Supporting Information

A simultaneous disulfide bond cleavage, N, S-bialkylation/N-protonation and self-assembly reaction: syntheses, structures and properties of two hybrid iodoargentates with thiazolyl-based heterocycles

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Table S1. Selected Bond Distances (Å) and Angles (°) for **1** and **2**.

1			
Bond	(Å)	Bond	(Å)
Ag(1)-Ag(2)#1	3.3212(5)	S(1)-C(1)	1.735(4)
Ag(1)-Ag(2)	3.0619(4)	S(1)-C(9)	1.716(3)
Ag(1)-I(1)	2.8009(5)	S(2)-C(9)	1.710(4)
Ag(1)-I(2)	2.9345(4)	S(2)-C(10)	1.823(4)
Ag(1)-I(3)	2.8642(4)	N(1)-C(6)	1.396(5)
Ag(1)-I(3)#2	2.9250(5)	N(1)-C(7)	1.474(4)
Ag(2)-Ag(1)#1	3.3213(5)	N(1)-C(9)	1.326(4)
Ag(2)-Ag(2)#1	2.9796(7)	C(1)-C(2)	1.406(5)
Ag(2)-I(1)	2.7815(5)	C(1)-C(6)	1.397(5)
Ag(2)-I(2)	3.0328(5)	C(2)-C(3)	1.388(5)
Ag(2)-I(2)#1	2.9014(4)	C(3)-C(4)	1.385(5)
Ag(2)-I(3)#3	2.8486(4)	C(4)-C(5)	1.370(6)
I(2)-Ag(2)#1	2.9014(4)	C(5)-C(6)	1.398(5)

I(3)-Ag(1)#2	2.9250(5)	C(7)-C(8)	1.513(5)
I(3)-Ag(2)#4	2.8486(4)	C(10)-C(11)	1.511(5)
Angle	(°)	Angle	(°)
Ag(2)-Ag(1)-Ag(2)#1	55.474(12)	I(3)#3-Ag(2)-Ag(1)	150.216(15)
I(1)-Ag(1)-Ag(2)	56.433(11)	I(3)#3-Ag(2)-Ag(2)#1	105.548(18)
I(1)-Ag(1)-Ag(2)#1	109.350(13)	I(3)#3-Ag(2)-I(2)	93.475(12)
I(1)-Ag(1)-I(2)	103.904(12)	I(3)#3-Ag(2)-I(2)#1	102.234(12)
I(1)-Ag(1)-I(3)#2	130.118(15)	Ag(2)-I(1)-Ag(1)	66.526(12)
I(1)-Ag(1)-I(3)	116.198(15)	Ag(1)-I(2)-Ag(2)	61.716(10)
I(2)-Ag(1)-Ag(2)#1	54.844(10)	Ag(2)#1-I(2)-Ag(1)	69.373(12)
I(2)-Ag(1)-Ag(2)	60.721(11)	Ag(2)#1-I(2)-Ag(2)	60.231(13)
I(3)-Ag(1)-Ag(2)#1	133.411(15)	Ag(1)-I(3)-Ag(1)#2	80.161(12)
I(3)-Ag(1)-Ag(2)	155.101(14)	Ag(2)#4-I(3)-Ag(1)	128.740(13)
I(3)#2-Ag(1)-Ag(2)	101.634(13)	Ag(2)#4-I(3)-Ag(1)#2	70.220(12)
I(3)#2-Ag(1)-Ag(2)#1	53.812(10)	C(9)-S(1)-C(1)	90.51(17)
I(3)-Ag(1)-I(2)	103.316(13)	C(9)-S(2)-C(10)	102.49(17)
I(3)#2-Ag(1)-I(2)	99.619(15)	C(6)-N(1)-C(7)	122.7(3)
I(3)-Ag(1)-I(3)#2	99.839(12)	C(9)-N(1)-C(6)	114.3(3)
Ag(1)-Ag(2)-Ag(1)#1	124.526(12)	C(9)-N(1)-C(7)	122.9(3)
Ag(2)#1-Ag(2)-Ag(1)	66.682(13)	C(2)-C(1)-S(1)	128.2(3)
Ag(2)#1-Ag(2)-Ag(1)#1	57.845(13)	C(6)-C(1)-S(1)	111.0(3)
Ag(2)#1-Ag(2)-I(2)	57.698(13)	C(6)-C(1)-C(2)	120.8(3)
I(1)-Ag(2)-Ag(1)#1	163.251(14)	C(3)-C(2)-C(1)	117.2(3)
I(1)-Ag(2)-Ag(1)	57.041(11)	C(4)-C(3)-C(2)	121.0(4)
I(1)-Ag(2)-Ag(2)#1	120.551(16)	C(5)-C(4)-C(3)	122.6(4)
I(1)-Ag(2)-I(2)	101.876(13)	C(4)-C(5)-C(6)	117.3(3)
I(1)-Ag(2)-I(2)#1	107.872(14)	N(1)-C(6)-C(1)	111.3(3)
I(1)-Ag(2)-I(3)#3	132.698(14)	N(1)-C(6)-C(5)	127.7(3)

I(2)#1-Ag(2)-Ag(1)	98.868(12)	C(1)-C(6)-C(5)	121.1(3)
I(2)-Ag(2)-Ag(1)	57.563(10)	N(1)-C(7)-C(8)	112.2(3)
I(2)-Ag(2)-Ag(1)#1	90.863(13)	S(2)-C(9)-S(1)	124.9(2)
I(2)#1-Ag(2)-Ag(1)#1	55.784(10)	N(1)-C(9)-S(1)	112.9(3)
I(2)#1-Ag(2)-Ag(2)#1	62.072(13)	N(1)-C(9)-S(2)	122.2(3)
I(2)#1-Ag(2)-I(2)	119.770(13)	C(11)-C(10)-S(2)	114.1(3)
I(3)#3-Ag(2)-Ag(1)#1	55.968(10)		

Symmetry transformations used to generate equivalent atoms: #1 -x, -y, -z; #2 –x-1, -y, -z; #3 x+1, y, z; #4 x-1, y, z.

