Supplementary Information for:

Optical and Computational Study of the *trans* ↔ *cis* Reversible Isomerization of the Commercial Bis-Azo Dye Bismarck Brown Y

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Photolysis Kinetics Analysis

Bismarck Brown Y can undergo two reversible *cis/trans* isomerization processes.

$$\underset{(x)}{EE} \underset{k_{-x}}{\overset{k_x}{\rightleftharpoons}} \underset{(y)}{EZ} \underset{k_{-y}}{\overset{k_y}{\rightleftharpoons}} \underset{(z)}{ZZ}$$

Isomerizations EE --> EZ and EZ --> ZZ are photo-driven. The reverse (*cis-trans*) processes are thermally driven. Concentrations *x*, *y*, and *z* are related to each other through differential equations (**5**)

$$\frac{dx}{dt} = -k_x \emptyset x + k_{-x} y$$

$$\frac{dy}{dt} = k_x \emptyset x - k_{-x} y - k_y \emptyset y + k_{-y} z \qquad (5)$$

$$\frac{dz}{dt} = k_y \emptyset y - k_{-y} z$$

where $\emptyset$ is the photon flux. We can determine the time profile of all concentrations by solving equations (**5**). This is best done numerically by defining a series of incremental time-slices, *i*, having period Δt, and solving the system numerically as shown in equation (**6**). Discretization gives:

$$\frac{x_i - x_{i-1}}{\Delta t} = -k_x \emptyset x_i + k_{-x} y_i$$

$$\frac{y_i - y_{i-1}}{\Delta t} = k_x \emptyset x_i - (k_{-x} + k_y \emptyset) y_i + k_{-y} z_i \qquad (6)$$

$$\frac{z_i - z_{i-1}}{\Delta t} = k_y \emptyset y_i - k_{-y} z_i$$

and collecting time-slices:

$$\left(\frac{1}{\Delta t} + k_x \emptyset\right) x_i - k_{-x} y_i = \frac{x_{i-1}}{\Delta t}$$

with corresponding expressions for *y* and *z*. This system can be solved recursively for each time-slice *i*, by matrix equation (**7**)

$$AC_i = \frac{1}{\Delta t} C_{i-1} \qquad (7)$$

where $\boldsymbol{C}_i$ is the concentration vector

$$C_i = \begin{bmatrix} x_i \\ y_i \\ z_i \end{bmatrix} \qquad (8)$$

expressed in expanded form as

$$\begin{bmatrix} \left(\frac{1}{\Delta t} + k_x\right) & -k_{-x} & 0 \\ -k_x\emptyset & \left(\frac{1}{\Delta t} + k_{-x} + k_y\emptyset\right) & -k_{-y} \\ 0 & -k_y\emptyset & \left(\frac{1}{\Delta t} + k_{-y}\right) \end{bmatrix} \begin{bmatrix} x_i \\ y_i \\ z_i \end{bmatrix} = \frac{1}{\Delta t} \begin{bmatrix} x_{i-1} \\ y_{i-1} \\ z_{i-1} \end{bmatrix} \qquad (9)$$

Calculation of Rate Constants

Rate constants, k_x, k_{-x}, k_y, and k_{-y} (equation **9**), were calculated from DFT energies of the corresponding species in accordance with transition state theory. The algorithm starts by loading vector $\boldsymbol{C}_{-1}$ with initial conditions ($x = [EE]_0$, $y = 0$, $z = 0$), and evaluating the elements of matrix $\boldsymbol{A}$. Vector $\boldsymbol{C}_i$ (equation **8**) is then determined by recursively solving equation (**3**) *via* a standard LU decomposition for each time-slice, *i*.

