# Supporting Information for: Unravelling the Photoprotection Properties of Mycosporine Amino Acid Motifs

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### A) TEAS in additional solvents

In addition to protic and polar aprotic environments, transient electronic absorption spectroscopy (TEAS) was also performed in dioxane where the solvent environment has significantly less perturbation on the solute. These transient absorption spectra (TAS) show similar dynamics to the observed dynamics in aprotic environments.

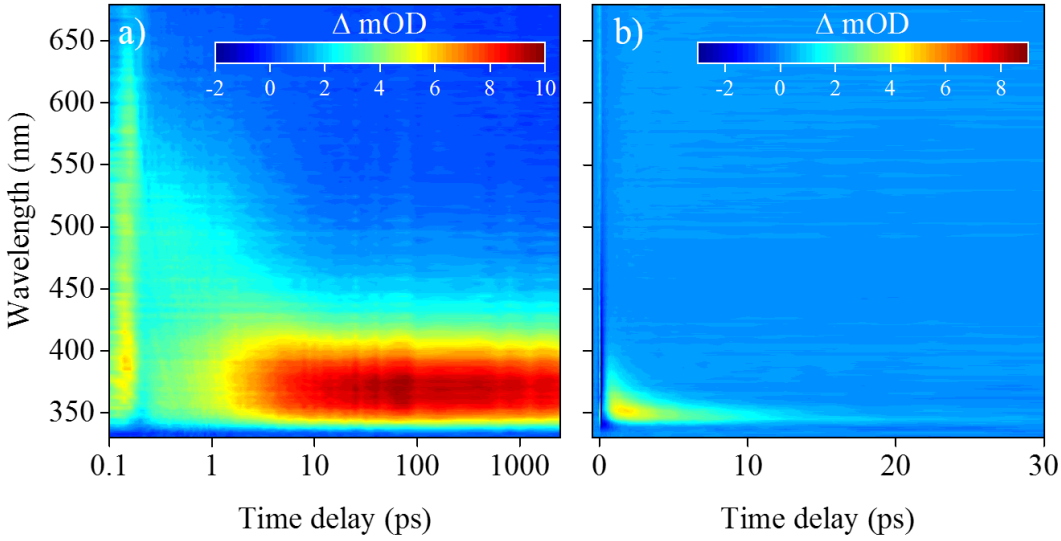


**Figure S1**: False colour maps of TAS in dioxane for a) 10 mM **ACyO** following 270 nm excitation and b) 10 mM **NN** following 328 nm excitation.

**B) Fitting residuals**

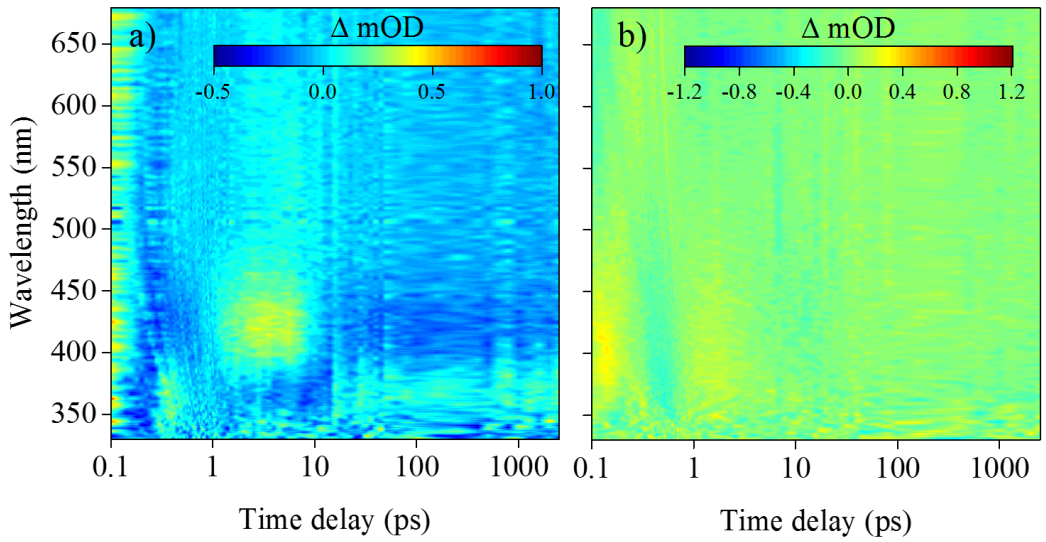


**Figure S2.** TAS residuals for **ACyO** in a) acetonitrile and b) methanol following excitation at 272 and 285 nm respectively.

