

Supplementary information for NEXAFS spectra of model sulfide chains: implications for sulfur networks obtained from inverse vulcanization

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1 Experimental peak fitting

1.1 Monosulfide

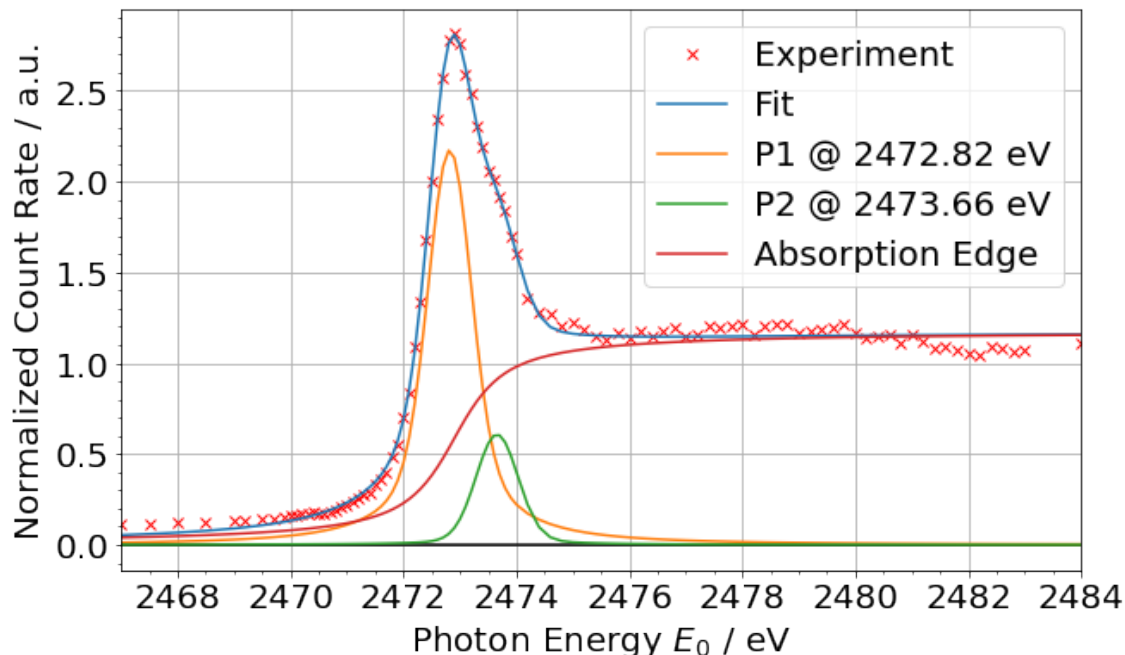


Figure S1: Experimentally acquired NEXAFS spectrum with the fitted dominant transition energies and the model of the absorption edge of dipropyl sulfide (DPS).

The only probed monosulfide was the dipropyl sulfide (DPS), which consists of one central sulfur atom connecting two propyl groups. The experimental spectrum shows one peak at the excitation energy of 2472.8 eV with a shoulder on the high-energy edge which was fitted with a second peak at 2473.6 eV. This spectrum looks qualitatively and quantitatively similar to the diheptyl sulfide spectrum presented by Qureshi et al.¹ The white line energy is significantly shifted towards higher energies compared to molecules with more than one sulfur atom reported below.

1.2 Disulfides

Five disulfide molecules have been investigated by sulfur K-edge NEXAFS spectroscopy: dimethyl disulfide (DMDS) and dipropyl disulfide (DPDS), which contain respectively a

