Supporting information

Facile fabrication and characterization of rare-earth complexes based on Keggin-polyoxometalate with highly efficient activity for photocatalytic degradation of MO

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Electronic Supplementary Information (ESI) available: crystal structure information, IR spectra, etc. CCDC 2262909-2262914. For ESI and crystallographic data in CIF or other electronic format See DOI: 10.1039/x0xx00000x

Caption of Figure

Fig. S1 (a)-(f) Micrographs of obtained crystals of complexes **1-6**.
Fig. S2 (a) Formation of 2D structural plane by hydrogen bonding for complex **2**; (b)-(d) molecular stacking structure of complex **2**. (some hydrogen atoms are omitted)
Fig. S3 (a) Formation of 2D structural plane by hydrogen bonding for complex **3**; (b)-(d) molecular stacking structure of complex **3**. (some hydrogen atoms are omitted)
Fig. S4 (a) Formation of 2D structural plane by hydrogen bonding for complex **4**; (b)-(d) molecular stacking structure of complex **4**. (some hydrogen atoms are omitted)
Fig. S5 (a) Formation of 2D structural plane by hydrogen bonding for complex **5**; (b)-(d) molecular stacking structure of complex **5**. (some hydrogen atoms are omitted)
Fig. S6 (a) Formation of 2D structural plane by hydrogen bonding for complex **6**; (b)-(d) molecular stacking structure of complex **6**. (some hydrogen atoms are omitted)
Fig. S7 The IR spectra for complex **1**.
Fig. S8 The IR spectra for complex **2**.

Caption of Table

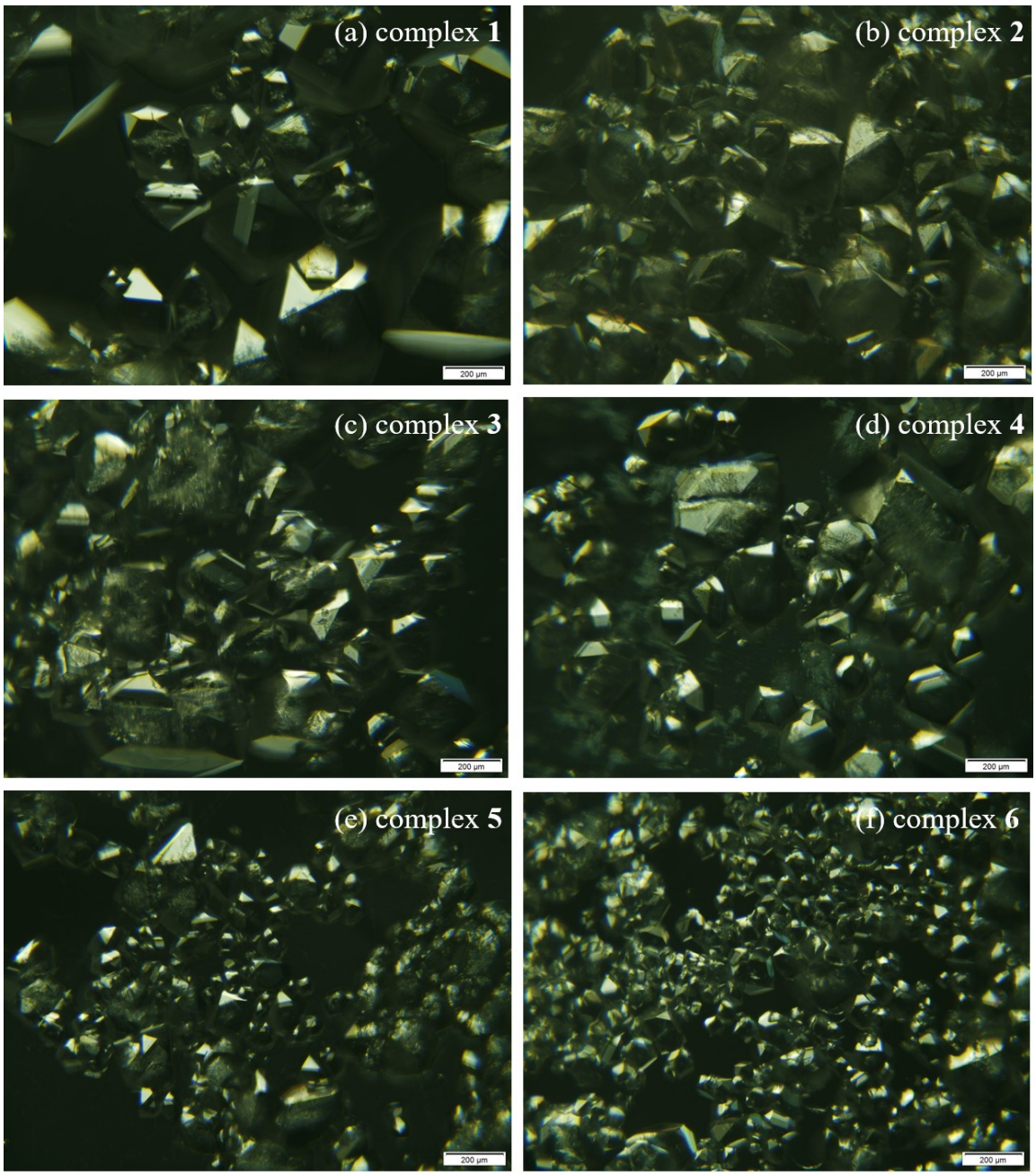

Fig. S1 (a)-(f) Micrographs of obtained crystals of complexes **1-6**.

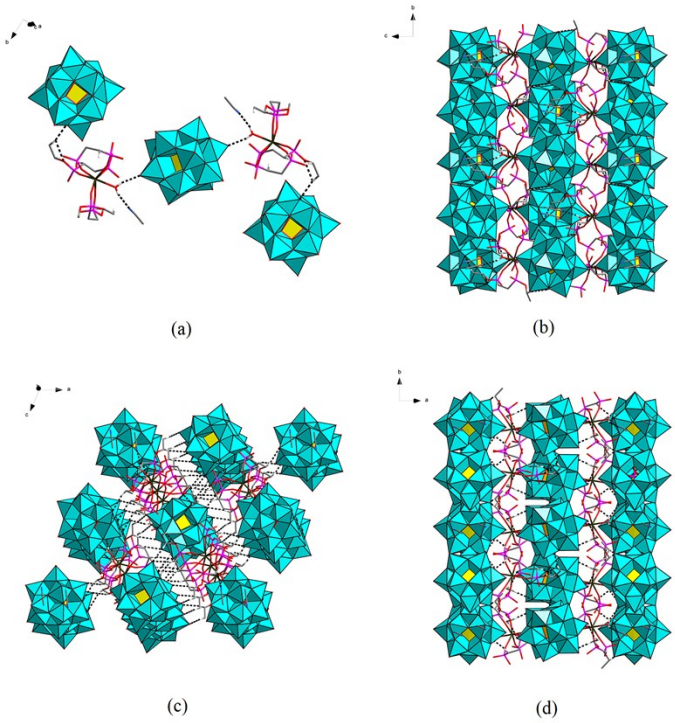

Fig. S2 (a) Formation of 2D structural plane by hydrogen bonding for complex **2**; (b)-(d) molecular stacking structure of complex **2**. (some hydrogen atoms are omitted)

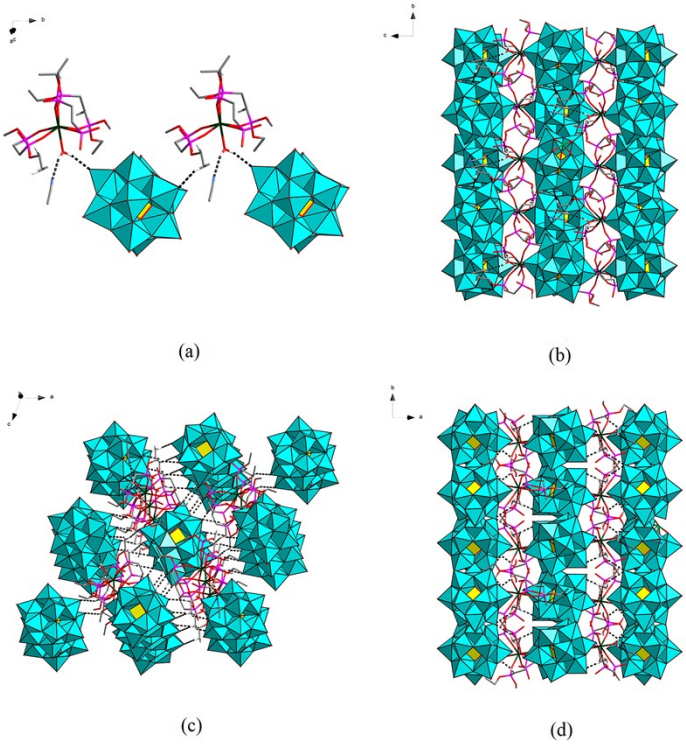

Fig. S3 (a) Formation of 2D structural plane by hydrogen bonding for complex **3**; (b)-(d) molecular stacking structure of complex **3**. (some hydrogen atoms are omitted)

