Supporting Information

Assembly of Novel Organic-Decorated Quaternary TM-Hg-Sb-Q Compounds (TM = Mn, Fe, Co; Q = S, Se) by the Combination of Three Types of Metal Coordination Geometries

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Table S1. Selected bond lengths (Å) and angles (°) for compound **1**[a].

Hg(1)-S(3)#1	2.364(2)	Mn(1)-N(1)	2.288(6)
Hg(1)-S(3)	2.364(2)	Mn(1)-S(2)#2	2.547(2)
Sb(1)-S(1)	2.369(2)	Mn(1)-S(2)	2.578(2)
Sb(1)-S(2)	2.430(3)	Mn(1)-S(1)	2.595(3)
Sb(1)-S(3)	2.496(2)	Mn(1)-S(3)#2	2.831(3)
Mn(1)-N(2)	2.236(6)		
S(3)#1-Hg(1)-S(3)	180.0	S(2)-Mn(1)-S(1)	88.14(8)
S(1)-Sb(1)-S(2)	97.13(8)	N(2)-Mn(1)-S(3)#2	82.76(19)
S(1)-Sb(1)-S(3)	97.40(8)	N(1)-Mn(1)-S(3)#2	83.90(18)
S(2)-Sb(1)-S(3)	94.49(8)	S(2)#2-Mn(1)-S(3)#2	84.38(8)
N(2)-Mn(1)-N(1)	73.4(2)	S(2)-Mn(1)-S(3)#2	90.64(8)
N(2)-Mn(1)-S(2)#2	163.0(2)	S(1)-Mn(1)-S(3)#2	174.67(9)
N(1)-Mn(1)-S(2)#2	94.29(17)	Sb(1)-S(1)-Mn(1)	87.45(8)
N(2)-Mn(1)-S(2)	98.17(17)	Sb(1)-S(2)-Mn(1)#2	94.45(8)
N(1)-Mn(1)-S(2)	170.40(18)	Sb(1)-S(2)-Mn(1)	86.54(7)
S(2)#2-Mn(1)-S(2)	93.03(7)	Mn(1)#2-S(2)-Mn(1)	86.97(7)
N(2)-Mn(1)-S(1)	92.28(19)	Hg(1)-S(3)-Sb(1)	100.96(8)
N(1)-Mn(1)-S(1)	96.57(18)	Hg(1)-S(3)-Mn(1)#2	104.75(9)
S(2)#2-Mn(1)-S(1)	100.86(9)	Sb(1)-S(3)-Mn(1)#2	86.39(8)

[a]Symmetric codes: #1 -*x*+2, -*y*+1, -*z*+1; #2 -*x*+1, -*y*+1, -*z*+1.

Table S2. Selected bond lengths (Å) and angles (°) for compounds **2-4**[a].

Sample	**2**	**3**	**4**
Hg(1)-Se(3)	2.5740(10)	2.5765(9)	2.5786(8)
Hg(1)-Se(4)	2.5973(11)	2.5956(10)	2.6001(8)

