

Rational Syntheses of Cd^{II} and Pb^{II} Metal-Organic Frameworks for Luminescence Sensing of Nitroaromatics, Ferric and Chromate Ions

Yu Wu,*^[a] Yulong Li,^[a] Like Zou,^[a] Jianshen Feng,^[a] Jianqiang Liu,*^[b] Miaomiao Luo,^[b] Jingwen Xu,^[b] Reena Yaday,^[c] and Abhinav Kumar*^[c]

Keywords: Coordination polymer; Photoluminescence; Sensing; Topology; Density functional calculations

Abstract. The metal-organic frameworks (MOFs), $\{[Cd(L)(H_2O)] \cdot CH_3OH \cdot DMF\}$ (1) and [Pb(L)(DMF)] (2) (L = 2,4-dihydroxybenzaldehyde nicotinoylhydrazone), were synthesized and characterized using microanalyses, IR spectroscopy, and single-crystal X-ray diffraction. Single crystal X-ray analyses revealed that both 1 and 2 exhibit 2D grid networks. The photoluminescence investigation

Introduction

Self-assembled metal organic frameworks (MOFs) comprising of organic linkers and metal ions or clusters provides impetus for developing new functional materials, e.g. development of porous materials.^[1–3] Also, because of the considerable specific surface area and recognition capability, the microporous MOFs have drawn a great deal of attention as an excellent candidate for the rapid recognition and sensing of cations, anions, small molecules.^[4–6] The MOF-based fluorescence sensor was firstly reported in 2009.^[7] After this investigation MOF-based fluorescence sensor represents a new sub-field of MOF research especially as explosive detectors.^[8–10] Some of these MOFs are used for the recognition and detection of electron-deficient nitroaromatic molecules.^[8–10] However, in comparison with the other applications of MOFs, this area of research still under progress.

To develop the luminescent metal-organic frameworks (LMOFs), three strategies ^[11,12] can be deployed at present: (1) Introducing functional organic sites in the ligand, (2) gener-

- E-Mail: wuyuhlj@163.com
- * Dr. J. Liu
 E-Mail: jianqiangliu2010@126.com
 * Dr. A. Kumar
- E-Mail: abhinavmarshal@gmail.com
- [a] College of Chemistry and Environmental Engineering Sichuan University of Science & Engineering
- Zigong, 643000, P. R. China [b] School of Pharmacy Guangdong Medical University Dongguan, 523808, P. R. China
- [c] Department of Chemistry Faculty of Science University of Lucknow
 - Lucknow 226 007, India
- Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/zaac.201600344 or from the author.

indicates that **1** and **2** could be a prospective candidate for developing luminescencent sensors for the selective sensing of nitrobenzene, which is used as a precursor for explosives. The luminescent properties of **1** and **2** in different solvents were investigated and corroborated by theoretical calculations. Additionally compounds **1** and **2** also show selective sensing ability for Fe³⁺ as well as for CrO_4^{2-} ions.

ating coordinatively unsaturated metal sites, and (3) constructing the mesoporous channels in the MOFs. The effectiveness of LMOFs can largely be improved by incorporating active functional groups (such as -NH2 and -COOH) in the ligands. From the aforementioned viewpoints one can say that the development of dual functional materials with high chemical stability, which can act as a fluorescent probe for different ions as well as can also detect nitrobenzene is a challenging task. To develop such type of LMOF, a salen type ligand was selected in the presented investigation due to the following reasons:^[13,14] (1) Salen type ligands form chemically stable materials; (2) this type of ligands comprises of electron pair rich nitrogen linkers and aromatic π ring, which could adjust the position of ligands to provide interactions and in turn modulate the luminescent character (Scheme 1); and (3) they can interact with electron deficient compounds such as nitrobenzene and its derivatives. Keeping these aspects in mind, herein, we wish to report the syntheses, characterization, and sensing capabilities of two new LMOFs comprising of central Cd^{II} and Pb^{II} atoms. The synthesized MOFs are capable of sensing not



Scheme 1. Illustration of rational design for stable MOFs based on Cd^{II}/Pb^{II} ions and the ligand involving different functional groups.

