

7-Cyanoindole Fluorescence as a Local Hydration Reporter: Application to Probe the Microheterogeneity of Nine Water-Organic Binary Mixtures

Debopreeti Mukherjee¹, Lilliana I. Ortiz Rodriguez², Mary Rose Hilaire¹, Thomas Troxler^{1,3}, and Feng Gai^{1,3,*}

¹*Department of Chemistry University of Pennsylvania, 231 South 34th Street, Philadelphia, PA 19104, USA*, ²*Department of Chemistry, University of Puerto Rico-Humacao, Humacao, Puerto Rico 00792* and ³*Ultrafast Optical Processes Laboratory, University of Pennsylvania, 231 South 34th Street, Philadelphia, PA 19104, USA*

Supporting Information

Table S1: Organic mole fraction (χ_{OM}) at which the fluorescence intensity (S_{Fmax}) of 7-CNI is the largest, and λ_{max} is the peak wavelength of the corresponding fluorescence spectrum of 7-CNI obtained at χ_{O} . Also shown for comparison are the peak emission wavelength (λ_{O}) of 7-CNI, and the respective peak wavenumber value (ω_{O}), obtained in the corresponding pure organic solvent.

| Organic Solvent | χ_{OM} | S_{Fmax} | $\lambda_{\text{max}} (\text{nm})$ | $\lambda_{\text{O}} (\text{nm})$ | $\omega_{\text{O}} (\text{cm}^{-1})$ |
|-----------------|--------------------|-------------------|------------------------------------|----------------------------------|--------------------------------------|
| ACN | 0.5 | 8.4 | 391 | 378 | 26455 |
| DMSO | 0.3 | 5.9 | 393 | - | - |
| THF | 0.2 | 10.8 | 391 | 370 | 27027 |
| Dioxane | 0.3 | 10.7 | 392 | 402 | 27248 |
| MeOH | 0.7 | 6.8 | 391 | 387 | 25840 |
| EtOH | 0.6 | 8.6 | 391 | 381 | 26247 |
| IPA | 0.5 | 9.6 | 392 | 379 | 26385 |
| TBA | 0.4 | 10.1 | 391 | 379 | 26385 |
| EtG | 1.0 | 9.7 | 393 | - | - |

Table S2: Dependence of the fluorescence lifetime (τ_F) of 7-CNI on the organic component and its mole fraction (χ_0) in the water-organic solvent binary system. Also listed are the χ^2 values resultant from fitting the corresponding fluorescence decay kinetics to a single-exponential function.

| Organic Solvents | χ_0 | τ_F (ns) | χ^2 |
|------------------|----------|---------------|----------|
| DMSO | 0.10 | 7.7 | 1.17 |
| DMSO | 0.15 | 11.7 | 1.11 |
| DMSO | 0.30 | 16.2 | 1.33 |
| DMSO | 0.80 | 14.6 | 1.19 |
| THF | 0.04 | 3.8 | 0.99 |
| THF | 0.10 | 10.4 | 0.99 |
| THF | 0.20 | 13.3 | 1.04 |
| THF | 0.40 | 13.2 | 1.23 |
| THF | 0.60 | 9.9 | 1.23 |
| THF | 0.80 | 8.4 | 1.06 |
| THF | 1.00 | 6.8 | 1.05 |
| ACN | 0.05 | 3.2 | 1.00 |
| ACN | 0.15 | 7.9 | 1.00 |
| ACN | 0.40 | 12.3 | 1.11 |
| ACN | 0.50 | 12.1 | 1.06 |
| ACN | 1.00 | 7.9 | 1.06 |
| DIO | 0.05 | 4.8 | 0.99 |
| DIO | 0.10 | 8.8 | 1.08 |
| DIO | 0.25 | 14.3 | 1.07 |
| DIO | 0.50 | 12.4 | 1.26 |
| DIO | 0.80 | 10.4 | 1.06 |
| EtOH | 0.00 | 1.9 | 0.95 |
| EtOH | 0.10 | 3.7 | 0.94 |
| EtOH | 0.20 | 7.4 | 1.06 |
| EtOH | 0.70 | 10.9 | 1.16 |
| EtOH | 1.00 | 8.8 | 0.96 |
| MeOH | 0.10 | 2.3 | 1.06 |
| MeOH | 0.40 | 6.7 | 1.04 |
| MeOH | 0.80 | 9.2 | 0.99 |
| MeOH | 1.00 | 8.2 | 1.01 |
| IPA | 0.05 | 3.1 | 1.08 |
| IPA | 0.15 | 9.3 | 1.17 |
| IPA | 0.50 | 11.7 | 1.01 |
| IPA | 0.90 | 9.7 | 1.14 |
| EtG | 0.10 | 2.9 | 0.92 |
| EtG | 0.50 | 8.4 | 1.16 |
| EtG | 1.00 | 12.3 | 0.96 |
| TBA | 0.10 | 9.0 | 1.22 |
| TBA | 0.40 | 12.1 | 1.30 |
| TBA | 1.00 | 9.4 | 1.15 |

