

A New Water Stable Zinc Metal Organic Framework as an Electrode Material for Hydrazine Sensing

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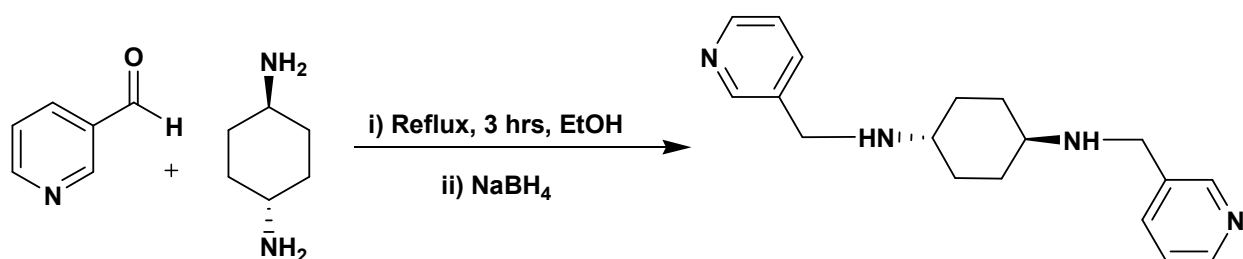
Supporting Information

Materials and Methods

Chemicals. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, Terephthalic acid (bdc), all reagents and solvents were purchased from Aldrich. These chemicals were used without further purification unless otherwise mentioned.

Synthesis of N,N' -bis(pyridin-3-ylmethyl)cyclohexane-1,4-diamine

3-Pyridylcarboxylaldehyde (5g, 46.68 mmol) and (1r,4r)-cyclohexane-1,4-diamine (5.33g, 46.68 mmol) were added in ethanol (30 mL). Then, triethylamine (7.08g, 70.02 mmol) was added slowly and refluxed for 4 hrs. Monitored the completion of reaction with TLC and first cooled down the reaction mixture to room temperature followed by further reduction in temperature in ice bath. Portion wise addition of NaBH_4 (4.41g, 116.7 mmol) was carried out and then allowed the stirring of reaction content for overnight at room temperature. 10 mL of water was added to quench the extra reducing agent While 40 ml of dichloromethane was added and separated the organic layer. Repeated the extraction with DCM and combined the organic layers. Dried by organic solvent by using anhydrous Na_2SO_4 and got the desired product by evaporating the solvent by rotary evaporated (yield = 70%).



Synthesis of precursor metal-organic framework (MOF). $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.297 g, 1.0 mmol), N,N' -bis(pyridin-3-ylmethylene)cyclohexane-1,4-diamine (3-bpcda) (0.297 g, 1.0 mmol) and H_2bdc (0.172 g, 1.0 mmol) were added in DMF / H_2O (10 mL, v/v: 3/1). The reaction mixture were placed in glass vial and heated at 105 °C for 72 h. Structures of both the ligands are shown in scheme 1S. Yellow block-shaped crystals of Zn-MOF were collected and washed with DMF three time (10 MI). The final product were dried in air at room temperature and used for further studies.

X-ray Crystallography

For Zn-MOF single crystal X-ray diffraction data were collected on an Oxford Diffraction Gemini CCD diffractometer employing $\text{Cu K}\alpha$ radiation (1.54180 Å) and operating in the ω -scan mode. Data reduction and empirical absorption corrections (multi-scan) were performed with Oxford Diffraction CrysAlisPro software Version 1.171.37.35. WINGX program suite was used to solve and refine the structure [1]. The structure was solved by direct methods with SIR-97 [2] and refined by full-matrix least-squares analysis with SHELXL97 [3].

Non-hydrogen atoms were refined with anisotropic thermal parameters, whereas H-atoms were included at estimated positions. Figure 1a of the compound 1 was produced with ORTEP3 [4]. A summary of the crystal data, structure solution and refinement parameters are given in Table 1S and selected bond lengths and angles are given in Table 2S. Asymmetric unit and unit cell structures are presented in Figures 1S, 2S and 3S.

