Supporting information

A series of porous 3D inorganic organic hybrid framework crystalline materials based on 5-Aminoisophthalic Acid for photocatalytic degradation of Crystal Violet

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Table S1 Crystallographic data for complexes **1-3***

Complexes	**1**	**2**	**3**
Formula	$C_{13}H_{13}N_2O_6Zn$	$C_{13}H_9N_2O_4Cu$	$C_{13}H_{13}N_2O_6Ni_{0.25}Zn_{0.75}$
M (g·mol^{-1})	358.62	320.76	351.96
Crystal system	*Monoclinic*	*Monoclinic*	*Monoclinic*
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$
a (Å)	12.3235(9)	12.5486(14)	12.4092(9)
b (Å)	7.6722(5)	7.6374(9)	7.6700(5)
c (Å)	16.1144(12)	16.0778(18)	16.0912(12)
α (°)	90	90	90
β (°)	108.5810(10)	109.037(2)	108.6420(10)
γ (°)	90	90	90
V (Å^3)	1444.17(18)	1456.6(3)	1451.18(18)
Z	4	4	4
D_c (g·cm^{-3})	1.649	1.463	1.611
F(000)	732	648	724
M(Mo-Kα) (mm^{-1})	1.732	1.512	1.368
θ (°)	1.743-29.599	1.717-24.999	1.732-24.994
Reflections collected	3642	3955	4864
Independent reflections(I>2σ(I))	3882	2557	2547
Parameters	200	181	200
Δ(ρ)(e Å^{-3})	1.322 and -0.874	0.320 and -0.268	2.146 and -0.717
Goodness of fit	1.114	1.158	1.106
R^a	0.0690(0.0532)[b]	0.0418(0.0373)[b]	0.0611(0.0583)[b]
$wR_2{}^a$	0.1731(0.1856)[b]	0.0831(0.0843)[b]	0.1695(0.1713)[b]

*[a]$R=\sum \left| F_O-F_C \right| / \sum \left| F_O \right|$, $wR_2=\{\sum[w(F_O^2-F_C^2)^2]/\sum[w(F_O^2)^2]\}^{1/2}$; [$F_O>4\sigma(F_O)$]. [b]Based on all data.

Table S2 Crystallographic data for complexes **4-7***

Complexes	**4**	**5**	**6**	**7**
Formula	$C_{13}H_{13}N_2O_6Cr$	$C_{13}H_{13}N_2O_6Co$	$C_{13}H_{13}N_2O_6Fe$	$C_{16}H_{16}N_2O_{10}Mn$
M ($g \cdot mol^{-1}$)	345.25	354.20	349.10	451.25
Crystal system	*Monoclinic*	*Monoclinic*	*Monoclinic*	*Monoclinic*
Space group	$P2_1/c$	$P2_1/c$	$P2_1/c$	$P2/n$
a (Å)	12.5435(9)	12.6083(16)	12.228(3)	7.040(4)
b (Å)	7.6671(6)	7.6426(9)	7.6950(16)	10.055(6)
c (Å)	16.1534(11)	16.1273(19)	16.114(4)	11.499(7)
α (°)	90	90	90	90
β (°)	108.7710(10)	109.076(2)	108.418(4)	95.072(10)
γ (°)	90	90	90	90
V ($Å^3$)	1470.88(19)	1468.7(3)	1438.5(5)	810.8(8)
Z	4	4	4	2
D_c ($g \cdot cm^{-3}$)	1.559	1.602	1.612	1.848
F(000)	708	728	716	462
M(Mo Kα) (mm^{-1})	0.808	1.199	1.199	0.883
θ (°)	1.715-28.105	1.709-24.993	1.755-28.223	2.025-25.242
Reflections collected	3585	4337	1135	945
Independent reflections($I>2\sigma(I)$)	3504	2555	3487	2008
Parameters	200	197	200	124
Δ(ρ)(e $Å^{-3}$)	1.817 and -1.360	3.047 and -1.506	1.177 and --0.498	1.021 and-0.694
Goodness of fit	1.079	1.061	1.022	1.044
R^a	0.0966(0.0835)[b]	0.0901(0.0844)[b]	0.1601(0.0730)[b]	0.0966(0.0537)[b]
$wR_2{}^a$	0.2395(0.2525)[b]	0.2520(0.2571)[b]	0.2046(0.2562)[b]	0.1209(0.1394)[b]

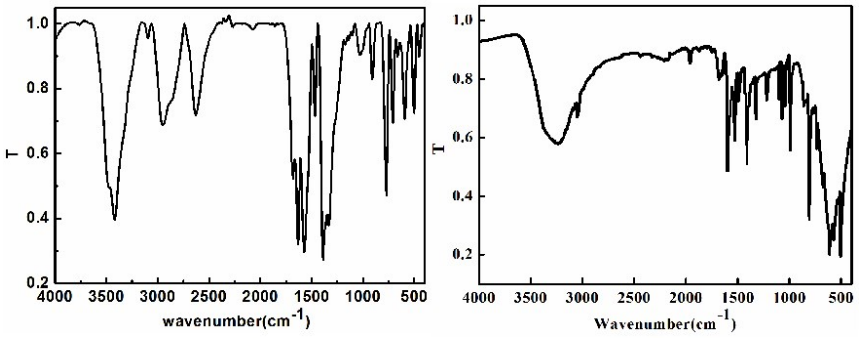
*[a]$R=\sum \left| F_O-F_C \right| / \sum \left| F_O \right|$, $wR_2=\{\sum[w(F_O^2-F_C^2)^2]/\sum[w(F_O^2)^2]\}^{1/2}$; $[F_O>4\sigma(F_O)]$. [b]Based on all data.

