

SYNTHESIS OF METAL-ORGANIC FRAMEWORKS FOR ENERGETIC APPLICATIONS

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ABSTRACT

Despite the fact that MOFs have been investigated in several application fields, the use of MOFs as energetic materials has not been fully explored yet. MOFs can be potential energetic materials because of their high densities and high heats of detonation. Additionally, they are expected to present some advantages compared to well established macromolecules such as organic polymers. Indeed, several reported MOFs have revealed their great potential as more stable new-generation high explosives.

A simple strategy for the synthesis of energetic MOFs consists of partially exchanging the ions within the framework with energetic ions. Herein, we present the results of a systematic study on the preparation of such materials. Three different metals (Zn, Co and Ni) were combined with 1,4-Di(4'-pyrazolyl)benzene (BDP), the metal was first exchanged with K^+ and subsequently with Guanidinium Nitrate (GUNI) and Guanylurea Dinitramide (FOX-12).

KEYWORDS

High-energy metal–organic frameworks (HE-MOFs), Synthesis, Nanomaterials

1. INTRODUCTION

The scientific attraction of metal-organic frameworks (MOFs) has achieved an exceptional level during the last decade (1). MOFs are composed of organic and inorganic building units, providing an infinite number of possible structures with variable properties and potential applications. They offer significant new scientific and technological opportunities by combining the attractive features of both their inorganic and organic units.

Considering the possible future applications of these materials, ranging from gas separation (2-4) to gas storage (5-6), drug delivery (7), catalysis (8-10) sensors (11), etc., a wide interdisciplinary technological advancement can be expected.

One of the most attractive characteristics of MOFs is certainly the possibility to finely tune their chemical and physical features. For example, the organic linkers can be either replaced or chemically

modified leading to a theoretically infinite number of materials with different properties. Additionally, due to their properties, such as high density, favorable thermal stability and excellent mechanical strength and hardness, it is predicted that MOFs could be applied as energetic materials reaching high heat of detonation. Nevertheless, it is found experimentally that once various nitrogen-rich energetic ligands combine with metal ions, the sensitivity of HE-MOFs grows exponentially as the energy increases, which, to a great extent, may restrict the applications of HE-MOFs in the field of energetic materials (12). A promising strategy to overcome this issue is represented by the introduction of ionic energetic materials within the framework, through an ion-exchange step between an ionic MOF and an energetic material (salt). Recently Feng et al. presented the synthesis of anionic MOFs constructed from Cu (or Co), azole ligands, and nitrogen-rich cations which show several advantageous features, making them superior to neutral HE-MOFs for developing eco-friendly energetic materials. Herein, we present the synthesis of Ni, Co and Zn 1,4-Di(4'-pyrazolyl)benzene and their subsequent post-synthetic modifications in order to introduce the energetic salts of Guanidinium Nitrate (GUNI) and Guanylurea Dinitramide (FOX-12) within the framework.

2. EXPERIMENTAL

2.1. Materials and methods

Chemicals and solvents were analytical grade, except methanol which was technical grade (98%), purchased from various commercial suppliers and used without further purification.

Powder diffraction measurements were performed on a Bragg-Brentano Diffractometer, D8 Advance from Bruker AXS, equipped with copper tube, 2.5° Soller collimators, 0.3 mm divergence slit, anti-scatter screen, flip-stick stage and silicon strip detector (LynxEye) with 3° 2 θ detector opening. The diffraction patterns were monitored between 5° and 65° 2 θ with 0.06° 2 θ step width and 3s counting time per step. Crystallite sizes were determined by Rietveld-Analysis.

TGA experiments were carried out on a TGA Q5000 TA Instruments device. Samples were heated under air at a heating rate of 10 K min⁻¹ up to 700°C.

Nitrogen adsorption/desorption isotherms were measured at 77 K using a Quantachrome Autosorb IQ-C surface area analyzer. Samples were degassed in vacuum for 18 h at 100°C prior to the analysis. BET pressure range varied between $3 \cdot 10^{-3}$ and $7.2 \cdot 10^{-2}$ bar. For the calculation of the BET surface area all the criteria for a correct estimation were taken into account.

IR spectra were recorded between 650 and 4000 cm⁻¹ at a resolution of 4 cm⁻¹ accumulating 64 scans using a diamond ATR/FT-IR spectrometer (Thermo Nicolet 6700; ATR-Durascope) with a MCT detector.