Elemental Analysis and FT-IR spectroscopy

Elemental analyses were performed on Perkin Elmer Series 11 (CHNS/O), Analyzer 2400. The solid state FT-IR spectra of the ligands and their Zn(II) MOF were recorded on a Perkin-Elmer FT-IR 180 spectrophotometer or NICOLET 6700 FT-IR using KBr pellets over the range 4000-400 cm^{-1} .

The CHN elemental analyses results matched well with the calculated results. Anal. Calc. for $\text{C}_{13}\text{H}_{18}\text{N}_2\text{O}_4\text{Zn}_{0.50}$: C 52.22, H 6.07, N 9.37%. Found; C 52.37, H 6.25, and N 9.77%.

FT-IR spectra of Zn-MOF displayed characteristic stretching and absorption bands (Figure 4S), around 3303 (broad) and 1600 cm^{-1} due to the water and N-H stretching (secondary amine) of ligand 3-bpcda and carboxylate group of bdc ligand respectively (Table 3S). In addition, the characteristic C-H stretching for aromatic and aliphatic functional groups at 3005 and 2914 cm^{-1} , respectively [5-7]. The FT-IR spectra and elemental analysis are consistent with the single crystal X-ray structure of Zn-MOF.

NMR Spectroscopy

^1H and ^{13}C NMR spectra were recorded on a LAMBDA 500 spectrophotometer operating at 500.01, 125.65 and 200.0 MHz respectively; corresponding to a magnetic field of 11.74 T. Tetra-methylsilane (TMS) was used as an internal standard for ^1H and ^{13}C NMR measurements. The ^{13}C NMR spectra were obtained with ^1H broadband decoupling, and the spectral conditions were: 32 k data points, 0.967 s acquisition time, and 1.00 s pulse delay and 45° pulse angle. The ^1H and ^{13}C NMR chemical shifts are given in Tables 4S and 5S respectively. The appearance of chemical shifts for N-H (Amine), C=O (Carbonyl), Ph (Phenyl), Cy (Cyclohexyl), $-\text{CH}_2-$ (Methylene) and Py (Pyridyl) groups of both ligands in ^1H and ^{13}C NMR spectra of compound **1** is consistence with single crystal X-ray structure.

Table 1S: Crystal data and structure refinement details of Zn-MOF.

Crystal data	
Empirical formula	$\text{C}_{18}\text{H}_{30}\text{N}_4\text{O}_4\text{Zn}$
Formula weight	298.98
Crystal system, space group	Triclinic, P-1'
Temperature (K)	190
a, b, c (\AA)	8.2199 (9), 8.3508 (10), 11.2244 (13)
α, β, γ ($^\circ$)	86.85 (1), 78.01(1), 66.22 (1)
V (\AA^3)	689.30 (15)
Z	2
Radiation type	Mo $\text{K}\alpha$
μ (mm^{-1})	0.95

Crystal size (mm)	0.3 × 0.1 × 0.1
Absorption correction	Multi-scan
T_{min}, T_{max}	0.971, 1.000
No. of measured, independent and observed	5198, 3117, 2600
[$I > 2\sigma(I)$] reflections	
R_{int}	0.031
$(\sin \theta/\lambda)_{max}$ (\AA^{-1})	0.686
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.040, 0.079, 1.04
No. of reflections	3117
No. of parameters	250
$\Delta\rho_{max}, \Delta\rho_{min}$ ($e \text{\AA}^{-3}$)	0.4, -0.43

Table 2S: Selected bond lengths (\AA) and bond angles ($^\circ$) of Zn-MOF.

Bond length(\AA)		Bond angles ($^\circ$)	
Zn1 -O1	2.106 (1)	O1 -Zn1 -O3	86.30 (5)
Zn1 -O3	2.131 (1)	O1 -Zn1 -O3 ⁱ	93.70 (7)
Zn1 -N1	2.149 (1)	O1 -Zn1 -N1	88.11 (3)
		O3 -Zn1 -N1	93.27 (7)
		N1 -Zn1 -N1 ⁱ	180.00

Table 3S: Selected mid-IR frequencies (cm^{-1}) of free ligands and Zn-MOF.

