Supplementary Information (SI) for Physical Chemistry Chemical Physics.
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Electronic Supplementary Information for: Spin Transport in the Phenalenyl Radical throughout Molecular Dynamics Trajectories

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S1 Snapshots from AIMD trajectories

Snapshots are presented of the Au-PLY-Au structure, taken every 1,000 fs from the 300 K, 500 K, and 700 K AIMD trajectories.

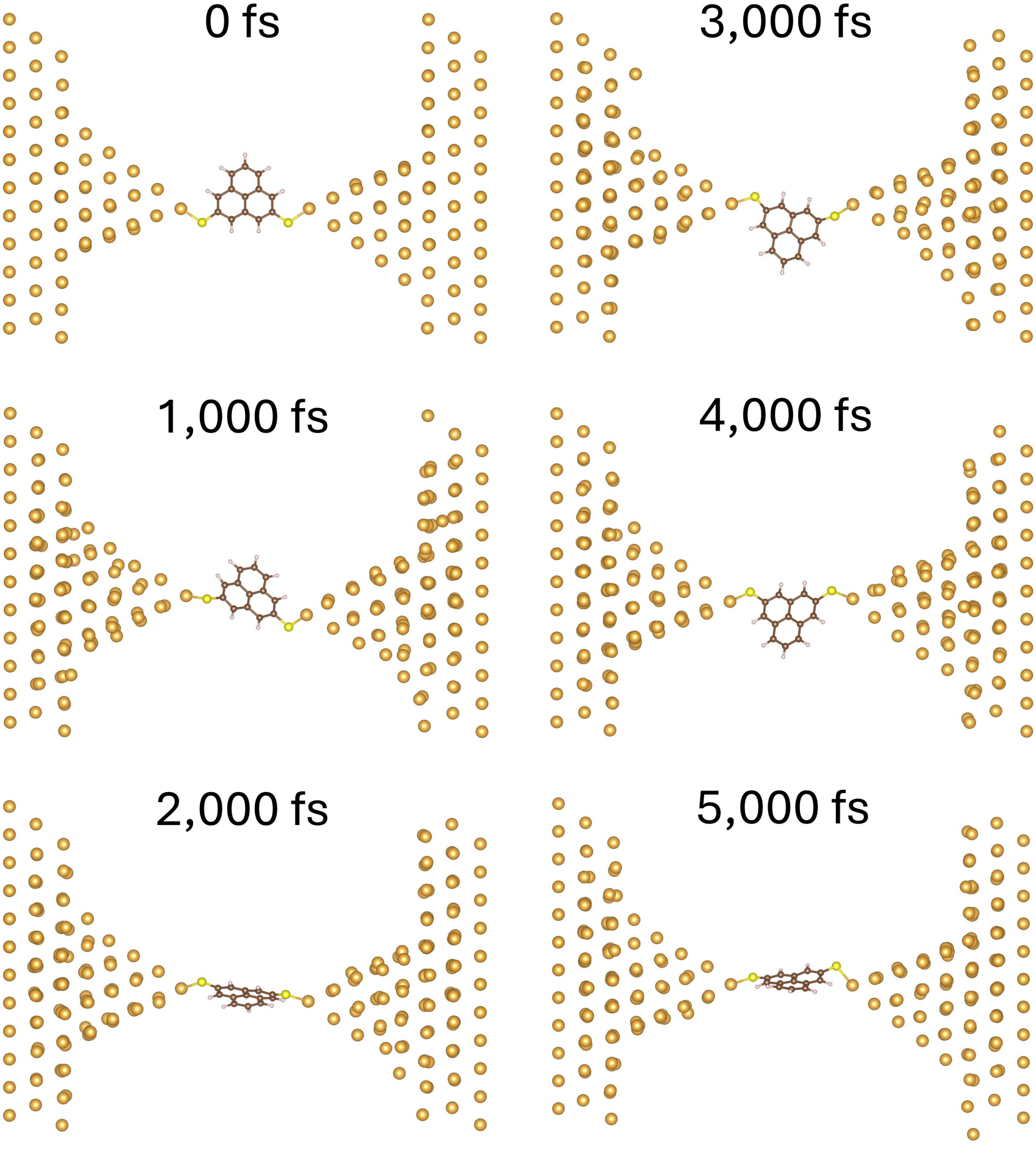
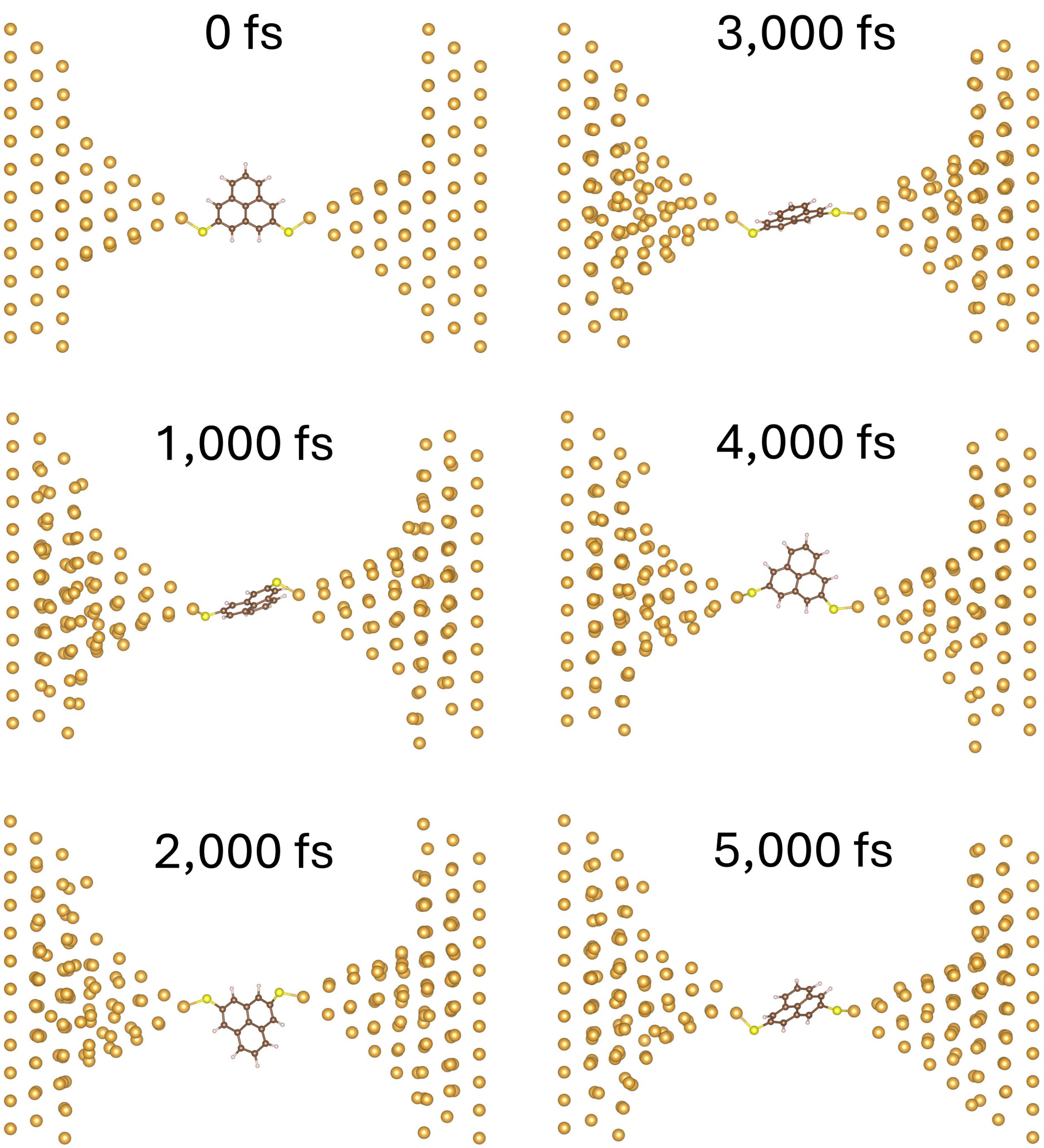


Figure S1: Structural snapshots of the 300 K AIMD trajectory taken at 1,000 fs intervals.



0 fs

3,000 fs

1,000 fs

4,000 fs

2,000 fs

5,000 fs

Figure S2: Structural snapshots of the 500 K AIMD trajectory taken at 1,000 fs intervals.

