Supporting Information for: Spatial Confinement Alters the Ultrafast Photoisomerization Dynamics of Azobenzenes

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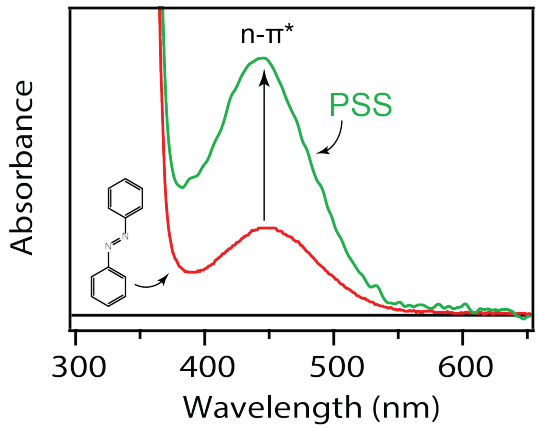

Figure S1: Ground-state absorption spectra in the region of the $n\pi^*$ absorption band for t-Az@OA_2 (red) and the mixture of t-Az@OA_2 and c-Az@OA_2 isomers at photo-stationary state (PSS; green). We obtain PSS by continuously irradiating the sample of encapsulated t-Az with a 310 nm UV LED. The stronger absorption at PSS is due to formation of the *cis* isomer. We estimate a relative concentration of 23% c-Az@OA_2 and 77% t-Az@OA_2 at PSS.

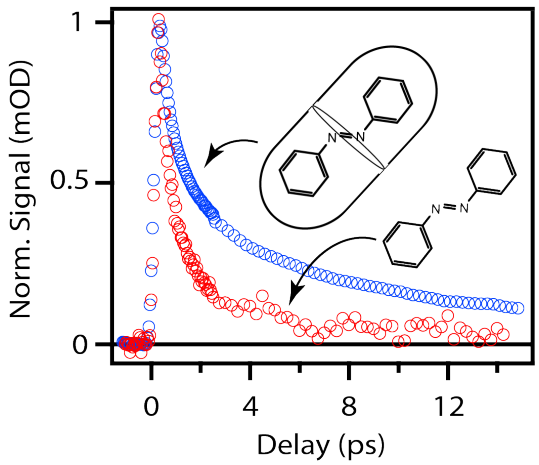

Figure S2: Comparison of excited-state decay at the absorption maximum near 400 nm following $\pi\pi^*$ excitation of t-Az in cyclohexane and t-Az@OA_2.

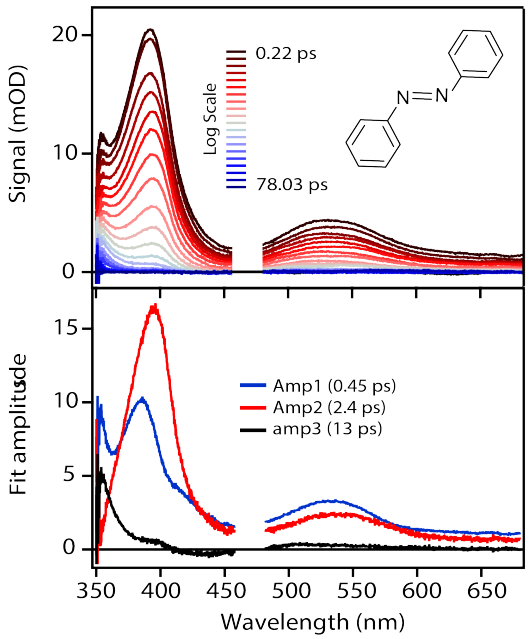

Figure S3: Top: Evolution of the TA spectrum following $n\pi^*$ excitation of t-Az in cyclohexane. Bottom: Decay associated spectra (DAS) from global fits to the TA data using a sum of 3 exponentials. The lifetimes associated with each spectrum are shown in the inset.

