Electronic Supplementary Information

Cobaloxime tethered pyridine-functionalized ethylene bridged periodic mesoporous organosilica as efficient HER catalyst

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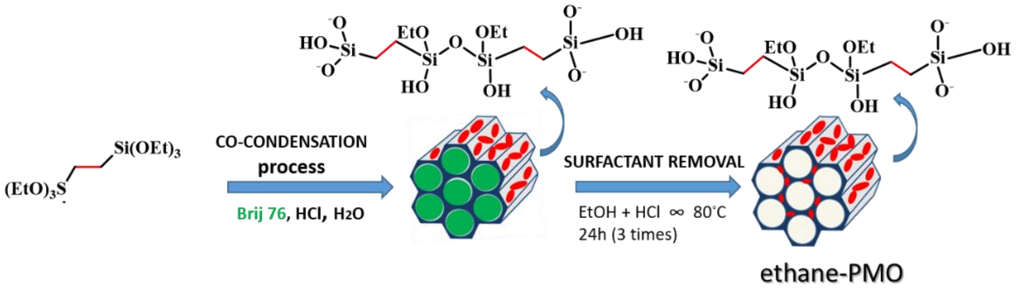
Synthesis of ethylene-bridged PMO

Ethylene-bridged PMO material was synthesized following a procedure described by Burleigh and col.[1] Typically, 6 gr of Brij 76 was added in a solution containing 19.6 ml of HCl and 279 ml of H_2O. The mixture was stirred at 50 ºC for 24 h. Afterwards, 15.9 ml of bis-silane precursor, 1,2-bis(triethoxysilyl)ethane, was added dropwise to the clear solution and it was stirred at 50 ºC for 24 h. Then, the mixture was aged at 90ºC overnight under static conditions. The final solid was filtered under vacuum and washed with plenty of water.

To remove the surfactant, 1g of synthetized material was refluxed in acid ethanolic solution (1ml conc. HCl:50 ml ethanol) for 12h. This process was repeated twice. Finally, the white solid was collected and dried under vacuum at 120 ºC overnight (Scheme S1).



Scheme S1. Synthesis route of ethylene-bridged PMO material.

[1] M. C. Burleigh, S. Jayasundera, C. W. Thomas, M. S. Spector, M. A. Markowitz and B. P. Gaber, *Colloid Polym. Sci.*, 2004, **282**, 728–733.

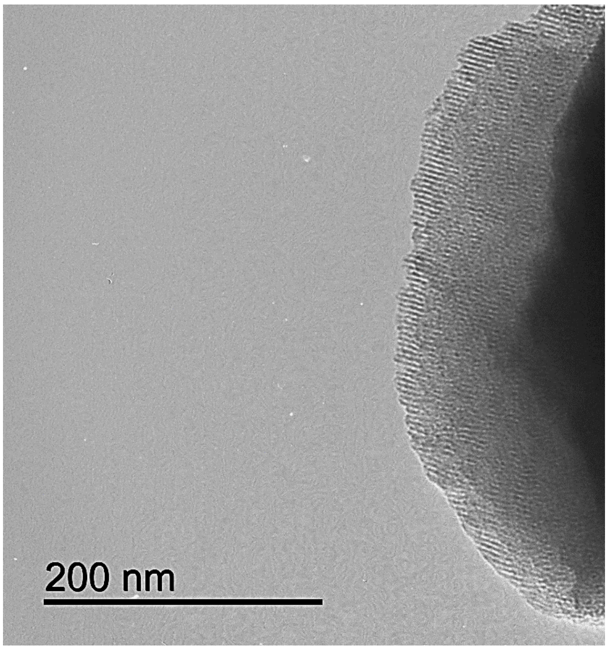


Fig S1. TEM image of py-etPMO.

