

Electronic Supporting Information

Unusual Concentration Dependence of the Photoisomerization Reaction in Donor-Acceptor Stenhouse Adducts

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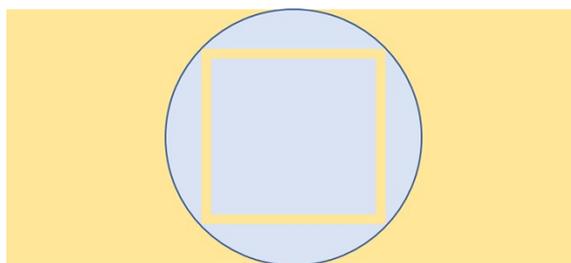
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1. Liquid sample preparation: 50 μmol and 10 μmol of **DASA** were placed in both chloroform and toluene, respectively to create 1×10^{-2} M and 1×10^{-3} M stock solutions. From here, 1×10^{-3} , 1×10^{-4} , 3×10^{-5} , 3×10^{-6} , and 8×10^{-6} M solutions were made via serial dilution.

- a. Solution absorption studies: For 3×10^{-6} M, a 1-cm cuvette was used. For higher concentrations in the range of 10^{-3} - 10^{-6} M, a commercial demountable cell with a variable path length O-rings was utilized to ensure that the optical densities remained at ~ 0.30 . The following table illustrates which path lengths were used with their respective concentrations:

Concentration (M)	Path length (mm)
1×10^{-2}	0.0005
1×10^{-3}	0.015
1×10^{-4}	0.2
3×10^{-5}	0.5
8×10^{-6}	2.5
3×10^{-6}	10

For $[\text{DASA}] = 10^{-2}$ M, a 0.5-micron path length cell was used. The fabrication of the cell was done by coating a microscope slide with photoresist and then patterning the shape of a square inscribed in a circle with a 1-cm diameter. The irradiated photoresist was dissolved away and gold was then deposited via electron beam evaporation. Finally, the remaining photoresist was washed away with acetone, leaving the pattern displayed in Schematic S1. The parameters of the OceanView software are described in the main paper.



Schematic S1. Diagram of the 0.5-micron cell used in the steady state absorption study. The gold regions on the slide is composed of 500 nm thick gold and the blue regions are vacant so that liquids can be placed inside.

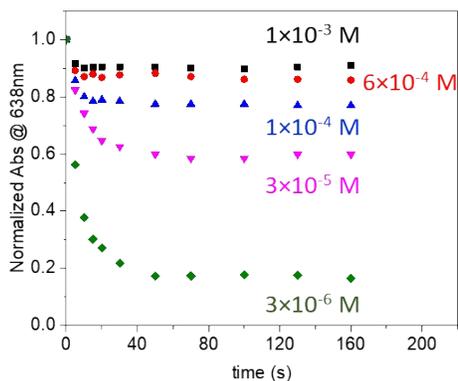


Figure S1. The absorption decay of **DASA** in toluene under 638 nm irradiation at 1.0 mW/cm². The PSS absorbance is lower due to a slower k_{back} .

