Supporting information for:

# Controlling Excited-State Dynamics via Protonation of Naphthalene-Based Azo Dyes

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## Summary of 1 – 4 Results:

Table S1. Photophysical Data and Excited-State Lifetimes Recorded of Azo **1**-**4**

| | $\tau_1$ (ps) $^*S_1 \rightarrow S_1$ | $\tau_2$ (ps) $S_1 \rightarrow {}^*S_0$ | $\tau_3$ (ps) $^*S_0 \rightarrow S_0$ | $\tau_4$ (ps) $^*S_0 \rightarrow$ *cis*-$S_0$ | $\tau_5$ (min)‡ *cis*-$S_0 \rightarrow$ *trans*- $S_0$ |
|---|---|---|---|---|---|
| **1** | 0.64 ± 0.20 | 2.9 ± 0.3 | 22 ± 3 | n/o | 280 |
| **2** | 1.19 ± 0.20 | 3.0 ± 0.5 | 32 ± 4 | n/o | 12 |
| **3** | 1.38 ± 0.14 | 3.7 ± 0.7 | 25 ± 1 | n/o | 24 |
| **4** | 0.70 ± 0.04 | 3.4 ± 0.9 | 16. ± 1 | 38 ± 5 | 8 |

n/o indicates that the process is not observed on our TAS measurements due to the spectral observation window available in our measurements. Based on the residual component (i.e. $\tau_5$ inf, we infer that the process does occur, but that we are not able to observe it in TAS).

‡ Based on steady-state reversion kinetics.

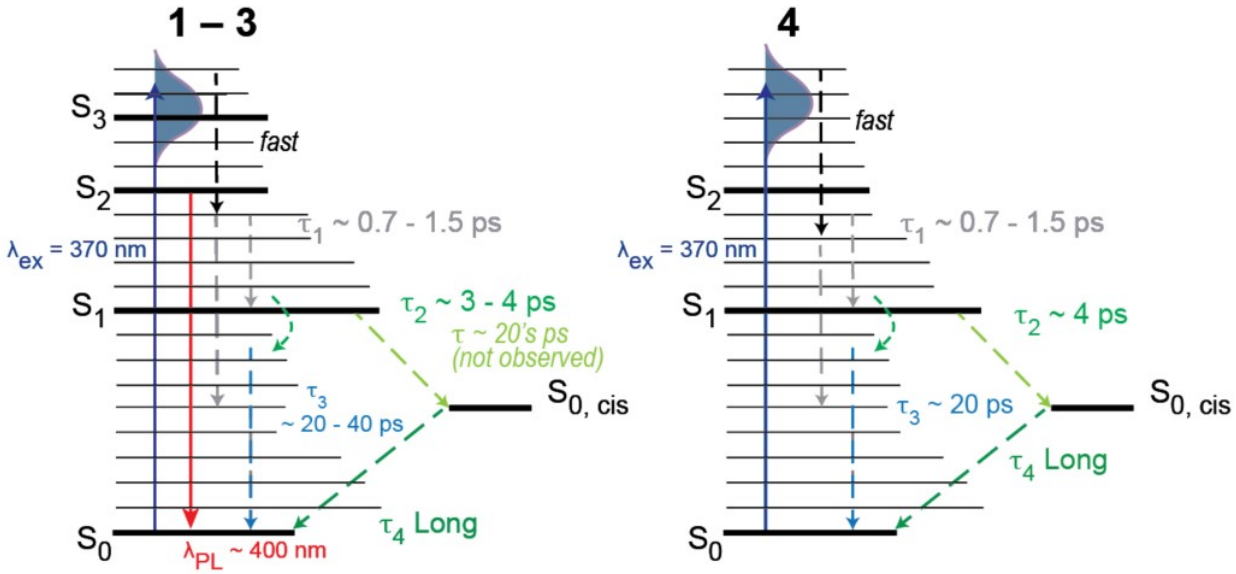


Figure S1. Figure summarizing the photophysics and proposed mechanism for the unprotonated naphthalene-based azo dyes for comparison to this work on the protonated moieties.

## Experimental Results

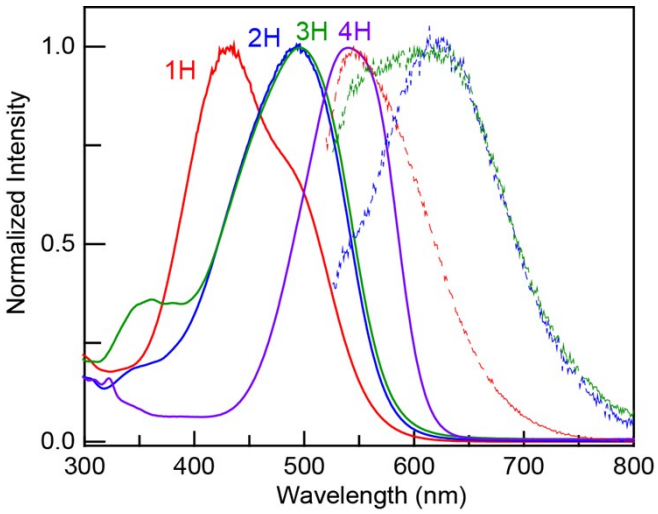


Figure S2. UV-visible and photoluminescence ($\lambda_{ex}$ = 500 nm) spectra of **1H** – **4H** in acetonitrile. **4H** shows no photoluminescence.

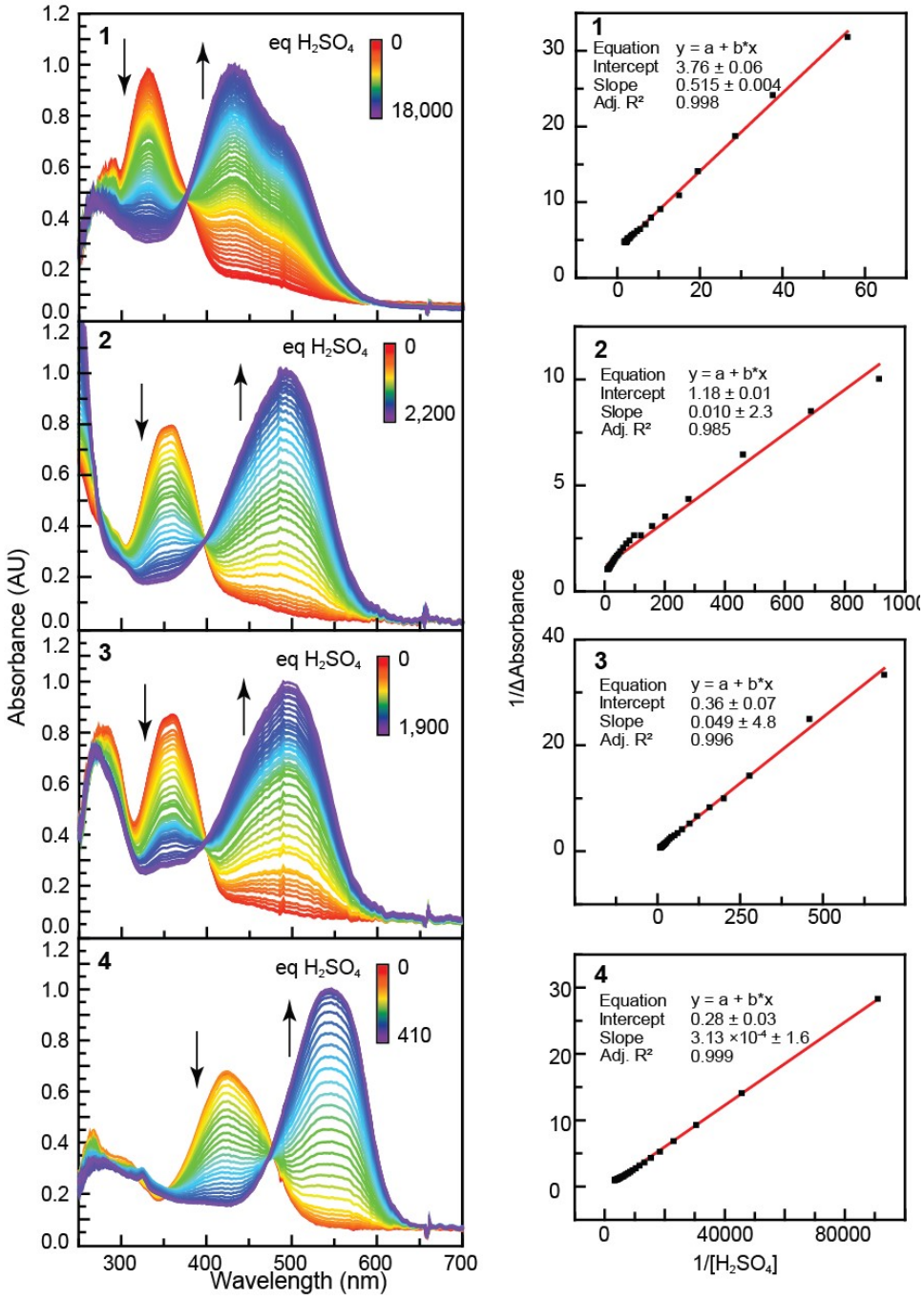


Figure S3. (left column) Protonation titration data for **1H** – **4H** and (right column) Benesi-Hildebrand plots with non-weighted fitting lines shown for the titration of **1** – **4** with $H_2SO_4$ to make **1H** – **4H**.

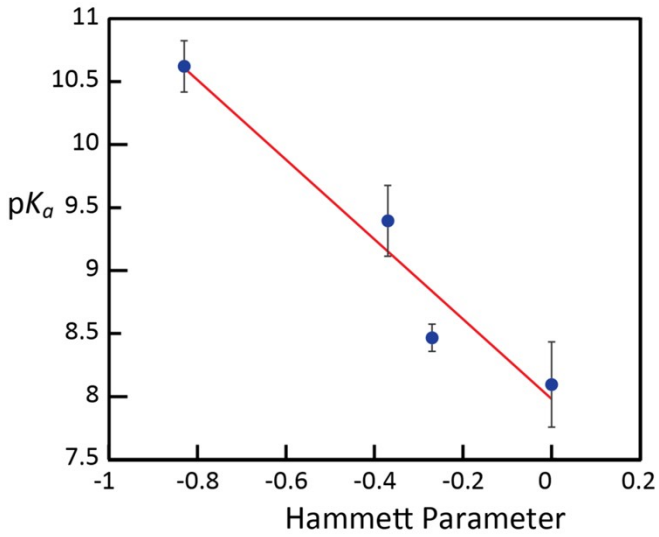


Figure S4. Hammett parameter plot with calculated p$K_a$s of **1** - **4**.

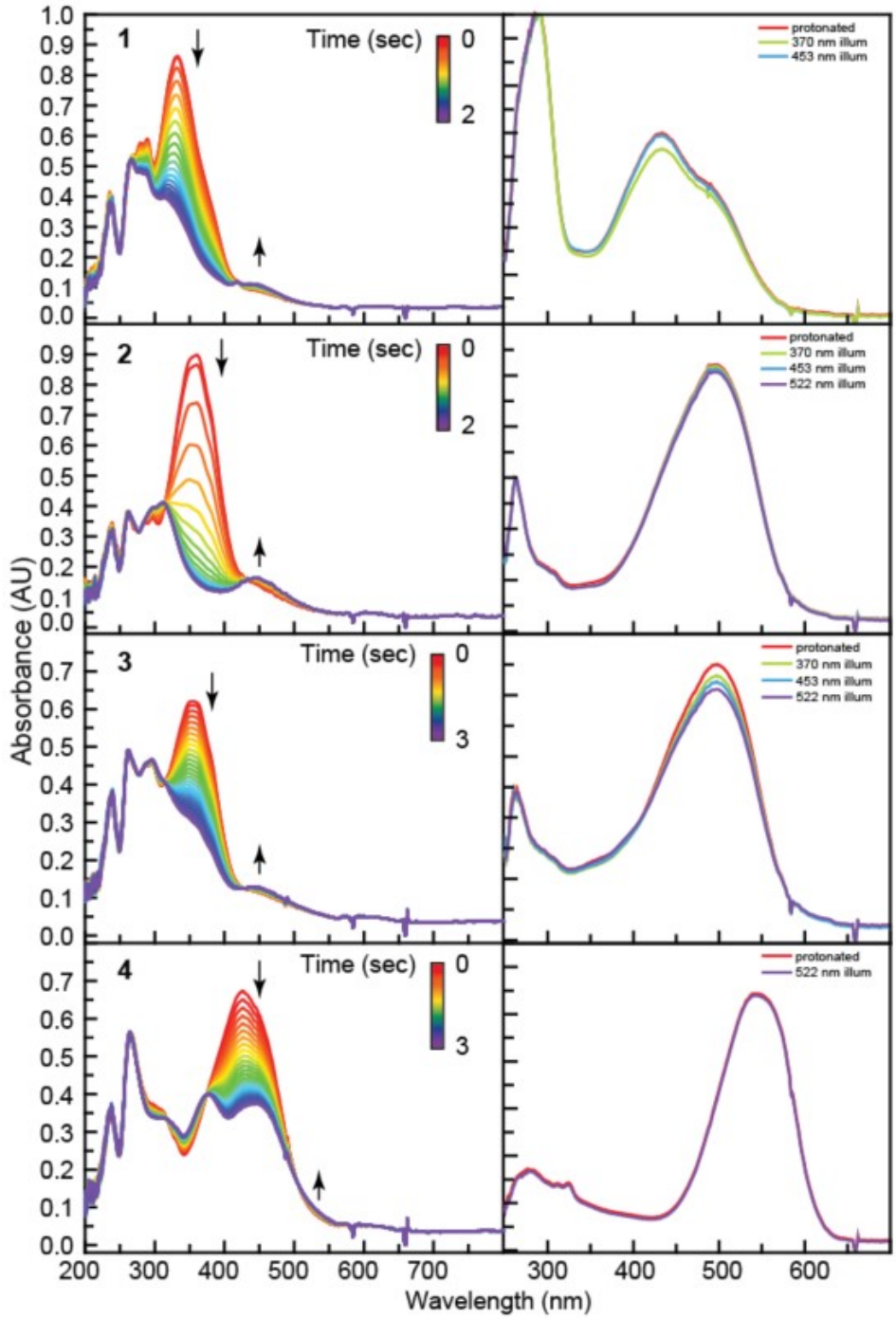


Figure S5. Photoisomerization spectra of (left column) **1** – **4** and (right column) **1H** – **4H**.

