Table S1 † Selected bond lengths (Å) and angles (°) for complexes **1**-**4**

Complex **1**			
Co(1)-O(1)	2.021(4)	Co(1)-O(2)$^{\#1}$	2.027(5)
Co(1)-N(2)	2.109(5)	Co(1)-N(6)	2.133(5)
Co(1)-O(6)	2.199(5)	Co(1)-O(5)	2.208(4)
Co(2)-O(8)$^{\#2}$	2.023(4)	Co(2)-O(7)$^{\#3}$	2.027(5)
Co(2)-O(4)$^{\#4}$	2.126(4)	Co(2)-N(4)	2.150(5)
Co(2)-N(8)$^{\#5}$	2.159(5)	Co(2)-O(3)$^{\#4}$	2.224(5)
O(8)-Co(2)$^{\#9}$	2.023(4)	N(8)-Co(2)$^{\#6}$	2.159(5)
O(2)-Co(1)$^{\#1}$	2.027(5)	O(3)-Co(2)$^{\#7}$	2.224(5)
O(4)-Co(2)$^{\#7}$	2.126(4)	O(7)-Co(2)$^{\#8}$	2.027(5)
O(3)$^{\#4}$-Co(2)-C(8)$^{\#4}$	30.1(2)	O(1)-Co(1)-O(2)$^{\#1}$	104.63(18)
O(1)-Co(1)-N(2)	87.46(19)	O(2)$^{\#1}$-Co(1)-N(2)	87.39(19)
O(1)-Co(1)-N(6)	95.27(19)	O(2)$^{\#1}$-Co(1)-N(6)	90.40(19)
N(2)-Co(1)-N(6)	176.9(2)	O(1)-Co(1)-O(6)	91.36(19)
O(2)$^{\#1}$-Co(1)-O(6)	163.80(18)	N(2)-Co(1)-O(6)	90.79(18)
N(6)-Co(1)-O(6)	90.70(19)	O(1)-Co(1)-O(5)	152.2(2)
O(2)$^{\#1}$-Co(1)-O(5)	103.13(19)	N(2)-Co(1)-O(5)	92.79(19)
N(6)-Co(1)-O(5)	85.52(19)	O(6)-Co(1)-O(5)	60.86(18)
O(8)$^{\#2}$-Co(2)-O(7)$^{\#3}$	101.55(18)	O(8)$^{\#2}$-Co(2)-O(4)$^{\#4}$	154.7(2)
O(7)$^{\#3}$-Co(2)-O(4)$^{\#4}$	103.7(2)	O(8)$^{\#2}$-Co(2)-N(4)	91.7(2)
O(7)$^{\#3}$-Co(2)-N(4)	91.82(18)	O(4)$^{\#4}$-Co(2)-N(4)	86.66(19)
O(8)$^{\#2}$-Co(2)-N(8)$^{\#5}$	89.32(19)	O(7)$^{\#3}$-Co(2)-N(8)$^{\#5}$	90.75(18)
O(4)$^{\#4}$-Co(2)-N(8)$^{\#5}$	91.21(19)	N(4)-Co(2)-N(8)$^{\#5}$	177.0(2)
O(8)$^{\#2}$-Co(2)-O(3)$^{\#4}$	93.87(18)	O(7)$^{\#3}$-Co(2)-O(3)$^{\#4}$	164.57(18)
O(4)$^{\#4}$-Co(2)-O(3)$^{\#4}$	60.90(18)	N(4)-Co(2)-O(3)$^{\#4}$	87.97(18)
N(8)$^{\#5}$-Co(2)-O(3)$^{\#4}$	89.14(18)	O(8)$^{\#2}$-Co(2)-C(8)$^{\#4}$	123.9(3)
O(7)$^{\#3}$-Co(2)-C(8)$^{\#4}$	134.5(3)	O(4)$^{\#4}$-Co(2)-C(8)$^{\#4}$	30.8(2)
N(4)-Co(2)-C(8)$^{\#4}$	85.8(2)	N(8)$^{\#5}$-Co(2)-C(8)$^{\#4}$	91.2(2)
Symmetry codes: #1: -x + 1, -y, -z + 1		#2: x + 1, -y + 1/2, z + 1/2	#3: -x + 1, y + 1/2, -z + 1/2
#4: x, -y + 1/2, z - 1/2		#5: x + 1, y + 1, z	#6: x - 1, y - 1, z
#7: x, -y + 1/2, z + 1/2		#8: -x + 1, y - 1/2, -z + 1/2	#9: x - 1, -y + 1/2, z - 1/2
Complex **2**			
Co(1)-O(1)$^{\#1}$	1.944(3)	Co(1)-O(1)	1.944(3)
Co(1)-N(2)$^{\#1}$	2.047(4)	Co(1)-N(2)	2.047(4)
O(1)$^{\#1}$-Co(1)-O(1)	113.9(2)	O(1)$^{\#1}$-Co(1)-N(2)	103.50(15)
O(1)-Co(1)-N(2)	118.41(15)	O(1)$^{\#1}$-Co(1)-N(2)$^{\#1}$	118.41(15)
O(1)-Co(1)-N(2)$^{\#1}$	103.50(15)	N(2)-Co(1)-N(2)$^{\#1}$	98.9(2)
Symmetry codes: #1: -x + 1, y, -z + 3/2		#2: -x + 3/2, -y + 5/2, -z + 2	
Complex **3**			
Co(1)-O(1)$^{\#1}$	2.083(2)	Co(1)-O(1)	2.083(2)
Co(1)-N(6)$^{\#2}$	2.150(3)	Co(1)-N(6)$^{\#3}$	2.150(3)
Co(1)-N(2)$^{\#1}$	2.167(3)	Co(1)-N(2)	2.167(3)

