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Supplementary information for

# Photochemical dynamics of indolylmaleimide derivatives

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**Table S1** The dominate coefficients of electron-configuration state functions (CSFs) for each state at optimized geometries of the electronic ground state, where the characters "a" and "b" designate demonstrate upward spin and downward spin, respectively.

| Electron occupation numbers [a] | **IM⁻′** | | | **IM²⁻** | | |
|---|---|---|---|---|---|---|
| | $S_0$ | $S_1$ | $S_2$ | $S_0$ | $S_1$ | $S_2$ |
| 22200 | 0.93 | 0.24 | 0.21 | 0.98 | 0.00 | 0.01 |
| 22ba0 [b] | 0.22 | -0.52 | -0.39 | 0.00 | -0.66 | 0.19 |
| 2b2a0 | 0.02 | 0.41 | -0.54 | 0.02 | -0.08 | -0.22 |
| 22b0a | --- | --- | --- | 0.00 | -0.15 | -0.60 |

[a] Electron occupation number in the active space which is defined as [(*53a*)(*54a*)(*55a*)(*56a*)(*57a*)]. For example, "22200" corresponds to "[$(53a)^2$ $(54a)^2$ $(55a)^2$ $(56a)^0$ $(57a)^0$]."

[b] 22ba0, for example,stand for (1/√2)(|22ab0>-|22ba0>), the singlet linear combination..

**Table S2**. Bond lengths of $R_1$ and $R_2$ and dihedral angles of $\theta$ for minimum structures in $S_0$, $S_1$ and $S_2$ states and at the conical intersections (ME-CoIns) between the $S_1$ and $S_0$ states and also between the $S_2$ and $S_1$ states for (a) **IM⁻′**, (b) **IM⁻″** and (c) **IM²⁻**

| **(a) IM⁻′** | | ME-CoIn | | ME-CoIn | |
|---|---|---|---|---|---|
| | $S_0$ min | ($S_0$-$S_1$) | $S_1$ min | ($S_1$-$S_2$) | $S_2$ min |
| bond length[a] | | | | | |
| C1-C2 | 1.412 | 1.417 | 1.432 | 1.410 | 1.410 |
| C2-C3 | 1.373 | 1.352 | 1.350 | 1.384 | 1.365 |
| C3-C4 | 1.416 | 1.477 | 1.467 | 1.453 | 1.445 |
| C4-C5 | 1.384 | 1.356 | 1.361 | 1.349 | 1.373 |
| C5-C6 | 1.405 | 1.464 | 1.450 | 1.440 | 1.432 |
| C6-C1 | 1.407 | 1.492 | 1.480 | 1.453 | 1.447 |
| C6-N7 | 1.383 | 1.256 | 1.286 | 1.303 | 1.312 |
| N7-C8($R_1$) | 1.296 | 1.482 | 1.404 | 1.393 | 1.386 |
| C8-C9 | 1.443 | 1.337 | 1.381 | 1.375 | 1.377 |
| C9-C1 | 1.458 | 1.428 | 1.406 | 1.423 | 1.427 |
| C9-C10 | 1.400 | 1.499 | 1.474 | 1.477 | 1.477 |
| C10-C11 | 1.527 | 1.393 | 1.437 | 1.441 | 1.442 |
| C11-N12($R_2$) | 1.361 | 1.395 | 1.388 | 1.390 | 1.390 |
| N12-C13 | 1.410 | 1.398 | 1.391 | 1.393 | 1.393 |
| C13-C14 | 1.434 | 1.411 | 1.436 | 1.436 | 1.438 |
| C14-C10 | 1.388 | 1.454 | 1.404 | 1.404 | 1.401 |
| bond angle[b] | | | | | |
| C1-C2-C3 | 119.5 | 117.4 | 118.5 | 118.2 | 118.5 |
| C2-C3-C4 | 121.4 | 124.2 | 122.8 | 121.8 | 122.0 |
| C3-C4-C5 | 119.9 | 121.0 | 121.3 | 121.4 | 121.0 |
| C4-C5-C6 | 118.7 | 117.3 | 118.1 | 118.5 | 118.2 |
| C5-C6-C1 | 121.6 | 120.0 | 119.8 | 120.1 | 119.9 |
| C6-C1-C2 | 118.8 | 120.1 | 119.5 | 120.1 | 120.4 |
| C1-C6-N7 | 112.6 | 111.0 | 112.2 | 111.7 | 111.7 |
| C6-N7-C8 | 105.2 | 104.2 | 103.9 | 104.8 | 104.9 |
| N7-C8-C9 | 115.0 | 114.8 | 115.1 | 114.4 | 114.2 |
| C8-C9-C1 | 102.5 | 102.6 | 103.2 | 103.4 | 103.6 |
| C9-C1-C6 | 104.7 | 107.3 | 105.6 | 105.8 | 105.6 |
| C10-C11-N12 | 106.0 | 105.0 | 105.3 | 104.9 | 104.9 |