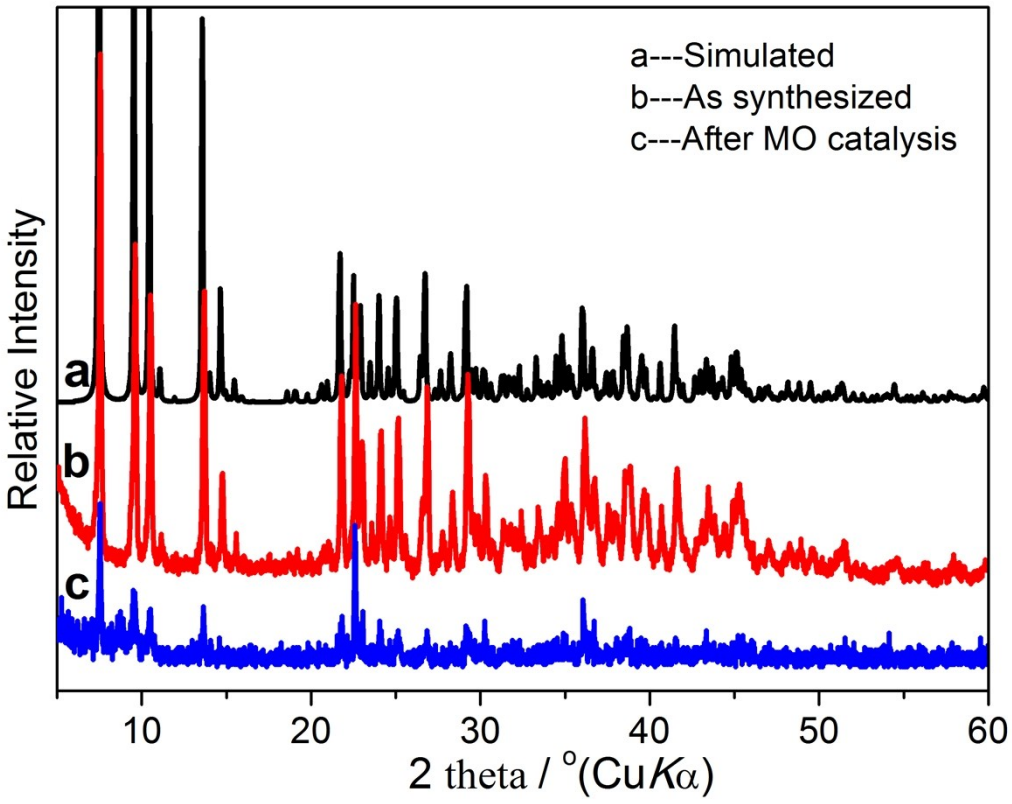
2

Bond	(Å)	Bond	(Å)
Ag(1)-Ag(1)#1	3.2386(8)	N(2)-C(27)	1.335(5)
Ag(1)-I(1)#2	2.8252(5)	C(11)-C(12)	1.396(6)
Ag(1)-I(1)	2.9330(5)	C(11)-C(16)	1.396(6)
Ag(1)-I(1)#1	2.8675(5)	C(12)-C(13)	1.366(6)
Ag(1)-S(2)	2.5501(12)	C(13)-C(14)	1.374(7)
Ag(2)-Ag(2)#3	3.1960(6)	C(14)-C(15)	1.392(7)
Ag(2)-Ag(2)#4	3.1960(6)	C(15)-C(16)	1.393(6)
Ag(2)-I(2)#4	2.8750(5)	C(21)-C(22)	1.379(6)
Ag(2)-I(2)	2.8303(5)	C(21)-C(26)	1.380(5)
Ag(2)-I(2)#5	2.9904(5)	C(22)-C(23)	1.378(7)
Ag(2)-S(4)	2.5240(11)	C(23)-C(24)	1.379(6)
I(1)-Ag(1)#1	2.8675(5)	C(24)-C(25)	1.381(6)
I(1)-Ag(1)#2	2.8252(5)	S(3)-C(21)	1.744(4)
I(2)-Ag(2)#6	2.9904(5)	S(3)-C(27)	1.746(4)
I(2)-Ag(2)#3	2.8749(5)	S(4)-C(27)	1.665(4)
S(1)-C(11)	1.750(4)	N(1)-C(16)	1.402(5)
S(1)-C(17)	1.723(4)	N(1)-C(17)	1.338(5)