Pump-Probe Isomerization Spectroscopy Data

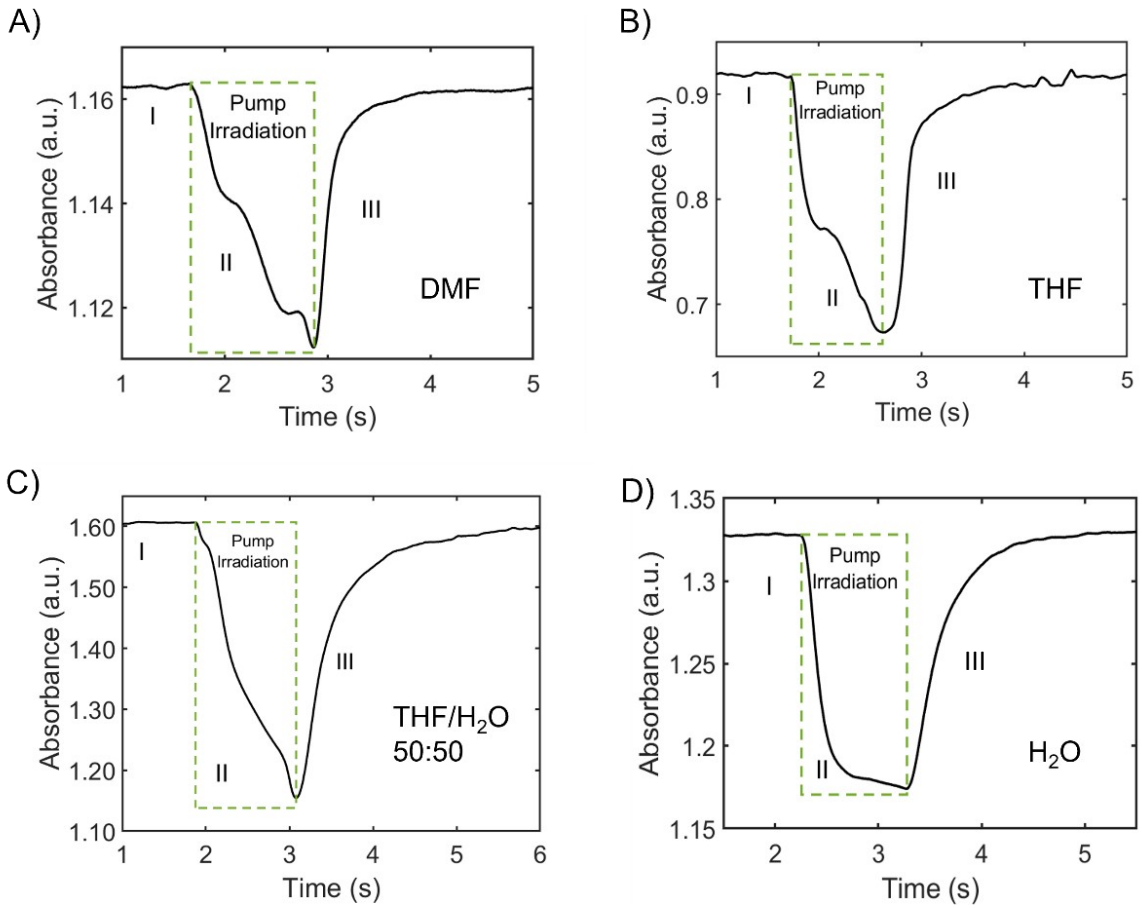


Figure S1. The absorbance *vs* time profiles of BBY in solvents (a) DMF, (b) THF, (c) THF/H_2O, and (d) H_2O. (I) Before irradiation, (II) during 1s pulse with 532nm laser, (III) *cis* decay in dark.

