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Solvent-Controlled Synthesis of Various Anderson-type Polyoxometalate-based Metal–Organic Complexes with Excellent Capacity for Chromatographic Separation of Dyes

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Table S1 Selected bond distances (Å) and angles (°) for complexes **1–5**.

Complex **2**

Cu(1)-O(1)	2.496(6)	Cu(2)-N(3)#3	2.019(5)
Cu(1)-O(13)	1.951(5)	Cu(2)-N(3)	2.019(5)
Cu(1)-O(1W)	1.971(5)	Cu(2)-O(2W)#3	1.98(5)
Cu(1)-O(15)#2	2.427(5)	Cu(2)-O(2W)	1.98(5)
Cu(1)-N(1)	1.978(6)	Cu(2)-O(10)	2.546(4)
Cu(1)-O(1F)	1.982(2)	Cu(2)-O(10)#3	2.546 (4)
O(1)-Cu(1)-O(13)	89.62(3)	N(1)-Cu(1)-O(1)	89.33(4)
O(1W)-Cu(1)-O(1)	91.7(4)	O(1W)-Cu(1)-N(1)	172.64(2)
O(13)-Cu(1)-O(1W)	89.88(2)	O(1F)-Cu(1)-O(1)	81.53(4)
O(13)-Cu(1)-N(1)	82.84(2)	O(1F)-Cu(1)-O(13)	170.81(9)
O(1F)-Cu(1)-N(1)	94.82(1)	O(1F)-Cu(1)-O(1W)	92.54(1)
O(1)-Cu(1)-O(15)#2	167.6(3)	O(13)-Cu(1)-O(15)#2	101.8(2)
O(1W)-Cu(1)-O(15)#2	83.6(2)	N(1)-Cu(1)-O(15)#2	96.8(2)
O(1F)-Cu(1)-O(15)#2	87.3(8)	N(3)#3-Cu(2)-N(3)	180.000(2)
N(3)#3-Cu(2)-O(2W)#3	91.5(19)	N(3)-Cu(2)-O(2W)#3	88.5(19)
N(3)#3-Cu(2)-O(2W)	88.5(19)	N(3)-Cu(2)-O(2W)	91.5(19)
O(2W)#3-Cu(2)-O(2W)	179.999(3)	N(3)#3-Cu(2)-O(10)#3	90.53(2)
N(3)-Cu(2)-O(10)#3	89.47(2)	O(2W)#3-Cu(2)-O(10)#3	85.27(1)
O(2W)-Cu(2)-O(10)#3	94.73(1)	N(3)#3-Cu(2)-O(10)	89.47(2)
N(3)-Cu(2)-O(10)	90.53(2)	O(2W)#3-Cu(2)-O(10)	94.73(1)
O(2W)-Cu(2)-O(10)	85.27(1)	O(10)#3-Cu(2)-O(10)	180.000(2)

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

Complex **3**

Cu(1)-N(1)	2.007(5)	Cu(1)-N(1)#2	2.007(5)
Cu(1)-Cl(1)	2.283(3)	Cu(1)-O(15)#2	2.334(4)
Cu(1)-O(1W)	2.07(7)	Cu(1)-O(15)	2.334(4)
Cu(2)-O(2W)	1.966(4)	Cu(2)-O(3)	1.971(4)
Cu(2)-O(3W)	1.976(4)	Cu(2)-N(3)	2.003(5)
Cu(2)-O(1)#3	2.355(4)	Cu(2)-O(4)	2.420(4)
N(1)-Cu(1)-N(1)#2	178.7(3)	N(1)-Cu(1)-O(1W)	89.37(15)
N(1)#2-Cu(1)-O(1W)	89.37(15)	N(1)-Cu(1)-Cl(1)	90.63(15)
N(1)#2-Cu(1)-Cl(1)	90.63(15)	O(1W)-Cu(1)-Cl(1)	180.000(1)