| | | | | | |
|---|---|---|---|---|---|
| C11-N12-C13 | 112.3 | 113.6 | 113.0 | 113.1 | 113.0 |
| N12-C13-C14 | 105.8 | 104.6 | 104.6 | 104.8 | 104.8 |
| C13-C14-C10 | 110.7 | 107.9 | 109.1 | 108.8 | 108.9 |
| C14-C10-C11 | 105.3 | 108.7 | 108.0 | 108.4 | 108.4 |
| dihedral angle[b] | | | | | |
| C8-C9-C10-C11($\theta$) | 0.0 | -62.2 | -21.6 | -84.8 | 74.1 |

| **(b) IM$^{-}$″** | | ME-CoIn | | ME-CoIn | |
|---|---|---|---|---|---|
| | $S_0$ min | ($S_0$-$S_1$) | $S_1$ min | ($S_1$-$S_2$) | $S_2$ min |
| bond length[a] | | | | | |
| C1-C2 | 1.396 | 1.401 | 1.402 | 1.401 | 1.402 |
| C2-C3 | 1.383 | 1.382 | 1.381 | 1.381 | 1.381 |
| C3-C4 | 1.401 | 1.403 | 1.404 | 1.404 | 1.404 |
| C4-C5 | 1.381 | 1.379 | 1.378 | 1.379 | 1.378 |
| C5-C6 | 1.394 | 1.397 | 1.398 | 1.397 | 1.398 |
| C6-C1 | 1.400 | 1.407 | 1.407 | 1.406 | 1.407 |
| C6-N7 | 1.379 | 1.365 | 1.365 | 1.367 | 1.364 |
| N7-C8($R_1$) | 1.389 | 1.387 | 1.382 | 1.387 | 1.384 |
| C8-C9 | 1.364 | 1.361 | 1.361 | 1.358 | 1.359 |
| C9-C1 | 1.466 | 1.464 | 1.463 | 1.462 | 1.461 |
| C9-C10 | 1.470 | 1.479 | 1.463 | 1.466 | 1.466 |
| C10-C11 | 1.554 | 1.431 | 1.431 | 1.450 | 1.450 |
| C11-N12($R_2$) | 1.319 | 1.449 | 1.444 | 1.390 | 1.392 |
| N12-C13 | 1.328 | 1.450 | 1.446 | 1.403 | 1.403 |
| C13-C14 | 1.540 | 1.411 | 1.416 | 1.436 | 1.435 |
| C14-C10 | 1.319 | 1.423 | 1.411 | 1.399 | 1.400 |
| bond angle[b] | | | | | |
| C1-C2-C3 | 118.7 | 119.3 | 119.3 | 119.2 | 119.2 |
| C2-C3-C4 | 121.0 | 121.1 | 121.2 | 121.1 | 121.1 |
| C3-C4-C5 | 121.2 | 120.9 | 120.9 | 121.0 | 121.0 |
| C4-C5-C6 | 117.5 | 117.7 | 117.6 | 117.6 | 117.6 |
| C5-C6-C1 | 122.1 | 122.5 | 122.6 | 122.4 | 122.4 |
| C6-C1-C2 | 119.5 | 118.4 | 118.5 | 118.7 | 118.6 |
| C1-C6-N7 | 108.6 | 108.2 | 108.0 | 108.0 | 107.9 |
| C6-N7-C8 | 108.0 | 108.5 | 108.7 | 108.3 | 108.7 |
| N7-C8-C9 | 110.8 | 111.1 | 111.1 | 111.2 | 111.0 |