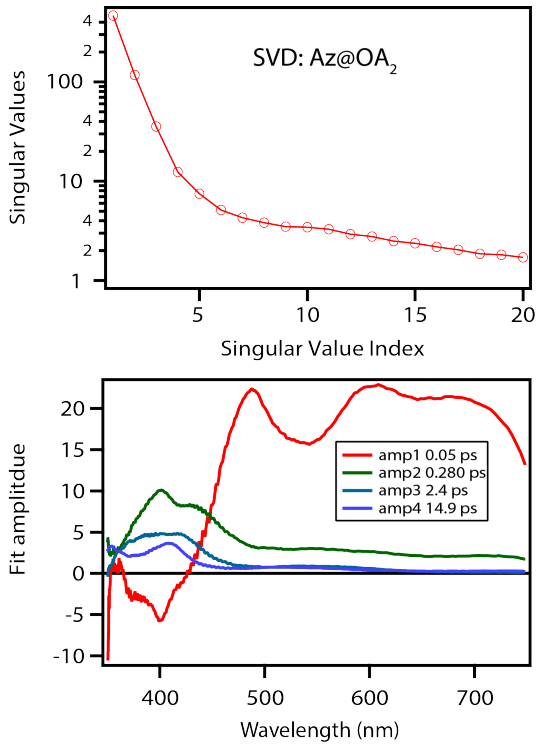

Figure S4: Top: Results from singular value decomposition (SVD) of the TA spectrum for *t*-Az@OA_2 indicating that at least four time constants are necessary to accurately reproduce the experimental data (at a threshold of 2%). The bottom panel shows the decay associated spectra (DAS) from global fits to the TA data using a sum of 4 exponentials. The associated lifetimes are shown in the inset. Notice that none of the DAS resemble the hot ground-state spectrum (S_0* in the main text) that becomes evident when including a fifth time constant in the target analysis (see main text).

