Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Copper Coordination Polymer Electrocatalyst for Strong Hydrogen Evolution Reaction Activity in Neutral Medium: Influence of Coordination Environment and Network Structure

Pandi Muthukumar,[a] Dohyun Moon,*[b] and Savarimuthu Philip Anthony*[a]

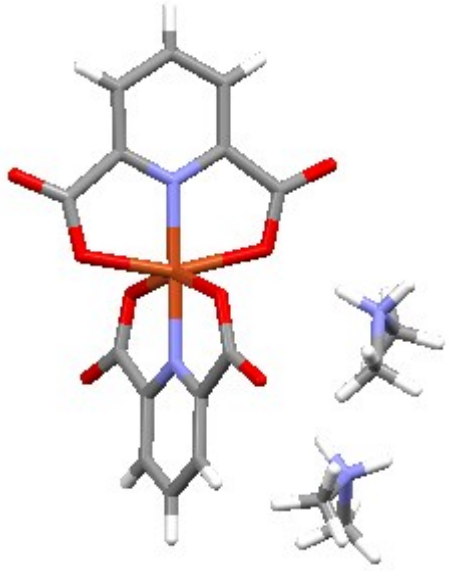
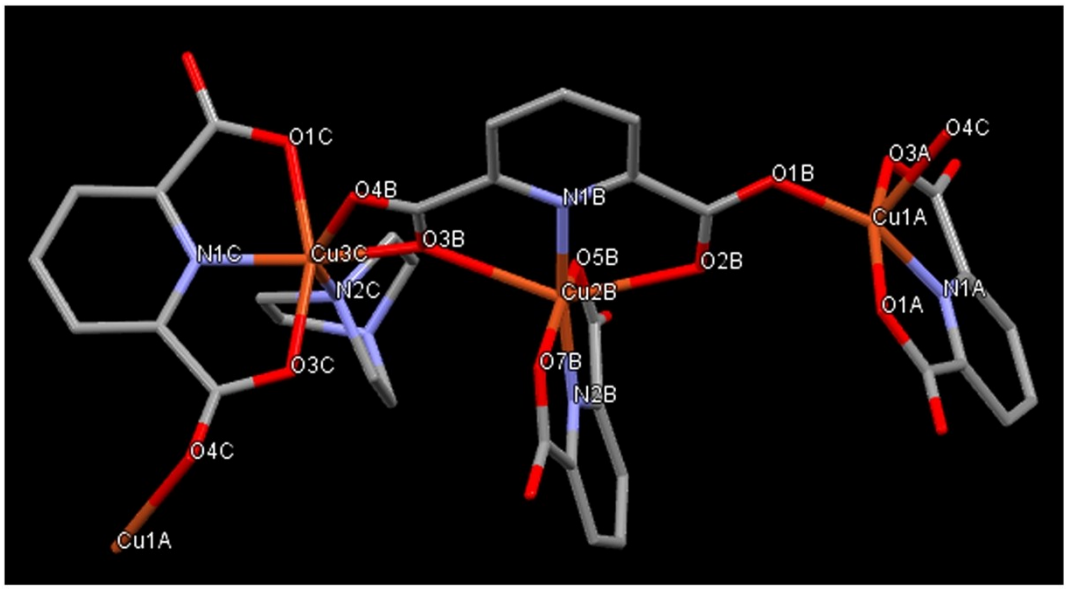
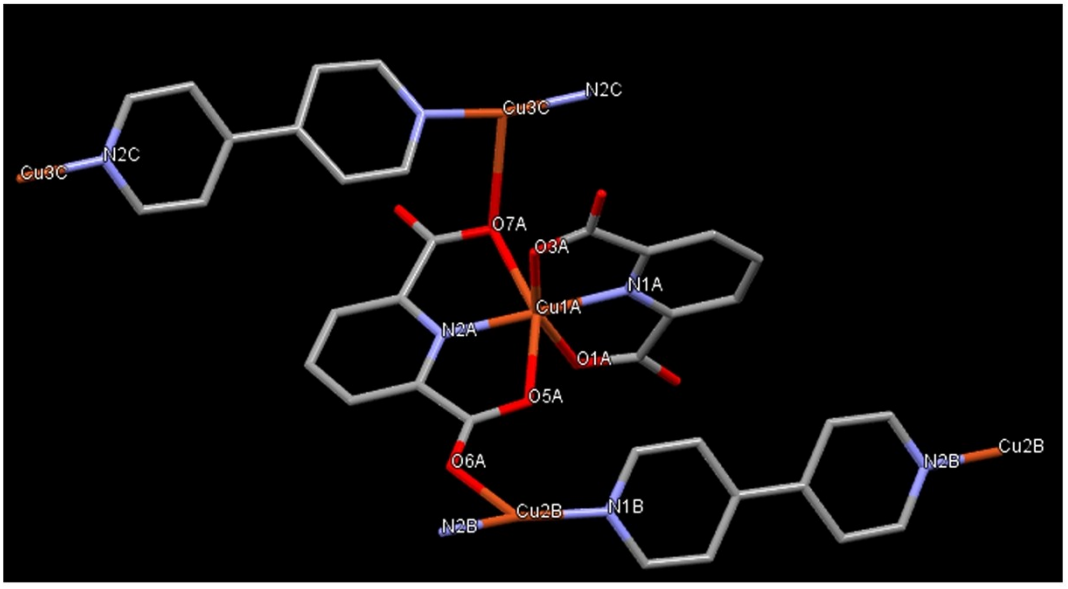


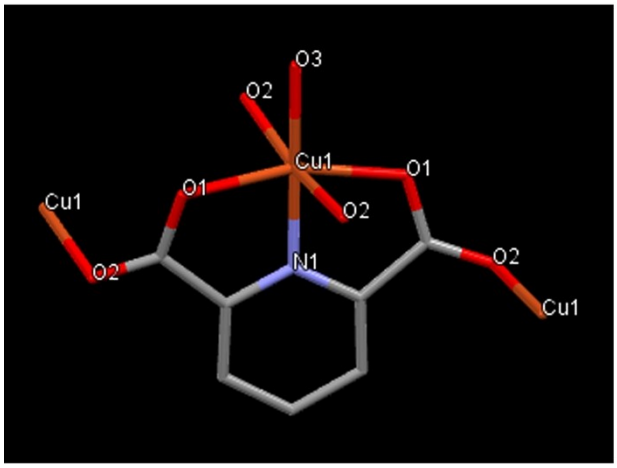
Figure S1. Molecular structure of green crystal. C (grey), N (blue), O (red), H (white) and Cu (orange).