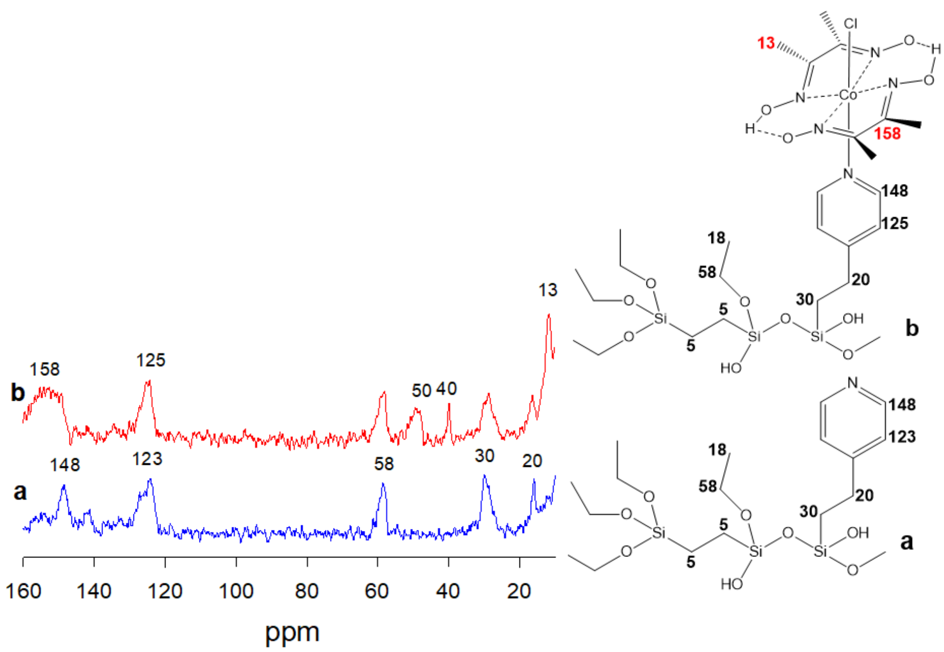


Fig S2. ^{13}C CP/MAS NMR spectra of py-etPMO (a) and py-etPMO-Co (b) excluding signal associated to Csp^3 of the ethylene bridges.

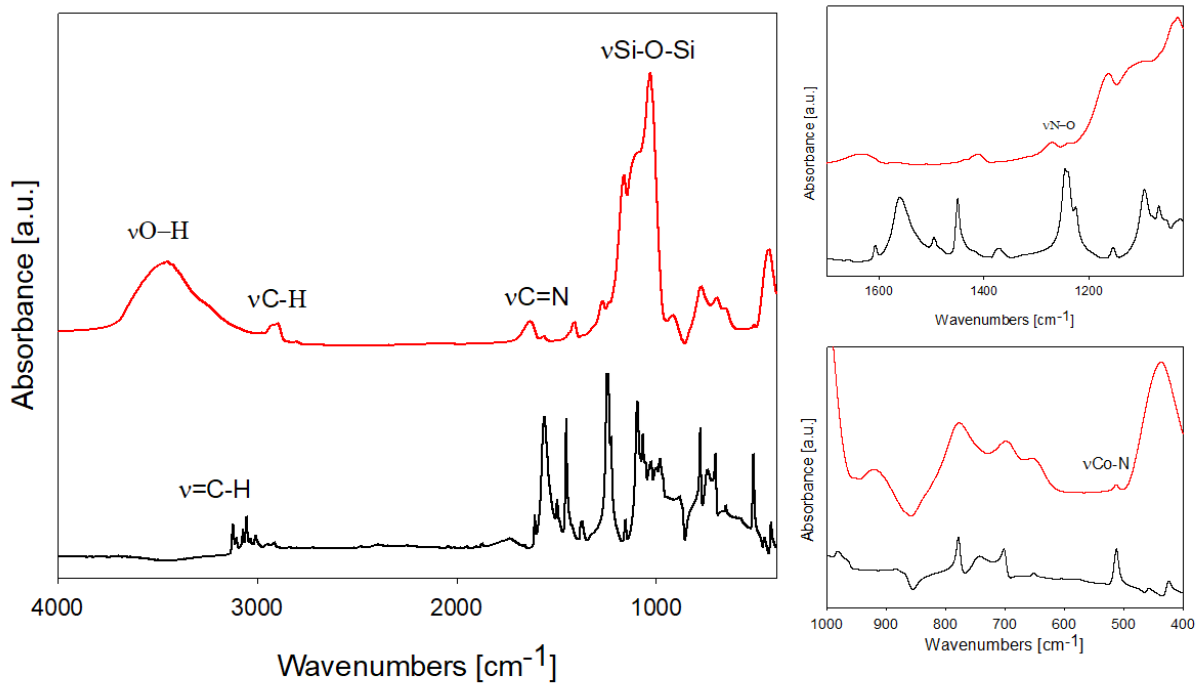


Fig S3. FT-IR spectra of Co(dmgH)$_2$pyCl complex (black) and py-etPMO-Co catalyst (red).

