SUPPLEMENTARY INFORMATION

Weak interactions in metallo-supramolecular grid crystals: an analysis of their effects

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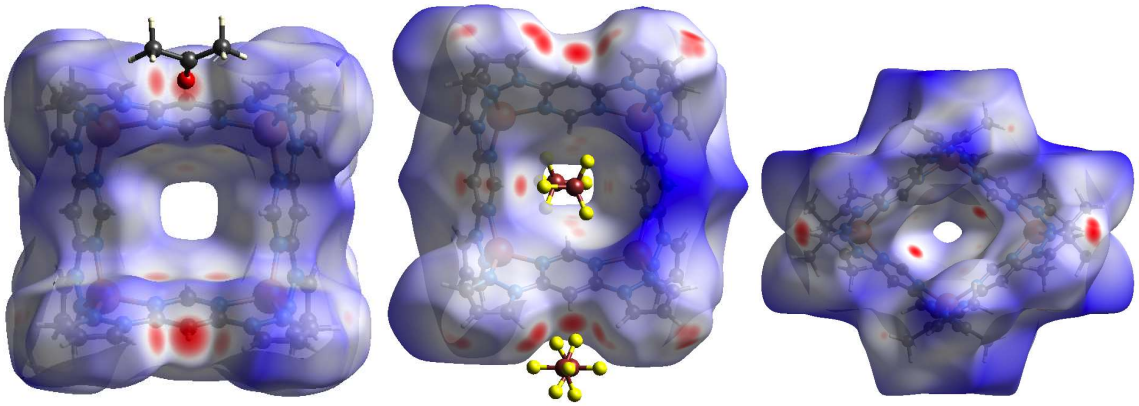
S1. Hirshfeld surface diagrams for the grid units (all views shown being approximately perpendicular to the grid mean plane and in "transparent" mode).



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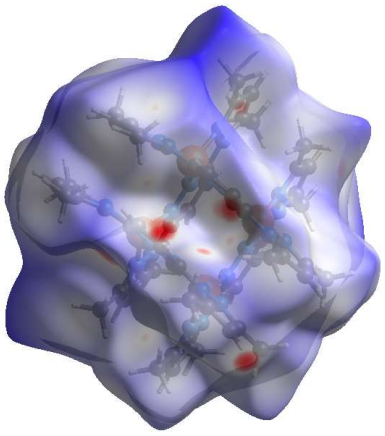

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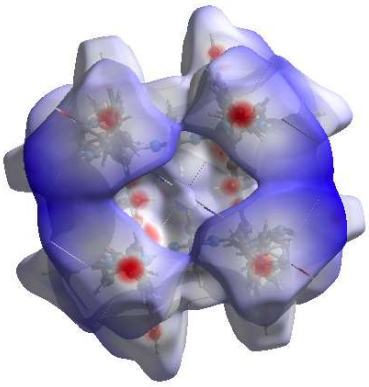

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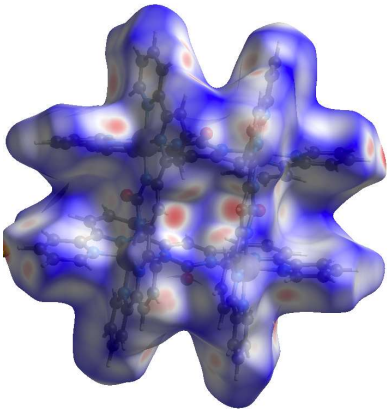

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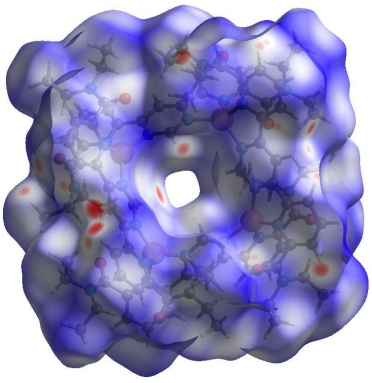

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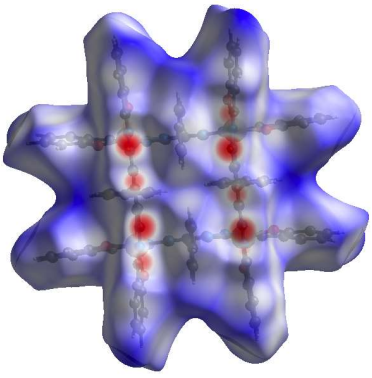

