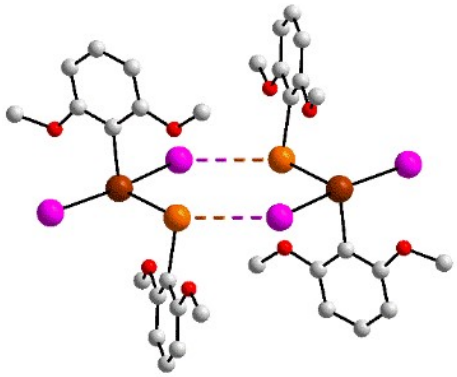
Electronic Supplementary Material (ESI) for CrystEngComm.

Te···I secondary-bonding interactions in crystals containing tellurium(II), tellurium(IV) and iodide atoms: supramolecular aggregation patterns, nature of the non-covalent interactions and energy considerations

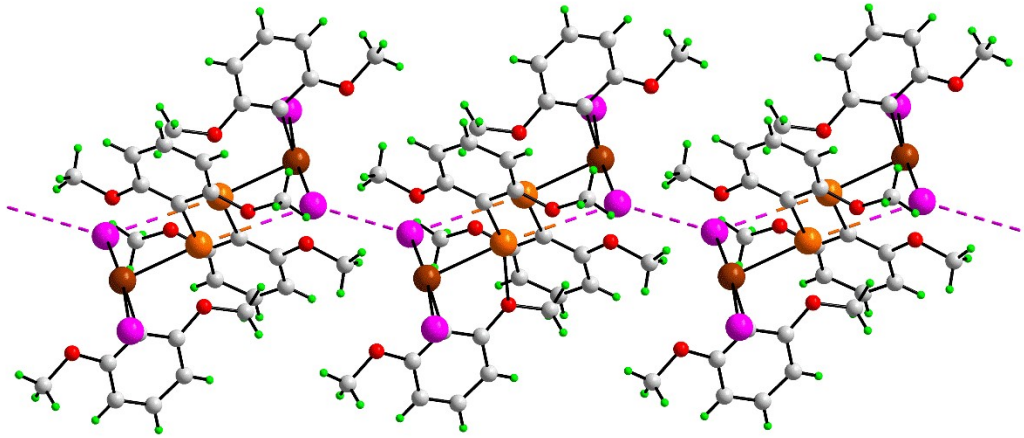
Rosa M. Gomila, Antonio Frontera* and Edward R. T. Tiekink*

Department of Chemistry, Universitat de les Illes Balears, Crta de Valldemossa km 7.5, 07122 Palma de Mallorca, Spain. E-mail: toni.frontera@uib.es; edward.tiekink@uib.es

ELECTRONIC SUPPLEMENTARY MATERIAL



(a)



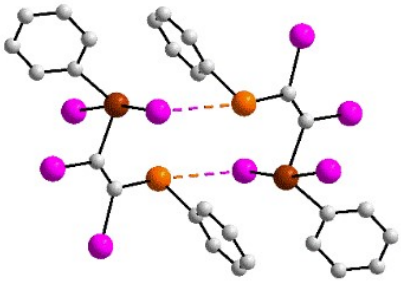
(b)

Figure S1. Supramolecular association in the crystal of 1,2-bis(2,6-dimethoxyphenyl)-1,1-bis(iodo)-1λ^4-ditellane (**1**):

