Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

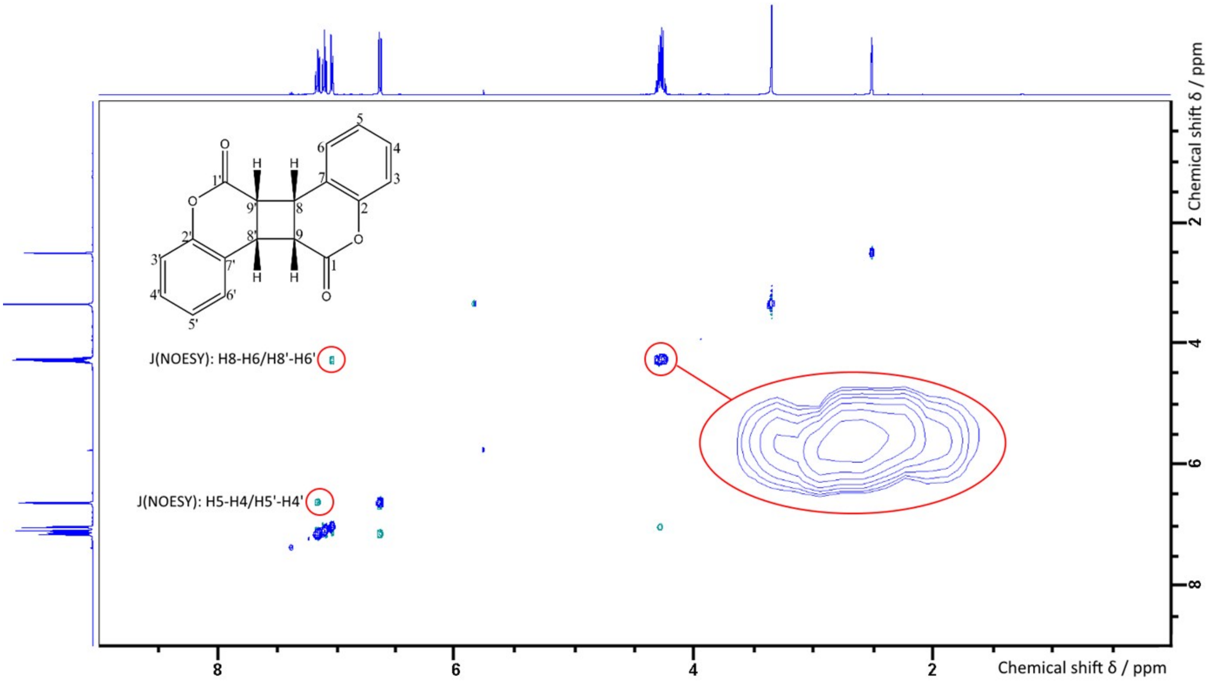
# Photocleavage of Coumarin Dimers Studied by Femtosecond UV Transient Absorption Spectroscopy

Man Jiang[1], Nicholas Paul[1], Nikolai Bieniek[2], Tiago Buckup[1], Norbert Hampp[2], Marcus Motzkus[1]

