Thiacalixarene-based {Co/Fe}$_{16}$ molecular clusters: the bimetallic synergistic effect for enhanced oxygen evolution reduction

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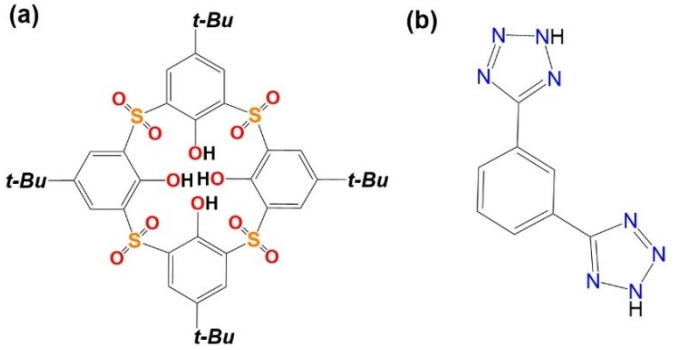
Additional Figures



Scheme S1. Molecular structures of H_4TC4A-SO_2 (a) and H_2BTTAB (b).

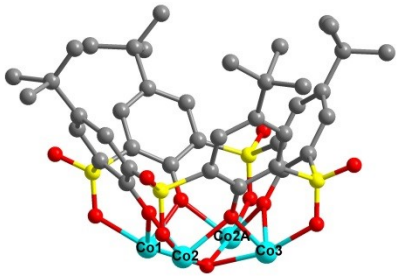


Figure S1. The structure of Co_4-(TC4A-SO_2) PSBU.

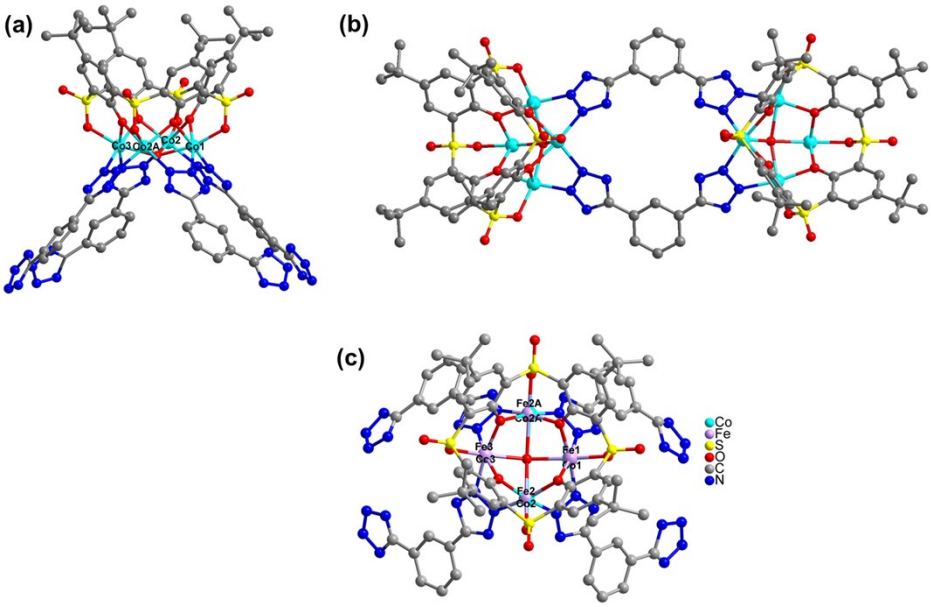


Figure S2. The coordination modes of (a) Co_4-(TC4A-SO_2) unit, (b) BTTAB ligand in **Co_{16}** and (c) $(Co/Fe)_4$-(TC4A-SO_2) unit in **{CoFe}$_{16}$-b**. Symmetry operators for equivalent positions are as follows: A = x, 1-y, 1-z for **Co_{16}** and A = x, y, 2-z for **{CoFe}$_{16}$-b**. Based on the single-crystal X-ray diffraction analysis, the ratio of Co and Fe is 3:2 in **{CoFe}$_{16}$-b**.

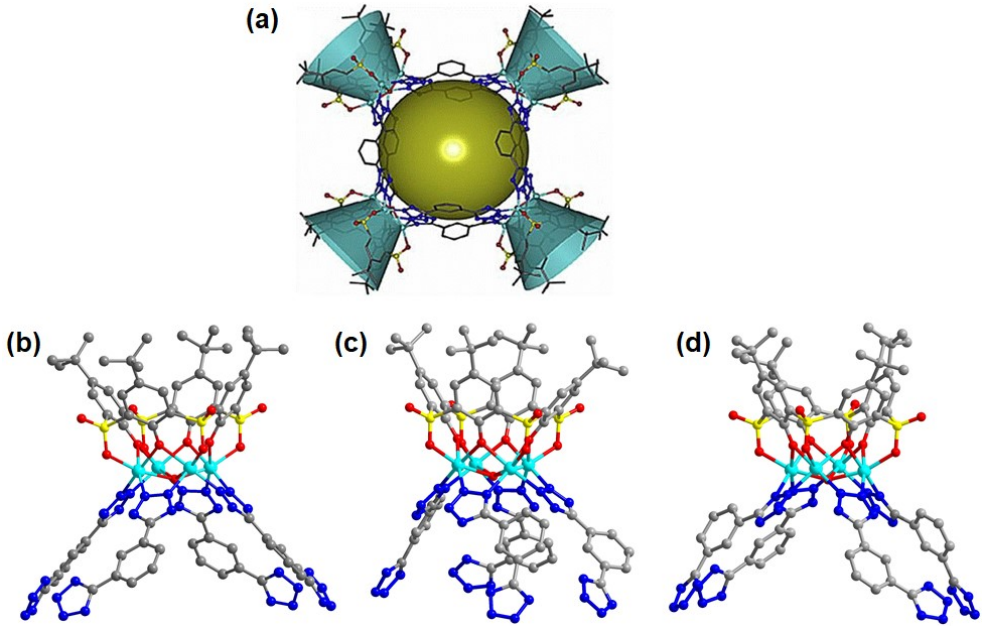


Figure S3. (a) $\{Co_{16}\}$ architecture (in literature) assembled from Co_4-(TC4A-SO_2) SBUs and BTTAB. (b-d) The coordination modes of Co_4-(TC4A-SO_2) units.