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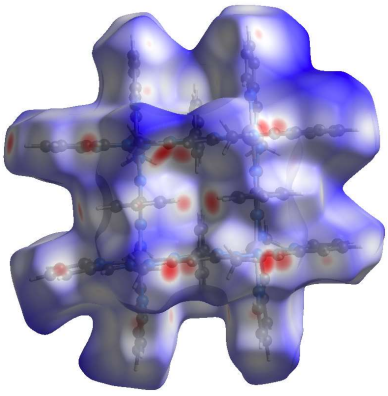

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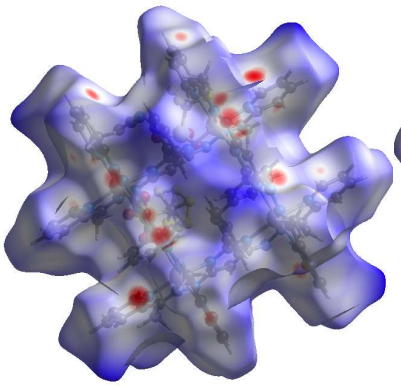

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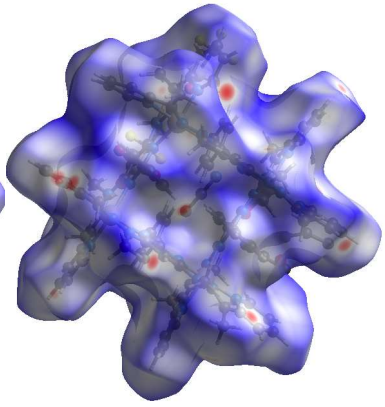

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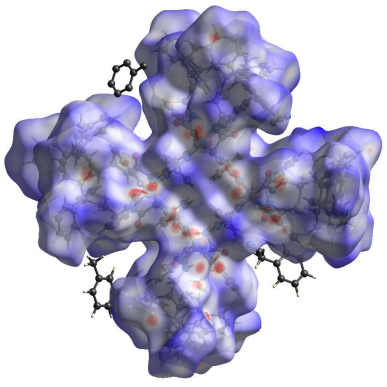

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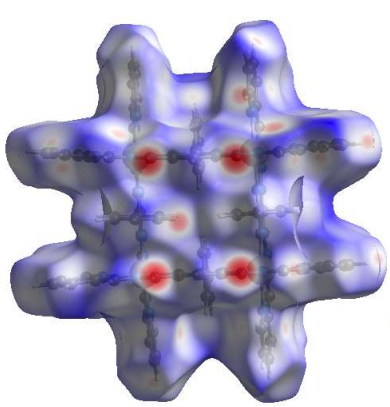

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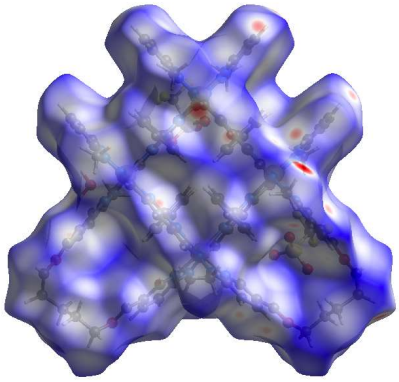

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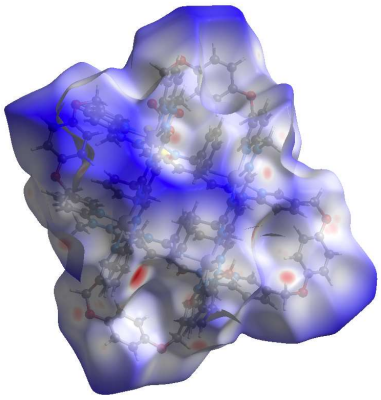

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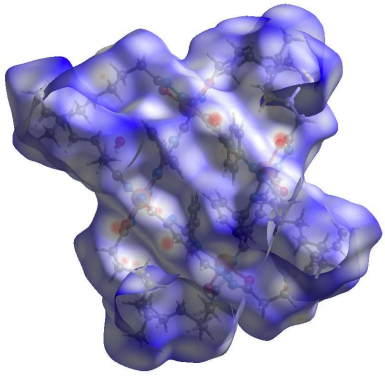