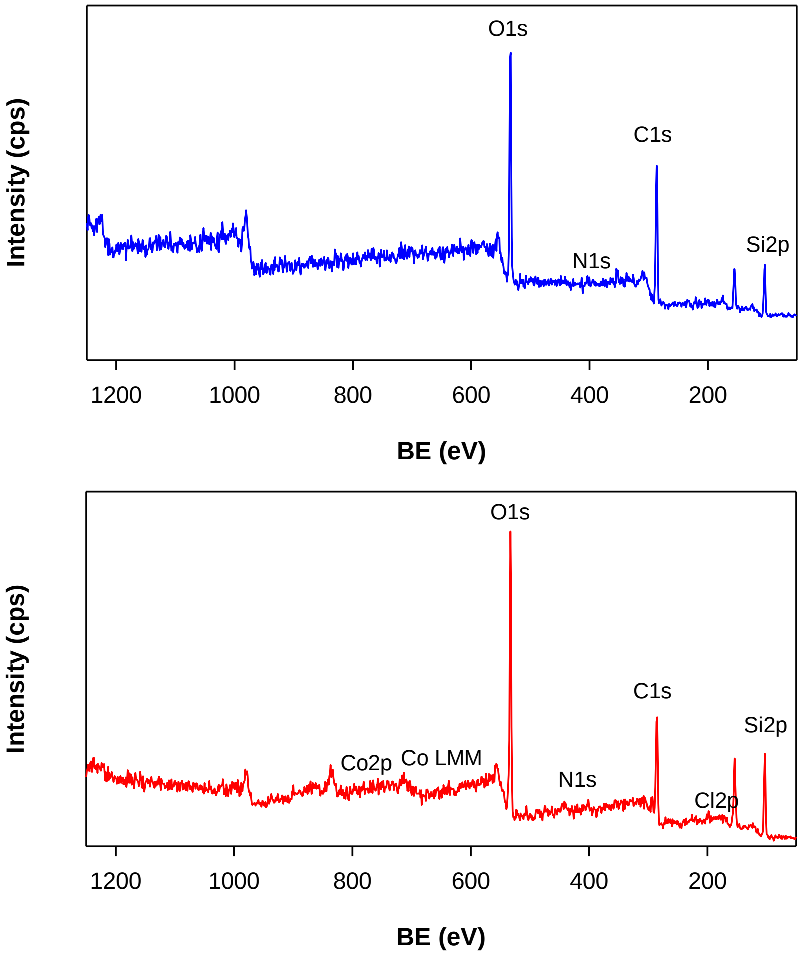


Fig S4. Survey spectra of py-etPMO (blue) and py-etPMO-Co (red).