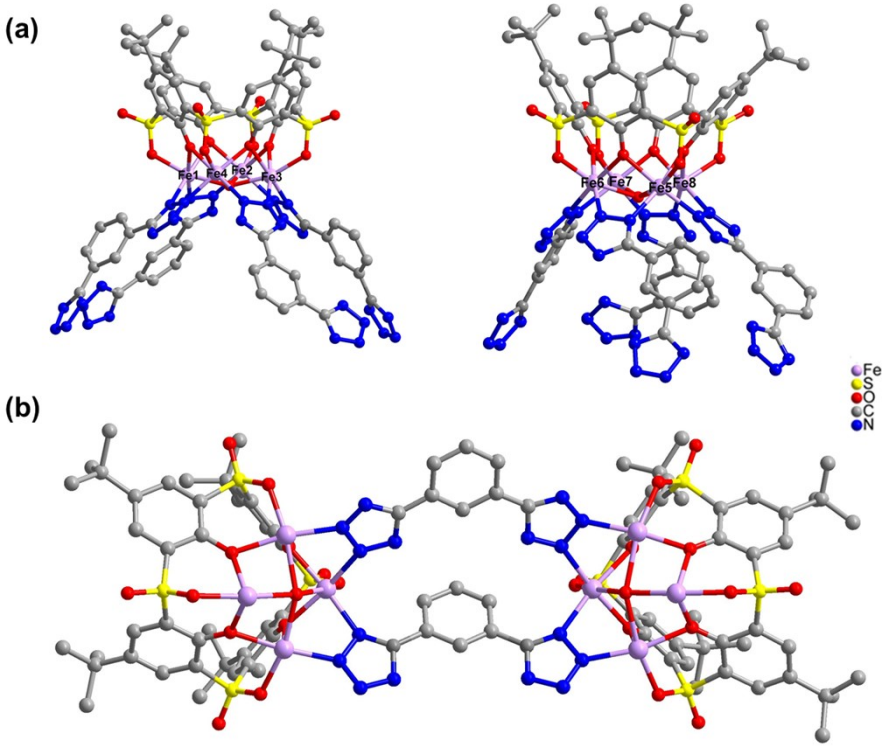


Figure S4. The coordination modes of two Fe_4-(TC4A-SO_2) units (a) and BTTAB ligand (b) in $\mathbf{Fe_{16}}$.

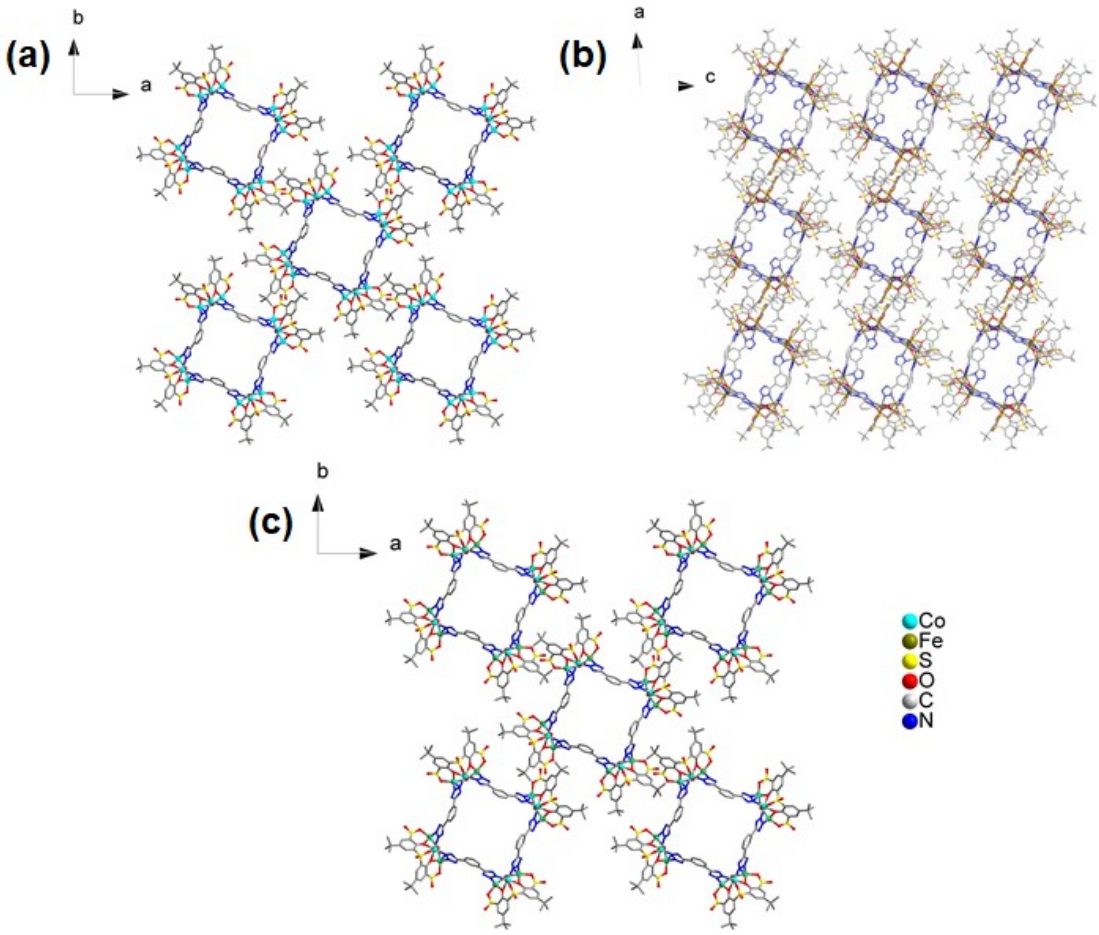


Figure S5. The packing diagrams of **Co_{16}** (a), **Fe_{16}** (b) and **$\{CoFe\}_{16}$-b** (c).

