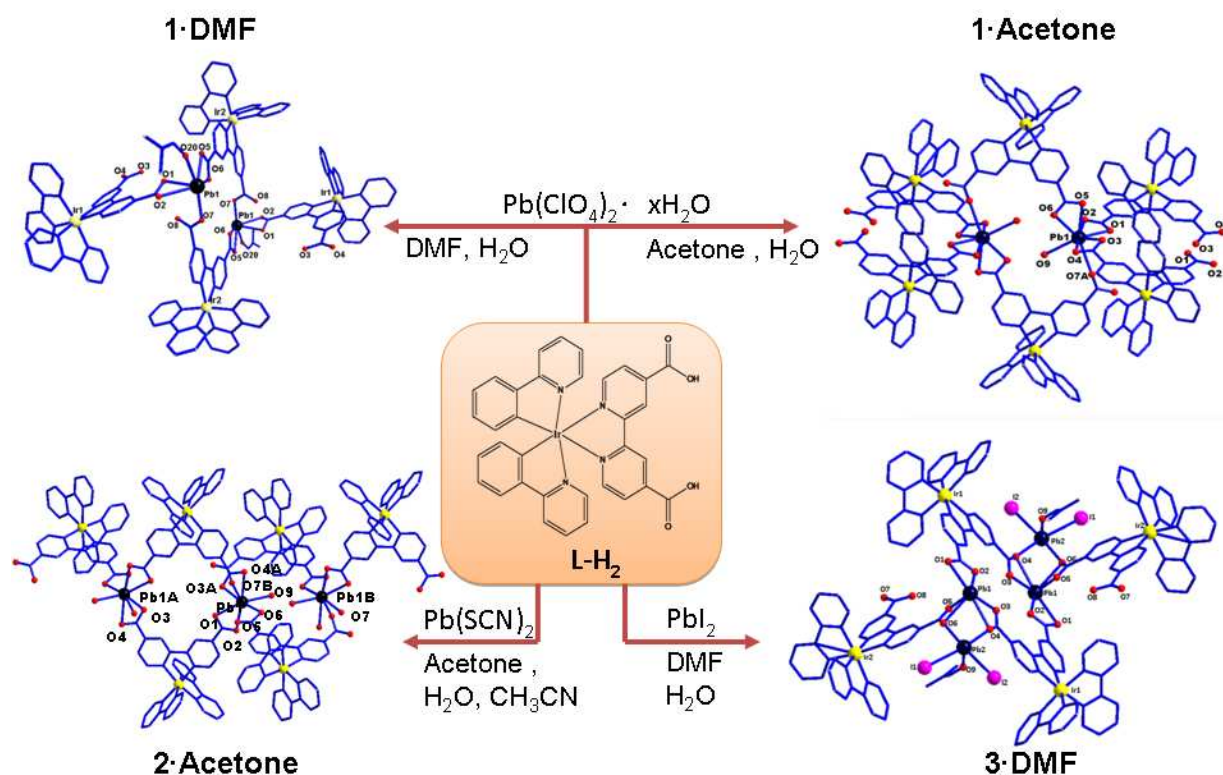
1. Introduction

The development and design of luminescent coordination polymers or metal-organic frameworks (MOFs) for applications in OLEDs, recognition devices, and biological labelling agents¹ have received much attention. Lead(II)-containing coordination polymers in particular have been the subject of considerable interest because of their unusual structural diversity, with two to ten coordination numbers.² This can be attributed to a large ion radius. Moreover, the intrinsic electronic property in Pb(II), which has a 6s² outer electronic configuration, has greater influence on diverse structure formation.²

In addition to the nature of metal atoms and ligands, the role of counter anions and solvents amid self-assembly processes has emerged as an increasingly active theme in recent studies.³ In the relevant approach, the anion effects in coordination polymers, particularly Cu(II),^{4(a)} Ag(I),^{3(c), 4(b)} Zn(II),^{4(c)} and Ln(III),^{4(d)} have been studied. The solvent effects in Cd(II) coordination

polymers^{4(e)} and Hg(II) complexes^{4(f)} have also been discussed. Conversely, to our knowledge, studies of structure-versus-anion/solvent behavior utilizing the Pb(II) framework are relatively scant. On the other hand, phosphorescent coordination polymers or complexes, such as iridium(III)- or ruthenium(II)-based materials, with luminophores that can be quenched by oxygen, are of interest in the fabrication of oxygen-sensing devices. The reason is that iridium(III)- or ruthenium(II)-based coordination polymers or complexes have high brightness owing to the high extinction coefficients from metal-to-ligand charge transfer.⁵

In our previous study,⁶ we reported the reversible oxygen-sensing performance of Iridium(III)-cations containing coordination polymers by using Ir(ppy)₂(H₂dcbpy)PF₆ (L-H₂, ppy = 2-phenylpyridine, H₂dcbpy = 4,4'-dicarboxy-2,2'-bipyridine) as the bridging ligand. The results of oxygen-sensing sensitivities and kinetics for the related compounds are much better in single crystal form than in powder form. The concept of molecular



Scheme 1. Illustration of the relationship between crystalline structures **1·DMF**—**3·DMF**, ligand **L-H₂** and Lead salts in different solvents.

design is that chromophores coordinated with heavy atoms promote an efficient intersystem crossing from the singlet to the triplet ³MLCT excited state.⁷ At this time, if oxygen molecules are present near the complex of chromophore-heavy atoms, bimolecular collisions between the excited dye molecules and the ground state oxygen will relax the luminophore nonradiatively, causing a quenching process. This oxygen quenching process is diffusion-limited and can be described by the Stern–Volmer relationship.⁸

To further increase the energy transfer to the triplet ³MLCT excited state and hence increase the oxygen-sensing ability, we have attempted to synthesize novel lead(II)-iridium(III) heterobimetallic coordination frameworks by taking the advantages of lead(II) and iridium(III). Bearing this in mind, as part of our continuous efforts, in this study, we report on the self-assembly of different lead(II) anions and solvents, including $\text{Pb}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$, $\text{Pb}(\text{SCN})_2$, PbI_2 , DMF, H_2O , acetone, and CH_3CN , respectively, with **L-H₂** ligand in an effort to investigate the influence of counter anions/solvents on the structural diversity, luminescence, and oxygen-sensing properties. Based on these building blocks, four new coordination polymers $[\text{Pb}_2\text{L}_4 \cdot (\text{DMF})_2] \cdot \text{ClO}_4 \cdot 2\text{DMF} \cdot 13\text{H}_2\text{O}$ (**1·DMF**), $[\text{PbL}_2 \cdot \text{H}_2\text{O}] \cdot \text{ClO}_4 \cdot 3\text{C}_3\text{H}_6\text{O} \cdot 3\text{H}_2\text{O}$ (**1·Acetone**), $[\text{PbL}_2 \cdot \text{H}_2\text{O}] \cdot 3\text{C}_3\text{H}_6\text{O} \cdot 3\text{H}_2\text{O} \cdot \text{CH}_3\text{CN}$ (**2·Acetone**) and $[\text{Pb}_4\text{L}_4 \cdot (\text{DMF})_2] \cdot 10\text{H}_2\text{O}$ (**3·DMF**), have been synthesized and structurally characterized (Scheme 1). The following sections are organized in a sequence of steps, where we unveil the synthesis of the four compounds. Subsequently, studies of thermal stability and photophysical and oxygen-sensing properties are presented, followed by the structural determination. Finally, the influences

of the oxygen-sensing kinetics, stability, interferences, temperature effect, reversibility, and a real gas test will be discussed in detail.

To gain further insight into the applicability, we developed a ratiometric oxygen sensor based on **3·DMF** mixed with a fluorescent C480 dye for monitoring oxygen levels in a real sample. Finally, the proposed method was successfully applied to detect oxygen content in real air.

2. Experimental Section

2.1 General Information and Materials

All solvents were obtained from commercial suppliers and were used without further purification unless otherwise noted. The infrared spectrum was measured with a PerkinElmer Spectrum 100 FTIR spectrometer with KBr pellets. Element analysis was performed on a PerkinElmer 2400 series II.

