Supplementary Material

Figure S1. One cation of the structure of **[**VO_2(**bptpy**)]ClO_4, **1**, showing its environment of other cations involved in C···C and CH···C interactions beyond dispersion with that cation. For clarity, only the ligand units of the surrounding cations involved in the interactions are shown (in yellow) and no H-atoms other than those involved in interactions are shown.

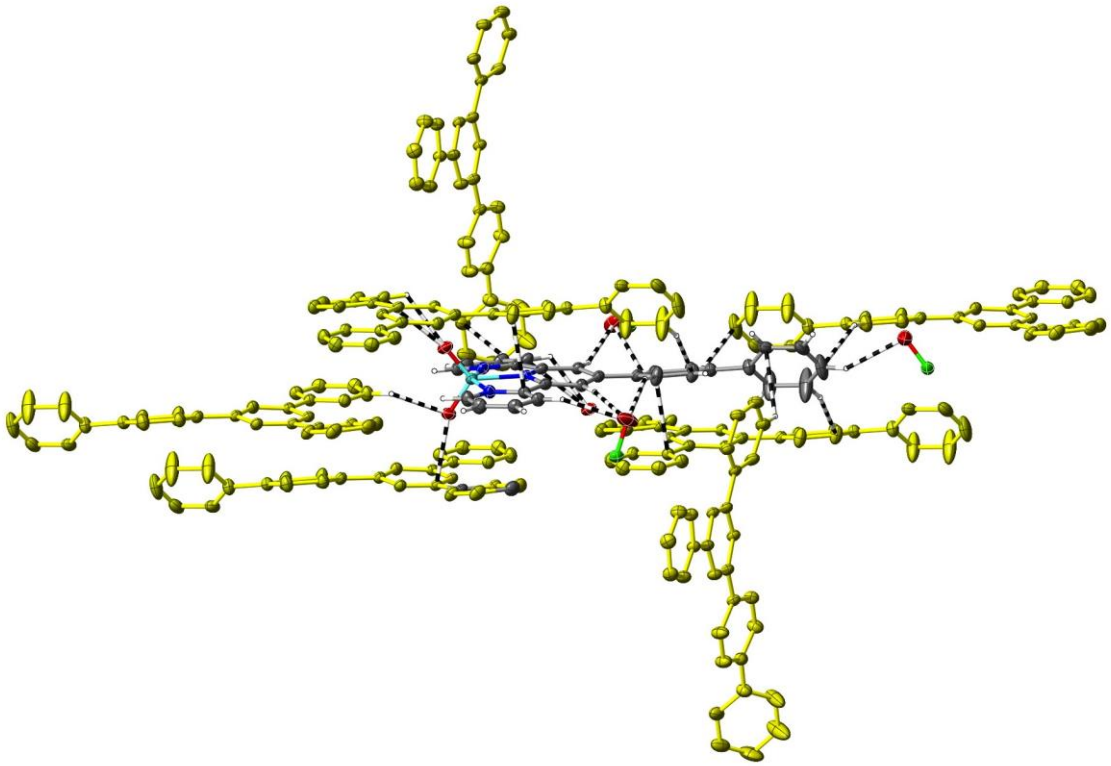
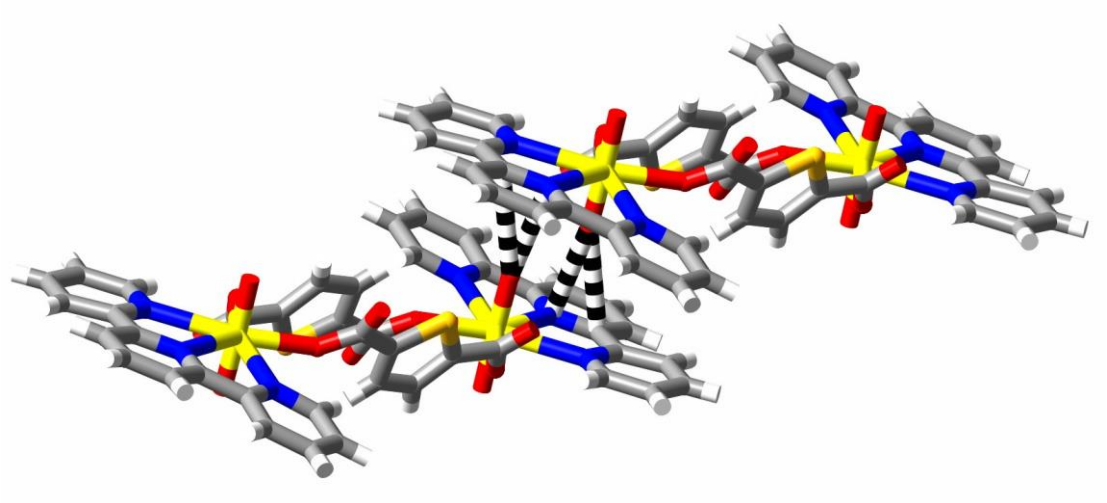


