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Various Polyoxomolybdate-based Hybrids Induced by pH and Solvents: Structures, Adsorption Activities for Dyes and Bifunctional Electrocatalytic Properties

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Table. S1 Selected bond distances (Å) and angles (°) for compounds **1–4**.

Compound **1**			
Co(1)-O(1W)	2.078(5)	N(4)-Co(1)-O(2W)	90.4(2)
Co(1)-N(2)#2	2.082(5)	O(1W)-Co(1)-O(11)	85.87(17)
Co(1)-O(2W)	2.112(5)	N(2)#2-Co(1)-O(11)	165.8(2)
Co(1)-N(4)	2.087(5)	O(2W)-Co(1)-O(11)	93.62(19)
Co(1)-O(11)	2.126(4)	N(4)-Co(1)-O(11)	78.43(19)
Co(1)-O(9)#2	2.173(5)	O(1W)-Co(1)-O(9)#2	90.28(19)
O(1W)-Co(1)-N(4) O(11)-	163.9(2)	N(2)#2-Co(1)-O(9)#2	78.5(2)
Co(1)-O(9)#2	90.28(19)	N(2)#2-Co(1)-N(4)	105.4(2)
O(1W)-Co(1)-N(2)#2	90.7(2)	O(2W)-Co(1)-O(9)#2	176.94(18)
O(1W)-Co(1)-O(2W)	87.1(2)	N(4)-Co(1)-O(9)#2	92.5(2)
N(2)#2-Co(1)-O(2W)	99.9(2)		
Symmetry code for **1**: #2 x – 1/2, –y + 1/2, z – 1/2;			
Compound **2**			
Co(1)-N(3)	2.049(8)	O(5)-Co(2)-O(4)	90.7(2)
N(1)-Co(1)	2.094(7)	O(6W)-Co(2)-O(4)	84.8(3)
Co(1)-O(1W)	2.103(6)	N(5)-Co(2)-O(4)	169.2(3)
Co(1)-O(1)	2.112(6)	N(12)-Co(2)-O(4)	76.7(2)
Co(1)-O(12)	2.123(5)	O(5W)-Co(2)-O(4)	93.9(3)
Co(1)-O(2)	2.128(6)	O(6W)-Co(2)-O(5)	85.5(3)
Co(2)-O(5W)	2.066(7)	N(5)-Co(2)-O(5)	79.1(3)
Co(2)-N(12)	2.067(7)	N(12)-Co(2)-O(5)	79.1(3)
Co(2)-N(5)	2.074(8)	O(5W)-Co(2)-O(5)	173.9(3)
Co(2)-O(6W)	2.132(6)	N(5)-Co(2)-O(6W)	90.8(3)
Co(2)-O(5)	2.134(6)	N(3)-Co(1)-O(2)	78.3(3)
Co(2)-O(4)	2.207(6)	N(1)-Co(1)-O(2)	88.9(3)
N(3)-Co(1)-N(1)	98.3(3)	O(1W)-Co(1)-O(2)	170.8(3)
N(3)-Co(1)-O(1W)	93.4(3)	O(1)-Co(1)-O(2)	88.0(2)
N(1)-Co(1)-O(1W)	96.4(3)	O(12)-Co(1)-O(2)	89.3(2)
N(3)-Co(1)-O(1)	165.8(3)	C(1)-O(1)-Co(1)	115.7(5)
N(1)-Co(1)-O(1)	77.6(2)	O(5W)-Co(2)-N(12)	97.8(3)
O(1W)-Co(1)-O(1)	100.5(3)	O(5W)-Co(2)-N(5)	96.0(3)