2. Powder X-Ray Diffraction & Polarized Microscopy

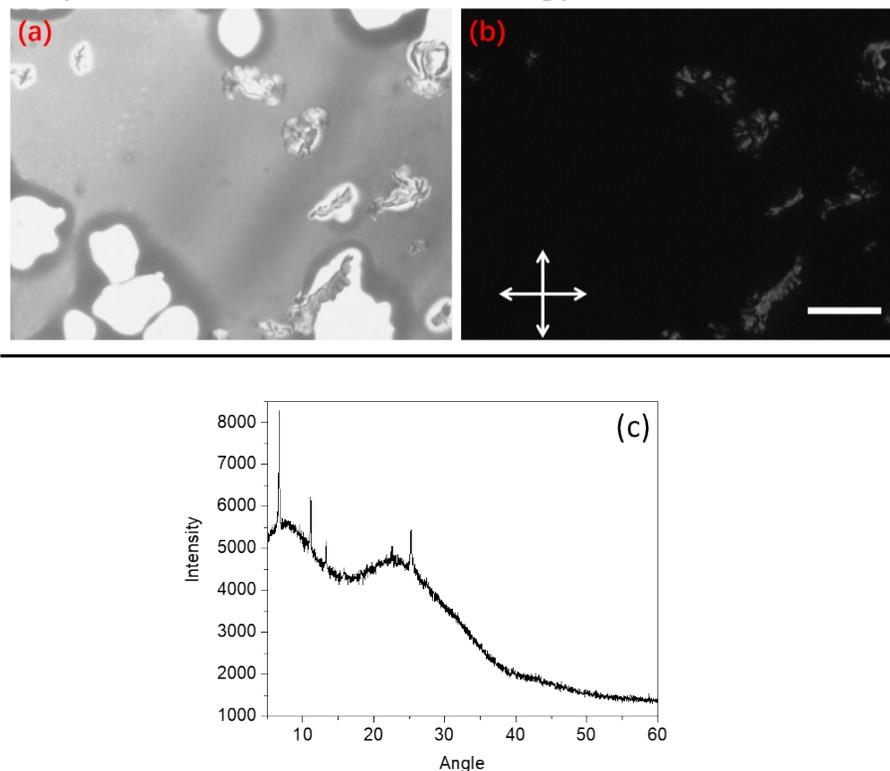


Figure S2. (a) Optical microscope image of **DASA** neat film at bright field. (b) Cross-polarized microscope image of **DASA** neat film of the same region as (a). Only a few regions exhibit birefringence. Scale bar: 50 μm . (c) X-ray diffraction pattern of **DASA** neat film.

3. Thin film preparation: 3 mM of **DASA** was prepared using methylene chloride as the solvent. From here, 6 μmol of **DASA** was dissolved with polystyrene ($\rho=1.04 \text{ g/cm}^3$) and polymethyl(methacrylate) ($\rho=1.18 \text{ g/cm}^3$) to create films of the following concentrations: 1×10^{-1} , 1×10^{-2} , 1×10^{-3} , and 1×10^{-4} M for PS and 1×10^{-1} , 1×10^{-2} , 8×10^{-3} , and 9×10^{-4} M for PMMA. The neat films were created by drop casting **DASA** dissolved in toluene on microscope slides. The films were then placed in an 80°C oven for approximately 10 minutes so that the residual solvent would be evaporated off.

b. Film absorption studies:

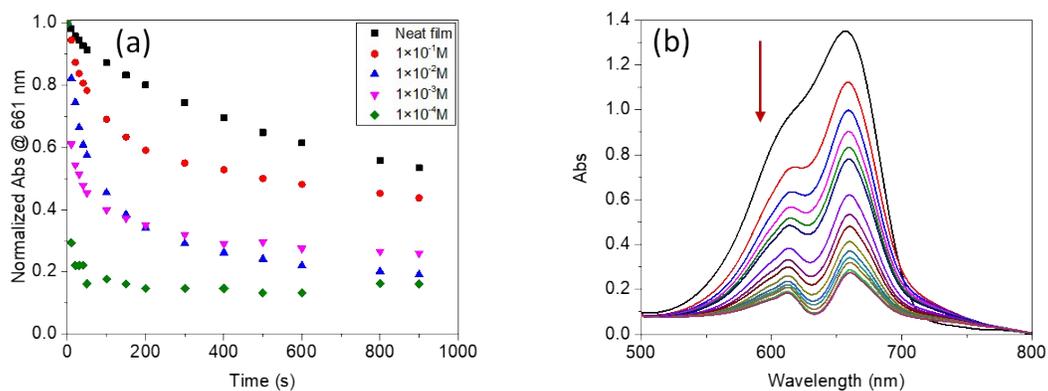


Figure S3. (a) The decay of absorption of **DASA/PS** films monitored at 661 nm (peak absorbance). (b) A sample of the decay of absorption of a **DASA/PS** film (1×10^{-2} M). The dip in the absorption at 638 nm is caused by the irradiation source.