Table S3 The selected bond distances (Å) of complexes **1-7***

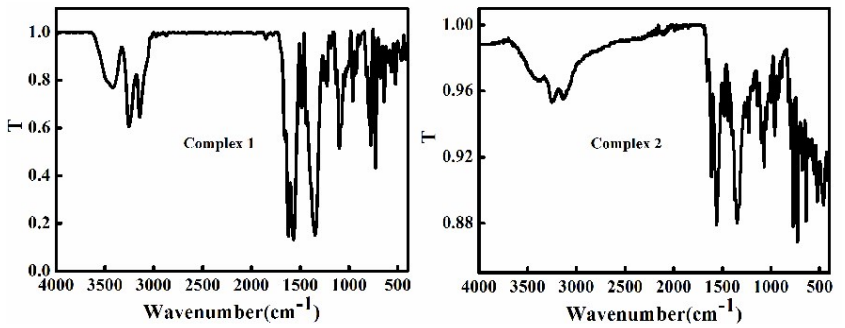
Complex **1**			
Zn(1)-N(2)	2.124(3)	Zn(1)-N(1)	2.043(3)
Zn(1)-O(4)$^{\#1}$	1.980(3)	Zn(1)-O(2)$^{\#2}$	1.937(3)
Complex **2**			
Cu(1)-N(1)	2.114(3)	Cu(1)-N(1AA)	2.036(3)
Cu(1)-O(3)$^{\#1}$	1.977(2)	Cu(1)-O(2)$^{\#2}$	1.954(2)
Complex **3**			
Ni(1)-N(1)	2.101(4)	Ni(1)-N(1)	2.044(4)
Ni(1)-O(2)$^{\#1}$	1.985(3)	Ni(1)-O(3)$^{\#2}$	1.937(3)
Complex **4**			

Cr(1)-N(1)	2.148(5)	Cr(1)-N(1)	2.049(4)
Cr(1)-O(3)$^{\#1}$	1.946(4)	Cr(1)-O(1)$^{\#2}$	1.986(4)
Complex **5**			
Co(1)-N(1)	2.113(5)	Co(1)-N(2)	2.041(5)
Co(1)-O(1)$^{\#1}$	1.984(4)	Co(1)-O(3)$^{\#2}$	1.942(5)
Complex **6**			
Fe(1)-N(1)	2.126(7)	Fe(1)-N(2)	2.038(6)
Fe(1)-O(1)$^{\#1}$	1.978(5)	Fe(1)-O(3)$^{\#2}$	1.939(5)
Complex **7**			
Mn(1)-O(4)$^{\#1}$	2.149(3)	Mn(1)-O(4)$^{\#2}$	2.149(3)
Mn(1)-O(1)	2.129(3)	Mn(1)-O(1)$^{\#3}$	2.129(3)
Mn(1)-O(5)$^{\#3}$	2.269(3)	Mn(1)-O(5)	2.269(3)

*Symmetry codes:Complex **1**: #1, +x, -1+y, +z; #2, +x, 3/2-y, 1/2+z; Complex **2**: #1, +x, 1+y, +z; #2, +x, 1/2-y, -1/2+z; Complex **3**: #1, +x, -1+y, +z; #2, +x, 3/2-y, 1/2+z; Complex **4**: #1, +x, 3/2-y, 1/2+z; #2, +x, 1+y, +z; Complex **5**: #1, +x, -1+y, +z; #2, +x, 3/2-y, 1/2+z; Complex **6**: #1, +x, 1+y, +z; #2, 2+x, 3/2-y, 1/2+z; Complex **7**: #1, 3/2-x,- 1+y, 1/2-z; #2,+x, -1+y, +z; #3, 3/2-x, +y, 1/2-z.



(a) (b)



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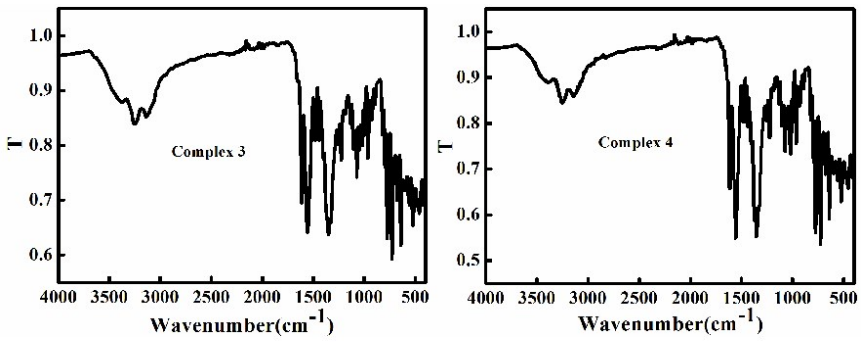


(e) (f)