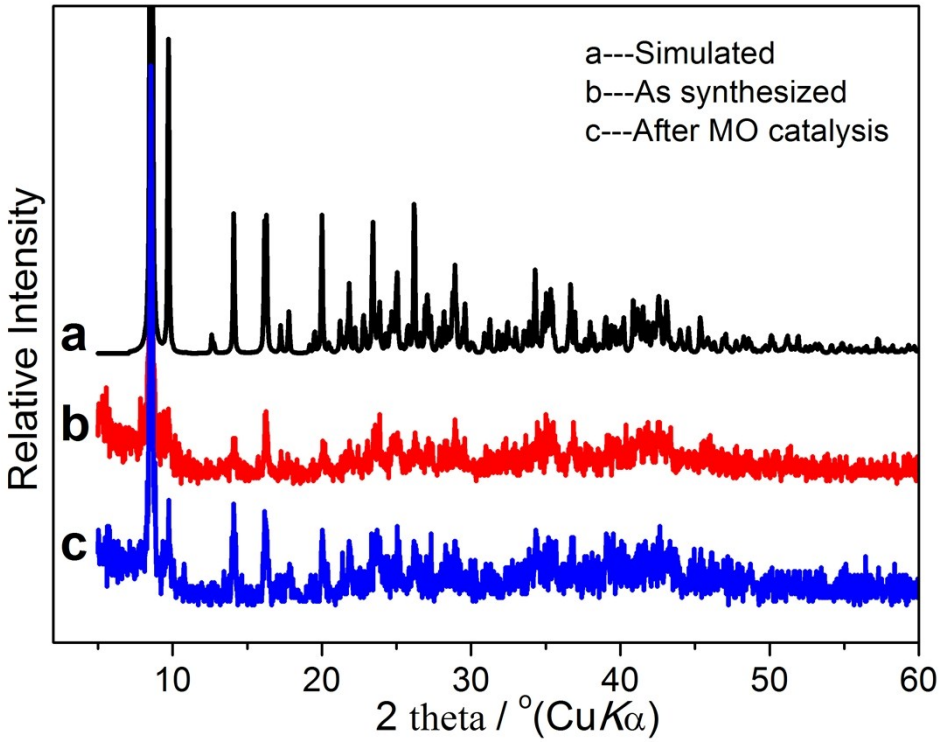
S(2)-C(17)	1.689(4)	N(2)-C(26)	1.385(5)
Angle	(°)	Angle	(°)
I(1)#1-Ag(1)-Ag(1)#1	57.025(14)	C(17)-S(2)-Ag(1)	108.48(15)
I(1)-Ag(1)-Ag(1)#1	55.104(13)	C(21)-S(3)-C(27)	91.88(19)
I(1)#2-Ag(1)-Ag(1)#1	116.68(2)	C(27)-S(4)-Ag(2)	107.68(14)
I(1)#2-Ag(1)-I(1)	106.580(15)	C(17)-N(1)-C(16)	116.2(3)
I(1)#2-Ag(1)-I(1)#1	102.436(16)	C(27)-N(2)-C(26)	116.5(3)
I(1)#1-Ag(1)-I(1)	112.129(14)	C(12)-C(11)-S(1)	130.0(3)
S(2)-Ag(1)-Ag(1)#1	118.21(4)	C(16)-C(11)-S(1)	110.2(3)
S(2)-Ag(1)-I(1)	102.68(3)	C(16)-C(11)-C(12)	119.9(4)
S(2)-Ag(1)-I(1)#2	125.08(3)	C(13)-C(12)-C(11)	118.2(4)
S(2)-Ag(1)-I(1)#1	108.02(3)	C(12)-C(13)-C(14)	121.6(4)
Ag(2)#3-Ag(2)-Ag(2)#4	87.937(19)	C(13)-C(14)-C(15)	122.2(4)
I(2)-Ag(2)-Ag(2)#3	56.597(10)	C(14)-C(15)-C(16)	116.0(4)
I(2)#4-Ag(2)-Ag(2)#4	55.271(15)	C(11)-C(16)-N(1)	111.1(3)
I(2)#5-Ag(2)-Ag(2)#4	55.267(10)	C(15)-C(16)-N(1)	126.7(4)
I(2)#4-Ag(2)-Ag(2)#3	58.736(16)	C(15)-C(16)-C(11)	122.1(4)
I(2)#5-Ag(2)-Ag(2)#3	120.615(18)	S(2)-C(17)-S(1)	125.8(2)
I(2)-Ag(2)-Ag(2)#4	119.113(18)	N(1)-C(17)-S(1)	110.6(3)
I(2)-Ag(2)-I(2)#4	115.279(16)	N(1)-C(17)-S(2)	123.6(3)
I(2)-Ag(2)-I(2)#5	99.316(14)	C(22)-C(21)-S(3)	130.0(3)
I(2)#4-Ag(2)-I(2)#5	110.488(16)	C(22)-C(21)-C(26)	120.1(4)
S(4)-Ag(2)-Ag(2)#4	126.08(3)	C(26)-C(21)-S(3)	109.8(3)
S(4)-Ag(2)-Ag(2)#3	136.34(3)	C(23)-C(22)-C(21)	118.9(4)
S(4)-Ag(2)-I(2)#4	115.18(3)	C(22)-C(23)-C(24)	121.1(4)
S(4)-Ag(2)-I(2)#5	102.34(3)	C(23)-C(24)-C(25)	121.0(4)
S(4)-Ag(2)-I(2)	112.19(3)	C(24)-C(25)-C(26)	117.3(4)
Ag(1)#1-I(1)-Ag(1)	67.870(14)	N(2)-C(26)-C(25)	126.1(4)

Ag(1)#2-I(1)-Ag(1)	73.419(15)	C(21)-C(26)-N(2)	112.4(4)
Ag(1)#2-I(1)-Ag(1)#1	102.434(16)	C(21)-C(26)-C(25)	121.5(4)
Ag(2)#3-I(2)-Ag(2)#6	66.003(12)	S(4)-C(27)-S(3)	123.3(2)
Ag(2)-I(2)-Ag(2)#3	68.133(12)	N(2)-C(27)-S(3)	109.4(3)
Ag(2)-I(2)-Ag(2)#6	99.317(14)	N(2)-C(27)-S(4)	127.3(3)
C(17)-S(1)-C(11)	91.95(19)		

Symmetry transformations used to generate equivalent atoms: #1 -x+1, -y, -z+1; #2 -x+1, -y+1, -z+1; #3 -x+3/2, y+1/2, -z+3/2; #4 -x+3/2, y-1/2, -z+3/2; #5 x, y-1, z; #6 x, y+1, z.



(a)



(b)

Fig. S1 The PXRD patterns of **1** (a) and **2** (b) under different conditions.