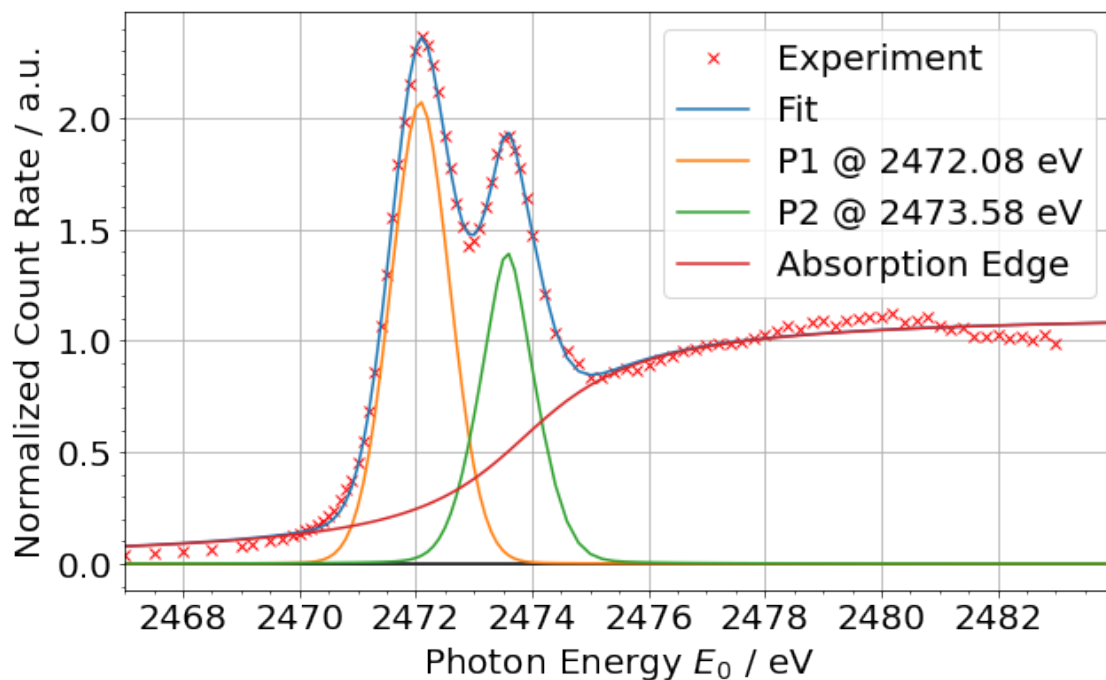


Figure S2: Experimentally acquired NEXAFS spectrum with the fitted dominant transition energies and the model of the absorption edge of dimethyl disulfide (DMDS).

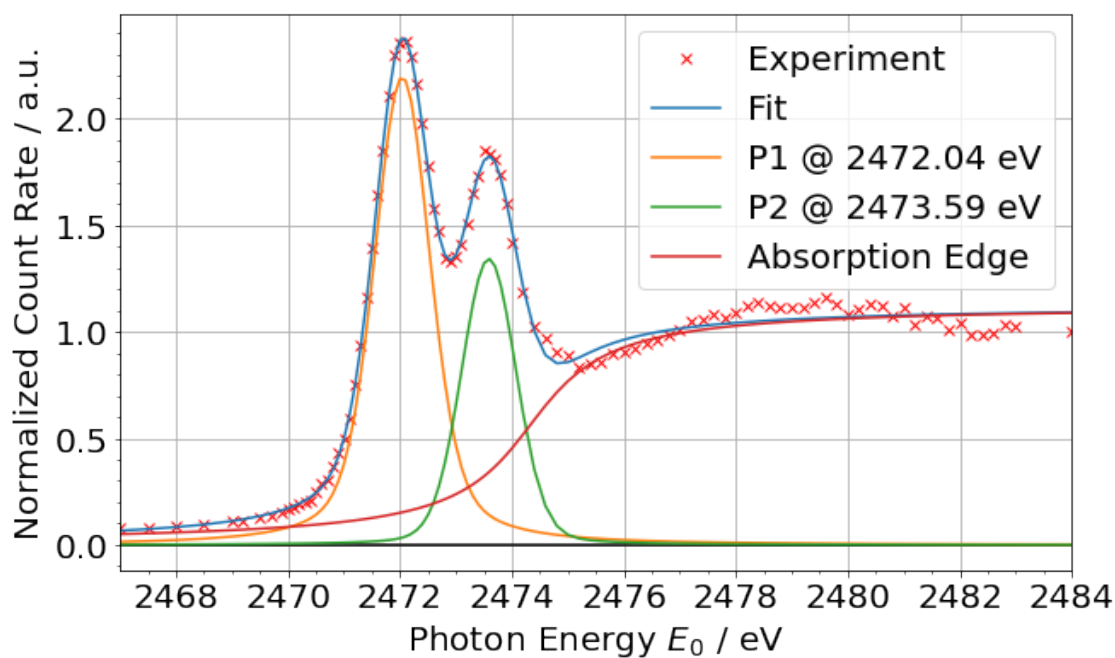


Figure S3: Experimentally acquired NEXAFS spectrum with the fitted dominant transition energies and the model of the absorption edge of dipropyl disulfide (DPDS).

