Supporting Information

Modulation of positional isomers on the photochromic behaviors of bipyridyltriazolium chloroantimonate hybrids

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Contents

1. Experimental section

Preparation of (2-bpt)Cl_2: 3,5-Bis(2-pyridyl)-1H-1,2,4-triazole (2-bpt) was synthesized according to the literature procedure.[1] Anal. Calc. for $C_{12}H_9N_5$ (223.24): C, 64.56; H, 4.06; N, 31.37. Found: C, 64.58; H, 4.00; N, 31.41. ^{1}H NMR (600 MHz, DMSO, δppm): 14.99 (s, 1H), 8.72 (s, 2H), 8.17 (s, 2H), 7.99 (s, 2H), 7.51 (s, 2H). (Fig. S1a).

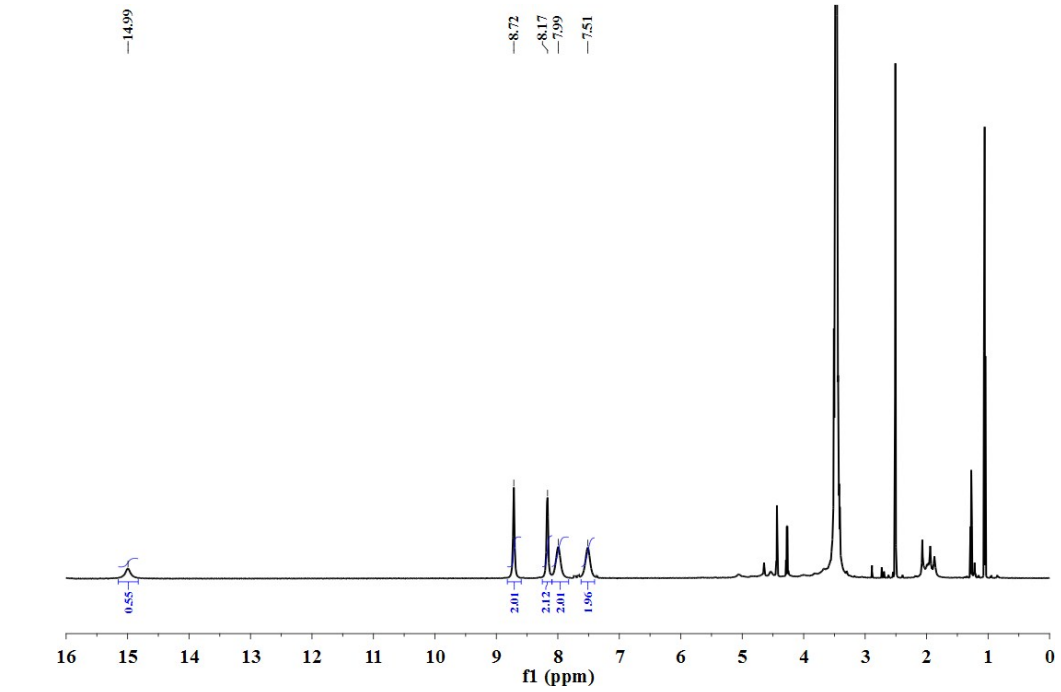
(2-bpt)Cl_2 was synthesized by dissolving 2-bpt (0.04 g, 0.18 mmol) in 3 mL concentrated HCl (37 %) and 3 mL acetonitrile and left for slow evaporation at room temperature for three days. The resulting colorless crystal was collected by filtration, washed with acetonitrile, and dried at air (yield: 63%). Anal. Calc. for $C_{12}H_{11}N_5Cl_2$ (295.84): C, 35.13; H, 3.72; N, 23.67. Found: C, 35.16; H, 3.67; N, 23.65.

Preparation of (4-bpt)Cl_2: 3,5-Bis(4-pyridyl)-1H-1,2,4-triazole (4-bpt) was synthesized *via* an in situ metal/ligand reaction and demetallation procedure according to the literature.[2] Anal. Calc. for $C_{12}H_9N_5$ (223.24): C, 64.56; H, 4.06; N, 31.37. Found: C, 64.60; H, 3.99; N, 31.40. 1H NMR (DMSO-d_6, dppm, 600 MHz): 8.70-8.71 (d, J = 5.5 Hz, 4H), 7.78-7.79 (d, J = 5.7 Hz, 4H) (Fig. S1b).

The synthesis procedure of pale yellow 4-bptCl_2 is similar to that of 2-bptCl_2 except 2-bpt was replaced by 4-bpt (yield: 58%). Anal. Calc. for $C_{12}H_{11}N_5Cl_2$ (295.84): C, 35.13; H, 3.72; N, 23.67. Found: C, 35.17; H, 3.66; N, 23.64.

TD-DFT and thermochemical calculations: All calculations were carried out using the Gaussian 09 program (Revision E.01)[3]. The ground-state geometries of 2-bpt^{2+} were optimized at the B3LYP/6-31+g(d, p) level. The widely used exchange correlation functional B3LYP[4] was chosen in view of its good compromise between accuracy and computational cost. Vibrational analyses were conducted to confirm each stationary point to be a minimum, and at the same time offered the thermochemical results. TD-DFT calculations[5] were performed on the basis of the ground-state geometry using the same functional and basis set.

