Coordination networks incorporating halogen-bond donor sites and azobenzene groups

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Electronic Supplementary Information

S.1 Crystallographic Notes

The single crystal X-Ray structure **3-5** were determined on a Bruker Kappa Apex II diffractometer at 103 K using a fine-focus MoKα tube, λ=0.71073 Å. Data collection and reduction were performed by SMART and SAINT and absorption correction, based on multi-scan procedure, by SADABS. The structure were solved by SHELXL2008 [1] and refined on all independent reflections by full-matrix least-squares based on F^2 by using SHELX-2008 [1]. All the non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined by using a riding model. Figures are obtained with Mercury 3.5 [2].

S.1.1. Experimental details for 3 and supplementary figures

Crystals were very small needles, nearly squared in section and usually assembled in bundles. The crystal used for data collection was the largest one in our hands and under the microscope it appeared untwinned. Notwithstanding this, the results suggested that it was a two-component twin, with the first component largely greater than the second one.

It was very difficult to understand and identify the solvent included in the system **3**. Various models were tested and refined, but, at the end, the adopted one was preferred because it was the simplest possible. However, we suspect that the structure might contain not only isopropanol but also some solvated water. The crystal is twinned, as suggested by the number of observed intensities greater than the calculated ones, but it was impossible to determine the second, minor component, probably because the two lattices are largely overlapped. The large second coefficient of the weighting scheme and the large residues on the final difference map strongly suggest that the crystal is twinned.

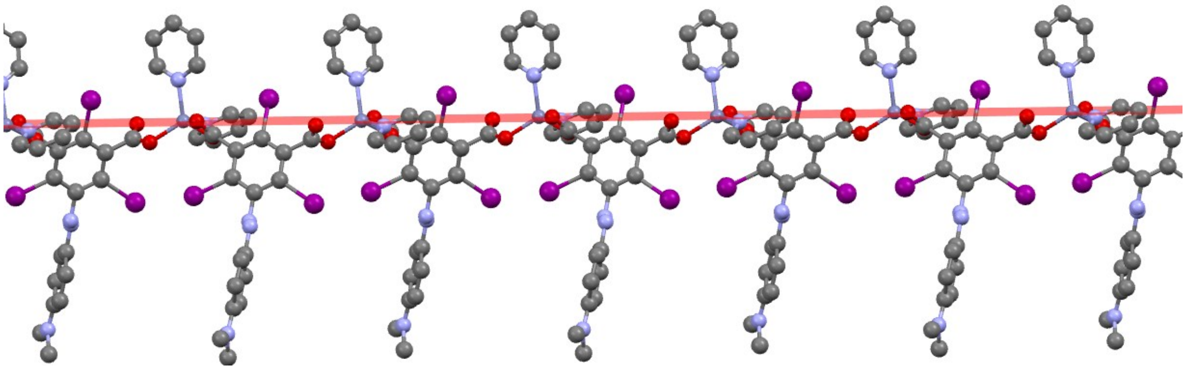

Fig. S.1.1.1. The coordination polymer **3**. Right: projection nearly along [1,0,-1]. The red trace is the plane through the Zn atoms.

