Supplementary data for the paper "Structural isomerism in (p–XC_6H_4)$SeCl_3$ and (p–XC_6H_4)$SeBr_3$ (X = F, Cl) compounds. Co–crystallisation of *cis*– and *trans*– dimeric forms of (p–ClC_6H_4)$SeCl_2$(μ–Cl)$_2$(p–ClC_6H_4)$SeCl_2$. A new structural modification for the "PhSeBr" reagent, $Ph_2Se_2Br_2$, containing an elongated Se–Se bond."

Crystal packing features:

(p–FC_6H_4)$SeCl_3$ and (p–FC_6H_4)$SeBr_3$:

The extended structures of (p-FC_6H_4)$SeCl_3$ and (p-FC_6H_4)$SeBr_3$ both show identical features as the two structures are isomorphous. The extended structures viewed down the *a*–axis are shown in Figure S1 below.

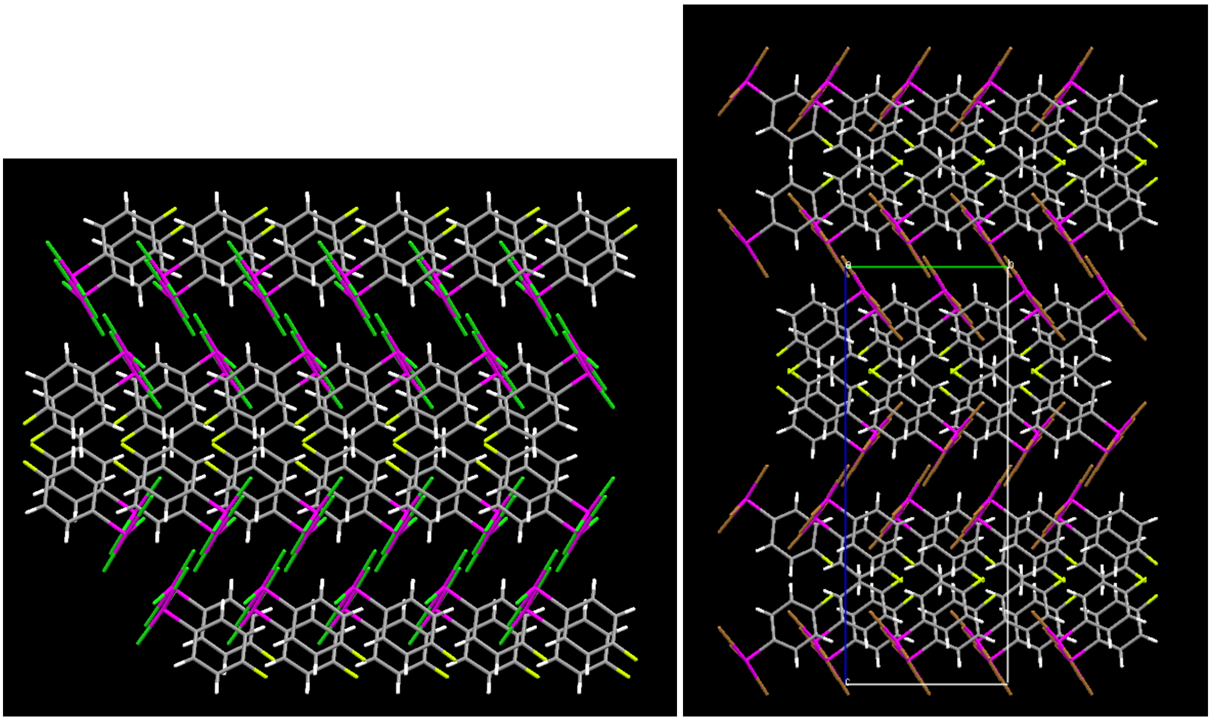

Figure S1 Extended structures of (p-FC_6H_4)$SeCl_3$ and (p-FC_6H_4)$SeBr_3$, viewed in each case down the crystallographic *a*–axis, showing the presence of a herringbone arrangement for the planar Se_2X_6 group of atoms throughout the crystal packing.

Alternating stacks of the dimer pairs are present, which pack in a herringbone fashion. The stacks link to neighbouring stacks via weak X···X contacts. In (p-FC_6H_4)$SeCl_3$ there is a weak Cl(6)···Cl(6) contact of 3.450(3) Å, which is slightly shorter than the sum of twice the van der Waals radii of chlorine (3.50 Å). Similarly, in (p-FC_6H_4)$SeBr_3$ there is a weak Br(1)···Br(1) contact of 3.568(3) Å (*c.f* twice the van der Waals radii of bromine, 3.70 Å).