OFEDOT

S2. Analysis of the Hirshfeld surfaces

As provided by *CrystalExplorer*, red regions on the Hirshfeld surface designate points where separations of inner and outer atoms are less than the sum of their van der Waals radii and thus indicative of weak interactions. Thus, by consideration of the positions of all entities surrounding the grids themselves, it is possible to identify the atoms involved in these interactions. Examples are shown in the above figures in the cases of TIWCOS and TIWDAF for just some of the components of the grids' surroundings. (The figures become extremely congested when all the surrounding species are shown.) Once the close atoms are identified, their separation can be obtained and we have found it convenient to do so using *CrystalMaker* version 11.5.1 from CrystalMaker Software Ltd, UK, as all figures in the main text have been prepared with this software. In most instances, the external atoms involved in interactions are part of larger anions or molecules and in the main text figures the whole entities are shown.

For each structure currently considered, the atomic "contacts" indicative of weak interactions exceeding dispersion, as identified by the use of *CrystalExplorer*, are the following:

(Atom numbering as in the cited cif files; separations in Å)

(i) TIWCOS (one twofold rotation axis of symmetry) F2···C17 3.05, F6···C3 3.02, F7···C13 3.10, F9···C6 2.96, F10···C4 2.96, F11···C16 3.07, F12···C14 3.08; H3A···Cl4S 2.56, H8A···Cl4S 2.62, H13A···O1S 2.41, H15A···O1S 2.36.

(ii) TIWCUY (vertical plane of symmetry; contacts for ordered, included anions only) F1···C7 3.08, F3···H16 2.39, F7···C14 3.01, F7···H7 2.57.

(iii) TIWDAF (one twofold rotation axis of symmetry) F1···C6 3.02, F2···H7A 2.43, F3···H13B 2.50.

(iv) TIWDEJ (no symmetry) F3···H6A 2.27, F4···H41A 2.34, F4···H34A 2.46, F6···H5A 2.39, F11···H30A 2.45, F11···H40A 2.48, F11···C49 2.95, F12···H23A 2.48, F15···H20A 2.37, F16···H19A 2.40, F21···H25B 2.45, F22···H42B 2.43, F30···C32 2.96, C29···H56C 2.72 (reciprocal interaction with neighbouring grids). Only cation-anion contacts are shown in Figure 3 of the main text.

(v) TIWDIN (no symmetry) O52···H17A 2.43, O53···H11E 2.40, O61···H13A 2.39, O62···H48A 2.39, O63···H27A 2.37, O63···H31E 2.58, C51···H11A 2.82, C52···H11A 2.78 plus other interactions involving adjacent grids C12···H21A 2.78, C13···H21A 2.78, C63···H11C 2.76, C73···H31F 2.74. Only cation-anion contacts are shown in Figure 3 of the main text.

(vi) FEKRET (twofold rotation axis perpendicular to the Fe_4 plane) O11···H31E 2.56, O14···H31E 2.55, Cl15···C1B 3.12, Cl15···C3B 3.30, Cl15···H21E 2.2.65, Cl15···H31A 2.68 are the only contacts clearly identifiable.

(vii) SIQPIR Extensive disorder in this structure negated application of *CrystalExplorer*.

(viii) IYUBEJ (twofold rotation axis perpendicular to the Fe_4 plane) Cl1···H3A 2.73, Cl1···H43A 2.53, Cl1···F14 2.92, N2A···C111 2.90, N2A···H49A 2.24, F13···H44A 2.44, F22···H1A 2.22. Some other seemingly very short F···H contacts involve disordered anions.

(ix) YENRUF (no symmetry) F12···H2A 2.39, F14···H5C 2.61, F14···H18C 2.47, F15···H12C 2.56, F21···H2S1 2.60, F21···H16B 2.49, F21···C19B 3.11, F22···H2B 2.62, F24···H2D 2.50, F31···H5D 2.40, F32···H5A 2.32, F32···H12A 2.37, F33···H12A 2.50, F36···H18D 2.43, F41···H12B 2.45, F42···H5B 2.39, F42···H10C 2.38, F42···H18B 2.56, F43···H12B 2.53, F44···H16D 2.38, O20B···H2S3 2.55, O1W···H32E 2.42. Presumed H-bond acceptance F13···O1W 2.90. Inter-grid C16D···H16C 2.78, O27C···H17B 2.66.