2.2 Synthesis of $[\text{Pb}_2\text{L}_4 \cdot (\text{DMF})_2] \cdot \text{ClO}_4 \cdot 2\text{DMF} \cdot 13\text{H}_2\text{O}$ (**1·DMF**)

Compound **1·DMF** was obtained by reaction of $\text{Pb}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$ (0.005 mmol, 2.03 mg) in H_2O (1 mL) and **L-H₂** (0.0025 mmol, 2.22 mg) in 2 mL mixed solvents of H_2O and DMF (1 : 1, v/v) at room temperature to give an orange-yellow solution. Orange-yellow needle crystals were obtained after several days (See Fig. 1(a)). Yield: 34.8% yield. Anal. Calc. for $\text{C}_{148}\text{H}_{142}\text{ClIr}_4\text{N}_{20}\text{O}_{37}\text{Pb}_2$ (Mr = 4011.45): C, 44.31; H, 3.57; N, 6.98. Found: C, 43.93; H, 3.61; N, 7.16. IR data (KBr pellet, Fig. S1 in the supporting information): $\nu = 3430(\text{m})$, $3044(\text{w})$, $1661(\text{s})$, $1607(\text{vs})$, $1584(\text{s})$, $1478(\text{s})$, $1420(\text{m})$, $1370(\text{vs})$, $1236(\text{m})$, $1164(\text{w})$, $1097(\text{w})$,

1031(w), 785(m), 762(m), 700(m) cm^{-1} .

2.3 Synthesis of $[\text{PbL}_2 \cdot \text{H}_2\text{O}] \cdot \text{ClO}_4 \cdot 3\text{C}_3\text{H}_6\text{O} \cdot 3\text{H}_2\text{O}$ (**1·Acetone**)

The synthesis procedure was similar to that for the preparation of compound **1·DMF** except that the solvent DMF was replaced by acetone to afford orange-red blocked crystals of **1·Acetone** in 43.1% yield (See Scheme 1). Anal. Calc. for $\text{C}_{77}\text{H}_{70}\text{ClIr}_2\text{N}_8\text{O}_{19}\text{Pb}$ ($M_r = 2038.45$): C, 45.37; H, 3.46; N, 5.50. Found: C, 44.44; H, 3.59; N, 5.33. IR data (KBr pellet, Fig. S1): $\nu = 3749(\text{m})$, 3498(m), 3494(m), 3419(m), 3111(m), 3042(m), 1711(m), 1608(vs), 1583(s), 1544(s), 1479(s), 1420(s), 1403(m), 1371(vs), 1315(m), 1287(m), 1269(m), 1233(m), 1166(m), 1103(s), 1066(m) cm^{-1} .

2.4 Synthesis of $[\text{PbL}_2 \cdot \text{H}_2\text{O}] \cdot 3\text{C}_3\text{H}_6\text{O} \cdot 3\text{H}_2\text{O} \cdot \text{CH}_3\text{CN}$ (**2·Acetone**)

Compound **2·Acetone** was synthesized by mixing 1 mL of $\text{Pb}(\text{SCN})_2$ (0.005 mmol, 1.62 mg) in H_2O , 1 mL of **L-H₂** (0.0025 mmol, 2.22 mg) in 2 mL mixed solvents of H_2O , acetone and CH_3CN (1 : 0.5 : 0.5, v/v/v) at room temperature to give an orange-red solution. Slow evaporation of the solvent resulted in the crystallization of **2·Acetone** as orange-red blocked crystals with a yield of 51.9%. Anal. Calc. for $\text{C}_{79}\text{H}_{73}\text{Ir}_2\text{N}_9\text{O}_{15}\text{Pb}$ ($M_r = 1980.05$): C, 47.92; H, 3.72; N, 6.37. Found: C, 47.29; H, 3.73; N, 6.29. IR data (KBr pellet, Fig. S1): $\nu = 3445(\text{m})$, 3111(m), 3041(m), 2059(m), 1709(m), 1607(vs), 1583(s), 1545(m), 1478(s), 1420(m), 1403(m), 1371(s), 1315(m), 1287(m), 1233(m), 1165(w), 1031(w), 845(m), 788(m), 759(s), 739(m), 702(m) cm^{-1} .

The chemical composition of **2·Acetone** (Fig. S2) was also examined using a SEM apparatus (FEI Nova200 NanoSEM) equipped an EDX system (OXFORD X-Max80) with a conventional Silico Drift detector with light-element capabilities. A typical setup consisted of a 15kV accelerating voltage, and the duration of the EDX scans on individual samples was ca. 30 s.

2.5 Synthesis of $[\text{Pb}_4\text{L}_4\text{I}_4 \cdot (\text{DMF})_2] \cdot 10\text{H}_2\text{O}$ (**3·DMF**)

Compound **3·DMF** was prepared in a mixture of PbI_2 (0.005 mmol, 2.31 mg) in H_2O (1 mL) and **L-H₂** (0.0025 mmol, 2.22 mg) in DMF (1 mL). After several weeks, orange-red blocked crystals of **3·DMF** were obtained with a yield of 55.6% (See Fig. 3(a)). Anal. Calc. for $\text{C}_{142}\text{H}_{122}\text{I}_4\text{Ir}_4\text{N}_{18}\text{O}_{28}\text{Pb}_4$ ($M_r = 4633.74$): C, 36.81; H, 2.65; N, 5.44. Found: C, 36.57; H, 3.43; N, 5.23. IR data (KBr pellet, Fig. S1): $\nu = 3435(\text{vs})$, 3106(s), 3048(s), 1637(s), 1584(s), 1543(s), 1478(s), 1419(s), 1375(s), 1315(m), 1270(m), 1237(m), 1163(w), 1126(w), 1103(w), 1064(w), 1032(w), 784(w), 756(m), 702(m) cm^{-1} .

2.6 Crystallographic Data Collection and Refinement

The chosen crystals were mounted on glass fibers. Data were collected on a NONIUS Kappa CCD diffractometer, with Mo radiation ($\lambda = 0.71073 \text{ \AA}$) at 150(2) K for compounds **1·DMF**, **1·Acetone**, and **2·Acetone**, and at 293(2) K for **3·DMF**, respectively. After data collection, the frames were integrated and absorption corrections were applied. The crystals of compound **1·Acetone** suitable for X-ray analysis were in twin form. The

crystallographic data were solved by twin refinement, and two molecules were present in the unit cell. The initial crystal structure was solved by direct method. The structure solution was expanded through successive least-squares cycles, and the final solution was determined. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms attached to the carbon and nitrogen were fixed at calculated positions and refined using a riding mode. Crystal data, data collection, and refinement parameters are summarized in Table 1. CCDC reference numbers 925662–925665 contain the supplementary crystallographic data in this paper. These data are available free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

2.7 Thermogravimetric analysis of compounds **1·DMF**, **1·Acetone**, **2·Acetone** and **3·DMF**

Thermogravimetric analysis (TGA) of **1·DMF**—**3·DMF** was performed with a computer-controlled TGA PerkinElmer 7 instrument (TA Instruments). Samples of **1·DMF**—**3·DMF** were loaded into platinum holders and heated with a ramp rate of 3 $^{\circ}\text{C}/\text{min}$ from room temperature to 800 $^{\circ}\text{C}$ in an airflow of 60 mL/min.

2.8 Spectral Measurement

UV–vis diffusive reflectance spectra of compounds **1·DMF**, **1·Acetone**, **2·Acetone** and **3·DMF**, and **L-H₂** were obtained with a HITACHI U-3900H spectrophotometer equipped with an integrating sphere accessory (Al_2O_3 was used as a reference).^{6, 9(a)} In order to investigate the possible differences in photoluminescence of **1·DMF**, **1·Acetone**, **2·Acetone** and **3·DMF** due to variations in topology, **1·DMF**, **1·Acetone**, **2·Acetone** and **3·DMF** were measured in the confocal mode of a MonoVista confocal Raman microscope system (Princeton Instruments/Acton).

The oxygen-sensing properties of **1·DMF**, **1·Acetone**, **2·Acetone** and **3·DMF** worked on the principle of luminescence intensity quenching. In this approach, a 405 nm laser line (diode laser, 405-50-COL-004, Oxiuss, France) was used as an excitation source throughout the measurement. A set of neutral density filters was then placed in the beam path to attenuate the laser power. N_2 (99.99%) and O_2 (99.99%) were mixed at different concentrations in mass flow controllers and passed into a Linkam FTIR600 hot stage (Linkam Scientific Instruments, United Kingdom) equipped with a video camera (QImage 5.0 RTV), in which the optics were specially made to allow both UV (up to 280 nm) excitation and emission. The microscope (Olympus BX51) had an upright-style frame in which all optics were modified to allow the passage of deep UV to infrared light. Simultaneously, a video camera (QImage 5.0 RTV) was used to capture images. The output flow rate of the gas mixture was maintained at 500 mL/min. The O_2 concentrations were accurate to 0.1%. The photoluminescence was separated from the scattering light of the excitation pulse by an edge filter with a cut-off wavelength of 420 nm (3RD420LP, Omega Optical). Subsequently, the luminescence was collected by an optical assembly at the entrance slit of a polychromator (blazed at 500 nm) coupled with a sensitive charge coupled detector (CCD, Princeton Instruments, PI-MAX). The CCD was operated in

Table 1. Crystal Data for **1·DMF**, **1·Acetone**, **2·Acetone** and **3·DMF**.