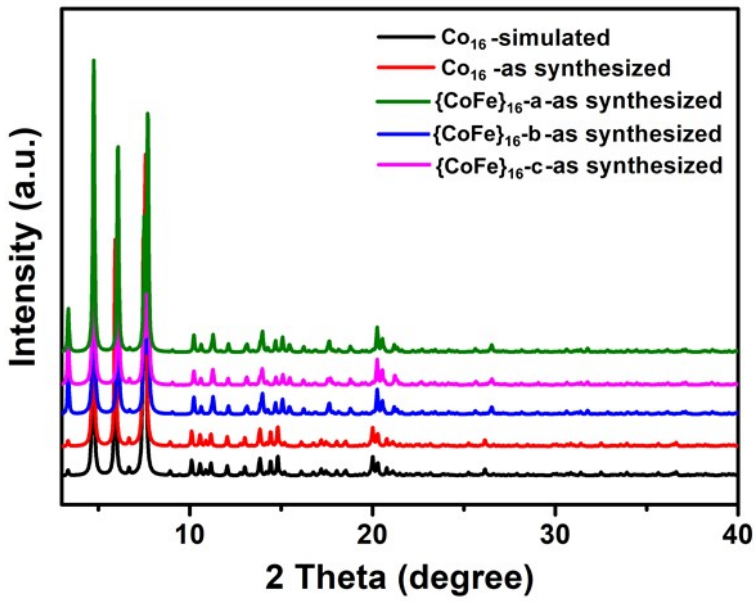


Figure S6. PXRD patterns of **Co_{16}**, **$\{CoFe\}_{16}$-a**, **$\{CoFe\}_{16}$-b**, and **$\{CoFe\}_{16}$-c**.

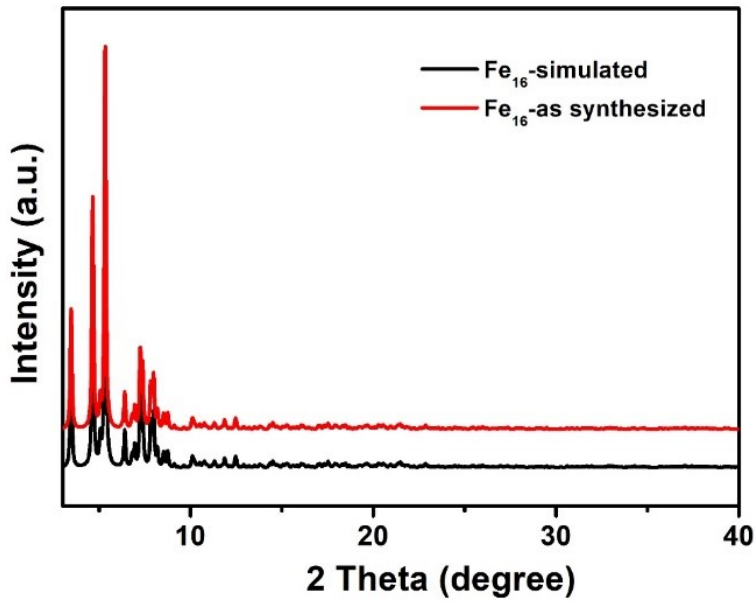


Figure S7. PXRD pattern of **Fe_{16}**.

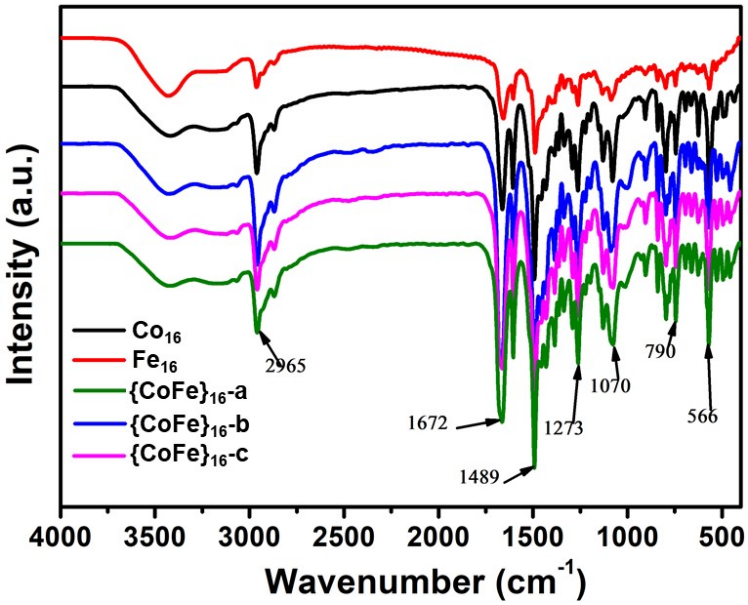


Figure S8. FT-IR spectra of **Co_{16}**, **Fe_{16}**, **$\{CoFe\}_{16}$-a**, **$\{CoFe\}_{16}$-b**, and **$\{CoFe\}_{16}$-c**.

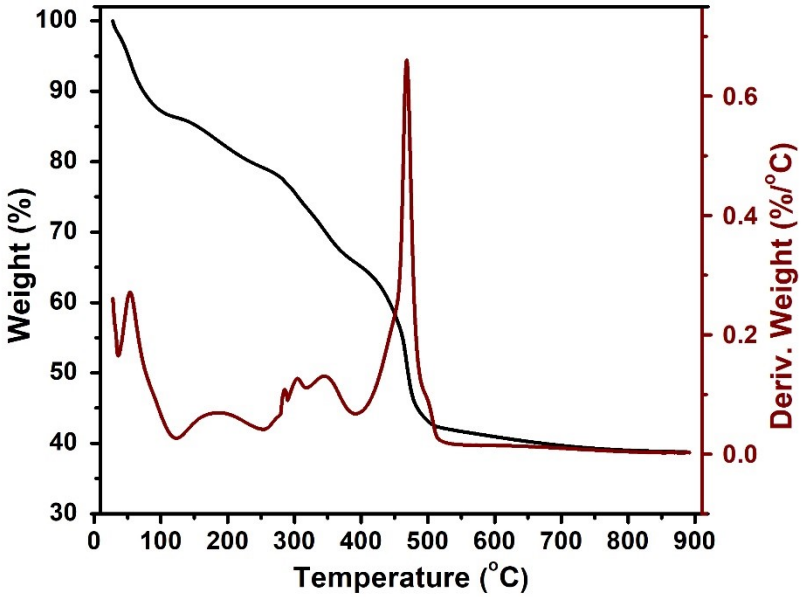


Figure S9. TGA curves of **Co_{16}**.

