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Balancing framework densification with charged, halogen-bonded-π-conjugated linkages: $[PPh_4]_2\{[E\text{-TTF–I}_2][Re_6Se_8(CN)_6]\}$ *versus* $[PPh_4]_2[\text{EDT-TTF–I}]_2\{[\text{EDT-TTF–I}][Re_6Se_8(CN)_6]\}$†

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The ionic character of a set of two redox linkages and strong, directional halogen bonding at the organic–inorganic interface compromise to produce two materials sharing a common two-dimensional net, eventually extended in a third dimension, although two of the six symmetrical halogen bond acceptors ultimately remain uninvolved as a result of charge densification.

Recent expectations call for the design of strongly correlated quantum materials where interchain hopping would be such that a direct transition between a one-dimensional metallic system and a three-dimensional one would occur at some (T,P) point in its phase diagram.[1] Not knowing with hindsight either the required subtle balance of transfer integrals—whose origin lies hidden within the entangled folds of the band structure topology in the momentum space[2]—or its explicit manifestation back into the direct space of the crystal, one wishes to address this formidable task by the making of materials, building upon our library of images. Hence, that of an ionic solid where molecular stacks would no longer be parallel to each other but interspersed rather within a three-dimensional template serving as a host for interacting metallic rods whose director orientations would be inherently polydispersed. Thus, the self-assembly by means of halogen bond interactions[3–5] of the redox active, expanded octahedral halogen bond acceptor anionic nodes,[6] $[Re_6Se_8(CN)_6^{(4-/3\bullet-)}]$, across *symmetrical* linkages, be they the single radical cation E-TTF–$I_2^{\bullet+}$, or the mixed valence dimers, $(\text{EDT-TTF–I})_2^{\bullet+}$ (ESI Scheme 1), was targeted, aiming to direct the construction of the simple three-dimensional, cubic host frameworks, formulated $(E\text{-TTF–}I_2^{\bullet+})_3[Re_6Se_8(CN)_6^{3\bullet-}]$ or $[(\text{EDT-TTF–I})_2^{\bullet+}]_3[Re_6Se_8(CN)_6^{3\bullet-}]$, respectively. As exemplified in the title compounds, coordination polymers do form based on strong $(C_{sp^2}\text{–I}\cdots N{\equiv}C\text{–Re})_n$ self-complementary halogen bonded infinite motifs, as anticipated, albeit primarily in one, then two directions only because charge densification occurs, as described herein.

Electrocrystallization in an H-shaped cell at a constant current of 0.5 μA for 3.5 weeks of I–TTF–I[7] (5 mg) in a 2/1, CH_3CN/THF (12 mL) solution and EDT-TTF–I[8] (5 mg) in a 5/1/0.5, CH_3CN/CH_2Cl_2/THF (13 mL) solution containing $(PPh_4)_4[Re_6Se_8(CN)_6]$,[6,9] (25 and 30 mg, respectively) affords shiny black needles of $[PPh_4]_2\{[E\text{-TTF–I}_2][Re_6Se_8(CN)_6]\}$, **1** and $[PPh_4]_2[\text{EDT-TTF–I}]_2\{[\text{EDT-TTF–I}][Re_6Se_8(CN)_6]\}$, **2** whose formulation was obtained by determination of their crystal structures‡. Both **1** and **2** crystallize in the triclinic, P-1 space group. In **1**, half molecules of I–TTF–I and the rhenium cluster anion lie about independent inversion centres and the PPh_4 moiety lies in a general position. In **2**, a half unit of the rhenium cluster anion lies about an inversion centre. There are two independent EDT-TTF–I molecules, one of which lies in a general position, and the other is disordered about an inversion centre. **1** and **2** share the common structural pattern shown in Fig. 1. Virtually identical two-dimensional nets develop upon two modes of polymerisation: one is the polymer built out of symmetrical, self-complementary halogen bonds across *trans* cyanide cluster ligands, as anticipated. Then, charge densification wins out because of a favorable, snug fit between the complementary shapes and curvatures of the radical cation cores and inorganic cluster anions, as observed earlier in the series of molecular anti-perovskites,[10] $(TTF)_3[X][Re_6Q_6Cl_8]$ ($X = Cl^-, Br^-, I^-$; Q = S, Se) (ESI Figures 1, 2 and 3). The latter tight fit stores an electrostatic stabilization energy which balances electrostatic halogen bonding interactions and eventually makes for robust hybrid stacks running along a direction essentially orthogonal to that of the former halogen-bonded polymers, as exemplified in Fig. 1.