There is also extensive π–stacking throughout both structures, which is best viewed down the *c*–axis, as shown in Figure S2 below.

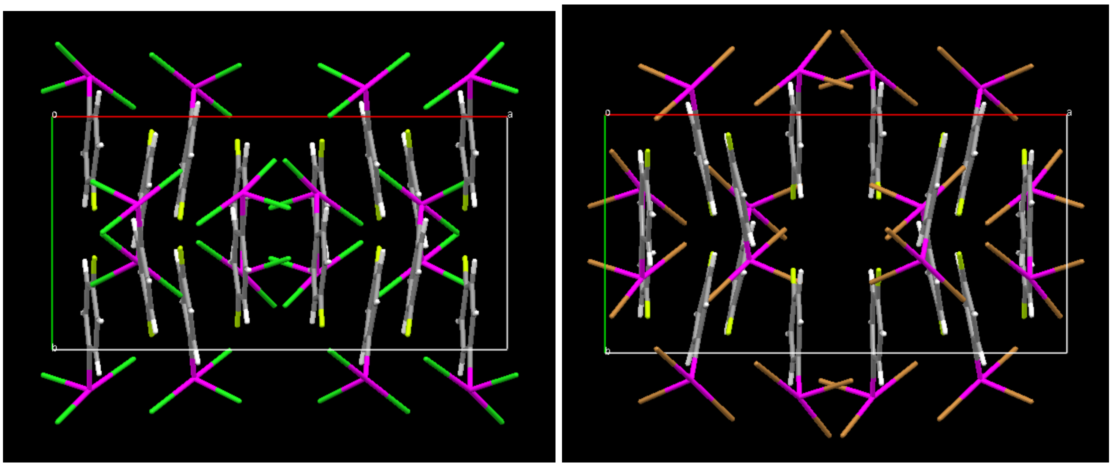

Figure S2 Extended structures of (*p*-FC$_6$H$_4$)SeCl$_3$ (left) and (*p*-FC$_6$H$_4$)SeBr$_3$ (right) viewed down the crystallographic *c*–axis, showing extensive π–stacking throughout the structures.

The presence of π–stacking of the *p*–FC$_6$H$_4$ rings, and aggregation of the fluorine atoms into fluorophilic regions, are also apparent in the crystal packing. Whilst there are no short F···F contacts in either structure, there are short F···H contacts in each structure, F(4)···H(11): 2.59 Å and F(10)···H(6): 2.56 Å in (*p*-FC$_6$H$_4$)SeCl$_3$, and F(1)···H(8): 2.53 Å in (*p*-FC$_6$H$_4$)SeBr$_3$.

(p–ClC_6H_4)$SeCl_3$:

In the extended structure of (p–ClC_6H_4)$SeCl_3$ the molecules of *cis*–dimers and *trans*–dimers stack down the crystallographic *b*–axis, and are linked by a combination of Se···Cl and Cl···Cl contacts, as shown in Figure S3 below.