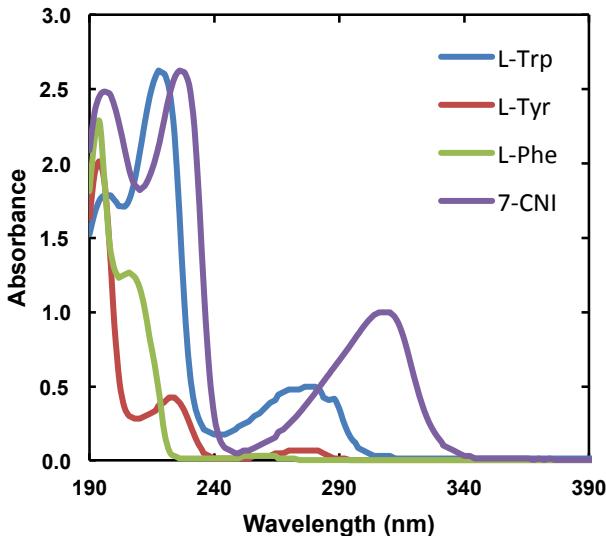


Figure S1. Absorption spectra of L-Trp, L-Tyr, L-Phe, and 7-CNI in water. For each solution, the concentration of the solute was $\sim 122 \mu\text{M}$.

