

# Fluorescent post-synthetic modified MOFs for methane sensing

Juan C. Cárdenas <sup>a,b</sup>, Laura A. Castillo <sup>a</sup>, William Molano <sup>b</sup>, Cesar A. Sierra <sup>b</sup>, Andreas Reiber <sup>a</sup>

<sup>a</sup> Universidad de los Andes, Carrera 1 N°18A-12, Bogotá, Colombia.

<sup>b</sup> Universidad Nacional de Colombia, Carrera 45 N° 26-85, Bogotá, Colombia.

## ABSTRACT

In order to obtain fluorescent materials for methane sensing, a series of post-synthetic modifications to UNMOF-1 and IRMOF-3 were carried out. Both MOFs were synthesized solvothermally and characterized by single-crystal X-Ray diffraction. Post-synthetic modifications to UNMOF-1 and IRMOF-3 proceeded following a cross coupling reaction and a condensation reaction (respectively). The modified products will be characterized by <sup>1</sup>H NMR and MALDI-TOF mass spectrometry. Fluorescence spectra with and without methane atmosphere will be performed in order to evaluate their capability of methane sensing. Additionally, fluorescence spectra of an already reported MOF (UNMOF-0) are shown under methane atmosphere to provide to the reader a perspective of the work that is being carried out.

**Keywords:** MOF, post-synthetic modification, fluorescence, methane sensing.

## 1 INTRODUCTION

In agree with recent studies and considerations of the Ministry of Mines and Energy of Colombia (MMEC), during the last decade colombian mining activity registered a significant increase in the volume and value of production. Therefore, its contribution to the overall growth of the colombian economy has been significant. According to the MMEC, the colombian mining scenery has two general components. The first one is characterized by a formal and large scale mining activity; the second one, characterized by a mining activity developed at minor scales and recognized by a lack of appropriate technology. In many cases also defined by its informality and subsistence purpose, which makes it unprofitable, non-competitive, environmentally not sustainable and mostly very insecure.[1]

In the short and medium term, coalmines are profitable promising in Colombia due to its relative abundance and their ease of operation. However, strip mining of coalmines carries imminent risks to workers and infrastructure. Among these risks, the presence of high methane concentrations stands out. Methane, in concentrations between 5 and 15% by volume is a very dangerous gas as it

promotes explosions of great magnitude, which often lead to numerous human and economic losses.

To mitigate this risk, several security measures have been taken, for example controlled mine ventilation or the use of methane commercial sensors. However, controlled ventilation depends on external factors that in many cases are impossible to manage in the field. For instance, the continuous power supply in the mining area that secures a proper ventilation is a difficult task in developing countries. In addition, methane detectors currently used have shown low efficiency. Clear sign of this are the recent fatal coalmines accidents in Colombia, China, Mexico and the United States. As a result there is an existing need of a real-time methane sensor easy to apply.

The use of MOFs with phenylenevinylene ligands (PVs) into its structure for the fabrication of a methane sensor arises as a promising option, due to the synergy between the MOF's high surface area [2] and the excellent luminescent properties of the PVs. However, the isolation of MOFs with PVs into its structure has been struggling because of the long length and extended conjugation of PVs, lead to a slight solubility in most of the common organic solvents, thereby avoiding the required conditions for the synthesis of the targeted MOF. However, here we present a PV ligand containing MOF in order to present the perspectives of the work that is being carried out.

In order to solve the situations mentioned above, we have proposed the post-synthetic modification of common MOFs, as IRMOF-3 and analogous thorough condensation reactions, and cross-coupling reactions.

## 2 METHODOLOGY

### 2.1 General

Commercially available precursors were used as received without further purification and solvents were dried according to standard procedures when needed. Melting points were determined on a Bibby Stuart Scientific SMP10 apparatus. <sup>1</sup>H and <sup>13</sup>C NMR spectra were taken using a Bruker Avance 400 spectrometer with CDCl<sub>3</sub> or DMSO – *d*<sup>6</sup> as solvent and internal standard for chemical shifts in ppm. UV/VIS spectra were measured in a double channel Thermo Scientific Evolution 300 UV/VIS spectrophotometer with xenon lamp based platform. Fluorescence spectra were registered in DMSO solutions or

in solid state on a PTI QuantaMaster 300 spectrofluorometer with xenon lamp.