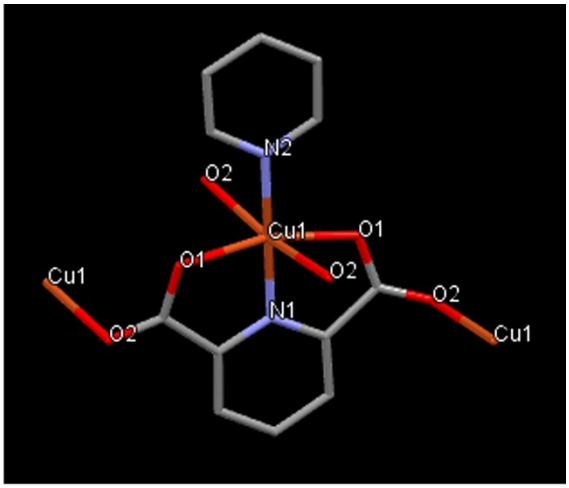
Cu PDA-1



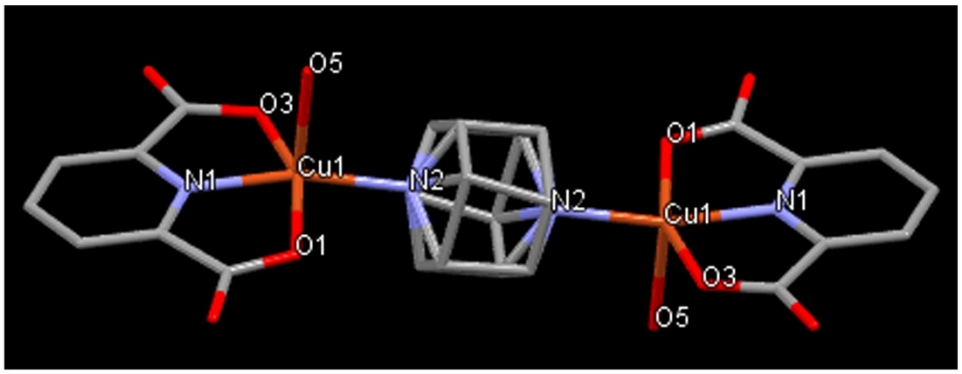
Cu PDA-2



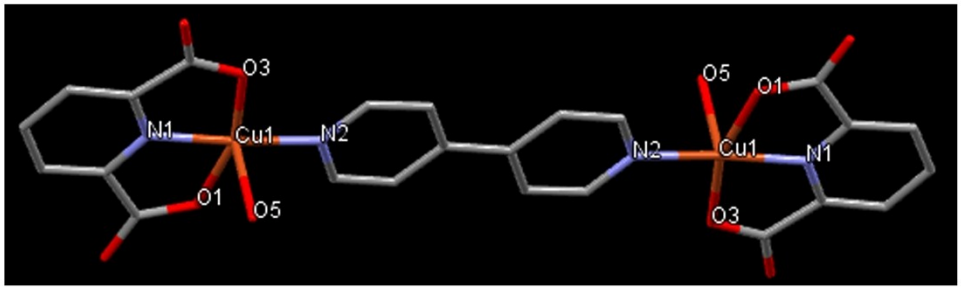
Cu PDA-3



Cu PDA-4



Cu PDA-5



Cu PDA-6

Figure S2. Different structural motifs of Cu-PDA CPs and complexes with different coordination geometry and mode. C (grey), N (blue), O (red), H (white) and Cu (orange).

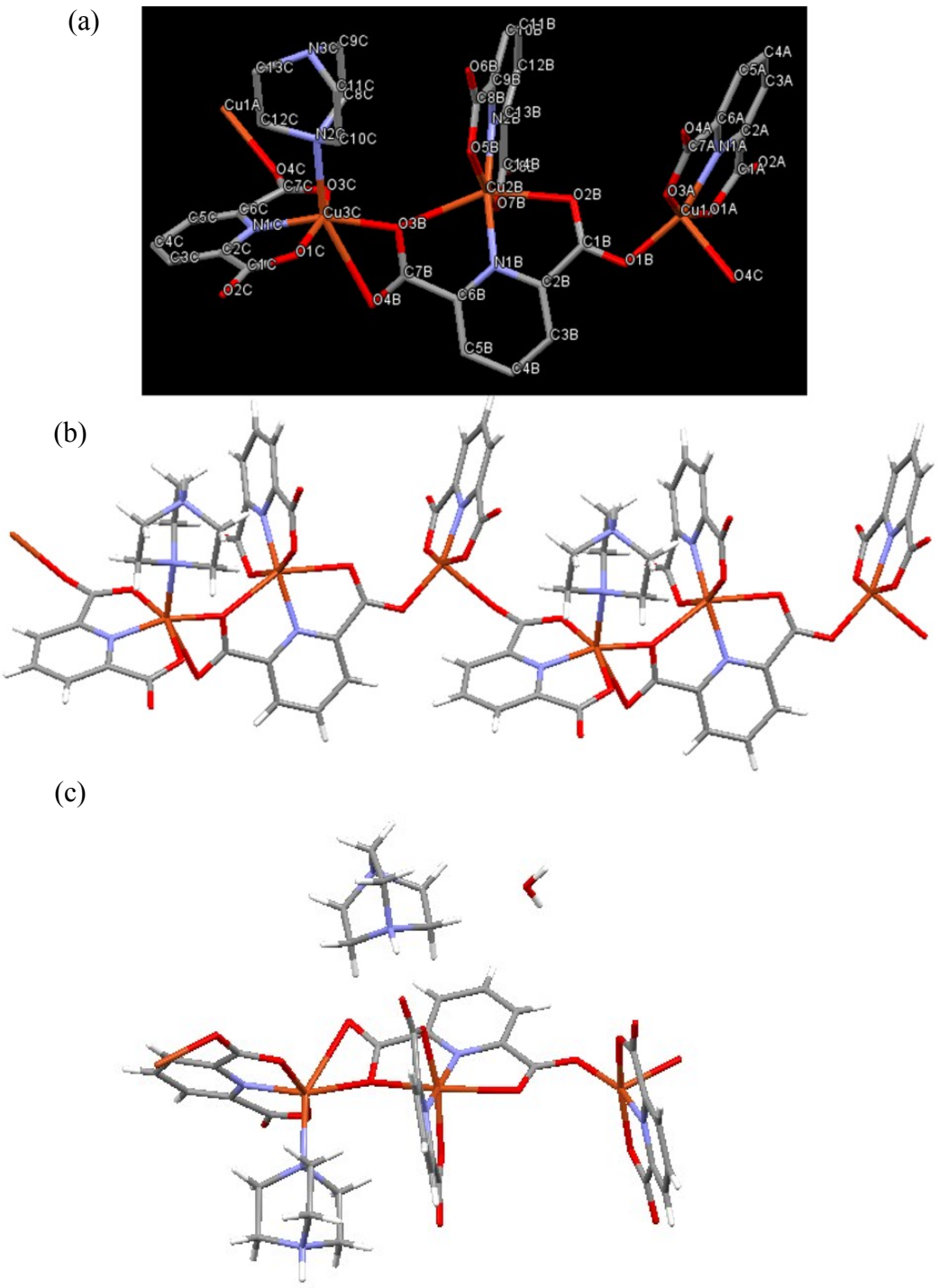


Figure S3. (a) Different coordination geometry of Cu and coordination mode of PDA in Cu PDA-1 with elemental labelling, (b) 1D coordination polymeric network and (c) Asymmetric unit of Cu PDA-1 with included DABCO and water molecule in the crystal lattice of Cu PDA-1. C (grey), N (blue), O (red), H (white) and Cu (orange).

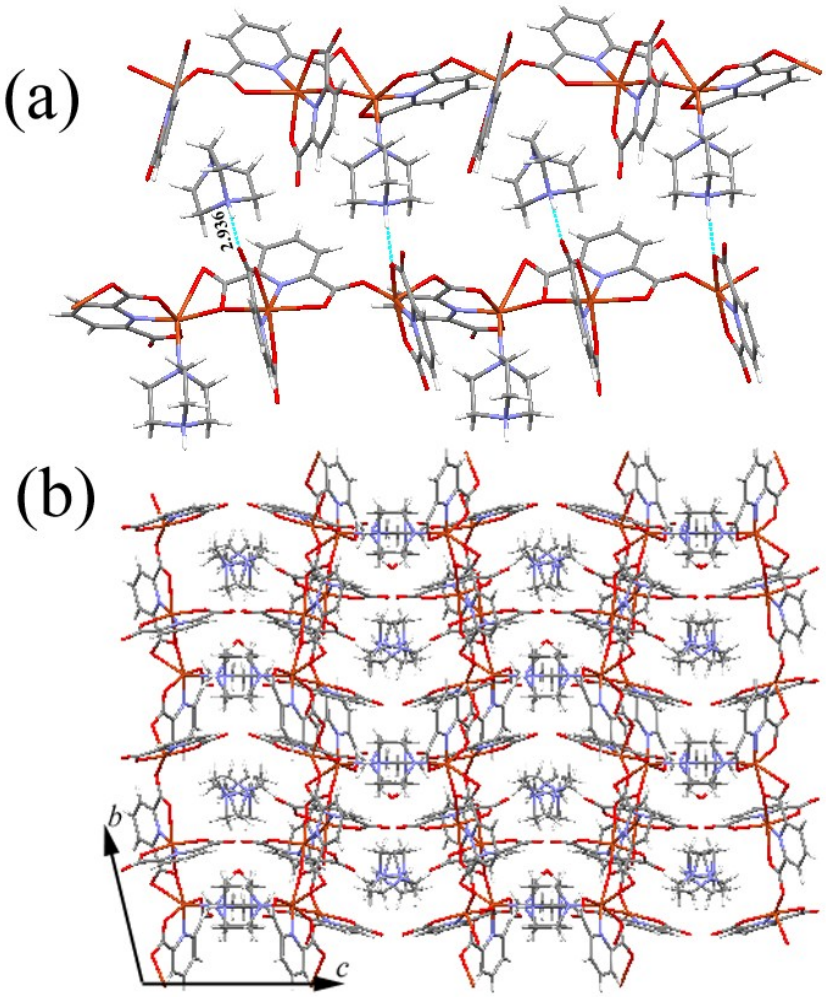


Figure S4. (a) H-bonding interaction between protonated DABCO and carboxylate oxygen (b) molecular packing in the crystal lattice of Cu PDA-1. C (grey), N (blue), O (red), H (white) and Cu (orange); H-bonds (broken line). $d_{D...A}$ distances are marked (Å).

