Hybrid QM/QM Simulations of Photochemical Reactions in the Molecular Crystal *N*-salicylidene-2-chloroaniline

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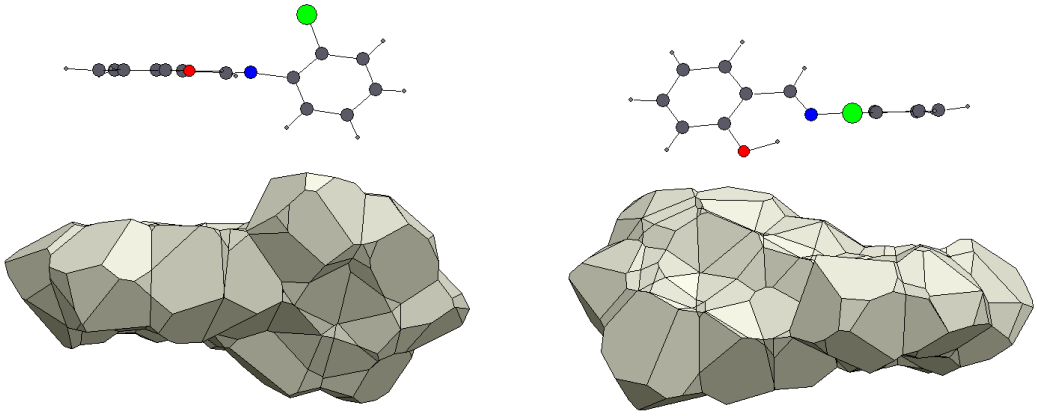
1 Molecular Packing in the Photochromic Polymorph of SCA

In order to further assess the crystal packing of SCA, we have carried out a Voronoi-Dirichlet tesselation[1] of the crystal structure using the computer program TOPOS 4.0.[2] This process assigns to each atom (which in this context is considered to be a point positioned at the nucleus) a Voronoi-Dirichlet polyhedron (VDP) that contains all points whose distance to that atom is not greater than the distance to any other atom. In this manner, space is partitioned completely and disjointly into VDPs associated with individual atoms. (The partitioning is not disjoint in the rigorous sense, because the surface of each polyhedron is shared with the neighbouring

polyhedra, but this fine point can be ignored here.) The VDP of an atom may be roughly interpreted as the region of space taken up by the atom and, by extension, the union of VPDs of atoms comprising a molecule may be regarded as the region of space belonging to that molecule. We must bear in mind, however, that although the Voronoi-Dirichlet tesselation provides a convenient means to analyze the molecular packing, the VDPs are purely geometric constructs that do not reflect the electronic structure of a crystal, and it would therefore be meaningless to use them to analyze system properties other than the spatial arrangement of atoms.

In Figure 1 we show two views of the union of atomic VDPs belonging to a single SCA molecule in the crystal lattice. It can be seen that the union of VDPs follows the shape of the molecule quite closely, consisting of two disk-like parts, which correspond to the two aromatic rings, joined at the edge. In particular, no significant bulge or protuberance is visible above or below the aromatic rings, indicating that the crystal structure contains no large voids on either side of the rings. This, in turn, suggests that a photoisomerisation mechanism involving a simple rotation around the C3-C4 bond is obstructed by intermolecular steric interactions, whereas the pedal-motion mechanism of Harada *et al.*, in which the two aromatic rings are less strongly displaced from their original positions, seems likely to be able to proceed with less steric hindrance.

Figure 1: Atomic VDPs of an SCA molecule in the crystal lattice. Above each view of the VDPs, the SCA molecule is displayed to scale and in the same orientation.



Note that in addition to the photochromic polymorph of SCA whose crystal structure is discussed above, a non-photochromic SCA polymorph has recently been reported[3] in which the molecules are planar and π-stacked. The density calculated from the crystal cell and contents of the non-photochromic polymorph at room temperature is slightly higher than that of the photochromic polymorph, at 1.405 g/cm^3 and 1.359 g/cm^3, respectively.

2 Construction of the $1 \times 1 \times 2$ Supercell Containing a *Trans*-keto Molecule

In the experimentally determined structure of the *trans*-keto tautomer of *N*-3,5-di-tert-butylsalicylidene-3-nitroaniline embedded in a lattice consisting predominantly of *cis*-enol molecules, the *trans*-keto molecule is positioned very similarly to the original *cis*-enol molecule.[4] Hence, in order to generate the starting geometry of the supercell containing a single *trans*-keto molecule, one molecule in the experimental crystal structure was converted from the *cis*-enol into the *trans*-keto form by manually moving the atoms H1, H2, C3 and N1 while preserving the position of the two aromatic rings. The structure obtained in this way was subsequently optimised at the periodic DFT level of theory (see Section 3.4.2 of the main body of the present

paper for a detailed description of the parameters of the DFT calculation). The default BFGS optimisation algorithm was applied, with the following convergence criteria: energy tolerance 2.0×10^{-5} eV/atom, maximum force tolerance 5.0×10^{-2} eV/Å, displacement tolerance 1.0×10^{-3} Å. The resulting optimised geometry of the supercell containing one *trans*-keto molecule and seven *cis*-enol molecules is shown in Figure 6(b) in the main body of the present paper.

References

[1] V. A. Blatov, *Cryst. Rev.*, 2004, **10**, 249.

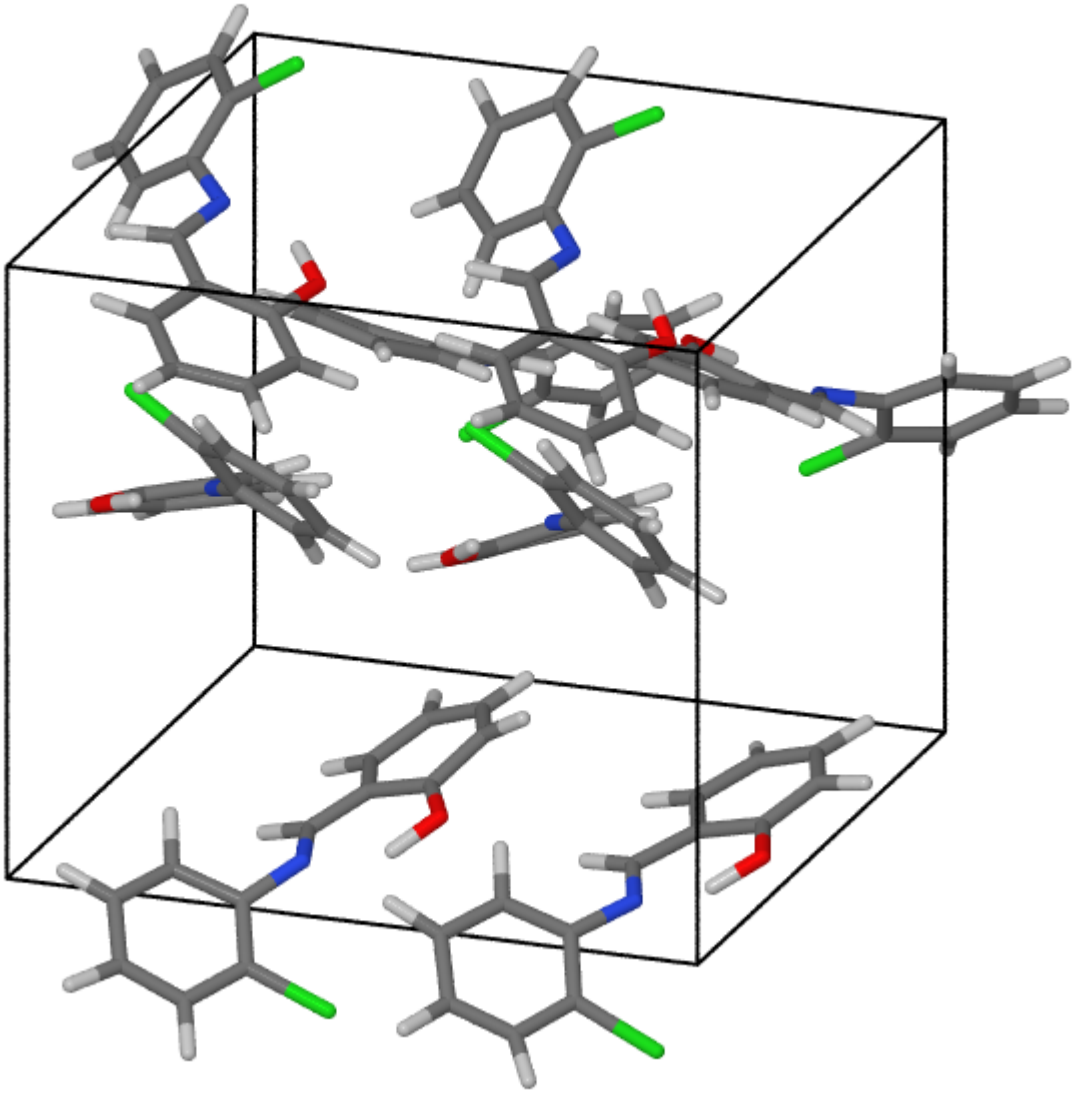
[2] TOPOS website: http://www.topos.ssu.samara.ru/

[3] K. Johmoto, T. Ishida, A. Sekine, H. Uekusa, Y. Ohashi, *Acta Cryst.*, 2012, **B68**, 297.

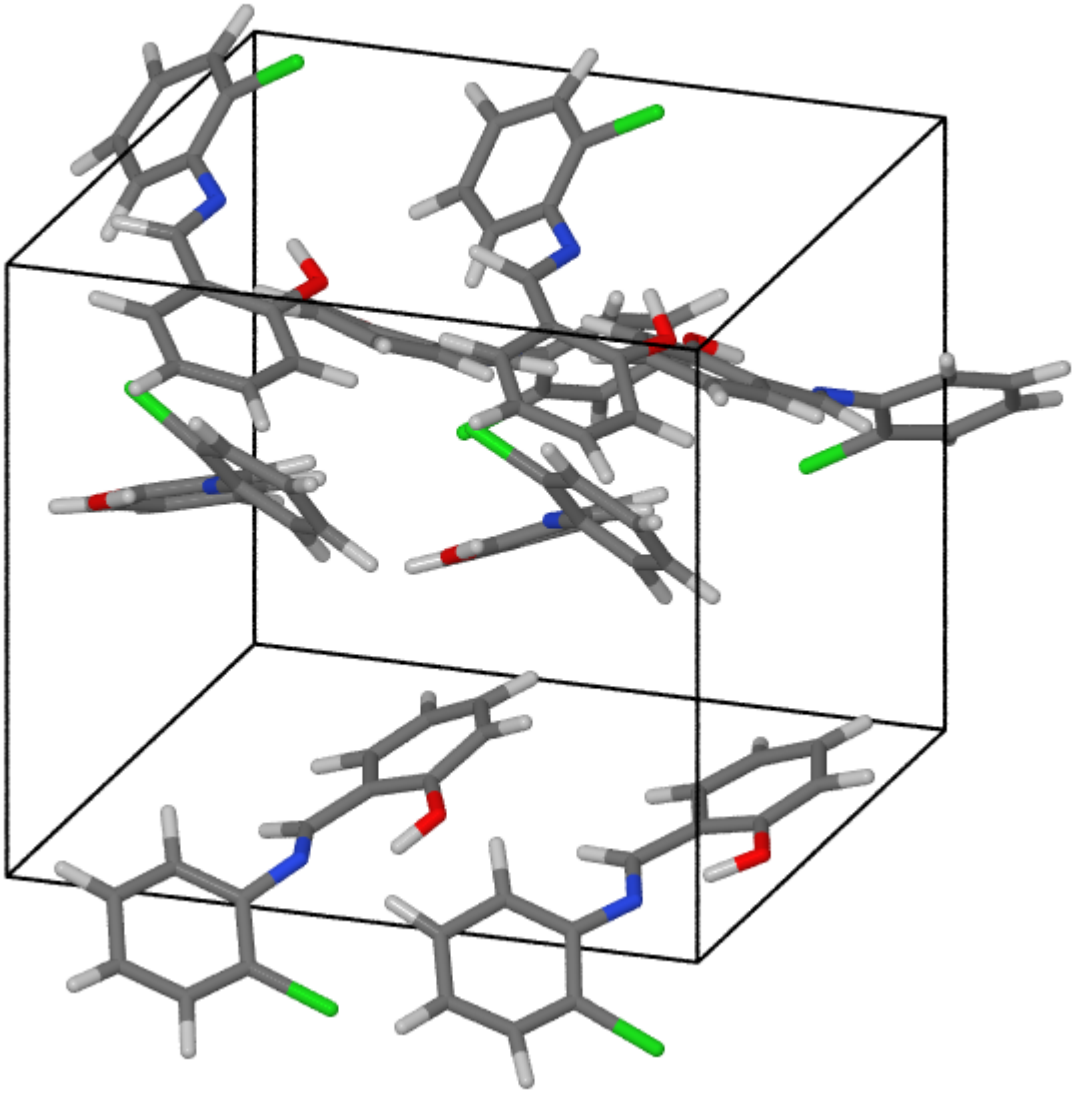
[4] J. Harada, H. Uekusa, Y. Ohashi, *J. Am. Chem. Soc.*, 1999, **121**, 5809.

Snapshots from Trajectory 1

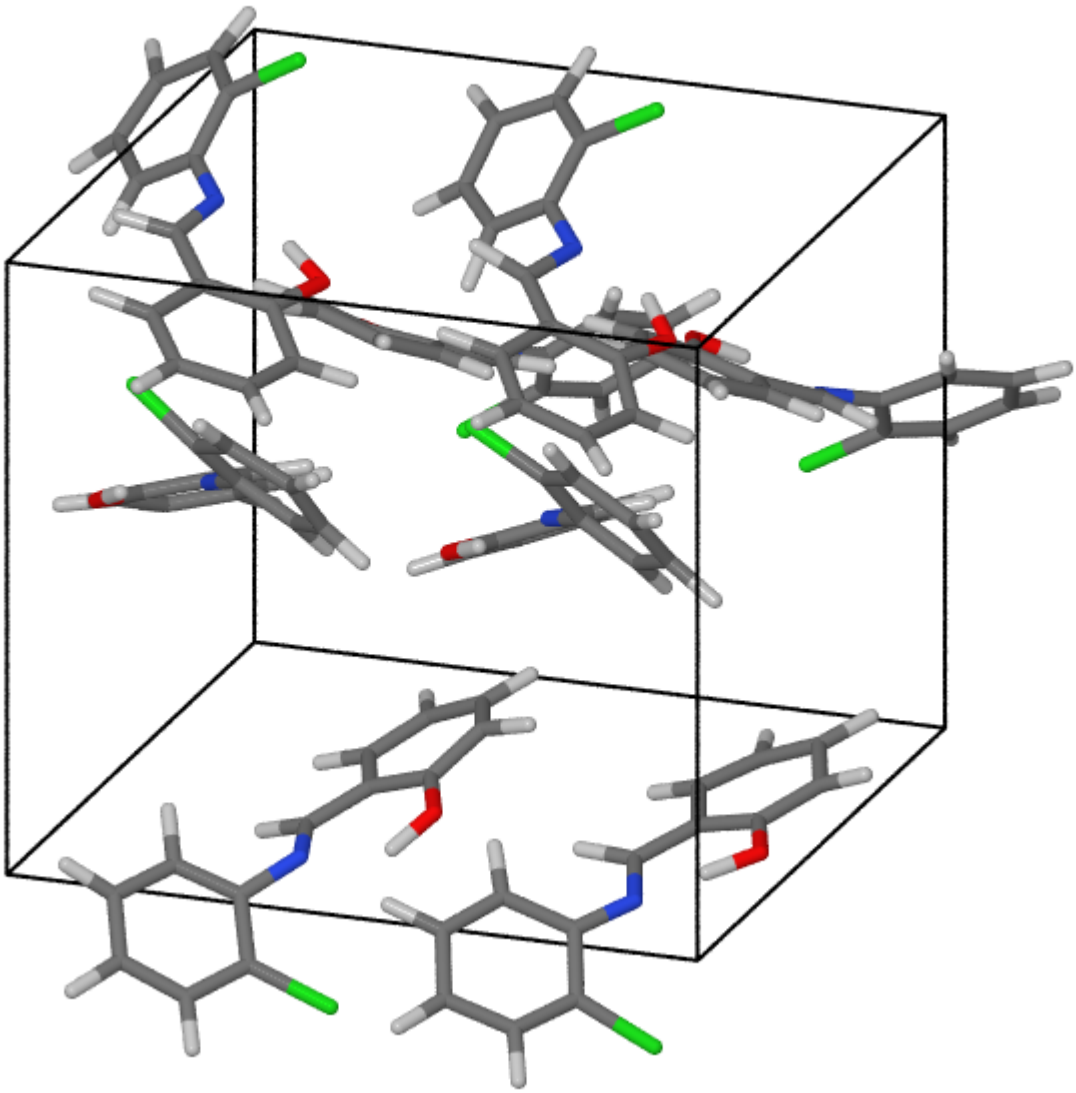
$t = 0$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 3.636$ eV



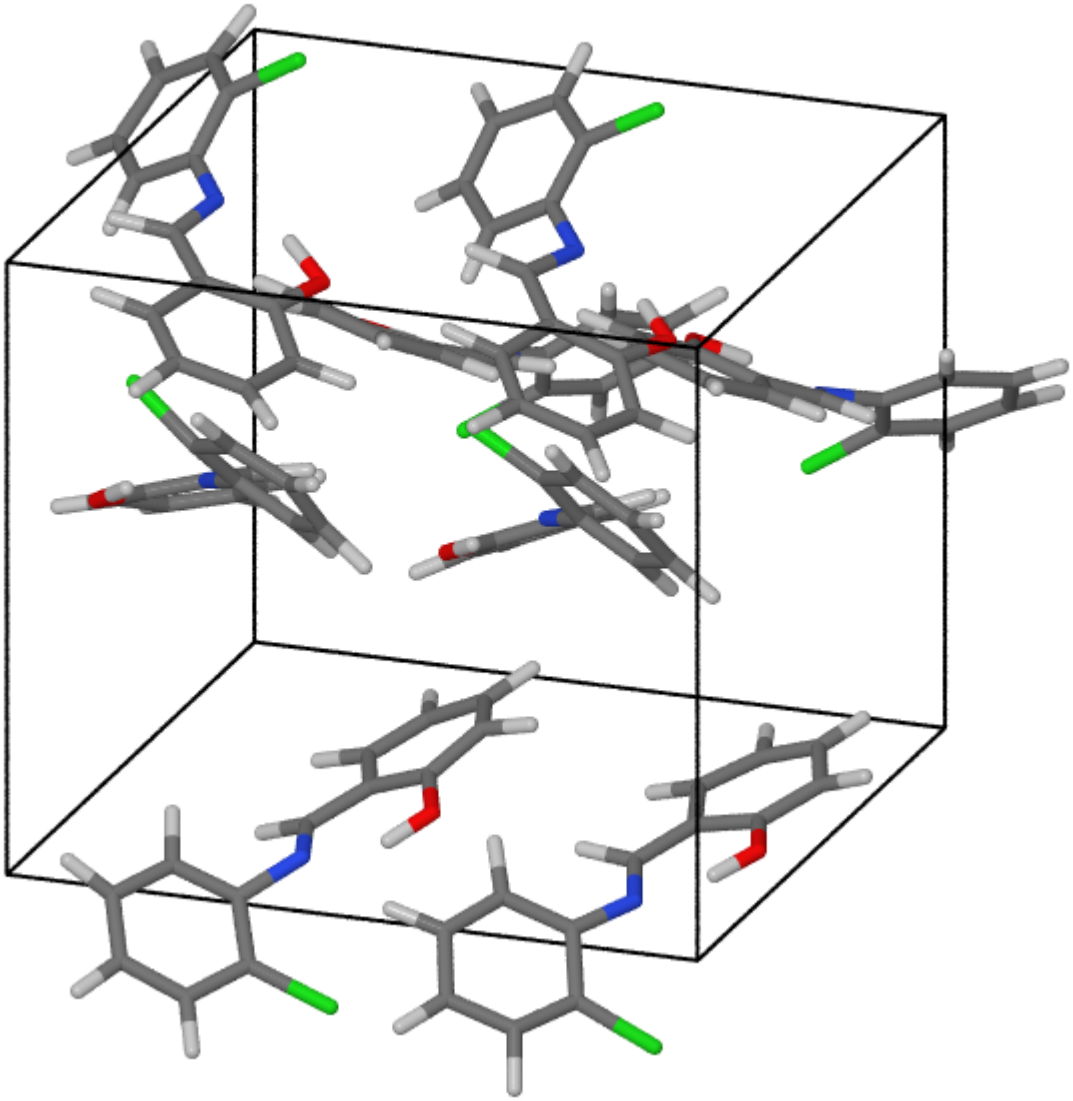
$t = 5$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 3.316$ eV