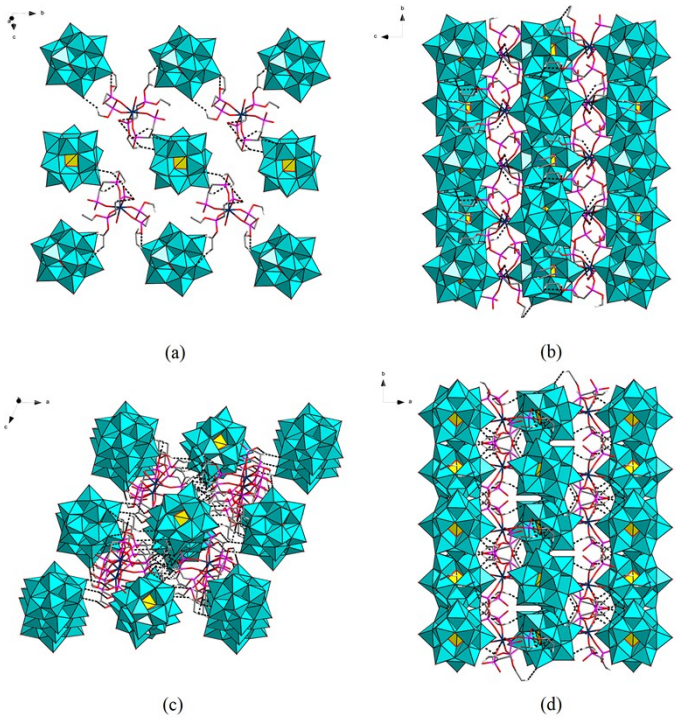

Fig. S4 (a) Formation of 2D structural plane by hydrogen bonding for complex **4**; (b)-(d) molecular stacking structure of complex **4**. (some hydrogen atoms are omitted)

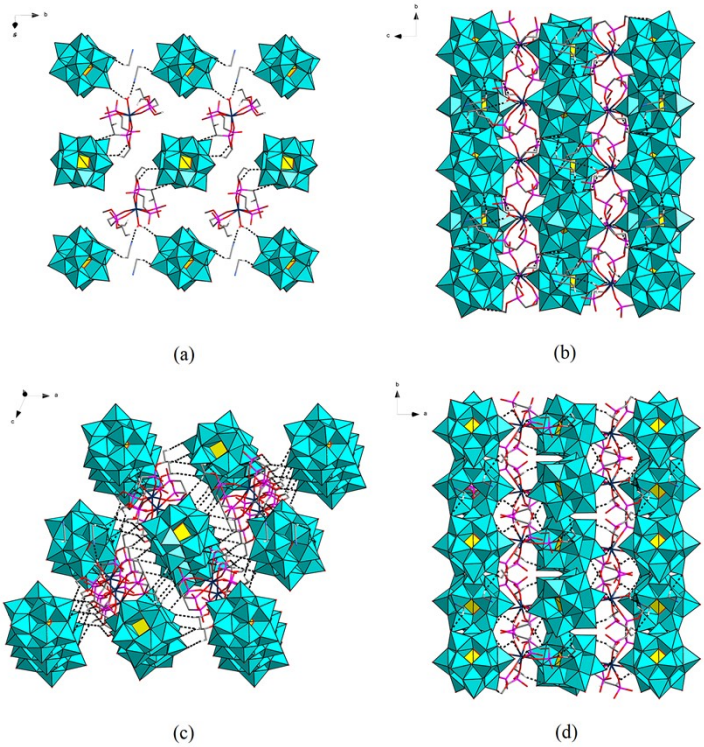

Fig. S5 (a) Formation of 2D structural plane by hydrogen bonding for complex **5**; (b)-(d) molecular stacking structure of complex **5**. (some hydrogen atoms are omitted)

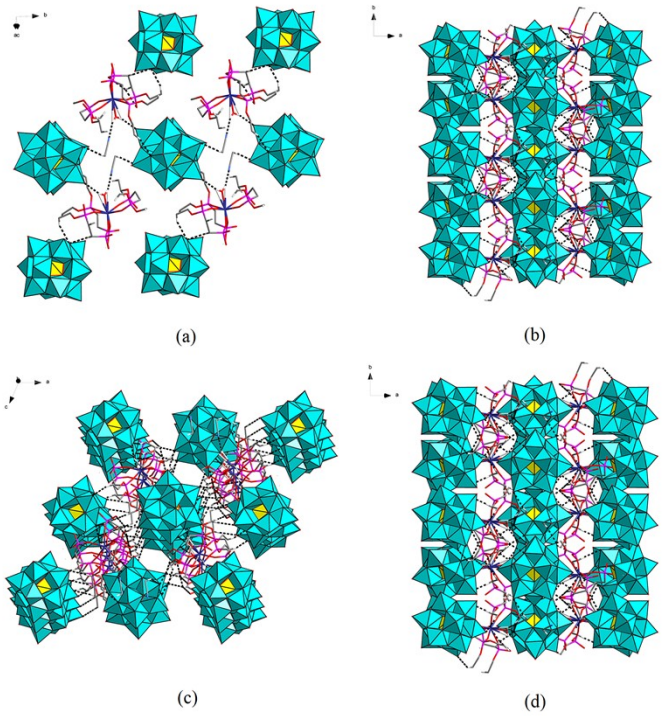

Fig. S6 (a) Formation of 2D structural plane by hydrogen bonding for complex **6**; (b)-(d) molecular stacking structure of complex **6**. (some hydrogen atoms are omitted)

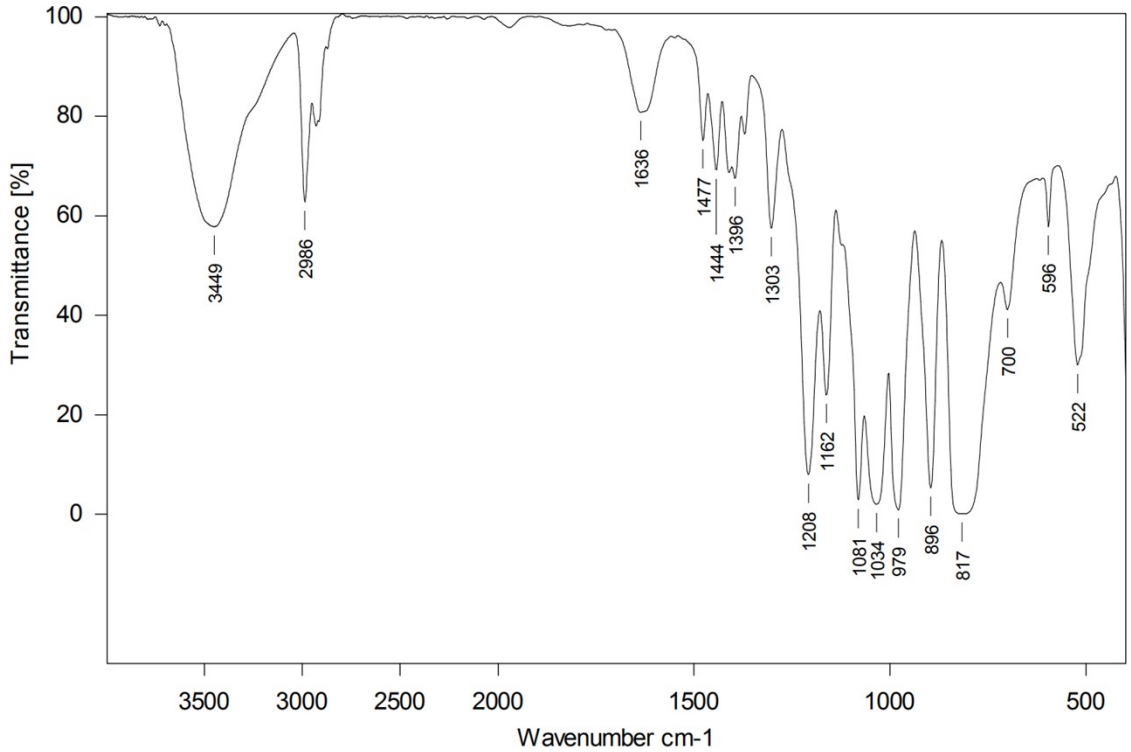

Fig. S7 The IR spectra for complex **1**.

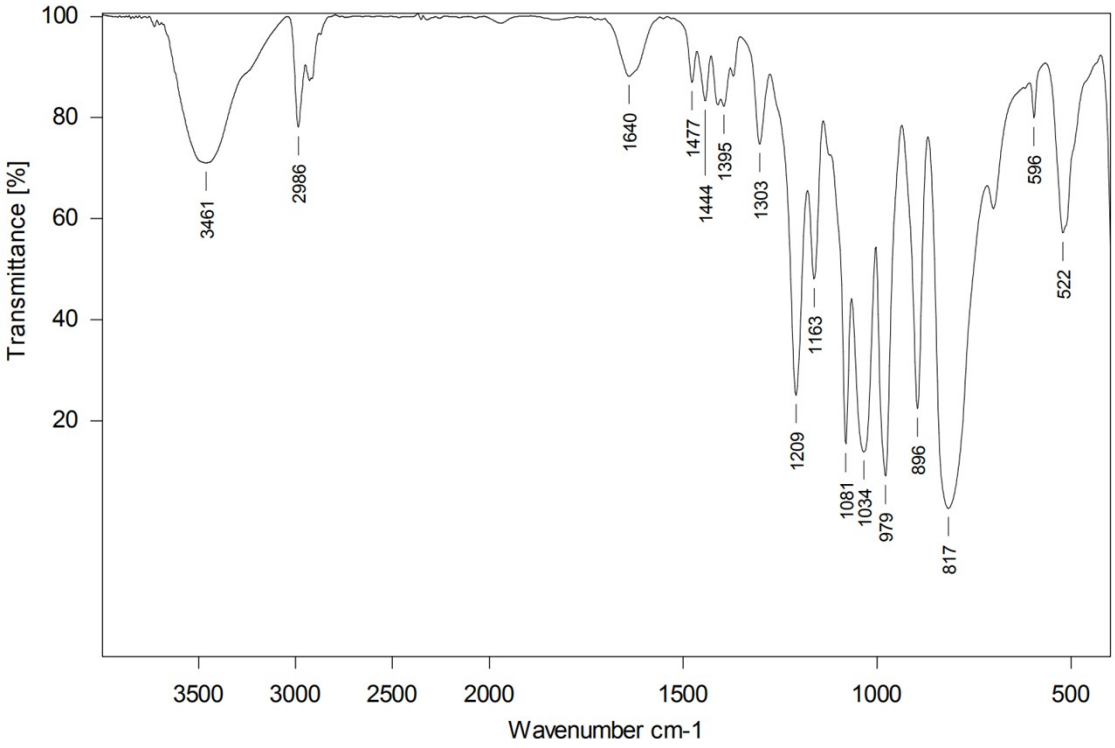

Fig. S8 The IR spectra for complex **2**.

