Supplementary Material (ESI) for *Dalton Trans.*

Various Anderson-type polyoxometalate-based metal–organic complexes induced by diverse solvents: Assembly, structures and selective adsorption for organic dyes

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Table S1 Selected bond distances (Å) and angles (°) for complexes **1–6**.

Complex **1**

Cu(1)-O(3)	1.946(15)	Cu(1)-N(1)	1.96(2)
Cu(1)-O(3)#2	1.946(15)	O(3)#2-Cu(1)-O(3)	179.998(13)
Cu(1)-N(1)#2	1.96(2)	O(3)#2-Cu(1)-N(1)	96.7(7)
O(3)-Cu(1)-N(1)#2	96.7(7)	N(1)#2-Cu(1)-N(1)	179.999(8)
O(3)#2-Cu(1)-N(1)#2	83.3(7)	O(3)-Cu(1)-N(1)	83.3(7)

Symmetry code:#1-x+1,-y+1,-z+1;#2 -x+2,-y+1,-z+2

Complex **2**

Zn(1)-O(4W)	2.061(8)	Zn(2)-O(2W)	2.130(10)
Zn(1)-O(6W)	2.064(8)	Zn(2)-O(12)#2	2.141(7)
Zn(1)-O(2)	2.104(7)	Zn(2)-O(3W)	2.175(10)
Zn(1)-N(1)	2.113(8)	Zn(2)-O(27)	2.243(9)
Zn(1)-O(5W)	2.136(8)	O(5W)-Zn(1)-O(3)#1	169.5(3)

Zn(1)-O(3)#1	2.238(8)	O(1W)-Zn(2)-O(2W)	175.4(5)
O(4W)-Zn(1)-O(6W)	94.6(3)	O(1W)-Zn(2)-O(12)#2	90.2(5)
O(4W)-Zn(1)-O(2)	173.2(3)	O(2W)-Zn(2)-O(12)#2	93.0(3)
O(6W)-Zn(1)-O(2)	91.6(3)	O(1W)-Zn(2)-O(3W)	88.4(5)
O(4W)-Zn(1)-N(1)	97.1(3)	O(2W)-Zn(2)-O(3W)	95.0(4)
O(6W)-Zn(1)-N(1)	162.5(3)	O(12)#2-Zn(2)-O(3W)	88.9(3)
O(2)-Zn(1)-N(1)	77.5(3)	O(1W)-Zn(2)-O(27)	85.4(5)
O(4W)-Zn(1)-O(5W)	90.7(3)	O(2W)-Zn(2)-O(27)	91.6(3)
O(6W)-Zn(1)-O(5W)	90.7(3)	O(12)#2-Zn(2)-O(27)	174.1(3)
O(2)-Zn(1)-O(5W)	86.4(3)	O(3W)-Zn(2)-O(27)	87.2(3)
N(1)-Zn(1)-O(5W)	102.1(3)	O(2)-Zn(1)-O(3)#1	101.3(3)
O(4W)-Zn(1)-O(3)#1	82.4(3)	N(1)-Zn(1)-O(3)#1	86.5(3)
O(6W)-Zn(1)-O(3)#1	82.1(3)		

Symmetry code:#1-x,-y+1,-z+1;#2 -x+1,-y+1,-z+1

Complex **3**

Zn(1)-N(3)#1	2.098(4)	O(1W)-Zn(2)	2.067(4)
Zn(1)-N(3)	2.098(4)	Zn(2)-O(2W)	2.085(4)
Zn(1)-O(13)	2.117(3)	Zn(2)-O(12)	2.150(3)
Zn(1)-O(13)#1	2.117(3)	Zn(2)-O(3)#3	2.186(4)

Zn(1)-O(3W)	2.159(7)	O(1)-Zn(2)	2.097(4)
Zn(1)-O(4W)	2.174(6)	O(1W)-Zn(2)-O(2W)	92.78(17)
N(3)#1-Zn(1)-N(3)	176.1(2)	O(1W)-Zn(2)-O(1)	92.41(14)
N(3)#1-Zn(1)-O(13)	89.71(14)	O(2W)-Zn(2)-O(1)	174.27(16)
N(3)-Zn(1)-O(13)	90.58(14)	O(1W)-Zn(2)-N(1)	169.46(15)
N(3)#1-Zn(1)-O(13)#1	90.59(14)	O(2W)-Zn(2)-N(1)	95.93(17)
N(3)-Zn(1)-O(13)#1	89.70(14)	O(1)-Zn(2)-N(1)	78.66(15)
O(13)-Zn(1)-O(13)#1	171.4(2)	O(1W)-Zn(2)-O(12)	88.71(14)
N(3)#1-Zn(1)-O(3W)	91.94(12)	O(2W)-Zn(2)-O(12)	91.42(16)
N(3)-Zn(1)-O(3W)	91.94(12)	O(1)-Zn(2)-O(12)	91.12(13)
O(13)-Zn(1)-O(3W)	85.71(11)	N(1)-Zn(2)-O(12)	96.98(15)
O(13)#1-Zn(1)-O(3W)	85.71(11)	O(1W)-Zn(2)-O(3)#3	82.43(14)
N(3)#1-Zn(1)-O(4W)	88.06(12)	O(2W)-Zn(2)-O(3)#3	83.81(16)
N(3)-Zn(1)-O(4W)	88.06(12)	O(1)-Zn(2)-O(3)#3	94.48(14)
O(13)-Zn(1)-O(4W)	94.29(11)	N(1)-Zn(2)-O(3)#3	92.59(15)
O(13)#1-Zn(1)-O(4W)	94.29(11)	O(12)-Zn(2)-O(3)#3	169.70(14)
O(3W)-Zn(1)-O(4W)	180.000(4)		

