

Supplementary Informations

Combined first principles-statistical mechanics approach to sulfur structure in organic cathode hosts for polymer based lithium-sulfur (Li-S) batteries

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S1: Conformational space sampling of product states

For the sampling of different conformations of the vulcanization product states DiTBT- S_n and DiTBT- $2S_n$ -DiTBT, we used the Avogadro software¹ employing the MMFF94 force field² with steepest descent minimization. The aim was to cover a wide range of sulfur chain conformations to estimate the structure-stability relationship of possible reaction products. Fig.S1 shows examples of the extreme cases probed by our sampling in terms of the dihedral angle γ_{SCCS} between the neighboring TBT units of a DiTBT. For $n = 1$, there is only one stable configuration for the *intra*- and *inter-chain* products. With increasing n , the chain's flexibility leads to various stable configurations with a broad range of dihedrals. Shown here are two extreme cases of the *intra*- and *inter-chain* process, respectively. For the former, a wide range of dihedrals is possible only for long chain lengths ($n = 16$), while for the latter, it can already be seen for short ranks ($n = 4$).

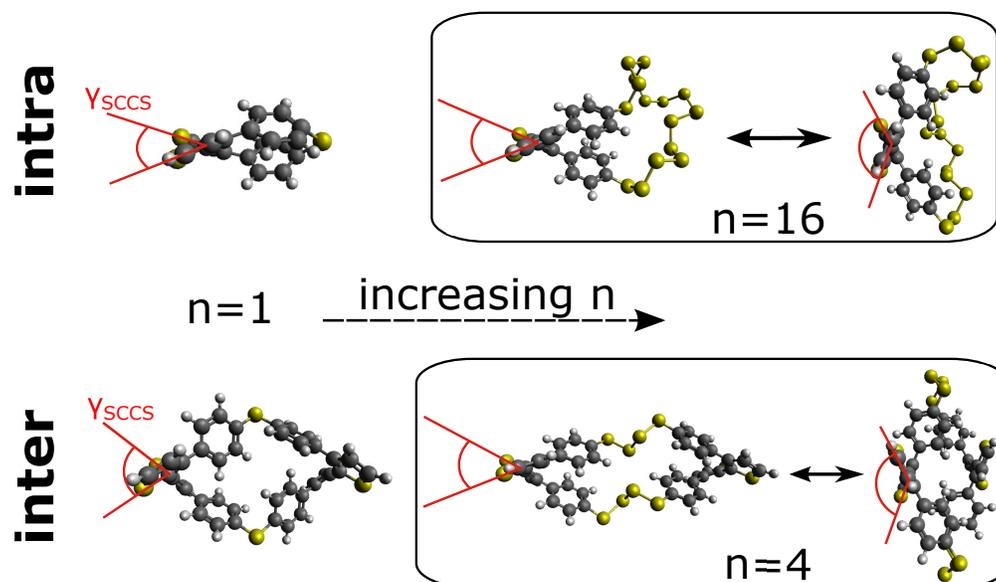


Fig. S1 Probing different configurations regarding the thiophene dihedral γ_{SCCS} in dependency of the sulfur rank n .

S2: Stability analysis - comparison of DFT functionals and van der Waals interaction methods

We also did the stability analysis of reaction products by using the hybrid DFT functional PBE0³ together with the pair-wise van der Waals correction^{4,5} (PBE0+vdW) and also the PBE functional⁶ together with the many-body dispersion method⁷ (PBE+MBD) and compared it with the PBE+vdW method presented in the main text. All DFT calculations were performed using the all-electron, full-potential density-theory package FHI-aims⁸⁻¹⁰ (convergence settings can be found in the computational details subsection of the main text). Fig.S2 shows that the two different functionals give relatively similar results for the vulcanization energies of the *inter-chain* process. The PBE0 results are decreased by about 0.03 eV against the PBE results. Using the MBD method instead of the pairwise vdW correction to account for the dispersion interaction, we observe that as the sulfur rank n increases, the larger structures are less stable. This is a consequence of the inclusion of many-body interactions in the dispersion energy. Contrary to including only an attractive pairwise interaction via the vdW-method, the inclusion of many-body effects becomes more relevant and less attractive when the chain consists of more sulfur atoms, yielding a less attractive long-range dispersion energy. This fact also points in the direction of an energy saturation in a real polymer chain, where the many-body effects would become even larger.