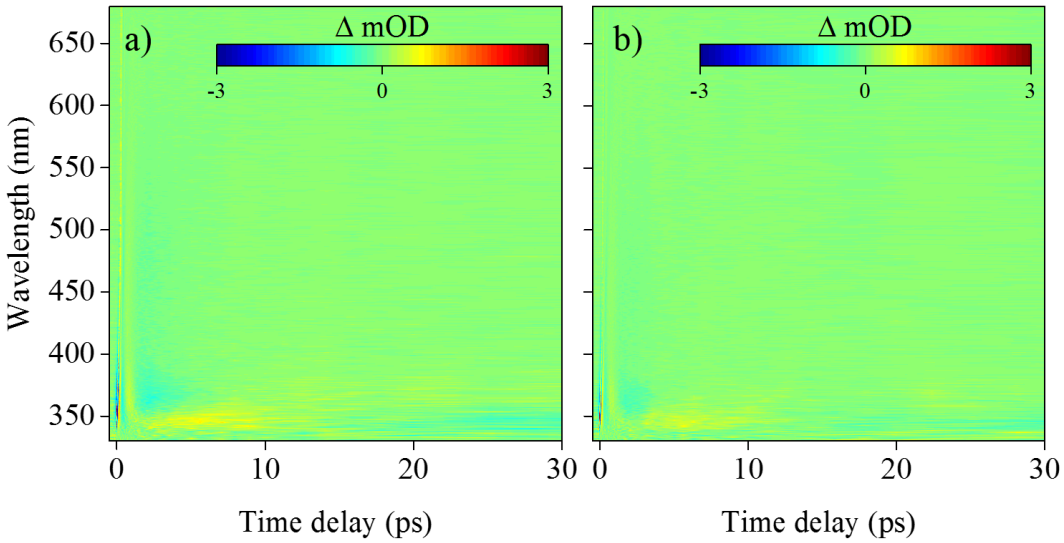


**Figure S3.** TAS residuals for **NN** in a) acetonitrile and b) methanol following excitation at 328 nm.

Averaged percentage errors for the four displayed residuals are approximately 30%. The large error can be reconciled by the sizeable percentage errors around time zero.

### C) Power dependencies

Power dependencies of **ACyO** and **NN** show a linear dependence across the spectral features of the TAS. These measurements were achieved by varying the TOPAS output power and taking a 10 nm integration window across a particular spectral window at a given pump probe time delay. Each TAS displays a linear relationship to the incident pump power (log(signal) *vs.* log(power) plots), strongly suggesting single photon induced dynamics.