| | | | | | |
|---|---|---|---|---|---|
| C8-C9-C1 | 105.6 | 105.1 | 105.1 | 105.1 | 105.1 |
| C9-C1-C6 | 106.8 | 107.1 | 107.2 | 107.2 | 107.3 |
| C10-C11-N12 | 110.3 | 107.2 | 107.0 | 102.3 | 102.5 |
| C11-N12-C13 | 108.8 | 107.0 | 107.1 | 116.8 | 116.5 |
| N12-C13-C14 | 109.6 | 106.1 | 105.9 | 101.3 | 101.4 |
| C13-C14-C10 | 106.5 | 110.3 | 110.2 | 111.0 | 111.1 |
| C14-C10-C11 | 104.7 | 106.9 | 107.3 | 108.6 | 108.5 |
| | | | | | |
| dihedral angle[b] | | | | | |
| C8-C9-C10-C11($\theta$) | -34.6 | -7.1 | -15.1 | -24.3 | -23.1 |

| **(c) IM$^{2-}$** | | ME-CoIn | | ME-CoIn | |
|---|---|---|---|---|---|
| | $S_0$ min | ($S_0$-$S_1$) | $S_1$ min | ($S_1$-$S_2$) | $S_2$ min |
| bond length[a] | | | | | |
| C1-C2 | 1.418 | 1.404 | 1.409 | 1.404 | 1.409 |
| C2-C3 | 1.381 | 1.384 | 1.381 | 1.383 | 1.381 |
| C3-C4 | 1.405 | 1.412 | 1.411 | 1.412 | 1.414 |
| C4-C5 | 1.396 | 1.379 | 1.380 | 1.379 | 1.379 |
| C5-C6 | 1.404 | 1.409 | 1.401 | 1.409 | 1.405 |
| C6-C1 | 1.438 | 1.435 | 1.431 | 1.434 | 1.434 |
| C6-N7 | 1.357 | 1.348 | 1.368 | 1.350 | 1.361 |
| N7-C8($R_1$) | 1.328 | 1.347 | 1.337 | 1.347 | 1.347 |
| C8-C9 | 1.413 | 1.395 | 1.411 | 1.391 | 1.400 |
| C9-C1 | 1.421 | 1.458 | 1.437 | 1.453 | 1.432 |
| C9-C10 | 1.454 | 1.462 | 1.452 | 1.475 | 1.472 |
| C10-C11 | 1.552 | 1.418 | 1.435 | 1.457 | 1.452 |
| C11-N12($R_2$) | 1.349 | 1.482 | 1.460 | 1.394 | 1.404 |
| N12-C13 | 1.352 | 1.455 | 1.444 | 1.394 | 1.403 |
| C13-C14 | 1.500 | 1.381 | 1.393 | 1.437 | 1.428 |
| C14-C10 | 1.363 | 1.452 | 1.433 | 1.406 | 1.411 |
| | | | | | |
| bond angle[b] | | | | | |
| C1-C2-C3 | 119.6 | 119.9 | 119.7 | 119.7 | 119.8 |
| C2-C3-C4 | 121.9 | 120.8 | 121.4 | 120.8 | 121.2 |
| C3-C4-C5 | 119.9 | 120.6 | 120.0 | 120.6 | 120.2 |
| C4-C5-C6 | 119.4 | 119.8 | 119.7 | 119.8 | 119.8 |
| C5-C6-C1 | 120.8 | 119.7 | 120.7 | 119.6 | 120.2 |
| C6-C1-C2 | 118.4 | 119.3 | 118.6 | 119.5 | 118.9 |

| | | | | | |
|---|---|---|---|---|---|
| C1-C6-N7 | 112.3 | 112.6 | 112.2 | 112.5 | 112.2 |
| C6-N7-C8 | 103.6 | 104.0 | 103.7 | 103.9 | 103.5 |
| N7-C8-C9 | 116.1 | 116.3 | 116.0 | 116.2 | 115.9 |
| C8-C9-C1 | 102.9 | 102.5 | 102.7 | 102.7 | 103.1 |
| C9-C1-C6 | 105.1 | 104.7 | 105.4 | 104.7 | 105.3 |
| C10-C11-N12 | 111.2 | 107.5 | 108.8 | 100.8 | 102.1 |
| C11-N12-C13 | 107.3 | 107.0 | 106.8 | 119.1 | 117.0 |
| N12-C13-C14 | 110.5 | 104.3 | 107.2 | 99.7 | 100.9 |
| C13-C14-C10 | 108.1 | 113.6 | 111.8 | 111.9 | 112.0 |
| C14-C10-C11 | 102.9 | 104.4 | 105.3 | 108.5 | 107.9 |
| dihedral angle[b] | | | | | |
| C8-C9-C10-C11($\theta$) | 0.0 | 2.9 | 0.0 | -25.0 | -21.3 |

[a] In angstroms. [b] In degrees.

