Electronic Supplementary Material for CrystEngComm

Aryl azo imidazoles assisted assembly of anion/anion-water through Salt formation

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SUPPORTING INFORMATION

Table S1. Selected bond length and bond angles.

Salt 1			
Br2 C16 1.889(3)	C14 C15 1.387(5)	N8 N7 1.101(4)	C3 C2 1.334(5)
Br1 C7 1.887(3)	C13 N8 1.632(5)	C7 C8 1.373(5)	C3 N2 1.367(4)
S1 C19 1.604(5)	C12 C11 1.325(5)	C7 C6 1.384(5)	C1 N1 1.309(5)
C16 C15 1.375(5)	C12 N5 1.344(4)	C9 C4 1.377(6)	C1 N2 1.331(5)
C16 C17 1.386(5)	C10 N5 1.284(5)	C9 C8 1.401(5)	C1 N3 1.537(5)
C17 C18 1.352(6)	C10 N6 1.323(5)	C6 C5 1.369(5)	C2 N1 1.350(4)
C18 C13 1.366(6)	C10 N7 1.643(5)	C5 C4 1.358(6)	N4 N3 1.129(4)
C14 C13 1.372(6)	C11 N6 1.359(5)	C4 N4 1.584(5)	C19 N9 1.151(4)
C15 C16 C17 120.9(3)	N5 C10 N6 111.5(4)	C6 C7 Br1 119.1(3)	N1 C1 N2 110.9(3)
C15 C16 Br2 119.5(3)	N5 C10 N7 114.6(4)	C4 C9 C8 120.0(4)	N1 C1 N3 115.9(4)
C17 C16 Br2 119.7(3)	N6 C10 N7 133.8(5)	C5 C6 C7 119.9(4)	N2 C1 N3 133.0(4)
C18 C17 C16 120.6(4)	C12 C11 N6 106.0(4)	C4 C5 C6 120.5(4)	C3 C2 N1 109.3(3)
C17 C18 C13 119.3(4)	N7 N8 C13 93.7(4)	C7 C8 C9 118.7(4)	N3 N4 C4 100.0(4)
C13 C14 C15 120.5(4)	N8 N7 C10 92.4(4)	C5 C4 C9 120.4(4)	C1 N2 C3 106.6(3)
C16 C15 C14 117.8(4)	C10 N6 C11 106.6(4)	C5 C4 N4 111.5(4)	N4 N3 C1 100.1(4)
C18 C13 C14 121.0(4)	C10 N5 C12 106.1(3)	C9 C4 N4 128.0(4)	C1 N1 C2 106.5(3)
C18 C13 N8 108.1(4)	C8 C7 C6 120.6(3)	C2 C3 N2 106.7(3)	N9 C19 S1 178.7(4) .
C14 C13 N8 130.7(5)	C8 C7 Br1 120.4(3)	C11 C12 N5 109.8(4)	