Co(2)-O(3)$^{\#4}$	1.948(3)	Co(2)-O(3)$^{\#5}$	1.948(3)
Co(2)-N(4)	2.049(3)	Co(2)-N(4)$^{\#6}$	2.049(3)
N(6)-Co(1)$^{\#7}$	2.150(3)	O(3)-Co(2)$^{\#8}$	1.948(3)
O(1)$^{\#1}$-Co(1)-O(1)	180.00(5)	O(1)$^{\#1}$-Co(1)-N(6)$^{\#2}$	85.08(10)
O(1)-Co(1)-N(6)$^{\#2}$	94.92(10)	O(1)$^{\#1}$-Co(1)-N(6)$^{\#3}$	94.92(10)
O(1)-Co(1)-N(6)$^{\#3}$	85.08(10)	N(6)$^{\#2}$-Co(1)-N(6)$^{\#3}$	180.000(1)
O(1)$^{\#1}$-Co(1)-N(2)$^{\#1}$	84.98(11)	O(1)-Co(1)-N(2)$^{\#1}$	95.02(11)
N(6)$^{\#2}$-Co(1)-N(2)$^{\#1}$	90.63(11)	N(6)$^{\#3}$-Co(1)-N(2)$^{\#1}$	89.37(11)
O(1)$^{\#1}$-Co(1)-N(2)	95.02(11)	O(1)-Co(1)-N(2)	84.98(11)
N(6)$^{\#2}$-Co(1)-N(2)	89.37(11)	N(6)$^{\#3}$-Co(1)-N(2)	90.63(11)
N(2)$^{\#1}$-Co(1)-N(2)	180.000(1)	O(3)$^{\#4}$-Co(2)-O(3)$^{\#5}$	97.1(2)
O(3)$^{\#4}$-Co(2)-N(4)	102.62(13)	O(3)$^{\#5}$-Co(2)-N(4)	124.19(14)
O(3)$^{\#4}$-Co(2)-N(4)$^{\#6}$	124.19(14)	O(3)$^{\#5}$-Co(2)-N(4)$^{\#6}$	102.62(13)
N(4)-Co(2)-N(4)$^{\#6}$	107.77(17)		

Symmetry codes: #1: -x + 3/2, -y + 1/2, -z + 1 #2: x, -y + 1, z - 1/2
#3: -x + 3/2, y - 1/2, -z + 3/2 #4: x, y + 1, z - 1
#5: -x + 1, y + 1, -z + 3/2 #6: -x + 1, y, -z + 1/2
#7: -x + 3/2, y + 1/2, -z + 3/2 #8: x, y - 1, z + 1

Complex **4**

Co(1)-N(2')	1.97(18)	Co(1)-N(2)	2.06(12)
Co(1)-O(1)	2.050(3)	Co(1)-O(2)$^{\#1}$	2.034(3)
Co(1)-O(3)	2.068(4)	Co(1)-O(4)$^{\#1}$	2.012(4)
N(2')-Co(1)-O(4)$^{\#1}$	105(6)	N(2')-Co(1)-O(2)$^{\#1}$	99(6)
O(4)$^{\#1}$-Co(1)-O(2)$^{\#1}$	91.15(14)	N(2')-Co(1)-O(1)	97(6)
O(4)$^{\#1}$-Co(1)-O(1)	90.05(15)	O(2)$^{\#1}$-Co(1)-O(1)	163.20(14)
N(2')-Co(1)-N(2)	1(9)	O(4)$^{\#1}$-Co(1)-N(2)	106(3)
O(2)$^{\#1}$-Co(1)-N(2)	99(4)	O(1)-Co(1)-N(2)	97(4)
N(2')-Co(1)-O(3)	92(6)	O(4)$^{\#1}$-Co(1)-O(3)	162.56(17)
O(2)$^{\#1}$-Co(1)-O(3)	88.10(15)	O(1)-Co(1)-O(3)	85.78(15)
N(2)-Co(1)-O(3)	91(3)		