4. Log-log plots of k_{back} & quantum yields vs concentration

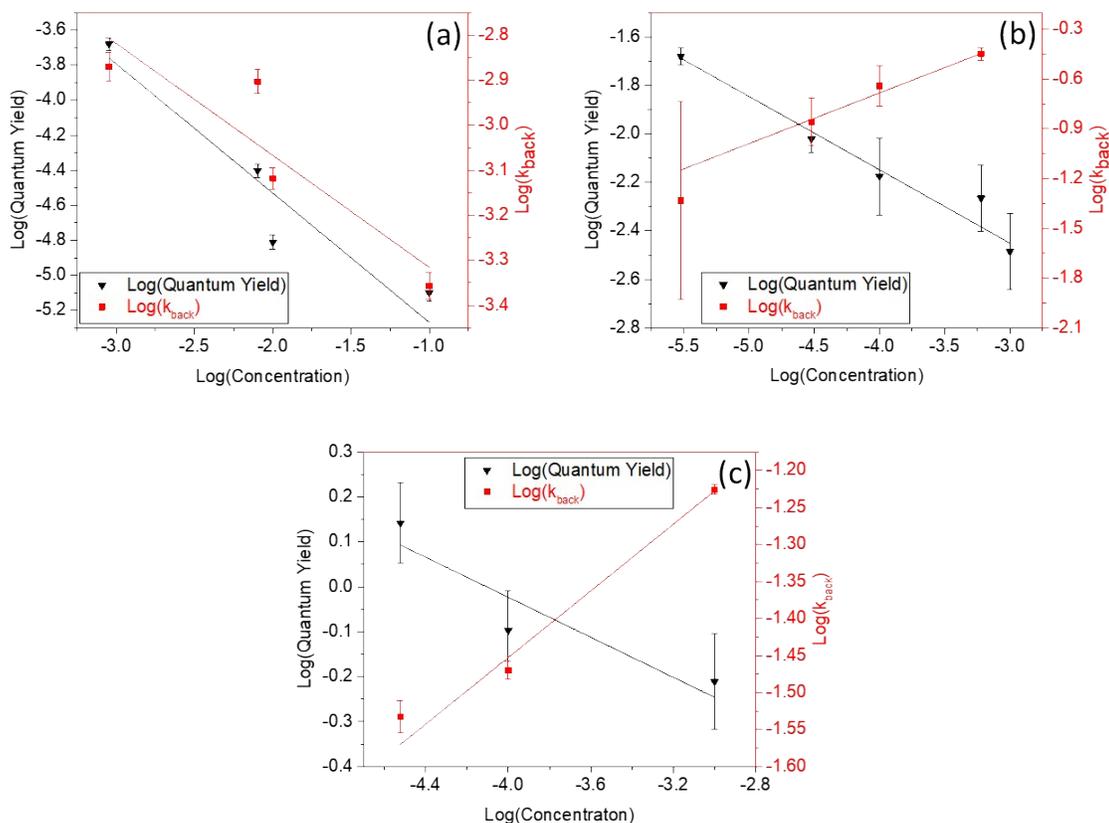


Figure S4. Log(QY) and $\log(k_{back})$ - $\log[\text{DASA}]$ plots for **DASA** in PMMA **(a)**, toluene **(b)**, and chloroform **(c)** are shown. A linear fit could be also shown for all cases. The slopes of k_{back} and the quantum yield in PMMA samples are -0.25 ± 0.09 and -0.74 ± 0.17 , respectively. The slopes for the toluene samples are $+0.31 \pm 0.03$ and -0.30 ± 0.02 . The slopes of the chloroform samples are $+0.23 \pm 0.02$ and -0.22 ± 0.09 .