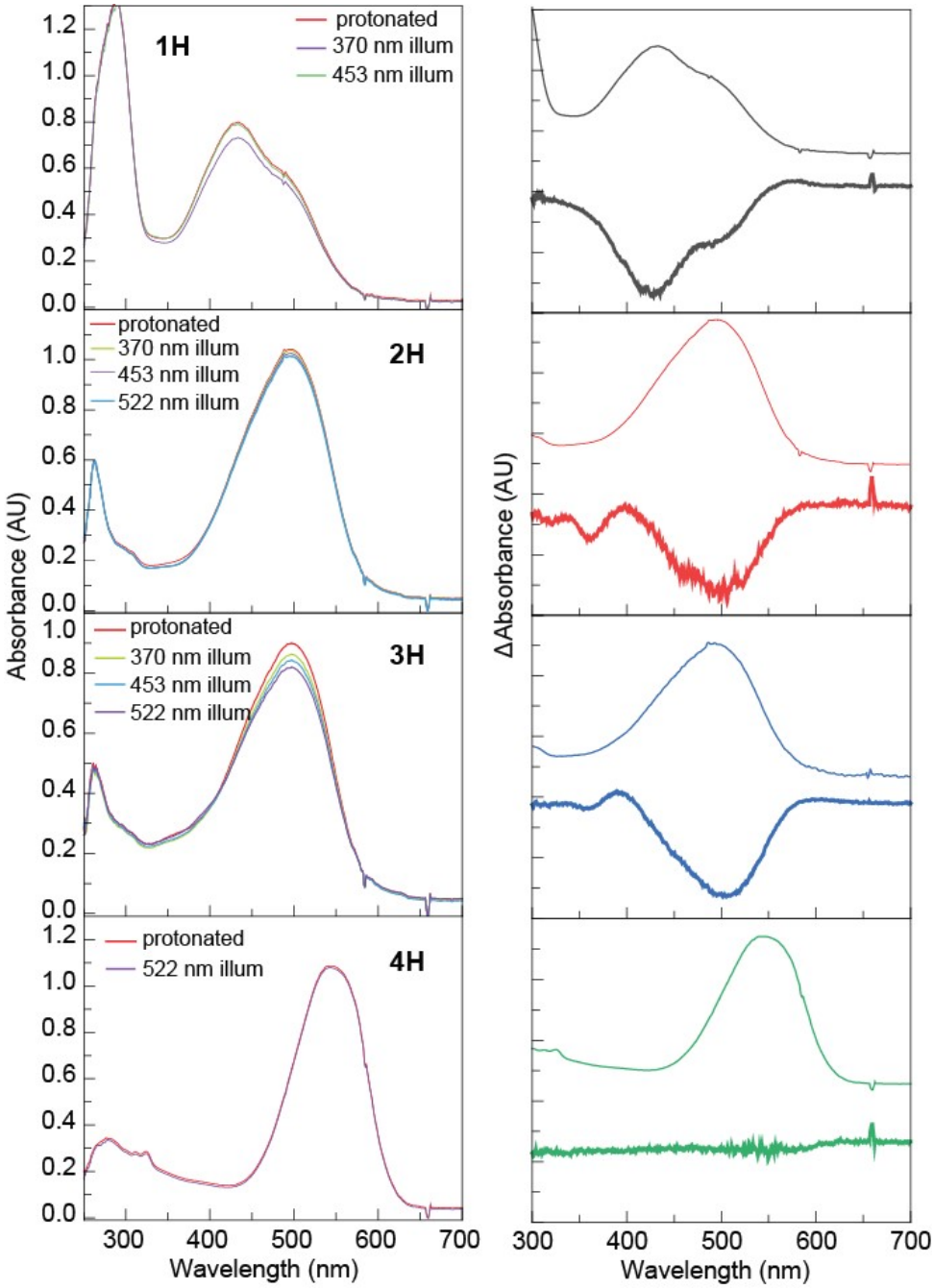


Figure S6. (left) Photoisomerization spectra for **1H** – **4H** at various illumination wavelengths. (right) Comparison of the initial protonated spectrum (thin line) with the difference spectrum (thicker line) obtained by subtracting the original protonated spectrum from the most changed isomerization spectrum for **1H** – **4H**. The difference spectra clearly show a small bleach of the protonated dye upon photoisomerization for **1H** – **3H**. While no photoisomerization occurs for 4H.

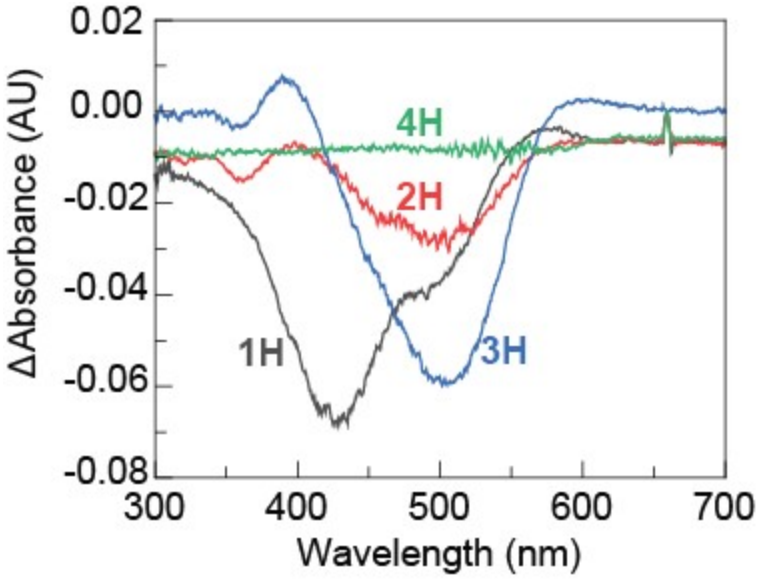


Figure S7. Comparison of difference spectra of photoisomerization endpoints for **1H** – **4H**.

## Transient Absorption Fitting

For each of the azo dyes **1H** – **4H**, we show the heat map of our TAS data before and after the chirp correction is applied in a single SI figure. In a second figure, we show a multi-panel series of data, fits and analysis of the fits. We provide here a detailed explanation of each panel of those figures below.

The top left panel labeled “Raw Data Surface” is the original data for each dye after chip correction, and other data preparation are applied. Global analysis fitting is performed providing a model featuring DADS and associated lifetimes reported in the text (and in the bottom left panel of the SI figure). Combining the DADS, lifetimes, time zero, and IRF produced by the fit model, the TAS surface is “reconstructed”. The reconstructed data surface is shown in the top middle panel, labeled “Reconstructed Surface”. From this surface a selection of spectra are presented in the bottom middle panel labeled “Reconstructed Representative Spectra”. Finally, the original data is compared to the reconstructed data in the right most column. Top right panel is a heat map of the residual between the original data surface and the reconstructed surface. The residual surface was used to evaluate the global analysis fit. Fit models were selected or modified in order to reduce or remove structure from the residual surface. Residual surfaces lacking distinct features and more closely resembling noise, resulted in a favoring of that fit. The root mean square error (RSE) value was calculated for each residual surface as a measure of how well that fit matched the data surface. This value was also used to identify fit improvements when differences became difficult to identify visually. RSE values were only used to judge improvements to fits for the same data surface, and were not assessed between data surfaces. On the lower right panel, single wavelength TAS data at a range of lifetime (dotted data points) are displayed. Solid lines representing the single wavelength traces constructed using the fitted lifetimes from global analysis overlay the data. This plot is another method of evaluating the fits obtained using global analysis.

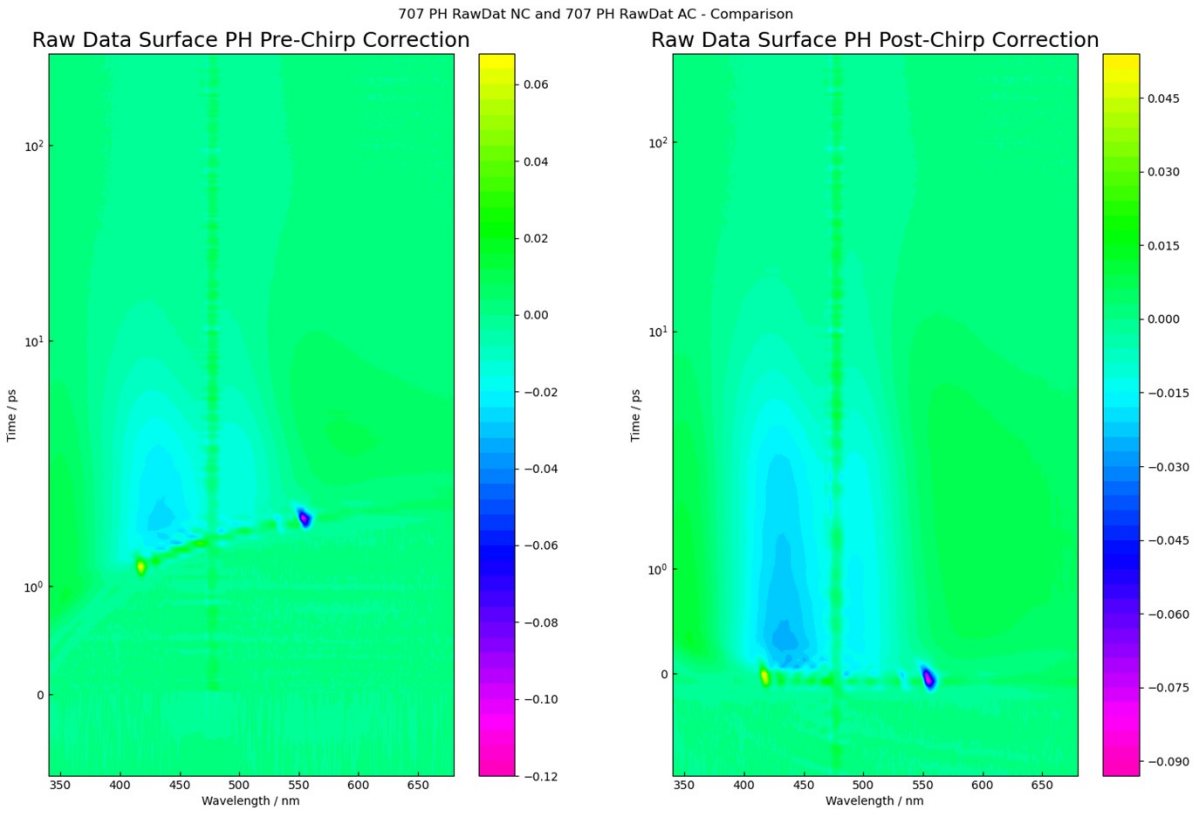


Figure S8. Heat map of **1H** TAS before (left), and after (right) chirp correction. Left) Raw pump-probe heat map at 475 nm excitation. x-axis = wavelength; y-axis = delay step position (exponential spacing); color map corresponds to ΔA. Right) corrected linear time pump-probe map at 475 nm excitation. x-axis = wavelength; y-axis = delay step position; color map corresponds to ΔA.

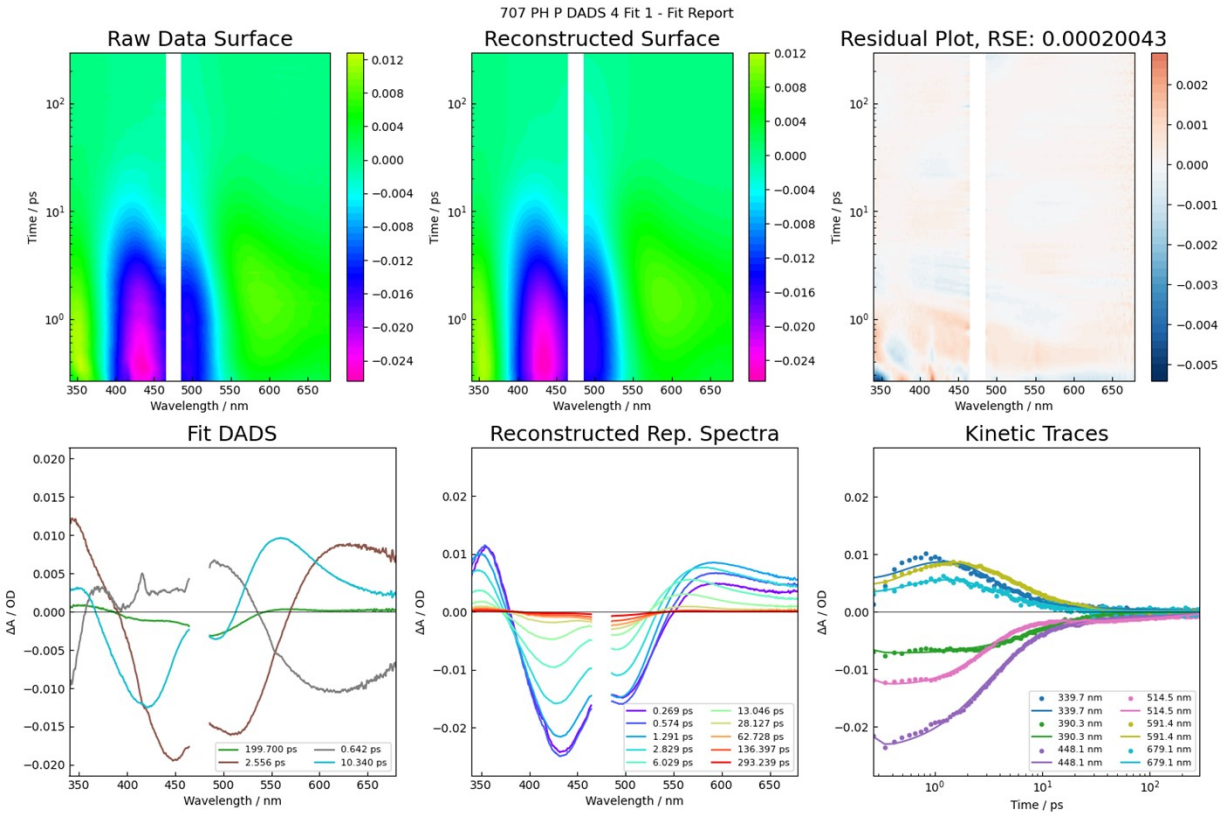


Figure S9. TAS data and fits of **1H** including: Top left) Chirp-corrected pump-probe heat map at 475 nm excitation. x-axis = wavelength; y-axis = delay step position; color map corresponds to ΔA. Top center) Reconstructed surfaces from fit DADS. Top right) Fit residual plots. Bottom right) SVD global fitting spectral components (DADS). Bottom center) Selected representative spectra depicting raw data surface. Bottom right) Single value kinetic traces of TAS data at select wavelengths.

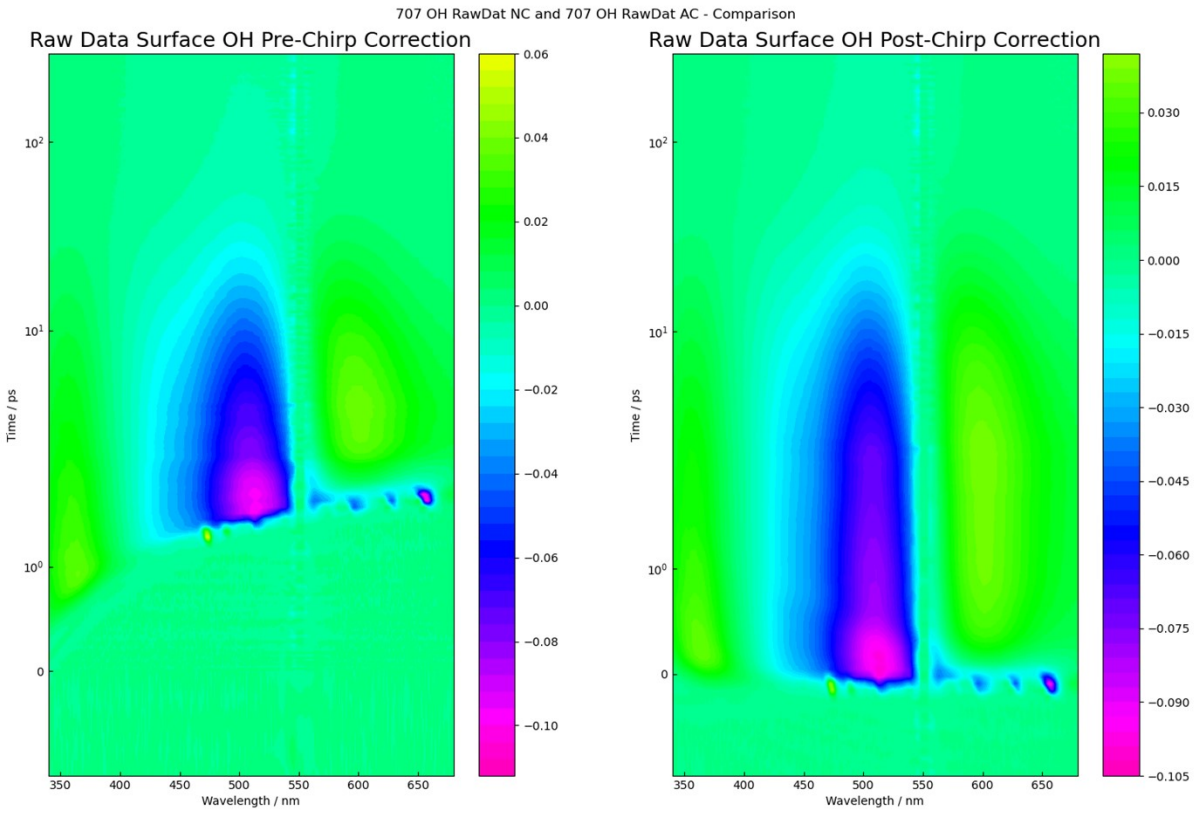


Figure S10. Heat map of **2H** TAS before (left), and after (right) chirp correction. Left) Raw pump-probe heat map at 550 nm excitation. x-axis = wavelength; y-axis = delay step position (exponential spacing); color map corresponds to ΔA. Right) corrected linear time pump-probe map at 550 nm excitation. x-axis = wavelength; y-axis = delay step position; color map corresponds to ΔA.