Figure S2. O···C contacts indicative of interactions beyond dispersion in stacked uranyl ion complexes. For clarity, stick representations are used and H-atoms are not shown.

(a) $[UO_2(\mathbf{tpy})(\mathbf{tdc})]_2$ (**tdc** = thiophene-1,4-dicarboxylate) [60]



(b) $[(UO_2)_2(OH)_2(\mathbf{tpy})_2](ClO_4)_2$ [62]

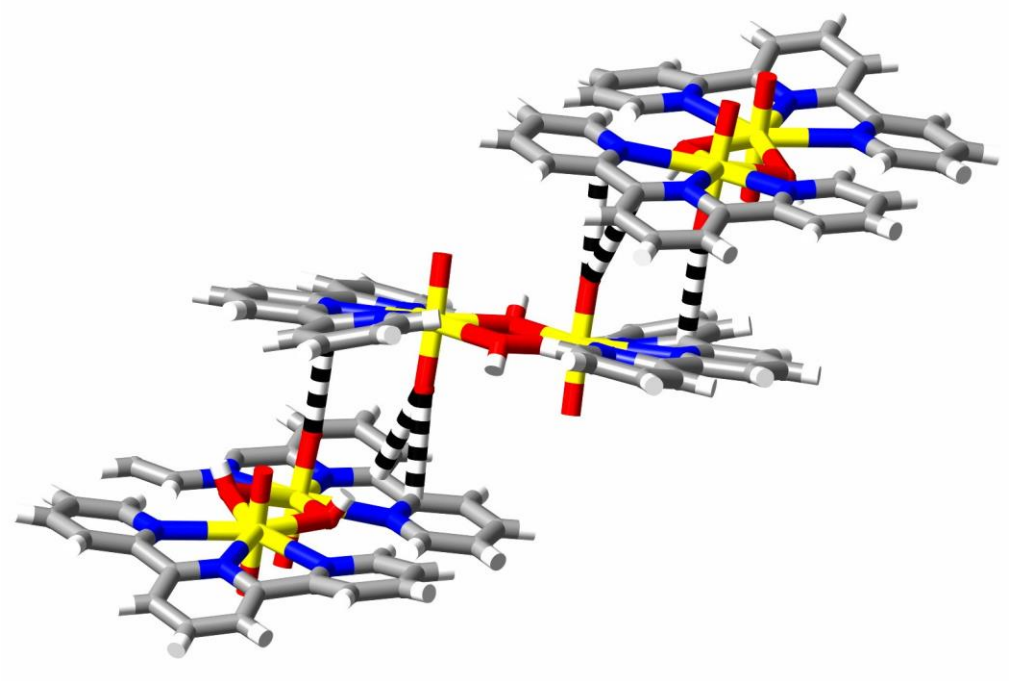
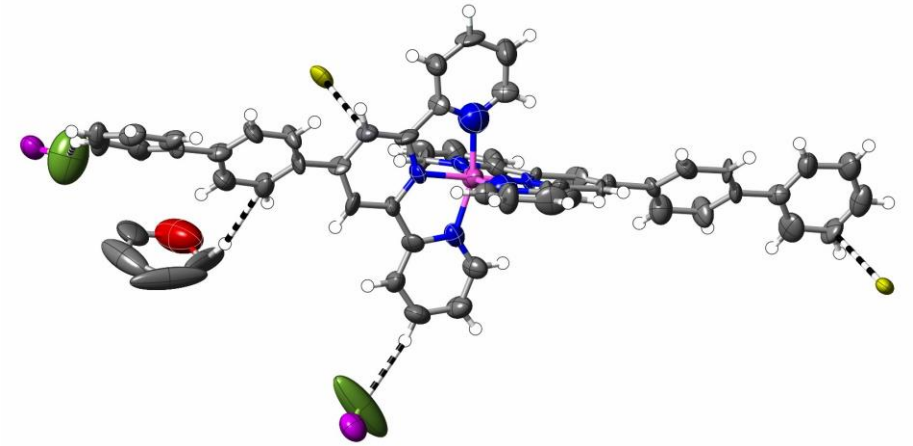
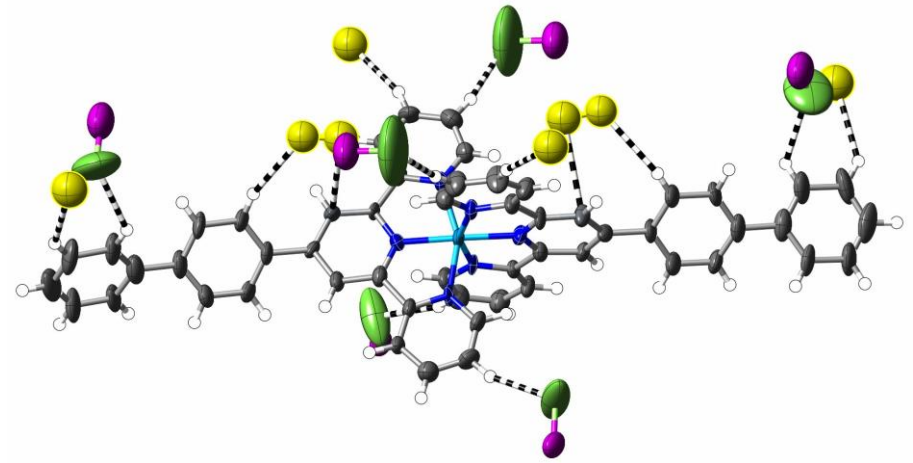