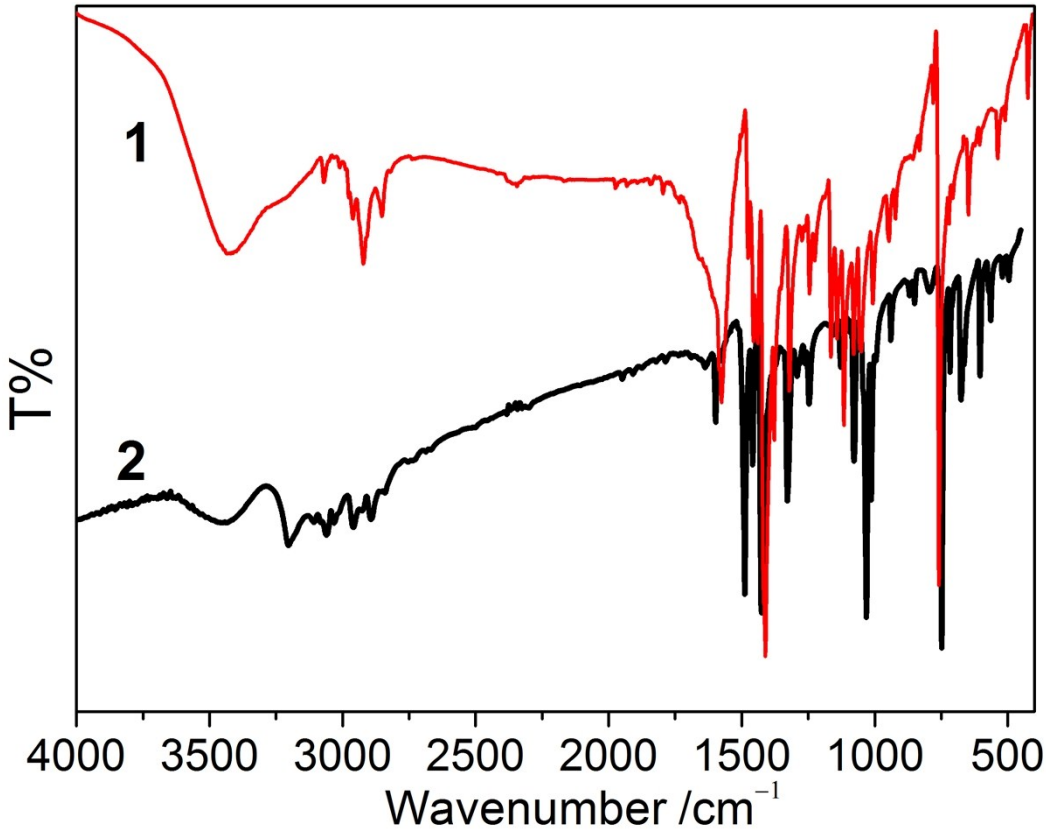


Fig. S2 IR spectra of **1** and **2**.

The IR spectra of **1**–**2** are shown in Fig. S4. For **1**, the bands in the region of 3000–2850 cm^{-1} correspond to the C–H vibrations of the ethyl group, ν(–C–H). Further, the occurrence of the characteristic band of $–CH_3$ at 1379 cm^{-1} confirms the presence of alkylated Hmbt in **1**. As for **1** and **2**, the relatively weak bands in the region of 3013–3109 cm^{-1} correspond to the C–H vibrations of the aromatic ring hydrogen atoms, ν(=C–H). The bands of ring vibrations of the conjugated ligand (ν(C=C) and ν(C=N)) are observed at 1606–1400 cm^{-1}, suggesting the existence of benzothiazole-based cation in **1** and **2**. The protonated products of mbt^- molecule in **1** can also be confirmed by the IR spectra. The IR bands at 2950–2845 cm^{-1} are attributed to the $N–H^+$ stretching vibrations of $=NH^+–$ for **2**. The broad bands in the range 3445–3408 cm^{-1} for **1**–**2** are assigned to the stretching of trace water since the measurements were conducted in air. In brief, the above results are all in agreement with the single crystal X-ray diffraction studies.

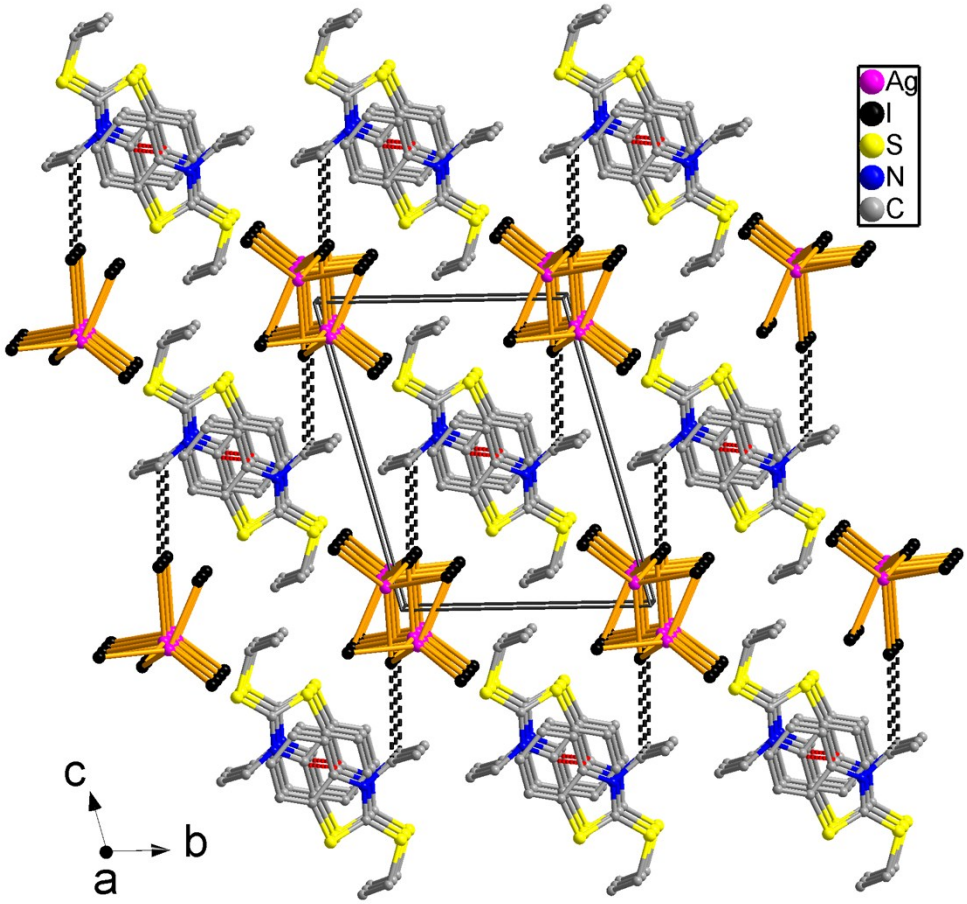


Fig. S3 The 3-D supramolecular structure of **1**.