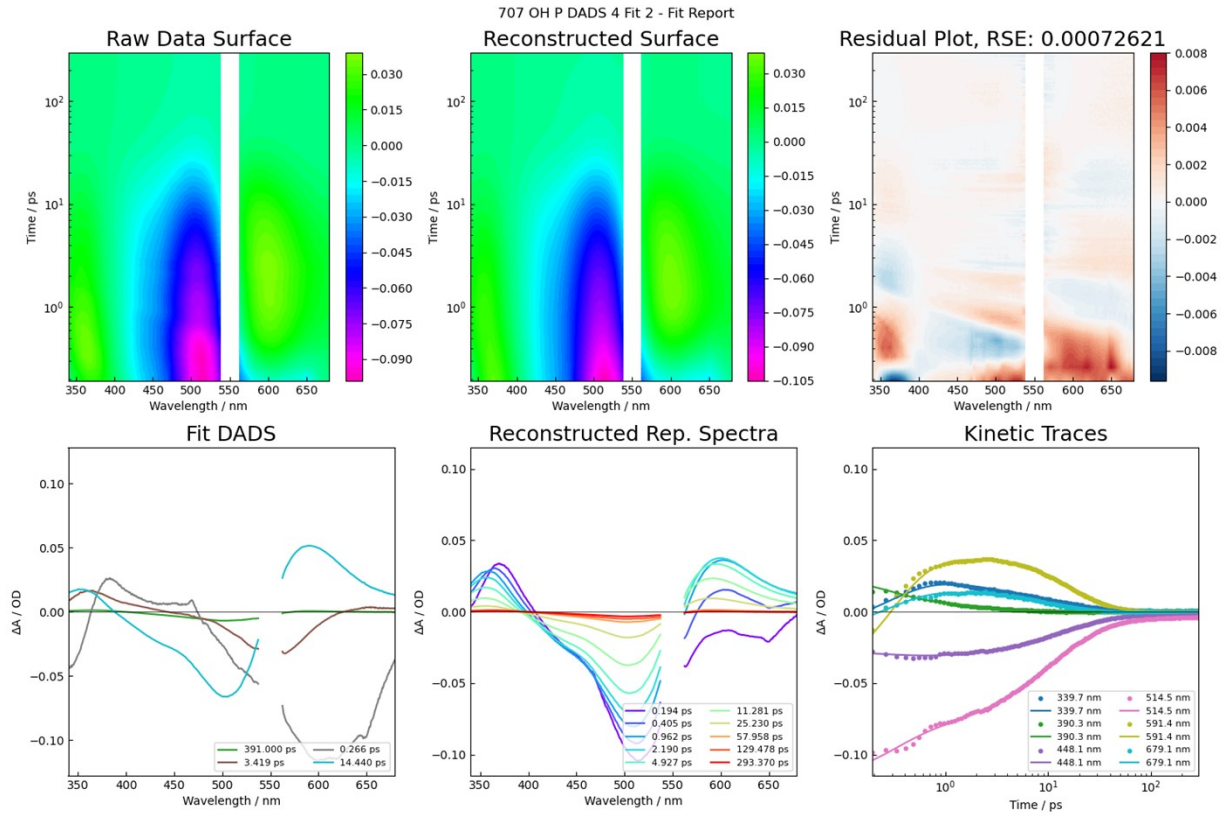


Figure S11. TAS data and fits of **2H** including: Top left) Chirp-corrected pump-probe heat map at 550 nm excitation. x-axis = wavelength; y-axis = delay step position; color map corresponds to ΔA. Top center) Reconstructed surfaces from fit DADS. Top right) Fit residual plots. Bottom right) SVD global fitting spectral components (DADS). Bottom center) Selected representative spectra depicting raw data surface. Bottom right) Single value kinetic traces of TAS data at select wavelengths.

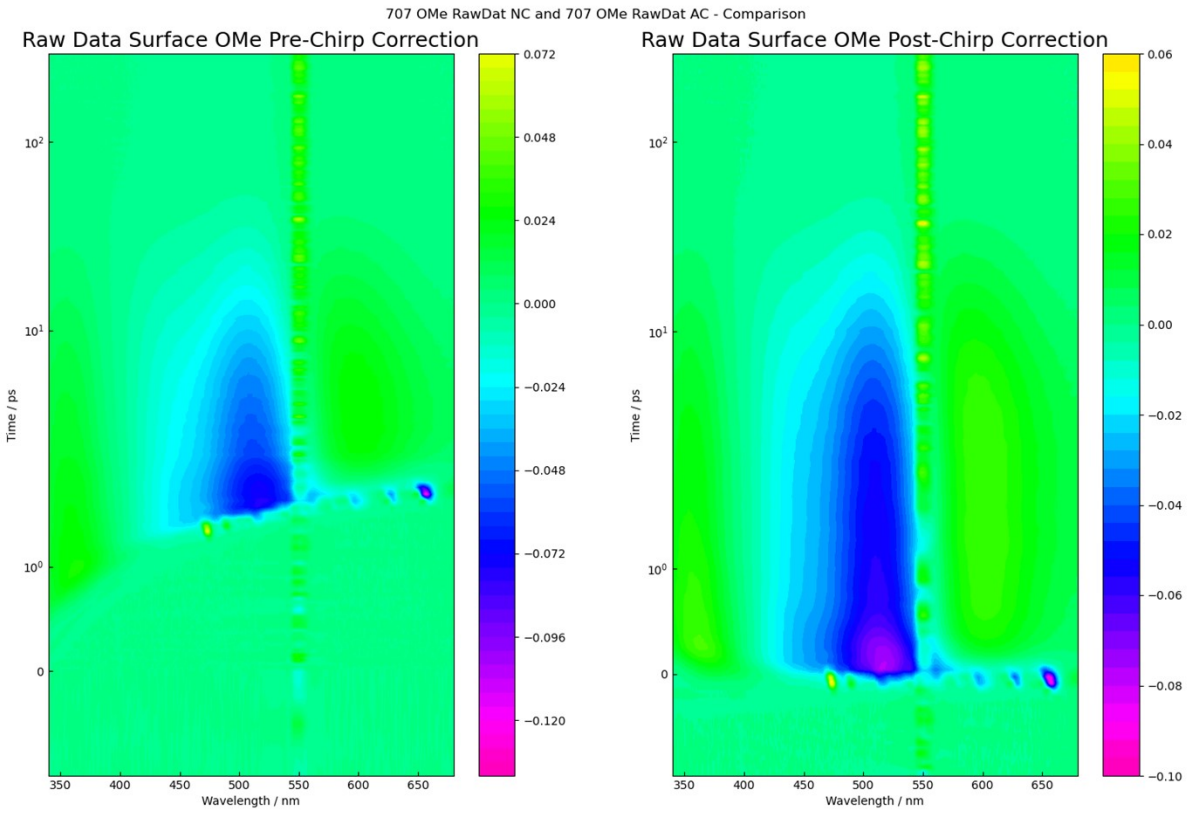


Figure S12. Heat map of **3H** TAS before (left), and after (right) chirp correction. Left) Raw pump-probe heat map at 550 nm excitation. x-axis = wavelength; y-axis = delay step position (exponential spacing); color map corresponds to ΔA. Right) corrected linear time pump-probe map at 550 nm excitation. x-axis = wavelength; y-axis = delay step position; color map corresponds to ΔA.

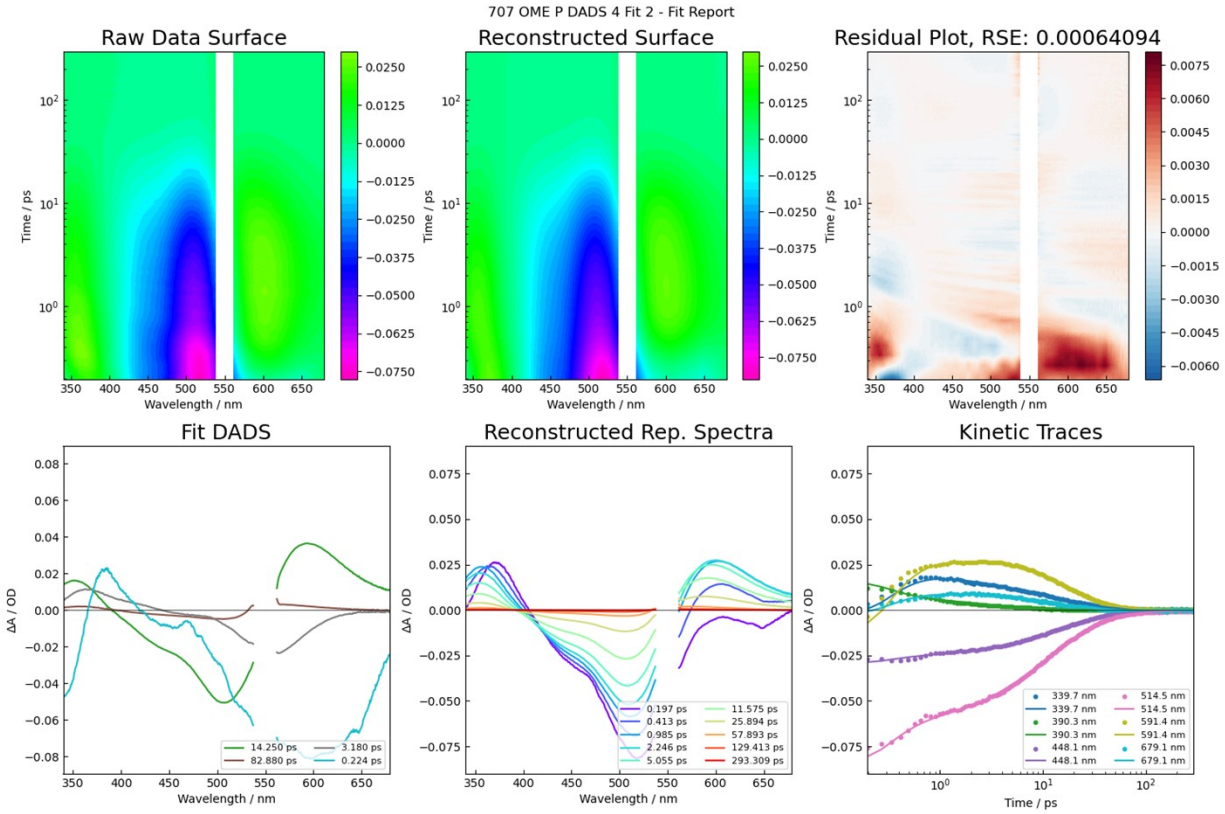


Figure S13. Heat map of **3H** TAS before (left), and after (right) chirp correction. Left) Raw pump-probe heat map at 590 nm excitation. x-axis = wavelength; y-axis = delay step position (exponential spacing); color map corresponds to ΔA. Right) corrected linear time pump-probe map at 590 nm excitation. x-axis = wavelength; y-axis = delay step position; color map corresponds to ΔA.

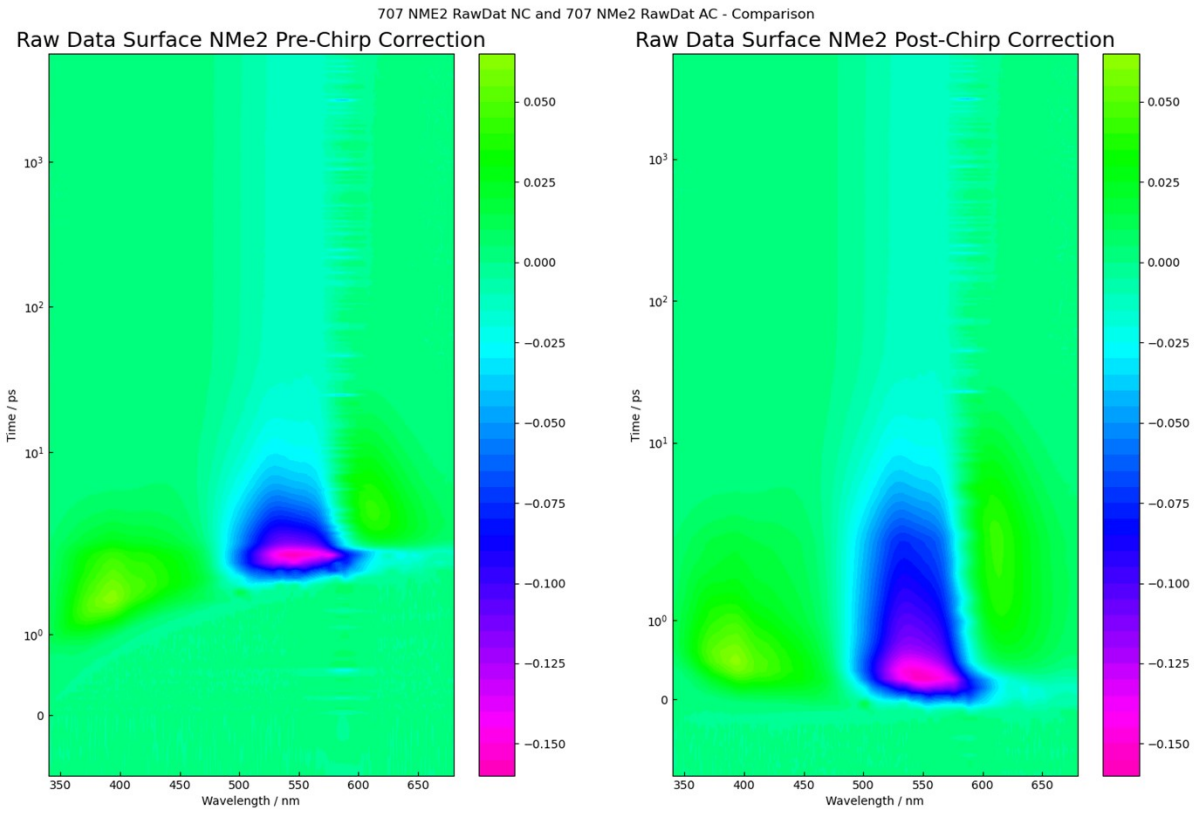


Figure S14. TAS data and fits of **4H** including: Top left) Chirp-corrected pump-probe heat map at 550 nm excitation. x-axis = wavelength; y-axis = delay step position; color map corresponds to ΔA. Top center) Reconstructed surfaces from fit DADS. Top right) Fit residual plots. Bottom right) SVD global fitting spectral components (DADS). Bottom center) Selected representative spectra depicting raw data surface. Bottom right) Single value kinetic traces of TAS data at select wavelengths.