Hg(1)-Se(5)	2.7266(11)	2.7219(10)	2.7263(9)
Hg(1)-Se(1)	2.8175(11)	2.8032(10)	2.8028(9)
Sb(1)-Se(5)	2.5515(13)	2.5586(11)	2.5566(10)
Sb(1)-Se(2)	2.5601(11)	2.5602(11)	2.5639(9)
Sb(1)-Se(1)	2.8006(11)	2.8087(10)	2.8124(9)
Sb(1)-Se(2)#4	3.0824(12)	3.0467(10)	3.0279(9)
Sb(2)-Se(4)#1	2.5361(11)	2.5380(10)	2.5350(9)
Sb(2)-Se(3)#2	2.5754(12)	2.5745(11)	2.5703(10)
Sb(2)-Se(1)	2.5996(12)	2.5927(10)	2.5896(9)
Se(2)-TM(1)	2.5960(19)	2.5374(15)	2.4996(13)
Se(3)-Sb(2)#2	2.5754(12)	2.5745(11)	2.5703(10)
Se(4)-Sb(2)#1	2.5361(11)	2.5380(10)	2.5350(9)
TM(1)-N(2)	2.162(8)	2.105(7)	2.050(6)
TM(1)-N(1)	2.191(8)	2.118(7)	2.090(7)
TM(1)-N(3)	2.213(9)	2.135(7)	2.078(6)
TM(1)-N(4)	2.362(8)	2.280(7)	2.256(6)
Se(3)-Hg(1)-Se(4)	115.00(3)	114.37(3)	113.98(3)
Se(3)-Hg(1)-Se(5)	127.34(4)	126.58(3)	126.51(3)
Se(4)-Hg(1)-Se(5)	107.67(4)	109.37(3)	110.10(3)
Se(3)-Hg(1)-Se(1)	103.23(3)	104.06(3)	104.53(3)
Se(4)-Hg(1)-Se(1)	110.12(4)	109.31(3)	108.72(3)
Se(5)-Hg(1)-Se(1)	89.02(3)	88.44(3)	88.09(3)
Se(5)-Sb(1)-Se(2)	98.89(4)	99.82(4)	100.07(3)
Se(5)-Sb(1)-Se(1)	93.03(4)	91.66(3)	91.33(3)
Se(2)-Sb(1)-Se(1)	88.74(3)	88.19(3)	88.17(3)
Se(4)#1-Sb(2)-Se(3)#2	97.31(4)	97.18(4)	97.07(4)
Se(4)#1-Sb(2)-Se(1)	95.49(4)	95.80(3)	95.90(3)
Se(3)#2-Sb(2)-Se(1)	95.45(4)	95.32(3)	95.19(3)
Sb(2)-Se(1)-Sb(1)	103.26(4)	102.73(3)	102.13(3)
Sb(2)-Se(1)-Hg(1)	97.55(3)	98.46(3)	98.59(3)
Sb(1)-Se(1)-Hg(1)	80.93(3)	81.07(3)	80.92(2)
Sb(1)-Se(2)-TM(1)	99.87(5)	102.40(4)	103.31(4)
Hg(1)-Se(3)-Sb(2)#2	96.77(4)	96.18(3)	95.62(3)
Sb(2)#1-Se(4)-Hg(1)	103.17(4)	103.31(3)	103.31(3)
Sb(1)-Se(5)-Hg(1)	87.32(4)	87.31(3)	87.16(3)
N(2)-TM(1)-N(1)	116.9(3)	116.8(3)	115.6(3)
N(2)-TM(1)-N(3)	109.0(3)	112.7(3)	113.7(3)
N(1)-TM(1)-N(3)	119.1(3)	119.6(3)	120.2(3)
N(2)-TM(1)-N(4)	77.5(3)	80.0(3)	79.5(2)
N(1)-TM(1)-N(4)	76.6(3)	78.5(3)	78.8(2)
N(3)-TM(1)-N(4)	76.6(3)	78.2(3)	79.0(2)
N(2)-TM(1)-Se(2)	113.3(3)	108.1(2)	107.25(19)
N(1)-TM(1)-Se(2)	97.4(2)	95.7(2)	95.5(2)

N(3)-TM(1)-Se(2)	99.0(2)	99.9(2)	100.35(18)
N(4)-TM(1)-Se(2)	169.14(19)	171.69(17)	172.70(16)

[a]TM = Mn for **2**, Fe for **3** and Co for **4**; Symmetric codes: #1 -*x*, -*y*, -*z*+1; #2 -*x*+1, -*y*, -*z*+1; #4 -*x*, -*y*+1, -*z*+1

Table S3. Distances (d/Å) and angles (°) for the π-π interactions in **1**.

ring(1)···ring(2)	d[Cg(1)···Cg(2)][a]	α[b]	β[c]	γ[d]	d[Cg(1)···P(2)][e]	d[Cg(2)···P(1)][f]
N(1),C(1)-C(4),C(12)···C(4)-C(7),C(11),C(12)	3.588(5)	1.56	22.47	24.02	3.278	3.316
C(4)-C(7),C(11),C(12)···C(4)-C(7),C(11),C(12)	3.430(5)	0.00	14.51	14.51	3.321	3.321

[a]Centroid-centroid distance.

[b]Dihedral angle between the ring planes.

[c]Angle between the centroid vector Cg(1)···Cg(2) and the normal to the plane 2.

[d]Angle vector Cg(1)···Cg(2) (between the centroid) and the normal to the plane 1.

[e]Perpendicular distance of Cg(1) on ring plane 2.

[f]Perpendicular distance of Cg(2) on ring plane 1.

Table S4. Selected hydrogen bonds data for **1-4** [a].

