Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information

The 8:1:1 ternary hybrid framework in the system, [EDT-TTF$^{\bullet+}$] / [1,4-bis(iodoethynyl)benzene] / $[Re_6Se_8(CN)_6]^{4-}$: dual noncovalent expression of the octahedral halogen-bond hexa-acceptor nanonode

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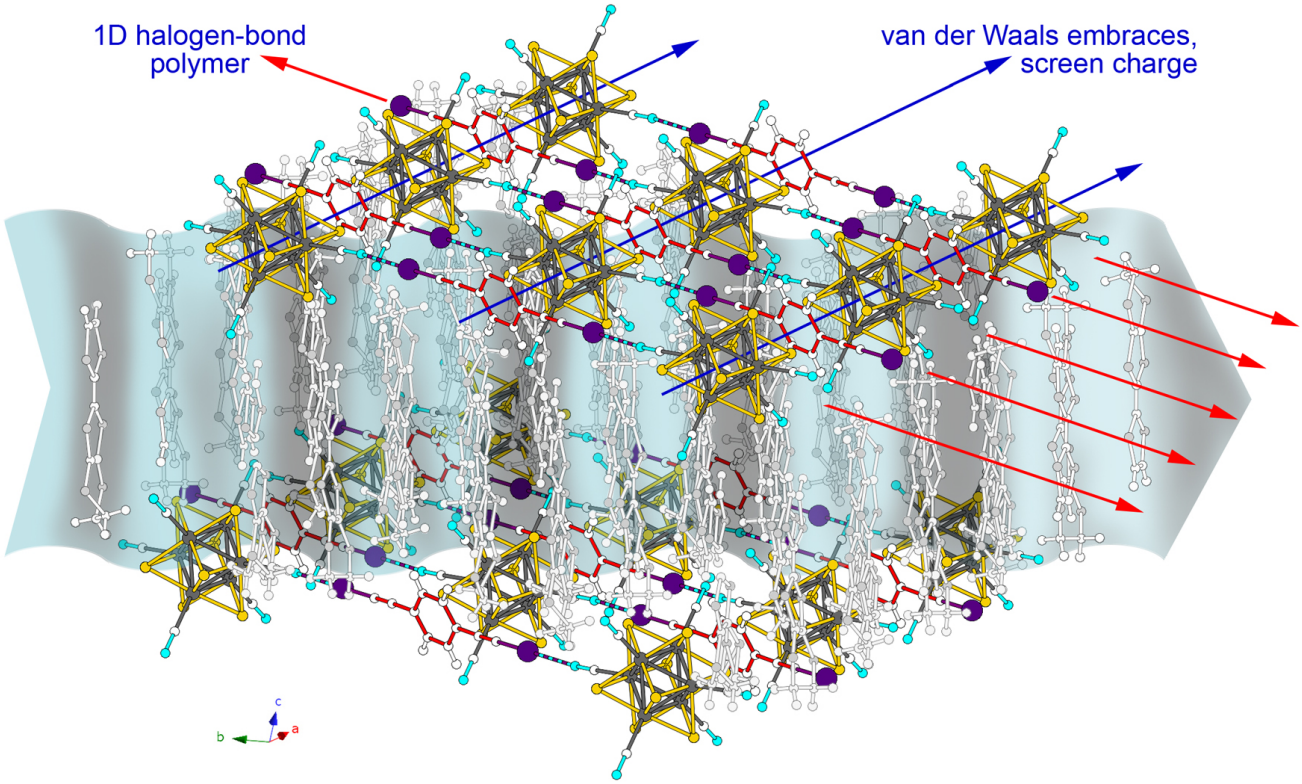

Fig. ESI 1 Illustration of the three types of nonvalent interactions whose balance direct the topology of the 8:1:1 ternary hybrid framework. The red arrows symbolize the halogen-bond self-assembly. The blue arrows symbolize how the flat, symmetrical neutral aromatic cores of the spacers and the inorganic cluter cores fit in, and screen the charge of the anionic node. The delocalization of charge carriers within the radical cation slab as a consequence of HOMO-HOMO interactions is also symbolized.

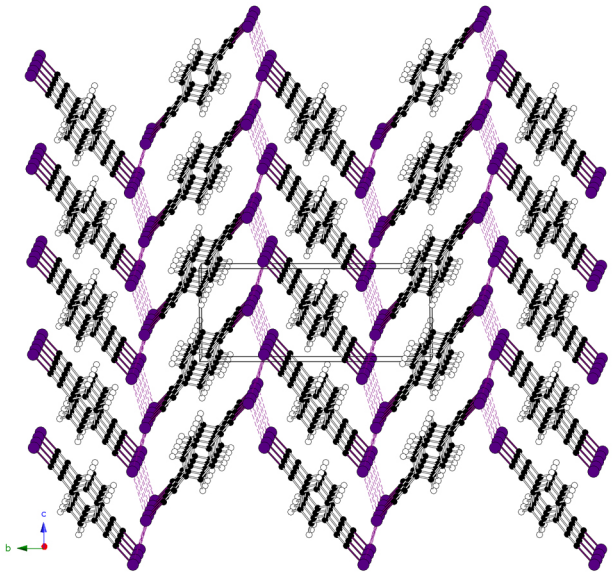

Fig. ESI 2 Three I•••I halogen bonds at 4.10, 4.24 and 4.45 Å are identified in the crystal structure of 1,4-bis(iodoethynyl)benzene. Note that the molecule lies about an inversion centre.

As pointed out rightly by one referee, changes in C-I bond-lengths in TTF-based structures containing short C-I…Cl-/Br- contacts are relevant to the discussion of the charge-assisted halogen-bond increase as it evolves herein. For example, one observes that the C-I bond-length increases from 2.08 in the monoconstituent solid[1] EDT-TTF-I to 2.10 in $(EDT\text{-}TTF\text{-}I)_2Br$.[2] Further in-depth investigations require extensive survey of published structures.

1 T. Devic, B. Domercq, P. Auban-Senzier, P. Molinié, M. Fourmigué, *Eur. J. Inorg. Chem.* 2002, 2844.
2 T. Imakubo, H. Sawa, R. Kato, *Synth. Met.* 1995, **73**, 117.