Salt 2			
I1 C7 2.096(4)	C3 N2 1.357(5)	C5 C4 1.400(5)	
C1 N1 1.325(5)	N4 N3 1.264(4)	C4 C9 1.392(5)	
C1 N2 1.340(4)	N4 C4 1.412(5)	C8 C9 1.384(5)	
C1 N3 1.389(5)	C7 C8 1.386(5)	O2 N5 1.236(4)	
C2 C3 1.327(6)	C7 C6 1.388(5)	O3 N5 1.255(4)	
C2 N1 1.366(5)	C5 C6 1.364(5)	O4 N5 1.220(4)	
N1 C1 N2 108.2(3)	N4 N3 C1 110.7(3)	C5 C4 N4 125.0(3)	
N1 C1 N3 129.6(3)	C8 C7 C6 120.2(3)	C9 C8 C7 119.9(3)	
N2 C1 N3 122.3(3)	C8 C7 I1 119.5(3)	C8 C9 C4 119.3(3)	
C3 C2 N1 108.2(4)	C6 C7 I1 120.2(3)	C5 C6 C7 120.7(4)	
C2 C3 N2 107.3(3)	C6 C5 C4 119.2(3)	O4 N5 O2 120.1(4)	
C1 N1 C2 107.9(4)	C9 C4 C5 120.6(3)	O4 N5 O3 121.6(3)	
C1 N2 C3 108.4(3)	C9 C4 N4 114.5(3)	O2 N5 O3 118.3(3)	
N3 N4 C4 114.9(3)			
Salt 3			
I1 C1 2.094(4)	C4 C5 1.368(5)		
Cl1 O4 1.399(3)	C4 C6 1.391(5)	C7 N5 1.332(5)	
Cl1 O3 1.404(3)	C2 C3 1.381(5)	C7 N3 1.391(5)	
Cl1 O2 1.418(3)	C3 C6 1.378(5)	C9 C8 1.355(5)	
Cl1 O1 1.421(4)	C6 N1 1.411(5)	C9 N4 1.365(5)	
C1 C2 1.381(5)	N1 N3 1.256(4)	C8 N5 1.362(5)	
C1 C5 1.394(5)	C7 N4 1.324(4)		
O4 Cl1 O3 110.6(2)	C5 C4 C6 119.8(3)	N4 C7 N5 108.0(3)	
O4 Cl1 O2 112.7(2)	C4 C5 C1 119.9(3)	N4 C7 N3 121.7(3)	
O3 Cl1 O2 109.3(2)	C1 C2 C3 119.6(3)	N5 C7 N3 130.3(3)	
O4 Cl1 O1 107.1(3)	C6 C3 C2 120.2(3)	N1 N3 C7 111.8(3)	
O3 Cl1 O1 109.8(3)	C3 C6 C4 120.2(3)	C8 C9 N4 106.9(3)	
O2 Cl1 O1 107.2(3)	C3 C6 N1 115.6(3)	C9 C8 N5 106.9(4)	
C2 C1 C5 120.2(3)	C4 C6 N1 124.2(3)	C7 N5 C8 109.0(3)	
C2 C1 I1 120.2(3)	N3 N1 C6 113.9(3)	C7 N4 C9 109.1(3)	
C5 C1 I1 119.6(3)			
Salt 4			