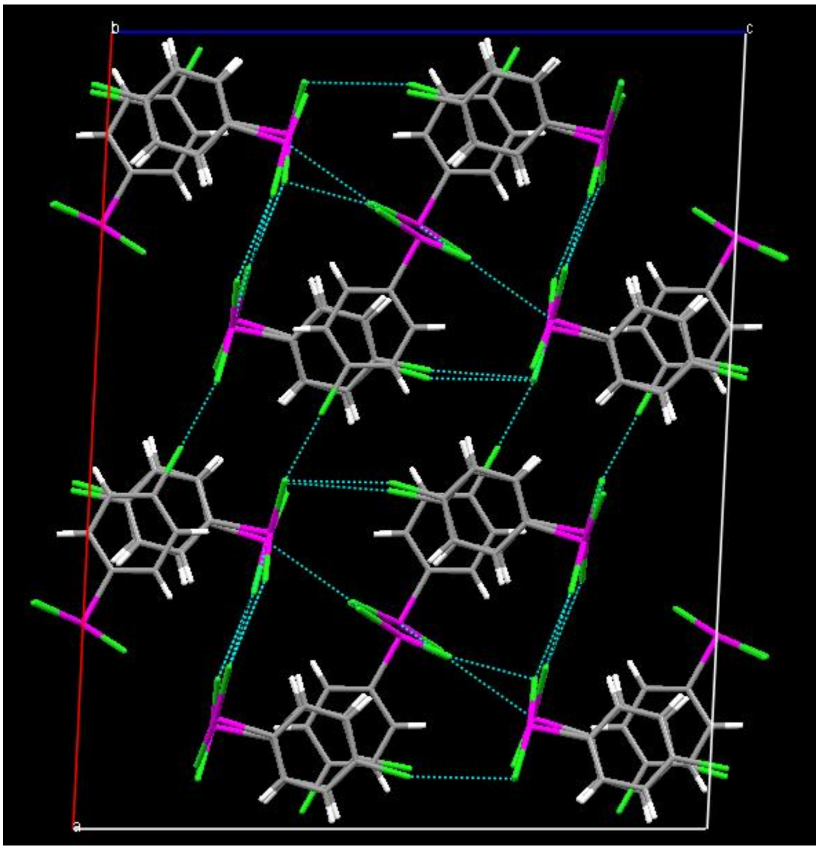

Figure S3 Packing of (p-ClC_6H_4)$SeCl_3$ viewed down the crystallographic *b*–axis.

The unusual co–crystallisation of both *cis*– and *trans*–dimers in the structure of (p-ClC_6H_4)$SeCl_3$ results in a number of interesting packing features. Stacks of *cis*– and trans–dimers are linked by an Se···Cl contact to the vacant sixth coordination site at atom Se(1) on the *cis*–dimer, Se(1)···Cl(11): 3.3542(19) Å. There are Cl···Cl contacts present between one of the terminal Se–Cl chlorine atoms and one of the bridging Se–Cl chlorine atoms on the *cis*–dimer with the aryl chlorine atoms of a neighbouring *cis*–dimer, Cl(4)···Cl(6): 3.423(3) Å, Cl(5)–Cl(8): 3.382(2) Å.

Extensive π–stacking of the p–ClC_6H_4 rings is observed in the crystal packing, as shown in Figure S4 below. Whilst stacking of p–ClC_6H_4 rings of the *cis*–dimer is close to parallel, more offset π–stacking also occurs with p–ClC_6H_4 rings of the *trans*–dimer.

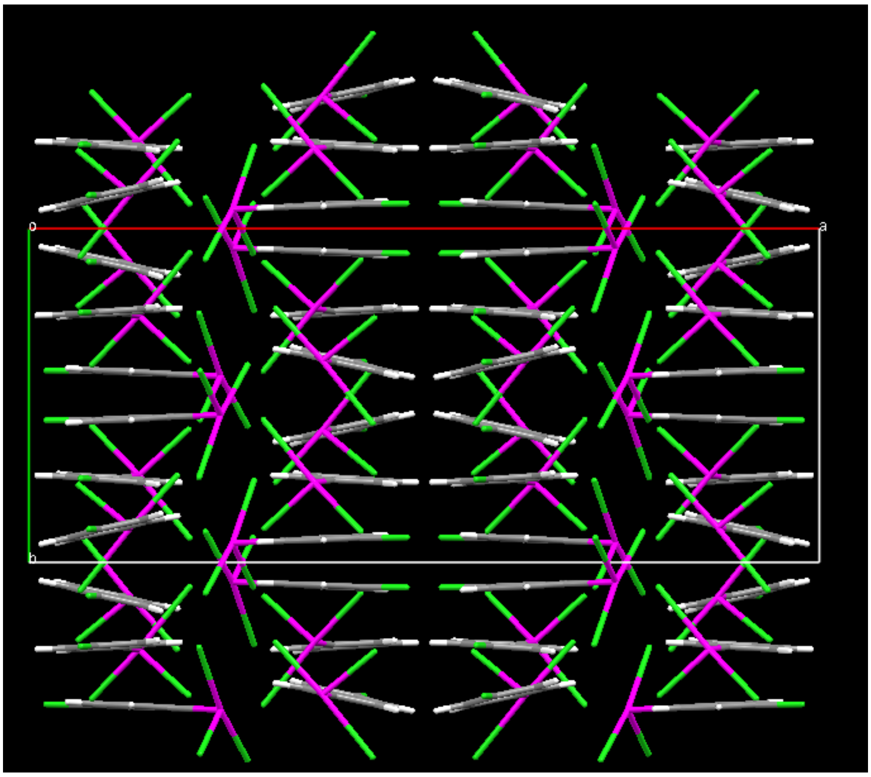

Figure S4 Crystal packing of (*p*-ClC$_6$H$_4$)SeCl$_3$ viewed down the *c*–axis, showing the extent of π–stacking throughout the structure.