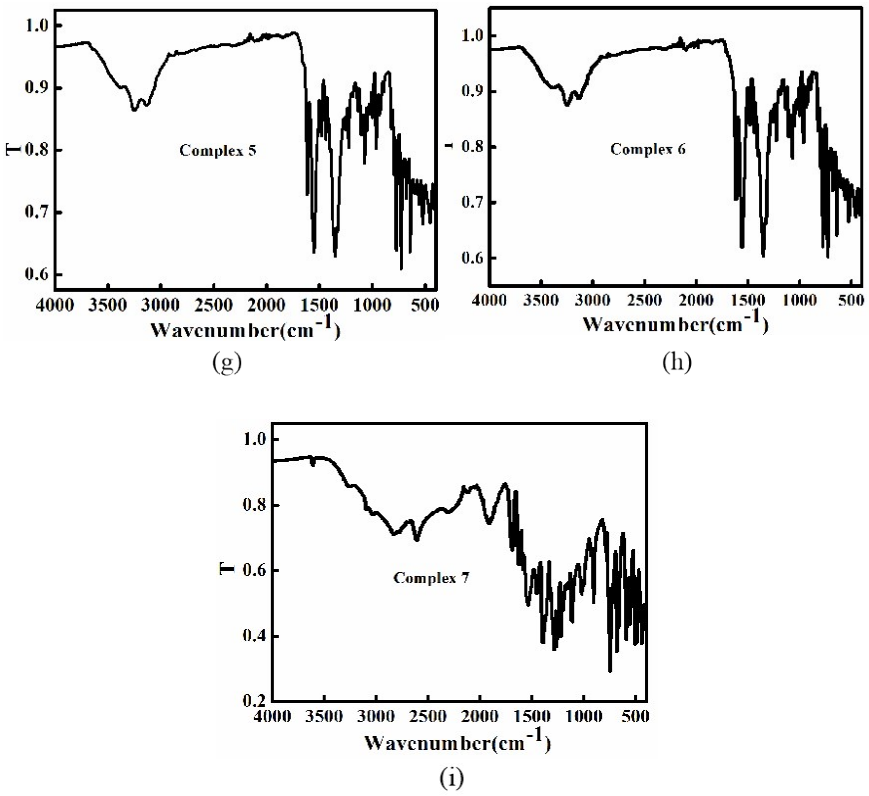
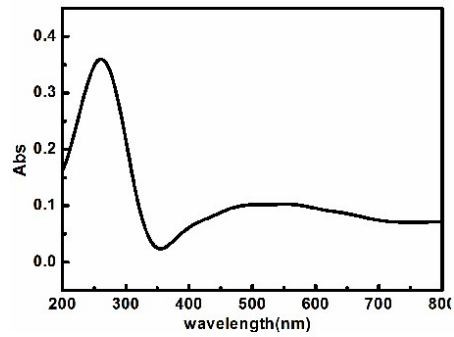


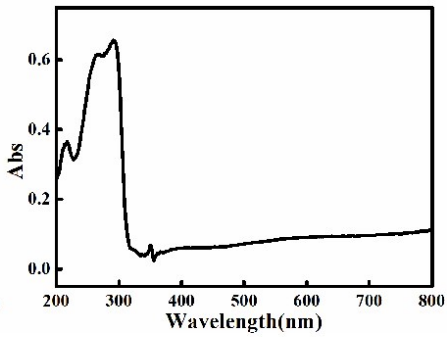
Figure S1 IR spectra of ligands and complexes **1-7**: (a)Ligand 5-aip; (b)Ligand 4,4′-bipy; (c) Complex **1**; (d) Complex **2**;(e) Complex **3**; (f) Complex **4**; (g) Complex **5**; (h) Complex **6**; (i) Complex **7**

Table S4 IR spectra (cm^{-1}) of ligands 5-aip, 4,4′-bipy and complexes **1-7**

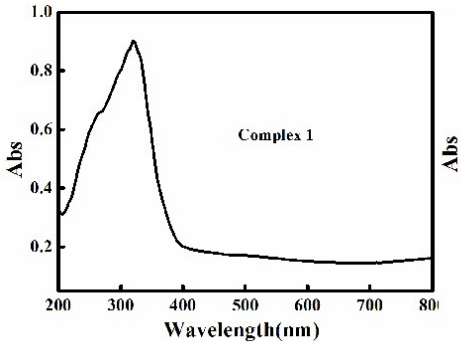
	5-aip	4,4′-bipy	**1**	**2**	**3**	**4**	**5**	**6**	**7**
ν_{O-H}	3442	3242	3418	3382	3376	3394	3400	3394	3423
ν_{N-H}	3107	-	3254	3248	3248	3254	3260	3260	3259
ν_{Ar-H}	3099	3053	3144	3126	3126	3132	3138	3138	3080
ν_{asCOO^-}	1691	-	1558	1552	1558	1558	1564	1552	1561
ν_{sCOO^-}	1395	-	1357	1351	1351	1351	1357	1345	1371
$\nu_{C=N}$	-	1679	1667	1667	1673	1671	1667	1661	-
$\nu_{C=C}$	1634, 1469	1600,1418	1613,1473	1619,1442	1613,1479	1613,1430	1625,1425	1619,1485	1641, 1458
ν_{C-C}	1145	1102	1187	1144	1193	1175	1181	1181	1176
ν_{C-N}	1105	1077	1103	1102	1102	1108	1114	1108	1053
ν_{C-O}	1035	-	1022	1071	1065	1077	1071	1041	1022
δ_{Ar-H}	778	797	773	773	767	779	778	779	781