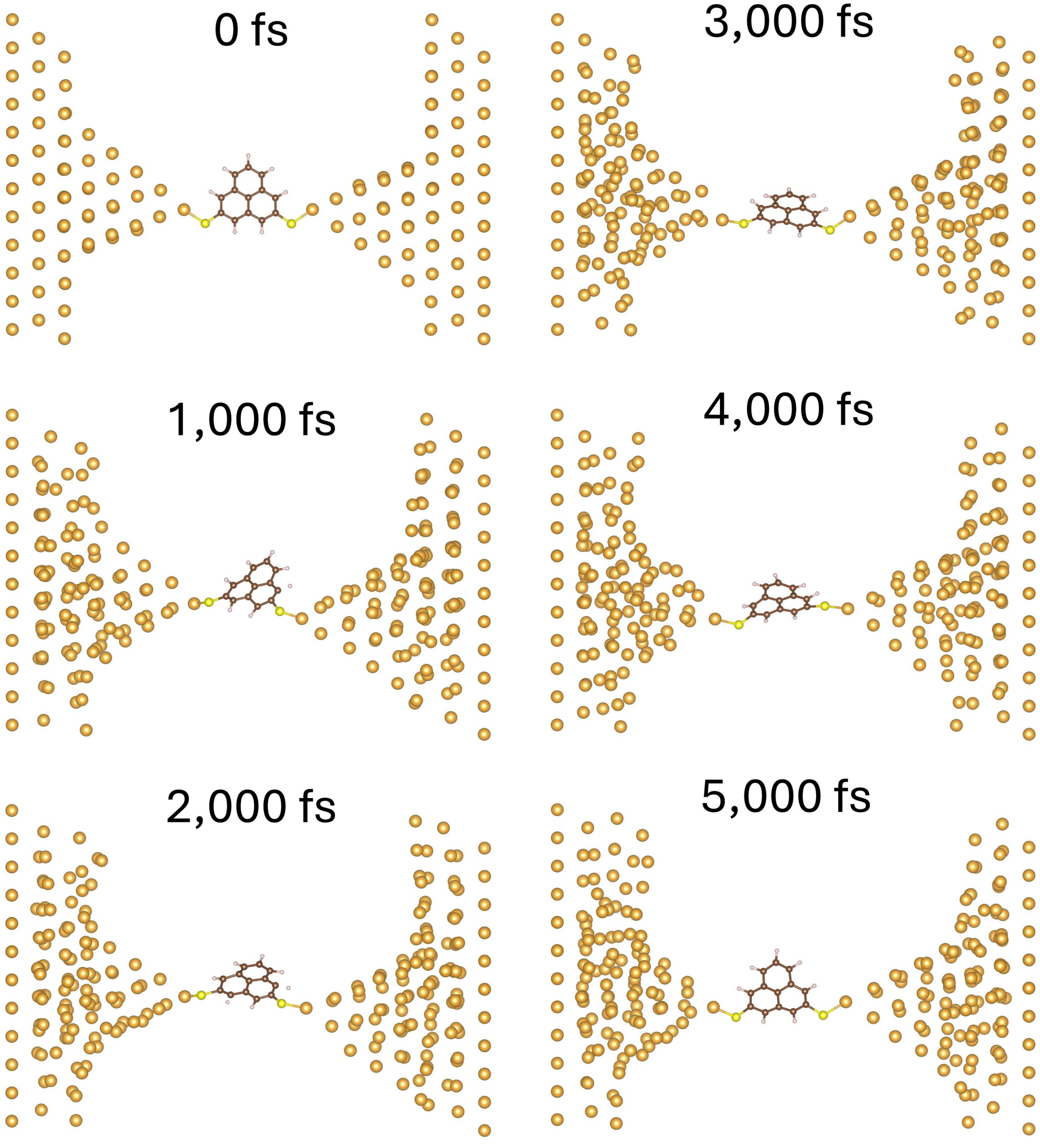


Figure S3: Structural snapshots of the 700 K AIMD trajectory taken at 1,000 fs intervals.

S2 Transmission peak assignments *via* scattering state calculations

Scattering state calculations are performed at the energies of resonances (peaks) in the transmission spectra of PLY. Eigenfunctions of the scattering states help identify the molecular orbital of PLY responsible for each of the resonances in the $T(E)$ function. Scattering states are not expected to exactly match the eigenfunction of the molecular orbitals in isolated PLY, however nodes and antinodes are expected to largely match in the two sets of eigenfunctions. The peak in the β transmission spectrum at -0.02 eV could not be directly assigned to a molecular orbital, as seen in Fig. S6. Thirty-three scattering states were generated at this energy; however, none of the scattering states matched the eigenfunction of the isolated SOMO. Based on the fact that the HOMO-1 orbital is responsible for the β transmission peak at ≈ -0.5 eV, combined with the similarity of the β transmission peak at -0.02 eV to the (α spectrum) SUMO peak at ≈ 0.5 eV, and comparison to previous literature,[1] we conclude that orbital mixing of the HOMO and SOMO levels cause the scattering state results at -0.02 eV. Furthermore, these facts give us high confidence that the peak at -0.02 eV is indeed caused by the SOMO peak.

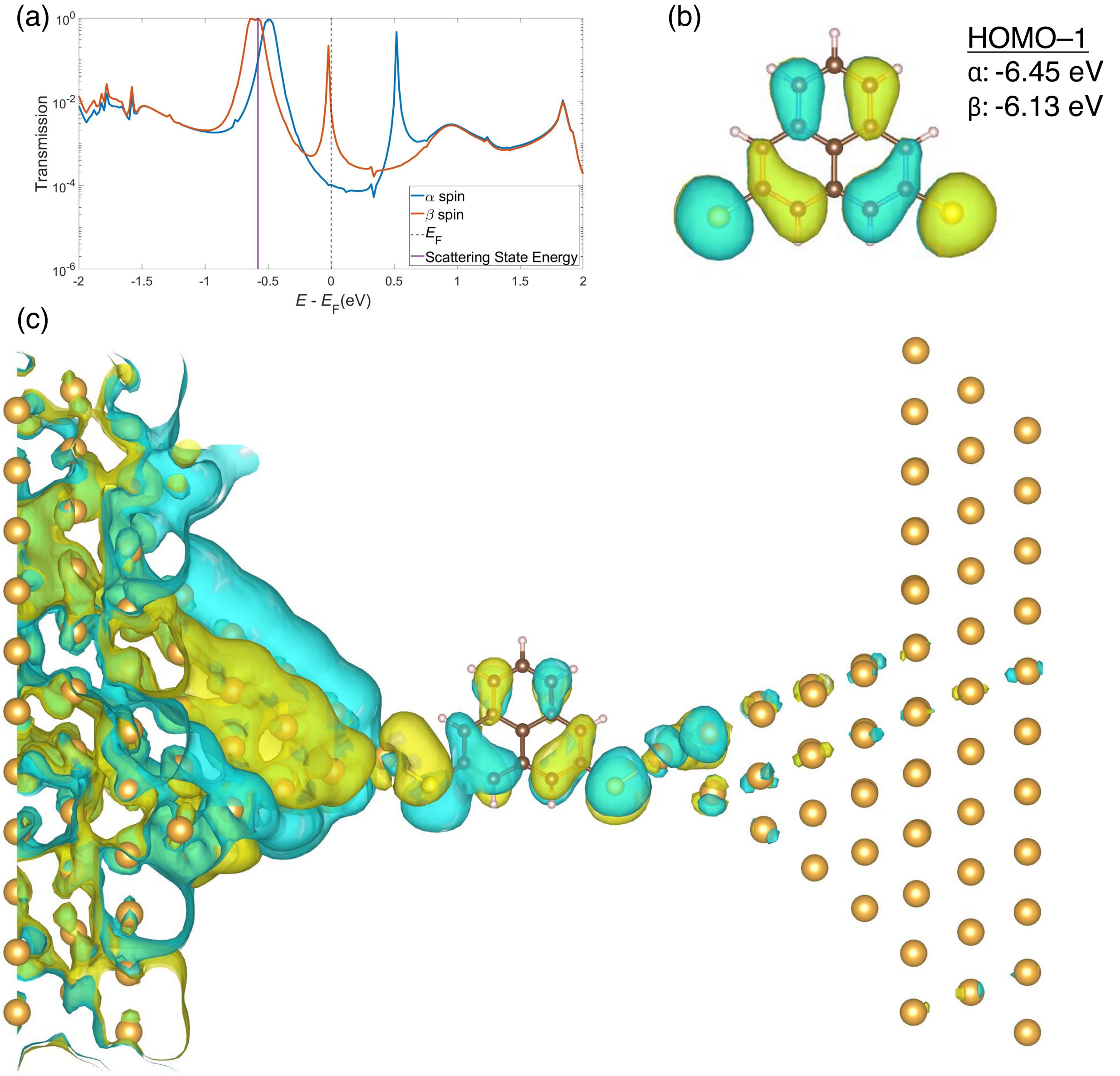


Figure S4: (a) $T(E)$ spectra showing the energy at which the scattering state calculation was performed (purple line). (b) Eigenfunction of the PLY β HOMO$-$1 molecular orbital. (c) Scattering state eigenfunction plotted for a scattering state at the energy indicated by the purple line in (a). The isosurface value was set to 0.005 a.u. Top right: energy of the HOMO$-$1 molecular orbital in isolated PLY, calculated using the B3LYP functional and a 6-311++G(d,p) basis set.