D-H···A	d(D-H)(Å)	D(H···A)(Å)	d(D···A)(Å)	<(DHA) (°)
$[Mn(phen)]_2HgSb_2S_6$ (**1**)				
C(3)-H(3A)···S(1)#3	0.93	2.91	3.749(9)	151.3
C(9)-H(9A)···S(2)#4	0.93	2.75	3.622(9)	156.5
$[Mn(tren)]HgSb_2Se_5$ (**2**)				
N(1)-H(1D)···Se(5)#3	0.90	2.89	3.736(9)	156.2
N(2)-H(2A)···Se(2)#3	0.90	2.88	3.651(9)	145.5
N(2)-H(2D)···Se(1)	0.92	2.87	3.455(9)	122.7
N(2)-H(2D)···Se(3)#2	0.92	2.79	3.618(9)	151.9
N(3)-H(3A)···Se(4)#1	0.91	2.78	3.614(8)	153.0
N(3)-H(3D)···Se(5)#4	0.90	2.81	3.634(8)	151.8
C(1)-H(1B)···Se(3)#3	0.97	2.97	3.689(10)	132.3
C(2)-H(2B)···Se(5)#5	0.97	2.93	3.878(12)	166.8
C(3)-H(3C)···Se(4)#2	0.97	2.87	3.599(10)	132.8
$[Fe(tren)]HgSb_2Se_5$ (**3**)				
N(1)-H(1D)···Se(5)#3	0.90	2.91	3.762(8)	157.1
N(2)-H(2A)···Se(2)#3	0.90	2.86	3.664(7)	148.7
N(2)-H(2D)···Se(1)	0.91	2.84	3.443(7)	124.9
N(2)-H(2D)···Se(3)#2	0.91	2.85	3.665(8)	150.8
N(3)-H(3A)···Se(4)#1	0.90	2.75	3.589(8)	154.0
N(3)-H(3D)···Se(5)#4	0.90	2.77	3.592(7)	153.3
C(1)-H(1C)···Se(3)#3	0.97	2.94	3.693(9)	135.4
C(2)-H(2B)···Se(5)#5	0.97	2.93	3.872(10)	164.4
C(3)-H(3C)···Se(4)#2	0.97	2.85	3.619(8)	136.5
$[Co(tren)]HgSb_2Se_5$ (**4**)				
N(1)-H(1D)···Se(5)#3	0.90	2.88	3.735(7)	158.1
N(2)-H(2A)···Se(2)#3	0.90	2.87	3.686(6)	151.5

N(2)-H(2D)···Se(1)	0.90	2.86	3.462(7)	125.8
N(2)-H(2D)···Se(3)#2	0.90	2.89	3.709(6)	151.2
N(3)-H(3A)···Se(4)#1	0.90	2.74	3.571(7)	154.3
N(3)-H(3D)···Se(5)#4	0.90	2.74	3.576(6)	154.6
C(1)-H(1C)···Se(3)#3	0.97	2.94	3.701(8)	136.0
C(2)-H(2C)···Se(5)#5	0.97	2.92	3.864(9)	163.8
C(3)-H(3C)···Se(4)#2	0.97	2.84	3.636(8)	139.8

[a]Symmetric codes for **1**: #3 -*x*+1, -*y*, -*z*; #4 -*x*, -*y*, -*z*+1; Symmetric codes for **2**-**4**: #1 -*x*, -*y*, -*z*+1; #2 -*x*+1, -*y*, -*z*+1; #3 -*x*+1, -*y*+1, -*z*+1; #4 -*x*, -*y*+1, -*z*+1; #5 *x*, *y*, *z*+1.

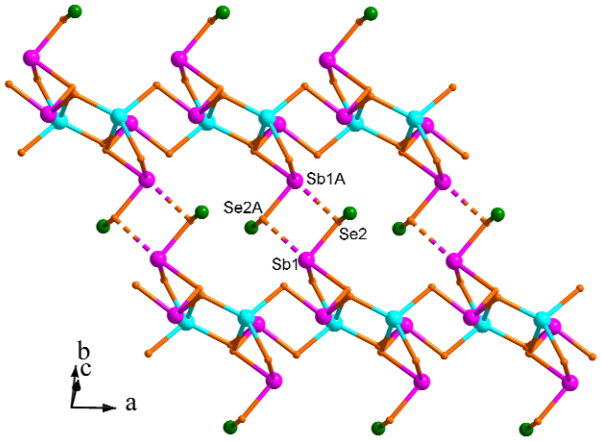

Figure S1. Secondary Sb(1)···Se(2A) interactions in the compound **2**. C, H, and N atoms have been omitted for clarity. [Symmetry operation: (A) -*x*, -*y*+1, -*z*+1]

Table S5. The state energies (eV) of the lowest conduction band (L-CB) and the highest valence band (H-VB) of **1** and **2**.