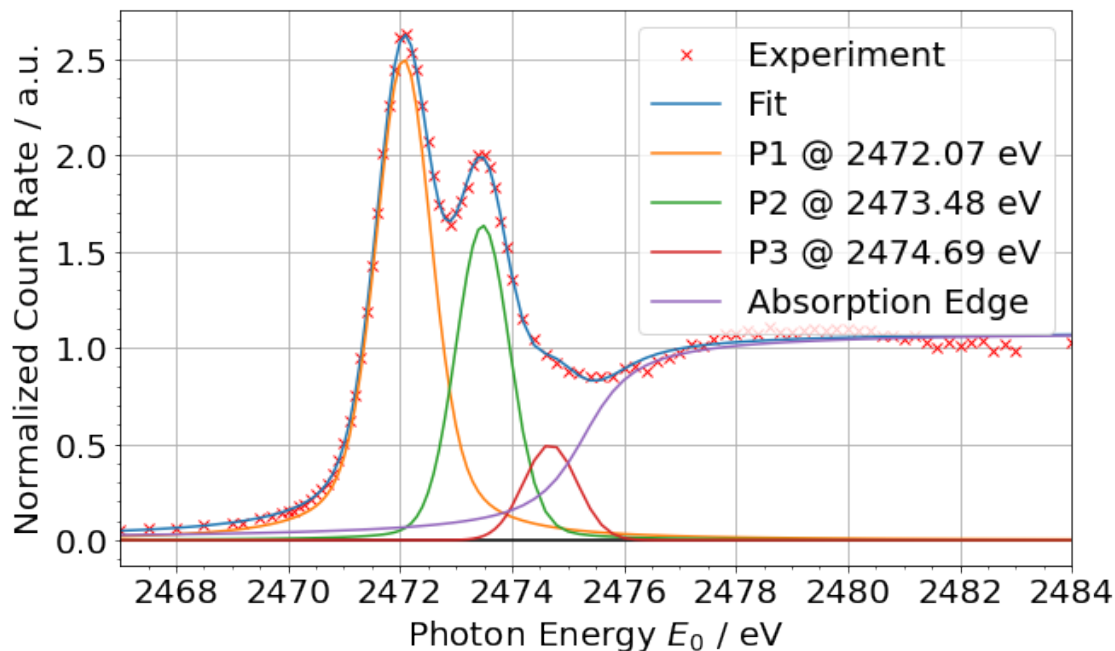


Figure S4: Experimentally acquired NEXAFS spectrum with the fitted dominant transition energies and the model of the absorption edge of diisopropyl disulfide (DIPDS).