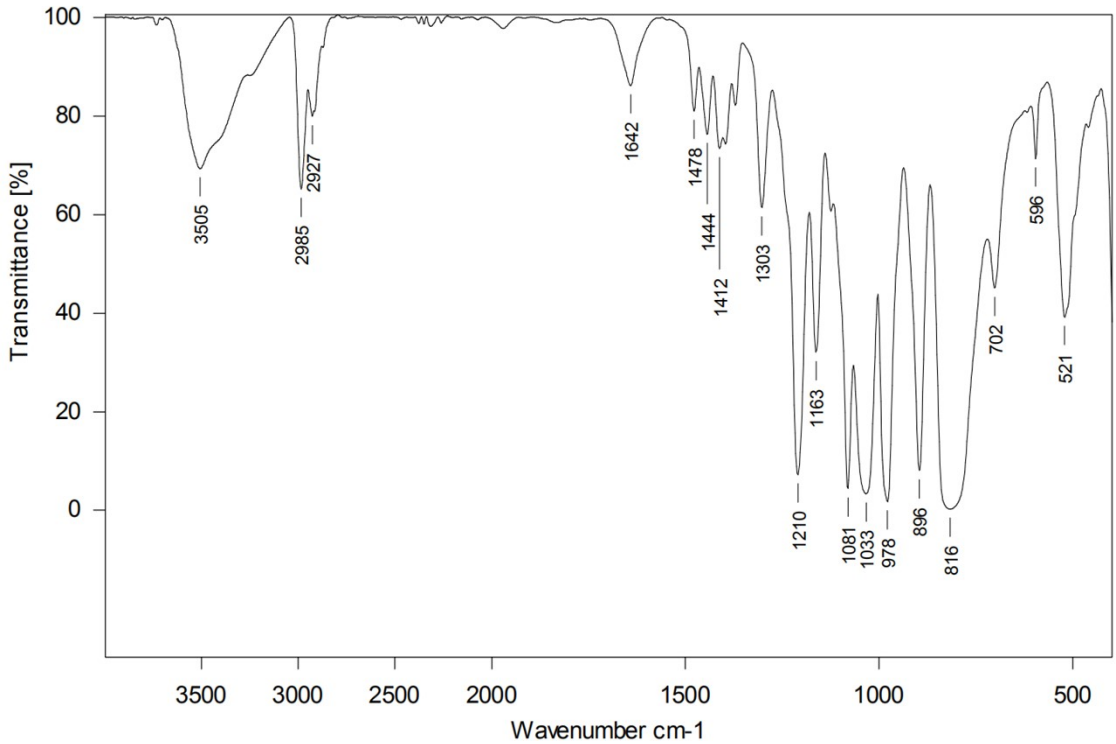

Fig. S9 The IR spectra for complex **3**.

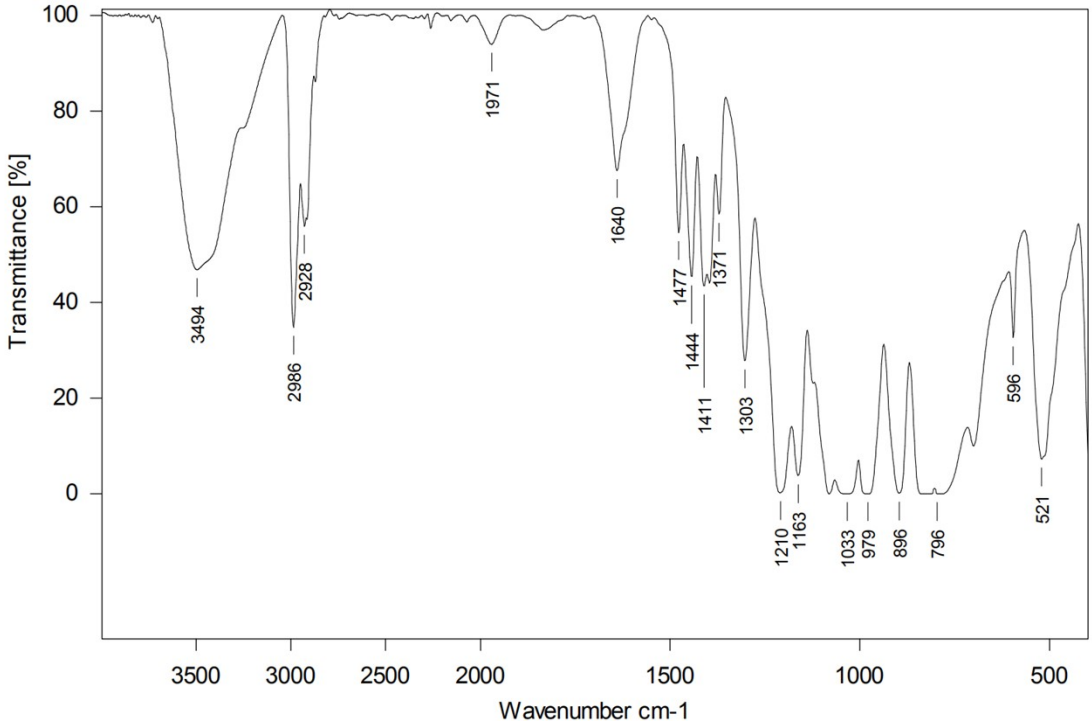

Fig. S10 The IR spectra for complex **4**.

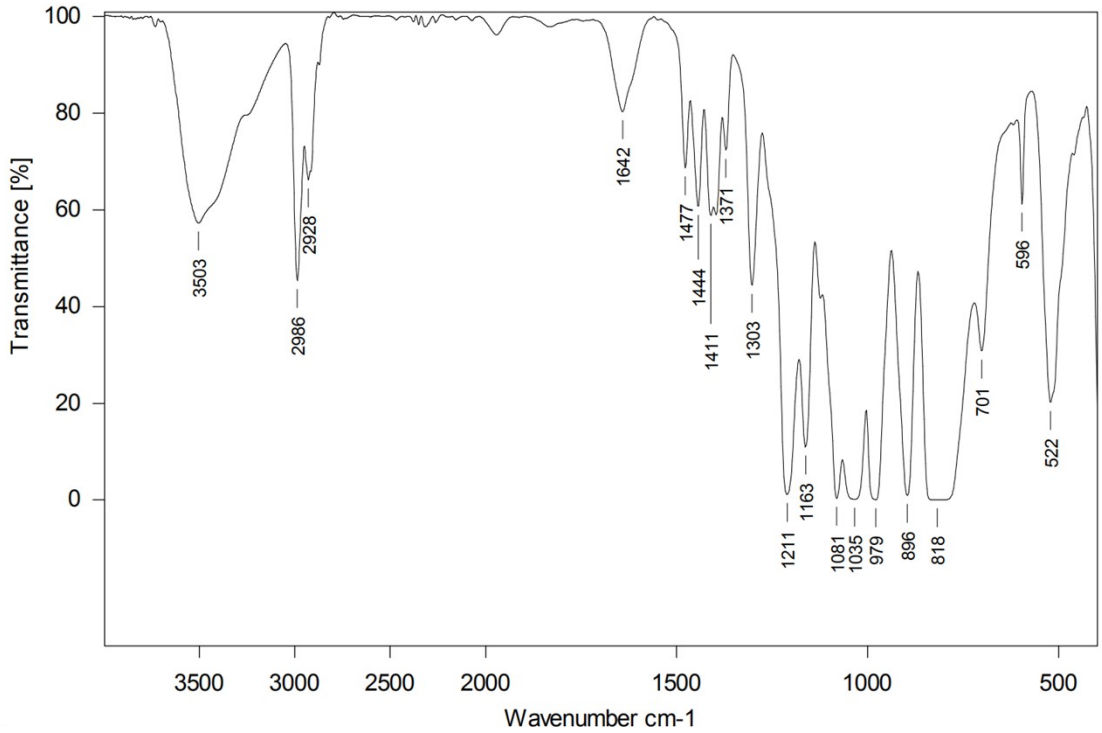

Fig. S11 The IR spectra for complex **5**.