N(3)-Co(1)-O(12)	99.6(3)	N(12)-Co(2)-N(5)	106.0(3)
N(1)-Co(1)-O(12)	161.2(3)	O(5W)-Co(2)-O(6W)	91.0(3)
O(1W)-Co(1)-O(12)	88.1(2)	N(12)-Co(2)-O(6W)	160.0(3)
O(1)-Co(1)-O(12)	83.6(2)		
Compound **3**			
Co(1)-N(3)	2.035(8)	O(4)-Co(1)-O(5)	94.8(2)
Co(1)-N(5)	2.071(7)	N(3)-Co(1)-O(3)	78.7(3)
Co(1)-N(4)	2.101(7)	N(5)-Co(1)-O(3)	170.7(3)
Co(1)-O(4)	2.104(5)	N(4)-Co(1)-O(3)	92.8(3)
Co(1)-O(5)	2.150(6)	O(4)-Co(1)-O(3)	92.5(2)
Co(1)-O(3)	2.156(6)	O(5)-Co(1)-O(3)	93.3(2)
O(1)-Co(2)	2.149(6)	N(2)-Co(2)-N(13)	97.3(3)
O(2)-Co(2)	2.196(5)	N(2)-Co(2)-N(16)	100.1(3)
N(2)-Co(2)	2.055(7)	N(13)-Co(2)-N(16)	93.6(3)
Co(2)-N(13)	2.093(7)	N(2)-Co(2)-O(6)	90.8(2)
Co(2)-N(16)	2.104(7)	N(13)-Co(2)-O(6)	169.1(3)
Co(2)-O(6)	2.116(5)	N(16)-Co(2)-O(6)	77.7(2)
N(3)-Co(1)-N(5)	97.3(3)	N(2)-Co(2)-O(1)	167.9(2)
N(3)-Co(1)-N(4)	93.7(3)	N(13)-Co(2)-O(1)	78.0(3)
N(5)-Co(1)-N(4)	95.9(3)	N(16)-Co(2)-O(1)	91.4(2)
N(3)-Co(1)-O(4) N(5)-Co(1)-	168.1(3)	O(6)-Co(2)-O(1)	95.5(2)
O(4)	92.6(3)	N(2)-Co(2)-O(2)	77.3(2)
N(4)-Co(1)-O(4)	78.6(2)	N(13)-Co(2)-O(2)	93.2(2)
N(3)-Co(1)-O(5)	93.7(3)	N(16)-Co(2)-O(2)	173.0(2)
N(5)-Co(1)-O(5)	78.5(2)	O(6)-Co(2)-O(2)	95.7(2)
N(4)-Co(1)-O(5)	171.2(3)	O(1)-Co(2)-O(2)	91.7(2)
Compound **4**			
Co(1)-N(2)	2.10(12)	N(5)#1-Co(1)-O(2)	97(4)
Co(1)-N(1)	2.10(11)	O(11)#1-Co(1)-O(2)	97(4)
Co(1)-N(5)#1	2.11(11)	N(1)-Co(1)-O(1)	78(4)
Co(1)-O(11)#1	2.12(9)	N(2)-Co(1)-O(1)	95(4)
Co(1)-O(2)	2.15(10)	N(5)#1-Co(1)-O(1)	164(4)
Co(1)-O(1)	2.16(9)	O(11)#1-Co(1)-O(1)	92(4)
N(5)-Co(1)#1	2.11(11)	O(2)-Co(1)-O(1)	97(4)
O(11)-Co(1)#1	2.12(9)	N(2)-Co(1)-O(2)	77(4)
N(1)-Co(1)-N(2)	92(4)	N(1)-Co(1)-O(2)	167(4)
N(1)-Co(1)-N(5)#1	91(4)	N(5)#1-Co(1)-O(11)#1	79(4)
N(2)-Co(1)-N(5)#1	95(4)	N(2)-Co(1)-O(11)#1	171(4)
N(1)-Co(1)-O(11)#1	95(4)		
Symmetry code for **4**: #1 – x, y , – z + 3/2;			

Table. S2 Selected hydrogen bonding geometry for compound **1**.