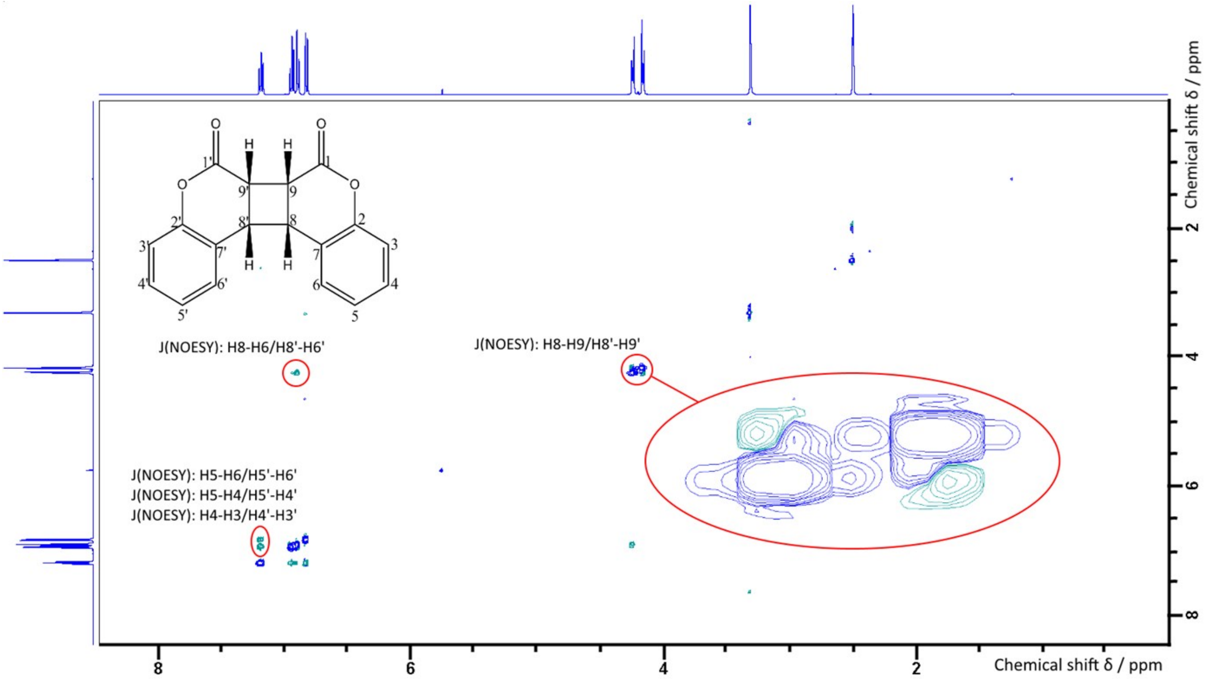
[1]*Institute of Physical Chemistry, Im Neuenheimer Feld 229, University of Heidelberg, D-69120 Heidelberg, Germany.*

[2]*Department of Chemistry, Hans-Meerwein-Str. 4, University of Marburg, D-35032 Marburg, Germany*

