Electronic Supplementary Material (ESI) for CrystEngComm.

Electronic Supplementary Information (ESI)

Turning Colour On and Off Using Molecular Disorder and Proton Transfer in Multi-Component Molecular Complexes

Charlotte L. Jones,[a] Chick C. Wilson[a] and Lynne H. Thomas[a]*

[a] Department of Chemistry, University of Bath, Bath, BA2 7AY, UK. Email: L.H.Thomas@bath.ac.uk

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1. Refinement Details for Complexes 2 and 4

The significant molecular disorder in complex **2** meant that significant constraints had to be applied in the refinement. The benzene rings were constrained to take a standard geometry using an AFIX 66 command. The C-C distances of the carboxylic acid groups and C-N distances of the disordered nitro groups were constrained to take standard values of 1.51 Å and 1.47 Å, respectively using a DFIX command. The N-O distances were constrained to take values of 1.22 Å. The C-O distances of the carboxylic acid groups were not restrained due to the ambiguity about the protonation state. These groups are 50:50 disordered between a carboxylic acid group and a carboxylate group. Pairs of C/N/O (A and B) atoms for the whole molecule were constrained to be equal to ensure sensible anisotropic displacement parameters were obtained; all atoms except the pivot nitro group were refined only isotropically. The occupancies of the two positions for each molecule were allowed to freely refine and these converged at approximately 50:50. The methanol molecule was also found to be disordered over two positions. The two positions were allowed to freely refine to approximately 50:50.

In complex **4**, one 4-iodoaniline molecule is 50:50 disordered over an inversion centre. In order to ensure chemically sensible bond lengths and angles were obtained, the benzene ring of this disordered molecule was constrained to take a standard geometry using an AFIX 66 command and the anisotropic displacement parameters for all carbon atoms in the ring (C70-C75) were constrained to take the same value using the EADP command.

Relaxation of this constraint resulted in unreasonable anisotropic displacement parameters for these atoms. The two positions for the 4IA molecule are displaced such that the I and N positions are very close. A series of constraints thus had to be applied to ensure that the C-C-N70/I2 angles and C-N70/I2 distances took approximately standard values. Firstly the EADP command was used to constrain the anisotropic displacement parameters of N70 and I2 to be the same; this was due to the close proximity of the two positions. SADI constraints were applied to ensure the C-C-I/N angles were chemically sensible; the C71-I2 bond length was constrained to be similar to the ordered C12-I1 bond length; the C74-N70 bond length was constrained to be similar to the C9-N4 bond length; the C-C-I/N bond angles on either side of the I/N group were constrained to be equal i.e. the C70-I2 distance should be the same as the C72-I2 distance and the C73-N70 distance should be the same as the C75-N70 distance.

2. Hydrogen bond details for 1 and 3-6

Table S1. Hydrogen bonding geometry (Å, °) for complexes **1** and **3-6**

D-H…A	**D-H**	**H···A**	**D···A**	**<(DHA)**
Complex **1**				
N1-H1A···O1(i)	0.93(3)	1.80(3)	2.727(3)	172(2)
N1-H1B···O1	0.94(3)	1.75(3)	2.681(3)	167(3)
N1-H1C···O1(ii)	0.94(3)	1.84(3)	2.763(3)	168(3)
Complex **3**				
O1-H10···O2	1.00(3)	1.50(3)	2.461(2)	159(3)
N3-H5···O2(iii)	0.90(3)	1.85(3)	2.744(2)	172(2)
N3-H6···O5(iv)	0.86(3)	2.41(2)	2.950(2)	122(2)
N3-H7···O3(v)	0.94(3)	1.80(3)	2.724(2)	168(2)
Complex **4**				
O2-H7···O1	0.89(7)	1.59(8)	2.441(5)	158(7)
N4-H20···O3(vi)	0.80(5)	2.12(5)	2.905(5)	166(5)
N4-H21···O3(vii)	0.94(7)	2.20(7)	2.944(6)	135(5)
N4-H22···O1(viii)	0.92(6)	1.96(6)	2.861(6)	165(5)
N4-H22···O7(viii)	0.92(6)	2.43(6)	3.026(6)	122(5)
Complex **5**				
N1-H1A···O4(ix)	0.92(2)	1.86(2)	2.755(2)	164(2)
N1-H3B···O3(x)	0.79(3)	1.94(3)	2.720(2)	165(2)
N1-H3C···O4(xi)	0.92(3)	1.87(3)	2.770(2)	168(2)
Complex **6**				
O1-H4···O2(xii)	0.82	1.81	2.625(2)	176
N3-H3A···O6(xiii)	0.86	2.46	3.257(2)	154
N3-H3B···O4(xiv)	0.86	2.46	2.921(2)	115

