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Five Monocyclic Pyridinium Derivatives Based Halo-argentate/cuprate Hybrids or Iodide Salts: Influence of Composition on Photochromic Behaviors

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Supporting Information (SI)

The asymmetric unit diagram (Fig. S1), High-Resolution mass spectra (Fig. S3), Infrared spectroscopy (Fig. S4), X–ray powder diffraction (XRPD) patterns (Fig. S5), Electron paramagnetic resonance (EPR) spectroscopy (Fig. S6), Selected bond lengths (Å) and angles (°) for **1** - **5** (Tables S1), Photochromic behaviors and UV-vis diffuse reflectance spectra of **4** and **5** (Fig. S7), Absorption changes with repeated UV irradiation/heating cycles for **1** - **2** (Fig. S8), Thermogravimetric analysis-differential scanning calorimetry (TG-DSC) curves for photochromic **1** - **3** (Fig. S9), ^{1}H NMR spectra for **1** - **2** and ^{13}C NMR spectra for **2** (Fig. S2).

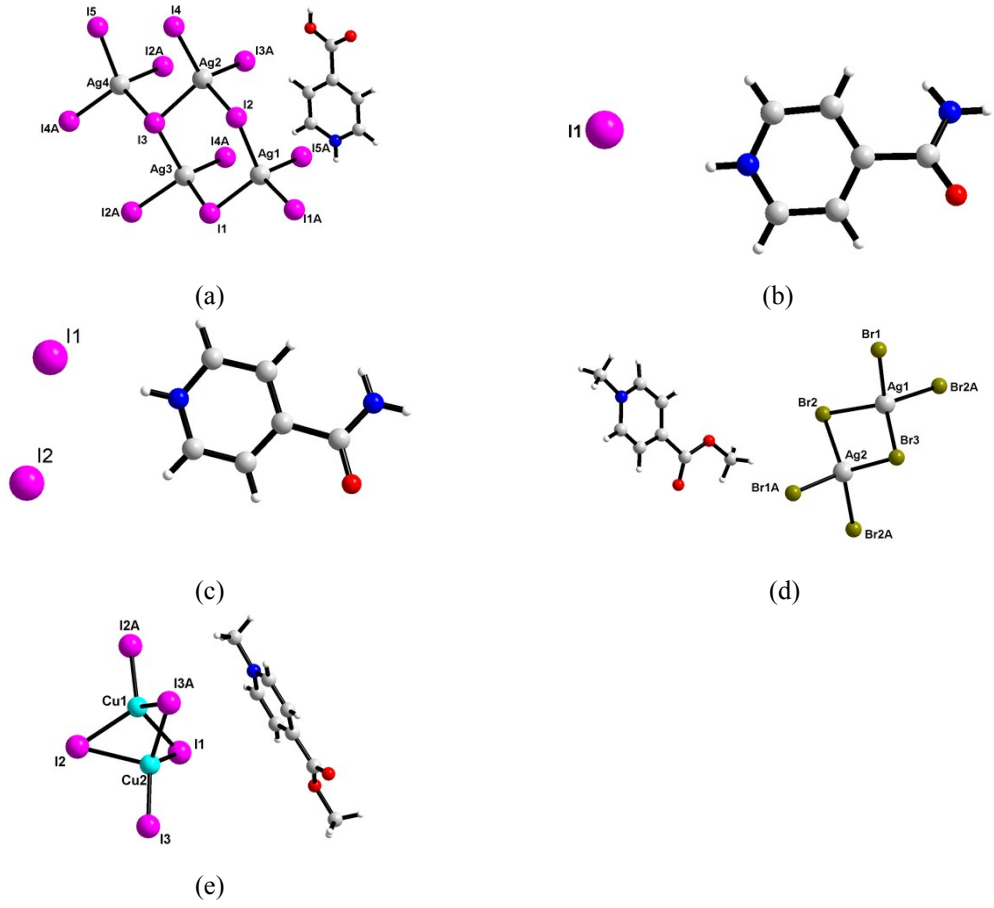
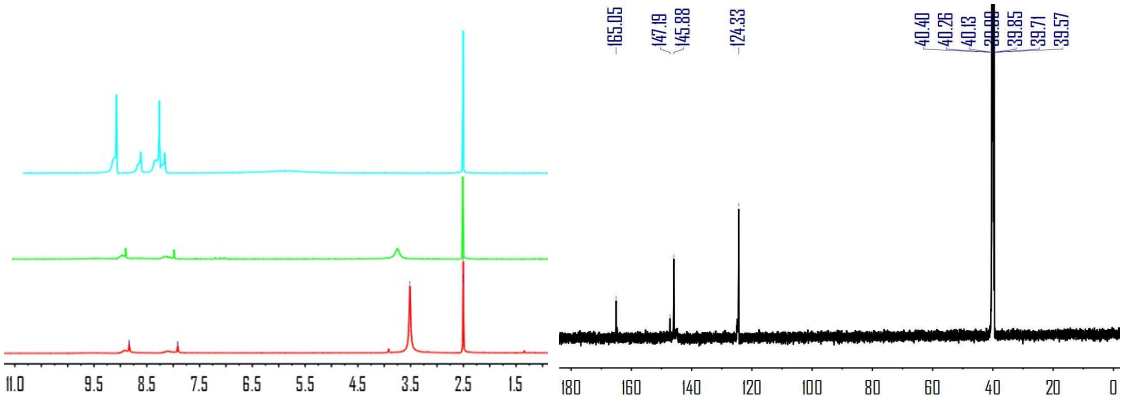


Fig. S1 The asymmetric unit diagram of **1** (a), **2** (b), **3** (c), **4** (d) and **5** (e).