Symmetry code:#1-x+1,y,-z+3/2;#2 -x+1,-y+1,-z+1;#3 -x+1/2,-y+3/2,-z+1

Complex **4**

Ni(1)-O(3)#1	2.026(10)	Ni(3)-O(24)#4	2.017(10)
Ni(1)-O(2W)	2.068(11)	Ni(3)-O(3W)	2.103(17)

Ni(1)-N(3)#1	2.069(13)	Ni(3)-O(4W)	2.073(18)
Ni(1)-O(1)	2.087(11)	Ni(3)-N(1)#5	2.099(13)
Ni(1)-O(14)	2.089(10)	N(1)-Ni(3)	2.099(13)
Ni(1)-O(1W)	2.092(11)	O(24)#3-Ni(3)-O(24)#4	175.9(6)
O(3)#1-Ni(1)-O(2W)	178.1(4)	O(24)#3-Ni(3)-O(3W)	92.1(3)
O(3)#1-Ni(1)-N(3)#1	80.7(5)	O(24)#4-Ni(3)-O(3W)	92.1(3)
O(2W)-Ni(1)-N(3)#1	97.4(5)	O(24)#3-Ni(3)-O(4W)	87.9(3)
O(3)#1-Ni(1)-O(1)	94.8(4)	O(24)#4-Ni(3)-O(4W)	87.9(3)
O(2W)-Ni(1)-O(1)	84.9(4)	O(3W)-Ni(3)-O(4W)	180.000(6)
N(3)#1-Ni(1)-O(1)	92.9(5)	O(24)#3-Ni(3)-N(1)#5	91.2(5)
O(3)#1-Ni(1)-O(14)	90.3(4)	O(24)#4-Ni(3)-N(1)#5	88.8(5)
O(2W)-Ni(1)-O(14)	90.3(4)	O(3W)-Ni(3)-N(1)#5	88.9(4)
N(3)#1-Ni(1)-O(14)	94.7(5)	O(4W)-Ni(3)-N(1)#5	91.1(4)
O(1)-Ni(1)-O(14)	171.4(4)	O(24)#3-Ni(3)-N(1)	88.8(5)
O(3)#1-Ni(1)-O(1W)	91.1(4)	O(24)#4-Ni(3)-N(1)	91.2(5)
O(2W)-Ni(1)-O(1W)	90.7(4)	O(3W)-Ni(3)-N(1)	88.9(4)
N(3)#1-Ni(1)-O(1W)	171.2(5)	O(4W)-Ni(3)-N(1)	91.1(4)
O(1)-Ni(1)-O(1W)	84.5(4)	N(1)#5-Ni(3)-N(1)	177.7(7)
O(14)-Ni(1)-O(1W)	88.5(4)		

Symmetry code:#1-x+1/2,-y+1/2 ,-z;#2 -x,-y,-z;#3 -x+1/2,y+1/2,-z+1/2;#4 x+1/2,y+1/2,z;#5 -x+1,y,-z+1/2

