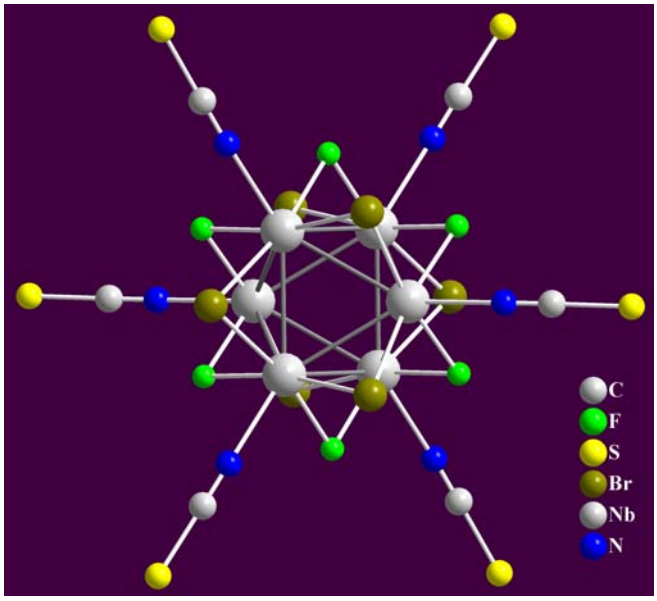
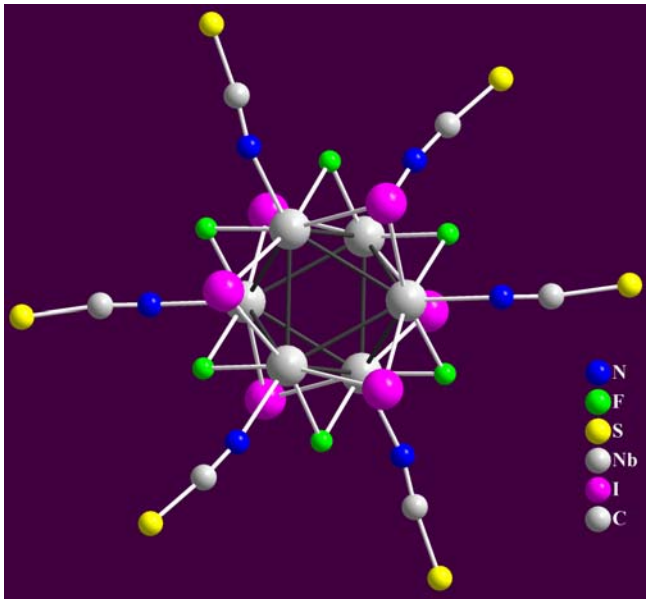
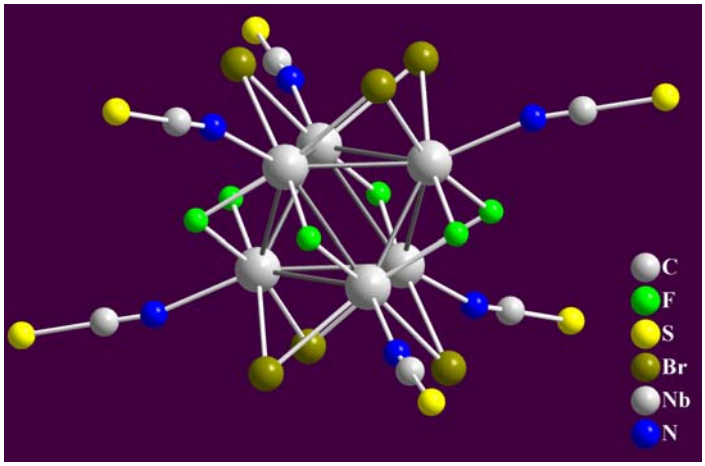
Figure S1.
Two orientations of isolated anions in $(Et_4N)_6[Nb_6F_6Br_6(NCS)_6]Br_2$ (**1**) and $Cs_{1.6}K_{2.4}[Nb_6F_6I_6(NCS)_6]$ (**2**)

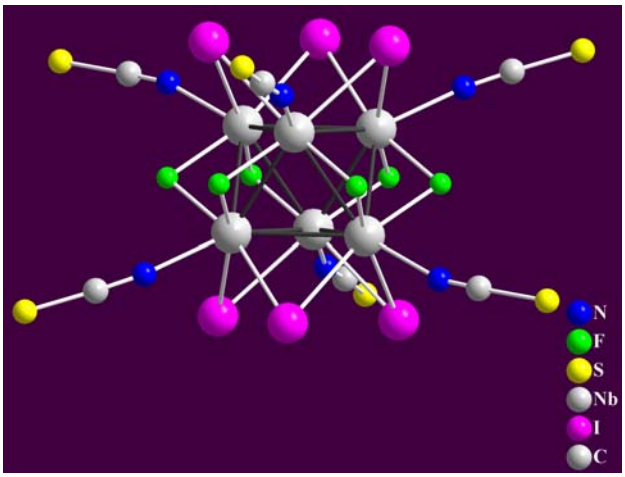
a) along three-fold axis;





b) showing plane of six fluoride ligands around Nb_6 cluster.