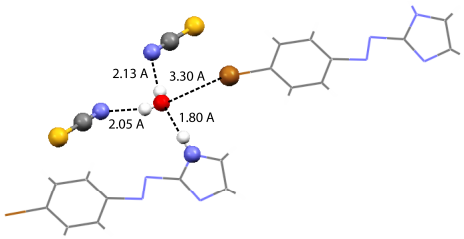
C13 C8 1.411(3)	C5 C6 1.390(3)	C2 C3 1.342(3)	
C13 C4 1.416(3)	C11 C10 1.397(3)	C2 N1 1.353(3)	
C13 C12 1.430(3)	C9 C10 1.346(3)	C3 N2 1.353(3)	
C4 C5 1.370(3)	C6 C7 1.357(3)	N3 N4 1.259(2)	
C4 N4 1.425(2)	C1 N1 1.320(2)	N5 O2 1.203(2)	
C8 C9 1.412(3)	C1 N2 1.327(2)	N5 O1 1.217(2)	
C8 C7 1.425(3)	C1 N3 1.383(2)	N5 O3 1.236(2)	
C12 C11 1.370(3)			
C8 C13 C4 118.19(18)	C13 C8 C7 119.4(2)	C9 C10 C11 120.4(2)	N3 N4 C4 114.30(16)
C8 C13 C12 118.53(19)	C9 C8 C7 121.0(2)	N1 C1 N2 107.73(19)	C1 N1 C2 109.21(18)
C4 C13 C12 123.28(19)	C11 C12 C13 119.3(2)	N1 C1 N3 121.44(19)	C1 N2 C3 108.83(18)
C5 C4 C13 120.72(19)	C4 C5 C6 120.8(2)	N2 C1 N3 130.83(19)	C6 C7 C8 120.3(2)
C5 C4 N4 123.49(19)	C12 C11 C10 121.4(2)	C3 C2 N1 107.0(2)	O2 N5 O1 119.6(2)
C13 C4 N4 115.79(17)	C10 C9 C8 120.8(2)	C2 C3 N2 107.2(2)	O2 N5 O3 122.0(2)
C13 C8 C9 119.6(2)	C7 C6 C5 120.5(2)	N4 N3 C1 112.11(16)	O1 N5 O3 118.5(2)
Salt 5			
C10 C1 1.415(5)	C7 C8 1.403(6)	C23 C14 1.436(5)	C24 N6 1.318(5)
C10 C9 1.422(5)	C11 N4 1.330(5)	C14 C15 1.384(5)	C24 N5 1.328(5)
C10 C5 1.429(5)	C11 N3 1.349(5)	C14 N8 1.407(5)	C24 N7 1.395(5)
C1 C2 1.363(5)	C11 N2 1.394(5)	C18 C17 1.414(6)	C26 C25 1.354(6)
C1 N1 1.419(5)	C12 C13 1.336(6)	C18 C19 1.414(5)	C26 N6 1.358(5)
C5 C4 1.412(6)	C12 N4 1.380(6)	C19 C20 1.343(6)	C25 N5 1.370(6)
C5 C6 1.414(5)	C13 N3 1.352(5)	C15 C16 1.399(7)	N8 N7 1.258(4)
C9 C8 1.363(6)	N2 N1 1.267(4)	C22 C21 1.369(6)	O8 N11 1.256(4)
C6 C7 1.361(6)	C23 C22 1.409(6)	C20 C21 1.383(6)	N11 O9 1.189(4)
C2 C3 1.395(6)	C23 C18 1.416(6)	C17 C16 1.357(6)	N11 O10 1.234(4)
C4 C3 1.352(5)			
C1 C10 C9 123.7(4)	C9 C8 C7 120.1(4)	C18 C23 C14 118.1(4)	C17 C16 C15 121.0(5)
C1 C10 C5 118.1(4)	C4 C3 C2 120.3(4)	C15 C14 N8 124.0(4)	N6 C24 N5 110.9(4)
C9 C10 C5 118.2(4)	N4 C11 N3 110.0(4)	C15 C14 C23 120.1(4)	N6 C24 N7 120.8(4)
C2 C1 C10 120.8(4)	N4 C11 N2 120.8(4)	N8 C14 C23 115.8(3)	N5 C24 N7 128.2(4)
C2 C1 N1 124.0(4)	N3 C11 N2 129.1(4)	C17 C18 C19 121.4(4)	C25 C26 N6 107.4(4)
C10 C1 N1 115.1(3)	C13 C12 N4 111.0(4)	C17 C18 C23 119.8(4)	C26 C25 N5 107.8(4)
C4 C5 C6 121.8(4)	C12 C13 N3 105.6(4)	C19 C18 C23 118.7(4)	N7 N8 C14 115.6(4)
C4 C5 C10 118.8(4)	N1 N2 C11 112.0(3)	C20 C19 C18 120.8(5)	N8 N7 C24 111.9(4)
C6 C5 C10 119.4(4)	N2 N1 C1 114.2(3)	C14 C15 C16 120.2(4)	C24 N6 C26 107.5(4)
C8 C9 C10 120.9(5)	C11 N4 C12 104.7(3)	C21 C22 C23 119.4(5)	C24 N5 C25 106.4(4)
C7 C6 C5 120.0(4)	C11 N3 C13 108.8(4)	C19 C20 C21 120.5(4)	O9 N11 O10 117.2(4)
C1 C2 C3 120.8(4)	C22 C23 C18 119.1(4)	C16 C17 C18 120.6(5)	O9 N11 O8 126.4(5)
C3 C4 C5 121.1(4)	C22 C23 C14 122.9(4)	C22 C21 C20 121.5(4)	O10 N11 O8 116.4(4)
C6 C7 C8 121.4(4)			