Abs
wavelength(nm)

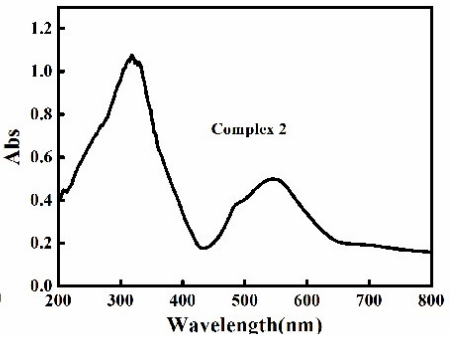
(a)


Abs
Wavelength(nm)

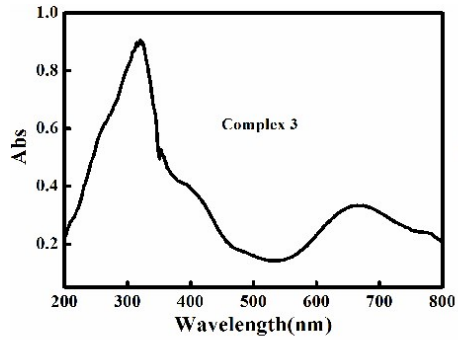
(b)


Complex 1
Abs
Wavelength(nm)

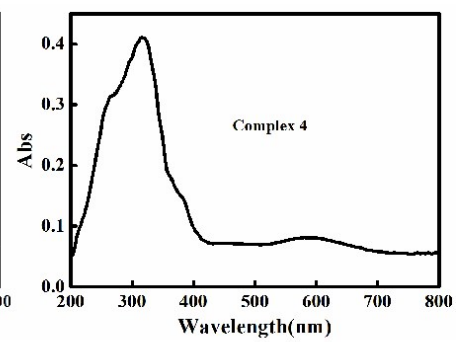
(c)


Complex 2
Abs
Wavelength(nm)

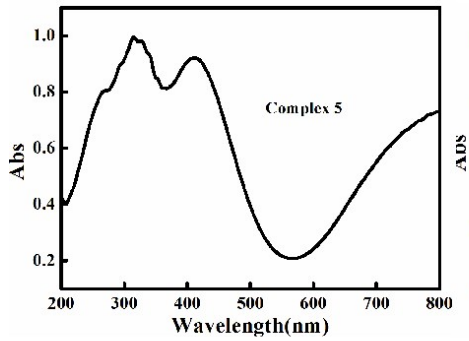
(d)


Complex 3
Abs
Wavelength(nm)

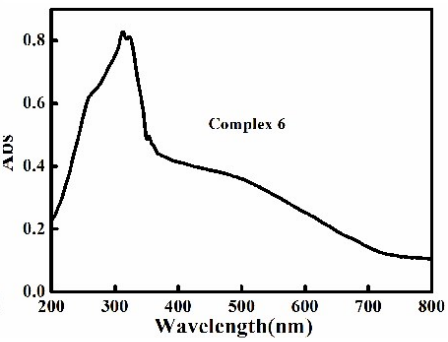
(e)


Complex 4
Abs
Wavelength(nm)

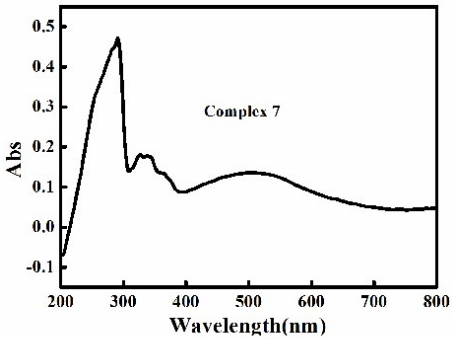
(f)


Complex 5
Abs
Wavelength(nm)

(g)


Complex 6
Abs
Wavelength(nm)

(h)

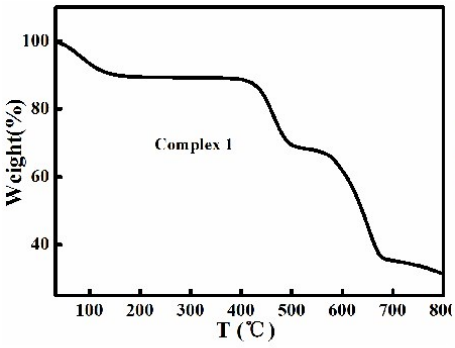


(i)

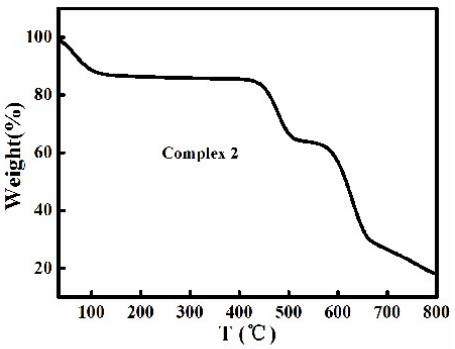
Figure S2 UV-Vis spectra of ligands and complexes **1-7**: (a) Ligand 5-aip; (b) Ligand 4,4′-bipy; (c) Complex **1**; (d) Complex **2**;(e) Complex **3**; (f) Complex **4**; (g) Complex **5**; (h) Complex **6**; (i) Complex **7**