Nuclear magnetic resonance (NMR) spectra were recorded on a Bruker Ascend^{TM}-600 MHz spectrometer in D_6-DMSO with tetramethylsilane (TMS) as internal reference. The organic moieties in compounds **1** and **2** were characterized at room temperature using ^{1}H NMR spectra. For the measurements, 10 mg of the samples was dissolved in 0.5 mL of D_6-DMSO. The chemical shifts of compound **1** in ^{1}H NMR at 8.84 ppm and 7.93 ppm are assigned to the proton on the pyridine, which clearly confirmed the existence of isonicotinic acid in the compound **1**[1]. Unfortunately, the proton signal on the carboxyl is missing due to the rapid exchange of active hydrogen with the high moisture content in D_6-DMSO. The ^{1}H NMR spectrum of compound **2** shows that proton signals at 8.99 ppm (s), 8.09 ppm (d) and 8.20 ppm (d) are the character of pyridine in isonicotinamide. The single peak of the proton on amide group is found at 8.54 ppm, proving that the organic moiety in the compound **2** was composed of isonicotinamide (Fig. S2a). The ^{13}C NMR data of compound **2** as an representative example was recorded on a Bruker AV-600 MHz spectrometer in D_6-DMSO with tetramethylsilane (TMS) as internal reference (Fig. S2b), the characterization ^{13}C NMR spectrum of **2** has been found (^{13}C NMR (150 MHz, DMSO) δ (ppm): 165.05, 147.19, 145.88, 124.33).

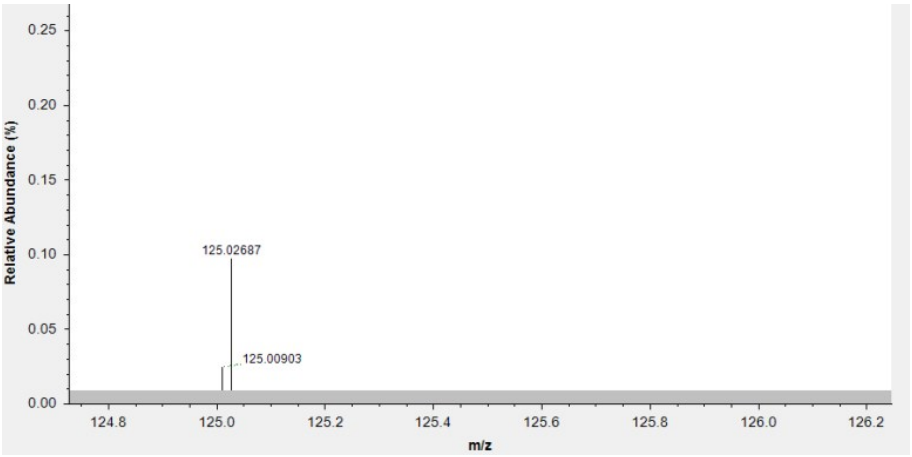
[1] Prajapati, P., Agrawal, Y. K. *Anal. Methods.* **2015**, 7, 7776-7783.



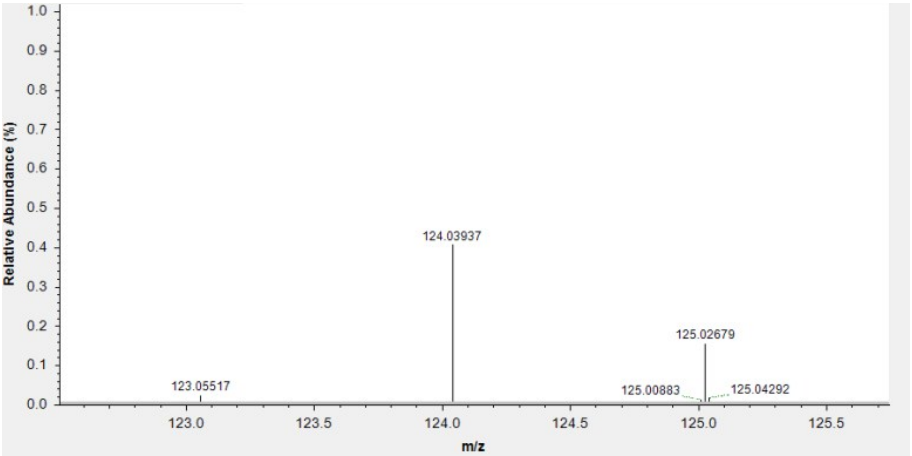
(a) (b)

Fig. S2 (a) ^{1}H NMR spectra for **1** prepared using isonicotinamide as starting reactants (red line); **1** prepared using isonicotinic acid as starting reactants (green line); **2** prepared using isonicotinamide as starting reactants (blue line); (b) the ^{13}C NMR spectrum for **2**.