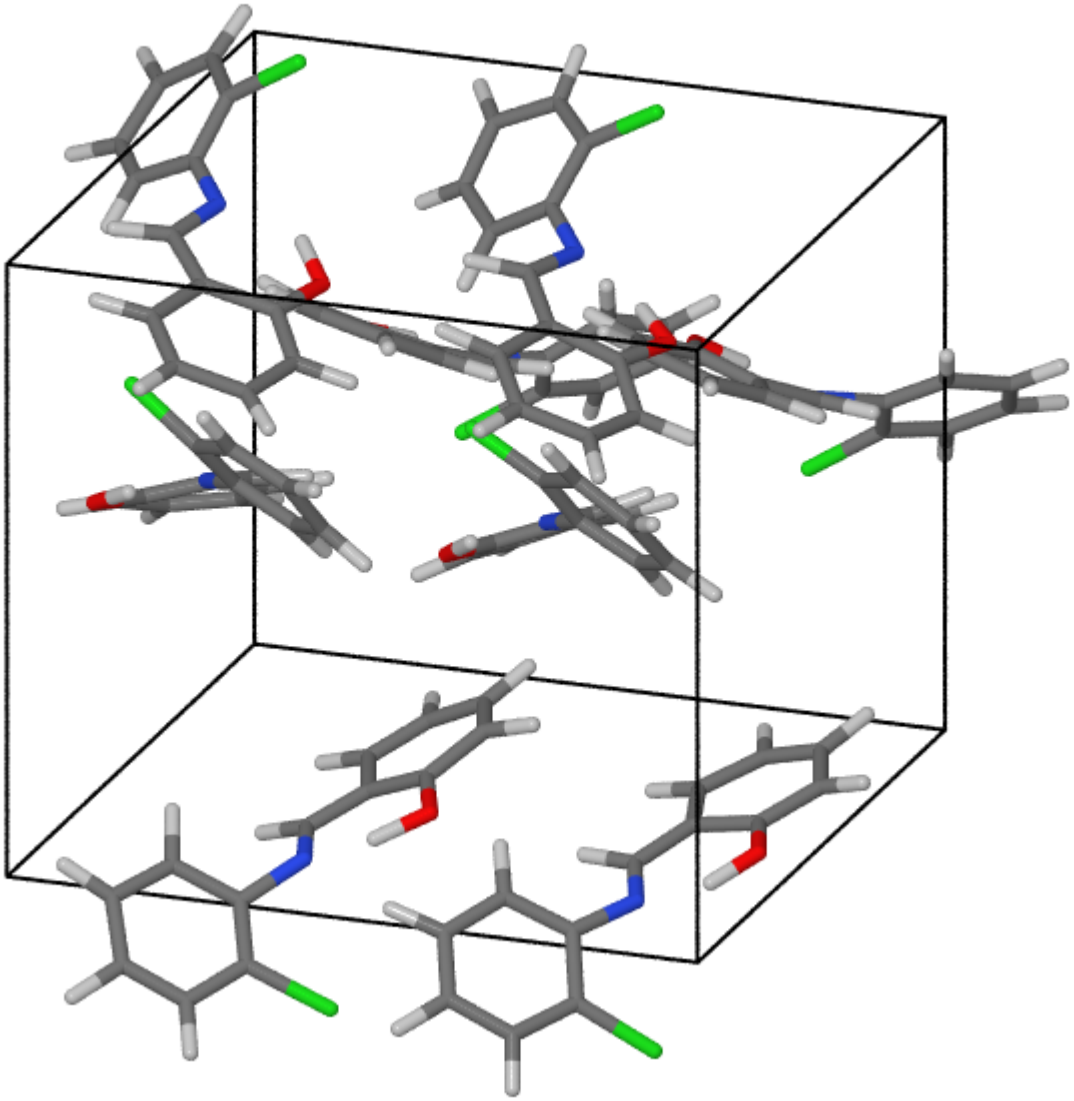
$t = 10\ \mathrm{fs} \quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 2.923\ \mathrm{eV}$



$t = 15\ \mathrm{fs} \quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 3.139\ \mathrm{eV}$



$t = 20$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 3.356$ eV



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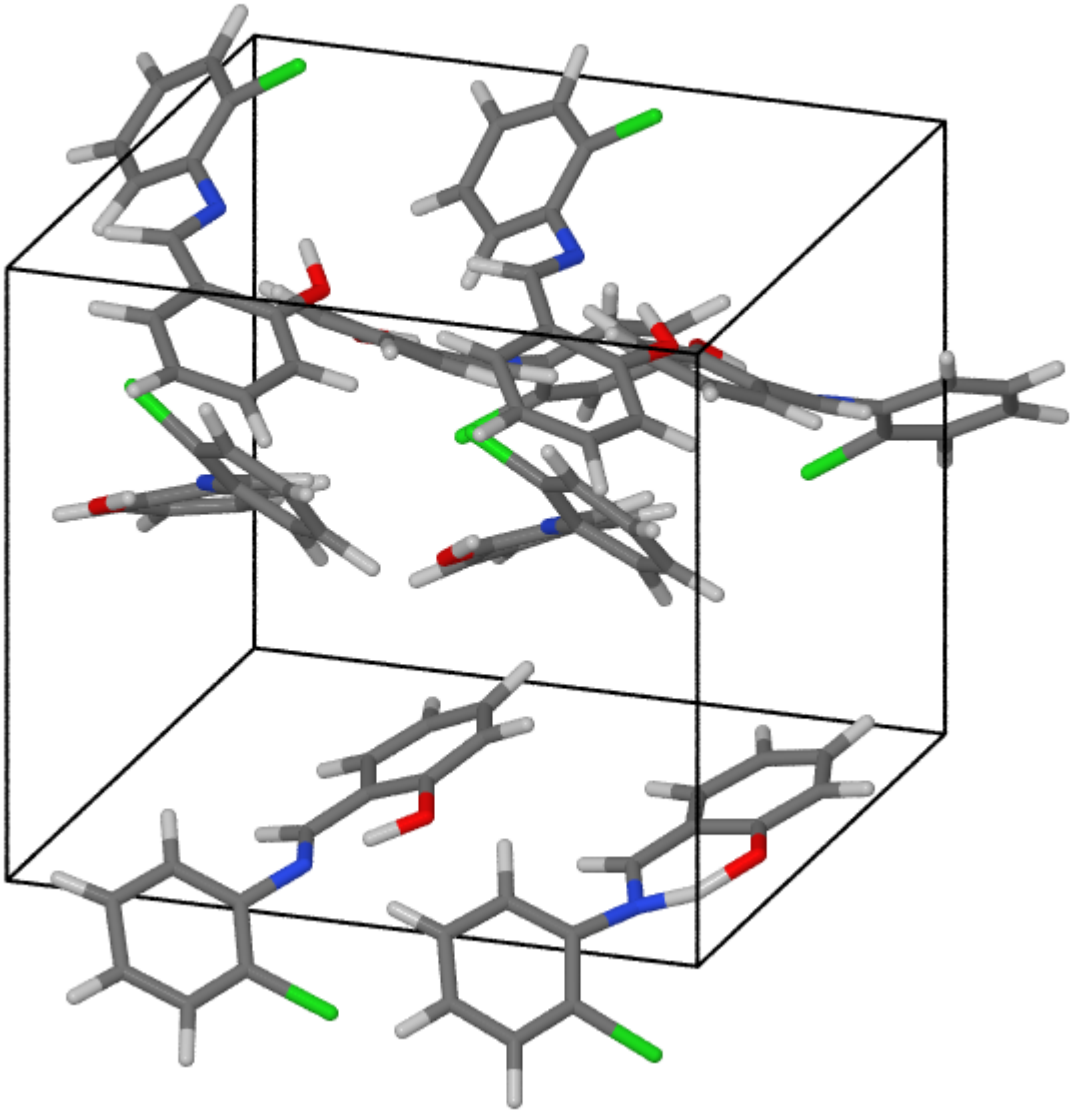

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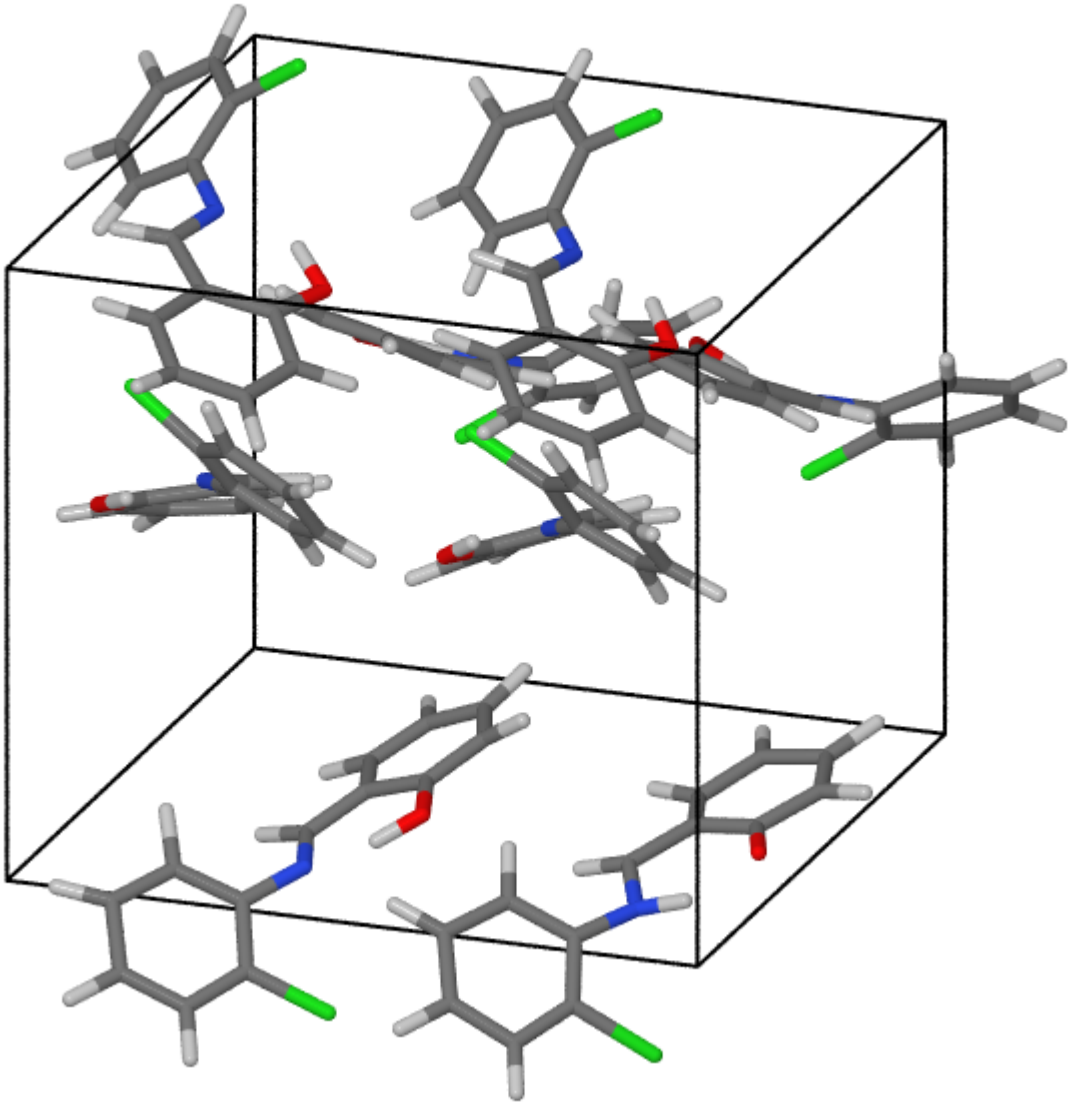
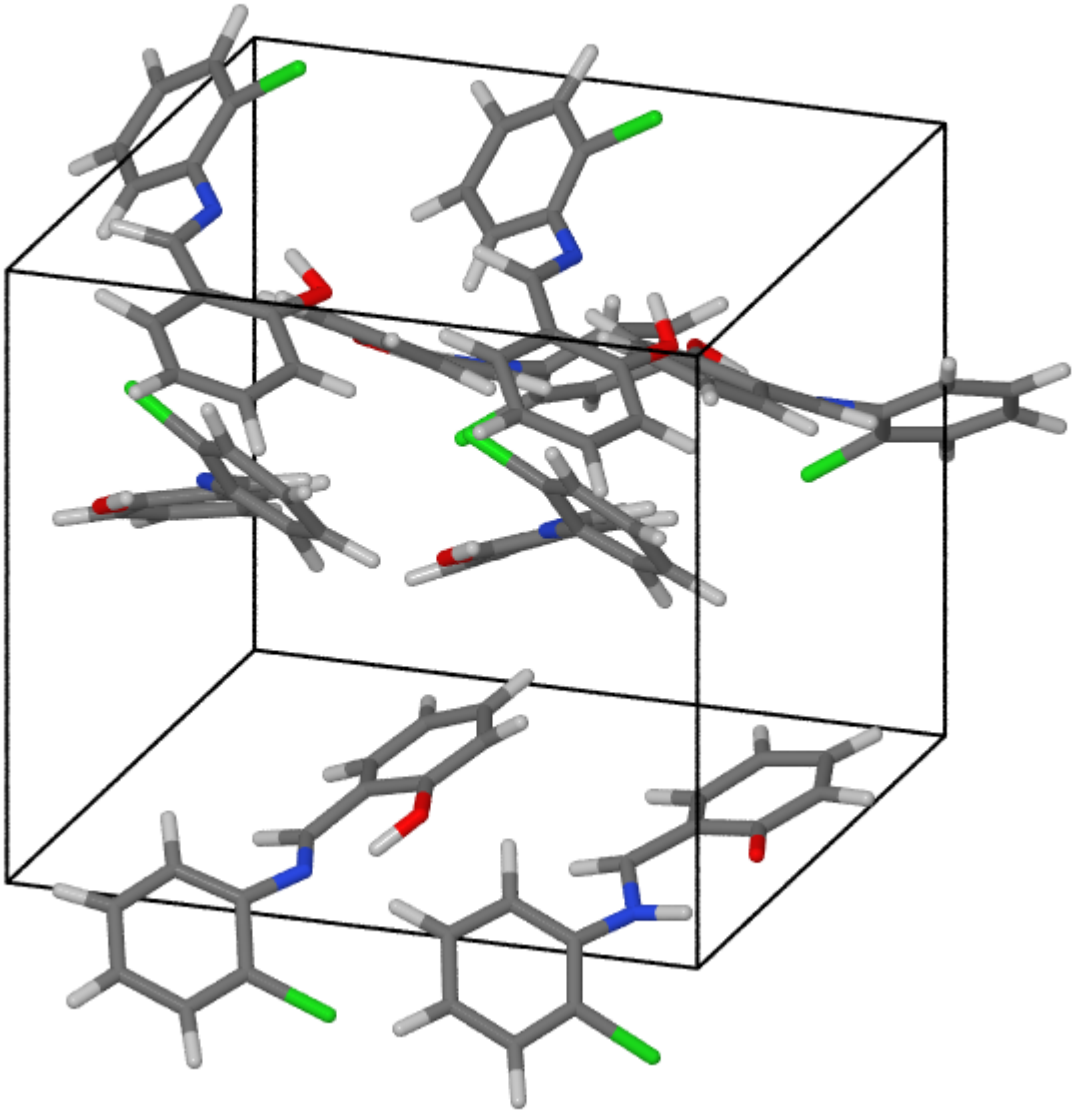


$t = 35$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 2.251$ eV



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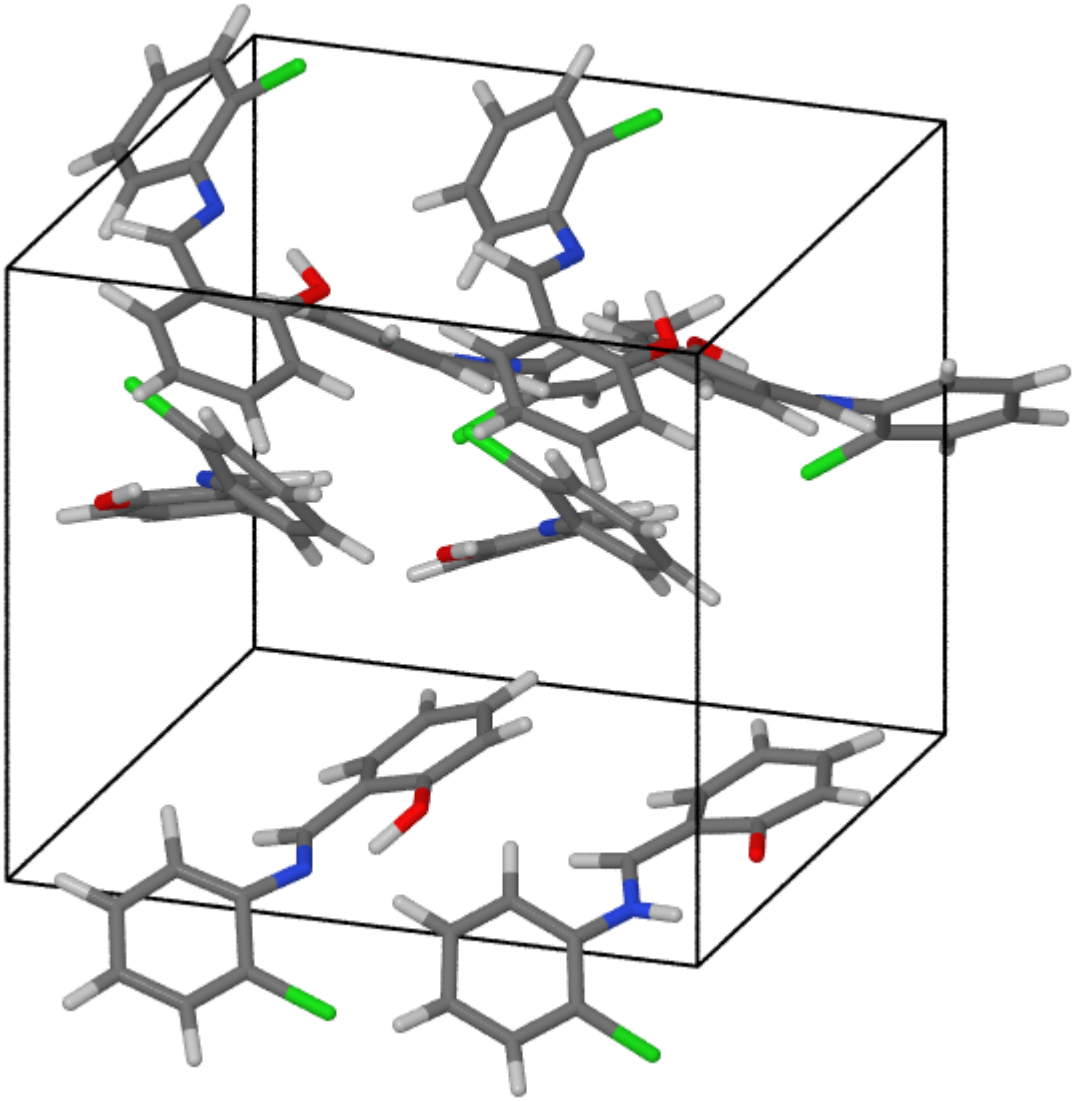
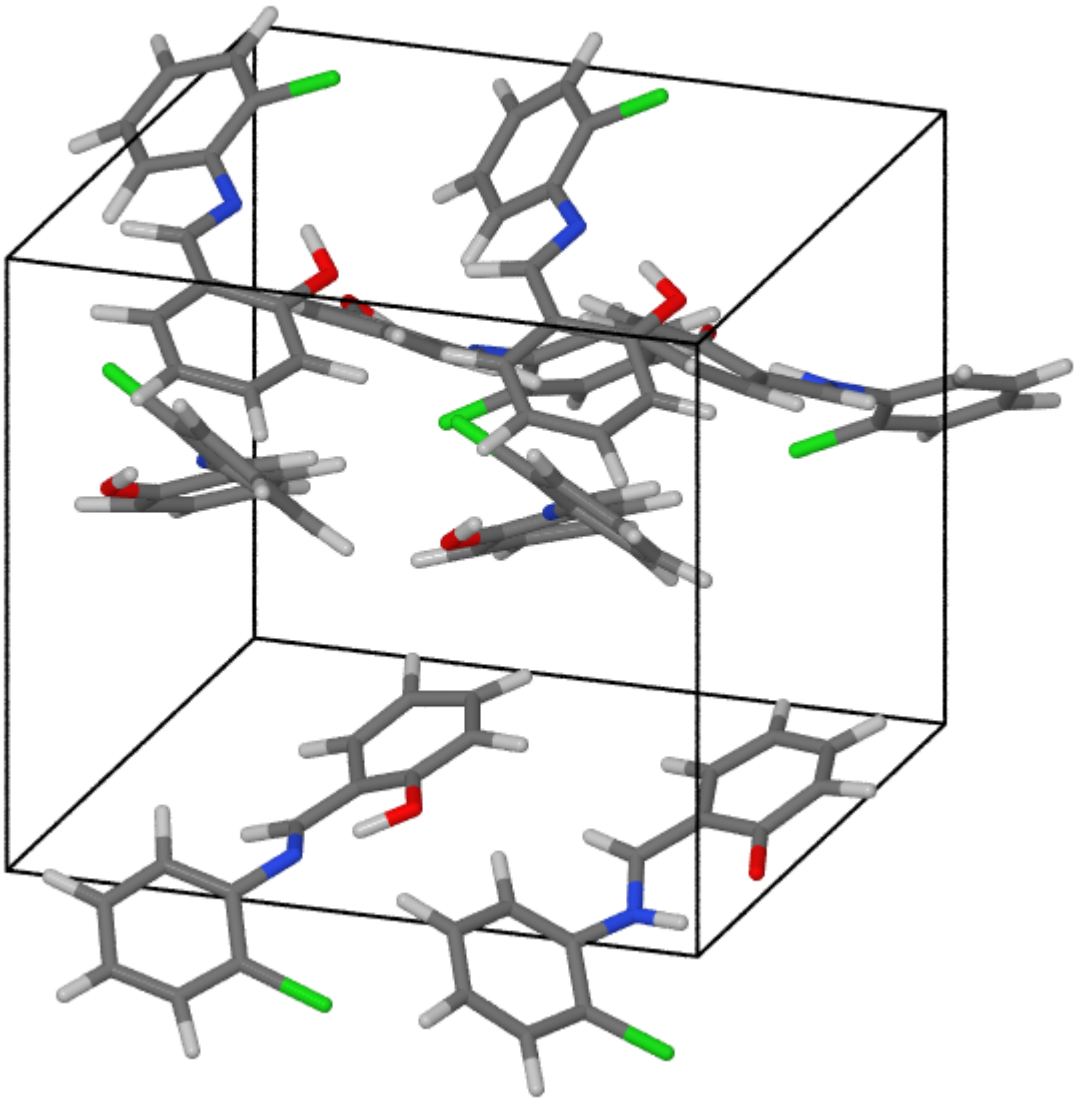
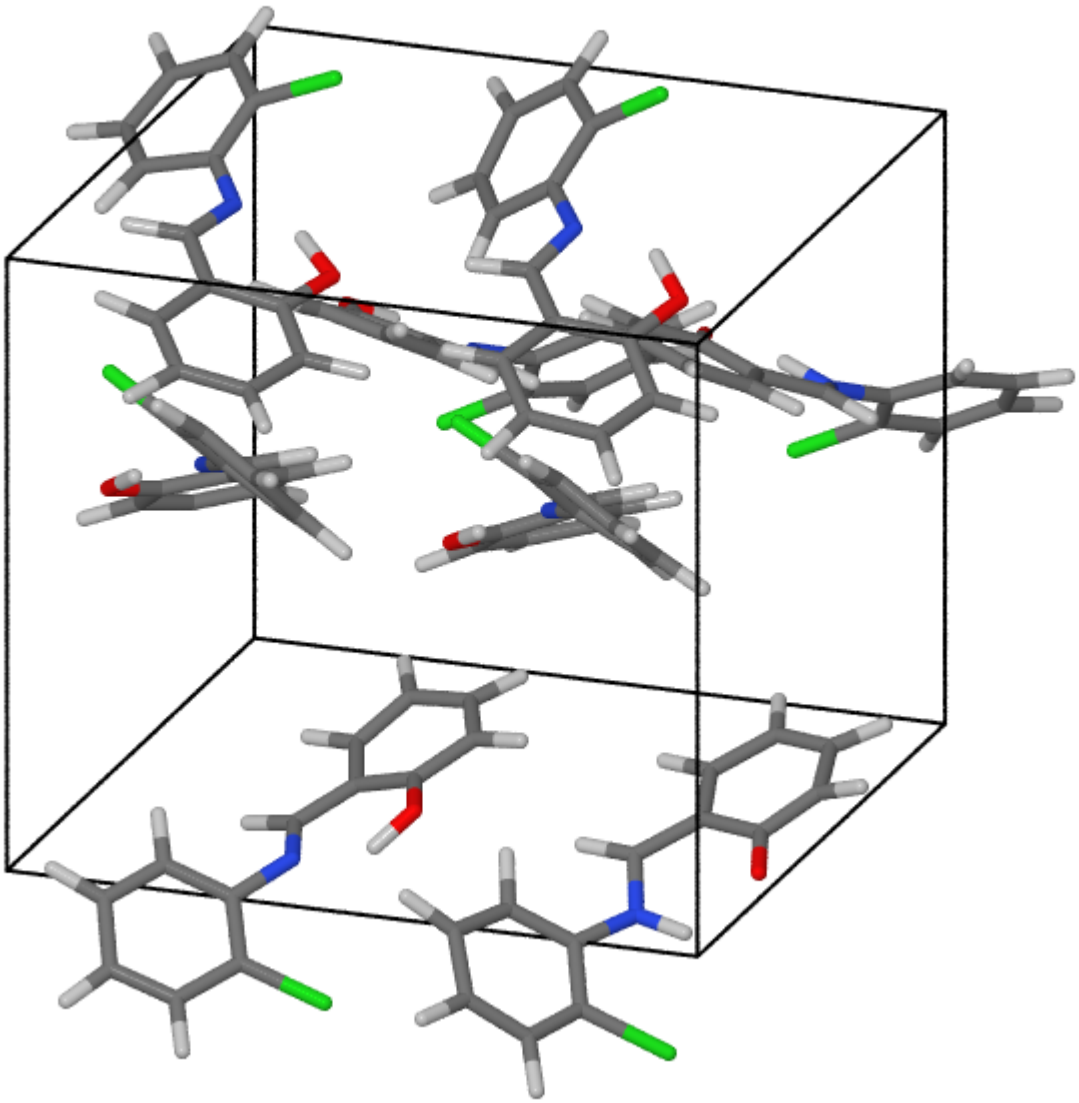