Table S2. Observed Non-covalent interactions in salt **1-5.**

D–H···A	H···A (Å)	D···A (Å)	D–H···A (◦)
Salt 1			
N1–H1N····O1	1.839 (40)	2.696 (5)	173.88 (26)
O1-H1O····N9	2.126 (70)	2.915 (6)	163.85 (95)
O1–H2O····N9	2.035 (45)	2.843 (6)	162.72 (61)
N5–H5N····N2	1.884 (3)	2.740 (5)	173.33 (26)
N6–H6N····N8	2.573 (5)	2.616 (7)	83.31 (32)
N5–H5N····N2	1.884 (3)	2.740 (5)	173.33 (26)
Salt 2			
N1–H1N····O1	1.851 (43)	2.656 (5)	160.35 (15)
O1–H1O····O3	1.942 (61)	2.753 (5)	175.95 (99)
O1–H2O····O3	2.109 (52)	2.806 (5)	150.51 (24)
N2–H2N····O2	1.807 (46)	2.705 (5)	173.41 (37)
N2–H2N····O4	2.634 (43)	3.188 (5)	120.54 (48)

O1–H2O····O2	2.779 (58)	3.405 (8)	139.87 (9)
N1–H1N····N4	2.500 (40)	2.684 (4)	93.43 (84)
Salt 3			
O5–H1O····O1	2.201 (10)	3.037 (6)	129.24 (98)
O5–H5O····O1	2.110 (63)	2.895 (6)	154.09 (69)
N4–H4N····O5	1.988 (45)	2.773 (4)	162.80 (48)
N5–H3N····O2	2.001 (41)	2.896 (5)	170.57 (75)
N5–H3N····N1	2.630 (40)	2.724 (5)	86.21 (48)
Salt 4			
N1–H1N····O3	1.845 (2)	2.703 (2)	174.72 (13)
N2–H2N····O1	2.364 (2)	2.913 (3)	165.98 (12)
N4–H4····N2	2.613 (2)	2.729 (3)	88.46 (13)
Salt 5			
N6–H6N····N1	1.815 (38)	2.685(.005)	177.74 (79)
N5–H5N····O4	1.754 (50)	2.818(.004)	160.93 (49)
O4–HOB····O2	1.778 (40)	2.841(.005)	170.10 (24)
O4–HOA····O3	1.947 (46)	2.923(.004)	158.89 (92)
N2–H2N····O1	2.340 (29)	3.166(.005)	169.47 (81)
N2–H2N····O2	2.472 (30)	3.078(.005)	130.17 (53)
N2–H2N····N4	2.647 (37)	2.726(.005)	86.40 (44)
N5–H5N····N8	2.553 (68)	2.687(.005)	84.81 (48)
O4–HOB····O3	2.346 (37)	3.139(.004)	129.41 (66)
O4–HOB····N9	2.422 (40)	3.450(.006)	159.82 (86)
N2–H2N····N2	2.797 (29)	3.567(.005)	154.12 (62)
O4–HOA····N9	2.854 (43)	3.864(.005)	170.24 (48)

(a)



(b)

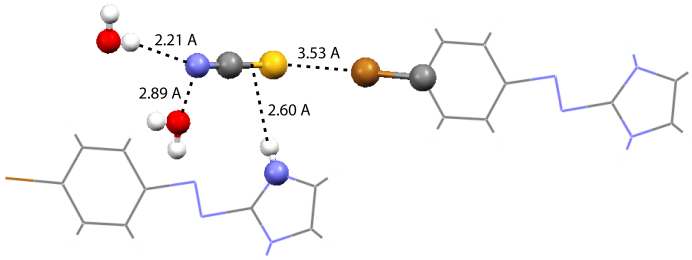


Figure S1. Hydrogen bonding pattern of (a) crystal water and (b) SCN^- anion in salt **1**.

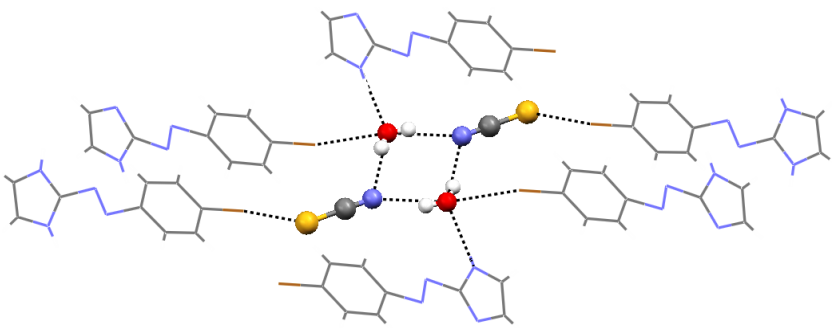


Figure S2. Water-thiocyanate-water-thiocyanate tetramer in salt 1.

(a) (b)

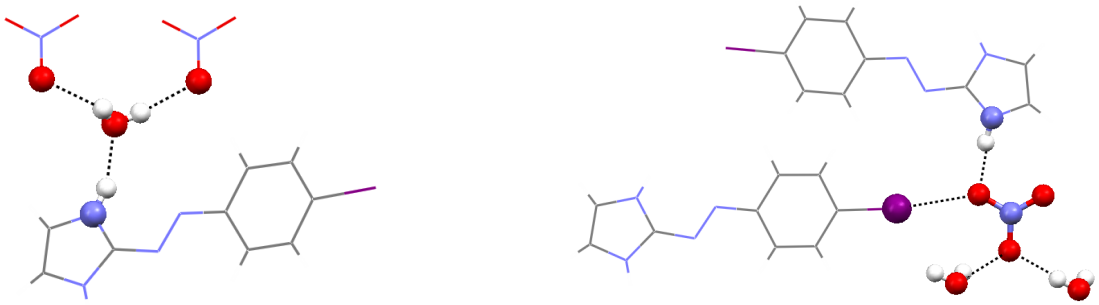


Figure S3. Hydrogen bonding pattern of (a) crystal water and (b) NO_3^- anion in salt **2**.