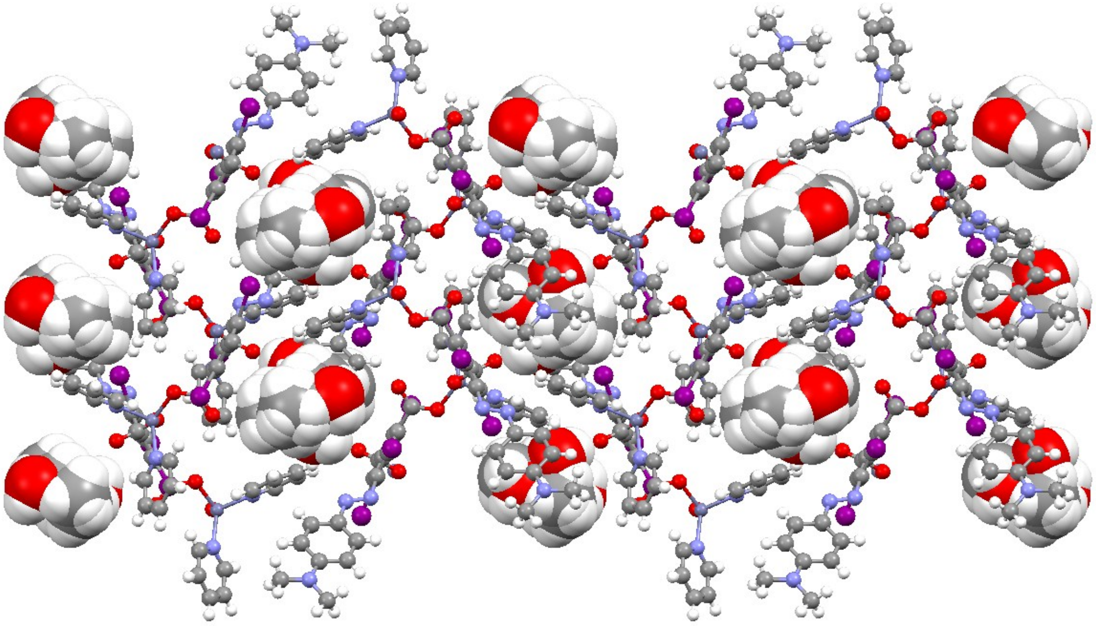

Fig. S.1.1.2. Crystal packing of **3** view along crystallographic *c* axis. Disordered 2-propanol molecules are in spacefill style. Color code: grey, carbon; sky blue, nitrogen; red, oxygen; violet, iodine; light green, zinc.

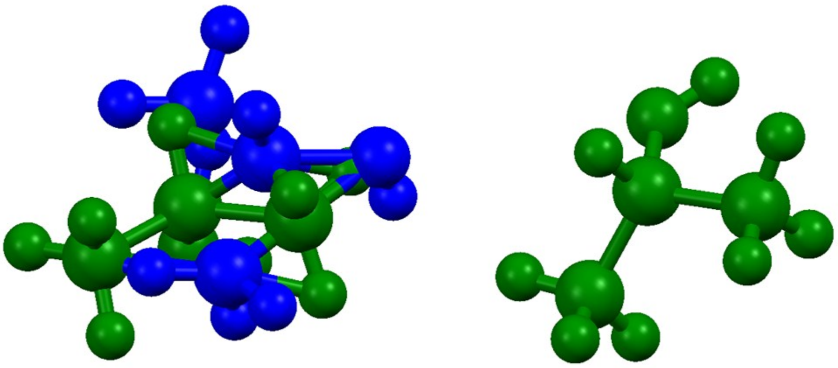

Fig. S.1.1.3. Left: Two configurations of the disordered 2-propanol molecule in **3**. The solvent molecule was splitted in two components and, here, are colored in green and blue. The population factor of the two components was set at 50:50. Right: One of the two components of the disordered 2-propanol.

S.1.2. Experimental details for 4 and supplementary figures

The crystals were always twinned needles. The sample use for data collection was apparently perfect. Some diffuse stripes in the frames were attributed to possible disorder. Notwithstanding this at the end of the refinement the list of the most disagreeable reflections showed a large number of Io

>> Ic, clear indication of a twinned systems, undetected in the first phase of the data collection. For these reason we omitted 17 reflections in the last cycles of the refinement.

The initial solution and refinement was very unsatisfactory, with very high R_1 and wR_2, coefficients of weighting scheme and residues larger than 6 e/Å^3. It was clear that the problem derived from the disorder of the molecule containing the diazo group. This molecule is present in two arrangement, approximately rotated of 180° around its longer axis. In both the conformations the couples of nearest atoms are separated by less than 0.6 Å, with the exception of the N=N group, the two methyl groups and the iodine I2.

