Electronic Supplementary Information for

Deciphering the photosensitization mechanisms of hypericin towards biological membranes

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TD-DFT Performance

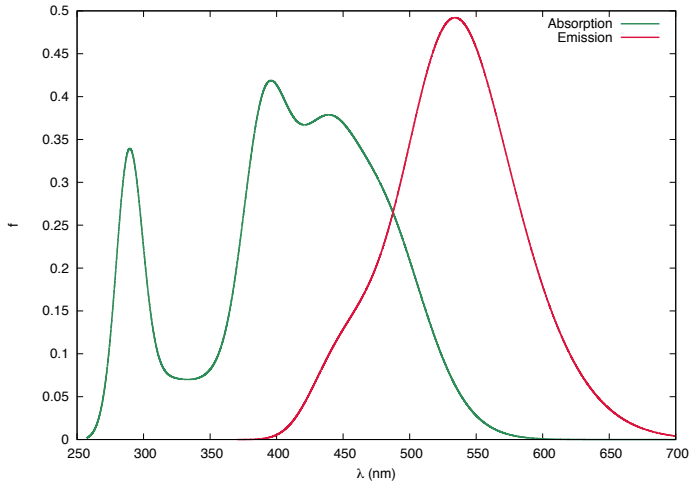

Figure S1) Calculated Absorption and Emission Spectrum from the Wigner distribution using the M06-2X functional. Note the important blue-shift compared to experience and B3LYP (see main text).

	S_1	S_2
B3LYP/DZP	2.37 (0.44)	2.85 (0.40)
PBE0/DZP	2.44 (0.46)	2.94 (0.45)
CAM-B3LYP/DZP	2.87 (0.43)	3.40 (0.42)
M06-2X/DZP	2.70 (0.55)	3.18 (0.59)
M06-2X/TZP	2.69 (0.55)	3.15 (0.61)

Table S1) Excitation energies calculated from the S_0 equilibrium geometries with different functionals. Oscillator strengths are given in parenthesis.

Comparison of Force Field and Wigner based Sampling

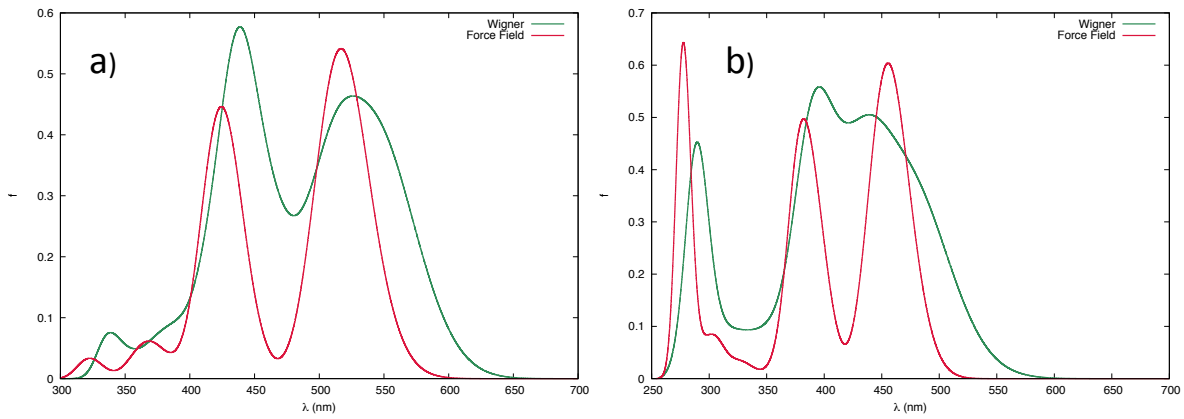

Figure S2) Comparison of the TD-DFT spectrum calculated at B3LYP/DZP (a) and M06-2X/DZP (b) level from a sampling of the ground state obtained via the Wigner distribution or a molecular dynamic trajectory in a water box. Note the global agreement with the position of the peaks.