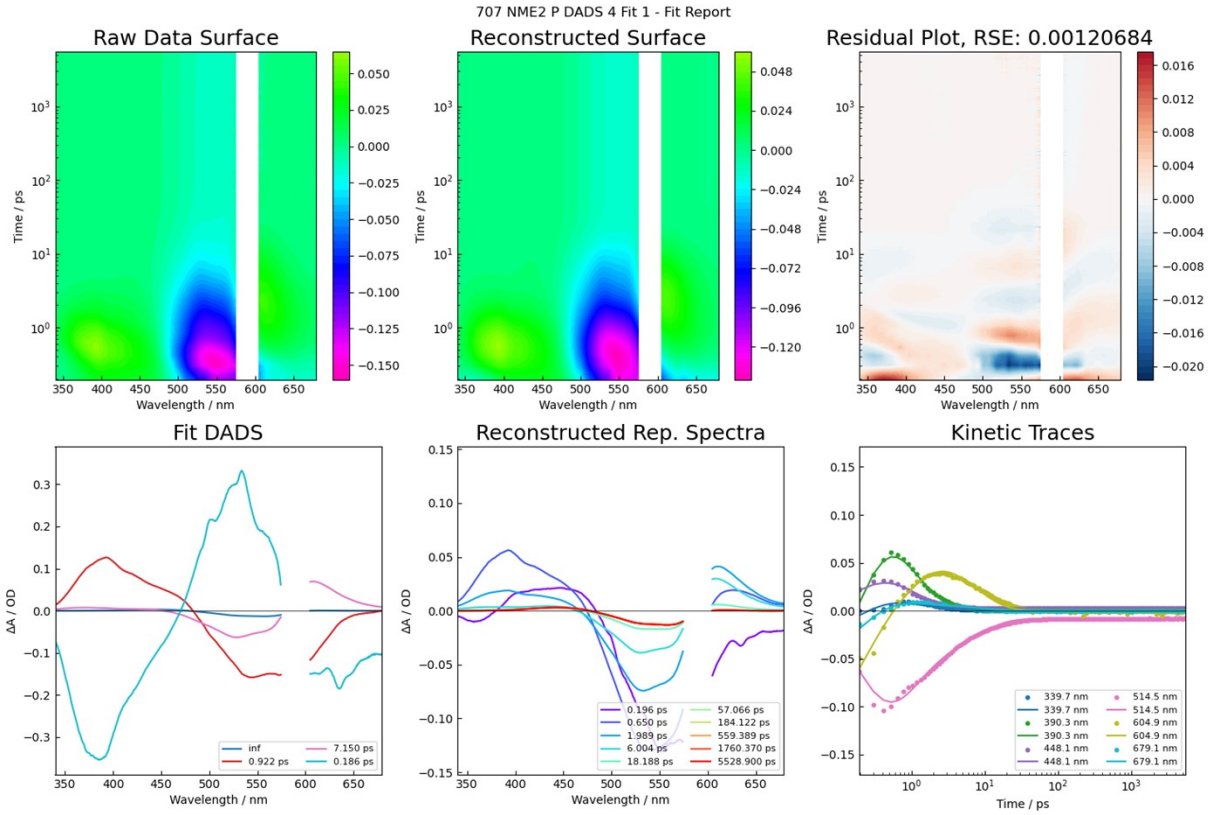


Figure S15. TAS data and fits of **4H** including: Top left) Chirp-corrected pump-probe heat map at 585 nm excitation. x-axis = wavelength; y-axis = delay step position; color map corresponds to ΔA. Top center) Reconstructed surfaces from fit DADS. Top right) Fit residual plots. Bottom right) SVD global fitting spectral components (DADS). Bottom center) Selected representative spectra depicting raw data surface. Bottom right) Single value kinetic traces of TAS data at select wavelengths.

## Computational Results

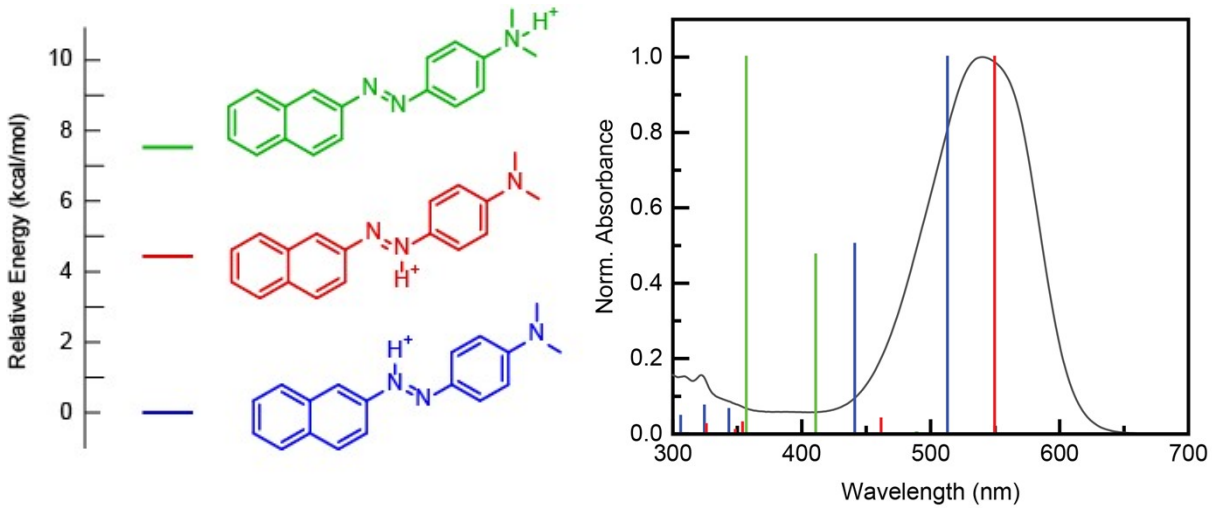


Figure S16. DFT relative energies of 4H protonated at each of the three nitrogen sites and the TDDFT predicted transitions for each protonation site in comparison to the experimental absorption spectrum.

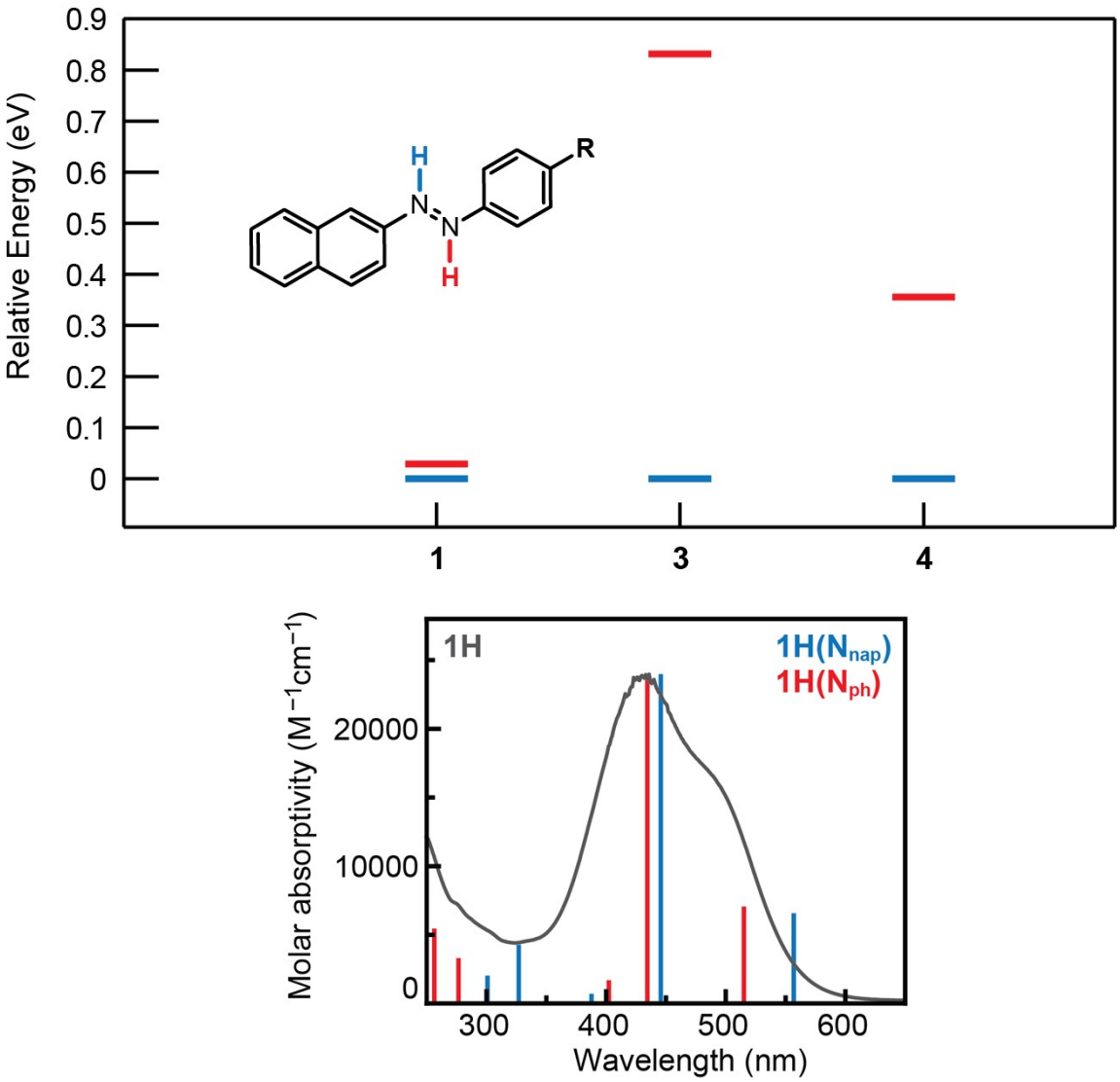


Figure S17. (top) Relative energies of the naphthalene-adjacent and phenyl-adjacent protonated **1**, **3**, and **4**. (bottom) TDDFT predicted transitions for the naphthalene-adjacent and phenyl-adjacent protonated **1H**. Relative SCF energies and TDDFT transitions of dyes protonated at the naphthalene-adjacent azo bond site are shown in blue, and those at the phenyl-adjacent azo bond site are shown in red. B3LYP/6-311G(d.p)/PCM(ACN)

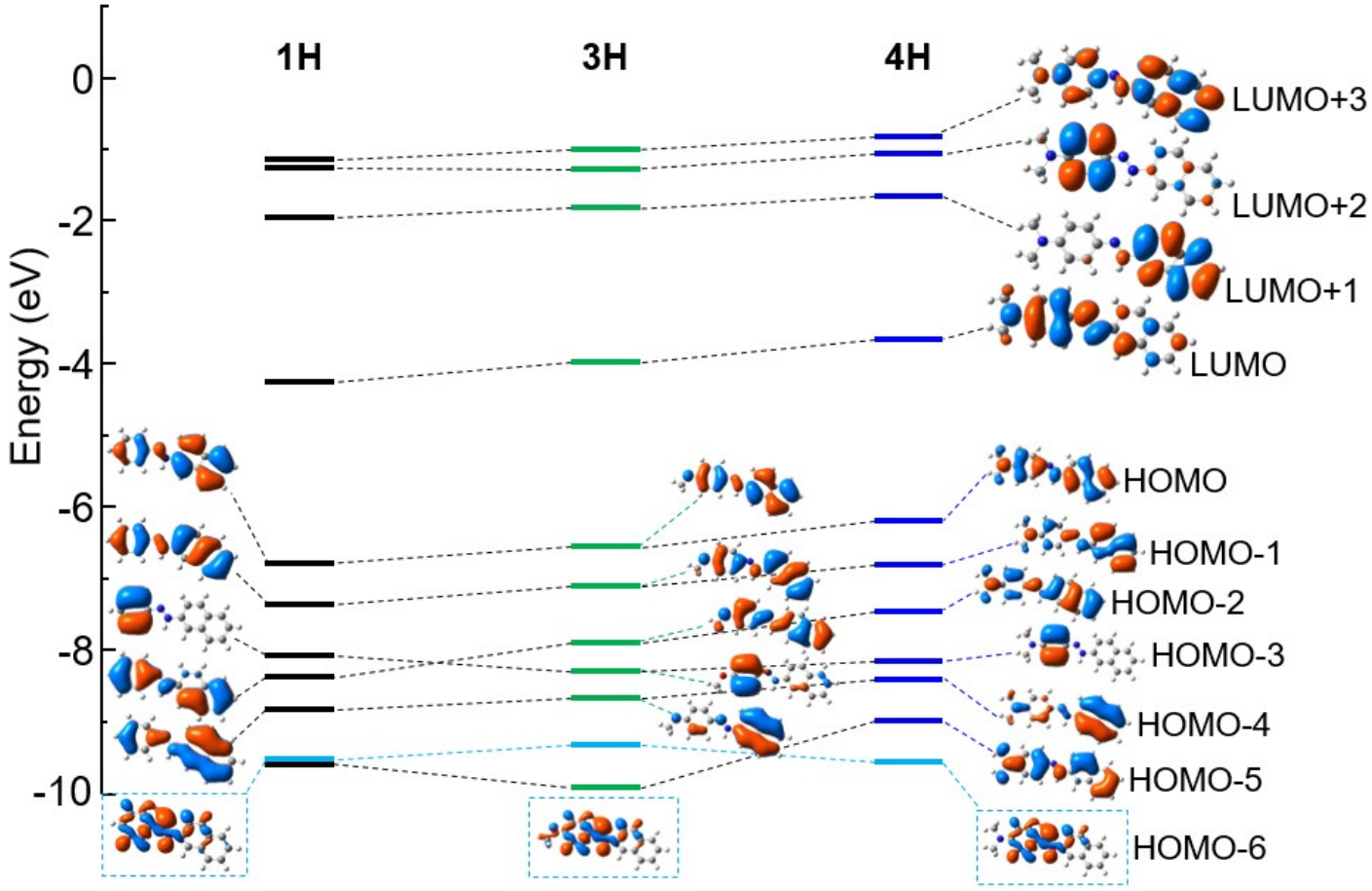


Figure S18. MO diagram for 1H, 3H, and 4H. B3LYP/6-311G(d.p)/PCM(ACN)

Potential Energy Curves of **1**, **1H**, **3**, **3H** and **4**, **4H**.

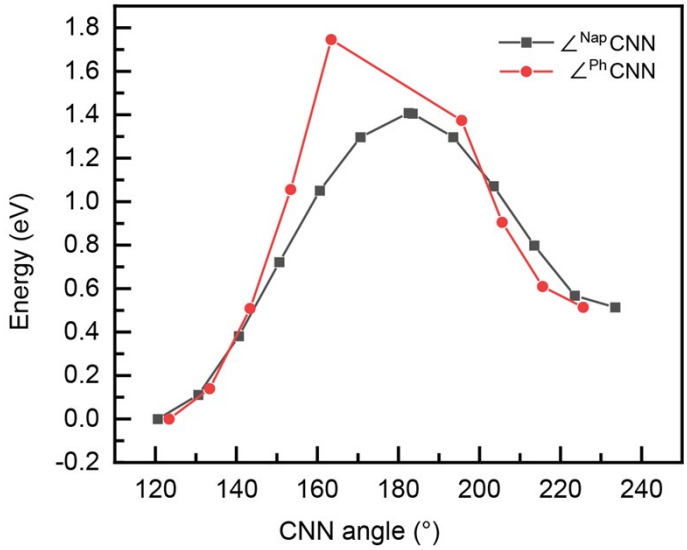


Figure S19. Comparison of the potential energy surfaces of **1H** along the phenyl and naphthalene moieties inversion (∠$^{Ph}$CNN and ∠$^{Nap}$CNN) *trans-cis* isomerization pathway. B3LYP/6-311G(d,p)/PCM(ACN).

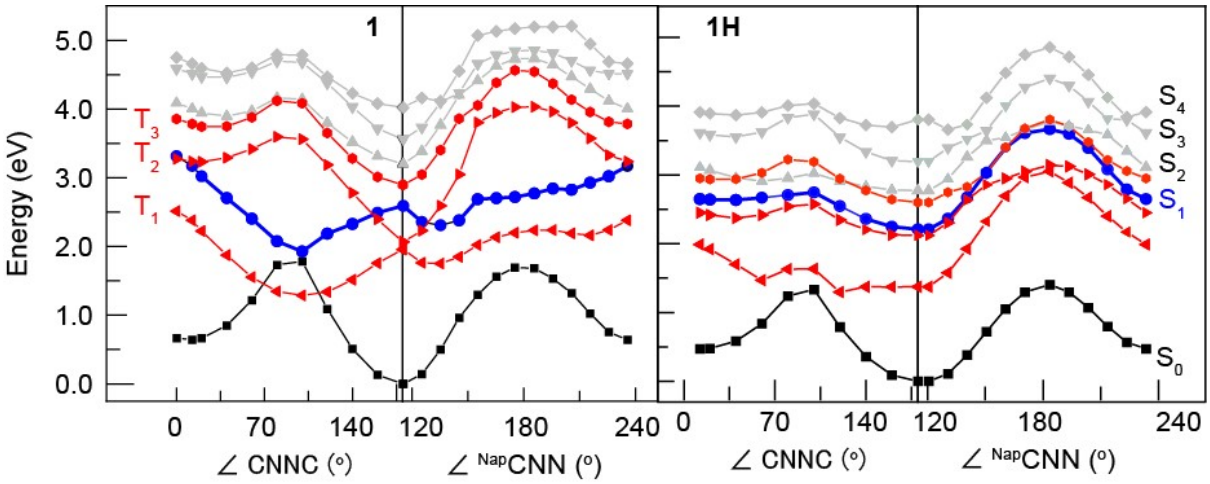


Figure S20. Comparison of the potential energy surfaces of **1** and **1H** along the torsional (∠CNNC) and inversion (∠$^{Nap}$CNN) *trans-cis* isomerization pathway. B3LYP/6-311G(d,p)/PCM(ACN). The $S_1$ PEC curve is emphasized with a bold, blue line (circle data points). Other singlet excited states are show in grey, and triplet states are red.