(i) x+1, y, z; (ii) x+1/2, y+5/2, -z; (iii) –x+1, -y, -z+1; (iv) x+2, y, z-1; (v) x+1, y+1, z-1; (vi) –x, -y, -z; (vii) x, y+1, z; (viii) x-1, y+1, z; (ix) x-1, y, z-1; (x) –x, y-1/2, -z+1; (xi) –x, y+1/2, -z+1; (xii) –x, -y-1, -z+1; (xiii) –x, -y, -z+2; (xiv) x, y-1, z

No hydrogen bond data is available for **2**. Due to the significant amount of crystallographic disorder in this molecular complex, it is not possible to accurately assign the protonation states of the molecules and therefore assign hydrogen atoms to the carboxyl and amine groups. The hydrogen atoms for these were therefore omitted from the model. There are also significant limitations in the determination of the hydrogen bond donor and acceptor atoms due to the close proximity of the two positions for the 3,5-dinitrobenzoic acid molecules. Therefore, no hydrogen bond details are recorded.

3. Photographs of complexes 1-6

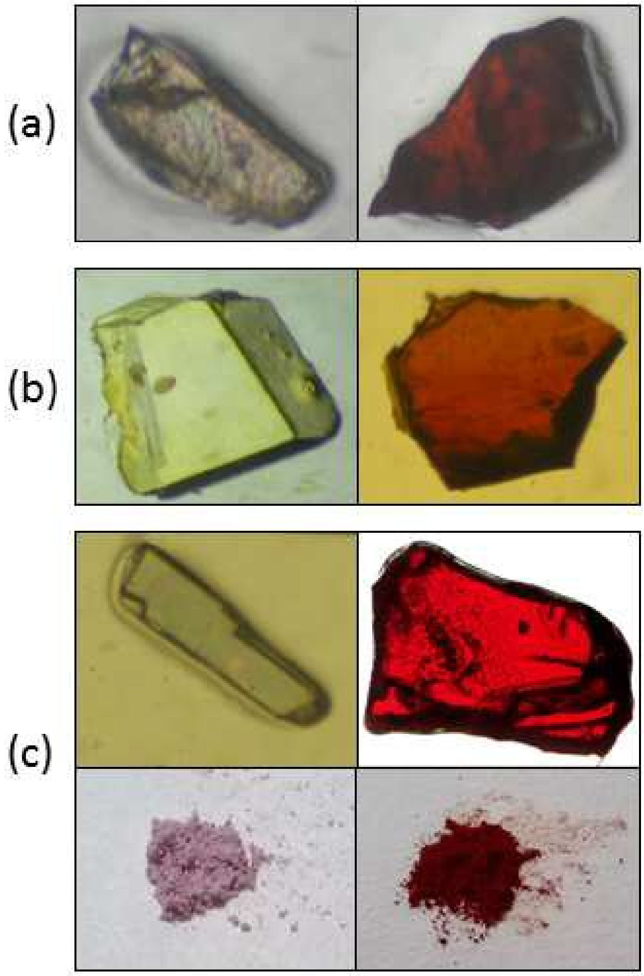

Fig. S1. Photographs of (a) crystals of **1** (left) and **2** (right); (b) crystals of **3** (left) and **4** (right); (c) crystals of **5** (top, left) and **6** (top, right), and powdered samples of **5** (bottom, left) and **6** (bottom, right).