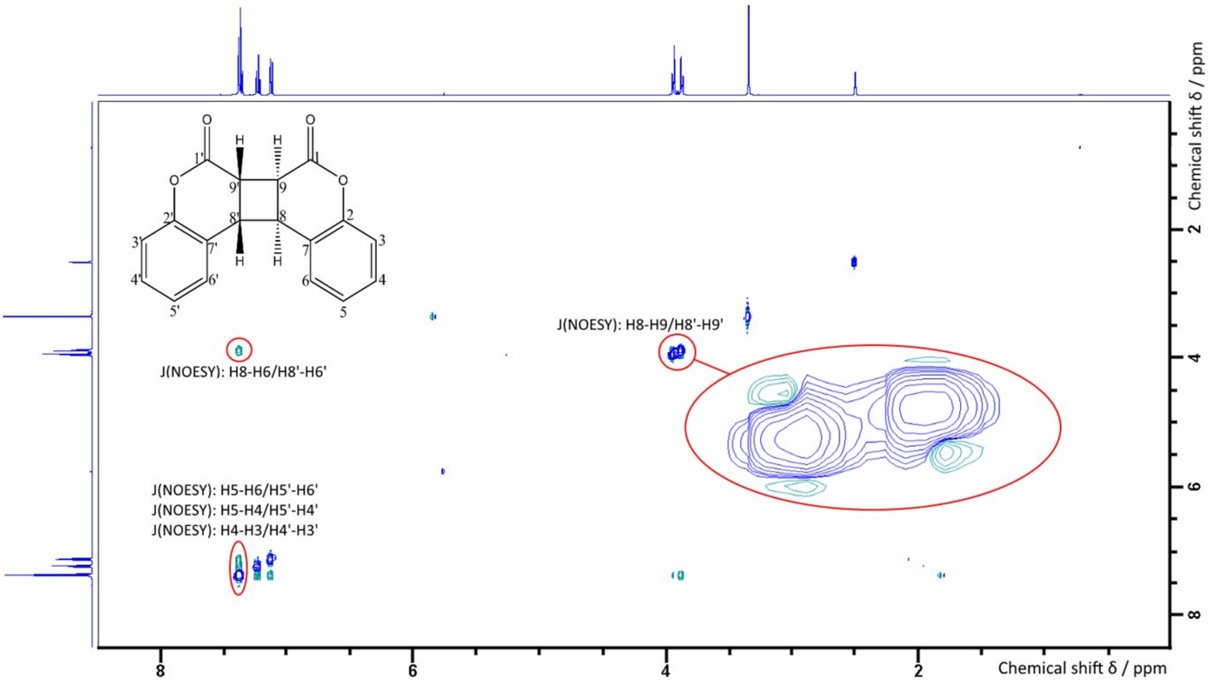
# Supplementary Information



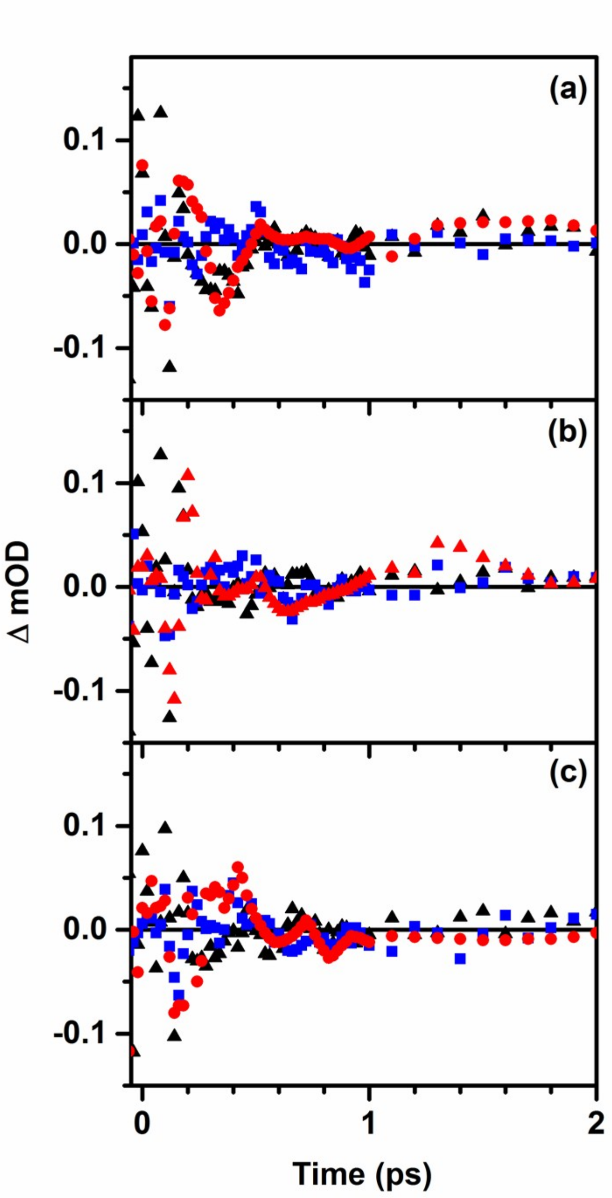
**SI 1:** NOESY syn-head-to-tail coumarin dimer



