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A phytochemical-containing metal–organic framework: Synthesis, characterization and molecular simulations for hydrogen adsorption

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ABSTRACT

As a result of involvement of all carboxylato/methoxo/oxo donor oxygen atoms of a phytochemical ferulic acid with zinc ions, a Zn-ferulate metal–organic framework (PhytoMOF-1), $\{[Zn_2(fer)_2]\}_n$ is formed. The structure of PhytoMOF-1 was characterized by single crystal X-ray diffraction studies. PhytoMOF-1 contains channels with a considerable diameter of $15.1(1) \times 17.2(1)$ Å. The total void volume of PhytoMOF-1 is ~3517 Å^3. N_2 adsorption/desorption analyses indicate that the PhytoMOF-1 is porous. Molecular simulations show that PhytoMOF-1 might store hydrogen. The luminescent properties of PhytoMOF-1 are quenched upon the adsorption of toluene and nitrobenzene.

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1. Introduction

Metal–organic frameworks (MOFs) are a unique class of crystalline organic–inorganic hybrid compounds constructed by joining metal-containing units (secondary building units or *SBUs*) with bridging organic linkers [1]. Among the classes of porous materials, MOFs have much higher surface areas and controllable porosity, thus they provide an excellent platform for catalysis [2], energy storage [3], adsorption/separation [4], sensors [5], magnetism [6], drug delivery [7], luminescence [8] and other useful applications.

Owing to the availability and flexibility of building blocks (metal SBUs and organic linkers) thousands of compounds have been reported within the last two decades [1]. Besides the many fascinating developments made in this field, MOFs are also ideal candidates for biomimetic materials due to their uniform controllable cavities that can provide excellent biomimetic active centers [2a]. The phytochemicals, chemicals derived from plants, are secondary metabolic compounds that naturally occur in plants and are responsible for color and other organoleptic properties of plants and known to provide protection against insects and diseases [9]. Although many attempts have been made to incorporate ideas from natural systems into general synthetic chemistry, to the best of our knowledge, the phytochemicals have rarely been used as linkers in MOFs [10]. Early examples of the compounds belonging to this family are a hydrogen-bonded framework of Co(II)-salicylate and $\{[Mn_2(L\text{-tartrate})_2(H_2O)]\cdot 3H_2O\}_n$, a 3D nano-porous homochiral MOF with a type III adsorption isotherms, which were obtained using sodium salicylate and L(+)-tartrate, respectively [10a,10b].

Our aim is to provide MOFs that have biomimetic character. For this purpose we used ferulic acid as linker, a derivative of cinnamic acid being a well known phytochemical. Ferulic acid is a ubiquitous phenolic compound in plant tissues. Therefore it constitutes a bioactive ingredient of many foods such as grain bran, whole grain foods, citrus fruits, banana, coffee, orange juice, eggplant, bamboo shoots, beetroot, cabbage, spinach and broccoli [11].

Herein we present the results of the synthesis and characterization of PhytoMOF-1. PhytoMOF-1 was characterized by single crystal X-ray diffraction, elemental analysis, IR, TG and surface area measurements. Grand Canonical Monte Carlo (GCMC) simulations were performed in order to establish H_2 adsorption properties of PhytoMOF-1. Furthermore, to assess the convenience of luminescence-based sensing application, the luminescent properties of PhytoMOF-1 were also investigated.

2. Experimental

2.1. Materials and instruments

IR spectra were recorded on a Perkin-Elmer 100 FTIR spectrophotometer as ATR in the wave number range of 4000–650 cm^{-1}.

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The elemental analyses (C and H contents) were determined with a LECO, CHNS-932 instrument. TG and DTA curves were obtained using a Seiko Exstar 6200 TG/DTA thermal analyzer under a dynamic air atmosphere. A sample size of 5–10 mg and a heating rate of 10 °C min^{-1} in the temperature range of 30–800 °C were used. Full data collection of single crystal was carried out on a Bruker Quest D8 device with microfocus Mo K$_\alpha$ radiation and Photon 100 CMOS detector. Powder X-ray diffraction (PXRD) data were recorded on a Rigaku/SmartLab diffractometer operated at 3000 W power (40 kV, 30 mA) using Cu K$_\alpha$ radiation. Fluorescence spectra of solid samples at room temperature were run on Molecular Devices Spectra M5 fluorescence spectrophotometer with emission slits of 4 nm, respectively. The Brunauer–Emmett–Teller (BET) specific surface area and N$_2$ adsorption–desorption-isotherms were measured using a Quantachrome NOVA 4200e instrument at 77 K.

2.2. Synthesis of PhytoMOF-1

A 10 mL DMF solution of Zn(NO$_3$)$\cdot$4H$_2$O (0.522 g, 2 mmol) was mixed with a 10 mL solution of ferulic acid (0.388 g, 2.0 mmol) in absolute ethanol with stirring at room temperature. The resulting solution was divided in 10 parts and filled in 4 mL vials which were kept at 90 °C in an oven for 24 h. 0.518 g product was obtained in total yield of 90%, calculated with respect to Zn.

The obtained crystals were severely twinned. This twin problem was overcome by using a different synthesis and crystallization method: mixing a 5 mL DMF solution of Zn(NO$_3$)$\cdot$4H$_2$O (0.261 g, 1 mmol) with a 5 mL ethanolic solution of ferulic acid (0.19 g, 1.0 mmol). Into the 2 mL stock solution, 1 mL methanol was added and kept at 90 °C. Single crystals suitable for X-ray diffraction experiment were collected after 24 h.