	1·DMF	1·Acetone	2·Acetone	3·DMF
Formula	C ₁₄₈ H ₁₄₂ ClIr ₄ N ₂₀ O ₃₇ Pb ₂	C ₇₇ H ₇₀ ClIr ₂ N ₈ O ₁₉ Pb	C ₇₉ H ₇₃ Ir ₂ N ₉ O ₁₅ Pb	C ₁₄₂ H ₁₂₂ Ir ₄ N ₁₈ O ₂₈ Pb ₄
FW	4011.45	2038.45	1980.05	4633.74
Crystal system	Monoclinic	Triclinic	Triclinic	Triclinic
Space group	P2/n	P-1	P-1	P-1
<i>a</i> (Å)	29.4296(7)	13.1493(4)	13.0965(2)	8.7126(2)
<i>b</i> (Å)	8.7352(2)	16.1900(5)	16.9698(3)	18.2978(4)
<i>c</i> (Å)	30.6568(7)	19.3364(6)	19.3066(3)	22.6191(5)
α (°)	90	66.7678(10)	67.1073(9)	87.0367(9)
β (°)	99.2586(7)	70.8605(9)	71.2175(10)	83.5709(9)
γ (°)	90	87.8194(9)	88.2966(10)	79.0030(10)
<i>V</i> (Å ³)	7778.4(3)	3553.78(19)	3719.82(10)	3515.79(14)
<i>Z</i>	2	2	2	1
Density (Mg/m ³)(calculated)	1.713	1.905	1.768	2.189
<i>F</i> (000)	3910	1986	1932	2172
Absorption coefficient (mm ⁻¹)	5.663	6.218	5.899	9.497
Reflections collected	46655	22806	55528	38459
Independent reflections	13714 [R(int) = 0.0533]	22806 [R(int) = 0.0000]	16945 [R(int) = 0.0671]	12290 [R(int) = 0.0536]
GOF on <i>F</i> ²	1.092	1.062	1.013	1.056
Final <i>R</i> indices [I > 2σ(I)] ^a	R1 = 0.0429, wR2 = 0.1263	R1 = 0.0671, wR2 = 0.1800	R1 = 0.0477, wR2 = 0.1171	R1 = 0.0449, wR2 = 0.0925
<i>R</i> indices (all data)	R1 = 0.0539, wR2 = 0.1368	R1 = 0.0971, wR2 = 0.2107	R1 = 0.0891, wR2 = 0.1341	R1 = 0.0849, wR2 = 0.1119
Largest diff. peak and hole	2.868 and -1.712 e.Å ⁻³	2.368 and -4.378 e.Å ⁻³	3.136 and -2.245 e.Å ⁻³	2.984 and -3.012 e.Å ⁻³

$$^a R(F) = \Sigma ||F_o - F_c| / \Sigma |F_o| \text{ and } wR(F^2) = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma w(F_o^4)]^{1/2}$$

shutter mode, and the measurements were taken with 100 ms exposure times. Typical-lifetime studies were performed with an Edinburgh FLSP 920P photon-counting system with a hydrogen-filled or nitrogen lamp as the excitation source. Data were analyzed by using the nonlinear least-squares procedure in combination with an iterative convolution method. The emission decays were analyzed by the sum of exponential functions, which allows partial removal of the instrument time broadening and provides a temporal resolution of approximately 300 ps. Quantum yields were measured using an absolute PL quantum yield measurement system (Edinburgh FLSP 920P).

2.9 Derivation of Stern–Volmer quenching constant (the K_{SV} value)

The peak intensity of emission was plotted against the mole fraction of O₂ in N₂. The quenching constant between complexes and oxygen can thus be deduced from the Stern–Volmer equation^{9(b)} from the relationship of the ratio between emission intensity, I_0/I , versus partial pressure of O₂ (P_{O_2}) expressed in the equation below, where I_0 denotes the total emission in the absence of oxygen.

$$\frac{I_0}{I} = 1 + K_{SV} P_{O_2}$$

3. Results and Discussion

3.1 Synthesis and General Characterization

In order to investigate the effects of the different counter anions/solvents on the structures and oxygen-sensing properties of lead(II)-iridium(III) heterobimetallic coordination polymers, the reactions of **L-H₂** with Pb(ClO₄)₂·xH₂O, Pb(SCN)₂, and PbI₂ in metal/ligand molar ratio of 2:1 and in DMF, H₂O, acetone, and CH₃CN, yielded the polymeric compounds **1·DMF**, **1·Acetone**, **2·Acetone** and **3·DMF** (see Scheme 1). All the complexes **1·DMF**, **1·Acetone**, **2·Acetone** and **3·DMF** are stable in air. The structures of **1·DMF**, **1·Acetone**, **2·Acetone** and **3·DMF** were identified by X-ray diffractometer methods, IR, and EDX.

To characterize the bonding information of **1·DMF**, **1·Acetone**, **2·Acetone** and **3·DMF**, IR measurements were conducted. Fig. S1 in the supporting information depicts the typical IR spectra of **1·DMF**, **1·Acetone**, **2·Acetone** and **3·DMF**. For comparison of the IR peaks, a control experiment was performed to acquire the spectra of **L-H₂**. The broad absorption band at around 3400 cm⁻¹ for **1·DMF**–**3·DMF** were attributed to the O–H stretching vibrations of the coordinated or lattice water molecules. The relatively weak absorption bands around 3040 cm⁻¹ were assigned to C–H stretching vibrations of -CH₃ group and aromatic ring.

A subtle change presented; namely, the vibration of the carbonyl group, C=O, shifted to lower wavenumbers, from ca. 1720 cm⁻¹ for **L-H₂** to 1661 cm⁻¹ for **1·DMF**, 1711 cm⁻¹ for **1·Acetone**, 1709 cm⁻¹ for **2·Acetone**, and 1637 cm⁻¹ for **3·DMF**, which supports the coordination of the carboxylate groups to the lead(II) ions. The binding modes between carboxylate groups and lead(II) cations were then determined from the magnitude of the separation between the carboxylate stretches (Δ), $\Delta = \nu_{\text{asymmetry}} - \nu_{\text{symmetry}}$.^{10(a)} The IR spectra exhibit peaks at ca. 1478 cm⁻¹, 1370

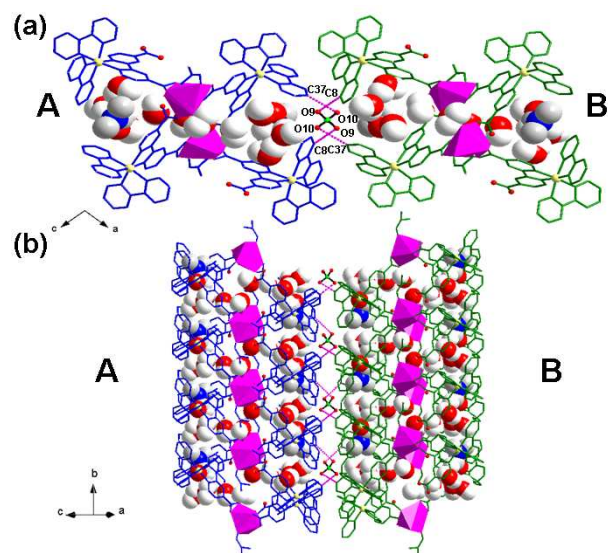


Fig. 1 (a) Polyhedral representation of the alternation in an AB/fashion (in blue and green) of **1·DMF** viewed down the *b*-axis. Magenta colored polyhedrons represent Pb(II) centers. (b) Encapsulation of 2D hydrogen-bonded lattice water and DMF molecules in **1·DMF**.

cm^{-1} for **1·DMF**, 1479 cm^{-1} , 1371 cm^{-1} for **1·Acetone**, 1478 cm^{-1} , 1371 cm^{-1} for **2·Acetone**, and 1478 cm^{-1} , 1375 cm^{-1} for **3·DMF**, respectively, were assigned to the asymmetric and symmetric C=O stretches, respectively.^{10(b)} The $\Delta\nu$ values were 108, 108, 107, and 103 cm^{-1} for **1·DMF**—**3·DMF**, respectively, indicating that carboxylate groups coordinated with Pb(II) in a bidentate fashion.