Due to this strong overlapping and the low population factor of the second conformation, its modelling and refinement was very demanding. Due to the high correlations factors between parameters of equivalent atoms we constrained all ADPs of equivalent couples to be identical and restrained the two conformer to be similar. Moreover, we refined the structure with an initially very large damping factor, which was reduced but not completely suppressed during the last least-squares cycles. The result was better in terms of R_1, wR_2, goodness-of-fit and residues on the difference map. Nevertheless the large second coefficient of the weighting scheme and the prevalence of strong reflections at low theta having Iobs > Icalc indicated that the undetected twinning was an unresolved problem. However, we considered this solution as correct. In particular, the translation of the halogen bond from the two N atoms of the diazo group is coherent with the rotation of the I2 atom and justify the rotation of the whole triiodo-di-carboxybenzyl group.

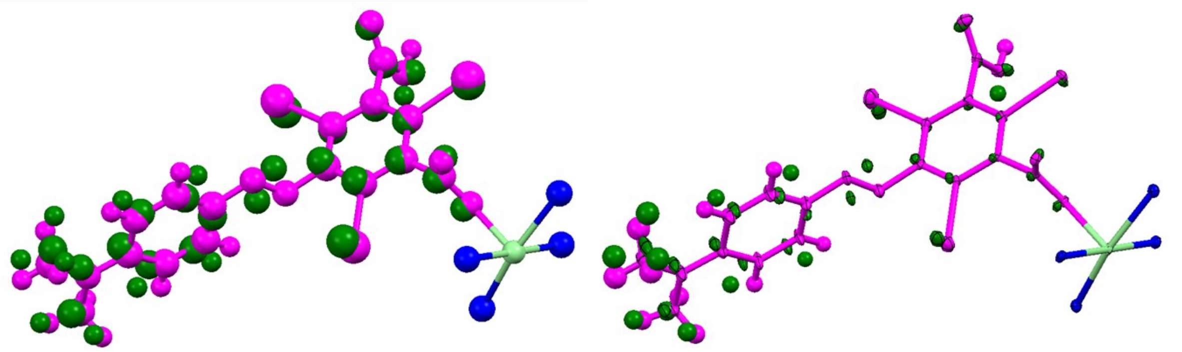

Fig. S.1.2.1. Disordered lingad **1** in **4**. The two conformations are colored in purple and green, both ball and stick (left) and ellipsoid (right) representation are reported. The population factor of the two conformations are very different; 93(purple):7(green). In light green Zn atom and in blu N atoms.

S.1.3. Experimental details for 5 and supplementary figures

The structure is partially disordered and a part of the solvent molecul was not clearly found and refined. We refined the structure with an initially very large damping factor, which was reduced but not completely suppressed during the last least-squares cycles. The disordered part was interpreted with two models (A and B) having population ratio p(A)/p(B) = 0.69/0.31. The difference between the two models consists in the rotation around the C5-N1 bond of the diazodimethylaminobenzene. As a consequence the solvent dimethylaminoformamide molecule (DMF 1.5 molecules per asymmetric unit) is also partially shifted. Plotting the two models independently, voids are evidenced, so large that, at least the most populated model may host an extra molecule such as unlinked dipyridylethylene. The void volumes of the two models partially superimpose. This makes the identification of the missing contect extremely difficult. Only for the A model we inserted an extra DMF molecule, but the refined population factor was < 0.5. Attempts to introduce dipyridylethylene instead of DMF or to insert extra DMF for model B failed because of the too large correlations between the relative parameters, so we interrupted the refinement at this point. Due to these problems we only refined anisotropically the ordered part of the structure.