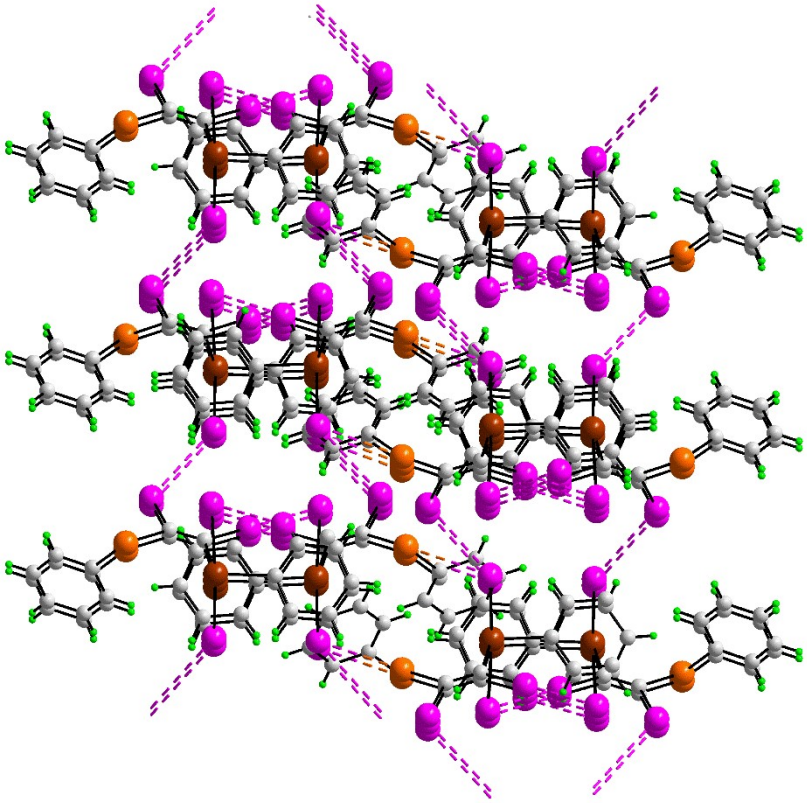
(a) the dimeric aggregate featuring $Te^{II}\cdots I$ interactions in the crystal of **1**.

(b) supramolecular chain whereby the dimeric aggregates of **1** assemble *via* long, end-on I···I interactions [d(I···I) = 4.0722(8) Å and Te–I···I = 139.727(16)°].

Colour code for this and subsequent diagrams: tellurium(II), orange; tellurium(IV), brown; iodide, pink; selenium, sky-blue; sulphur, yellow; oxygen, red; nitrogen, blue; carbon, grey; hydrogen, bright-green. The $Te^{II}\cdots I$, $Te^{IV}\cdots I$ and I···I interactions are represented as orange-pink, brown-pink and pink dashed lines, respectively. Non-acidic hydrogen atoms have been omitted for clarity in the molecular structure diagrams.



(b)



(b)

Figure S2. Supramolecular association in the crystal of *cis*-1,2-diiodo-1-(tellurophenyl)-2-(diodo-tellurophenyl)ethylene (**2**):

(a) the dimeric aggregate featuring $Te^{II}\cdots I$ interactions.

(b) a view of the three-dimensional architecture whereby the dimeric aggregates of **2** assemble *via* I···I interactions: 3.5845(4) Å [Te^{IV}–I···I = 97.31(1)° & ethylene-C–I···I = 176.18(11)°] and 3.8359(4) Å [Te^{IV}–I···I = 145.98(12)° & ethylene-C–I···I = 124.77(12)°].