The linear, type I[3,4] halogen bonds identified in Fig. 1a and 1b extend along the direction of maximum electrostatic attractive interaction between the electron deficient region in the vicinity of the covalently bounded halogen atoms and the electron rich (lone pair) domain of the cyanide ligands. The I···N distances are even shorter than those recorded for $(\text{EDT-TTF–I})_2[Ag(CN)_2]$,[11] 2.88 Å, and $(\text{EDT-TTF–I})_4[M(CN)_4]$,[12] M = Pt, Pd, 3.07 Å and 3.14 Å. Of particular note are the disordered, equiprobable molecular orientations observed in **2** (Fig. 1b), allowing one single dissymmetrical EDT-TTF–I to be accommodated on the very same site as E-TTF–I_2.

In addition, a fine design element is identified in **2** and described in Fig. 2 where the tendency[11,12] to form centrosymmetrical $(\text{EDT-TTF–I})_2$ dimers is shown to be fulfilled. Hence, as anticipated at the outset of this research, symmetrical, halogen-bond-donor linkages direct the self-assembly across *trans* cyanide acceptors and make for a third polymerisation direction and the three-dimensional framework illustrated in Fig. 2.

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† Electronic supplementary information (ESI) available: Scheme 1, synthesis of I–TTF–I and EDT-TTF–I by adapted published procedures. See DOI: 10.1039/b600159a

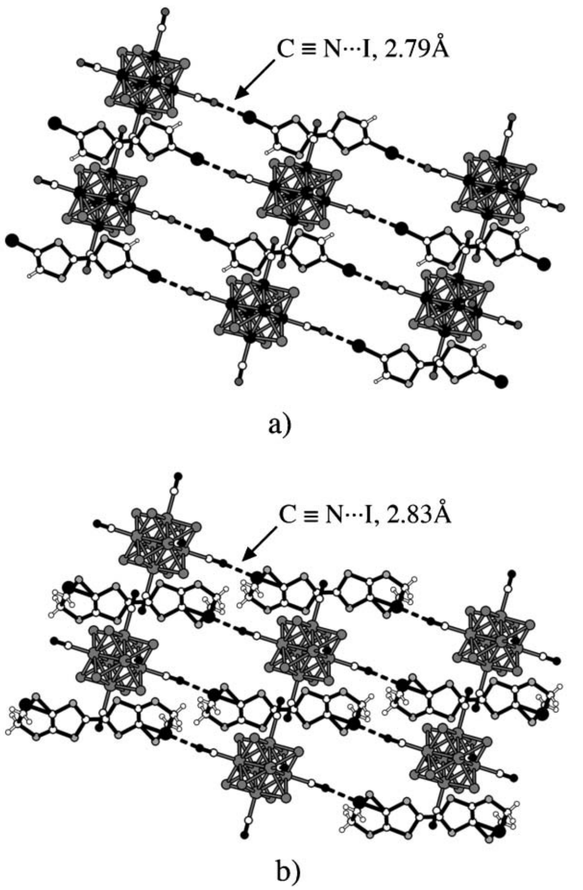

Fig. 1 Identical two-dimensional nets, formulated a) [E-TTF–$I_2^{\bullet+}$][$Re_6Se_8(CN)_6^{3-}$] in **1** with C–I···N, 177° and I···N≡C, 172°; b) [EDT-TTF–$I^{\bullet+}$][$Re_6Se_8(CN)_6^{4-}$] in **2**, with C–I···N, 176° and I···N≡C, 175°. PPh_4^+ cations have been omitted for clarity.