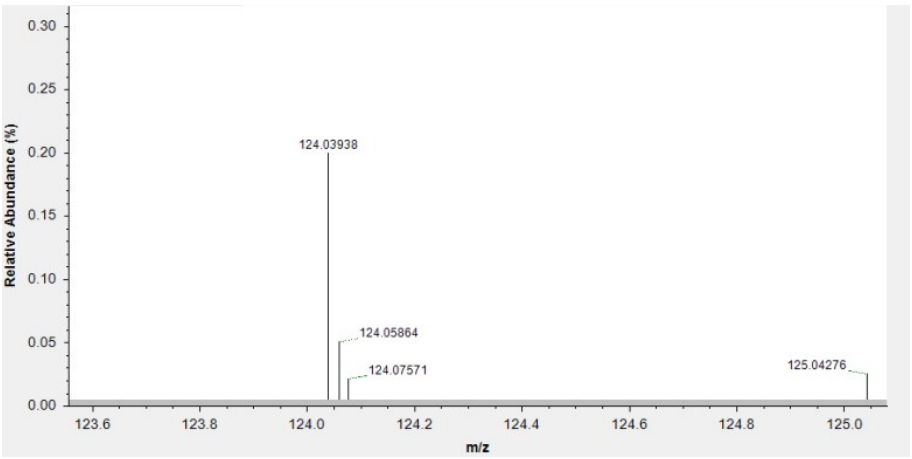
High-Resolution mass spectral analyses were performed on aquadrupole high resolution Orbitrap mass spectrometry (QOrbitrap MS, ThermoFisher, USA) detector using source type of a heated electrospray ionization (HESI) source and positive standard methods. All samples were dissolved in methanol (sample **2** and **3**) or dimethyl sulfoxide (sample **1**, **4** and **5**) to form 50 μM solutions and were infused directly into the ESI source at a flow rate of 3 μL/min (Note: the microsolubility for sample **1** and **4**). The characterization data were presented (HR-ESI-MS for **1** obsd 125.02687, calcd 125.04713 [(M + H)$^+$, M = $C_6H_6NO_2$]; HR-ESI-MS for **2** obsd 124.03937, calcd 124.06311 [(M + H)$^+$, M = $C_6H_7N_2O$]; HR-ESI-MS for **3** obsd 124.03938, calcd 124.06311 [(M + H)$^+$, M = $C_6H_7N_2O$]; HR-ESI-MS for **4** obsd 153.07397, calcd 153.07843 [(M + H)$^+$, M = $C_8H_{10}NO_2$]; HR-ESI-MS for **5** obsd 153.07361, calcd 153.07843 [(M + H)$^+$, M = $C_8H_{10}NO_2$]).



