

“Exploring Physical and Chemical Properties in new Multifunctional Indium, Bismuth and Zinc based 1D and 2D Coordination Polymers”

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Section S1: Synthesis procedure details.

Bi-1, Bi-2, In-1 and **Zn-1**, were obtained as crystalline solids under solvothermal conditions. The solid reactants and solvents were used as received without purification from Across Organics and Sigma-Aldrich.

Synthesis of Bi-1 ([Bi(1,2,4,5-BTC)_{0.5}(2,2'-bipyridine)(NO₃)(DMF)]) was obtained under mild solvothermal conditions for an extended time (60 °C, 120 h), mixing 1 mmol of 1,2,4,5-benzenetetracarboxylic acid (Across Organics) (0.254 g), 2 mmoles of 2,2'-bipyridine (Sigma-Aldrich) (0.31 g) and 1 mmol of Bi(NO₃)₃·5H₂O (0.485 g) (Sigma-Aldrich) in 15 mL of N,N'-dimethylformamide (DMF). After that, transparent “block shape” crystals were obtained (Yield: 72% respect to bismuth metal). The crystalline product was washed with DMF and dried at room temperature. BiC₁₈H₁₆N₄O₈ (624.69 g·mol⁻¹): calcd. C 34.6, H 2.6, O 20.5, N 8.96 ; found C 34.9, H 2.44, O 20.2, N 8.22.

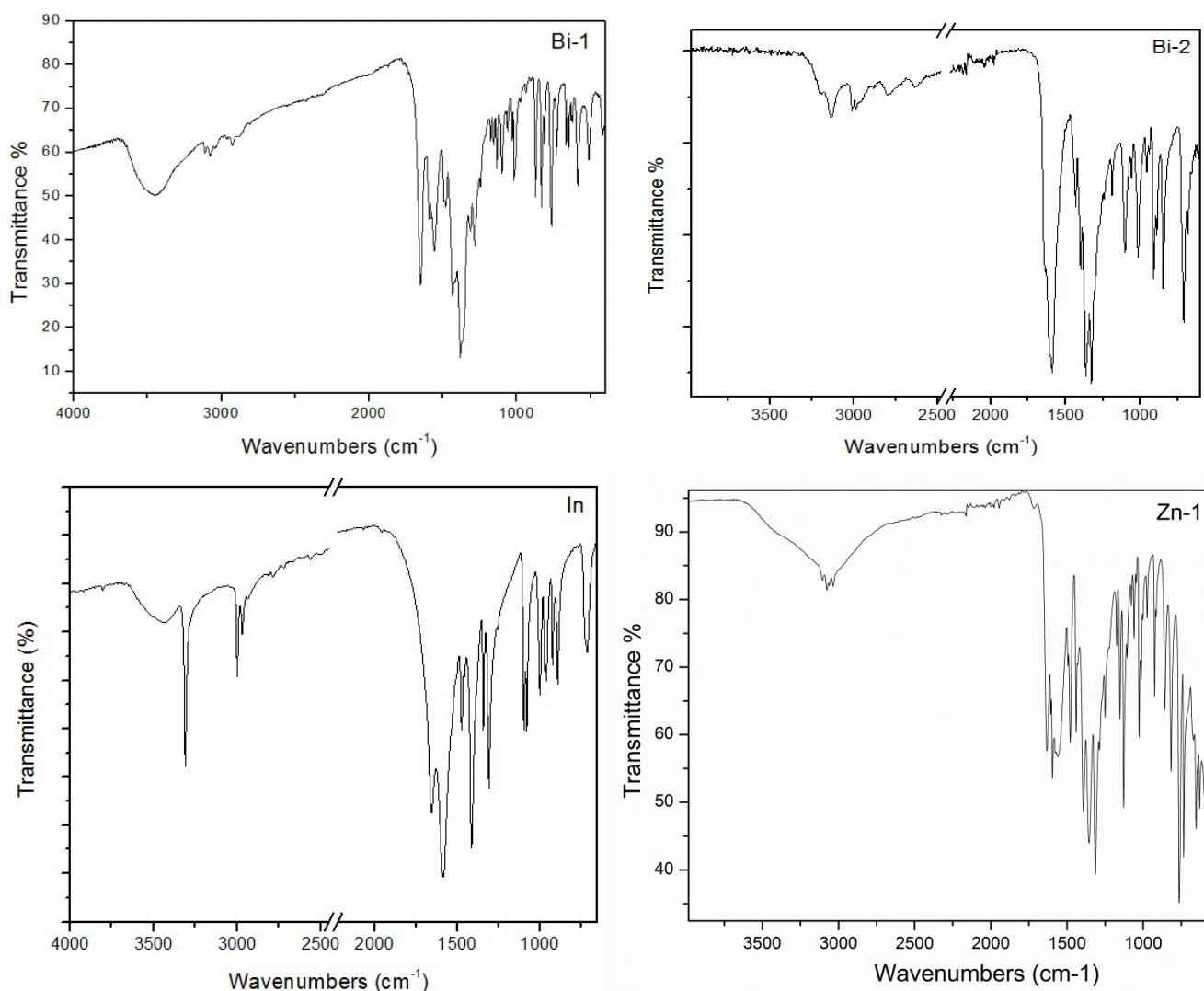
Synthesis of Bi-2 ([Bi(IDA)(IDAH)]): the compound was obtained under mild synthetic conditions, mixing 2 mmol of H₂IDA (Sigma Aldrich) (0.266 g), and 1 mmol of Bi(NO₃)₃·5H₂O (0.485 g) (Sigma-Aldrich) in 15 mL of N,N'-dimethylformamide and 5 mL of distilled water. The mixture was stirred at room temperature for 30 minutes to ensure total dissolution of all the reactants. Then, the clear solution was heated at 60 °C in a glass vessel for 48 h. Subsequently, the reactor was cooled to room temperature. Colorless crystals (Yield: 82% based on bismuth) suitable for single-crystal X-ray diffraction were obtained (see Figure 1). Finally, the crystalline product was washed with DMF and ethanol and dried at room temperature. The main difference with the synthetic route reported by Davidovich *et al.*¹ is that **Bi-2** crystals were obtained with higher quality denoted by an R factor of 0.031 (compared with a value of 0.0351 obtained previously). BiC₈H₁₁N₂O₈ (472.17 g·mol⁻¹): calcd. C 20.29, H 2.3, O 27.06, N 5.9 ; found C 20.5, H 2.21, O 26.88, N 5.62.

