Electronic Supporting Information for

Metal-organic hybrid materials involving the $[UO_2Cl_3(NO_3)]^{2-}$ tecton and the role of halogen polarizability

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Experimental

Synthesis. Caution! *Whereas the uranium oxynitrate hydrate* $(UO_2)(NO_3)_2{\bullet}6H_2O$ *used in this investigation contain* depleted *uranium, standard precautions for handling radioactive substances should be followed.*

Materials. The materials used in this study were purchased from Sigma Aldrich.

General synthesis of compounds 1 – 3 Uranium oxynitrate hexahydrate $UO_2(NO_3)_2{\bullet}6H_2O$ (100 mg, 0.2 mmol, 1 eq.) was mixed with 4-halopyridine (0.4 mmol, 2 eq.) and 1M HCl (2 ml) and the mixture was sonicated to ensure complete dissolution. The solution was allowed to evaporate in a petri dish and after several days yielded crystals suitable for single crystal X-ray diffraction.

Several attempts were made to form the bromide equivalent of the metal-based tecton studied here. Even at low concentrations of HBr, however, this unit could not be isolated. The reasons for this are unclear, as the affinity of the Br- anion for UO_2^{2+} is lower than that of Cl^- and in fact on the same order as that of NO_3^-,[1] it may, however, relate to the greater steric demands of three bromide ligands resulting in a preference for a fourth bromide over a more bulky nitrate ligand.

Crystal Structure Determination. Single crystals isolated from each bulk sample were mounted on MiTeGen micromounts. For structure determinations reflections were collected using 0.5 φ scans on a Bruker SMART X2S bench-top diffractometer using Mo Kα radiation. All data was integrated using the *SAINT* software package[2] and an absorption correction was applied using *SADABS*.[3] All structures were solved using direct methods (*SHELXS-97*[4]) and refined using *SHELXL-97* within the WinGX software package,[5] in which all the non-hydrogen atoms were refined anisotropically with satisfactory refinements. Tests for additional symmetry were done using *PLATON*.[6]

Characterization. Powder X-Ray Diffraction patterns were obtained for each sample using a Rigaku Miniflex diffractometer (Cu Kα, 3-60°) and analyzed using the Jade software package.[7] Calculated powder patterns were overlaid on observed patterns to identify phases present. Compounds 2 and 3 showed signs of impurities (Figures S5 and S6) however no single crystals other than those described could be found. The PXRD patterns were therefore overlaid with the calculated patterns of the corresponding $[UO_2Cl_4]^{2-}$ material[8] as well as that of various ligand and uranyl salts, however no matches could be found. Solid-state fluorescent studies were carried out on a Shimadzu RF-5301 PC Spectrofluorophotometer with a UV-35 filter.

