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Structure of a Novel Amorphous Organic-Inorganic Hybrid Tin Cluster Exhibiting Nonlinear Optical Effects by Low-Energy XAFS Measurements

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Tailored light sources have greatly advanced technological and scientific progress by optimizing colour and brilliance, improving energy efficiencies or the quantum properties of light. So called supercontinuum generators are premier examples for media with nonlinear optical (NLO) effects – far superior in some respects to other sources such as phosphorescent white light-emitting diodes (LEDs). However, unlike LEDs, most of these advanced light sources are only used for scientific purposes, as they require extreme electric field strengths which are commonly realized by high-power pulsed lasers. In contrast, the materials of interest for this research project represent a new generation of supercontinuum emitters that are readily obtained from ubiquitous resources in a simple synthesis.

These compounds are of the general composition Sn4S6R4 (R=Methyl, Phenyl, Naphtyl, Cyclopentadienyl) and exhibit strong NLO effects, making it possible to use them as cheap and efficient warm-white supercontinuum emitters when driven by a commercially available low-power continuous-wave infrared laser diode [1]. Quantum chemical calculations suggest that these compounds consist of Sn4S6 clusters. On the other hand, it was also confirmed that the NLO effect is linked to the amorphous nature of the materials, but the structural properties of the amorphous phase, and thereby the apparent origin of this effect, is difficult to determine [2].

Recent investigations indicate that the relative orientation of neighboring clusters comprise key information concerning the strength of the NLO effect.[3] These inter-cluster correlations can be probed by low-energy EXAFS measurements, which were conducted at BL11 for a sample with R=Methyl. The analysis is complicated by the multitude of different EXAFS paths, therefore a good resolution in

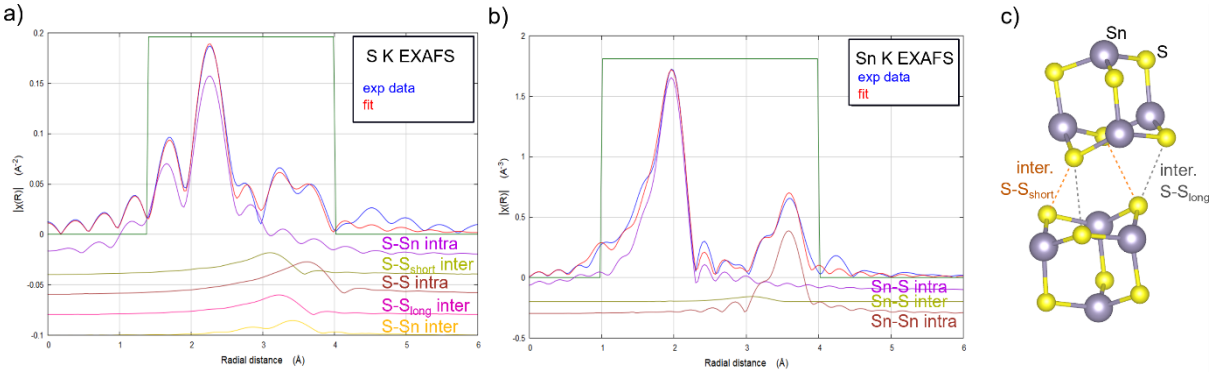

FIGURE 1. S K-edge EXAFS data (a) in comparison with Sn K-edge EXAFS data, and their fitting results. The model used for the fit is shown in (c), where the organic side groups are omitted for clarity.

real-space, corresponding to a wide *k*-range in the raw data, is essential. A simplified model based on the calculation of the dimer structure [3] gives a very good fit to the data (Fig. 1a) and is also in agreement with higher energy EXAFS data from the Sn K-edge (Fig. 1b). The model is illustrated in Fig. 1c, and comprises two different inter-cluster S-S distances, one short (about 3.70 Å) and one long (about 3.85 Å) distance.

The results indicate an inter-cluster S-S coordination number of 0.7, tantamount to a dimerization of the Sn4S6R4-clusters (expected CN is 0.66). A formation of a further network of arranged clusters (equivalent to a larger inter-cluster S-S coordination number) is demonstrated to be unlikely for the clusters with Methyl side groups. Further work is necessary to investigate samples with other organic side groups to reveal possible links between the network formation and the NLO effect.

REFERENCES

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