3. Infrared spectra

Complex **2** has significant molecular disorder resulting in ambiguity in the assignment of protonation states of the 4-iodoaniline (4IA) and 3,5-dinitrobenzoic acid (3,5-DNBA) molecules; the geometry around the molecules was consistent with either neutral molecules, protonated 4IA molecules or deprotonated 3,5-DNBA molecules and it was not possible to resolve any H atom positions due to the disorder. IR spectra were therefore recorded. Spectra were recorded for the single component 4IA (Figure S2), 3,5-DNBA (Figure S3) and 3,5-dinitrosalylic acid (Figure S4) compounds. The spectra in the 3500-3000 cm^{-1} region are clearly different; the features corresponding to an NH_2 group in 4IA could therefore clearly be identified in this region.

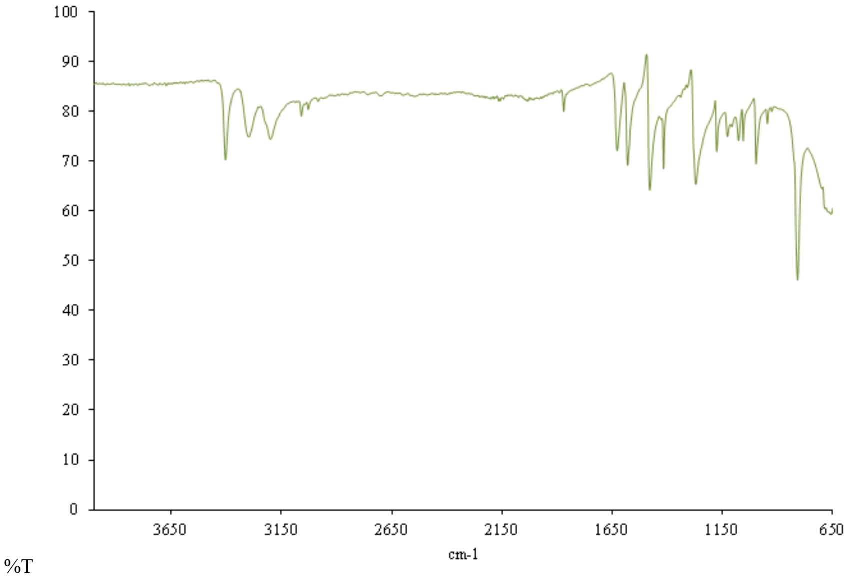

Fig. S2. IR spectrum for 4-iodoaniline

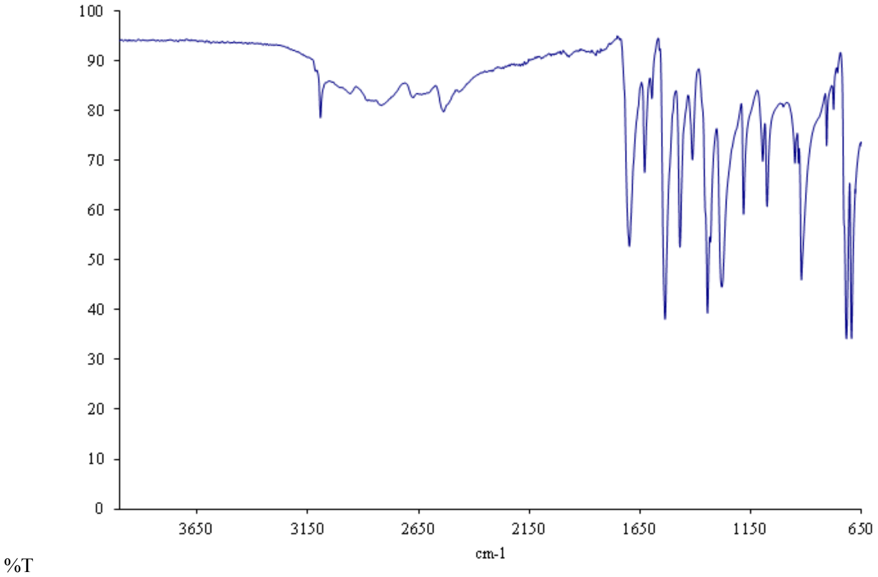

Fig. S3. IR spectrum for 3,5-dinitrobenzoic acid

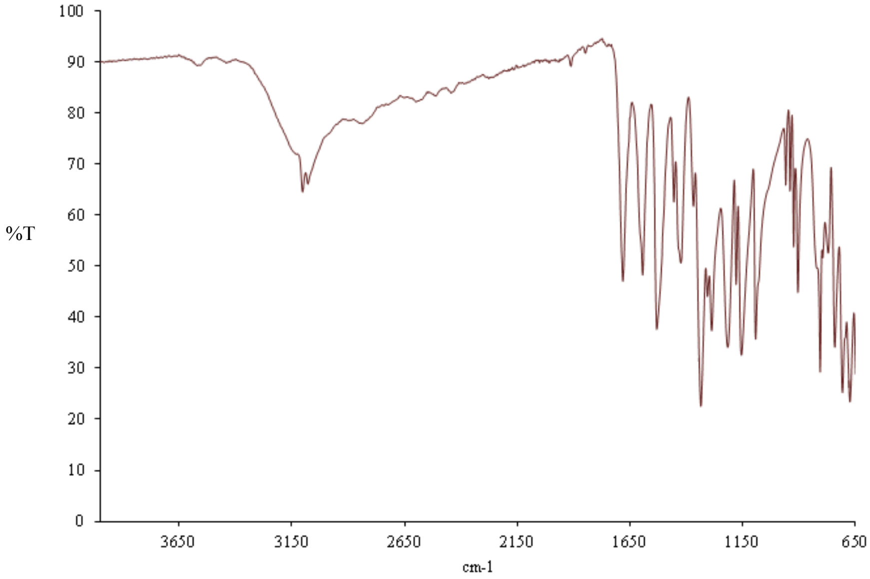

