A 2D porous Pb-MOF based on 2-nitroimidazole: CO₂ adsorption, electronic structure and luminescence

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Abstract

A new porous metal-organic framework, $[\text{Pb}_5(\text{Ac})_7(\text{nIm})_3]_n$ (**1**), has been successfully synthesized by employing 2-nitroimidazole ligand and Pb^{2+} ion. **1** contains novel the ribbon-shaped Pb-O SBU and reveals a 2D porous framework with a 1D tubular channel. Moreover, **1** shows moderate adsorption uptake towards CO_2 and luminescence properties from intraligand charge transfer. We further confirmed nitro group and metal ion are important adsorption sites by GCMC simulations, and the electronic structures of **1** was investigated.

1. Introduction

Metal-organic frameworks (MOFs), assembled from organic ligands and metal ions/clusters[1–3], have been attracted researcher's attention over the last few years by virtue of their fascinating architectures and topologies[4] as well as broad potential applications such as gas adsorption/separation[5, 6], luminescence[7, 8], catalysis[9, 10], magnetic[11, 12], sensing[13, 14], and so on. Many chemists are working hard to explore new strategies in order to synthesize target materials, but it is very challenging to synthesize MOFs owning expected structure and performance[15, 16]. Compared with traditional porous materials, the greatest advantage of MOFs is that it can control the metal nodes and organic linkers in the synthesis process, thus resulting in a variety of MOFs materials possessing different surface areas, pore environments and chemical functions[17–19]. Therefore, judicious selection of ligands with different size, shape and functional group together with metal ions can effectively build novel and functional MOFs[20–22]. Moreover, the highly crystalline nature of MOFs enables its structure can be precisely determined from single crystal X-ray diffraction and molecular level information can be obtained, which make the research of mechanism is clearer[23].

2-Nitroimidazole (nIm), a nitro-functionalized imidazole connector, has been extensively employed to prepare Zeolitic Imidazolate Frameworks (ZIFs)[24–27]. On one hand, the nitro group has the higher dipole moment, which is conducive to formation of dipole-quadrupole interactions with CO_2 molecules[28]. On the other hand, imidazole N atoms and nitro O atoms can provide robust coordination abilities in bridging metal ions[29]. In contrast to widely-used transition metal ions, main group Pb^{2+} ion features a flexible coordination preference and $6s^25d^{10}$ electronic configuration, giving rise to more opportunities for the construction of unique frameworks and excellent luminescent properties[30]. However, to the best of our knowledge, MOFs building from Pb^{2+} ions and 2-nitroimidazole have never been reported.

Based on the above considerations, a MOF comprising Pb^{2+} ion and nIm, $[\text{Pb}_5(\text{OAc})_7(\text{nIm})_3]_n$ (**1**), has been successfully prepared. **1** is based on the ribbon-shaped Pb-O secondary building unit (SBU) and shows a 2D porous framework with a 1D tubular channel. Moreover, **1** reveals moderate CO_2 adsorption capability, and nitro groups together with metal ions play an important role in adsorption process which is

confirmed by GCMC simulations. We also explored the electronic structures and luminescence properties, and **1** presents a broad emission band originated from intraligand charge transfer.

2. Experimental Section

2.1. Materials and general methods

All reagents were commercially available. Fourier transform infrared spectrum (FTIR) was obtained with a Nicolet FTIR 170 SX spectrophotometer in the range of 4000 – 400 cm^{-1} . The fluorescent spectra for the solid samples were measured with a Hitachi F-4500 fluorescence spectrophotometer at room temperature. Elemental analyses for C, H, and N were performed with a Perkin-Elmer 2400C Elemental analyzer. Thermogravimetric analysis (TGA) was measured with a NETZSCH TG 209 thermal analyzer under a nitrogen atmosphere with a heating rate of 10°C min^{-1} . Powder X-ray diffraction (PXRD) pattern was recorded on a Bruker D8 ADVANCE X-ray powder diffractometer (Cu $K\alpha$, 1.5418 Å). Gas sorption was tested with a Micrometrics ASAP 2020M apparatus.

2.2 Crystallography

Crystal structure was determined at 296(2) K by a Bruker SMART APEX II CCD diffractometer with a Mo $K\alpha$ radiation source. The structure was solved by direct methods and refined on F^2 by full-matrix least-squares methods using the Olex2 program[31]. The non-H atoms were refined anisotropically, while the H atoms fixed to their geometrically ideal positions were refined isotropically. It was failed to determine the right model of solvent molecules from the difference Fourier map, thereby the SQUEEZE routine of PLATON program was used in structural refinement[32]. The refinement result and selected bond distances/angles are given in Tables 1 and S1, respectively. CCDC Number: 2041796.