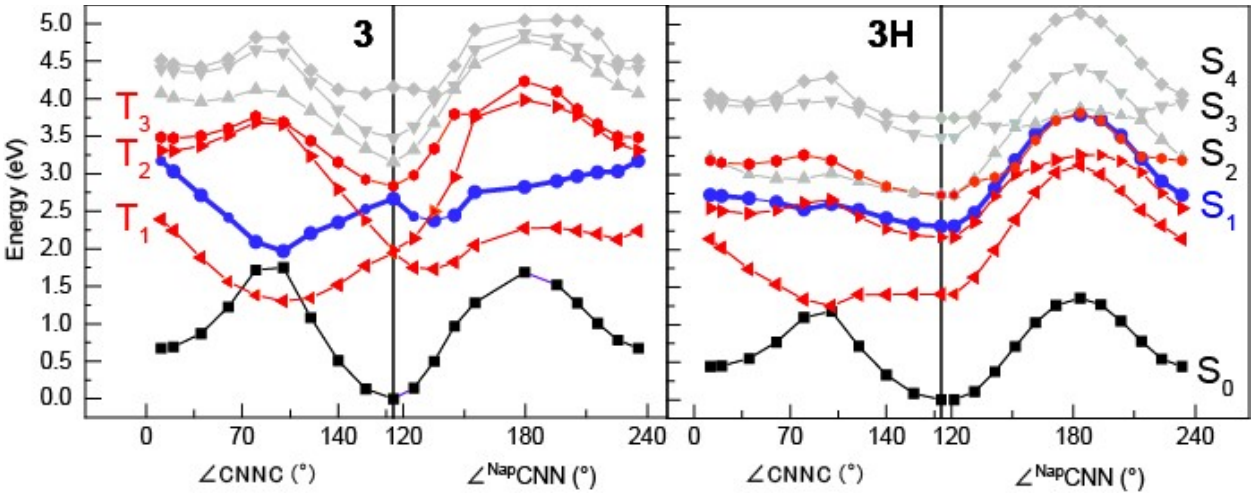


Figure S21. Comparison of the potential energy surfaces of **3** and **3H** along the torsional (∠CNNC) and inversion (∠$^{Nap}$CNN) *trans-cis* isomerization pathway. B3LYP/6-311G(d,p)/PCM(ACN). The $S_1$ PEC curve is emphasized with a bold, blue line (circle data points). Other singlet excited states are show in grey, and triplet states are red.

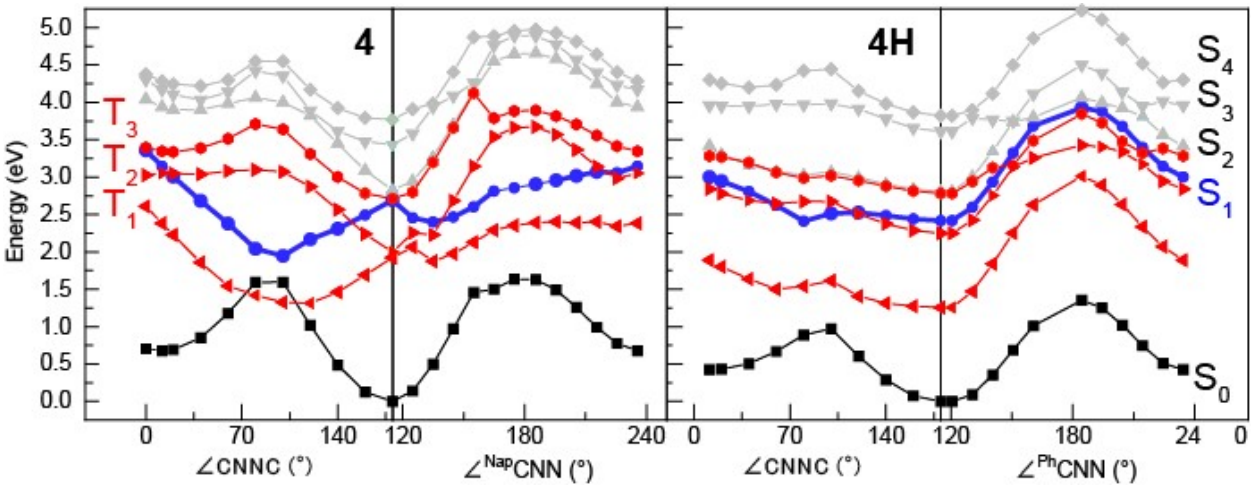


Figure S22. Comparison of the potential energy surfaces of **4** and **4H** along the torsional (∠CNNC) and inversion (∠$^{Nap}$CNN) *trans-cis* isomerization pathway. B3LYP/6-311G(d,p)/PCM(ACN). The $S_1$ PEC curve is emphasized with a bold, blue line (circle data points). Other singlet excited states are show in grey, and triplet states are red.

TDDFT tables

Table S2: TDDFT energies of singlet excitations for 1H in its optimized ground state geometry

| Excited States | Energy (eV) | Wavelength (nm) | Oscillator Strength | Transition | Transition Contribution |
|---|---|---|---|---|---|
| 1 | 2.2095 | 561.14 | f=0.2392 | HOMO-1 -> LUMO | -0.25619 |
| | | | | HOMO -> LUMO | 0.65781 |
| 2 | 2.7710 | 447.43 | f=0.8816 | HOMO-1 -> LUMO | 0.65559 |
| | | | | HOMO -> LUMO | 0.26224 |
| 3 | 3.1923 | 388.39 | f=0.0225 | HOMO-2 -> LUMO | 0.70108 |
| 4 | 3.8023 | 326.08 | f=0.1547 | HOMO-4 -> LUMO | -0.25140 |
| | | | | HOMO-3 -> LUMO | 0.64090 |
| 5 | 3.9614 | 312.98 | f=0.0013 | HOMO-5 -> LUMO | 0.69661 |
| 6 | 4.1403 | 299.45 | f=0.0715 | HOMO-4 -> LUMO | 0.64720 |
| | | | | HOMO-3 -> LUMO | 0.22733 |
| 7 | 4.4018 | 281.66 | f=0.0687 | HOMO-3 -> LUMO | -0.10123 |
| | | | | HOMO-1 -> LUMO+1 | 0.11853 |
| | | | | HOMO-1 -> LUMO+3 | 0.12029 |
| | | | | HOMO -> LUMO+1 | 0.66190 |
| 8 | 4.6461 | 266.86 | f=0.0592 | HOMO-1 -> LUMO+1 | 0.51284 |
| | | | | HOMO -> LUMO+1 | -0.13863 |
| | | | | HOMO -> LUMO+2 | 0.17230 |
| | | | | HOMO -> LUMO+3 | -0.40979 |
| 9 | 4.9631 | 249.81 | f=0.0000 | HOMO-7 -> LUMO | 0.69483 |
| 10 | 5.1302 | 241.68 | f=0.0725 | HOMO-6 -> LUMO | 0.53293 |
| | | | | HOMO -> LUMO+2 | 0.41146 |
| | | | | HOMO -> LUMO+3 | 0.10245 |
| 11 | 5.1655 | 240.02 | f=0.0055 | HOMO-6 -> LUMO | -0.41803 |
| | | | | HOMO -> LUMO+2 | 0.51482 |
| | | | | HOMO -> LUMO+3 | 0.16708 |
| 12 | 5.3244 | 232.86 | f=0.0000 | HOMO-9 -> LUMO | 0.20730 |
| | | | | HOMO-8 -> LUMO | 0.66602 |
| 13 | 5.4228 | 228.64 | f=0.0000 | HOMO-9 -> LUMO | 0.66610 |
| | | | | HOMO-8 -> LUMO | -0.21036 |
| 14 | 5.5772 | 222.31 | f=0.4155 | HOMO-3 -> LUMO+1 | -0.27699 |
| | | | | HOMO-1 -> LUMO+1 | 0.35205 |
| | | | | HOMO-1 -> LUMO+2 | -0.24231 |
| | | | | HOMO -> LUMO+3 | 0.40505 |
| | | | | HOMO -> LUMO+5 | -0.14543 |
| 15 | 5.6834 | 218.15 | f=0.0272 | HOMO-3 -> LUMO+1 | -0.16407 |
| | | | | HOMO-2 -> LUMO+1 | -0.37264 |
| | | | | HOMO-2 -> LUMO+3 | -0.11248 |
| | | | | HOMO-1 -> LUMO+1 | 0.12037 |

| | | | | | |
|---|---|---|---|---|---|
| | | | | HOMO-1 -> LUMO+2 | 0.50027 |
| | | | | HOMO -> LUMO+2 | -0.10907 |
| 16 | 5.7542 | 215.47 | f=0.0073 | HOMO-3 -> LUMO+1 | -0.22127 |
| | | | | HOMO-2 -> LUMO+1 | 0.56431 |
| | | | | HOMO-1 -> LUMO+2 | 0.26882 |
| | | | | HOMO -> LUMO+4 | 0.14293 |
| | | | | HOMO -> LUMO+5 | -0.14938 |
| 17 | 5.7798 | 214.51 | f=0.0007 | HOMO-12 -> LUMO | 0.10201 |
| | | | | HOMO-10 -> LUMO | 0.69409 |
| 18 | 5.7931 | 214.02 | f=0.0963 | HOMO-4 -> LUMO+1 | 0.15108 |
| | | | | HOMO-3 -> LUMO+1 | -0.27682 |
| | | | | HOMO-2 -> LUMO+1 | -0.19267 |
| | | | | HOMO-1 -> LUMO+1 | -0.13762 |
| | | | | HOMO-1 -> LUMO+2 | -0.22905 |
| | | | | HOMO -> LUMO+3 | -0.24290 |
| | | | | HOMO -> LUMO+4 | 0.34912 |
| | | | | HOMO -> LUMO+5 | -0.28608 |
| 19 | 5.8984 | 210.20 | f=0.0497 | HOMO-4 -> LUMO+1 | 0.18147 |
| | | | | HOMO-3 -> LUMO+1 | 0.16138 |
| | | | | HOMO-2 -> LUMO+2 | 0.13562 |
| | | | | HOMO-1 -> LUMO+3 | 0.52011 |
| | | | | HOMO -> LUMO+4 | -0.19798 |
| | | | | HOMO -> LUMO+5 | -0.27124 |
| 20 | 6.0081 | 206.36 | f=0.1838 | HOMO-11 -> LUMO | -0.11779 |
| | | | | HOMO-4 -> LUMO+1 | -0.18668 |
| | | | | HOMO-1 -> LUMO+1 | 0.13415 |
| | | | | HOMO-1 -> LUMO+3 | 0.34317 |
| | | | | HOMO -> LUMO+4 | 0.40391 |
| | | | | HOMO -> LUMO+5 | 0.33563 |
| 21 | 6.1651 | 201.11 | f=0.0001 | HOMO-12 -> LUMO | 0.68836 |
| 22 | 6.1774 | 200.70 | f=0.2293 | HOMO-11 -> LUMO | -0.33191 |
| | | | | HOMO-3 -> LUMO+1 | 0.39707 |
| | | | | HOMO-1 -> LUMO+3 | -0.20712 |
| | | | | HOMO-1 -> LUMO+5 | 0.13118 |
| | | | | HOMO -> LUMO+4 | 0.24783 |
| | | | | HOMO -> LUMO+5 | -0.22715 |
| 23 | 6.2203 | 199.32 | f=0.0487 | HOMO-11 -> LUMO | 0.51886 |
| | | | | HOMO-4 -> LUMO+1 | 0.16164 |
| | | | | HOMO-3 -> LUMO+1 | 0.20251 |
| | | | | HOMO-2 -> LUMO+2 | -0.19636 |
| | | | | HOMO-2 -> LUMO+3 | -0.17768 |
| | | | | HOMO-1 -> LUMO+1 | 0.12773 |
| | | | | HOMO -> LUMO+3 | 0.15161 |
| | | | | HOMO -> LUMO+4 | 0.12553 |

| | | | | | |
|---|---|---|---|---|---|
| 24 | 6.3270 | 195.96 | f=0.0410 | HOMO-4 -> LUMO+1 | -0.11018 |
| | | | | HOMO-4 -> LUMO+3 | 0.13572 |
| | | | | HOMO-3 -> LUMO+2 | 0.37621 |
| | | | | HOMO-2 -> LUMO+3 | 0.31177 |
| | | | | HOMO-2 -> LUMO+4 | -0.12963 |
| | | | | HOMO-1 -> LUMO+2 | 0.17503 |
| | | | | HOMO-1 -> LUMO+5 | -0.27821 |
| | | | | HOMO -> LUMO+4 | 0.15319 |
| | | | | HOMO -> LUMO+5 | -0.12534 |
| 25 | 6.3499 | 195.25 | f=0.0021 | HOMO-4 -> LUMO+1 | 0.18474 |
| | | | | HOMO-4 -> LUMO+2 | 0.13870 |
| | | | | HOMO-4 -> LUMO+3 | -0.13801 |
| | | | | HOMO-3 -> LUMO+2 | 0.15849 |
| | | | | HOMO-3 -> LUMO+3 | 0.23060 |
| | | | | HOMO-2 -> LUMO+3 | 0.26920 |
| | | | | HOMO-1 -> LUMO+2 | 0.11920 |
| | | | | HOMO-1 -> LUMO+4 | -0.22447 |
| | | | | HOMO-1 -> LUMO+5 | 0.40831 |
| 26 | 6.5103 | 190.44 | f=0.0075 | HOMO-13 -> LUMO | 0.19554 |
| | | | | HOMO-4 -> LUMO+1 | 0.50070 |
| | | | | HOMO-3 -> LUMO+2 | 0.10618 |
| | | | | HOMO-3 -> LUMO+3 | -0.20446 |
| | | | | HOMO-1 -> LUMO+4 | 0.21905 |
| | | | | HOMO -> LUMO+5 | 0.27898 |
| 27 | 6.5289 | 189.90 | f=0.1142 | HOMO-13 -> LUMO | -0.10004 |
| | | | | HOMO-4 -> LUMO+1 | -0.13700 |
| | | | | HOMO-3 -> LUMO+3 | 0.15606 |
| | | | | HOMO-2 -> LUMO+2 | -0.30302 |
| | | | | HOMO-1 -> LUMO+3 | 0.11783 |
| | | | | HOMO-1 -> LUMO+4 | 0.51557 |
| | | | | HOMO-1 -> LUMO+5 | 0.18633 |
| 28 | 6.5671 | 188.80 | f=0.0010 | HOMO -> LUMO+6 | 0.69595 |
| 29 | 6.7102 | 184.77 | f=0.0409 | HOMO-3 -> LUMO+2 | 0.30623 |
| | | | | HOMO-3 -> LUMO+3 | -0.11024 |
| | | | | HOMO-2 -> LUMO+2 | 0.34523 |
| | | | | HOMO-2 -> LUMO+3 | -0.32735 |
| | | | | HOMO-2 -> LUMO+4 | -0.23277 |
| | | | | HOMO-1 -> LUMO+4 | 0.17694 |
| | | | | HOMO-1 -> LUMO+5 | 0.16842 |
| 30 | 6.7569 | 183.49 | f=0.0000 | HOMO-7 -> LUMO+1 | 0.53299 |
| | | | | HOMO-5 -> LUMO+1 | 0.45007 |

