Formation of Trigons in a Metal-Organic Framework: The Role of Metal-Organic Polyhedron Subunits as Meta-Atoms

Jiyoung Lee[†], Jae Sun Choi[‡], Nak Cheon Jeong[‡] and Wonyoung Choe[*,†]

[†]Department of Chemistry, Ulsan National Institute of Science and Technology, Ulsan 44919, Korea

[‡]Department of Emerging Materials Science, Daegu Gyeongbuk Institute of Science and Technology, Daegu 42988, Korea

*Corresponding authors choe@unist.ac.kr

Materials and instrumentation

1,4-diazabicyclo[2.2.2]octane (dabco) (Sigma-Aldrich), $Cu(NO_3)_2 \cdot 2.5H_2O$ (Sigma-Aldrich), and $Zn(NO_3)_2 \cdot 6H_2O$ (JUNSEI) were used without further purification. 2,7-Naphthalenedicarboxylate (NDC) was obtained from dimethyl 2,7-Naphthalenedicaroxylate by hydrolyzing with THF/MeOH/20 % KOH solution at 50 ˚C.

Chloroform, and 99.0 % of dimethyl sulfoxide (DMSO) were obtained from JUNSEI and 99.5% of *N,N*-dimethylformamide (DMF) were obtained from JUNSEI.

A single crystal of Zn/Cu-UMOM-10 coated with paratone-N oil and the diffraction data were collected at 100 K with ADSC Quantum-210 detector at 2D SMC with a silicon (111) DCM at the Pohang Accelerator Laboratory, Korea. The ADSC Q210 ADX program[1] was used for data collection, and HKL3000[2] was used for cell refinement, reduction, and absorption correction. All crystal structures were solved by the directed method and were refined by full-matrix least-squares calculations using the SHELXL program package[3].

Powder X-ray diffraction data was obtained from Bruker D2 phaser. Inductively coupled plasma **(**ICP) analysis was performed on Varian 700-ES. Field emission scanning electron microscopy (FE-SEM) images were obtained from Hitachi S-4800 at an acceleration voltage of 5 kV. Raman spectra were recorded using a Nicolet Almega XR dispersive Raman spectrometer (Thermo Scientific). Excitation of the samples was performed by focusing a 0.5 mW and 532 nm of wavelength laser beam on a crystal with a 10× magnifying objective lens. Gas sorption isotherm was performed on Micromeritics ASAP 2020 instrument. Pore size distributions were obtained using oxide surface cylindrical model with a N_2 isotherm. Focused ion beam (FIB) SEM images were obtained from FEI Helios 4850 HP and the FIB milling was performed with Ga ion beam. Mercury porosimetry data were obtained from AutoPore IV

9500, after activation process during 12 hours under vacuum at room temperature. Pore size distributions in macropore range (50-5000nm) were obtained from Hg isotherm.

Synthesis of Zn-UMOM-10. A 1 mL of 97.5% of DMF (20μL of distilled water in 1mL of 99.5% DMF) solution of $Zn(NO_3)_2 \cdot 6H_2O$ (57.8 mg, 0.194 mmol) was mixed with a 97.5% of DMF (1.0 mL) solution of 2,7-NDC (42.4 mg, 0.196 mmol) in a capped vial (16 ml). After mixing, dabco (11.2 mg, 0.1 mmol) was added to this solution and then sonicated. Clear solution was obtained after centrifuge and the resulting solution was heated at 115 °C for 12h, then cooled at 80 °C for 4 h, 60 °C for 30 h, and 30 °C. After reaction, decanting the solution and then allowed the vial stand at room temperature. After few hours, colorless crystals were crystallized.

Synthesis of Zn/Cu-UMOM-10. The as-synthesized Zn-UMOM-10 was immersed in the 0.1 M $Cu(NO_3)_2 \cdot 2.5H_2O$ solution with 5 mL of DMF and then left to react at room temperature. After 2 days, blue crystals were obtained.