Photophysical Properties Using the M06-2X functional

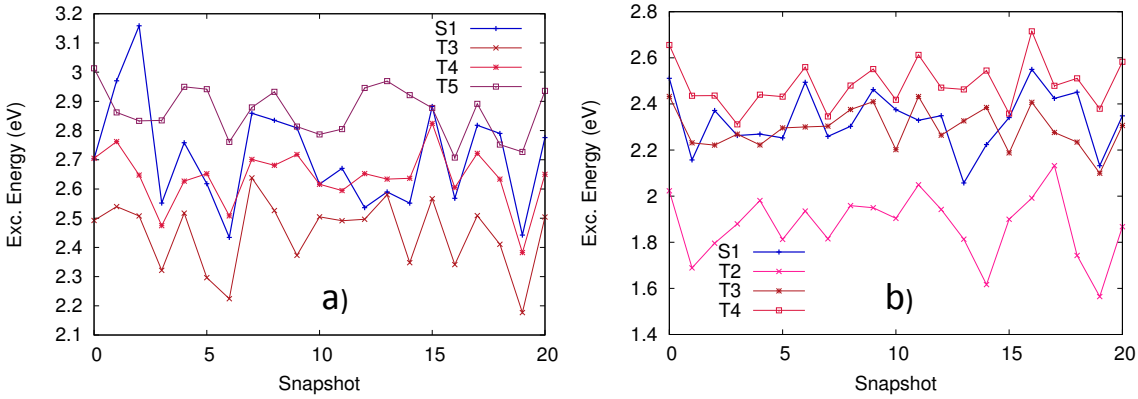

Figure S3) Relative energies of the lowest lying excited singlet and nearby triplet states as obtained with M06-2X/DZP theory level around the Franck-Condon (a) and S_1 equilibrium geometry (b).

Photophysical Properties Using the B3LYP Functional

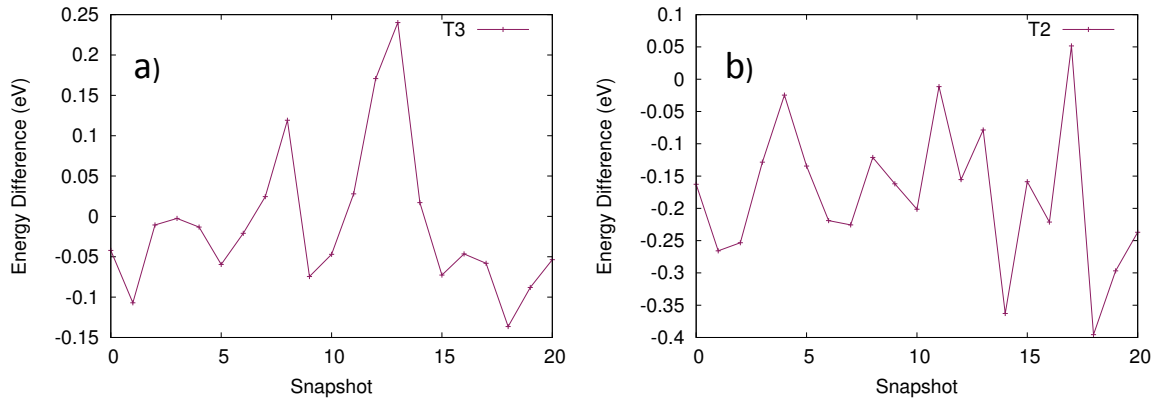

Figure S4) Energy difference between S_1 and the closest triplet at the Franck-Condon region (a) and close to the S_1 minimum (b).