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

Table S2 † The coordination modes of H_2dpb ligand and the roles of ancillary ligands in complexes **1-4**

Complex	Coord. modes	Ancillary ligands/role	Dihedral angles (°) of H_2dpb	Structure and topology
1	Mode III	4,4′-Bibp/bridging	41.52(9)/41.96(6)/43.63(7)	3D 4-connected $(6^5\cdot8)$-**cds** net
2	Mode I	4,4′-Bibp/bridging	20.87(6)/34.16(6)/47.50(7)	1D chain ⟶ 3D based supramolecular
3	Mode II	Tib/chelating	24.61(4)/43.71(3)/56.83(3)	3D (3,4,6)-connected $(6^2\cdot7)^2(6^4\cdot7^5\cdot8^4\cdot9\cdot10)(6^4\cdot8^2)$

				unprecedented net
4	Mode IV	Bimb/bridging	29.61(5)/57.67(5)/32.86(4)	3D 6-connected $(4^4 \cdot 6^{11})$ unprecedented net

Fig. S1 † (a-d)

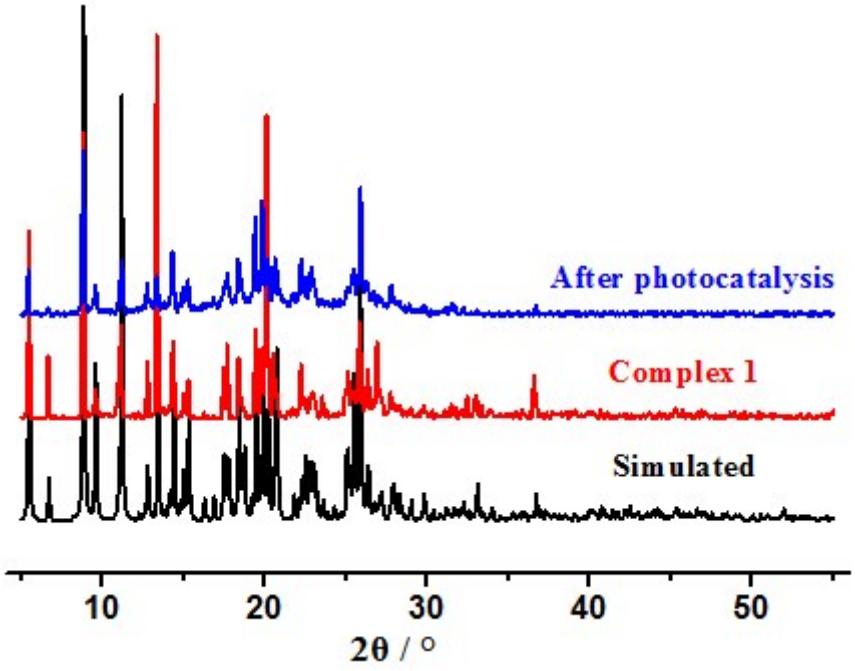

Fig. S1 † (a) PXRD patterns of complex **1** before and after photocatalysis process.

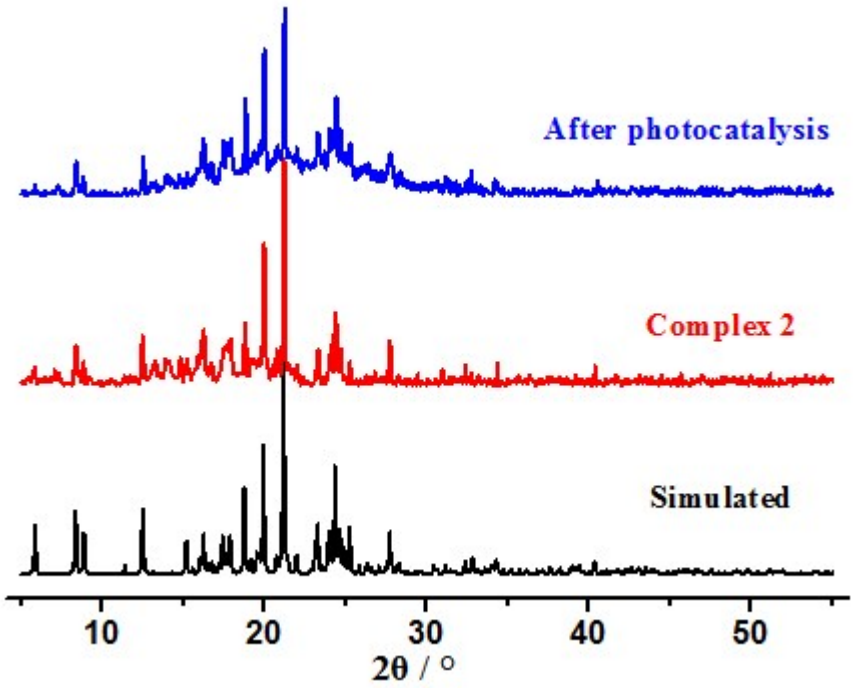

Fig. S1 † (b) PXRD patterns of complex **2** before and after photocatalysis process.