Synthesis of Zn/Cu-UMOM-10-ce. A DMF (1.0 mL) solution of $Zn(NO_3)_2 \cdot 6H_2O$ (57.8 mg, 0.194 mmol) was mixed with a DMF (1.0 mL) solution of 2,7-NDC (42.4 mg, 0.196 mmol). After mixing, dabco (11.2 mg, 0.1 mmol) was added to this solution and then sonicated. Clear solution was obtained after centrifuge and the resulting solution was heated at 115 °C for 12h, then cooled at 80 °C for 4 h, 60 °C for 30 h, and 30 °C. After reaction, decanting the solution and then allowed the vial stand at room temperature until few hundred microns size of colorless crystals was crystallized. The as-synthesized crystals were immersed in the 3.0 mL of DMSO/98.5% of DMF (10μL of distilled water in 1mL of 99.5% DMF) mixture (v:v=3:1)

solution for a 7, 12 and 24 h. After that, collected crystals were immersed in 0.1 M $Cu(NO_3)_2 \cdot 2.5H_2O$ solution with 5 mL of DMF and then left to react at 30 °C. After 2 days, blue crystals were collected.

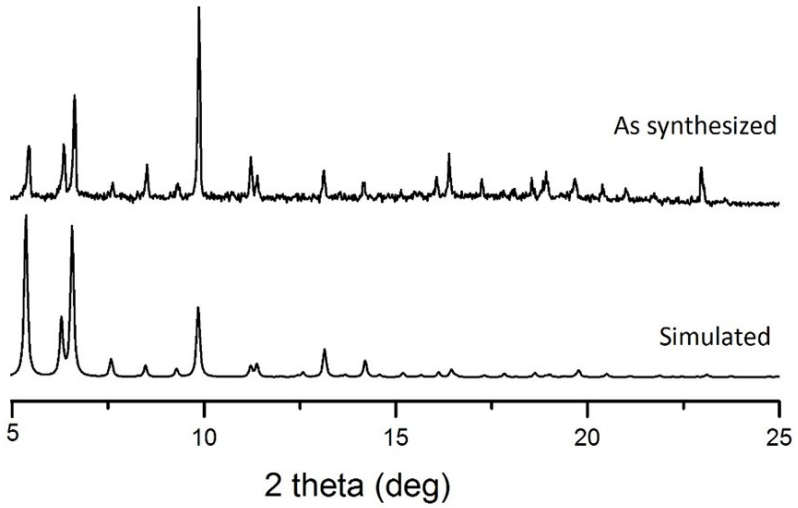

Figure S1. The as synthesized (top) and simulated (bottom) powder X-ray diffraction patterns of Zn-UMOM-10.

Table S1. Crystal data for Zn/Cu-UMOM-10

Complex	Zn/Cu-UMOM-10
Empirical formula	$C_{324}\,H_{228}\,N_{12}\,O_{108}\,Zn_{12}\,Cu_{12}$
Formula weight	7564.09
Crystal system	Cubic
Space group	*Fm-3m*
a (Å)	46.455(5)
b (Å)	46.455(5)
c (Å)	46.455(5)
V (Å^3)	100252(35)
Z	4
ρ_{calc} (g/cm^3)	0.501
μ (mm^{-1})	0.536
R_1, $I > 2\sigma(I)$	0.0663
wR_2, $I > 2\sigma(I)$	0.2289

Table S2. Paddlewheel conformation comparison

	ZND[4]	Zn/Cu-UMOM-10	UMOM-2[5]
d_{MM}	2.93Å	2.74Å	2.67Å
d_{MN}	2.04Å	2.03Å	2.18Å
θ_1	128.08˚	128.34˚	122.95 ˚
θ_2	127.70˚	123.53 ˚	123.63 ˚