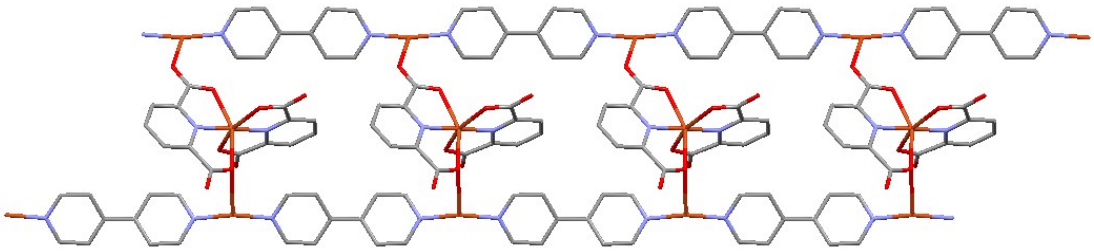


Figure S5. 1D coordination network structure with different coordination geometry of Cu and PDA coordination mode in the crystal lattice of Cu PDA-2. C (grey), N (blue), O (red), H (white) and Cu (orange).

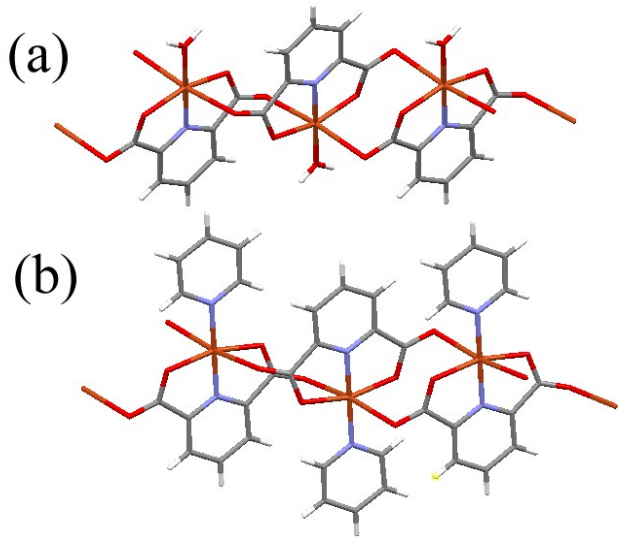


Figure S6. 1D coordination network structure in the crystal lattice of (a) Cu PDA-3 and (b) Cu PDA-4. C (grey), N (blue), O (red), H (white) and Cu (orange).

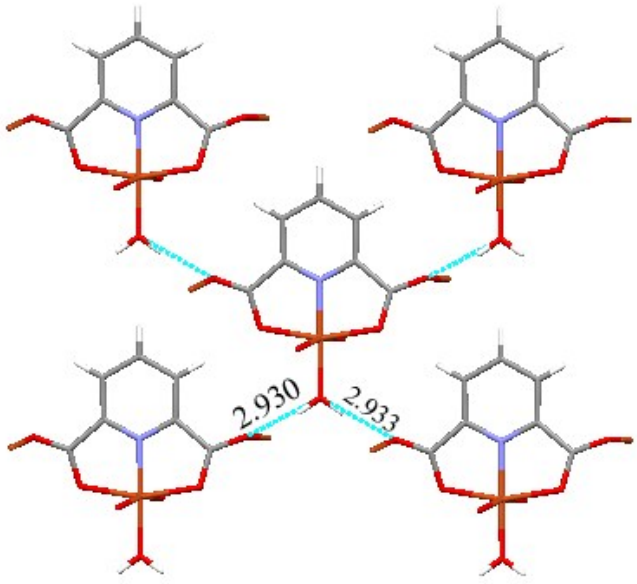


Figure S7. H-bonding interactions between coordinated water molecules and carboxylate oxygen in the crystal lattice of Cu PDA-3. C (grey), N (blue), O (red), H (white) and Cu (orange); H-bonds (broken line). $d_{D...A}$ distances are marked (Å).

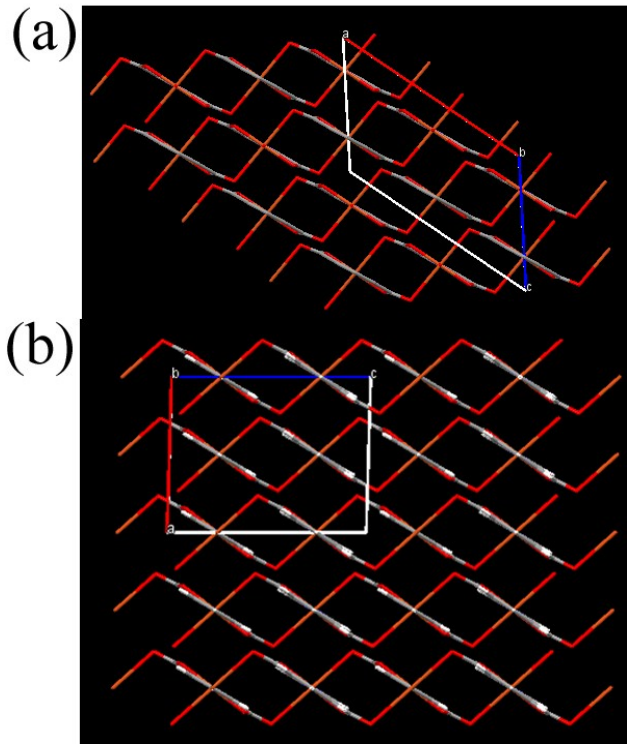


Figure S8. Molecular packing in the crystal lattice of (a) Cu PDA-3 and (b) Cu PDA-4. C (grey), N (blue), O (red), H (white) and Cu (orange).

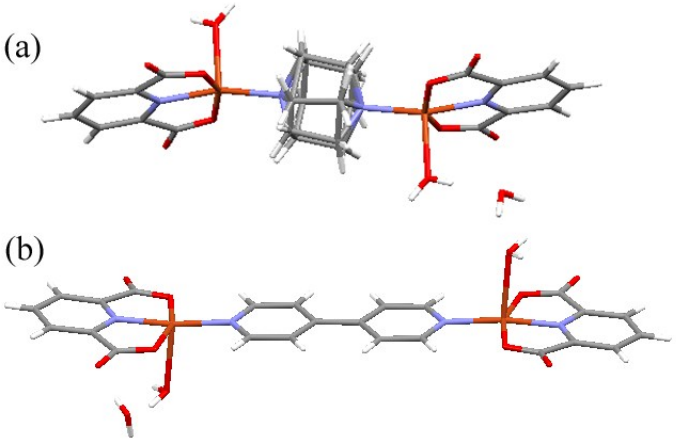


Figure S9. Molecular structure in the crystal lattice of (a) Cu PDA-5 and (b) Cu PDA-6. C (grey), N (blue), O (red), H (white) and Cu (orange).

