Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences

SUPPLEMENTARY INFORMATION

Temperature Dependent Femtosecond-Resolved Hydration Dynamics of Water in Aqueous Guanidinium Hydrochloride Solution

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Time resolved fluorescence measurements

Fluorescence transients have been measured and fitted by using commercially available spectrophotometer (LifeSpec-ps) from Edinburgh Instrument, U.K (excitation wavelength 409 nm, 80 ps instrument response function (IRF)) with an attachment for temperature dependent studies (Julabo, Model F 32). The observed fluorescence transients are fitted by using a nonlinear least square fitting procedure to a function $\left(X(t) = \int_0^t E(t') R(t - t') dt' \right)$ comprising of convolution of the IRF (E(t)) with a sum of exponentials $\left(R(t) = A + \sum_{i=1}^{N} B_i e^{-t/\tau_i} \right)$ with pre-exponential factors (B_i), characteristic lifetimes (τ_i) and a background (A). Relative concentration in a multi-exponential decay is finally expressed as; $a_n = \frac{B_n}{\sum_{i=1}^{N} B_i}$. The quality of the curve fitting is evaluated by reduced chi-square and residual data.

To construct time-resolved emission spectra (TRES) we follow the technique described in references[1, 2]. As described above the emission intensity decays are analyzed in terms of the multi-exponential model,

$$I'(\lambda, t) = H(\lambda) I(\lambda, t) = \sum_{i=1}^{N} \alpha_i'(\lambda) \exp\left(-t/\tau_i(\lambda)\right) \qquad \text{(S1)}$$

where $\alpha_i(\lambda)$ are the pre-exponential factors, with $\Sigma\alpha_i(\lambda)=1.0$. In this analysis, we compute a new set of intensity decays, which are normalized so that the time-integrated intensity at each wavelength is equal to the steady-state intensity at that wavelength. Considering $F(\lambda)$ to be the steady-state emission spectrum, we calculate a set of $H(\lambda)$ values using,

$$H(\lambda) = \frac{F(\lambda)}{\int_0^\infty I(\lambda, t)dt} \quad \text{(S2)}$$

which for multi-exponential analysis becomes,

$$H(\lambda) = \frac{F(\lambda)}{\sum_i \alpha_i(\lambda)\tau_i(\lambda)} \quad \text{(S3)}$$

Then, the appropriately normalized intensity decay functions are given by,

$$I'(\lambda, t) = H(\lambda)I(\lambda, t) = \sum_{i=1}^{N} \alpha_i'(\lambda)\exp[-t/\tau_i(\lambda)] \quad \text{(S4)}$$

where $\alpha'_i(\lambda) = H(\lambda)\alpha_i(\lambda)$. The values of $I'(\lambda,t)$ are used to calculate the intensity at any wavelength and time, and thus the TRES. The values of the emission maxima and spectral width are determined by nonlinear least-square fitting of the spectral shape of the TRES. The spectral shape is assumed to follow a lognormal line shape[2]

$$I(\bar{\nu}) = I_0 \exp\left\{-\left[\ln 2\left(\frac{\ln(\alpha+1)}{b}\right)^2\right]\right\} \quad \text{(S5)}$$

with $\alpha = \frac{2b(\bar{\nu} - \bar{\nu_{max}})}{\Delta} - 1$, where I_0 is amplitude, $\bar{\nu}_{max}$ is the wavenumber of the emission maximum and spectral width is given by, $\Gamma = \Delta\left[\frac{\sinh(b)}{b}\right]$. The terms b and Δ are asymmetry and width parameters. The equation (S5) reduces to a Gaussian function for b=0.

Design of the Temperature Dependent Accessory:

Figure S1 detail on the temperature dependent setup in the commercially available fluorescence up-conversion setup, FOG100, CDP. The setup is made from a solid aluminum plate (width 7.5cm, height 7.8cm, thickness 1.3cm) that is bored inside to make hollow channel

(Figure S1a). In this system another bore (3.1cm) has been made along the breadth of the setup. This setup is the base of the sample holder. The sample holder (Figure S1b) is made from another solid aluminum tube in which 3.1cm pore has been bored. The outer diameter of this cell holder (3.0cm) is such that this can fit well and rotate in the axis of hollow of 3.1cm bore of Figure S1a. The sample holder consists of three different parts (b, c, e). The liquid sample is taken between two quartz plates with a Teflon spacer of required sample thickness and placed in the body of the sample holder (Figure S1b) and the top cover of the sample holder "c" is tightened by using 3 screws. The other part "e" is the safety bolt of the sample holder. This sample holder is then inserted into the hole of the temperature dependent setup "a" and fitted with "e". The "e" is inner threaded with the same pitch of the thread of "b". Top view of the sample holder after fitting all the components is shown in "d".