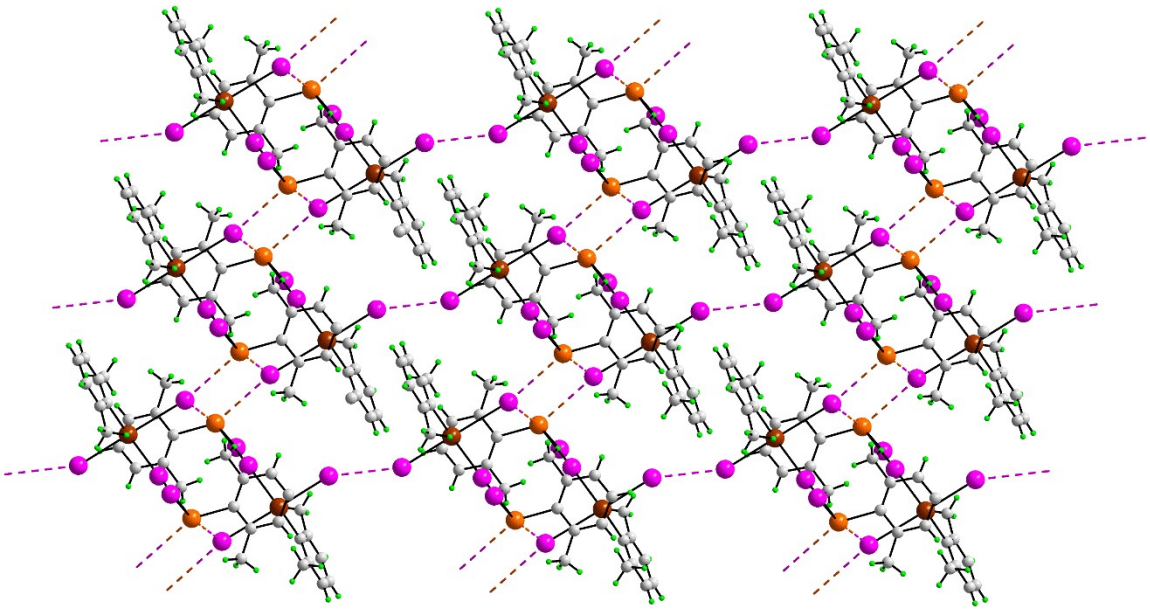


Figure S3. Supramolecular association in the crystal of (μ_2-iodido)-bis(2,6-dimethylphenyl)-tris(iodido)-tellurium(II)-tellurium(IV) (**3**): supramolecular two-dimensional array whereby the chains of **3** assemble *via* long, end-on I···I interactions [d(I···I) = 3.8166(5) Å and Te–I···I = 150.13(14)°].