Table S5 UV-Vis spectra (nm) of ligand 5-aip, 4,4′-bipy and complexes **1-7**

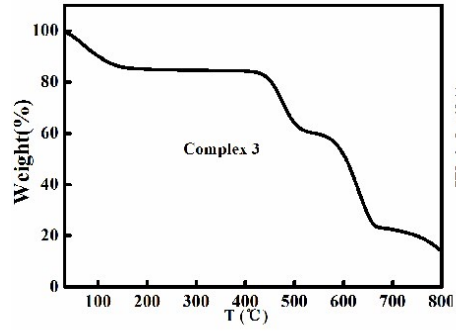
	LLCT		LMCT	MMCT
	π-π*	n-π*		
5-aip	217	298	-	-
4,4′-bipy	215	290	-	-
1	265	289	-	-
2	265	314	412	-
3	263	323	398	659
4	265	317	383	592
5	208	318	331	549
6	257	312	351	-
7	216	289	367	503



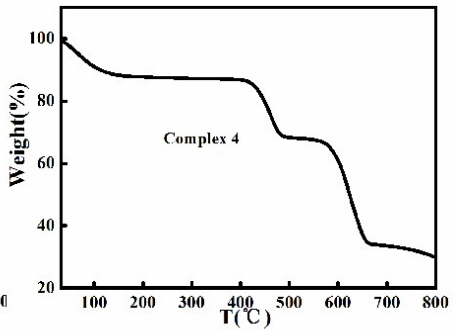
(a)



(b)



(c)



(d)

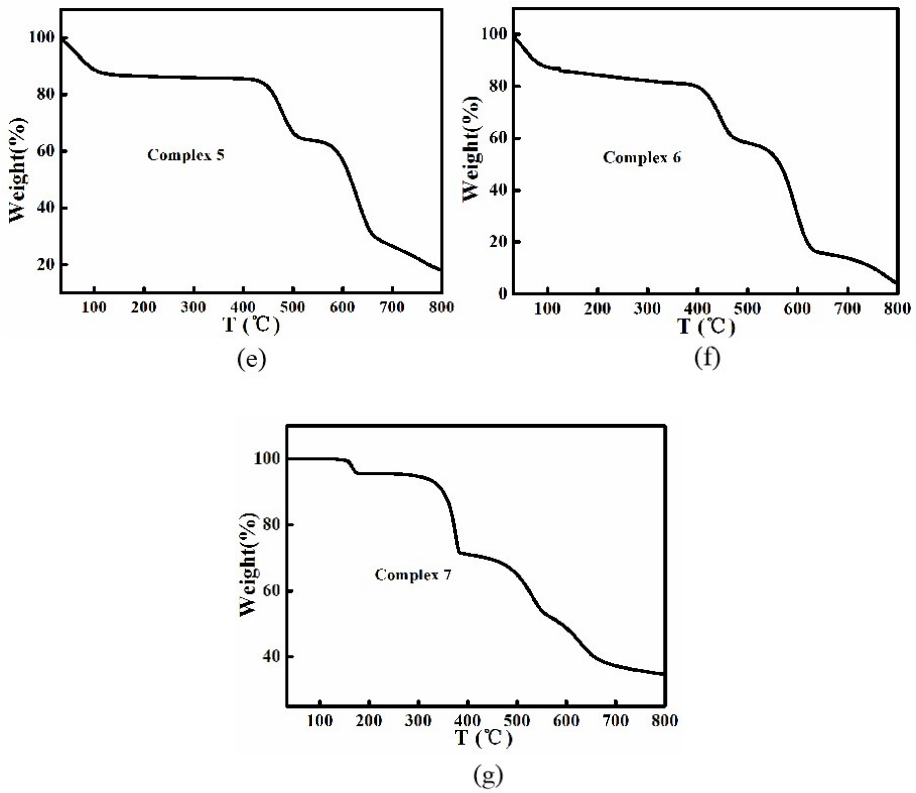


Figure S3 TG curves of complexes **1**−**7** (a) Complex **1**; (b) Complex **2**;(c) Complex **3**; (d) Complex **4**; (e) Complex **5**; (f) Complex **6**; (g) Complex **7**

Table S6 TG analysis data of complexes **1-6**

complexes		**1**	**2**	**3**	**4**	**5**	**6**
The first stage	T(°C)	30-373	30-356	30-380	30-388	30-344	30-180
	Cal. value	10.1%	10.1%	10.2%	8.3%	10.1%	8.2%
	Mea. value	10.08%	10.08%	11.5%	9.6%	9.5%	9.7%
The second stage	T(°C)	373-518	356-520	380-525	388-491	344-530	180-478
	Cal. value	21.7%	21.5%	22.2%	17.9%	22.2%	17.8%
	Mea. value	20.5%	21.9%	23.9%	18.2%	21.7%	18.7%
The third stage	T(°C)	518-800	520-800	525-800	497-800	530-800	478-800
	Cal. value	37.02%	38.2%	47.3%	38.1%	44.3%	53.6%
	Mea. value	37.88%	37.02%	46.01%	37.6%	45.1%	52.41%