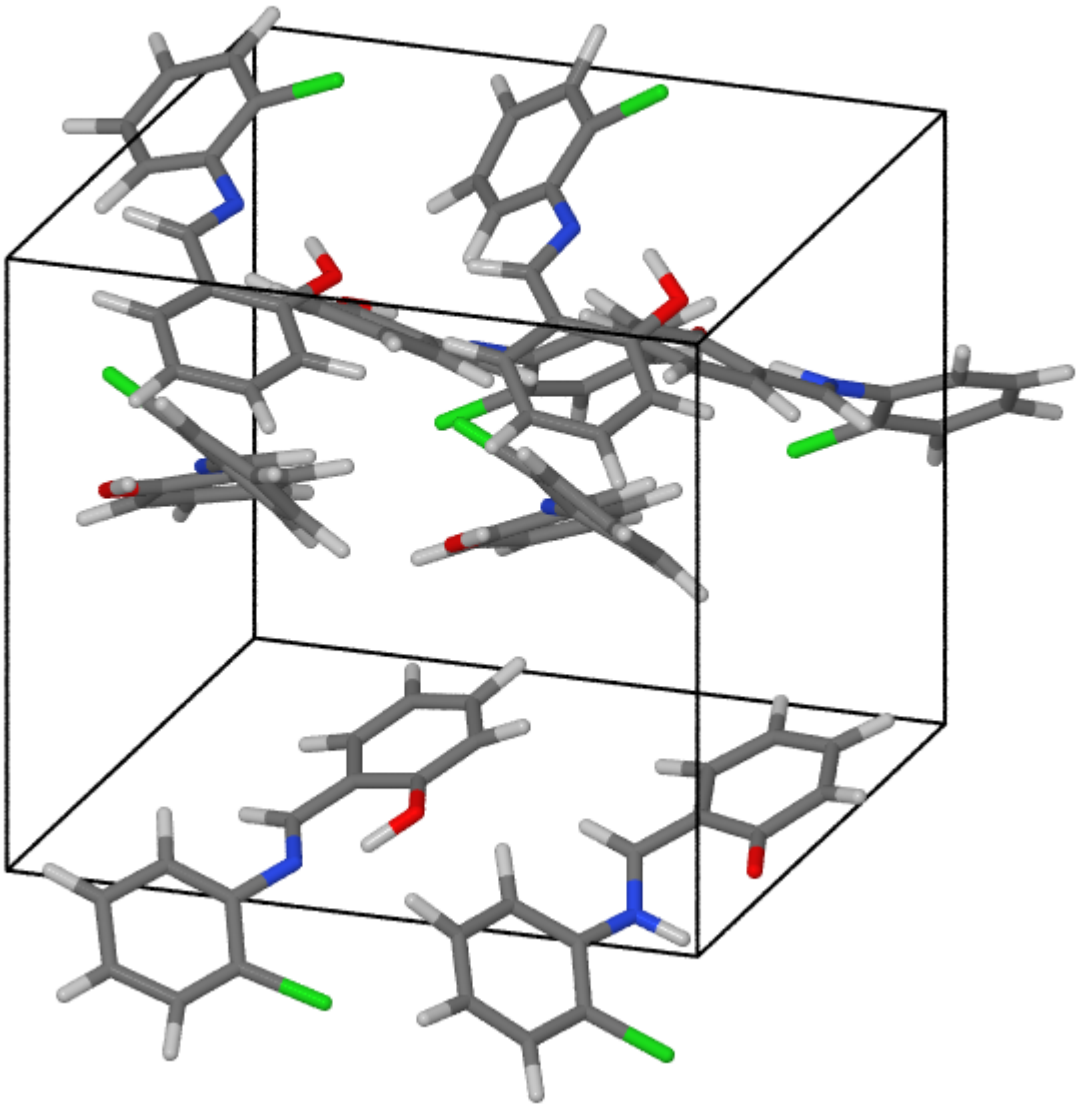
$t = 240$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 2.429$ eV



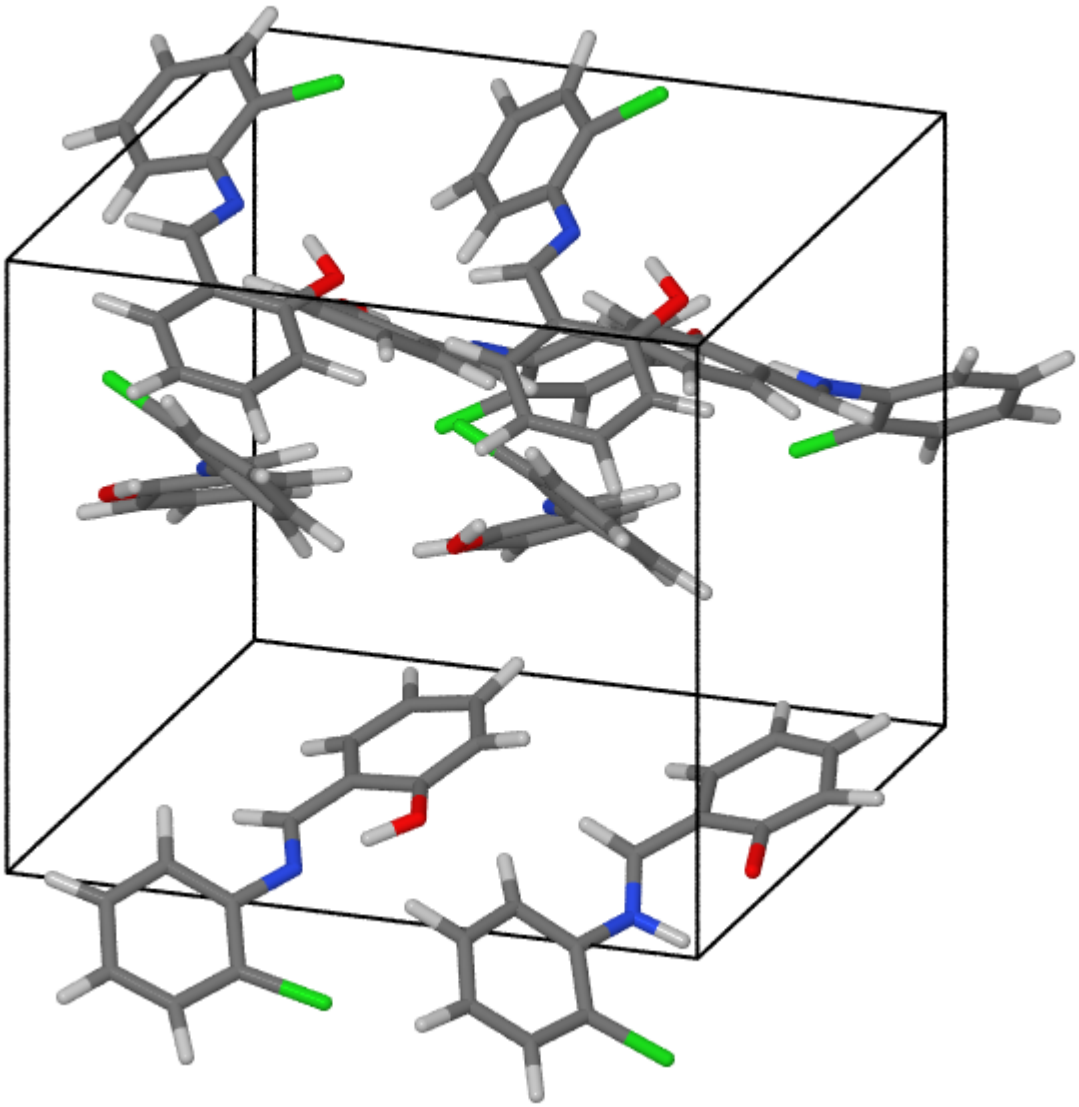
$t = 250$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 2.120$ eV



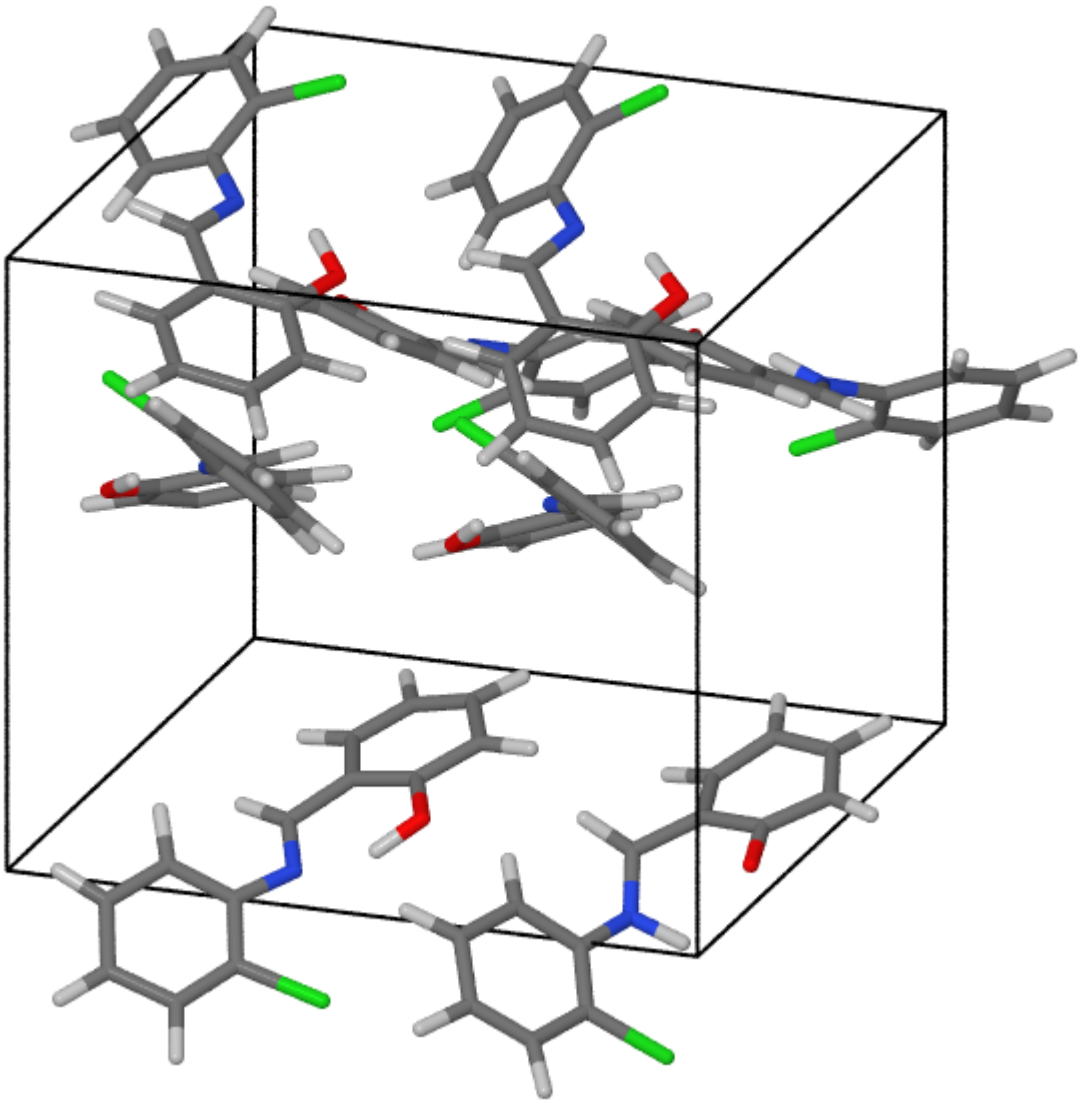
$t = 260$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 2.185$ eV



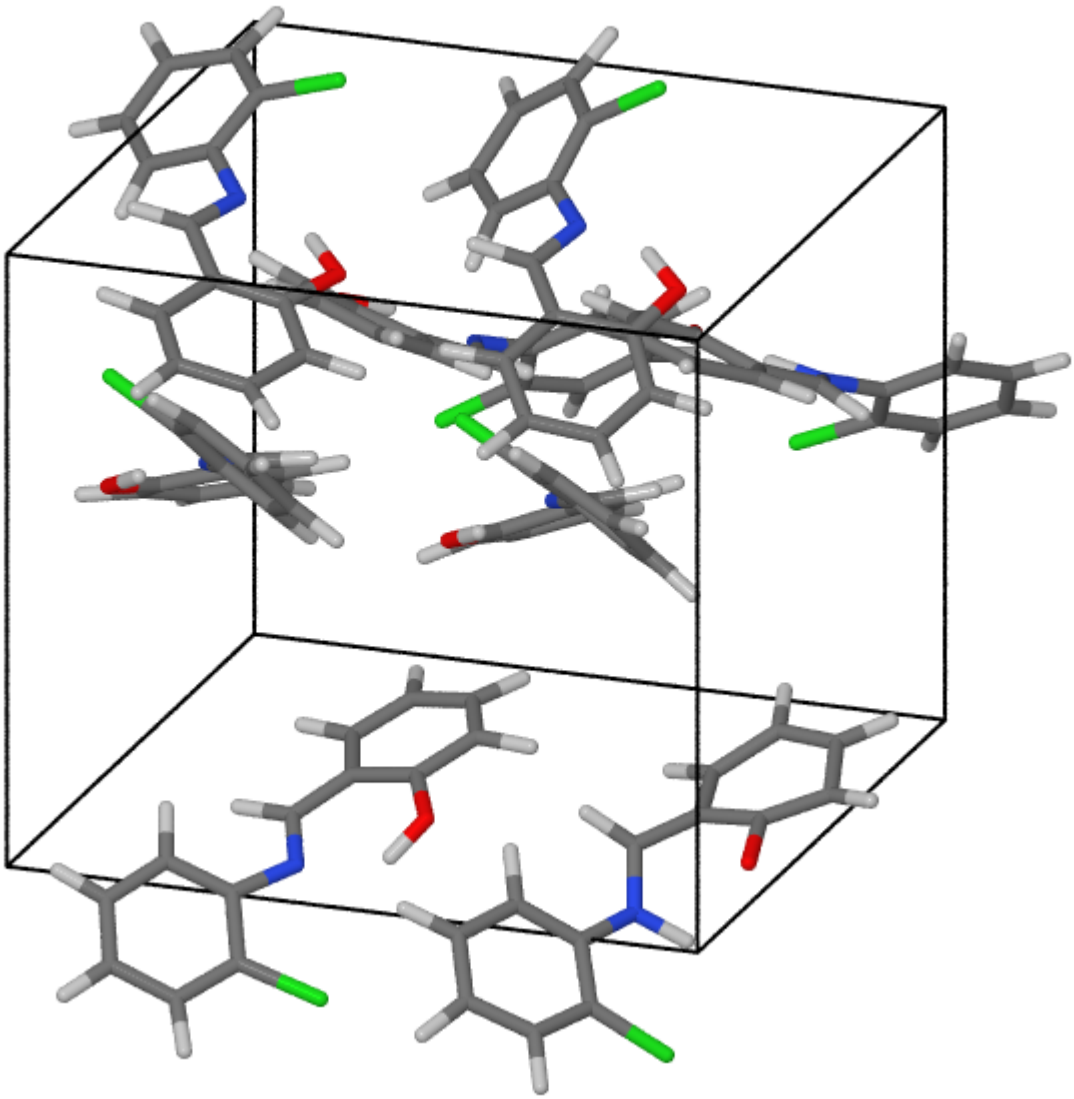
$t = 270$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 1.496$ eV



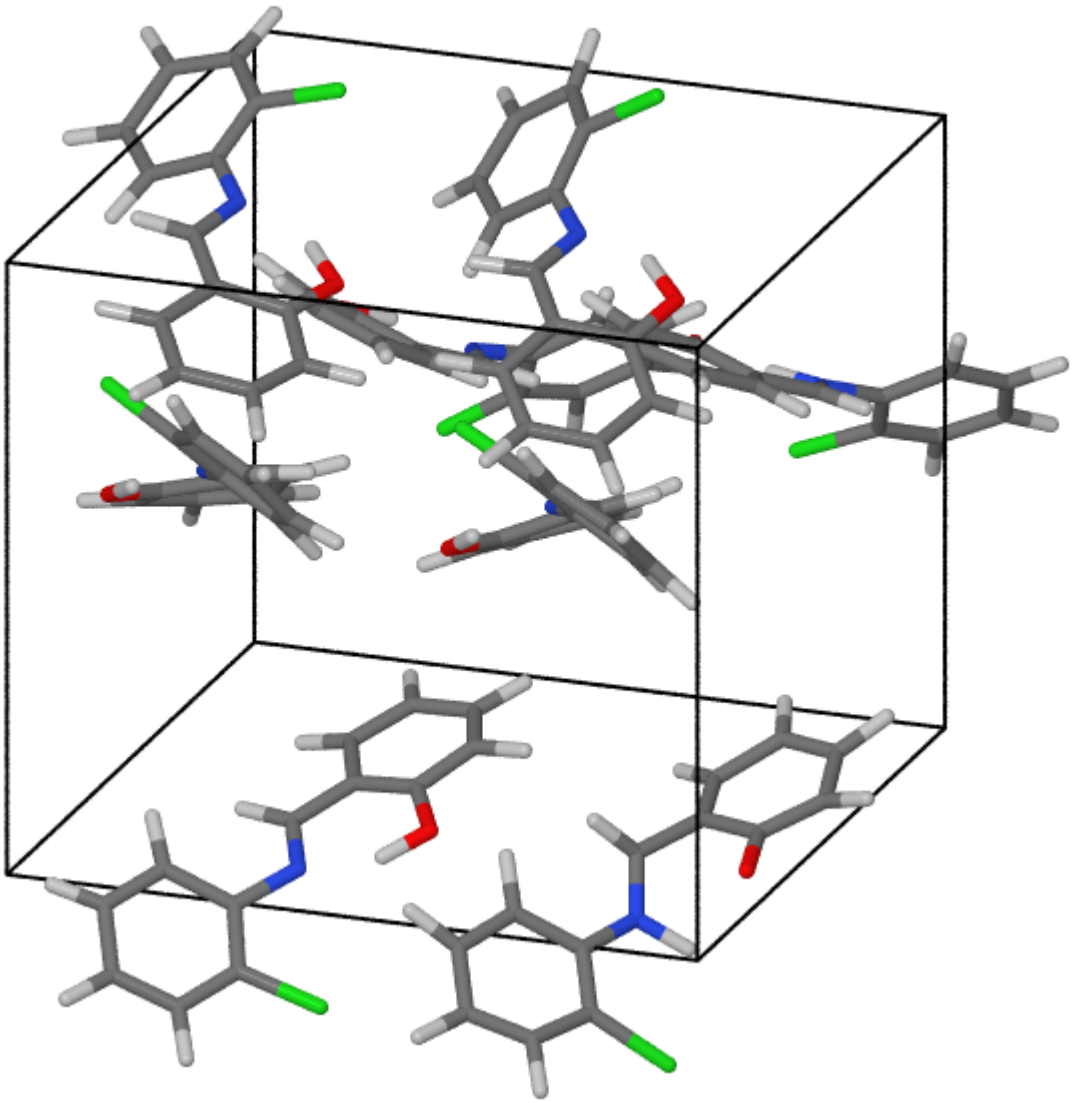
$t = 280$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 1.752$ eV