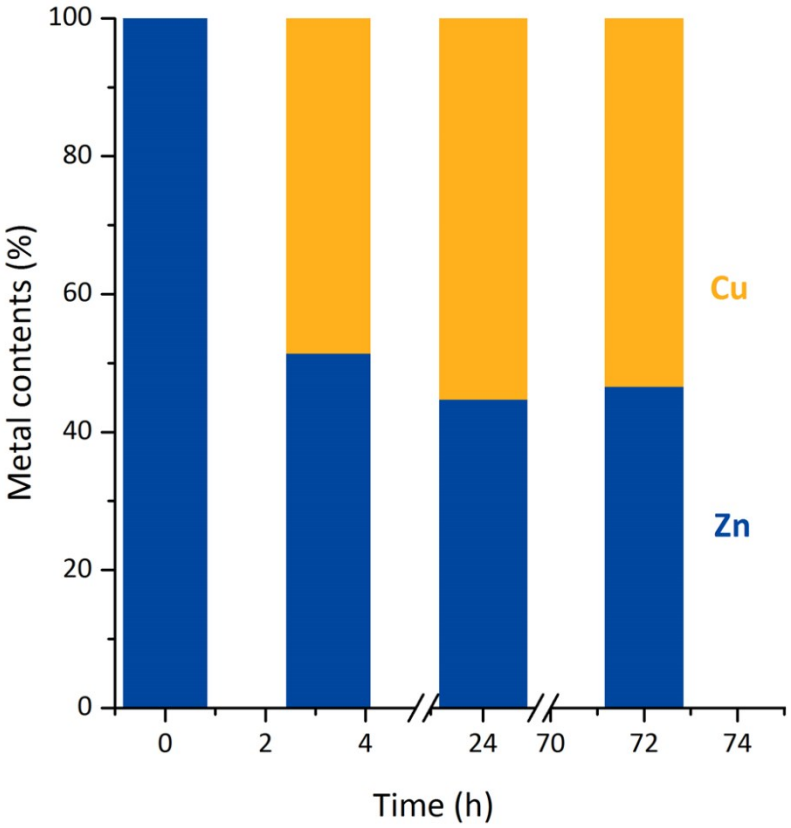

Figure S2. Kinetic profile of the Zn(II) to Cu(II) transmetalation procedure based on inductively coupled plasma analysis data.

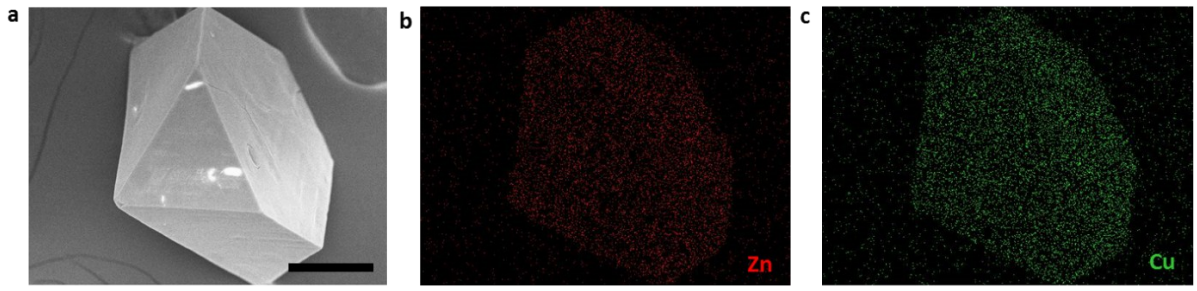

Figure S3. Energy-dispersive spectroscopy mapping analysis of Zn/Cu-UMOM-10. SEM image (a), elemental distribution of zinc (b) and copper (c). Scale bar, 50 μm.

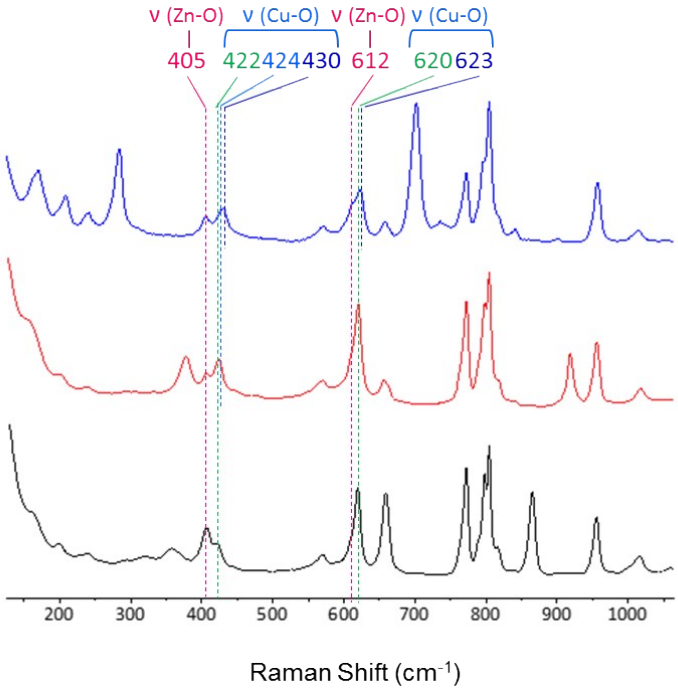

Figure S4. Raman shift data for DMF exchanged Zn/Cu-UMOM-10 (bottom), acetonitrile exchanged Zn/Cu-UMOM-10 (middle) and DCM exchanged Zn/Cu-UMOM-10 (top). There is *ν*(Cu-O) peak shift under different solvent conditions due to the different coordinated solvent molecules on the paddlewheel; peak at 422 cm^{-1} (in DMF) was blue shift to 424 cm^{-1} (in acetonitrile) and 430 cm^{-1} (in DCM), peak at 620 cm^{-1} (in DMF) was blue shift to 623 cm^{-1} (in DCM). However, there is no *ν*(Zn-O) peak shift at 405 and 612 cm^{-1}.

