Tetrathiafulvalene-2,3,6,7-tetrathiolate Linker Redox-State Elucidation via S K-edge X-ray Absorption Spectroscopy

Ningxin Jiang, Jan-Niklas Boyn, Arun Ramanathan, Henry S. La Pierre, and John S. Anderson

Sulfur K-edge XAS data provide a unique tool to examine oxidation states and covalency in electronically complex S-based ligands. We present sulfur K-edge X-ray absorption spectroscopy on a discrete redox-series of Ni-based tetrathiafulvalene tetra(thiolate) (TTFtt) complexes as well as on a 1D coordination polymer (CP), NiTTFtt. Experiment and theory suggest that Ni—S covalency decreases with oxidation which has implications for charge transport pathways. Finally, a characteristic peak for doubly oxidized TTFtt verifies this formal redox state in the CP, NiTTFtt.

Dithiolene and tetrathiafulvalene (TTF)-based compounds have generated significant interest due to their remarkable properties. For instance, high electric conductivity has been observed in dithiolene-based CPs, such as Ni_3(BHT)_(2) (BHT = benzenehexathiolate), Cu_4(BHT), and cobalt dithiolenes, as well as in TTF-based metal organic frameworks. Some sulfur-based materials, such as [(TTF)Ni(dmit)]_2 and (TTF)[Pd(dmit)]_2 (dmit = 1,3-dithiole-2-thione-4,5-dithiolate), which possess both dithiolene motifs and TTF, are also superconductors.

Tetrathiafulvalene-2,3,6,7-tetrathiolate (TTFtt) is a particularly attractive sulfur-based ligand for developing novel materials since it has features of both dithiolene and TTF cores. Exciting physical properties have been observed in TTFtt-based molecules and materials. For example, [(FeTPA)_2TTFtt][BARF_4]_2 exhibits reversible switching of diradical character via metal-centered spin crossover, while Pt-based TTFtt molecules show bright, modular, and switchable near-infrared II emission, and NITTFtt CPs display glassy-metallic conductivity.

TTFtt can be oxidized twice leading to three distinct redox states which can have a dramatic effect on properties. The CP NiTTFtt has formally doubly oxidized TTFtt linkers with high conductivity and n-type carriers. In contrast NiTTFtt with neutral TTF cores is a p-type semiconductor. While the formal redox state and charge for these materials is evident from composition analysis, determining the localization of oxidation, namely between the linker and the metal center, is more challenging. Direct correlation between spectroscopic evidence and TTFtt oxidation state is lacking even though differences can be observed in vibrational, UV-visible, and NIR data between different molecular TTFtt redox isomers.

X-ray absorption spectroscopy (XAS) enables experimental examination of oxidation states and covalency. In particular, S K-edge XAS enables analysis of the redox states of non-innocent S-based ligands in dithiolene compounds. For instance, in [Ni(S_2C_2Me_2)_2]_n, S K-edge XAS suggests that oxidation primarily occurs on the ligand as opposed to Ni. We therefore collected sulfur K-edge XAS data on a series of [(dppe)Ni]_2TTFtt molecules as well as the nickel-based CP. We also performed time-dependent density functional theory (TD-DFT) calculations to interpret this data. We find that the covalency of the metal sulfur bond decreases with higher TTFtt redox states. A characteristic peak is observed for the doubly oxidized TTFtt-based moieties. Calculations are in good agreement with the experimental data and suggest that this characteristic peak can be assigned to excitation into a π-based lowest unoccupied molecular orbital (LUMO). These results elucidate the electronic structures of TTFtt systems and provide insights into how these electronic structures are linked to the observed bulk properties in TTFtt-based materials.

Three previously reported Ni-based TTFtt molecules with different TTFtt redox states were chosen for XAS characterization (Fig. 1a). The complex [(dppe)Ni]_2TTFtt (1-TTFtt) contains a neutral TTF, while [(dppe)Ni]_2TTFtt[BARF_4]_2 (2-TTFtt) has a singly-oxidized TTF and the TTF in [(dppe)Ni]_2TTFtt[BARF_4]_2 (3-TTFtt) is doubly oxidized (BARF_4 =
tetrakis[3,5-bis(trifluoromethyl)phenyl]borate. Experimental S K-edge XAS data of these complexes are shown in Fig. 1b. Both 1-(TTF\(^+\)), 2-(TTF\(^+\)) display one pre-edge feature at 2471.5 eV. In contrast, 3-(TTF\(^+\)) displays three distinct pre-edge shoulders at ~2470.5, 2471.5 and 2472.5 eV. Curve-fitting analyses were performed using pseudo-Voigt line shapes and a step function, as shown in the bottom of Fig. 2 (further details in SI). Fitting provides pre-edge peak positions of 2471.2 (1-(TTF\(^+\))) and 2471.4 (2-(TTF\(^+\))) eV. For 3-(TTF\(^+\)), three pre-edge peaks are fit at 2470.6, 2471.5, and 2472.5 eV.