2. Figures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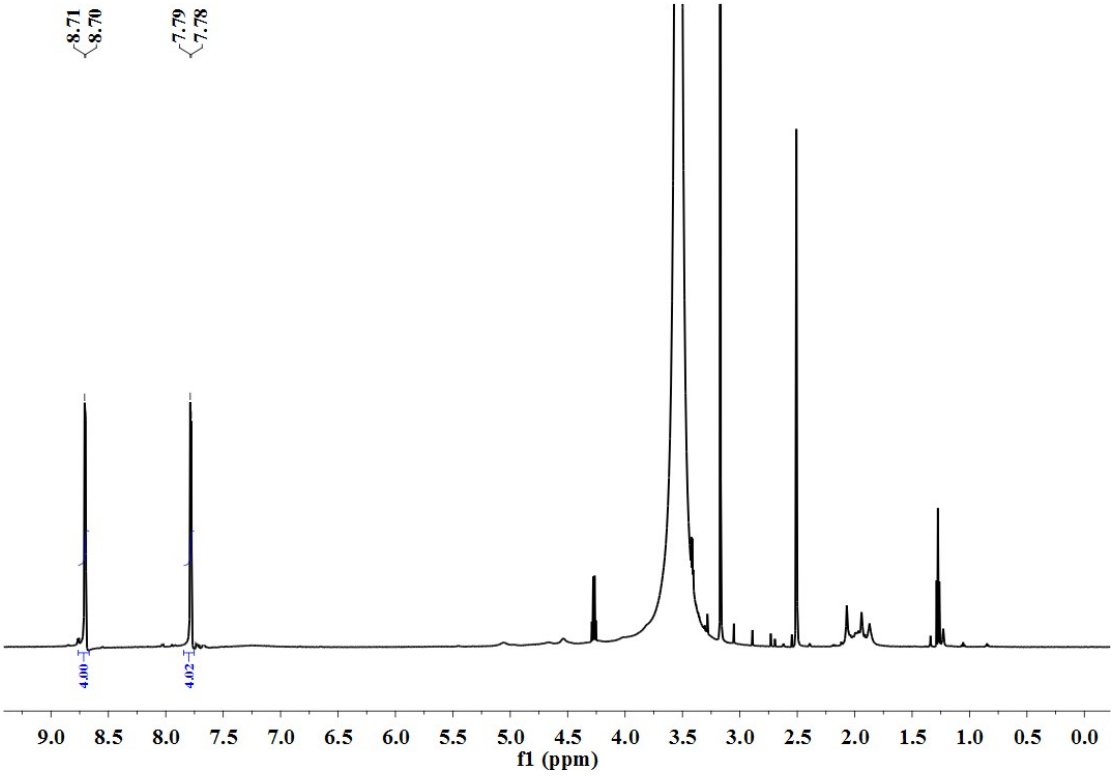
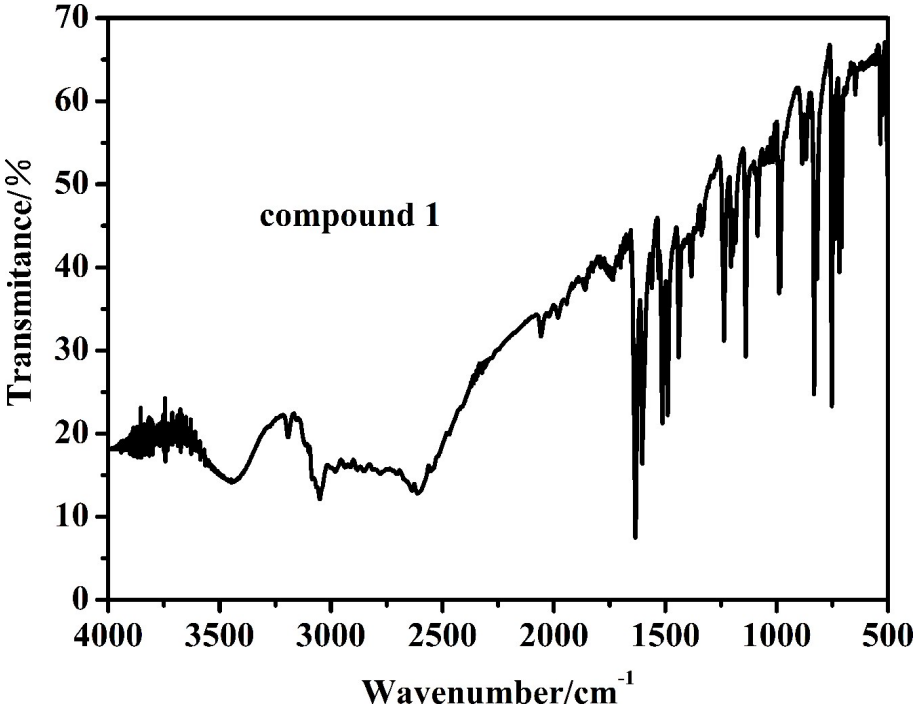
8.72
8.17
7.99
7.51
0.55
2.01
2.12
2.01
1.96
16 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1 0
f1 (ppm)

(a)


8.71
8.70
7.79
7.78
4.00
4.02
9.0 8.5 8.0 7.5 7.0 6.5 6.0 5.5 5.0 4.5 4.0 3.5 3.0 2.5 2.0 1.5 1.0 0.5 0.0
f1 (ppm)

(b)

Fig. S1 The ^{1}HNMR spectra of 2-bpt (a) and 4-bpt (b)