Figure S3. Interactions beyond dispersion for cations in complexes of 4'-biphenyl-2,2':6',2''-terpyridine (**bptpy**). Structures reported by N. W. Alcock, P. R. Barker, J. M. Haider, M. J. Hannon, C. L. Painting, Z. Pikramenou, E. A. Plummer, K. Rissanen, P. Saarenketo, *J. Chem. Soc., Dalton Trans* **2000**, 1447–1461 (Ref. 43). Colour coding as for Figure 1.

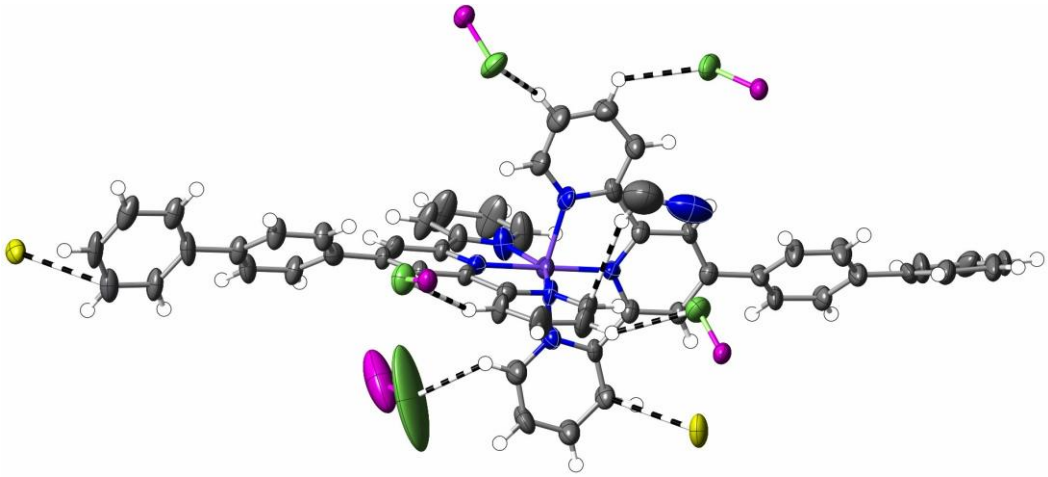
(a) **$[Co(bptpy)_2](PF_6)_2 \cdot THF$**