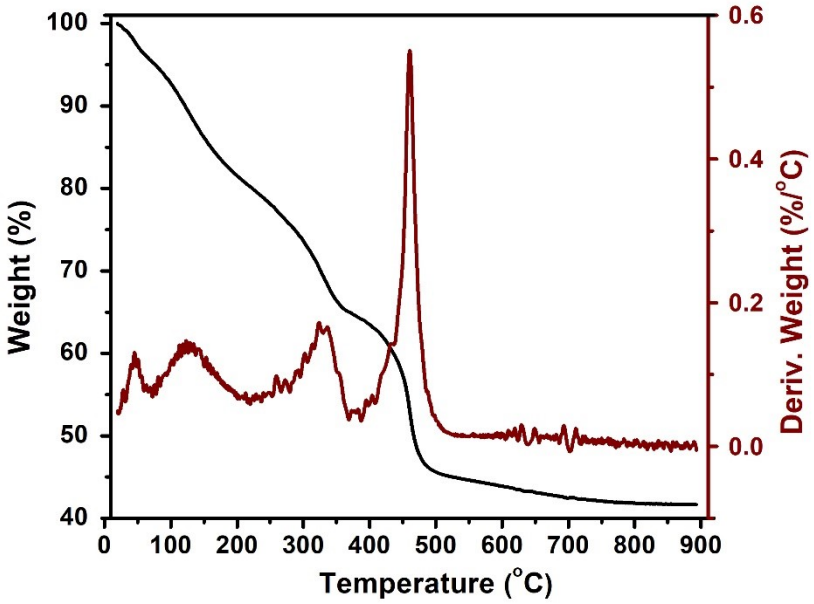


Figure S10. TGA curves of **$\{CoFe\}_{16}$-b**.

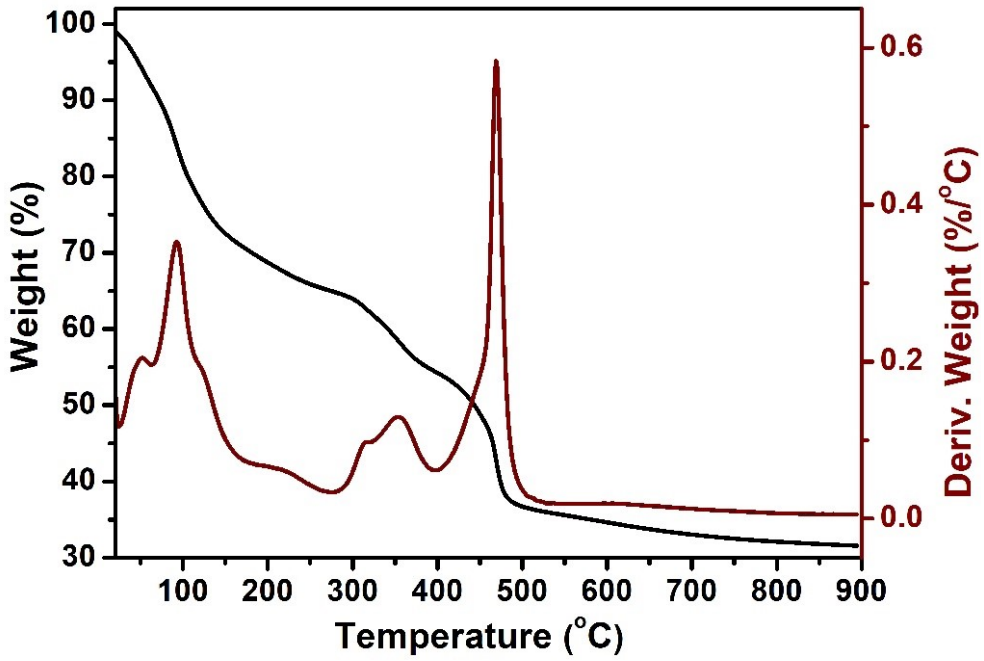


Figure S11. TGA curves of **Fe_{16}**.

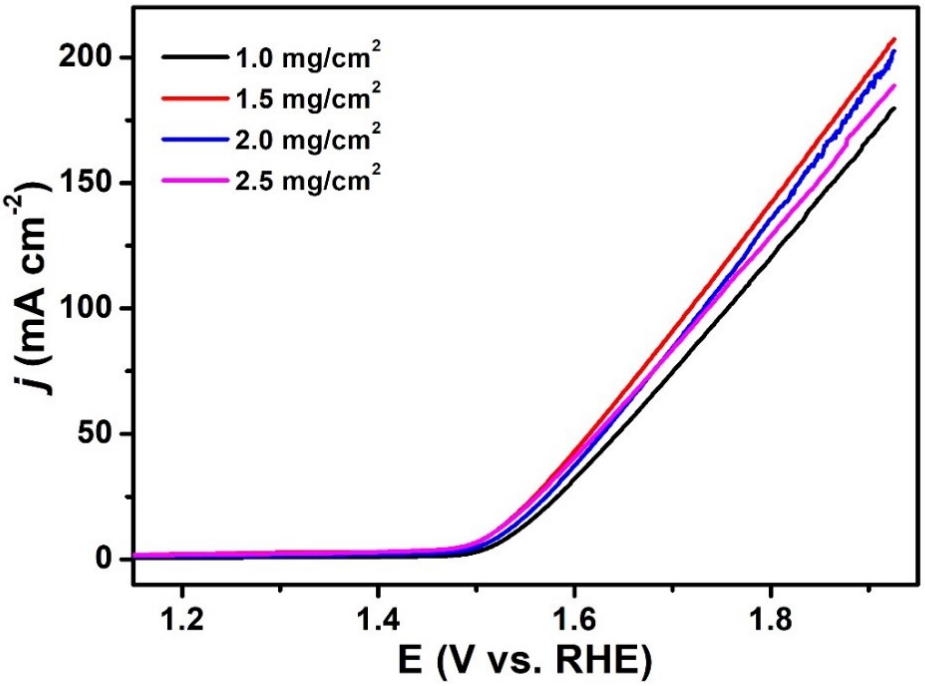


Figure S12. LSV curves of **{CoFe}$_{16}$-b**/CP at different loading.