Complex **5**

Cu(1)-O(1)	1.956(5)	Cu(2)-N(2)#3	2.010(6)
Cu(1)-O(1W)	1.987(6)	Cu(2)-O(2W)	2.093(9)
Cu(1)-O(4W)	1.988(5)	Cu(2)-O(3W)	2.284(5)
Cu(1)-N(1)	1.996(6)	Cu(2)-O(13)#3	2.312(5)
Cu(1)-O(8)#1	2.344(5)	Cu(2)-O(13)	2.312(5)
Cu(1)-O(10)	2.418(5)	N(2)-Cu(2)-N(2)#3	178.7(4)
O(1)-Cu(1)-O(1W)	179.1(2)	N(2)-Cu(2)-O(2W)	89.34(19)
O(1)-Cu(1)-O(4W)	91.1(2)	N(2)#3-Cu(2)-O(2W)	89.34(19)
O(1W)-Cu(1)-O(4W)	89.8(2)	N(2)-Cu(2)-O(3W)	90.66(19)
O(1)-Cu(1)-N(1)	83.0(2)	N(2)#3-Cu(2)-O(3W)	90.66(19)
O(1W)-Cu(1)-N(1)	96.1(3)	O(2W)-Cu(2)-O(3W)	180.000(1)
O(4W)-Cu(1)-N(1)	174.0(2)	N(2)-Cu(2)-O(13)#3	89.7(2)
O(1)-Cu(1)-O(8)#1	94.3(2)	N(2)#3-Cu(2)-O(13)#3	90.1(2)
O(1W)-Cu(1)-O(8)#1	85.5(2)	O(2W)-Cu(2)-O(13)#3	83.90(14)
O(4W)-Cu(1)-O(8)#1	82.1(2)	O(3W)-Cu(2)-O(13)#3	96.10(14)
N(1)-Cu(1)-O(8)#1	97.2(2)	N(2)-Cu(2)-O(13)	90.1(2)
O(1)-Cu(1)-O(10)	90.1(2)	N(2)#3-Cu(2)-O(13)	89.7(2)
O(1W)-Cu(1)-O(10)	90.3(2)	O(2W)-Cu(2)-O(13)	83.90(14)
O(4W)-Cu(1)-O(10)	86.7(2)	O(3W)-Cu(2)-O(13)	96.10(14)
N(1)-Cu(1)-O(10)	94.4(2)		

Symmetry code:#1-x-1/2,-y-1/2 ,-z;#2 -x,-y,-z;#3 -x,y,-z+1/2

Complex **6**

O(1W)-Co(2)	2.115(6)	Co(1)-O(2W)	2.021(5)
Co(1)-O(4W)	2.026(5)	Co(2)-O(5W)	2.041(5)
Co(1)-O(1)	2.078(4)	Co(2)-O(5W)#3	2.041(5)
Co(1)-N(1)	2.135(5)	Co(2)-O(4)#3	2.088(5)
Co(1)-O(3)#1	2.193(5)	Co(2)-O(4)	2.088(5)
Co(1)-O(3W)	2.235(5)	Co(2)-O(1W)#3	2.115(6)
O(2W)-Co(1)-O(4W)	96.7(2)	O(5W)-Co(2)-O(5W)#3	180.000(2)
O(2W)-Co(1)-O(1)	167.4(2)	O(5W)-Co(2)-O(4)#3	89.7(2)
O(4W)-Co(1)-O(1)	92.7(2)	O(5W)#3-Co(2)-O(4)#3	90.3(2)
O(2W)-Co(1)-N(1)	95.7(2)	O(5W)-Co(2)-O(4)	90.3(2)
O(4W)-Co(1)-N(1)	162.9(2)	O(5W)#3-Co(2)-O(4)	89.7(2)
O(1)-Co(1)-N(1)	76.99(18)	O(4)#3-Co(2)-O(4)	180.0(3)
O(2W)-Co(1)-O(3)#1	84.4(2)	O(5W)-Co(2)-O(1W)	91.8(2)
O(4W)-Co(1)-O(3)#1	83.1(2)	O(5W)#3-Co(2)-O(1W)	88.2(2)
O(1)-Co(1)-O(3)#1	105.14(19)	O(4)#3-Co(2)-O(1W)	90.3(2)
N(1)-Co(1)-O(3)#1	86.44(19)	O(4)-Co(2)-O(1W)	89.7(2)
O(2W)-Co(1)-O(3W)	87.3(2)	O(5W)-Co(2)-O(1W)#3	88.2(2)
O(4W)-Co(1)-O(3W)	89.0(2)	O(5W)#3-Co(2)-O(1W)#3	91.8(2)
O(1)-Co(1)-O(3W)	84.50(19)	O(4)#3-Co(2)-O(1W)#3	89.7(2)

N(1)-Co(1)-O(3W)	103.4(2)	O(4)-Co(2)-O(1W)#3	90.3(2)
O(3)#1-Co(1)-O(3W)	167.71(18)	O(1W)-Co(2)-O(1W)#3	179.999(1)

Symmetry code:#1 -x,-y,-z+1;#2 -x,-y+1,-z+2;#3 -x,-y,-z+2;#4 -x+1,-y+2,-z+3

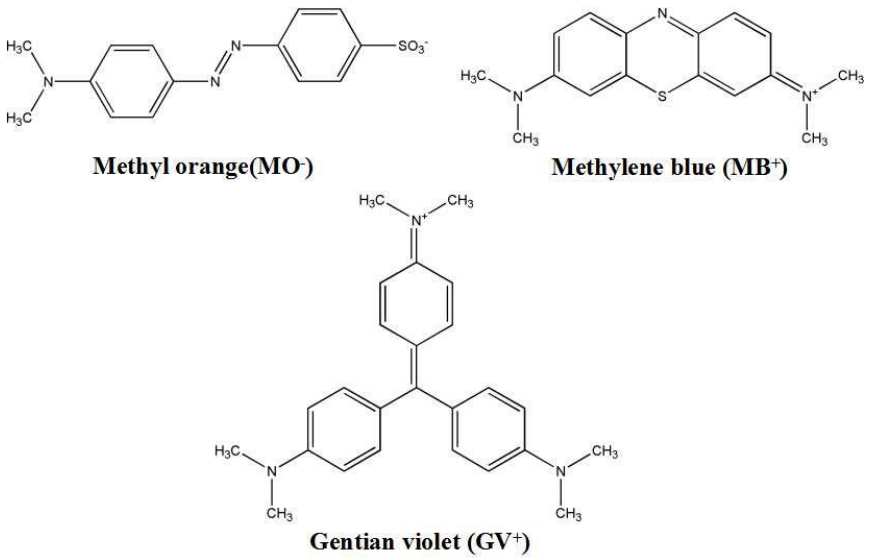
Table S2. Selected hydrogen-bonding geometry (Å, º) for complexes **1**–**6**