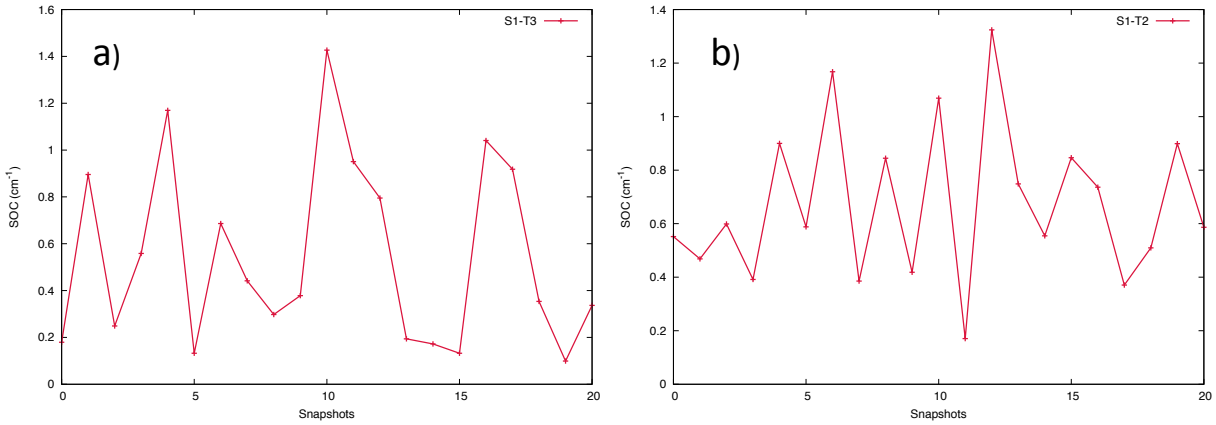

Figure S5) Maximum component of the SOC, in cm^{-1}, between S_1 and T_3 at the Franck-Condon region (a) and between S_1 and T_2 at the S_1 minimum (b).

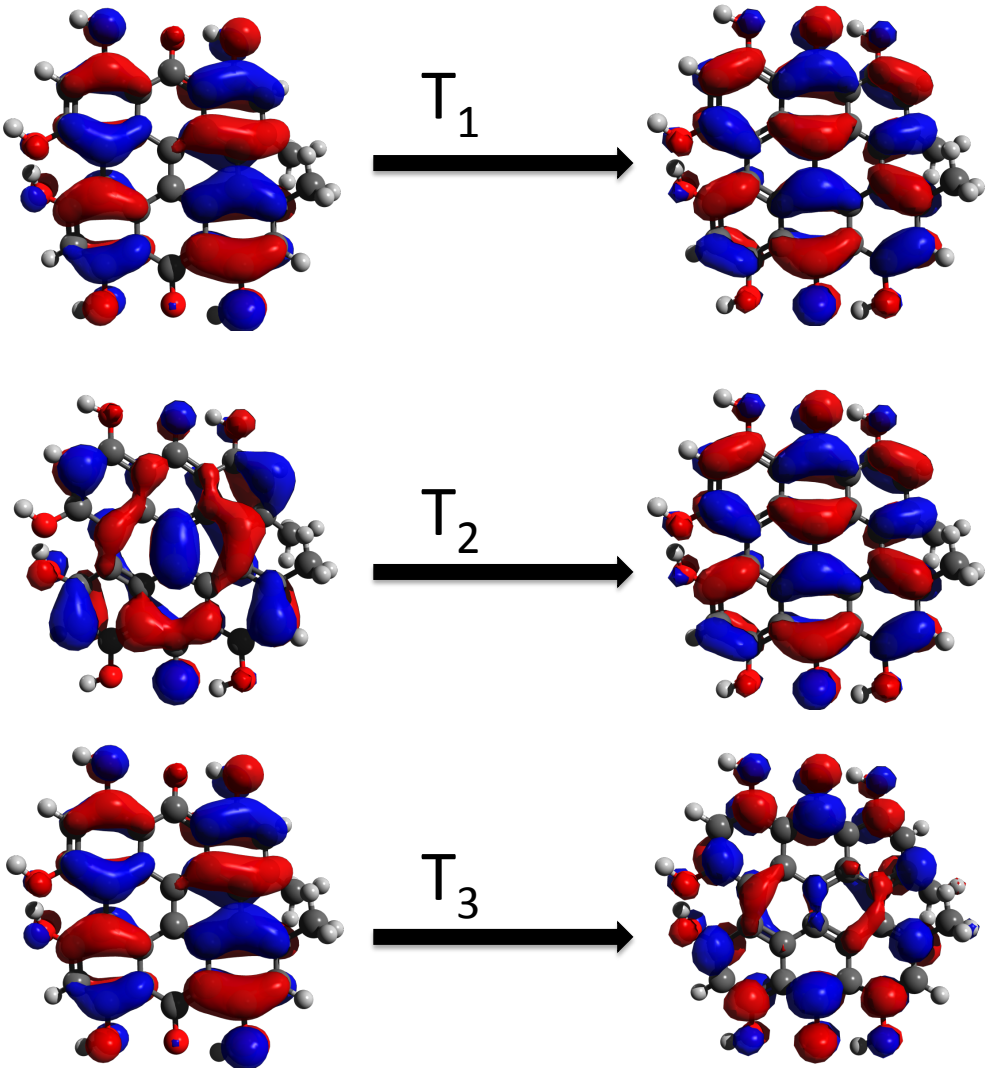

Figure S6) NTOs for the lowest three triplet states.