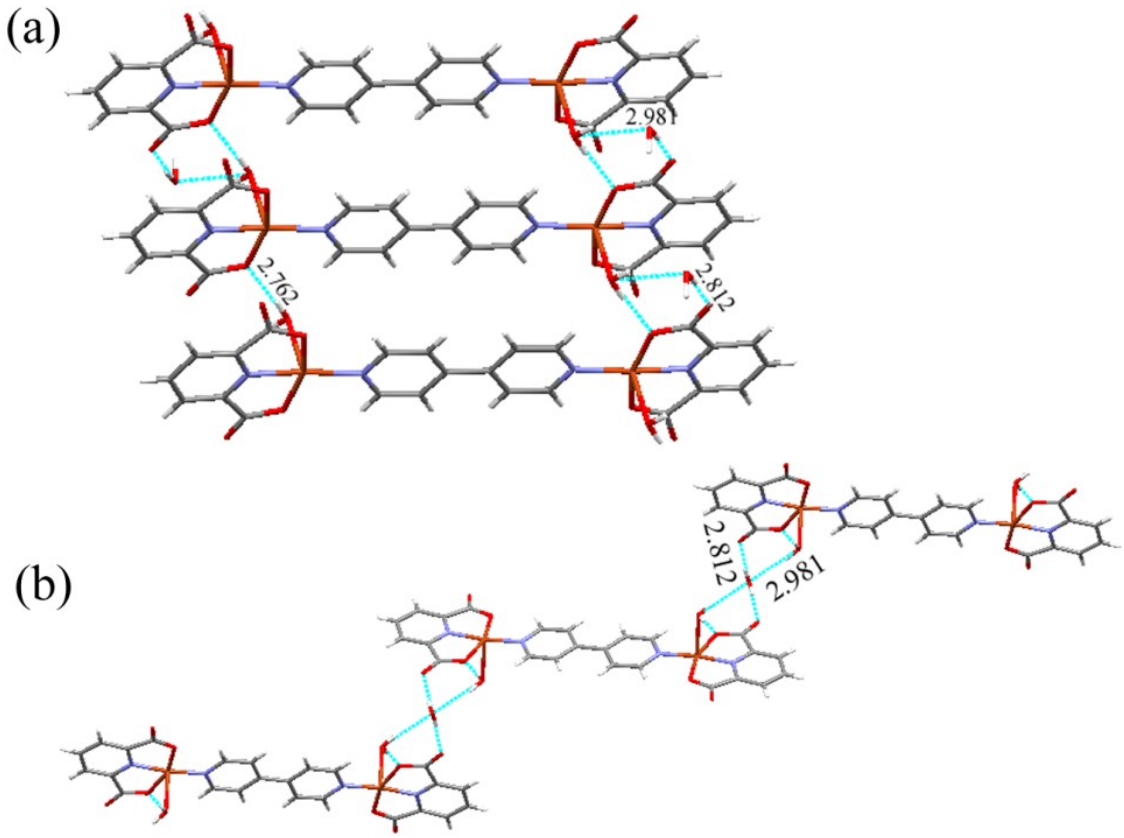


Figure S10. H-bonding interactions between coordinated water molecules and carboxylate oxygen in the crystal lattice of Cu PDA-6. C (grey), N (blue), O (red), H (white) and Cu (orange); H-bonds (broken line). $d_{D...A}$ distances are marked (Å).

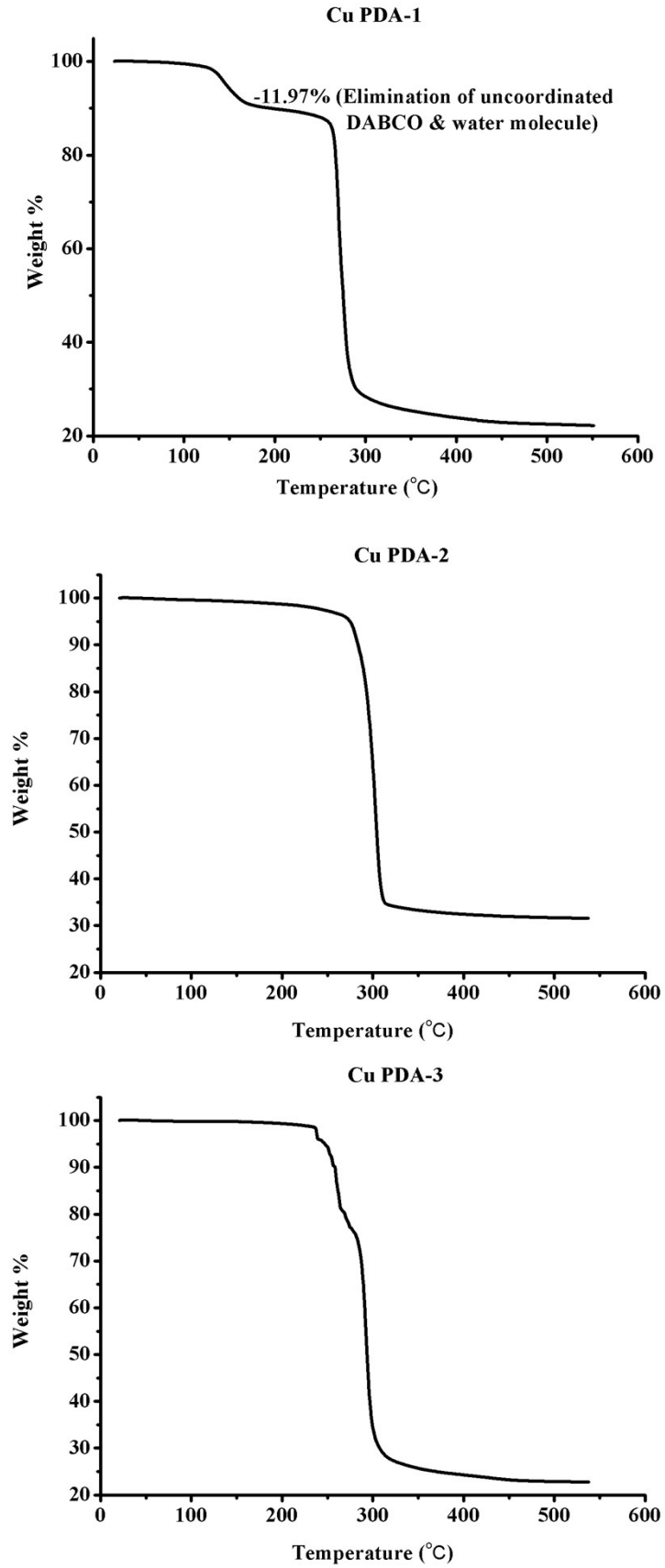


Figure S11. TGA analysis of Cu PDA-1 to Cu PDA-3.

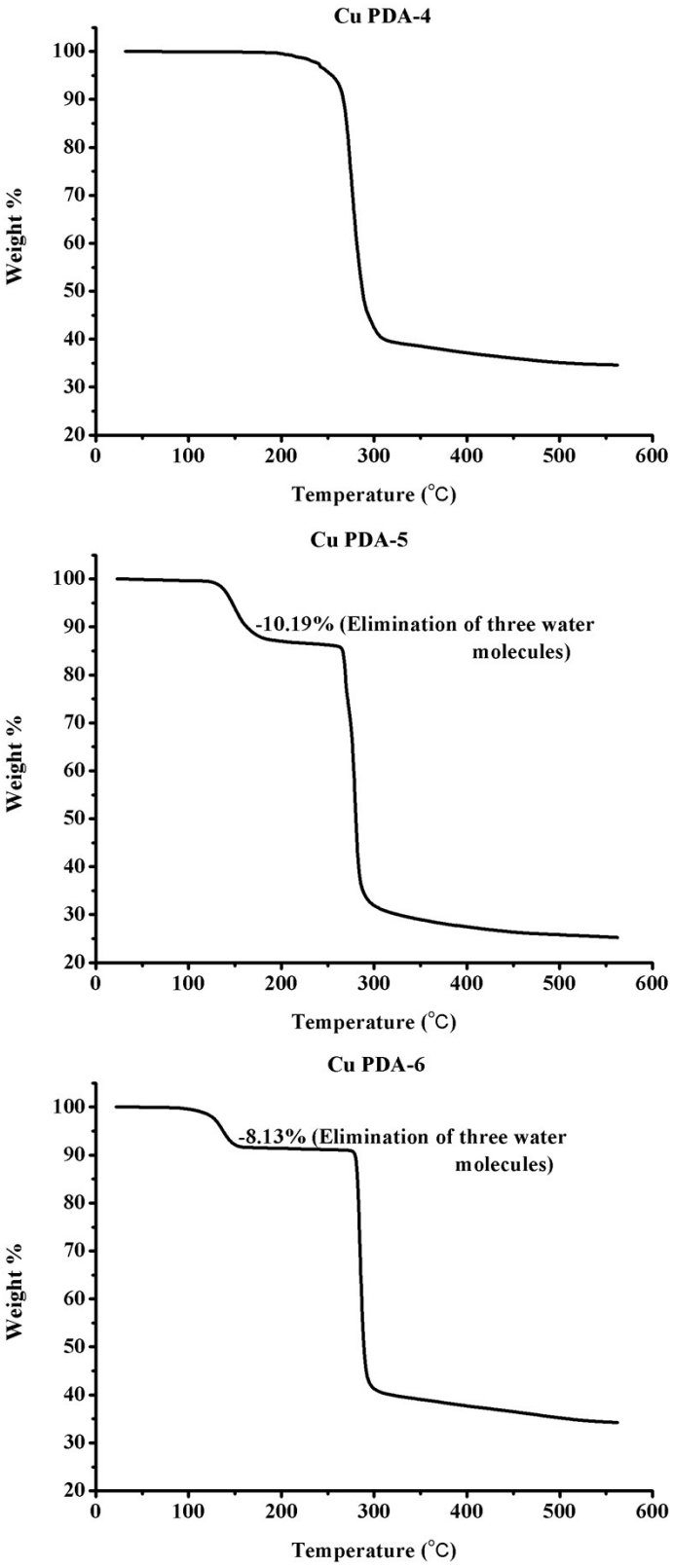


Figure S12. TGA analysis of Cu PDA-4 to Cu PDA-6.