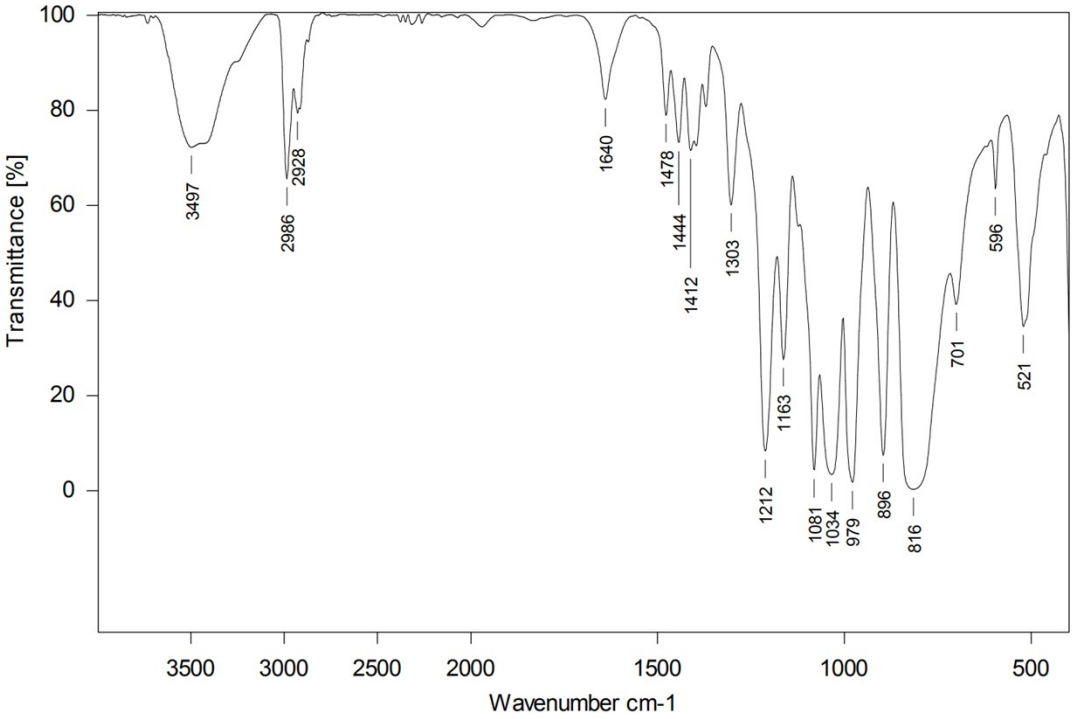

Fig. S12 The IR spectra for complex **6**.

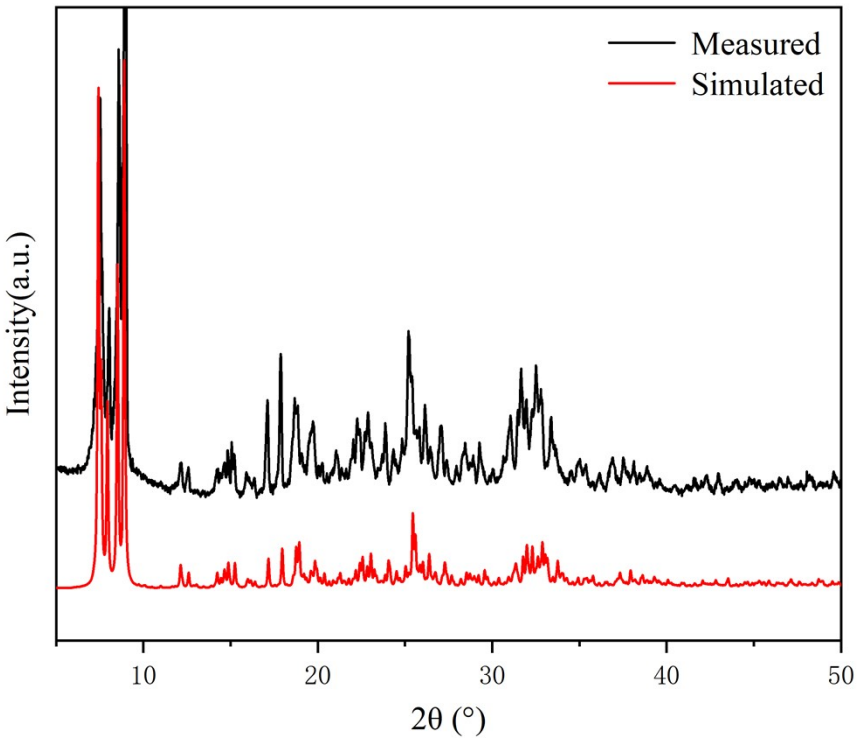

Fig. S13 Powder X-ray diffraction of complex **1**.

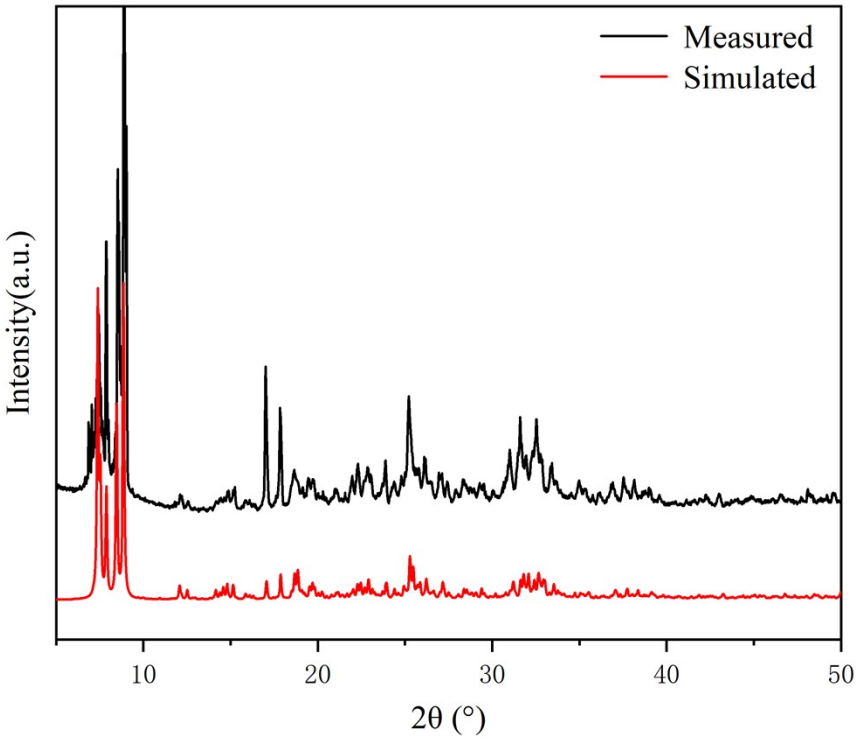

Fig. S14 Powder X-ray diffraction of complex **2**.

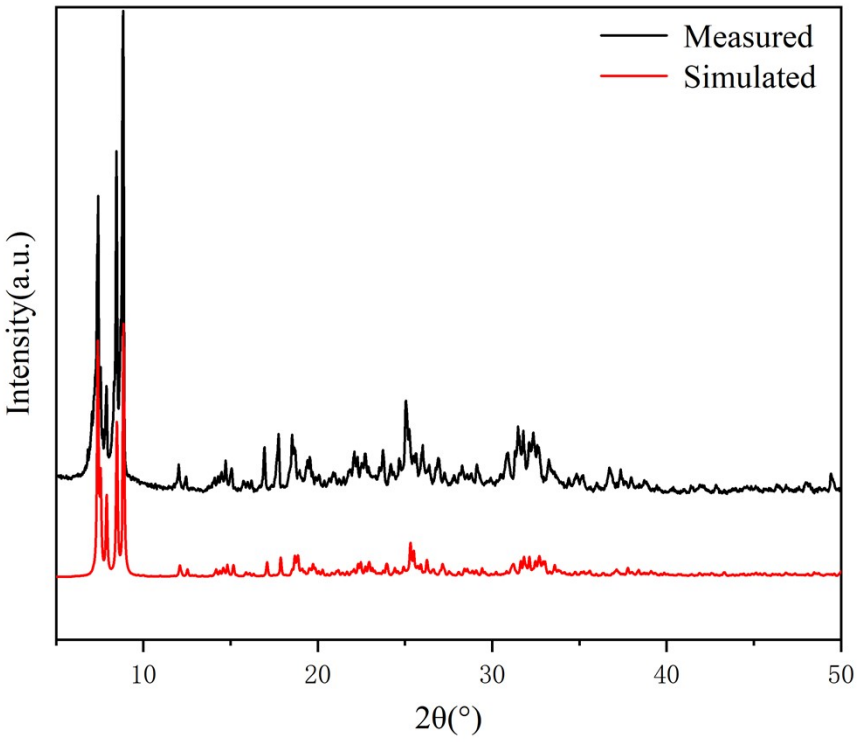

Fig. S15 Powder X-ray diffraction of complex **3**.

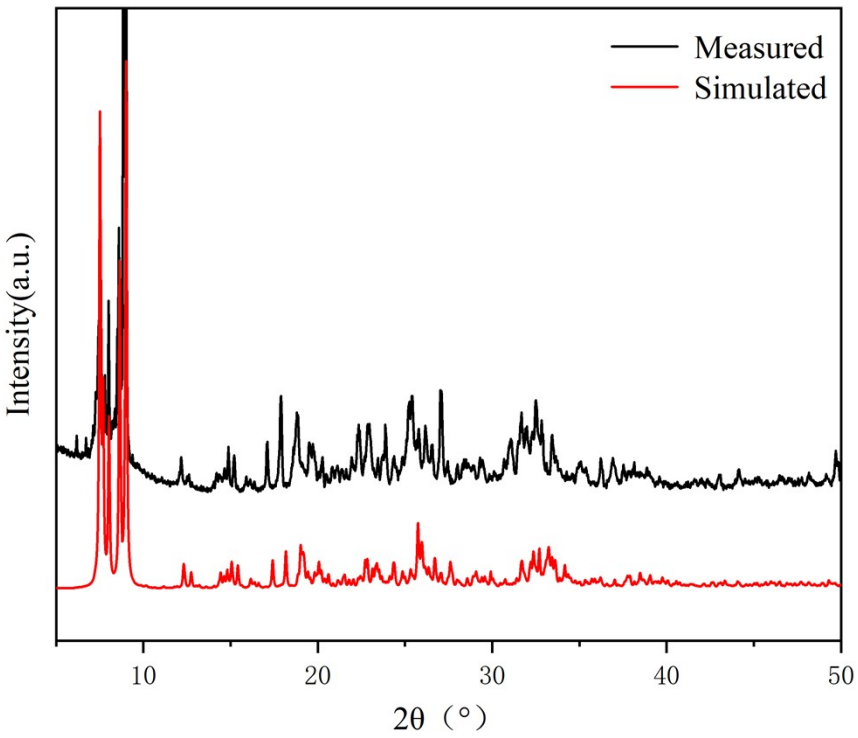

Fig. S16 Powder X-ray diffraction of complex **4**.