Table 1
Crystal data and structure refinement for **1**.

Complex	1
Molecular formula	C ₂₃ H ₂₇ N ₉ O ₂₀ Pb ₅
Formula weight	1785.48
Temperature	296(2)
Crystal system	Triclinic
Space group	P-1
<i>a</i> (Å)	8.7930(13)
<i>b</i> (Å)	15.691(2)
<i>c</i> (Å)	16.094(3)
<i>α</i> (°)	98.050(2)
<i>β</i> (°)	100.411(2)
<i>γ</i> (°)	91.176(2)
<i>V</i> (Å ³)	2160.1(6)
<i>Z</i>	2
<i>ρ</i> (g/cm ³)	2.745
<i>F</i> (000)	1596
Reflections collected	10836
Goodness-of-fit on <i>F</i> ²	1.010
<i>R</i> ₁ ^a [<i>I</i> > 2σ(<i>I</i>)]	0.0488
<i>wR</i> ₂ ^b [<i>I</i> > 2σ(<i>I</i>)]	0.1214
^a <i>R</i> ₁ = Σ(<i>F</i> _o - <i>F</i> _c)/Σ <i>F</i> _o . ^b <i>wR</i> ₂ = [Σ <i>w</i> (<i>F</i> _o ² - <i>F</i> _c ²) ² /Σ <i>w</i> (<i>F</i> _o ²) ²] ^{1/2} .	

2.3 Synthesis of [Pb₅(OAc)₇(nlm)₃]_n (**1**)

A mixture of nlm (11.3 mg, 0.1 mmol), Pb(OAc)₂ (32.5 mg, 0.1 mmol) and 10 mL MeCN were sealed in a Teflon-lined vessel (25 mL) and heated at 140°C for 72 h. After cooling to room temperature, the colorless block-shaped crystals were gained in 7.8 mg. Anal. Calcd. for C₂₃H₂₇N₉O₂₀Pb₅: C, 15.47; H, 1.52; N, 7.06. Found: C, 15.55; H, 1.54; N, 7.10. IR data (KBr, cm⁻¹): 1510(s), 1432(s), 1351(s), 1172(m), 1155(m), 1095(w), 1011(w), 1114(w), 935(m), 985(w), 829(m), 785(w), 671(m), 557(w).

3. Results And Discussion

3.1 Crystal structure of **1**

Single crystal X-ray diffraction analysis reveals that **1** exhibits a 2D porous framework crystallizing in the triclinic P-1 space group. The asymmetric unit of **1** contains five crystallographically different Pb(II) ions, three nlm ligands and seven coordinated acetate. Both Pb1 and Pb4 are seven coordination configurations, forming a distorted decahedron geometry, in which Pb1 is coordinated by three O atoms of two different acetates [Pb-O = 2.347–2.653 Å], two O atoms from two nlm ligands [Pb-O = 2.883–2.929 Å] and two N atoms of two nlm ligands [Pb-N = 2.511–2.554 Å], while Pb4 is ligated by five atoms of four different acetates [Pb-O = 2.431–2.880 Å], one O atom of one nlm ligand [Pb-O = 2.878 Å] and one N atom of one nlm ligand [Pb-N = 2.505 Å]. Pb2 and Pb3 adopt eight coordination modes in which Pb2 is ligated by eight carboxylate O atoms of five acetates [Pb-O = 2.453–2.824 Å], while Pb3 is surrounded by eight carboxylate O atoms of six acetates [Pb-O = 2.557–2.752 Å]. Pb5 is a six coordinated mode that displays a distorted four-corner biconical configuration, which is encircled by two carboxylate O atoms of one acetate [Pb-O = 2.393–2.640 Å], one O atom of one nlm ligand [Pb-O = 2.898 Å] and three N atoms of three nlm ligands [Pb-N = 2.473–2.597 Å]. Adjacent Pb1, Pb2, Pb3 and Pb4 atoms link O atoms of acetates forming the infinite ribbon-shaped SBU along the *a* axis. Then the ribbon is further linked to neighboring ribbons by nlm ligand, acetate and Pb5 forming a 2D open framework with a 1D tubular channel. The nlm ligand in **1** shows two coordination modes, one of which adopt $\mu_2\text{-}\eta^1\text{:}\eta^2$ coordination mode and the other possess $\mu_2\text{-}\eta^2\text{:}\eta^2$. The adjacent 2D frameworks are further connected through C-H $\cdots$ O hydrogen bonds [C-O = 3.406–3.535 Å, $\angle\text{CHO} = 126.9\text{--}139.0^\circ$] generated by O atoms of acetates and H atoms of imidazoles or methyl groups developing a 3D supramolecular framework.