Fig. S4. IR spectrum for 3,5-dinitrosalicylic acid

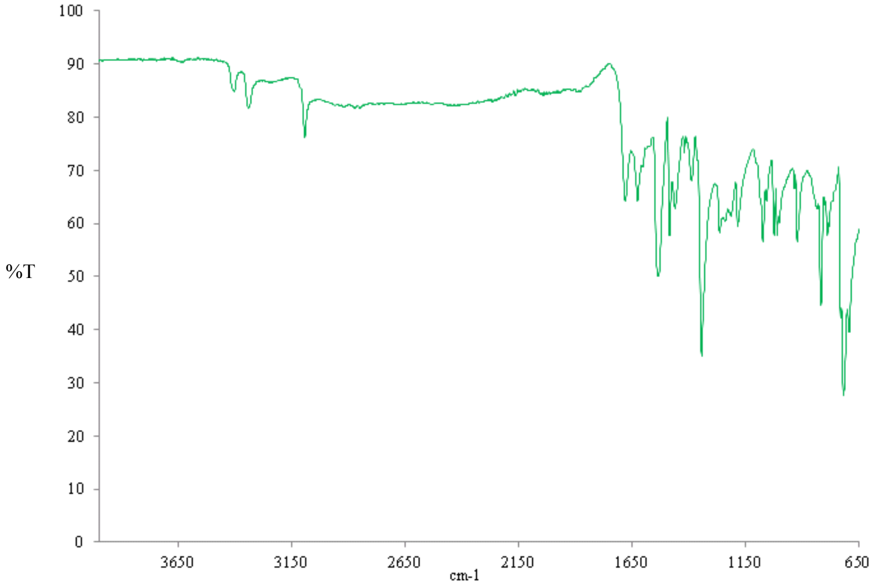

Fig. S5. IR spectrum for **2**

The IR spectrum of complex **2** (Figure S5) was therefore compared to that of 4IA and complexes **3** (Figure S6) and **4** (Figure S7) in which the protonation states could clearly be resolved from single crystal X-ray diffraction. Complex **3** contains only protonated 4IA molecules (with NH_3^+ groups) and the region 3500-3000 cm^{-1} shows significant differences to that of neutral 4IA consistent with a lowering of symmetry (Figure S6). Complex **4** contains a mixture of neutral and ionic 4IA molecules (and therefore a mixture of NH_2 and NH_3^+ groups; Figure S7). The IR spectra of complex **2** shows similarities to that of complex **4** and shows a pattern which has characteristics of both 4IA and complex **3**. Combined with crystallographic arguments, this is consistent with complex **2** being comprised of both neutral and ionic 4IA molecules.