N(1)-Cu(1)-O(15)#2	89.91(16)	N(1)#2-Cu(1)-O(15)#2	89.97(17)
O(1W)-Cu(1)-O(15)#2	84.41(11)	Cl(1)-Cu(1)-O(15)#2	95.59(11)
N(1)-Cu(1)-O(15)	89.97(17)	N(1)#2-Cu(1)-O(15)	89.91(16)
O(1W)-Cu(1)-O(15)	84.42(11)	Cl(1)-Cu(1)-O(15)	95.58(11)
O(15)#2-Cu(1)-O(15)	168.8(2)	O(2W)-Cu(2)-O(3)	179.35(18)
O(2W)-Cu(2)-O(3W)	89.10(18)	O(3)-Cu(2)-O(3W)	91.50(17)
O(2W)-Cu(2)-N(3)	97(2)	O(3)-Cu(2)-N(3)	82.40(18)
O(3W)-Cu(2)-N(3)	173.84(18)	O(2W)-Cu(2)-O(1)#3	86.12(19)
O(3)-Cu(2)-O(1)#3	93.72(16)	O(3W)-Cu(2)-O(1)#3	81.99(16)
N(3)-Cu(2)-O(1)#3	97.49(17)	O(2W)-Cu(2)-O(4)	89.44(18)
O(3)-Cu(2)-O(4)	90.85(15)	O(3W)-Cu(2)-O(4)	86.73(16)
N(3)-Cu(2)-O(4)	94.18(17)	O(1)#3-Cu(2)-O(4)	167.93(15)

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

Complex **4**

Co(1)-O(15)	2.082(3)	Co(1)-O(15)#2	2.082(3)
Co(1)-O(3W)	2.100(5)	Co(1)-O(4W)	2.107(5)
Co(1)-N(1)	2.124(3)	Co(1)-N(1)#2	2.125(3)
Co(2)-O(1W)	2.074(3)	Co(2)-O(3)	2.076(3)
Co(2)-O(2W)	2.090(3)	Co(2)-N(3)	2.110(3)
Co(2)-O(4)	2.122(3)	Co(2)-O(1)#3	2.135(3)
O(15)-Co(1)-O(15)#2	172.49(17	O(15)-Co(1)-O(3W)	86.25(9)
O(15)#2-Co(1)-O(3W)	86.25(9)	O(15)-Co(1)-O(4W)	93.75(9)
O(15)#2-Co(1)-O(4W)	93.75(9)	O(3W)-Co(1)-O(4W)	180.000(2)
O(15)-Co(1)-N(1)	91.34(11)	O(15)#2-Co(1)-N(1)	88.90(11)
O(3W)-Co(1)-N(1)	91.86(10)	O(4W)-Co(1)-N(1)	88.14(10)
O(15)-Co(1)-N(1)#2	88.91(11)	O(15)#2-Co(1)-N(1)#2	91.34(11)
O(3W)-Co(1)-N(1)#2	91.86(10)	O(4W)-Co(1)-N(1)#2	88.14(10)
N(1)-Co(1)-N(1)#2	176.3(2)	O(1W)-Co(2)-O(3)	173.76(12)
O(1W)-Co(2)-O(2W)	92.06(13)	O(3)-Co(2)-O(2W)	93.50(11)
O(1W)-Co(2)-N(3)	95.85(14)	O(3)-Co(2)-N(3)	78.39(12)
O(2W)-Co(2)-N(3)	170.81(12)	O(1W)-Co(2)-O(4)	92.36(12)
O(3)-Co(2)-O(4)	90.55(11)	O(2W)-Co(2)-O(4)	89.28(11)
N(3)-Co(2)-O(4)	95.07(13)	O(1W)-Co(2)-O(1)#3	83.41(12)
O(3)-Co(2)-O(1)#3	94.44(11)	O(2W)-Co(2)-O(1)#3	83.02(12)
N(3)-Co(2)-O(1)#3	93.21(12)	O(4)-Co(2)-O(1)#3	171.05(11)

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

Complex **5**

Co(1)-O(2W)#2	2.043(3)	Co(1)-O(2W)	2.043(3)
Co(1)-O(1W)	2.079(4)	Co(1)-O(1W)#2	2.079(4)
Co(1)-O(17)	2.091(3)	Co(1)-O(17)#2	2.091(3)
Co(2)-O(4W)	2.016(3)	Co(2)-O(3W)	2.016(3)
Co(2)-O(3)	2.077(2)	Co(2)-O(1)#3	2.203(2)
Co(2)-O(5W)	2.222(3)	Co(2)-N(1)	2.131(3)
O(2W)#2-Co(1)-O(1W)	90.82(2)	O(2W)-Co(1)-O(1W)	89.18(2)