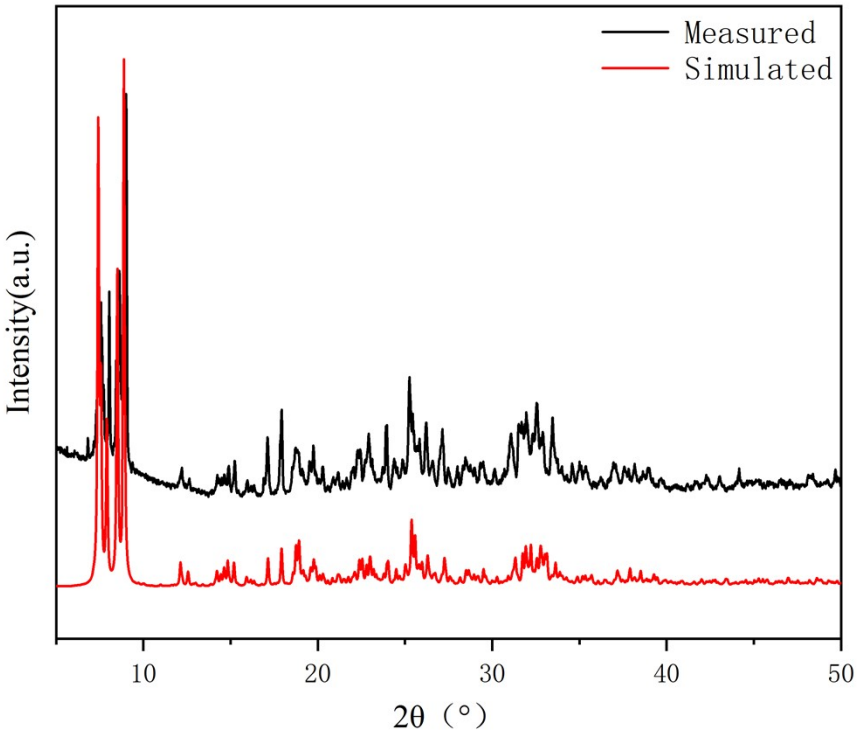

Fig. S17 Powder X-ray diffraction of complex **5**.

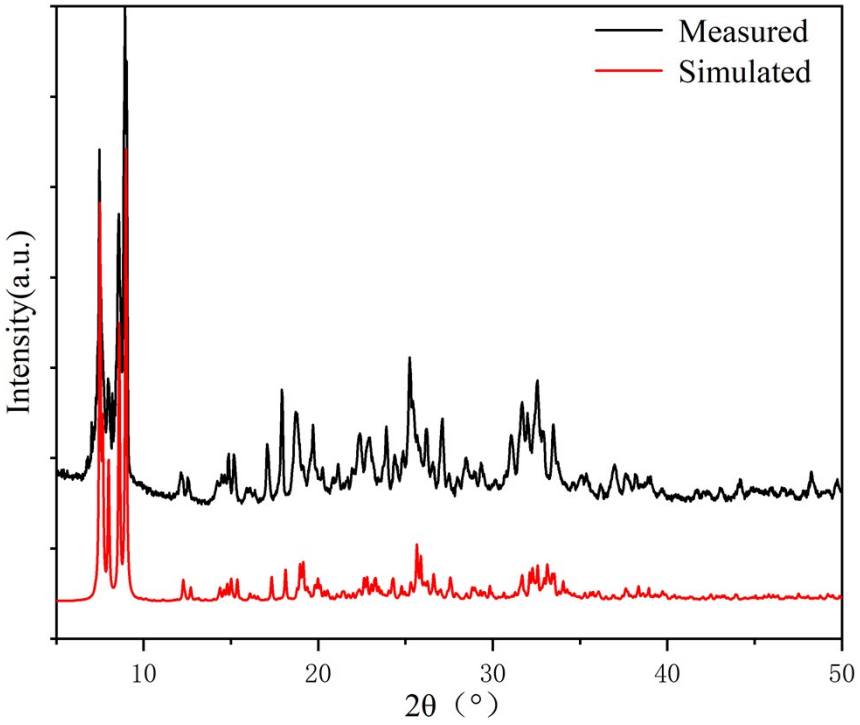

Fig. S18 Powder X-ray diffraction of complex **6**.

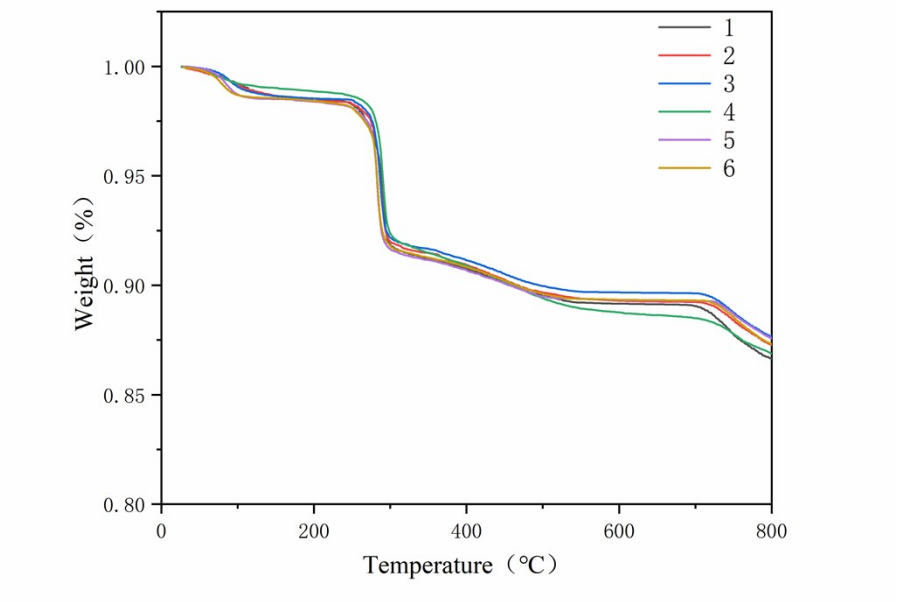

Fig. S19 Thermogravimetric curves of complexes **1-6**.

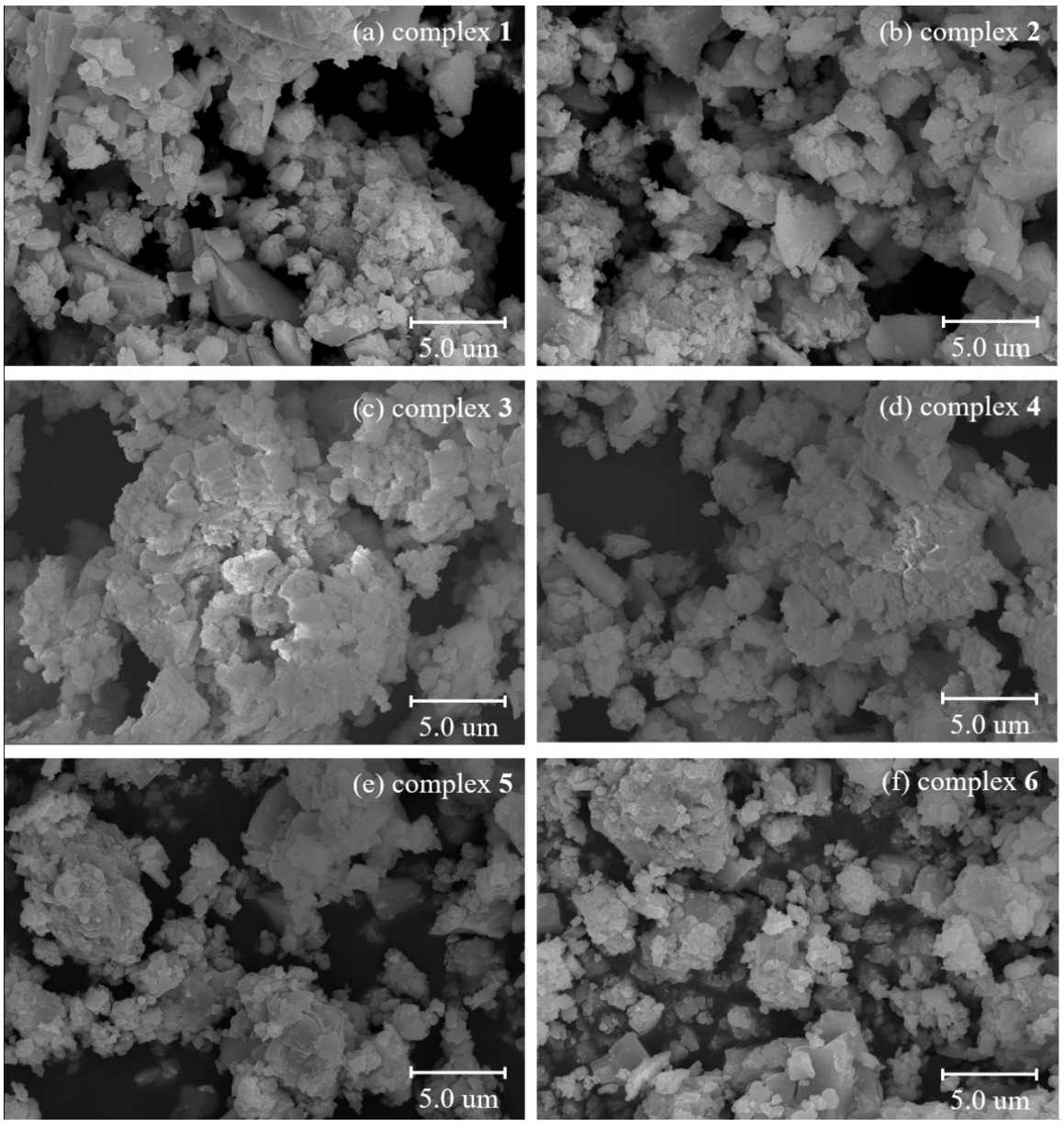

Fig. S20 Scanning electron micrographs of complexes **1-6**.