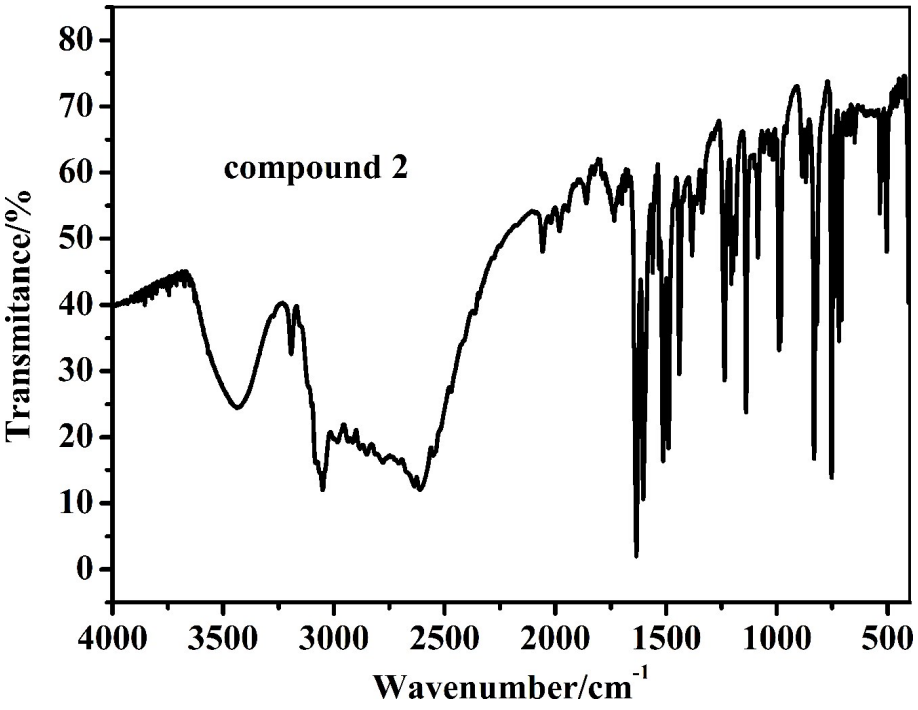
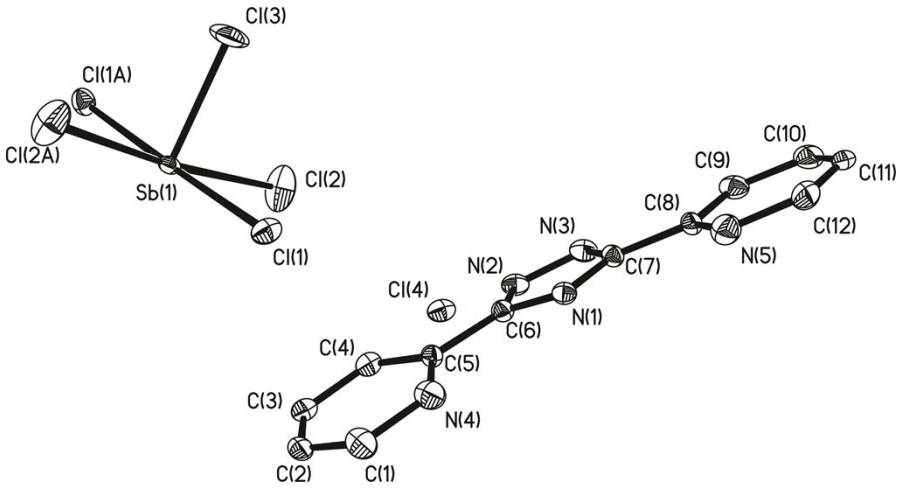
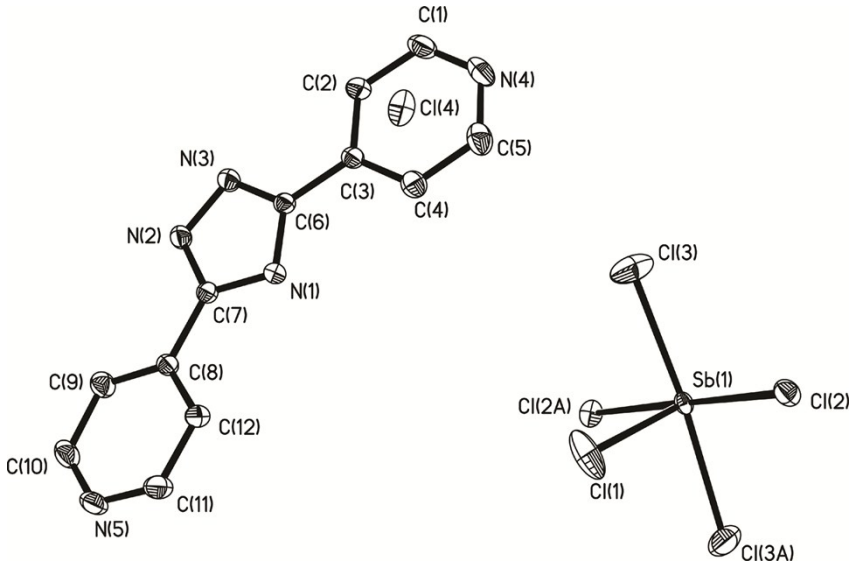


Fig. S2 IR spectra of **1** and **2**



(a)



(b)

Fig. S3 The asymmetric units of **1** (a) and **2** (b).