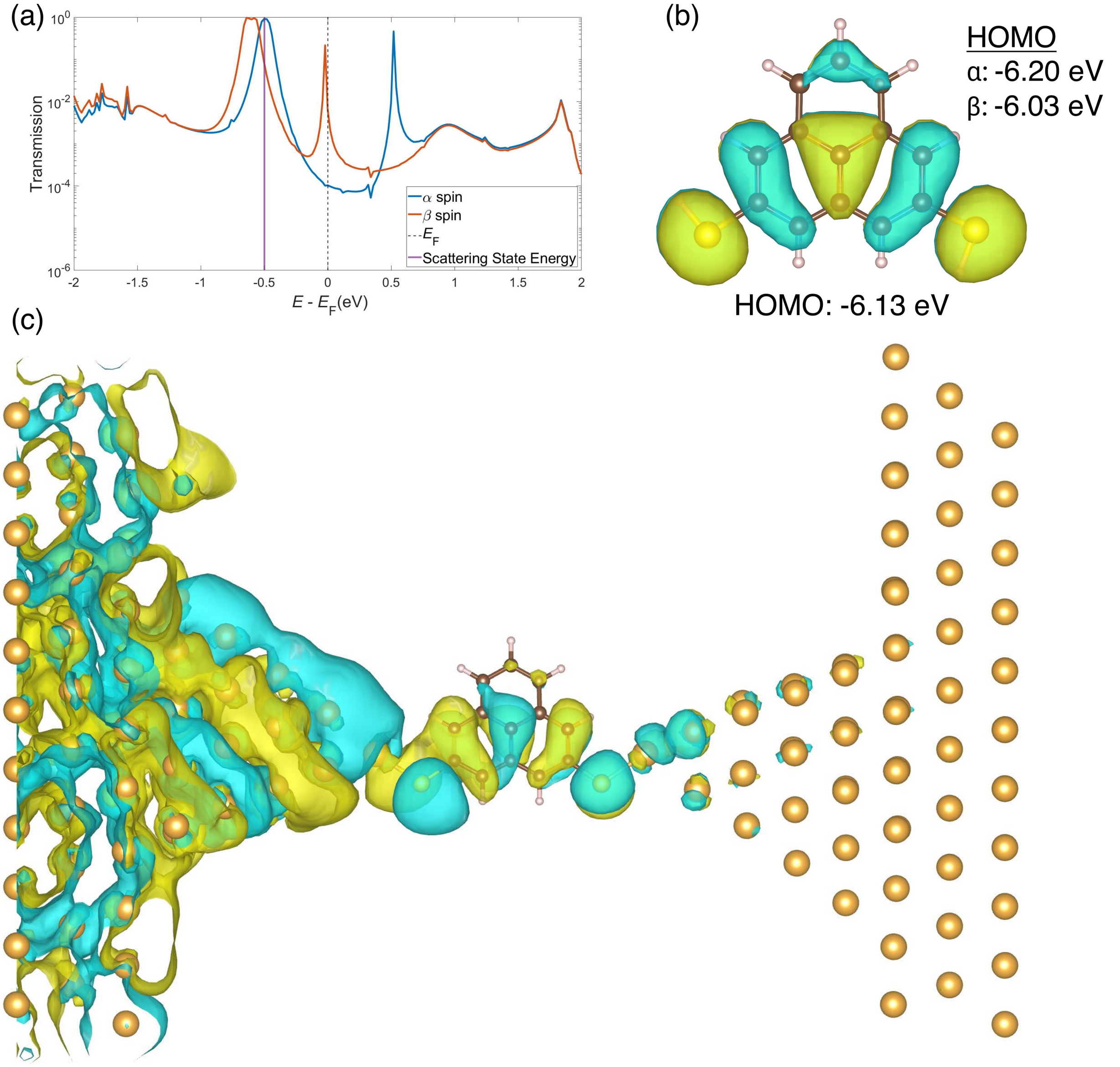


Figure S5: (a) $T(E)$ spectra showing the energy at which the scattering state calculation was performed (purple line). (b) Eigenfunction of the PLY α HOMO molecular orbital. (c) Scattering state eigenfunction plotted for a scattering state at the energy indicated by the purple line in (a). The isosurface value was set to 0.02 a.u. Top right: energy of the HOMO molecular orbital in isolated PLY, calculated using the B3LYP functional and a 6-311++G(d,p) basis set.

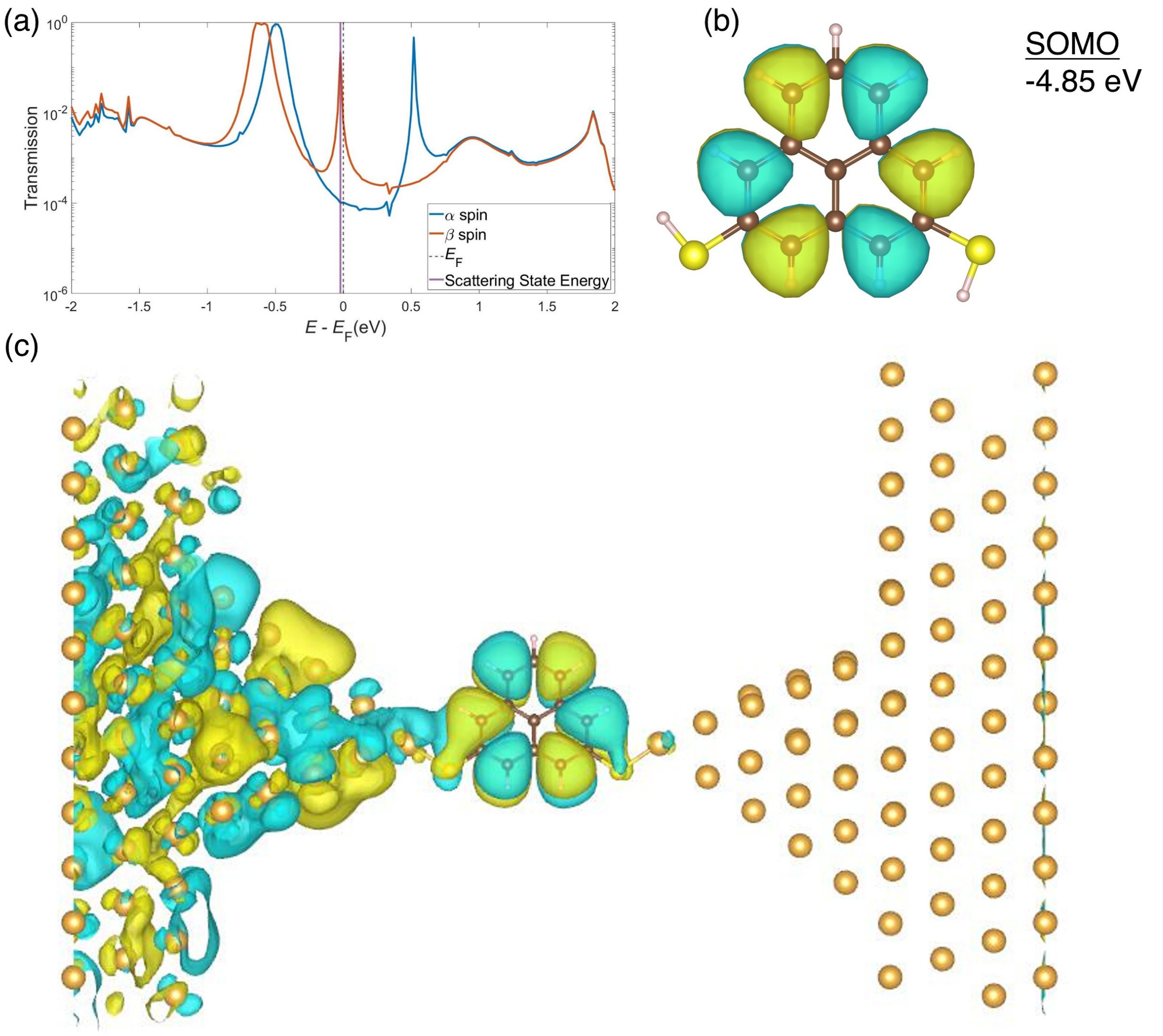


Figure S6: (a) $T(E)$ spectra showing the energy at which the scattering state calculation was performed (purple line). (b) Eigenfunction of the PLY β SOMO molecular orbital. (c) Scattering state eigenfunction plotted for a scattering state at the energy indicated by the purple line in (a). The isosurface value was set to 0.05 a.u. Top right: energy of the SOMO molecular orbital in isolated PLY, calculated using the B3LYP functional and a 6-311++G(d,p) basis set.