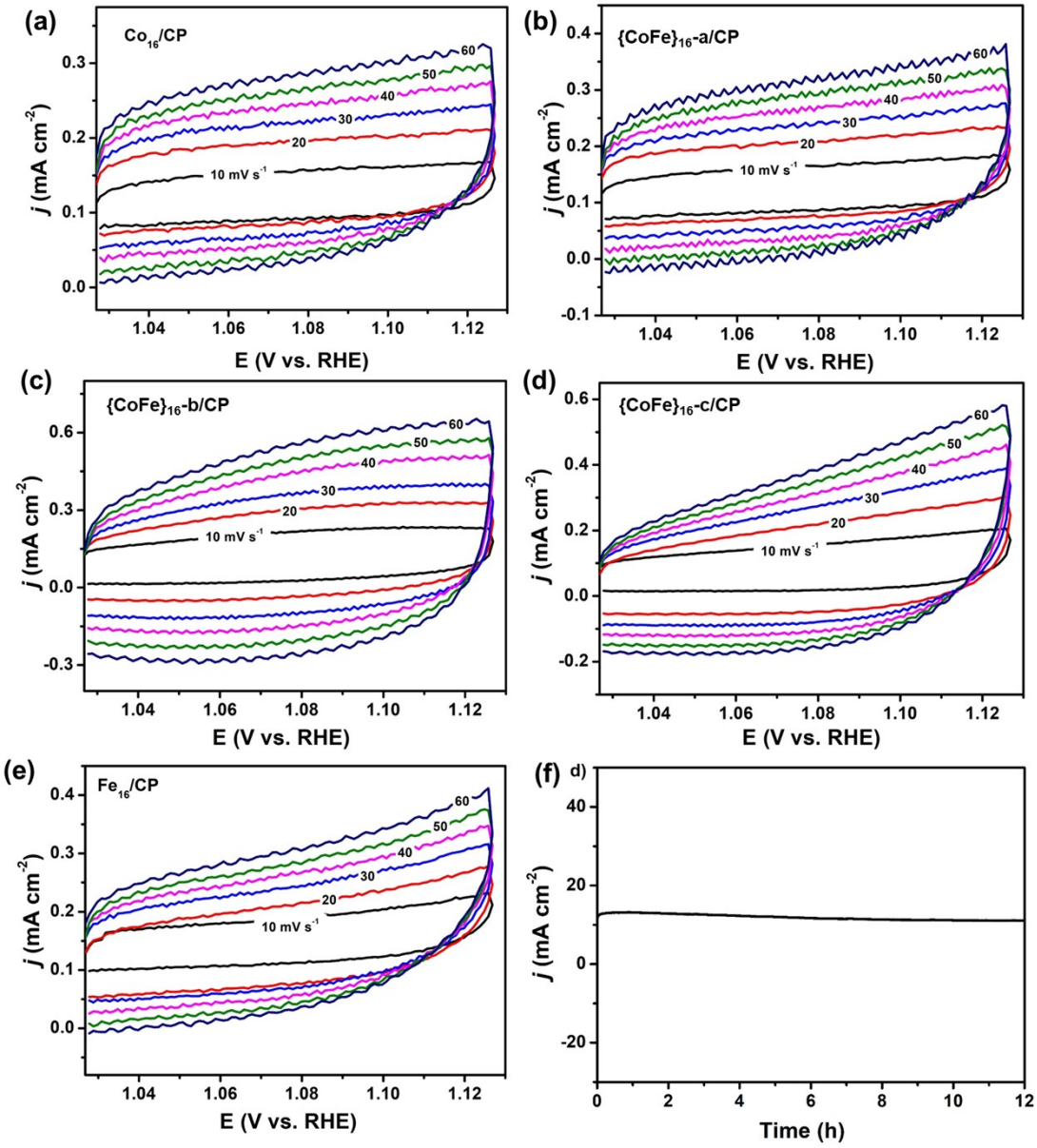


Figure S13. Cyclic voltammetry (CV) curves of **Co_{16}**/CP (a), **{CoFe}$_{16}$-a**/CP (b), **{CoFe}$_{16}$-b**/CP (c), **{CoFe}$_{16}$-c**/CP (d) and **Fe_{16}**/CP (e); (f) *i-t* curve of the **{CoFe}$_{16}$-b**/CP catalyst recorded at 1.60 V *vs* RHE.