5. Transient absorption

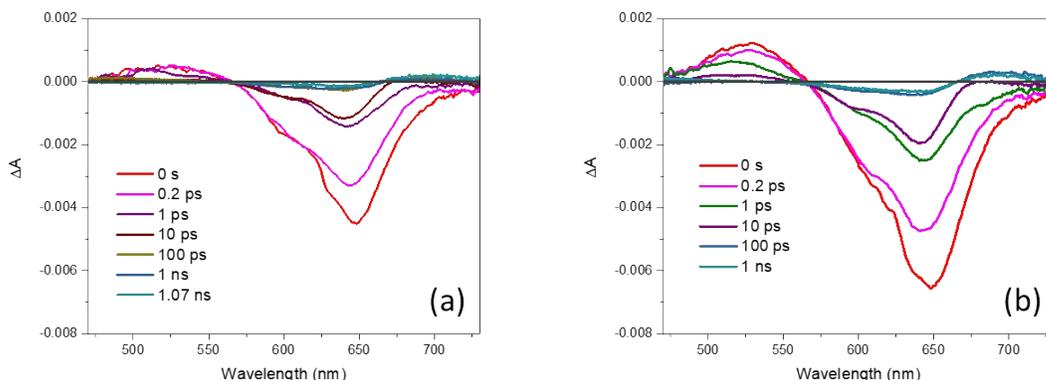


Figure S5. Raw transient absorption spectra of both **(a)** 30 μM and **(b)** 1 mM **DASA** in CHCl_3 . The long-time derivative feature between both concentrations are comparable relative to their initial bleaches.

- 6. Obtaining T_g of DASA/PS films:** Approximately 0.5 mL of the PS/**DASA** mixture was drop cast into differential scanning calorimetry (DSC) pans specifically designed for the Netzsch 241 Polyma differential scanning calorimeter. The pans were placed into an 80°C oven for 10 minutes to encourage solvent evaporation. Once the pans were dry, they were placed into the instrument to collect the glass transition temperatures (T_g) of the films.

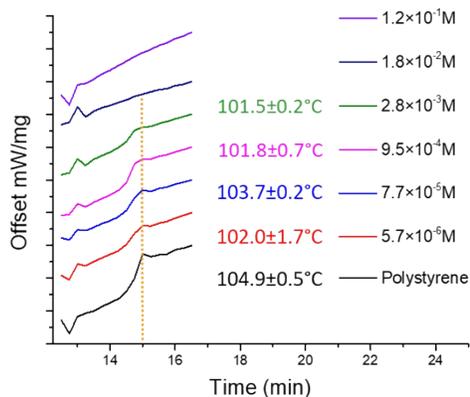


Figure S6. T_g of pure PS and various concentrations of **DASA-PS** were collected via DSC. The T_g appears to decrease slightly as concentration is increased. At the two highest concentrations, the T_g diminishes and is not observed.