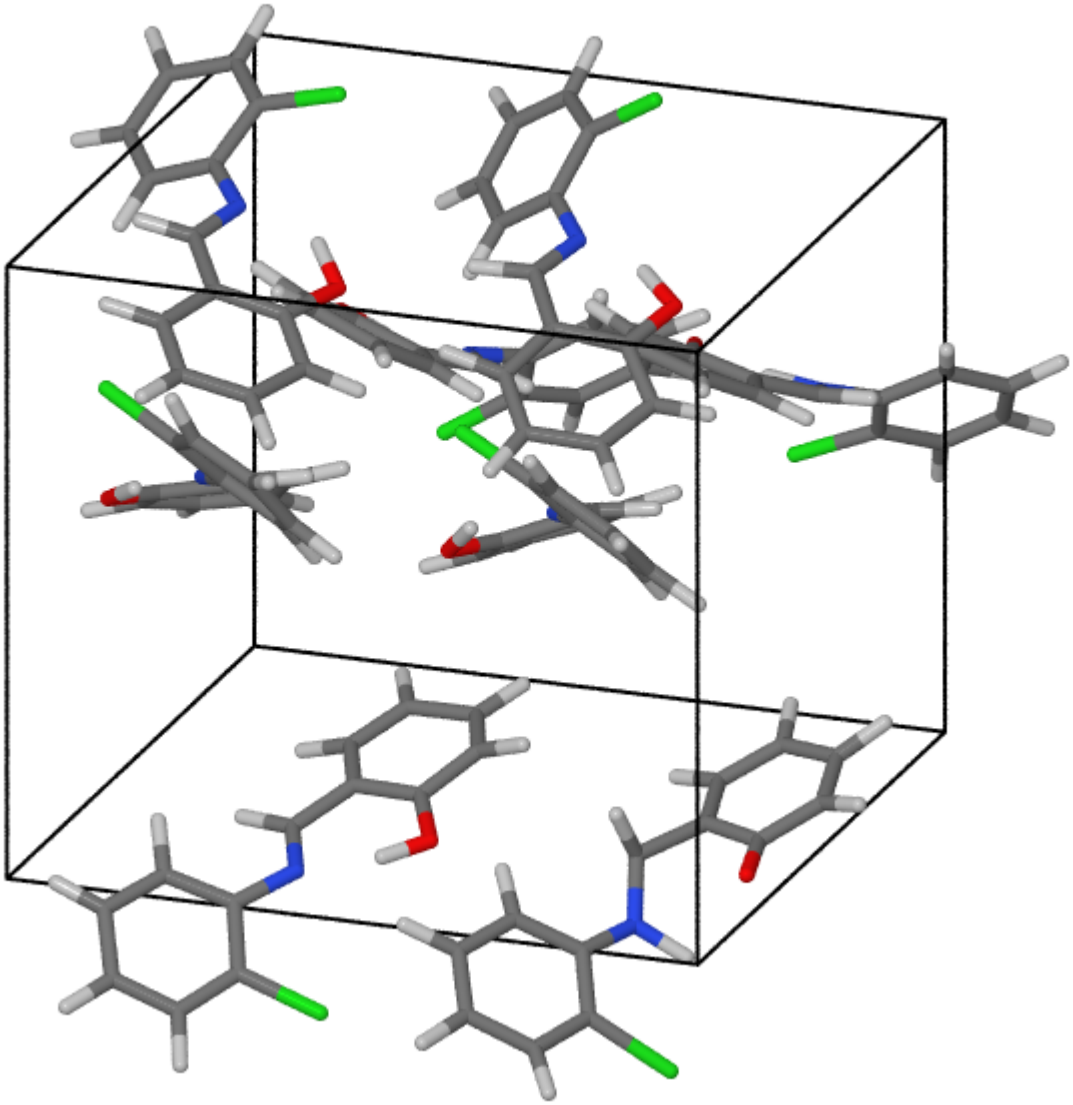
$t = 290$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 1.036$ eV



$t = 300$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 0.768$ eV



$t = 310$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 0.264$ eV



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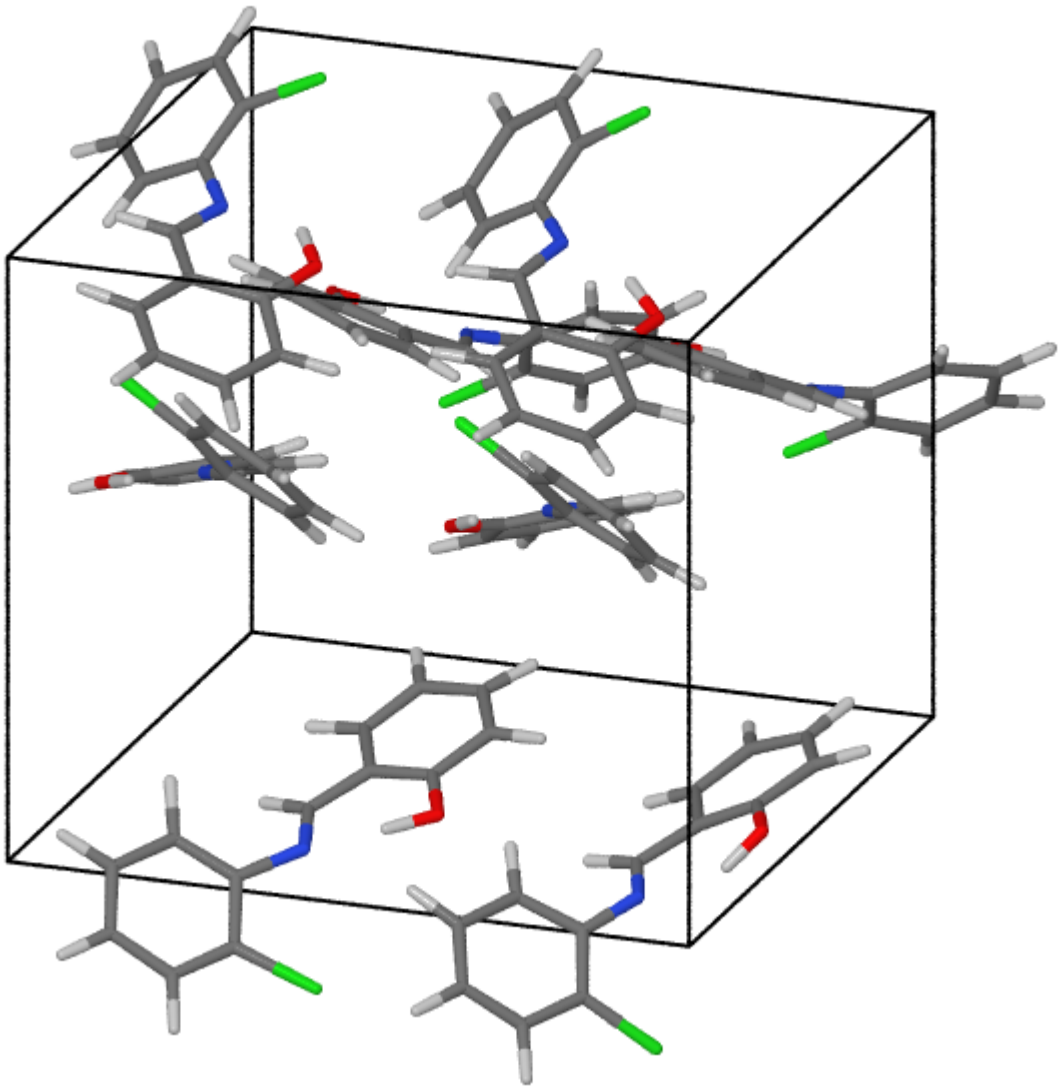
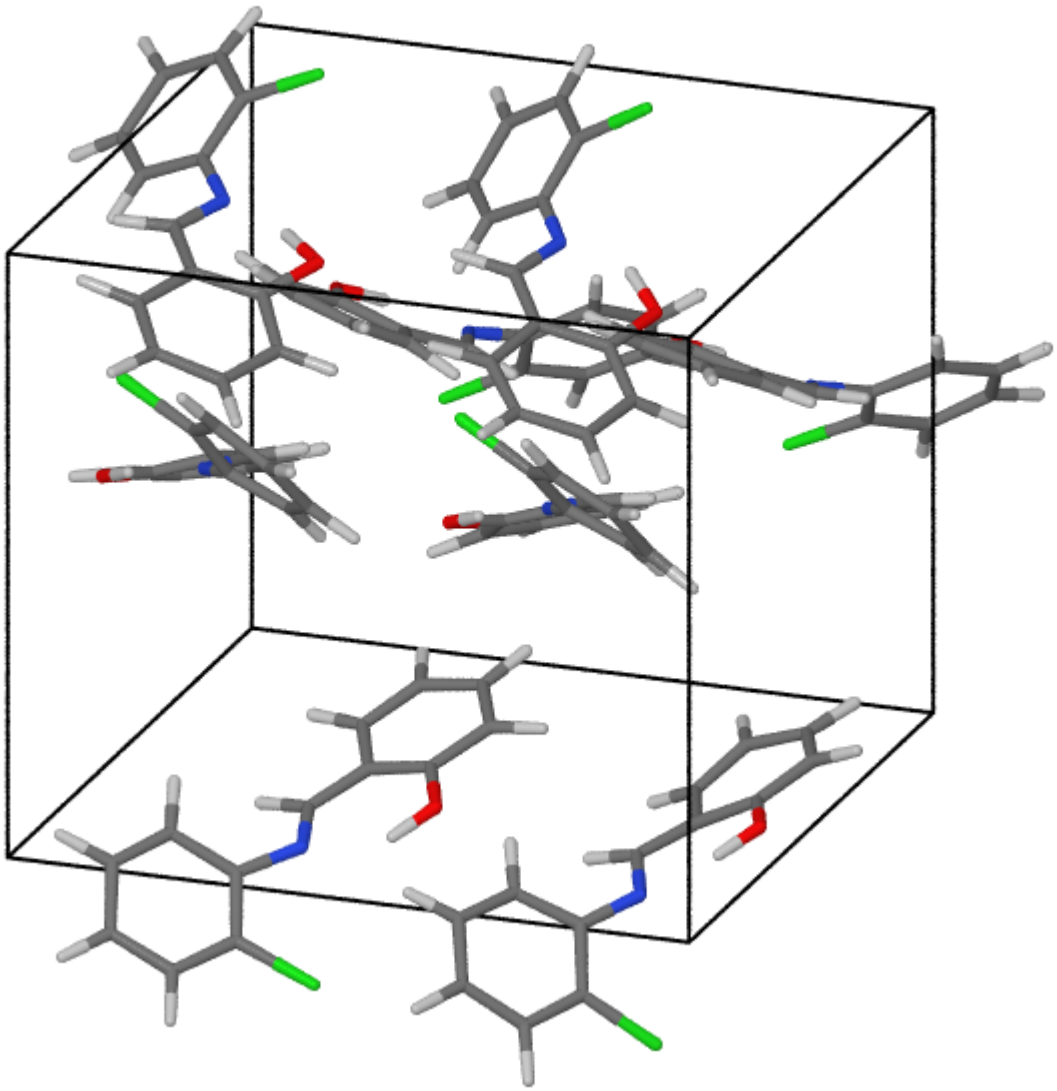
Snapshots from Trajectory 3

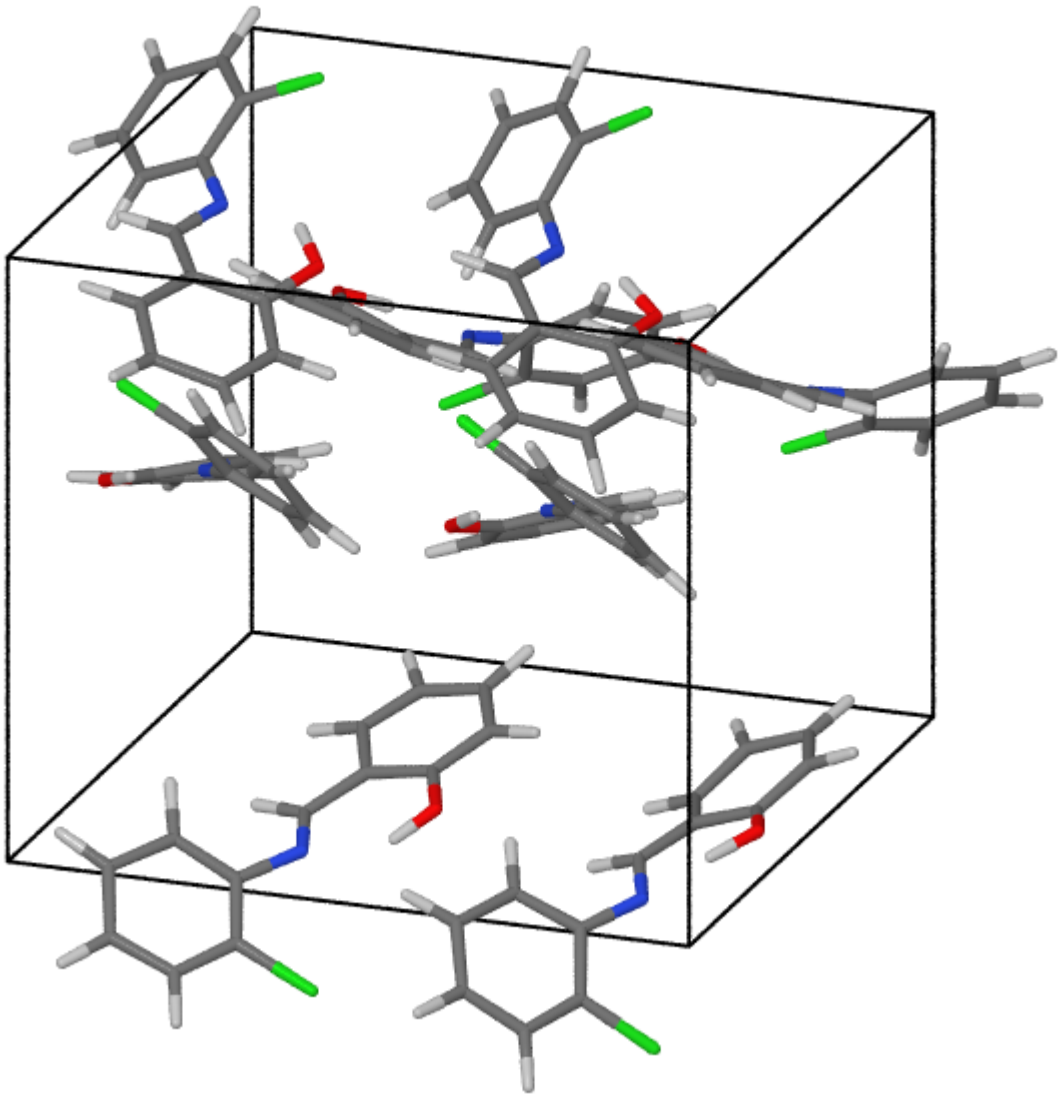
$t = 0$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 3.699$ eV



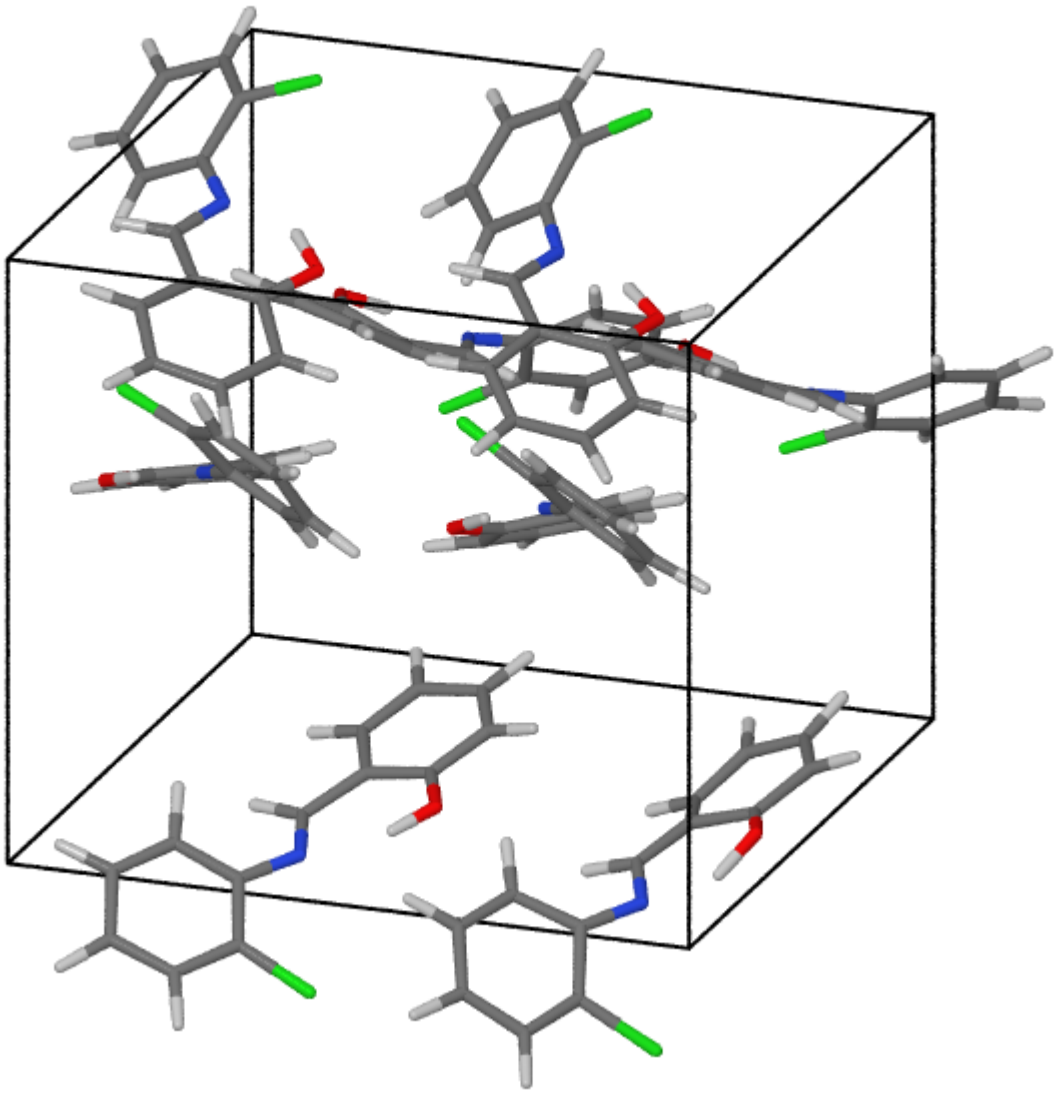
$t = 10$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 2.986$ eV



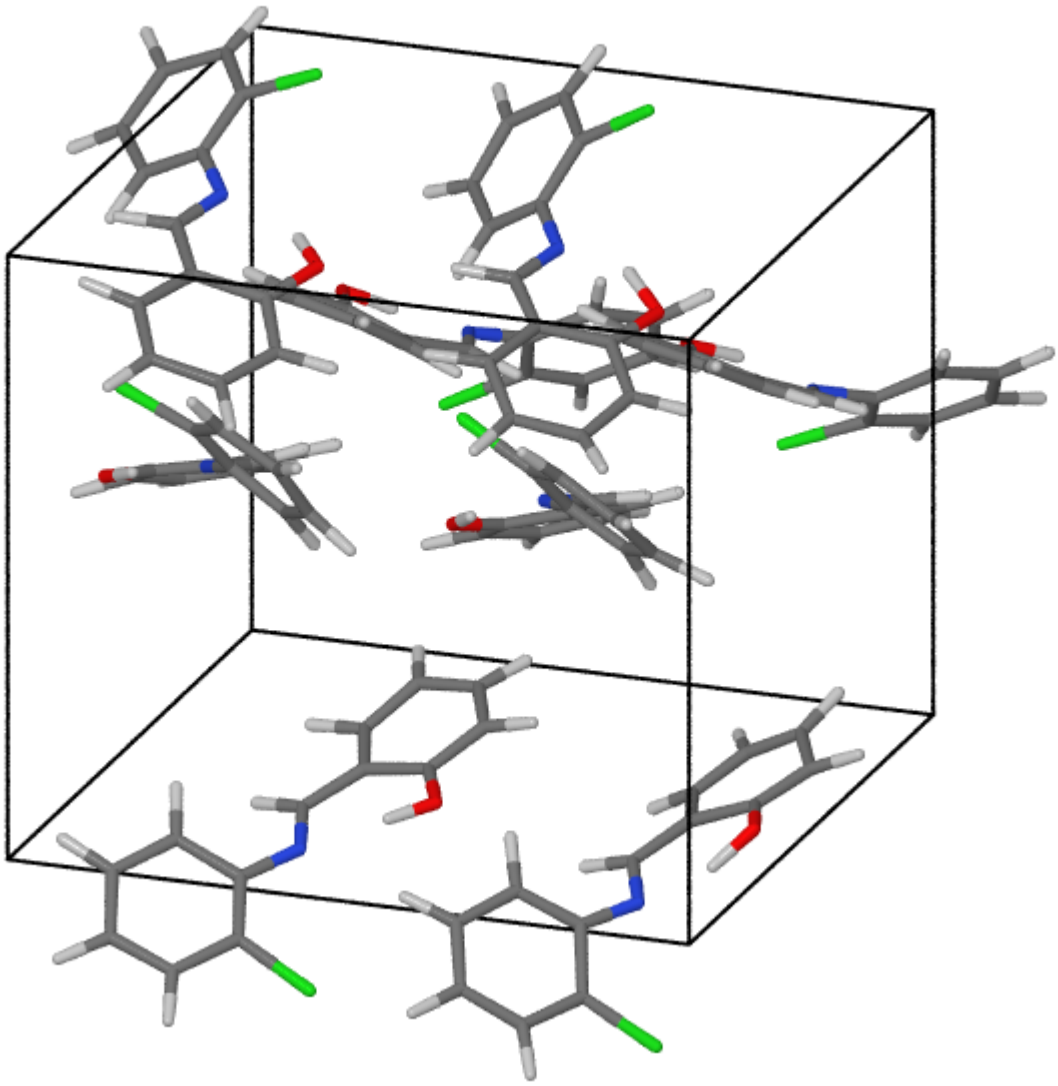
$t = 20$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 3.096$ eV