Table S2. Selected Hydrogen Bonds Data for **1**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	∠(DHA) (°)
C7-H7A···I3[a]	0.97	3.08	3.936(4)	148.3

Symmetry code: a (-x, 1-y, 1-z).

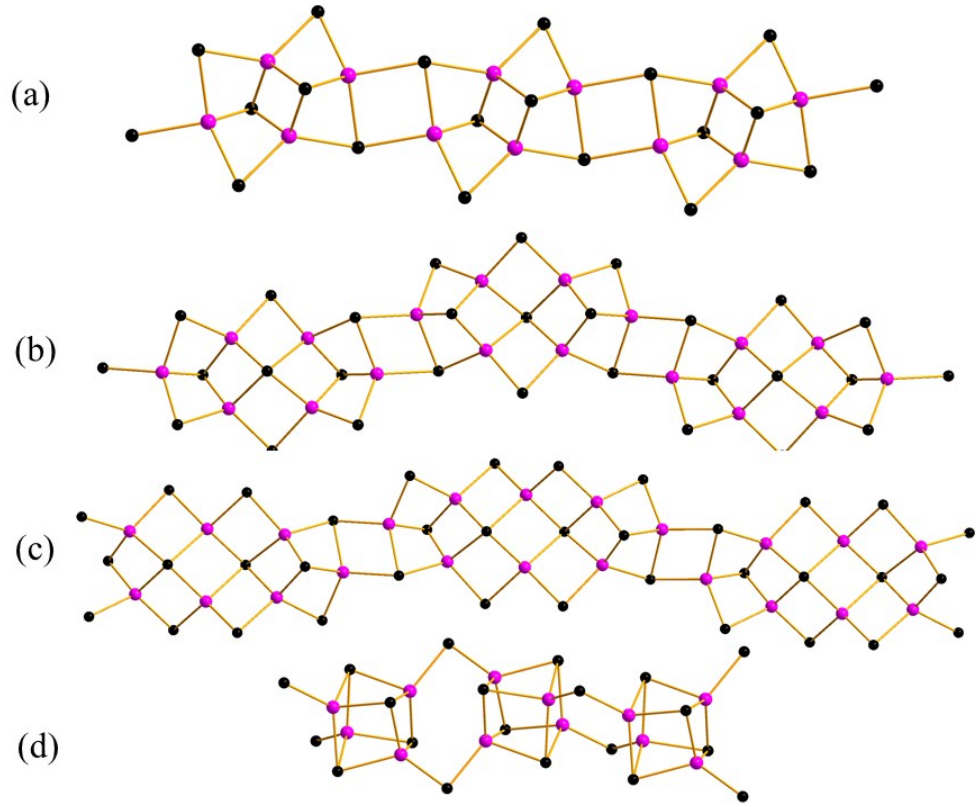


Fig. S4 (a) The $(Ag_2I_3)_n^{n-}$ anionic chain like that in **1**. (c-d) The other three isomers of 1-D $(Ag_2I_3)_n^{n-}$ anion.

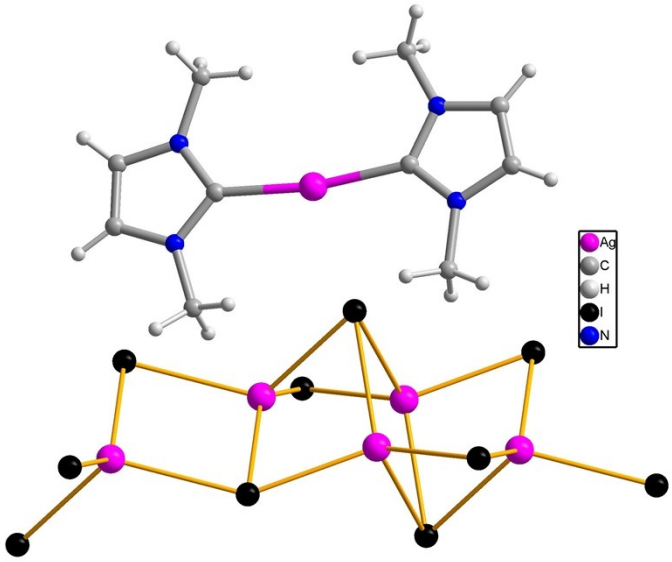


Fig. S5 The organometallic compound $[Ag(carbene)_2](Ag_2I_3)$.