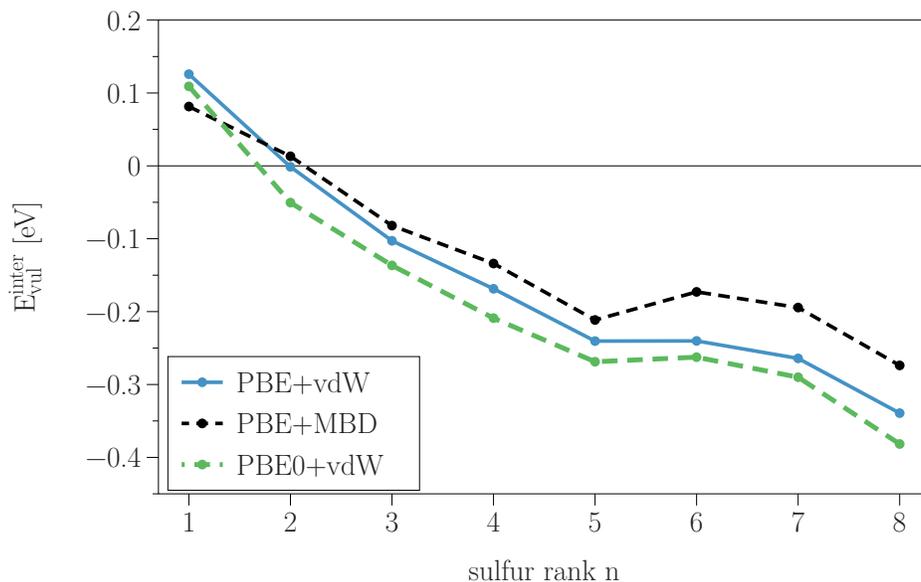


Fig. S2 The comparison of vulcanization energies $E_{\text{vul}}^{\text{inter}}$ of the most stable *inter-chain* products for different exchange-correlation functionals and different van der Waals interactions: PBE+vdW (solid blue line), PBE+MBD (dashed black line), and PBE0+vdW (dashed green line).

S3: Raman spectroscopy of *intra-chain* and *inter-chain* bonds

Raman spectroscopy may be sensitive to the conformational modes of thiol groups. Therefore, we have repeated the Raman backscattering experiments with higher spectral resolution using an exposition time of 300 s. Fig. S3 shows the Raman spectra measured with lower (3 cm^{-1} , blue curve) and higher (1 cm^{-1} , green curve) spectral resolution. The spectrum with higher resolution shows some pronounced shoulders for the vibrational modes of the -S-S- group around 500 cm^{-1} . As shown in the inset of Fig. S3, the peak centered around 500 cm^{-1} can be deconvoluted in three components: the peaks at 478 cm^{-1} , 492 cm^{-1} , and 516 cm^{-1} originate from the S-S stretching modes in the *gauche-gauche-gauche* (GGG), *gauche-gauche-trans* (GGT), and the *trans-gauche-trans* (TGT) configurations^{11,12}, respectively. These peaks have been shifted by about 30 cm^{-1} to lower energy with respect to those from ref. 11,12. This may be a result of a different environment (polymer vs. human hair).

The three components were found for the as-prepared polymer PTBT leading to the assumption that all these configurations co-exist in the polymeric layer. So far, it is not possible to discriminate any preferential conformation for the molecules and associate them to the types of inter- and intra-molecular bonds by Raman spectroscopy. To do so, we need polymers with only GGG, GGT, TGT configuration and with only inter- or only intra-molecular bonding, which is nearly impossible from a synthesis point of view.