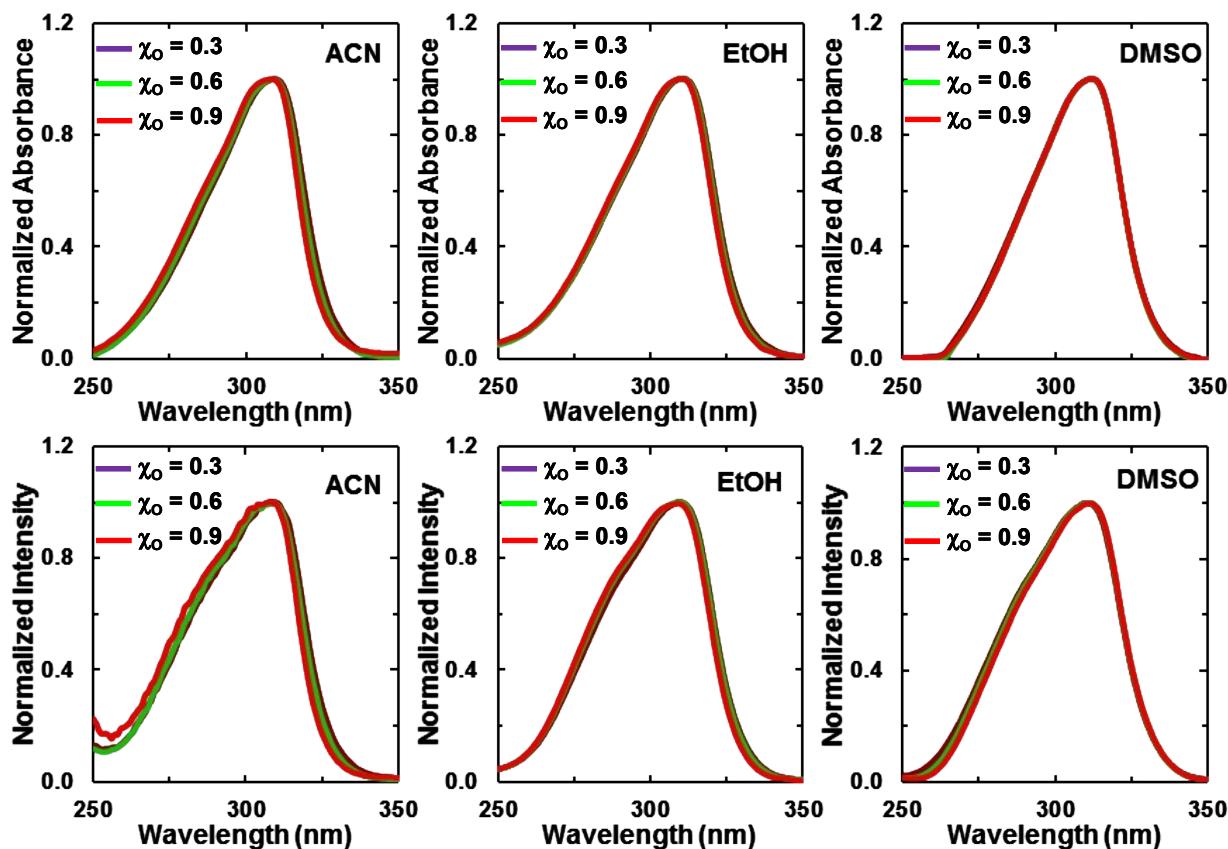


Figure S2. Top panel: normalized absorption spectra of 7-CNI ($\sim 10 \mu\text{M}$) in representative water-organic binary mixtures and at different organic mole fractions, as indicated. Bottom panel: corresponding fluorescence excitation spectra of 7-CNI for each case measured at λ_{\max} .

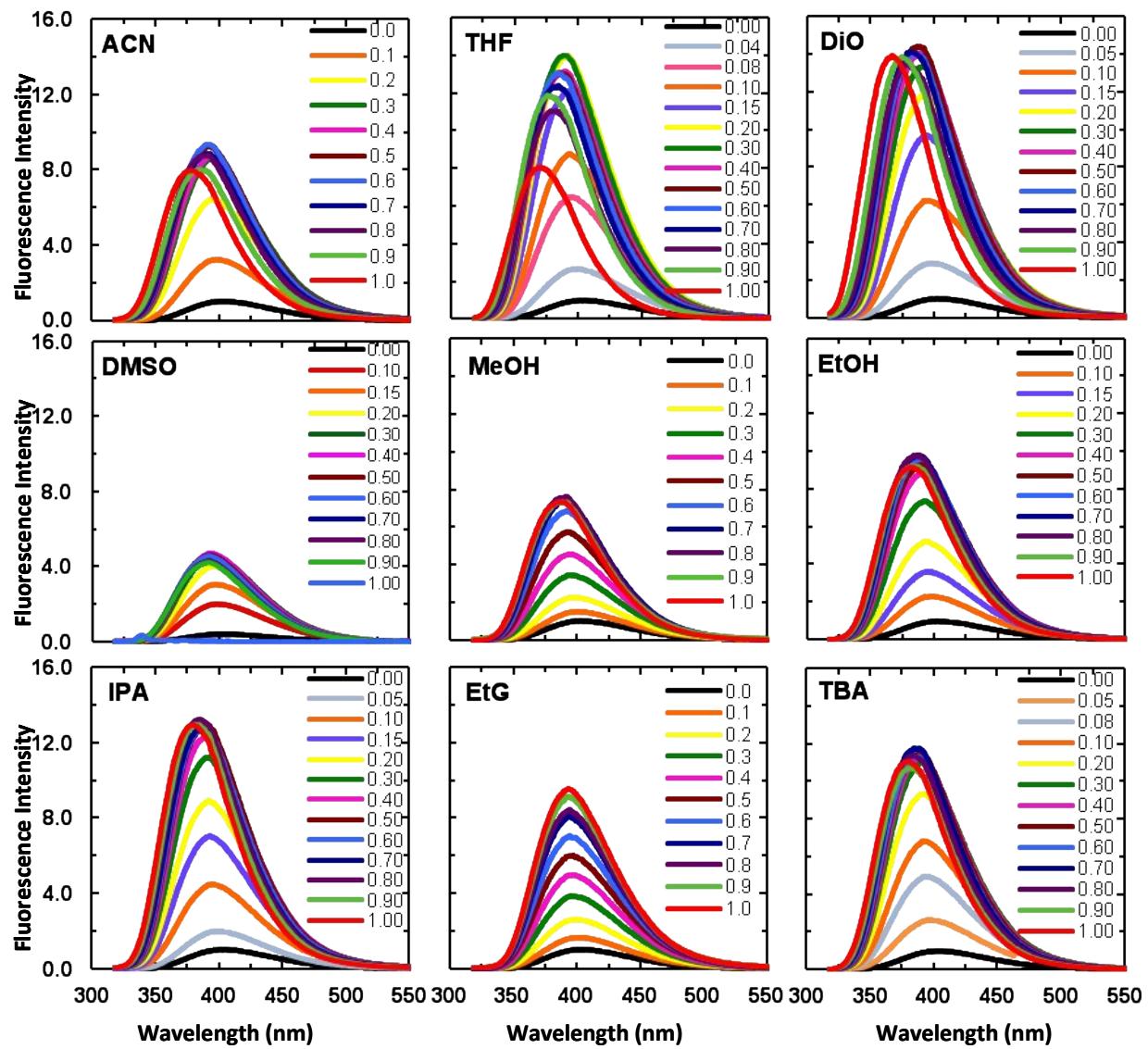


Figure S3. Normalized fluorescence spectra of 7-CNI in different water-organic binary systems, as indicated. In each panel, the numbers indicate the mole fractions of the organic solvent.