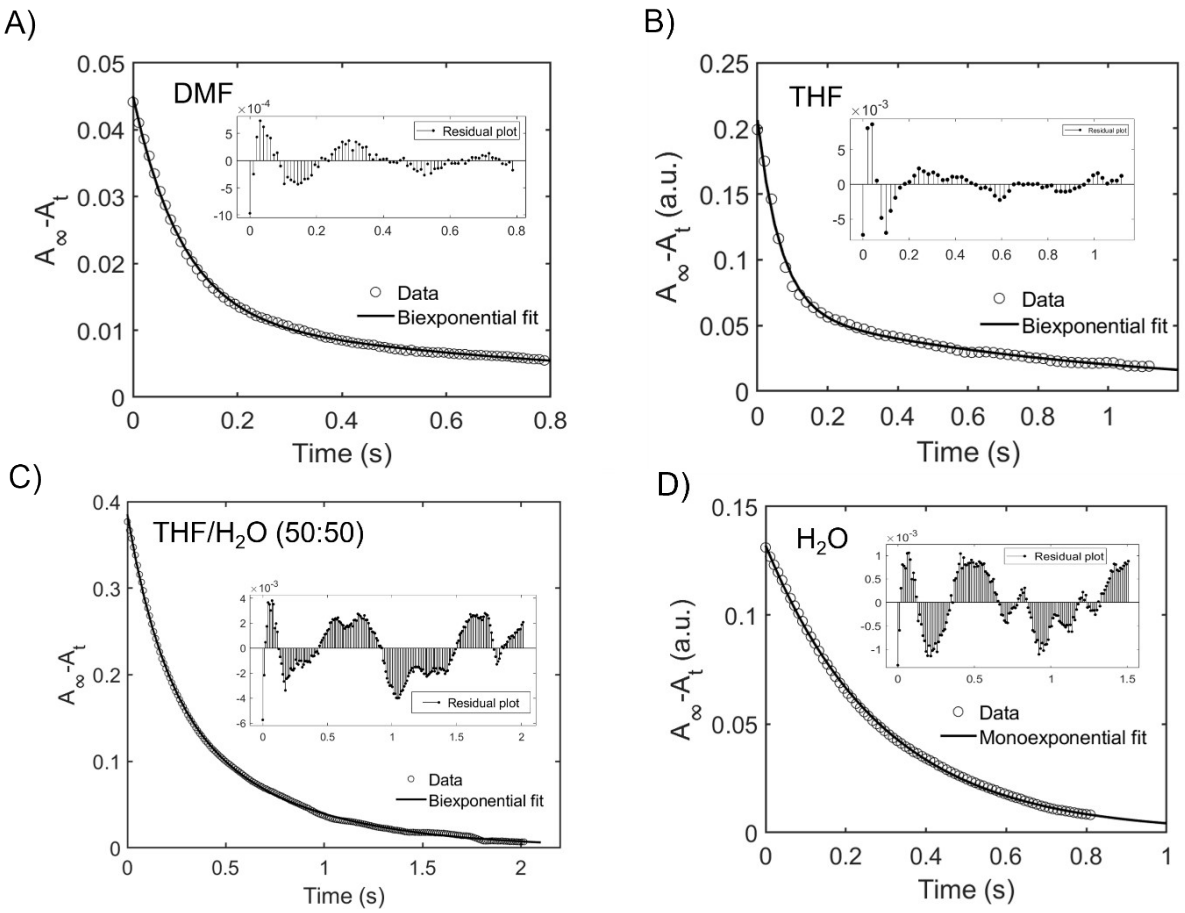
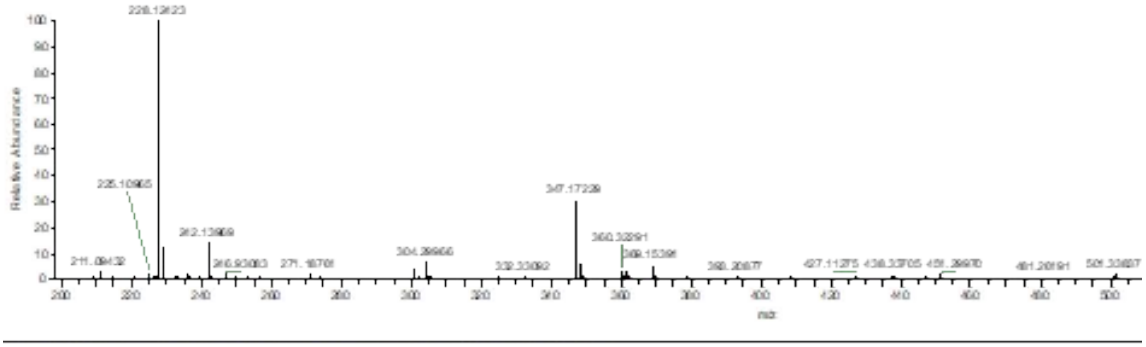
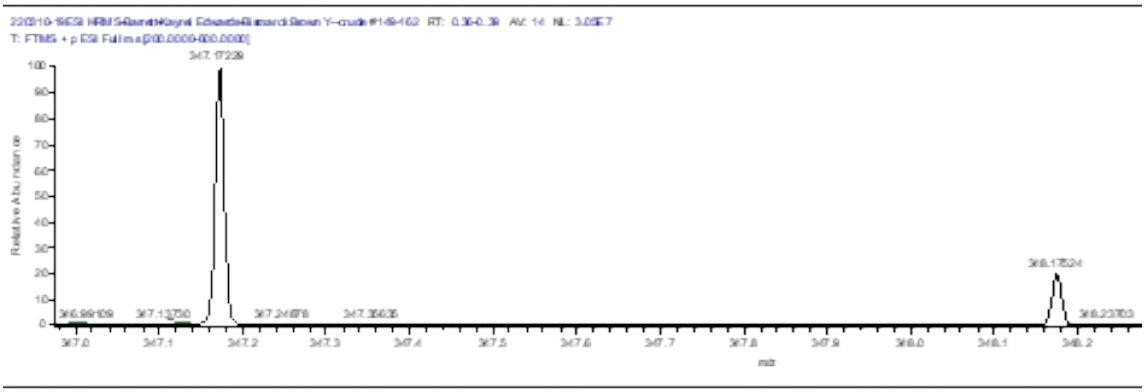