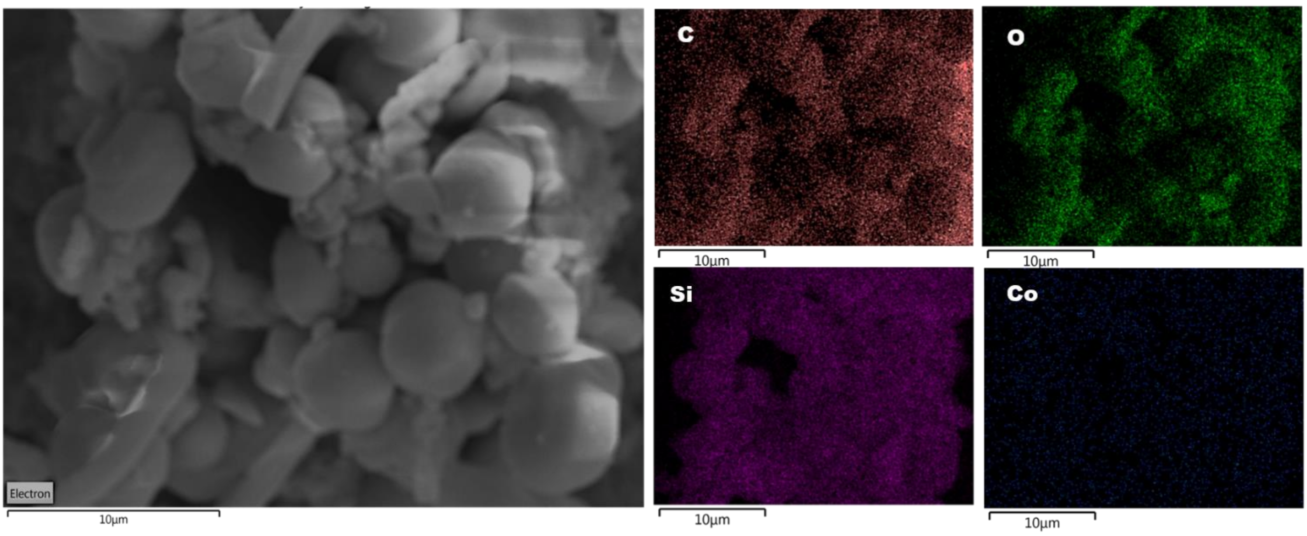


Fig S5. SEM image of py-etPMO-Co and corresponding EDX elemental analysis maps.

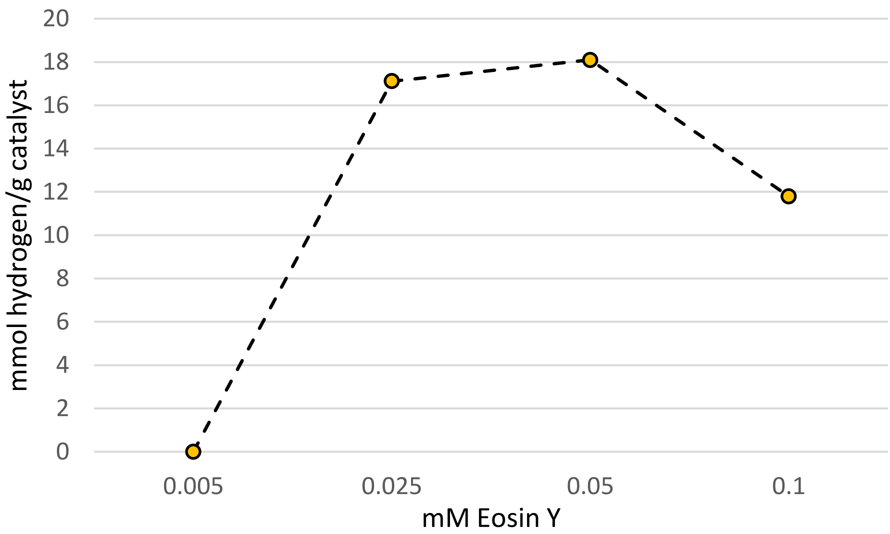


Fig S6. Effect of EY concentration on hydrogen production activity of py-etPMO-Co (catalyst, 1 mg; TEOA, 0.75 mM; reaction time, 4 h).