O(2W)#2-Co(1)-O(1W)#2	89.18(2)	O(2W)-Co(1)-O(1W)#2	90.82(2)
O(1W)-Co(1)-O(1W)#2	180.0(0)	O(2W)#2-Co(1)-O(17)	89.95(12)
O(2W)-Co(1)-O(17)	90.05(12)	O(1W)-Co(1)-O(17)	89.89(15)
O(1W)#2-Co(1)-O(17)	90.11(15)	O(2W)#2-Co(1)-O(17)#2	90.05(12)
O(2W)-Co(1)-O(17)#2	89.95(12)	O(1W)-Co(1)-O(17)#2	90.11(15)
O(1W)#2-Co(1)-O(17)#2	89.89(15)	O(17)-Co(1)-O(17)#2	180(5)
O(4W)-Co(2)-O(3W)	97.24(14)	O(4W)-Co(2)-O(3)	168.03(11)
O(3W)-Co(2)-O(3)	91.47(12)	O(4W)-Co(2)-N(1)	96.42(12)
O(3W)-Co(2)-N(1)	161.67(13)	O(3)-Co(2)-N(1)	77 (1)
O(4W)-Co(2)-O(1)#1	84.23(11)	O(3W)-Co(2)-O(1)#3	82.6(12)
O(3)-Co(2)-O(1)#3	105.11(10)	N(1)-Co(2)-O(1)#3	86.67(10)
O(4W)-Co(2)-O(5W)	87.28(10)	O(3W)-Co(2)-O(5W)	89.44(12)
O(3)-Co(2)-O(5W)	84.6(10)	N(1)-Co(2)-O(5W)	103.38(11)
O(1)#3-Co(2)-O(5W)	167.53(10)		

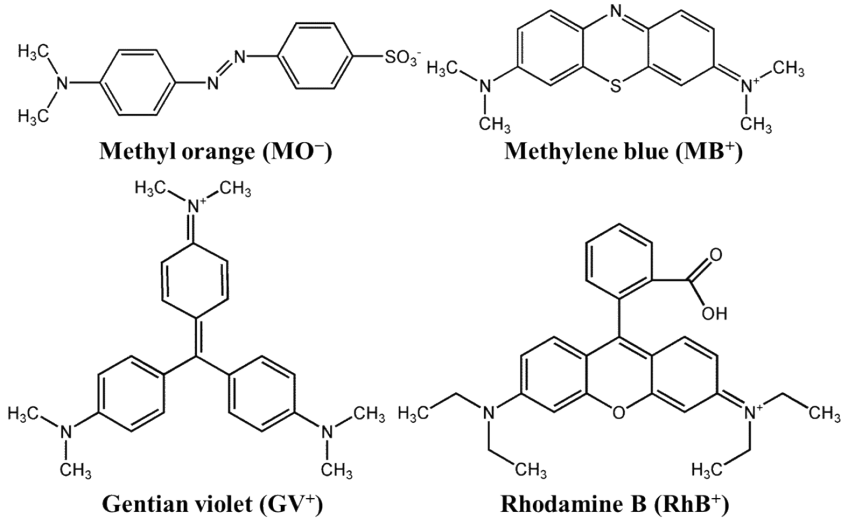
Symmetry code for **5**: #1 -x+2,-y+1,-z+2; #2 -x+2, -y+2,-z+2; #3 -x+2,-y,-z+1; #4 -x+1,-y,-z+1