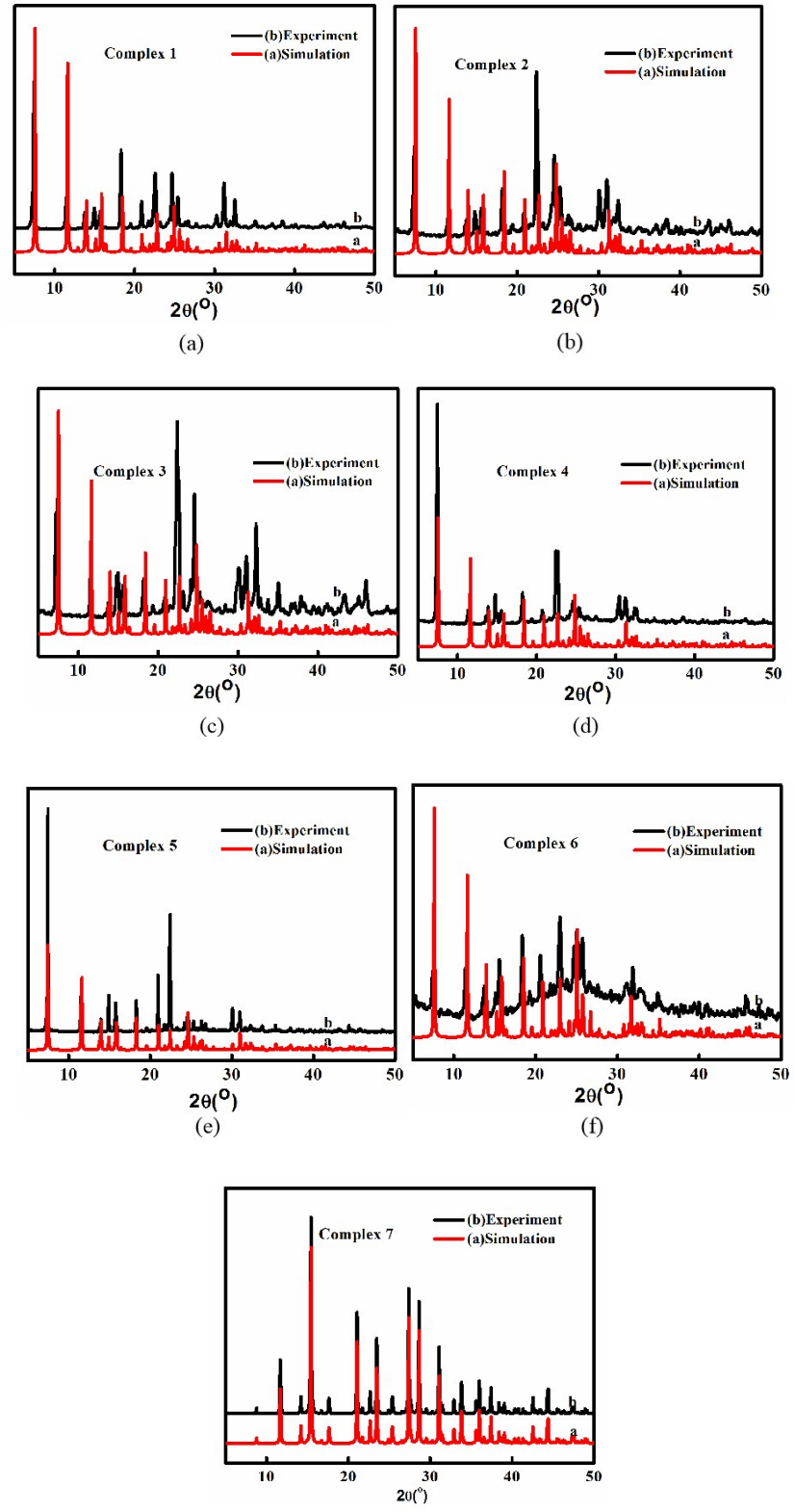
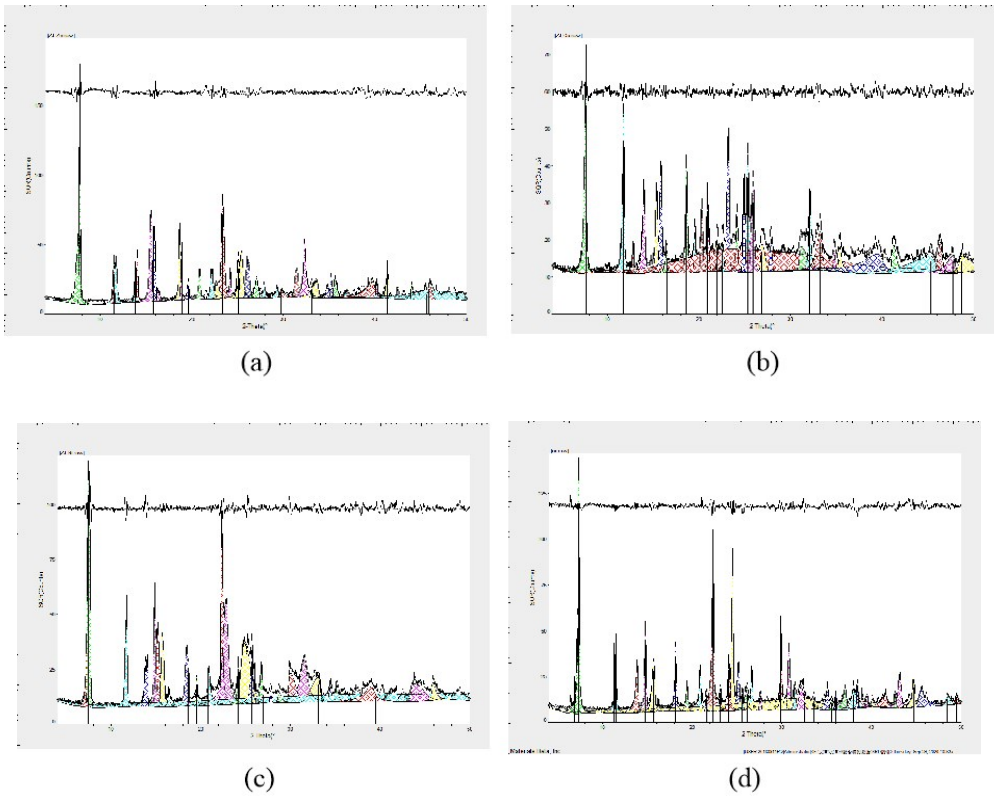
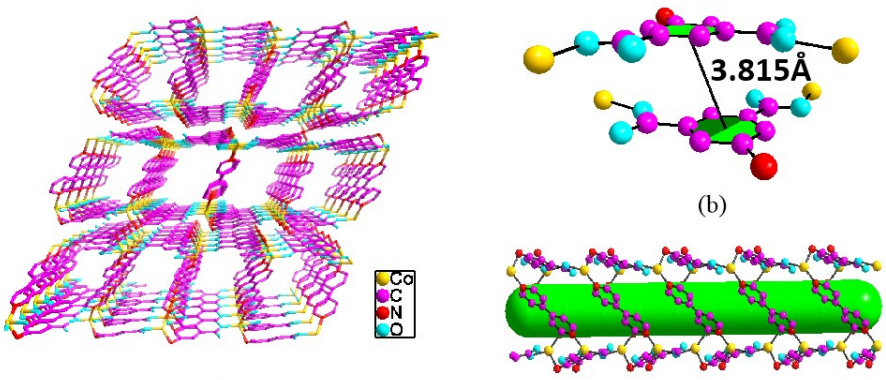