PhytoMOF-1 as-synthesized : IR (ATR, cm^{-1}): 3416bw, 3037vw, 2936vw, 2864vw, 1664vs, 1633s, 1599m, 1571w, 1522m, 1499vs, 1405vs, 1384vs, 1328m, 1300m, 1262vs, 1217m, 1154m, 1130s, 1090m, 1021m, 979m, 922w, 847w, 831s, 808s, 710m, 658m.

PhytoMOF-1 activated: *Anal.* Calc. for C$_{20}$H$_{16}$O$_8$Zn$_2$: C, 46.63; H, 3.13. Found C, 44.86; H, 3.18%. IR (ATR, cm^{-1}): 3046vw, 2988vw, 2943vw, 1633s, 1597m, 1568w, 1540s, 1504vs, 1448m, 1422m, 1399vs, 1295m, 1262vs, 1245m, 1214m, 1165w, 1129s, 1027m, 1011m, 982m, 929w, 879w, 850m, 822s, 781m, 704m (see Supp. Figs. 2 and 3 for IR spectra).

2.3. Details of molecular simulations

In order to assess H$_2$ adsorption properties of the synthesized MOF, molecular simulations were performed. GCMC simulations were used to compute single-component adsorption of H$_2$ at 77, 87 and 298 K. The atomic positions of MOF were obtained from the XRD study and rigid structure was used in all simulations. The universal force field (UFF) [12] was used for the framework atoms. Unfortunately we do not possess any experimental data for H$_2$ uptake of PhytoMOF-1, therefore it is not possible to make a direct comparison between the experiments and simulation results to validate the force field. However, the previous studies have shown that adsorption simulation results based on UFF agree well with the experimental measurements for several other MOFs [13]. Spherical Lennard-Jones (LJ) 12-6 potentials were used to model the H$_2$ molecule [14]. This potential model has been successfully adopted in the past to predict the adsorption behavior of H$_2$ in various MOFs [15]. The Lorentz–Berthelot mixing rules were employed to calculate the adsorbate-adsorbent and adsorbate–adsorbate LJ cross interaction parameters. Interactions between the adsorbate molecules and PhytoMOF-1 atoms were modeled using pair-wise interactions between the adsorbates and each atom in the framework. By specifying the temperature and fugacity of the adsorbing gases, the number of adsorbed molecules was calculated at equilibrium using GCMC simulations. Three types of trial moves, attempts to translate a molecule, attempts to create a new molecule, and attempts to delete an existing molecule were included. The size of the simulation box was set to $2 \times 2 \times 2$ crystallographic unit cells. Simulations at the lowest fugacity for each system were started from an empty matrix and each subsequent simulation at higher fugacity was started from the final configuration of the previous run. The intermolecular potentials were truncated at 13 Å. Simulations consisted in total of 1×10^7 steps to guarantee the equilibration, followed by 1×10^7 steps to sample the desired properties.

2.4. Crystal structure determination

A single crystal of PhytoMOF-1 suitable for X-ray diffraction analysis was carefully chosen from a sample affected by twinning problems. On initial examination of the crystal weak superstructure reflections were found on the diffraction pattern. This phenomenon was reproducible for other single crystals found in the examined sample. Omission of the superstructure reflections led to a small *C*-centered monoclinic cell ($a = 17.144(4)$, $b = 15.145(3)$, $c = 6.519(3)$ Å, $\beta = 92.06(3)°$ for 4316 reflections). Attempt to solve the structure assuming this cell led to a solution with chemically unreasonable disorder of the ferulate ligand. The presence of the weak superstructure reflections was accounted for at the stage of planning the final full measurement strategy. Basic crystallographic data are shown in Table 1.

The structure of PhytoMOF-1 was solved by direct methods in SHELXS97 and refined by full-matrix method in SHELXL97 [16]. All H atoms were generated in their calculated positions and a riding model was applied with $U_{eq} = 1.2/1.5\ U_{eq}$(parent atom) for phenyl/methyl H atoms, respectively. Very large voids in the structure were found (total void volume of ∼3517 Å^3), containing heavily disordered solvent molecules. The contribution of these molecules was removed by application of the PLATON SQUEEZE procedure [17]. On the final difference Fourier map the highest maximum of 2.64 e Å^{-3} is situated in the neighborhood of the Zn1 atom.

Table 1
Selected X-ray data for PhytoMOF-1.

	PhytoMOF-1
Formula	C$_{20}$H$_{16}$O$_8$Zn$_2$
Formula weight	515.07
T (K)	100(2)
λ (Å)	0.71073
Crystal system	monoclinic
Space group	$C2/c$
a (Å)	13.006 (3)
b (Å)	31.084 (4)
c (Å)	17.660 (4)
β (°)	108.39 (3)
V (Å^3)	6775 (2)
Z	8
ρ_{calc} (g cm^{-3})	1.010
μ (mm^{-1})	1.44
$F(000)$	2080
Crystal size (mm)	$0.31 \times 0.12 \times 0.07$
θ range(°)	2.43–25.00
Reflections: total/unique	11 158/5729
R_{int}	0.028
Absorption correction	numerical
Min., max. transmission factors	0.772, 1.00
Data/parameter/restraints	5729/274/0
Goodness-of-fit (GOF) on F^2	1.02
R_1 ($I > 2\sigma(I)$)	0.063
wR_2 (all data)	0.160
Maximum, minimum $\Delta\rho_{elect}$ (e Å^{-3})	2.64, −0.69