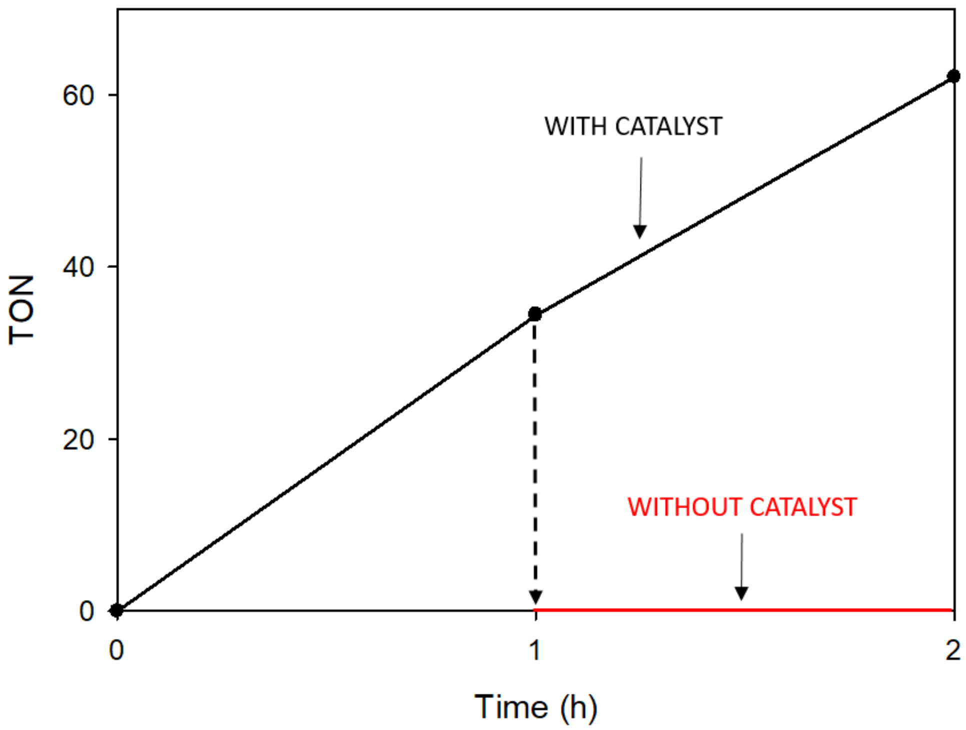


Fig S7. Catalytic test after removing catalyst.

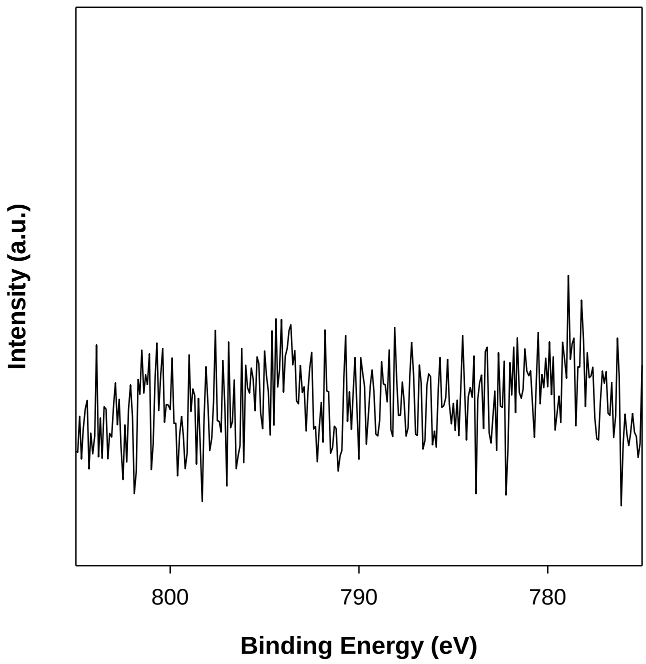


Fig S8. Co2p XPS spectrum of py-etPMO-Co after photocatalysis.

Table S1. Compositional analysis of py-etPMO and py-etPMO-Co

Sample	%wt. Nitrogen[a]	mmol of Nitrogen per gram	mmol of Co per gram[b]
py-etPMO	0.57	0.41	n.d
py-etPMO-Co	n.d	n.d	0.16
ethane-PMO	-	-	0.792×10^{-3}

[a] Determined by elemental analysis

[b] Obtained by ICP-MS

Table S2. Comparison of the photocatalytic performance of py-etPMO-Co for HER with previously reported heterogenized molecular hydrogen evolution reaction catalysts.

Catalyst	Support	External Sensitizer	Time (h)	H_2 evolution rate (mmol g^{-1})	TON	Ref.
$Co(dmgH_2)(dmgH)Cl_2$	py-etPMO	Eosin Y	4	18.1	113	This work
$Co(dmgH)_2$(4-HEP)Cl[a]	MIL-101(Cr)	Eosin Y	5	8	20	2
$Co(dmgH_2)(dmgH)pyCl$	COF	-	13	11.8	170	3
Cobaloxime - complex	Polymer	$Ru(bpy)_3Cl_2$	5	0.9	2.8	4
$Fe_2(dcbdt)(CO)_6$[b]	Zr(IV)-MOF	$Ru(bpy)_3Cl_2$	2.5	3.5	5.9	5
$Fe_2(cbdt)(CO)_6$[c]	MIL-101(Cr)	$Ru(bpy)_3Cl_2$	2.3	3	18.5	6
$Fe_2S_2(CO)_6$-complex	UiO-MOF	polypyridyl ruthenium	50	0.032	16	7
[FeFe]-hydrogenase	SH-PMO	$Ru(bpy)_3Cl_2$		0.0009	12	8

[a]4-HEP: 4-(2-hydroxyethyl)pyridine
[b]dcbdt: 1,4-dicarboxylbenzene-2,3-dithiolate
[c]cbdt: 3-carboxybenzene-1,2-dithiolate

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