Intriguingly, the IR spectrum of **2·Acetone** had a moderate peak at ca. 2059 cm^{-1} , which is characteristic of the nitrile group, R—CN, from the solvent, whereas our reactant was of the isothiocyanate group, S—CN. The chemical composition of **2·Acetone** was also characterized by energy-dispersive X-ray (EDX) spectroscopy (see Fig. S2) and revealed that the elemental constituents had no S signal. The above results were also confirmed by single-crystal structure analysis. A similar result was also reported by Oyama *et al.*^{10(c)}

3.2 Description of Crystal Structures

Single-crystal X-Ray structure determination revealed that the complexes **1·Acetone**, **2·Acetone** and **3·DMF** crystallized in the triclinic *P*-1 space group, while compound **1·DMF** belonged to the monoclinic *P*2₁/*n* space group (see Table 1).

3.2.1 Crystal Structure of 1·DMF

The coordination environment of Pb(II) in **1·DMF** is depicted in Scheme 1, and the selected bond distances and angles are listed in Table S1. The Pb(II) center is six-coordinated and is defined by four oxygen atoms of two **L** ligands, one oxygen atom of the third **L** ligand, and one oxygen atom from one solvent DMF molecule. The Pb—O bond lengths range from $2.476(9)$ to $2.703(11)\text{ Å}$, and O—Pb—O bond angles vary from $45.9(3)^\circ$ to $156.4(4)^\circ$.

In **1·DMF**, the **L** ligand adopts a bidentate-chelating coordination mode through monodentate-chelating bidentate

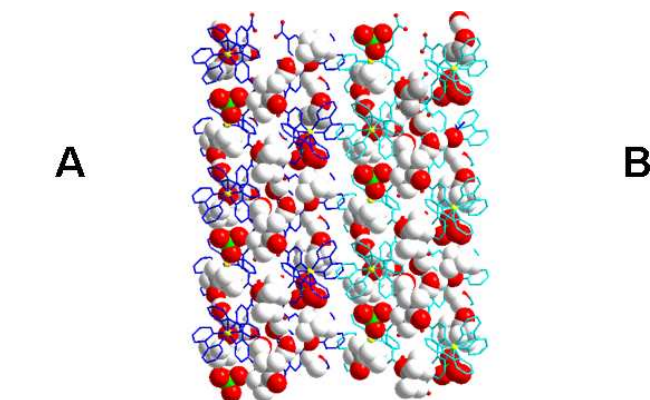


Fig. 2 Encapsulation of 2D hydrogen-bonded lattice water and acetone molecules along the crystallographic *a*-axis in **1·Acetone**. Polyhedral representation of the alternation in an AB/fashion (in blue and cyan) of **1·Acetone**.

carboxylate moieties,¹¹ and the oxygen atom of DMF links to a pair of Pb(II) centers to form $[\text{Pb}_2\text{L}_4(\text{DMF})_2]$ units with separations of Pb...Pb of $11.367(2)\text{ Å}$. The adjacent $[\text{Pb}_2\text{L}_4(\text{DMF})_2]$ chains (see A or B chain in Fig. 1(a)) are then mutually interlinked through hydrogen bonds between the framework of the ligand **L** and perchlorate oxygen atom $[\text{C}8\cdots\text{O}9^{\text{iv}} = 3.361(12)$, $\text{C}37\cdots\text{O}10^{\text{vii}} = 3.443(13)\text{ Å}$, symmetry codes: ^{iv} $1-x, -y, -z$; ^{vii} $-1+x, y, z$, see Table S2] to give rise to the formation of a 2D layer in the *ac*-plane and form rhombus-shaped channels along the *a*-axis. These channels have a cross sectional area of around $9.2 \times 9.6\text{ Å}^2$ and are filled with lattice water and DMF molecules in the symmetric unit shown in Fig. 1(b).

3.2.2 Crystal Structure of 1·Acetone

To investigate the influence of the solvent on the structure of the complex, acetone was introduced to obtain a new complex $[\text{PbL}_2(\text{H}_2\text{O})]\cdot\text{ClO}_4\cdot 3\text{C}_3\text{H}_6\text{O}\cdot 3\text{H}_2\text{O}$ (**1·Acetone**), and the structure was determined. Unlike **1·DMF**, the coordination environment of which is shown in Scheme 1, Pb(II) is eight-coordinated by three carboxylate oxygen atoms (O1—O6), a carboxylate O atom (O7A) of **L** ligands, and a coordinated water molecule. The bond distances around the Pb(II) center of **1·Acetone** range from $2.409(7)$ – $2.815(9)\text{ Å}$, comparable to those reported for other Pb—O distances.¹² The O—Pb—O angles are from $47.6(2)$ to $169.8(3)^\circ$. As illustrated in Fig. S3(a), in **1·Acetone**, the oxygen atoms (O1—O7) in carboxylate groups of **L** ligand, which act as chelating and bridging ligands, are connected by Pb(II) atoms and extend into infinite 1D chains running parallel to the *a*-axis.

As can be seen in Fig. S3(b) and Table S3, intermolecular edge-to-face π – π interactions were also observed to stabilize the 3D structure. The first one, between rings I and II, presents a distance between phenyl ring centroids of $4.828(4)\text{ Å}$ and a dihedral angle between the two aryl rings of 79.1° . The second edge-to-face interaction, between I and III, has a value of $4.502(3)\text{ Å}$ and a dihedral angle of 76.7° . The cross sectional area of this 1D pore between AB chains is around $9.6 \times 12.9\text{ Å}^2$ and is filled with the perchlorate anion, lattice acetone, and water molecules Fig. 2.

3.2.3 Crystal Structure of 2·Acetone

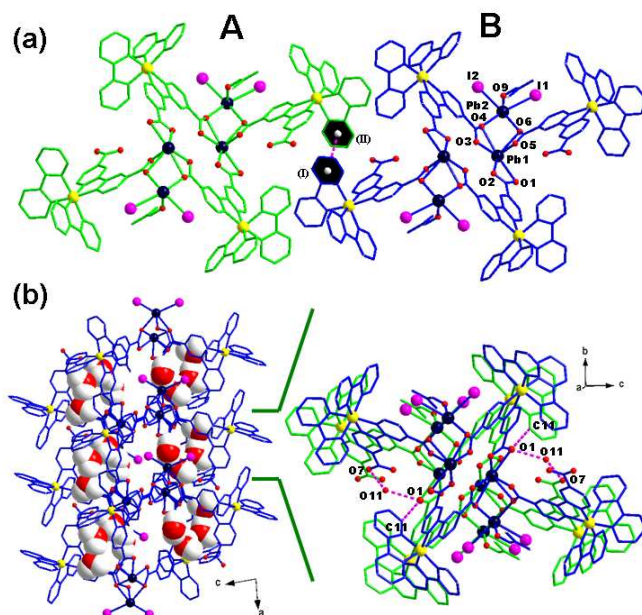


Fig. 3 (a) The coordination environment of Pb(II) in **3-DMF** and representation of the alternation in an AB/fashion (in blue and green). Hydrogen atoms are omitted for clarity. Dotted lines indicate the π - π interactions found. (b) View of a 1D linear chain in **3-DMF** along the crystallographic *b*-axis (left). Selected pairs of molecules from the structure of **3-DMF** along the *a*-axis. Dotted lines indicate the H-bond interactions found.

When the lead(II) salts, i.e., $\text{Pb}(\text{ClO}_4)_2 \cdot x\text{H}_2\text{O}$, in the synthesis of **1-DMF** and **1-Acetone** were replaced by $\text{Pb}(\text{SCN})_2$, **2-Acetone** was obtained. Similar to the structure of **1-Acetone**, the coordination environment around Pb(II) is also eight-coordinated (Scheme 1). The Pb—O bond distances are similar to those in **1-DMF** and **1-Acetone** and range from 2.426(5)–2.814(6) Å. The O—Pb—O angles are from 49.94(17) to 173.70(19)°.

As observed in the compound **2-Acetone**, rhombus channels between A and B column form by packing of iridium(III) and Pb(II) heterobimetallic complexes, which were observed along the *b*-axis direction (Fig. S4(a)), and contain acetone, water and acetonitrile solvent molecules. The cross sectional area of the channel is around $9.6 \times 13.0 \text{ Å}^2$. The rhombus packing forms a three-dimensional network provided by two sets of edge-to-face π - π interactions (Fig. S4(b)). One set of edge-to-face interactions, between rings I and II, presents a distance between phenyl ring centroids of 4.550(3) Å and a dihedral angle between two aryl rings of 78.2°. The second set of edge-to-face interactions, between rings I and III, has a ring centroid distance of 4.930(4) Å and a dihedral angle of 82.6°.

