Supporting Information for

Ion Pair Charge-Transfer Thiogermanate Salts $[MV]_2Ge_4S_{10}$·xSol: Solvent Induced Crystal Transformation and Photocurrent Responsive Properties

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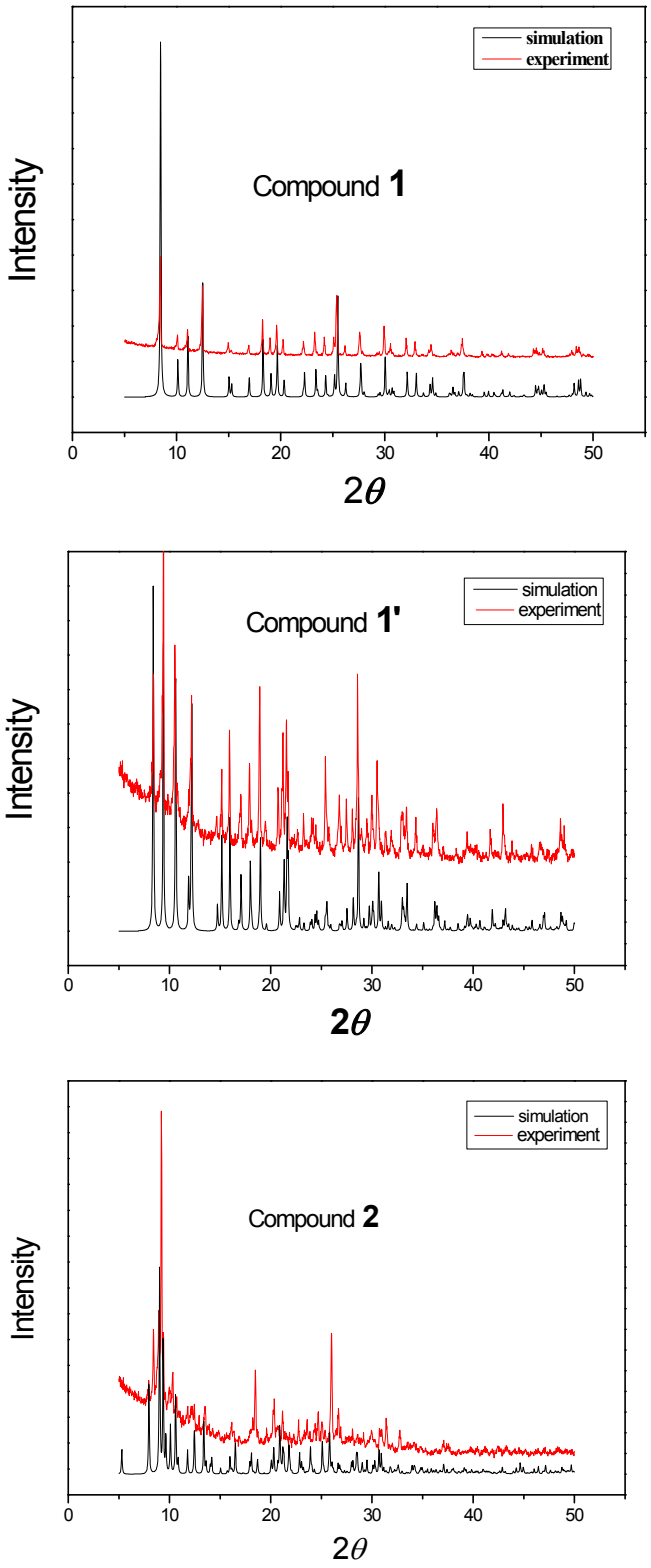


Figure S1. The experimental XRD patterns and the simulated patterns from the crystal data of compound **1** (yellow crystals), **1'** (orange crystals) and **2** (red crystals, that is sensible to moisture)