Complex	D–H···A	D–H	H···A	D···A	D–H···A
1	N(2)–H(2A)···O(11)	0.86	2.41	3.2252	158
2	C(5)–H(5A)···O(2W)	0.93	2.56	3.3277	140
	N(2)-H(2A)···O(16)	0.86	2.25	2.7942	121
	N(3)–H(3B)···O(16)	0.86	2.64	3.2165	126
6	C(2)–H(2A)···O(5W)	0.93	3.39	3.1778	69
	C(12)–H(12)···O(25)	0.93	2.64	2.8941	97

Table S3 Molecular weight and dimensions of different dyesmolecules.

Abbr.	MB	MO	GV
M_W	284.40	304.33	372.53
x(Å)	4.00	5.31	4.00
y(Å)	7.93	7.25	16.32

z(Å)	16.34	17.39	14.15



Scheme S1 Chemical structures of MO, MB and GV

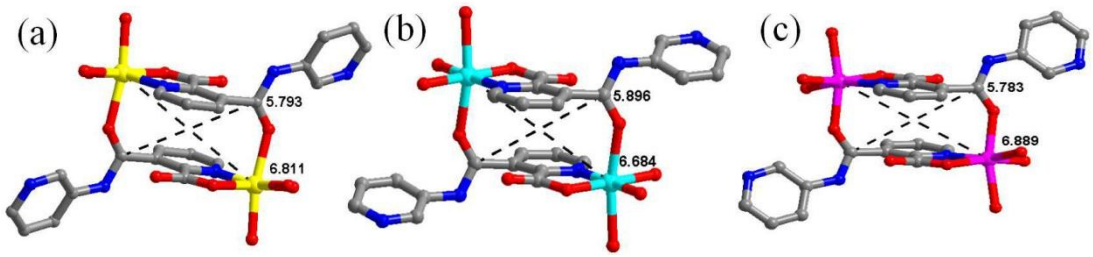


Fig. S1 The $[M_2(PCAP)_2]$ metal-organic loop of (a) **2**, (b) **5** and (c) **6**.

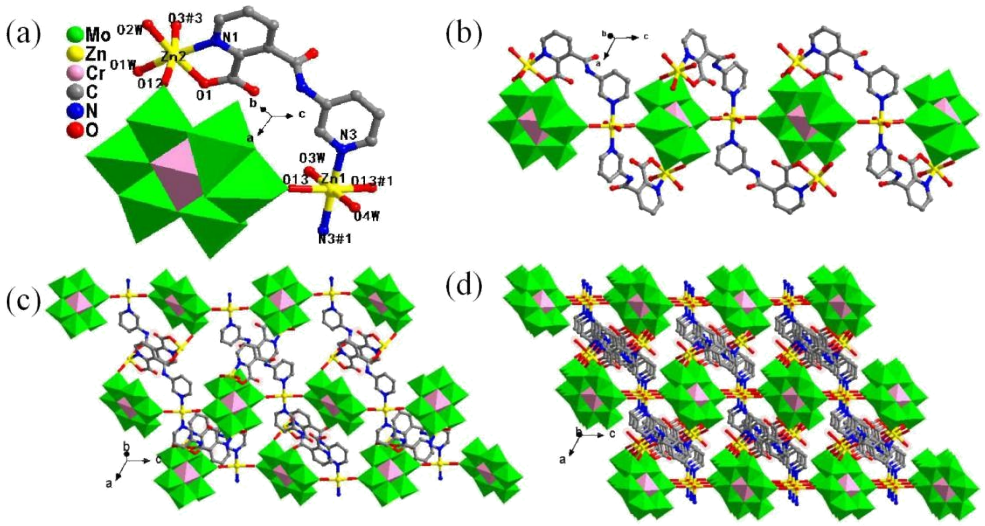


Fig. S2 (a)The coordination environment of the Zn^{II} ions in **3**. (b) View of the 1D chain in **3**. (c) View of the 2D layer in **3**. (d). The 3D $CrMo_6$-based metal organic framework in **3**.