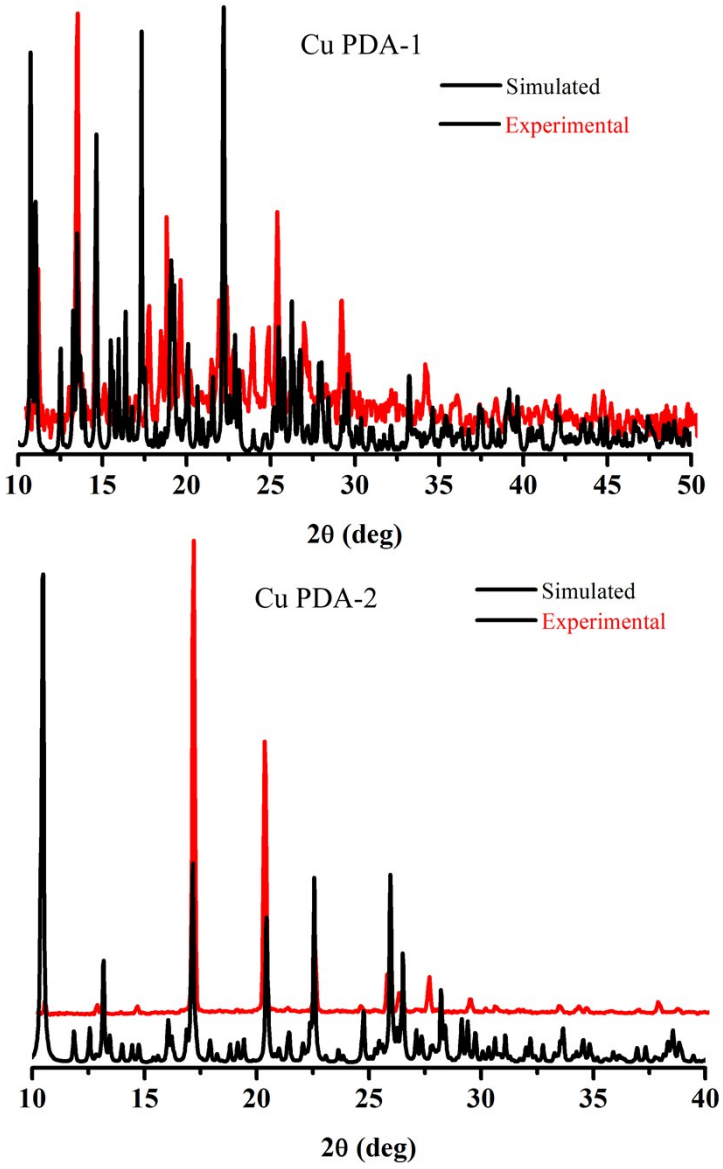


Figure S13. Comparison of simulated and experimental PXRD of Cu PDA-1 and Cu PDA-2.

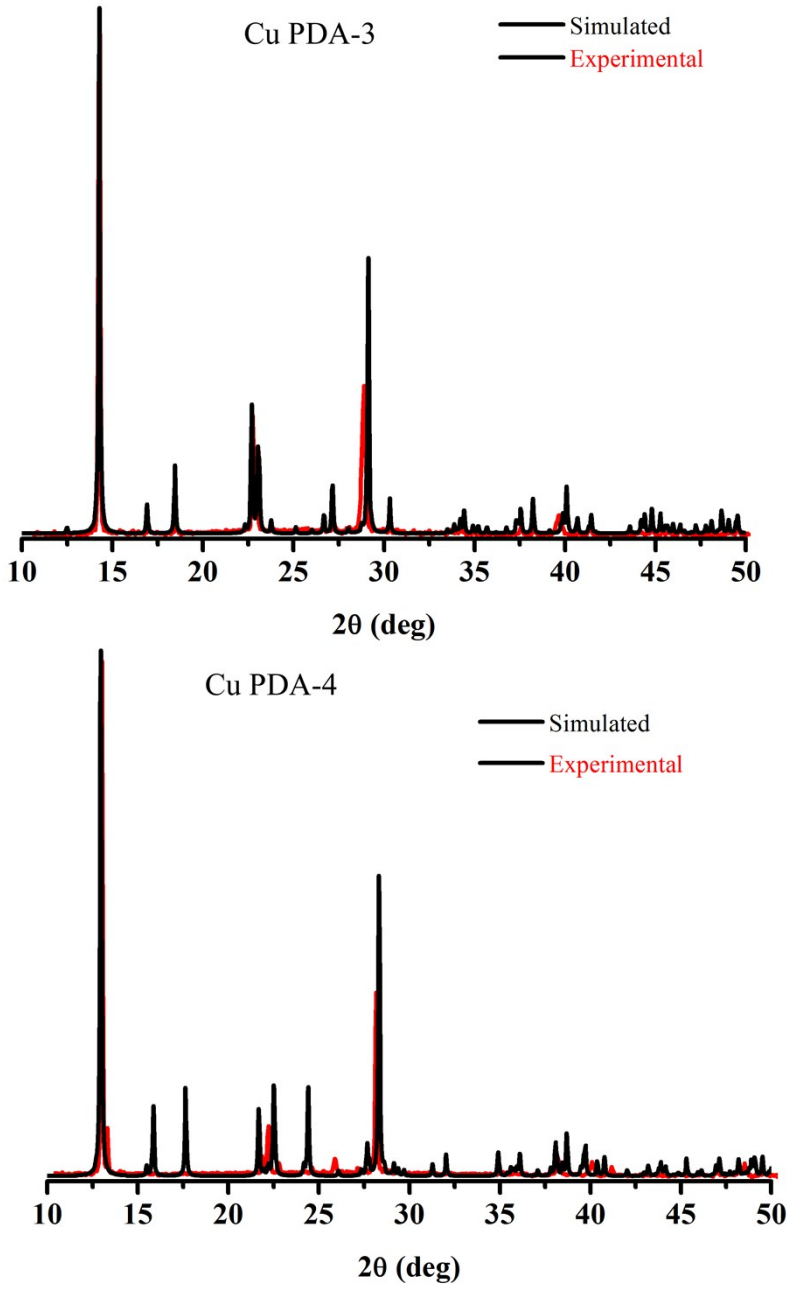


Figure S14. Comparison of simulated and experimental PXRD of Cu PDA-3 and Cu PDA-4.

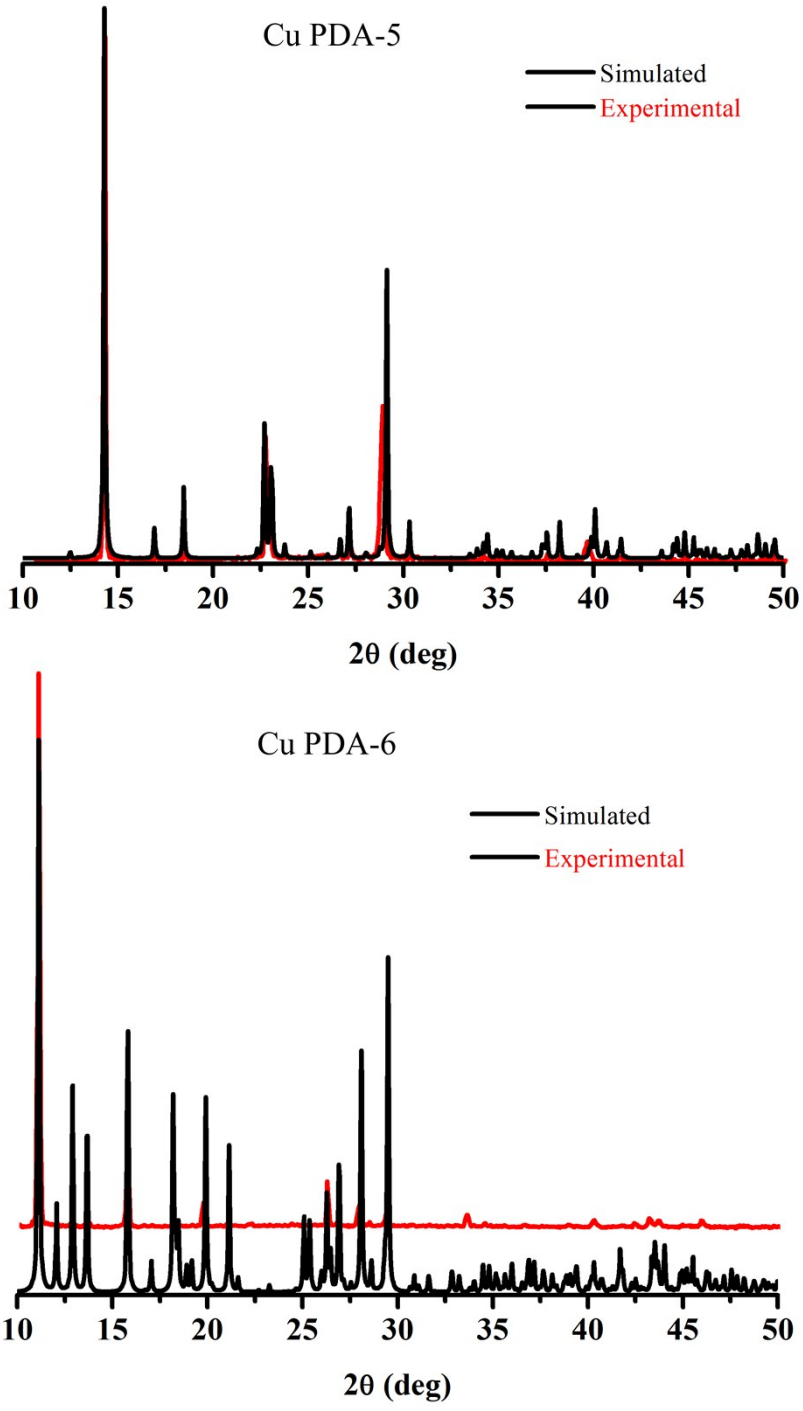


Figure S15. Comparison of simulated and experimental PXRD of Cu PDA-5 and Cu PDA-6.