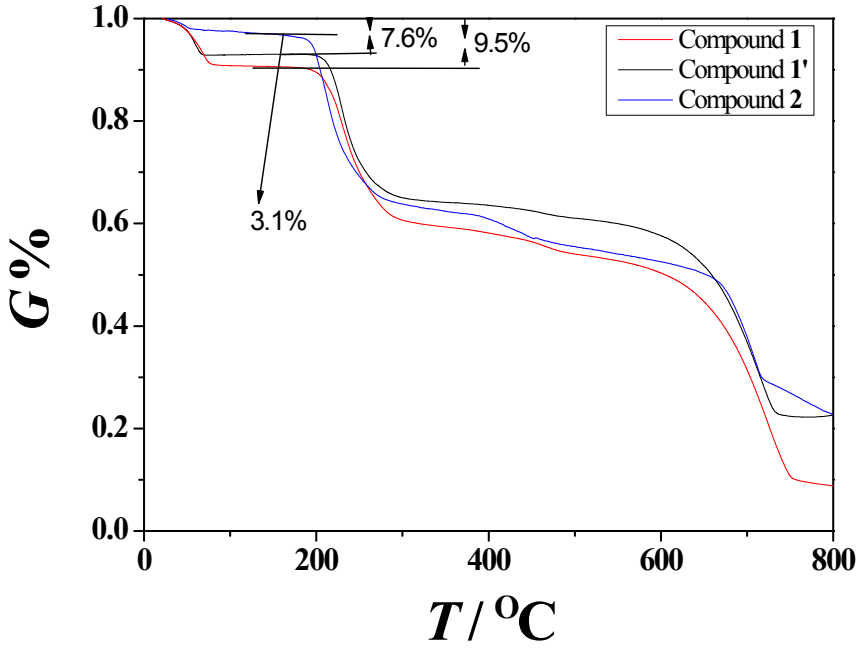


Figure S2. Thermal gravimetric measurements of **1**(red line), **1'**(black line) and **2** (blue line)

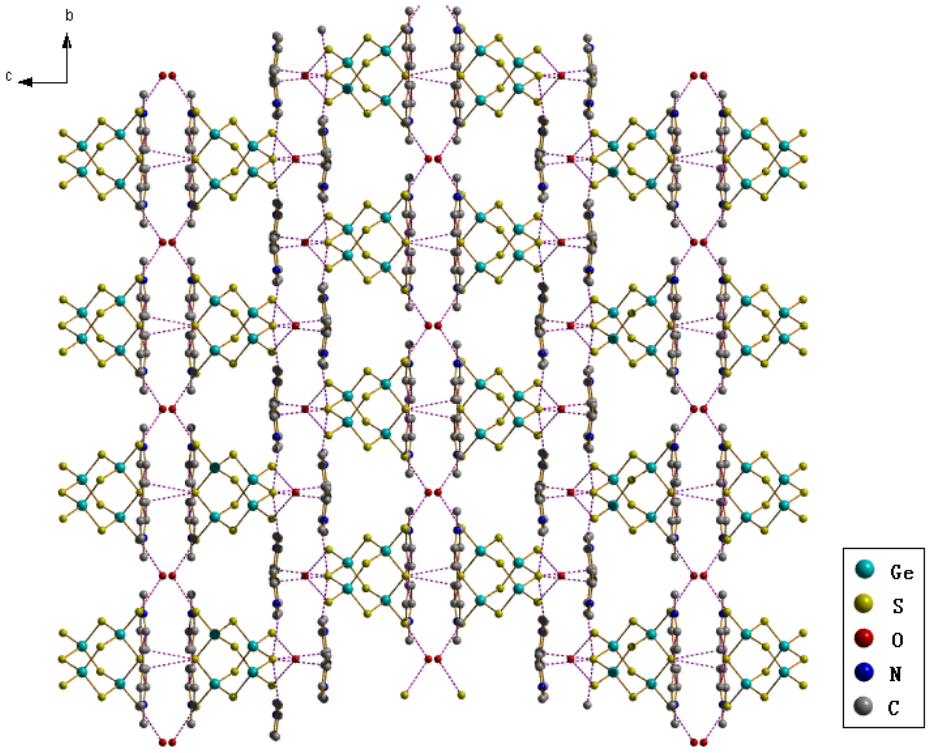
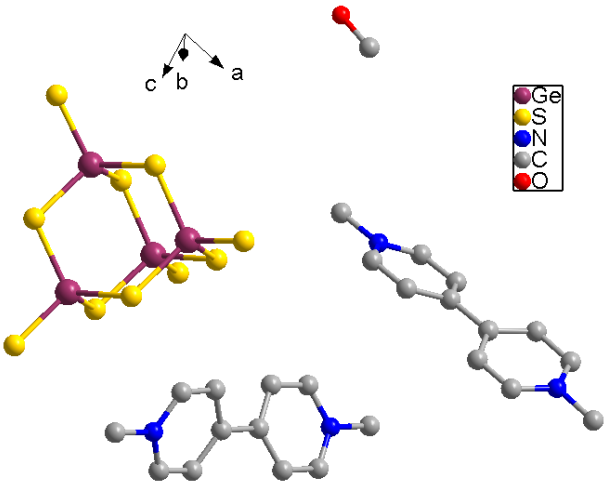
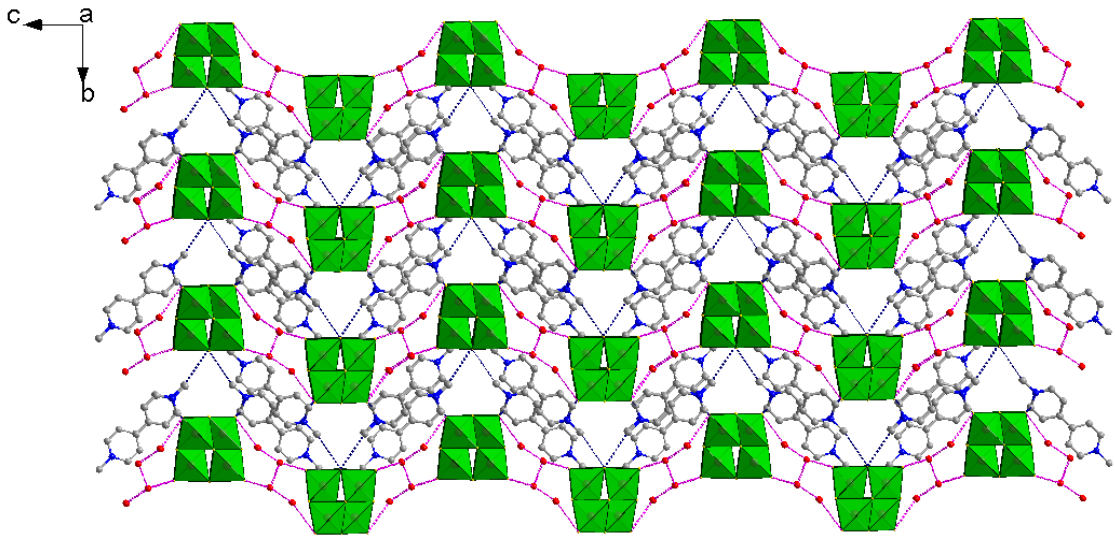