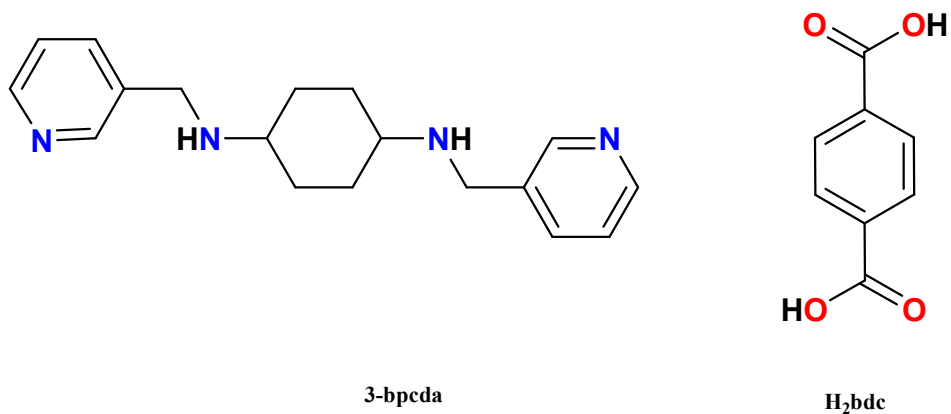
Species	$\nu(\text{C}=\text{O})$	$\nu(\text{N}-\text{H})$	$\nu(\text{C}-\text{H})_{\text{aromatic}}$	$\nu(\text{C}-\text{H})_{\text{aliphatic}}$
1,4-bdc and 3- bpcda	1705.8	3335.2, 743.8	3055.7, 3029.8	2928.5, 2856.1
Zn-MOF	1594.6	3305.8, 748.6	3005.8	2914.0

Table 4S: ^1H chemical shifts (ppm) of the Zn-MOF in DMSO- d_6 .

N-H	-CH ₂ -	Cy	Py	Ph
5.35	4.36	3.00, 3.39, 3.65	8.69, 9.25	9.68

Table 5S: ^{13}C chemical shifts (ppm) of Zn-MOF in DMSO-d_6 .

C=O	-CH ₂ -	Cy	Py	Ph
153.05	48.57	29.48, 55.37	127.75, 141.88	130.18



Scheme 1S. Structures of N,N'-bis(pyridin-3-ylmethylene)cyclohexane-1,4-diamine (3-bpcda) and benzene dicarboxylic acid (H₂bdc) linkers used in this work.

