



Synthesis of novel nanoporous metal-organic gels with tunable porosity and sensing of aromatic compounds

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ABSTRACT

Herein we report the bottom up design of novel porous metal-organic gels (MOGs) Fe-ndc (H₂ndc – 2,6-naphthalene dicarboxylic acid) and Fe-btc (H₄btc – 1,2,4,5-benzenetetracarboxylic acid) based on Fe³⁺. The effective strategy to obtain MOGs with controllable porosity by changing the concentrations of precursors was studied. The MOGs were dried in vacuum and the resultant xerogels were fully characterized using PXRD, TGA, FT-IR spectroscopy and SEM techniques. The resultant materials demonstrated a wide range of BET surface area 0–290 m²/g. Presence of micro (< 2 nm), meso (2–50 nm) and macropores (> 50 nm) in obtained xerogels was found. Furthermore, Fe-ndc demonstrated strong dependence of photoluminescence properties on the nature of the guest molecules. A unique enhancement effect of maximum luminescence intensity of the host framework Fe-ndc in the presence of toluene (862%). Introduction of benzene led to just 42% increase of luminescence intensity of material compared to Fe-ndc. Quenching effects of maximum luminescence intensity of the host framework upon introduction of nitrobenzene (67%) and 1,3-dinitrobenzene (46%) were found. These features make Fe-ndc an efficient fluorescent material for selective detection of hazardous highly energetic aromatic compounds.

1. Introduction

Metal-organic gels (MOGs) are supramolecular porous solid networks containing low-molecular-weight gelators (LMWGs), metal ions, and trapped intra-channel solvent [1–3]. There are two types of MOGs according to the type of connectivity published up to date [4]. The first one is presented by MOGs with metal complexes connected to the structure of gelator units by non-covalent interactions. Usually these materials contain inert metal ions and are characterized by a limited degree of tuning their properties. Another type of MOGs consists of compounds constructed from metal ions connected to each other through organic ligands (linkers) by strong covalent bonds [5–7]. Metal ions in these materials are essential parts of the framework structure and form diverse secondary building units (SBUs). This opens a wide range for structural variety according to coordination properties of metals and ligands. These compounds are similar to metal-organic frameworks (MOFs) and zeolites that showed potential in adsorption, sensing, catalysis and optoelectronics [8–10]. One of the strong disadvantages of MOFs is their crystallinity, which strongly limits their application in device fabrication.

Chemically and mechanically stable materials with controlled porosities are especially required in such technologies as gas separation and sensors. These applications require rather delicate control of pore size and pore size distribution combined with processability. However it is extremely hard to rationally design and predictably construct MOFs with necessary porosity. All attempts to increase the length of linkers in practice lead to arrangement of SBUs and linkers in the space of MOF channels [11,12]. It leads to the formation of interpenetrated networks, which significantly decreases the surface area of the material. In this regard, thanks to sol-gel physical state of MOGs, they exhibit much easier processability and simplicity in creation of flexible devices. The sol-gel process affords many strategies for the syntheses of compounds with controllable porosity [13–16]. The pore size is established by structure of gels which depends on condensation rate and value of collapse upon drying. MOGs demonstrate high stability during very rough drying in vacuum of a membrane pump [17,18]. This may be explained by highly stable bonds metal-ligand and obtained strengthened gel network.

Owing to presence of electron rich aromatic carboxylates conjugated with metal ions and porous structure MOGs have a great

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potential in photoluminescent sensing [19–25]. This technique is one of the most effective methods for detection of a variety of chemicals with different electron withdrawing or releasing properties [26]. It is very sensitive, commercially available and easy to use technique. Photoluminescent sensing of compounds with environmental importance is a growing field of research. Despite all mentioned advantages, MOGs are still strongly undeveloped especially in the area of photoluminescent sensing.