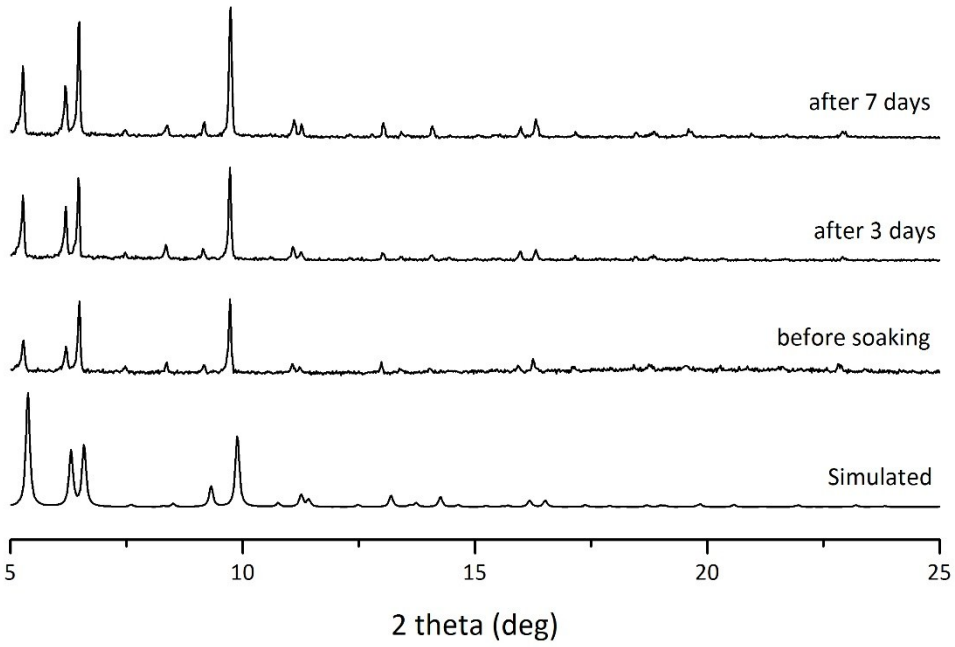

Figure S5. The powder X-ray diffraction patterns of Zn/Cu-UMOM-10 before and after DMSO soaking.