Water, from an automated temperature bath (Julabo, model F32), is pumped to the container from one side (scheme S1) and filling the whole container, returns to the bath from another side. The temperature of the sample changes due to the thermal contact of the sample holder and the setup. The sample temperature of the system is calibrated by our own designed temperature sensor. We have observed that upon insertion of the temperature controlled cell-holder in the up-conversion setup does not affect the instrument response function compared to that of the original setup supplied by CDP Company.

Refrences

1. J. R. Lakowicz, *Principles of fluorescence spectroscopy*, Kluwer Academic/Plenum, New York, 1999.
2. M. L. Horng, J. A. Gardecki, A. Papazyan and M. Maroncelli, *J. Phys. Chem.*, 1995, **99**, 17311-17337.

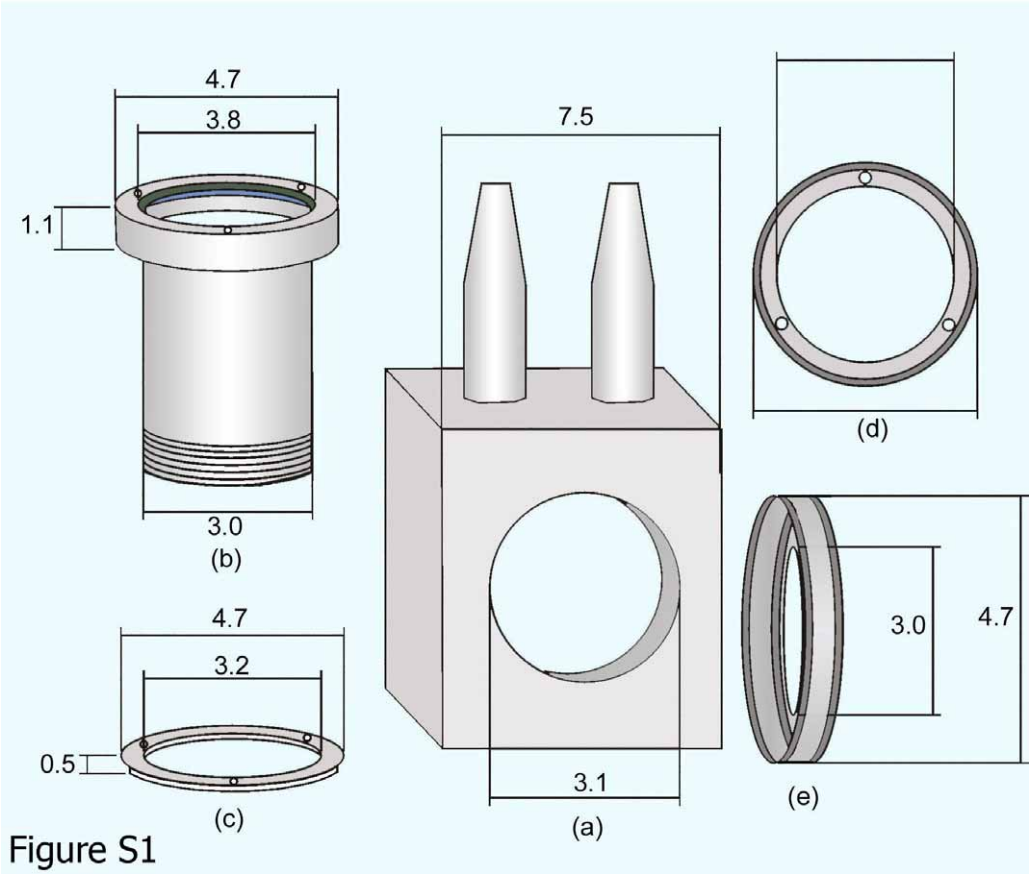
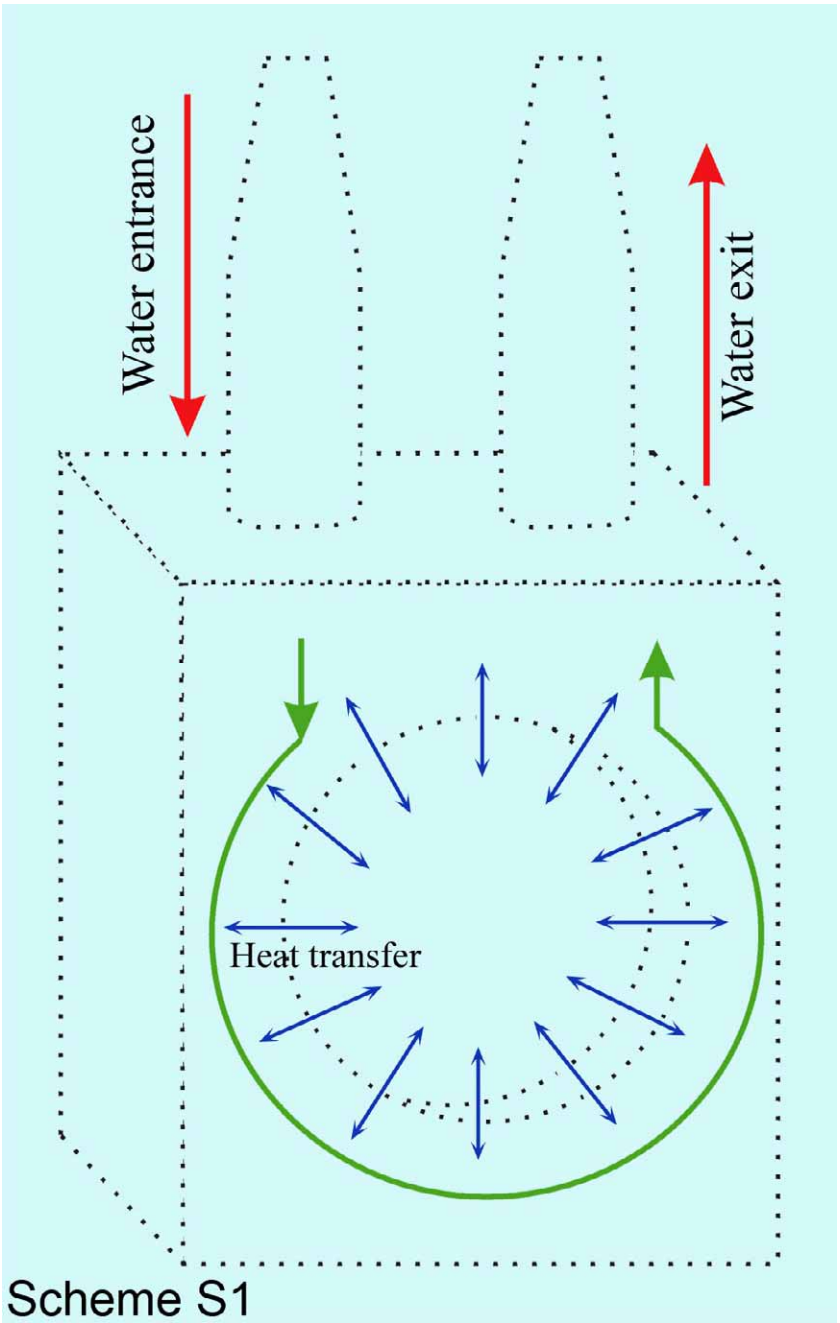
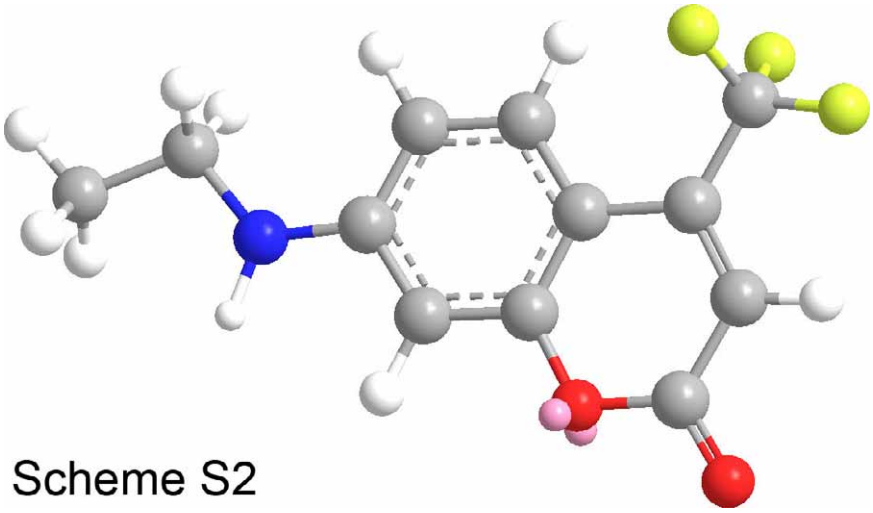


Figure S1



Scheme S1



Scheme S2

Figure Captions:

Figure S1: Temperature dependent setup unit. (a) Temperature bath, (b) sample holder (c) top cover of the sample holder, (d) top view of the sample holder,(e) screw bolt of the sample holder.

Scheme S1: Schematic representation of the temperature controlling unit.

Scheme S2: Optimized structure of the molecular probe coumarin 500.