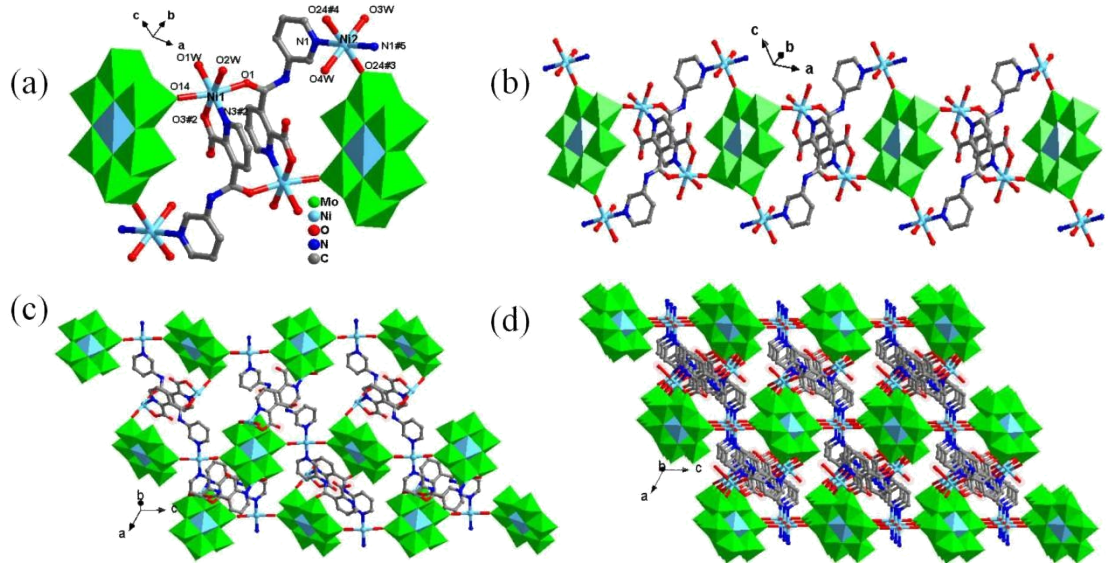
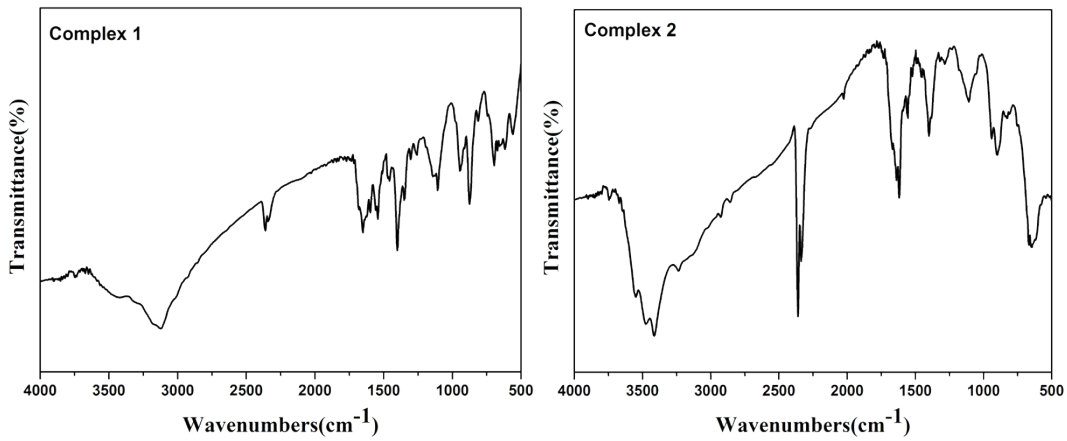


Fig. S3 (a) The coordination environment of the Ni^{II} ions in **4**. (b) View of the 1D chain in **4**. (c) View of the 2D layer in **4**. (d) The wave chain consists of 3D $CrMo_6$-based metal organic framework in **4**.