(x) TIKXUI (centrosymmetric, all Fe centres equivalent) F1···H2A 1.92, F3···H18 2.25, F4···H5A 1.92. No interactions beyond dispersion of the water molecules were evident.

(xi) VEDJIY (twofold rotation axis about the Zn2-Zn3 vector) F8···H2 2.58, F12···H12 2.61, N17···H27 2.40, N20···H23 2.58, O1···H41 2.49, O1···H42 2.42, O1···H43 2.41, O3···H25 2.30, O4···H19 2.50, O6···H22 2.48, O7···H6 2.21, O7···H5 2.38, O9···H4 2.61, O11···H11 2.49, O9···H20 2.43, O11···H11 2.49, O11···H35 2.24, O12···H31 2.28.

(xii) VEDJOE (twofold rotation axes about both ZnZn diagonals, all Zn centres equivalent) N3···O5 2.75, N6···O2 2.80, O1···H20 2.43, O2···H16 2.57, O4···H17 2.27, O5···H5 2.48, O5···H8 2.48.

(xiii) VEDJUK (no symmetry) N33···H23 2.62, N34···H8 2.59, O2···C53 3.06, O3···H46 2.56, O4···H95 2.59, O5···H52 2.43, O7···H50 2.34, O12···H72 2.46, O13···H24 2.59, O15···H81 2.39, O16···H36 2.47, O16···H37 2.59, O17···H59 2.52, O20···H71 2.63, O22···H78 2.59, O23···H43 2.38, O24···H104 2.52.

(xiv) GUGTAE (no symmetry) C99···H18C 2.52, C183···H126 2.59, N45···H227 2.33, N50···H87 2.32, F1···H19A 2.29, F2···H18B 2.29, F5···H9 2.11, F5···H25D 2.30, F5···H23C 2.36, F6···H25D 2.33, F8···H23C 2.41, F9···H159 2.52, F17···H29A 2.22, F17···H11A 2.41, F17···H93B 2.37, F17···H78 2.41, F18···H11A 2.43, F19···H146 2.38, F20···H93B 2.43, F22···H39A 2.17, F24···H23D 2.34, F24···H39A 2.27, F26···H17 2.37, F26···H19 2.40, F28···H10 1.91 (H-bond), O3···H30F 2.24, O4···H30D 2.39, O5···H30A, 2.30, O6···H232 2.33.

(xv) BARYUP (no symmetry) C124···O44 2.89, C217···O7C 3.15, C416···H128 2.74, O3B···H22D 2.55, O3C···H119 2.59, O6C···H118 2.63, O8B···H417 2.57, O10B···H312 2.60, O11B···H314 2.58, O11B···H116 2.55, O12B···H422 2.46, O33···H413 2.34, O42···H326 2.43, O51···H318 2.60, O51···H328 2.58, O53···H329 2.54, O61···H324 2.33, O64···H116 2.52, O73···H31A 2.07, O73···H314 2.46, O81A···H429 2.53, O82A···HAB 2.37, O82B···H418 2.34, O82B···H428 2.35 (* O81 and 82 are part of disordered perchlorate ions). H-bonds: O1W···H12A 1.90, O2W···H11A 1.91, O3W···H32A 1.80, O4W···H21A 1.94, O4W···H21 2.55, O5W···H22C 1.89, O6W···H41A 1.88, O7W···H42A 1.89.

(xvi) ODAQOD (one twofold rotation axis of symmetry about the Zn2-Zn3vector) C013···N1-5 3.13, F2-4···H4A 2.44, O0W···H15C 2.41, O1-1···H17A 2.62, O1-3···H12A 2.57, O2-1···H5B 2.53, O2-1···H16A 2.54, O2-4···H15D 2.19, O4A···H6B 2.56. Reciprocal contacts to other grids: C17B···H6A 2.74, O4A···H6B 2.56, O4A···H6B 2.56.

(xvii) ODAWOJ (twofold rotational symmetry) C29A···H51B 2.69, C41···O8 2.98, C50···O8 2.88, O2A···H3A 2.54, O2B···H37 2.38, O3···H9 2.55, O3···H18 2.50, O6···H14 2.46, O7···H25A 2.37, O10···H54A 2.37 (H disorder), O13···H60 2.36.