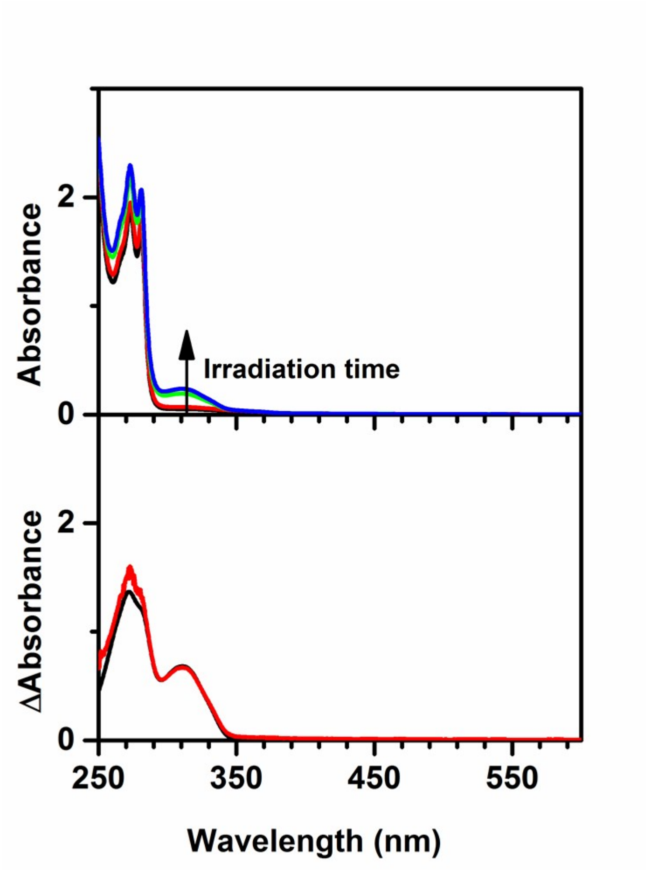
**SI 2:** NOESY syn-head-to-head coumarin dimer



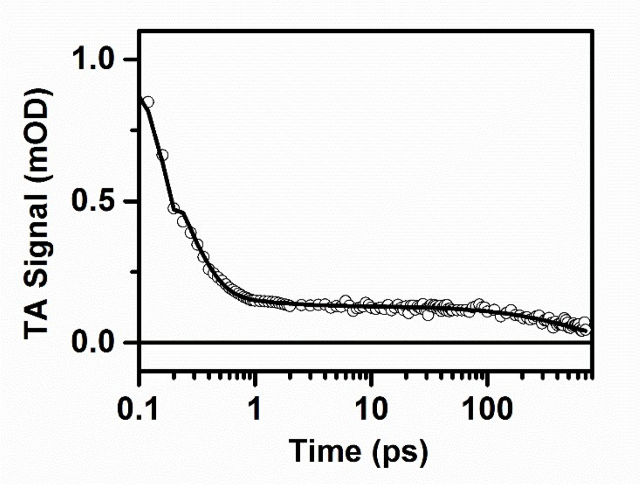
**SI 3:** NOESY anti-head-to-head coumarin dimer