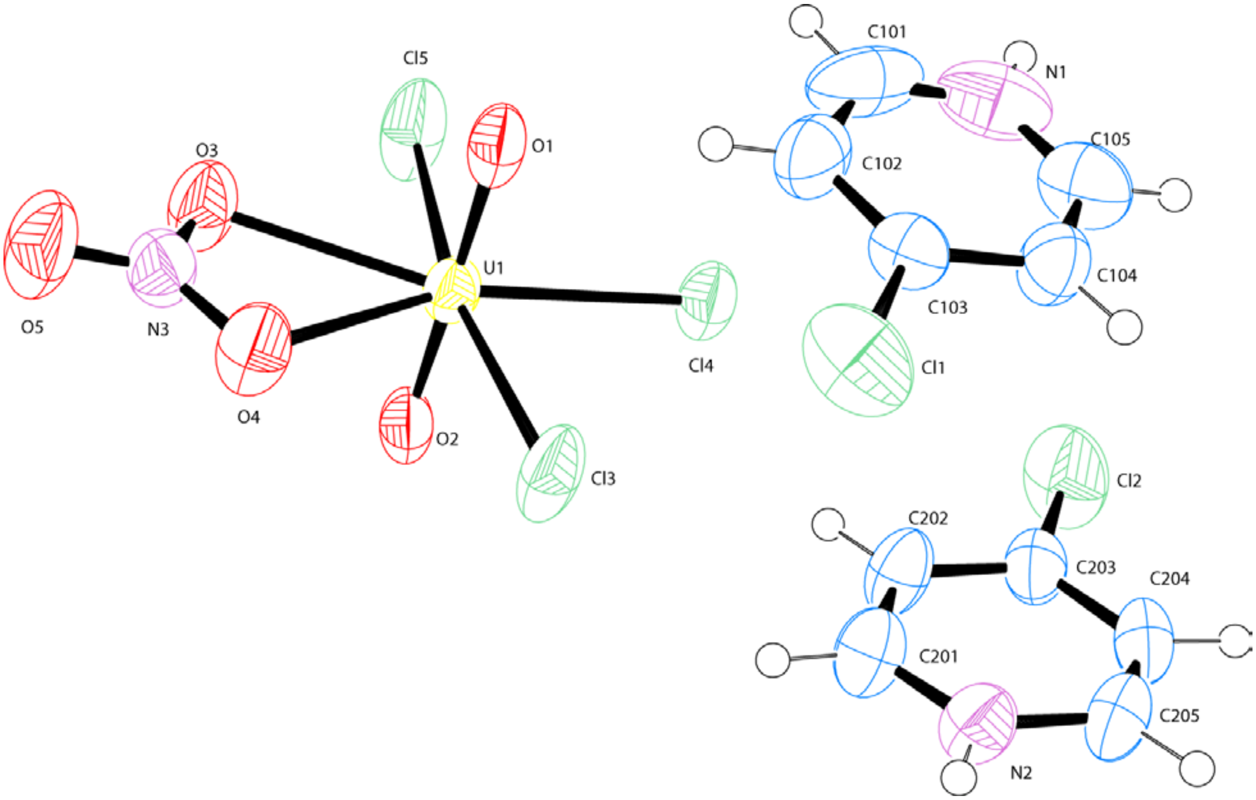

Figure S1 ORTEP of Compound **1** (ellipsoids at 50 % probability level)

