



Research paper

New Zinc functionalized metal organic Framework for selective sensing of chromate ion



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ABSTRACT

A modified metal organic framework have been prepared by the solvothermal process of 2-(4-carboxyphenyl)-1, 3-dioxoisindoline-5-carboxylic acid with $Zn(OAc)_2 \cdot 2H_2O$. The framework has a PtS – type net. The obtained porous material has been characterized by X-ray diffraction, Scanning electron microscopy, UV–vis spectroscopy, FTIR spectroscopy and BET surface area analysis. The BET surface area was $757 \text{ m}^2/\text{g}^{-1}$. The synthesized MOF exhibits reasonably good fluorescence characteristics. The luminescent studies indicates that the obtained Zn-MOF could be an efficient material for selectively sensing anion especially CrO_4^{2-} . The mechanism of sensing is also studied in detail. The Zn-MOF senses the anion without altering its structural integrity. This post-synthesis route can be used for synthesis of isomorphous metal–organic frameworks that cannot be obtained by direct synthesis.

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1. Introduction

MOFs represent a promising new classes of porous crystalline solids because they exhibit largest pore volumes and highest surface areas [1–3]. MOFs are considered as organic analogs of inorganic zeolites in which oxygen atoms are replaced by rigid organic ligands that bridge the metal ions. The resulting crystalline solids are comprised of rigid frameworks of molecules coordinated to metal ions in two or three dimensions that form open networks that render the crystalline structure highly porous. MOFs have already shown promising performances in a number of applications, including catalysis [4], energy storage [5], drug delivery system [6], nonlinear optics [7] and gas storage [8]. Hydrogen sorption in the microporous functionalized MOF structures has been proposed as one of their most useful applications [9]. Recently, the MOFs have found new and interesting applications in the sensing of small molecules, solvents and explosives [10]. Detectable changes in the luminescence of MOFs by tuning the host–guest chemistry along with the tunable porosity and high surface area makes MOFs the excellent candidates for sensing applications.

In general, anions are of particular interest in our day to day life, as they are responsible in maintaining many biological and environmental processes for example, controlling osmotic pressure,

maintaining cell volume etc. The interference of anion is recognized as being the primary factor of many diseases that includes cystic fibrosis, Dent diseases etc. Allergic reaction in human being is generally caused by the interference of chromates anion. Exposure to chromate ion can leads to contact dermatitis, irritant dermatitis and chrome ulcer [11]. So it is necessary to track the chromate ion directly and efficiently. The detection method is generally carried out with the aid of electro-sensors which are generally very complicated and expensive [12,13]. By trapping the guest harmful molecules inside the porous material, recognition and sensing of harmful material can be achieved.

To construct a porous metal organic sensor material, the essential need is to detach the solvent molecule from the framework. On this basis many metal organic framework has been used for the molecular recognition of anion. In particular NH_2 -MIL-101Al is used for the detection of fluoride ions in aqueous solutions [14]; the detection is based on the decomposition of the host scaffold which induces the release of the fluorescent dye molecule. And MOF ZIF 90 is used in sensing the chromate ion which has low Langmuir surface area and low binding constant [15]. The lanthanides metal organic frameworks have been widely used for sensing studies since they involve a mechanism of ligand to metal charge transfer. Only few transition metal based MOFs without any incorporation of fluorophore are used in sensing studies [16].

Zeolites acts as host moieties which facilitate the exchange of its metal ion with other transition metal ion [16–19]. Surprisingly, metal organic framework also exhibits same properties. The

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exchange technique has been used extensively to enhance the properties of nanocrystals and molecules, but the extent of its applications for MOFs is still expanding. Cation exchange is an emerging synthetic route for modifying the secondary building units (SBUs) of metal–organic frameworks (MOFs). Delving through journals [20–22], most examples of cation exchange at SBUs involve Cu^{2+} replacing Zn^{2+} or Cd^{2+} . And majority of the MOF tends to show the exchange property only in the presence of solvents like methanol [23,24] and DMF, but this exchange phenomena yet not reported in propanol. In this work, propanol has been used as solvent and exchange of Cu^{2+} and Ni^{2+} does happen.

In this present work we have synthesized a new metal organic framework with imide based ligand[2-(4-carboxyphenyl)-1,3-dioxoisindoline-5-carboxylic acid] which is referred as Zn-MOF. The photophysical property of the Zn-MOF have been studied and it shows selectivity towards chromate anion over other competing anions. The metal exchange of the MOF has been studied in propanol for Cu^{2+} and Ni^{2+} .

2. Experimental

All reagents were obtained from commercial sources and unless otherwise stated were used without further purification.

2.1. Synthesis of ligand

Into a 250-mL, round-bottom flask 0.5 g (2.5 mmol) of trimellitic anhydride, 0.34 g (2.5 mmol) of *p*-amino benzoic acid (PABA), 20 mL of acetic acid and a stirring bar were placed. The mixture was stirred at room temperature overnight and then refluxed for 4 h. The solvent was removed under reduced pressure, and the residue was dissolved in 100 mL of cold water; then, 5 mL of concentrated HCl was added. The solution was stirred until a white precipitate was formed, and then the precipitate was filtered off and dried; this yielded 0.73 g (90.3%) of white powder. ^1H NMR (500 MHz, $\text{DMSO}-d_6$) δ (ppm): 7.63 (1H), 8.11 (d, 1H.), 8.34(d, 1H.), 8.4 (d, 1H), FTIR (KBr, cm^{-1}) ν =3100–2200 (m, br), 1770 (sh), 1720 (s), 1710 (m), 1405 (m), 1400–1610 (s).