2.2. Synthesis of 1,4-Di(4'-pyrazolyl)benzene MOFs (14)

In a typical synthesis, 280 mg (1.33 mmol) of 1,4-Di(4'-pyrazolyl)benzene were dissolved in 70 mL of DMF and 1.8 mmol of metal (Ni, Co or Zn) acetate were dissolved in 18 mL of H₂O. The two limpid solutions were mixed together and refluxed for 6 h under stirring. The solids obtained were filtered and washed with EtOH and Et₂O and characterized. The materials obtained were denominated Ni-BDP, Co-BDP and Zn-BDP.

2.3 Synthesis of K@M-BDP (15)

Each M-BDP MOF was dried under high vacuum ($1 \cdot 10^{-2}$ mbar) for 6 hours. A solution of KOH 0.5 M in methanol (15 mL) was added to 450 mg of MOF and the suspension was allowed to stir overnight. The solids were recovered by filtration, washed with plenty of methanol and characterized. The materials obtained were denominated K@Ni-BDP, K@Co-BDP and K@Zn-BDP.

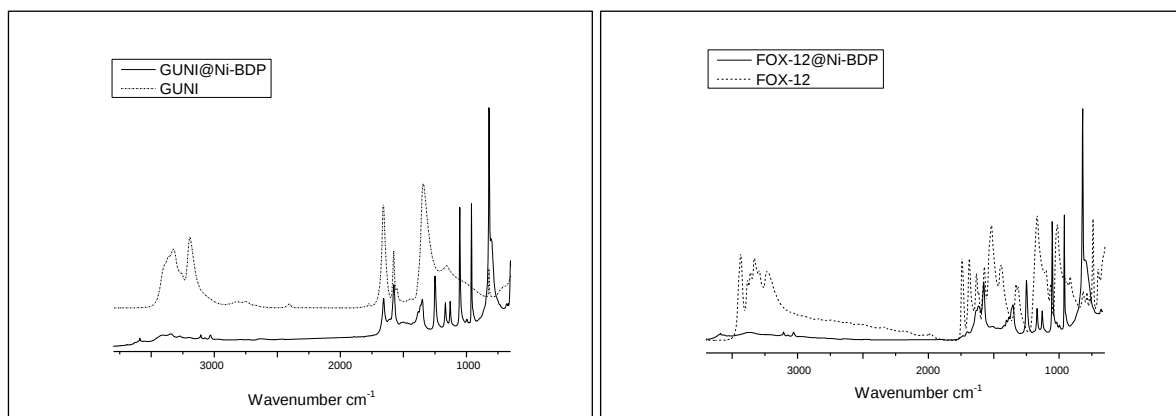
2.4 Synthesis of GUNI@M-BDP and FOX-12@M-BDP

Each K@M-BDP MOF was dried under high vacuum ($1 \cdot 10^{-2}$ mbar) for 6 hours. A solution of Guanidinium Nitrate (GUNI) in methanol (50 mg in 5 mL) was added to 80 mg of MOF and the suspension was allowed to stir overnight. Following the same procedure, a solution of Guanylurea Dinitramide (FOX-12) in methanol and DMF (50 mg in 5+1 mL) was added to 80 mg of MOF and the suspension was allowed to stir overnight. The solids were recovered by filtration, washed with plenty of methanol and characterized. The materials obtained were denominated GUNI@Ni-BDP, GUNI@Co-BDP, GUNI@Zn-BDP, FOX-12@Ni-BDP, FOX-12@Co-BDP and FOX-12@Zn-BDP.