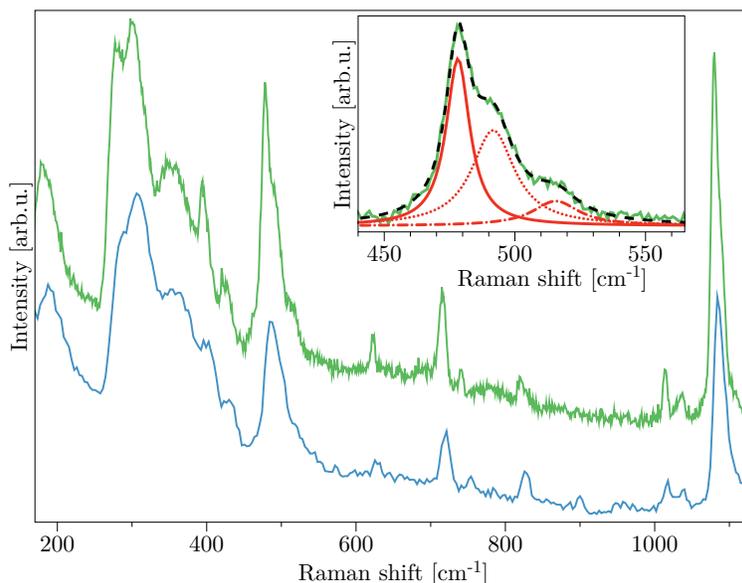


Fig. S3 Raman spectra measured with lower (3 cm^{-1} , blue curve) and higher (1 cm^{-1} , green curve) spectral resolution. The spectrum recorded at higher resolution shows some pronounced shoulders for the vibrational modes of the -S-S- group around 500 cm^{-1} . The inset shows the peak centered around 500 cm^{-1} and its deconvolution into three components as described in the text.

S4: Binding probability distributions for the *intra-chain* process

In Fig.S4, the individual binding probabilities for the *intra-chain* process $p_n^{\text{intra}}([x])$ are displayed versus the molar ratio of free sulfur and binding sites $y = [x]/[\text{BS}]$. The maximum *intra-chain* binding probability p_{14}^{intra} is four orders of magnitude lower than for the *inter-chain* process (cf. Fig.8 in main text). This shows that the connection of adjacent TBT units of the same polymer backbone by a sulfur chain is the side reaction during vulcanization.

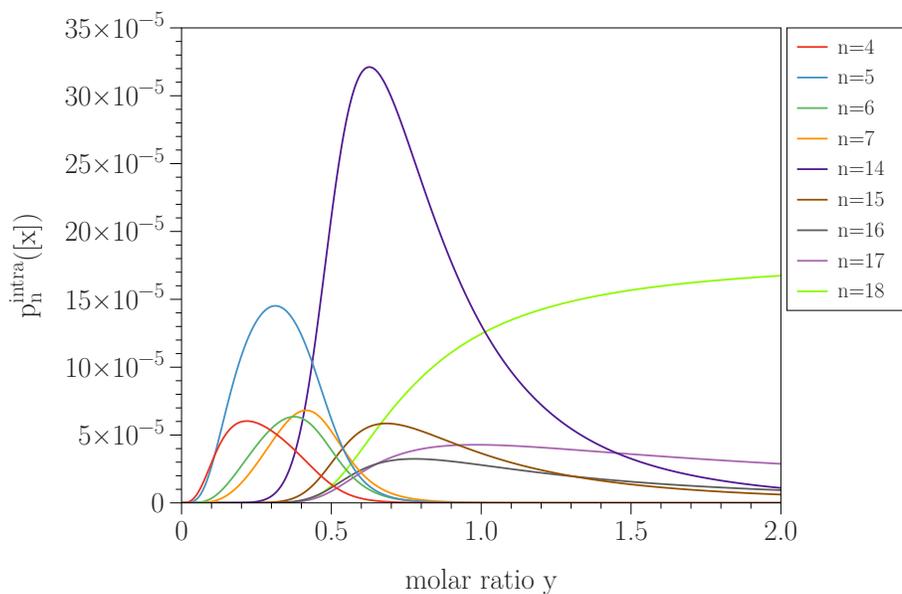


Fig. S4 The individual binding probabilities for the *intra-chain* process $p_n^{\text{intra}}(x)$.

Notes and references

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