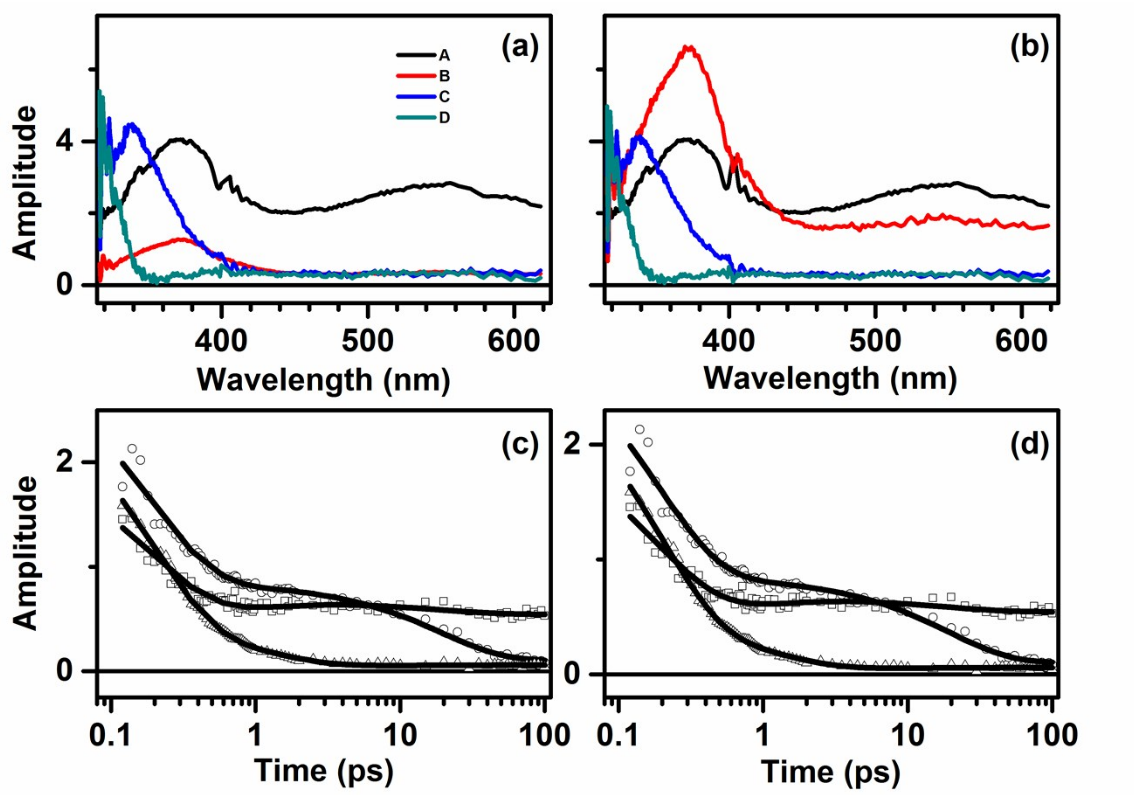
**SI 4:** Fitting residual of (a) syn-ht, (b) syn-hh, (c) anti-hh at 325 nm (black triangle), 340 nm (blue square) and 540 nm (red circle).



**SI 5:** Direct irradiation of the syn-ht dimer by a UV lamp at 252 nm for 3 hours: (a) absorption change upon irradiation time, (b) absorption difference after 3 hours irradiation time (red) and the static absorption of coumarin monomers.