D–H···A	D–H / Å	H···A / Å	D···A / Å	D–H···A / º
N(1)–H(1B)···O(4)	0.859	2.191	2.967	150.06
N(3)–H(3B)···O(13)	0.86	2.109	2.844	143.08

Table S3 Selected hydrogen bonding geometry for compound **2**.

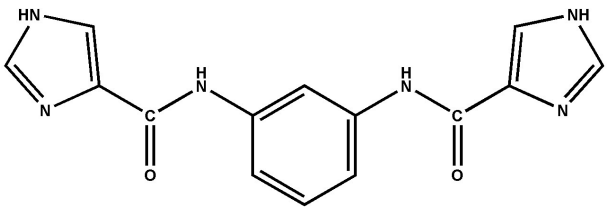
D–H···A	D–H / Å	H···A / Å	D···A / Å	D–H···A / º
N(6)–H(6A)···O(17)	0.86	2.594	2.979	108.35
N(8)–H(8A)···O(21)	0.861	2.307	3.044	143.72

Table S4 Selected hydrogen bonding geometry for compound **3**.

D–H···A	D–H / Å	H···A / Å	D···A / Å	D–H···A / º
N(1)–H(1B)···O(13)	0.859	2.384	2.956	124.34
N(17)–H(17B)···O(23)	0.86	1.891	2.751	179.5
N(14)–H(14A)···O(21)	0.859	2.313	3.011	138.52

Table S5 Selected hydrogen bonding geometry for compound **4**.

D–H···A	D–H / Å	H···A / Å	D···A / Å	D–H···A / º
N(4)–H(4D)···O(6)	0.859	2.112	2.93	158.91
N(6)–H(6B)···O(14)	0.861	1.968	2.809	165.19
N(11)–H(11D)···O(10)	0.862	2.028	2.853	160.06



Scheme. S1. The ligand **L** used in this work.

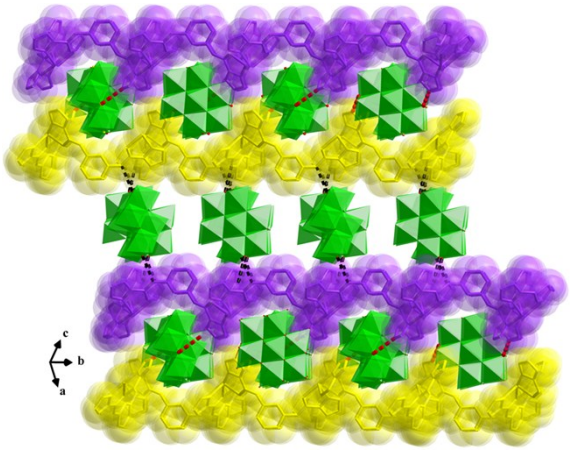


Fig. S1. View of the 3D supramolecular structure of **1**.