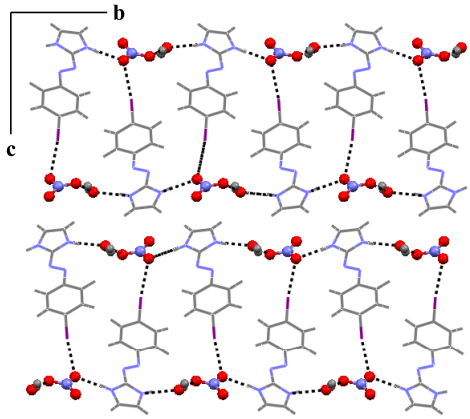


Figure S4. Packing of salt **2** along *a* axis.

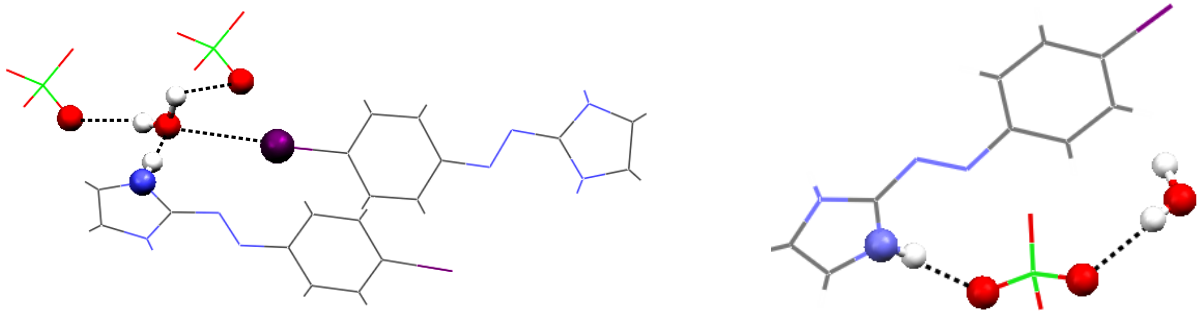


Figure S5. Hydrogen bonding pattern of (a) crystal water and (b) ClO_4^- anion in salt **3**.

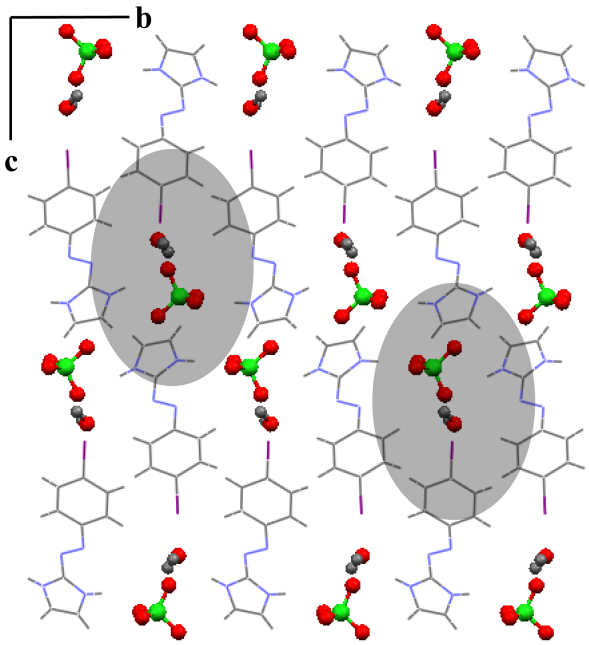


Figure S6. Elliptical pocket for anion and water in salt **3** along *a* axis.

