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).

<table>
<thead>
<tr>
<th></th>
<th>$S_1$</th>
<th>$S_2$</th>
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<tbody>
<tr>
<td>B3LYP/DZP</td>
<td>2.37</td>
<td>2.85</td>
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<tr>
<td>PBE0/DZP</td>
<td>2.44</td>
<td>2.94</td>
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<tr>
<td>CAM-B3LYP/DZP</td>
<td>2.87</td>
<td>3.40</td>
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<tr>
<td>M06-2X/DZP</td>
<td>2.70</td>
<td>3.18</td>
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<tr>
<td>M06-2X/TZP</td>
<td>2.69</td>
<td>3.15</td>
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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.