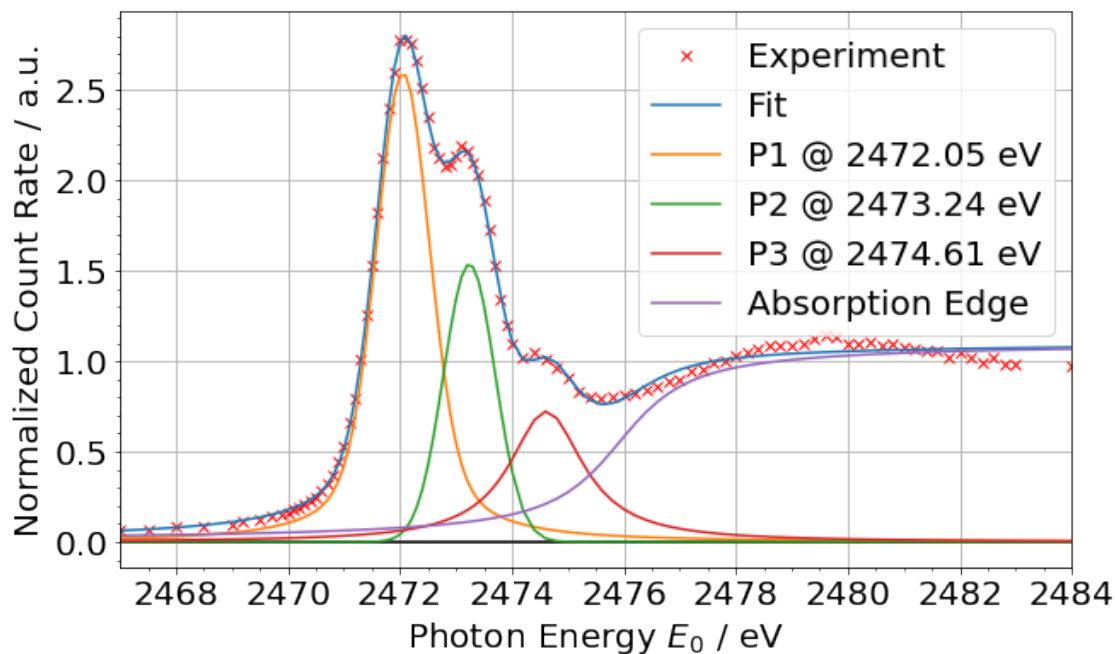


Figure S5: Experimentally acquired NEXAFS spectrum with the fitted dominant transition energies and the model of the absorption edge of di-tert-butyl disulfide (DTBDS).

methyl or propyl group at both of the sulfur atoms, diisopropyl disulfide (DIPDS) and di-tert-butyl disulfide (DTBDS), which have differing levels of substitution at the S-bonded

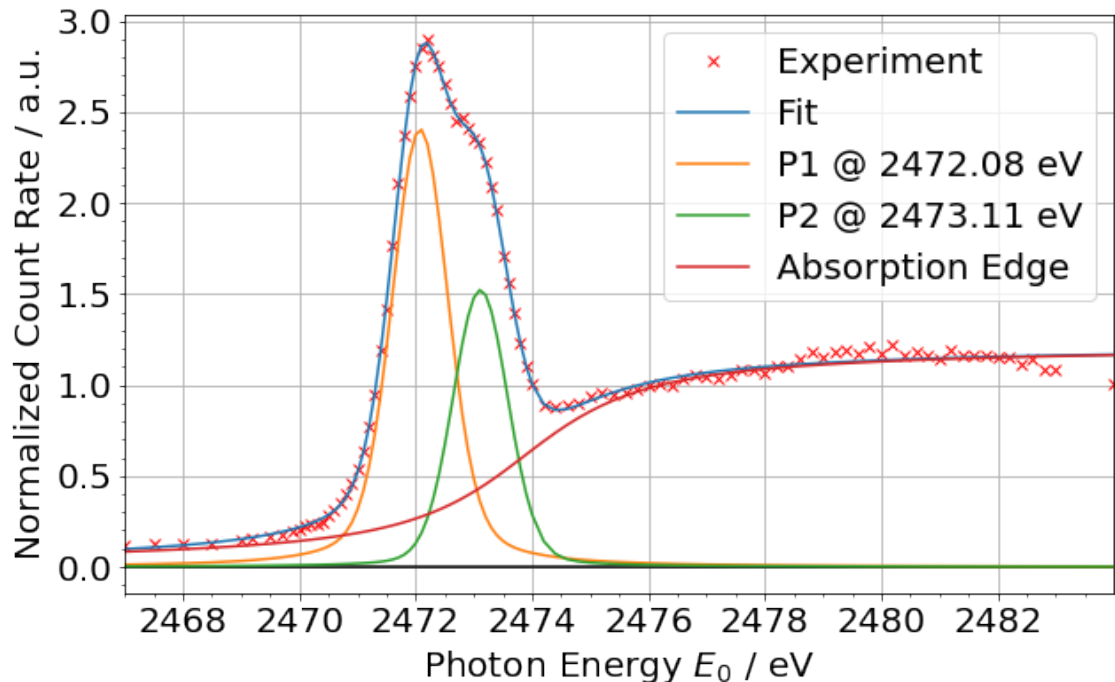


Figure S6: Experimentally acquired NEXAFS spectrum with the fitted dominant transition energies and the model of the absorption edge of dibenzyl disulfide (DBDS).