Table S3: TDDFT energies of singlet excitations for 3H in its optimized ground state geometry

| Excited States | Energy (eV) | Wavelength (nm) | Oscillator Strength | Transition | Transition Contribution |
|---|---|---|---|---|---|
| 1 | 2.3111 | 536.48 | f=0.4743 | HOMO-1 -> LUMO | -0.26084 |
| | | | | HOMO -> LUMO | 0.65647 |
| 2 | 2.7364 | 453.09 | f=0.8251 | HOMO-2 -> LUMO | -0.10207 |
| | | | | HOMO-1 -> LUMO | 0.64579 |
| | | | | HOMO -> LUMO | 0.26782 |
| 3 | 3.4943 | 354.82 | f=0.0138 | HOMO-3 -> LUMO | 0.50929 |
| | | | | HOMO-2 -> LUMO | 0.47470 |
| 4 | 3.7579 | 329.93 | f=0.1671 | HOMO-4 -> LUMO | -0.12121 |
| | | | | HOMO-3 -> LUMO | -0.47249 |
| | | | | HOMO-2 -> LUMO | 0.47497 |
| | | | | HOMO-1 -> LUMO | 0.10087 |
| 5 | 4.0746 | 304.29 | f=0.0013 | HOMO-5 -> LUMO | 0.69507 |
| 6 | 4.1547 | 298.42 | f=0.0052 | HOMO-4 -> LUMO | 0.66387 |
| | | | | HOMO-2 -> LUMO | 0.12975 |
| | | | | HOMO -> LUMO+1 | 0.16360 |
| 7 | 4.2889 | 289.08 | f=0.0569 | HOMO-4 -> LUMO | -0.16846 |
| | | | | HOMO-1 -> LUMO+3 | 0.11685 |
| | | | | HOMO -> LUMO+1 | 0.64656 |
| | | | | HOMO -> LUMO+3 | -0.10407 |
| 8 | 4.5887 | 270.20 | f=0.0620 | HOMO-2 -> LUMO+1 | -0.11519 |
| | | | | HOMO-1 -> LUMO+1 | 0.51886 |
| | | | | HOMO -> LUMO+1 | -0.14814 |
| | | | | HOMO -> LUMO+2 | 0.19988 |
| | | | | HOMO -> LUMO+3 | -0.37049 |
| 9 | 4.8784 | 254.15 | f=0.1698 | HOMO-6 -> LUMO | 0.13326 |
| | | | | HOMO-1 -> LUMO+1 | -0.15161 |
| | | | | HOMO -> LUMO+2 | 0.64328 |
| | | | | HOMO -> LUMO+3 | 0.12520 |
| 10 | 5.0114 | 247.41 | f=0.0282 | HOMO-6 -> LUMO | 0.66144 |
| | | | | HOMO -> LUMO+2 | -0.11549 |
| | | | | HOMO -> LUMO+3 | -0.13245 |
| 11 | 5.1169 | 242.31 | f=0.0000 | HOMO-8 -> LUMO | 0.60389 |
| | | | | HOMO-7 -> LUMO | 0.34312 |
| 12 | 5.1530 | 240.61 | f=0.0001 | HOMO-8 -> LUMO | -0.32804 |
| | | | | HOMO-7 -> LUMO | 0.60709 |
| 13 | 5.2856 | 234.57 | f=0.1604 | HOMO-6 -> LUMO | 0.10171 |
| | | | | HOMO-2 -> LUMO+1 | 0.44310 |
| | | | | HOMO-1 -> LUMO+1 | 0.34872 |
| | | | | HOMO-1 -> LUMO+2 | -0.11359 |

| | | | | | |
|---|---|---|---|---|---|
| | | | | HOMO-1 -> LUMO+3 | -0.13494 |
| | | | | HOMO -> LUMO+3 | 0.32390 |
| 14 | 5.3910 | 229.98 | f=0.0085 | HOMO-2 -> LUMO+1 | 0.16796 |
| | | | | HOMO-1 -> LUMO+2 | 0.65885 |
| 15 | 5.5222 | 224.52 | f=0.0000 | HOMO-9 -> LUMO | 0.69662 |
| 16 | 5.6605 | 219.03 | f=0.1316 | HOMO-10 -> LUMO | -0.23783 |
| | | | | HOMO-3 -> LUMO+2 | -0.10267 |
| | | | | HOMO-2 -> LUMO+1 | -0.25293 |
| | | | | HOMO-1 -> LUMO+1 | 0.12574 |
| | | | | HOMO-1 -> LUMO+3 | 0.40381 |
| | | | | HOMO -> LUMO+3 | 0.34369 |
| | | | | HOMO -> LUMO+4 | -0.14471 |
| 17 | 5.7744 | 214.71 | f=0.0924 | HOMO-10 -> LUMO | -0.14481 |
| | | | | HOMO-4 -> LUMO+1 | 0.28872 |
| | | | | HOMO-1 -> LUMO+3 | -0.26659 |
| | | | | HOMO -> LUMO+4 | -0.27400 |
| | | | | HOMO -> LUMO+5 | 0.44848 |
| 18 | 5.8204 | 213.02 | f=0.0398 | HOMO-10 -> LUMO | 0.63239 |
| | | | | HOMO -> LUMO+3 | 0.16603 |
| 19 | 5.9071 | 209.89 | f=0.0831 | HOMO-4 -> LUMO+1 | 0.15872 |
| | | | | HOMO-3 -> LUMO+1 | 0.14154 |
| | | | | HOMO-2 -> LUMO+1 | 0.22990 |
| | | | | HOMO-1 -> LUMO+3 | 0.37677 |
| | | | | HOMO -> LUMO+4 | 0.31490 |
| | | | | HOMO -> LUMO+5 | 0.35310 |
| 20 | 6.0099 | 206.30 | f=0.0861 | HOMO-3 -> LUMO+1 | 0.55756 |
| | | | | HOMO-2 -> LUMO+1 | 0.21674 |
| | | | | HOMO -> LUMO+4 | -0.28410 |
| | | | | HOMO -> LUMO+5 | -0.16792 |
| 21 | 6.0552 | 204.76 | f=0.1322 | HOMO-3 -> LUMO+1 | 0.26787 |
| | | | | HOMO-2 -> LUMO+1 | -0.19374 |
| | | | | HOMO-2 -> LUMO+2 | 0.48037 |
| | | | | HOMO-1 -> LUMO+3 | -0.13036 |
| | | | | HOMO-1 -> LUMO+5 | 0.13135 |
| | | | | HOMO -> LUMO+3 | 0.10340 |
| | | | | HOMO -> LUMO+4 | 0.23879 |
| 22 | 6.1169 | 202.69 | f=0.0000 | HOMO-4 -> LUMO | -0.37995 |
| | | | | HOMO-11 -> LUMO | 0.57976 |
| 23 | 6.1299 | 202.26 | f=0.3199 | HOMO-3 -> LUMO+1 | -0.27303 |
| | | | | HOMO-3 -> LUMO+2 | -0.14157 |
| | | | | HOMO-2 -> LUMO+1 | 0.17433 |
| | | | | HOMO-2 -> LUMO+2 | 0.44235 |
| | | | | HOMO-1 -> LUMO+2 | -0.10093 |
| | | | | HOMO-1 -> LUMO+3 | 0.17952 |

| | | | | | |
|---|---|---|---|---|---|
| | | | | HOMO -> LUMO+4 | -0.31335 |
| 24 | 6.2149 | 199.49 | f=0.0170 | HOMO-4 -> LUMO+1 | -0.29417 |
| | | | | HOMO-4 -> LUMO+3 | 0.18957 |
| | | | | HOMO-2 -> LUMO+3 | -0.20044 |
| | | | | HOMO-2 -> LUMO+5 | -0.10660 |
| | | | | HOMO-1 -> LUMO+4 | -0.23149 |
| | | | | HOMO-1 -> LUMO+5 | 0.41870 |
| | | | | HOMO -> LUMO+4 | -0.11835 |
| | | | | HOMO -> LUMO+5 | 0.21012 |
| 25 | 6.3426 | 195.48 | f=0.0000 | HOMO-12 -> LUMO | 0.57903 |
| | | | | HOMO-11 -> LUMO | 0.38486 |
| 26 | 6.3835 | 194.23 | f=0.0006 | HOMO -> LUMO+6 | 0.69608 |
| 27 | 6.4314 | 192.78 | f=0.0298 | HOMO-13 -> LUMO | 0.19919 |
| | | | | HOMO-4 -> LUMO+1 | 0.42805 |
| | | | | HOMO-3 -> LUMO+2 | -0.10710 |
| | | | | HOMO-2 -> LUMO+3 | -0.29477 |
| | | | | HOMO-1 -> LUMO+4 | -0.30872 |
| | | | | HOMO -> LUMO+5 | -0.21794 |
| 28 | 6.5122 | 190.39 | f=0.0861 | HOMO-13 -> LUMO | 0.17536 |
| | | | | HOMO-4 -> LUMO+1 | 0.14652 |
| | | | | HOMO-2 -> LUMO+3 | -0.15396 |
| | | | | HOMO-1 -> LUMO+4 | 0.54384 |
| | | | | HOMO-1 -> LUMO+5 | 0.29842 |
| 29 | 6.5439 | 189.46 | f=0.0286 | HOMO-14 -> LUMO | -0.14557 |
| | | | | HOMO-13 -> LUMO | -0.37052 |
| | | | | HOMO-3 -> LUMO+2 | 0.39275 |
| | | | | HOMO-2 -> LUMO+2 | 0.10826 |
| | | | | HOMO-2 -> LUMO+3 | -0.35850 |
| | | | | HOMO-1 -> LUMO+5 | -0.10782 |
| 30 | 6.6373 | 186.80 | f=0.1221 | HOMO-14 -> LUMO | -0.19888 |
| | | | | HOMO-13 -> LUMO | -0.29783 |
| | | | | HOMO-4 -> LUMO+1 | 0.24041 |
| | | | | HOMO-4 -> LUMO+2 | -0.10462 |
| | | | | HOMO-4 -> LUMO+3 | 0.15341 |
| | | | | HOMO-3 -> LUMO+2 | 0.10340 |
| | | | | HOMO-3 -> LUMO+3 | 0.11182 |
| | | | | HOMO-2 -> LUMO+3 | 0.38600 |
| | | | | HOMO-1 -> LUMO+5 | 0.23910 |
| | | | | HOMO -> LUMO+5 | -0.12615 |

Table S4: TDDFT energies of singlet excitations for **4H** in its optimized ground state geometry

| Excited States | Energy (eV) | Wavelength (nm) | Oscillator Strength | Transition | Transition Contribution |
|---|---|---|---|---|---|
| 1 | 2.4167 | 513.03 | f=1.0069 | HOMO-1 -> LUMO | -0.22713 |

| | | | | | |
|---|---|---|---|---|---|
| | | | | HOMO -> LUMO | 0.67122 |
| 2 | 2.8112 | 441.04 | f=0.5068 | HOMO-4 -> LUMO | -0.17628 |
| | | | | HOMO-1 -> LUMO | 0.64453 |
| | | | | HOMO -> LUMO | 0.22177 |
| 3 | 3.6105 | 343.40 | f=0.0656 | HOMO-5 -> LUMO | 0.22486 |
| | | | | HOMO-4 -> LUMO | 0.63572 |
| | | | | HOMO-1 -> LUMO | 0.13778 |
| 4 | 3.8219 | 324.41 | f=0.0749 | HOMO-5 -> LUMO | 0.66231 |
| | | | | HOMO-4 -> LUMO | -0.20084 |
| 5 | 4.0510 | 306.06 | f=0.0473 | HOMO-6 -> LUMO | -0.13029 |
| | | | | HOMO-1 -> LUMO+3 | 0.11625 |
| | | | | HOMO -> LUMO+1 | 0.66950 |
| 6 | 4.1711 | 297.25 | f=0.0013 | HOMO-8 -> LUMO | 0.70171 |
| 7 | 4.3327 | 286.16 | f=0.0052 | HOMO-6 -> LUMO | 0.67531 |
| | | | | HOMO -> LUMO+1 | 0.10706 |
| 8 | 4.5188 | 274.37 | f=0.0343 | HOMO-4 -> LUMO+1 | -0.12937 |
| | | | | HOMO-1 -> LUMO+1 | 0.38938 |
| | | | | HOMO -> LUMO+2 | 0.47530 |
| | | | | HOMO -> LUMO+3 | -0.25887 |
| 9 | 4.5854 | 270.39 | f=0.1621 | HOMO-1 -> LUMO+1 | -0.38529 |
| | | | | HOMO-1 -> LUMO+2 | 0.10404 |
| | | | | HOMO -> LUMO+2 | 0.48835 |
| | | | | HOMO -> LUMO+3 | 0.25733 |
| 10 | 4.8647 | 254.86 | f=0.0458 | HOMO-7 -> LUMO | 0.62945 |
| | | | | HOMO-4 -> LUMO+1 | -0.13088 |
| | | | | HOMO-1 -> LUMO+3 | 0.10120 |
| | | | | HOMO -> LUMO+3 | -0.18531 |
| 11 | 4.9988 | 248.03 | f=0.0348 | HOMO-7 -> LUMO | 0.25250 |
| | | | | HOMO-4 -> LUMO+1 | 0.44418 |
| | | | | HOMO-1 -> LUMO+1 | 0.34640 |
| | | | | HOMO-1 -> LUMO+3 | -0.17141 |
| | | | | HOMO -> LUMO+3 | 0.24012 |
| 12 | 5.2622 | 235.61 | f=0.0428 | HOMO-4 -> LUMO+1 | 0.13100 |
| | | | | HOMO-1 -> LUMO+2 | 0.60472 |
| | | | | HOMO-1 -> LUMO+3 | -0.10764 |
| | | | | HOMO -> LUMO+3 | -0.27063 |
| 13 | 5.3663 | 231.04 | f=0.1153 | HOMO-4 -> LUMO+1 | -0.22543 |
| | | | | HOMO-1 -> LUMO+1 | 0.14158 |
| | | | | HOMO-1 -> LUMO+2 | 0.30716 |
| | | | | HOMO-1 -> LUMO+3 | 0.38778 |
| | | | | HOMO -> LUMO+2 | -0.10346 |
| | | | | HOMO -> LUMO+3 | 0.36872 |
| 14 | 5.4078 | 229.27 | f=0.0000 | HOMO-9 -> LUMO | 0.69764 |
| 15 | 5.6534 | 219.31 | f=0.0356 | HOMO-6 -> LUMO+1 | 0.25289 |

| | | | | | |
|---|---|---|---|---|---|
| | | | | HOMO -> LUMO+4 | 0.47704 |
| | | | | HOMO -> LUMO+5 | 0.39768 |
| 16 | 5.6890 | 217.94 | f=0.0132 | HOMO-10 -> LUMO | 0.64474 |
| | | | | HOMO -> LUMO+4 | -0.16993 |
| | | | | HOMO -> LUMO+5 | 0.11883 |
| 17 | 5.7033 | 217.39 | f=0.0001 | HOMO-12 -> LUMO | 0.67925 |
| | | | | HOMO-11 -> LUMO | 0.13873 |
| 18 | 5.7965 | 213.89 | f=0.1140 | HOMO-10 -> LUMO | -0.19530 |
| | | | | HOMO-4 -> LUMO+1 | -0.21710 |
| | | | | HOMO-1 -> LUMO+3 | -0.36025 |
| | | | | HOMO -> LUMO+4 | -0.27238 |
| | | | | HOMO -> LUMO+5 | 0.41465 |
| 19 | 5.7972 | 213.87 | f=0.0000 | HOMO-12 -> LUMO | -0.13889 |
| | | | | HOMO-11 -> LUMO | 0.68569 |
| 20 | 5.8875 | 210.59 | f=0.0781 | HOMO-4 -> LUMO+1 | -0.14494 |
| | | | | HOMO-4 -> LUMO+2 | 0.61773 |
| | | | | HOMO-1 -> LUMO+3 | -0.11793 |
| | | | | HOMO -> LUMO+4 | 0.10193 |
| | | | | HOMO -> LUMO+5 | -0.14815 |
| 21 | 5.9716 | 207.62 | f=0.4423 | HOMO-6 -> LUMO+1 | -0.17505 |
| | | | | HOMO-4 -> LUMO+1 | 0.29581 |
| | | | | HOMO-4 -> LUMO+2 | 0.30265 |
| | | | | HOMO-1 -> LUMO+3 | 0.26015 |
| | | | | HOMO-1 -> LUMO+4 | 0.12436 |
| | | | | HOMO-1 -> LUMO+5 | 0.13103 |
| | | | | HOMO -> LUMO+4 | -0.20235 |
| | | | | HOMO -> LUMO+5 | 0.28207 |
| 22 | 6.0534 | 204.82 | f=0.1850 | HOMO-6 -> LUMO+1 | -0.28414 |
| | | | | HOMO-6 -> LUMO+3 | 0.10463 |
| | | | | HOMO-5 -> LUMO+1 | 0.34660 |
| | | | | HOMO-4 -> LUMO+1 | -0.12080 |
| | | | | HOMO-4 -> LUMO+3 | 0.15574 |
| | | | | HOMO-1 -> LUMO+3 | -0.19925 |
| | | | | HOMO-1 -> LUMO+4 | 0.29757 |
| | | | | HOMO-1 -> LUMO+5 | 0.18384 |
| | | | | HOMO -> LUMO+4 | 0.24453 |
| 23 | 6.0678 | 204.33 | f=0.0024 | HOMO-6 -> LUMO+1 | 0.21453 |
| | | | | HOMO-5 -> LUMO+1 | 0.60679 |
| | | | | HOMO-1 -> LUMO+4 | -0.17616 |
| | | | | HOMO-1 -> LUMO+5 | -0.14268 |
| 24 | 6.1117 | 202.86 | f=0.0001 | HOMO -> LUMO+6 | 0.69358 |
| | | | | HOMO -> LUMO+7 | 0.10048 |
| 25 | 6.3719 | 194.58 | f=0.1681 | HOMO-14 -> LUMO | -0.14949 |
| | | | | HOMO-6 -> LUMO+1 | 0.27458 |