Figure S2. The decay of *cis* isomer fit to biexponential kinetics of BBY in solvents (a) DMF, (b) THF, (c) THF/H_2O, and (d) H_2O. The inset shows the residual plot between our least-squares four-parameter biexponential fit and the data.





220310-19ESI HRMS-Barrett-Kayrel Edwards-Bismarck Brown Y--crude#149-162 RT: 0.36-0.39 AV: 14
T: FTMS + p ESI Full ms [200.0000-600.0000]
m/z= 347.16072-347.18676

m/z	Intensity	Relative	Resolution	Charge	Theo. Mass	Delta	RDB	Composition

Figure S3. Mass spectra of crude BBY.

- Crude BBY (ESI +p, m/z= 347 ($C_{18}H_{19}N_8$), 228 ($C_{12}H_{14}N_5$), 242 ($C_{13}H_{16}N_5$), expected mass ($C_{18}H_{18}N_8$.2HCl, FW=419.3 g/mol).
- Recrystallized BBY (ESI +p, m/z= 347 ($C_{18}H_{19}N_8$), 228 ($C_{12}H_{14}N_5$), 242 ($C_{13}H_{16}N_5$), expected mass ($C_{18}H_{18}N_8$.2HCl, FW=419.3 g/mol)
- Chrysoidine (ESI +p, m/z= 213 ($C_{12}H_{13}N_4$), expected mass ($C_{12}H_{12}N_4$.HCl, FW=248 g/mol).