**Table S3** Average time of $S_1 \rightarrow S_0$ transitions, the ratio of deactivated trajectories and the total number of calculated trajectories for **IM⁻′** and **IM²⁻**

| | Ratio/% | Average time/fs | Qty. |
|---|---|---|---|
| **IM⁻′** | 60.0 | 36.19[a] | 40 |
| **IM²⁻** | 0 | --- | 20 |

[a] The average of trajectories deactivated to $S_0$ of 60.0 %.

**TableS4** Average time of $S_2 \rightarrow S_1$ and $S_1 \rightarrow S_0$ transitions, the ratio of deactivated trajectories and the total number of calculated trajectories for **IM⁻′** and **IM²⁻**

| | Ratio of $S_2 \rightarrow S_1$ transition/% | Avarage time/fs | Qty. |
|---|---|---|---|
| **IM⁻′** | 100 | 5.71 | 34 |
| **IM²⁻** | 100 | 5.84 | 18 |
| | Ratio of $S_1 \rightarrow S_0$ transition/% | Avarage time/fs | Qty. |
| **IM⁻′** | 76.5 | 26.16[a] | 34 |
| **IM²⁻** | 0 | --- | 18 |

[a] The average of trajectories deactivated to $S_0$ of 76.5 %.

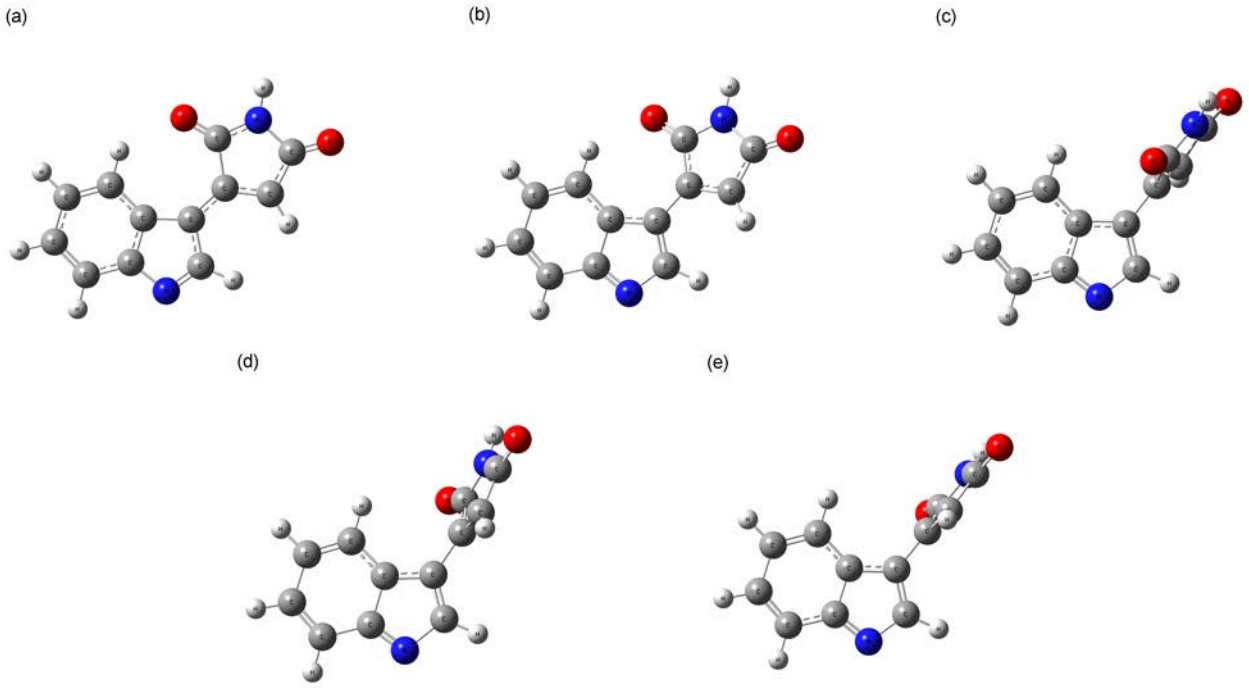


**Fig. S1** Top views of optimized geometries of indolylmaleimides of monovalent anion with a deprotonated indole NH group (**IM**$^{-\prime}$) ((a) $S_0$, (b) $S_1$, (c) $S_2$, (d) minimum energy conical intersection (ME-CoIn) structure between the $S_0$ and $S_1$ states, and (e) ME-CoIn structure between the $S_2$ and $S_1$ states.).