Table S2. Selected hydrogen-bonding geometry (Å, º) for complexes 1–**5**

Complex	D–H···A	D–H	H···A	D···A	D–H···A	Symop for A
1	C4 –H(4A)···O7	0.93	2.4	3.046(3)	125	-x,1-y,-z
	C2 –H(2A)···O5	0.93	2.25	3.152(1)	164	-1+x,-1+y,z
	C10 –H(10A)···O12	0.93	2.54	3.332(5)	143	-x,1-y,1-z
	C(11) –H(11A)···O(1)	0.93	2.31	3.238(1)	175	-1+x,y,z
2	C(3) –H(3A)···O(6)	0.93	2.42	3.287(2)	155	1-x,1-y,1-z
	C(5)–H(4A)···O(7)	0.93	2.31	3.119(5)	145	-1+x,y,z
5	N(3) –H(3A)···O(24)	0.86	1.91	2.752(4)	168	x,y,1+z
	C(10) –H(10A)···O(6)	0.93	2.59	3.202(10)	123	1-x,1-y,1-z

Table S3 Molecular weight and dimensions of different dyes molecules.

Abbr.	MB	MO	GV	RhB
M_W	284.40	304.33	372.53	479.02
x(Å)	4.00	5.31	4.00	6.8
y(Å)	7.93	7.25	16.32	11.8
z(Å)	16.34	17.39	14.15	15.8



Scheme S1 Chemical structures of MO, MB, GV and RhB.

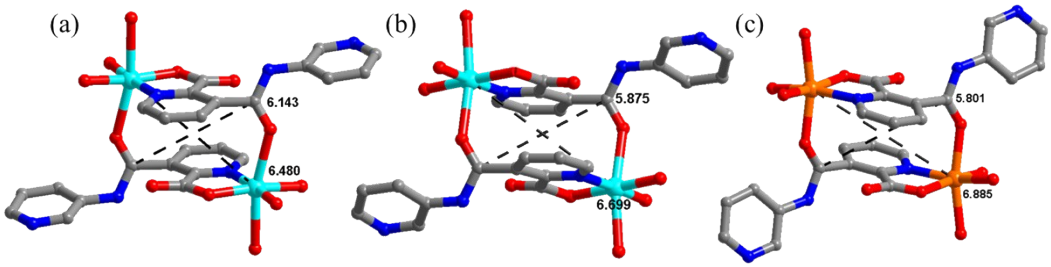


Fig. S1 The $[M_2(PCAP)_2]$ metal-organic loop of (a) **2**, (b) **3** and (c) **5**.

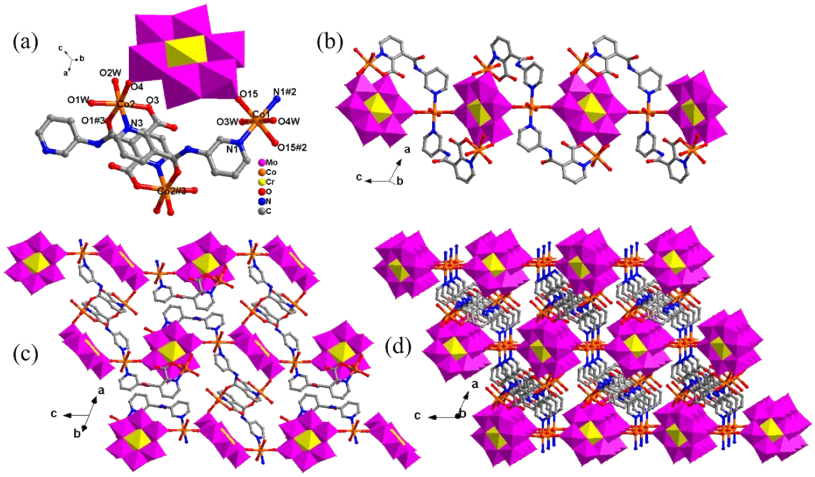


Fig. S2 (a)The coordination environment of the Co^{II} ions in **4**. Symmetry code: #2 -x+1,y,-z+1/2; #3 -x+3/2,-y+1/2,-z+1 (b) View of the 1D chain in **4**. (c) View of the 2D layer in **4**. (d). The 3D $CrMo_6$-based metal organic framework of **4**.