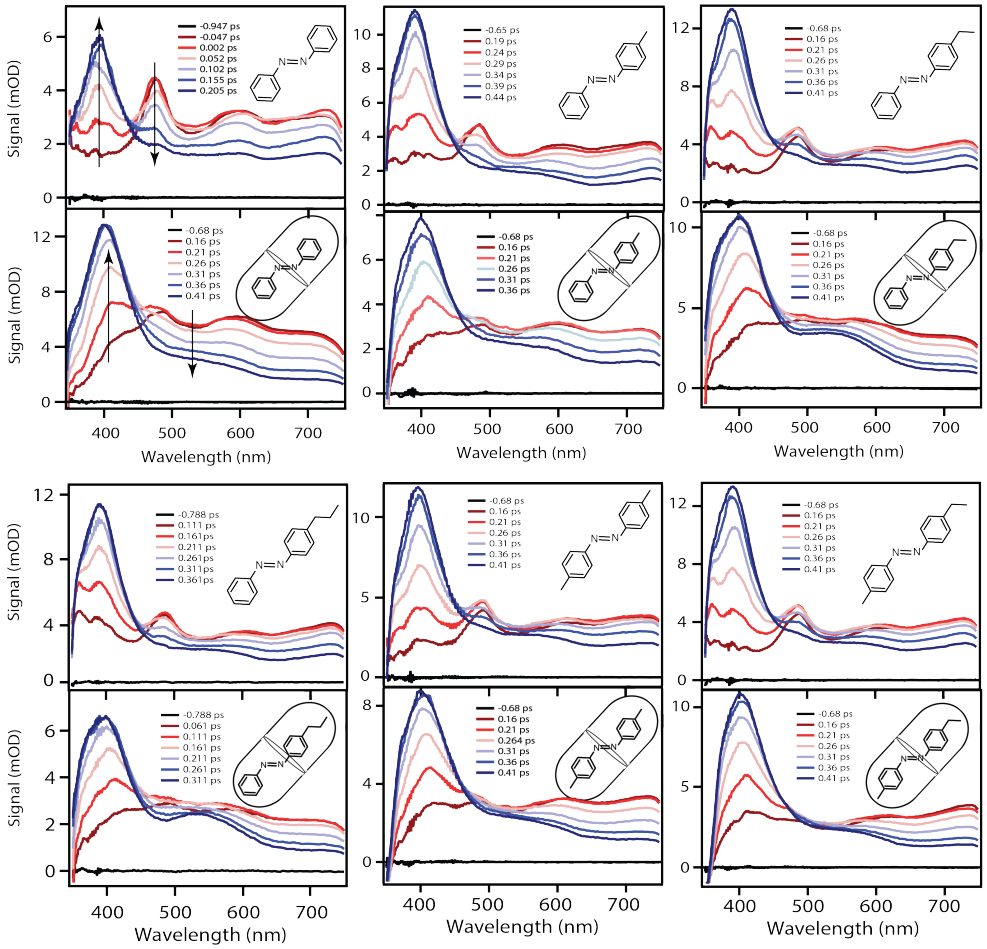

Figure S5: Evolution of the TA spectrum over the first ∼400 fs following $\pi\pi^*$ excitation of *t*-Az in cyclohexane and *t*-Az@OA_2. See Figure S6 for longer time delays.

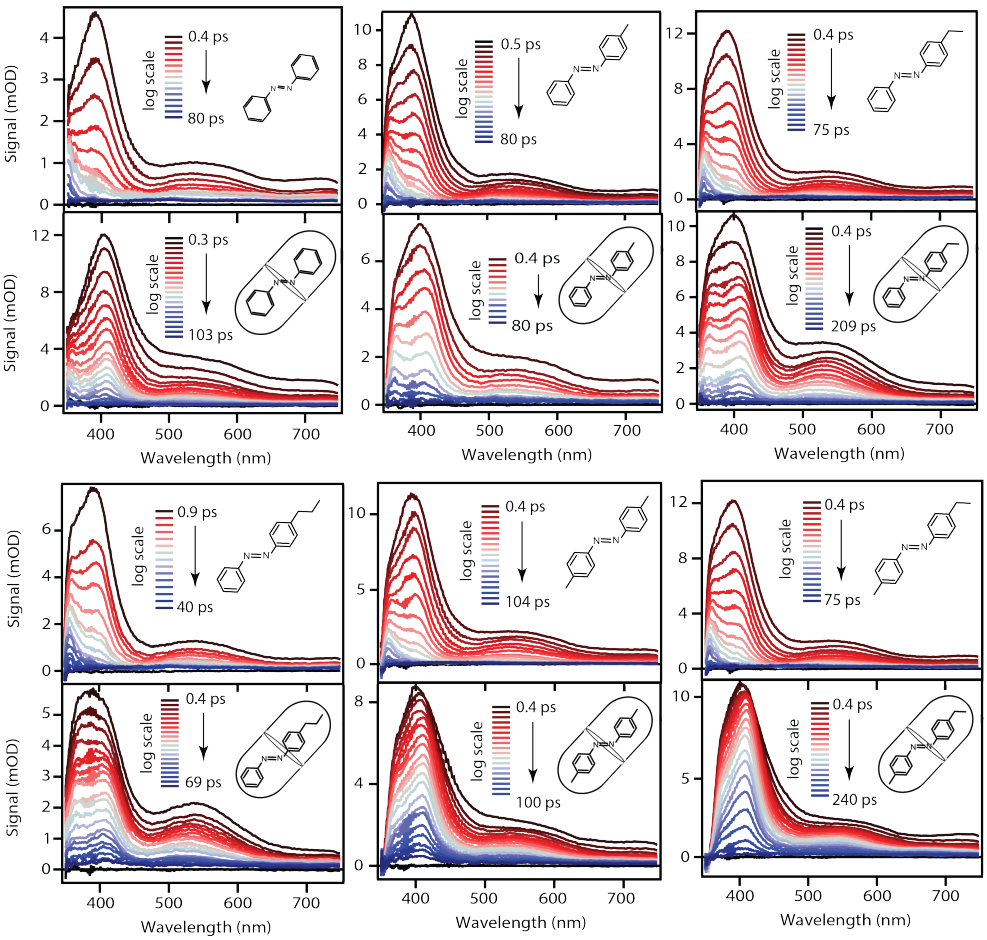

Figure S6: Evolution of the TA spectrum from ∼0.3 ps to ∼100 ps following $\pi\pi^*$ excitation of *t*-Az in cyclohexane and *t*-Az@OA_2. See Figure S5 for shorter time delays.