Synthesis of In-1: the compound ([In(IDA)(Cl)]) was obtained by mixing 0.5 mmoles of anhydrous InCl₃ (0.11 g) and 0.75 mmoles of H₂IDA (Sigma-Aldrich) (0.1 g) were mixed in 7 mL of water and 2 mL of ethanol. The mixture was kept under constant stirring for 30 minutes and then it was heated at 200 °C in a 43 mL Teflon-lined Parr reactor for 72 hs. After that period, the crystalline product was washed with distilled water and ethanol and dried at room temperature. As can be seen in Figure 1, twinned crystals of **In-1(a)** were obtained and no single crystals were isolated. Diring *et al.*² have demonstrated the increase of size and uniformity of diverse crystalline structures in HKUST-1 phases by the controlled addition of *capping* and *modulating agents*. Besides, Pham *et al.*³ studied the influence of the addition of pyridine in the formation of uniformed cube MOF crystals, which reinforces the use of amines as modulating agents. Reformulating the synthetic conditions of **In-1(a)**, big single crystals were obtained by adding a double function size-modulator such as 4,4'-bipyridine. In this case, 0.5 mmoles of InCl₃ and 0.75 mmoles of H₂IDA (Sigma Aldrich) were mixed into a clear solution of 7 mL of distilled water and 2 mL of ethanol containing 1 mmol of 4,4'-bipyridine (0.156 mmoles). The temperature was set at 180 °C, incrementing the reaction time to 96 h (Yield: 63% based on indium metal). InC₄H₅NO₄Cl (281.36 g·mol⁻¹): calcd. C 17.06, H 1.77, O 22.75, N 4.9 ; found C 17.12, H 1.73, O 22.96, N 4.81. The main difference with the synthetic route reported by Song *et al.*⁴ is that **In-1** crystals were obtained in less time (96 h respect to 168 h) increasing the temperature up to 180 °C.

Synthesis of Zn-1 ([Zn(1,2,4,5-BTC)_{0.5}(2,2'-bipyridine)(H₂O)]): the compound was obtained by a mixture of 1.5 mmoles of Zn(NO₃)₂·6H₂O (Sigma-Aldrich) (0.45 g), 1.5 mmoles (0.234 g) of 2,2'-bipyridine (Sigma-Aldrich) and 1 mmol of 1,2,4,5-benzenetetracarboxylic acid (Across Organics) (0.254 g) (Sigma-Aldrich) in 10 mL of water and 1 mL of ethanol. After 30 minutes of constant stirring at room temperature, the transparent solution was heated up at 150 °C in a 43 mL Teflon-lined Parr reactor for 72 h. Finally, the reactor was cooled down to room temperature. Colorless “block shape” crystals (Yield: 55% based on zinc metal) suitable for single-crystal X-ray diffraction were obtained (see SI section S4). After that, the crystalline product was washed with water and ethanol and dried at room temperature. The main difference between our synthetic approach and that reported previously⁵ is the employed less time and using ethanol to obtain suitable good quality crystals for SCXRD (reported in the present work). ZnC₁₅H₁₁N₂O₅ (364.63 g·mol⁻¹): calcd. C 49.36, H 3.02, O 21.94, N 7.7; found C 49.55, H 2.89, O 22.02, N 7.62.

Section S2: Vibrational analysis of **Bi-1**, **Bi-2**, **In-1** and **Zn-1**.

The interpretation of the FTIR spectra was performed to compare the internal vibrations of the organic groups to those observed in related compounds⁶. The corresponding assignment of bands is shown as follow: **Bi-1**: $\nu_{\text{as}}\text{COO}^-$ 1594 cm^{-1} , $\nu_{\text{s}}\text{COO}^-$ 1367 cm^{-1} , $\nu\text{C}=\text{O}$ (DMF) 1652 cm^{-1} , νNH (DMF) 1101 cm^{-1} , νCN (2,2'-bipyridine) 1496 cm^{-1} , $\nu\text{CH}_{\text{aromatic}}$ 3077 cm^{-1} , $\nu_3(\text{NO}_3^-)$ 1384 cm^{-1} . **Bi-2**: νNH 3207 cm^{-1} , νCH_2 3011 and 2987 cm^{-1} , $\nu_{\text{as}}\text{COO}^-$ 1590 cm^{-1} , $\nu_{\text{s}}\text{COO}^-$ 1366 cm^{-1} , $\nu\text{C}-\text{N}$ 1327 cm^{-1} . **In-1**: νNH 3309 cm^{-1} , νCOO^- 1413 cm^{-1} , $\nu\text{C}-\text{N}$ 1307 cm^{-1} . **Zn-1**: νCH 3105-3030 cm^{-1} , $\nu_{\text{as}}\text{COO}^-$ 1596 cm^{-1} , $\nu_{\text{s}}\text{COO}^-$ 1356 cm^{-1} , νCN (2,2'-bipyridine) 1494 cm^{-1} , $\rho(\text{OH})$ 1633 cm^{-1} .



Section S3: Thermal analysis.

To study the thermal properties, TGA and DSC experiments on **Bi-1**, **Bi-2**, **In-1** and **Zn-1** were carried out. Between parentheses are shown the calculated values.