Figure S4 PXRD spectra of complexes **1**-**7**: (a) Complex **1**; (b) Complex **2**; (c) Complex **3**; (d) Complex **4**;(e) Complex **5**; (f) Complex **6**; (g) Complex **7**



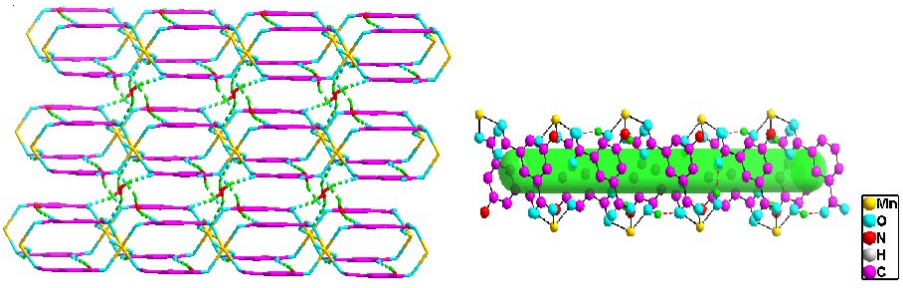
(a) (b) (c) (d)

Figure S5 The crystallinity rate of (a) complex **1** (b) complex **2** (c) complex **3** (d) complex **4**



(a) (b) (c)

Figure S6 Complex **1**: (a) 3D network structure; (b) π-π stacking interaction; (c) pore.



(a) (b)

Figure S7 Complex **7**: (a) 3D network structure; (b) pore.