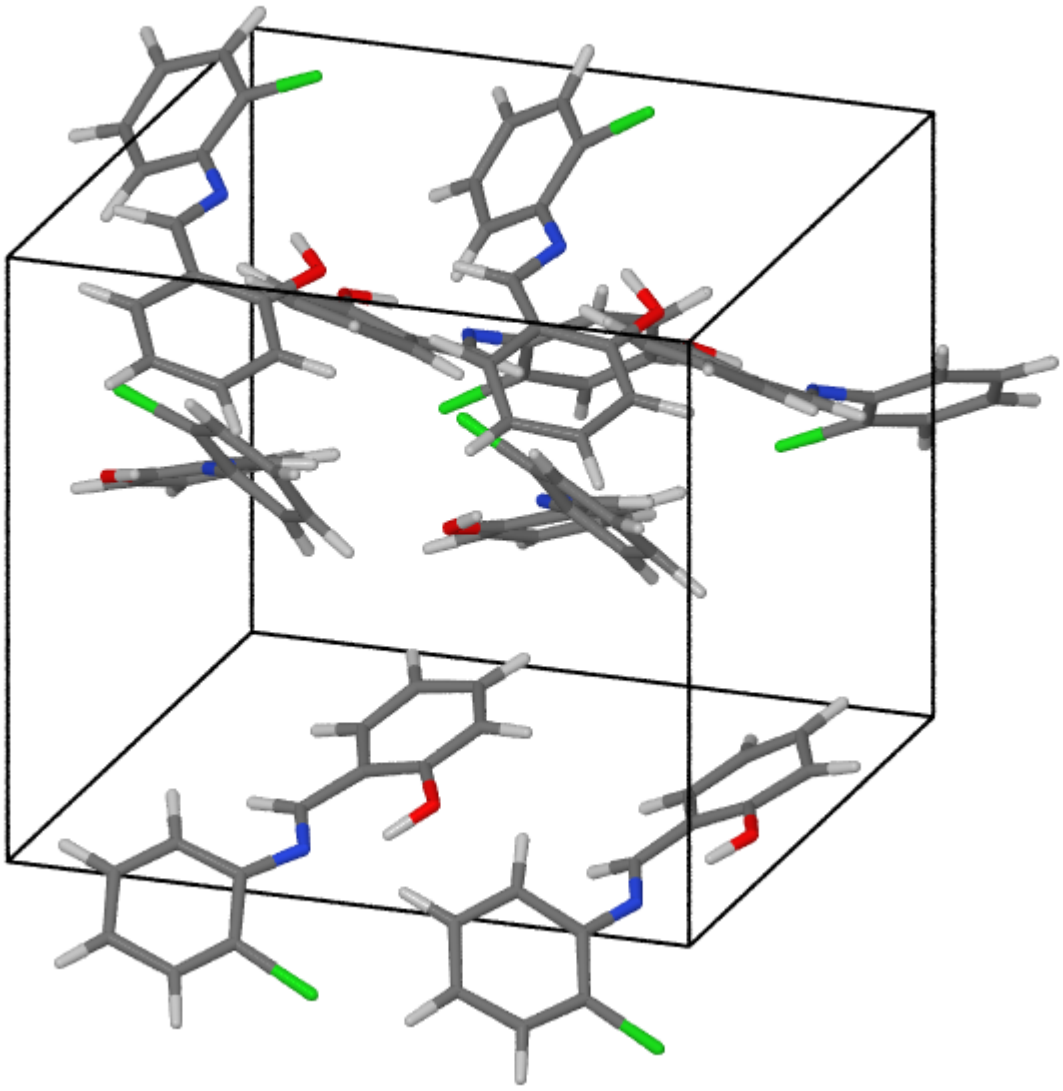
$t = 30$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 2.960$ eV



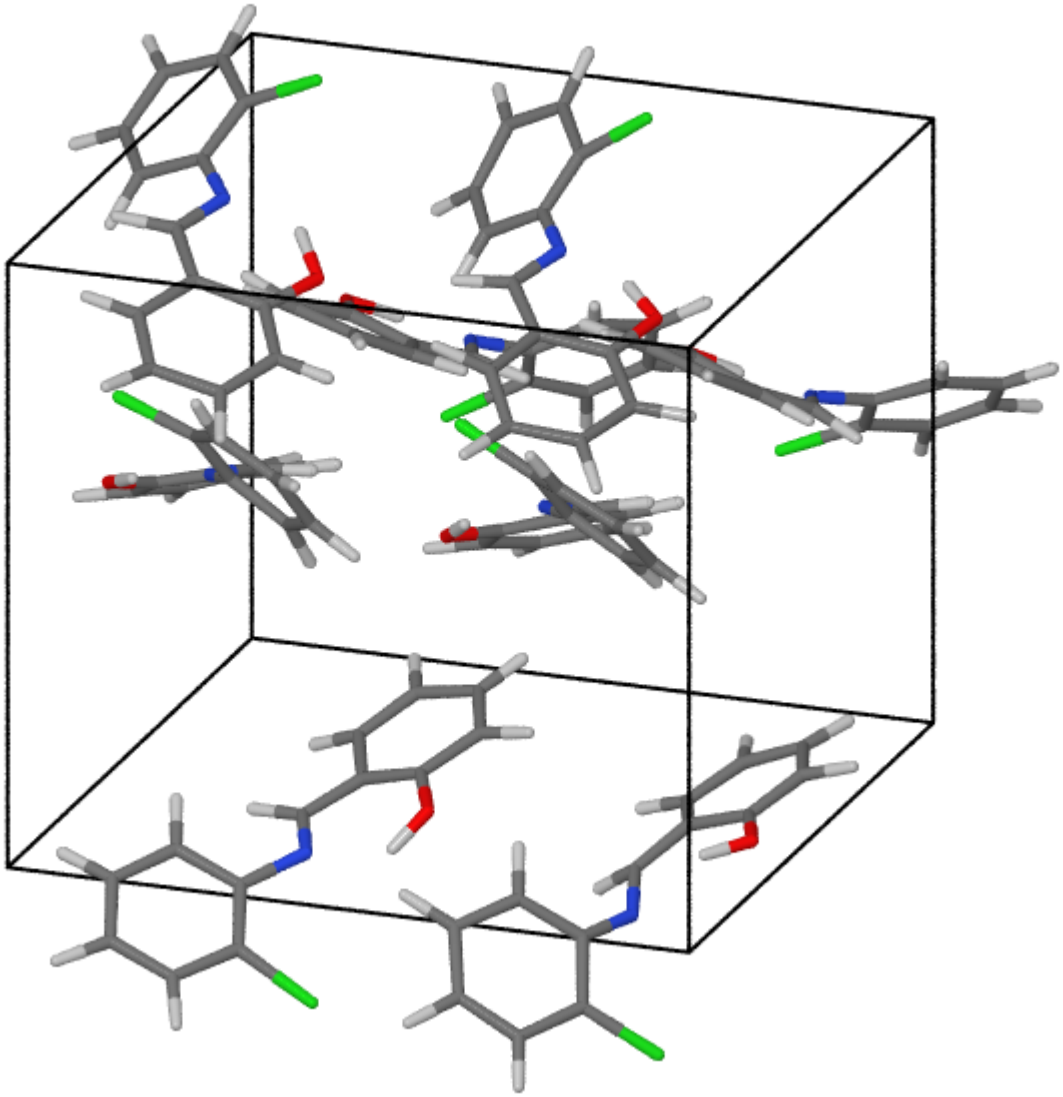
$t = 40$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 2.880$ eV



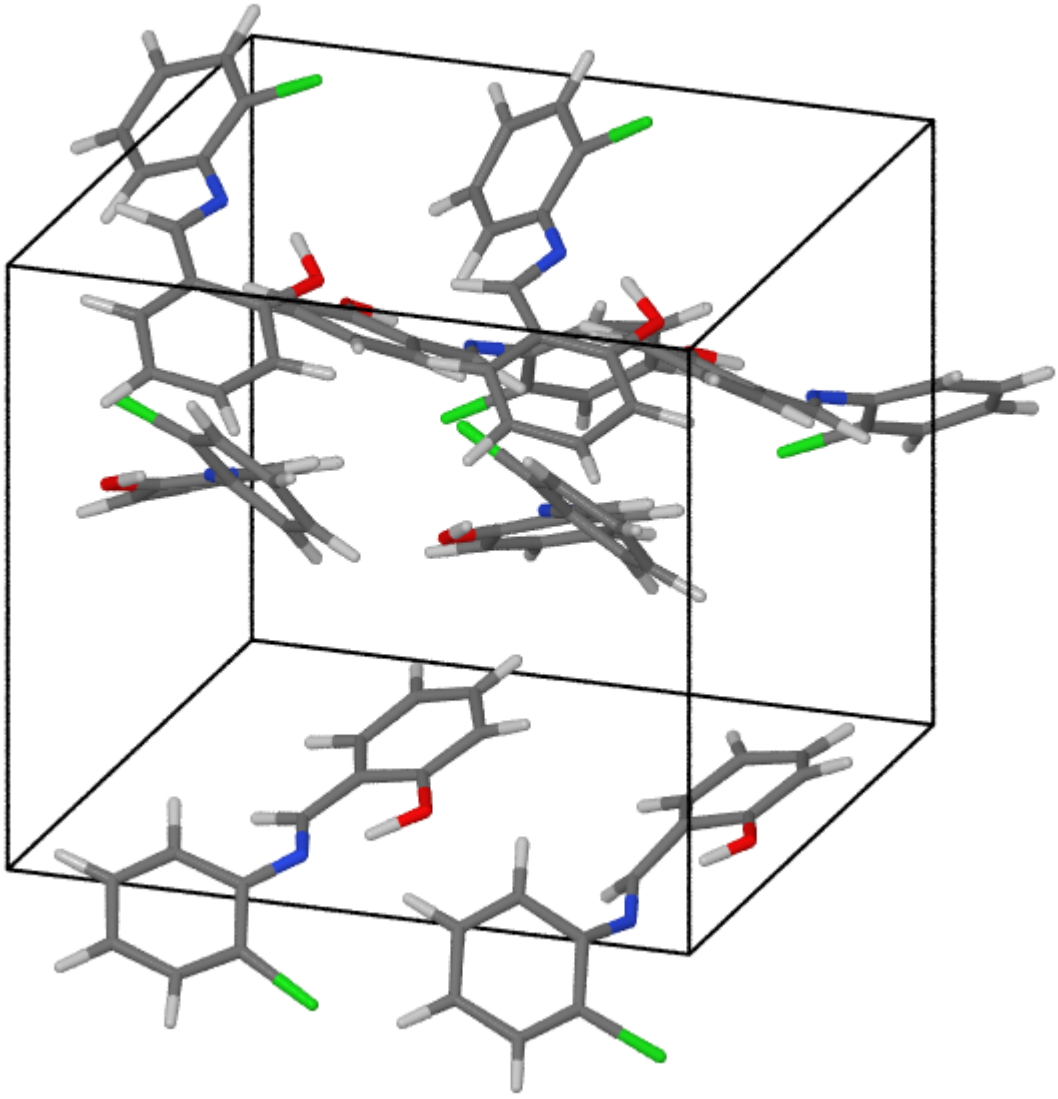
$t = 50\ \mathrm{fs} \quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 2.854\ \mathrm{eV}$



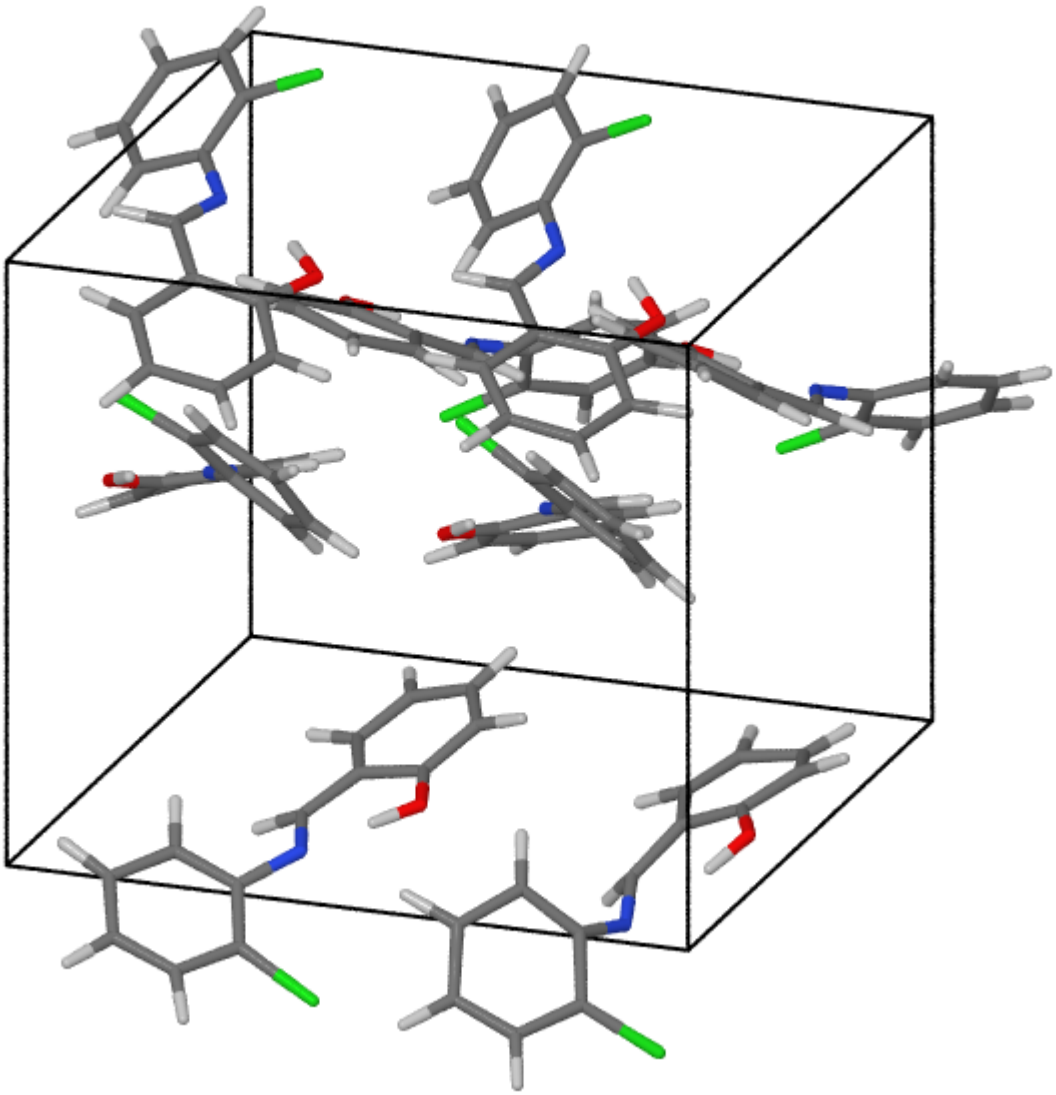
$t = 60$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 1.675$ eV



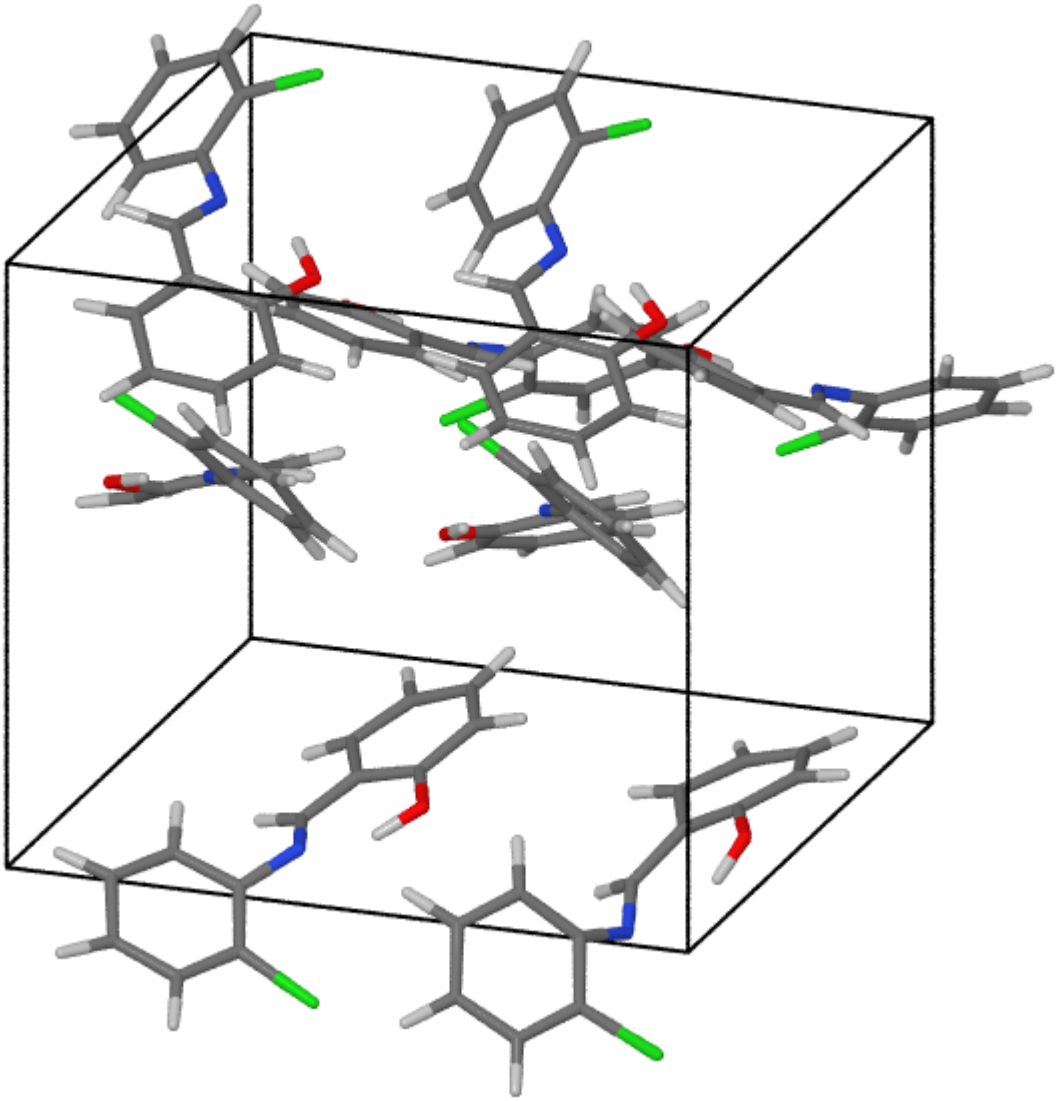
$t = 70$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 1.586$ eV



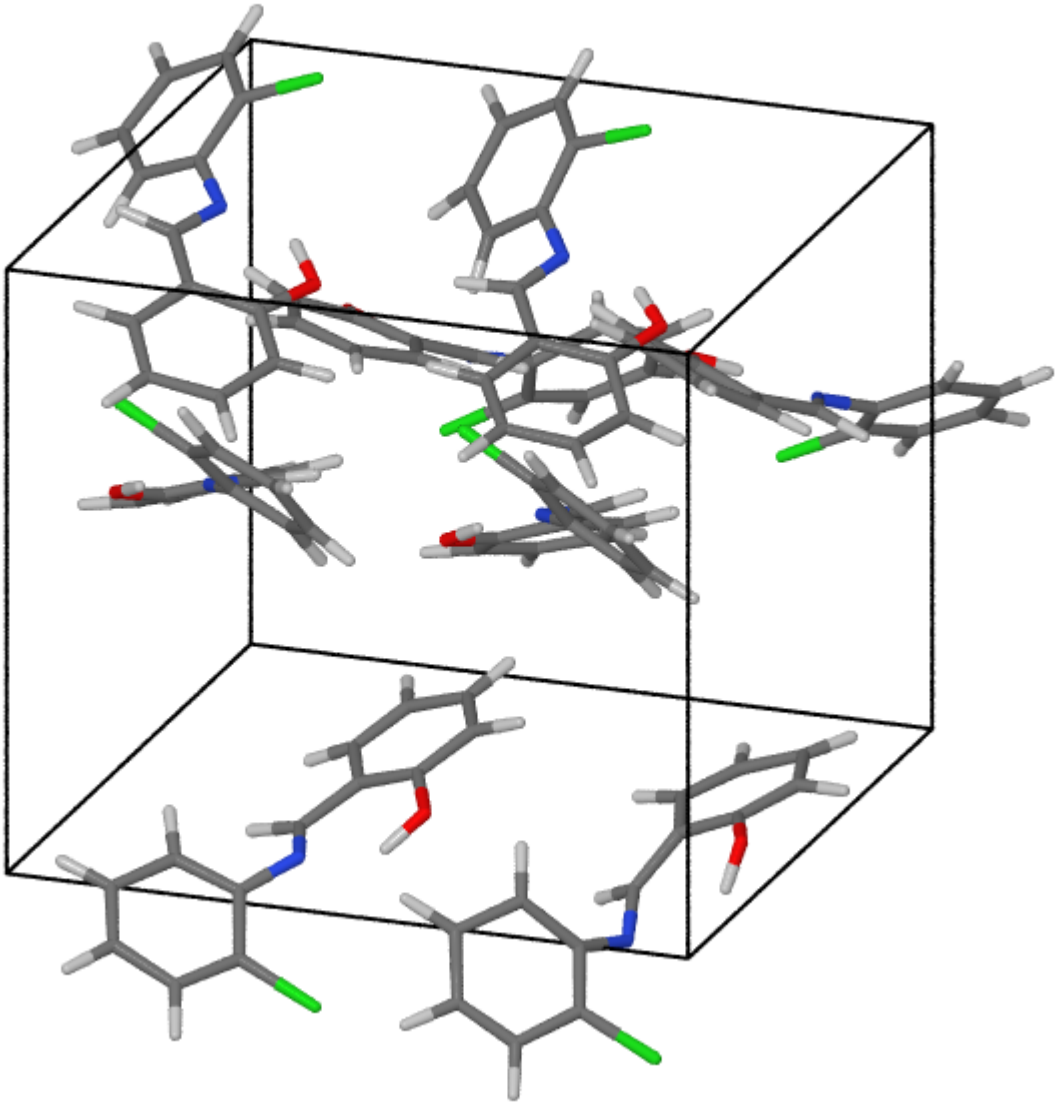
$t = 80$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 0.399$ eV