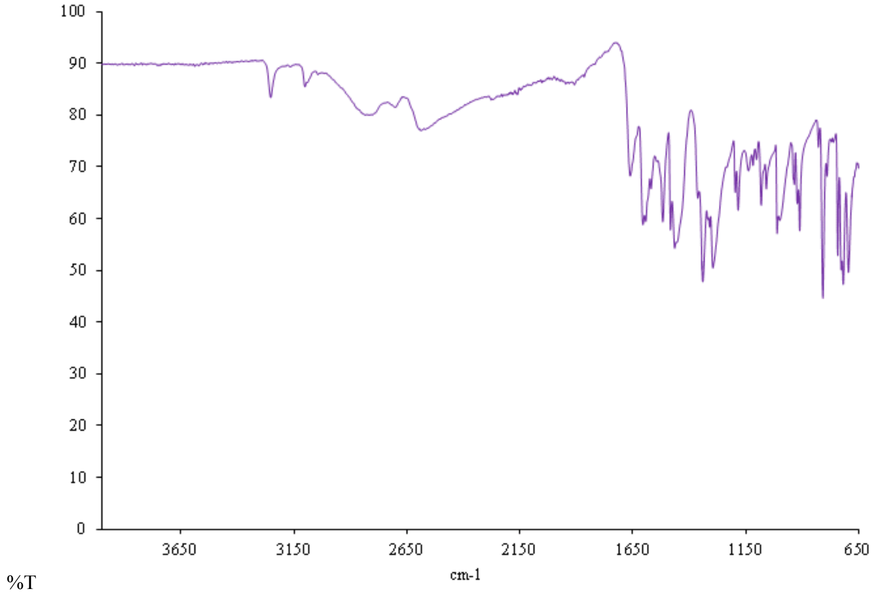

Fig. S6. IR spectrum for **3**

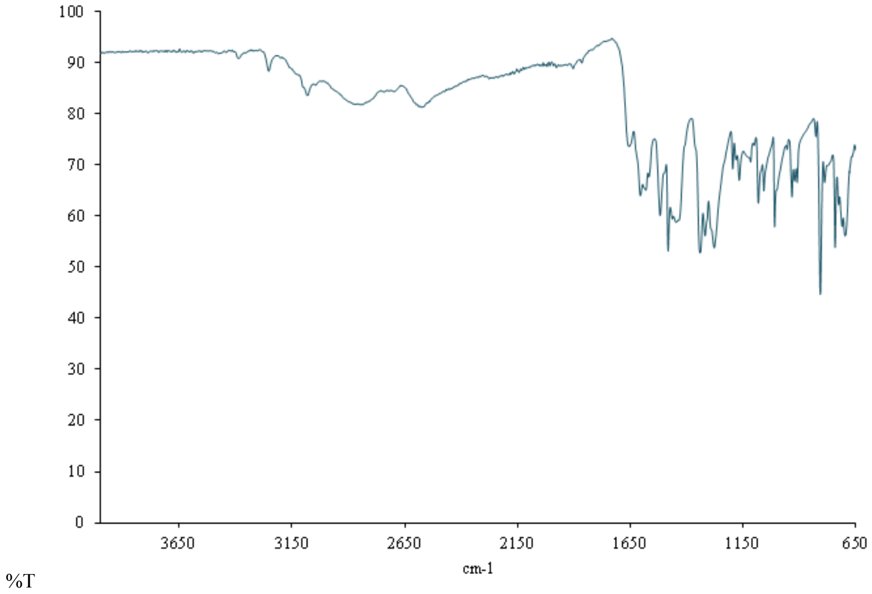

Fig. S7. IR spectrum for **4**

4. PXRD data for complexes 5 and 6