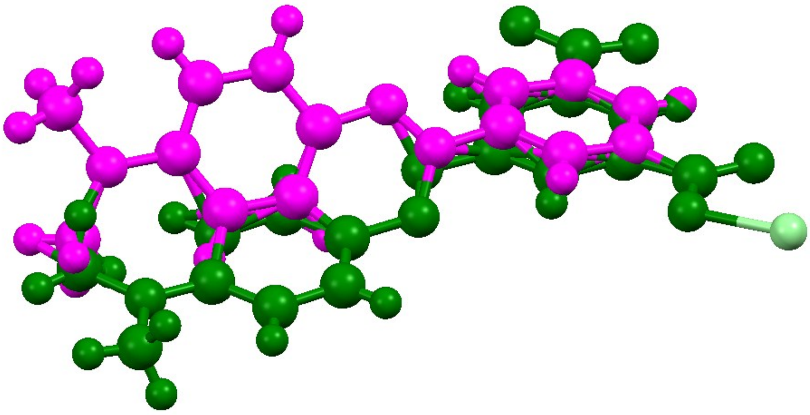

Fig. S.1.3.1. Disordered ligand **2** in **5**. The two conformations are colored in purple and green. The population factor of the two conformations are 69 (green):31 (purple). In light green Zn atom.

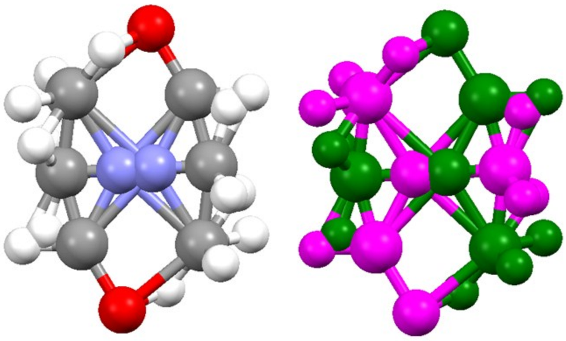

Fig. S.1.3.2. Representation of the disordered DMF molecule in **5**. The two conformations are shown using color as in Fig. 1.3.2 (left) and colored in purple and green (right).

S.2 Photochemistry

The UV-Vis spectra of **1** and **2** in dilute DMF solution are shown in Fig. S.2.1 and S.2.2, displaying absorption maxima at 400 and 435 nm, respectively. Upon irradiation with a 457 nm laser, the absorbances of both **1** and **2** decreased due to *trans*-to-*cis* isomerization. The decrease is much more notable for **2**, indicating that its photostationary state is much more *cis*-rich. This is likely due to the presence of the bulky iodine atoms in **1**, which may prevent and efficient isomerization to the *cis* isomer due to steric hindrance. The thermal half-lives of the *cis*-isomer can be estimated by monitoring the recovery of the absorption spectra, and we obtained the values of τ = 3000 s and τ = 850 s for **1** and **2**, respectively. The longer half-life of **1** can be attributed to the *ortho*-substitution of one of the benzene rings, which is known to stabilize the *cis*-isomer [3].