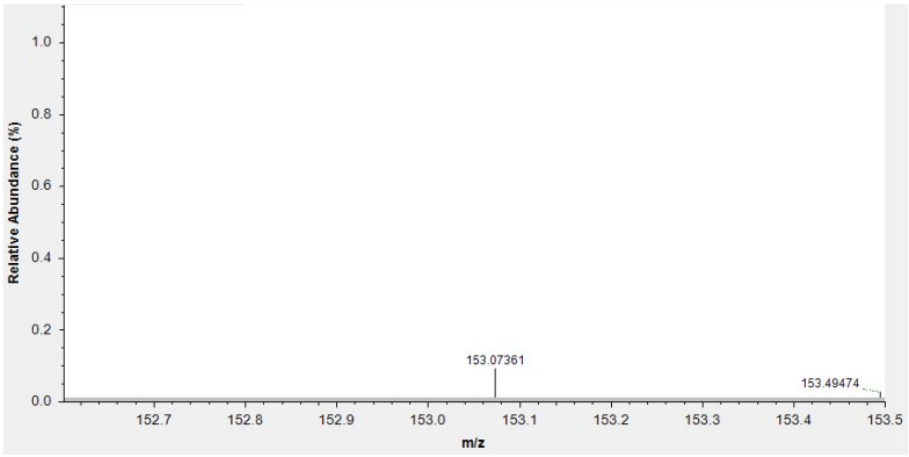
compound **1**



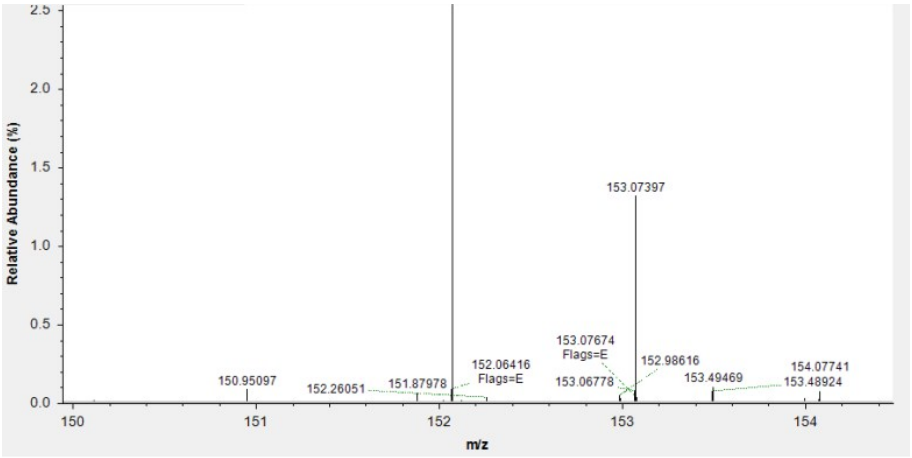
compound **2**



compound **3**



compound **4**

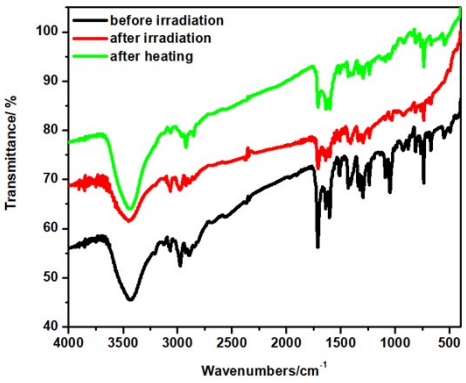


compound **5**

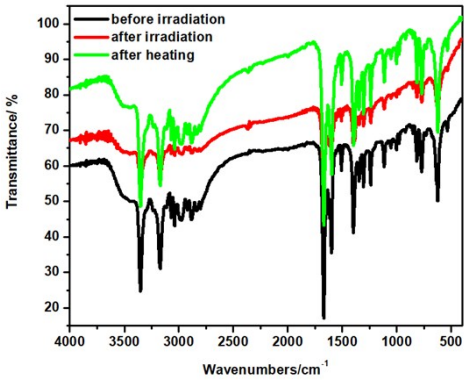
Fig. S3 High resolution ESI(+)-MS of compounds **1-5** solutions.

The IR spectra of **1** - **5** were obtained with a Nicolet 5DX spectrometer by use of KBr pellets. The band about ν = 1700 cm^{-1} indicates the existence of C=O groups in five compounds. The two strong bands at 3347 cm^{-1} and 3173 cm^{-1} in the compounds **2** and **3** denote the existence of N-H stretching absorptions of isonicotinamide[2].

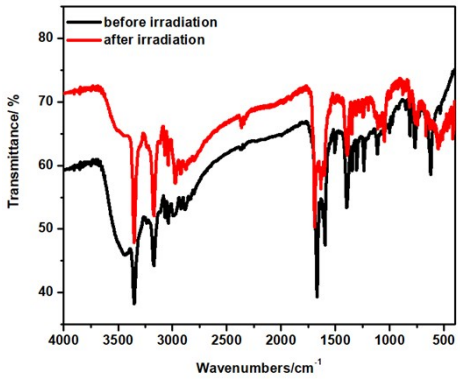
[2] Mukherjee, A., Tothadi, S., Chakraborty, S., Ganguly, S., Desiraju, G. R. *Crystengcomm.* **2013**, 15, 4640-4654.



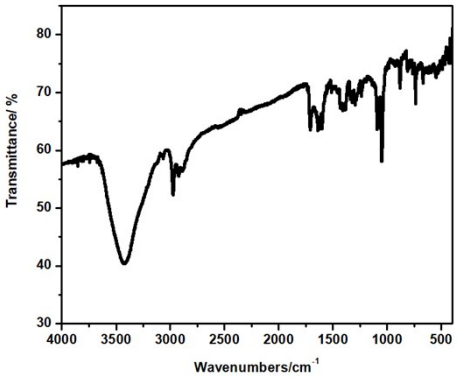
compound **1**



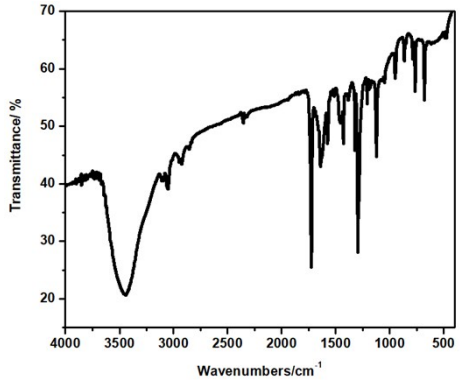
compound **2**



compound **3**

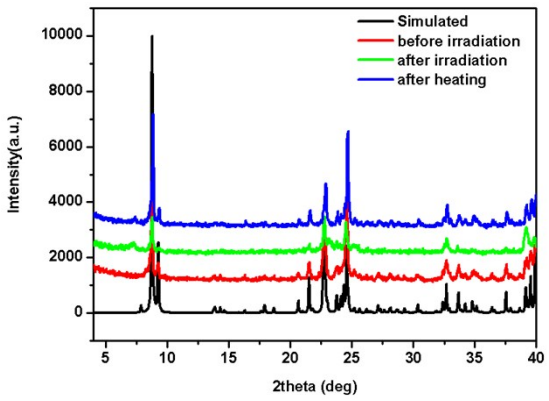


compound **4**

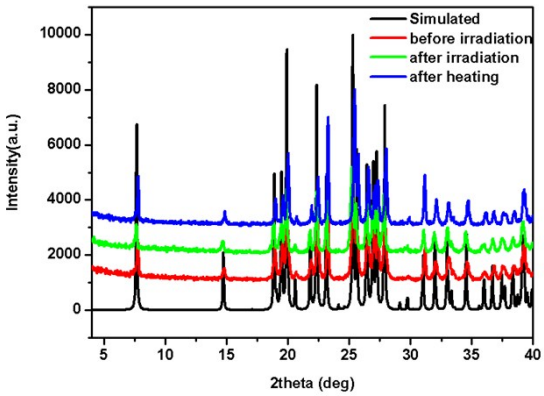


compound **5**

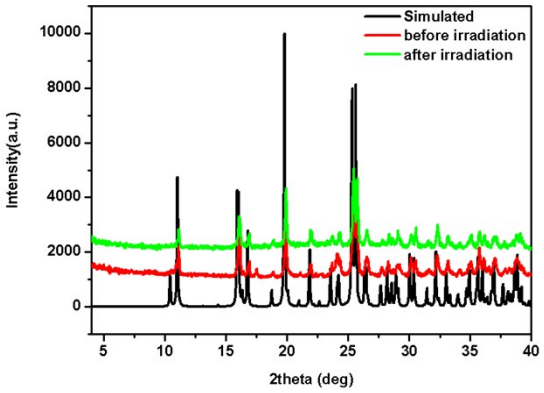
Fig. S4 IR spectra of compounds **1** – **5.**