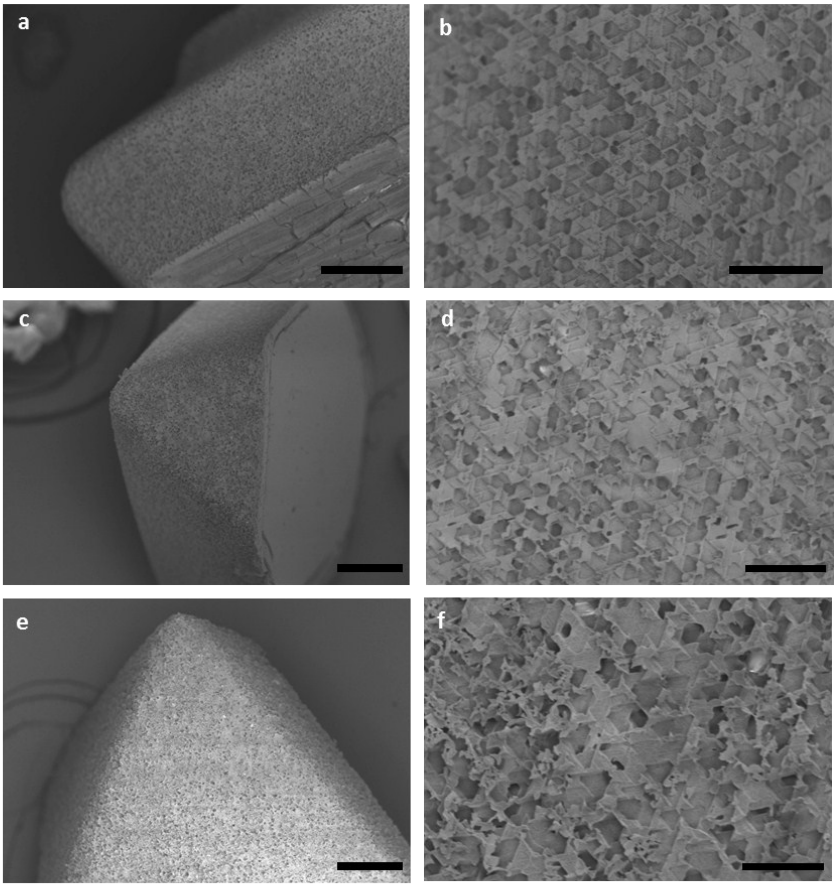

Figure S6. SEM images of Zn/Cu-UMOM-10-ce with etching time is (a, b) 7 h, (c, d) 12 h (e, f) 24 h. Scale bar, 50 μm (a, c and e), 10 μm (b, d and f).

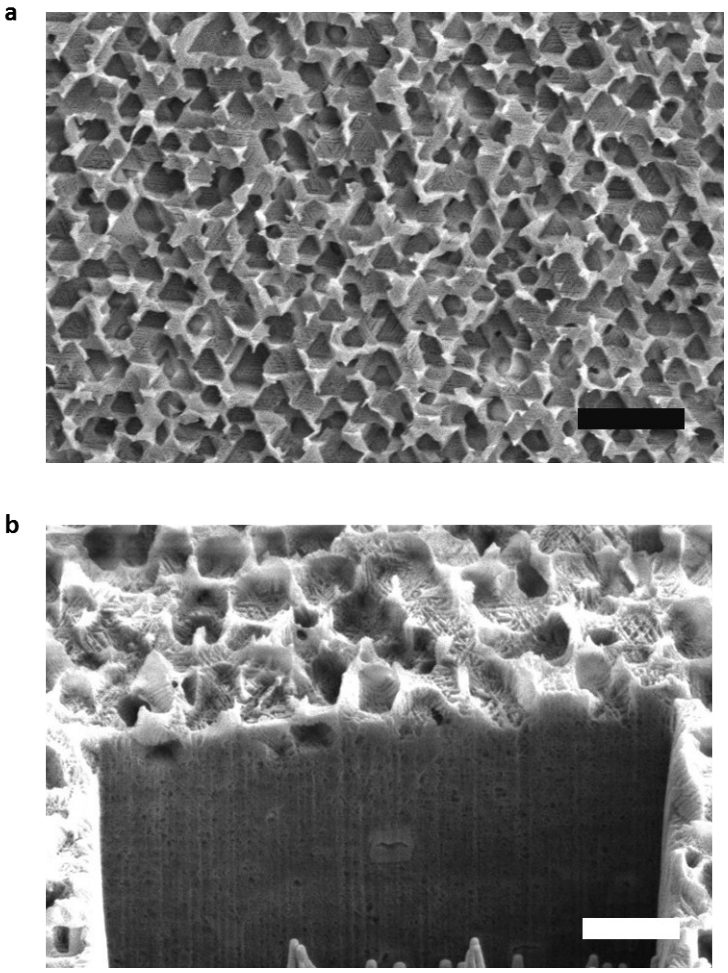

Figure S7. Focused ion beam images of single crystal of Zn/Cu-UMOM-10-ce with 7 h of etching time: (a) before the milling and (b) after milling with 52° rotation. Scale bar, (a) 5 μm and (b)2.5 μm.

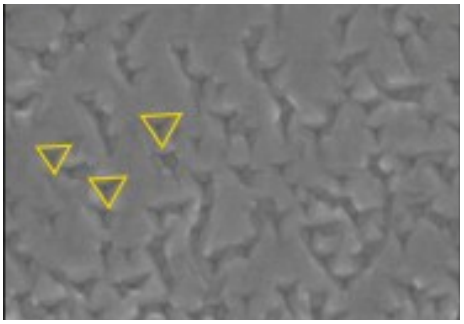

Figure S8. SEM images of etching patterns on a (111) face of fcc packed platinum electrode.[6] Copyright 2016 Rights Managed by Nature Publishing Group.