carbon atoms, and dibenzyl disulfide (DBDS), in which the sulfur atoms are bonded to carbon atoms which are bonded to aromatic carbon atoms. For all five molecules, two main transitions are visible in both the experimental spectra reported in Figs. S2-S6, with the first peaks being consistently between 2472.0 and 2472.1 eV. For DMDS and DPDS, the second peak is at 2473.6 eV and has an intensity which is about 2/3 compared to the first peak. The second carbon atom in the DIPDS leads to the second peak being shifted down by 0.1 eV while the intensity ratio stays similar. In the DTBDS, there occurs a structure between the energies of the first peaks and the edge which has been fitted by a third peak in Fig. S5. The second peak shifts down to 2473.2 eV. The smallest energy gap between the two peaks is present in the DBDS where the second peak was fitted at 2473.1 eV, only slightly more than 1 eV above the first peak and on the edge of being identified significantly. The approximate intensity ratio of 2/3 remains the same, also throughout the latterly mentioned samples.

In Qureshi's¹ data, the dihexyl disulfide behaves comparably in terms of a clear double-peak structure with the first peak being more intense than the second one and its energy

shifted to lower energies compared to the monosulfide representative. This trend is confirmed by this series of measurements. The shift of the higher energy peak depending on the substituted functional group following the results of Behyan² for two representative disulfides could by this measurement series be extended to some intermediate peak energies for related ligands.

1.3 Trisulfide

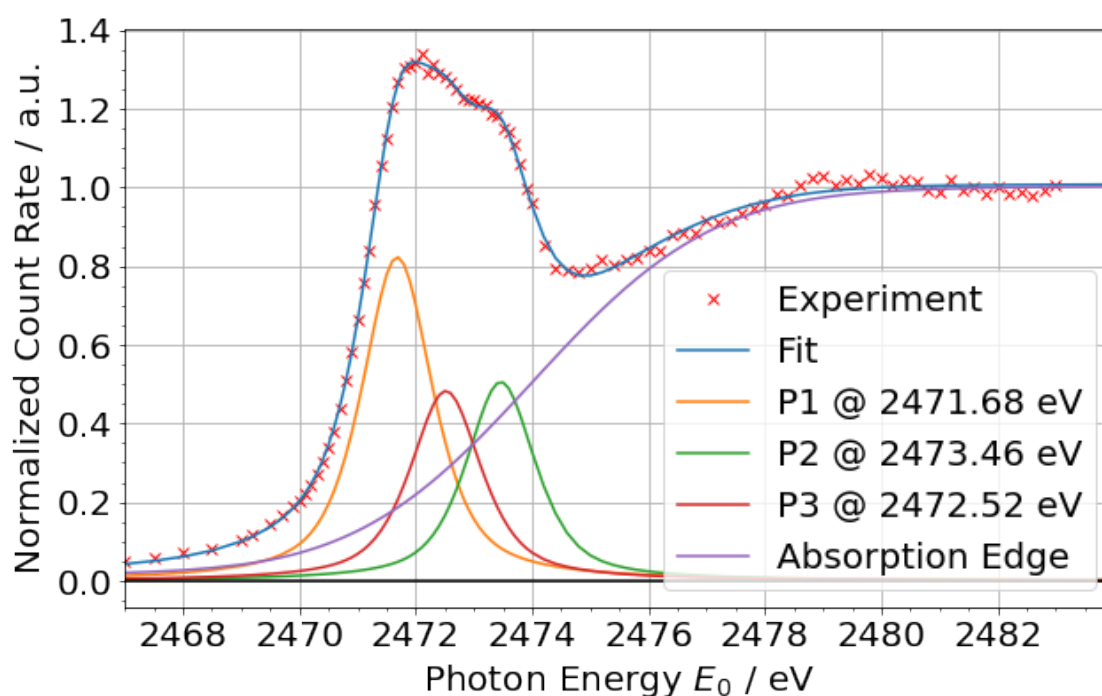


Figure S7: Experimentally acquired NEXAFS spectrum with the fitted dominant transition energies and the model of the absorption edge of dimethyl trisulfide (DMTS).