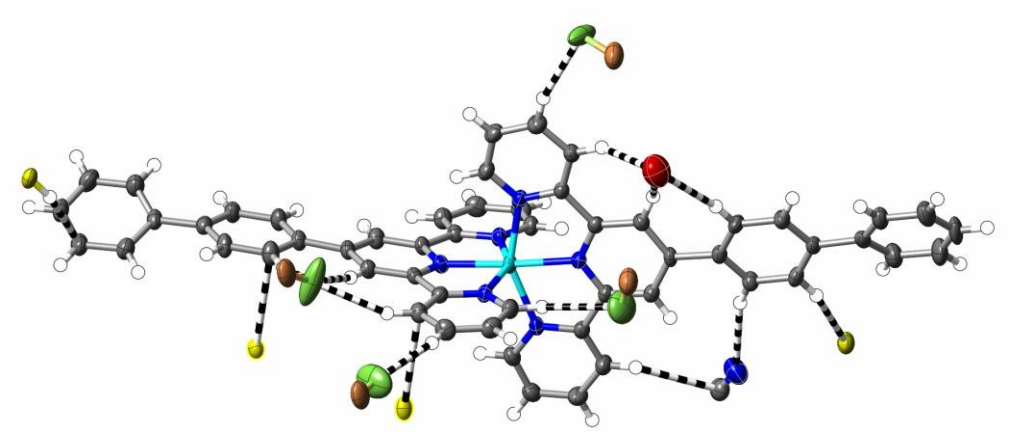
(b) **$[Ni(bptpy)_2](PF_6)_2 \cdot CH_3NO_2$**



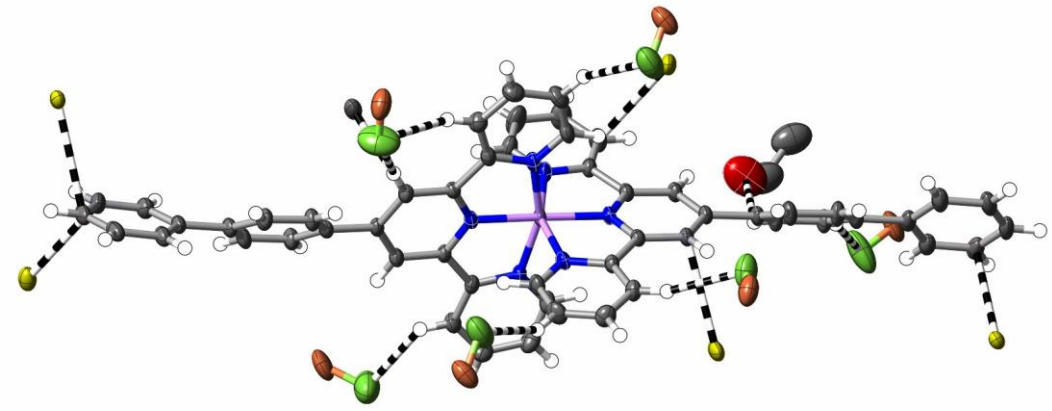
(c) **[Cu(bptpy)$_2$](PF$_6$)$_2$·CH$_3$NO$_2$**