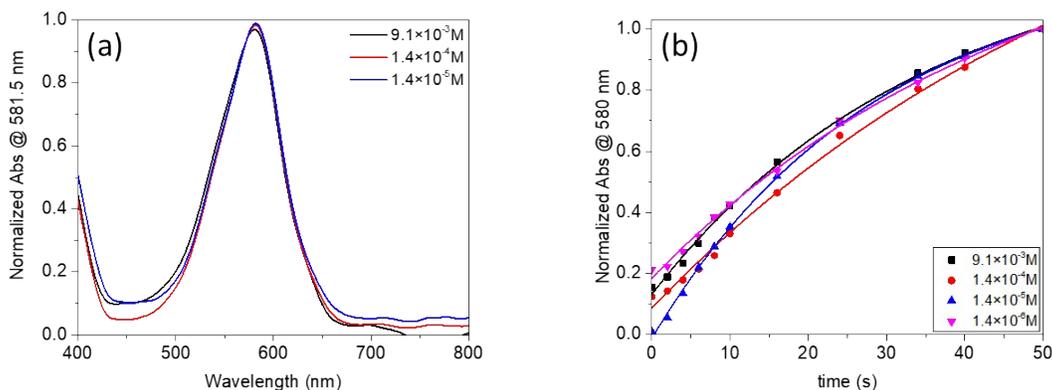
7. Spiropyran studies

a. Liquid sample preparation: The spiropyran derivative, 1,3,3-trimethylindolino-6'-nitrobenzopyrylospiran, was used as a control in this study. Spiropyran undergoes a ring-opening reaction upon irradiation with UV light to form its polar counterpart, merocyanine. The merocyanine form can thermally relax back to recover the original spiropyran. 91 mmol of the spiropyran derivative was used to create a 9.1 mM stock solution with chloroform as the solvent. From here, 1.4×10^{-6} - 1.4×10^{-4} M concentrations were prepared by method of serial dilution.

b. Steady-state absorption studies: Just as with **DASA**, we wanted to ensure that the absorption at the irradiation wavelength (365 nm) was ~ 0.30 to ensure uniform irradiation about the sample. The extinction coefficient ($\epsilon_{343 \text{ nm}}$) was estimated to be $22,000 \text{ M}^{-1}\text{cm}^{-1}$. The following table represents the path lengths used with their respective concentrations:

Concentration (M)	Path length (mm)
9.1×10^{-3}	0.015
1.4×10^{-4}	1
1.4×10^{-5}	10
1.4×10^{-6}	100

For 1.4×10^{-5} M and 1.4×10^{-6} M, a 1 cm and 10 cm cuvette was used respectively. The samples were irradiated with a 365 nm lamp at 1.52 mW/cm^2 . Figure S5 (a) visualizes the absorption spectra of merocyanine of the various concentrations overlaid on one another. Both the formation of merocyanine (b) and recovery of the spiropyran (c) are observed through the increase and decrease of absorption in the 580 nm regime. It is worth noting that the spiropyran samples were not irradiated to a photostationary state (PSS) because at low concentrations ($\leq 10^{-4}$ M), the intensity of the UV lamp damaged the samples irreversibly. To circumvent this, the samples were only irradiated to upwards of 50 seconds.



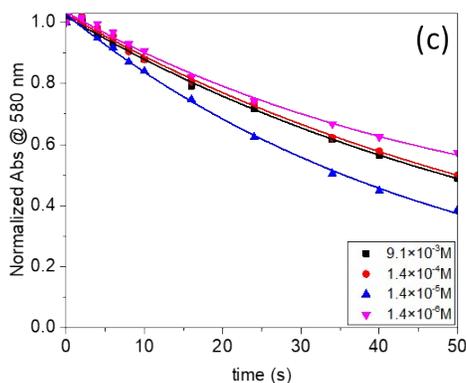


Figure S7. The steady state absorption of the spiropyran derivative is shown. **(a)** illustrates the merocyanine spectra overlaid on each other. We note that the spectral lineshape remains constant despite increasing orders of magnitude in concentration. The 10^{-6} M absorbance was omitted due to poor signal-to-noise. **(b)** The increase of absorption at 580 nm due to the formation of merocyanine during irradiation with 365 nm light. **(c)** Decay of the 580 nm absorbance due to the thermal relaxation of the merocyanine derivative back to the spiropyran form after the light is removed.

c. Kinetics of 1,3,3-trimethylindolino-6'-nitrobenzopyrylospiran: The quantum yields and k_{back} are summarized in the following table.

Concentration (M)	k_{back} (s^{-1}) ($\times 10^{-3}$)	$k_{forward}$ (s^{-1}) ($\times 10^{-3}$)	Φ (%)
9.1×10^{-3}	15 ± 3	30 ± 3	12 ± 2
1.4×10^{-4}	14 ± 5	16 ± 4	7 ± 2
1.4×10^{-5}	21 ± 4	35 ± 3	15 ± 2
1.4×10^{-6}	20 ± 5	21 ± 3	9 ± 2

Here, Φ was calculated by using $k_{forward} = I\sigma\Phi$.