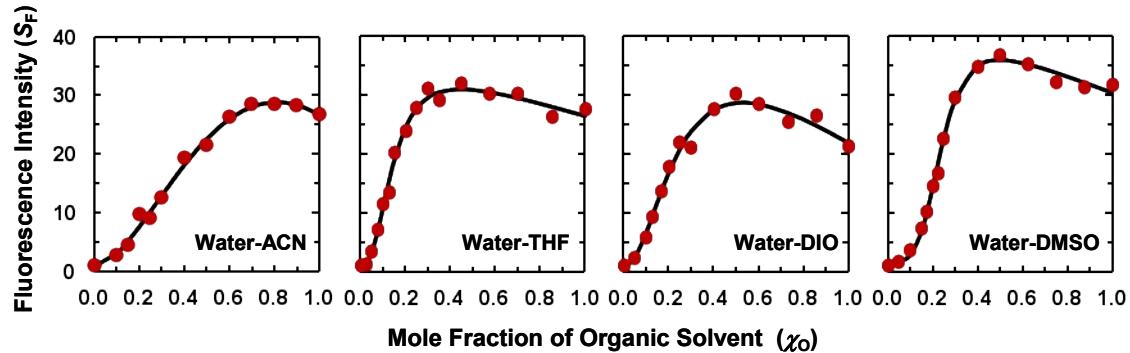


Figure S4. Normalized fluorescence intensity (S_F) of 5-CNI as a function of χ_0 in different water-organic binary mixtures, as indicated. In each case, the smooth line serves to guide the eyes.

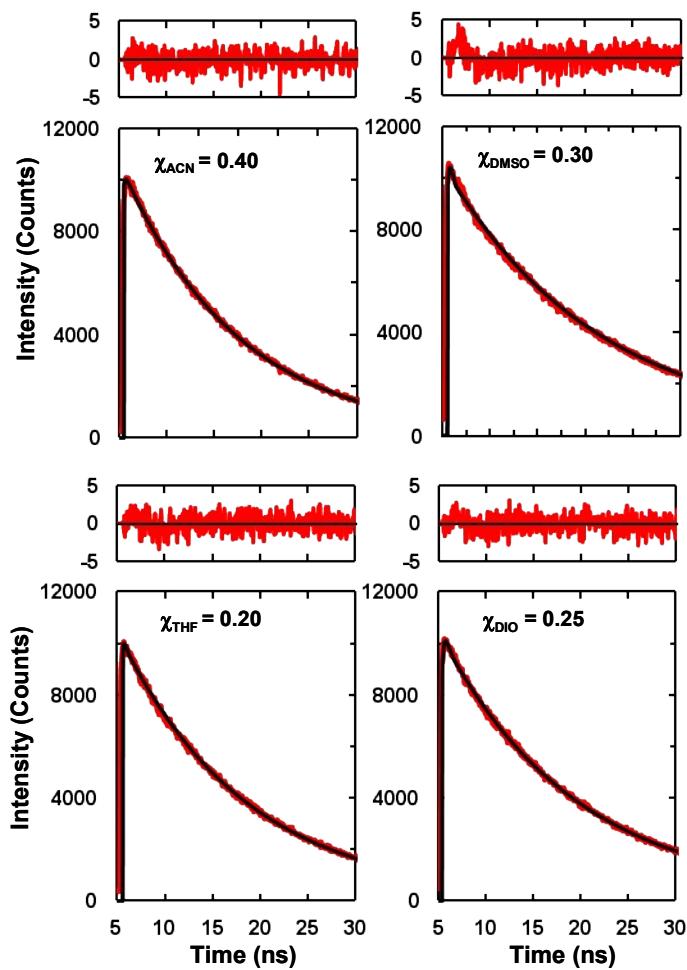


Figure S5. Representative fluorescence decay kinetics (red) of 7-CNI obtained in different water-organic solvent binary mixtures with the indicated mole fraction of the corresponding organic component. In each case, the black line represents the best fit of the kinetics to a single-exponential function with the resultant residues shown in the top panel.