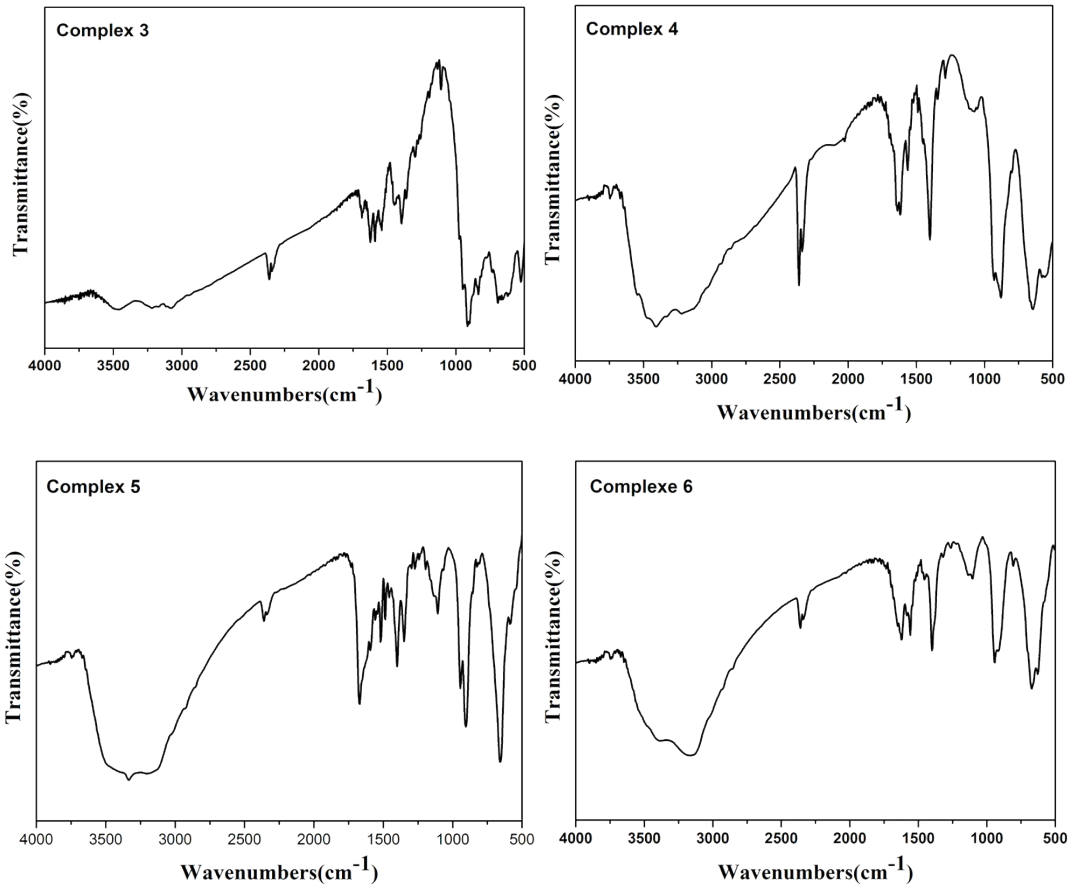
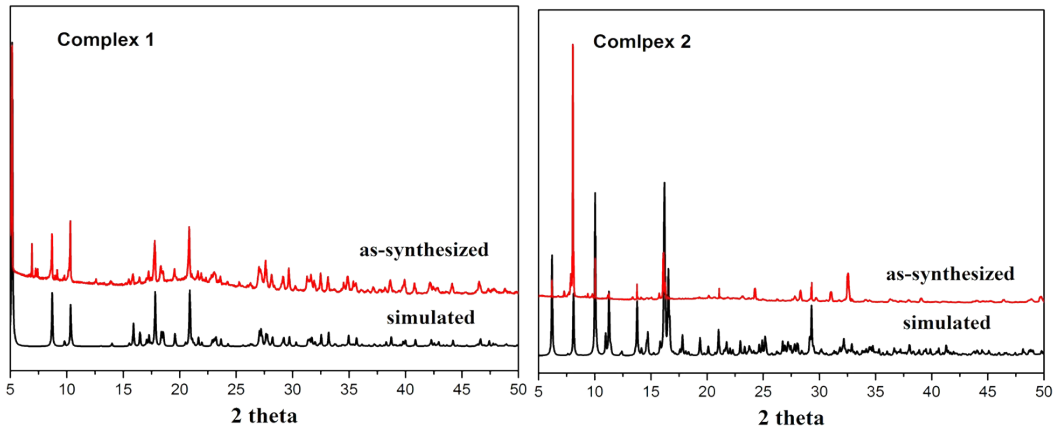


Fig. S4 The IR spectra of complexes **1**–**6**.