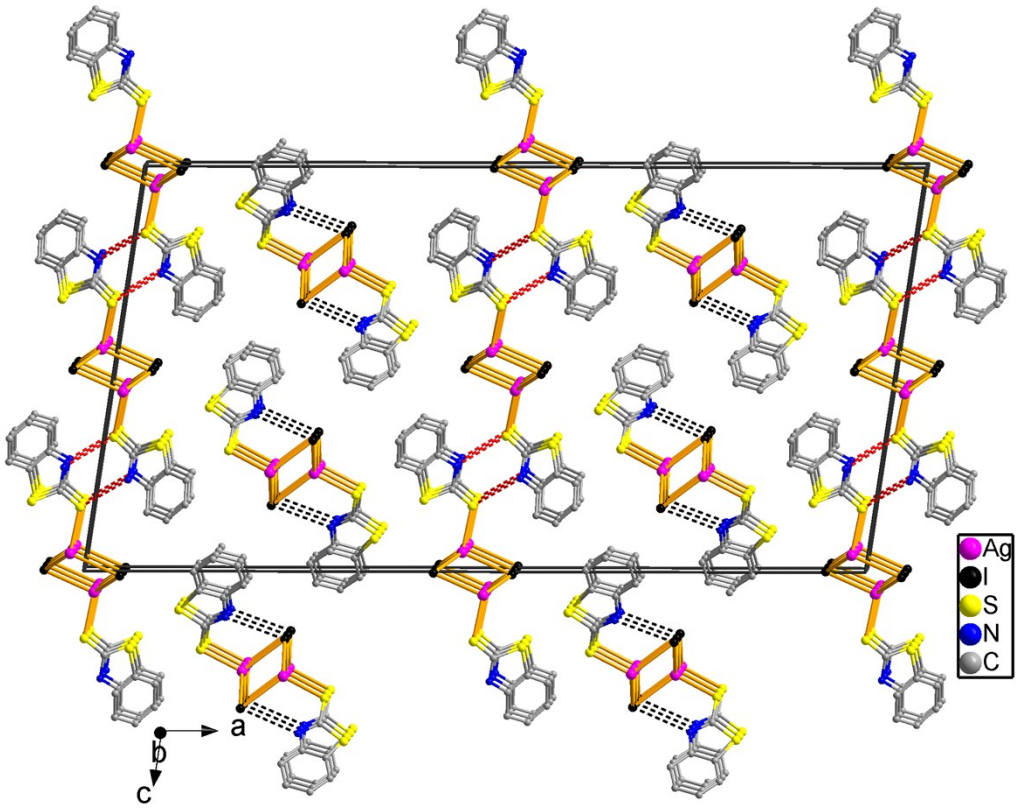


Fig. S6 The 3-D supramolecular structure of **2**.

Table S3. Selected Hydrogen Bonds Data for **2**.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	∠(DHA) (°)
N1-H1A···S2[a]	0.86	2.45	3.308(3)	176.3
N2-H2A···I2[b]	0.86	2.89	3.731(3)	167.6

Symmetry code: a (1-x, y, 3/2-z); b (3/2-x, -1/2+y, 3/2-z).