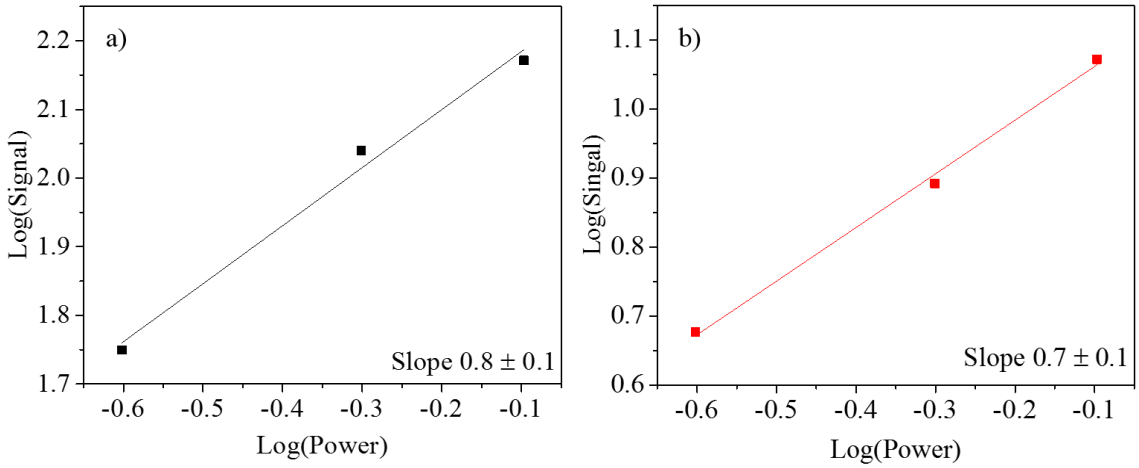


**Figure S4.** Power dependencies for the integrated intensity for **ACyO** in: a) Acetonitrile following excitation at 272 nm; 10 nm integration window, 365-375 nm, at $\Delta t$ = 1 ns pump-probe delay. b) Methanol following excitation at 285 nm; 10 nm integration window, 395-405 nm, at $\Delta t$ = 1 ns pump-probe delay.

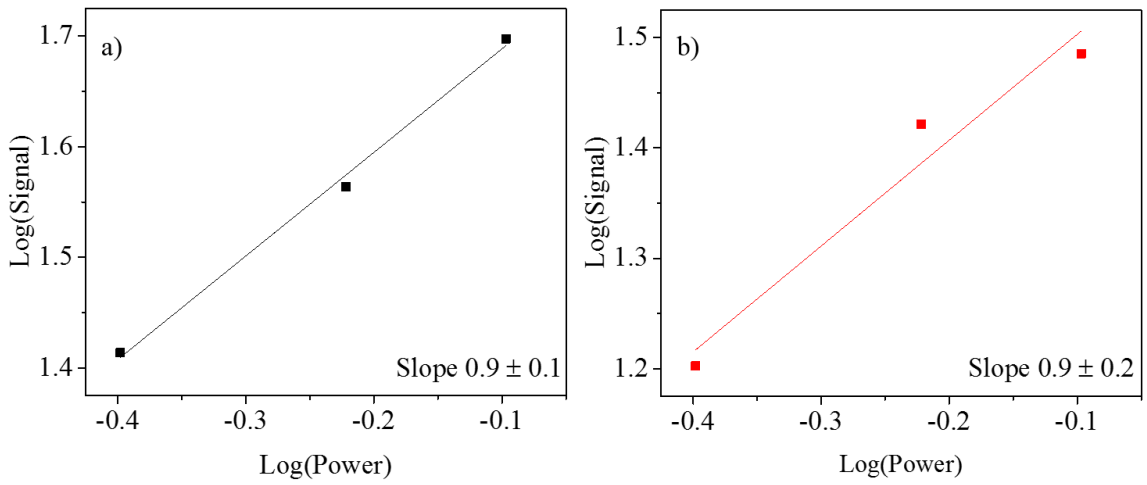


**Figure S5.** Power dependencies for the integrated intensity for **NN** following excitation at 328 nm for the integrated intensity of a 10 nm window, 345-355 nm at $\Delta t$ = 1 ps probe delay a) acetonitrile and b) methanol.

### D) Calculations

Calculations were carried out in Molpro[1], using 2 state-averaged CASSCF with a 6-31G* basis set. The CASSCF calculations used 8 electrons in 6 orbitals, the four occupied orbitals being the 3 π-orbitals as well as the lone pair perpendicular to the CO bond and the 2 unoccupied orbitals being the π* orbitals. Configuration interaction singles calculations indicated that the excited states contained mainly contributions from these orbitals, with none from the second lone pair on the oxygen (parallel to the CO bond).