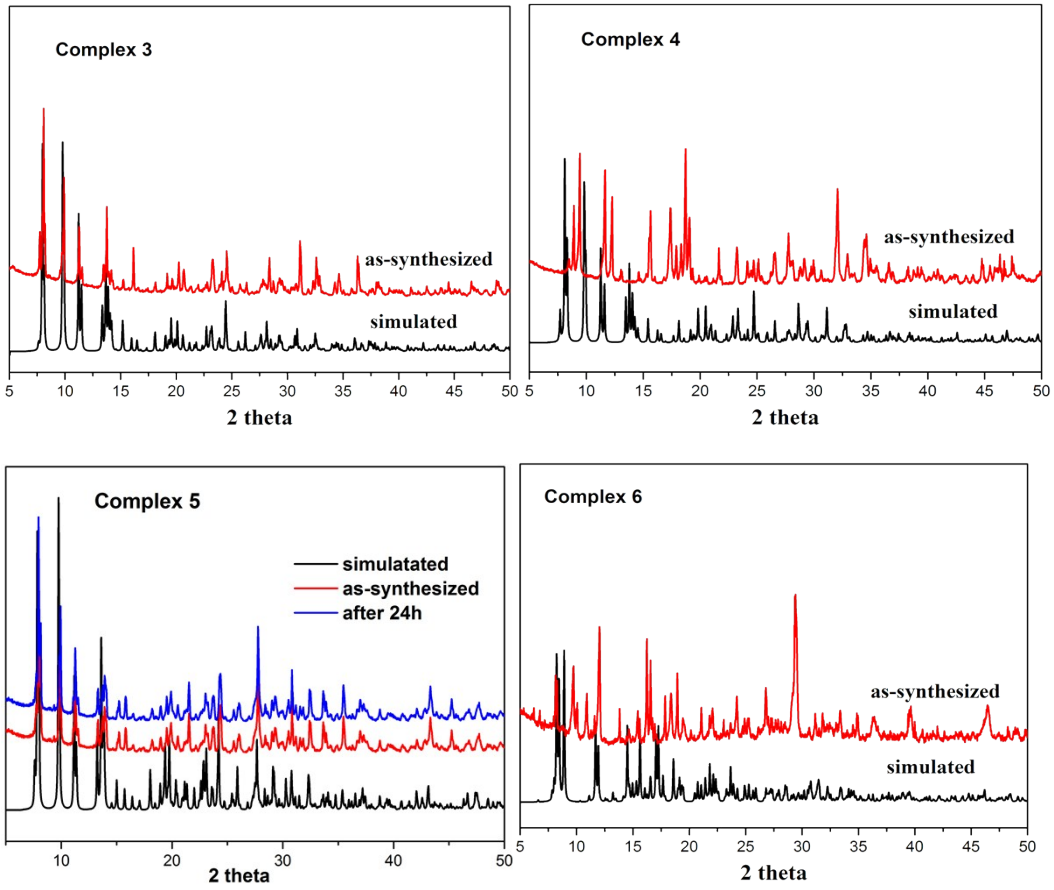


Fig. S5 The PXRD patterns of complexes **1**-**6**.

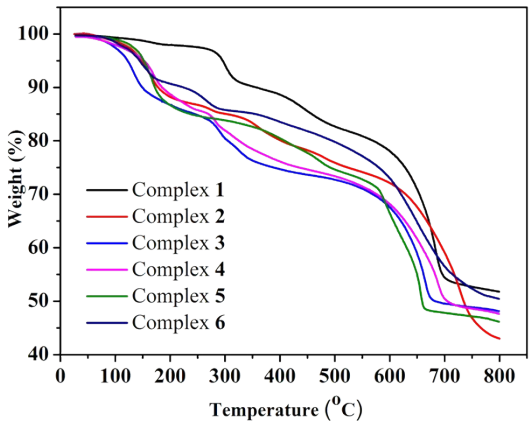


Fig. S6 The TG curves of complexes **1**–**6**.