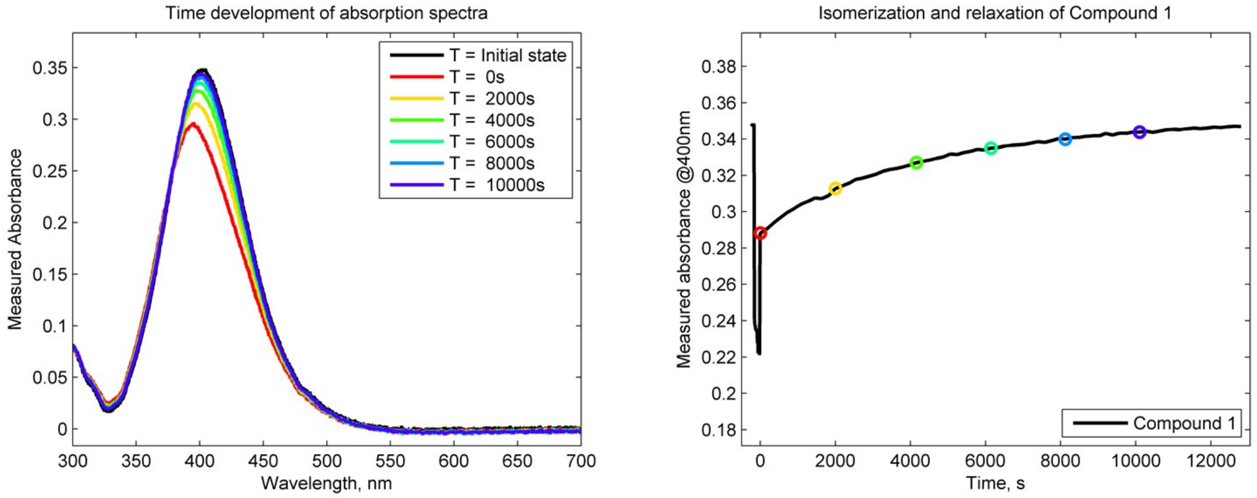

Fig. S.2.1: Left, UV-vis spectra of **1** before (black curve) and after (coloured curves) irradiation using 457 nm light. Right, time development of the absorbance of **1**.

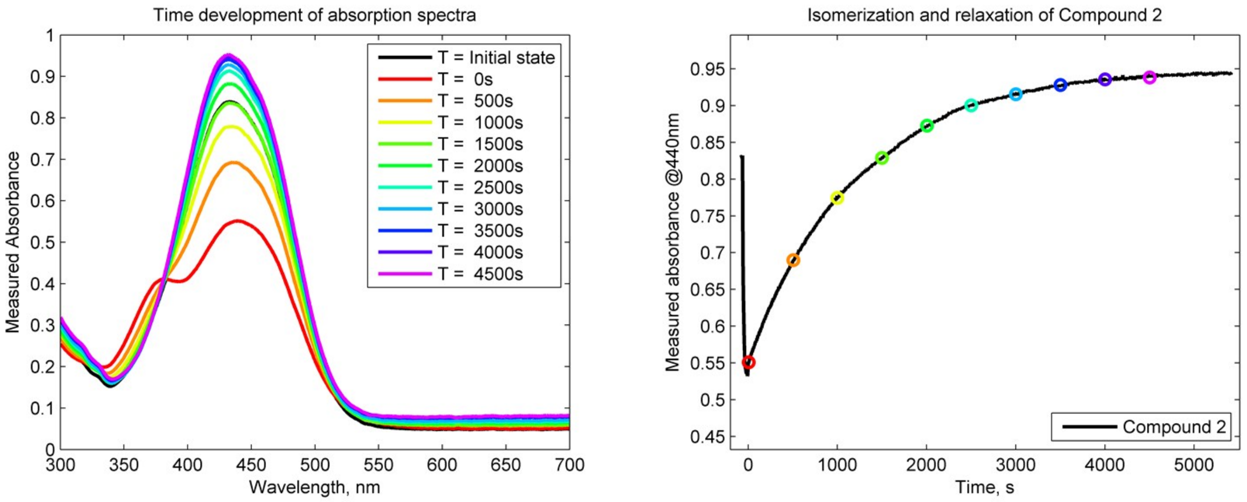

Fig. S.2.2: Left, UV-vis spectra of **2** before (black curve) and after (coloured curves) irradiation using 457 nm light. Right, time development of the absorbance of **2**.

S.3 References

[1] G. M. Sheldrick, *Acta Crystallogr.* 2008, **A64**, 112-122.

[2] C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler, J. van de Streek, *J. Appl. Crystallogr.* 2006, **39**, 453-457.

[3] C. Knie, M. Utrecht, F. Zhao, H. Kulla, S. Kovalenko, A. M. Brouwer, P. Saalfrank, S. Hecht, D. Bléger, *Chem. Eur. J.*, 2014, **20**, 16492; D. Bléger, J. Schwarz, A. M. Brouwer, S. Hecht, *J. Am. Chem. Soc.*, 2012, **134**, 20597.