**Table S1.** Calculated energies for the critical points for **ACyO** along the $S_1$ surface.

| Vertical Excitation (eV) / (nm) | $S_1$ Minimum (eV) | $S_1/S_0$ CI (eV) |
|---|---|---|
| 4.03 (307) | 3.54 | 3.58 |

## E) Calculated geometries

$S_0$ Minimum Energy Geometry

| | | | |
|---|---|---|---|
| C | -2.4816619373 | 0.5879608421 | 0.2498375135 |
| C | -2.3562204628 | -0.7531347247 | -0.4726044793 |
| C | -1.0796422502 | -1.4841391663 | -0.0563804486 |
| C | 0.1343316058 | -0.5882776607 | -0.1211981324 |
| C | 0.0359253429 | 0.7566941410 | -0.1051254939 |
| C | -1.2563323629 | 1.4532041767 | 0.0213998219 |
| O | -1.3279577459 | 2.6616309673 | -0.0308174117 |
| N | 1.3575808363 | -1.2605060812 | -0.0880101908 |
| H | -3.3582995686 | 1.1382132570 | -0.0693596414 |
| H | -2.5760335442 | 0.4188851358 | 1.3211009219 |
| H | -3.2219252055 | -1.3740212470 | -0.2666319997 |
| H | -2.3379207422 | -0.5827553253 | -1.5460742567 |
| H | -0.9233855320 | -2.3496626976 | -0.6960422662 |
| H | -1.1713847526 | -1.8682781249 | 0.9572684115 |
| H | 0.9108149178 | 1.3811811669 | -0.1592024944 |
| H | 1.3898999010 | -2.0843029186 | -0.6513641313 |
| H | 2.1511005004 | -0.6805177404 | -0.2637377223 |

S1 Minimum Energy Geometry

| | | | |
|---|---|---|---|
| C | -2.4934927461 | 0.6040483057 | 0.2091029577 |
| C | -2.3539335580 | -0.7710587639 | -0.4558333858 |
| C | -1.0758643896 | -1.4968216551 | -0.0211414247 |
| C | 0.1390035559 | -0.6310373778 | -0.2161647591 |
| C | 0.0207613618 | 0.7652542899 | -0.1010871635 |
| C | -1.2022270475 | 1.3629183796 | 0.0822350967 |
| O | -1.3176586214 | 2.7190102156 | 0.2016734568 |
| N | 1.3900795757 | -1.2731457020 | -0.1358794378 |
| H | -3.2979477578 | 1.1643905915 | -0.2584302547 |
| H | -2.7577257330 | 0.4953328470 | 1.2594303512 |
| H | -3.2238456059 | -1.3778638071 | -0.2261864868 |
| H | -2.3342727340 | -0.6364956136 | -1.5334907832 |
| H | -0.9726524399 | -2.4186255247 | -0.5900949405 |
| H | -1.1480745049 | -1.7931696117 | 1.0252859816 |
| H | 0.9013639425 | 1.3830165321 | -0.1560933363 |
| H | 1.4565781893 | -2.0641070304 | -0.7455746378 |
| H | 2.1587975130 | -0.6594720751 | -0.3146932337 |

$S_0/S_1$ Minimum Energy Geometry

| | | | |
|---|---|---|---|
| C | -1.6860444652 | 0.2525565354 | 1.1102245225 |
| C | -2.1779517284 | -0.9005108526 | 0.2049872616 |
| C | -1.0958942565 | -1.4353034574 | -0.7990651765 |
| C | 0.1450790764 | -0.6108573096 | -0.6004922054 |
| C | -0.0169845177 | 0.8241820170 | -0.6607441524 |
| C | -0.9830483785 | 1.3355764233 | 0.2916642889 |
| O | -1.3165228038 | 2.5068323233 | 0.3670344920 |
| N | 1.0733974510 | -1.1145667226 | 0.2465427664 |
| H | 1.8757582353 | -0.5658760424 | 0.4585479588 |
| H | -2.5244005934 | 0.7029781189 | 1.6260129981 |
| H | -1.0060221954 | -0.1342632441 | 1.8630697538 |
| H | -2.5241020193 | -1.7184324682 | 0.8273884425 |
| H | -3.0352616940 | -0.5518947125 | -0.3598296174 |
| H | -1.4480925433 | -1.3118059613 | -1.8159996777 |
| H | -0.9088547457 | -2.4941098258 | -0.6435892586 |
| H | 0.1549696405 | 1.3824249707 | -1.5620284345 |
| H | 1.1301945378 | -2.0909507918 | 0.4312610380 |