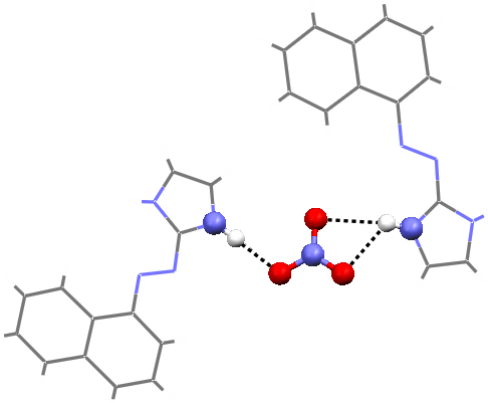


Figure S7. Hydrogen bonding pattern of anion in salt **4**.

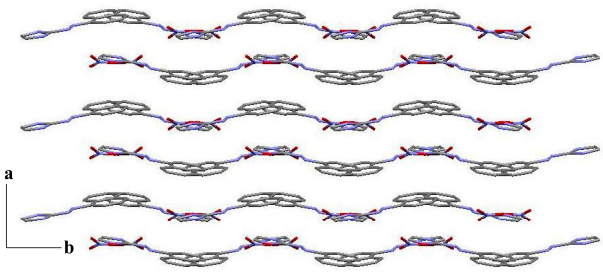


Figure S8. Packing of salt **4** along *c* axis.

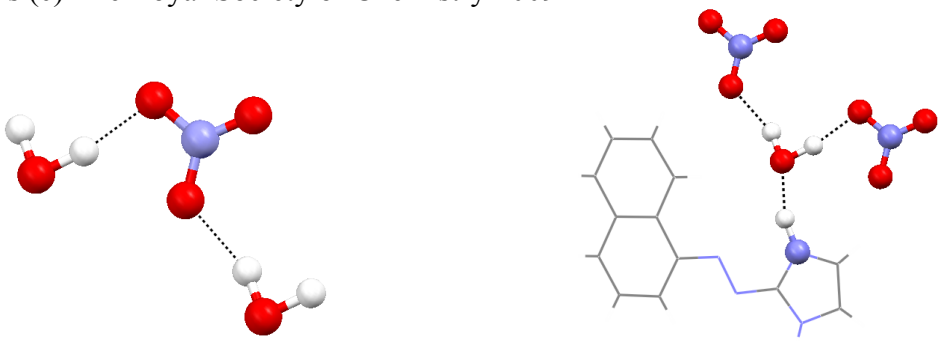


Figure S9. Hydrogen bonding pattern of (a) crystal water and (b) ClO_4^- anion in salt **5**.

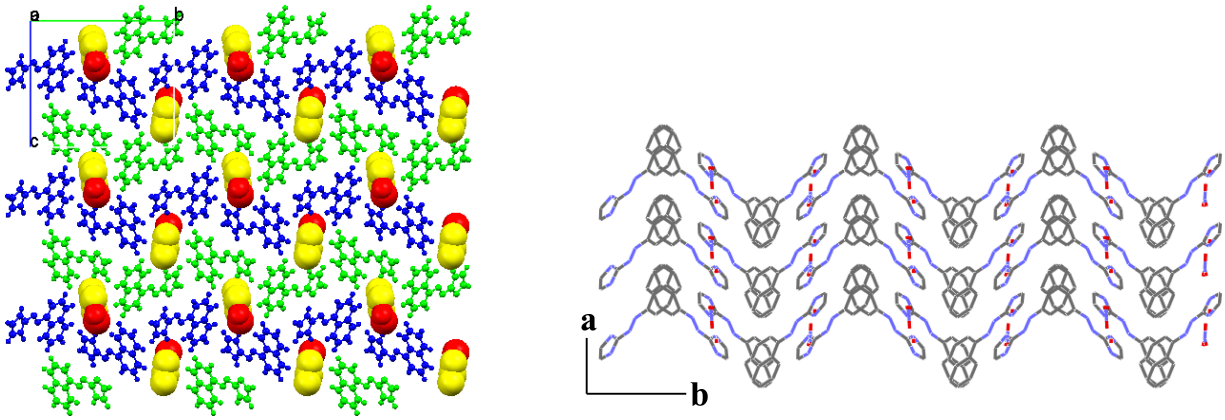


Figure S10. Packing of salt **5** along *a* axis and *c* axis.