(xviii) OFEDOT (twofold rotation axis perpendicular to the Cu_4 mean plane) C11···O56 3.27, C19···H64B 3.15, N14···H81B 2.17, O1···H51A 2.46, O41···H81A 2.11, O56···H11A 2.36.

S3. Representations of the hydrogen bonding in neutral grid hydrates referred to in the main text using O···O and O···N separations obtained by analysis of the structure OFEDOT. In all these figures, water molecule O-atoms are shown in green.

Fig. S3(i) CCDC 637557

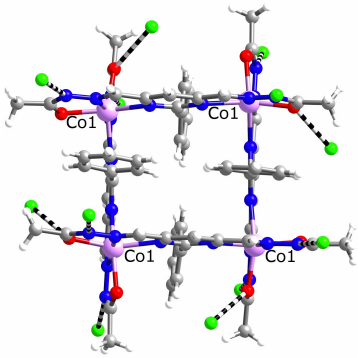

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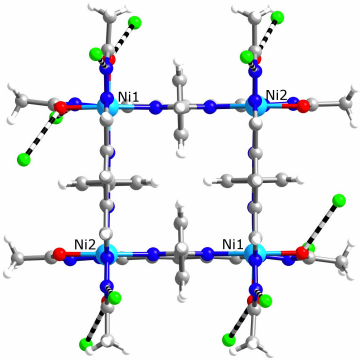
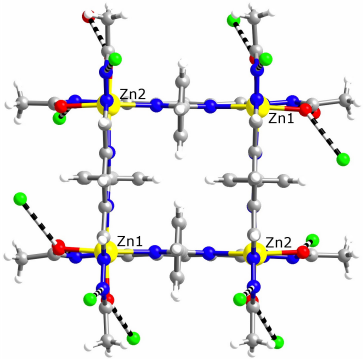
Fig. S3(ii) CCDC 637558



(twofold rotation about Ni1Ni1)

Fig. S3(iii) CCDC 637559



(twofold rotation about Zn1Zn1)

Fig. S3(iv) CCDC 637560

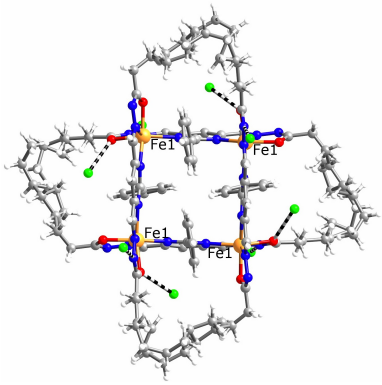


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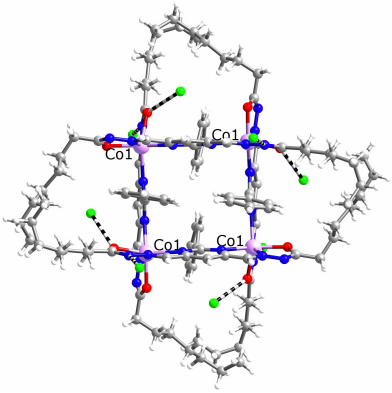
Fig. S3(v) CCDC 637561



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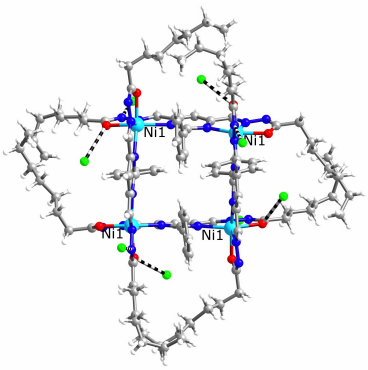

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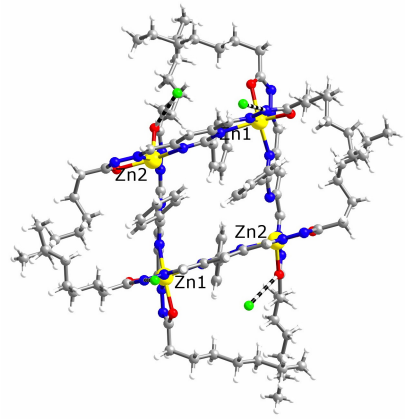

(twofold rotation axes)