$t = 90$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 0.502$ eV



$t = 100$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 0.325$ eV



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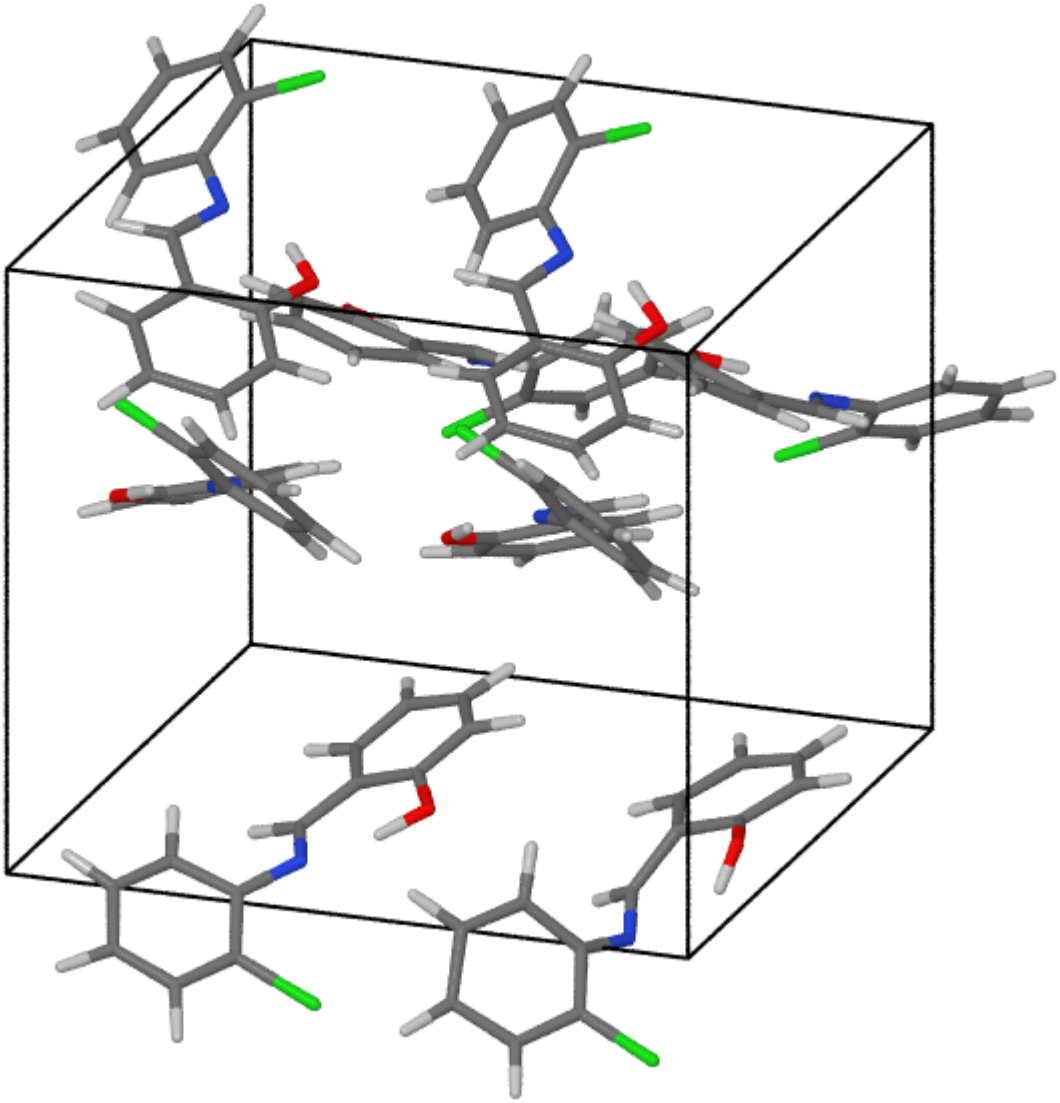
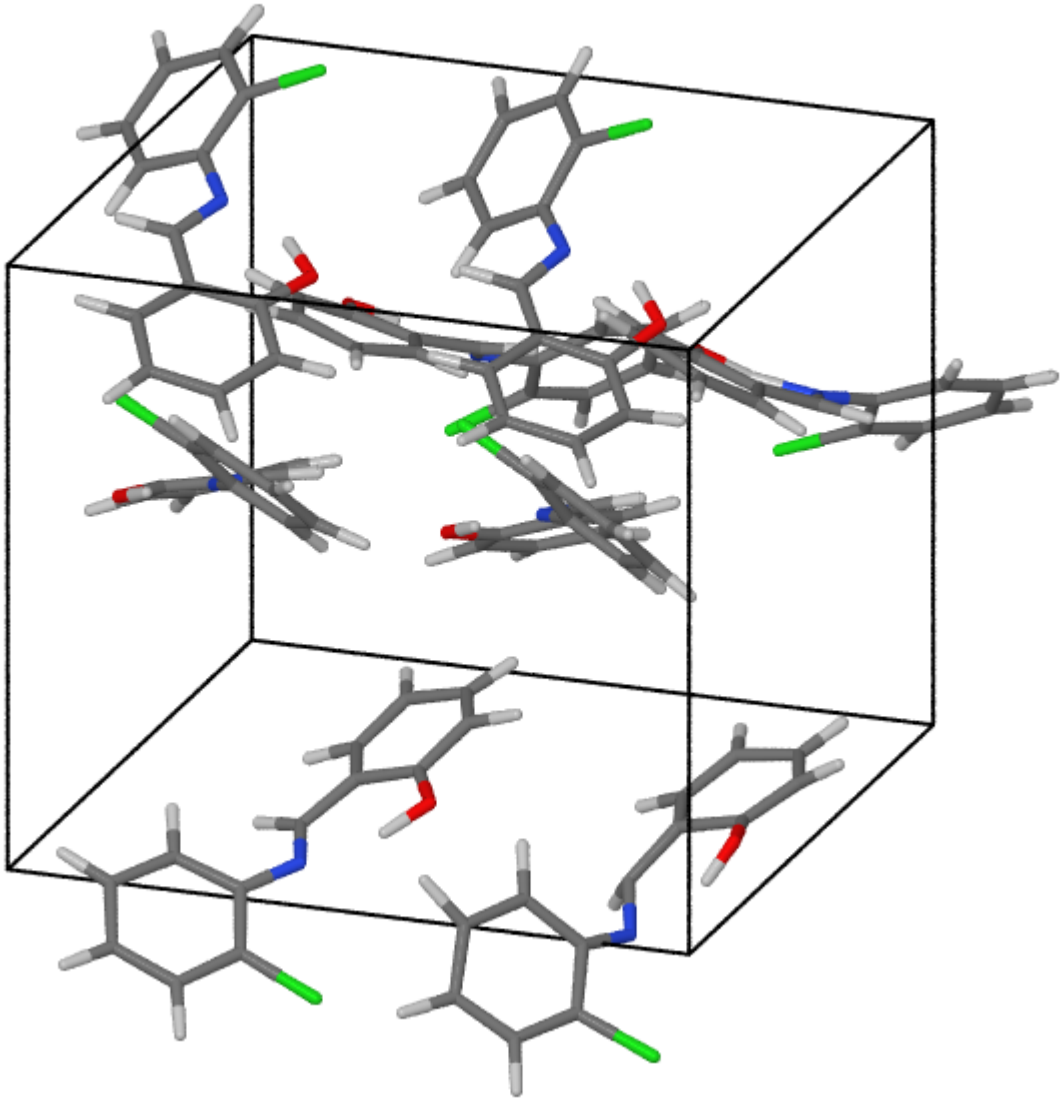


$t = 120$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 0.073$ eV



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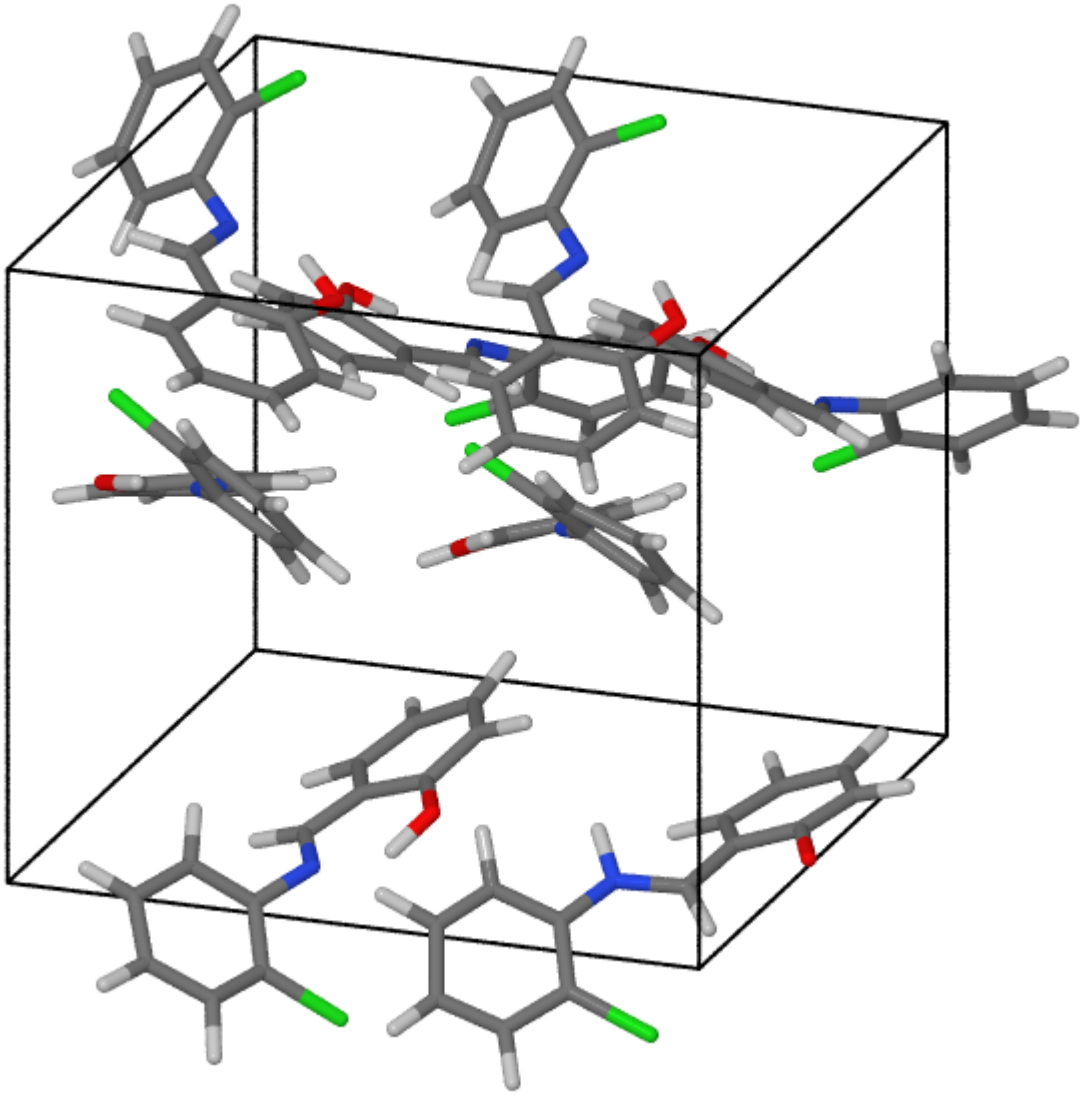
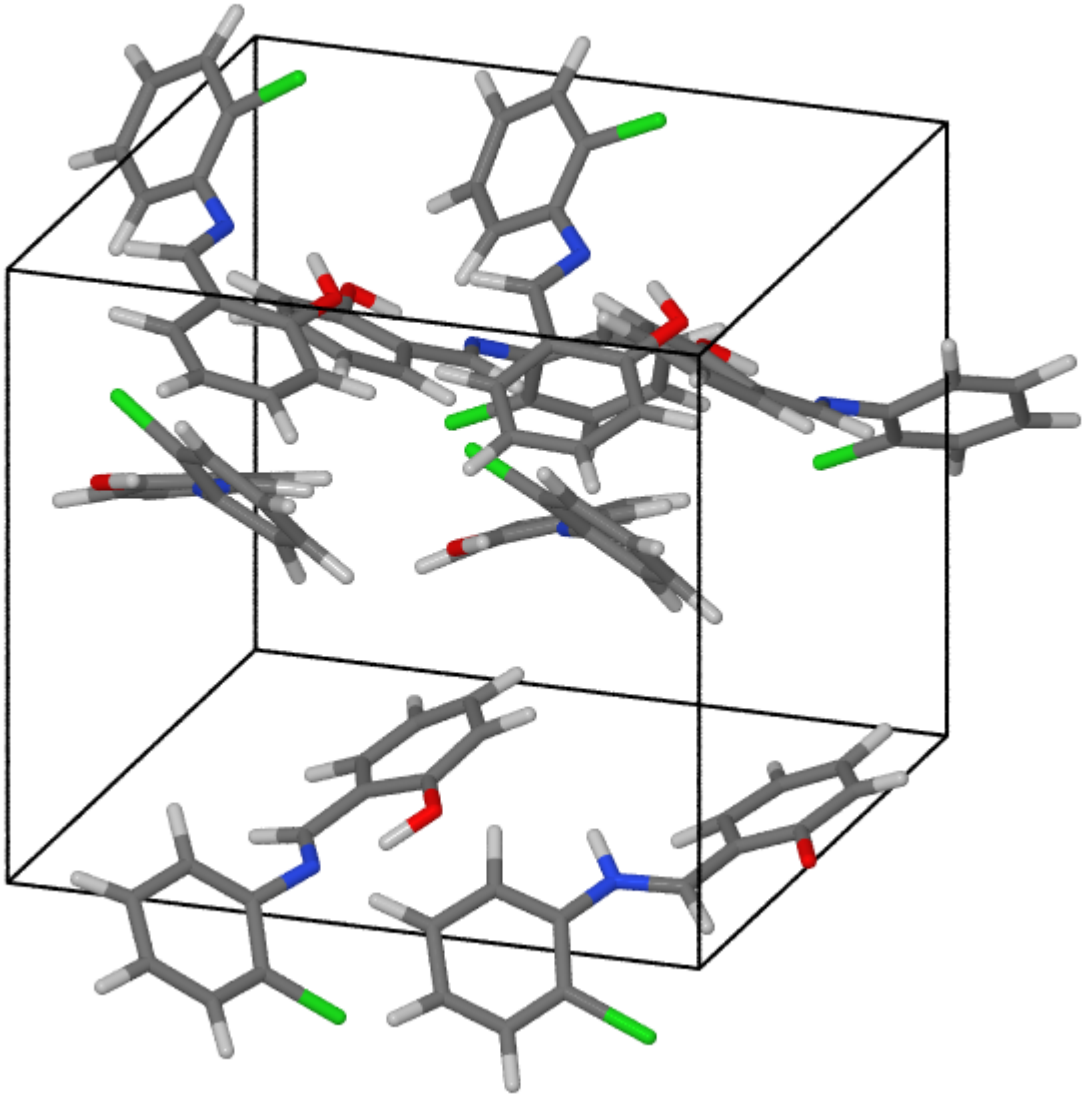
Snapshots from Trajectory 3′

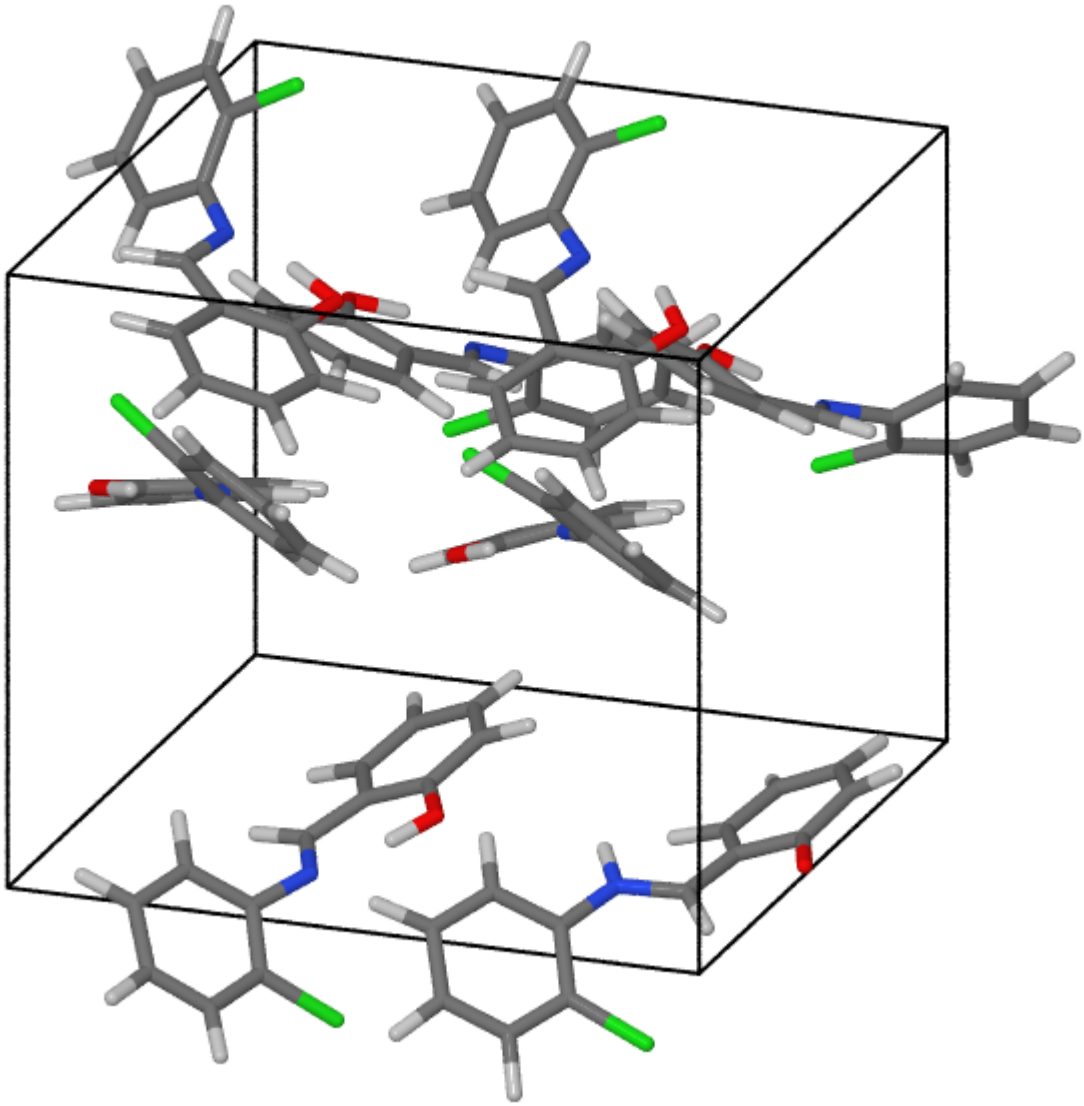
$t = 440$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 1.987$ eV



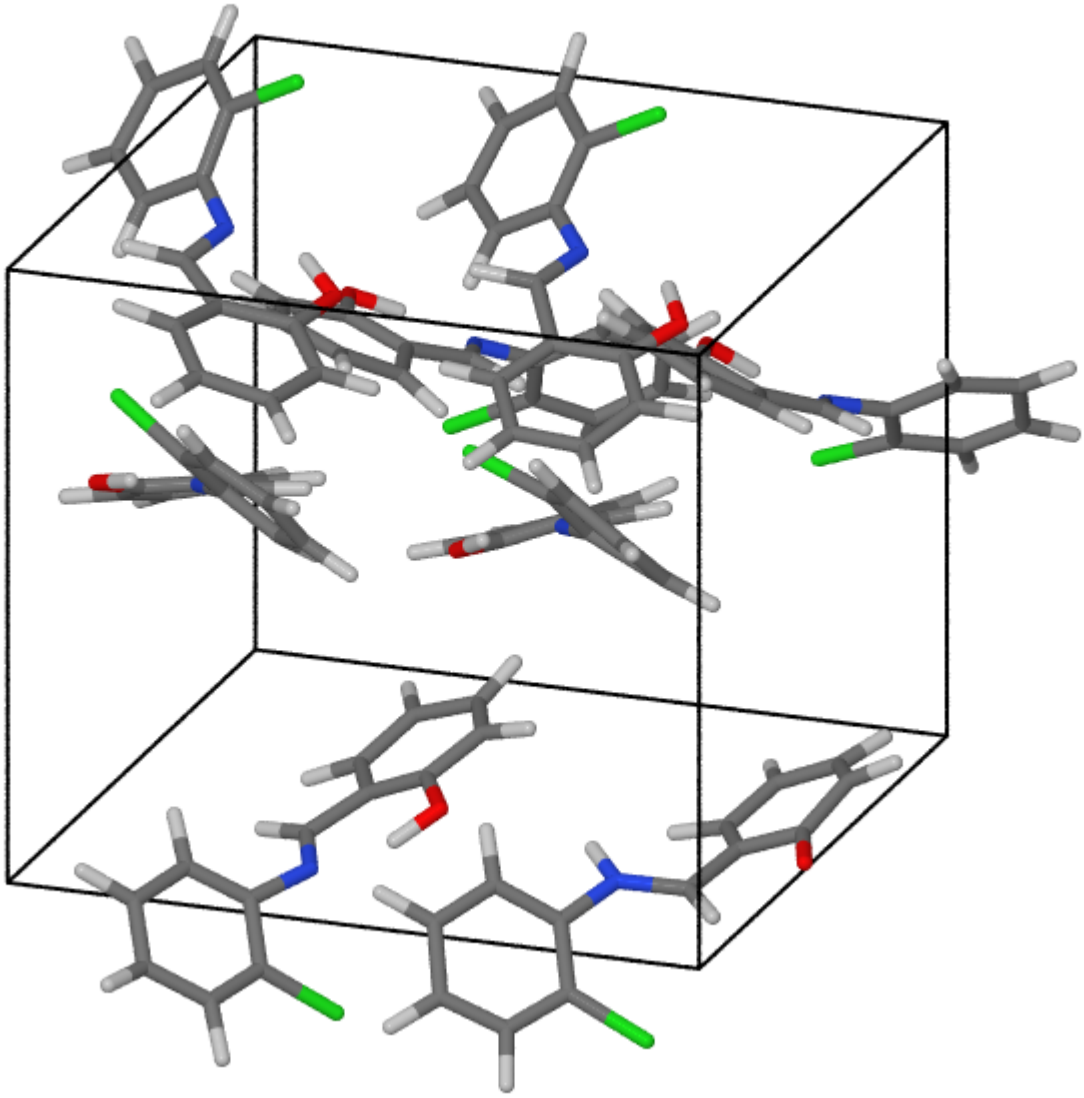
$t = 450$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 1.516$ eV