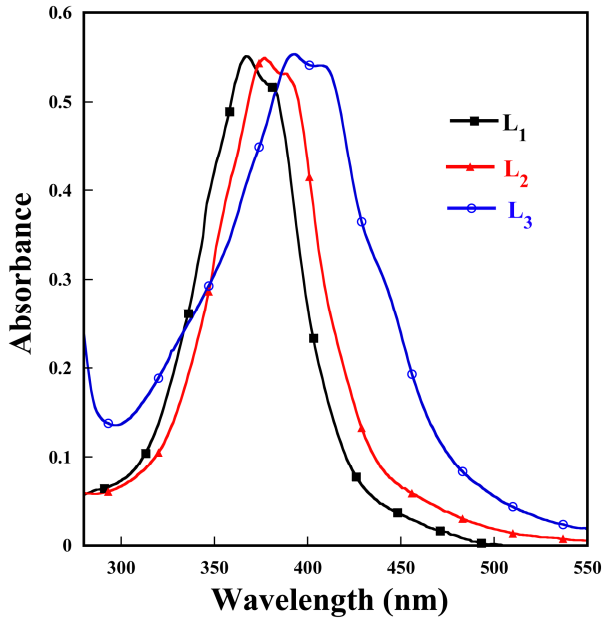


Figure S11. UV-vis absorption spectra of $\mathbf{L_{1\text{-}3}}$.

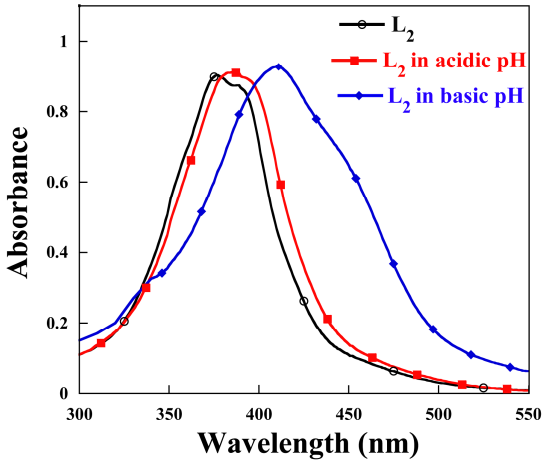


Figure S12. UV-vis absorption spectra of **L_2** in presence of acid and base.

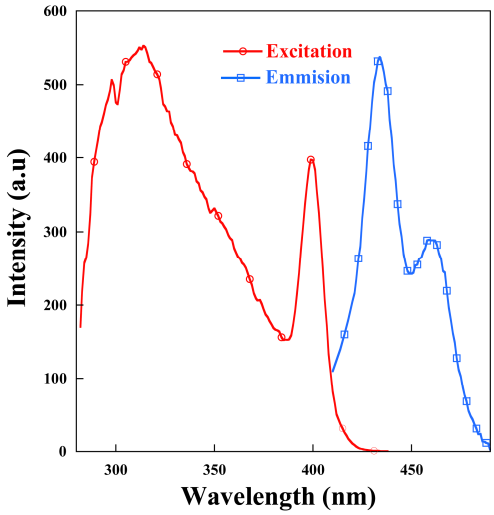


Figure S13. Excitation and emission spectra of **L_3**.

Table S3. Fluorescence quantum yield of **L_3** with different anionic input.

Sr. No.	Anionic input	Φ_F	$\Phi_F - \Phi_q$
1	Nil	0.025	0.000
2	Br^-	0.019	0.006
3	Cl^-	0.022	0.003
4	SCN^-	0.018	0.007
5	NO_3^-	0.014	0.011
6	ClO_4^-	0.001	0.024
7	CH_3COO^-	0.016	0.009
8	$CF_3SO_3^-$	0.014	0.008

9	BF_4^-	0.020	0.005

Table S4. Fluorescence quantum yield of **L_3** with different concentration of ClO_4^-.

Sr. No.	$[ClO_4^-]$ (M)	Φ_q	Φ_F/Φ_q
1	4×10^{-6}	0.0060	3.5000
2	8×10^{-6}	0.0031	6.7000
3	12×10^{-6}	0.0025	8.3000
4	16×10^{-6}	0.0018	11.700
5	20×10^{-6}	0.0016	13.000
6	24×10^{-6}	0.0013	16.000
7	28×10^{-6}	0.0011	18.900
8	32×10^{-6}	0.0010	21.000