8. Derivation of N_{open} as a function of t

Starting from equation 1a, $\frac{dN_{open}}{dt} = -\sigma I \varphi_{OC} N_{open} + k_{back} N_{closed}$, recall that $N_{open} + N_{closed} = N_0$ and that N_{closed} can be expressed in terms of N_{open} and N_0 , yielding

$$\frac{dN_{open}}{dt} = -\sigma I \varphi_{OC} N_{open} + k_{back}(N_0 - N_{open}) \quad (S1)$$

Rearranging S1 and grouping the N_{open} terms gives the following

$$\frac{dN_{open}}{dt} = N_0 k_{back} - N_{open}(\sigma I \varphi_{OC} + k_{back}) \quad (S2)$$

Recall $k = \sigma I \varphi_{OC} + k_{back}$ and substituting k into S2

$$\frac{dN_{open}}{dt} = N_0 k_{back} - N_{open} k \quad (S3)$$

We recognize that S3 is a separable differential equation and upon solving, yields

$$-\frac{1}{k} \ln(k_{back} N_0 - N_{open} k) = t + C \quad (S4)$$

Where C is the constant of integration. Equation S4 can be rearranged so that N_{open} is a function of t

$$N_{open}(t) = \frac{N_0 k_{back}}{k} - \frac{e^{-kt}}{k e^{kC}} \quad (S5)$$

Recall that $N_{open}(t=0) = N_0$, which enables us to solve for C (the work is omitted and the exercise is left to the reader), which gives $C = -\frac{1}{k} \ln(N_0 k_{back} - N_0 k)$. Substituting C into S5 yields

$$N_{open} = \frac{N_0 k_{back}}{k} - \frac{e^{-kt}}{k e^{-\left(\frac{k}{k}\right) \ln(N_0 k_{back} - N_0 k)}} \quad (S6)$$

Finally, simplifying and grouping like-terms yields the final equation that describes N_{open} as a function of t

$$N_{open} = \frac{N_0 k_{back}}{k} + N_0 \left(1 - \frac{k_{back}}{k}\right) e^{-kt} \quad (S7)$$

9. Determination of ϵ and σ of DASA

The molar extinction coefficient (ϵ) at the maximum absorbance ($\lambda=652$ nm) was estimated to be $10^5 \text{ M}^{-1}\text{cm}^{-1}$.¹ From here, the absorbances were converted to ϵ so that the $\epsilon_{638 \text{ nm}}$ could be found. The extinction coefficient used to calculate the quantum yields is estimated to be $80,600 \pm 986 \text{ M}^{-1}\text{cm}^{-1}$, which is then converted to a cross section by multiplying by a conversion factor of 3.826×10^{-21} .

(1) Helmy, S.; Leibfarth, F. A.; Oh, S.; Poelma, J. E.; Hawker, C. J.; Alaniz, J. R. d., Photoswitching Using Visible Light: A New Class of Organic Photochromic Molecules. *J. Am. Chem. Soc.* **2014**, *136*, 8169–8172.

10. FWHM & peak absorbance of DASA/polymer films

PMMA			PS		
Concentration (M)	FWHM (cm^{-1})	λ_{peak} (nm)	Concentration (M)	FWHM (cm^{-1})	λ_{peak} (nm)
1×10^{-1}	138,831	637.7	Neat film	46,089	674.1
1×10^{-2}	165,371	668.7	1×10^{-1}	74,482	656.7
8×10^{-3}	167,842	638.1	1×10^{-2}	104,134	656.6
9×10^{-4}	170,416	635.6	1×10^{-3}	146,049	657.3
			1×10^{-4}	158,403	655.1