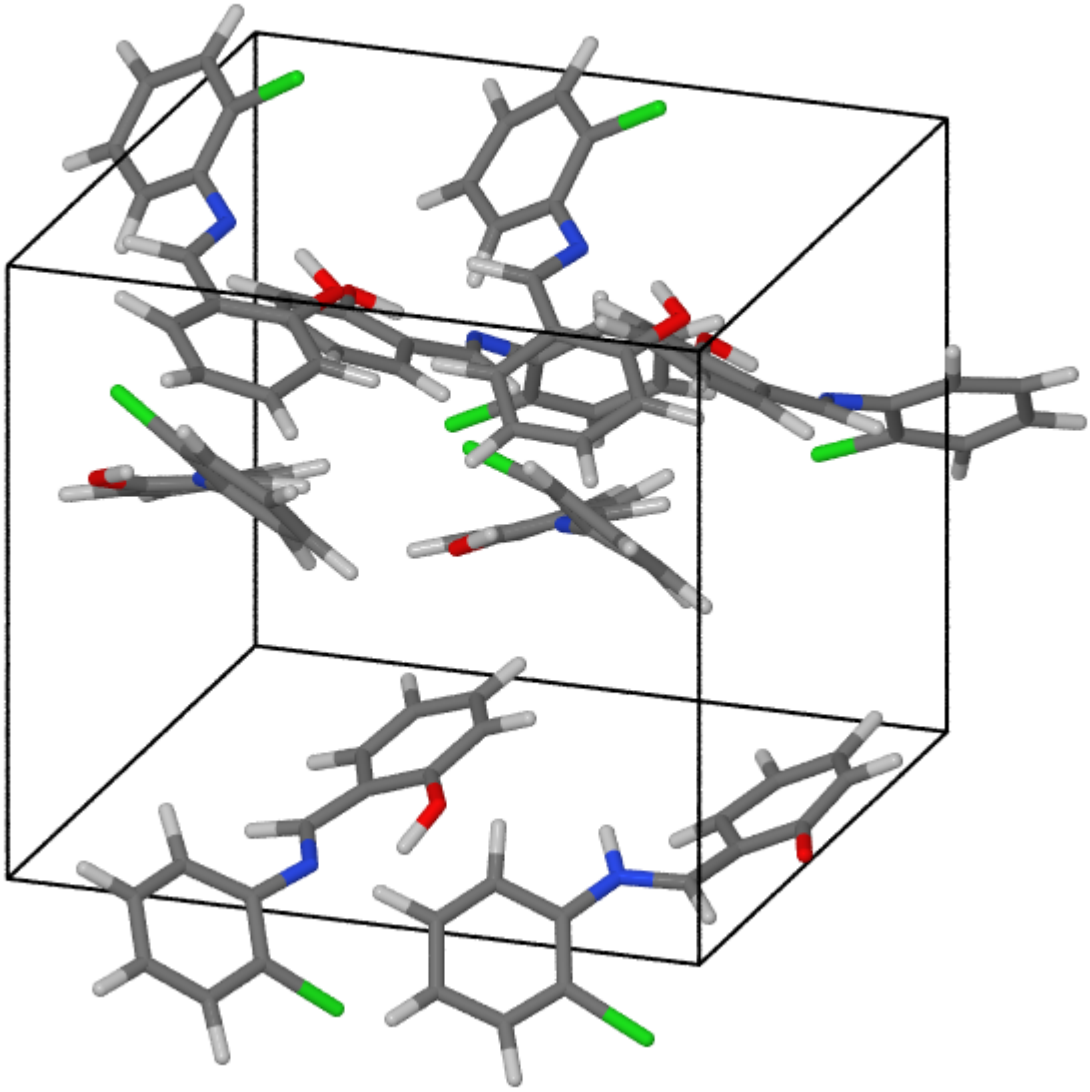
$t = 460\ \mathrm{fs} \quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 1.617\ \mathrm{eV}$



$t = 470$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 1.421$ eV



$t = 480$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 1.335$ eV



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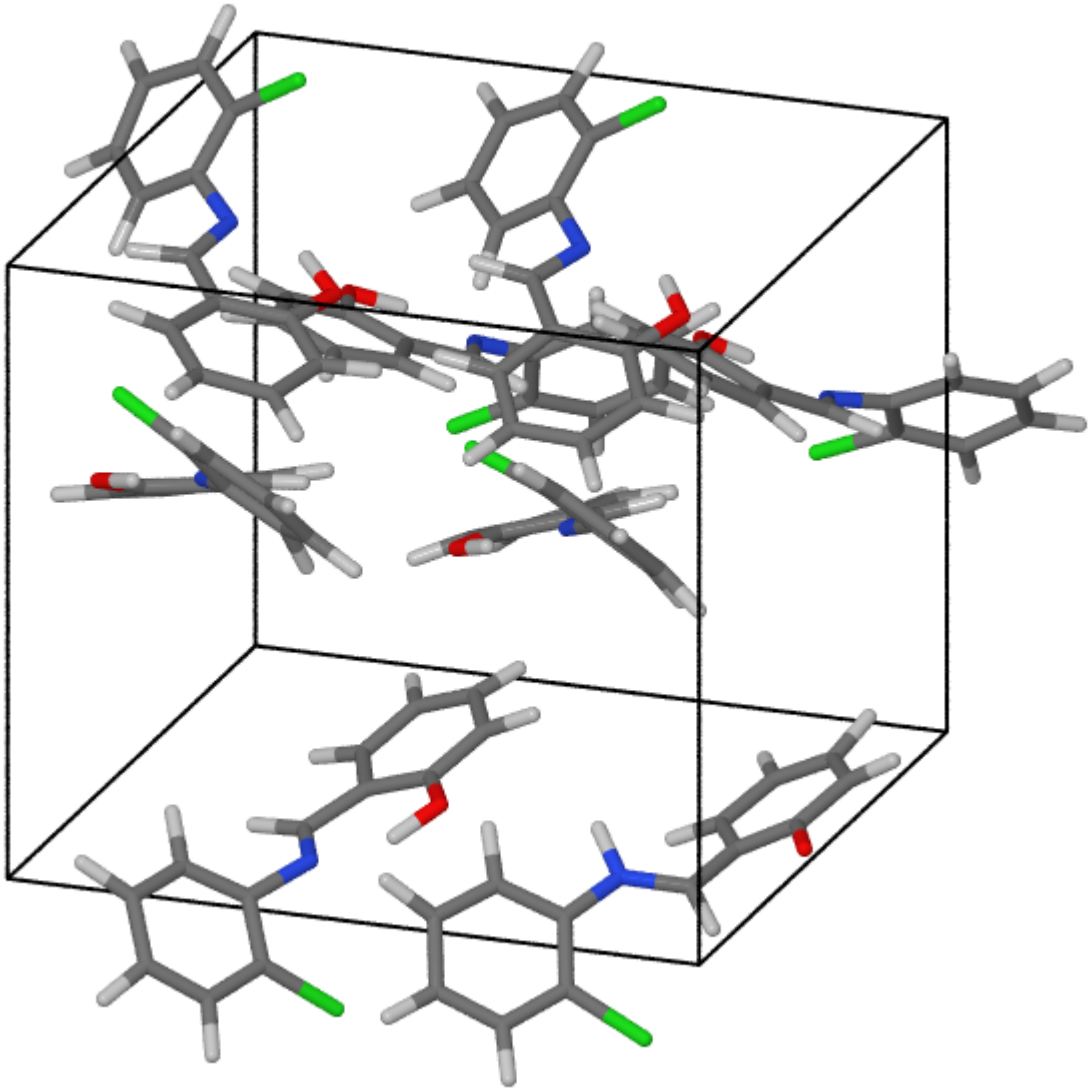
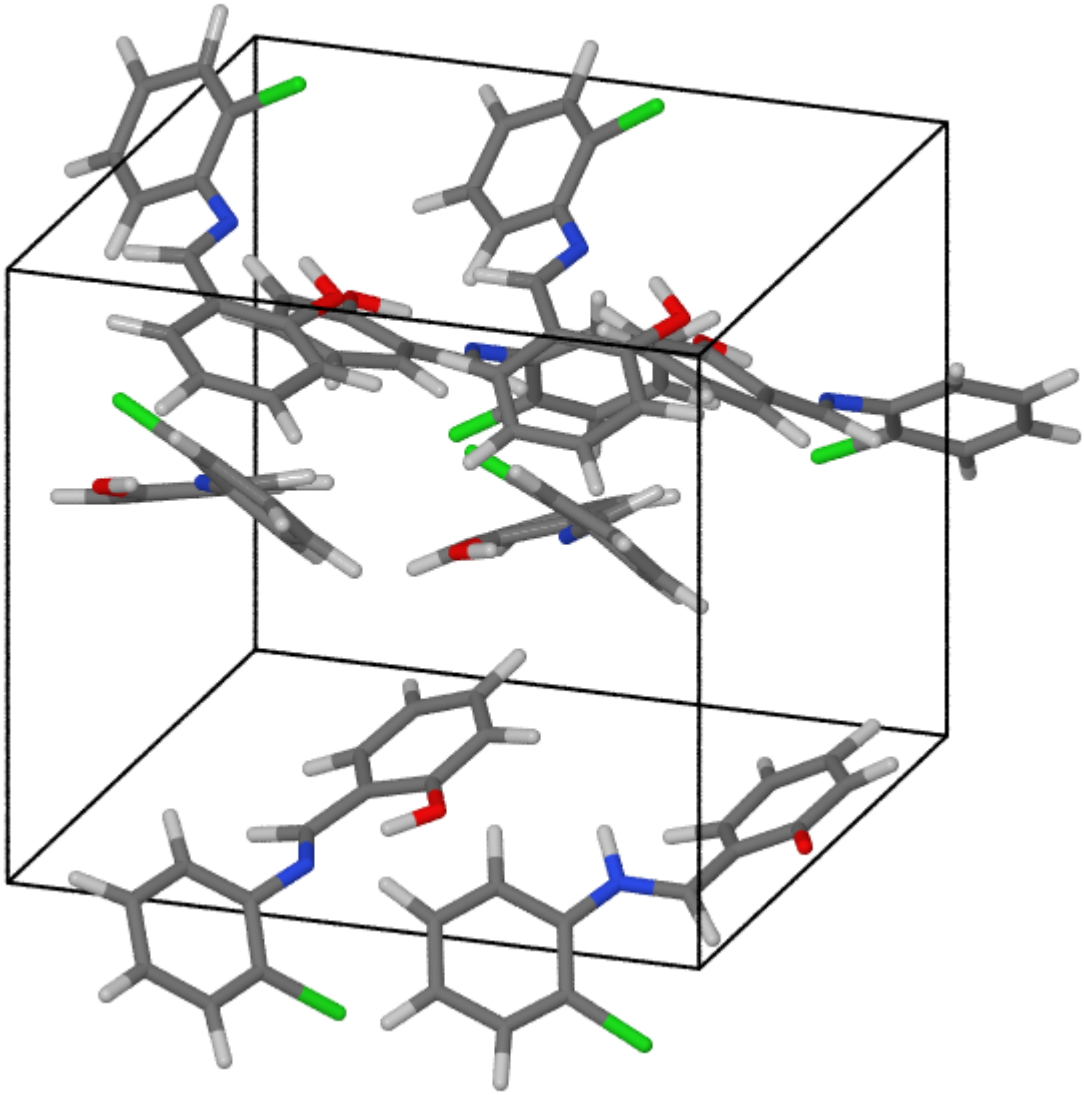
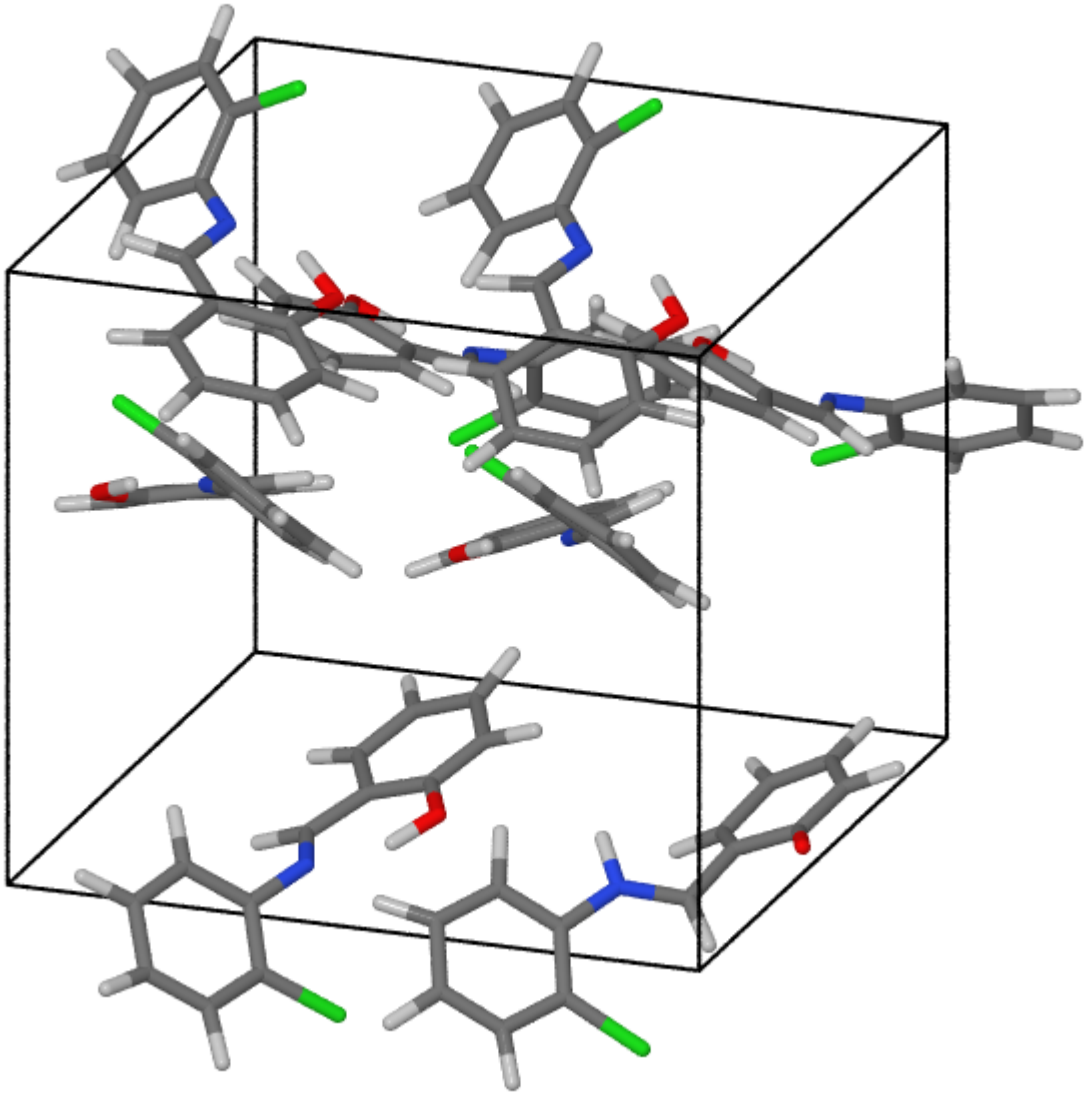


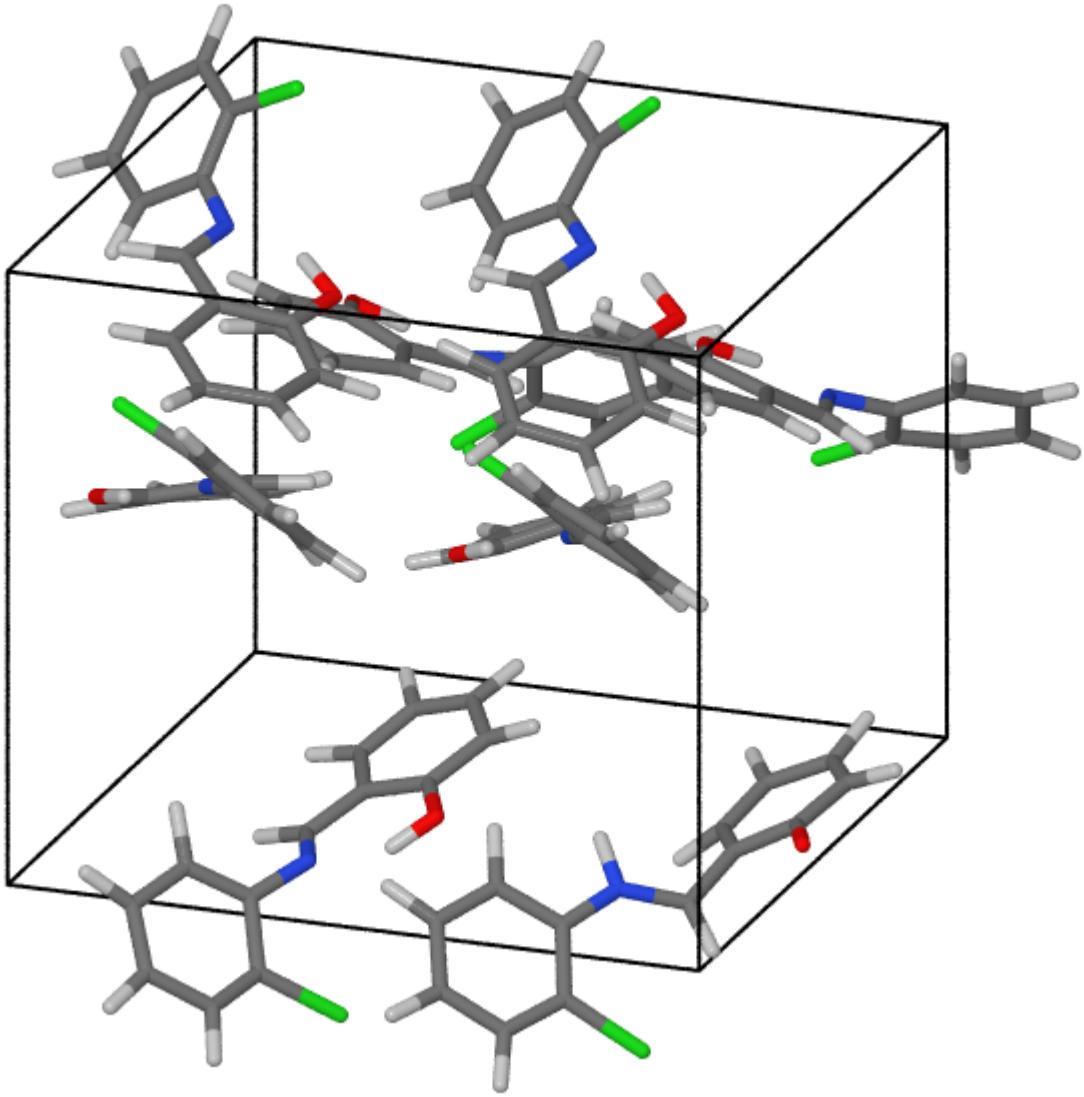
$t = 500\ \mathrm{fs} \quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 1.254\ \mathrm{eV}$