The only trisulfide compound commercially available was the dimethyl trisulfide (DMTS) which is a chain of three sulfur atoms capped by a methyl group at each of the external sulfur atoms. The spectrum depicted in Fig. S7 shows rather a plateau than clearly separated peaks. It can be fitted by 3 peaks where the energy of the first peak shifts to smaller values by 0.4 eV compared to the disulfide spectra. A possible interpretation is given in the main text.

2 Total energy correction

2.1 XPS and NEXAFS first peak energies

Table S1: Molecules and values used for determining the empirical S(1s) shift for PBE. Upper part of the table lists XPS values and the lower part NEXAFS first peak (white line) values.

XPS molecule	E_{exp} [eV]	E_{unpol} [eV]	Δ_{unpol} [eV]	E_{spin} [eV]	Δ_{spin} [eV]
SF ₄	2487.34 ³	2499.37	12.03	2482.25	-5.09
COS	2478.87, ⁴ 2478.70, ⁵ 2478.87 ³	2492.19	13.38± 0.11	2475.08	-3.73± 0.11
C ₂ H ₆ OS ₂	2476.20 ⁴	2489.23	13.03	2472.09	-4.11
C ₂ H ₆ OS ₂	2477.90 ⁴	2490.98	13.08	2473.92	-3.98
CS ₂	2478.10, ⁵ 2477.96 ³	2491.41	13.38± 0.07	2474.30	-3.73± 0.07
SF ₅ Cl	2490.10, ⁶ 2489.29 ³	2501.36	11.66± 0.40	2484.22	-5.47± 0.40
SO ₂	2483.70, ⁶ 2484.11 ³	2496.65	12.74± 0.20	2479.53	-4.37± 0.20
C ₂ F ₆ S ₂	2479.76 ³	2492.31	12.55	2475.20	-4.56
SPCl ₃	2477.42 ³	2490.24	12.82	2473.13	-4.29
SH ₂	2478.50, ⁶ 2478.92 ³	2491.70	12.99± 0.21	2474.59	-4.12± 0.21
S(CH ₃) ₂	2478.17 ³	2490.49	12.32	2473.38	-4.79
SF ₆	2490.10, ⁶ 2490.10, ⁷ 2490.45 ³	2502.34	12.13± 0.12	2485.20	-5.01± 0.12
NEXAFS first peak					
molecule	E_{exp} [eV]	E_{unpol} [eV]	Δ_{unpol} [eV]	E_{spin} [eV]	Δ_{spin} [eV]
DBDS	2471.61 ²	2485.24	13.63	2468.01	-3.60
C ₅ H ₅ SH	2472.46 ²	2485.96	13.50	2468.66	-3.80
S ₈	2471.70, ⁸ 2472.00, ⁹ 2472.70 ¹⁰	2484.65	12.52± 0.43	2467.53	-4.61± 0.43
S(CH ₃) ₂	2472.11 ¹¹	2486.03	13.92	2468.81	-3.30
S ₂	2467.50, ¹² 2468.95 ⁸	2482.18	13.96± 0.72	2464.96	-3.27± 0.72

2.2 First peak energies of model compounds

Table S2: NEXAFS first peak (white line) energies (eV) in semi-empirically corrected theory and from experiment.

Short	Molecule	Experiment	PBE unpol.	PBE spin
DPS	dipropyl sulfide	2472.82	2473.04	2472.83
DMDS	dimethyl disulfide	2472.08	2472.36	2472.08
DPDS	dipropyl disulfide	2472.04, 2471.6 ¹³	2472.28	2472.01
	dibutyl disulfide	2471.61 ²		
DIPDS	diisopropyl disulfide	2472.07	2472.27	2472.05
DTBDS	di-tert-butyl disulfide	2472.05, 2471.5 ¹³	2472.23	2472.04
DBDS	dibenzyl disulfide	2472.08 (2471.68 ²)	2472.18	2472.10
DMTS	dimethyl trisulfide	2471.68	2472.07	2472.09