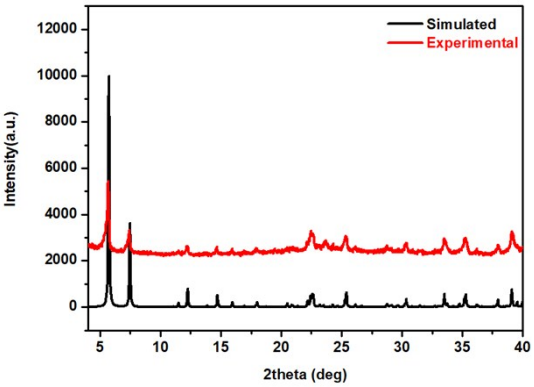
compound **1**



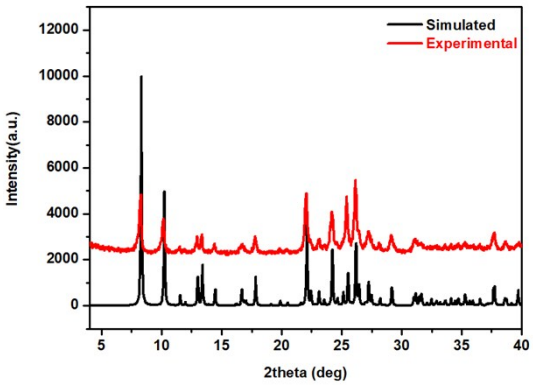
compound **2**



compound **3**

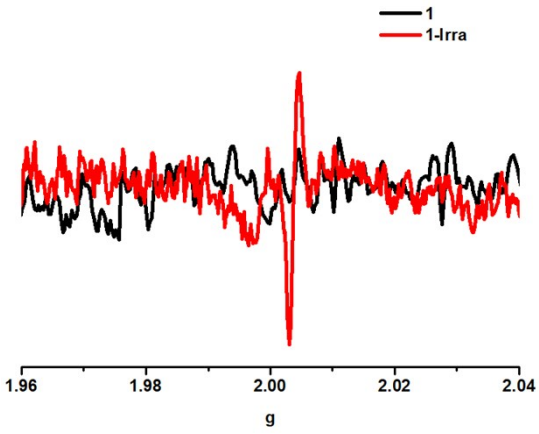


compound **4**

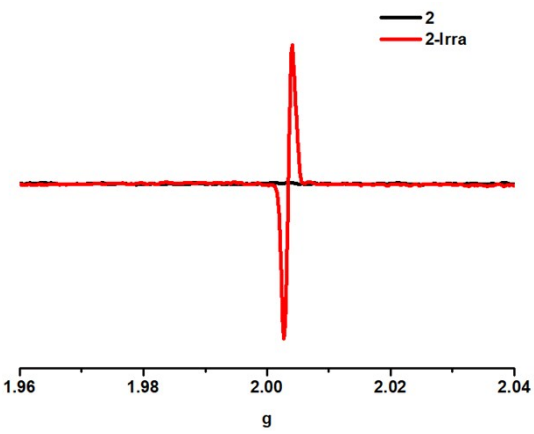


compound **5**

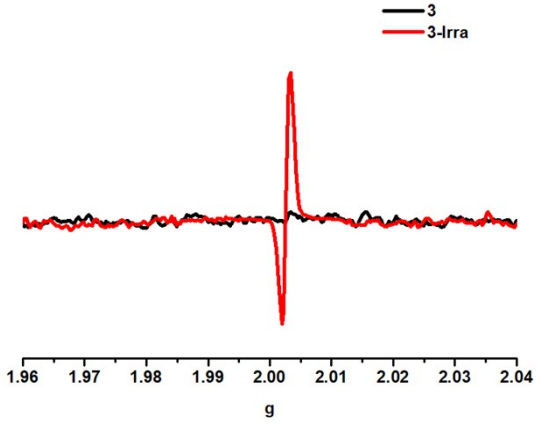
Fig. S5 X-ray powder diffraction (XRPD) patterns of **1** - **5**.