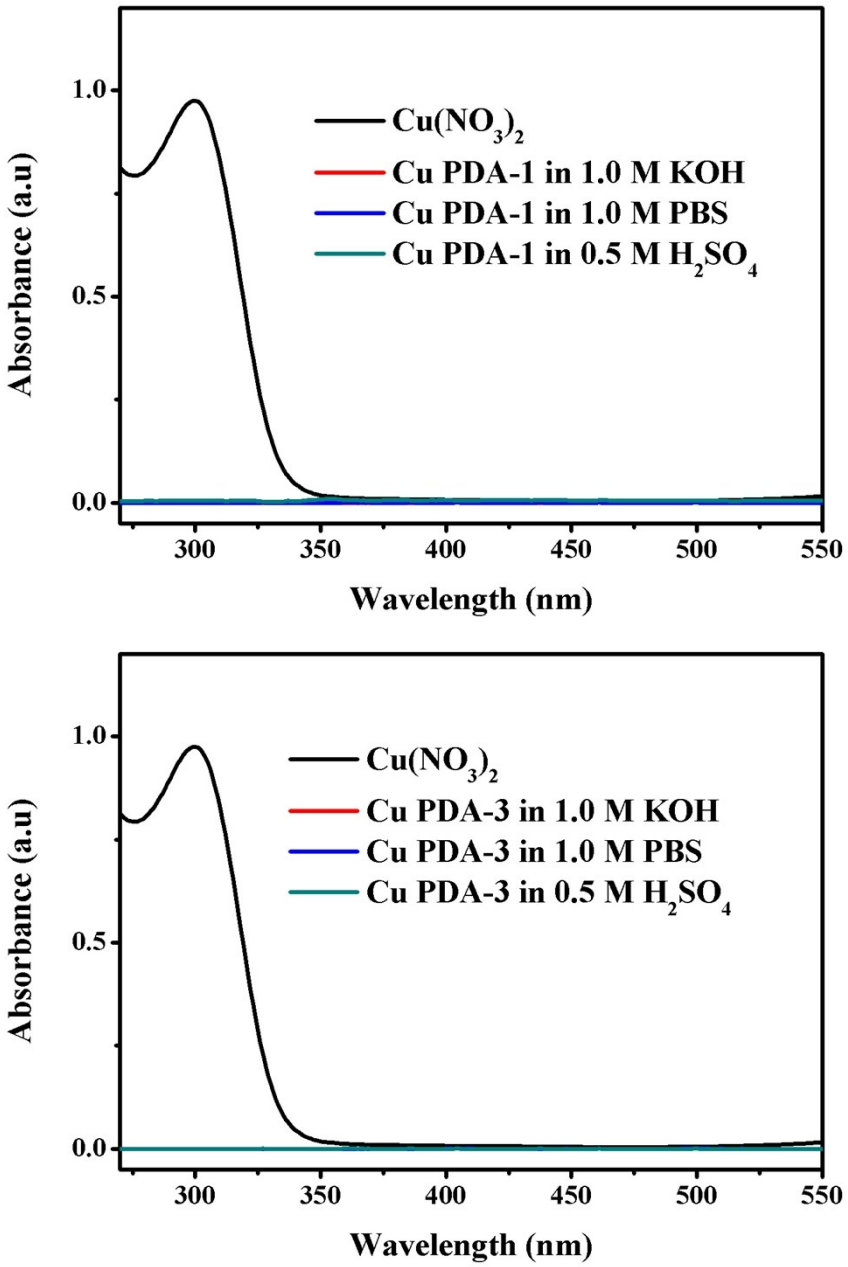


Figure S16. Absorption spectra of Cu PDA-1 and 3 in different water medium after immersing in 1h.

Table S2. HER electrocatalytic activities of CPs/MOFs in presence of conducting composites. (*0.5M H_2SO_4 was used as electrolyte for all catalysts)

Catalyst (*)	**Overpotential [mV] @ 10 mA/cm²**	**Tafel slope [mV/dec]**	**Stability tests**	**Ref**
(GO 8 wt%) Cu-MOF	209 (30 mA/cm²)	84	N/A	1
1.7 wt% AB &Cu.BTC	208	80	2000 cycles and 18h	2
AB&CTGU-5 (1:4) (Co)	44	45	96 h	3
AB&CTGU-9 (3:4) (Co)	128	87	2000 cycle and 21h	4
Gr(4wt%) &Co-MOF	125	91	1000 cycle	5
UiO-66-NH2-Mo-5 (Zr& Mo)	200	59	5000 cycles and 7h	6
MSZIF-900 (Co)	233	N/A	2.5 h	7

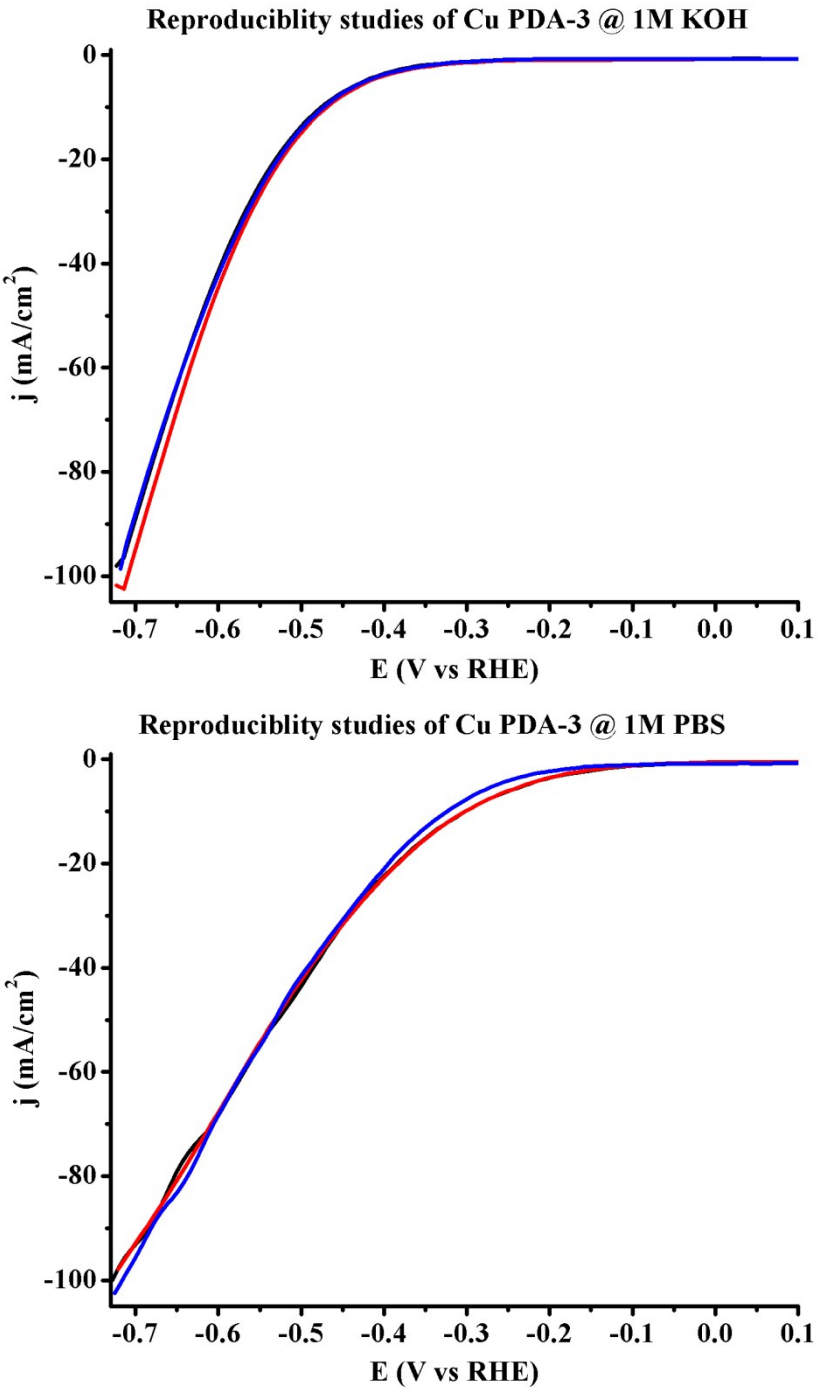


Figure S17. HER Polarization curves of two more batch prepared Cu PDA-3 in 1.0 M KOH and 1.0 M PBS.