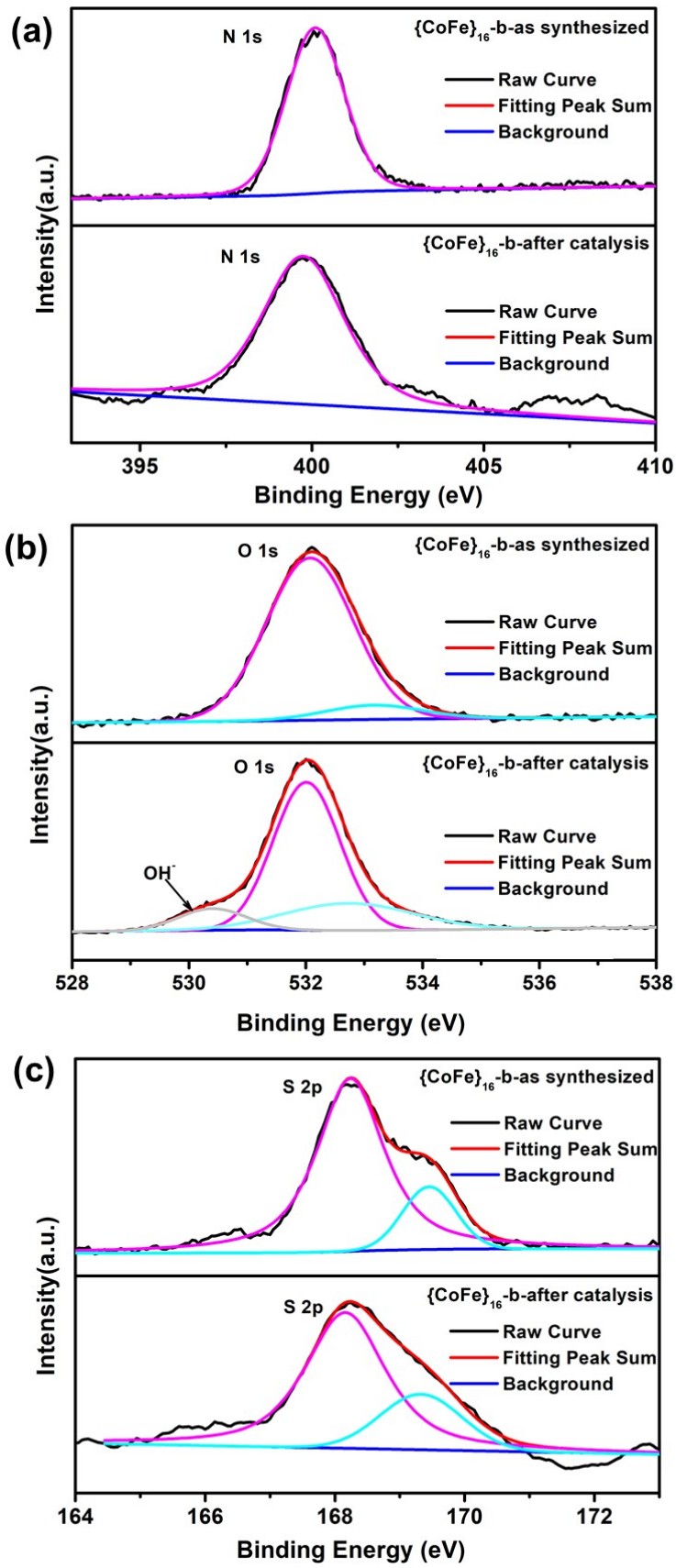


Figure S14. High-resolution N 1s (a), O 1s (b), and S 2p (c) XPS spectra of as-synthesized **{CoFe}$_{16}$-b** and **{CoFe}$_{16}$-b** after catalysis (after stabilized LSV).

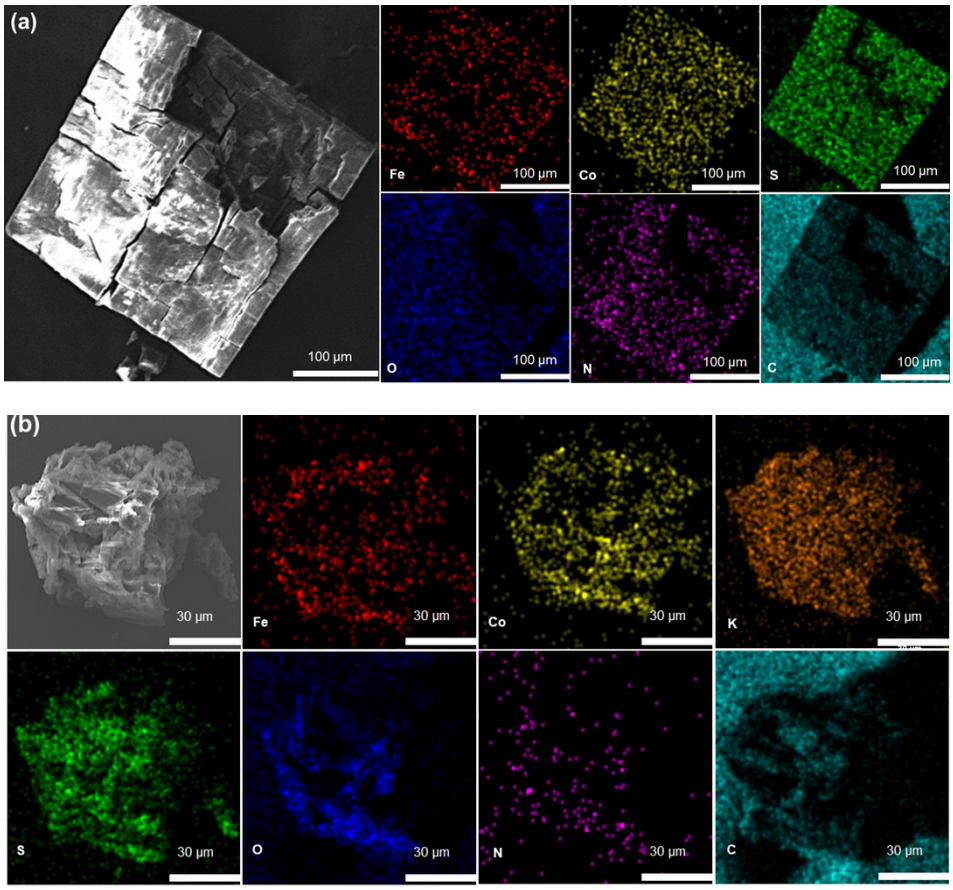


Figure S15. Scanning electron microscope (SEM) elemental mapping images of **{CoFe}$_{16}$-b** at different stage: (a) **{CoFe}$_{16}$-b**-as-prepared, (b) **{CoFe}$_{16}$-b** after OER catalysis.