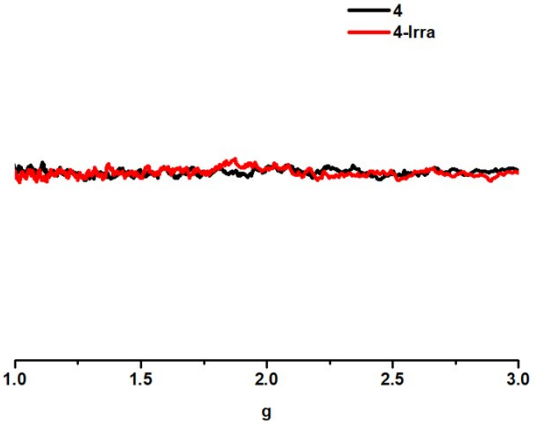
compound **1**



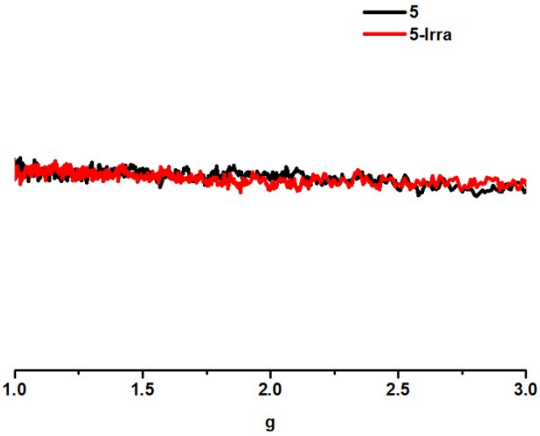
compound **2**



compound **3**

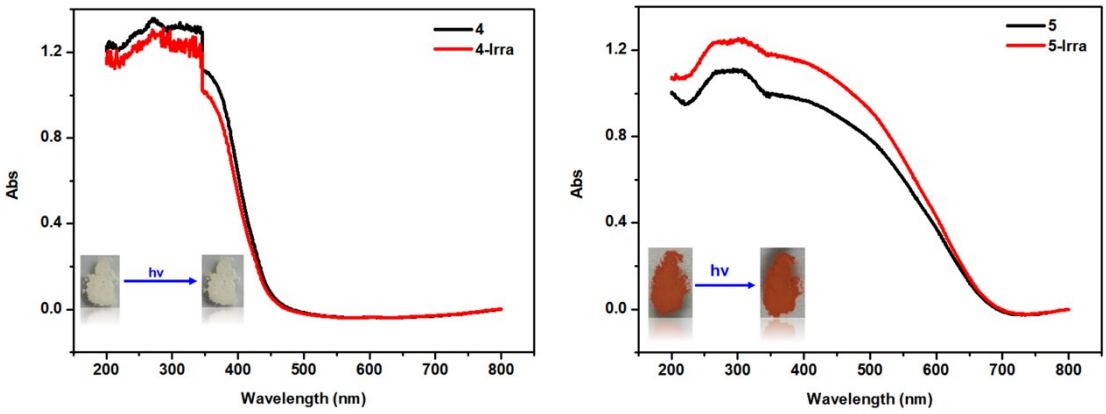


compound **4**



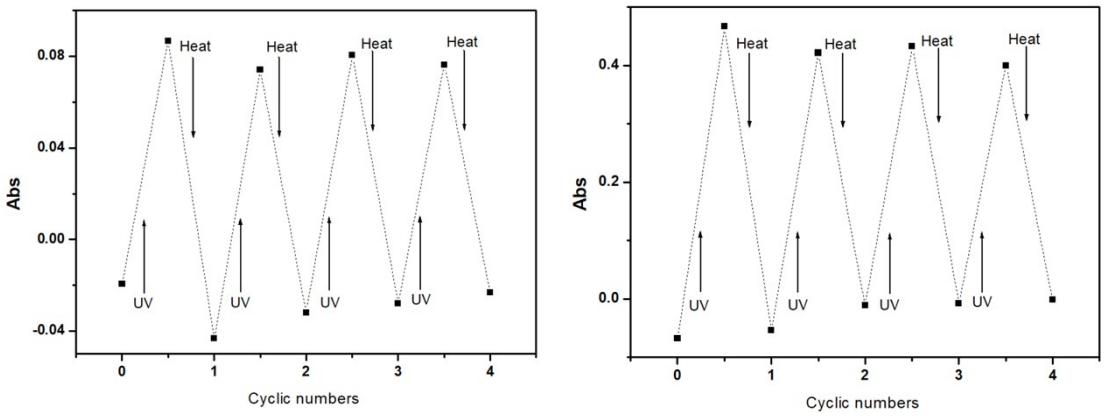
compound **5**

Fig. S6 EPR spectra for **1** - **5**.



compound **4** compound **5**

Fig. S7 Photochromic behaviors and UV-vis diffuse reflectance spectra of **4** and **5**.



(a) (b)

Fig. S8 The absorption changes with repeated ultraviolet irradiation/heat cycles of **1** (a) at 585 nm and **2** (b) at 490 nm.