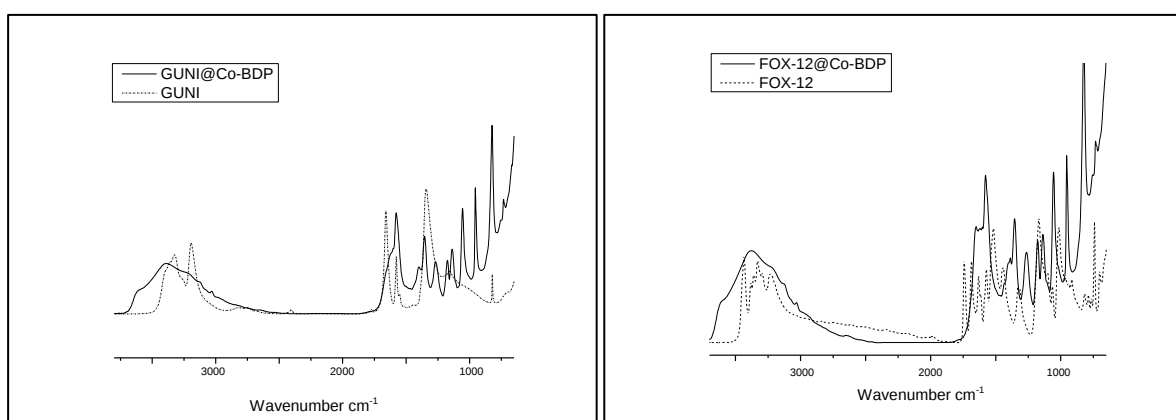
3. RESULTS AND DISCUSSION

A Nickel / 1,4-Di(4'-pyrazolyl)benzene (BDP) MOF has been recently synthesized by Cirujano et al. aiming to introduce Cu(II) into the framework through post-synthetic modifications for catalytic purposes (15). The same approach was used in this work to introduce Guanidinium cations, derived from the energetic salts Guanidinium nitrate (GUNI) and Guanylurea Dinitramide (FOX-12) into Nickel-, Cobalt- and Zinc-BDP MOFs. Following this strategy a series of BDP-MOFs were synthesized, using Nickel, Cobalt and Zinc acetate as metal precursors. These materials were subsequently treated with methanolic solutions of KOH in order to allow the partial cation exchange with K⁺, which, thanks to its mobility, can be further exchanged with other cations.

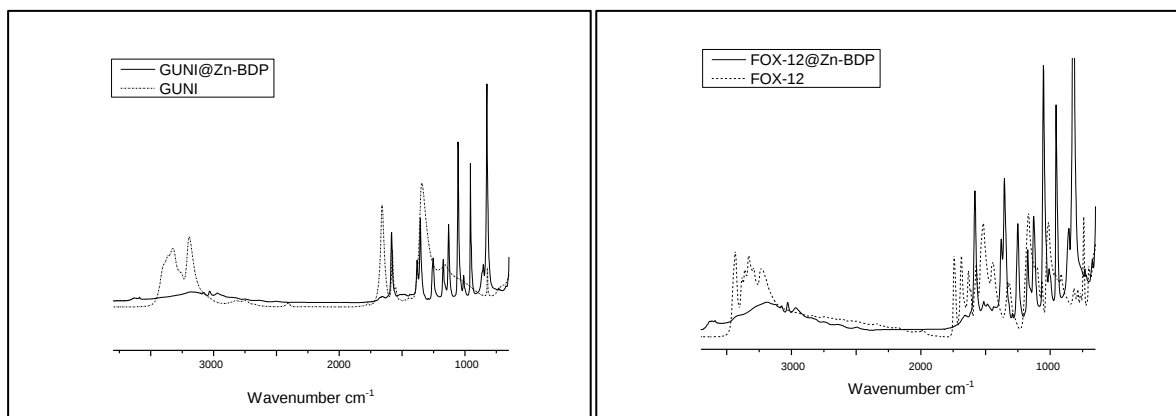
The obtained materials were characterized through pXRD, B.E.T., TGA and FT-IR. Once the porosity and crystallinity of the MOFs has been assessed, FT-IR proved the introduction of the energetic salts within the frameworks. Figures 1-3 show the FT-IR spectra of the GUNI@M-BDP and FOX-12@M-BDP in comparison with the energetic salts.



a **b**
Figure 1. FT-IR comparison of Guanidinium nitrate with GUNI@Ni-BDP (a) and FOX-12 with FOX-12@Ni-BDP (b).



a **b**
Figure 2. FT-IR comparison of Guanidinium nitrate with GUNI@Co-BDP (a) and FOX-12 with FOX-12@Co-BDP (b).



a **b**
Figure 3. FT-IR comparison of Guanidinium nitrate with GUNI@Zn-BDP (a) and FOX-12 with FOX-12@Zn-BDP (b).

4. CONCLUSION

The possibility to introduce energetic salts within the network of ionic MOFs has been tested and confirmed. FT-IR measurements show that the ions are present in the solid materials, which preserved their porosity. Further studies (DSC, friction and impact sensitivity) will provide the necessary information to evaluate the potential energetic applications of these new materials.

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