Supplementary Information

The fundamental structural motif that both structures have in common is the layer depicted in Fig. S1, for the rhombohedral polymorph, view direction *c*. The only difference is thus different stacking patterns.

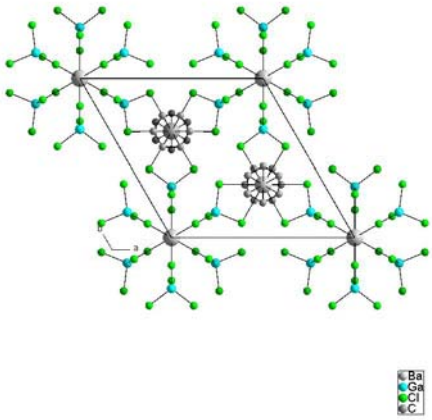

Fig. S1 First layer of the rhombohedral dimorph (**1**).

In the rhombohedral form, the two different Ba atoms are labelled Ba1 (both Cl and benzene ligands) and Ba2 (Cl ligands only). The layers are stacked along *c* in such a fashion that the sequence along the axis is Ba2-Ba1-Ba1-Ba2-… and that the Ba atoms lie on a perfectly straight line parallel with *c*. Hence, each Ba2 polyhedron has Ba1 as the closest neighbours in the adjacent layers, whereas each Ba1 has one Ba1 and one Ba2 neighbour. The distance between Ba1 and Ba2 is 923.5(3) pm, the Ba1-Ba1 distance 1466.1(5) pm.

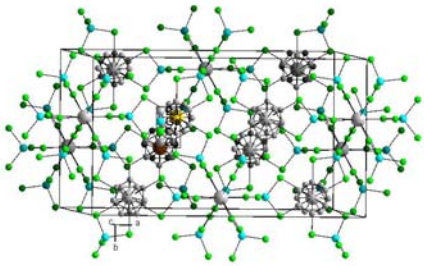

Fig. S2 Packing of two layers in the monoclinic dimorph (**2**), showing the *a*,*b*-shift.

In the monoclinic form, the stacking is more complex. While the basic structural feature, the layer containing two different types of Ba atoms, remains the same, the adjacent layer in +c direction appears to be shifted by -148 pm and -268 pm, respectively, in the *a* and *b* direction, respectively.