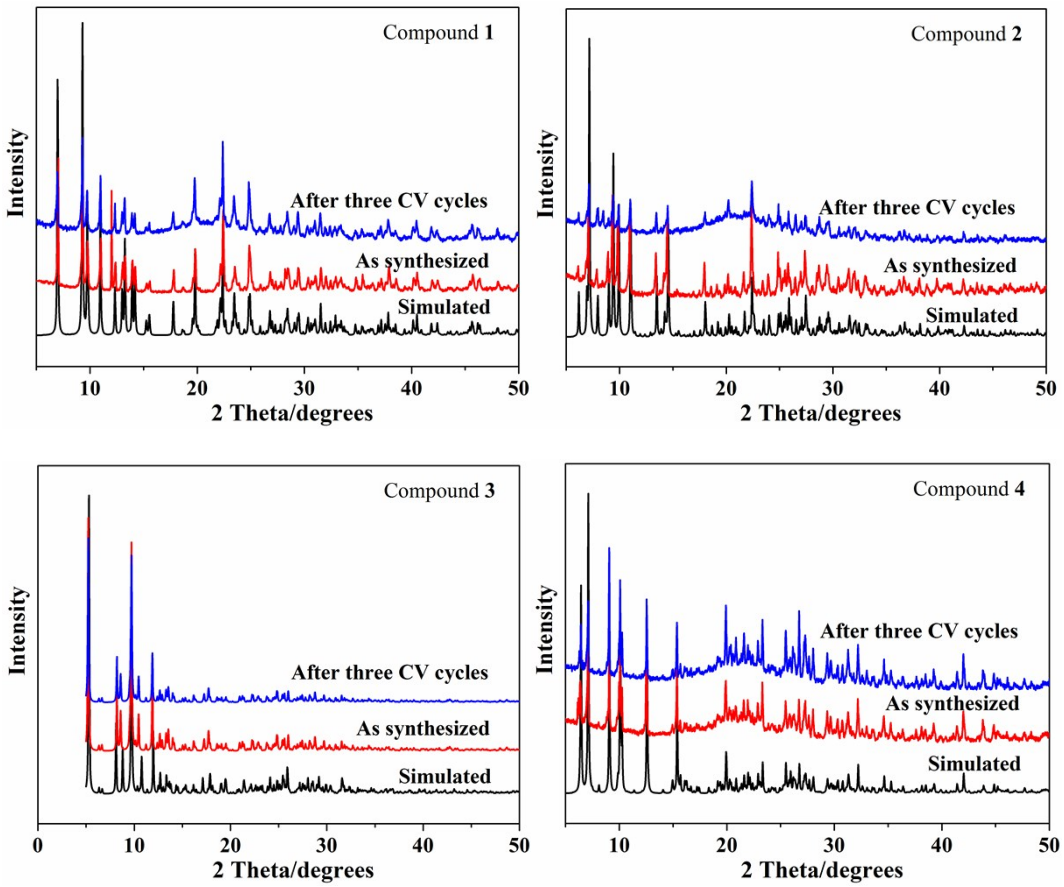


Fig. S2. PXRD patterns of compounds **1**–**4** (simulated, as synthesized and after three CV cycles).