## 2.2 Synthesis of ligands

### 2.2.1 Synthesis of 1,4-bis((*E*)-2-(pyridin-4-yl)vinyl)benzene (PV1)

4-vinylpyridine (0.5g, 4.75mmol, Alfa Aesar), dibromobenzene (0.56g, 2.38mmol, Alfa Aesar), Pd(dba)<sub>2</sub> (0.0273g, 1% cat, 0.0475mmol, Sigma-Aldrich), triphenylphosphite (0.147g, 0.475mmol, Sigma-Aldrich) and triethylamine (0.485g, 4.75mmol, Panreact) were poured into a 5mL vial and dissolved in 2mL of dried N,N-dimethylformamide (Merck SeccoSolv. Max. 0.003% H<sub>2</sub>O). The vial was purged with nitrogen before sealing. The reaction mixture was introduced in an oven at 110°C with stirring, for 24h. After completion of reaction time, a yellow powder was obtained. The product was washed with cold methanol and dried at room temperature for 24h. A total of 0.568g was obtained (1.99mmol, 84% yield). <sup>1</sup>H NMR (400MHz, DMSO-d<sub>6</sub>, d, ppm): 7.25 (d, 2H, J<sub>trans</sub> = 15.9Hz), 7.33 (s, 4H), 7.47 (d, 4H, J = 7.8Hz), 7.91 (d, 2H, J<sub>trans</sub> = 15.9Hz), 8.54 (d, 4H, J = 7.8Hz). Melting Point 274-275°C (ref.[3] 273°C).

### 2.2.2 Synthesis of 2,5-diiodoterephthalic acid

Terephthalic acid (1.0g, 6 mmol, Alfa Aesar), KIO<sub>4</sub> (1.4 g, 6 mmol, Alfa Aesar) and I<sub>2</sub> (2.3 g, 9 mmol Alfa Aesar) were dissolved in 50 mL acetic acid and refluxed during 24 h in a 100mL round bottom flask. After completion, the reaction mixture was filtered out, washed several times with cold methanol and dried at 45 °C during 24 h to yield 0.98 g (2.3 mmol, 39% yield) of 2,5-diiodoterephthalic acid. <sup>1</sup>H NMR (400MHz, DMSO-d<sub>6</sub>, d, ppm): 8.59 (s, 2H). <sup>13</sup>C NMR (400MHz, DMSO-d<sub>6</sub>, d, ppm): 94.8, 140.3, 142.1, 170.1.

## 2.3 Synthesis of MOFs

### 2.3.1 Synthesis of UNMOF-0

1,3,5-benzenetricarboxylic acid (21mg, 0.1mmol), PV1 (28.4mg, 0.1mmol) and Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (29.7mg, 0.1mmol) were poured into a Parr® Teflon autoclave, and dissolved in 3 mL mixture of acetonitrile/water 1:1. The autoclave was sealed and left in an oven at 150°C during 20h. After this time, the reaction mixture was cooled to 100° during another 14h. Finally, the oven was turned off and the autoclave was cooled to room temperature to yield yellow fluorescent needles. The UNMOF-0 was characterized through single crystal XRD. This MOF was already obtained from different reaction conditions than those used in this project. [4]

### 2.3.2 Synthesis of UNMOF-1

UNMOF-1 (Zn<sub>4</sub>O(C<sub>8</sub>H<sub>2</sub>O<sub>4</sub>)<sub>3</sub>) was synthesized by a solvothermal treatment involving 2,5-diiodoterephthalic acid (14mg, 0.03mmol) and zinc nitrate hexahydrate (30mg, 0.1mmol Panreac) dissolved in dry N,N-dimethylformamide (2.5 mL, SeccoSolv. Max. 0.003% H<sub>2</sub>O, Merck) and placed in an Ace pressure tube (Aldrich). The reaction vessel was placed in a oven for 40 hours at 100°C. Cubic white crystals were obtained. The mother liquor was decanted and the crystals were washed with dried DMF. Activation was performed by immerse in chloroform for 3 days (each day the solvent was decanted and replenished).