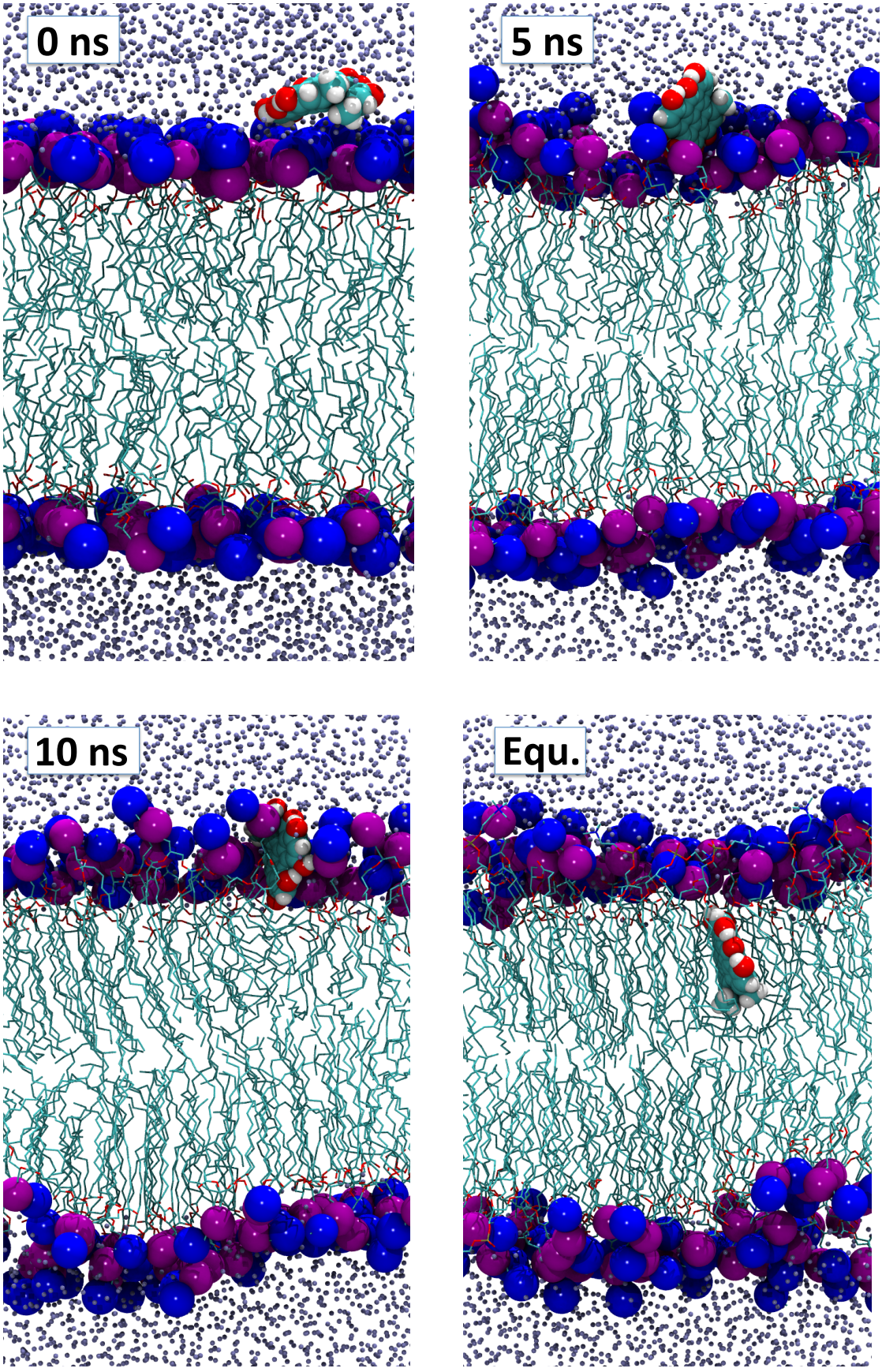

Figure S7) Representative snapshots of the MD trajectory showing HYP insertion in the lipid core