Figure S3. The molecular packing of **1**, viewed along the *a* direction.



(a)



(b)

Figure S4. (a) Asymmetric unit of **2**. (b) The molecular packing, viewed along the *a* direction, showing polyhedral view of the anion.

Table S1. Selected Ge–S and C–N bond lengths (Å) and angles (deg) for **1**，**1'** and **2**

1			
Ge1–S1	2.1262(9)	Ge1–S3	2.2317(8)
Ge1–S2	2.2513(7)	Ge1–S4	2.2382(8)
N1-C1	1.334(5)	N1-C5	1.343(4)
N1-C6	1.475(4)		
1'			
Ge1 #1–S1(t)	2.129(3)	Ge1–S3(b)	2.229(3)
Ge1–S2(b)	2.221(2)	Ge1–S4(b)	2.247(3)
Ge2 #1–S5(t)	2.126(3)	Ge2–S3(b)	2.232(3)
Ge2–S4(b)	2.233(3)	Ge2–S6(b)	2.238(2)
Ge1#2–S2(b)	2.221(2)	Ge2#2–S4(b)	2.233(3)
Ge2–S6(b)	2.238(2)		
N1–C5	1.312(15)	N1–C1	1.346(13)
N1–C11	1.488(13)	N2–C10	1.319(12)
N2–C6	1.326(13)	N2–C12	1.468(12)
2			
Ge1–S1(t)	2.123(3)	Ge1–S3(b)	2.247(3)
Ge1–S2(b)	2.241(3)	Ge1–S4(b)	2.229(3)
Ge2–S5(t)	2.119(3)	Ge2–S2(b)	2.240(3)
Ge2–S7(b)	2.257(3)	Ge2–S6(b)	2.242(3)
Ge3–S8(t)	2.126(3)	Ge3–S9(b)	2.246(3)
Ge3–S6(b)	2.238(3)	Ge3–S3(b)	2.232(3)

Ge4–S10(t)	2.132(3)	Ge4–S9(b)	2.248(3)
Ge4–S7(b)	2.249(3)	Ge4–S4(b)	2.216(3)
N1–C1	1.342(16)	N1–C5	1.342(17)
N1–C11	1.496(17)	N2–C6	1.322(16)
N2–C10	1.374(14)	N2–C12	1.480(15)
N3–C17	1.337(15)	N3–C13	1.333(15)
N3–C23	1.455(13)	N4–C22	1.337(14)
N4–C18	1.348(12)	N4–C24	1.471(14)

Symmetry transformations used to generate equivalent atoms: #1) *x*, *y*, *z*; #2) 1–*x*, *y*, 1/2–*z*; t) terminal; b) bridged.

Table S2. C–H···S hydrogen bonds and C···S short contacts for **1**，**1'** and **2**

C–H···S hydrogen bonds

D–H···A	D–H (Å)	H···A (Å)	D–H···A (Å)	D–H···A (deg)
		1		
C2–H2···S1	0.940	2.855	3.730	155.47
C5–H5···S2	0.940	3.801	3.536	135.78
		1'		
C2–H2···S1	0.940	2.879	3.696	146.10
C9-H9···S5	0.942	2.821	3.689	153.61
C12-H12···S5	0.971	2.873	3.542	126.88
		2		
C9–H9···S1	0.930	2.812	3.466	128.29
C7–H7···S5	0.930	2.749	3.518	140.56
C5–H5···S8	0.930	2.854	3.620	140.49

C···S short contacts (Å)

1			
C3···S2	3.492		
1'			
C1···S2	3.346	C6···S5	3.435
2			
C8···S2	3.465	C10···S3	3.157
C13···S3	3.252	C14···S3	3.495
C14···S9	3.345	C22···S9	3.368