### 2.3.3 Synthesis of IRMOF-3

IRMOF-3 (Zn<sub>4</sub>O(C<sub>8</sub>H<sub>5</sub>NO<sub>4</sub>)<sub>3</sub>) was synthesized by a solvothermal treatment involving 2-aminoterephthalic acid (0.12g, 0.63mmol, Alfa Aesar) and zinc nitrate hexahydrate (0.5g, 1.67mmol, Panreac) dissolved in dry N,N-dimethylformamide (15mL, Merck SeccoSolv. Max. 0.003% H<sub>2</sub>O). The reaction mixture was placed in an Ace pressure tube (Aldrich) and carried out in a oven for 40 hours at 100°C. After completion, the mother liquor was decanted and the crystals were washed with dried DMF. Activation was performed by immerse in chloroform for 3 days (each day the solvent was decanted and replenished). Posterior activation to alleviate water sensibility was done by an additional immersion in toluene.[5]

## 2.4 Post-synthetic modifications

### 2.4.1 Post-synthetic modification of UNMOF-1

UNMOF-1 (0.018g, 0.012mmol), butyl acrylate (0.015g, 0.12 mmol), Pd(dba)<sub>2</sub> (0.69mg, 0.0012mmol), triphenylphosphite (4mg, 0.12 mmol) and triethylamine (0.012g, 0.12 mmol) were dissolved in DMF (0.2 mL, SeccoSolv. Max. 0.003% H<sub>2</sub>O, Merck) and placed into a microwave reaction system. The reaction mixture was stirred and heated at 100 °C during 30 minutes to yield a white-yellow powder. The solid was filtered out and sonicated in a DCI 1.0 M solution in diethyl ether, 97.5% D. The solution is analyzed through NMR and MALDI – TOF.

### 2.4.2 Post-synthetic modification of IRMOF-3

IRMOF-3 (0.47g, 0.58mmol), salicylaldehyde (0.68g, 5.6mmol, Alfa Aesar) and toluene (2mL) were introduced in a 25mL round bottom flask. The reaction mixture was left for 7 days without stirring or heating. After completion, the crystals were decanted and washed with toluene.

## 2.4 Methane sensing test

40 mg of UNMOF-0 were adhered carefully to the quartz lens of the integrating sphere of the spectrofluorometer. Thereafter the quartz lens with UNMOF-0 was placed into a vial and the vial was sealed with a septum. Methane was injected for 10 minutes to allow adsorption of the gas into the pores of the MOF. Finally, the lens was carefully removed from vial and placed into the integrating sphere for measurements of fluorescence with irradiation at 333nm.

### 3 RESULTS AND DISCUSSION

Various attempts have been made in our research group to build MOFs containing 2½ phenylenevinylene (PV) length units as the only building ligand. However, those syntheses produce polycrystalline mixtures, making the crystal characterization impossible.

As an alternative, this project outlines the use of PVs as an auxiliary ligand in a MOF whose main framework is assembled by common ligands (benzenedicarboxylate (BDC) and benzenetricarboxylate (BTC)). Following this idea, the UNMOF-0 using BTC and PV1 (Figure 1) as co-building ligands, was synthesized.

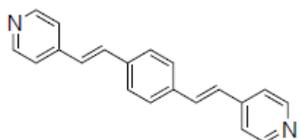


Figure 1: PV1 ligand structure.

As shown in Figure 2, UNMOF-0 presents pores available for adsorption of guest molecules by interaction with the metal clusters or the ligands. Additionally, it can be observed how the 2D interpenetrated crystal framework is constructed by BTC molecules linked together through zinc metal clusters organized in a paddle wheel form [6]. The pores serve as well as containers for PV1 ligands located in an axial position in relation to the 2D layers. This incorporation of PV1 inside the framework, makes it in principle appropriate for fluorescent sensing.