| | | | | | |
|---|---|---|---|---|---|
| | | | | HOMO-4 -> LUMO+3 | 0.56640 |
| | | | | HOMO-1 -> LUMO+4 | 0.16122 |
| | | | | HOMO -> LUMO+4 | -0.13785 |
| 26 | 6.4479 | 192.28 | f=0.0419 | HOMO-14 -> LUMO | 0.15413 |
| | | | | HOMO-7 -> LUMO+1 | 0.11179 |
| | | | | HOMO-4 -> LUMO+3 | -0.11606 |
| | | | | HOMO-1 -> LUMO+4 | 0.44792 |
| | | | | HOMO-1 -> LUMO+5 | -0.44767 |
| 27 | 6.4845 | 191.20 | f=0.0083 | HOMO-14 -> LUMO | -0.19476 |
| | | | | HOMO-6 -> LUMO+1 | 0.36979 |
| | | | | HOMO-6 -> LUMO+3 | 0.10639 |
| | | | | HOMO-5 -> LUMO+2 | 0.13797 |
| | | | | HOMO-4 -> LUMO+3 | -0.28782 |
| | | | | HOMO-4 -> LUMO+5 | -0.10994 |
| | | | | HOMO-1 -> LUMO+4 | 0.24086 |
| | | | | HOMO-1 -> LUMO+5 | 0.31311 |
| | | | | HOMO -> LUMO+5 | -0.10802 |
| 28 | 6.5280 | 189.93 | f=0.0153 | HOMO-1 -> LUMO+7 | 0.12083 |
| | | | | HOMO -> LUMO+7 | 0.67487 |
| 29 | 6.5463 | 189.40 | f=0.1131 | HOMO-16 -> LUMO | -0.16666 |
| | | | | HOMO-14 -> LUMO | 0.43174 |
| | | | | HOMO-7 -> LUMO+1 | -0.11183 |
| | | | | HOMO-6 -> LUMO+1 | 0.16922 |
| | | | | HOMO-5 -> LUMO+2 | -0.38681 |
| | | | | HOMO-1 -> LUMO+5 | 0.22109 |
| 30 | 6.5804 | 188.41 | f=0.0000 | HOMO-13 -> LUMO | 0.66921 |
| | | | | HOMO-9 -> LUMO+1 | 0.13358 |
| | | | | HOMO-8 -> LUMO+1 | 0.13804 |

Table S1. TDDFT Energies of **1H** along the torsional ∠ CNNC of the S0 trans-cis isomerization.

| ∠ CNNC | S0 | S1 | S2 | S3 | S4 | T1 | T2 | T3 |
|---|---|---|---|---|---|---|---|---|
| 12.3 | 0.47336 | 2.64936 | 3.11046 | 3.60936 | 3.91156 | 1.98726 | 2.44966 | 2.94986 |
| 20 | 0.47877 | 2.64167 | 3.06787 | 3.58287 | 3.89217 | 1.91987 | 2.41717 | 2.93607 |
| 40 | 0.58447 | 2.63447 | 2.95727 | 3.55137 | 3.86907 | 1.70007 | 2.37257 | 2.93897 |
| 60 | 0.83732 | 2.66882 | 2.90852 | 3.62192 | 3.90832 | 1.46972 | 2.41752 | 3.02992 |
| 80 | 1.23937 | 2.70677 | 2.95147 | 3.83237 | 4.00747 | 1.62966 | 2.54197 | 3.22277 |
| 100 | 1.33568 | 2.74558 | 3.02348 | 3.88178 | 4.03618 | 1.63464 | 2.57498 | 3.18928 |
| 120 | 0.78869 | 2.54579 | 2.90579 | 3.54769 | 3.82659 | 1.29619 | 2.34559 | 2.94419 |
| 140 | 0.36032 | 2.36032 | 2.83292 | 3.33502 | 3.72392 | 1.37382 | 2.20442 | 2.77312 |
| 160 | 0.09215 | 2.24705 | 2.78155 | 3.20705 | 3.69465 | 1.37225 | 2.12835 | 2.64265 |
| 180 | 0 | 2.20945 | 2.77095 | 3.19225 | 3.80225 | 1.37275 | 2.12035 | 2.59945 |

| ∠ CNN | S0 | S1 | S2 | S3 | S4 | T1 | T2 | T3 |
|---|---|---|---|---|---|---|---|---|
| 120.6 | 0 | 2.20945 | 2.77095 | 3.19225 | 3.80225 | 1.37275 | 2.12035 | 2.59945 |
| 130.6 | 0.11087 | 2.36287 | 2.94047 | 3.39237 | 3.65687 | 1.57657 | 2.30387 | 2.74617 |
| 140.6 | 0.38129 | 2.67169 | 3.26009 | 3.51789 | 3.73029 | 1.92359 | 2.63639 | 2.82469 |
| 150.6 | 0.72183 | 3.04533 | 3.49823 | 3.64313 | 4.12013 | 2.32333 | 2.85653 | 3.03113 |
| 160.6 | 1.05076 | 3.39526 | 3.54186 | 4.00116 | 4.48176 | 2.69366 | 2.94766 | 3.39926 |
| 170.6 | 1.29692 | 3.60842 | 3.65572 | 4.27132 | 4.74722 | 2.96542 | 3.04822 | 3.67412 |
| 183.5 | 1.40515 | 3.66325 | 3.77585 | 4.40205 | 4.85435 | 3.05105 | 3.14095 | 3.80385 |
| 193.5 | 1.29706 | 3.59656 | 3.71226 | 4.29796 | 4.71566 | 2.88466 | 3.12256 | 3.70536 |
| 203.5 | 1.07116 | 3.38996 | 3.65126 | 4.06526 | 4.45246 | 2.67056 | 3.00686 | 3.47726 |
| 213.5 | 0.79837 | 3.08137 | 3.58397 | 3.81517 | 4.12557 | 2.40077 | 2.85797 | 3.21747 |
| 223.5 | 0.56758 | 2.78798 | 3.34608 | 3.79988 | 3.84068 | 2.16888 | 2.65368 | 3.05608 |
| 233.5 | 0.47336 | 2.64936 | 3.11046 | 3.60936 | 3.91156 | 1.98726 | 2.44966 | 2.94986 |

Table S2. TDDFT Energies of **1H** along the inversion ∠ $^{Nap}$CNN of the $S_0$ trans-cis isomerization.

Table S3. TDDFT Energies of **3H** along the torsional ∠ CNNC of the $S_0$ trans-cis isomerization.

| ∠ CNNC | S0 | S1 | S2 | S3 | S4 | T1 | T2 | T3 |
|---|---|---|---|---|---|---|---|---|
| 11.8 | 0.67467 | 3.16977 | 4.06897 | 4.39837 | 4.51427 | 2.39181 | 3.30987 | 3.48557 |
| 20 | 0.69312 | 3.03172 | 4.01362 | 4.36192 | 4.46112 | 2.24287 | 3.30442 | 3.47522 |
| 40 | 0.86911 | 2.71321 | 3.95881 | 4.34481 | 4.42241 | 1.88258 | 3.37101 | 3.50181 |
| 60 | 1.22682 | 2.41722 | 4.01332 | 4.42912 | 4.53082 | 1.56177 | 3.51652 | 3.60432 |
| 80 | 1.7172 | 2.0903 | 4.1225 | 4.651 | 4.8184 | 1.37925 | 3.6814 | 3.7636 |
| 100 | 1.74982 | 1.96852 | 4.08212 | 4.61012 | 4.81402 | 1.30254 | 3.65932 | 3.68782 |
| 120 | 1.08176 | 2.20616 | 3.84076 | 4.21566 | 4.37806 | 1.3427 | 3.23496 | 3.44026 |
| 140 | 0.51103 | 2.34923 | 3.57953 | 3.84943 | 4.12303 | 1.51775 | 2.79283 | 3.15343 |
| 160 | 0.13265 | 2.52965 | 3.33685 | 3.57065 | 4.07035 | 1.77211 | 2.37855 | 2.92265 |
| 180 | 0 | 2.6648 | 3.1557 | 3.478 | 4.1519 | 1.94018 | 1.9787 | 2.8358 |

Table S4. TDDFT Energies of **3H** along the inversion ∠ $^{Nap}$CNN of the $S_0$ trans-cis isomerization.

| ∠ CNN | S0 | S1 | S2 | S3 | S4 | T1 | T2 | T3 |
|---|---|---|---|---|---|---|---|---|
| 115.17371 | 0 | 2.6648 | 3.1557 | 3.478 | 4.1519 | 1.9416 | 1.9787 | 2.8358 |
| 125.17371 | 0.14269 | 2.42889 | 3.32029 | 3.62729 | 4.12499 | 1.74929 | 2.13799 | 2.98049 |
| 135.17371 | 0.49998 | 2.37508 | 3.67668 | 3.98258 | 4.07878 | 1.72888 | 2.49698 | 3.33448 |
| 145.17371 | 0.96895 | 2.44535 | 4.12725 | 4.17065 | 4.43895 | 1.81975 | 2.95405 | 3.79395 |
| 155.17371 | 1.27928 | 2.75398 | 4.45708 | 4.65408 | 4.91938 | 2.04588 | 3.75058 | 3.79418 |
| 179.6 | 1.68555 | 2.82215 | 4.78615 | 4.86655 | 5.04095 | 2.27335 | 3.98365 | 4.23285 |
| 195.54038 | 1.5187 | 2.902 | 4.6975 | 4.8074 | 5.047 | 2.2785 | 3.8932 | 4.0953 |
| 205.54038 | 1.2774 | 2.9665 | 4.5466 | 4.684 | 5.0346 | 2.2392 | 3.7778 | 3.8595 |
| 215.54038 | 1.00742 | 3.01862 | 4.34882 | 4.52972 | 4.86582 | 2.19622 | 3.57882 | 3.66012 |
| 225.54038 | 0.78191 | 3.03211 | 4.16921 | 4.40691 | 4.49751 | 2.12341 | 3.39401 | 3.49491 |
| 235.54038 | 0.67467 | 3.16977 | 4.06897 | 4.39837 | 4.51427 | 2.23787 | 3.30987 | 3.48557 |

Table S5. TDDFT Energies of **4H** along the torsional ∠ CNNC of the $S_0$ trans-cis isomerization.

| ∠ CNNC | S0 | S1 | S2 | S3 | S4 | T1 | T2 | T3 |
|---|---|---|---|---|---|---|---|---|
| 11.2 | 0.42431 | 3.00181 | 3.41441 | 3.95811 | 4.30061 | 1.88781 | 2.84001 | 3.28231 |
| 20 | 0.42997 | 2.94697 | 3.30837 | 3.95137 | 4.25287 | 1.80157 | 2.77837 | 3.26937 |
| 40 | 0.50545 | 2.80645 | 3.16135 | 3.94785 | 4.19825 | 1.63645 | 2.68705 | 3.19635 |
| 60 | 0.66841 | 2.62351 | 3.07571 | 3.97551 | 4.23351 | 1.49991 | 2.64431 | 3.06291 |
| 80 | 0.88958 | 2.41118 | 3.03058 | 3.96658 | 4.42238 | 1.54028 | 2.67258 | 2.98808 |
| 100 | 0.97107 | 2.51367 | 3.07167 | 3.98207 | 4.44397 | 1.61407 | 2.67137 | 3.01867 |
| 120 | 0.60472 | 2.52642 | 2.99712 | 3.91182 | 4.15212 | 1.40662 | 2.50622 | 2.95432 |
| 140 | 0.2896 | 2.4855 | 2.9084 | 3.7768 | 3.9811 | 1.3141 | 2.3753 | 2.88 |
| 160 | 0.07556 | 2.43986 | 2.84126 | 3.65636 | 3.86706 | 1.27396 | 2.28596 | 2.81496 |
| 180 | 0 | 2.4167 | 2.8112 | 3.6105 | 3.8219 | 1.2546 | 2.2493 | 2.7828 |

Table S6. TDDFT Energies of **4H** along the inversion ∠ $^{Nap}$CNN of the $S_0$ trans-cis isomerization.

| ∠ CNN | S0 | S1 | S2 | S3 | S4 | T1 | T2 | T3 |
|---|---|---|---|---|---|---|---|---|
| 120.6 | 0 | 2.4167 | 2.8112 | 3.6105 | 3.8219 | 1.2546 | 2.2493 | 2.7828 |
| 130.6 | 0.09197 | 2.59837 | 3.00167 | 3.78727 | 3.89767 | 1.47097 | 2.42527 | 2.93937 |
| 140.6 | 0.35419 | 2.93549 | 3.34569 | 3.76529 | 4.11639 | 1.83939 | 2.75439 | 3.12589 |
| 150.6 | 0.68602 | 3.32252 | 3.74032 | 3.74852 | 4.49692 | 2.25002 | 3.13352 | 3.15922 |
| 160.6 | 1.01004 | 3.68434 | 3.79984 | 4.10934 | 4.85594 | 2.62934 | 3.25684 | 3.48794 |
| 184.4 | 1.35323 | 3.92563 | 4.06293 | 4.49903 | 5.22913 | 3.01233 | 3.42703 | 3.84543 |
| 194.4 | 1.25033 | 3.87923 | 3.99283 | 4.38993 | 5.10633 | 2.89273 | 3.40313 | 3.72703 |
| 204.4 | 1.02135 | 3.67925 | 3.92285 | 4.13735 | 4.84385 | 2.63275 | 3.34195 | 3.47595 |
| 214.4 | 0.74613 | 3.39493 | 3.81213 | 3.94783 | 4.51923 | 2.33403 | 3.17043 | 3.32133 |
| 224.4 | 0.51038 | 3.14378 | 3.56798 | 4.01308 | 4.26668 | 2.07018 | 2.94508 | 3.38358 |
| 234.4 | 0.42431 | 3.00181 | 3.41441 | 3.95811 | 4.30061 | 1.88781 | 2.84001 | 3.28231 |

Spin orbit coupling tables

Table S7. Spin-orbit coupling constants between $S_0 - S_6$ and $T_1 - T_6$ states of azo **1H** in its optimized ground-state geometry B3LYP/6-311G(d.p)/PCM(ACN)

| | S0 | S1 | S2 | S3 | S4 | S5 | S6 |
|---|---|---|---|---|---|---|---|
| T1 | 0.08927 | 0.27182 | 0.29764 | 0.23561 | 0.13338 | 5.54583 | 0.1481 |
| T2 | 0.19227 | 0.25176 | 0.27071 | 0.23934 | 0.1181 | 0.90985 | 0.22675 |
| T3 | 0.41134 | 0.02164 | 0.1499 | 0.04221 | 0.20313 | 0.55793 | 0.23615 |
| T4 | 0.16993 | 0.37845 | 0.02745 | 0.31156 | 0.06253 | 6.74246 | 0.03729 |
| T5 | 0.20246 | 0.11667 | 0.00657 | 0.0816 | 0.05504 | 3.06563 | 0.00942 |
| T6 | 31.74461 | 2.70851 | 4.16059 | 1.04862 | 3.34948 | 0.6222 | 5.5808 |