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^{*} Dr. Y. Wu

only the nitrobenzene but also having capability to sense Fe^{3+} and CrO_4^{2-} ions. The results of these investigations are presented herein.

Results and Discussion

Molecular Structures

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Single-crystal X-ray analysis revealed that the asymmetric unit of 1 is comprising of one Cd^{II} ion, one L ligand, one coordinated water molecule, one free CH₃OH, and one DMF molecule. The central Cd^{II} atom adopts a distorted octahedral coordination environment with O1, N1, N3, O1W, O2, and O2A (A: -x, -1-y, -1-z) (Figure 1a). The structure contains a crystallographically imposed inversion center in the middle of a $M_2(\mu_2-O)_2$ core, where M refers to Cd1 and the oxygen atoms (O2) belong to the hydroxyl group. The doubly deprotonated H₂L ligand behaves as a tetradentate fashion coordinated to Cd^{II} via carbonyl, azomethine nitrogen atom, phenolic oxygen, as well as pyridyl nitrogen atoms. The Cd^{II} ion is found to be displaced by 0.22 Å from the plane constituting atoms N3, N1, O1, and O2. Based on the above connection, adjacent Cd^{II} ions are connected by L ligand into 2D layer along the ab plane (Figure 1b). As observed for the neutral complex 1, in this case the ONO coordination generates two chelation rings, all planar within 0.09 Å, but not perfectly coplanar to each other, having a dihedral angle of ca. 8°. Accordingly, the overall skeletons of the two ligands are slightly bent and deviate from planarity by 0.12 Å. It is interesting to compare the reported complex of [Fe(HPNO)₂]³⁺, which differs only in the substituent at the ester terminus and shows an identical coordination mode.^[14b]



Figure 1. (a) Local structure of the $Cd_2(O_2C)_2$ cluster in the structure of 1. (b) Extended view of 2D layer constructed by the cluster and the complete attached ligands.

In that case the overall planarity of the two ligands was more pronounced, while the chelate rings were relatively less planar.

Like for complex 1, a 2D grid layer coordination polymer of 2 was obtained. The asymmetric unit of 2 consists of a Pb^{II} ion on a crystallographic inversion center, having L ligand and one coordinated DMF molecule. The Pb^{II} ion is coordinated in a *trans* {PbN₂O₄} octahedral fashion (Figure 2a). Two *trans* coordination sites are taken up by a carbonyl oxygen atom and a pyridyl nitrogen atom. The remaining sites are occupied by azomethine nitrogen atom, phenolic oxygen atom, as well as DMF. Selected bond lengths and angles are given in Table S1 (Supporting Information). Pairs of exobidentate L ligands, binding two Pb^{II} ions via pyridyl and carbonyl donor, construct a 2D layer (Figure 2b).



Figure 2. (a) Local structure of the $Pb_2(O_2C)_2$ cluster in the structure of 2. (b) Extended view of 2D layer constructed by the cluster and the complete attached ligands.

Li et al. have reported four Zn polymers based on aroylhydrazone Schiff base ligand (H₃L). These polymers displayed Zn₄O₄ boat-shaped core and discrete linear tetranuclear central Zn^{II} atom, mononuclear and dinuclear units, respectively. They explored the effect of the hydroxyl group substituent in salicylaldehyde on the fluorescent properties.^[15a,15b] Using an unsymmetrical bis-pyridylhydrazone ligand, series of solid materials were synthesized by *Mahmoudi* and his coworkers.^[15c,15g] The Schiff base acted as a tridentate N₂O-donor ligand through the oxygen, the imine and pyridine nitrogen atoms in all the complexes. Also, the central metal atom is hemidirectionally coordinated and consequently sterically ideal for establishing tetral bonding interactions. Furthermore, theoretical calculations (DFT) were employed to analyze some relevant noncovalent interactions observed in the solid state.

