Electronic Supplementary Information

Two-photon Absorption Spectra of a Near-Infrared 2-Azaazulene Polymethine Dye: Solvation and Ground-State Symmetry Breaking

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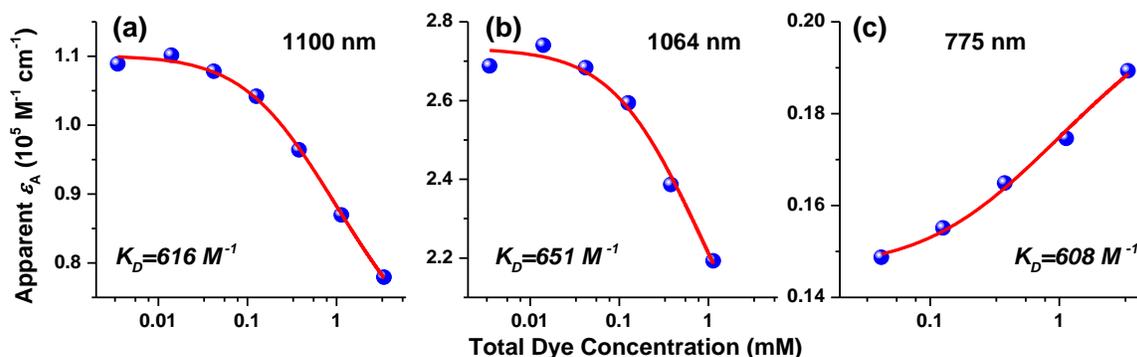
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Figure S1: The fitting (red curve) of the experimental apparent ε (blue dot) using dimerization model at three different wavelengths: 1100 nm (a), 1064 nm (b), and 775 nm (c)
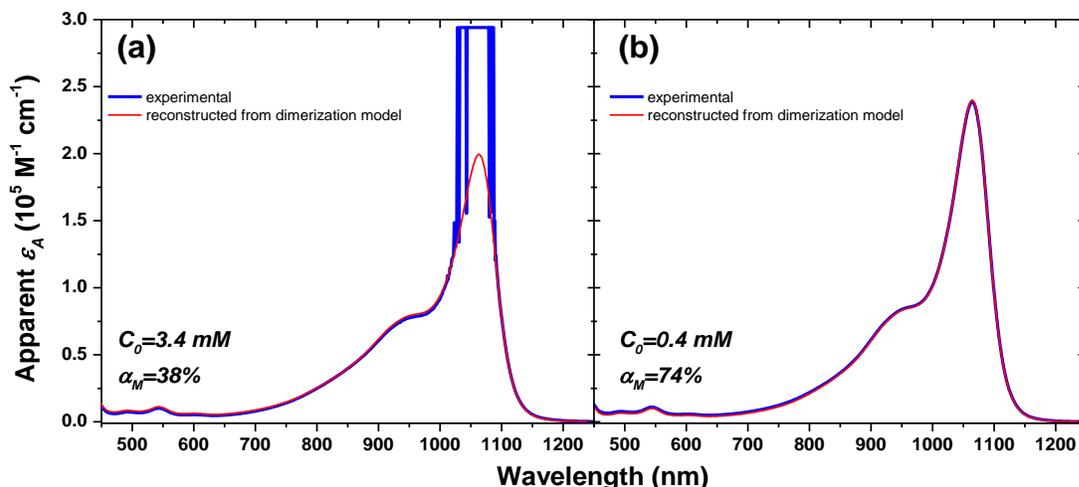
Figure S2: Comparison of apparent ε_A spectra of JB17-08 in DCM (red curves), based on dimerization model, with experimental results (blue curves) at C_0=3.4 mM (a) and C_0=0.4 mM (b).
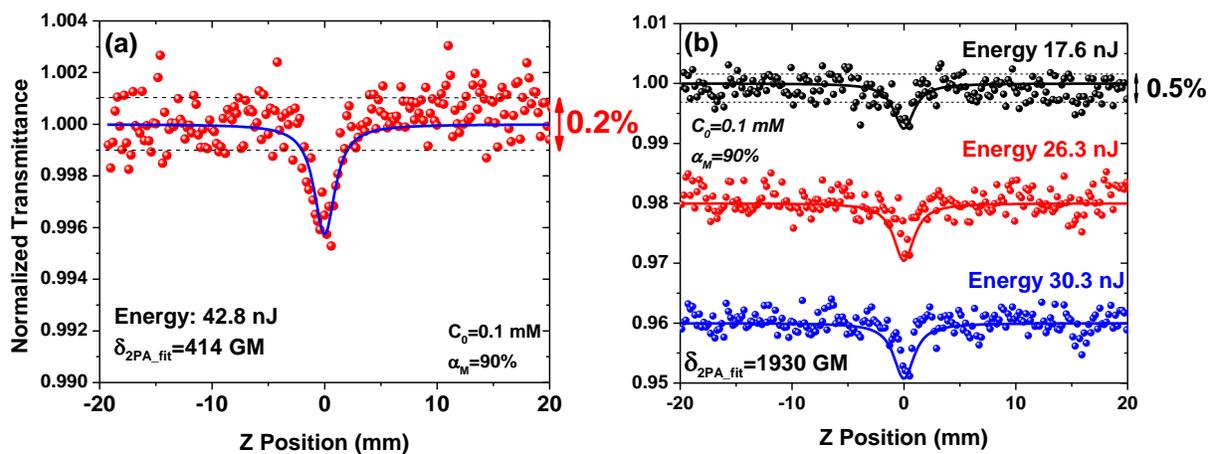