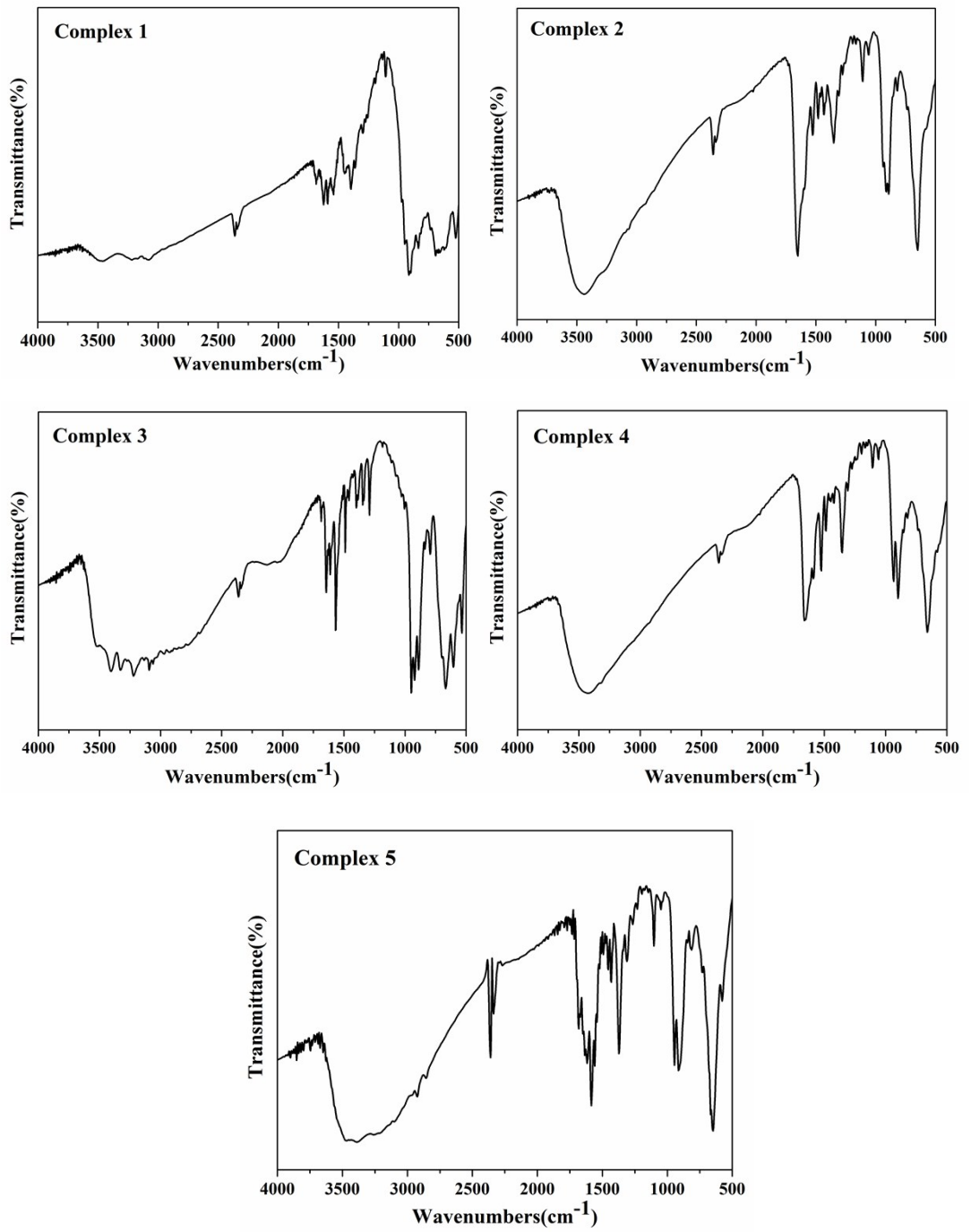


Fig. S3 The IR spectra of complexes **1–5**.