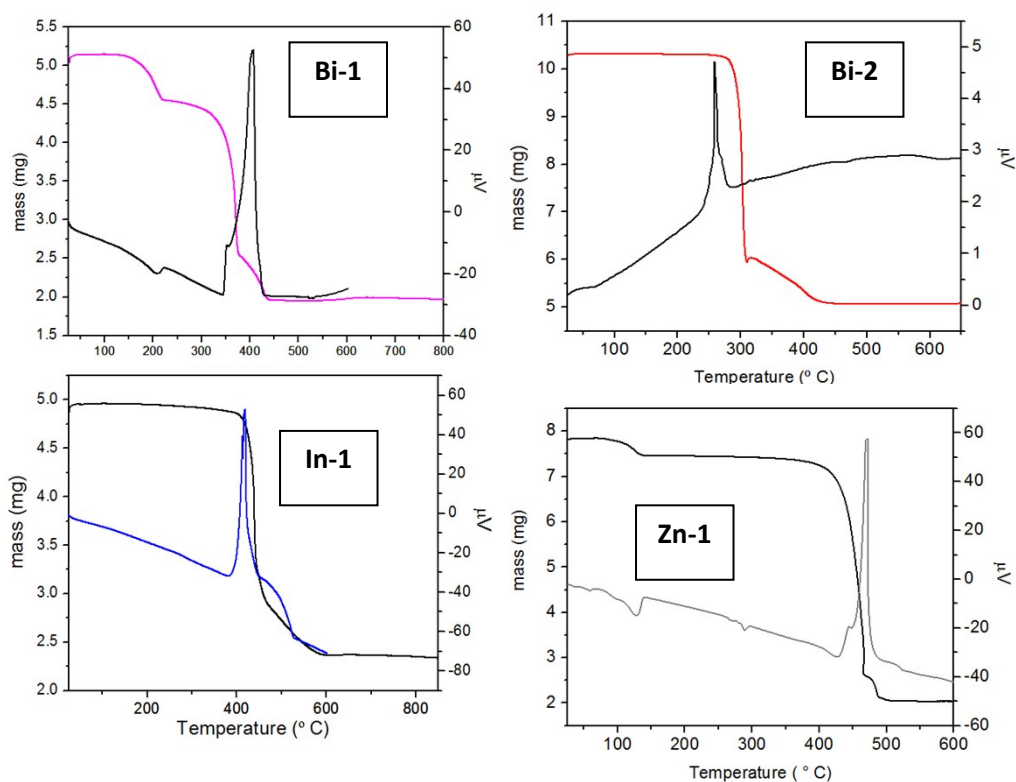
Bi-1, exhibits two thermal decomposition steps with weight loss of ca. 12.04 % (11.7 %) and 51.5 % (51.04 %). The first stage, due to DMF removal, is characterized with an endothermic peak in the DSC located at 207 °C. Moreover, the second step due to the total decomposition till Bi₂O₃ presents an exothermic peak in the DSC profile centered at 407 °C.

Bi-2, exhibits only one thermal decomposition step till Bi_2O_3 with a weight loss of ca. 50.93 % (52.3 %) characterized with an exothermic peak in the DSC located at 260 °C.

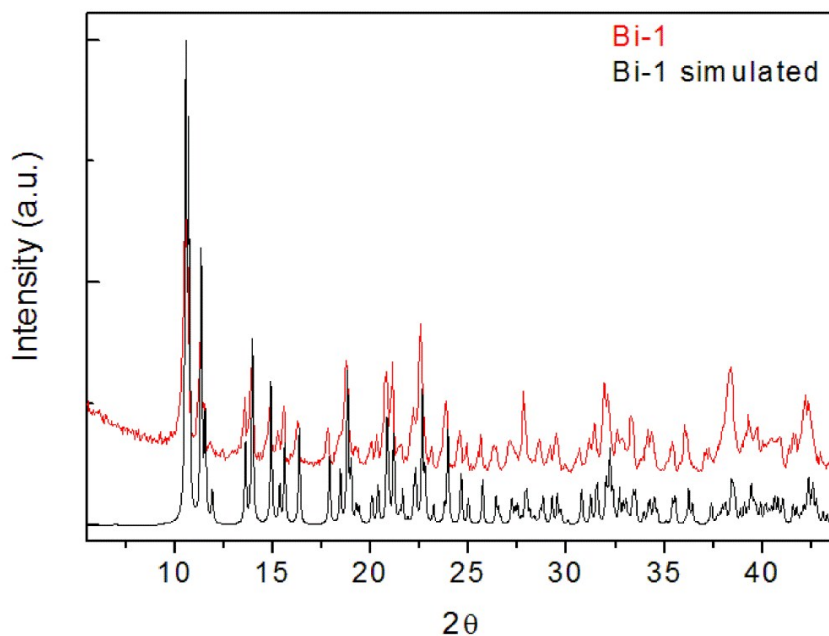
The TGA and DSC curves of **In-1** present a unique event denoted by a weight loss of 52.8 % (53.3 %), accompanied with an exothermic peak at 420 °C, demonstrating an important thermal stability till reaching total pyrolysis (In_2O_3 as final product). This result reveals an important thermal stability exhibited by **In-1** compound.