Figure S3: Z-scan traces for JB17-08 in DCM at C_0=0.1 mM at 1.55 μm (a) and 1.8 μm (b). Note for 1.55 μm, the spot size at the focus is 23.5 μm (HW1/e^{2}M) and the pulsewidth is 80 fs (FWHM); for 1.8 μm the spot size at the focus is 25 μm (HW1/e^{2}M) and the pulsewidth is 100 fs (FWHM). The noise level at 1.55 μm is 0.2%, while the noise level at 1.8 μm is 0.5%, as marked in the figure.
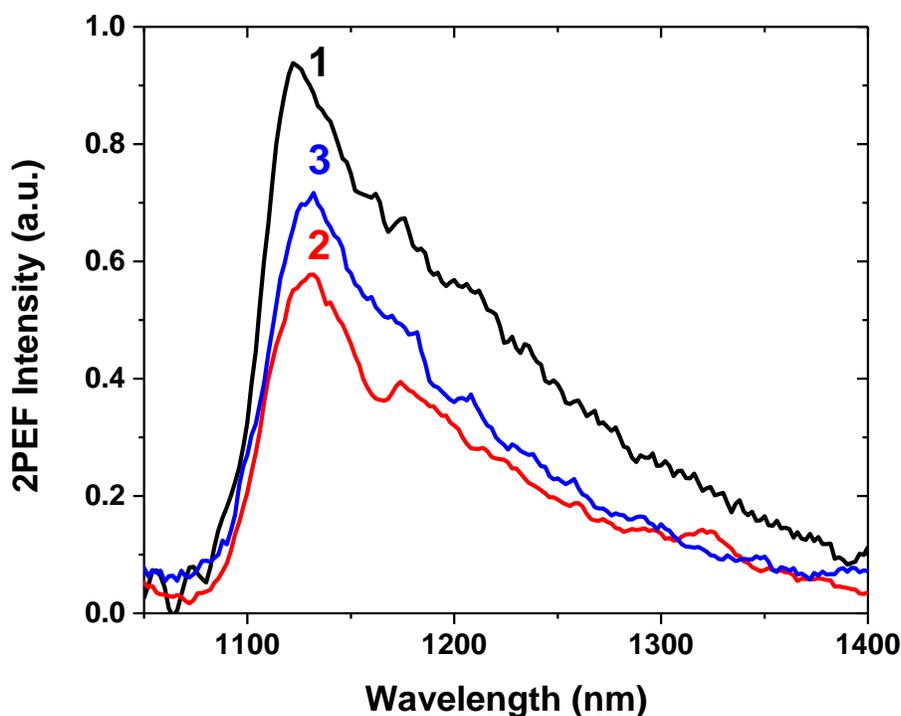
Figure S4: 2PEF signal of JB17-08 in DCM at C_0=0.1 mM, at the excitation wavelengths of 1800 nm (1), 1850 nm (2), and 1900 nm (3), with the same excitation irradiance. The δ_{2PA} is thus proportional to the integrated area of the 2PEF signal.