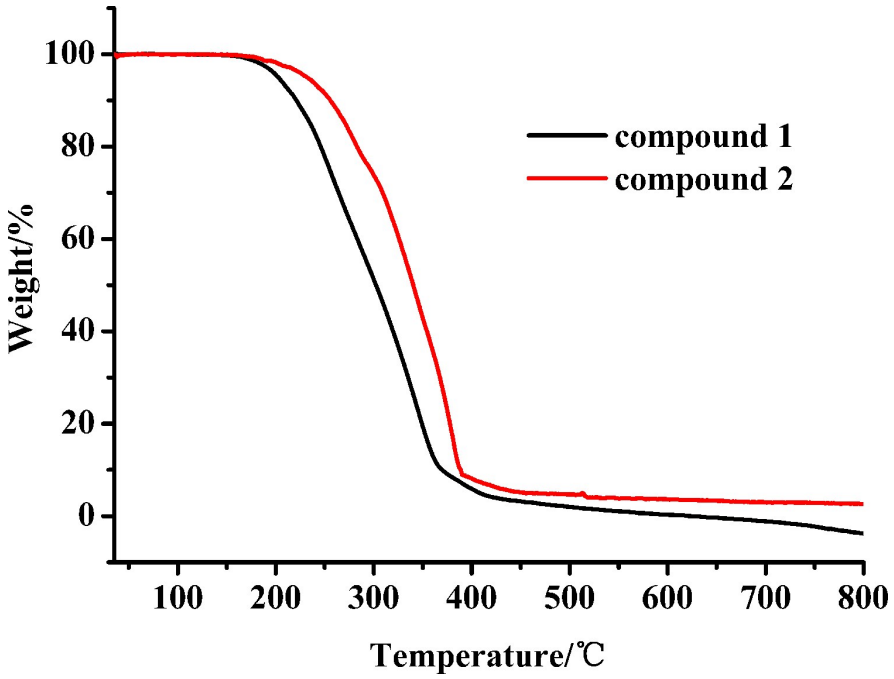


Fig. S4 Thermogravimetric (TG) curves of **1** and **2**.

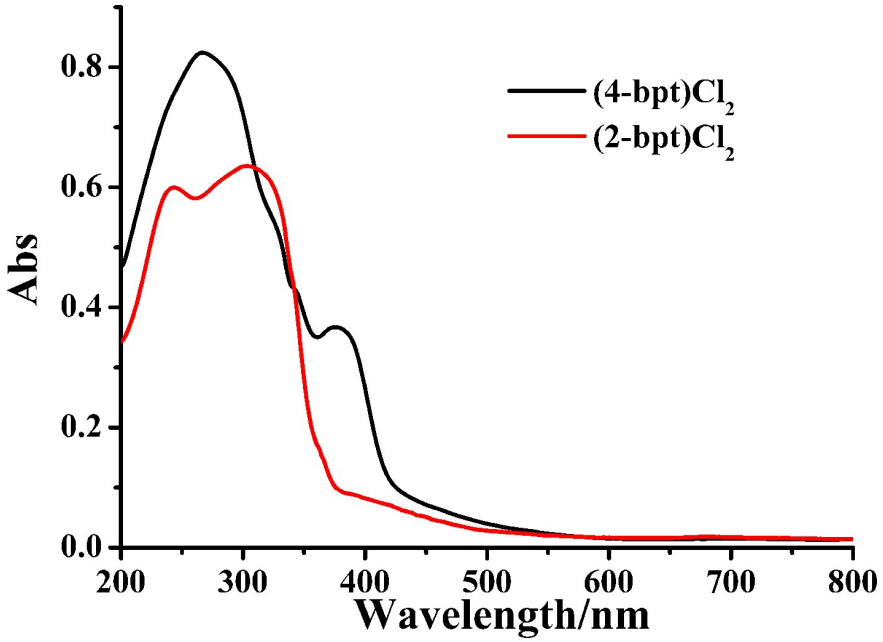
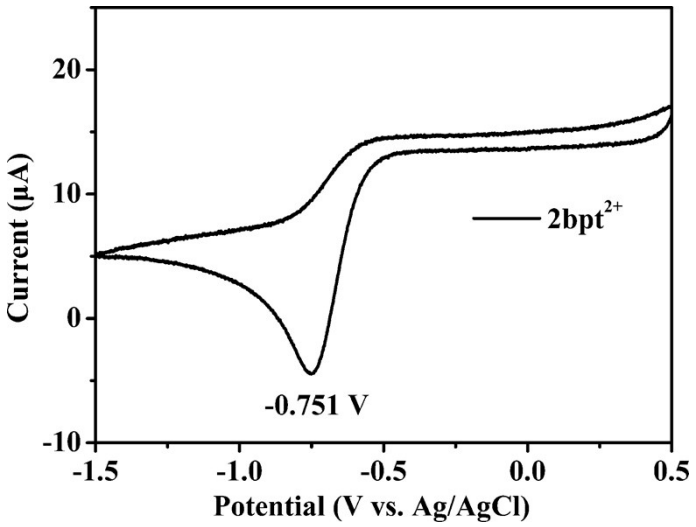
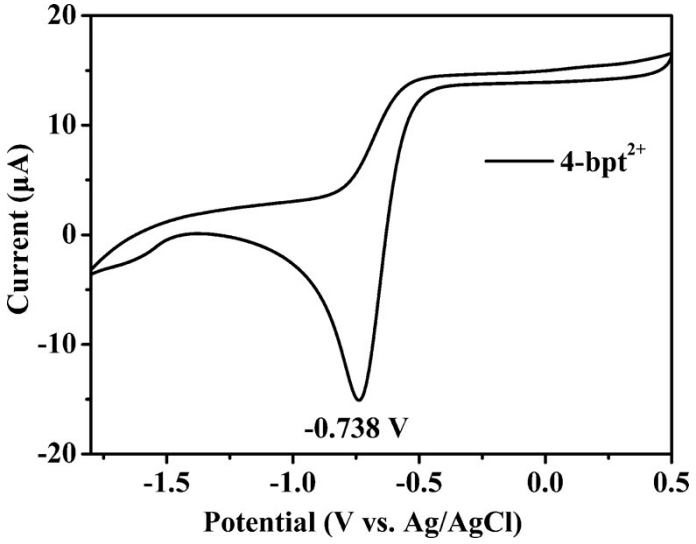


Fig. S5 The UV-vis absorption spectra of (2-bpt)Cl_2 and (4-bpt)Cl_2.