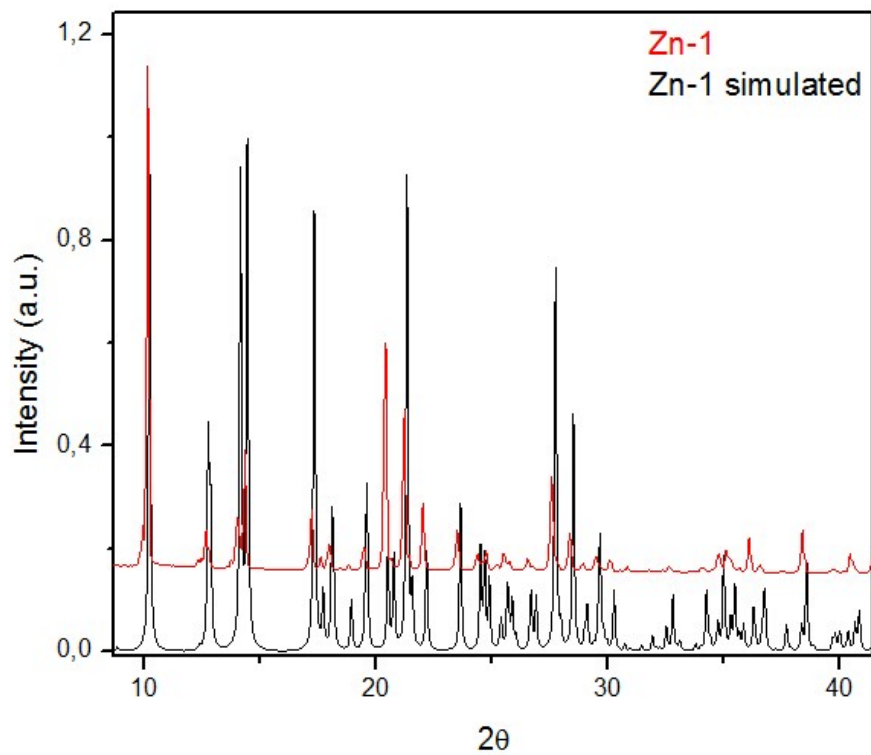
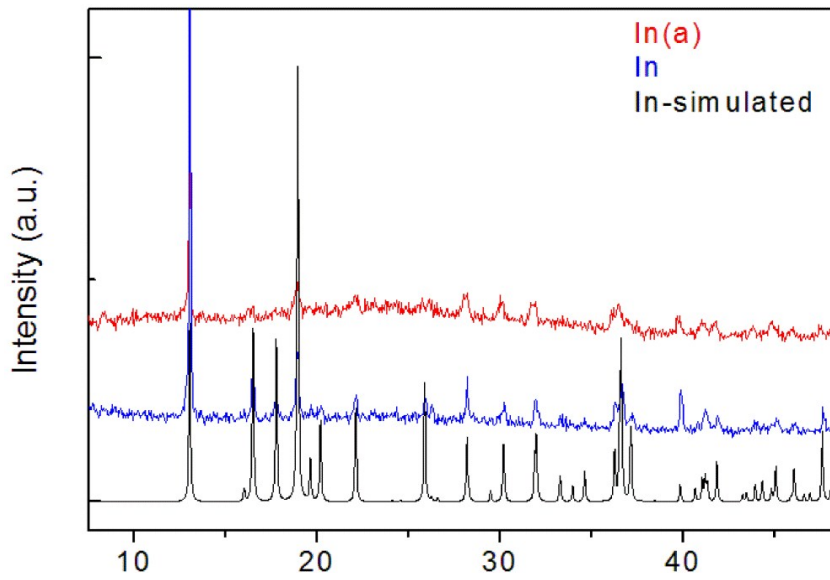
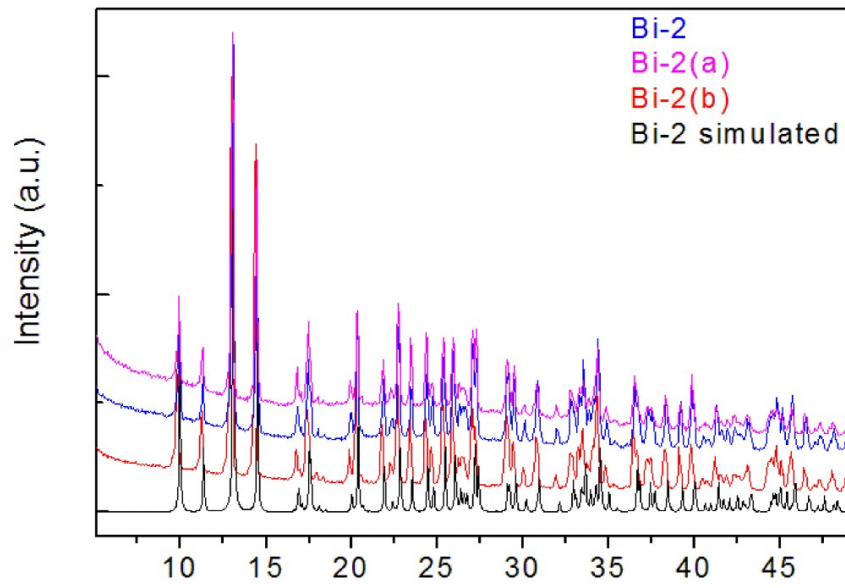
No evidence of phase transitions was found in the three compounds.

The TGA and DSC curves of **Zn-1** present two events denoted by a weight loss of 4.94 % (4.9 %) and 69.8 % (71.1 %). The first step, because of water removal, is accompanied with an endothermic peak located at 128 °C; meanwhile the second one, due to total decomposition (ZnO as final product), is characterized by an exothermic peak centered at 472 °C.

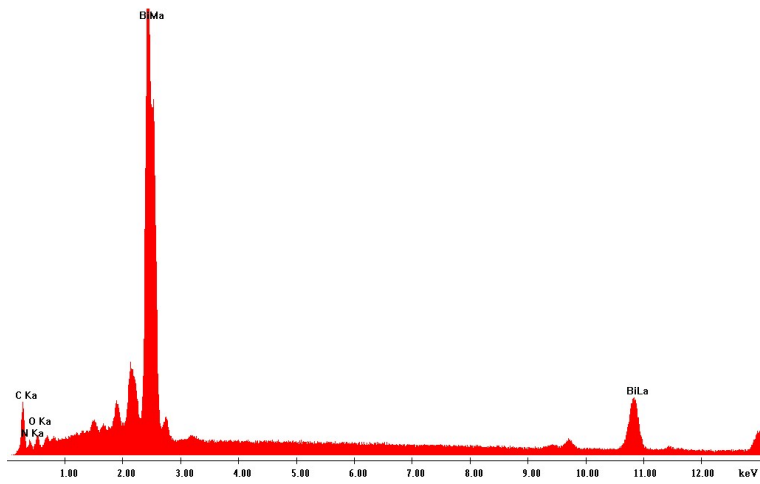
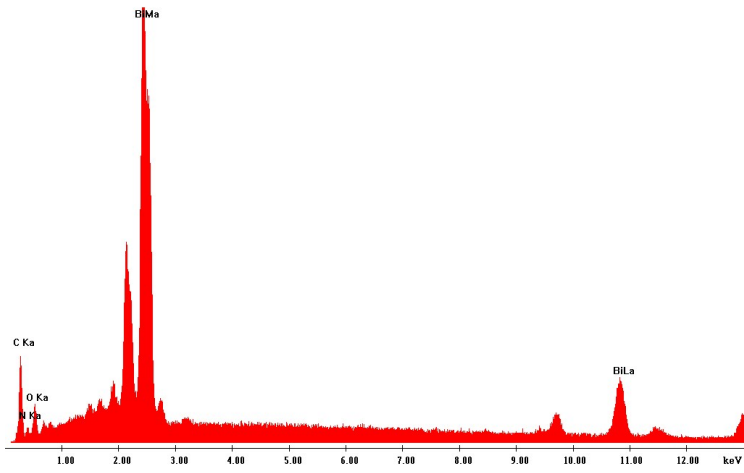


Section S4: PXRD patterns of **Bi-1**, **Bi-2**, **In-1** and **Zn-1** in comparison with their respective simulated profiles.