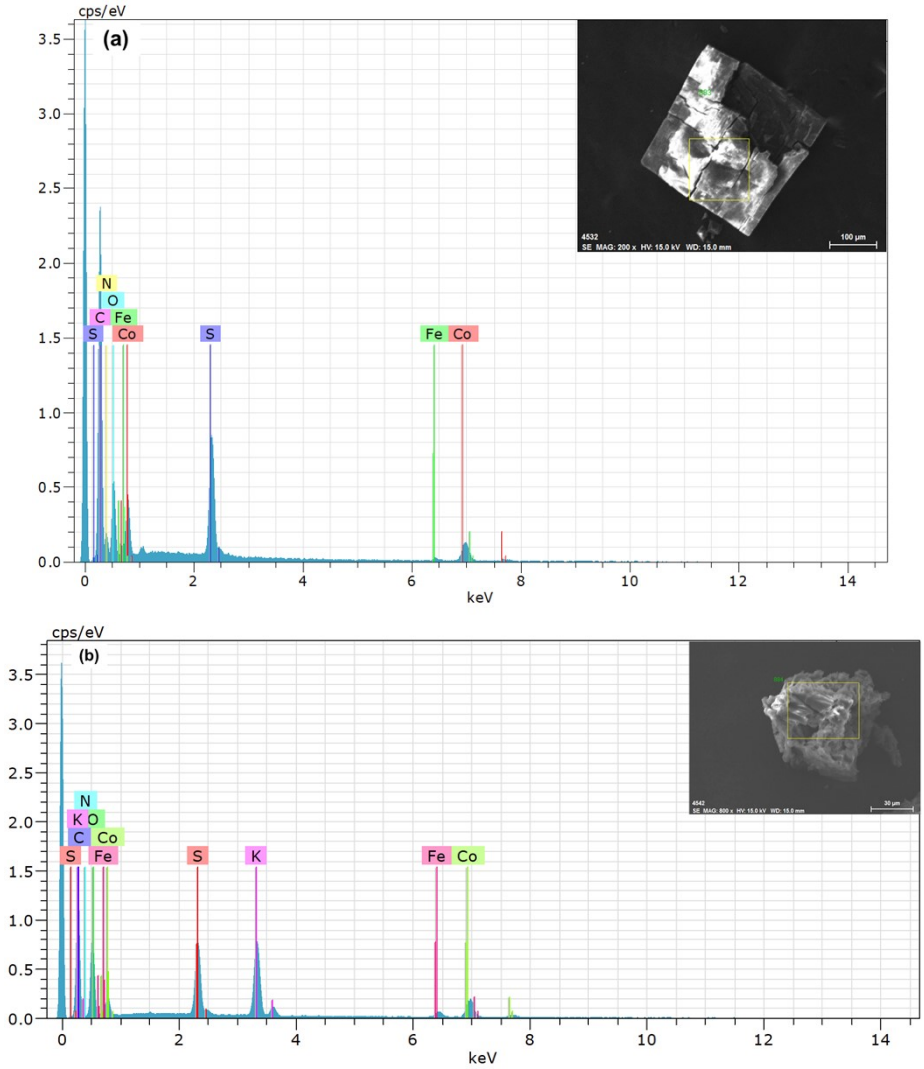


Figure S16. Energy-dispersive X-ray spectroscopy (EDS) analysis of **{CoFe}$_{16}$-b** at different stage: (a) **{CoFe}$_{16}$-b**-as-prepared, (b) **{CoFe}$_{16}$-b** after OER catalysis.

Table S1. Selected Crystal Data for Clusters **Co_{16}**, **Fe_{16}** and **$\{CoFe\}_{16}$-b**.

	Co_{16}	**Fe_{16}**	**$\{CoFe\}_{16}$-b**
Formula*	$C_{224}H_{216}N_{64}Co_{16}O_{52}S_{16}$	$C_{224}H_{216}N_{64}Fe_{16}O_{52}S_{16}$	$C_{224}H_{216}N_{64}Co_{9.60}Fe_{6.40}O_{52}S_{16}$
Formula Weight*	6092.44	6035.27	6072.72
Crystal System	Tetragonal	Monoclinic	Tetragonal
Space Group (no.)	*I4/m* (*No.* 87)	*C2/c* (*No*. 15)	*I4/m* (*No.* 87)
Temperature (*K*)	150 K	150 K	150 K
a(Å)	37.4109(13)	51.070(3)	37.212(3)
b(Å)	37.4109(13)	17.5178(11)	37.212(3)
c(Å)	16.2505(7)	52.146(3)	15.8033(13)
α (°)	90	90	90
β (°)	90	94.784(2)	90
γ (°)	90	90	90
V (Å^3)	22743.8(19)	46489(5)	21883(4)
Z	2	4	2
D_c (g/cm^{-3}) *	0.890	0.862	0.920
μ (mm^{-1})	0.689	0.602	0.685
F (000)	6224	12352	6195
Total Data	36053	132196	51005
Unique data	7443	34333	10093
R_{int}	0.070	0.0752	0.067
GOF on F^2	1.03	1.00	1.026
R_1[a] [I>2 $\sigma(I)$]	0.0559	0.0599	0.0611
wR_2[b]	0.1933	0.1798	0.2115

[a]$R_1 = \Sigma||F_0|-|F_c||/\Sigma|F_0|$; [b]$wR_2=\{\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$

Table S2. Selected bond distances (Å) and BVS calculations for **Co_{16}**, **$\{CoFe\}_{16}$-b**, and **Fe_{16}**

Co_{16}							
Band	Distance	r	Value	Band	Distance	r	Value
Co(1)-O(3)	2.071(4)	1.69	0.359	Co(3)-O(7)	2.069(5)	1.69	0.361
Co(1)-O(1)	2.088(3)	1.69	0.343	Co(3)-N(8)	2.099(4)	1.84	0.497
Co(1)-O(1)[b]	2.088(3)	1.69	0.343	Co(3)-N(8)[b]	2.099(4)	1.84	0.497
Co(1)-N(2)	2.108(4)	1.84	0.485	Co(3)-O(2)	2.106(4)	1.69	0.327
Co(1)-N(2)[b]	2.108(4)	1.84	0.485	Co(3)-O(2)[b]	2.106(4)	1.69	0.327
Co(1)- O(9)	2.171(4)	1.69	0.274	Co(3)-O(9)	2.190(4)	1.69	0.260
valence			**2.288**	valence			**2.268**
Co(2)-N(9)[a]	2.070(4)	1.84	0.537				
Co(2)-O(5)	2.071(4)	1.69	0.359				
Co(2)-N(3)	2.074(4)	1.84	0.531				
Co(2)-O(1)	2.075(3)	1.69	0.355				
Co(2)-O(2)	2.077(3)	1.69	0.353				
Co(2)-O(9)	2.2045(14)	1.69	0.250				
valence			**2.386**				
Symmetry Code a: 1-y, x, z; b: x, y,1-z; c: 1-y, x, 1-z.							
$\{CoFe\}_{16}$-b							
Band	Distance	r	Value	Band	Distance	r	Value
Co(1)-O(3)	2.058(5)	1.69	0.332	Fe(1)-O(3)	2.055(12)	1.73	0.487
Co(1)-O(1)	2.094(4)	1.69	0.305	Fe(1)-N(1)[a]	2.102(10)	1.86	0.444
Co(1)-O(1)[a]	2.094(4)	1.69	0.305	Fe(1)-N(1)	2.102(10)	1.86	0.444
Co(1)-N(1)	2.113(4)	1.84	0.527	Fe(1)-O(1)[a]	2.107(10)	1.73	0.426
Co(1)-N(1)[a]	2.114(5)	1.84	0.527	Fe(1)-O(1)	2.107(10)	1.73	0.426
Co(1)-O(9)	2.164(5)	1.69	0.302	Fe(1)-O(9)	2.225 (5)	1.73	0.276
valence			**2.299**	valence			**2.504**
Co(2)-N(2)	2.060(5)	1.84	0.565	Fe(2)-O(2)	2.056(7)	1.73	0.429
Co(2)-N(6)[b]	2.070(5)	1.84	0.531	Fe(2)-N(6)[b]	2.065(7)	1.86	0.581
Co(2)-O(1)	2.070(5)	1.69	0.363	Fe(2)-O(1)	2.071(7)	1.73	0.399
Co(2)-O(5)	2.076(5)	1.69	0.356	Fe(2)-O(5)	2.082(6)	1.73	0.387
Co(2)-O(2)	2.093(5)	1.69	0.331	Fe(2)-N(2)	2.096(7)	1.86	0.517
Co(2)-O(9)	2.238(4)	1.69	0.226	Fe(2)-O(9)	2.225(5)	1.73	0.267
valence			**2.373**	valence			**2.581**
Co(3)-O(7)	2.073(5)	1.69	0.338	Fe(3)-O(7)	2.054(13)	1.73	0.449
Co(3)-N(7)[b]	2.116(4)	1.84	0.498	Fe(3)-O(2)	2.108(9)	1.73	0.393
Co(3)-N(7)[c]	2.116(4)	1.84	0.498	Fe(3)-O(2)	2.109(9)	1.73	0.393
Co(3)-O(2)[a]	2.122(4)	1.69	0.296	Fe(3)-N(7)[b]	2.131(8)	1.86	0.444
Co(3)-O(2)	2.122(4)	1.69	0.296	Fe(3)-N(7)[c]	2.131(8)	1.86	0.444
Co(3)-O(9)	2.151(5)	1.69	0.299	Fe(3)-O(9)	2.165(13)	1.73	0.300
valence			**2.226**	valence			**2.423**
Symmetry Code a: x, y,2-z; b: y,1-x, z; c: y, 1-x, 2-z.							