3.2.4 Crystal Structure of **3-DMF**

Besides those in compounds **1-DMF**, **1-Acetone**, and **2-Acetone**, the **L-H₂** ligands in compound **3-DMF** contain two crystallographic independent Pb(II) ions (Pb1 and Pb2). As shown in Fig. 3(a), Pb1 ion is six-coordinated by six carboxylate oxygen atoms (O1—O6) from three iridium complexes. Pb2 ion is five-coordinated by two carboxylate oxygen atoms (O4 and O6) from two iridium complexes, one oxygen atom (O9) from a coordinated DMF solvent molecule, and two iodide anions (I1

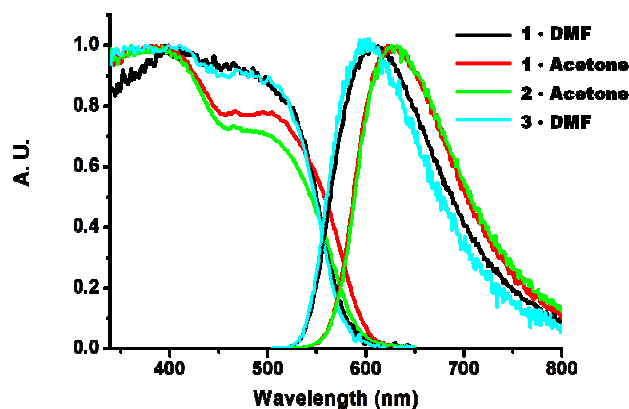


Fig. 4 UV-vis diffusive reflectance and emission spectra of **1-DMF**—**3-DMF**. $\lambda_{\text{exc}} = 405 \text{ nm}$.

and I2). The structural feature of **3-DMF** is that an unusual Pb—O cluster is fused by the bridging μ_2 -O (O1, O2, O3, and O5; two-fold coordination) atoms and μ_3 -O (O4 and O6; three-fold coordination) atoms around the Pb1 atom and the other type of Pb(II) metal center, imposing Pb...Pb separation (4.151(2) and 4.430(1) Å, see Fig. S5). The Pb—O bond lengths are in the range of 2.391(9)–2.77(2) Å and the O—Pb—O angles are from 50.1(2) to 169.3(4)°, comparable to those reported for other lead(II) carboxylates.^{2(a)} The observed Pb—I bond distances (3.0479(10) to 3.0732(10) Å) and I—Pb—I, O—Pb—I angles fall in the normal range.¹³

Moreover, the H-bonds through O7—O11—O1—C11 linkage $[\text{O}(11) \dots \text{O}(7)]^{\text{ii}} = 2.844(13)$, $[\text{O}(11) \dots \text{O}(1)]^{\text{i}} = 3.043(13)$, $[\text{C}(11) \dots \text{O}(1)]^{\text{ii}} = 3.351(16) \text{ Å}$, symmetry code: ⁱ1-x, 1-y, 1-z; ⁱⁱx, 1-y, 1-z] construct a 1D chain (Fig. 3(b)), which further combines with an π - π stacking (A, B columns) interaction between phenyl rings of the **L-H₂** ligands to extend the 2D layer to a 3D network (see Table S2 and Fig. 3(a)–3(b)).

3.3 Thermogravimetric analysis

Thermogravimetric analysis (TGA) was conducted to explore the thermal stability of the as-synthesized compounds (see Fig. S6). The TG curve of **1-DMF** reveals three main steps of weight loss. The first and second weight losses of 14.0% (calcd ca. 15.6%) are in the temperature range from 21 to 150 °C, which corresponds to the release of two coordinated DMF, two lattice DMF, thirteen lattice water, and one perchlorate molecules. The framework was stable up to 150 °C and started to decompose above 230 °C, which is consistent with the decomposition of the main organic building ligand. This observed weight loss of 53.9% is close to the calculated value (54.9 %).

The curve also exhibits three main stages weight loss for **1-Acetone**. The first step, with 13.8% weight loss from 20 to 280 °C, is attributed to the gradual loss of three lattice water, three acetone, and one perchlorate molecules (calcd ca. 16.0%), following by a second and a third stage after 280 °C. Compound **1-Acetone** has a higher thermal stability than **1-DMF**, which can be rationalized by the fact that the bonding mode around the Pb(II) center and the bonding strength of the 1D infinite chain of **1-Acetone** are stronger than those of **1-DMF** (*vide supra*). A

Table 2. Photophysical properties and oxygen-quenching fitting parameters of **1·DMF—3·DMF**.

	$\lambda_{\text{max}}(\text{nm})^a$	Q.Y.	$\tau_{\text{obs}}(\text{ns})^d$	K_{SV}	R^2	LOD	95% response time (s)	95% recovery time (s)
L-H₂	613	0.178 ^b	314.12	2.48	0.9966	N.A.	N.A.	N.A.
1·DMF	610	0.13 ^c	285.08	1.44	0.9879	0.65%	28	45
1·Acetone	631	0.15 ^c	314.64	1.60	0.9966	0.70%	85	86
2·Acetone	630	0.17 ^c	363.42	2.85	0.9946	0.61%	46	91
3·DMF	602	0.05 ^c	146.10	5.11	0.9802	0.52%	50	24

^aThe emission was detected in single crystal at 298K upon excitation at 405 nm. ^bQuantum yield was measured in the solid state. ^cQuantum yield was measured in the crystal. ^dLifetime was detected in the solid state. Note that lifetimes for **1·DMF—3·DMF** were beyond the system limit of 300 ps.

similar trend has also been observed in the case of **2·Acetone**. The TGA trace for **2·Acetone** shows a gradual weight loss of 11.3% (calcd ca. 13.6%), corresponding to the escape of all lattice solvent. Further weight loss (~56.5%) indicates the loss of coordinated water, followed by the decomposition of the framework. Weight loss calculations showed that the final product was PbO and Ir₂O₃. The thermal stability of **1·Acetone** and **2·Acetone**, the bonding strengths around the Pb(II) center, and π - π interactions for both have been compared. **2·Acetone** has higher thermal stability than **1·Acetone**, which may be attributed to the small differences between the bond lengths around the Pb(II) center in **2·Acetone**. Finally, the TG curve of **3·DMF** indicates that the release of two DMF and lattice water molecules takes place at 20 to 195°C with a weight loss of 6.6% (calcd ca. 7.1%), and decomposition of the iodide anion and main framework cause further weight loss of 55.6% (calcd ca. 55.0%). Compound **3·DMF** has better thermal stability than the others, which may be attributed to the binding modes around the Pb-O cluster (*vide supra*).

3.4 Photophysical properties

The solid-state adsorption and emission properties of **1·DMF—3·DMF** were also investigated at room temperature. As shown in Fig. 4, the adsorption and emission bands of **1·DMF—3·DMF** in single crystal form are broad and structureless. Pertinent data are summarized in Table 2. From a previous study,⁶ we know that free ligand **L-H₂** in single crystal exhibits a low-lying characteristic adsorption band with $\lambda > 400$ nm, which is assigned to metal-to-ligand charge transfer (MLCT) in the triplet manifold. Upon excitation at ~405 nm, the origin of emission for **1·DMF—3·DMF** in single crystal is attributed to ³MLCT; i.e., phosphorescence. This is supported by the long lifetimes and blue-shifted emission peaks at 77K for **1·DMF—3·DMF** (see Table 2 and Fig. S7). First, let us discuss the spin-orbital coupling effect directed by the heavy metal cation, Pb²⁺, to the emission wavelength. Comparing Zn²⁺, Cd²⁺, Co²⁺, and Ni²⁺-iridium(III) coordination polymers and the **L-H₂** in our previous work⁶ with this study, the absorption and emission peaks of lead(II)-iridium(III) coordination frameworks are more red-shifted, and quantum yields are lowered. These indicate that the lead(II)

cation is heavier than the other cation, provoking the intersystem crossing to another lower-lying triplet state for the host molecule *via* an enhanced spin-orbit coupling. Consequently, the emission wavelength and intensity will plausibly be quenched due to a smaller T₁-S₀ energy gap.⁶