Thermogravimetric Analyses

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Thermogravimetric analysis (TGA) of complexes 1 and 2 indicated two step weight loss (Figure S2, Supporting Information). The first major weight loss of complex 1 is in the range between 25 and 256 °C. The observed weight loss of 25.6% corresponds to the loss of the free DMF, CH₃OH and coordinated H₂O molecules (calcd. 25.1%). The second weight loss at 400 °C may be due to the elimination of coordinated L (calcd. 52.4%; found 52.0%). The final residual mass of 25.8% is nearly indicating the formation of CdO (calcd. 26.1%, found 24.8%). Complex **2** has the similar decomposition behavior. The observed weight loss of 14.2% corresponds to the loss of the coordinated DMF molecule (calcd. 13.6%).

Photoluminescence Measurements and Sensing Experiments

Complexes **1** and **2** having central Cd^{II} and Pb^{II} atoms with d¹⁰ configuration are coordinated to the luminescent ligand and hence show strong luminescence with emission peaks at 499 and 503 nm ($\lambda_{ex} = 350$ nm) for **1** and **2**, respectively. This emission band can be assigned to H₂L ligand-centered emission, because the emission for the free H₂L was observed at 555 nm ($\lambda_{ex} = 360$ nm) (Figure S3, Supporting Information). The hypochromatic shift in the emission may arise from the aggregation induced emission for **1** and **2**, where the coordination of the ligand to the metal ions can reduce the freedom of the ligands and enhance their non-radiative transitions.^[16–18]

To investigate the fluorescence sensing ability of 1 and 2, the emission spectra of 1 and 2 crystal powder dispersed in DMF with different solvent emulsions were measured (Figure S5, Supporting Information). It has been reported that the photoluminescence (PL) intensities are solvent dependent, mainly in the case of nitrobenzene (NB), $^{[22-23]}$ which exhibits signifi-

cant quenching behavior due to the solute and solvent interaction.

In order to gain insight into the sensing process, 1 and 2 were titrated with various NB in DMF at room temperature (Figure 3). This facilitated possible host-guest interactions as a result of electron transfer from the electron-donating framework to the highly electron-deficient NB molecule upon excitation, resulting in fluorescence quenching.^[21-24] Excellent linear dependencies of luminescence intensities on the NB concentration were obtained ($R^2 = 0.9973$ for 1 and $R^2 = 0.9972$ for 2). The luminescence intensity decreased to 50% at 15×10^{-4} and 24×10^{-4} M for **1** and **2**, respectively, and complete quenching in the luminescence was observed at 48×10^{-4} and 75×10^{-4} M (Figure 3), suggesting that the two luminescent MOFs sensor can be used for detecting the concentration of NB.^[25] The absorption spectrum for NB exhibits a massive overlap with the emission of 1 and 2 (Figure S4, Supporting Information), which suggests that both electronand energy-transfer mechanisms are present for the fluorescence quenching by NB.[22]

To substantiate this point and to gain insight into the quenching mechanism associated with the analytes mentioned in the presented investigation, the HOMO-LUMO energies of the nitrobenzene along with the other analytes were calculated using density functional theory (DFT) at the B3LYP/6-31G* level (Table S2, Supporting Information). The most probable reason behind quenching may be the charge transfer from the 1 and 2 framework to the LUMO of the analytes and this charge transfer will occur when the LUMO of the donor (1 and 2) lie at the higher energy scale than the LUMO of the acceptor in the analyte. Maximum fluorescence intensity quenching observed in the case of nitrobenzene is due to easy electron transfer from the excited metal-organic framework to the LUMO of nitrobenzene.^[29,30] Also, the LUMOs of 1 and 2 are at the lower energy level than that of LUMO of other analytes, which rules out the effective charge transfer from the 1 and 2 to these analytes and hence the efficient quenching. However, the observed order of quenching with other analytes is not in full agreement with the corresponding LUMO energies of the other analytes, which indicates that electron transfer is not the sole mechanism for the intensity quenching.