Herein we report the syntheses of two new porous MOGs, Fe-ndc and Fe-btc, based on Fe^{3+} ions connected by carboxylate groups of naphthalene dicarboxylic acid (H_2ndc) and benzenetetracarboxylic acid (H_4btc), correspondingly. The small size and robustness of these ligands make them highly attractive for syntheses of stable and porous MOGs. Furthermore, they possess high electron density that can serve as a $\pi \rightarrow \pi$ stacking center with guest molecules. This allows one to produce excited complexes with the following change of the luminescence intensity of the material. Iron(3+) is a strong coordination center with acid properties and a broad structural variety. This opens wide opportunities for syntheses of a range of MOGs with sensing properties. We found that porosity of these materials is in strong dependence on the concentration of reagents. Usual change of the concentrations of reagents and amount of trapped solvent in MOGs leads to the formation of Fe-ndc (1) and Fe-btc (2) xerogels with different and controlled porosity ranging from nonporous materials to the systems with a BET surface area of $290 \text{ m}^2/\text{g}$. Xerogel 1 demonstrated high ability for sensing of aromatic compounds. Strong sensitivity of the luminescence intensity of 1 depending on the nature of detected molecules makes it a perspective material in sensing of high energetic compounds, like nitro compounds.

2. Experimental

2.1. Materials and physical measurements

All compounds were synthesized under solvothermal conditions. Starting materials include iron(III) nitrate nonahydrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O} \geq 99.95\%$ trace metals basis, Aldrich), 2,6-naphthalenedicarboxylic acid ($\text{C}_{12}\text{H}_8\text{O}_4$, 99%, Aldrich), 1,2,4,5-benzenetetracarboxylic acid ($\text{C}_{10}\text{H}_6\text{O}_8$, 94%, Aldrich). Ethanol was dried according to the literature method by distillation over Na [27].

Powder samples were put between two glass sheets and fixed in powder holder. wder X-ray diffraction (PXRD) data were obtained on Shimadzu XRD 7000S diffractometer (Cu K α radiation, $\lambda = 1.54178 \text{ \AA}$): 2θ step = .03, counting time = 1.0–2.5 s, 2θ scan range = 3–25°. Powder X-ray diffraction patterns of 1 and 2 are present in Fig. S1, Supporting Information. Fourier-transform infrared (FT-IR) spectra in the range $4000 - 300 \text{ cm}^{-1}$ were measured on a Vertex 80 spectrometer. The IR spectra are presented in Figs. S4–S5, Supporting Information. Thermogravimetric analyses (TGA) were obtained on a NETZSCH TG 209 F1 device and are presented in Figs. S2–S3, Supporting Information. The sample quantity ranged from 2 to 10 mg. All samples were heated under a He atmosphere from room temperature up to $250 \text{ }^\circ\text{C}$ at a $2 \text{ }^\circ\text{C}/\text{min} - 1$ heating rate. Elemental C, H, N analysis data were obtained on a Eurovector 600 analyzer. An ICP-AES spectrometer (iCAP 6000) was used to prove the absence of $\text{Fe}(\text{NO}_3)_3$ impurities in the materials by checking [Fe] in mother liquids. Samples of 1 and 2 (20 mg) were boiled in 10 ml of water or ethanol and studied by ICP-AES afterward.

2.1.1. Surface area and porous structure

Analysis of the porous structure was performed on a Quantochrome Autosorb iQ analyzer at 77 K. Samples of 1 and 2 were first degassed under a vacuum at $90 \text{ }^\circ\text{C}$ for 8 h. N_2 adsorption – desorption isotherms were measured within the range of relative pressures of $10^{-6} - 0.99$ bar. The specific surface area was calculated from the data based on the Brunauer – Emmett – Teller (BET) equation. The Saito

Foley and density functional theory (DFT) approaches, the most appropriate for the studied materials, were employed to estimate the total pore volume and the pore-size distribution, respectively.

2.1.2. CO_2 sorption experiments

The CO_2 adsorption isotherms were measured volumetrically on a Quantochrome Autosorb iQ analyzer at 273 K using an ice – water bath. The samples (ca. 50 mg) were activated before measurements using the standard “outgas” option of the equipment at 323 K. Adsorption – desorption isotherms were measured within the range of pressures of $10^{-3} - 1$ bar. The database of the National Institute of Standards and Technology was used as a source of $p - V - T$ relations at experimental pressures and temperatures.