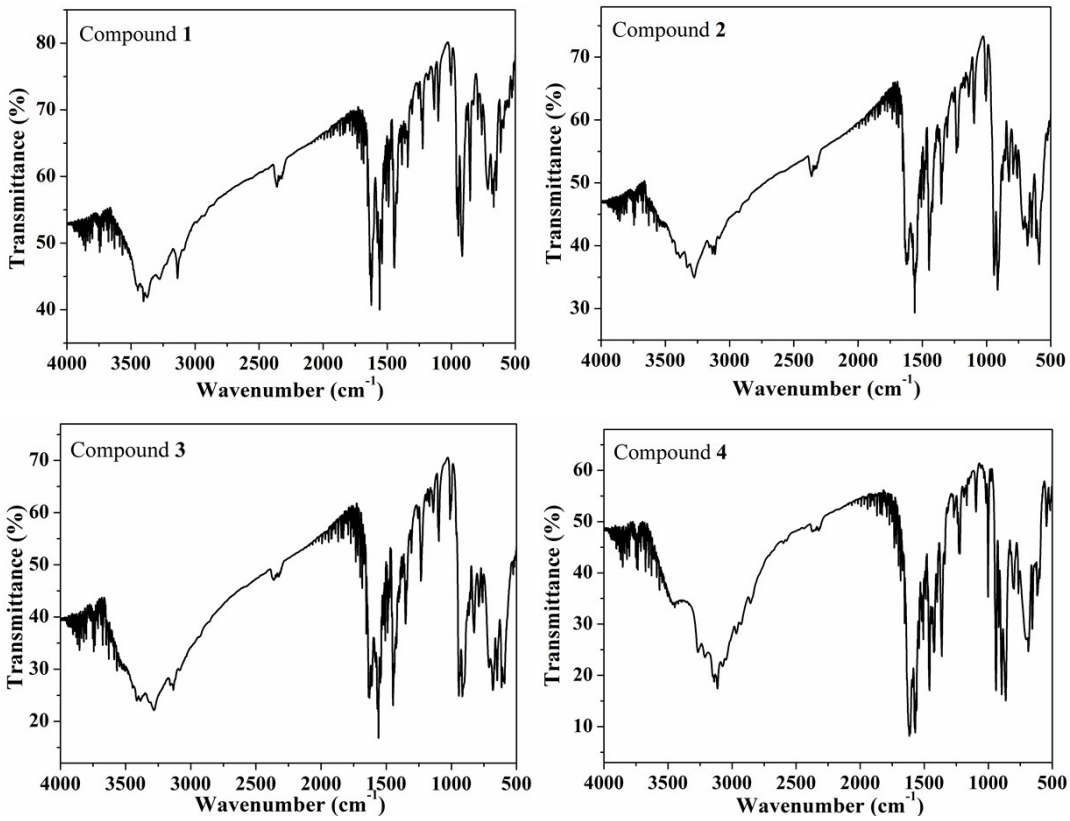


Fig. S3. The IR spectra of compounds **1**–**4**.

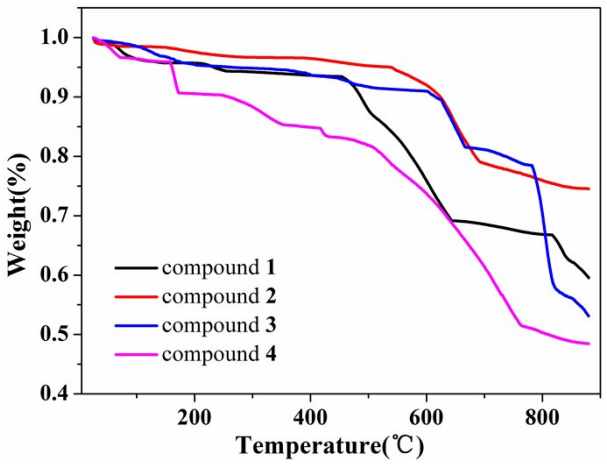


Fig. S4. The TG curves of compounds **1**–**4.**

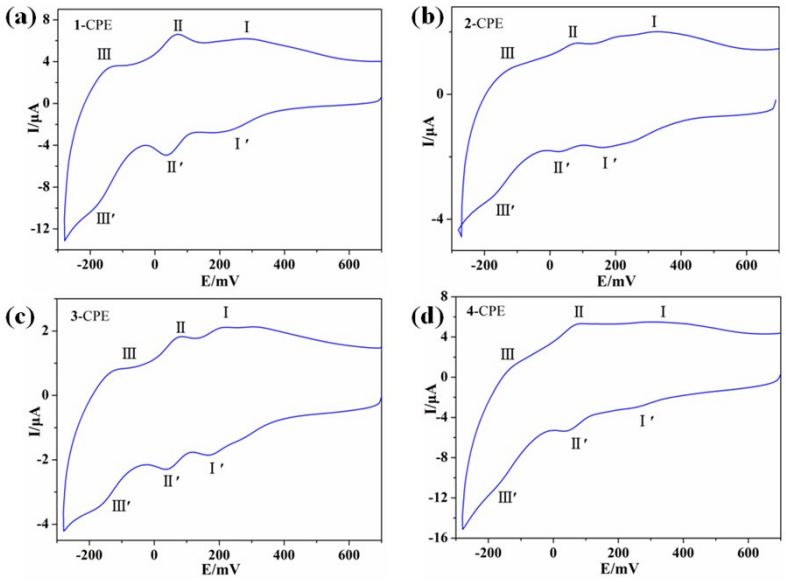


Fig. S5. (a) Cyclic voltammograms of **1**, **2, 3** and **4**–CPEs in 0.1M H_2SO_4 + 0.5 M Na_2SO_4 aqueous. Scan rate: 200 mV s^{-1}.