Section S5: EDS profiles of **Bi-1** (top) and **Bi-2** (down).

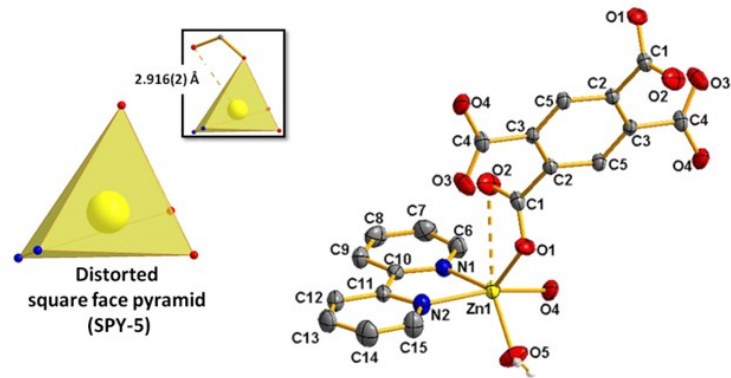


Section 6: Crystallographic data and refinement parameters for **Bi-1**, **Bi-2**, **Zn-1** and **In-1** compounds.

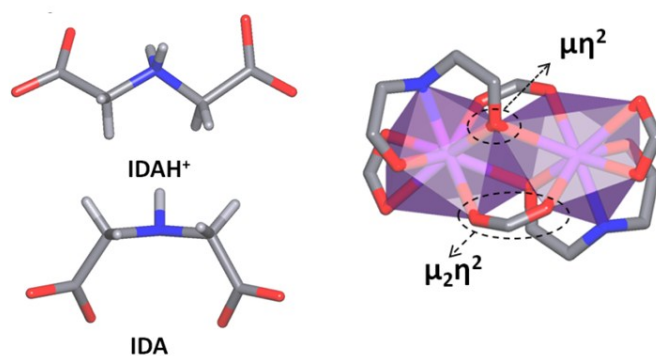
Compound	Bi-1	Bi-2	Zn-1	In-1
Empirical Formula	C ₁₈ H ₁₆ N ₄ O ₈ Bi	C ₈ H ₁₁ N ₂ O ₈ Bi	C ₁₅ H ₁₁ N ₂ O ₅ Zn	C ₄ H ₅ N ₄ O ₄ ClIn
FW (g·mol ⁻¹)	624.69	472.17	364.63	281.36
Temp. (K)	293	293	293	296
λ (Å)	0.71073			
Crystal system	Triclinic	Monoclinic	Triclinic	Orthorombic
Space Group	<i>P</i> $\bar{1}$	<i>C</i> 2/ <i>c</i>	<i>P</i> $\bar{1}$	<i>Pnma</i>
Unit cell				
<i>a</i> (Å)	9.3852(6)	18.337(5)	7.6958(6)	13.5719(4)
<i>b</i> (Å)	9.6474(7)	12.223(3)	8.8864(7)	8.7940(3)
<i>c</i> (Å)	13.4442(9)	10.707(3)	10.6748(9)	6.0584(2)
α (°)	72.378(6)	90	80.941(7)	90
β (°)	74.943(6)	104.479(9)	70.420(8)	90
γ (°)	62.844(7)	90	78.138(7)	90
Volume (Å ³)	1021.6(1)	2323.6(1)	670.01(10)	723.08(4)
Z	2	8	2	2
ρ calcd (mg·m ⁻³)	2.031	2.700	1.808	1.292
Abs.Coeff (mm ⁻¹)	8.683	15.217	1.863	1.800
F(000)	597	1760	370	268
θ range (°)	1.6-34.3	2.0-27.3	2.8-34.3	3.0 to 27.5
Reflections collected /	15325/7804	12026/2604	10016/5108	3412/878
Unique [R(int)]	[0.042]	[0.061]	[0.034]	[0.016]
Completeness (%)	91.3	99.5	91.5	99.4
Data / restraints	7804/0/288	2604/0/172	5108/0/216	878/0/55
/ parameters				
Gof on F ²	1.03	1.06	1.03	1.098
R1 [I>2σ(I)]	0.0416	0.0312	0.0421	0.0136
wR2 [I>2σ(I)]	0.0766	0.0734	0.0931	0.0360

Section S7: Crystalline description of **Zn** compound.

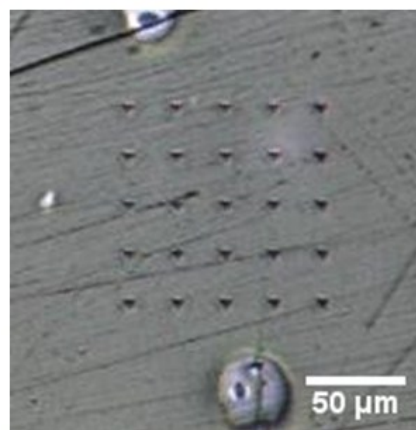
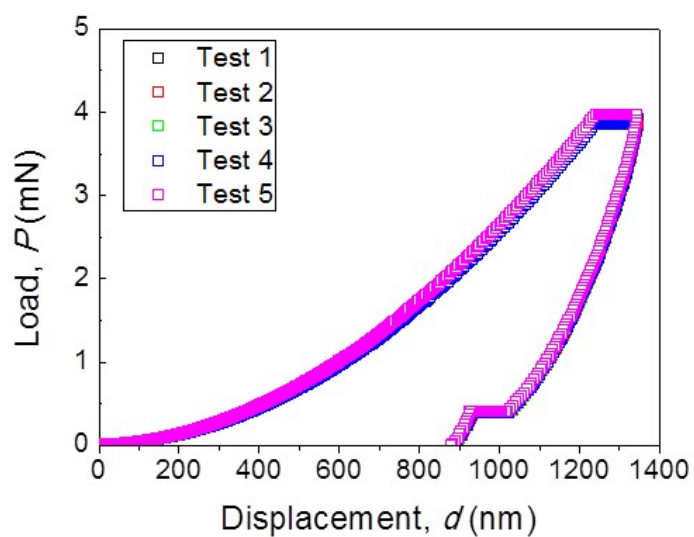
The crystal structure of **Zn** is formed by one divalent Zn atom, one 1,2,4,5-BTC, one 2,2'-bipyridine and one crystallographically independent water molecule. The coordination sphere is formed by two nitrogen atoms of the 2,2'-bipyridine, two oxygen atoms from the ligand and one water molecule forming a distorted square-face pyramid arrangement (SPY-5). In this structure, the distance Zn1-O2 = 2.916(2) Å and the angle Zn1-O2-C1 = 71.08° are not in agreement with the tendency observed for this type of bonds (Figure 3). A search in the CCDC database show that a normal Zn-O distances and Zn-O-C angles ranging between 1.761-2.761 Å and 73.51-135.52°, respectively.



