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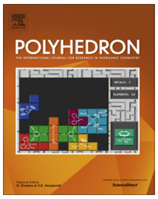

Two new alkaline earth metal organic frameworks with the diamino derivative of biphenyl-4,4′-dicarboxylate as bridging ligand: Structures, fluorescence and quenching by gas phase aldehydes

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A B S T R A C T

Alkaline earth metal ion organic frameworks (AEMOFs) represent a relatively underexplored subcategory of MOFs. Two new MOFs $[Ca_6(bpdc\text{-}(NH_2)_2)_5(\mu_3\text{-}HCO_2)_2(H_2O)_{2.5}(DMF)_{0.5}]\cdot 0.5H_2O\cdot 2.5DMF$ (**1**) and $[Sr_4(bpdc\text{-}(NH_2)_4)(\mu_2\text{-}DMF)_2(DMF)_{1/3}]\cdot 2/3(DMF)$ (**2**) [$H_2bpdc\text{-}(NH_2)_2$ = 2,2′-diamino-[1,1′-biphenyl]-4,4′-dicarboxylic acid); DMF = N,N-dimethylformamide] are presented here. These MOFs display structural variety with diverse topologies and new structural features. Luminescence studies revealed that both MOFs display ligand based fluorescence with small differences in emission profiles possibly attributable to the difference in charge density of the metal ions combined with the different conformation adopted by the ligand in the crystal structures of **1** and **2**. Furthermore, initial sensing studies reveal that both MOFs can potentially function as fluorescent sensors for gas phase aldehydes.

1. Introduction

Metal organic frameworks (MOFs) or Porous Coordination Polymers (PCPs) are a class of hybrid crystalline materials, assembled by metal ions or clusters and bridging polydentate organic ligands to form polymeric network structures containing potential voids [1–3]. Due to their properties such as structural and functional diversity, porosity, high surface area, and adsorption affinity towards various guest species, MOFs have been used for a variety of applications including gas storage and separation [4–10], catalysis [11–13], ion exchange [14–20], and proton conduction [21]. One more important advantage of MOFs is the facile introduction of interesting physical properties such as luminescence through the use of photoactive ligands, metal ions or their combinations. Thus, luminescent MOFs (LMOFs), represent an important rapidly growing subcategory of MOFs [22]. These luminescent crystalline materials show great prospects in a range of technological applications from phosphors in lighting devices [23–28], photocatalysts [29–34], luminescent molecular thermometers [35–37], biomedical imaging [38–42] and luminescent sensors [14,20,43–49].

Alkaline earth metal-based MOFs (AEMOFs) are still relatively rare in comparison to their transition metal and rare earth based counterparts. Nevertheless, AEMOFs display unique advantages over transition and lanthanide-based MOFs such as: (i) low cost because of the high natural abundance of alkaline earths, (ii) reduced toxicity, (iii) low density of the early members of the alkaline earth series which is an important property for gas storage applications and (iv) stability in air and various solvents. Despite the fact that the research on AEMOFs remains on a rather preliminary level, AEMOFs exhibit interesting properties and they have been used in several applications [50–62]. Recently, our group reported a series of AEMOFs based on the bridging ligand 2,5-dihydroxy terephthalate, which exhibits unusual luminescence properties because of excited state intramolecular proton transfer (ESIPT). The ESIPT process has been shown to be partly hindered due to electrostatic repulsion between the mobile proton and the coordinated alkaline earth ion with the lighter ions inducing a more pronounced effect as a result of their higher charge density [63,64]. Among the AEMOFs studied by our group, a Mg^{2+} based MOF can

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be used for real time detection of water traces in organic solvents via an “turn on” luminescence sensing mechanism [63].

In this contribution, we present two new alkaline earth metal ion MOFs, namely $[Ca_6(bpdc\text{-}(NH_2)_2)_5(\mu\text{-}HCO_2)_2(H_2O)_{2.5}(DMF)_{0.5}]\cdot 0.5H_2O\cdot 2.5DMF$ (**1**) and $[Sr_4(bpdc\text{-}(NH_2)_4)(\mu\text{-}DMF)_2(DMF)_{1/3}]\cdot 2/3DMF$ (**2**). The compounds display structural diversity forming three dimensional frameworks with different secondary building units (SBUs) [65] and network topologies. These AEMOFs exhibit bright blue fluorescence following population of the ligand based $^1\pi\pi^*$ and $^1n\pi^*$ excited states. Furthermore, the presence of free amino groups which are possibly able to react with carbonyl compounds in the frameworks of **1** and **2** prompted us to study their fluorescence properties in the presence of gas phase aldehydes. Indeed, preliminary studies revealed that both MOFs display significant fluorescence quenching upon their exposure to vapors of volatile aldehydes thereby showing potential as gas phase aldehyde sensors.

2. Experimental part

2.1. Materials and methods

All starting materials and solvents were used as received from the usual commercial sources (Sigma Aldrich, Alfa Aesar and TCI).