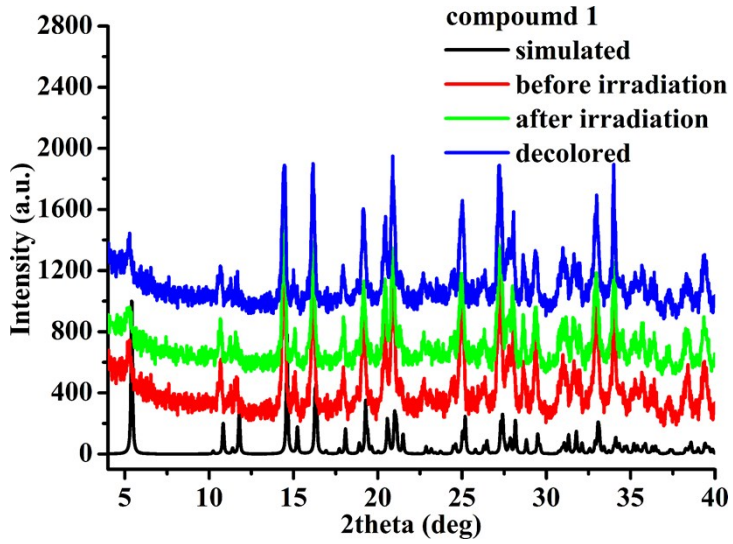


(a)

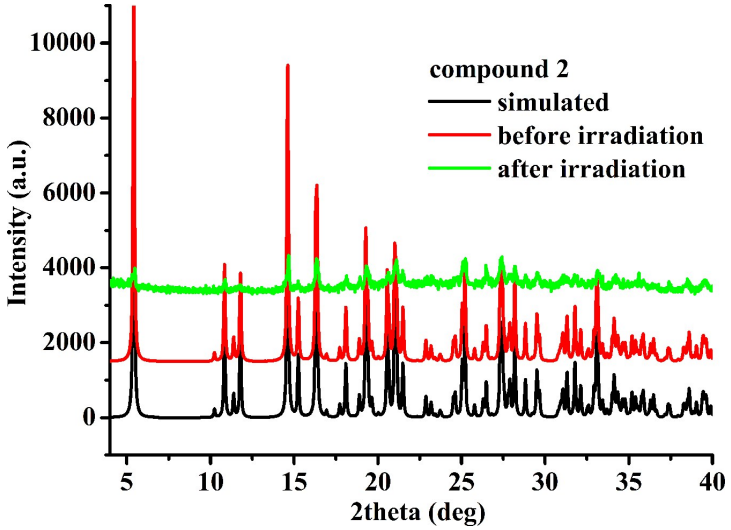


(b)

Fig. S6 Cyclic voltammograms of 1 mmol L^{-1} 2-bpt^{2+} (a) and 4-bpt^{2+} (b) in a 0.1 mol L^{-1} [Bu_4N][PF_6] DMF solution with 100 mV s^{-1} scan rate.



(a)



(b)

Fig. S7 Powder X-ray diffraction (PXRD) patterns of **1** (a) and **2** (b).