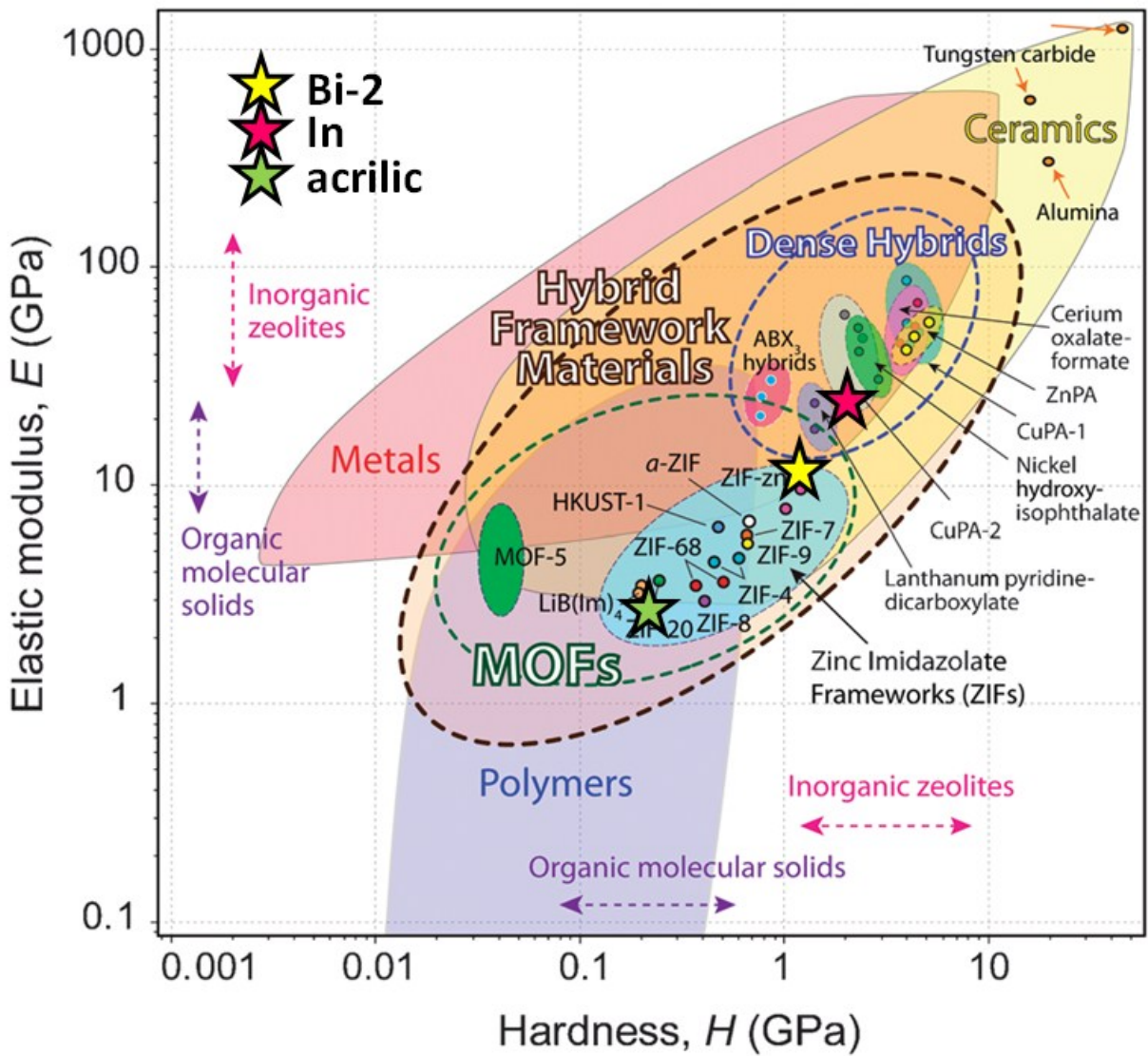
Section S8: Coordination polyhedra (left) and coordination modes of the IDA ligand in **Bi-2** (right).