Compound	k-point	L-CB	H-VB
1	G (0.000, 0.000, 0.000)	1.32246	-0.17062
	F (0.000, 0.500, 0.000)	1.28701	-0.00092
	Q (0.000, 0.500, 0.500)	1.2696	0
	Z (0.000, 0.000, 0.500)	1.22417	-0.17955
2	G (0.000, 0.000, 0.000)	1.1638	-0.00791
	F (0.000, 0.500, 0.000)	1.15748	-0.0016
	Q (0.000, 0.500, 0.500)	1.15412	0
	Z (0.000, 0.000, 0.500)	1.15957	-0.00807

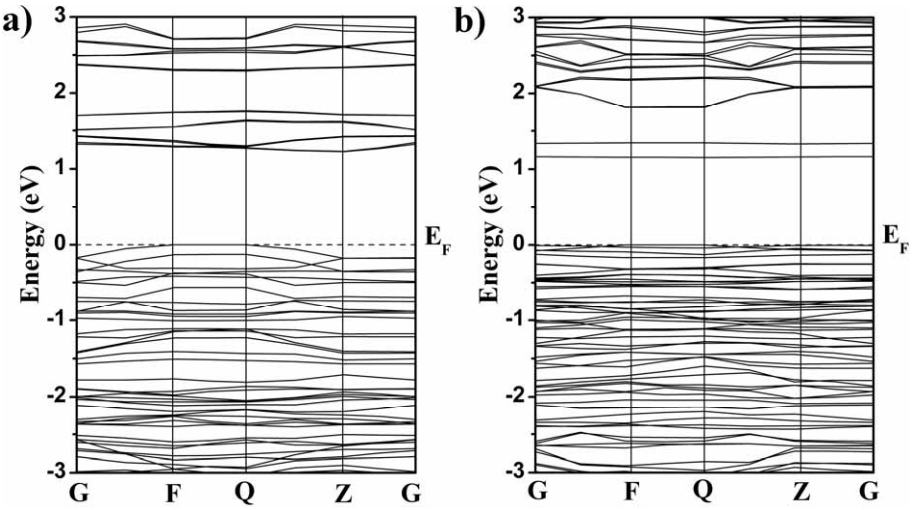

Figure S2. The band structure of **1** (a) and **2** (b). Fermi level is set at 0 eV (dot line).

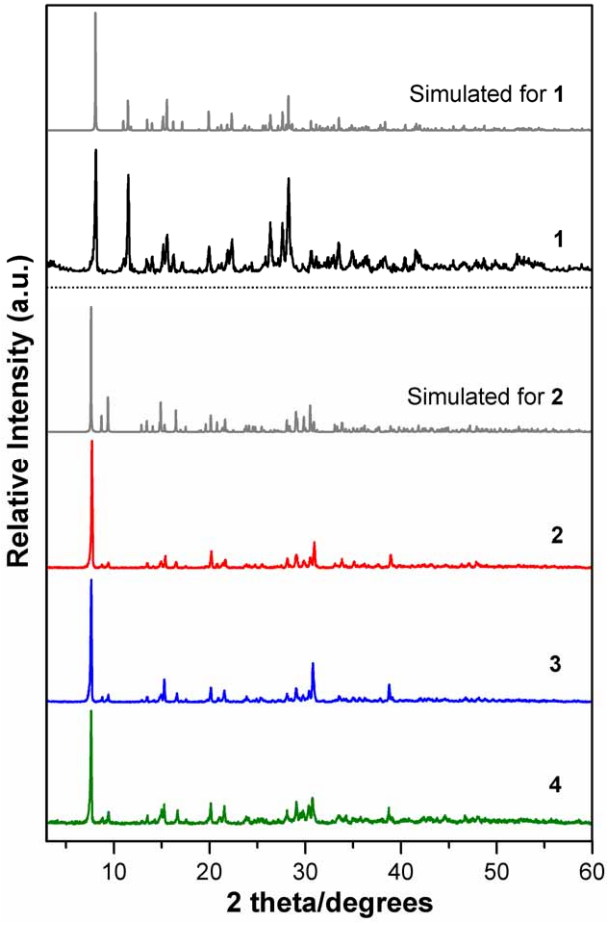

Figure S3. PXRD patterns for compounds **1**-**4**.

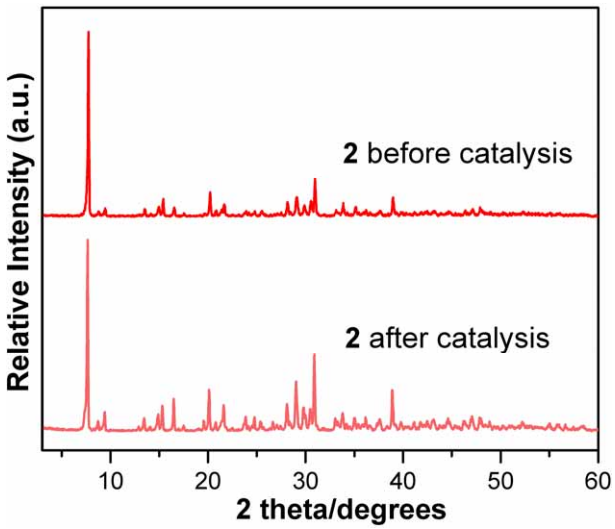

Figure S4. PXRD patterns of sample **2** before and after the 300min VIS photocatalysis.