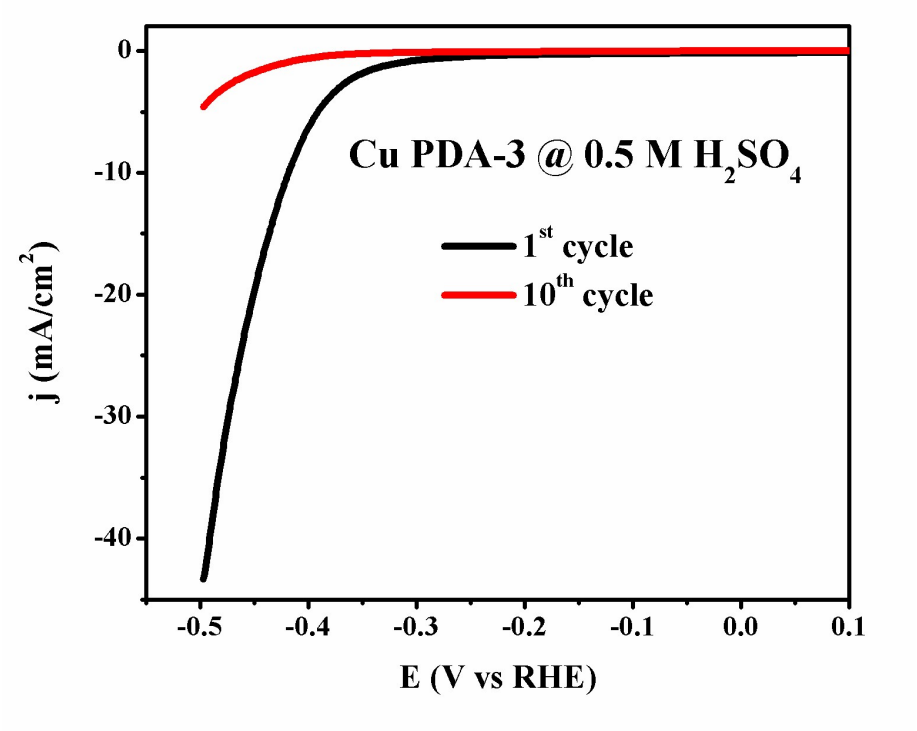


Figure S18. HER polarization curves of Cu PDA-3 in 0.5 M H_2SO_4.

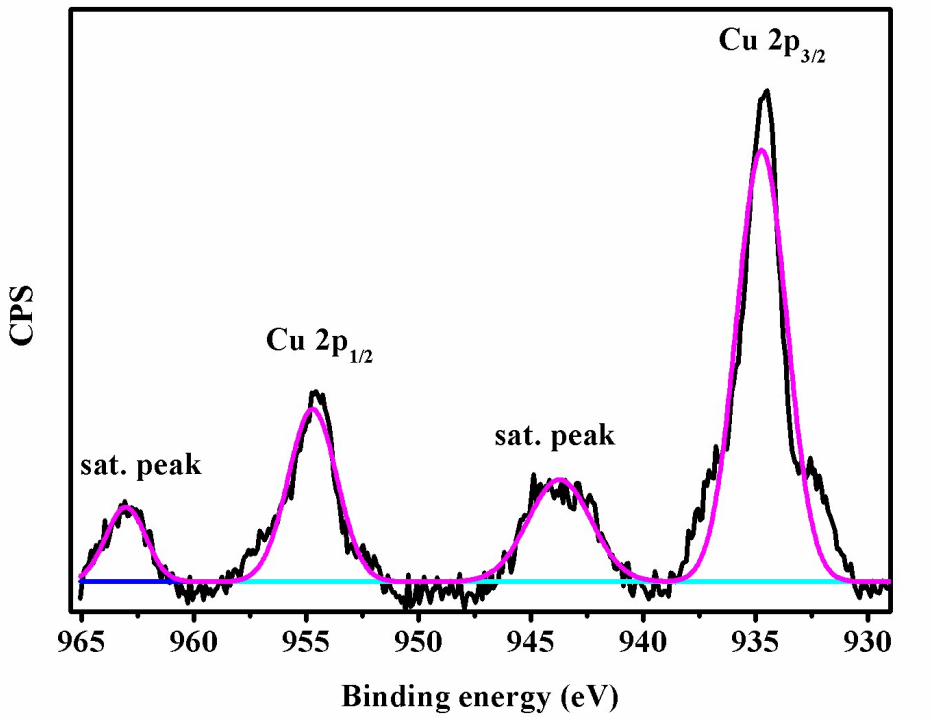


Figure S19. High resolution XPS spectrum of Cu^{2+} after catalysis of Cu PDA-3 in 1.0 M PBS.

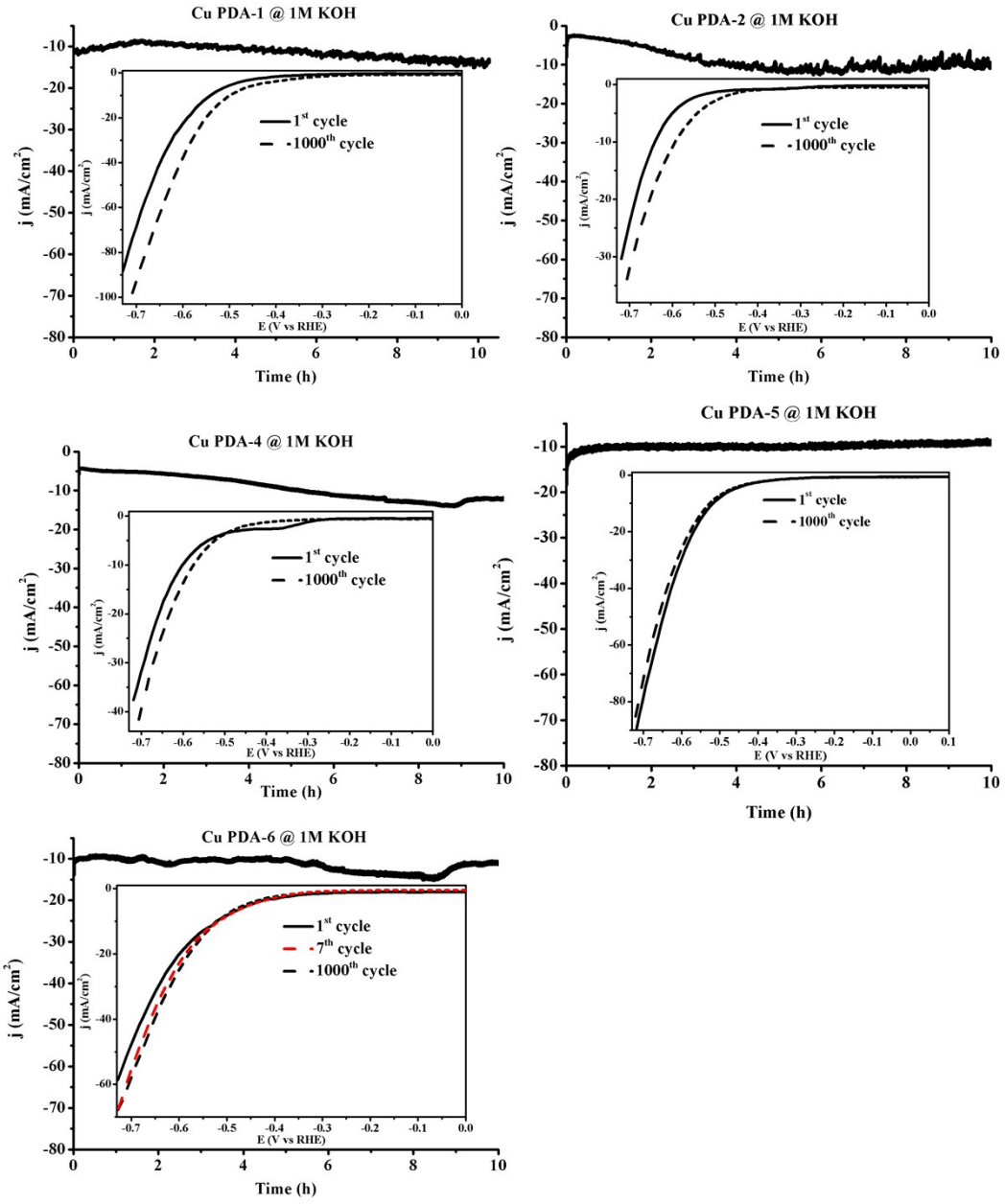


Figure S20. Current−time chronoamperometric response of Cu PDA-1, Cu PDA-2, Cu PDA-4, Cu PDA-5 and Cu PDA-6 in 1.0 M KOH.