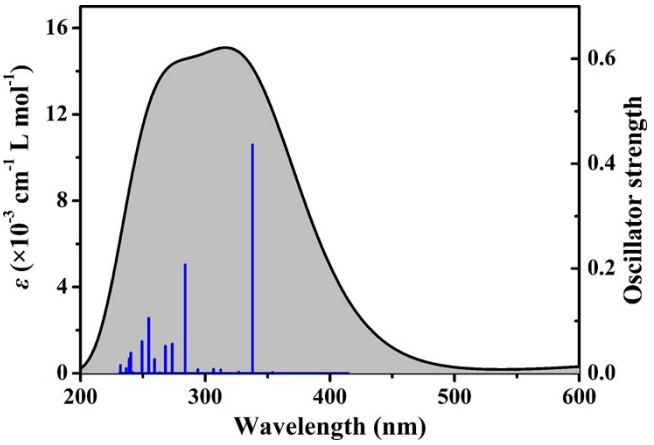


Fig. S8 The UV-vis spectra of 2-bpt$^{+\bullet}$ obtained by TD-DFT calculation

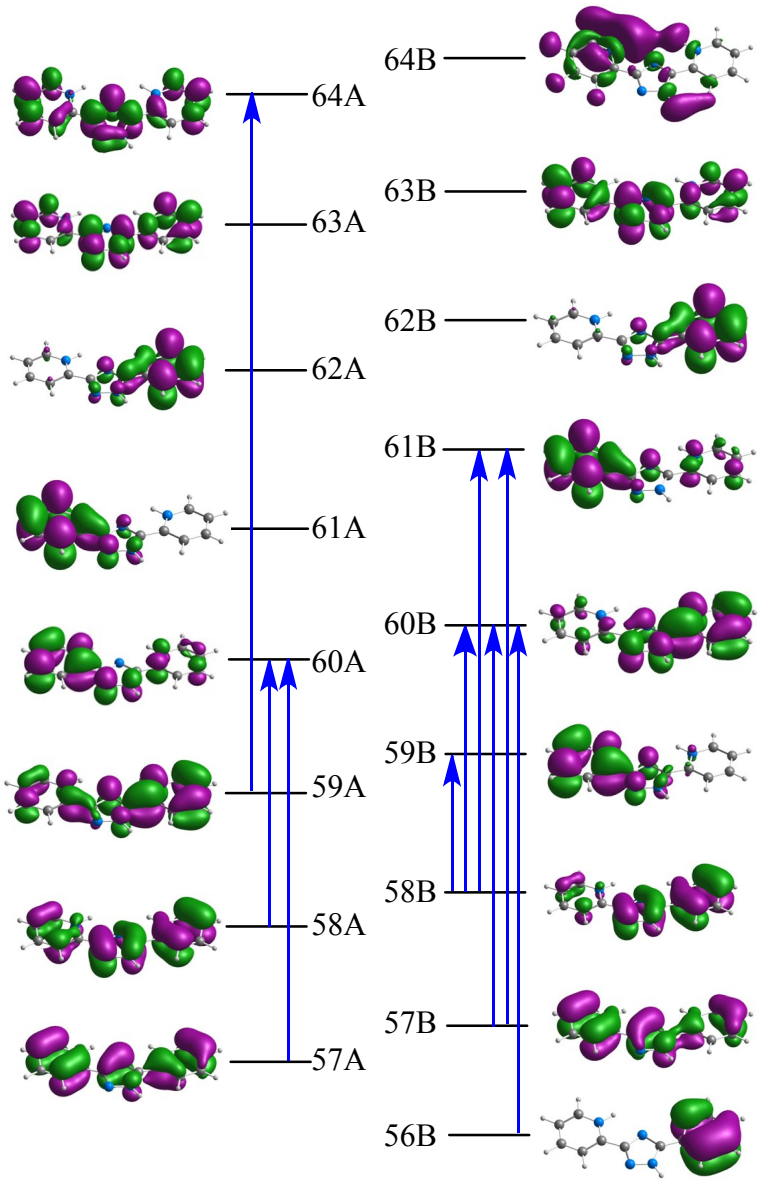
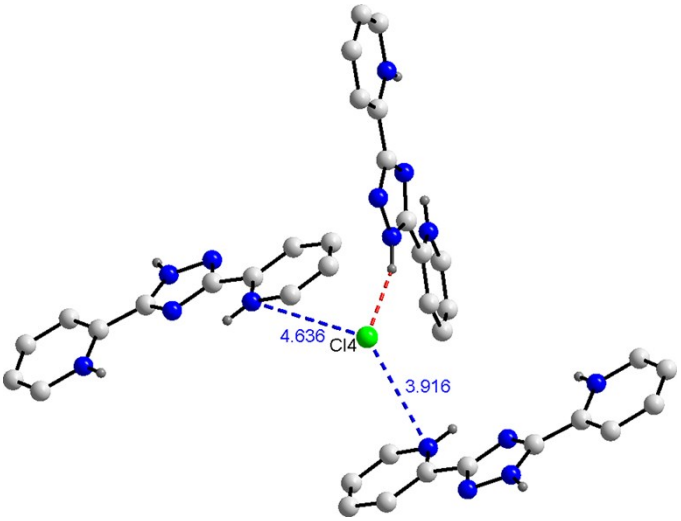
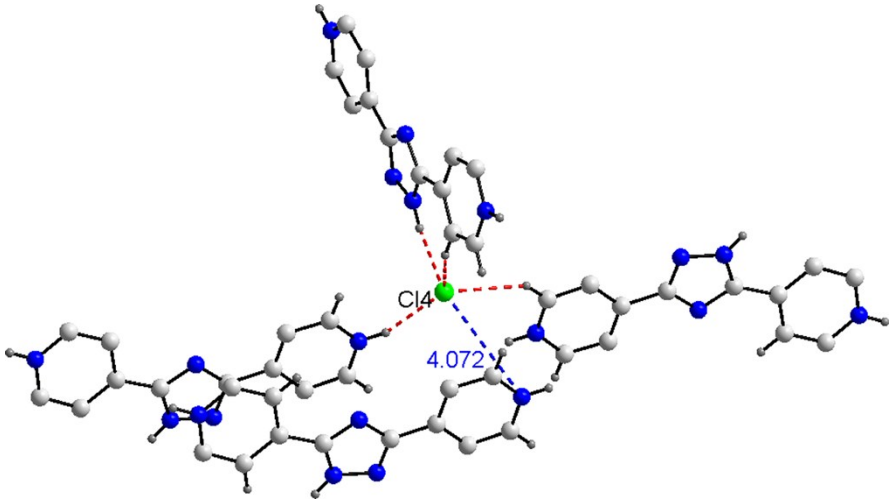


Fig. S9 Orbitals transition types of 2-bpt$^{+\bullet}$ at the B3LYP/6-31+g(d, p) level



(a)



(b)

Fig. S10 Interactions between isolated Cl^- and 2-bpt^{2+}/4-bpt^{2+} cations in **1** (a) and **2** (b).