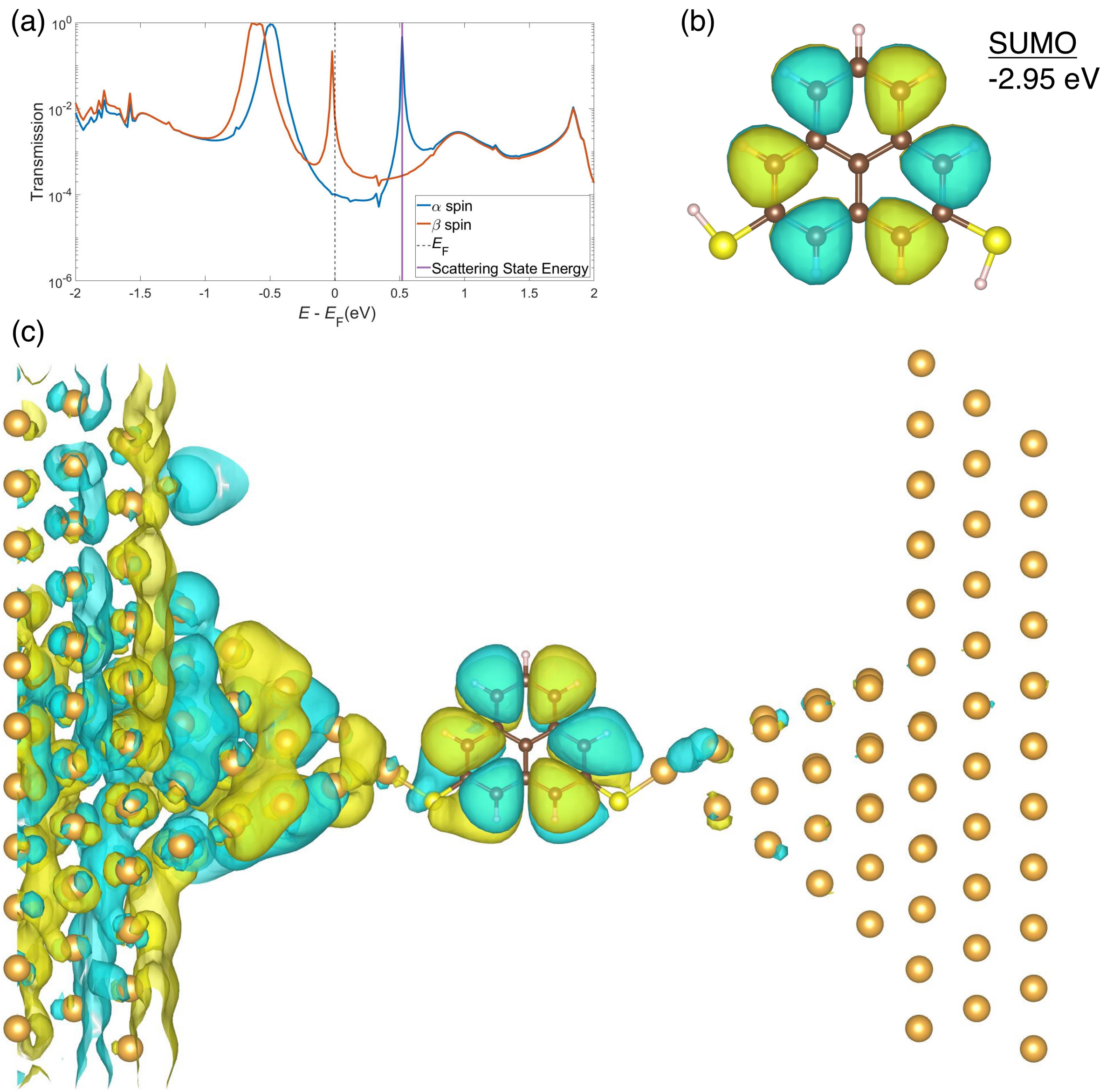


Figure S7: (a) $T(E)$ spectra showing the energy at which the scattering state calculation was performed (purple line). (b) Eigenfunction of the PLY α SUMO molecular orbital. (c) Scattering state eigenfunction plotted for a scattering state at the energy indicated by the purple line in (a). The isosurface value was set to 0.05 a.u. Top right: energy of the SUMO molecular orbital in isolated PLY, calculated using the B3LYP functional and a 6-311++G(d,p) basis set.

S3 $T(E)$ spectra around SFE dips in the 300 K, 500 K, and 700 K trajectories

Transmission spectra are plotted for points around SFE dips in the 300 K, 500 K, and 700 K AIMD trajectories.

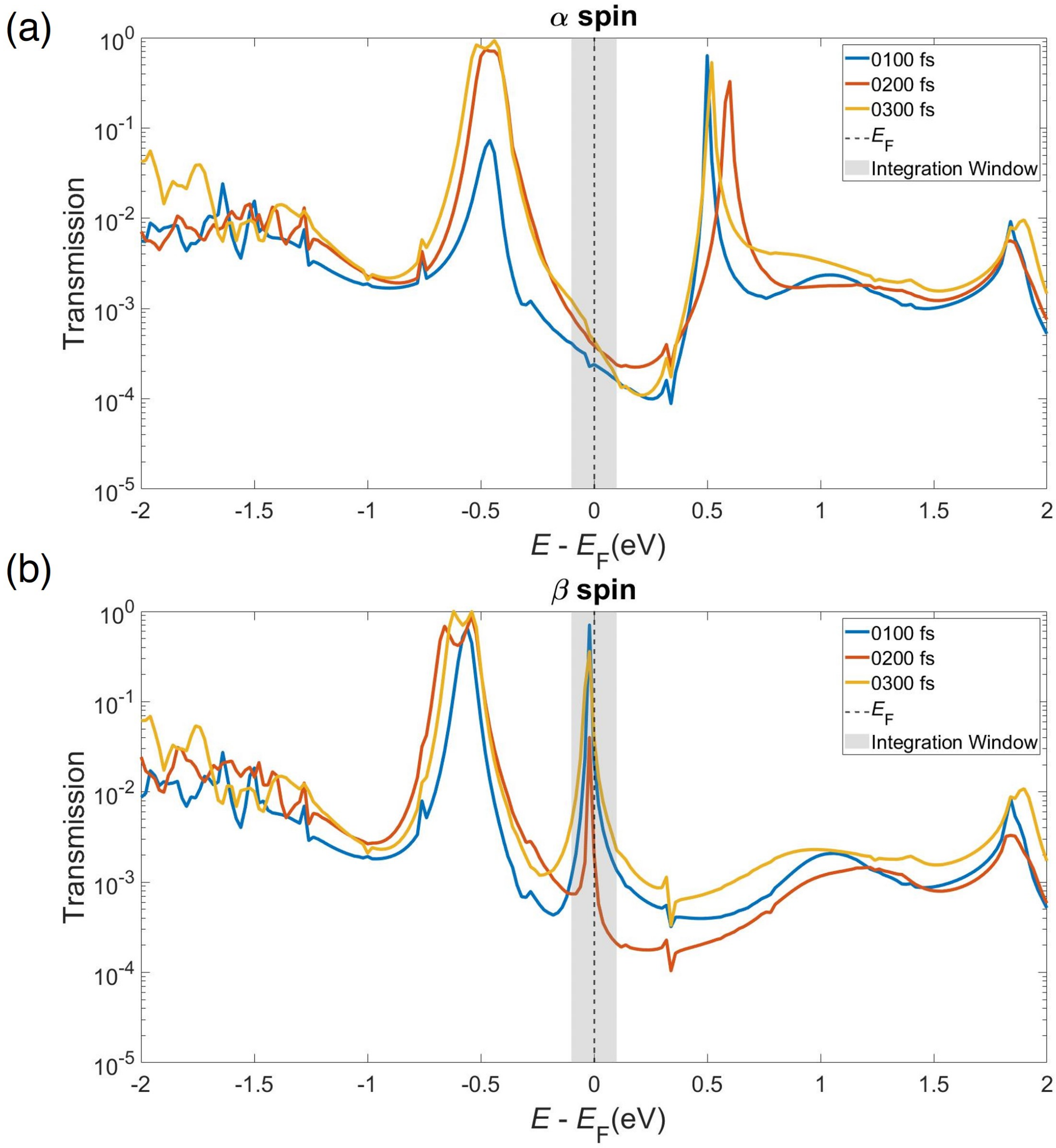


Figure S8: (a) α and (b) β transmission spectra from around the 300 K AIMD trajectory taken from around the 200 fs SFE dip.

