

## **A Cluster Fullerene Containing Only Non Group III Metal inside the Carbon Cage: $\text{Ti}_2\text{S}@D_{3h}(5)\text{-C}_{78}$ with a Linear Sulfide Cluster inside the Cage**

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After the discovery of the first nitride cluster metallofullerenes (NCFs),  $\text{Sc}_3\text{N}@C_{80}$ , in 1999, numerous cluster metallofullerenes have been prepared. However, the types of "clusterfullerenes" reported so far are quite limited: nitride cluster fullerenes (NCFs), carbide cluster metallofullerenes (CCFs), oxide cluster metallofullerenes (OCFs) and sulfide cluster fullerenes (SCFs). Given that almost all of the encaged metals for all of these reported cluster fullerenes are limited to group-III (Sc, Y, and lanthanide) metals, there are very few reports of the synthesis of cluster fullerenes with a non-group III metal, titanium (Ti), trapped inside a carbon cage. However, the Ti is normally accompanied by other metals. This suggests that it is difficult to encage a cluster containing only Ti metal inside a fullerene cage. There is only one report with a titanium-only cluster,  $\text{Ti}_2\text{C}_2@C_{78}$ , and it showed particular interactions between the Ti atoms and the carbon cage. In this work, a titanium sulfide fullerene,  $\text{Ti}_2\text{S}@C_{78}$ , was synthesized. Multistage HPLC methods were utilized to isolate and purify the  $\text{Ti}_2\text{S}@C_{78}$ . The purified  $\text{Ti}_2\text{S}@C_{78}$  was characterized by mass spectrometry, UV-Vis-NIR absorption spectroscopy and its electrochemical behavior was studied by cyclic voltammetry. Computational studies suggest that the  $\text{Ti}_2\text{S}$  cluster is linear, as opposed to the geometry of the  $\text{Sc}_2\text{S}$  cluster.