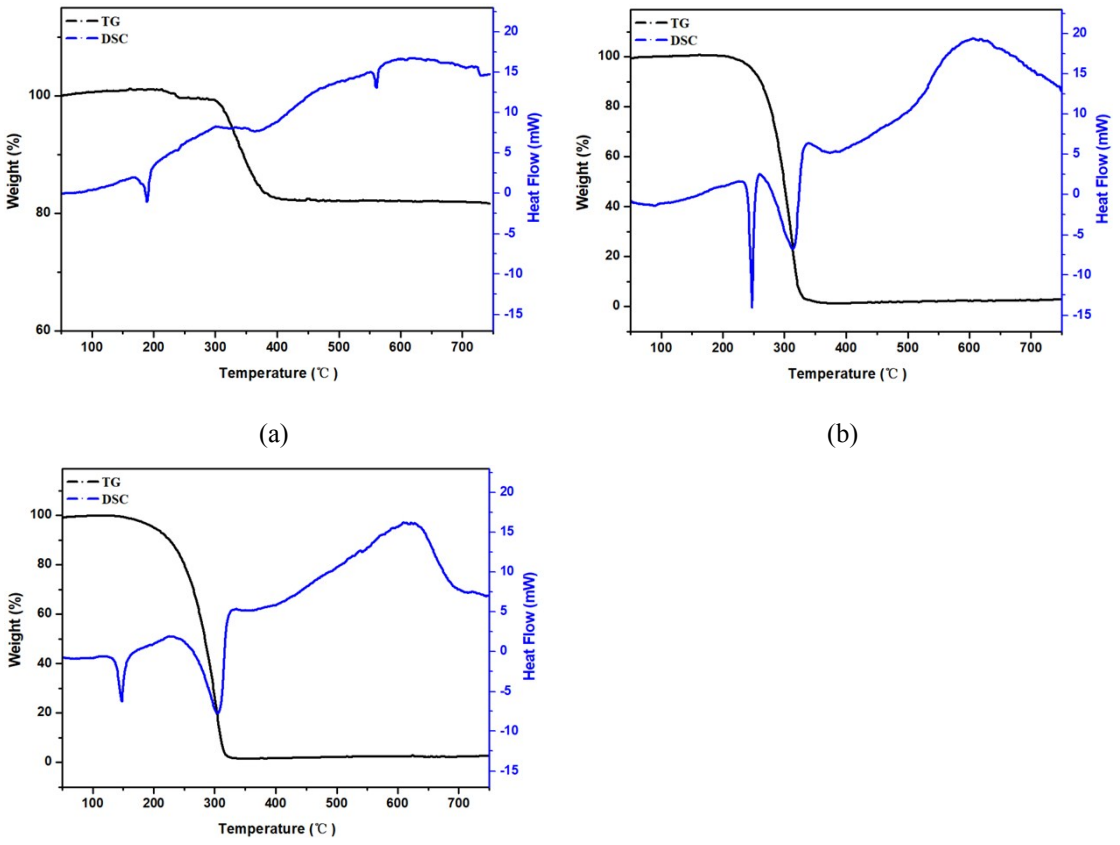


Fig. S9 TG-DSC curves for compounds **1** (a), **2** (b) and **3**(c).

Table S1. Selected bond lengths (Å) and angles (°) for **1** - **5** at 293(2) K

Compound 1			
Ag(1)-I(1)	2.7842(11)	Ag(1)-I(1)#2	2.8491(11)
Ag(1)-I(5)#1	2.8230(11)	Ag(1)-I(2)	2.8796(12)
Ag(2)-I(4)	2.8265(12)	Ag(2)-I(3)	2.8657(11)
Ag(2)-I(2)	2.8484(12)	Ag(2)-I(3)#1	2.9207(11)
Ag(3)-I(1)	2.7904(11)	Ag(3)-I(2)#3	2.8629(11)
Ag(3)-I(4)#1	2.8301(11)	Ag(3)-I(3)	2.9168(12)
Ag(4)-I(5)	2.8086(12)	Ag(4)-I(3)	2.8360(12)
Ag(4)-I(4)#3	2.8328(11)	Ag(4)-I(2)#1	2.9666(11)

Ag(2)-Ag(3)#1	3.0974(14)	Ag(3)-Ag(2)#1	3.0975(14)
Ag(2)-Ag(2)#1	3.2802(19)	Ag(3)-Ag(4)#4	3.3256(14)
Ag(2)-Ag(4)#1	3.3575(15)	Ag(4)-Ag(3)#4	3.3256(14)
Ag(4)-Ag(2)#1	3.3575(15)		
I(1)-Ag(1)-I(5)#1	112.99(4)	I(1)-Ag(1)-I(2)	110.66(4)
I(1)-Ag(1)-I(1)#2	107.32(3)	I(5)#1-Ag(1)-I(2)	108.32(3)
I(5)#1-Ag(1)-I(1)#2	110.12(4)	I(1)#2-Ag(1)-I(2)	107.28(4)
I(4)-Ag(2)-I(2)	109.82(4)	I(4)-Ag(2)-I(3)#1	114.75(4)
I(4)-Ag(2)-I(3)	110.25(4)	I(2)-Ag(2)-I(3)#1	109.55(4)
I(2)-Ag(2)-I(3)	100.61(3)	I(3)-Ag(2)-I(3)#1	110.94(3)
I(1)-Ag(3)-I(4)#1	118.38(4)	I(1)-Ag(3)-I(3)	103.31(3)
I(1)-Ag(3)-I(2)#3	104.45(3)	I(4)#1-Ag(3)-I(3)	114.76(3)
I(4)#1-Ag(3)-I(2)#3	110.76(3)	I(2)#3-Ag(3)-I(3)	103.68(4)
I(5)-Ag(4)-I(4)#3	111.73(4)	I(5)-Ag(4)-I(2)#1	106.32(3)
I(5)-Ag(4)-I(3)	113.06(4)	I(4)#3-Ag(4)-I(2)#1	107.75(3)
I(4)#3-Ag(4)-I(3)	109.16(4)	I(3)-Ag(4)-I(2)#1	108.60(4)
Compound 2			
C(1)-N(1)	1.335(13)	C(2)-N(1)	1.323(14)
C(1)-C(4)	1.386(11)	C(2)-C(4)	1.399(11)
C(1)-C(3)	1.377(14)	C(4)-C(5)	1.370(14)
C(5)-C(6)	1.516(13)	C(6)-N(2)	1.336(13)
C(6)-O(1)	1.227(13)		
N(1)-C(1)-C(4)	116.2(14)	N(1)-C(2)-C(3)	121.0(15)
C(2)-C(3)-C(5)	116.1(14)	O(1)-C(6)-C(5)	120.2(14)
C(4)-C(5)-C(3)	120.8(14)	N(2)-C(6)-C(5)	115.1(14)
C(4)-C(5)-C(6)	117.9(12)	C(2)-N(1)-C(1)	125.2(14)
C(3)-C(5)-C(6)	121.2(13)	C(5)-C(4)-C(1)	120.6(14)