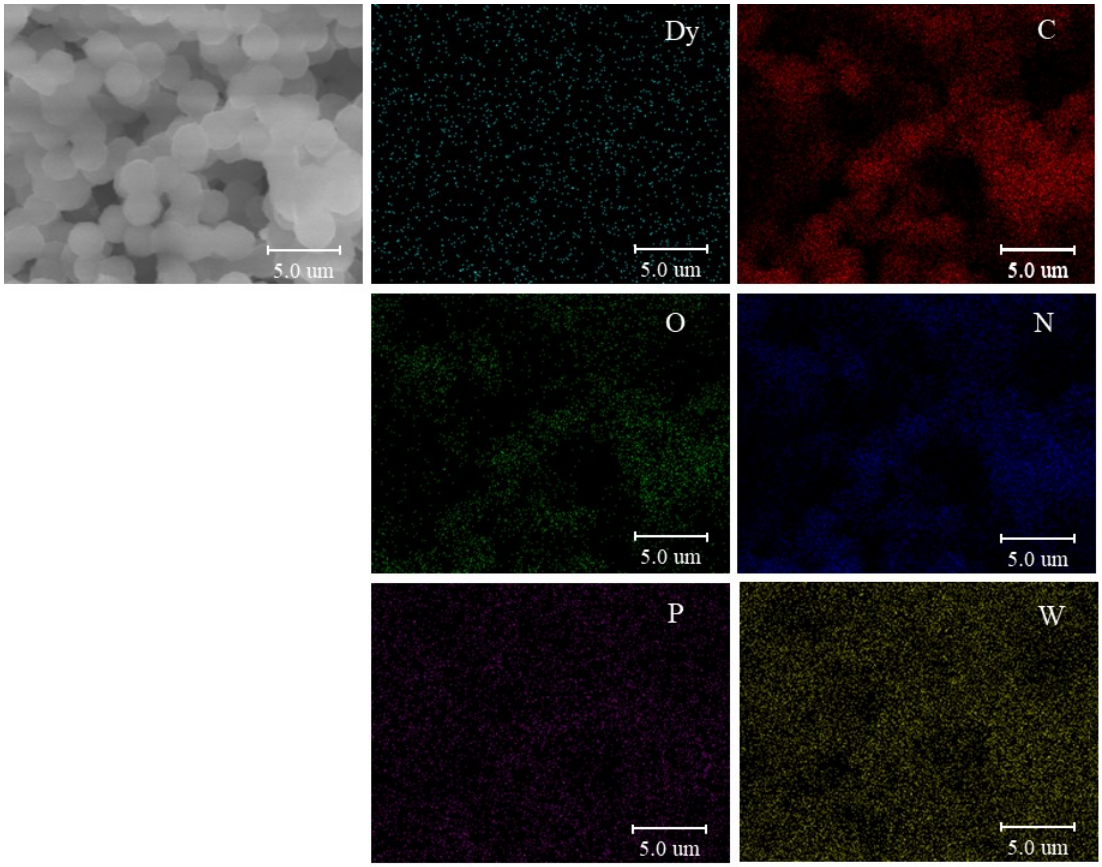

Fig. S21 EDS mapping of $[DyL_3(H_2O)]PW_{12}O_{40}\cdot CH_3CN$@PVDF.

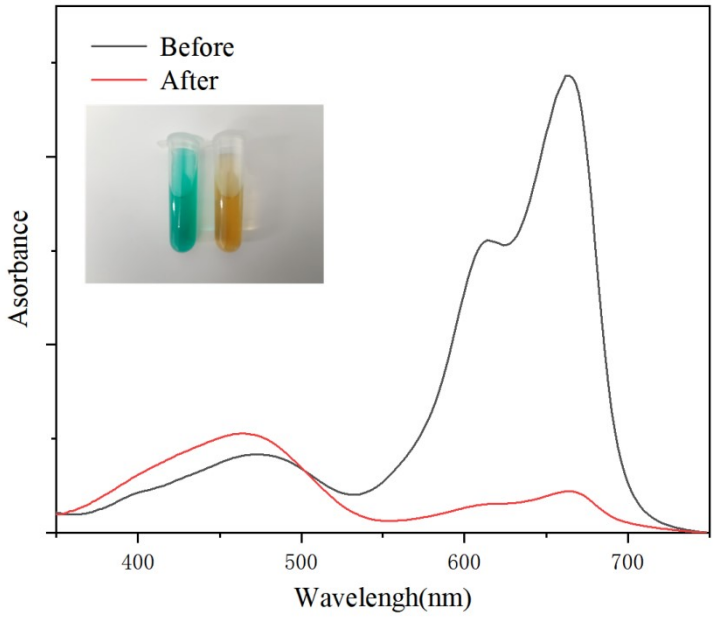

Fig. S22 Selective adsorption properties of complex **1**.

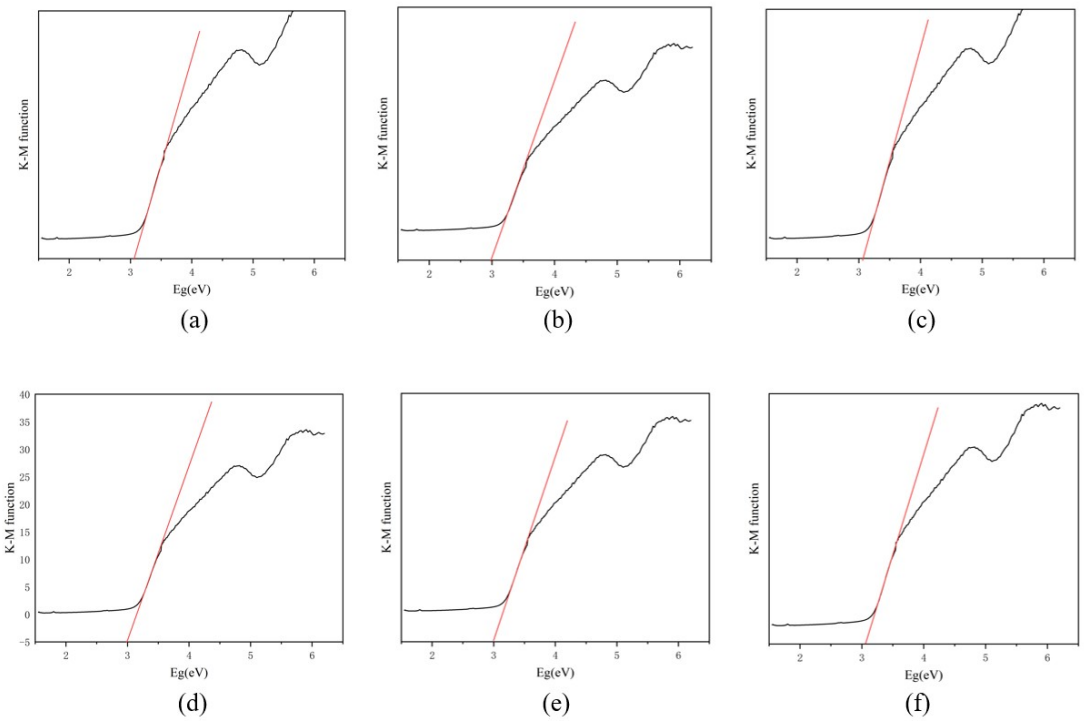

Fig. S23 Solid UV-Vis diffuse reflectance spectrum of K-M function vs Eg for complexes **1-6**.