In order to perform the methane sensing test for UNMOF-0, a preliminary study over the PV1 ligand was performed. By implementing UV-Vis technique, it was possible to recognize the PV1 absorption maximum ( $\lambda_{max} = 333\text{nm}$ ) used later for excitation during the fluorescence analysis.

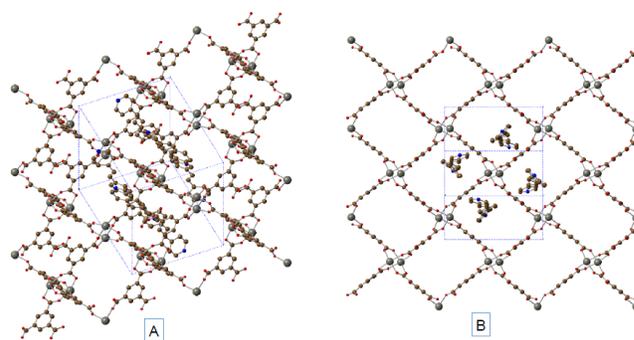


Figure 2: UNMOF-0 Crystalline structure. A: MOF's general view. B: view through the plane (100). Zn: grey, C: brown, O: red, N: blue

PV1 shows an adequate emission profile for a fluorescent promising ligand as shown in figure 3. The profile displays 2 wavelengths of maximum emissions at 460nm and 490nm. Once the UNMOF-0 is built, the wavelength at 490nm disappears in the emission spectra and the maximum emission wavelength at 460nm undergoes a red shift of 10nm (figure 4.)

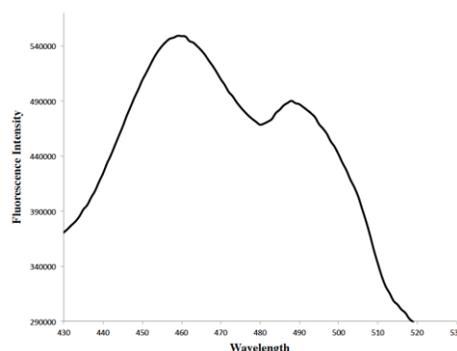


Figure 3: Fluorescent emission spectra of PV1

For the methane-sensing test, the UNMOF-0 fluorescence spectra were again measured after methane loading. The emission spectrum exhibits 5% increased intensity in relation to the UNMOF-0 alone, followed by a small red shift.

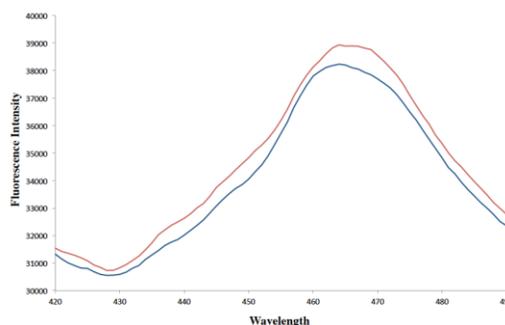


Figure 4: Relative emission intensities of UNMOF-0 (red) and UNFMO-0 under methane atmosphere (blue)

As presented above, UNMOF-0 displays indeed a variation, though small, of the fluorescent emission spectra when subjected to methane atmosphere. This indicates the utility of the mentioned material as a fluorescent sensor for methane under laboratory conditions.

## 4 CONCLUSIONS

A metal-organic framework (UNMOF-0) was synthesized with BTC and PV1 as co-ligands. The framework consists of 2D interpenetrated layers build up by BTC molecules joined together by metal zinc clusters with PV1 ligands located inside the framework pores. This material displayed an increase of 5% intensity when subjected to methane atmosphere, in relation to the MOF alone. This property makes it suitable for methane sensing at laboratory conditions.

After completing the analysis of UNMOF-0, we have decided to build MOFs comprising shorter ligands, which can be then modified to yield fluorescent MOFs. For this reason we have synthesized UNMOF-1 and IRMOF-3 that have been post-synthetic modified to obtain MOFs with analogous fluorescent characteristics in relation to UNMOF-0. Their analyses are still being developed and the results until now are promising.

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