(a) (b)

Fig. S11 Photochromic behaviors of (2-bpt)Cl_2 and (4-bpt)Cl_2 under irradiation of Hg lamp

3. Tables

Table S1. Selected bond lengths [Å] and angles [˚] for **1** and **2**

Compound **1**			
Sb(1)-Cl(1)	2.6438(8)	Sb(1)-Cl(1)#1	2.6438(8)
Sb(1)-Cl(2)	2.6014(11)	Sb(1)-Cl(2)#1	2.6014(11)
Sb(1)-Cl(3)	2.3859(14)	Sb(1)-Cl(3)#4	3.1048(11)
Cl(1)#1-Sb(1)-Cl(1)	178.48(3)	Cl(1)-Sb(1)-Cl(2)	88.37(3)
Cl(1)-Sb(1)-Cl(2)#1	91.55(3)	Cl(1)-Sb(1)-Cl(3)	89.240(16)
Cl(1)-Sb(1)-Cl(3)#4	90.760(16)	Cl(1)#1-Sb(1)-Cl(2)	91.55(3)
Cl(1)#1-Sb(1)-Cl(2)#1	88.37(3)	Cl(1)#1-Sb(1)-Cl(3)	89.240(16)
Cl(1)#1-Sb(1)-Cl(3)#4	90.760(16)	Cl(2)-Sb(1)-Cl(2)#1	173.93(8)
Cl(2)-Sb(1)-Cl(3)	86.968(4)	Cl(2)-Sb(1)-Cl(3)#4	93.032(4)
Cl(3)-Sb(1)-Cl(2)#1	86.97(4)	Cl(3)#4-Sb(1)-Cl(2)#1	93.032(4)
Cl(3)-Sb(1)-Cl(3)#4	180.00		
Compound **2**			
Sb(1)-Cl(1)	2.3855(9)	Sb(1)-Cl(1)#6	3.1028(4)
Sb(1)-Cl(2)	2.6419(6)	Sb(1)-Cl(2)#1	2.6419(6)
Sb(1)-Cl(3)	2.5988(7)	Sb(1)-Cl(3)#1	2.5988(7)
Cl(1)#6-Sb(1)-Cl(1)	180.00	Cl(1)-Sb(1)-Cl(2)	89.220(10)
Cl(1)-Sb(1)-Cl(2)#1	89.221(10)	Cl(1)-Sb(1)-Cl(3)	86.99(2)
Cl(1)-Sb(1)-Cl(3)#1	86.99(2)	Cl(1)#6-Sb(1)-Cl(2)	90.78(1)
Cl(1)#6-Sb(1)-Cl(2)#1	90.78(1)	Cl(1)#6-Sb(1)-Cl(3)	93.006(22)
Cl(1)#6-Sb(1)-Cl(3)#1	93.006(22)	Cl(2)-Sb(1)-Cl(2)#1	178.44(2)
Cl(2)-Sb(1)-Cl(3)	88.51(2)	Cl(2)-Sb(1)-Cl(3)#1	91.41(2)
Cl(3)-Sb(1)-Cl(2)#1	91.41(2)	Cl(3)#1-Sb(1)-Cl(2)#1	88.50(2)
Cl(3)-Sb(1)-Cl(3)#1	173.99(4)		

Symmetry code: for **1 :** #1 -x+3/2, y, -z+1; #4 x, y+1, z. for **2 :** #1 -x+2, y, -z+3/2; #6 x, y+1, z.

Table S2. Hydrogen bonds for **1** and **2** (Å and °)

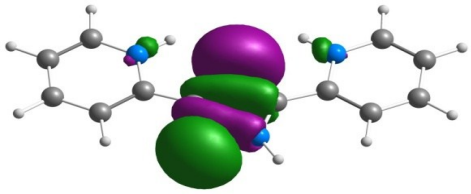
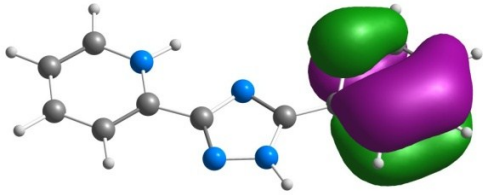
D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
		Compound **1**		
N(2)-H(2)...Cl(4)	0.93	2.12	3.018	163.1
		Compound **2**		
N(2)-H(2A)...Cl(4)#3	0.86	2.18	3.019	163.4
N(4)-H(4A)...Cl(4)#6	0.86	2.27	3.073	155.2
N(5)-H(5A)...Cl(2)#4	0.86	2.91	3.491	126.9
N(5)-H(5A)...Cl(2)#3	0.86	2.38	3.167	152.6
C(1)-H(1)...Cl(4)#2	0.93	2.63	3.409	142.4
C(5)-H(5)... Cl(3)	0.93	2.96	3.565	124.2
C(9)-H(9)... Cl(4)#3	0.93	2.94	3.781	151.4
C(10)-H(10)...Cl(3)#3	0.93	2.98	3.893	169.1
C(11)-H(11)...Cl(2)#4	0.93	2.82	3.459	126.9
C(12)-H(12)...Cl(3)#5	0.93	2.95	3.865	169.3

Symmetry code: for **1** #1 -x+1, y, -z+3/2. for **2** #1 -x+2, y, -z+3/2; #2 -x+3/2, -y+3/2, -z+1; #3 x, -y, z-1/2; #4 -x+2, y-2, -z+3/2; #5 x, y-1, z; #6 x, y+1.