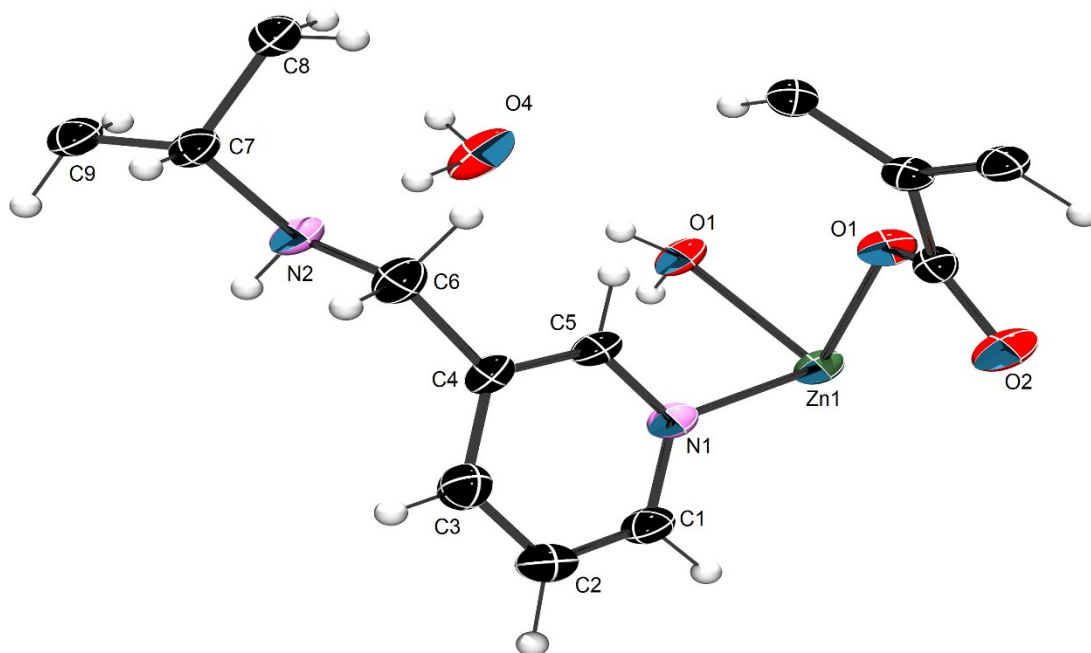


Figure 1S: A view of asymmetric unit of X-ray structure of Zn-MOF. Hydrogen atoms were omitted for clarity of structure.

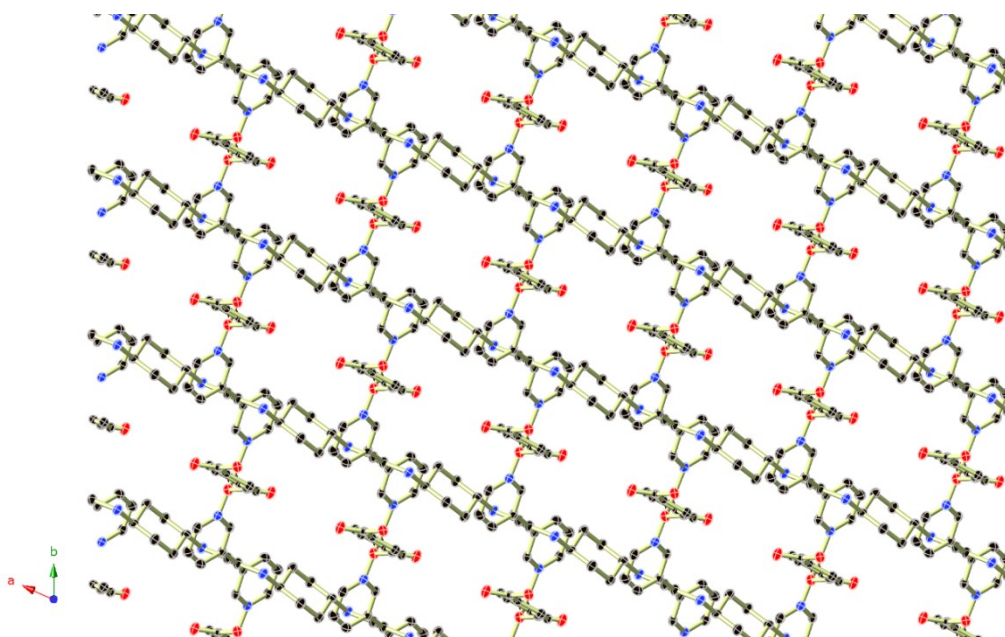


Figure 2S: A view of the three-dimensional extended structure of Zn-MOF. The displacement ellipsoids are drawn at the 50% probability level.