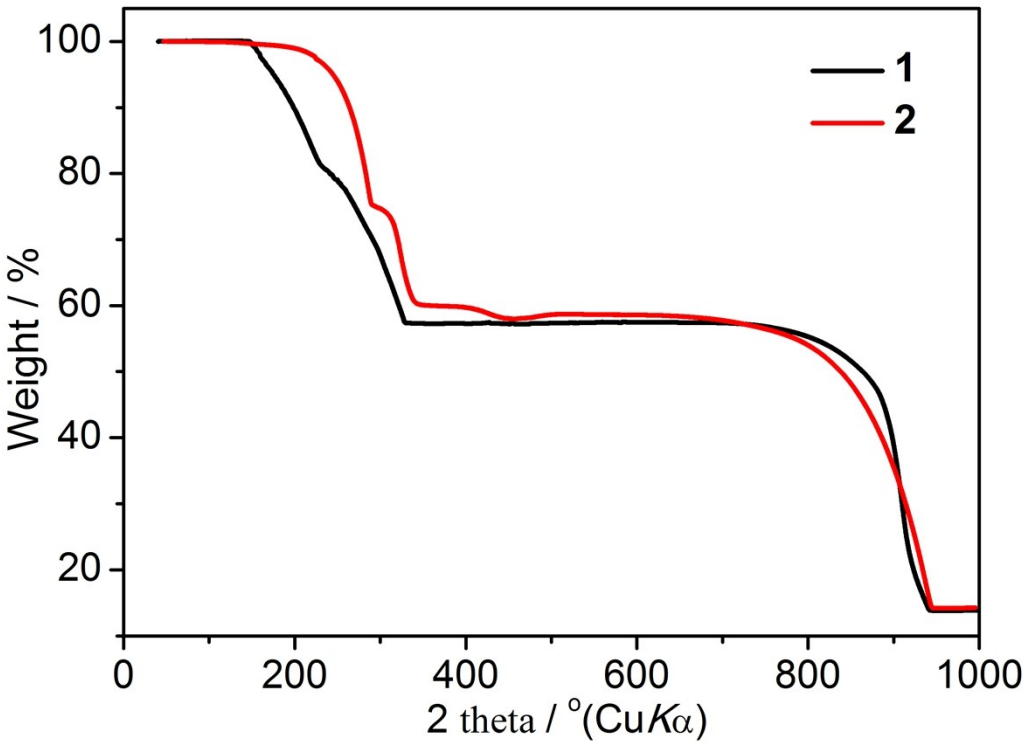
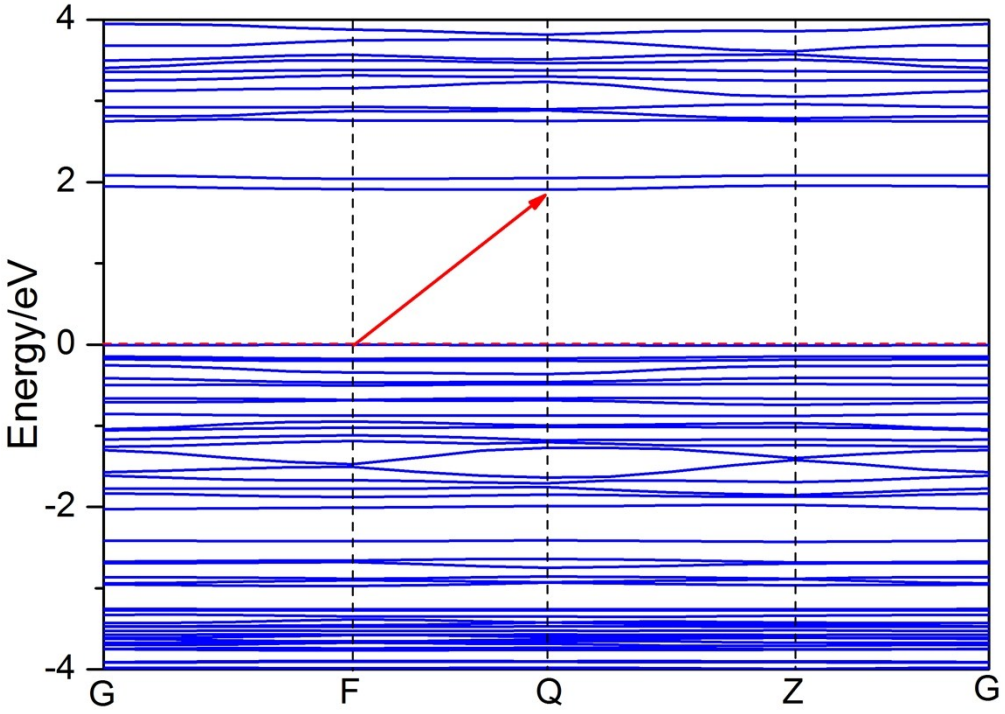
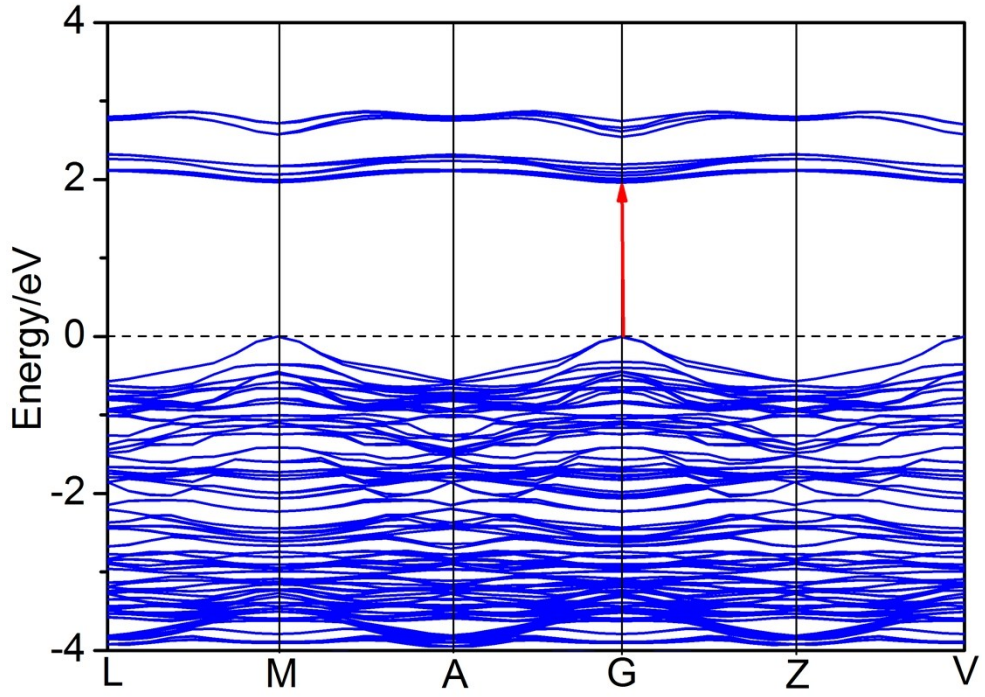


Fig. S7 TGA curves of **1** and **2**.



(a)



(b)

Fig. S8 Band structures of **1** (a) and **2** (b). The Fermi level is set at 0 eV.