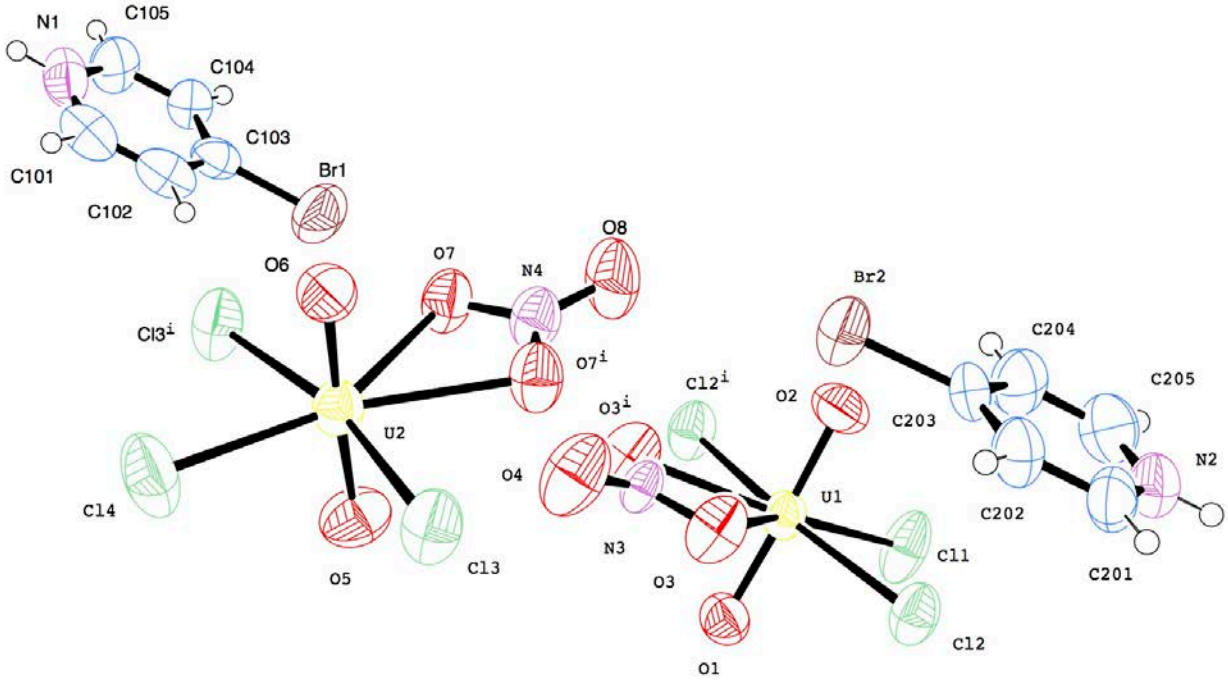

Figure S2 ORTEP of Compound **2** (ellipsoids at 50 % probability level). Superscript indicates symmetry equivalent: i = x, -y+2/3, z

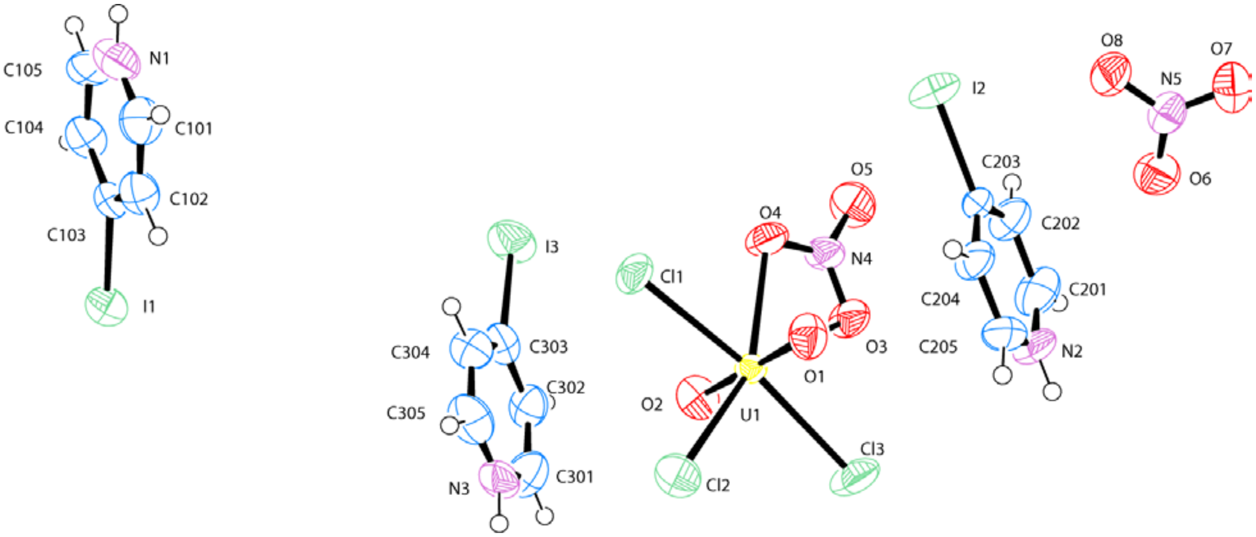

Figure S3 ORTEP of Compound **3** (ellipsoids at 50 % probability level)