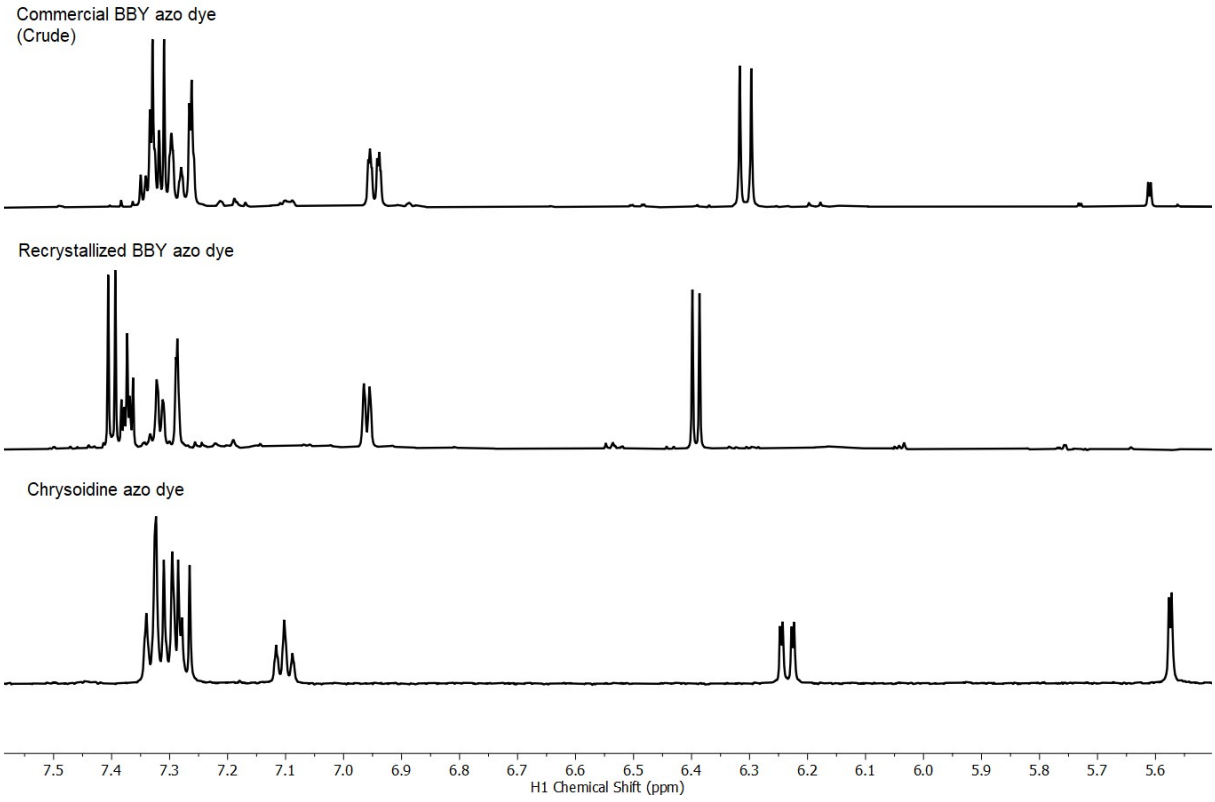


Figure S4. H^1 - NMR spectra of crude commercial BBY, recrystallized BBY, and Chrysoidine azo dyes.

- Crude commercial BBY azo dye (500 MHz, D_2O) δ 7.37 – 7.24 (m, 4H), 6.98 – 6.92 (m, 1H), 6.31 (d, *J* = 9.9 Hz, 1H).
- Recrystallized BBY azo dye (800 MHz, D_2O) δ 7.40 (d, *J* = 9.9 Hz, 2H), 7.39 – 7.35 (m, 2H), 7.32 (dd, *J* = 8.1, 2.2 Hz, 1H), 7.29 (t, *J* = 2.2 Hz, 1H), 6.96 (dd, *J* = 8.0, 2.1 Hz, 1H), 6.39 (d, *J* = 9.9 Hz, 2H).
- Chrysoidine azo dye (500 MHz, D_2O) δ 7.37 – 7.24 (m, 5H), 7.11 (d, *J* = 7.2 Hz, 1H), 6.24 (dd, *J* = 9.9, 2.3 Hz, 1H), 5.57 (d, *J* = 2.3 Hz, 1H).