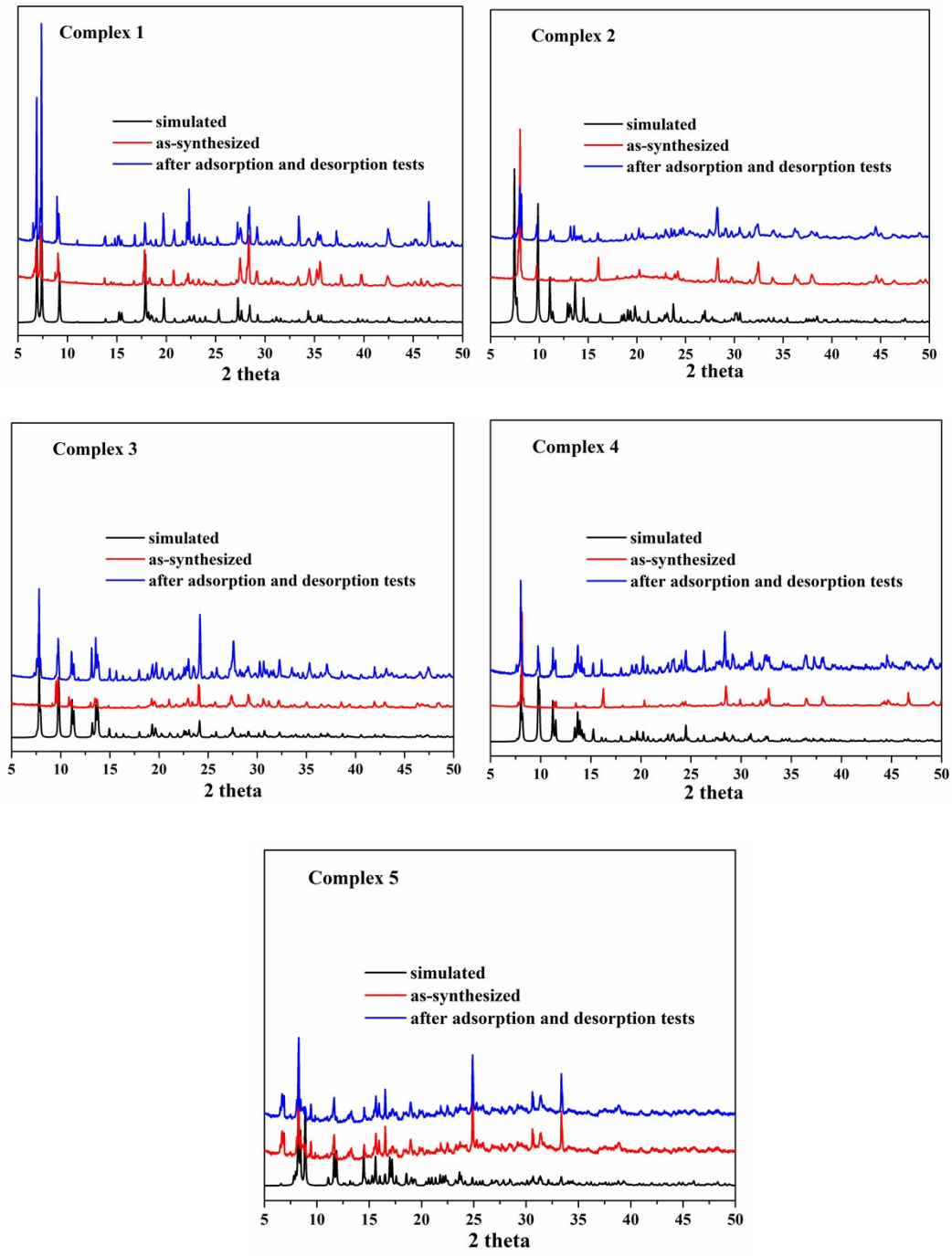


Fig. S4 The PXRD patterns of complexes **1**–**5**.

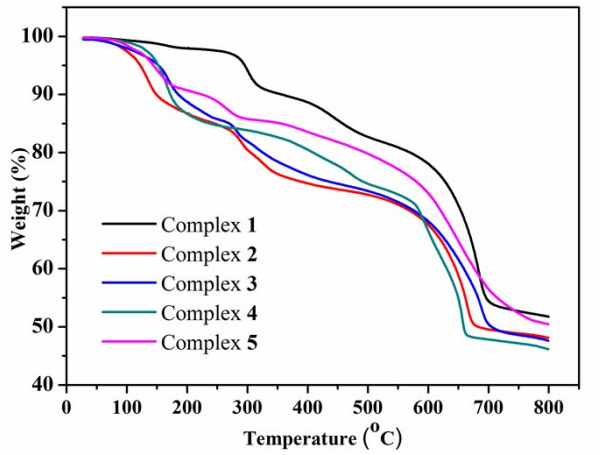


Fig. S5 The TG curves of complexes **1–5**.