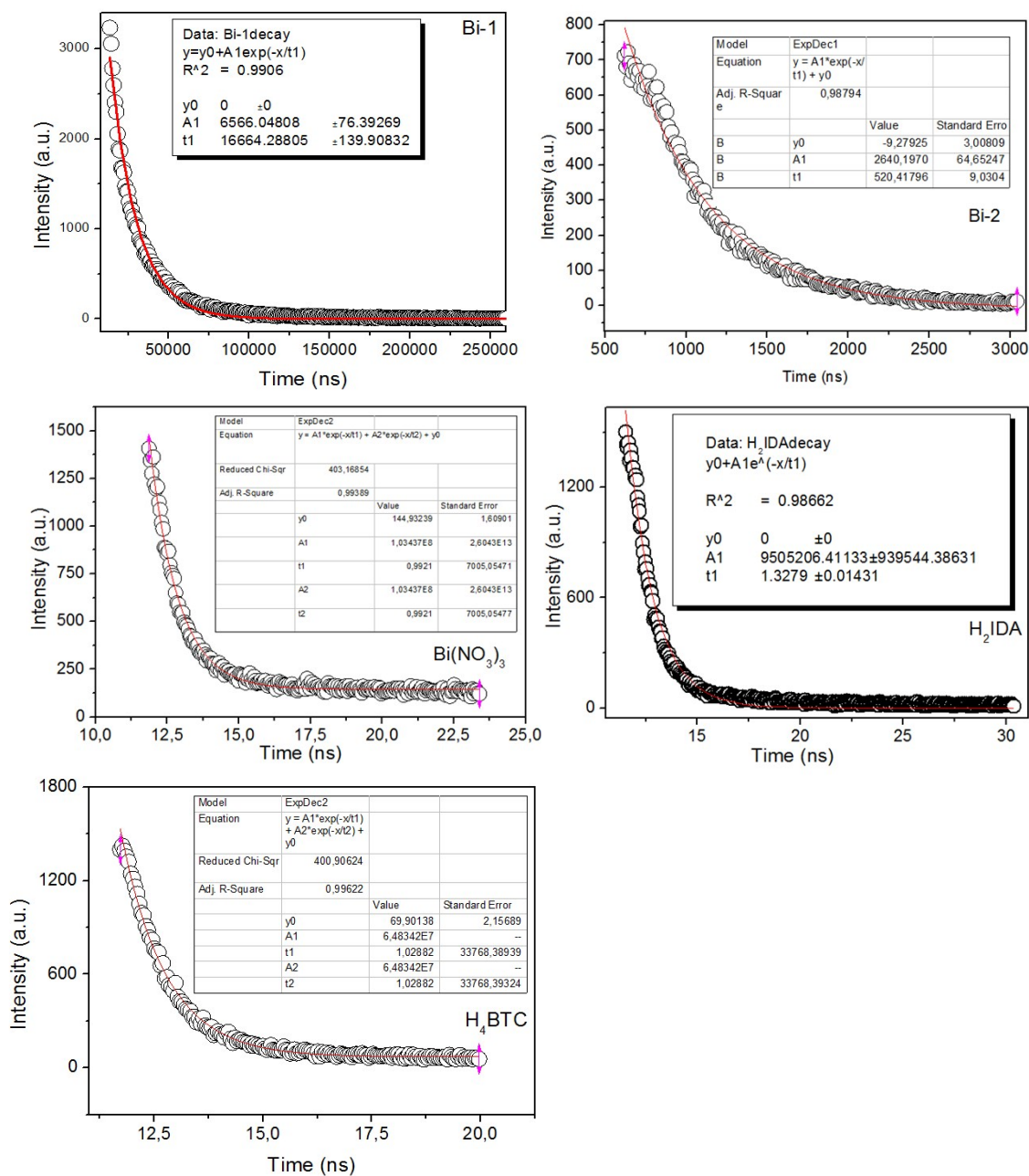
Section S9: Fifteen consecutive *P-h* profiles of the acrylic without crystals (left), and optical micrograph of the corresponding indented acrylic (right).



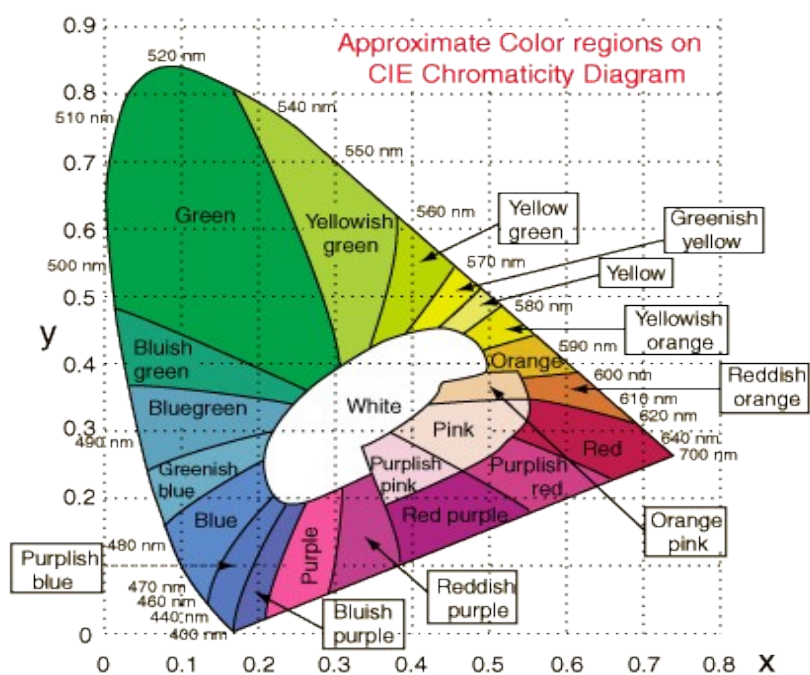
Section S10: Young's modulus vs hardness for different materials⁴¹ The E and H values from **Bi-2**, **In-1** and the acrylic are included in comparison with other CP and MOFs-type materials



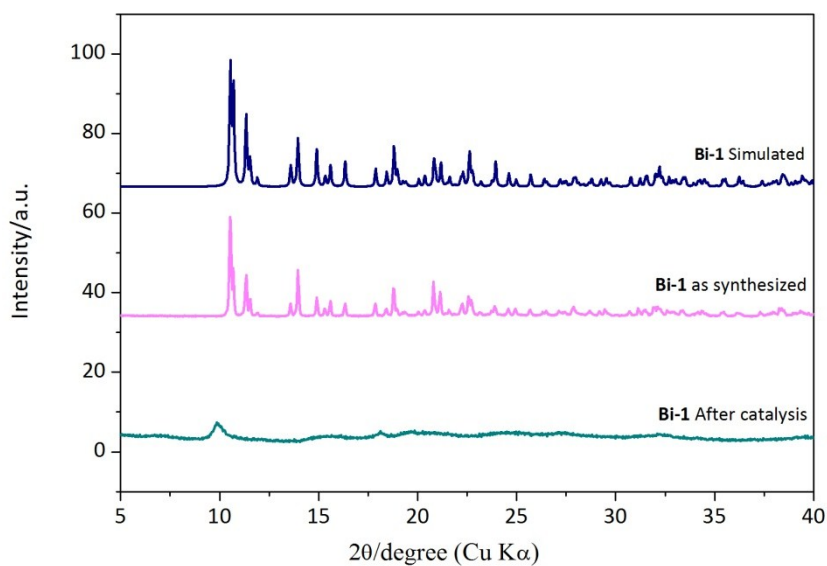
Section S11: Decay luminescence profiles of **Bi-1**, **Bi-2**, $\text{Bi}(\text{NO}_3)_3$, H_2IDA and H_4BTC (the red lines show the best exponential fit in both cases).