O(1)-C(6)-N(2)	124.7(14)		
Compound 3			
I(2)-I(2)#1	2.7892(12)	C(1)-C(4)	1.419(16)
N(1)-C(2)	1.327(16)	C(2)-C(3)	1.385(15)
N(1)-C(1)	1.349(17)	C(3)-C(5)	1.377(12)
C(4)-C(5)	1.377(12)	C(5)-C(6)	1.503(11)
N(2)-C(6)	1.324(11)	O(1)-C(6)	1.214(11)
C(2)-N(1)-C(1)	123.3(8)	N(1)-C(2)-C(4)	118.4(9)
N(1)-C(1)-C(3)	120.5(9)	C(5)-C(4)-C(2)	119.1(10)
C(5)-C(3)-C(1)	117.3(9)	C(4)-C(5)-C(3)	121.3(9)
C(4)-C(5)-C(6)	117.2(9)	O(1)-C(6)-N(2)	124.4(8)
C(3)-C(5)-C(6)	121.5(9)	O(1)-C(6)-C(5)	119.9(6)
N(2)-C(6)-C(5)	116.0(9)		
Compound 4			
Ag(1)-Br(3)	2.6534(11)	Ag(1)-Br(1)	2.6578(10)
Ag(1)-Br(2)#1	2.9034(9)	Ag(1)-Br(2)	2.9373(9)
Ag(2)-Br(1)#2	2.6484(11)	Ag(2)-Br(2)	2.8829(9)
Ag(2)-Br(3)	2.6636(10)	Ag(2)-Br(2)#3	2.9557(8)
Ag(1)-Ag(1)#1	2.9563(14)	Ag(2)-Ag(2)#3	3.0242(14)
Ag(1)-Ag(2)	3.3601(9)		
Br(3)-Ag(1)-Br(1)	118.89(4)	Br(3)-Ag(1)-Br(2)#1	110.60(3)
Br(1)-Ag(1)-Br(2)#1	98.77(3)	Br(1)-Ag(1)-Br(2)	105.32(3)
Br(3)-Ag(1)-Br(2)	104.75(3)	Br(2)#1-Ag(1)-Br(2)	119.19(3)
Br(1)#2-Ag(2)-Br(3)	120.55(4)	Br(1)#2-Ag(2)-Br(2)#3	97.70(3)
Br(1)#2-Ag(2)-Br(2)	106.46(3)	Br(3)-Ag(2)-Br(2)#3	109.12(3)
Br(3)-Ag(2)-Br(2)	105.99(3)	Br(2)-Ag(2)-Br(2)#3	117.62(3)
Compound 5			

Cu(1)-I(2)#1	2.5153(12)	Cu(1)-I(2)	2.7997(18)
Cu(1)-I(1)	2.6454(16)	Cu(1)-I(3)#2	2.8129(17)
Cu(2)-I(1)	2.6274(15)	Cu(2)-I(3)	2.5336(12)
Cu(2)-I(2)	2.8175(18)	Cu(2)-I(3)#2	2.8355(15)
Cu(1)-Cu(2)	2.4497(16)	Cu(2)-Cu(2)#2	2.607(3)
Cu(1)-Cu(1)#1	2.651(3)		
I(2)#1-Cu(1)-I(1)	116.99(6)	I(2)#1-Cu(1)-I(3)#2	110.98(6)
I(2)#1-Cu(1)-I(2)	120.45(6)	I(1)-Cu(1)-I(3)#2	102.76(5)
I(1)-Cu(1)-I(2)	105.45(5)	I(2)-Cu(1)-I(3)#2	97.13(5)
I(3)-Cu(2)-I(1)	122.36(6)	I(3)-Cu(2)-I(3)#2	122.23(5)
I(3)-Cu(2)-I(2)	103.70(6)	I(1)-Cu(2)-I(3)#2	102.61(5)
I(1)-Cu(2)-I(2)	105.43(5)	I(2)-Cu(2)-I(3)#2	96.21(5)

Symmetry code:

For 1: #1 -x+1, -y+1, -z+2; #2 -x+1/2, y-1/2, -z+3/2; #3 x, y+1, z; #4 -x+1, -y+2, -z+2; #5 -x+1/2, y+1/2, -z+3/2; #6 x, y-1, z. For 3: #1 -x+1, -y+1, -z. For 4: #1 -x, -y+2, -z+1; #2 x+1, y, z; #3 -x+1, -y+2, -z+1; #4 x-1, y, z. For 5: #1 -x, -y+1, -z+1; #2 -x+1, -y+1, -z+1.