Figure 3. Emission spectra of (a) 1 and (b) 2 dispersed in DMF with the titration of NB, and the quenching of the original emission.



Figure 4. Comparison of the luminescence intensity of different concentrations of Fe³⁺ ions added to (a) 1 and (b) 2 in 10^{-2} M aqueous solution.

The luminescence spectra of 1 and 2 dispersed in DMF solution containing the same concentrations of $M(NO_3)_{x}$ ($M = Li^+$, Na⁺, K⁺, Mg²⁺, Ca²⁺, Pb²⁺, Al³⁺, Ca²⁺, Ni²⁺, Fe³⁺, Co²⁺) were studied. The luminescent properties of $M^{n+}@1$ and $M^{n+}@2$ were recorded and compared (Figure S6, Supporting Information). On addition of Mg²⁺ to MOFs 1 or 2 the intensity of $M^{n+}@1$ and $M^{n+}@2$ gets slightly enhanced, whereas the emission intensities declined on addition of other metal ions. Particularly, the Fe³⁺ ion shows a significant quenching effect on the luminescence intensity to a degree. According to the reported literature, Lewis basic sites, such as pyridyl, amide, hydroxyl sites,^[28-31] containing porous MOFs could have an effect on metal ions. As the possible reason of the quenching by Fe³⁺, we consider that it might be related to the interaction between the Fe³⁺ ions and hydroxyl sites on the $M^{n+}@1$ and $M^{n+}@2.^{[32]}$ The energy transfer efficiency from L to the Cd^{II}/Pb^{II} ions within $M^{n+}@1$ and $M^{n+}@2$ gets minimized by the interaction between the Fe³⁺ ions and the L ligand, which may lead to the decrease in the luminescent intensity. As illustrated in Figure 4, the luminescent intensity is almost completely quenched at a Fe(NO₃)₃ concentration of 21×10^{-4} and 87×10^{-4} M for 1 and 2, respectively. Therefore, 1 and 2 can be used as a highly sensitive luminescent probe for the quantitative detection of Fe³⁺ ions.

The luminescence investigations were also carried out to explore the influence of various anions on the luminescence of 1 and 2. Using ultrasonic method the suspensions of MOFs 1 and 2 were prepared in 4 mL of DMF, and 0.4 mL of Na_nX (1×10⁻² м) (X = PO₄³⁻, F⁻, Cl⁻, Br⁻, I⁻, NO₃⁻, OAc⁻, SO₄²⁻, CO32-, C2O42-, or CrO42-) were added in dropwise manner into the suspensions of **1** and **2** (1×10^{-3} M). The resultant suspensions were monitored under the perturbation of various anions, using a fluorescence spectrophotometer, and only dominant emission peaks were recorded. Interestingly, most of the anions have insignificant effect on the luminescence of 1 and 2, while CrO_4^{2-} exhibits a drastic quenching effect on emission (Figure S7, Supporting Information). The quenching effects on the emission of CrO₄²⁻ are obviously observed, indicating that 1 and 2 can be considered as a promising luminescent probe for detecting CrO42- among various colorless anions.^[33] To gain information about the fate of LMOFs 1 and

2 after interacting with CrO_4^{2-} , powder XRD were performed after soaking the LMOFs **1** and **2** in Na₂CrO₄ for 24 h. As evidenced by powder XRD, the samples soaked in Na₂CrO₄ solution for 24 h still maintains their crystallinity (Figure S11, Supporting Information). As shown in Figure S12, the absorption band of **1** and **2** is located from 350 to 450 nm, which is largely overlapped by the absorbing band of CrO_4^{2-} . Upon excitation, there is a competition of absorption of the light source energy between CrO_4^{2-} ions and **1** or **2**. Combined with the absorption and luminescent spectra, it can be expected that the energy absorbed by **1** or **2** is transferred to CrO_4^{2-} , resulting in a decrease in the luminescence intensity. This quenching mechanism is in agreement with that proposed previously by *Chen* et al.^[34]