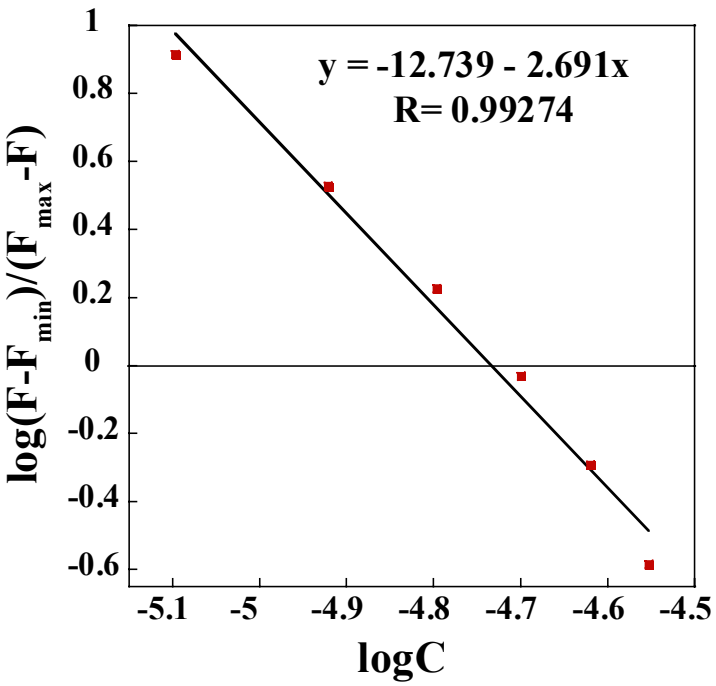


Figure S14. Determination dissociation constant (K_d). The apparent K_d is at the X intercept, at a value of –4.73. The inverse log of this is 1.9×10^{-5} M.

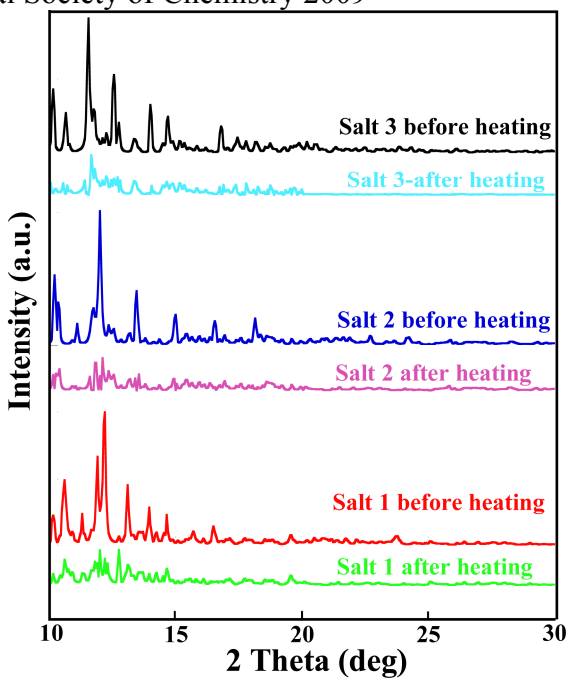


Figure S15. PXRD patterns of crystalline salt 1, salt 2 and salt 3 before and after heating.

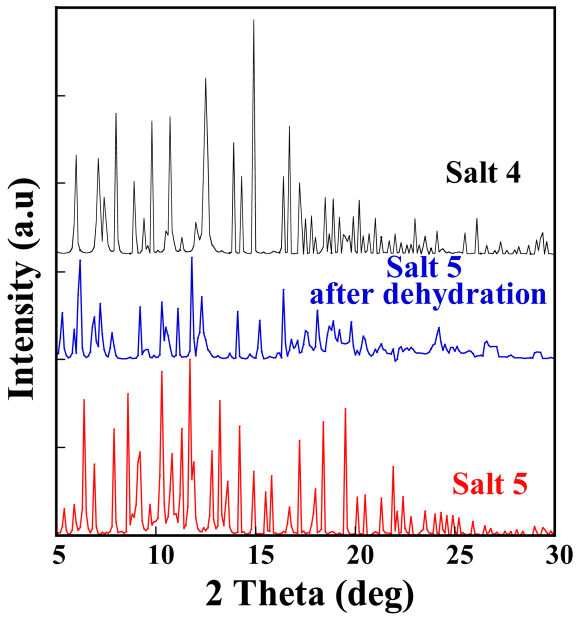


Figure S16. PXRD patterns of crystalline salt 4, salt 5 and salt 5 after removal of water.