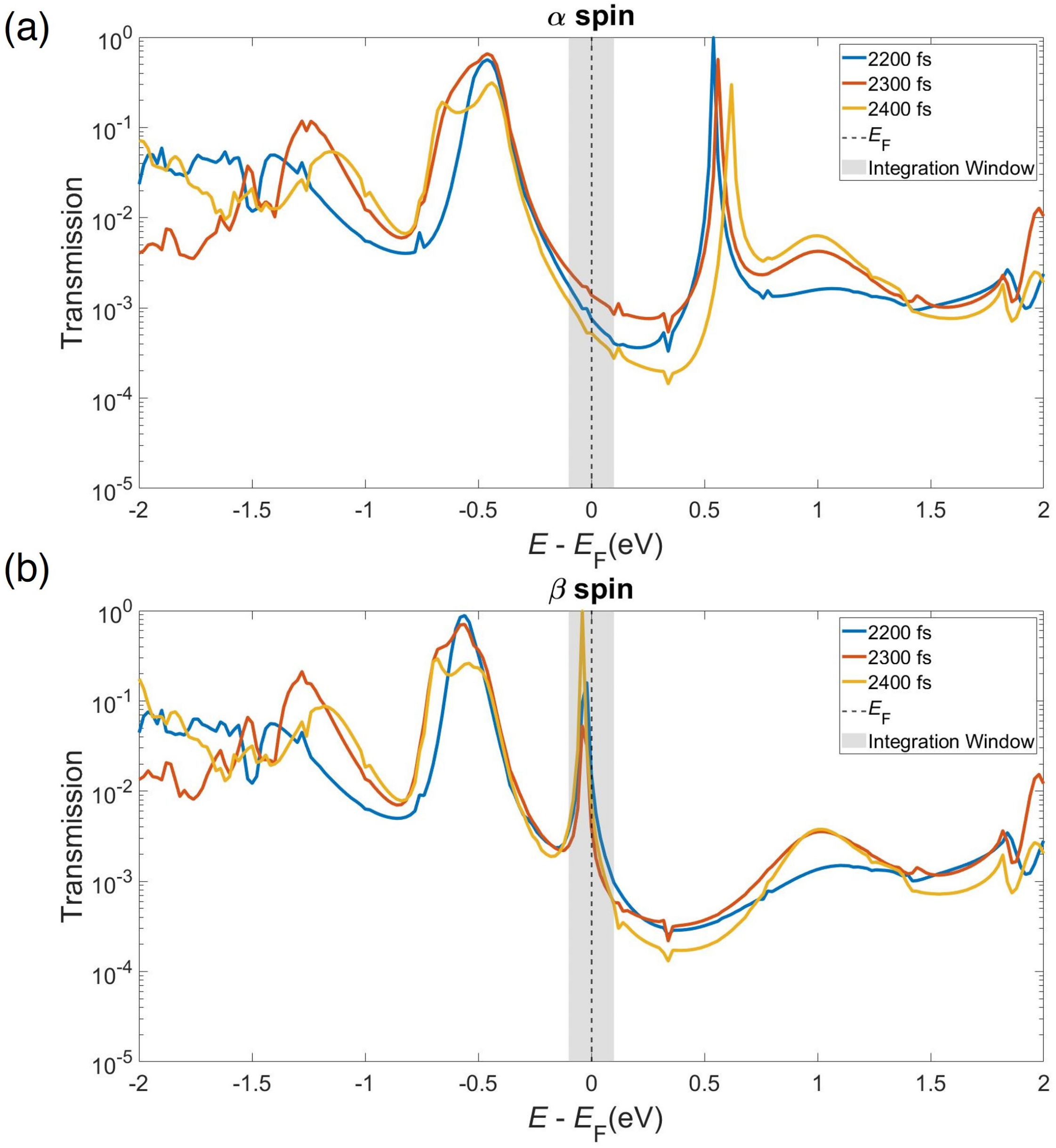


Figure S9: (a) α and (b) β transmission spectra from around the 300 K AIMD trajectory taken from around the 2,300 fs SFE dip.

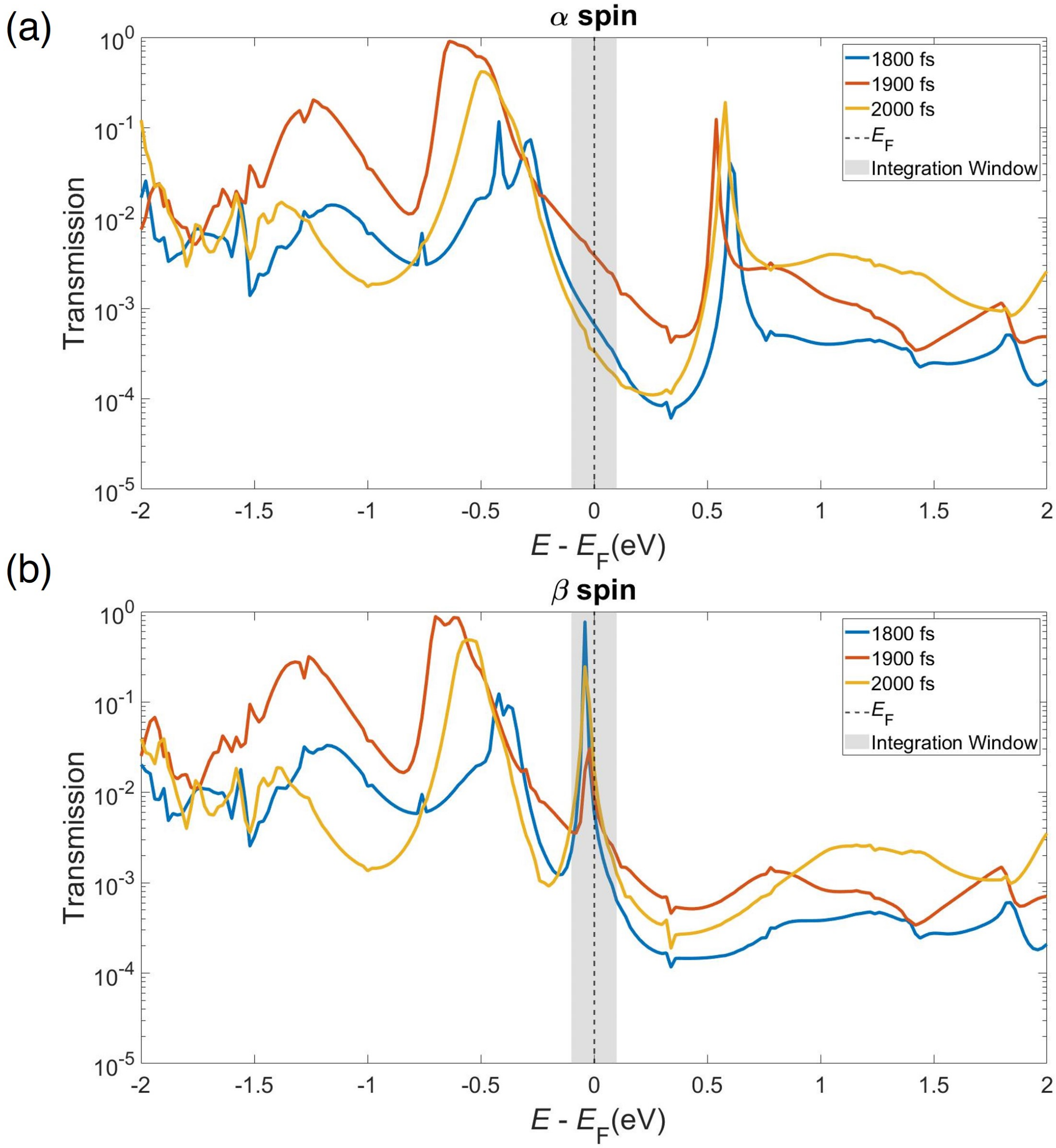


Figure S10: (a) α and (b) β transmission spectra from around the 500 K AIMD trajectory taken from around the 1,900 fs SFE dip.

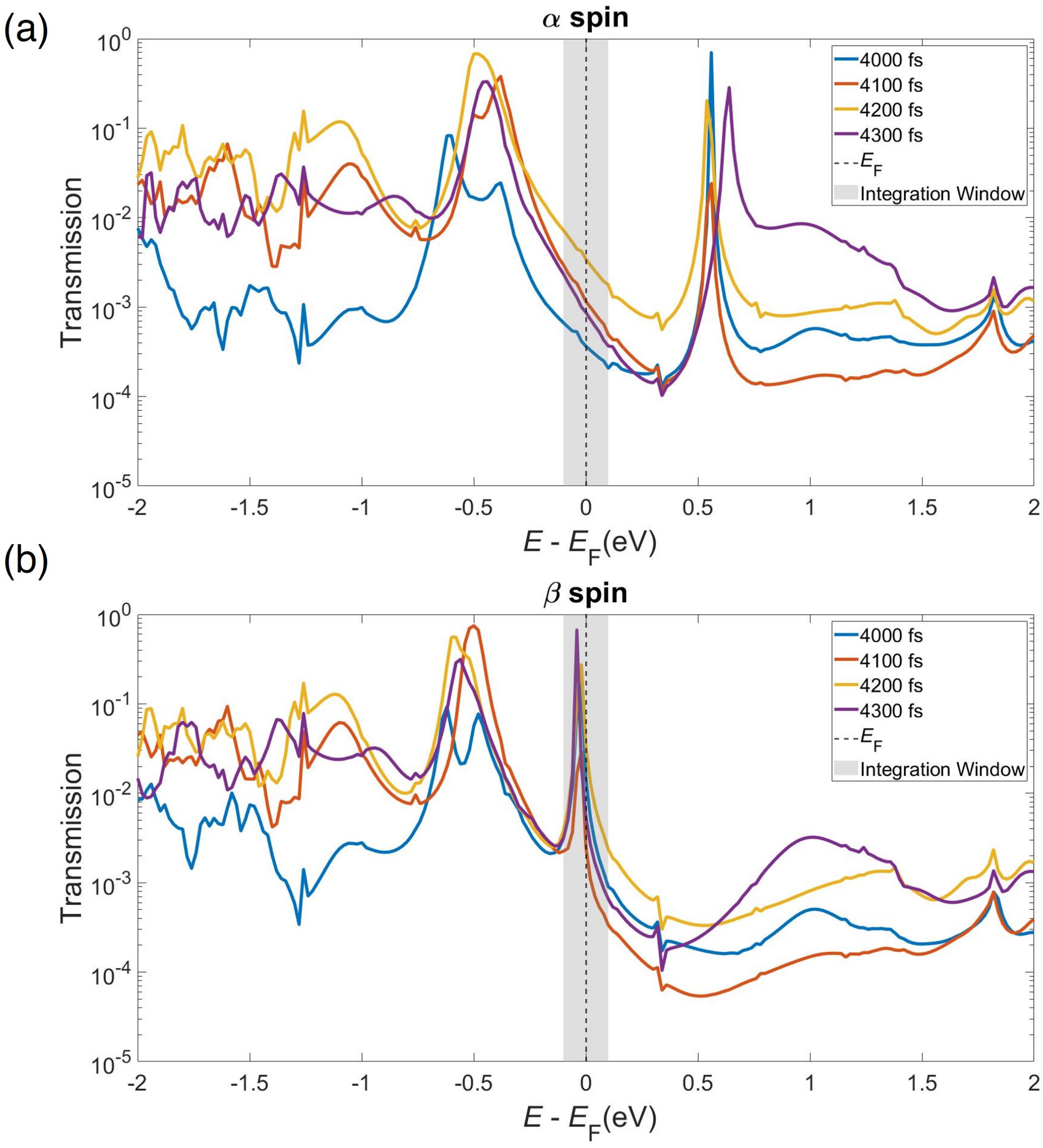


Figure S11: (a) α and (b) β transmission spectra from around the 500 K AIMD trajectory taken from around the 4,100 fs SFE dip.