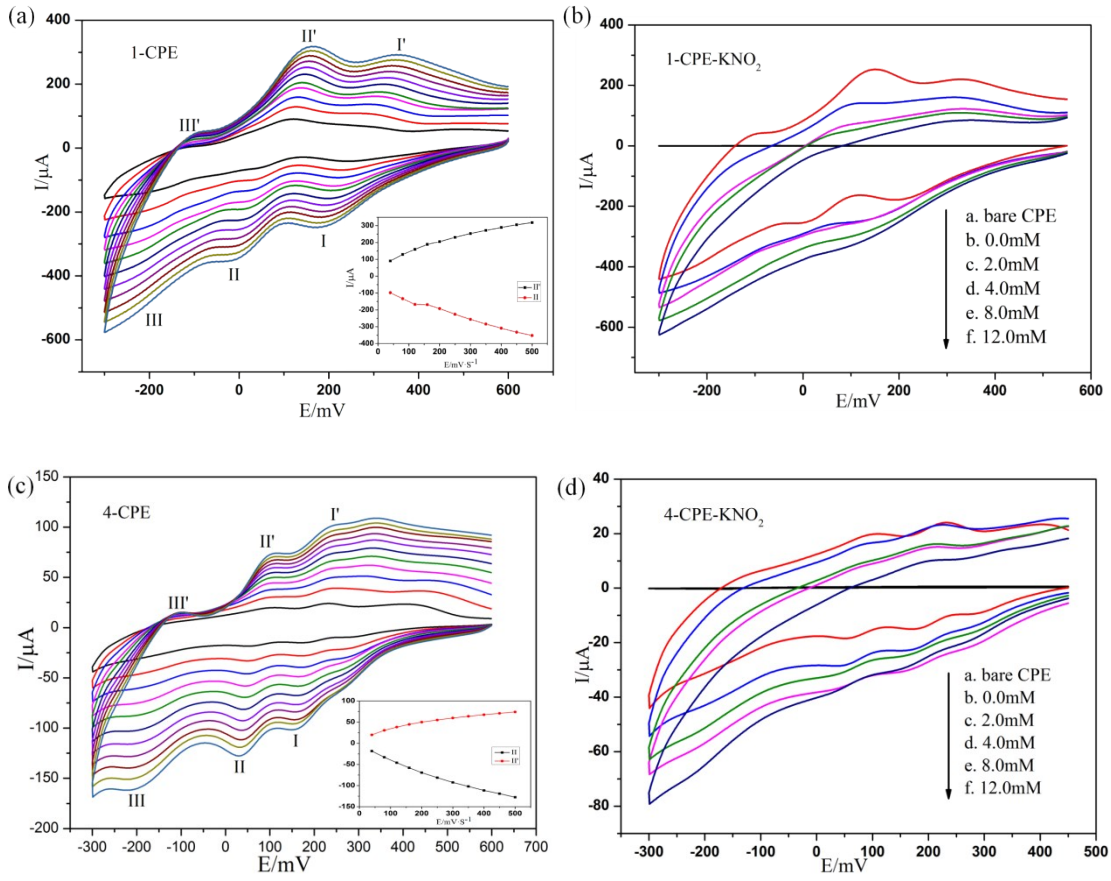


Fig. S7 (a) Cyclic voltammograms of the**1**-CPE and (c) **4**-CPE in 0.1 M H_2SO_4 + 0.5M Na_2SO_4 aqueous solution at different scan rates (from inner to outer: 40, 80, 120, 160, 200, 250, 300, 350, 400, 450, 500mV·s^{-1}); Inset: The plots of peak currents vs. scan rates for **1**- and **4**-CPE. Cyclic voltammograms of (c) **1**- and (d) **4**-CPE in 0.1 M H_2SO_4 + 0.5M Na_2SO_4 aqueous solution containing 0.0–12.0 mM KNO_2 . Scan rate: 30 mV·s^{-1}.

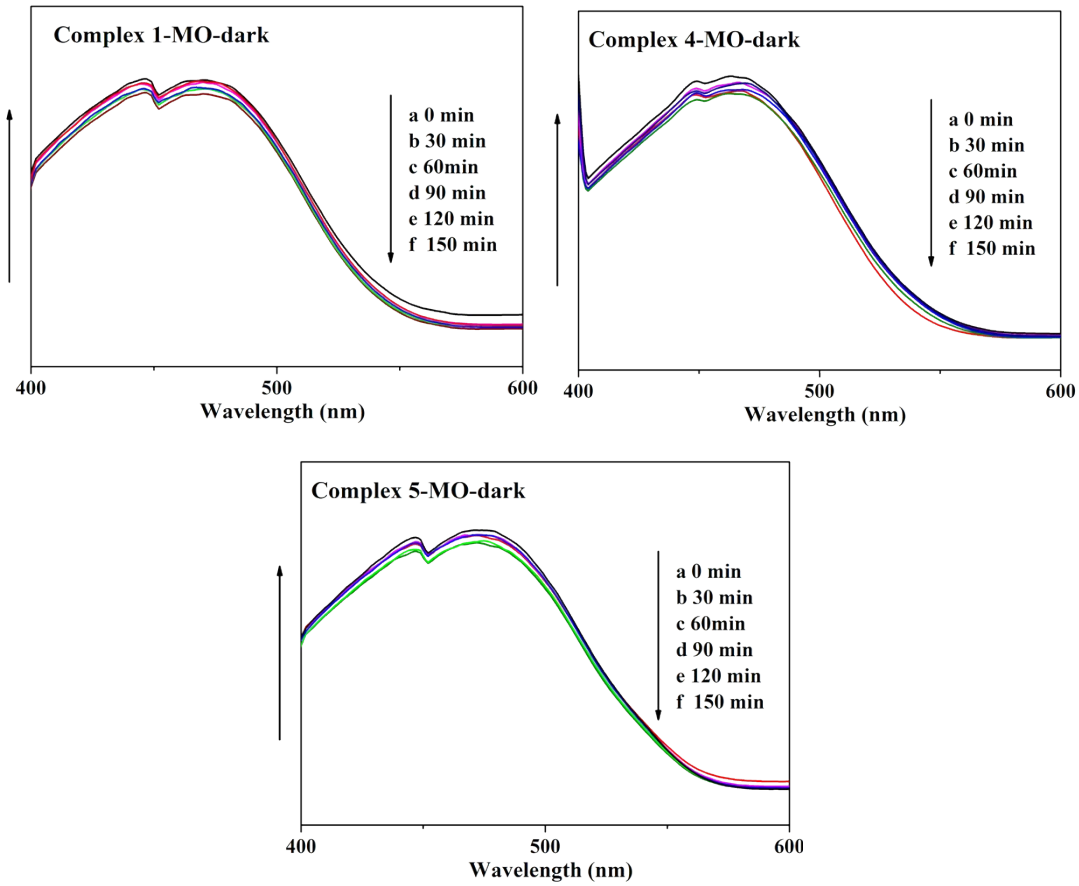


Fig. S8 Absorption spectra of the MO aqueous solution during adsorption with complexes **1, 4** and **5**, respectively.