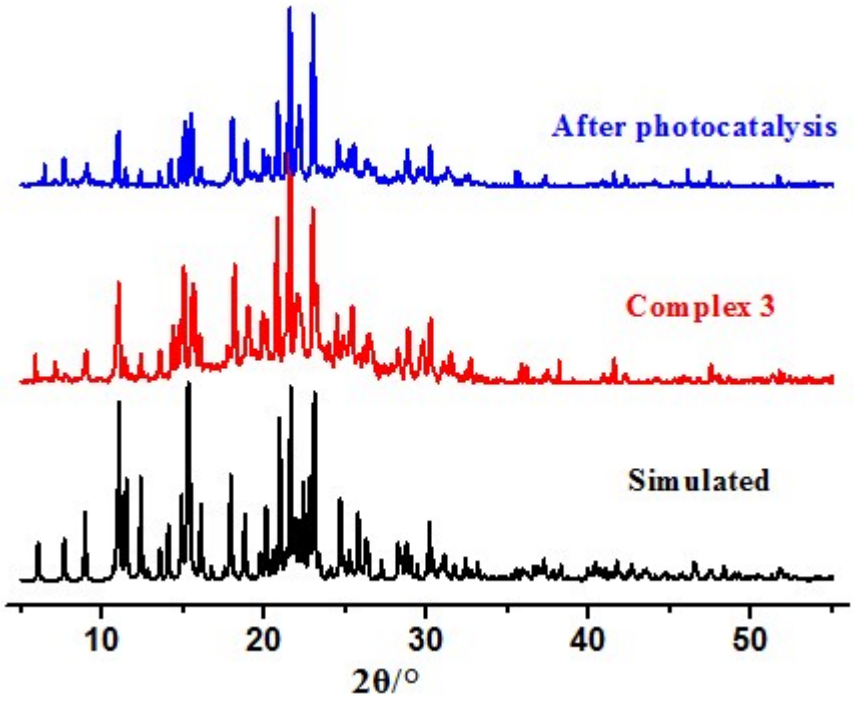

Fig. S1 † (c) PXRD patterns of complex **3** before and after photocatalysis process.

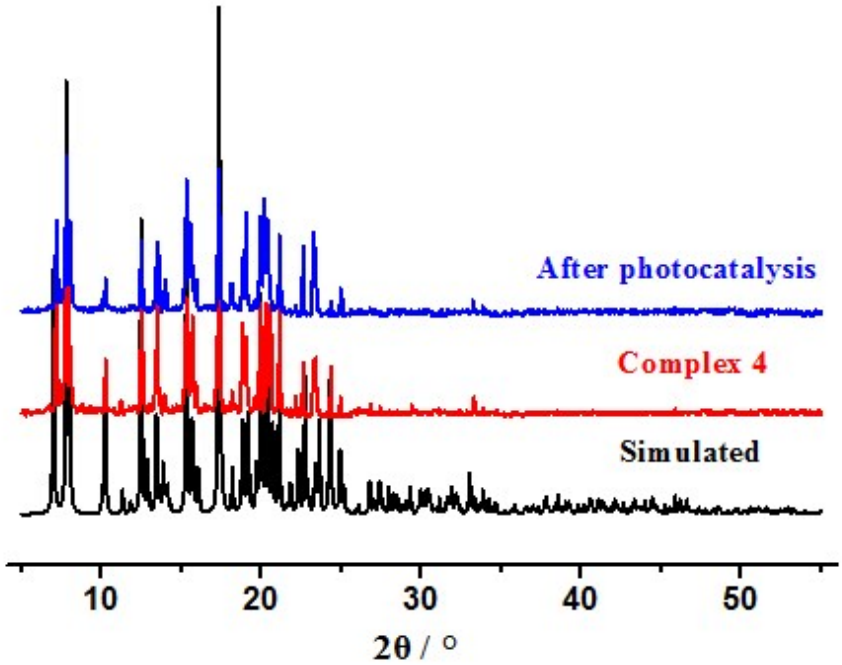

Fig. S1 † (d) PXRD patterns of complex **4** before and after photocatalysis process.