Probe dependent anomalies in solvation dynamics of coumarin dyes in dimethyl sulfoxide-glycerol binary solvent: confirming the local environments are different for coumarin dyes.

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1. Experimental Section

1.1 Materials used
All coumarin dyes, HPLC grade Dimethyl Sulfoxide and glycerol (molecular biology, purity ≥99%) were purchased from Sigma-Aldrich chemical and used without further purification.

1.2 Preparation of DMSO/GLY solutions containing coumarin dyes
DMSO/GLY mixtures were prepared by mixing the two solvents in correct ratios. Coumarin dyes were incorporated to the binary solvent by spreading the required amount of “coumarin dye in methanol” stock solution into a 5 mL glass vial and methanol was completely evaporated by air blowing. The thin film of coumarin dye was dissolved with 3 ml binary mixture. Concentrations of coumarin dyes in binary mixture were always kept in the range of 3-6 μM/liter range.

1.3 Instruments used
The steady state absorption spectra and fluorescence spectra were recorded in Perkin-Elmer Lambda-750 spectrophotometer and Perkin-Elmer LS 55 spectrofluorimeter, respectively. Picosecond lifetimes were measured in a time-correlated single-photon counting (TCSPC) spectrometer (Edinburgh, OB920). We used 375 nm laser head to excite coumarin 480 (C480) and 405 nm laser head to excite coumarin 153 (C153) and coumarin 343 (C343), respectively. Fluorescence was collected at right angle by using MCP photomultiplier (Hamamatsu R3809U-50). The excitation lamp profiles were obtained from a scatterer sample (dilute Ludox solution) and used in the deconvolution fitting function. From the lamp profile we obtained the Instrument Response Function (IRF) of our instrument which was found to be ~70 ps (IRF) for all laser diodes. Data were fitted by using F900 decay analysis software. All experiments were done at room temperature (24°C). Viscosities of binary solvents were measured by using Ubbelohde viscometer.

Rotational anisotropy decay was measured by changing the emission polarizer at regular intervals to parallel and perpendicular direction with respect to the excitation polarizer. Anisotropy correlation function r(t) was calculated from the decay of parallel intensity \( I_{\text{parallel}}(t) \) and perpendicular intensity \( I_{\text{perpendicular}}(t) \) using the following equation,

\[
r(t) = \frac{I_{\text{parallel}}(t) - GI_{\text{perpendicular}}(t)}{I_{\text{parallel}}(t) + 2I_{\text{perpendicular}}(t)} \tag{S1}
\]
The $G$ value in the above equation was obtained from the calibration of the setup using a dye whose rotational relaxation is very fast (i.e., C480 in methanol). The details of this technique has been described elsewhere.¹

2. Figure captions

**Fig. S1.** Time-resolved emission spectra (TRES) of (A-B) C480 ($\lambda_{\text{ex}}=405$ nm) and (C-D) C343 ($\lambda_{\text{ex}}=405$ nm) in DMSO/GLY binary mixtures with GLY concentrations 10 (A, C) and 60 (B, D) mole %, respectively.

**Fig. S2.** Decay of rotational correlation function $r(t)$ of (A) C153 ($\lambda_{\text{ex}}=405$ nm), (B) C480 ($\lambda_{\text{ex}}=375$ nm) and (C) C343 ($\lambda_{\text{ex}}=405$ nm) in DMSO-GLY binary mixtures with $X_{\text{GLY}}=0.1$ (red), 0.4 (blue), 0.6(cyan), and 0.8 (magenta). Emissions were collected at 20 nm blue-end of their respective steady state emission peaks.

3. References

Fig. S1

A

Normalized intensity

Wavelength (cm$^{-1}$)

B

Normalized intensity

Wavenumber (cm$^{-1}$)
Fig. S2

A

B

C

$X_{GLY} = 0.8$

$0.8$

$0.6$

$0.4$

$0.1$

Time(ns)

$R(t)$

$X_{GLY} = 0.8$

$0.8$

$0.6$

$0.4$

$0.1$

Time(ns)

$R(t)$

$X_{GLY} = 0.8$

$0.8$

$0.6$

$0.4$

$0.1$

Time(ns)

$R(t)$

$X_{GLY} = 0.8$

$0.8$

$0.6$

$0.4$

$0.1$

Time(ns)