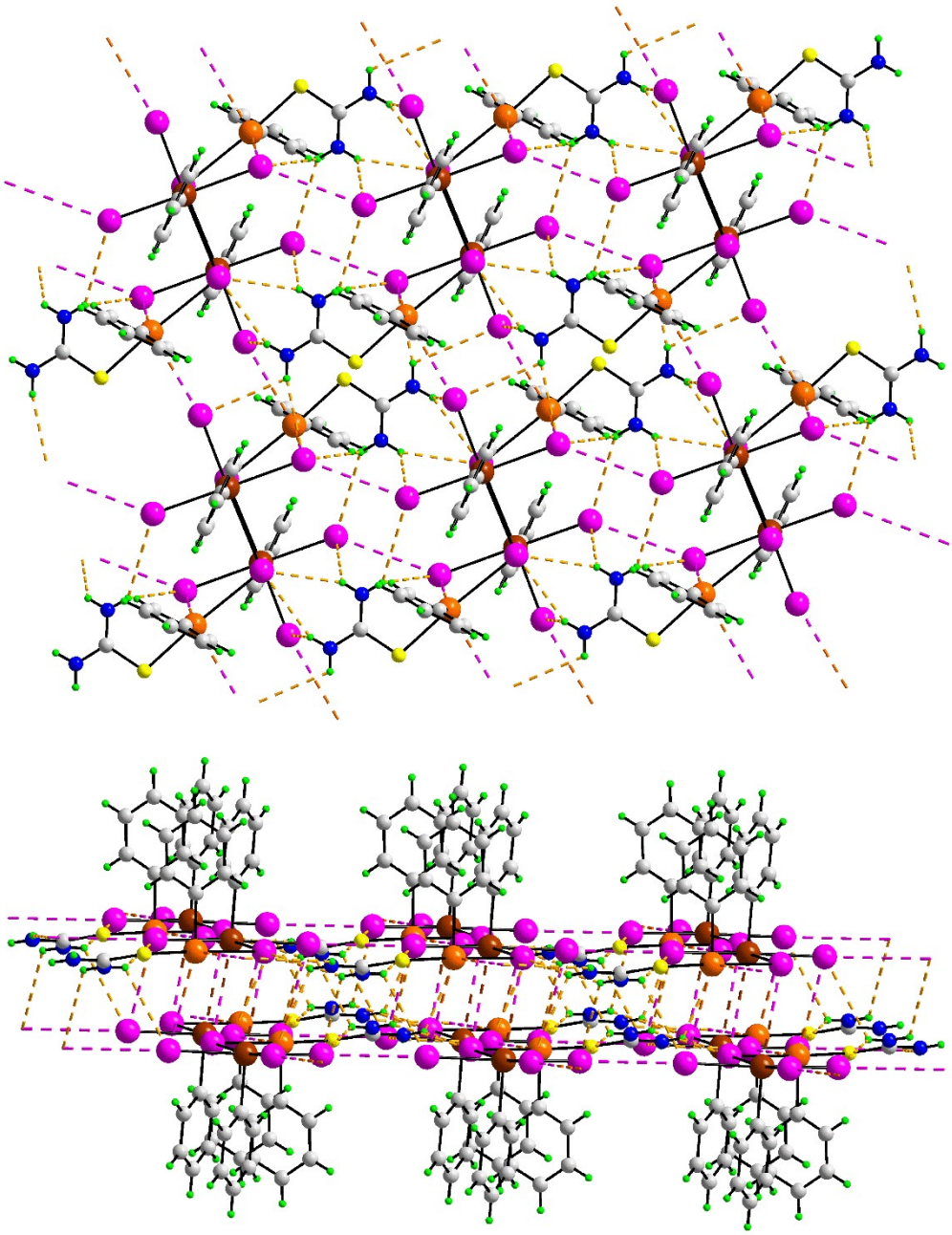


Figure S4. Supramolecular association in the crystal of (μ_2-iodido)-tris(iodido)-diphenyl-(thiourea-S)-tellurium(II)-tellurium(IV) (**4**): plan and side-on views of the two-dimensional supramolecular array, two molecules thick, whereby the chains of **4** assemble *via* I···I [4.0494(10) Å; Te^{II}–I···I = 109.021(16) and Te^{IV}–I···I = 140.67(2)°] interactions over a centre of inversion with supporting N–H···I hydrogen-bonds [d(H···I) = 2.97 to 3.39 Å], shown as orange dashed lines.

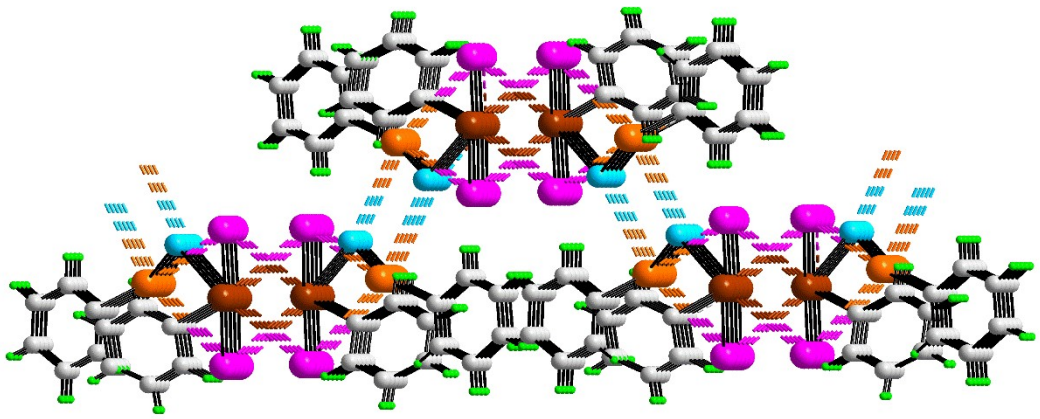
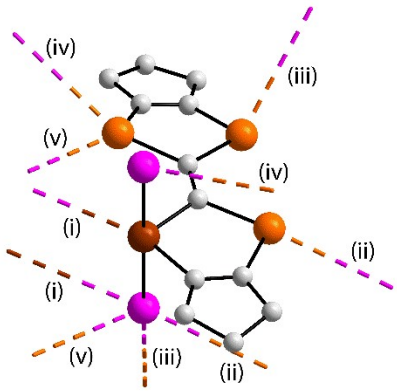
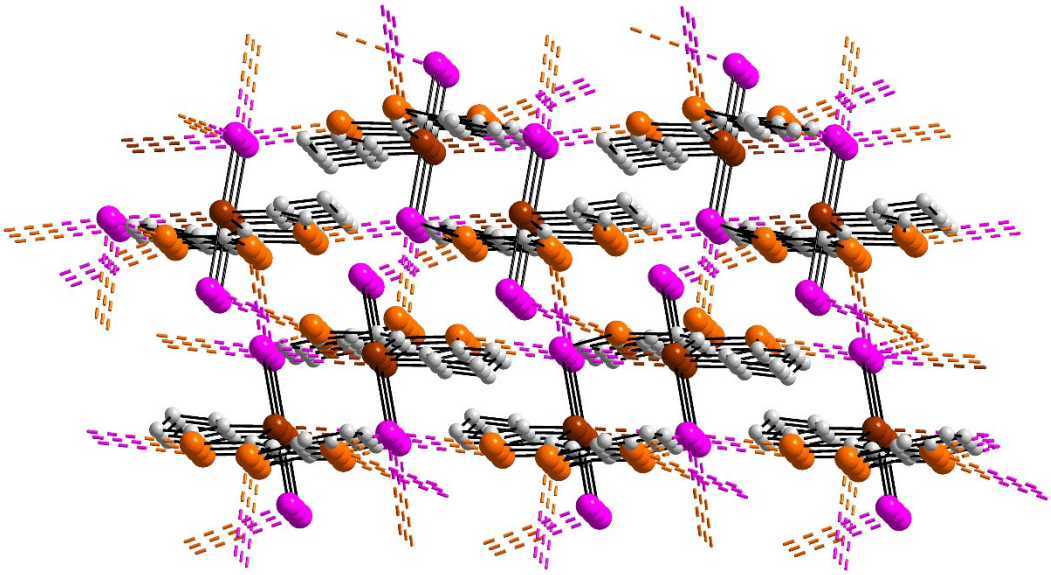