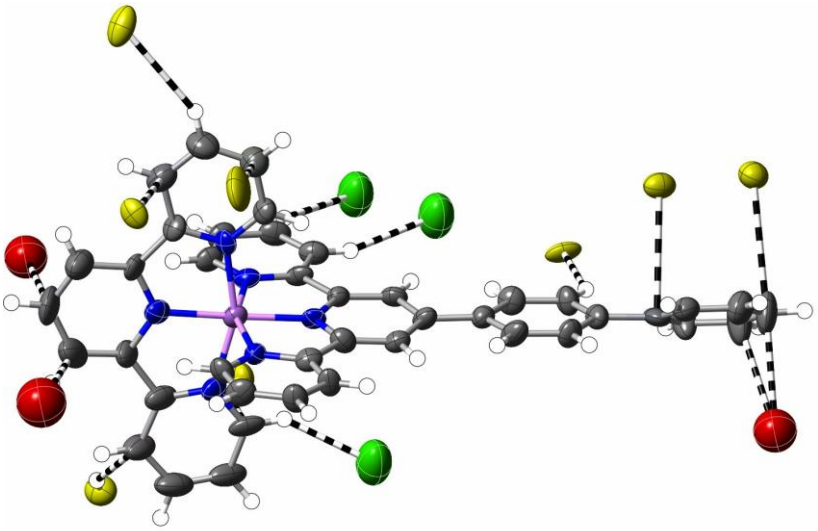
(d) **[Zn(bptpy)$_2$](PF$_6$)$_2$·0.5H$_2$O**



(e) **[Ru(bptpy)$_2$](BF$_4$)$_2$·2.5CH$_3$NO$_2$**



(f) **[Ru(bptpy)(tpy)]Cl_2·10H_2O**



(g) **[Cd(bptpy)$_2$](PF_6)$_2$·0.5CH_3NO_2** (Cd1 only)