Several singular features complement the former deciphering of the role of halogen bonding in directing the framework construction in **1** and **2**. It is observed that as no dimerization of E-TTF–I_2 occurs, **1** remains a two-dimensional framework; here, the chalcogenide cluster anion is stabilized in its open-shell 23-electron paramagnetic form, as demonstrated by the observed formulation and geometric characteristics of the cluster unit, especially Re–C bond lengths (2.008(1), 2.103(3) Å) shorter[13] than those (2.104(9), 2.145(11) Å) within its 24-electron congener in **2**. Thus, two types of spins ½ co-exist in the lattice, yet they are essentially uncoupled as demonstrated by magnetic susceptibility and ESR experiments. Indeed the susceptibility follows a Curie–Weiss law with a Weiss constant of about −1 K (ESI Fig. 4) indicating the presence of very weak antiferromagnetic interactions between spin carriers. This result is confirmed by ESR measurements on powder sample and single-crystal. As expected for non-interacting or weakly interacting species, two resonance lines are observed for each of the spin carriers (ESI Fig. 5). On the powder spectra, both lines can be observed at 4.2 K: a broad resonance line ($\Delta H \approx 160$ Oe) attributed to [$Re_6Se_8CN)_6^{3-}$] and a sharp, "composite" organic line ($\Delta H \approx 30$ Oe). This resonance line has been observed on a single crystal with a line width of 7 Oe. The magnetic characterisation of **1** clearly establishes the quasi-absence of magnetic exhange interaction between the organic and the inorganic spins either across the I···N≡C halogen bond or through space despite the van der Waals close fit.

The hydrogen bond acceptor ability of all six cyanides supported by the cluster core was shown to be fulfilled recently, with all six cyanides satisfied by redox amide donors.[6] The present study demonstrates that the cluster also serves as an halogen bond multi-acceptor, albeit only two, then four out of the six cyanides are coordinated. This suggests the exploration of ternary assemblages, involving admixtures of hydrogen-bond π-donors such as EDT-TTF–CONHR[4,14] and the present halogen-bond π-donors, to form for example [EDT-TTF–$CONHR^{\bullet+}$]$_2${[I–TTF–I][$Re_6Se_8(CN)_6$]} and [EDT-TTF–$CONHR^{\bullet+}$]$_2$[EDT-TTF–I]$_2$-{[EDT-TTF–I][$Re_6Se_8(CN)_6$]}. The goal here is to counterbalance the electrostatic driving force and the van der Waals fit of the complementary shapes of the organic radical cation and inorganic cluster anion to promote halogen-bonding polymerisation in all