Conclusions

The 2,4-dihydroxybenzaldehyde nicotinoylhydrazone ligand H_2L with free recognition sites was coordinated with Cd^{II} and Pb^{II} ions to yield two robust 2D coordination polymers 1 and 2. The resulting material emits blue luminescence, which exhibits quenching effect in presence of nitro aromatics. It was shown that observed quenching is due to the efficient electron transfer from the conduction band of 1 and 2 to the LUMO of the nitrobenzene. Also, dispersed suspensions of 1 and 2 in DMF solution display good selectivity and sensitivity toward Fe³⁺ and CrO₄²⁻ ions.

Experimental Section

Materials and Methods: All chemicals were purchased and used without further purification except for the L ligand. Powder X-ray diffraction (PXRD) was collected with a Bruker D8 ADVANCE X-ray diffractometer with Cu- K_{α} radiation ($\lambda = 1.5418$ Å) at 50 kV, 20 mA with a scanning rate of 6°·min⁻¹ and a step size of 0.02°. The simulated powder patterns were calculated using Mercury 2.0. The purity and homogeneity of the bulk products were determined by comparison of the simulated and experimental X-ray powder diffraction patterns. Fourier transform infrared (FT-IR) spectra as KBr pellet were measured with a Nicolet Impact 750 FTIR in the range of 400–4000 cm⁻¹. Thermogravimetric analysis was performed in a nitro-

gen atmosphere from room temperature to 800 °C at a heating rate of 10 K·min⁻¹, with a SDT Q600 thermogravimetric analyzer.

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X-ray Crystallography: Room-temperature single-crystal X-ray diffraction data collection were carried out with a Bruker SMART APEX diffractometer that was equipped with a graphite monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å) by using an ω -scan technique. The intensities were corrected absorption effects by using SADABS. The structures were solved by direct methods (SHLEXS-97)^[35a] and refined by a full-matrix least-squares procedure based on F^2 (Shelxl-97).^[35b] All the hydrogen atoms were generated geometrically and refined isotropically using the riding model. All non-hydrogen atoms were refined with anisotropic displacement parameters. The relatively high wR_2 value for **2** are really small measurable crystals and the relatively bad quality of data (the effects of weak high angle data), which cause the high wR_2 value.

Crystal Data for 1: $C_{17}H_{22}CdN_4O_6$, M = 490.79, monoclinic, $P2_1/n$, a = 11.698(9) Å, b = 13.324(10) Å, c = 14.837(11) Å, $\beta = 92.552(13)^\circ$, V = 2310(3) Å³, Z = 4, $D_{calc} = 1.411$ mg·m⁻³, F(000) = 992, reflections collected 11119, independent reflections 4010, Final indices $[I > 2\sigma(I)] R_1 = 0.0739$, $wR_2 = 0.1767$, R indices (all data) $R_1 = 0.1043$, $wR_2 = 0.1996$, gof 1.146.

Crystal Data for 2: $C_{16}H_{16}PbN_4O_4$, M = 535.52, monoclinic, $P2_1/n$, a = 11.132(10) Å, b = 13.901(11) Å, c = 13.431(9) Å, $\beta = 122.43(5)^\circ$, V = 1754(3) Å³, Z = 4, $D_{calc} = 2.028$ mg·m⁻³, F(000) = 1016, reflections collected 10104, independent reflections 4240, Final indices $[I > 2\sigma(I)]$ $R_1 = 0.0879$, $wR_2 = 0.2314$, R indices (all data) $R_1 = 0.1196$, $wR_2 = 0.2712$, gof 1.098.

Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC-1479617 for **1** and CCDC-1479619 for **2** (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, http:// www.ccdc.cam.ac.uk).