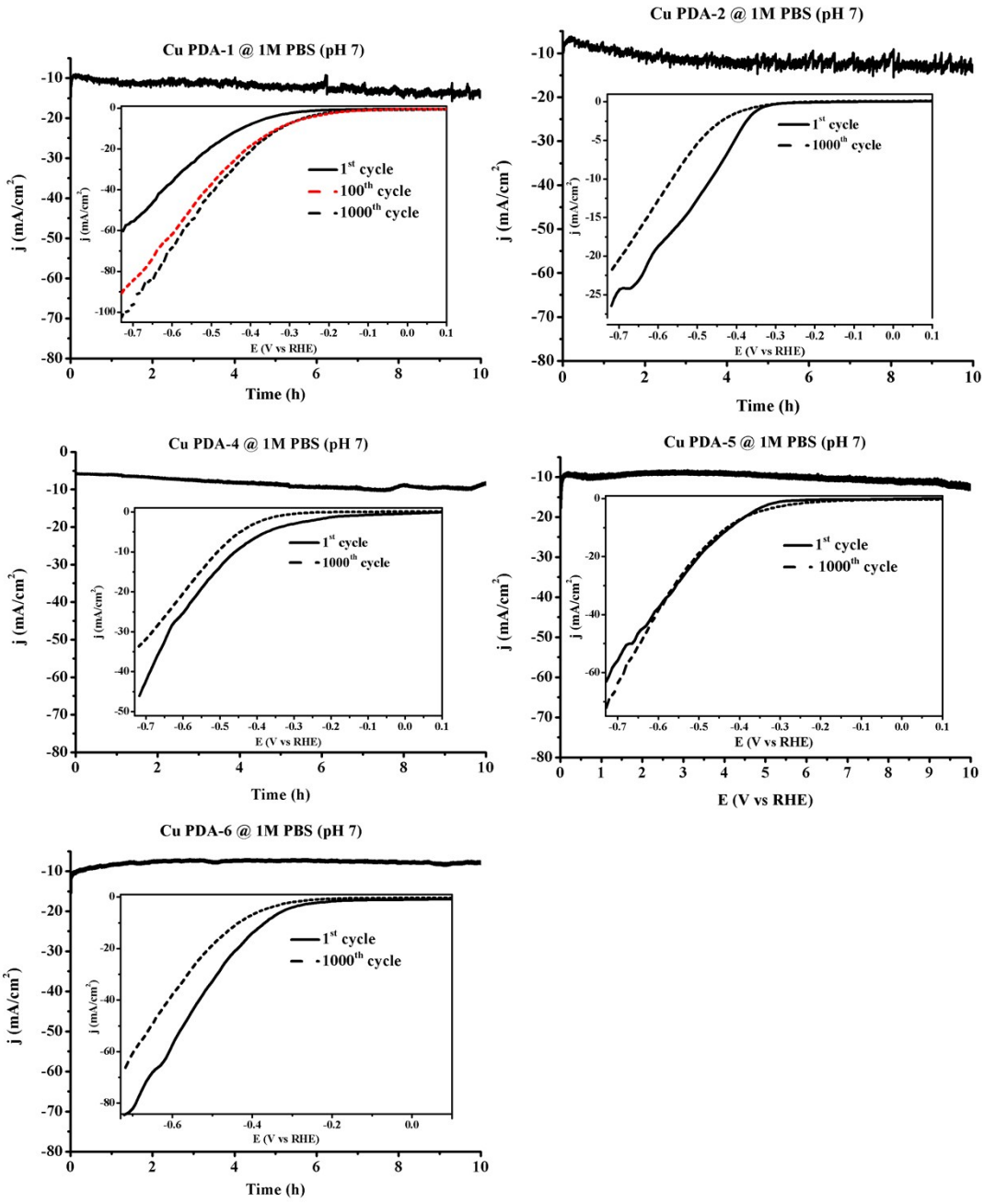


Figure S21. Current−time chronoamperometric response of Cu PDA-1, Cu PDA-2, Cu PDA-4, Cu PDA-5 and Cu PDA-6 in 1.0 M PBS.

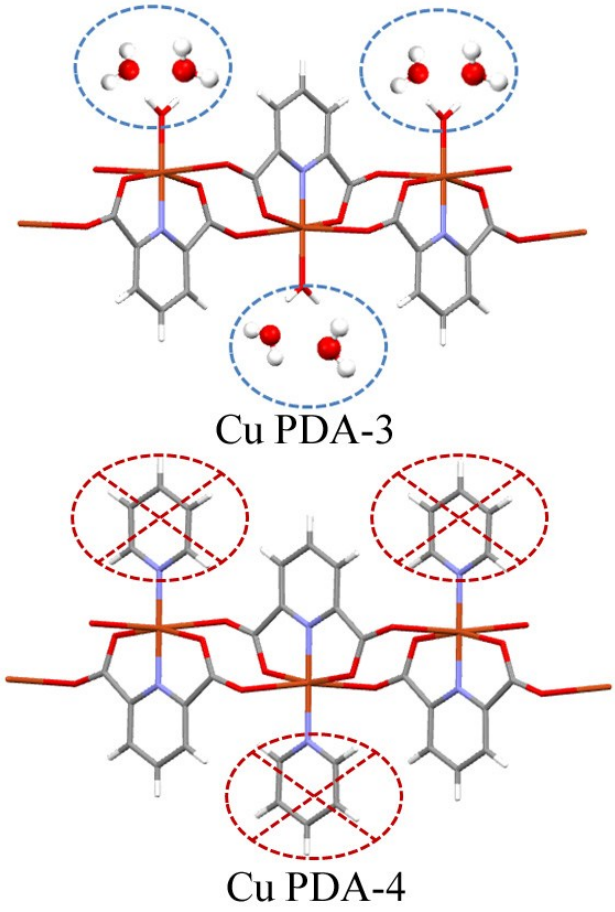


Figure S22. Possible H-bonding site of water molecule with Cu PDA-3 is shown in blue circle whereas crossed red circle shows the absence of such H-bonding site in Cu PDA-4.

References:

1) M. Jahan, Z. Liu, K. P. Loh, *Adv. Funct. Mat*. **2013**, *23*, 5363–5372.
2) X. Wang, W. Zhou, Y.-P. Wu, J.-W. Tian, X.-K. Wang, D.-D. Huang, J. Zhao, D.-S. Li, *J. All. Comp*. **2018**, *753*, 228–233.
3) Y.-P. Wu, W. Zhou, J. Zhao, W.-W. Dong, Y.-Q. Lan, D.-S. Li, C. Sun, X. Bu, Angew. Chem. Int. Ed. 2017, 56, 13001–13005.
4) W. Zhou, Y.-P. Wu, X. Wang, J.-W. Tian, D.-D. Huang, J. Zhao, Y.-Q. Lan, D.-S. Li, Cryst. Eng. Comm. 2018, 20, 4804–4809.
5) J.-W. Tian, M.-X. Fu, D.-D. Huang, X.-K. Wang, Y.-P. Wu, J. Y. Lu, D.-S. Li, *Inorg. Chem. Comm.* **2018**, *95*, 73-77.
6) X. Dai, M. Liu, Z. Li, A. Jin, Y. Ma, X. Huang, H. Sun, H. Wang, X. Zhang, *J. Phys. Chem. C* **2016**, *120*, 12539−12548.
7) G. Jia, W. Zhang, G. Fan, Z. Li, D. Fu, W. Hao, C. Yuan, Z. Zou, *Angew. Chem. Int. Ed.* **2017**, *56*, 13781 –13785.