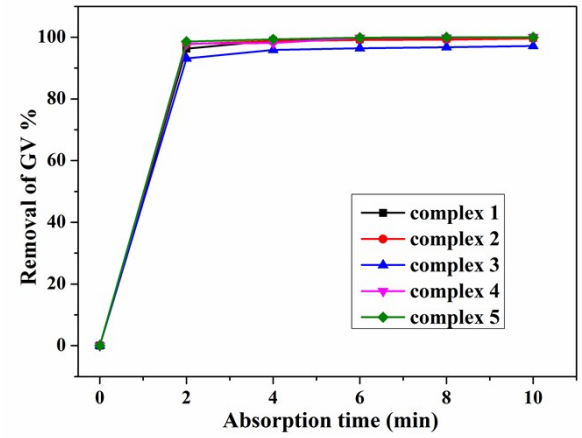


Fig. S6 The corresponding removal efficiency on the GV dye for complexes **1-5**.

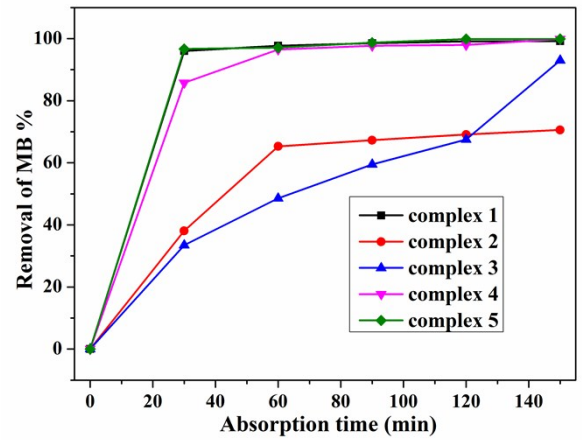


Fig. S7.The corresponding removal efficiency on the MB dye for **1-5**.