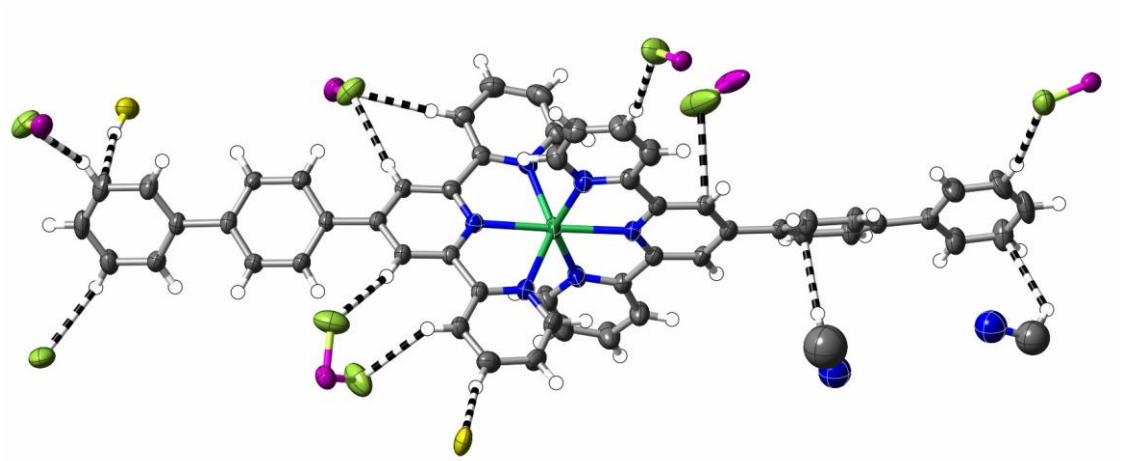
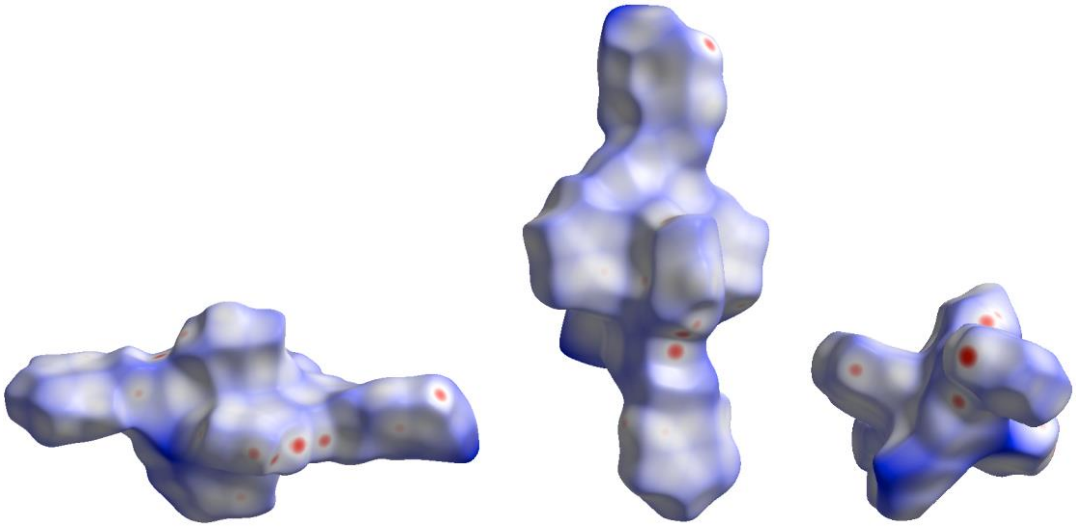
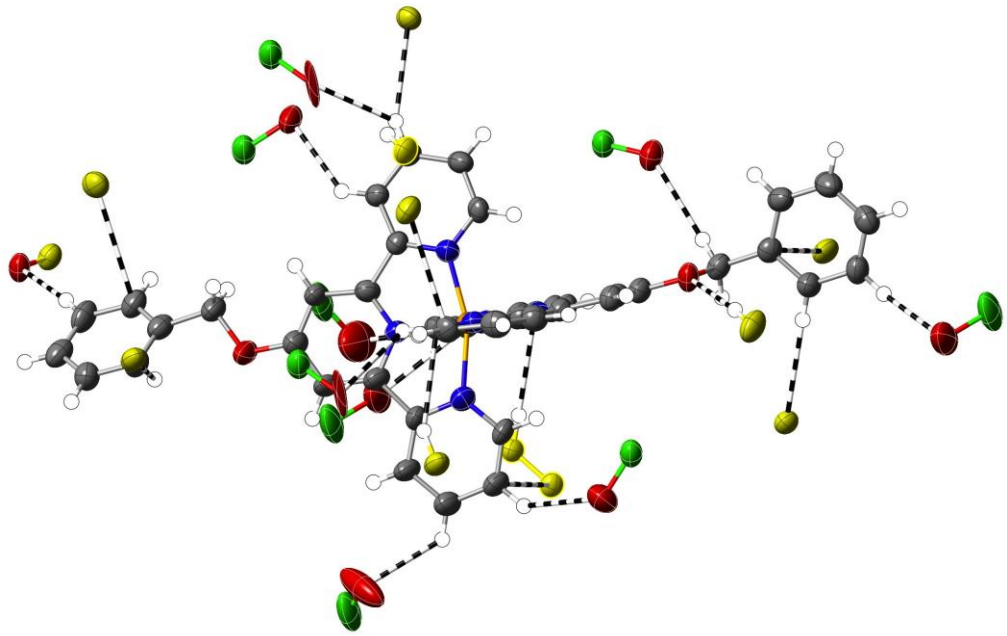


Figure S4. Hirshfeld surfaces, d_{norm} representations in non-transparent mode to render more obvious the red regions indicative of interactions beyond dispersion, for (a) [Fe(**bzOtpy**)$_2$](ClO$_4$)$_2$, **28**, and (b) [Ni(**bzOtpy**)$_2$](ClO$_4$)$_2$, **29**, along with representations of the full interactions of the cations