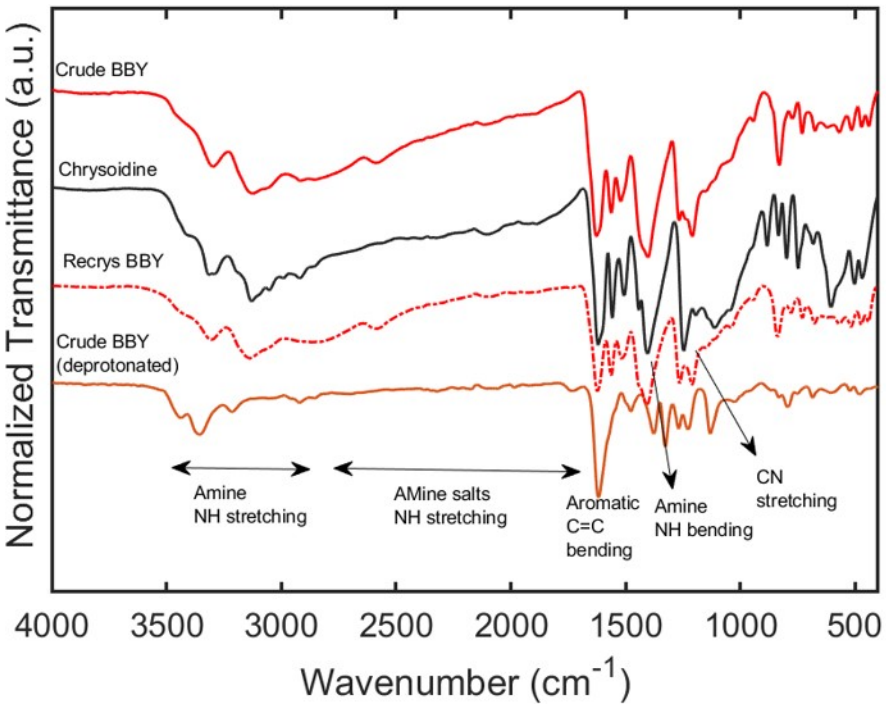


Figure S5. FTIR spectra of crude commercial BBY, Chrysoidine, recrystallized BBY and crude BBY (deprotonated) azo dyes.

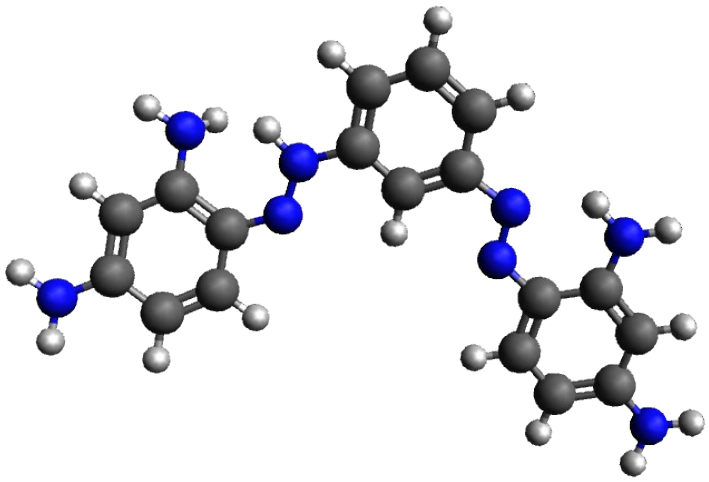


Figure S6. DFT optimized geometry of the protonated EE (*trans*) isomer of BBY.