3 Methyl capped sulfur strands

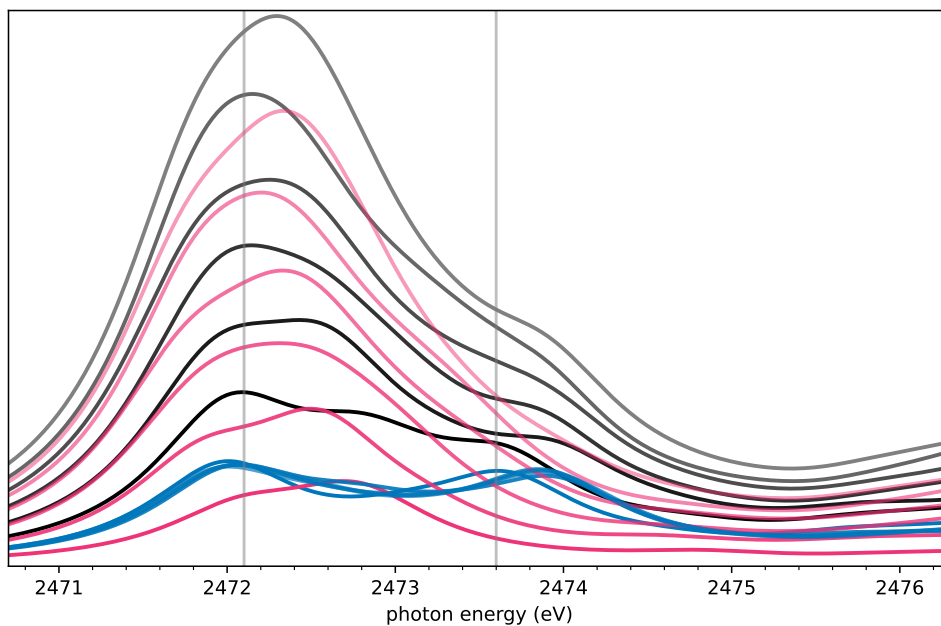


Figure S8: Folded theoretical spectra of the dimethyl sulfides of rank 3 to 8. These spectra are based on the lowest energy conformers determined for each species. Compare figure 5 in the main text, showing the Boltzmann-weighted spectra for the same molecules.

4 DIB cathodes

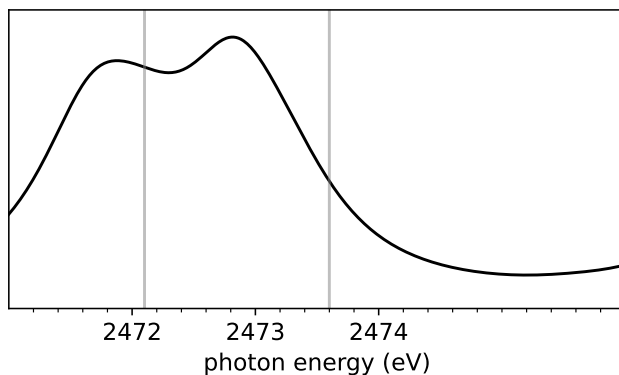


Figure S9: Folded theoretical spectra of S_8 . Guiding lines at the experimental DMDS peak energies are shown in grey.