**F) NMR spectrum of NN**

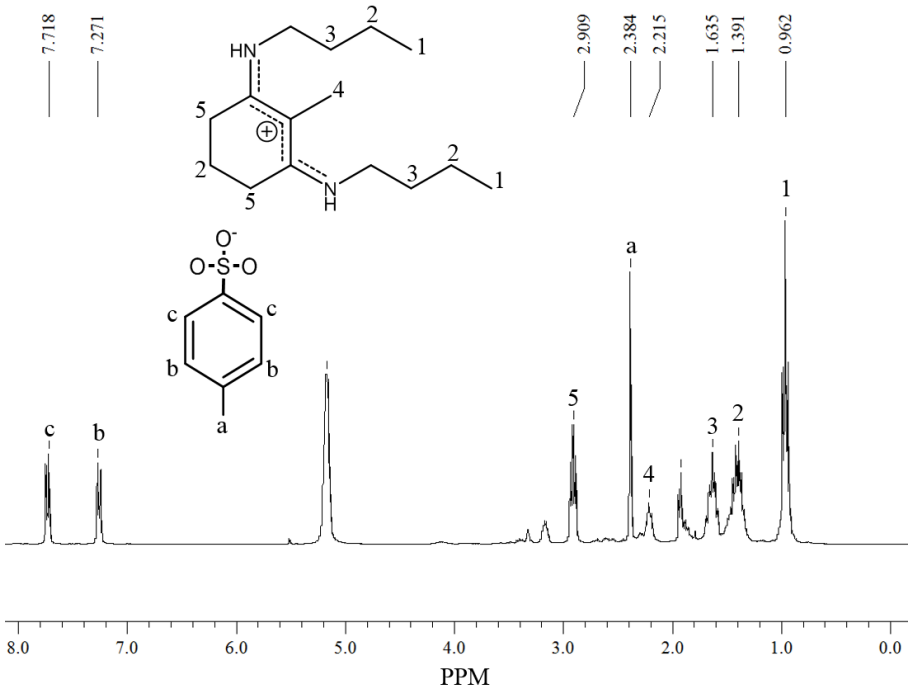


**Figure S6.** NMR of **NN** and $TsO^-$ counter ion (MeOD solvent, 400 Hz).

From analysis of the NMR, samples also contained small quantities of the salt (butan-1-aminium 4-methylbenzenesulfonate). To confirm that the TAS collated for **NN** did not contain contributions from the butan-1-aminium 4-methylbenzenesulfonate salt, TAS of the salt only (following photoexcitation at 328 nm) were collated which clearly showed only instrument limited dynamics (i.e. a time zero response). The associated false colour map is shown in Figure S8.

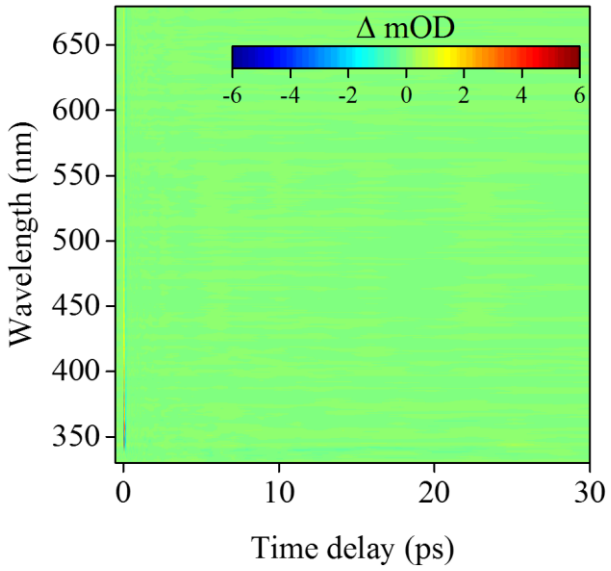


**Figure S7.** False colour heat map of 10 mM butan-1-aminium 4-methylbenzenesulfonate, photoexcited at 328 nm.

## G) References

(1) Werner, H. J.; Knowles, P. J.; Knizia, G.; Manby, F. R.; Schütz, M. Molpro: A general-purpose quantum chemistry program package. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2012**, *2*, 242–253.