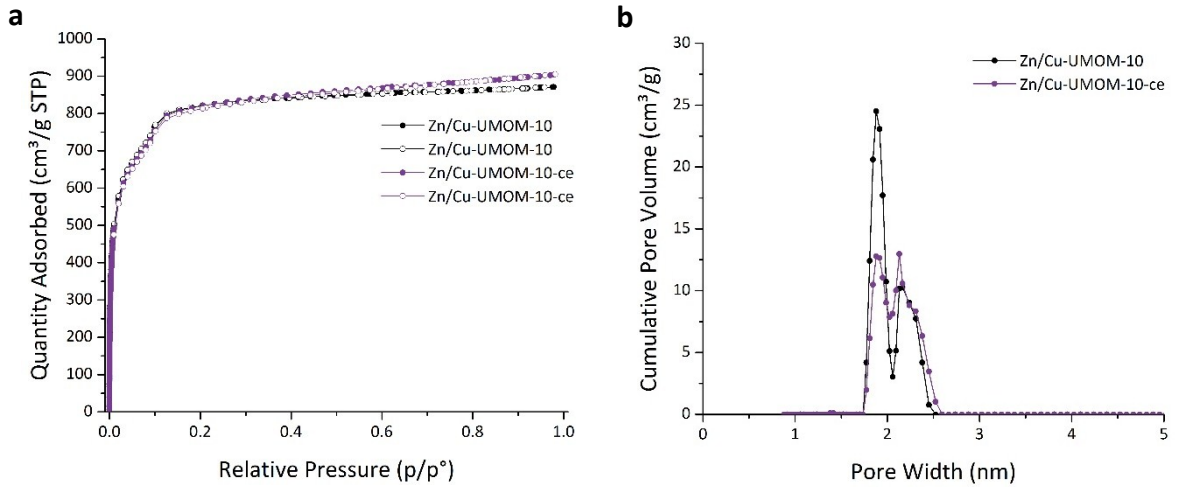

Figure S9. (a) N_2 sorption isotherm of Zn/Cu-UMOM-10 (black) and Zn/Cu-UMOM-10-ce (purple) with etching reaction time 12 h. (b) Pore size distribution of Zn/Cu-UMOM-10 and Zn/Cu-UMOM-10-ce with 12 h of etching reaction time measured by the N_2 sorption isotherm using oxide surface cylindrical model.

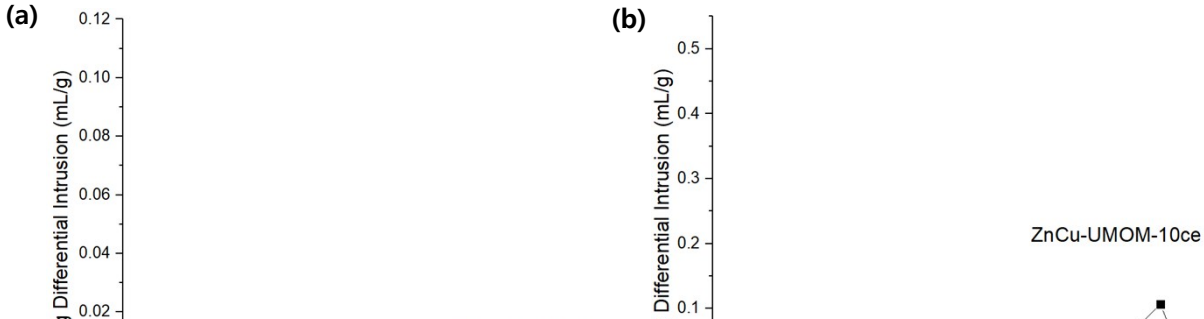

Figure S10. Pore size distribution for (a) Zn/Cu-UMOM-10 and (b) Zn/Cu-UMOM-10-ce.

References

1. A. J. Arvai and C. Nielsen, ADSC Quantum-210 ADX, Area Detector System Corporation; Poway, CA, USA, 1983.

2. Z. Otwinowski and W. Minor, *Methods Enzymol*., 1997, **276**, 307-326.

3. G. M. Sheldrick, *Acta Cryst. Sect. A*, 2008, **64**, 112-122.

4. H. Chun, H. Jung and J. Seo, *Inorg, Chem.*, 2009, **48**, 2043-2047.

5. J. Lee, J. H. Kwak and W. Choe, *Nat. Commun.*, 2017, **8**, 14070.

6. T. J. P. Hersbach, A. I. Yanson and M. T. M. Koper, *Nat. Commun.,* 2016, **7**, 12653.