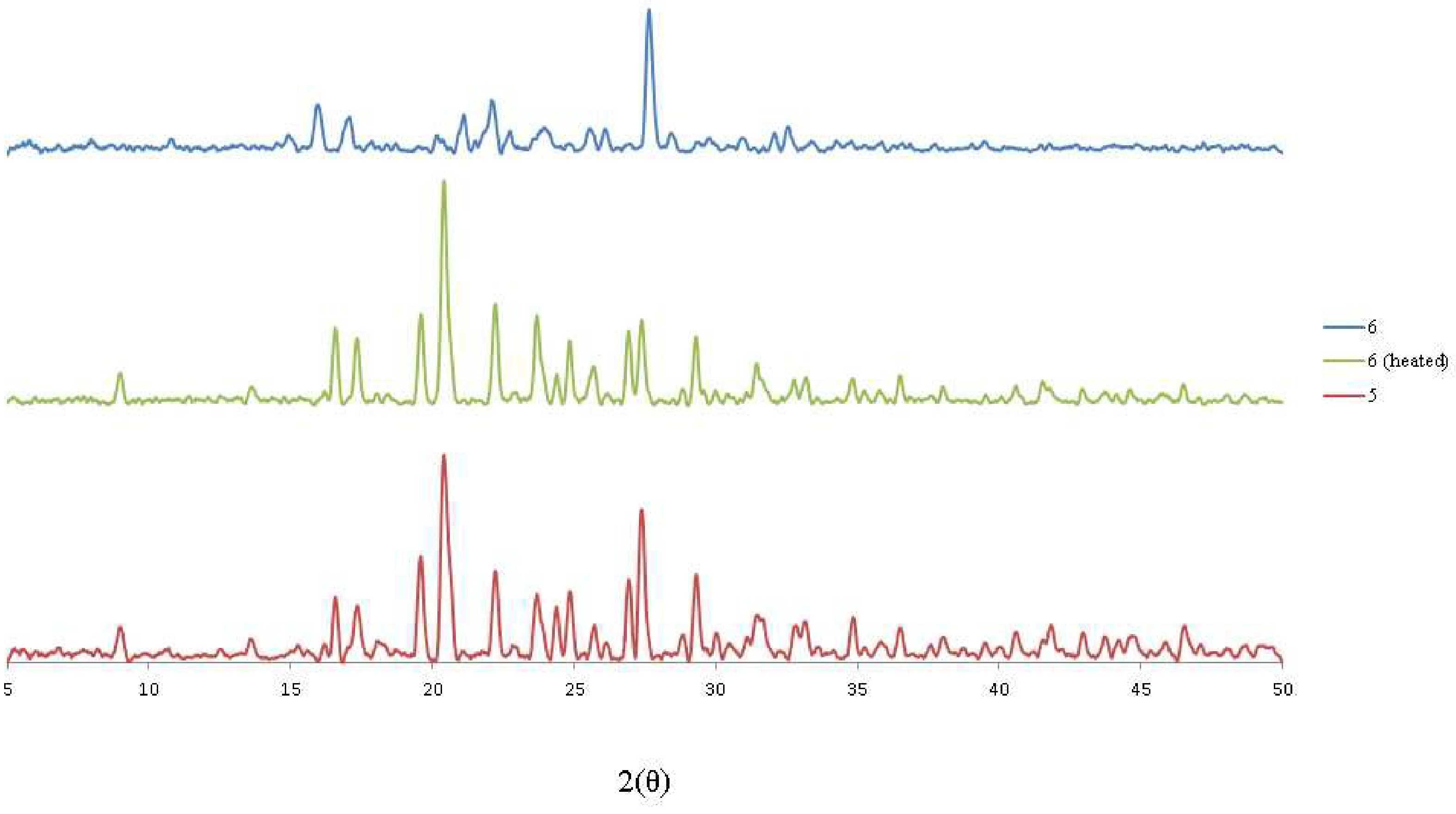

Fig. S8. PXRD data for complexes **5** and **6**, and a sample of **6** which has been heated to 80°C which had converted to **5**