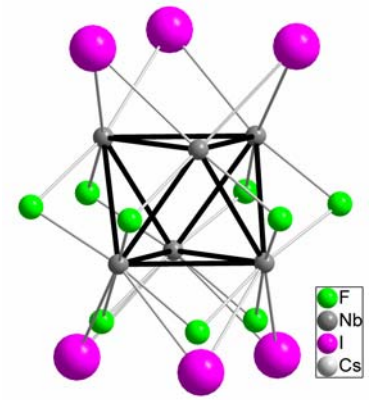


$[Nb^i_6F^i_6Br^a_6(NCS)^a_6]^{4-}$ anion

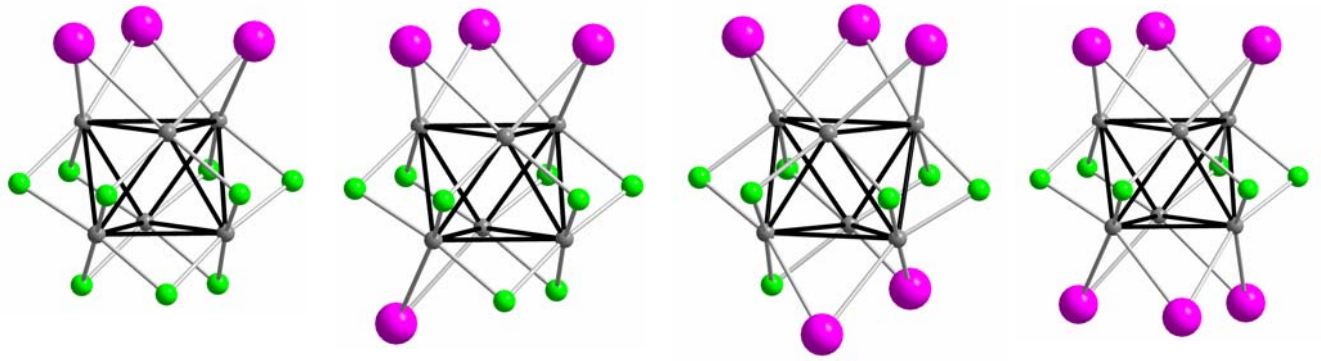
$[Nb^i_6F^i_6I^a_6(NCS)^a_6]^{4-}$ anion

Figure S2.

a) Environment of Nb_6 cluster in parent $Cs_4Nb_6F_{8.5}I_{9.5}$. Occupancies of disordered I^i and F^i in $Cs_4Nb_6F^i_{8.5}I^i_{3.5}I^a_6$ are 0.5 and 2.5, respectively.

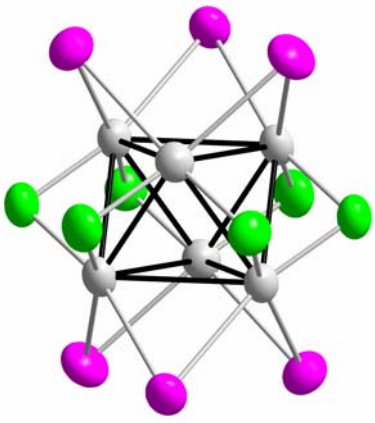


b) Possible isomers of $Nb_6L^i_{12}$ cluster core in parent $Cs_4Nb_6F_{8.5}I_{9.5}$:



$Nb^i_6F^i_9I^a_3$ $Nb^i_6F^i_8I^a_4$ $Nb^i_6F^i_7I^a_5$ $Nb^i_6F^i_6I^a_6$

c) Cluster core in isolated $[Nb^i_6F^i_6I^a_6(NCS)^a_6]^{4-}$ anion:



The experimental I/F ratio (9.5/8.5) in $Cs_4[Nb_6F^i_{8.5}I^i_{3.5}I^a_6]$ could result from an equimolar mixture of $Nb_6F^i_8I^i_4$ and $Nb_6F^i_9I^i_3$ units, or a mixture of $Nb_6F^i_9I^i_3$ and $Nb_6F^i_6I^i_6$ with ratio 5:1. The isolation of **2** with low yield favors the latter possibility altough the presence of traces other isomers units ($Nb_6F^i_9I^i_3$, $Nb_6F^i_8I^i_4$, $Nb_6F^i_7I^i_5$ and $Nb_6F^i_6I^i_6$) is also assumed.