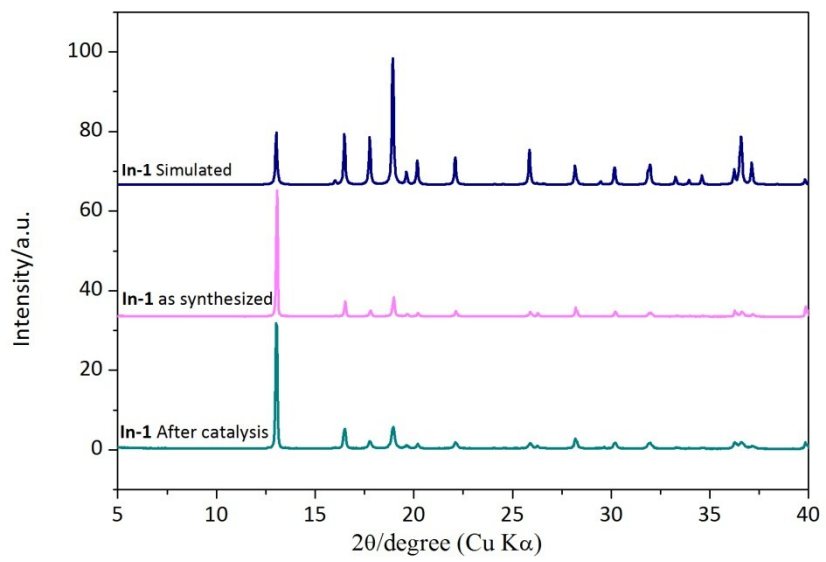
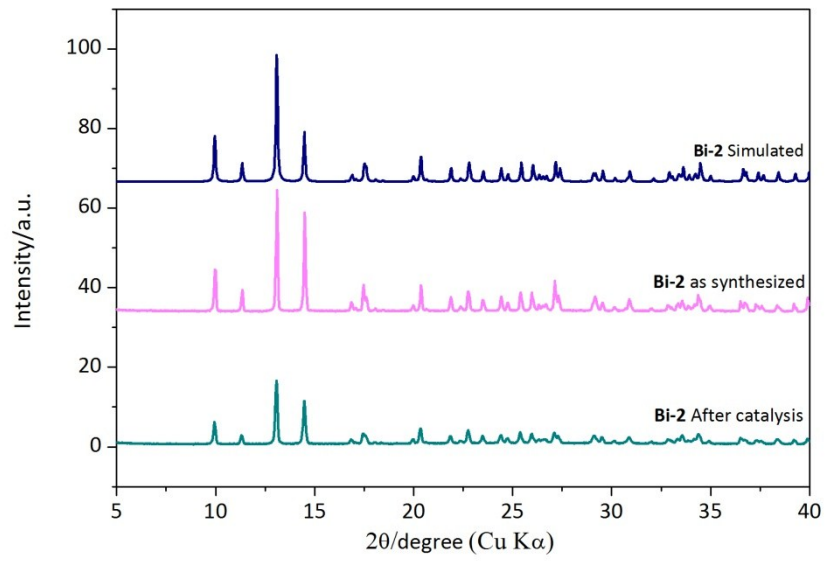


Section S12: Classic Bidimensional CIE 1931 diagram for color assignation.

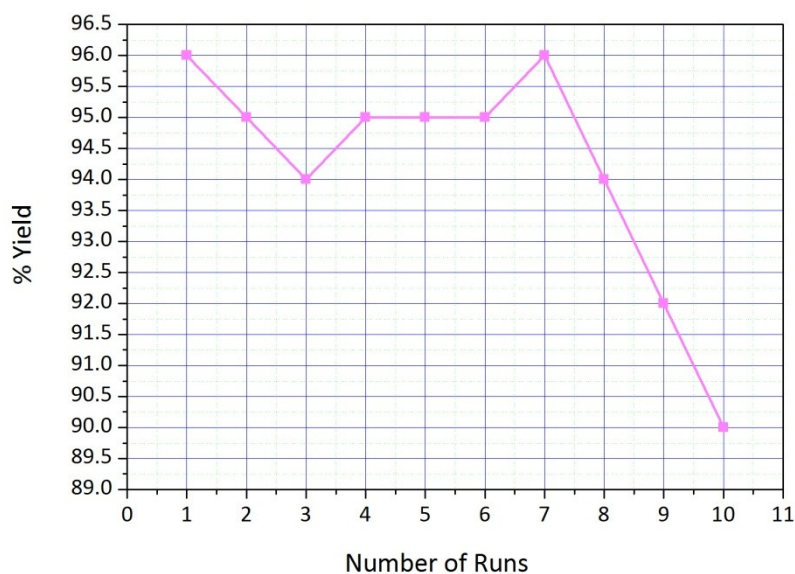


Section S13: PXRD patterns of **Bi-1**, **Bi-2** and **In-1** as synthesized and after catalytic reactions.





Section S14: Catalysis recyclability test using In-1 material.



References

- ¹ R. L. Davidovich, A. V. Gerasimenko, V. B. Logvinova, *Russ. J. Inorg. Chem.*, **2001**, 46(8), 1178-1183 .
- ² S. Diring, S. Furukawa, Y. Takashima, T. Tsuruoka, S. Kitagawa, *Chem. Mater.*, **2010**, 22, 453-4538.
- ³ M.-H. Pham, G.-T. Vuong, F.-G. Fontaine, T. O. Do, *Cryst. Growth Des.*, **2012**, 12, 3091-3095.
- ⁴ R.-F. Song, J. Yang, Q. Zhong, M.-Y. Sun, *Chinese J. Struct. Chem.*, **2011**, 30 (8), 1127-1131.
- ⁵ Xu, X.; Lu, Y.; Wang, E.; Ma, Y.; Bai, X., *J. Mol. Struct.*, **2006**, 825, 124-129.
- ⁶ K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons Inc., USA, **1997**.
- ⁷ Powder X-ray diffraction (PXRD) patterns were measured with a Bruker D8 diffractometer, with step size = 0.02 ° and exposure time = 0.5 s/step. PXRD measurements were used to check the crystalline preservation of materials by comparison of the experimental results with the simulated patterns obtained from single-crystal X-ray diffraction data.