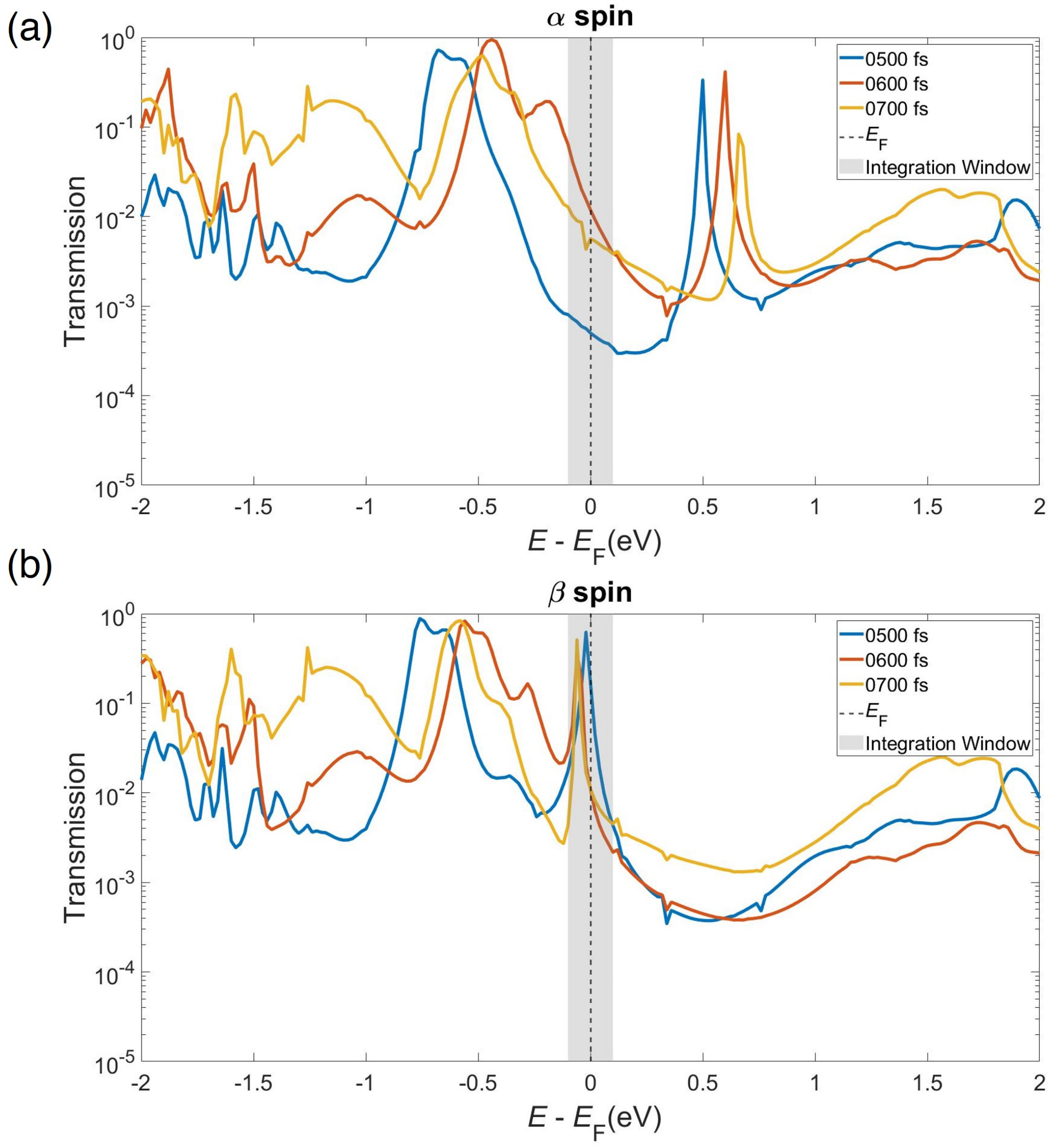


Figure S12: (a) α and (b) β transmission spectra from around the 700 K AIMD trajectory taken from around the 600 fs SFE dip.

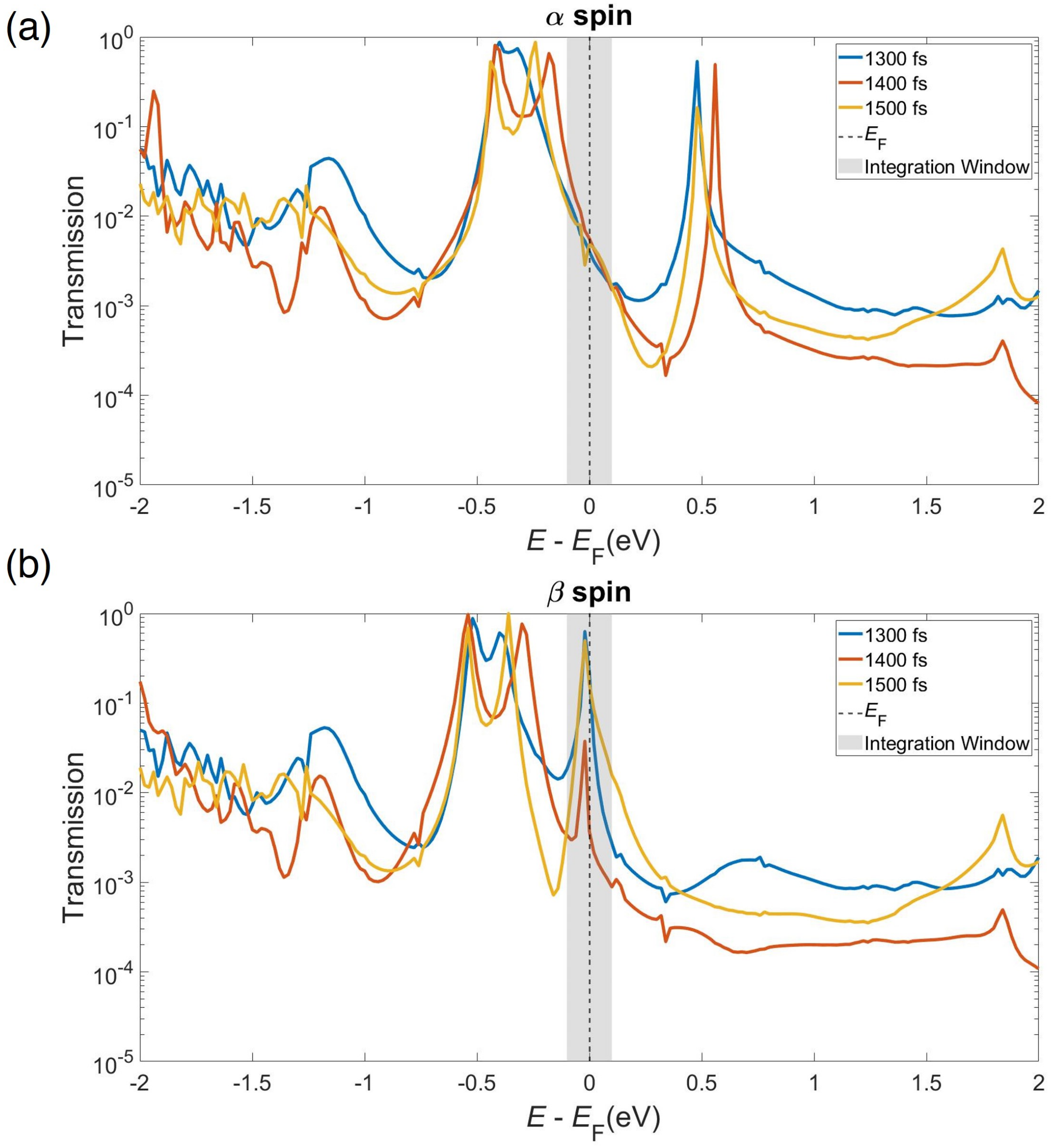


Figure S13: (a) α and (b) β transmission spectra from the 700 K AIMD trajectory taken from the 1,300 fs, 1,400 fs, and 1,500 fs timesteps in the trajectory.