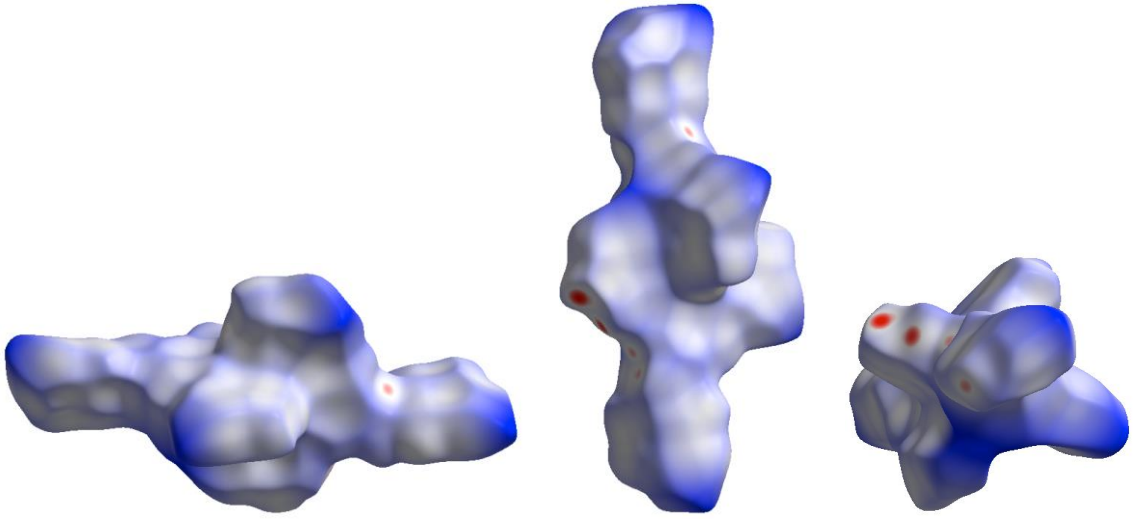
(a)



down *a* down *b* down *c*



(b)



down *a* down *b* down *c*

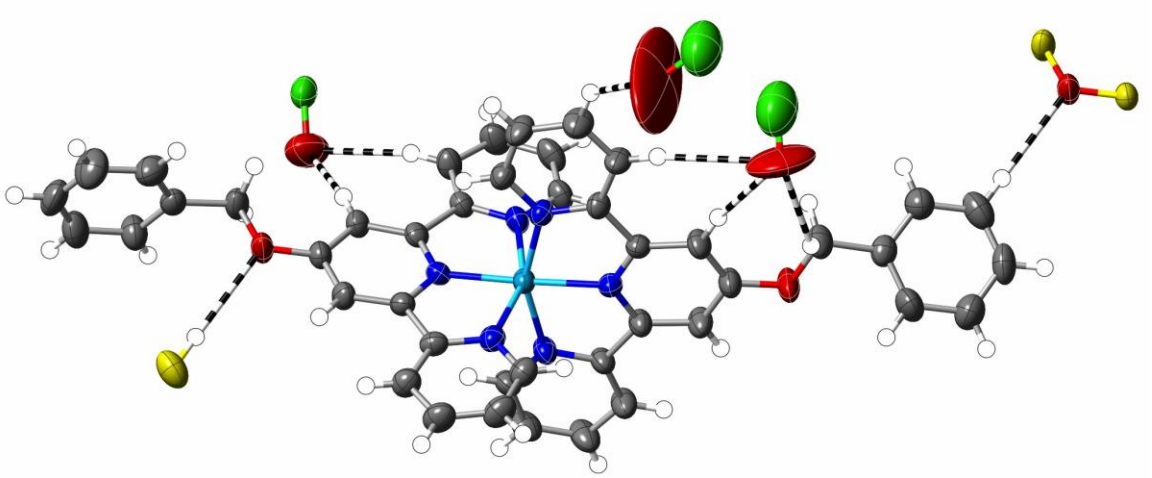


Figure S5. Hirshfeld surface diagrams, d_{norm} representations, transparent mode, as obtained with CrystalExplorer for complexes of benzyloxy-substituted terpyridine ligands with or without methoxyl functionalisation