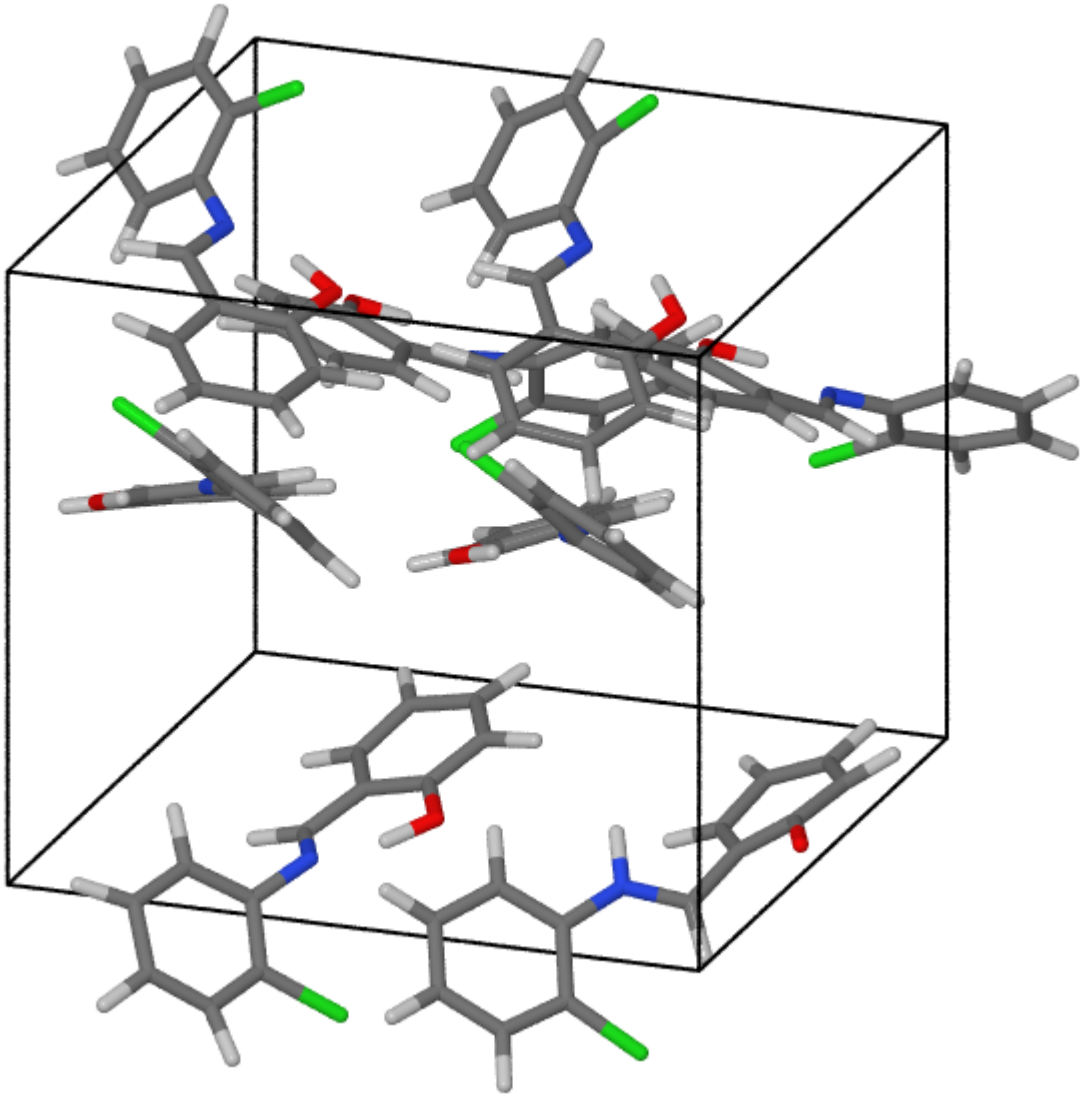
$t = 510$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 1.865$ eV



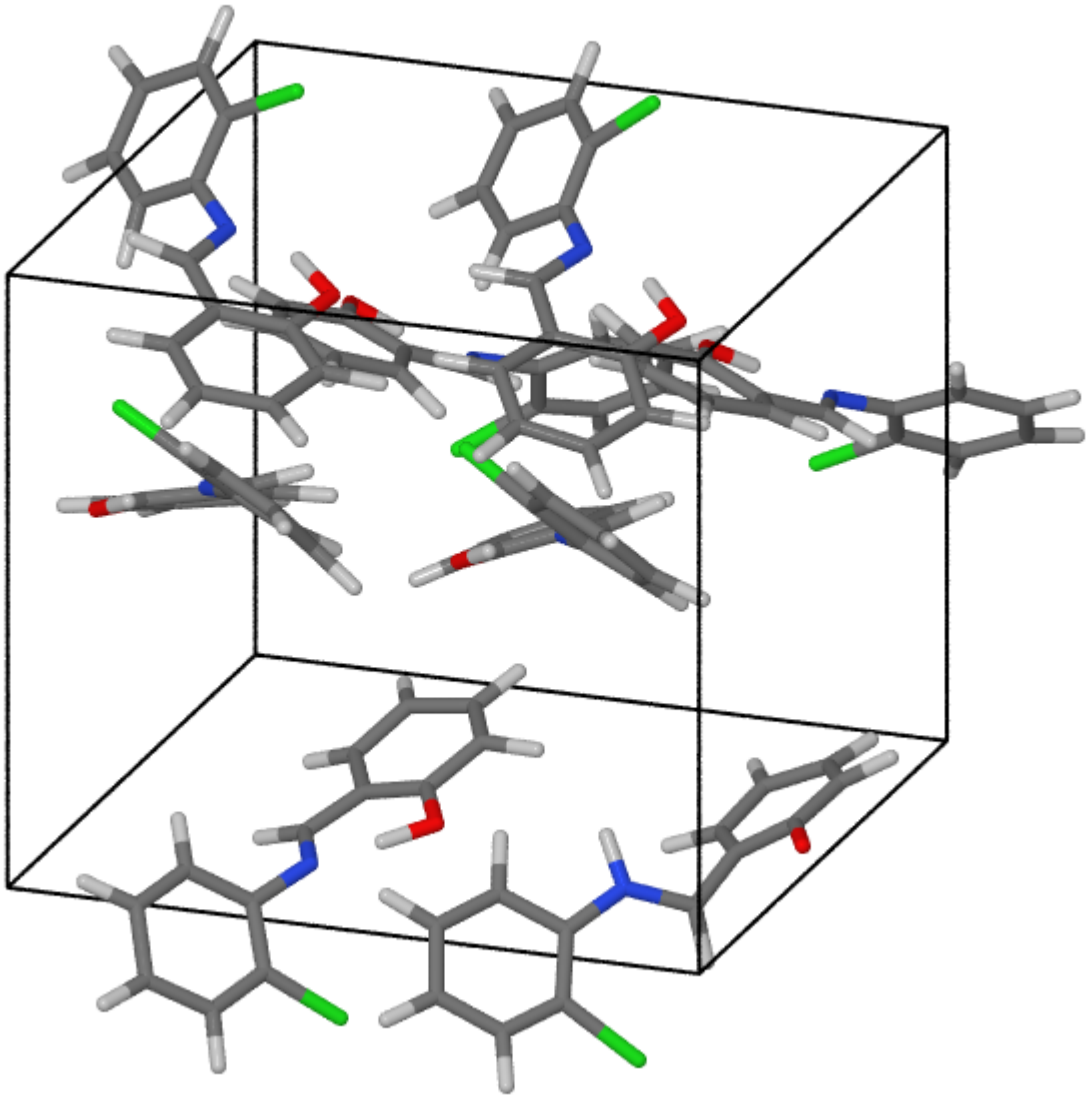
$t = 520\ \mathrm{fs} \quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 1.437\ \mathrm{eV}$



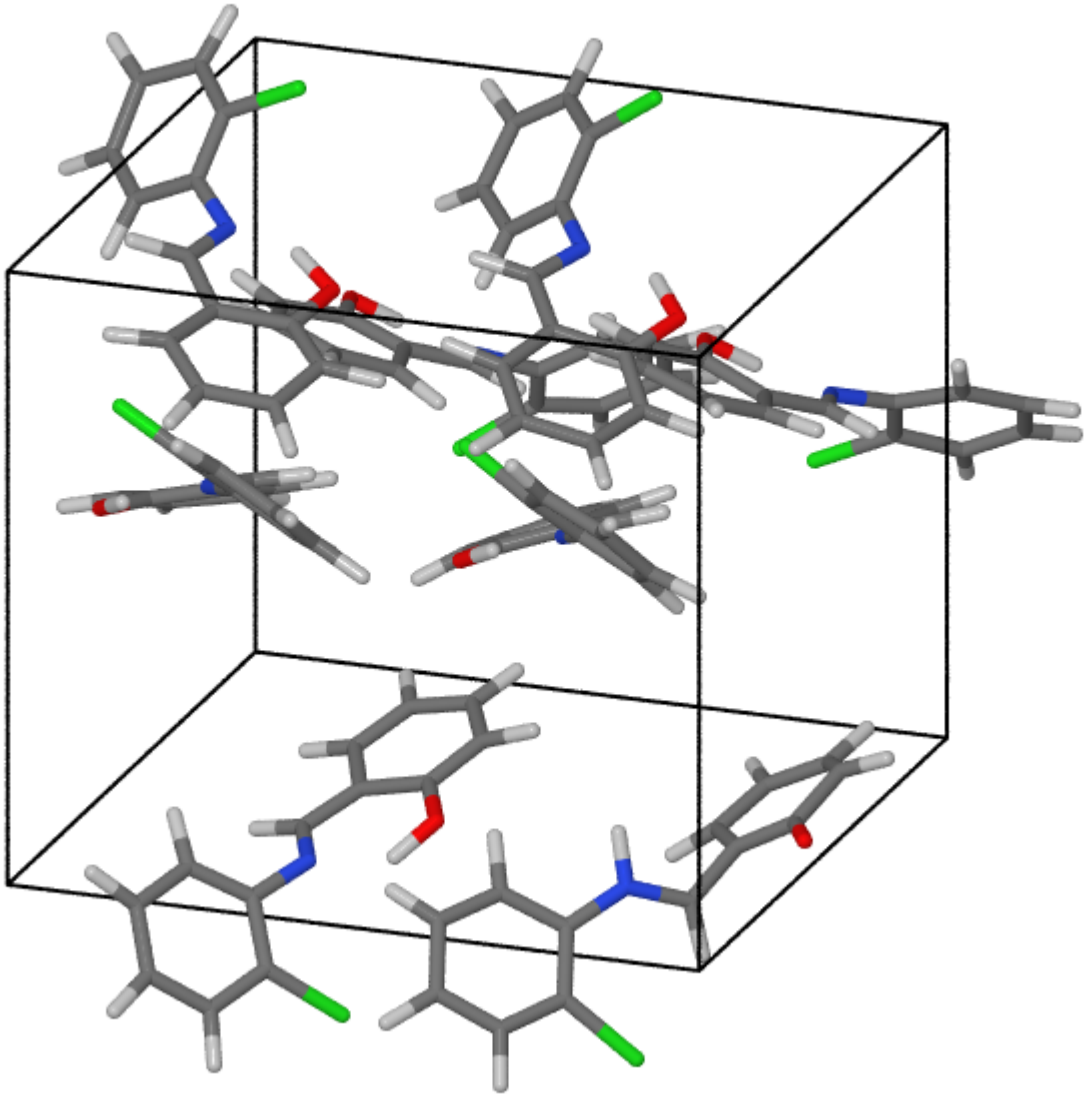
$t = 530\ \mathrm{fs} \quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 1.388\ \mathrm{eV}$



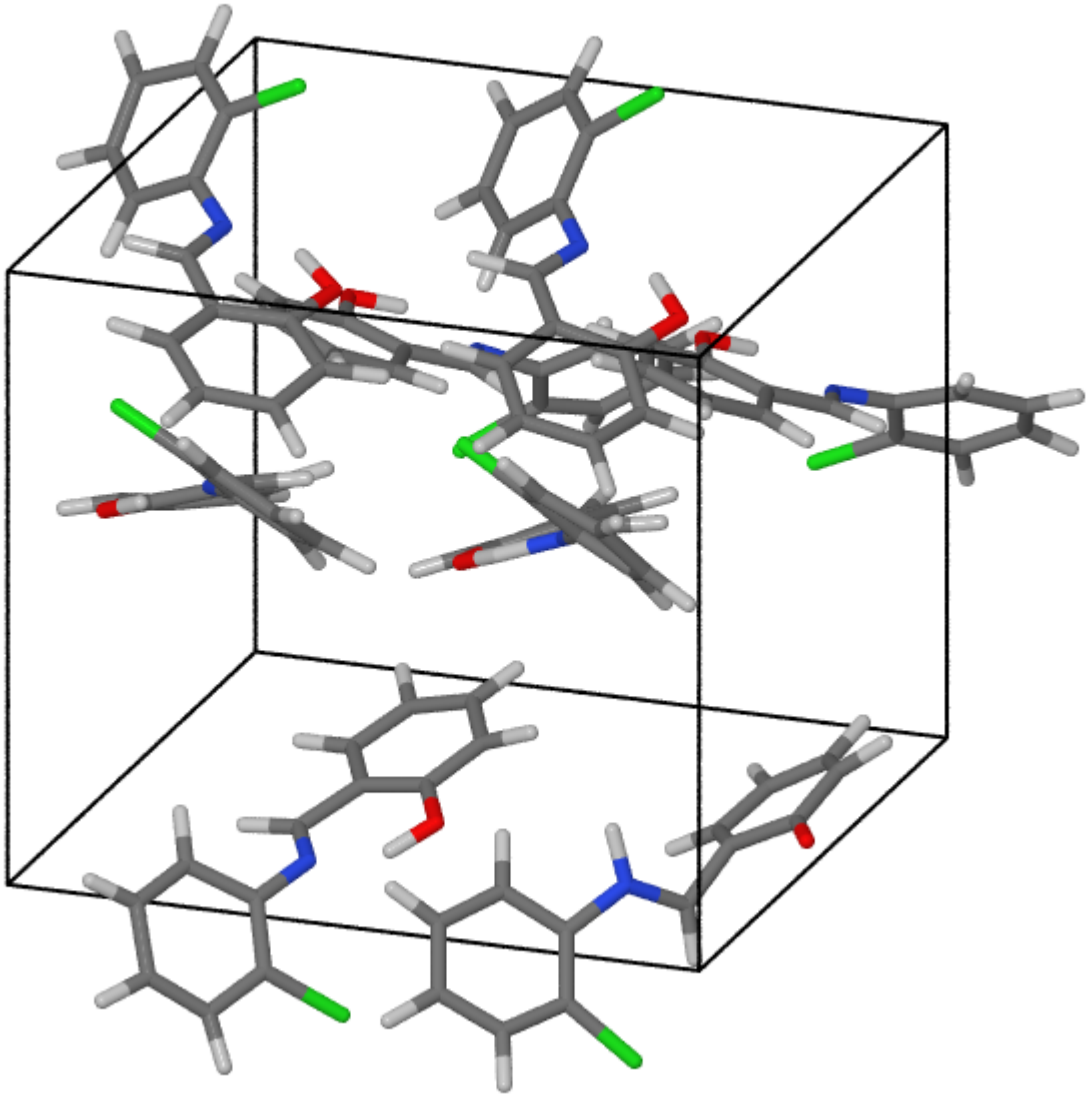
$t = 540$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 1.060$ eV



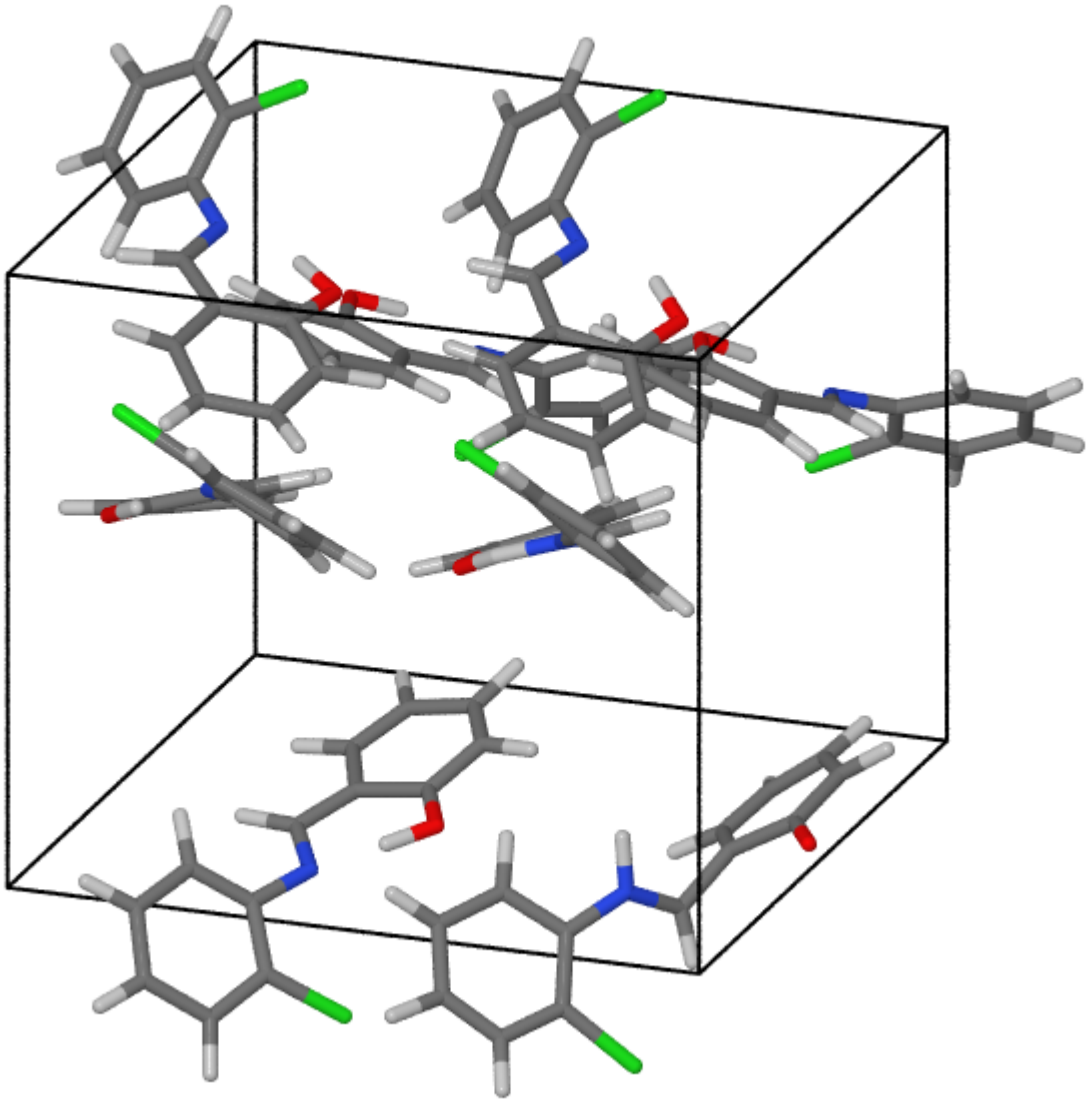
$t = 550\ \mathrm{fs} \quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 0.927\ \mathrm{eV}$



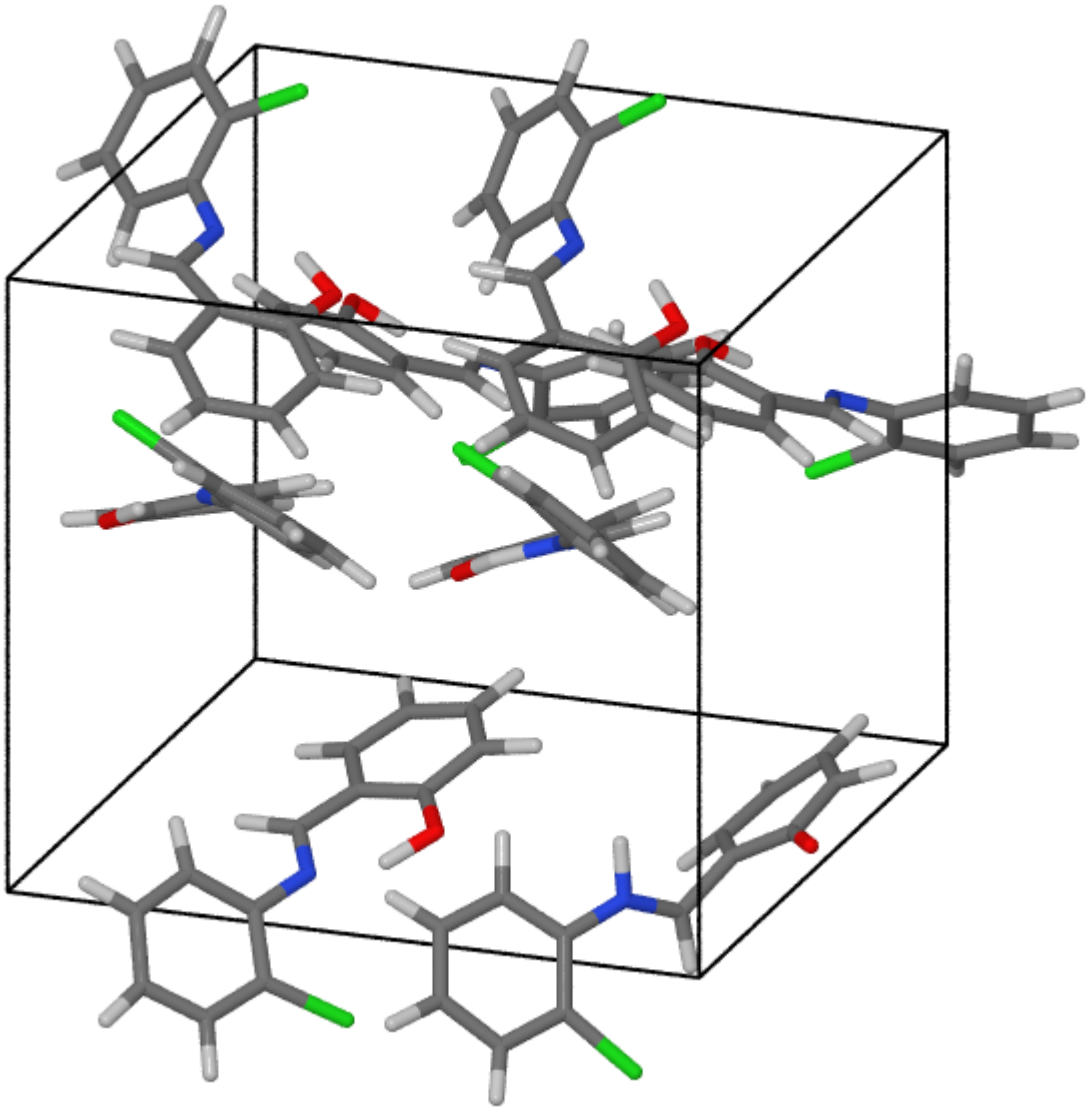
$t = 560$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 0.691$ eV



$t = 570\ \mathrm{fs} \quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 0.310\ \mathrm{eV}$



$t = 580$ fs $\quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 0.509$ eV



$t = 590\ \mathrm{fs} \quad E(\mathrm{S}_1) - E(\mathrm{S}_0) = 0.253\ \mathrm{eV}$