Fe_{16}							
Band	Distance	r	Value	Band	Distance	r	Value
Fe(1)-O(5)	2.060(3)	1.73	0.414	Fe(5)-O(17)	2.097(3)	1.73	0.394
Fe(1)-N(10)	2.119(4)	1.86	0.497	Fe(5)-O(13)	2.118(3)	1.73	0.354
Fe(1)-O(4)	2.131(3)	1.73	0.342	Fe(5)-N(14)	2.125(4)	1.86	0.489
Fe(1)-O(25)	2.138(3)	1.73	0.336	Fe(5)-O(26)	2.166(3)	1.73	0.311
Fe(1)-N(1)	2.161(4)	1.86	0.443	Fe(5)-N(5)	2.182(4)	1.86	0.419
Fe(1)-O(1)	2.197(3)	1.73	0.286	Fe(5)-O(16)	2.211(3)	1.73	0.275
valence			**2.318**	valence			**2.242**
Fe(2)-O(2)	2.057(3)	1.73	0.418	Fe(6)-O(19)	2.095(3)	1.73	0.377
Fe(2)-N(11)	2.100(4)	1.86	0.523	Fe(6)-O(13)	2.103(3)	1.73	0.369
Fe(2)-O(7)	2.109(3)	1.73	0.363	Fe(6)-N(6)	2.110(4)	1.86	0.509
Fe(2)-N(30)[a]	2.123(4)	1.86	0.491	Fe(6)-O(14)	2.119(3)	1.73	0.353
Fe(2)-O(1)	2.146(3)	1.73	0.328	Fe(6)-N(26)	2.123(4)	1.86	0.491
Fe(2)-O(25)	2.264(3)	1.73	0.239	Fe(6)-O(26)	2.190(3)	1.73	0.292
valence			**2.362**	valence			**2.391**
Fe(3)-O(9)	2.062(3)	1.73	0.412	Fe(7)-O(21)	2.088(3)	1.73	0.384
Fe(3)-O(25)	2.135(3)	1.73	0.338	Fe(7)-O(15)	2.106(3)	1.73	0.366
Fe(3)-O(2)	2.145(3)	1.73	0.329	Fe(7)-N(23)[a]	2.118(4)	1.86	0.498
Fe(3)-N(19)	2.147(4)	1.86	0.460	Fe(7)-N(25)	2.030(5)	1.86	0.481
Fe(3)-N(29)[a]	2.166(4)	1.86	0.437	Fe(7)-O(14)	2.139(3)	1.73	0.335
Fe(3)-O(3)	2.198(3)	1.73	0.285	Fe(7)-O(26)	2.2532(3)	1.73	0.246
valence			**2.263**	valence			**2.309**
Fe(4)-O(4)	2.047(3)	1.73	0.429	Fe(8)-O(23)	2.076(3)	1.73	0.397
Fe(4)-N(18)	2.088(4)	1.86	0.540	Fe(8)-O(15)	2.091(3)	1.73	0.381
Fe(4)-O(11)	2.107(3)	1.73	0.365	Fe(8)-N(22)[a]	2.105(4)	1.86	0.516
Fe(4)-O(3)	2.110(3)	1.73	0.362	Fe(8)-N(15)	2.110(4)	1.86	0.509
Fe(4)-N(2)	2.127(4)	1.86	0.486	Fe(8)-O(16)	2.110(3)	1.73	0.362
Fe(4)-O(25)	2.308(3)	1.73	0.212	Fe(8)-O(26)	2.616(2)	1.73	0.262
valence			**2.394**	valence			**2.426**
Symmetry Code a: 3/2-x,3/2-y,1-z.							

Note: BVS calculations reveal that all the ions in these clusters are divalent.

Table S3. ICP-AES analysis of catalysts **{CoFe}$_{16}$-a**, **{CoFe}$_{16}$-b**, and **{CoFe}$_{16}$-c**.

Catalysts	Co (ppm)	Fe (ppm)	Co: Fe (molar ratio)	Experimental value
{CoFe}$_{16}$-a	1362.0	56.55	24.10 : 1	$Co_{15.4}Fe_{0.6}$
{CoFe}$_{16}$-b	977.6	635.1	1.54 : 1	$Co_{9.7}Fe_{6.3}$
{CoFe}$_{16}$-c	639.5	910.9	1 : 1.42	$Co_{6.4}Fe_{9.6}$