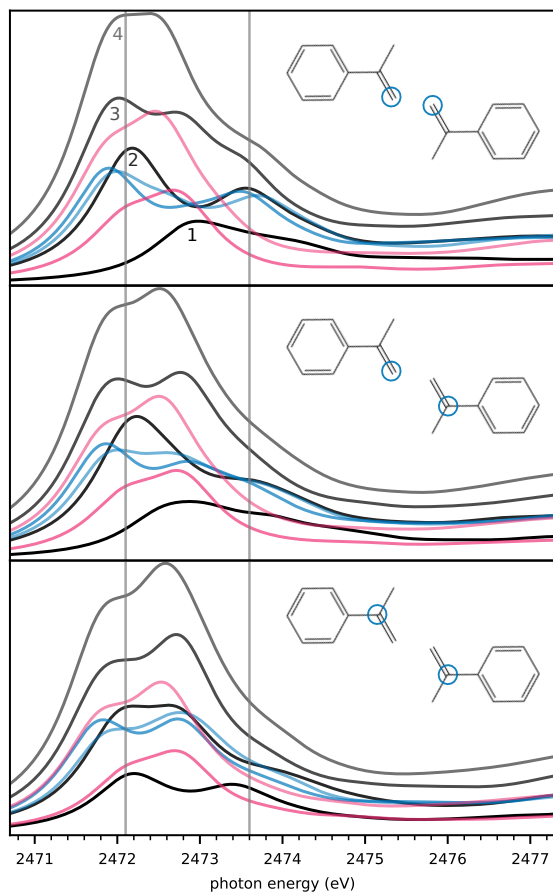


Figure S10: Comparison of simulated NEXAFS spectra of α -methylstyrene monomers linked by 1 to 4 S atoms. The S-chains connecting in a primary-to-primary, primary-to-tertiary, and tertiary-to-tertiary carbons as indicated. Total spectra are shown in black, spectra of C-bonded S atoms in blue, and of internal S atoms in magenta. Guiding lines at the experimental DMDs peak energies are shown in grey.

1,3-diisopropenylbenzene (DIB) is a common co-monomer used in inverse vulcanization.¹⁴ Fig. S10 shows simulated NEXAFS spectra of sulfur strands between α -methylstyrene monomers, which we have used as a model for DIB for computational simplicity. When the S-strand bonding is primary-to-primary carbons, the C-bonded S atom spectrum resembles that of dibenzyl disulfide, and the S-C resonances are at higher energies than the S-S. When the bonding is tertiary-to-tertiary, the S-C and S-S resonances overlap. This effect is very similar to the spectrum of DBDS in Fig. 3 in the main text.

Fig. S11 shows the experimental NEXAFS spectra of S-DIB cathodes. The peak forms of 20% to 50% sulfur are rather similar so that S-S antibonding peaks can hardly be separated

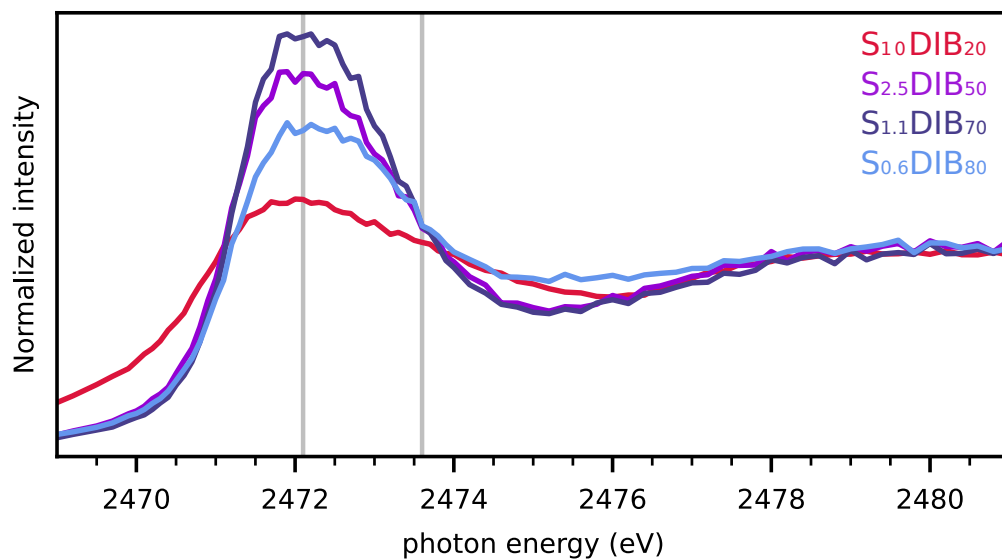


Figure S11: Experimental NEXAFS spectra of S-DIB cathodes with different sulfur loads. The subscript to S indicates the nominal average S-rank, and the subscript to DIB indicates its weight per cent.

from S-C antibonding peaks in agreement with simulations in Fig. S10. The damped white line signal of the 80% sulfur cathode indicates a self-absorption regime which suggests that below 50% sulfur, the self-absorption effect seems to be negligible. Remnant elemental sulfur content would contribute in this energy region also, c.f. Fig. S9.

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