Second, we then inspected the effects of stereochemistry of the ligand-metal complex and architectures of the associated crystal packing on the emission maxima of **1·DMF** (610 nm), **1·Acetone** (631 nm), **2·Acetone** (630 nm), and **3·DMF** (602 nm), respectively. As shown in Fig. 2, S3(b), S4(b), and table S3, iridium(III) has the same coordination number and two sets of π - π interactions between the A and B columns in **1·Acetone** and **2·Acetone**, but the distances of π - π interactions in **1·Acetone** are slightly shorter than those in **2·Acetone**. As a result, **1·Acetone** exhibits lower energy emission than **2·Acetone**. Theoretically, the distances of π - π interactions are shorter in **1·Acetone** than in **2·Acetone**, which would increase the rigidity of the whole backbone and thus reduce the loss of energy by radiationless decay of the interligand emission excited state.^{14, 15} However, the quantum yield and lifetime of **1·Acetone** are small and shorter than those of **2·Acetone**, which can most likely be attributed to the optical energy gap law. The nonradiative decay rate increases as the triplet energy decreases.¹⁶

Next, unlike **1·Acetone** and **2·Acetone**, the absorption and emission bands for **1·DMF** and **3·DMF** tend to be blue-shifted relative to those of **1·Acetone** and **2·Acetone**. Although **1·DMF** and **3·DMF** exhibit similar coordination environments (*vide supra*), i.e., they are six-coordinated around the Pb(II) center and have one set of infinite intermolecular π - π interaction stacking of pyridyl and pyridyl moieties between AB stacking fashion in **3·DMF**, **3·DMF** exhibits a blue-shifted emission peak with respect to that of **1·DMF**. The hypsochromic shift can be tentatively rationalized by the existence of Pb/Pb interactions in **3·DMF** that enhance the cooperative association of the intermolecular π - π interaction (see table S3), for example, in an H-type of arrangement, which is similar to our previous report.¹⁷ The emission quantum yield for **3·DMF** in single crystal was the lowest among the four compounds, which can be attributed to the number of heavy atoms in the unit cell larger than others and hence decreased emission (*vide supra*).

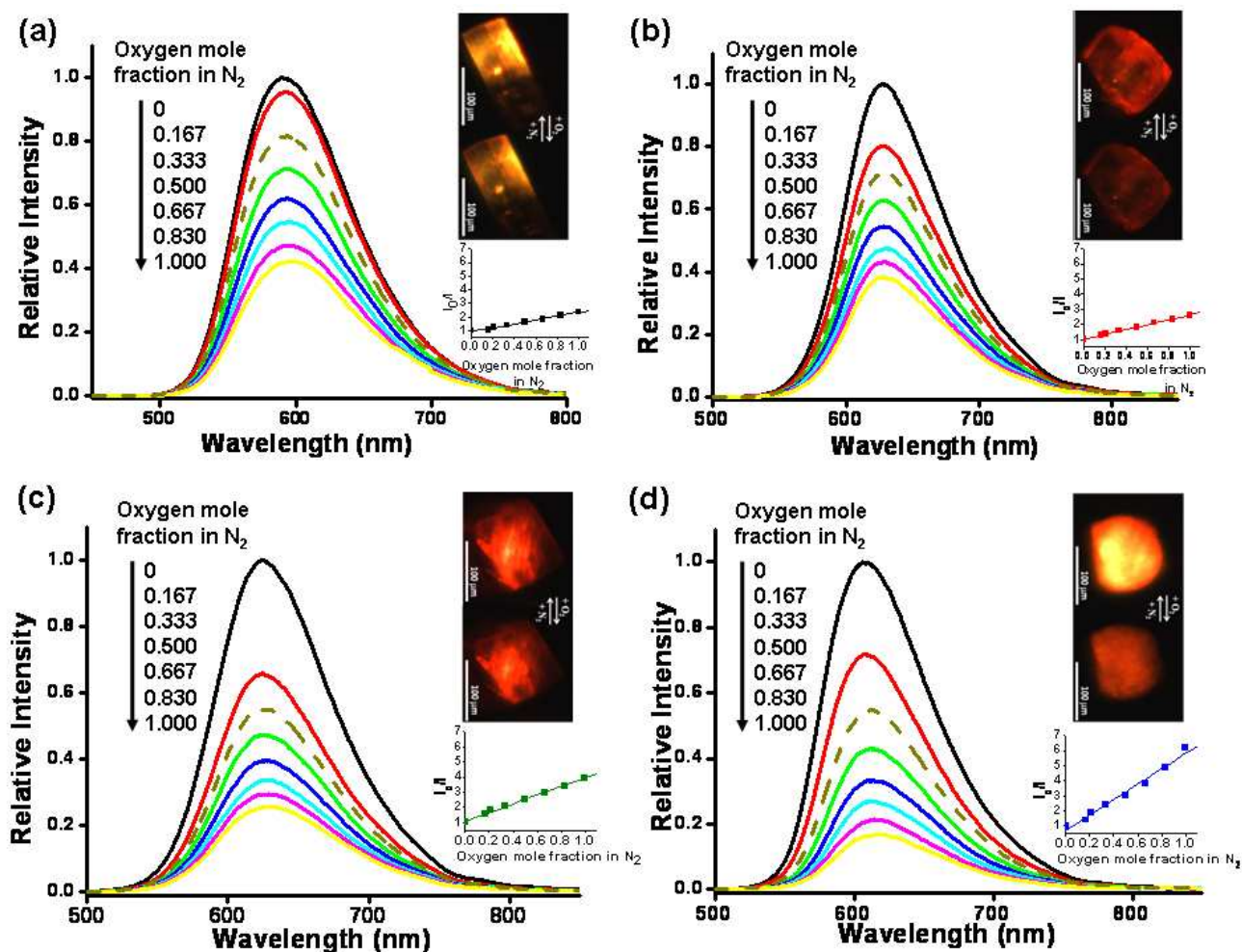


Fig. 5 (a)-(d) Response of **1·DMF–3·DMF** in single crystal under different mole fractions of $O_2(g)$ in nitrogen (solid line). $\lambda_{ex} = 405$ nm. And response of complexes exposed to standard air (dash line). Inset: Luminescence changes of **1·DMF–3·DMF** with 100% N_2 and 100% O_2 , respectively. Scale bar is 100 μm . Stern–Volmer plot for the oxygen quenching of **1·DMF–3·DMF**. The solid lines are the best fitting lines using the equation described in the experimental section.

Although the quantum yields for **1·DMF–3·DMF** were not larger than those of Zn^{2+} , Cd^{2+} , Co^{2+} , Ni^{2+} -iridium(III) coordination polymers, the magnitude was still greater than that of relevant iridium complexes (~ 0.02) and should be more suitable for oxygen-sensing application.¹⁸

3.5 Oxygen-sensing properties

Oxygen-sensing properties and the response and recovery performances of **1·DMF–3·DMF** were subsequently examined. As shown in Fig. 5(a)-5(d), after exposure to different concentrations of O_2 at room temperature, phosphorescence intensities decreased. Likewise, the confocal images of the four compounds were visibly luminescent under 100% N_2 , but intensities decreased when exposed to 100% O_2 (see inset of figures). At 1 atm O_2 , the emission intensities of **1·DMF–3·DMF** were quenched by 58%, 62%, 74%, and 83%, respectively. Subsequently, the Stern–Volmer equation⁶ was used for studying the kinetics of a photophysical intermolecular deactivation process between **1·DMF–3·DMF** and oxygen. The peak intensity of emission was plotted against the mole fraction

of O_2 in nitrogen (see inset of Fig. 5(a)-5(d)). Accordingly, the quenching constants, or K_{SV} values, between **1·DMF–3·DMF** and oxygen were deduced from the slope to be 1.44 ($R^2 = 0.9879$), 1.60 ($R^2 = 0.9966$), 2.85 ($R^2 = 0.9946$), and 5.11 ($R^2 = 0.9802$), respectively (also see Table 2).

For **1·DMF** to **3·DMF**, the K_{SV} values were larger than the reported values and even larger than our previous report in the solid interface.^{6, 19-22} To support this contention, the K_{SV} values of various iridium oxygen sensors are listed in Table 3. This result can be rationalized by the fact that the enhancement of the quenching constant for different lead(II)-iridium(III) heterobimetallic coordination frameworks can be attributed to increased energy transfer to the triplet 3MLCT excited state by lead(II) atoms, the result of which increases the triplet state deactivation between sensitizer and ground-state oxygen. We found that increasing the number of lead(II) atoms, i.e. heavy atoms, in the unit cell results increased the K_{SV} value; that is, **1·Acetone** < **2·Acetone** < **3·DMF**. Among these, the K_{SV} value for **1·Acetone** is larger than for **1·DMF** even though the amount of lead(II) in **1·Acetone** is smaller than that in **1·DMF**. The difference in the K_{SV} values among **1·DMF** and **1·Acetone** may

Table 3. Comparison of the performances of the various types of optical oxygen sensor based on the coordination polymers.