Table S8. Spin-orbit coupling constants between $S_0 - S_6$ and $T_1 - T_6$ states of azo **3H** in its optimized ground-state geometry B3LYP/6-311G(d.p)/PCM(ACN)

| | S0 | S1 | S2 | S3 | S4 | S5 | S6 |
|---|---|---|---|---|---|---|---|
| T1 | 0.13733 | 0.21115 | 0.27609 | 0.14462 | 0.22818 | 1.96105 | 0.01961 |
| T2 | 0.08791 | 0.11611 | 0.2665 | 0.26713 | 0.15259 | 4.51259 | 0.10094 |
| T3 | 0.31331 | 0.42457 | 0.10183 | 0.03538 | 0.1556 | 7.28802 | 0.06723 |
| T4 | 0.39133 | 0.15303 | 0.11821 | 0.06905 | 0.14801 | 0.94904 | 0.06675 |
| T5 | 0.19754 | 0.11134 | 0.02578 | 0.00322 | 0.02498 | 3.0266 | 0.0865 |
| T6 | 31.3139 | 2.16921 | 0.79127 | 4.51323 | 5.95197 | 0.41317 | 4.45763 |

Table S9. Spin-orbit coupling constants between $S_0 - S_6$ and $T_1 - T_6$ states of azo **4H** in its optimized ground-state geometry B3LYP/6-311G(d.p)/PCM(ACN)

| | S0 | S1 | S2 | S3 | S4 | S5 | S6 |
|---|---|---|---|---|---|---|---|
| T1 | 0.13989 | 0.10394 | 0.20334 | 0.01297 | 0.20859 | 0.2405 | 4.63169 |
| T2 | 0.07856 | 0.00127 | 0.29948 | 0.2764 | 0.08903 | 0.2134 | 6.78772 |
| T3 | 0.14561 | 0.43277 | 0.17533 | 0.16238 | 0.03745 | 0.18807 | 4.59596 |
| T4 | 0.27077 | 0.08211 | 0.02397 | 0.06977 | 0.01856 | 0.37031 | 3.0215 |
| T5 | 0.52722 | 0.1281 | 0.12364 | 0.07922 | 0.06896 | 0.01973 | 0.51262 |
| T6 | 29.59469 | 0.60486 | 2.38889 | 8.24098 | 2.86528 | 0.30722 | 0.04398 |

Coordinates

Table S10. nap-azoH-ph: **1** with protonation of N on the phenyl side

```
1 1
C -5.52866329 0.01669600 0.00000877
C -4.61383535 -1.01826136 -0.00000666
C -3.23155250 -0.74686956 -0.00000950
C -2.79636447 0.62002180 0.00000434
C -3.76168256 1.66323174 0.00002011
C -5.10300091 1.36348157 0.00002228
H -2.59267499 -2.81827662 -0.00003476
H -6.58932214 -0.20491733 0.00001074
H -4.95177751 -2.04778067 -0.00001663
C -2.25240076 -1.78941937 -0.00002503
C -1.41833227 0.88817799 0.00000310
H -3.42263407 2.69261707 0.00003074
H -5.83938754 2.15757193 0.00003446
C -0.48192508 -0.15056201 -0.00001338
C -0.91786496 -1.51547827 -0.00002750
H -1.05493676 1.90847559 0.00001408
H -0.21394998 -2.33815194 -0.00003965
N 0.81588920 0.28701147 -0.00001395
C 3.13007868 -0.15017766 0.00000782
C 4.08764767 -1.17010268 0.00003557
C 3.49646300 1.20053453 -0.00002463
C 5.43464596 -0.82955097 0.00003077
H 3.78138887 -2.21004735 0.00005993
C 4.84549720 1.52034006 -0.00002906
H 2.73512888 1.96792363 -0.00004606
C 5.81488177 0.51180826 -0.00000152
H 6.18413790 -1.61069333 0.00005196
H 5.14634947 2.56055791 -0.00005421
H 6.86559839 0.77480926 -0.00000534
N 1.77396046 -0.53933908 0.00001169
H 1.60157936 -1.54901535 0.00003756
```

Table S11. nap-Hazo-ph: also called **1H**

```
1 1
C 5.53580824 0.05176483 0.00000065
C 4.59827256 1.06222805 0.00000127
C 3.21797164 0.76027189 0.00000058
C 2.81215120 -0.61430942 -0.00000073
C 3.80150953 -1.63326808 -0.00000139
C 5.13586181 -1.30394055 -0.00000070
H 2.53276544 2.81529813 0.00000225
H 6.59161507 0.29550425 0.00000127
H 4.91034320 2.10022630 0.00000228
C 2.21872546 1.77803583 0.00000122
C 1.43433347 -0.91687536 -0.00000128
H 3.48797494 -2.67098101 -0.00000244
H 5.88794712 -2.08359543 -0.00000121
C 0.50352652 0.10666135 -0.00000058
C 0.88699334 1.47291226 0.00000067
H 1.11430866 -1.95322154 -0.00000214
H 0.12811608 2.24209302 0.00000126
C -3.11051823 0.14381732 0.00000023
C -4.05050989 1.19502732 -0.00000188
C -3.54911709 -1.19994031 0.00000220
C -5.40739724 0.91201509 -0.00000174
H -3.68281573 2.21302345 -0.00000351
C -4.90476465 -1.46598850 0.00000222
H -2.85573833 -2.03221362 0.00000373
C -5.83421425 -0.41554715 0.00000031
H -6.12955347 1.71825668 -0.00000327
H -5.25007761 -2.49194965 0.00000367
H -6.89365716 -0.64151079 0.00000034
N -1.79761348 0.57145593 -0.00000008
N -0.85086830 -0.26239774 -0.00000090
H -1.03365048 -1.27152457 -0.00000164
```

Table S12. nap-azoH-phOMe: **3** with protonation of N on the phenyl side

```
1 1
C -6.39375802 -0.26626120 -0.00018821
C -5.54483495 0.82210590 -0.00009006
C -4.14685709 0.63667145 -0.00002270
C -3.62606575 -0.69896647 -0.00004647
C -4.52543750 -1.79904644 -0.00014526
C -5.88297429 -1.58359286 -0.00021833
H -3.63631152 2.74244790 0.00008022
H -7.46624722 -0.11167834 -0.00024677
H -5.94466778 1.82941351 -0.00006752
C -3.23437402 1.73604644 0.00006617
C -2.23183572 -0.88097587 0.00004130
H -4.12365084 -2.80563091 -0.00016060
H -6.56755878 -2.42298933 -0.00029689
C -1.36240389 0.21083255 0.00013191
C -1.88428524 1.54439398 0.00013878
H -1.80796128 -1.87774212 0.00003783
H -1.23554108 2.41174599 0.00019870
C 2.23551353 0.47806879 0.00019937
C 3.12105223 1.56926870 -0.00018544
C 2.72051619 -0.83566834 0.00049876
C 4.47971135 1.34306596 -0.00030396
H 2.74099510 2.58451727 -0.00041661
C 4.08414365 -1.06142223 0.00039255
H 2.02724678 -1.66530405 0.00085681
C 4.97895913 0.02673596 -0.00006695
H 5.18259197 2.16572965 -0.00061439
H 4.44889135 -2.07828942 0.00075151
O 6.31492543 -0.09021151 -0.00013391
C 6.91267278 -1.39694950 -0.00038618
H 7.98538513 -1.22239509 -0.00114703
H 6.63028348 -1.95375266 0.89601451
H 6.62904150 -1.95397745 -0.89624297
N 0.86334170 0.75246154 0.00025435
H 0.61254962 1.74538391 0.00016464
N -0.03375658 -0.14269408 0.00021254
```

Table S13. nap-Hazo-phOMe: also called **3H**

```
1 1
C -6.41433418 -0.15675248 0.00007331
C -5.52806405 0.89757253 0.00089254
C -4.13286982 0.66426810 0.00055654
C -3.65701583 -0.68665493 -0.00062544
C -4.59550813 -1.75247042 -0.00144691
C -5.94490877 -1.49044427 -0.00110367
H -3.54931331 2.74975103 0.00233001
H -7.48117261 0.03331371 0.00033382
H -5.88984761 1.91951402 0.00181624
C -3.18569660 1.72862321 0.00139188
C -2.26355415 -0.92049628 -0.00091462
H -4.23143198 -2.77370414 -0.00233036
H -6.65630699 -2.30771331 -0.00172965
C -1.38436419 0.14498653 -0.00009757
C -1.83954664 1.48859927 0.00110250
H -1.89517454 -1.94074047 -0.00179149
H -1.12115282 2.29576000 0.00177457
N 0.88985292 0.74932408 -0.00010704
C 2.21265555 0.42906480 0.00034670
C 3.08703140 1.54828242 -0.00157471
C 2.76806253 -0.87691866 0.00255395
C 4.44674802 1.37710642 -0.00194703
H 2.64857321 2.53788108 -0.00295534
C 4.13058642 -1.05261409 0.00231707
H 2.14437214 -1.76280359 0.00471996
C 4.98972757 0.07399471 -0.00020949
H 5.12484303 2.22021319 -0.00358655
H 4.53673344 -2.05345516 0.00407253
O 6.31646274 -0.00099564 -0.00112863
C 6.97335327 -1.28495910 0.00016460
H 8.03587514 -1.05944122 -0.00102122
H 6.71330927 -1.84737333 0.89849215
H 6.71184271 -1.84995551 -0.89612922
N -0.00863007 -0.14902742 -0.00034332
H 0.23477478 -1.14248435 -0.00069191
```

Table S14. nap-azoH-phNMe2: **4** with protonation of N on the phenyl side

```
1 1
C 6.81970565 -0.14540945 0.00002462
C 5.93418277 0.91158171 -0.00002515
C 4.54114778 0.67903358 -0.00002393
C 4.06318797 -0.67163008 0.00002672
C 5.00081910 -1.73936907 0.00007913
C 6.35058377 -1.47881974 0.00007908
H 3.95737064 2.76486585 -0.00009764
H 7.88662594 0.04427206 0.00002263
H 6.29843955 1.93259221 -0.00006592
C 3.59218590 1.74420599 -0.00006797
C 2.67333200 -0.90038548 0.00002316
H 4.63430944 -2.75964422 0.00011882
H 7.06201835 -2.29594950 0.00012021
C 1.76648526 0.15705153 -0.00002652
C 2.24797524 1.50499266 -0.00006658
H 2.28619141 -1.91211587 0.00005613
H 1.57335634 2.35263151 -0.00009100
N 0.44270244 -0.23508548 -0.00004398
N -0.47301646 0.65057945 -0.00003622
C -1.82847408 0.37250096 -0.00001903
C -2.73032868 1.45381739 0.00003174
C -2.31893251 -0.94803840 -0.00005125
C -4.08497293 1.23058118 0.00004749
H -2.35685097 2.47199698 0.00004998
C -3.67067264 -1.17669772 -0.00003926
H -1.62322841 -1.77586375 -0.00009635
C -4.60891329 -0.09628732 0.00002116
H -4.75029246 2.08043498 0.00006979
H -4.02136206 -2.19785162 -0.00007265
N -5.94100371 -0.32676837 0.00003577
C -6.88951577 0.78827203 0.00014276
H -7.90008461 0.38996703 0.00032394
H -6.76499613 1.41279127 0.88915208
H -6.76527792 1.41271914 -0.88896229
C -6.46571724 -1.69392886 -0.00011533
H -7.55118260 -1.65242895 0.00006855
H -6.14286456 -2.24202495 -0.88955061
H -6.14257441 -2.24234684 0.88901670
H -0.23284333 1.64605007 0.00000355
```

Table S15. nap-Hazo-phNMe2: also called **4H**

```
1 1
C 6.83310950 -0.04129912 -0.00018626
C 5.91360338 0.98300584 -0.00011049
C 4.52487106 0.70603417 -0.00003862
C 4.08954215 -0.65790072 -0.00004484
C 5.06270363 -1.69242927 -0.00012112
C 6.40354214 -1.38884939 -0.00018919
H 3.87368411 2.77069023 0.00004687
H 7.89364939 0.18167742 -0.00023991
H 6.24223235 2.01640214 -0.00010204
C 3.54435559 1.73770087 0.00004445
C 2.70235232 -0.93541167 0.00002876
H 4.73177584 -2.72513735 -0.00011613
H 7.13937819 -2.18448568 -0.00024284
C 1.78711812 0.09790302 0.00011999
C 2.20561309 1.45372764 0.00012098
H 2.36773330 -1.96739237 0.00000548
H 1.46317415 2.23885510 0.00019024
N 0.41898452 -0.23103895 0.00020239
N -0.50458069 0.66179273 0.00016684
C -1.80544896 0.32805352 0.00021171
C -2.71039505 1.43021567 0.00003806
C -2.35801618 -0.99057415 0.00038671
C -4.06237459 1.24999087 -0.00004762
H -2.28823219 2.42734924 -0.00003253
C -3.70712669 -1.18109978 0.00026561
H -1.72398998 -1.86914720 0.00064763
C -4.62057313 -0.06899006 -0.00006069
H -4.70857136 2.11441213 -0.00016369
H -4.09002106 -2.19044237 0.00048273
N -5.94662695 -0.26649564 -0.00018989
C -6.87366405 0.87214252 -0.00026532
H -7.89142706 0.49453704 -0.00047497
H -6.73177735 1.48943455 0.88963151
H -6.73145487 1.48958085 -0.89001117
C -6.51363133 -1.62159260 -0.00022324
H -7.59660368 -1.54559324 -0.00096567
H -6.20509432 -2.17432613 -0.89030467
H -6.20626968 -2.17387619 0.89055354
H 0.19388994 -1.22610935 0.00026698
```

Table S16. nap-azo-phNMe2H: **4** with protonation of N on the dimethylamine functionality

```
1 1
C 6.83667700 -0.09204363 0.01544263
C 5.93894039 0.95215049 -0.00761927
C 4.54495140 0.70544688 -0.00975184
C 4.08309357 -0.64976692 0.01126499
C 5.03362970 -1.70434063 0.03460649
C 6.38120303 -1.43047978 0.03689480
H 3.94065231 2.78460439 -0.04957860
H 7.90167272 0.10952739 0.01726674
H 6.29084114 1.97781389 -0.02416975
C 3.58499388 1.75994254 -0.03232893
C 2.68930677 -0.89361145 0.00797749
H 4.67896930 -2.72912668 0.05089643
H 7.10084953 -2.24058616 0.05517358
C 1.78358992 0.15038681 -0.01179686
C 2.24294359 1.49936993 -0.03267438
H 2.31403314 -1.91042648 0.02289458
H 1.51411492 2.29773962 -0.04943926
N 0.42527772 -0.22646679 -0.01049961
N -0.39997825 0.72047297 -0.00051112
C -1.76158745 0.31982718 -0.00824520
C -2.69755148 1.35433763 0.09415846
C -2.19987007 -1.00678585 -0.11754649
C -4.05998768 1.08007755 0.09654489
H -2.34182264 2.37351174 0.17448519
C -3.55783038 -1.28780650 -0.12109115
H -1.47218856 -1.80168105 -0.19996896
C -4.47126891 -0.24246308 -0.01301863
H -4.77039733 1.89202401 0.18246775
H -3.89919811 -2.31316735 -0.20873888
N -5.91899522 -0.57252603 -0.01917464
C -6.64870133 0.00012438 -1.21125293
H -7.67050514 -0.37190817 -1.19086591
H -6.63968775 1.08426363 -1.14050274
H -6.13833200 -0.32797963 -2.11314320
C -6.60440200 -0.22288841 1.28042656
H -7.62639271 -0.59187190 1.23268324
H -6.06074017 -0.70008036 2.09144272
H -6.59647493 0.85703483 1.39914803
H -5.97830266 -1.58891557 -0.11069730
```