Table S3 Wavelengths, transition types and oscillator strengths of UV-vis absorption spectrum for 2-bpt$^{+\bullet}$ at the B3LYP/6-31+g(d, p) level

Wavelength (nm)	Transition types	Oscillator strength
337.70	58A→60A 0.29902 59A→64A 0.57568 58B→59B 0.60780 58B→60B 0.31064	0.4362
283.78	57A→60A 0.35739 58B→60B 0.57762 58B→61B 0.28599	0.2072
254.57	56B→60B 0.2312 57B→60B 0.6585 57B→61B 0.2023	0.1055

Table S4 Orbitals representations of 2-bpt$^{+\bullet}$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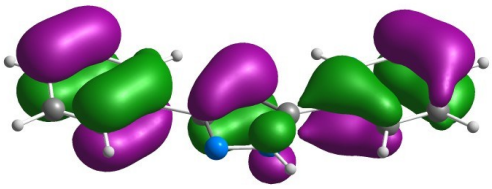	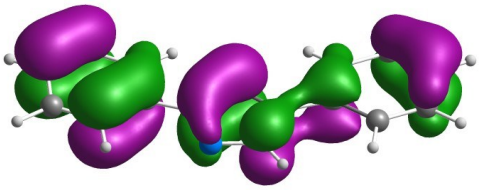
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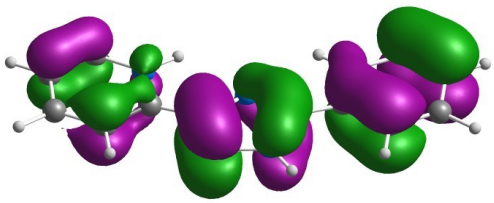	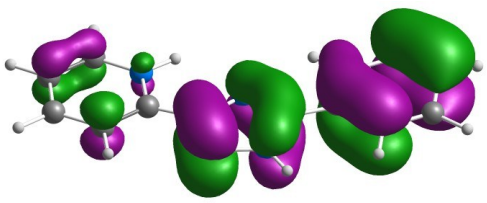
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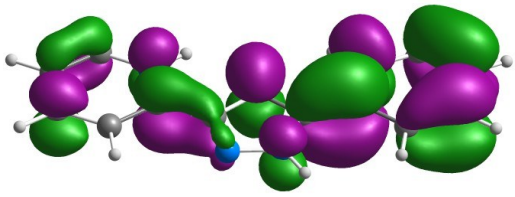	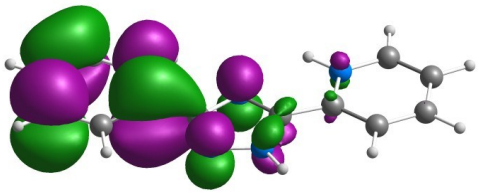
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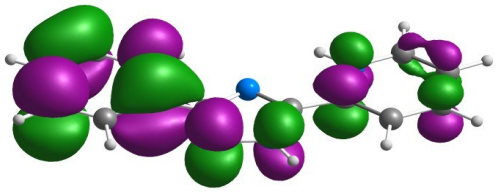	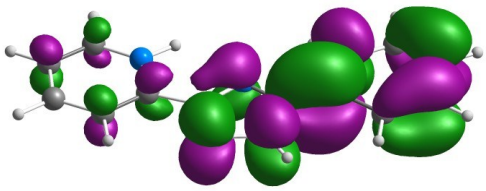
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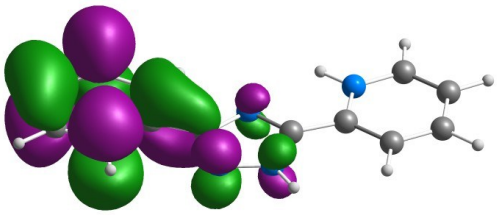	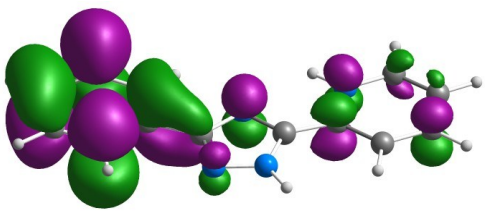
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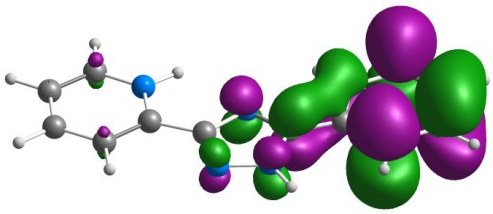	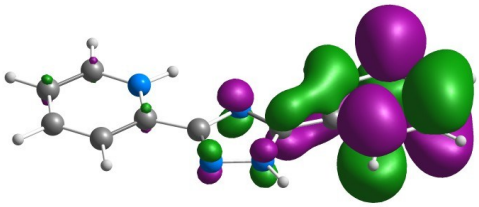
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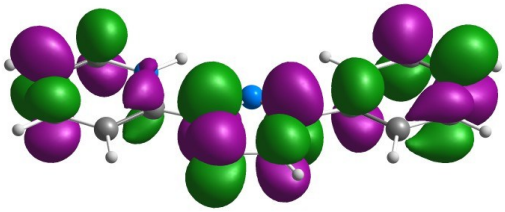	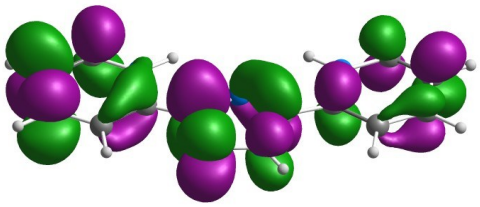
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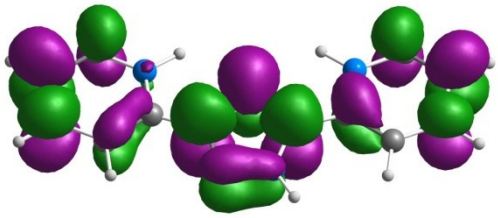	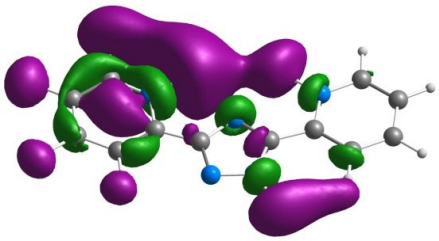
64A	64B

References

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