We used TD-DFT calculations to understand the pre-edge features in the XAS spectra (Fig. 1c and 2). Computations used the PBE0 functional\(^\text{18}\) with the zero-order regular approximation (ZORA) and the ZORA-def2-TZVP and SARC/J basis sets\(^\text{19-21}\) utilizing the Tamm-Dancoff approximation\(^\text{22}\) as implemented in Orca 5.0.3.\(^\text{23}\) A uniform shift of 36.5 eV was applied to the TD-DFT spectra for alignment with experimental data. We note that there are two distinct sets of S atoms in the TTF\(^{t+}\) ligand: the four S's bound to Ni (M-S's) and the four S's located in the TTF core (TTF-S's). The TD-DFT calculations enable differentiation between these different S types.

Each calculated spectrum in Fig. 2 (black curve) is composed of the M–S contribution (red curve) and the TTF–S contributions (blue curve). For 1-(TTF\(^{t+}\)), the pre-edge feature at 2471.2 eV primarily arises from M–S based transitions. For 2-(TTF\(^{t+}\)), the calculations suggest that the pre-edge feature at 2471.4 eV arises from both M–S and TTF–S based transitions. For 3-(TTF\(^{t+}\)), the first feature at 2470.6 eV can be assigned to a M–S based transition, however, assignment of the features at 2471.5 eV and 2472.5 eV is more complicated. One broader feature is found in the calculated spectrum (2472.2 eV), but examination of the constitutive transitions of this feature suggests that it is a convolution of two distinct transitions, similar to the pre-edge feature in 2-(TTF\(^{t+}\)) (see below). The experimental spectrum evinces greater resolution of these features which may be due to multiplet effects not captured in the calculation. Based on the calculated relative intensity and the experimental intensity of peaks, the peak at 2471.5 eV is assigned to a M–S transition and the peak at 2472.5 eV primarily arises from TTF–S transitions (see details in SI).

The intensities of pre-edge peaks in ligand K-edge XAS data are proportional to the bond covalency.\(^\text{16, 17, 24, 25}\) Since TD-DFT calculations allow for deconvolution of the M–S contributions the Ni–S bond covalency can be determined. Calculations indicate that the pre-edge feature in 2-(TTF\(^{t+}\)) at 2471.4 eV arises from both M–S and TTF–S based transitions which precludes assigning the fitted intensity to a single transition. For 1-(TTF\(^{t+}\)), the Ni–S relative covalency of the peak at 2471.2 eV can be determined from the intensity of the peak which is ~0.56(3). For 3-(TTF\(^{t+}\)), the Ni-S covalency is from both peaks at 2470.6 and 2471.5 eV. The combined intensity of these peaks is 0.47(5); smaller than in 1-(TTF\(^{t+}\)). The lower value in 3-(TTF\(^{t+}\)) suggests a lower bond covalency in 3-(TTF\(^{t+}\)) and, therefore, a higher ionic character for the Ni–S bonds. DFT calculations also show a decrease of the Ni–S Mayer bond order from 0.888 in 1-(TTF\(^{t+}\)) to 0.802 in 3-(TTF\(^{t+}\)).

In previous S K-edge XAS data on Ni dithiolene compounds, the hole-weighted covalencies were also found to decrease with higher ligand oxidation states which was rationalized with an inverted bonding description.\(^\text{16}\) In the present example, oxidation of the TTF\(^{t+}\) increases S-bonding in the organic core of the linker, thereby decreasing covalency with Ni. An increase in C–S bonding covalency is supported by a similar increase in the computed C–S bond order (Table S2). Thus, while similar trends with oxidation are observed between these TTF\(^{t+}\)-based compounds and previous dithiolene examples, we propose that the origins of these effects are subtly different.
It should be noted that there is a distinctive peak at 2470.6 eV in 3-(TTF$^2+$) which is not observed in 1-(TTF$^0+$) and 2-(TTF$^1+$). TD-DFT calculations also provide insight into this unique pre-edge feature. The natural transition orbitals (NTOs) of the XAS transitions are shown in Fig. 3 and Fig. S3. All three compounds have a feature between 2471-2472 eV which stems from a transition from the M–S S-based s-orbitals into an orbital localized on the respective half of the molecule. For 3-(TTF$^2+$), the low energy peak at 2470.6 eV can be assigned to a transition from the M–S s-orbitals into the TTFtt π LUMO. This DFT-predicted peak is also present in 2-(TTF$^1+$) but displays significantly lower intensity of the transition because this orbital is singly occupied in the monocationic complex. The increased intensity in 3-(TTF$^2+$) provides a diagnostic signal for this formally doubly oxidized TTFtt oxidation state. A 2470.5 eV peak has also been observed in a TTF-BA (BA = bromanil, C$_6$Br$_4$O$_2$) compound. This peak in TTF-BA is of comparatively higher intensity than those observed here, although the calculations from this previous work predict a similar low-intensity feature.