5. Thermal analyses for complexes 5 and 6

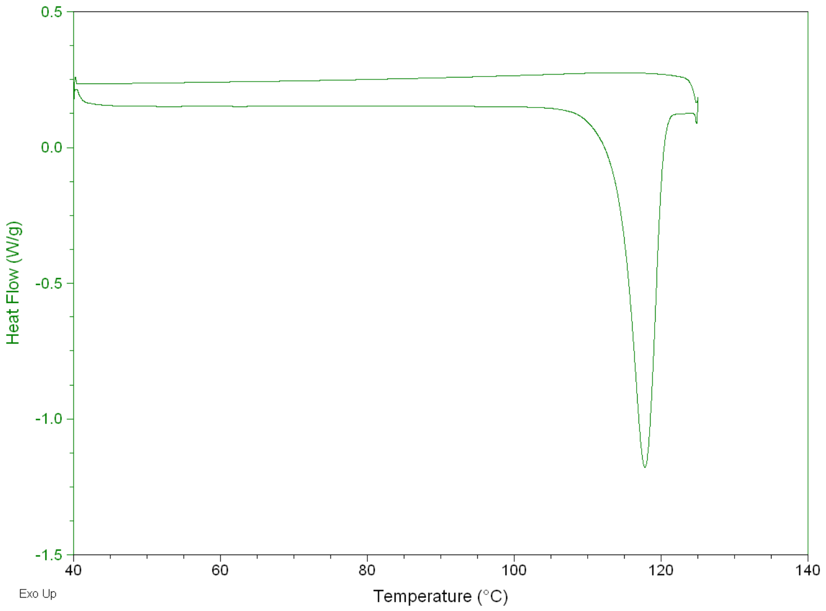

Fig. S8. DSC thermogram for complex **5**

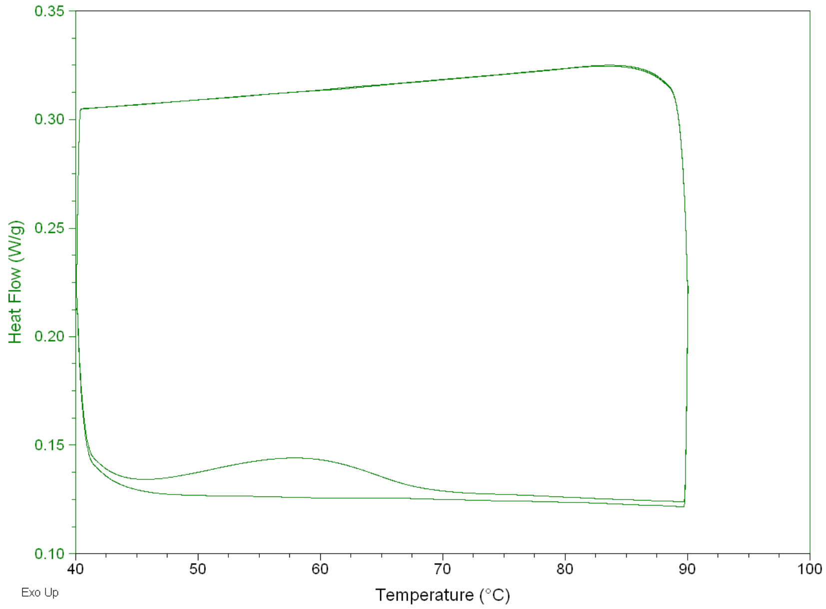

Fig. S9. Two-cycle DSC thermogram for complex **6**. The thermochromic conversion from **6** to **5** is irreversible.