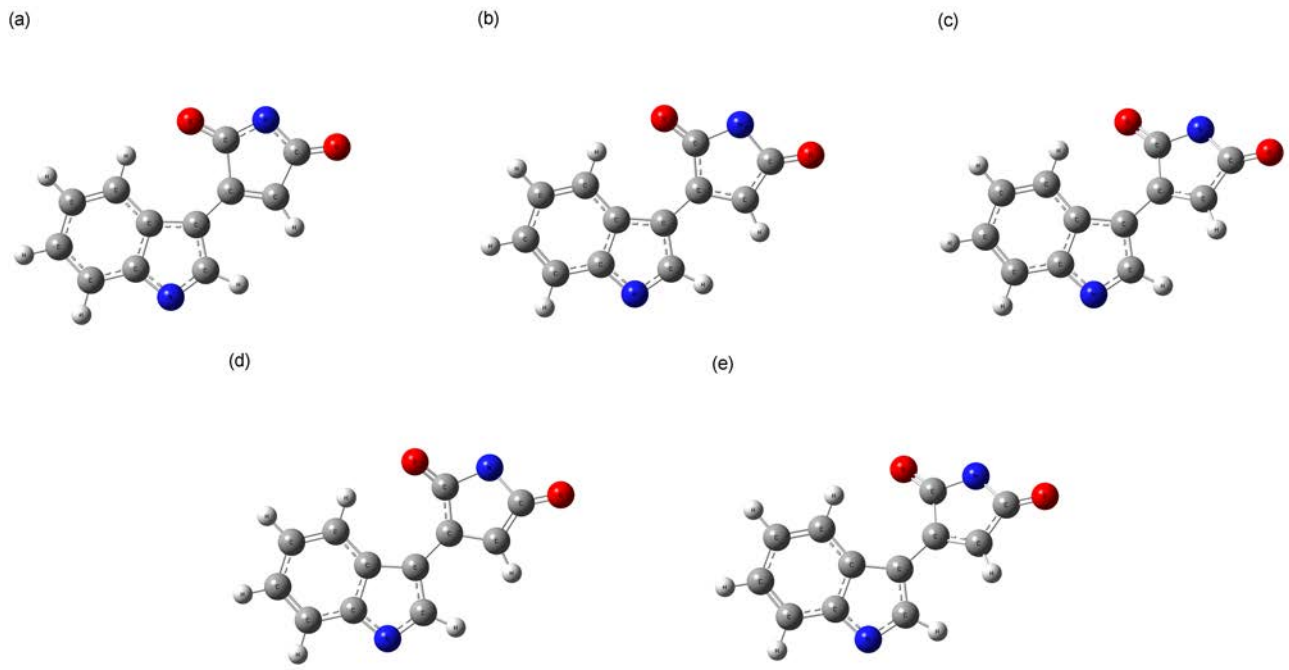


**Fig. S2** Top views of optimized geometries of indolylmaleimides of divalent anion with doubly deprotonated indole and the maleimide NH groups (**IM**$^{2-}$) ((a) $S_0$, (b) $S_1$, (c) $S_2$, (d) ME-CoIn structure between the $S_0$ and $S_1$ states, and (e) ME-CoIn structure between the $S_2$ and $S_1$ states.).