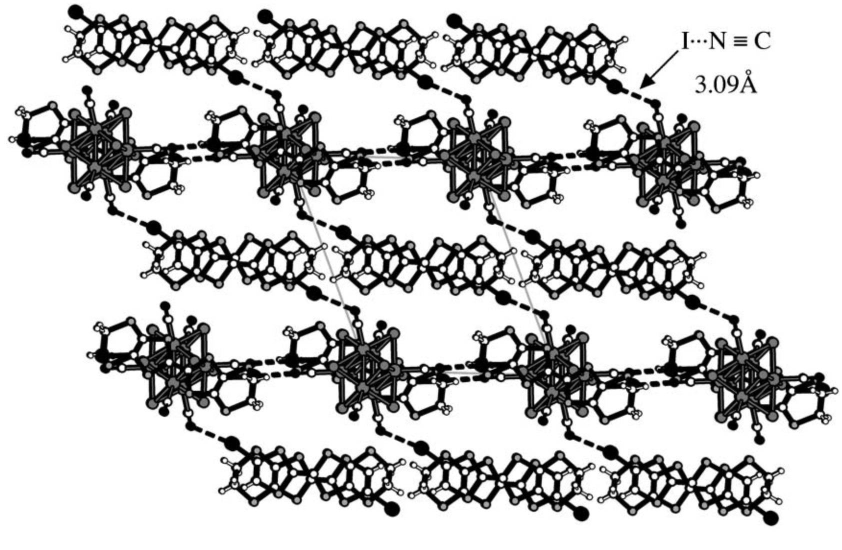

Fig. 2 Three-dimensional framework construction in **2**: rotating Fig. 1b by 90° reveals another type of self-complementary polymers developing along the diagonal of the Figure out of centrosymmetrical mixed valence dimers, halogen-bonded to another set of *trans* cyanide ligands *via* bent, type II interactions with characteristic angles, C–I···N, 164° and I···N≡C, 110°. PPh_4^+ cations have been omitted for clarity.

three directions and favor charge dilution and framework expansion.

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Notes and references

‡ Crystal structure analysis for $[PPh_4]\{[E\text{-TTF–}I_2]_{1/2}[Re_6Se_8(CN)_6]\}_{1/2}$ $C_{30}H_{21}IN_3PRe_3S_2Se_4$, triclinic, space group P-1, a = 12.618(5), b = 12.87(3), c = 13.317(8) Å, α = 92.24(9), β = 106.25(3), γ = 90.97(10)°, V = 2074(5) Å^3, D_c = 2.434 g cm^{-3}, Z = 2. Black needle-like crystal (0.10 × 0.09 × 0.05 mm). Data were collected on a Bruker four-circle diffractometer attached to a CCD area detector and a graphite monochromator for the MoKα radiation (50 KV, 30 mA), λ = 0.71073 Å at 293(2) K. Absorption correction was applied using the SADABS program (Siemens, USA, 1995). A total of 17895 reflections were collected up to θ = 29.9° of which 10466 are independent among 4030 observed [$F_o > 4\sigma(F_o)$]. The structure solution (SHELXS-97) and refinements on F_o^2 (SHELXL-97) gave R(obs.) = 0.1025 [R(all) = 0.2516] and Rw(obs.) = 0.2486 [Rw(all) = 0.3526] for 267 parameters; min. and max. residual electron densities were −7.19 and 2.77 e Å^{-3}. The latter electron density lies near the rhenium cluster anion. There are 26 non-H atoms that have only been treated isotropically, as they enter non-positive definites. This is also attributed to a disorder of the PPh_4 cation. All crystals tested gave comparable X-ray data of somewhat poor quality. Crystal structure analysis for $[PPh_4][\text{EDT-TTF–I}]\{[\text{EDT-TTF–I}][Re_6Se_8(CN)_6]\}_{1/2}$ $C_{26}H_{18.33}IN_2P_{0.67}Re_2S_6Se_{2.67}$, triclinic, space group P-1, a = 12.860(1), b = 13.371(1), c = 16.230(1) Å, α = 65.92(1), β = 74.42(1), γ = 74.69(1)°, V = 2416.1(3) Å^3, D_c = 2.642 g cm^{-3}, Z = 3. Black needle-like crystal (0.11 × 0.12 × 0.08 mm). Data were collected on a Bruker four-circle diffractometer attached to a CCD area detector and a graphite monochromator for the MoKα radiation (50 KV, 30 mA), λ = 0.71073 Å at 293(2) K. Absorption correction was applied using the SADABS program (Siemens, USA, 1995). A total of 62262 reflections were collected up to θ = 35.0° of which 20406 are independent among 11443 observed [$F_o > 4\sigma(F_o)$]. The structure solution (SHELXS-97) and refinements on F_o^2 (SHELXL-97) gave R(obs.) = 0.0542 [R(all) = 0.1251] and Rw(obs.) = 0.1364 [Rw(all) = 0.1741] for 569 parameters; min. and max. residual electron densities were −4.05 and 4.33 e Å^{-3}. The latter essentially lies near the rhenium chalcogenide cluster. The CCDC deposition numbers for **1** and **2** are CCDC 292268 and 292269, respectively. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b600159a

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