Luminescence materials	K_{SV}	Response time ^g	Recovery time ^g	Ref
Ir-Zn derivative ^a	$\sim 1.33 \text{ (atm}^{-1}\text{)}$	?	?	Xie <i>et al.</i> (2010) ¹⁹
Ir complex doped into the framework of $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bpdc})_6$	$2.01 \text{ (atm}^{-1}\text{)}$	?	?	Barrett <i>et al.</i> (2012) ²⁰
Tb^{3+} -indium trimesate MOFs film-3.5wt% ^c	0.78	90 s	60 s	Dou <i>et al.</i> (2014) ²¹
Tb^{3+} -indium trimesate MOFs film-5.1wt% ^d	7.59	6 s	53 s	Dou <i>et al.</i> (2014) ²¹
Tb^{3+} -indium trimesate MOFs film-1.5wt% ^d	13.13	4 s	48 s	Dou <i>et al.</i> (2014) ²¹
Tb^{3+} -indium trimesate MOFs film-1.0wt% ^d	14.05	4 s	41 s	Dou <i>et al.</i> (2014) ²¹
$[\text{Ru}_{0.1}\text{Zn}_{6.9}(\text{ip})_{12}](\text{OH})_2$ ^e	2.97	?	?	Qi <i>et al.</i> (2013) ²²
$[\text{Ru}_{0.13}\text{Zn}_{6.87}(\text{ip})_{12}](\text{OH})_2$ ^e	4.1	?	?	Qi <i>et al.</i> (2013) ²²
$[\text{Ru}_{0.15}\text{Zn}_{6.85}(\text{ip})_{12}](\text{OH})_2$ ^e	5.3	?	?	Qi <i>et al.</i> (2013) ²²
$[\text{Ru}_{0.16}\text{Zn}_{6.84}(\text{ip})_{12}](\text{OH})_2$ ^e	6.9	?	?	Qi <i>et al.</i> (2013) ²²
Cd-Ir coordination polymers ^f	2.82	70	30	Our previous results. (2012) ⁶

^a Ir[3-(2-pyridyl)benzoate]₃ derivative.

^b $[\text{Ir}^{\text{III}}(\text{ppy})_2(\text{dcbpy})]\text{Cl}$, dcbpy = 2,2'-bipyridinyl-5,5'-dicarboxylate) doped $\text{Zr}_6\text{O}_4(\text{OH})_4(\text{bpdc})_6$, bpdc = *para*-biphenyldicarboxylate.

^c $[(\text{CH}_3)_2\text{NH}_2][\text{In}_3\text{O}(\text{BTC})_2(\text{H}_2\text{O})_3]_2[\text{In}_3(\text{BTC})_4]$, BTC = 1,3,5-benzenetricarboxylate, 3.5wt% means content of Tb^{3+} in MOF film.

^d $\text{In}_3\text{O}(\text{OH})(\text{H}_2\text{O})_2[\text{BTC}]_2$, 5.1, 1.5, 1.0wt% means content of Tb^{3+} in MOF films, respectively.

^e $[\text{Ru}_x\text{Zn}_{7-x}(\text{ip})_{12}](\text{OH})_2$, Hip = 1*H*-imidazo-[4,5-*f*][1,10]phenanthroline

^f $[\text{CdL}_2(\text{H}_2\text{O})_2] \cdot 3\text{DMF} \cdot 6\text{H}_2\text{O}$

^g ? means not mentioned in the article.

be attributed to the optical energy gap law (*vide supra*).

Moreover, the inset of Fig. 5(a)-5(d) shows that the linear calibration curve for **1·DMF—3·DMF** with the correlation coefficient (R^2) was 0.9879, 0.9966, 0.9946, and 0.9802, respectively, suggesting that there is only one environment in which quenching takes place between the framework and oxygen. As shown in Fig. 5(a)-5(d), the limit of detection was the lowest quantity of oxygen exposure to the framework that could be distinguished from the absence of that oxygen. The minimum detectable concentrations (LODs) of oxygen for **1·DMF—3·DMF** were calculated to be 0.65%, 0.70%, 0.61%, and 0.52%, respectively, from three times signal to noise.

In addition, the recovery test was used to test the oxygen sensing accuracy of **1·DMF—3·DMF**. Commercially available, standard air containing oxygen gas of 0.21% with a purity of 99.9999% was analyzed. The recovery test for oxygen was performed by purging this standard gas to **1·DMF—3·DMF**. The results are also shown in Fig. 5(a)-5(d) (see the dash line). The concentrations of oxygen (and recovery) were then evaluated separately to be 0.220% (105%), 0.231% (110%), 0.252% (120%), and 0.227 (108%) for **1·DMF—3·DMF**, respectively, which clearly indicates that **1·DMF—3·DMF** offer an accurate, precise method for the determination of oxygen.

3.6 Reversibility, response time, recovery time, and stability of the oxygen-sensing behavior of **1·DMF—3·DMF**

Since good reproducibility and reversibility are desirable for an oxygen sensor, a reversible sensing test of **1·DMF—3·DMF** for

oxygen was performed. The reproducibility and reversibility of the sensing framework was evaluated by repeatedly switching the compound in an alternating atmosphere of O_2 . Fig. 6(a)-(d) shows the changes in relative phosphorescence intensity for at least ten cycles at the emission maximum of **1·DMF—3·DMF** under excitation at 405 nm versus time recording for the framework when it was exposed to oxygen. The 72.1%, 61.0%, and 50.3% recoveries of intensity after ten cycles for **1·Acetone—3·DMF**, respectively, demonstrate the high degree of reproducibility and reversibility during the sensing process. The recovery of intensity of **1·DMF** was 42.4% lower than those of the others, possibly due to the lower thermal stability.

When 100% nitrogen was replaced with 100% oxygen, the observed 95% average response times were 28, 85, 46, and 50 s for **1·DMF—3·DMF**, respectively, for the decrement of emission intensity by 95% (Fig. 6(a)-6(d)). The 95% observed average recovery times were 45, 86, 91 and 24 s for **1·DMF—3·DMF**, respectively, for the increase of emission intensity to 95% after exposing 100% O_2 to 100% N_2 . From the above, it appears that **3·DMF** represents the best oxygen-sensing ability, shortest response time, and fastest recovery time. Moreover, it should be noted that the evaluated recovery time for **3·DMF** is even faster than those reported for rare-earth MOF films (also see Table 3).²³ In summary, the large quenching constant, the short response time, the fast recovery time, and the reversibility for sensing oxygen, especially **3·DMF**, allows efficient, reversible, and rapid detection of O_2 molecules. Fig. 6(e) plots the long-term stability of **3·DMF**. This sensor retained 99.9% of its original response even after 60 days in a testing concentration of air containing

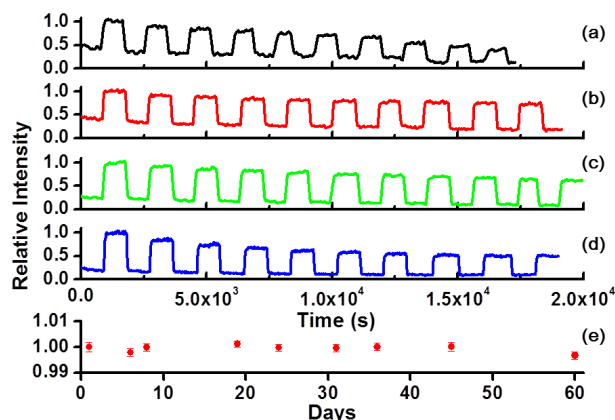


Fig. 6 Reversibility, response time, and recovery time of (a)-(d) **1-DMF-3-DMF** in single crystals when cycling from 100% N₂ to 100% O₂ atmosphere. (e) Long-term stability of **3-DMF** exposed to air containing 21% oxygen.

21% oxygen.