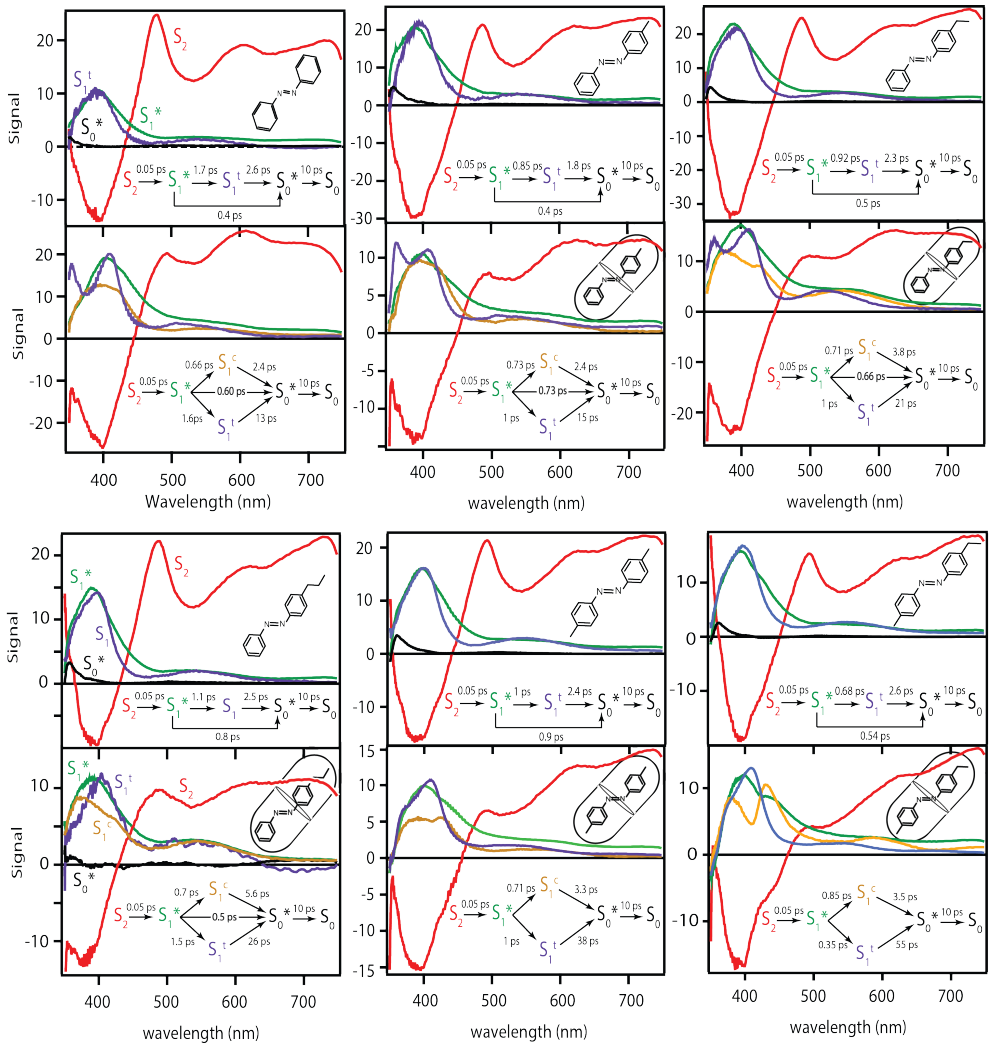

Figure S7: Species associated spectra (SAS) from global fits to the TA data using the kinetic models shown as insets following $\pi\pi^*$ excitation of each *t*-Az derivative in cyclohexane and in the OA_2 capsule. Lifetimes from each fit are shown in the insets. See main text for details.