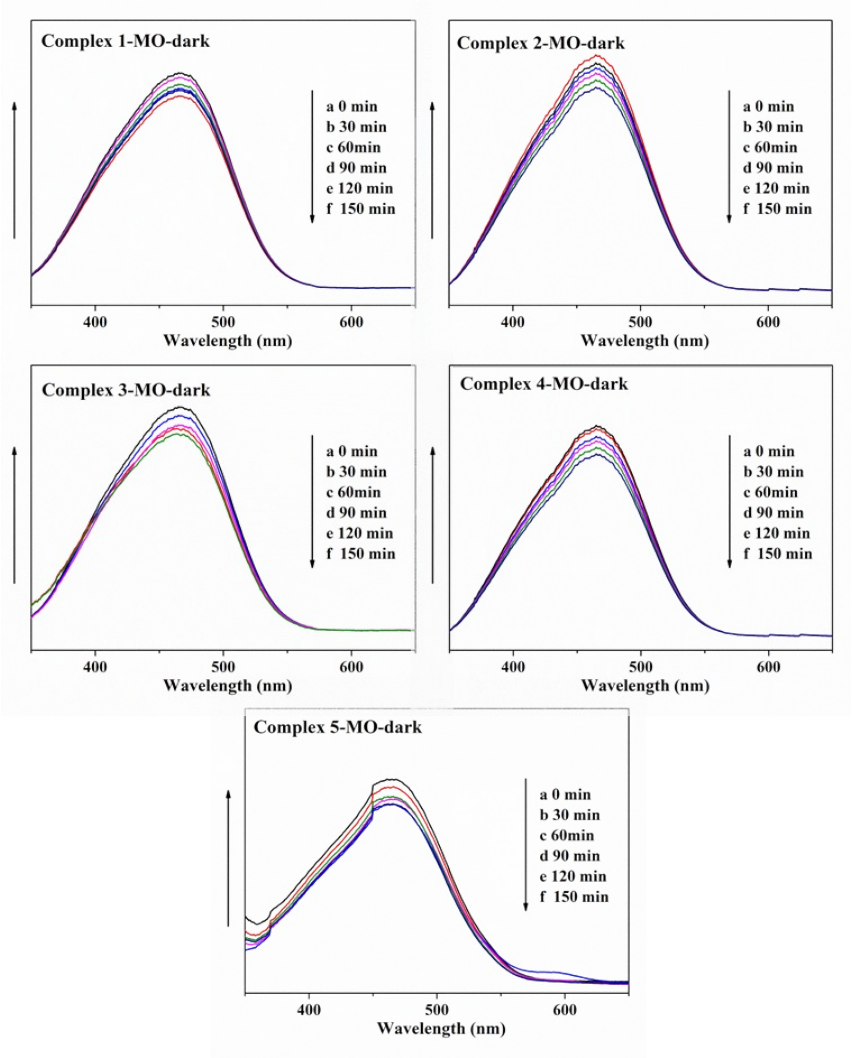


Fig. S8 Absorption spectra of the MO aqueous solution during adsorption with complexes **1-5**, respectively.

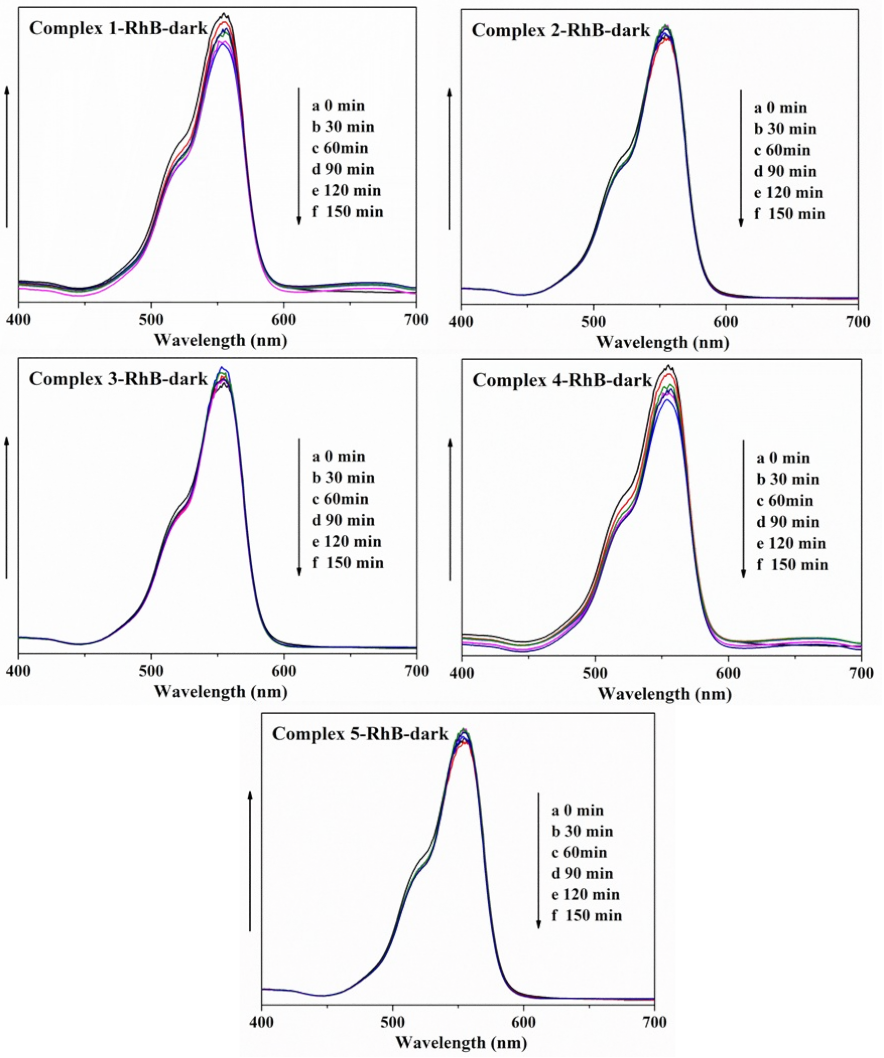


Fig. S9 Absorption spectra of the RhB aqueous solution during adsorption with complexes **1**-**5**, respectively.