3.7 Effect of temperature on oxygen-sensing behavior of 3-DMF

All of the above results, taken together, indicated that **3-DMF** was suitable for use as a potential oxygen sensor for testing subsequent experiments. It is known that phosphorescence intensity is affected by temperature. Fig. S8 illustrates the effect of environmental temperature on the emission intensity of **3-DMF** in an alternating atmosphere of 100% O₂ and 100% N₂ at 0, 10, 20, 30, 40, and 50 °C. As shown in that figure, the emission intensity decreases as temperature increases. At lower temperatures, the frequency of molecular collisions between framework and oxygen is greatly reduced, thereby increasing phosphorescence signals.^{24(a)} At elevated temperatures, emission is very rapidly thermally quenched, hence decreasing the emission intensity.^{24(b)} Fig. S8 indicates that **3-DMF** can respond to oxygen at temperatures even up to 50 °C.

3.8 Effect of interferences on oxygen-sensing behavior of 3-DMF

To examine the possible interference from other gases on the luminescence intensity of **3-DMF**, the phosphorescence responses of **3-DMF** to other gases were examined. All gases (CO, CO₂, and O₃) were at 1-atm pressure except HCl, which was at its maximum room-temperature vapor pressure. The gray bar reveals the interfering effects of these gases on the phosphorescence quenching of **3-DMF**, and the white bar represents purging of 100% N₂ with respect to every competing gas. As shown in Fig. 7, **3-DMF** has a distinct quenching effect upon recognizing oxygen gas, while other gases induce much smaller phosphorescence decrements. This experiment confirms the noteworthy selectivity of **3-DMF** for oxygen.

3.9 Ratiometric Oxygen-sensing properties of 3-DMF

Finally, in order to further increase the application of this oxygen sensor, **3-DMF** was mixed with a commercial dye, Coumarin 480

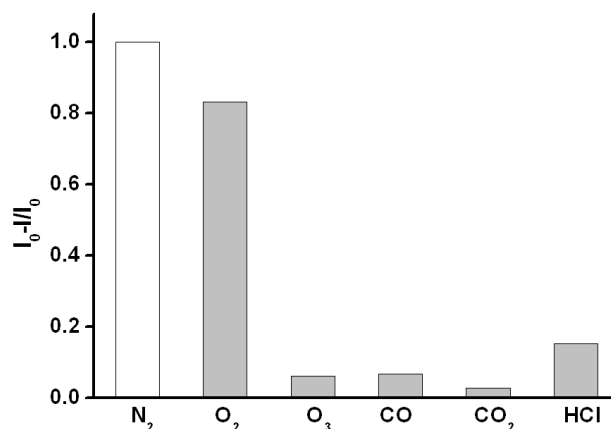


Fig. 7 Relative phosphorescence response of **3-DMF** to various gases under excitation at 405 nm. The gray bar reveals the interfering effects of these gases on the phosphorescence quenching of **3-DMF**, and white bar represents purging of 100% N₂ with respect to every competing gas.

(C480)^{25(a)}, as a ratiometric oxygen sensor^{25(b)} for analysis of real oxygen gas in air. Combining a fluorescent blue-emissive dye with a phosphorescent orange-emissive MOFs upon excitation of UV light as a strategy enables ratiometric oxygen-sensing measurement, and makes the result easily visible to the naked eye.

At first, C480 (10⁻²M, 500 μL in ethanol)-doped polydimethylsiloxane (PDMS, 550 μL) was prepared as a useful blue emissive fluorescent probe. Then the prepared gel solution was mixed with **3-DMF** and applied to sense oxygen. Fig. 8 shows the emission spectra of **3-DMF** containing C480 in PDMS under 0%, 50%, 75%, and 100% O₂ after excitation at 325 nm. The emission of **3-DMF**, with its maximum at 608 nm, was easily quenched by 100% O₂; this was simultaneously accompanied by a slight fluorescence decrease at 442 nm. The ratios of emission intensities at λ_{em} = 608 nm/442 nm ranged from 5.23 to 1.07 under 100% N₂ to 100% O₂, indicating that **3-DMF** containing C480 in PDMS acts as a ratiometric sensor for oxygen gas sensing. In addition, compared to their individual framework emissions, this mixed emission is slightly shifted, possibly due to an intermolecular interaction between luminophore and PDMS in the solid state. The inset of Fig. 8 plots the ratio of emission intensity of this oxygen sensor as a function of concentration of O₂ gas. This fitting curve was quite linear (Y = 5.3758 - 3.9594 X; R² = 0.9824). After exposure to real air containing 21% oxygen (Fig. 8), the recovery was evaluated to be 93.2%, clearly indicating that **3-DMF** containing C480 in PDMS offers an excellent, accurate, and precise method for the determination of oxygen in real gas. This indicates that the model compound **3-DMF** mixed with fluorescent dye should spark a broad spectrum of interest in application.

4. Conclusions

Four new lead(II)-iridium(III) heterobimetallic coordination frameworks, i.e., [Pb₂(L)₄(DMF)₂]·ClO₄·2DMF·13H₂O (**1-DMF**), [PbL₂·H₂O]·ClO₄·3C₃H₆O·3H₂O (**1-Acetone**), [PbL₂·H₂O]·3C₃H₆O·3H₂O·CH₃CN (**2-Acetone**), and [Pb₄L₄I₄·(DMF)₂]·10H₂O (**3-DMF**), have been successfully

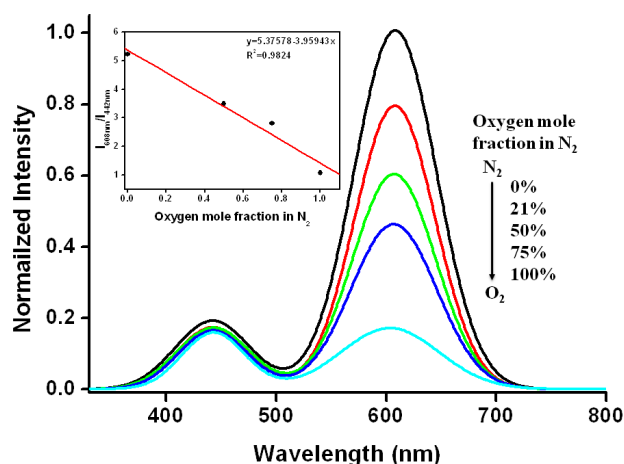


Fig. 8 Normalized emission spectra of C480-doped PDMS mixed with **3-DMF** under 0%, 50%, 75%, 100% O₂ and real air (containing 21% oxygen), $\lambda_{\text{ex}} = 325$ nm. Inset: Plots of $I_{608 \text{ nm}}/I_{442 \text{ nm}}$ as a function of oxygen pressure.

synthesized. These four structures, containing heavy atoms, i.e., lead(II) atoms, make an exquisite case in point for oxygen selective sensing. The detection limit, e.g. **3-DMF**, was in the 0.52% concentration range for oxygen gas. At 1 atm O₂, the emission intensity of **3-DMF** was quenched by 83% with a quenching constant, or K_{SV} value, between **3-DMF** and oxygen of 5.11 ($R^2 = 0.9802$). Moreover, **3-DMF** exhibits a short response time (50 s), fast recovery time (24 s), high reproducibility, satisfactory temperature response range (at least to 50 °C), and long-term stability (for at least 60 days) to oxygen. CO, CO₂, O₃ and HCl gases have no obvious interference toward oxygen-sensing. Finally, for further practical application, **3-DMF** was mixed with Coumarin 480 (C480) as a ratiometric oxygen sensor for analysis of real oxygen gas in air. The fitting curve was still quite linear. The model compound **3-DMF** mixed with fluorescent dye should spark a broad spectrum of interest in application.

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Notes and references

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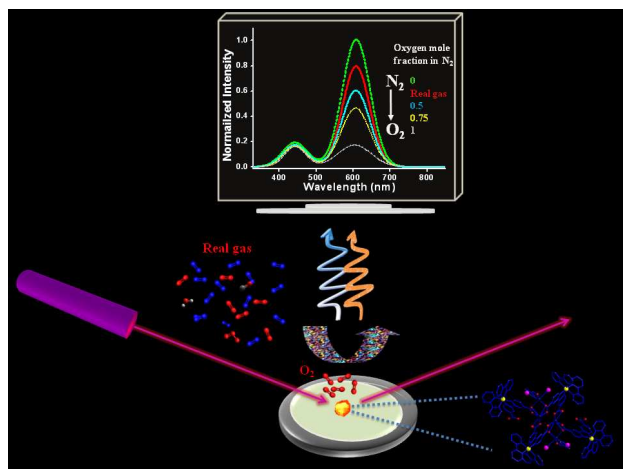
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Table of Content



The crystalline lead(II)-iridium(III) heterobimetallic coordination frameworks mixed with C480 as ratiometric oxygen sensor are prepared and applied to the determination of oxygen in real gas.