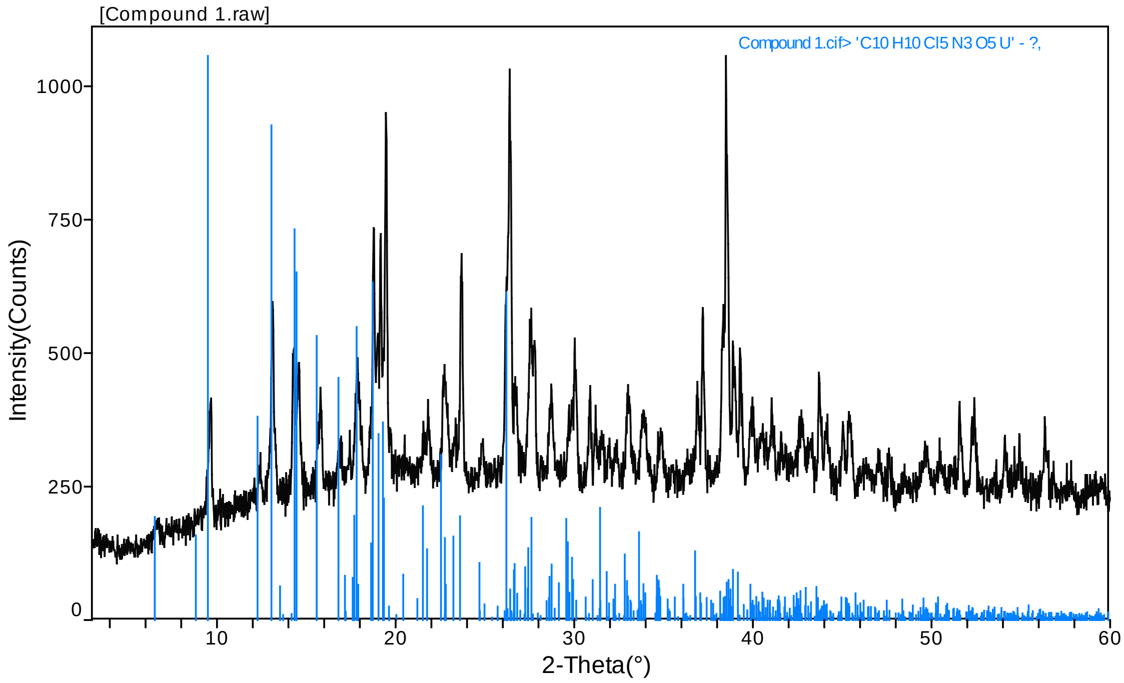

Figure S4 The powder x-ray diffraction (PXRD) pattern of **1**

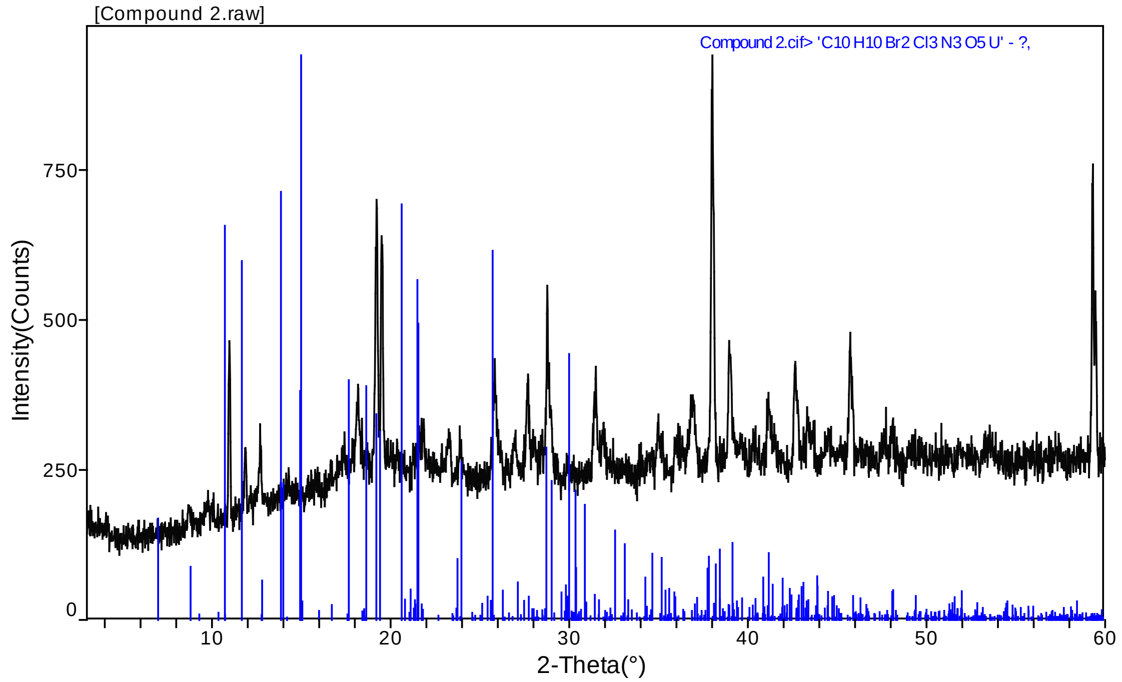

Figure S5 The PXRD pattern of **2**

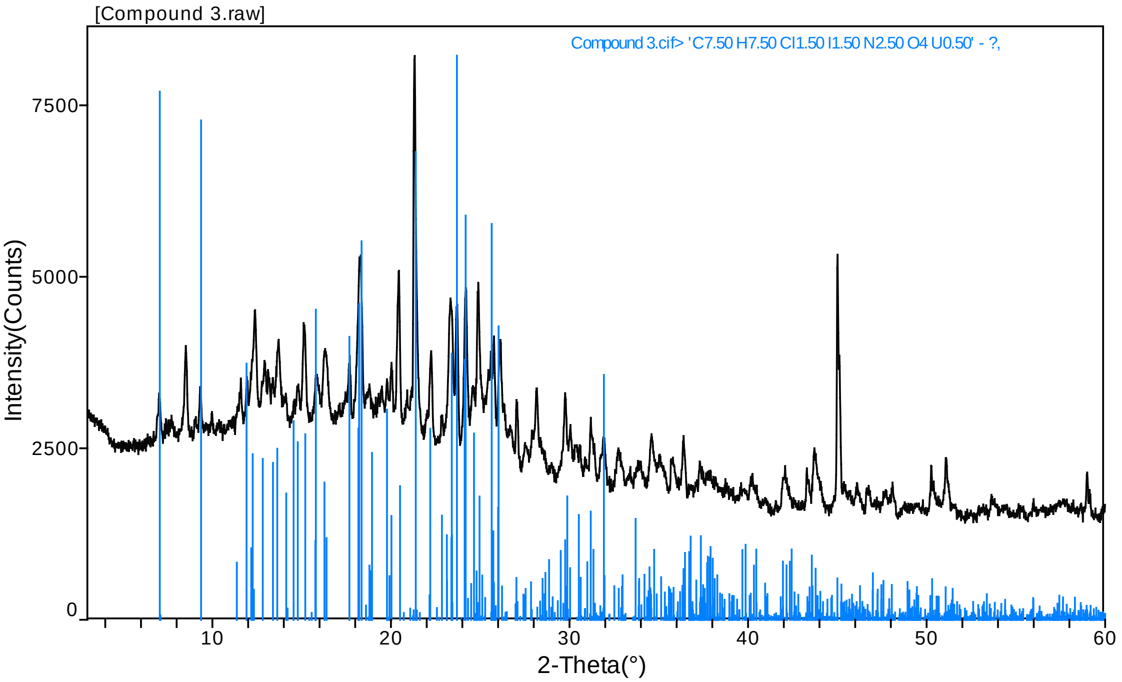

Figure S6 The PXRD pattern of **3**

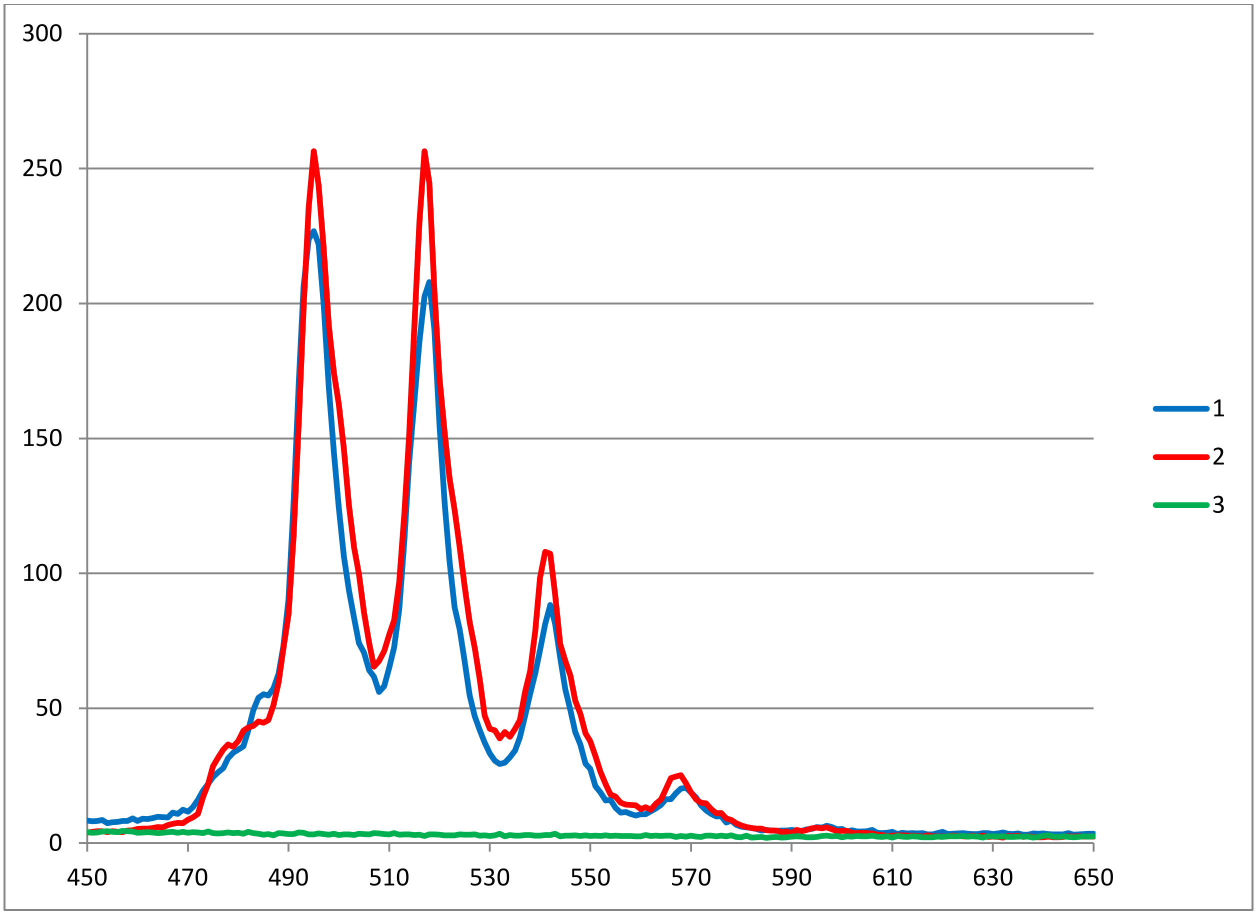

Figure S7 The fluorescence spectra (λ_{ex} = 350 nm) of compound 1 – 3.

References

1. C. Nguyen Trung, G. M. Begun and D. A. Palmer, *Inorganic Chemistry*, 1992, **31**, 5280-5287.
2. Saint Area-Detector Integration Software, Siemens Industrial Automation, Inc., Madison, WI, 1998
3. G. M. Sheldrick SADABS, v. 2.03, University of Gottingen, Germany, 2002
4. G. M. Sheldrick, *Acta Crystallogr., Sect. A: Found. Crystallogr.*, 2008, **A64**, 112-122.
5. L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837-838.
6. A. Spek, *Journal of Applied Crystallography*, 2003, **36**, 7-13.
7. JADE, v. 6.1, Materials Data Inc., Livermore, CA, 2002.
8. M. B. Andrews and C. L. Cahill, *Dalton Transactions*, 2012.