Figure S5. Supramolecular association in the crystal of (μ_2-selenido)-diiodo-diphenyl-di-tellurium (**5**): side-on view of the supramolecular two-dimensional array whereby the ribbons of **5** assemble *via* $Te^{II}\cdots Se$ interactions and centrosymmetric $\{\cdots Te^{II}Se\}_2$ synthons [$d(Te^{II}\cdots Se)$ = 3.5188(14) Å, Te^{II}–$Se\cdots Te^{II}$ = 99.22(4)°, Te^{IV}–$Se\cdots Te^{II}$ = 152.87(4)°].



(a)



(b)

Figure S6. Supramolecular association in the crystal of hexamethylenetetratellurafulvalene di-iodide (**6**): (a) view of the asymmetric-unit and the Te···I interactions it forms and (b) a portion of the three-dimensional framework. (i) d(Te^{IV}···I) = 4.0256(17) Å, Te^{IV}–I···Te^{IV} = 75.96(4)°, I–Te^{IV}···I = 76.15(4) & 104.04(4)°, C–Te^{IV}···I = 117.1(3) & 148.4(4)°; (ii) d(Te^{II}···I) = 3.7166(17) Å; Te^{IV}–I···Te^{II} = 107.35(5)°, C–Te^{II}···I = 92.9(4) & 170.6(3)°; (iii) d(Te^{II}···I) = 4.000(2) Å, Te^{IV}–I···Te^{II} = 170.44(6)°, C–Te^{II}···I = 93.9(4) & 126.4(3)°; (iv) d(Te^{II}···I) = 3.9196(19) Å, Te^{IV}–I···Te^{II} = 78.85(4)°, C–Te^{II}···I = 119.2(3) & 146.9(3)° and (e) d(Te^{II}···I) = 3.9353(17) Å; Te^{IV}–I···Te^{II} = 101.77(5)°, C–Te^{II}···I = 85.4(3) & 160.2(3)°.

Description of the molecular packing: The tellurium(IV) is tetra-coordinated within a C_2I_2 donor set with the iodide atoms projecting above and below the plane through the molecule encompassing the remaining non-hydrogen atoms. The tellurium(II) atoms are coordinated in a bent fashion by two ring-carbon atoms. Two of the tellurium(II) atoms, one from each ring, and the tellurium(IV) atom form a single Te···I interaction with the remaining tellurium(II)

atom forming two Te···I interactions. A disparity in connectivity also exists for the iodide atoms in that one iodide forms a single Te···I interaction whereas the second iodide participates in four Te···I interactions. Thus, there are five independent Te···I interactions in the crystal, (left-hand image).

Two Te^{IV}–I bonds self-associate about an inversion centre to form a centrosymmetric $\{\cdots Te^{IV}I\}_2$ synthon, entry (i) in the (a); this corresponds to the longest of the Te···I interactions in the crystal of **6**. The tellurium(II) atom of the same ring forms a Te···I interaction with the tellurium(IV)-bound iodide atom that forms four interactions, entry (ii) in (a), leading to a centrosymmetric, eight-membered $\{\cdots Te^{II}CTe^{IV}I\}_2$ synthon. This iodide also forms an interaction with each of the tellurium(II) atoms of the second ring, entries (iii) and (iv) in (a), respectively, and serves to link two independent molecules. The tellurium(II) atom forming the interaction specified as "(iv)" forms a further Te···I interaction with the second iodide atom, *i.e*. the iodide atom forming a single Te···I interaction only, *i.e*. (v) in (a), and occurs within a zigzag chain along the glide plane. A view of the three-dimensional architecture is shown in the Fig. S6(b); the closest I···I separation in the crystal of **6** is 4.38 Å.