Synthesis of H₂L: An ethanol solution (30 mL) of 2,4-dihydroxybenzaldehyde (1.38 g, 10 mmol) and one drop of acetic acid were added with stirring to an ethanol solution (30 mL) of nicotinoylhydrazine (1.37 g, 10 mmol). After stirring under reflux for 2 h, a yellow precipitate was isolated by filtration and washed with ethanol and ether. ¹H NMR ([D₆]DMSO): $\delta = 12.13$ (s, 1 H, OH); 11.27 (s, 1 H, OH); 10.02 (s, 1 H, NH); 8.56 (s, 1 H, CH); 8.81–6.34 (m, 7 H, Ar–H).

Synthesis of {[Cd (L)(H₂O)]·CH₃OH·DMF} (1): A DMF solution (15 mL) of the H₂L (0.257 g, 1 mmol) was added with stirring to a methanol solution (15 mL) of Cd(OAc)₂·2H₂O (0.230 g, 1 mmol). After adding two drops of triethylamine, the reaction solution were stirred at room temperature for 2 h. X-ray quality single crystals were formed by slow evaporation of the solutions in air after a few days (yield 45% based on Cd). $C_{17}H_{22}CdN_4O_6$: calcd. C 41.60; H 4.52; N 11.42%; found C 41.49; H 4.46; N 11.37%. **IR** (KBr): $\tilde{v} = 3432$ (vs); 2971 (m); 1616 (vs); 1528 (v); 1489 (v); 1321 (m), 1214 (m); 1161 (m); 983 (v); 701 (v) cm⁻¹.

Synthesis of [Pb(L) (DMF)] (2): A mixture of Pb(OAc)₂·3H₂O (0.379 g, 1 mmol) and the H₂L (0.257 g, 1 mmol) were dissolved in 15 mL DMF: methanol mixture (2:1 V/V) and refluxed for 3 h. The resulting solution was treated with ether diffusion at room temperature for several days, X-ray quality single crystals were formed (yield 38 %

based on Pb). $C_{16}H_{16}N_4O_4Pb$: calcd. C 35.88; H 3.01; N 10.46%; found C 35.73.; H 3.06; N 10.29%. **IR** (KBr): $\tilde{v} = 3070$ (s); 1646 (vs); 1599 (v); 1516 (v); 1422 (m); 1339 (m); 1221 (m); 983 (m); 842 (v); 720 (v); 594 (m) cm⁻¹.

Computational Details: In order to ascertain the nature of highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbital (LUMO) of different analytes, the ligand H₂L as well as **1** and **2** density functional theory (DFT) calculations were performed. Optimized molecular geometries were calculated using the B3LYP exchange-correlation functional.^[36] The 6-31G** basis set for C, H, N and O atoms were used, whereas for Cd MWB28 and for Pb MWB78 basis sets were used for geometry optimization. All the calculations were performed using the Gaussian 09 program.^[37]

Supporting Information (see footnote on the first page of this article): IR, UV-Vis, and fluorescence spectra; TGA plots, pXRD patterns, and HOMO-LUMO plots.

Acknowledgements

The authors acknowledge financial assistance from National Natural Science Foundation of China (21501124), the Opening Project of Key Laboratory of Green Catalysis of Sichuan Institutes of High Education (No: LYJ1301, LYJ1306, LZJ1203, LZJ14201), the Education Committee of Sichuan Province (Nos. 12ZA090, 13ZB0131, 14ZB0212, 14ZB0220, 15ZB0222, 15ZB0214), the Start-up Foundation of Sichuan University of Science & Engineering (Nos. 2014RC05, 2014RC34, 2015RC23, 2015RC26), the Institute of Functionalized Materials (Nos. 2014PY01, 2015PY03), and the Project of Zigong Science & Technology and Intellectual Property Bureau (No. 2014HX02, 2015HX16, 2015HX18).

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Received: September 20, 2016 Published Online: ■

Y. Wu,* Y. Li, L. Zou, J. Feng, J. Liu,* M. Luo, J. Xu, R. Yadav, A. Kumar* 1–7

Rational Syntheses of Cd^{II} and Pb^{II} Metal-Organic Frameworks for Luminescence Sensing of Nitroaromatics, Ferric and Chromate Ions