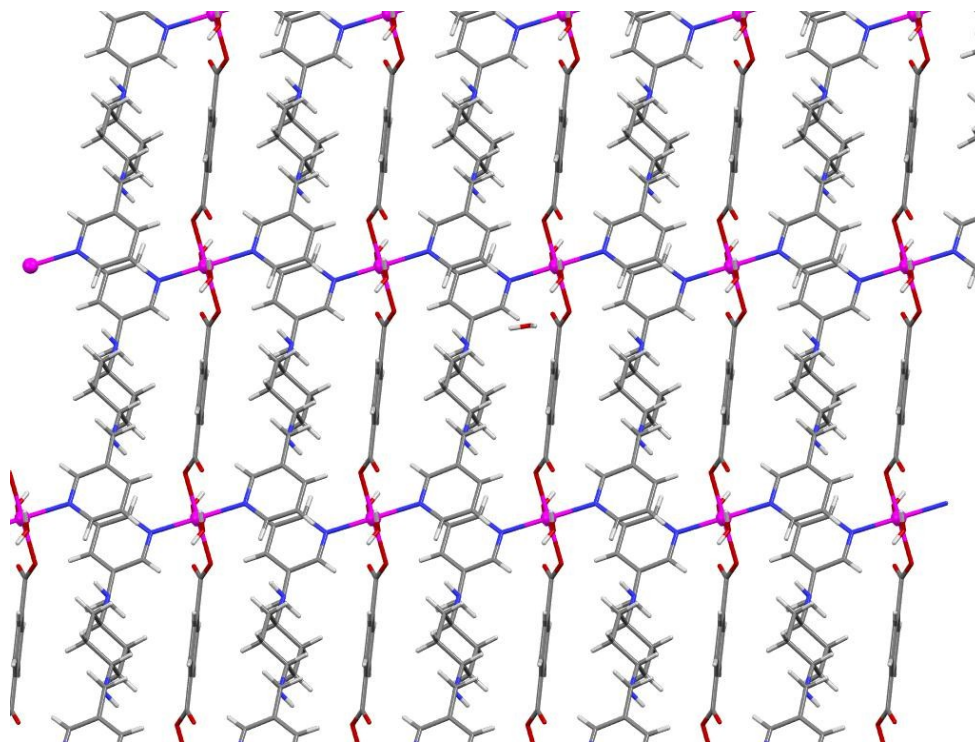


Figure 3S: A view of two-dimensional framework of Zn-MOF along *a*-axis.

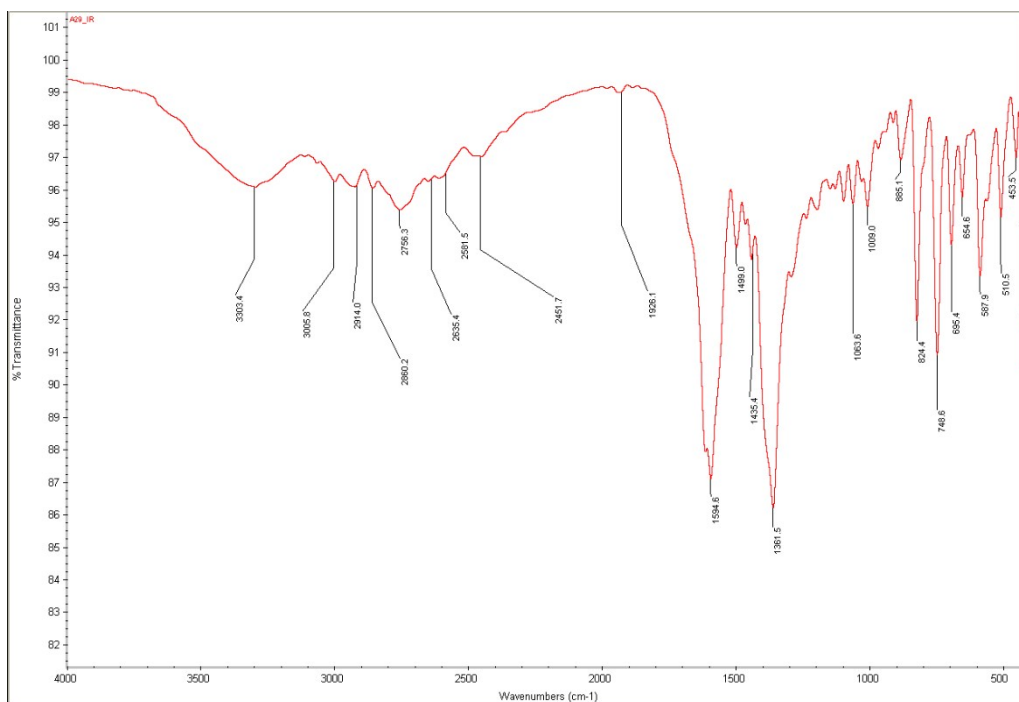


Figure 4S. IR spectrum of Zn-MOF.