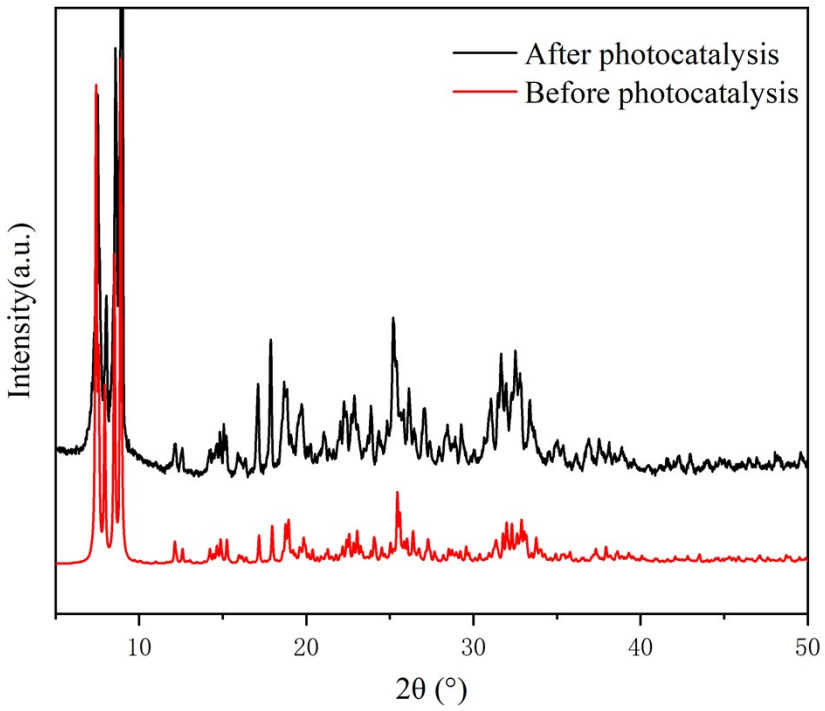

Fig. S24 Comparison of PXRD before and after catalysis of complex **1**.

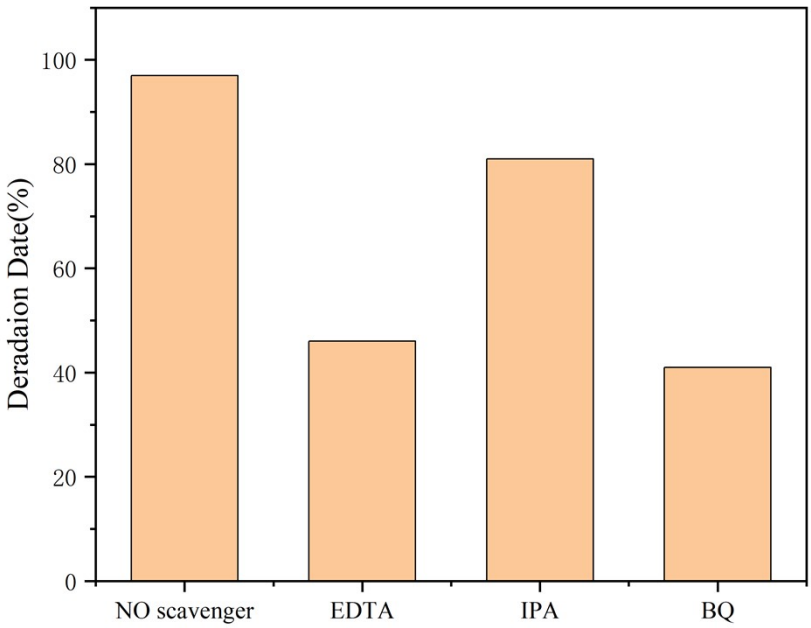

Fig. S25 Degradation efficiency of complex **1**@PVDF in different inhibitors.

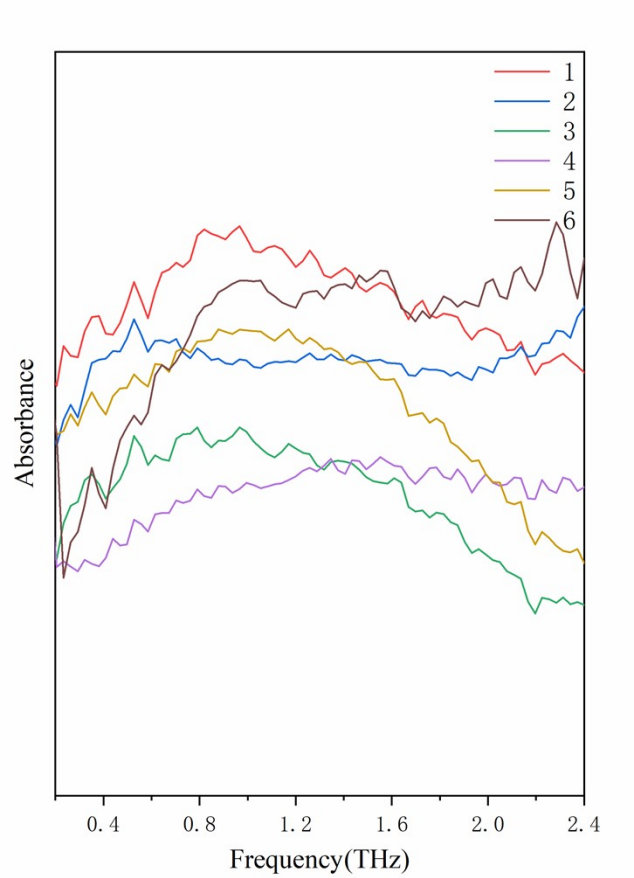

Fig. S26 Terahertz spectra of complexes **1-6**.

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

Complex **1**					
Dy(1)–O(16)	2.24(3)	Dy(1)–O(7)	2.25(3)	Dy(1)–O(10)	2.27(3)
Dy(1)–O(13)	2.27(3)	Dy(1)–O(1)	2.28(3)	Dy(1)–O(4)	2.33(3)
Dy(1)–O(19)	2.41(3)				
O(1)–Dy(1)–O(4)	76.4(10)	O(7)–Dy(1)–O(10)	77.5(10)	O(13)–Dy(1)–O(16)	79.1(11)
Complex **2**					
Ho(1)–O(16)	2.2233(17)	Ho(1)–O(7)	2.250(16)	Ho(1)–O(4)	2.291(16)
Ho(1)–O(13)	2.292(16)	Ho(1)–O(1)	2.297(17)	Ho(1)–O(10)	2.298(15)
Ho(1)–O(19)	2.370(16)				
O(1)–Ho(1)–O(4)	75.9(6)	O(7)–Ho(1)–O(10)	77.5(6)	O(13)–Ho(1)–O(16)	78.9(6)
Complex **3**					
Er(1)–O(1)	2.227(15)	Er(1)–O(4)	2.270(16)	Er(1)–O(7)	2.249(15)
Er(1)–O(10)	2.260(15)	Er(1)–O(13)	2.249(15)	Er(1)–O(16)	2.227(17)
Er(1)–O(19)	2.378(14)				
O(1)–Er(1)–O(4)	76.4(5)	O(7)–Er(1)–O(10)	78.8(5)	O(13)–Er(1)–O(16)	78.6(6)
Complex **4**					
Tm(1)–O(1)	2.23(2)	Tm(1)–O(4)	2.23(2)	Tm(1)–O(7)	2.18(2)
Tm(1)–O(10)	2.20(2)	Tm(1)–O(13)	2.25(2)	Tm(1)–O(16)	2.18(2)
Tm(1)–O(19)	2.29(2)				
O(1)–Tm(1)–O(4)	76.2(8)	O(7)–Tm(1)–O(10)	77.9(8)	O(13)–Tm(1)–O(16)	80.6(9)
Complex **5**					
Yb(1)–O(1)	2.247(16)	Yb(1)–O(4)	2.261(13)	Yb(1)–O(7)	2.244(13)
Yb(1)–O(10)	2.283(14)	Yb(1)–O(13)	2.290(15)	Yb(1)–O(16)	2.182(15)
Yb(1)–O(19)	2.377(14)				
O(1)–Yb(1)–O(4)	75.8(5)	O(7)–Yb(1)–O(10)	78.0(5)	O(13)–Yb(1)–O(16)	78.7(6)
Complex **6**					

Lu(1)–O(1)	2.200(17)	Lu(1)–O(4)	2.232(15)	Lu(1)–O(7)	2.172(14)
Lu(1)–O(10)	2.200(15)	Lu(1)–O(13)	2.216(15)	Lu(1)–O(16)	2.218(15)
Lu(1)–O(19)	2.297(17)				
O(1)–Lu(1)–O(4)	75.5(6)	O(7)–Lu(1)–O(10)	78.2(6)	O(13)–Lu(1)–O(16)	79.0(6)

Table S2 Weak interactions in the stacking structure of complex **1**.

Intermolecular hydrogen bonds in the stacking structure of complex **1**

Donor-H···Acceptor	D-H (Å)	H···A (Å)	D-H···A (°)
O(19)-H(19E)···N(1)	0.86	2.12	162
O(19)-H(19F)···O(28)	0.86	2.03	166
C(7)-H(7A)···O(39)	0.97	2.58	141
C(10)-H(10C)···O(58)	0.96	2.53	160
C(19)-H(19A)···O(53)	0.97	2.57	128
C(20)-H(20B)···O(2)	0.96	2.58	153
C(23)-H(23A)···O(57)	0.97	2.59	159
C(24)-H(24C)···O(33)	0.95	2.17	148
C(27)-H(27A)···O(39)	0.96	2.56	142
C(27)-H(27B)···O(33)	0.98	2.57	157
C(32)-H(32A)···O(33)	0.96	2.4	146

Intramolecular hydrogen bonding in the stacking structure of complex **1**

Donor-H···Acceptor	D–H (Å)	H···A (Å)	D–H···A (°)
C(7)-H(7B)···O(6)	0.97	2.45	141
C(13)-H(13A)···O(9)	0.96	2.60	103
C(17)-H(17A)···O(15)	0.97	2.43	163
C(25)-H(25A) ···O(14)	0.97	2.55	101

C(29)-H(29A) ···O(16)	0.97	2.53	110

Table S3 Weak interactions in the stacking structure of complex **2**.