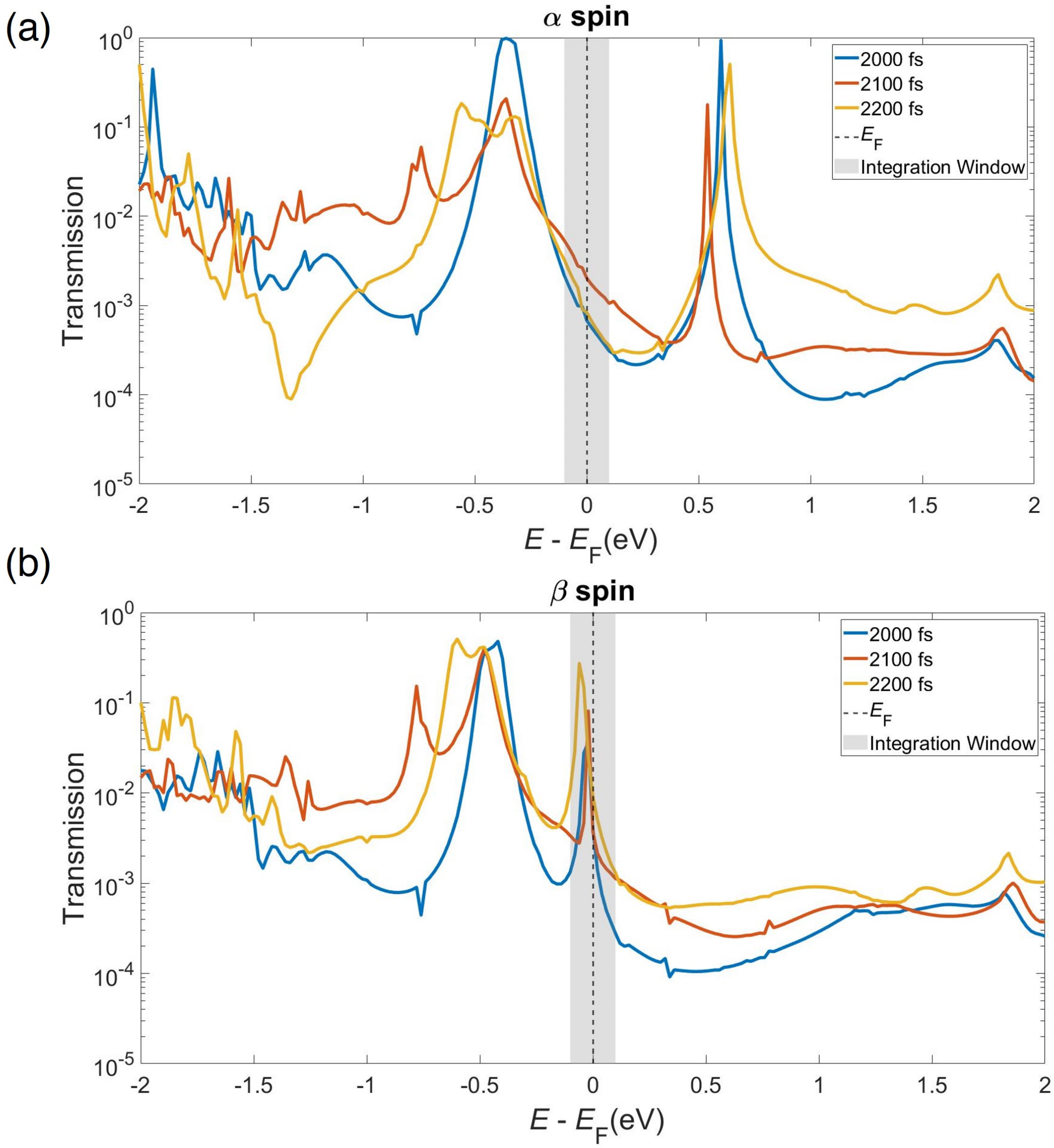


Figure S14: (a) α and (b) β transmission spectra from the 700 K AIMD trajectory taken from around the 2,100 fs SFE dip.

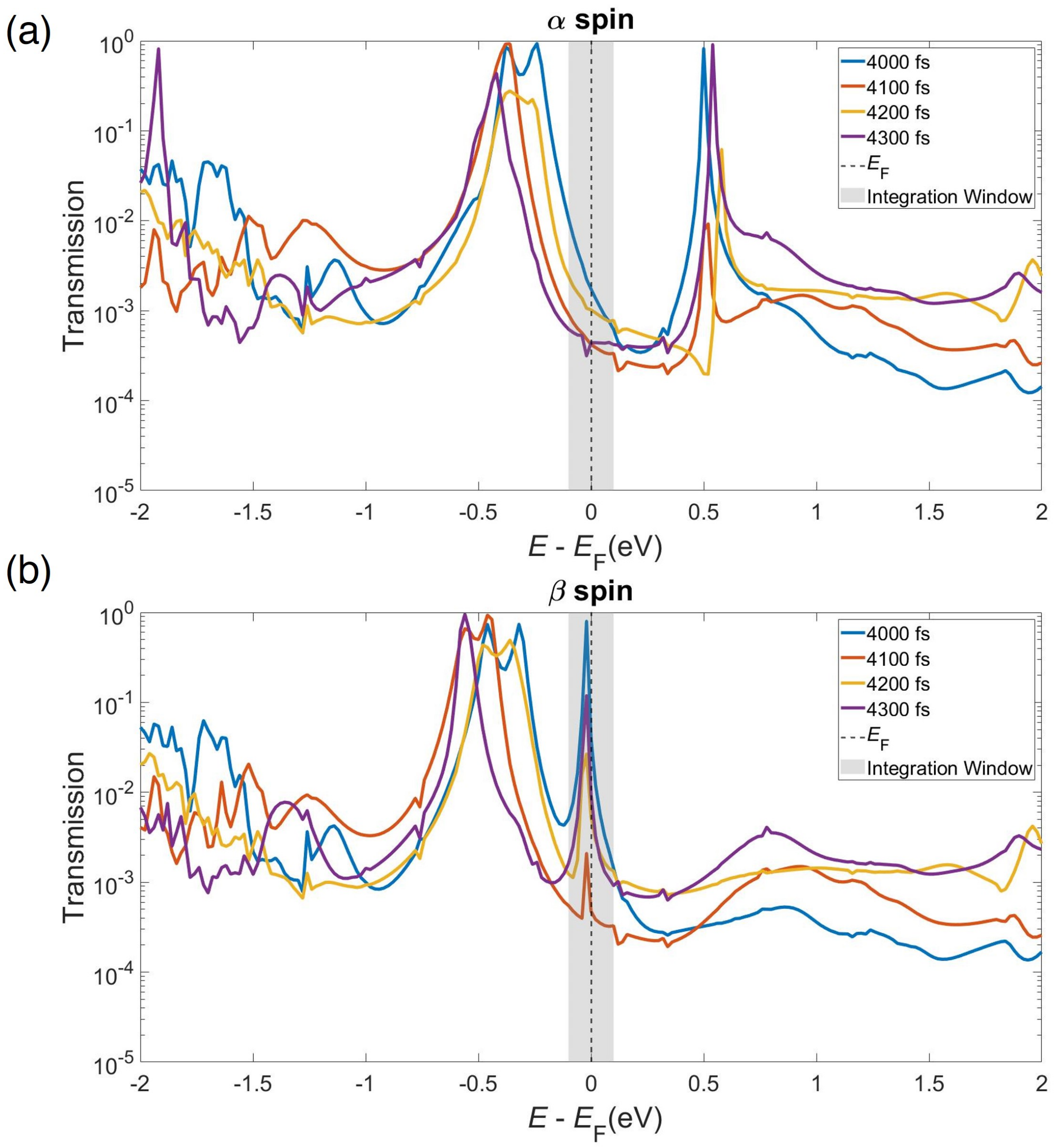


Figure S15: (a) α and (b) β transmission spectra from the 700 K AIMD trajectory taken from around the 4,100 fs SFE dip.

S4 Analyses performed on conductance and spin filter efficiency data

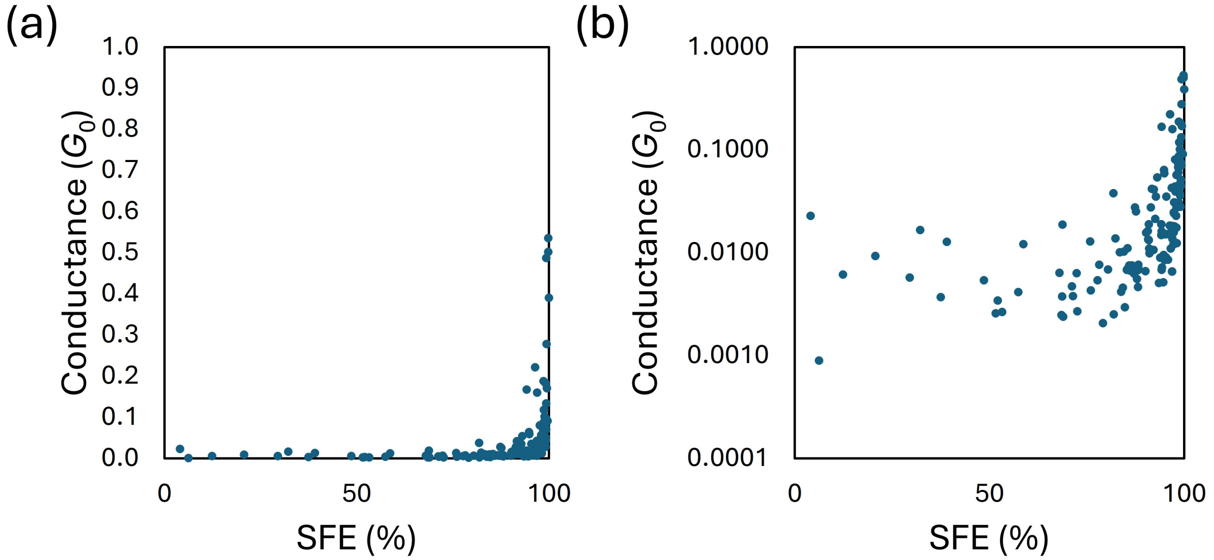


Figure S16: Regression analysis between SFE and conductance with SFE plotted on a linear x-axis and conductance on an (a) linear and (b) logarithmic y-axis. This analysis consists of all spin and charge transport data generated *via* AIMD trajectories.