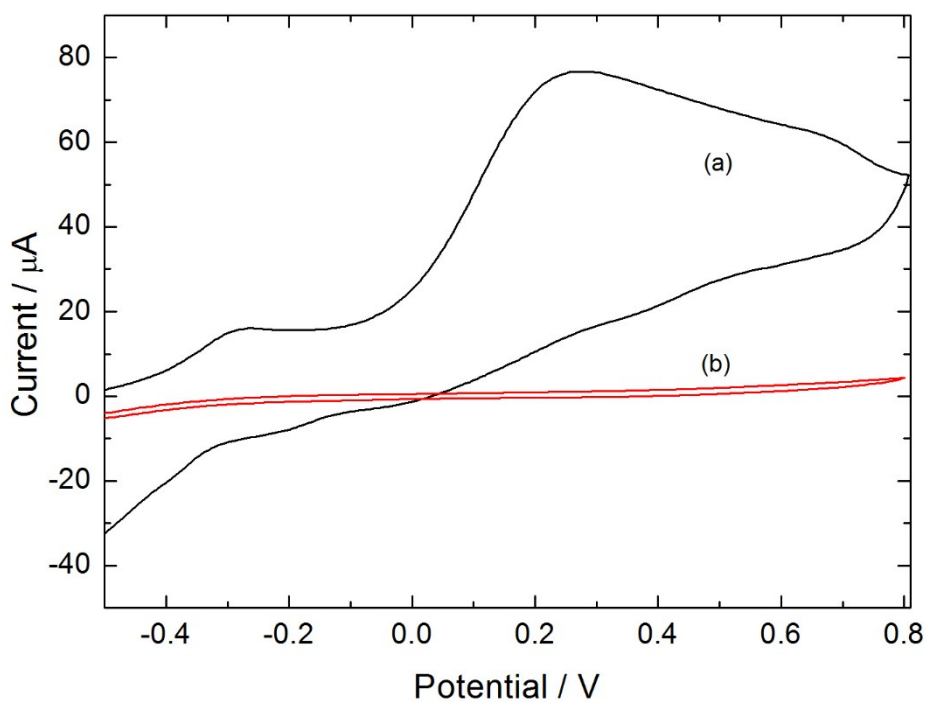


Figure 5S. The CV response with ZnMOF/ETH500/nafion modified GCE for (a) 0.350 mM hydrazine in 0.1 M K₂SO₄ solution, scan rate 50 mV /s and (b) in absence of hydrazine.

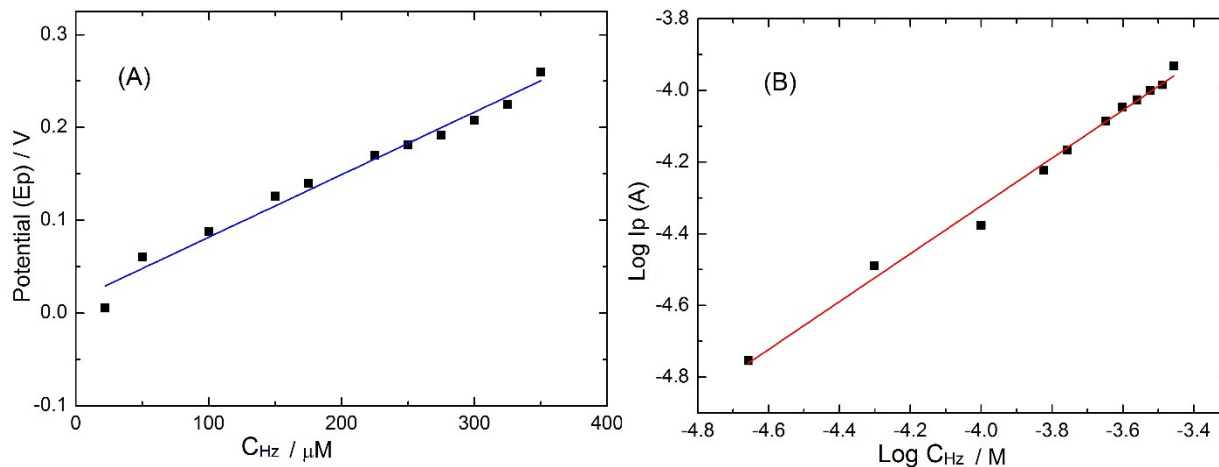


Figure 6S. (A) Plots between change in E_p (potential for maximum oxidation peak current) with change in hydrazine concentration and (B) change in log of I_p with log of hydrazine concentration ($\text{log } C_{Hz}$).