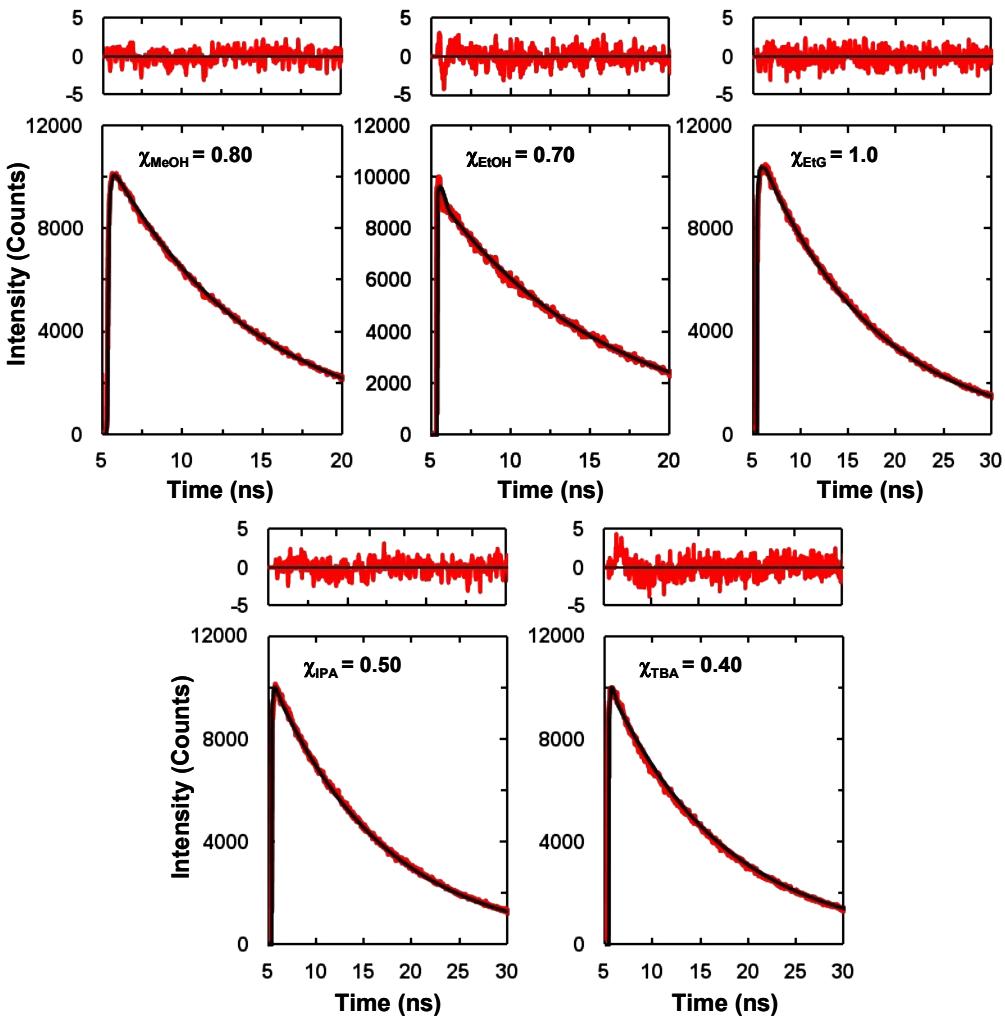


Figure S6. Representative fluorescence decay kinetics (red) of 7-CNI obtained in different water-alcohol binary mixtures with the indicated alcohol mole fraction. In each case, the black line represents the best fit of the kinetics to a single-exponential function with the resultant residues shown in the top panel.

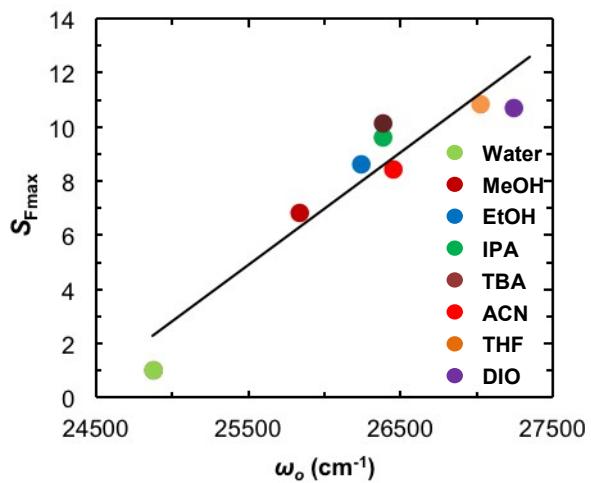


Figure S7. Dependence of $S_{F\max}$ on ω_0 .