(a) [Fe(**bzOtpy**)$_2$](ClO$_4$)$_2$, **28** (b) [Co(**tmbzOtpy**)$_2$](BF$_4$)$_2$ [36] (c) [Cu(**tmbzOtpy**)$_2$](ClO$_4$)$_2$ [36]

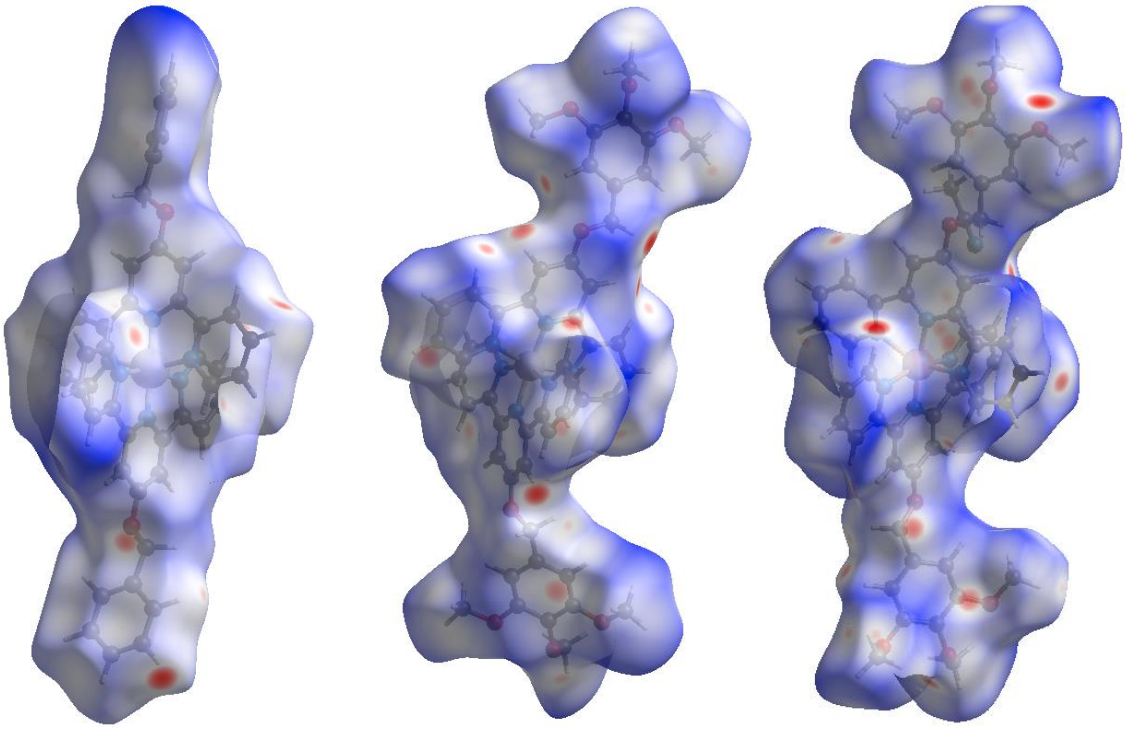


Table S1. Volume of voids per unit cell, number of electrons per void, and possible solvent molecules occupying the voids, as deduced from SQUEEZE results.

Complex	Void volume (Å^3)	Number of electrons per void	Possible solvent molecules
7	296	51	2 CH_3CN
	322	68	3 CH_3CN
9	92	29	CH_3CN
13	67	19	CH_3OH
14	145	36	$CH_3CN + H_2O$
18	2 × 300	2 × 59	2 × (DMF + H_2O)
20	2 × 317	2 × 67	2 × (DMF + 2 H_2O)
28	83	20	CH_3OH
29	158	68	3 CH_3CN
	95	27	CH_3CN
32	315	39	$CH_3CN + H_2O$
34	390	68	3 CH_3CN