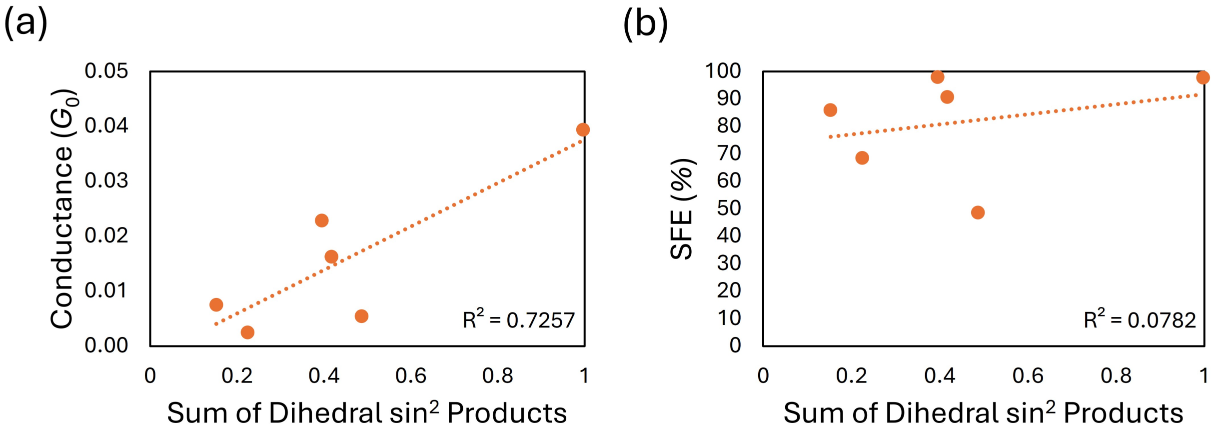


Figure S17: Regression analysis between (a) conductance and (b) SFE against the sum of dihedral $\sin^2$ products around the SFE dips at 200 and 2300 fs in the 300 K AIMD trajectory. Correlation does exist between the sum of dihedral $\sin^2$ products and conductance, although SFE is not strongly correlated to the dihedral values.

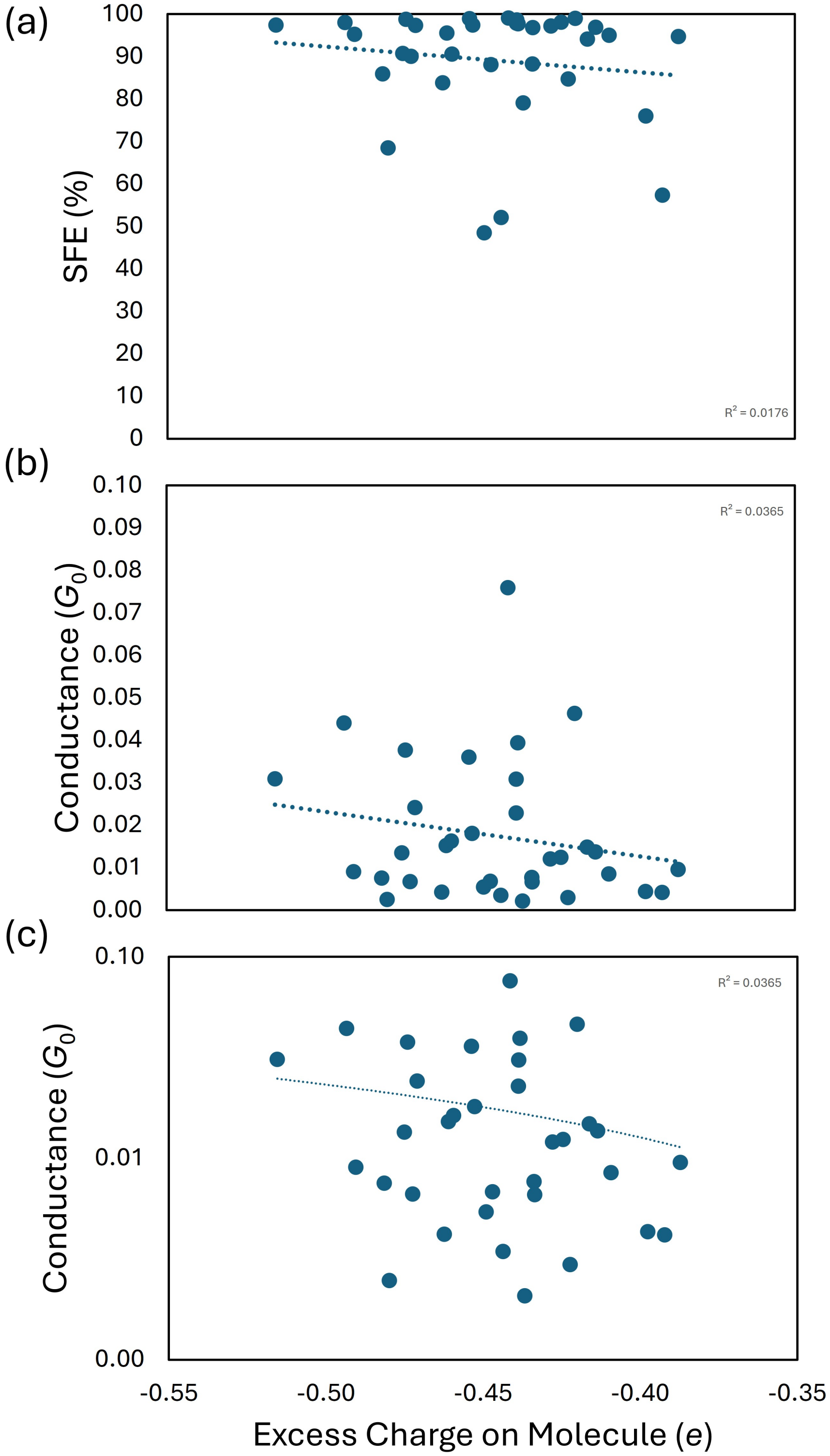


Figure S18: Regression analysis between excess charge on the molecule and (a) SFE, (b) conductance on a linear scale, and (c) conductance on a logarithmic scale, with these data coming from the first 3300 fs of the 300 K AIMD trajectory. Strong correlation between charge and SFE/conductance data does not exist in these data.

S5 DZP calculations performed on isolated PLY

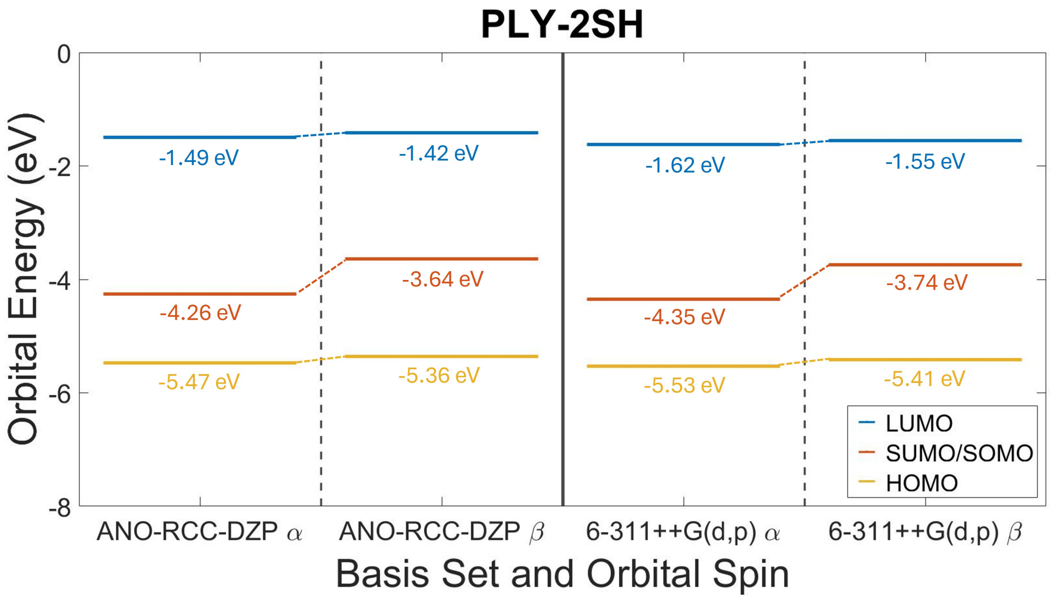


Figure S19: Data are presented comparing the HOMO, SOMO, SUMO, and LUMO molecular orbital energies calculated using the ANO-RCC-DZP[2] basis set and the 6-311++G(d,p) basis set. Both calculations were performed using the PBE exchange correlation functional. The orbital splitting values for HOMO, SOMO-SUMO, and LUMO were 0.11 eV, 0.61 eV, and 0.07 eV, respectively, for both the ANO-RCC-DZP and 6-311++G(d,p) basis sets, although the exact energies differ between the two basis sets.

References

(1) Smeu, M.; Monti, O.; McGrath, D. Phenalenyls as tunable excellent molecular conductors and switchable spin filters. *Phys. Chem. Chem. Phys.* **2021**, *23*, 24106–24110.

(2) Roos, B.; Lindh, R.; Malmqvist, P.; Veryazov, V.; Widmark, P.; Borin, A. New Relativistic Atomic Natural Orbital Basis Sets for Lanthanide Atoms with Applications to the Ce Diatom and LuF3. *J. Phys. Chem. A* **2008**, *112*, 11431–11435.