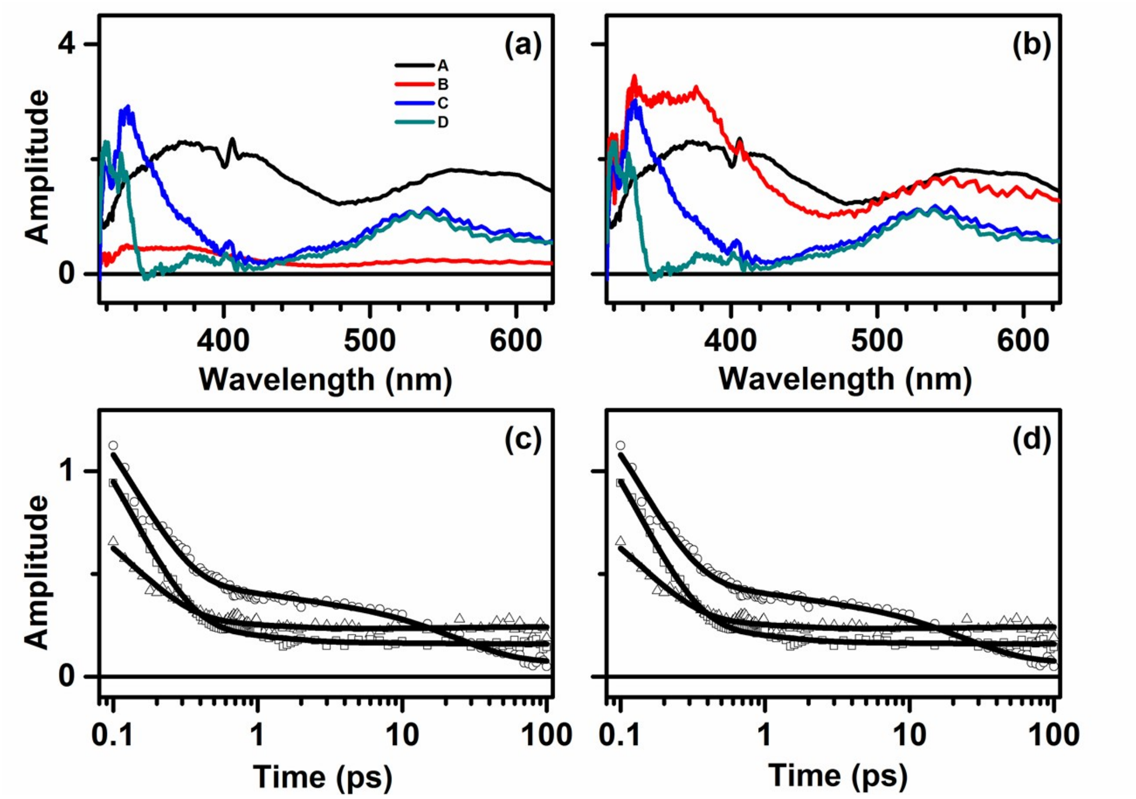
**SI 6:** Transient absorption trace (up to 700 ps) of the syn-ht dimer at 540 nm (empty circle) with the fitting (solid line). Three exponential contributions are obtained: $t_1$ =150 fs, $t_2$ =1.4 ps and $t_3$ = 600 ps.



**SI 7**: Global target analysis results of the syn-hh dimer: SAS obtained for the model I (a) and model II (b), transient absorption traces for the model I (c) and model II (d). Open points are experimental data, lines are global target fittings.