2.2. Synthesis of metal organic framework

Zn-MOF was prepared by mixing $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ (0.0183 g, 0.1 mmol) and ligand (0.0155 g, 0.05 mmol) in DMF (15 mL) and heating the mixture in a 100 mL Teflon-lined Parr autoclave for 48 h in an oven at 120°C. The as-synthesized product was recovered by filtration and washed with DMF, which was then soaked in CHCl_3 for two days and exchanged once with fresh CHCl_3 during the period. The mixture was finally filtered to get crystals, which were then evacuated under a high vacuum overnight to yield the activated MOF. FTIR (KBr cm^{-1}): ν =3358 water peak from zinc acetate, 1788, 1709 (C=O) (trimellitic imide) 1658 (C=O) (carboxylate of carboxylic acid) (Supporting information).

2.3. Luminescence studies

The photoluminescence properties of MOF in various anions were investigated at room temperature. For the properties of

sensing with respect to metal ions, the emulsion of Zn-MOF was obtained by diffusing Zn-MOF powder (1.0 mg) into (3 mL) deionized water. The prepared emulsion of Zn-MOF were treated with 200 μL of various anions like F^- , Cl^- , Br^- , I^- , OAc^- , CN^- , HSO_4^- , NO_3^- , OH^- , HPO_4^- , CrO_4^{2-} to study the sensitivity and selectivity towards particular anion over other anions.

2.4. Metal ion exchange

The crystals of Zn-MOF were immersed in a solution of $\text{Cu}(\text{NO}_3)_2 \cdot 2.5\text{H}_2\text{O}$ and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in propanol. A small amount of solid sample was removed at specific time intervals. The compound was decomposed with concentrated HNO_3 , and the ratio of Zn/Cu and Zn/Ni was determined by ARCOS Simultaneous ICP spectrometer at a wavelength range of 130–770 nm (SPECTRO Germany).

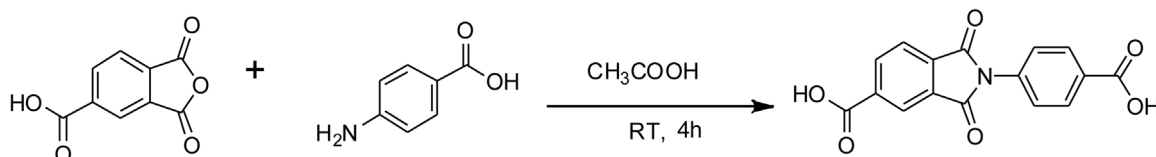
2.5. Materials and instrumentation

All chemicals were obtained from commercial suppliers and used without further purification unless otherwise mentioned. X-ray powder diffraction (XRD) was conducted on a diffractometer with $\text{CuK}\alpha$ (1.5404Å) radiation. Scans were made in the 2θ range 0.5 to 10° with a scan rate of $2^\circ/\text{min}$. Surface area and pore size distributions were measured by N_2 adsorption/desorption using Micromeritics Gemini V-2380 surface area analyzer. Absorption spectra were recorded with a Shimadzu UV-2600 spectrophotometer using 1 cm path length quartz cell. Fluorescence spectra were taken on RF-5301PC spectrofluorophotometer at a scan rate of 500 nm/min, the excitation wavelength was 372 nm. The ^1H NMR and ^{13}C NMR spectra were recorded on a Bruker AV-500 spectrometer (500 MHz for ^1H and 125 MHz for ^{13}C) (Bruker, Switzerland). IR spectra were obtained with a Nicolet IS 5 FTIR spectrometer (KBr pressed disc method). Tetra butyl ammonium salts of various anions such as cyanide, fluoride, chloride, bromide, iodide, acetate, dihydrogen phosphate, sulphate, nitrate and hydroxide and potassium salt of chromate ion was purchased from Sigma-Aldrich and used without further purification. 1 mg of Zn-MOF was dispersed in H_2O , 1.5×10^{-5} M anions in H_2O were prepared and used for sensing studies.

3. Results and discussion

3.1. X-Ray diffraction and BET analysis

The imide based ligand was synthesized (Scheme 1) according to the procedure reported in literature [25]. The structure of the ligand was confirmed by ^1H NMR and FT-IR spectroscopic characterization. The IR stretching frequencies and the ^1H NMR peaks of all functional groups present in the ligand was observed in the expected region (Supporting information). Zn-MOF was synthesized by solvothermal method with synthesized imide based ligand and Zn-acetate as metal salt. The structure of synthesized metal organic framework is similar to PtS topology [26]. Pt and S are substituted with Zn^{2+} and ligand respectively. The powder X-ray diffraction (PXRD) patterns (Fig. 1) of as-synthesized are almost similar to the simulated XRD pattern, indicating that the struc-



Scheme 1. Synthesis of ligand.

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