2.2. Physical methods

Thermogravimetric analysis (TGA) data were recorded on a Mettler-Toledo TGA/DSC1 instrument. Thermal analysis was conducted from 25 to 800 °C under a N_2 atmosphere (50 mL min^{-1}) with a heating rate of 5 °C min^{-1}. The ^1H NMR spectra of the ligand were recorded at room temperature and on Agilent 500 MHz instrument, with the use of the solvent proton as an internal standard. PXRD patterns were recorded on a Bruker D8 Advance X-ray diffractometer with Cu-Kα radiation (λ = 1.5418 Å). IR spectra were recorded on KBr pellets in the 4000–400 cm^{-1} range using a PerkinElmer Fourier Transform IR spectrophotometer. The UV–vis spectra in solution were recorded on a Hitachi-2001 spectrophotometer in the wavelength range of 200–500 nm while UV–vis diffuse reflectance spectra were obtained at room temperature on a Shimadzu 1200 PC spectrophotometer in the wavelength range of 200–800 nm. $BaSO_4$ powder was used both as a reference (100% reflectance) and a base material on which the powder sample was coated. The reflectance data were converted to absorption using the Kubelka-Munk function. The fluorescence spectra were measured on a Hitachi F-7000 spectrofluorometer equipped with a red sensitive Hamamatsu R928 photomultiplier tube detector. Appropriate long pass filters were used to remove scattering from the sample and the monochromators.

2.3. Single-crystal X-ray crystallography

Single crystals of the MOFs were obtained from reaction mixtures according to the described synthetic procedures. For the structural determination of **1** and **2**, single crystals of the respective MOF were mounted on a Bruker Kappa APEX II diffractometer, equipped with a triumph monochromator at ambient temperature. Diffraction measurements were recorded using MoKα radiation. The data were collected at 130 K over a full sphere of reciprocal space. Intensity data were collected using φ and ω scan mode. The frames collected for each crystal were integrated with the Bruker SAINT software package [66] using a narrow-frame algorithm. Data were corrected for absorption using the numerical method (SADABS) based on crystal dimensions [67]. The powder X-ray diffraction (PXRD) data of **1** and **2** show excellent agreement with the simulated PXRD patterns of the compounds (Fig. S1 and Fig. S2 respectively) thereby confirming that the analyzed single crystals are representative of the bulk samples.

All structures were solved using the SUPERFLIP [68] package and were refined by the full-matrix least-squares method on F^2 using the CRYSTALS package version 14.40b [69]. All non-hydrogen atoms have been refined anisotropically except in the case of disordered atoms.

All hydrogen atoms were found at their expected positions and refined using soft constraints. By the end of the refinement, they were positioned using riding constraints. CCDC 1833862–1833863 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif. The crystal data, details of data collection and structure refinement for both MOFs are given in Table 1. Illustrations were drawn by the Mercury program [70]. Further details on the crystallographic studies as well as atomic displacement parameters are given as Supporting Information in the form of cif files.

2.4. Compound preparation

2.4.1. Synthesis of $H_2bpdc\text{-}(NH_2)_2$

Dimethyl-2,2′-dinitro-[1,1′-biphenyl]-4,4′-dicarboxylate. Dimethyl-biphenyl-4,4́-dicarboxylate (1.00 g, 3.7 mmol) was added into concentrated H_2SO_4 (10 mL). The mixture was stirred at room temperature for 10 min. Nitric acid (760 μL, 3 eq.) was added into concentrated H_2SO_4 (2 mL). This solution was added dropwise into the first mixture at room temperature over a period of 20 min. The mixture was stirred at room temperature for 4 h and then poured into ice (300 mL) to form a beige solid. The resulting solid was dissolved in dichloromethane and the aqueous phase was extracted with dichloromethane (3 × 70 mL). The combined organic layers were dried over Na_2SO_4 and evaporated under reduced pressure to afford a beige solid. The crude mixture was recrystallized from 2-propanol and washed with diethyl ether to give the pure product. Yield: 1.2 g (3.33 mmol, 90%). ^1H NMR (500 MHz, $CDCl_3$): δ (ppm): 8.90 (s, 2H), 8.37 (d, J = 8.4 Hz, 2H), 7.40 (d, J = 8 Hz, 2H), 4.02 (s, 6H).

Dimethyl-2,2′-diamino-[1,1′-biphenyl]-4,4′-dicarboxylate. Dimethyl-2,2′-dinitro-[1,1′-biphenyl]-4,4′-dicarboxylate (1.2 g, 3.33 mmol) was dissolved in 20 mL acetic acid and the solution was stirred under Ar for 10 min. To this solution iron powder (3.7 g, 10 eq.) was added and the mixture was stirred at room

Table 1
Selected crystal data for **1** and **2**.

Compound	1	2
Chemical formula	$C_{81}H_{77}Ca_6N_{13}O_{30}$	$C_{75}H_{81}Sr_4N_{13}O_{21}$
Formula mass	1953.05	1851.02
Crystal system	monoclinic	monoclinic
a (Å)	13.782(3)	12.4481 (16)
b (Å)	30.575 (7)	25.930 (4)
c (Å)	11.112 (2)	13.2612 (19)
α (°)	90	90
β (°)	105.628 (7)	109.292 (4)
γ (°)	90	90
Unit Cell Vol ($Å^3$)	4509.1 (17)	4040.1 (10)
Temperature (K)	130	130
Space group	$P2_1/c$	$P2_1/c$
Z	2	2
No. of reflections measured	50 527	56 760
No. of independent reflections	8284	7749
No of observed reflections [$I > 2.0\sigma(I)$]	5984	5646
R_{int}	0.028	0.053
$R[F^2 > 2\sigma(F^2)]$	0.038	0.047
$wR(F^2)$	0.090	0.086