Intermolecular hydrogen bonds in the stacking structure of complex **2**

Donor-H···Acceptor	D-H (Å)	H···A (Å)	D-H···A (°)
O(19)-H(19E)···N(1)	0.87	2.1	164
O(19)-H(19F)···O(28)	0.86	2.11	165
C(2)-H(2B)···O(36)	0.97	2.48	162
C(12)-H(12B)···O(53)	0.97	2.58	160
C(19)-H(19A)···O(53)	0.97	2.34	156
C(20)-H(20A)···O(56)	0.96	2.5	160
C(23)-H(23A)···O(57)	0.97	2.56	171
C(24)-H(24B)···O(63)	0.96	2.54	159
C(27)-H(27B)···O(33)	0.97	2.49	165

Intramolecular hydrogen bonding in the stacking structure of complex **2**

Donor-H···Acceptor	D–H (Å)	H···A (Å)	D–H···A (°)
C(3)-H(3B)···O(58)	0.97	2.58	100
C(15)-H(15A)···O(8)	0.97	2.38	106
C(25)-H(25A)···O(14)	0.97	2.55	101

Table S4 Weak interactions in the stacking structure of complex **3**.

Intermolecular hydrogen bonds in the stacking structure of complex **3**

Donor-H···Acceptor	D-H (Å)	H···A (Å)	D-H···A (°)
O(19)-H(19E)···N(1)	0.86	2.11	165
O(19)-H(19F)···O(28)	0.86	2.1	164

C(2)-H(2B)···O(36)	0.97	2.49	162
C(19)-H(19A)···O(53)	0.97	2.36	161
C(23)-H(23A)···O(57)	0.97	2.57	173
C(24)-H(24A)···O(33)	0.96	2.53	125
C(24)-H(24B)···O(63)	0.96	2.53	156

Intramolecular hydrogen bonding in the stacking structure of complex **3**

Donor-H···Acceptor	D–H (Å)	H···A (Å)	D–H···A (°)
C(3)-H(3B)···O(58)	0.97	2.58	130
C(5)-H(5B)···O(17)	0.97	2.56	129
C(25)-H(25A)···O(14)	0.97	2.57	102

Table S5 Weak interactions in the stacking structure of complex **4**.

Intermolecular hydrogen bonds in the stacking structure of complex **4**

Donor-H···Acceptor	D-H (Å)	H···A (Å)	D-H···A (°)
O(19)-H(19E)···N(1)	0.85	2.14	163
O(19)-H(19F)···O(28)	0.85	2.09	163
C(1)-H(1B)···O(58)	0.97	2.56	143
C(2)-H(2B)···O(36)	0.97	2.42	159
C(12)-H(12B)···O(53)	0.97	2.57	158
C(13)-H(13A)···O(27)	0.97	2.58	138
C(14)-H(14B)···O(30)	0.96	2.52	169
C(16)-H(16B)···O(50)	0.96	2.51	141
C(19)-H(19A)···O(53)	0.97	2.21	150
C(20)-H(20A)···O(56)	0.96	2.59	140
C(23)-H(23A)···O(57)	0.97	2.56	154

C(24)-H(24C)···O(33)	0.95	2.25	168
C(27)-H(27A)···O(39)	0.97	2.38	140
C(32)-H(32C)···O(33)	0.96	2.45	152

Intramolecular hydrogen bonding in the stacking structure of complex **4**

Donor-H···Acceptor	D–H (Å)	H···A (Å)	D–H···A (°)
C(2)-H(2B)···O(3)	0.97	2.58	112
C(3)-H(3B)···O(1)	0.97	2.47	101
C(3)-H(3B)···O(12)	0.97	2.50	112
C(5)-H(5A)···O(17)	0.97	2.59	112
C(17)-H(17A)···O(15)	0.97	2.47	117
C(22)-H(22A)···O(51)	0.97	2.56	104
C(25)-H(25A)···O(14)	0.97	2.57	100

Table S6 Weak interactions in the stacking structure of complex **5**.

Intermolecular hydrogen bonds in the stacking structure of complex **5**

Donor-H···Acceptor	D-H (Å)	H···A (Å)	D-H···A (°)
O(19)-H(19E)···N(1)	0.86	2.06	163
O(19)-H(19F)···O(28)	0.86	2.09	165
C(1)-H(1B)···O(58)	0.97	2.6	148
C(2)-H(2B)···O(36)	0.97	2.48	161
C(19)-H(19A)···O(53)	0.97	2.39	154
C(20)-H(20A)···O(56)	0.96	2.46	156
C(23)-H(23A)···O(57)	0.97	2.49	161
C(24-H(24B)···O(63)	0.96	2.49	170
C(27)-H(27B)···O(33)	0.97	2.57	159
C(29)-H(29A)···O(36)	0.97	2.58	137

C(32)-H(32C)···O(33)	0.96	2.49	156

Intramolecular hydrogen bonding in the stacking structure of complex **5**

Donor-H···Acceptor	D–H (Å)	H···A (Å)	D–H···A (°)
C(2)-H(2B)···O(3)	0.97	2.58	111
C(3)-H(3B)···O(1)	0.97	2.58	102
C(3)-H(3B)···O(12)	0.97	2.51	112
C(17)-H(17A)···O(15)	0.97	2.52	160
C(23)-H(23B)···O(13)	0.97	2.47	111

Table S7 Weak interactions in the stacking structure of complex **6**.

Intermolecular hydrogen bonds in the stacking structure of complex **6**

Donor-H···Acceptor	D-H (Å)	H···A (Å)	D-H···A (°)
O(19)-H(19E)···N(1)	0.85	2.1	162
O(19)-H(19F)···O(28)	0.85	2.11	164
C(1)-H(1B)···O(58)	0.97	2.51	147
C(2)-H(2B)···O(36)	0.97	2.4	161
C(10)-H(10C)···O(58)	0.96	2.59	147
C(14)-H(14B)···O(30)	0.96	2.54	162
C(16)-H(16B)···O(50)	0.96	2.6	142
C(19)-H(19A)···O(53)	0.97	2.3	156
C(23)-H(23A)···O(57)	0.97	2.53	177
C(24)-H(24B)···O(63)	0.96	2.35	176
C(27)-H(27B)···O(33)	0.97	2.55	156
C(29)-H(29A)···O(36)	0.97	2.43	133
C(32)-H(32A)···O(33)	0.96	2.54	143

Intramolecular hydrogen bonding in the stacking structure of complex **6**

Donor-H···Acceptor	D–H (Å)	H···A (Å)	D–H···A (°)
C(2)-H(2B)···O(3)	0.97	2.59	111
C(3)-H(3B)···O(12)	0.97	2.54	129
C(5)-H(5B)···O(17)	0.97	2.53	121
C(17)-H(17A)···O(15)	0.97	2.44	160
C(25)-H(25A)···O(14)	0.97	2.56	100

Table S8 Efficiency of methyl orange degradation by complexes **1-6**.

	0min	3min	6min	9min	12min	15min
Complex **1**	0%	40.27%	70.35%	92.35%	95.48%	95.78%
Complex **2**	0%	22.51%	64.33%	92.53%	96.35%	97.41%
Complex **3**	0%	33.45%	70.32%	91.58%	95.06%	96.38%
Complex **4**	0%	34.05%	66.22%	86.93%	94.71%	95.84%
Complex **5**	0%	37.27%	65.28%	87.34%	94.62%	95.32%
Complex **6**	0%	26.75%	70.17%	87.07%	94.45%	95.02%

Table S9 Comparison of the photocatalytic activities of reported polyacid-based complexes.

Catalysts	Light source	Degradation rate	Stability (cycle)	Ref.
$Pt/H_3PMo_{12}O_{40}/TiO_2$	300 W Xe lamp	82.56% in 180 min	5	1
$TiO_2/POM/Fe_3O_4@SiO_2$	300 W Hg lamp UV	97.32% in 100 min	1	2
$H_3PW_{12}O_{40}/SiO_2$	500 W Xe lamp	98.3% in 120 min	5	3
$[\{Ag_5(pz)_7\}\{AlW_{12}O_{40}\}]\cdot 4H_2O$	125 W Hg lamp UV	90.33% in 175 min	1	4
$Na(BiHEDTA\cdot 2H_2O)_3(PW_{12}O_{40})\cdot 2H_2O$	300 W Xe lamp	96% in 80 min	5	5

$Li_4(H_2O)_6[(H_2V_6O_{18})\cdot(Me_{10}CB[5]@H_2O)_2]\cdot 14H_2O$	500W Xe lamp	75% in 180 min	5	6
$[Cu_4(OH)_3Cl(H_2O)_3(4\text{-bpo})_3](SiW_{12}O_{40})\cdot 5H_2O$	500 W Xe lamp	68.6% in 180 min	1	7
$H_9Na_3[WZn_3(H_2O)_2(ZnW_9O_{34})_2]\cdot 24H_2O$	400W Hg lamp UV	99% in 7 min	1	8
$Cu_2(L_1)_3(H_2O)_2(Mo_4O_{13})_2$	200 W Hg lamp UV	56% in 90 min	5	9
$H_3PW_{12}O_{40}/Ag_3PO_4$ Powder	300 Xe lamp	99% in 6 min	4	10
$H_3PW_{12}O_{40}/Ag_3PO_4$@PVDF-F127	300 Xe lamp	75% in 60 min	4	11
$[DyL_3(H_2O)]PW_{12}O_{40}\cdot CH_3CN$	400 W Hg lamp UV	95.8% in 15min	4	This work
$[DyL_3(H_2O)]PW_{12}O_{40}\cdot CH_3CN$@ PVDF	400 W Hg lamp UV	97.4% in 50 min	4	This work

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