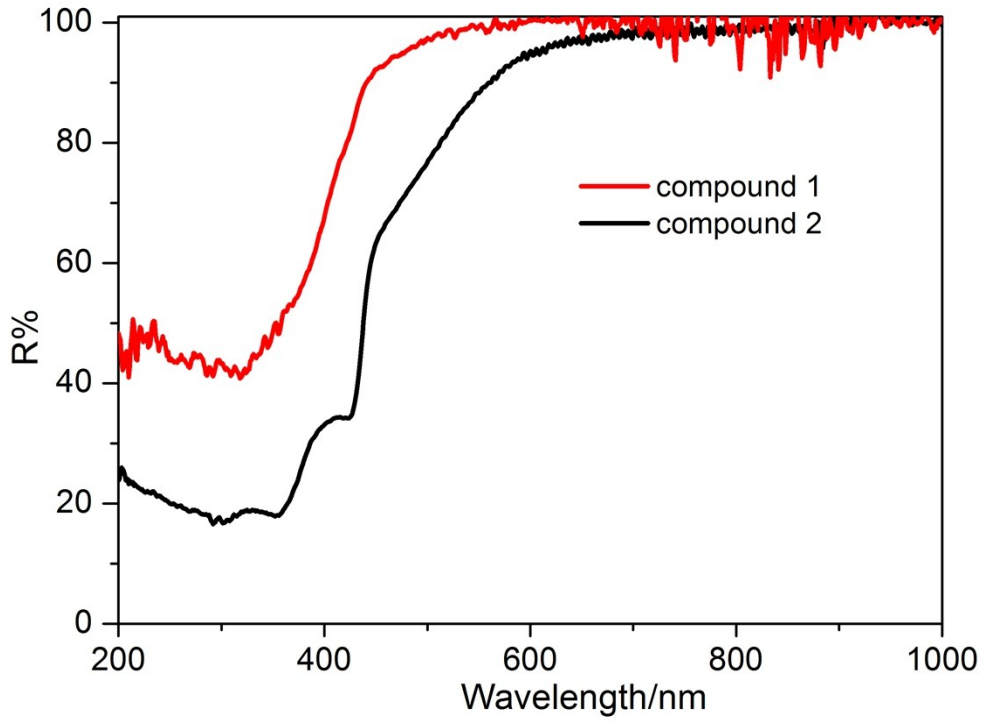
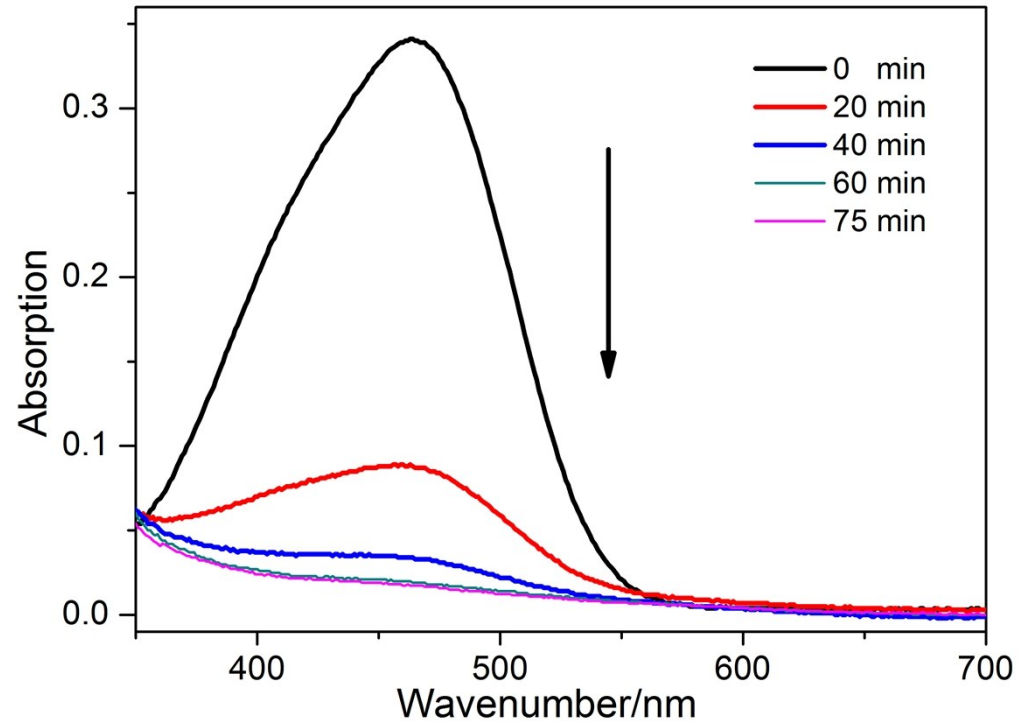
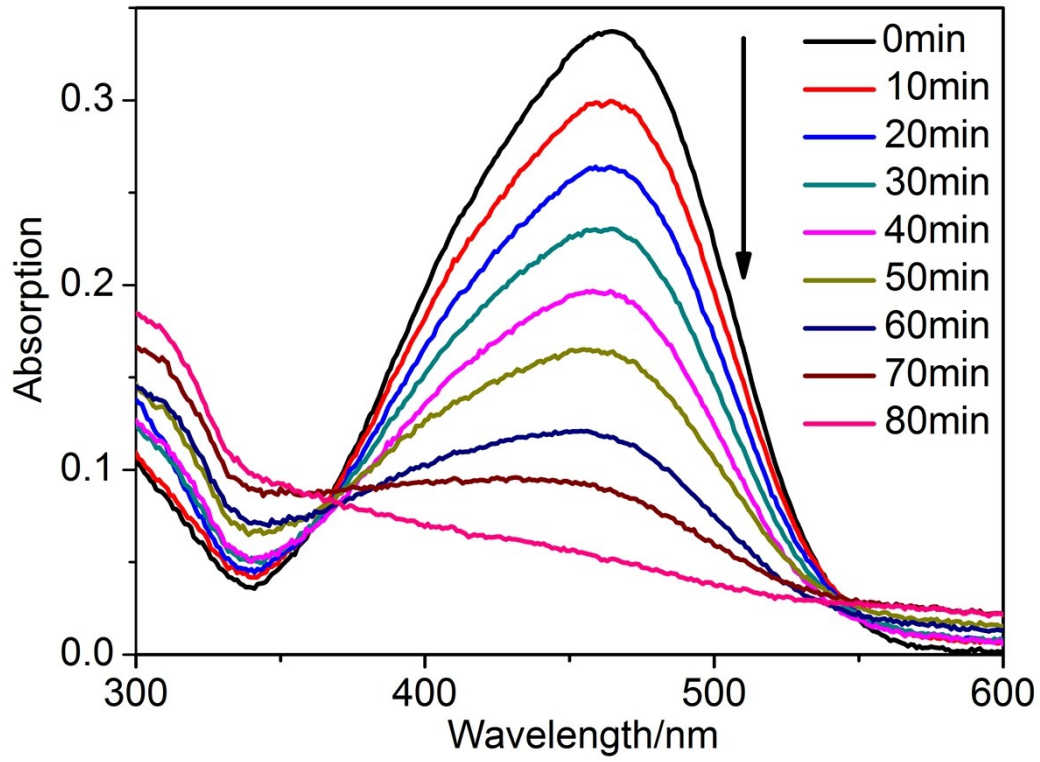


Fig. S9 UV absorption spectrum for **1** and **2**. The UV light between 250–380 nm is used for photocatalytic degradation of organic dye.



(a)



(b)

Fig. S10 Time-dependent UV/vis spectra of MO over **1** (a) and **2** (b).

Table S4. Linear relationship of $\ln(C_0/C)$ and reaction time for the photodegradation of MO.

	$ln(C_0/C) = kt$	k
1	$\ln(C_0/C) = 0.0481t$	0.0481
2	$\ln(C_0/C) = 0.0185t$	0.0185