2.2. Luminescence and excitation spectra for the powder samples

The excitation and emission spectra of the powder samples (see Fig. 5) were recorded at room temperature on PerkinElmer LS 55 photoluminescence spectrometer. A xenon discharge lamp was used as a source of excitation. Powder samples were put between two quartz sheets and fixed in powder holder. Excitation and emission slits were set 15.0 and 20.0 nm respectively. A UG-5 excitation filter was used during all emission spectra measurements to remove spurious emission. Emission spectra were recorded under $\lambda_{\text{exc}} = 250, 275, 300, 330, 350, 375 \text{ nm}$ excitation wavelengths and were corrected for photomultiplier spectral sensitivity using built-in correction file. The excitation spectra were recorded by varying the excitation energy while fixing the emission wavelength λ_{em} (λ_{em} is a wavelength of luminescence spectrum maximum) and were corrected for varying intensity of xenon lamp using built-in correction file.

Effect of guest molecules on maximum luminescence intensity of 1 (Tables 3 and 4) was determined using calibrated AvaSpec-ULS2048-USB2 spectrometer (Avantes) equipped with FCR-7UVIR400-1-ME fiber optic reflection probe (Avantes). The reflection probe was fixed in RPH-1 holder (Avantes) under 90° against powder sample. 355 nm LED was used as source of excitation. For all powder samples luminescence signal was collected from exactly the same surface area of dense powder layer. This allowed us to compare maximum luminescence intensities of different samples quantitatively. The enhancement efficiency (%) is defined as $(I - I_0)/I_0 \times 100$ in which I_0 = the maximum fluorescence intensity of guest-free sample and I is the corresponding intensity maximum after exposure to a selected guest@1.

2.2.1. Activation of xerogels 1 and 2

In a typical procedure, xerogels 1 and 2 were activated by soaking of as-synthesized gel in CH_2Cl_2 with the following filtration and heating under a reduced pressure ($1.5 \cdot 10^{-1} \text{ mbar}$) at $90 \text{ }^\circ\text{C}$ during 8 h. Elemental Anal. Calcd for $1 \cdot (\text{C}_{36}\text{H}_{22}\text{Fe}_3\text{NO}_{18})$ (%): C, 46.8; H, 2.40; N, 1.52. Found: C, 46.72; H, 2.65; N, 1.44. Elemental Anal. Calcd for $2 \cdot (\text{C}_{10}\text{H}_6\text{FeO}_{9.5})$ (%): C, 35.02; H, 2.06. Found: C, 35.11; H, 2.34.

2.2.2. Guest exchange in MOGs 1*guests

Activated 1 was immersed in an organic solvent during 2 days, then it was filtered off and dried in a vacuum of a membrane pump during 10 min at $25 \text{ }^\circ\text{C}$. *Meta*-dinitrobenzene were dissolved in CH_2Cl_2 (10^{-2} M). Elemental Anal. Calcd for $1 \cdot 4\text{C}_6\text{H}_5\text{NO}_2$ ($\text{C}_{60}\text{H}_{38}\text{Fe}_3\text{N}_5\text{O}_{24}$) (%): C, 52.20; H, 2.77; N, 5.07. Found: C, 52.50; H, 2.65; N, 5.02. Anal. Calcd for $1 \cdot 5\text{C}_6\text{H}_6$ ($\text{C}_{66}\text{H}_{48}\text{Fe}_3\text{NO}_{16}$) (%): C, 62.00; H, 3.78; N, 1.10. Found: C, 62.30; H, 3.42; N, 1.31. Anal. Calcd for $1 \cdot 4\text{C}_6\text{H}_5\text{CH}_3$ ($\text{C}_{64}\text{H}_{50}\text{Fe}_3\text{NO}_{16}$) (%): C, 61.17; H, 4.01; N, 1.11. Found: C, 60.92; H, 4.32; N, 1.21. Anal. Calcd for $1 \cdot 4\text{C}_6\text{H}_4(\text{NO}_2)_2$ (*meta*-) ($\text{C}_{60}\text{H}_{34}\text{Fe}_3\text{N}_9\text{O}_{32}$) (%): C, 46.18; H, 2.20; N, 8.08. Found: C, 46.30; H, 2.45; N, 8.19.

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