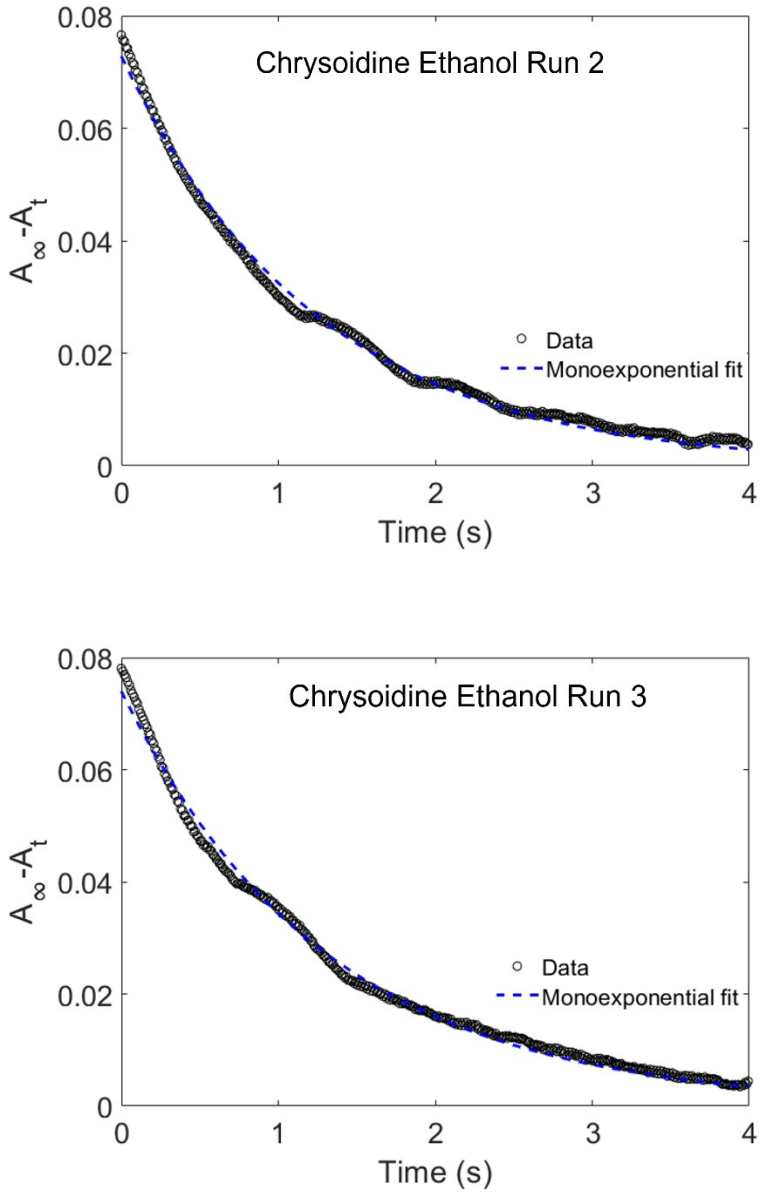


Figure S7. Runs '2' and '3' showing the decay of *cis* isomer fit to monoexponential kinetics of Chrysoidine.

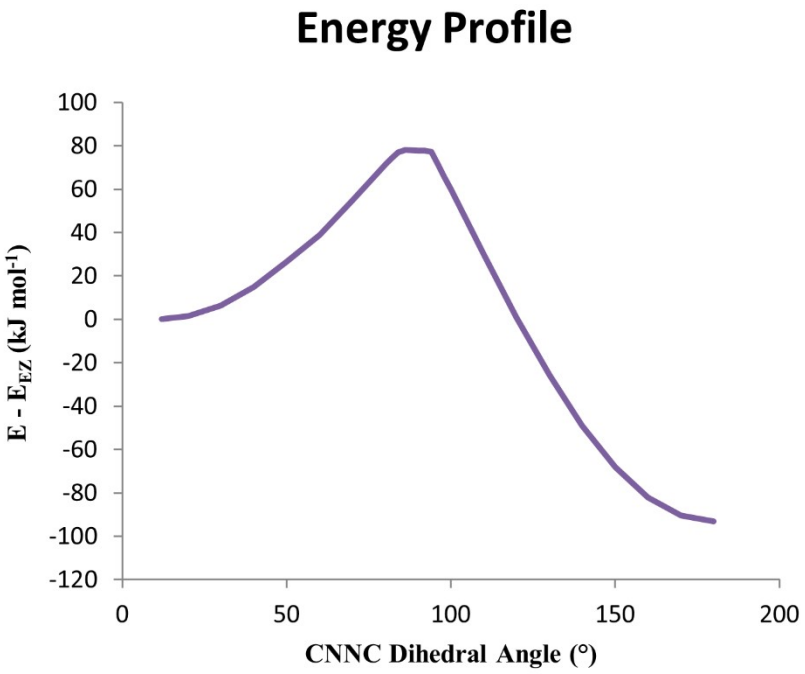


Figure S8. **E**nergy profile showing a typical monotonic rise from the *cis* isomer to the activation energy, followed by a monotonic fall to the *trans* isomer, as a plot of relative Energy *vs* CNNC bond angle.