(*p*–ClC$_6$H$_4$)SeBr$_3$:

The extended structure of (*p*–ClC$_6$H$_4$)SeBr$_3$ shows many similar features to the analogous trichloride. Dimer pairs stack down the *a*–axis (as shown in Figure S5 below), and are linked by Cl···H contacts from aryl chlorine to aryl protons, Br···H contacts from Se–Br atoms to aryl protons, and again by off–set π-stacking.

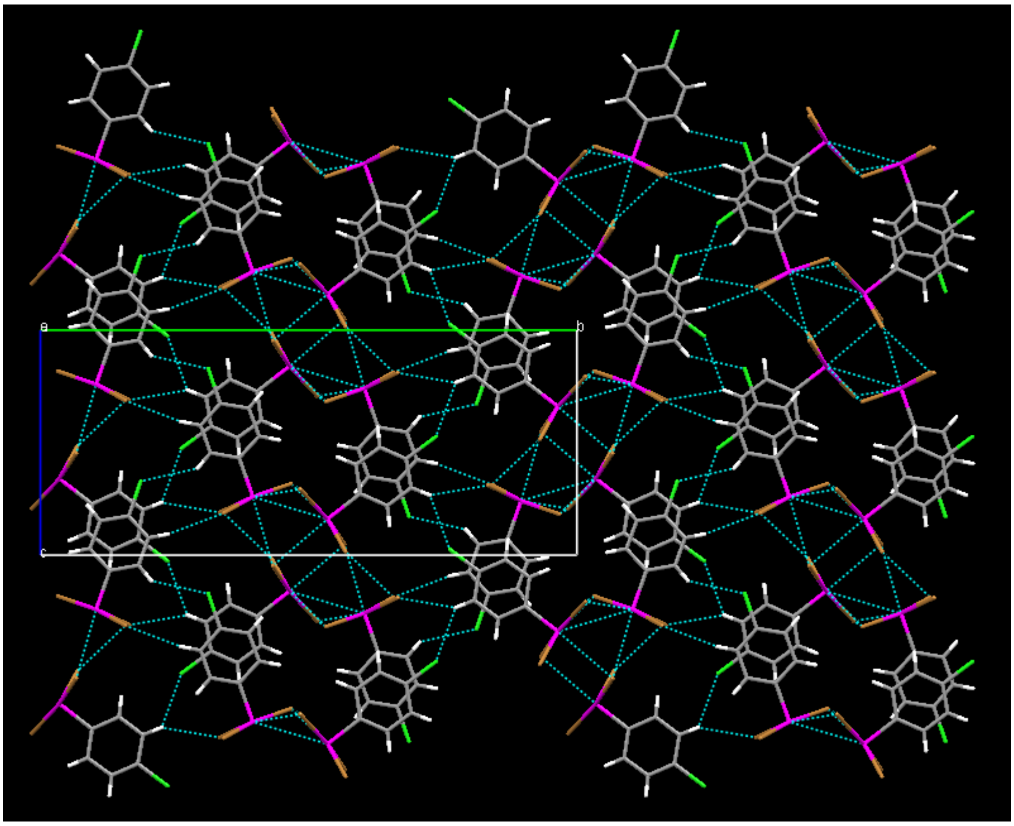

Figure S5 Packing of (*p*-ClC$_6$H$_4$)SeBr$_3$ viewed down the crystallographic *a*–axis.

One noticeable difference between the structures of (*p*-ClC$_6$H$_4$)SeCl$_3$ and (*p*-ClC$_6$H$_4$)SeBr$_3$, is that in the former the Se–Cl bonds participated directly in Se···Cl and Cl···Cl interactions between stacks. In (*p*-ClC$_6$H$_4$)SeBr$_3$ this is not observed. Instead, non–classical hydrogen bonding (either Cl···H or Br···H) is observed between the stacks. There are two short Cl···H contacts present, one to each of the two aryl chlorine atoms, Cl(1)···H(3): 2.85 Å and Cl(2)···H(12): 2.90 Å. The folded nature of the dimer results in only the two terminal bromine atoms Br(4) and Br(5) participating in hydrogen bonding, Br(4)···H(3): 3.02 Å and Br(5)···H(9): 3.02 Å. It should be noted that atom H(3) acts as a bifurcated H–bond donor interacting with both Cl(1) and Br(4).