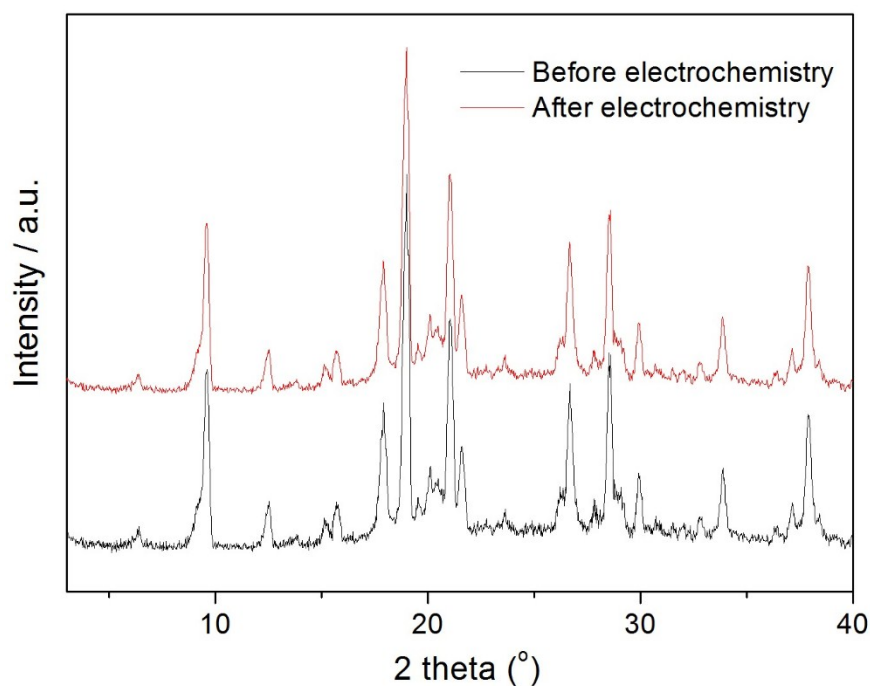


Figure 7S. PXRD patterns of ZnMOF/ETH500/nafion modified FTO electrode before and after electrochemical experiments for 0.350 mM of hydrazine in 0.1 M K_2SO_4 .

References

- [1] L.J. Farrugia, WinGX suite for small-molecule single-crystal crystallography, *Journal of Applied Crystallography*, 32 (1999) 837-838.
- [2] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, A.G. Moliterni, G. Polidori, R. Spagna, SIR97: a new tool for crystal structure determination and refinement, *Journal of Applied Crystallography*, 32 (1999) 115-119.

- [3] G.M. Sheldrick, A short history of SHELX, *Acta Crystallographica Section A: Foundations of Crystallography*, 64 (2008) 112-122.
- [4] S. Weber, XRDIF: Simulation of X-ray diffraction patterns, *Journal of Applied Crystallography*, 30 (1997) 565-566.
- [5] H.-J. Hao, F.-J. Liu, H.-F. Su, Z.-H. Wang, D.-F. Wang, R.-B. Huang, L.-S. Zheng, Syntheses, structures and fluorescence of two coordination complexes of Zn (II) and 1, 3-bis (2-methylimidazolyl) propane: solvent effect, *CrystEngComm*, 14 (2012) 6726-6731.
- [6] D.K. Maity, B. Bhattacharya, R. Mondal, D. Ghoshal, Five diverse bivalent metal coordination polymers based on benzene dicarboxylate and bent dipyriddy ligands: syntheses, structures, and photoluminescent properties, *CrystEngComm*, 16 (2014) 8896-8909.
- [7] W.-G. Yuan, F. Xiong, H.-L. Zhang, W. Tang, S.-F. Zhang, Z. He, L.-H. Jing, D.-B. Qin, Syntheses, structures and luminescent properties of six divalent metal terephthalate coordination polymers based on three new flexible bis (imidazole) ligands, *CrystEngComm*, 16 (2014) 7701-7710.