3.2 PXRD and TGA

The phase purity of sample of **1** was confirmed by coincident PXRD patterns between the simulated and experimental (Fig. 2). TGA of **1** was obtained in a N₂ atmosphere (Fig. 3). **1** is stable up to 150 °C, beyond this temperature, the framework begins to collapse.

3.3 Luminescence properties

As shown in Fig. 4, luminescent spectra of free ligand and **1** in solid state were recorded at room temperature. The ligand exhibits a broad emission band with two emission peaks at 470 and 485 nm when excited at 300 nm, which may be attributed to the $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$ transitions of the intraligands. **1** also shows two fluorescence maximum emissions centered at 470 and 485 nm upon excitation at 423 nm, which is similar to that of free ligand. Therefore, the emission band of **1** can probably be ascribed to the intraligand charge transfer of nlm ligand[33].

3.4 Frontier molecular orbital analysis

In order to further explore the electronic structures of MOFs, density functional theoretical (DFT) calculations were performed. As shown in Fig. 5, the frontier molecular orbital (FMO) includes the highest

occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) in which HOMO value determines a molecule's ability to provide electron whereas LUMO value determines the electron-accepting nature.

The HOMO-LUMO energy plot reveals that HOMO of **1** is primarily contributed from the coordinated carboxylate groups (donor). In LUMO, the electron density is mainly focused on the nitro groups. The energy of HOMO is -6.489 eV whereas of LUMO is -4.343 eV. The energy gap ΔE of HOMO-LUMO is 2.146 eV which is slightly high, indicating that the complex is stable[34].

3.5 Sorption properties

Due to the existence of channels in **1**, sorption properties were assessed by gas adsorption experiment. The adsorption isotherms of N₂ at 77 K reveal no uptake, but **1** reveals a CO₂ loading of 25.8 cm³ cm⁻¹ at 298 K and 760 mmHg (Fig. 6a), which is higher than that of 1-Eu[35] and {[Cd(bdc)(4-bpmh)]}_n·2 n(H₂O)[36], but lower than that of {[Cd(2-NH₂bdc)(4-bpmh)]}_n·2 n(H₂O)[36]. In order to further understanding of the interaction details of **1** with CO₂, GCMC simulations have been carried out at 298 K and 100 kPa. The obtained density contours uncovered the mostly populated sites are located in the vicinity of O atoms of -NO₂ groups and Pb atoms in pore (Fig. 6d). Two preferential CO₂ binding sites in **1** were found. For CO₂-I, two electronegative O atoms of two -NO₂ groups simultaneously attract one electropositive C atom of one CO₂-I molecule by O_{-NO₂}...C_{CO₂} electrostatic interactions (O...C = 2.96–3.19 Å), which less than the sum of van der Waals radii of C (1.70 Å) and O (1.52 Å) atoms, denoting intense contacts (Fig. 6b). For CO₂-II, one electronegative O atom of CO₂-II links one Pb atom, in which the Pb...O distances of 3.66 Å approximate to the sum of van der Waals radii of Pb (2.02 Å) and O (1.52 Å) atoms, indicating moderate interaction (Fig. 6c).

4. Conclusions

In summary, a porous Pb-MOF based on ribbon-shaped SBUs and 2-nitroimidazole has been constructed. In addition, **1** shows not only moderate CO₂ adsorption capability which is confirmed by GCMC simulations and experiment, but also luminescence emission band with two emission peaks resulting from intraligand charge transfer. And the frontier molecular orbital of **1** was analyzed.

Declarations

Acknowledgments

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Figures

Figure 1

(a) The ribbon-shaped SBU viewed along the c axis. (b) A 2D open framework viewed along the a axis. (c) A 3D supramolecular framework connected by C-H...O hydrogen bonds.

Figure 2

PXRD pattern of as-synthesized 1.

Figure 3

TG curve of 1.

Figure 4

Emission spectra of nlm and 1.

HOMO

LUMO

Figure 5

Frontier molecular orbitals of 1.

Figure 6

(a) Gas sorption isotherm of 1 for CO₂ at 298 K. (b) Interactions between CO₂ and 1. (c) Density contours of CO₂ in 1.

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