Derivation of mathematical equivalence between dimerization model and ion pair model

To prove that the ion pair model: *Cation+Counter-Ion↔Ion Pair*, is mathematically equivalent to dimerization model: 2M↔D, we can write the relation between the concentration of the cations, C_{cation}, and the concentration of the ion pairs, $C_{ion\,pair}$, as

$$K_{ion\,pair} = \frac{C_{ion\,pair}}{C_{cation} \cdot C_{counter\text{-}ion}} = \frac{C_{ion\,pair}}{C_{cation}^2} = \frac{1-\alpha_{cation}}{\alpha_{cation}^2 C_0}, \tag{S 1}$$

where $K_{ion\,pair}$ is the constant of dynamic equilibrium, C_0 is the total dye concentration, and α_{cation} =($C_{counter\text{-}ion}$ /C_0) is the fraction of cations. Note that the concentrations of cations and its counter-ions are equal.

Equation S1 can be rewritten as

$$\frac{K_{ion\,pair}}{2} = \frac{1 - \alpha_{cation}}{2\alpha_{cation}^2 C_0} \equiv K_D', \tag{S 2}$$

where we define K_D' as the constant equivalent to the dimerization constant K_D. Note that equation S 2 is mathematically equivalent to Equation 2 in the dimerization model. Similar to Equation 2, Equation S 2 yields α_{cation} as:

$$\alpha_{cation} = \frac{\sqrt{8K_D'C_0 + 1} - 1}{4K_D'C_0}. \tag{S 3}$$

Thus, the apparent absorptivity, ε_A, representing the averaged molar absorptivities of cations and the ion pairs, can be expressed as:

$$\varepsilon_A = \alpha_{cation}\varepsilon_{cation} + (1 - \alpha_{cation})\varepsilon_{ion\,pair}, \tag{S 4}$$

where ε_{cation} and $\varepsilon_{ion\,pair}$ are the molar absorptivity of the cations and the ion pairs, respectively. Note that the absorption from the counter-ions is placed in the UV range, not contributing to the absorption in the NIR range. Combining Equations S3 and S 4, we obtain:

$$\varepsilon_A = \frac{\sqrt{8K_D'C_0 + 1} - 1}{4K_D'C_0}(\varepsilon_{cation} - \varepsilon_{ion\,pair}) + \varepsilon_{ion\,pair}. \tag{S 5}$$

Equations S2 to S5 are mathematically equivalent to Equation 2 to 5. Therefore, we may conclude that the following nonlinear regression fitting yields the same K_D' and the same relation between ε_A and C_0 as shown in Figure 2b.

Details of experimental procedures for 2PA study

To obtain a relatively accurate shape of the δ_{2PA} spectrum of JB17-08 in DCM and ACN, we performed single-wavelength, single-arm Z-scan on the solutions with a concentration of 3 mM for DCM solution and 1.3 mM for ACN solution between 1350 nm to 2100 nm. Lead Sulfide (PbS) detector (PDA30G, Thorlabs) was used due to it wide spectral response range (1.0 – 2.9 μm). However, at several wavelengths between 1550 and 1800 nm, where the δ_{2PA} is relatively large, we performed dual-arm Z-scans [1] on a series of solutions with C_0 ranging from 5 mM down to 0.1 mM for the DCM solution using homemade Germanium (Ge) detectors. In comparison to PdS detectors, the noise level of Ge detectors is much reduced, which, in

combination with the dual-arm Z-scan technique, allows detection of extremely small Z-scan signals for a 0.1 mM solution in DCM and 0.18 mM solution in ACN ; however, due to the absorption gap at 0.67 eV (1850 nm) of Ge [2], the sensitivity of Ge detectors deteriorates dramatically beyond a wavelength of 1800 nm. Therefore, at the wavelengths 1850 nm and 1900 nm, we determined the δ_{2PA} in 0.1 mM solution in DCM and 0.07 mM solution in ACN by comparing their two-photon fluorescence (2PF) intensity against the 2PF excited at 1800 nm normalized to the same excitation irradiance. [3, 4] This allows us to extrapolate the correct δ_{2PA} spectrum of the monomer species in DCM.

References

1.   M. R. Ferdinandus, M. Reichert, T. R. Ensley, H. Hu, D. A. Fishman, S. Webster, D. J. Hagan and E. W. Van Stryland, *Opt. Mater. Express*, 2012, **2**, 1776-1790.
2.   P. Klocek, *Handbook of Infrared Optical Materials*, Marcel Dekker Inc., New York, 1991.
3.   C. Xu and W. W. Webb, *J. Opt. Soc. Am. B*, 1996, **13**, 481-491.
4.   N. S. Makarov, J. Campo, J. M. Hales and J. W. Perry, *Opt. Mater. Express*, 2011, **1**, 551-563.