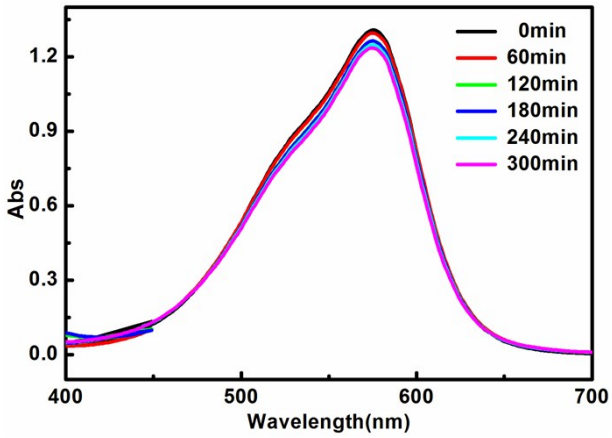


Figure S8 Photocatalytic degradation of CV (10 mg/L) with H_2O_2 only

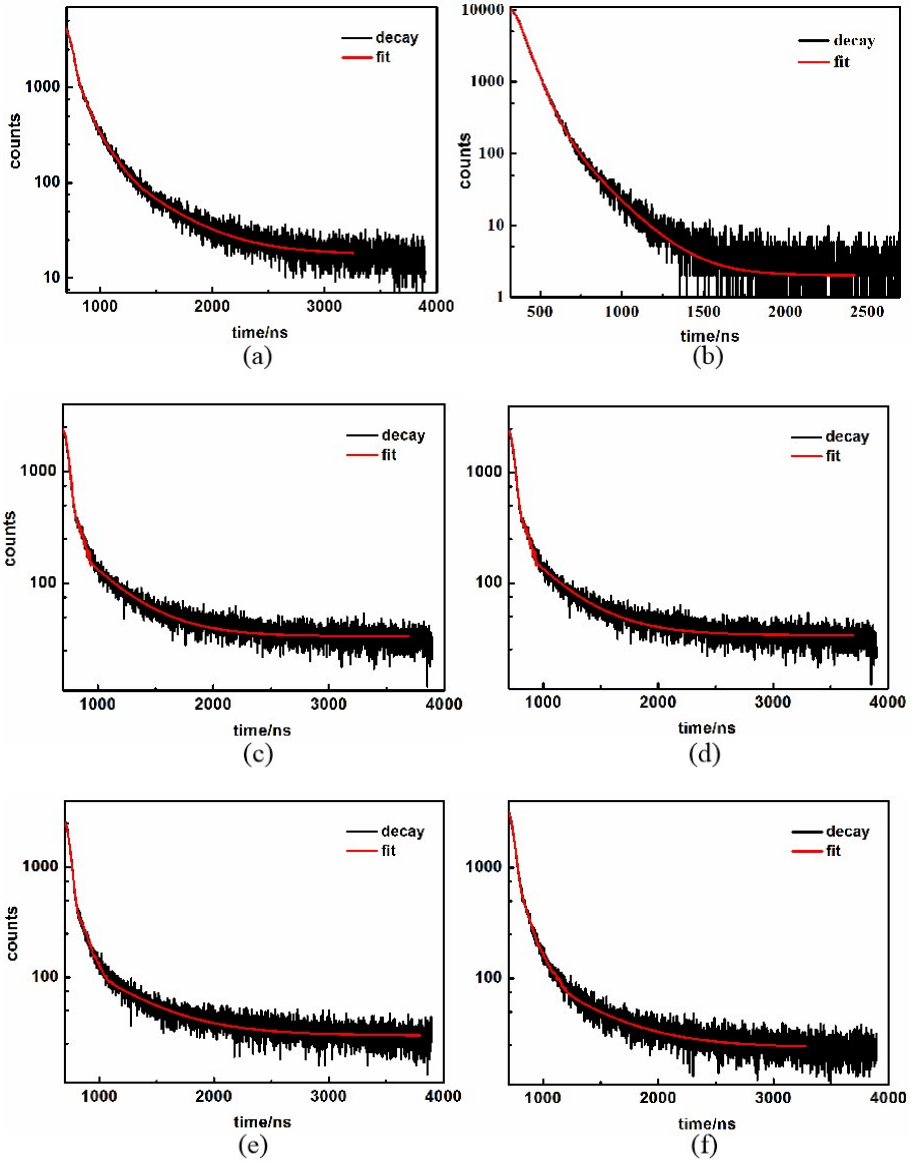


Figure S9 Lifetime of samples (a) 5-aip; (b) 4,4′-bipy ; (c) Complex **1**;(d) Complex **2**; (e) Complex **3**; (f) Complex **4**;

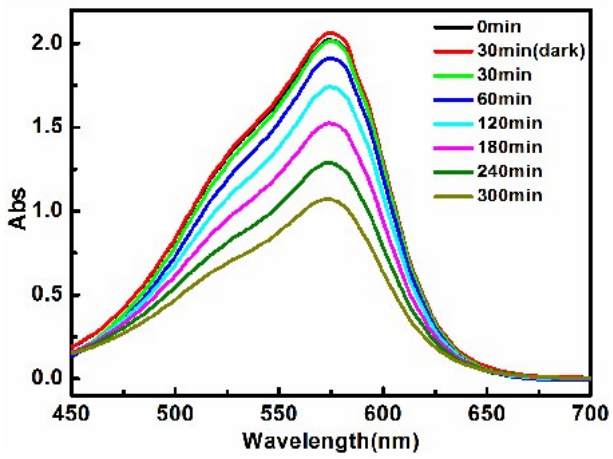


Figure S10 Photocatalytic degradation of CV with 5-aip

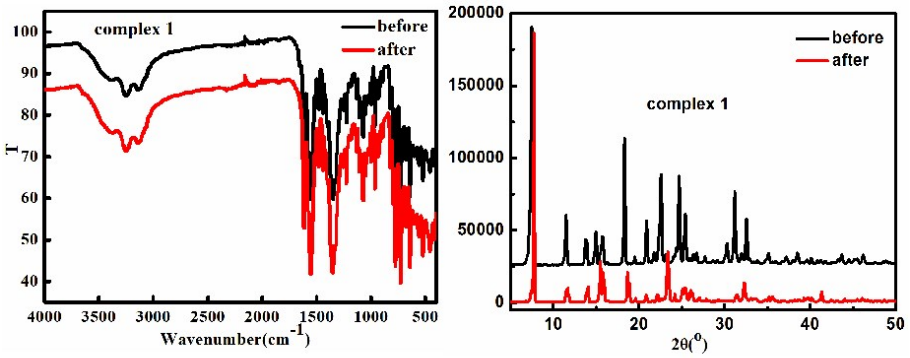


Figure S11 (a) The IR spectra before and after photocatalytic degradation, (b) The PXRD spectra before and after photocatalytic degradation