Table 1 Time constants of syn-hh obtained by global target analysis

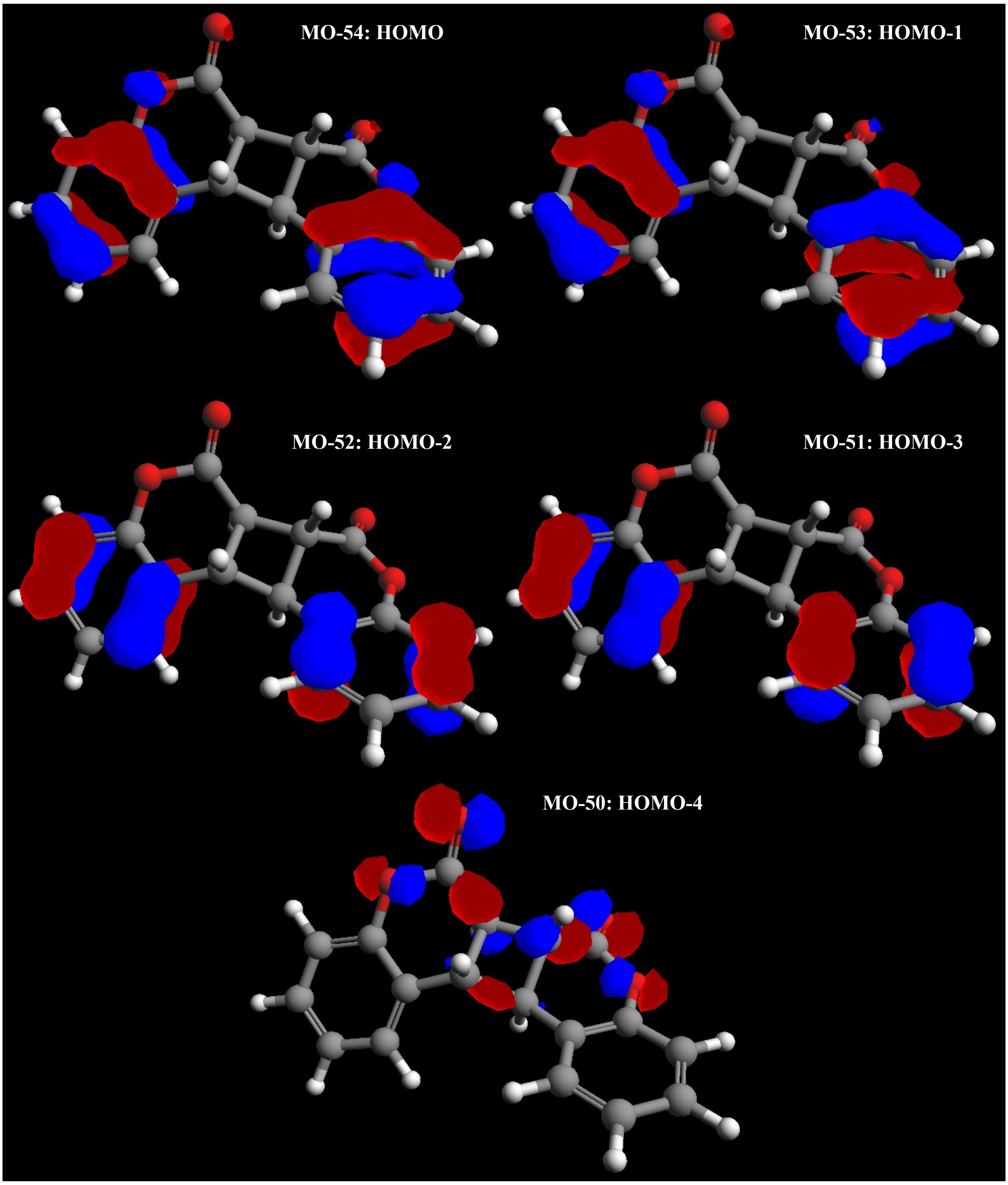
| Model | $\tau_1$ (ps) | $\tau_2$ (ps) | $\tau_3$ (ps) | $\tau_4$ (ps) | Residual |
|---|---|---|---|---|---|
| I | 0.19 | 1.50 | 6.95 | 19.20 | 47.96 |
| II | 0.23 | 0.98 | 1.23 | 19.20 | 47.96 |