The $S$ K-edge XAS data on the NiTTFTt-(TTF$^0+$) CP which has formally doubly oxidized TTTT linkers (Fig. 4) were also examined. This material exhibits glassy metallic conductivity, and more detailed understanding of its electronic structure and how it relates to its bulk properties is valuable. Unfortunately, the corresponding reduced CP with neutral TTTT linkers, Li-NiTTFTt-(TTF$^0+$), is too air-sensitive for reliable acquisition of XAS data. NiTTFTt-(TTF$^0+$) shows only one prominent pre-edge feature at ~2470.7 eV which is very close to the position of the lowest energy pre-edge peak observed in 3-(TTF$^2+$). This similar peak position suggests that the formal TTTT oxidation states are similar in NiTTFTt-(TTF$^0+$) and 3-(TTF$^2+$), namely that they both have a doubly oxidized linker with a formally 2+ TTF core. The peak position was determined from 2nd derivative analysis due to the trailing absorption in NiTTFTt-(TTF$^0+$) which is putatively due to disordered sites and a band-like electronic structure. Similar trailing features have been observed in MoS$_2$ S K-edge data.

The structures of 1-(TTF$^0+$) and 3-(TTF$^2+$) are similar to the smallest repeat units of Li-NiTTFTt-(TTF$^0+$) and NiTTFTt-(TTF$^2+$) and thus the XAS data on these molecular compounds can provide insights on the properties of TTTT-based CPs. Indeed, such dimensional reduction studies of molecular compounds have been performed on several extended solids. The electrical conductivity of NiTTFTt-(TTF$^0+$) (470 S/cm) is significantly higher than that of Li-NiTTFTt-(TTF$^0+$) (10 S/cm). Limiting charge transport pathways in CPs include hopping and band-like transport. For band-like transport, increasing the metal-ligand covalency should, in principle, increase conductivity. A trend of decreasing covalency upon oxidation from 1-(TTF$^0+$) to 3-(TTF$^2+$) is observed along with similar overall electronic structures for 3-(TTF$^2+$) and NiTTFTt-(TTF$^2+$). These observations suggest an apparent dichotomy, namely decreasing Ni–S covalency but increasing conductivity upon oxidation. Previous calculations on NiTTFTt-(TTF$^2+$) suggest that
the metallic character arises primarily from linker-linker interactions.\textsuperscript{12} Therefore the decreased Ni–S covalency may not be as important for bulk conductivity. However, the observed decrease in the LUMO energy indicated from the low-energy pre-edge features at \(\sim 2470.5\) eV in \(3\)-(TTF\(^{3+}\)) and NiTTFTt-(TTF\(^{3+}\)) may instead indicate better linker-linker \(\pi\)-stacking interactions which lead to enhanced conductivity.\textsuperscript{13}

In conclusion, \(K\)-edge XAS and TD-DFT studies were conducted on Ni-based TTFt systems with different TTFt redox states. The Ni–S bonding covalency decreases with higher TTFt redox states. A unique feature is observed at \(\sim 2470.5\) eV for the doubly oxidized TTFt linkers and can be assigned to a transition into a \(\pi\)-type orbital. Importantly, while Ni–S covalency decreases upon oxidation, conductivity increases, supporting previous studies that suggest the major conductivity pathways in TTFt based materials are through linker-linker interactions. Thus, the results presented here anchor formal TTFt redox states with spectroscopic signatures and provide insights into the unusual charge transport behavior observed in TTFt CPs.

This work was supported by the ARO (W911NF-20-1-0091). J.S.A. acknowledges support from the DOE (DE-SC0019215), and from the NSF (DMR-2002367). A.R. and H.S.L acknowledge support for spectroscopic studies through NSF grant CHE-1943452. Use of the Stanford Synchrotron Radiation Lightsource, SLAC National Accelerator Laboratory, is supported by the U.S. DOE, BES (DE-AC02-76SF00515). The SSRL Structural Molecular Biology Program is supported by the DOE BER, and by the NIGMS (P41GM103393).

Notes and references