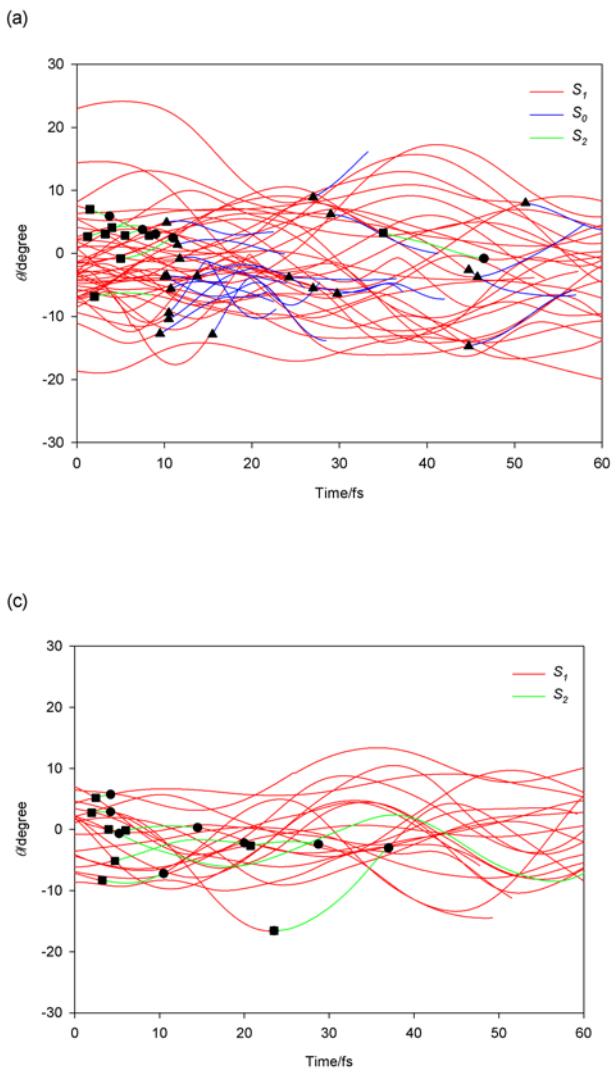


**Fig. S3** Time-evolution of $\theta$ after excitation $S_1$ state for (a) **IM⁻′** and (c) **IM²⁻**. The blue, red and green lines represent that the trajectories run on the $S_0$, $S_1$ and $S_2$ states, respectively. The black circles, triangles and squares indicate the projections of the nonadiabatic transitions of $S_2 \rightarrow S_1$, $S_1 \rightarrow S_0$ and $S_1 \rightarrow S_2$, respectively.

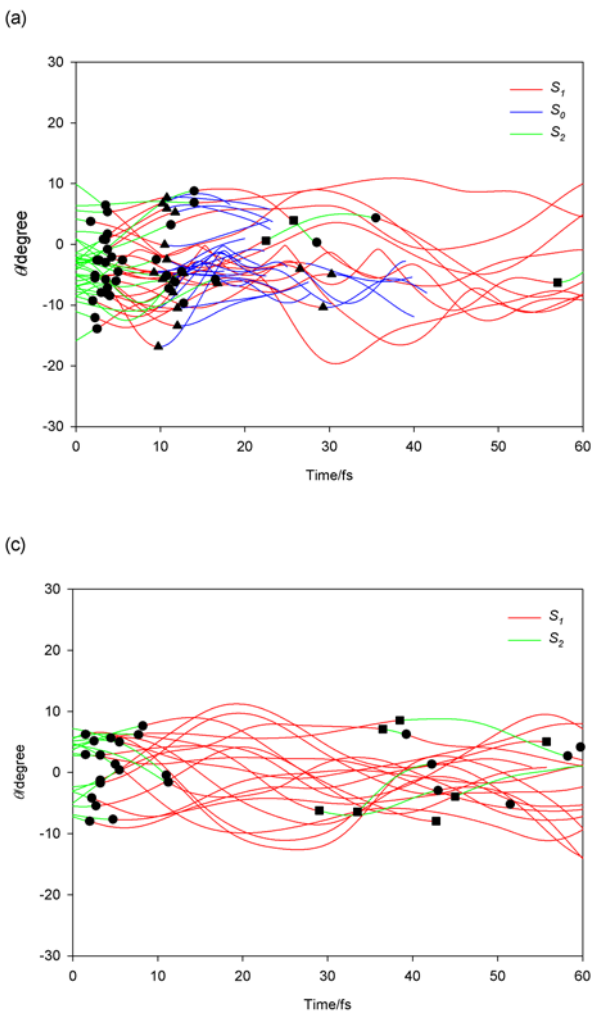


**Fig. S4** Time-evolution of $\theta$ after the excitation to the $S_2$ state for (a) **IM⁻′** and (b) **IM$^{2-}$**. The blue, red and green lines represent that the trajectories run on the $S_0$, $S_1$ and $S_2$ states, respectively. The black circles, triangles and squares indicate the projections of the nonadiabatic transitions of $S_2 \rightarrow S_1$, $S_1 \rightarrow S_0$ and $S_1 \rightarrow S_2$, respectively.