Supporting Information

Excited-State Proton Transfer from the Photoacid 2-Naphthol-8-Sulfonate to Acetonitrile/Water Mixtures

Oren Gajst,⁷ Luís Pinto da Silva,^{a,b} Joaquim C.G. Esteves da Silva^{b,c} and Dan Huppert^{7,*}

^{*γ*} Raymond and Beverly Sackler Faculty of Exact Sciences, School of Chemistry,

Tel Aviv University, Tel Aviv 69978, Israel

^a Chemistry Research Unit (CIQUP), Department of Chemistry and Biochemistry, Faculty of Sciences of University of Porto, R. Campo Alegre 687, 4169-007 Porto, Portugal.

^b LACOMEPHI, GreenUP, Department of Geosciences, Environment and Territorial Planning, Faculty of Sciences of University of Porto, R. Campo Alegre 687, 4169-007 Porto, Portugal.

^a Chemistry Research Unit (CIQUP), Department of Geosciences, Environment and Territorial Planning, Faculty of Sciences of University of Porto, R. Campo Alegre 687, 4169-007 Porto, Portugal.

*Corresponding author: Dan Huppert

E-mail: dhuppert@post.tau.ac.il

Phone: 972-3-6407012

Fax: 972-3-6407491

Supporting Information Available:

- A. Preferential solvation.
- B. Absorption spectra of 2N8S in the presence of water.
- C. 2-naphthol-6-sulfonate Time-resolved fluorescence.

A. Preferential solvation

Suppan¹ studied the absorption and emission of polar solutes in solvent mixtures of different dielectric polarities. In such solvent mixtures, a process of preferential solvation, described as "dielectric enrichment", occurs near polar solute molecules. The polarity of a solvent is defined by Onsager's function, F, of the dielectric constant, ε .

$$F = \frac{2(\varepsilon - 1)}{2\varepsilon + 1}$$

The solute-solvent interaction energy is a linear function of the solvent polarity. The polarity of an "ideal" mixture of two solvents, composed of apolar, N, and polar, P, solvents, with dielectric constants ε_N and ε_P , respectively, is a simple linear combination of their mole fractions, χ_N and χ_P

$$F_{\text{Linear,Bulk}} = \chi_{\text{N}} F_{\text{N}} + \chi_{\text{P}} F_{\text{P}}$$

Dielectric "nonideality" of a binary solvent system refers to the deviation of the Onsager reaction field function from linearity with the polar mole fraction of the solvent mixture. A polar fluorophore, dissolved in an ideal dielectric mixture, exhibits a solvatochromic shift that is linear with the polar solvent mole fraction in its solvation sphere. As a result, the "local composition" can easily be determined from the absorption or the fluorescence band-peak shift. Kauffman and coworkers^{2,3} found, that in most cases, a linear approximation will not provide the local solvent composition around a polar fluorophore. Water molecules have the tendency to form hydrogen bonds with nearby water molecules and tend to strongly solvate hydroxyl groups of photoacids and sulfonate groups. They also tend to form a bridge of water molecules in acetonitrile-rich CH₃CN/H₂O mixtures tend to form such a bridge. In 2-naphthol-8-sulfonate a bridge of water molecules connects the 2-OH with the 8-sulfonate, and a unique intramolecular ESPT between the two sites takes place.

B. Absorption spectra of 2N8S in the presence of water



Figure S1: Shows the absorption spectra of 2N8S in CH₃CN rich CH₃CN-H₂O mixtures in the water range $0 < \chi_{water} < 0.367$.

C. 2-naphthol-6-sulfonate Time-resolved fluorescence



Figure S2: Normalized TCSPC signals of the ROH form of 2N6S (measured at 360nm) in CH₃CN/H₂O mixtures of varying mole ratio of water, χ_{water} . Panel a shows the range of $0 \le \chi_{water} \le 0.72$ on semilog scale. Panel b shows the range of $0.75 \le \chi_{water} \le 1$ on semilog scale.

References

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