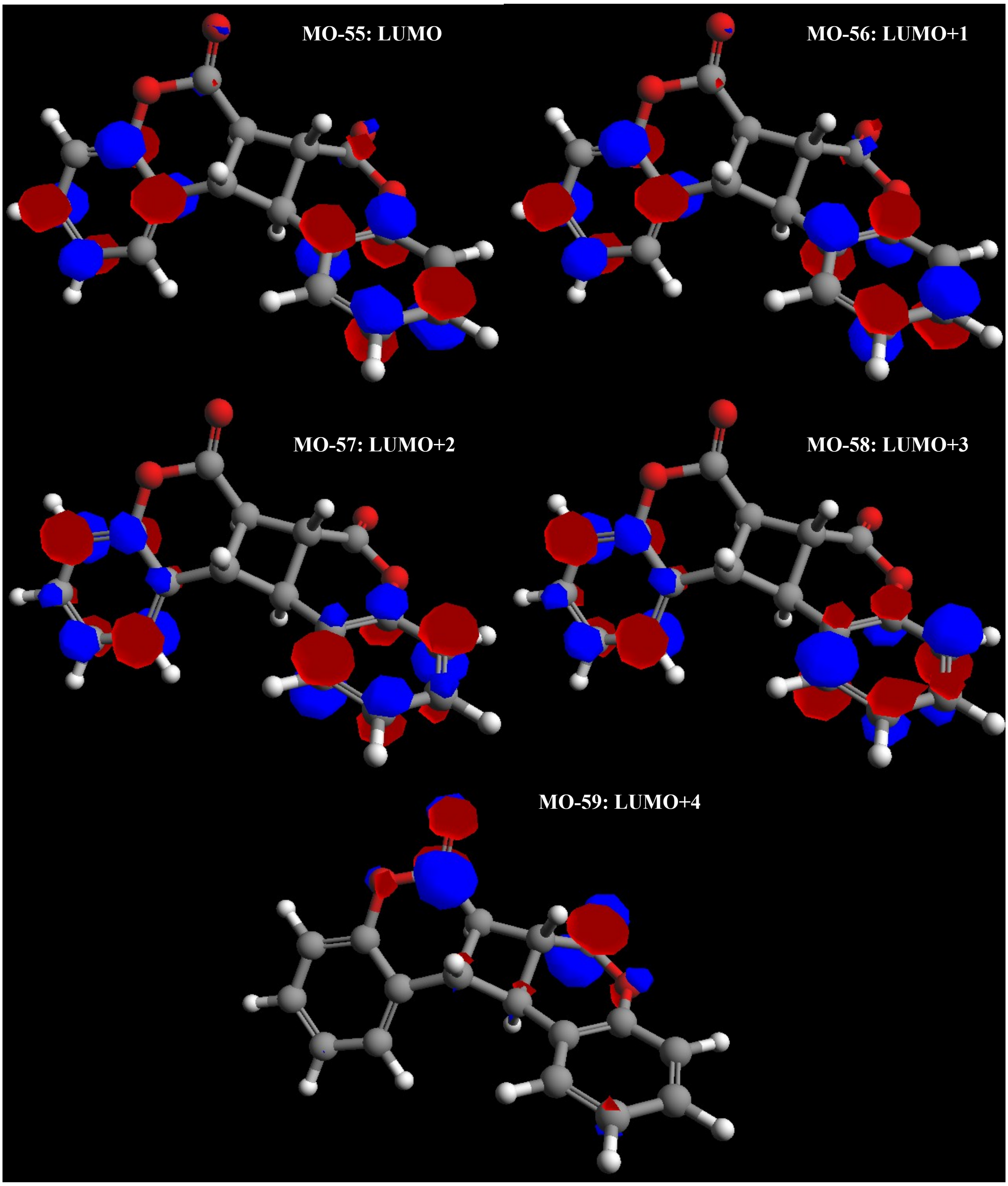
**SI 8**: Global target analysis results of the syn-ht dimer: SAS obtained for the model I (a) and model II (b), transient absorption traces for the model I (c) and model II (d). Open points are experimental data, lines are global target fittings.

Table 2 Time constants of syn-ht obtained by global target analysis

| Model | $\tau_1$ (ps) | $\tau_2$ (ps) | $\tau_3$ (ps) | $\tau_4$ (ps) | Residual |
|---|---|---|---|---|---|
| I | 0.14 | 1.33 | 7.40 | 23.00 | 15.17 |
| II | 0.16 | 0.94 | 1.12 | 23.00 | 15.16 |



**SI9:** Occupied, ground state molecular orbitals for the Anti-HH dimer in its relaxed (energy minimum) geometric arrangement.



**SI10:** Vacant, ground state molecular orbitals for the Anti-HH dimer in its relaxed (energy minimum) geometric arrangement.

## Experimental method for computational calculations

Calculations were performed using the freely available ArgusLab (4.0.1, 2004 Mark Thompson and Planaria Software) package. Geometry optimisation was performed in a step wise manner. Molecular mechanics (Unified Force Field, UFF) was used to relax the geometry to a local, ground state minimum. After successful minimisation, semi-empirical methods using the PM3 model were used to further minimise the equilibrium geometry.

Careful attention was paid to ensure the cyclobutane ring was in the expected, distorted, “boat” geometry. Optimisations were susceptible to local minima where the cyclobutane ring is in the higher energy, flat arrangement.  Once completed, the energies and molecular orbitals were generated.