Supplementary Material: Fluorescent molecular rotor probes nanosecond viscosity changes

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S1. SPECTRAL PROPERTIES OF 4-DASPI

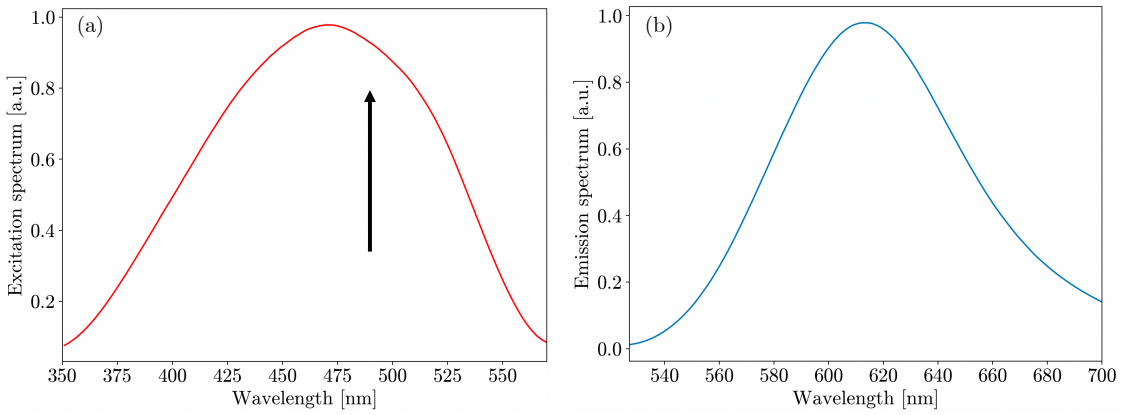

FIG. S1. (a): excitation spectrum of 4-DASPI dissolved in glycerol, detected at 600 nm. The arrow indicates the excitation wavelength (490 nm) used to excite 4-DASPI during the T-jump experiment. (b): Emission spectrum of 4-DASPI in glycerol, excited at 490 nm.

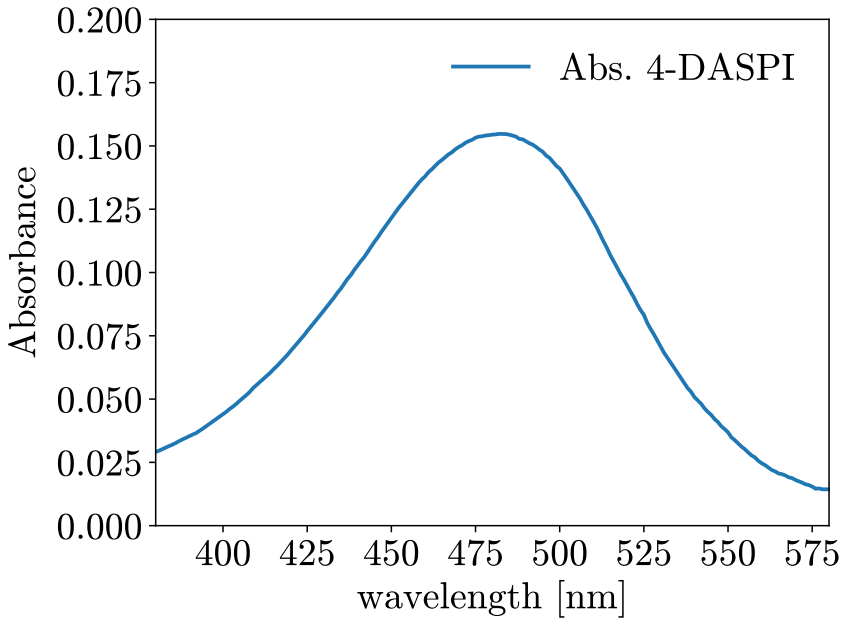

FIG. S2. Absorption spectrum of 4-DASPI in glycerol (1 mm optical path length).

S2. RELATIONSHIP BETWEEN LIFETIME AND VISCOSITY

The dependence of the fluorescence lifetime on the solvent viscosity can be described by the Föster-Hoffman equation[S1]:

$$\tau_f = k \cdot \eta^x \,. \tag{1}$$

The calibration of the molecular rotor response to the viscosity has been performed by using aqueous solutions with different molar fractions of glycerol. Their macroscopic viscosities are obtained by conventional rheology at ambient temperature. Measurements were performed on an Anton Paar MCR 302 rheometer using a cone-plate geometry (diameter 50 mm, angle 1°). The fluorescence decay of 4-DASPI has been probed using a time-correlated single photon counting setup (TCSPC) (more details in Ref. S2), which has a time response of roughly $\simeq$ 24 ps (see black curve in Fig.S3). Fig.S3 shows, as an example, the fluorescence decay probed from a 95%wt glycerol-water mixture. The decay is well described by a bi-exponential function (red-line). Fig. S4 shows the dependence of the amplitude-averaged lifetime on the macroscopic viscosity (red diamonds) while the black line is the calibration curved obtained by fitting Eq. S1 to the experimental data. The circles shows the viscosity obtained from our T-jump setup for different pump-probe delay line. In absence of the temperature jump (green circle in Fig.S4), the extracted lifetime is agreement with the value expected for 99% pure glycerol at 295K, even though the single-shot detection scheme used during the temperature jumps has a longer instrumental response $\simeq$0.5ns).

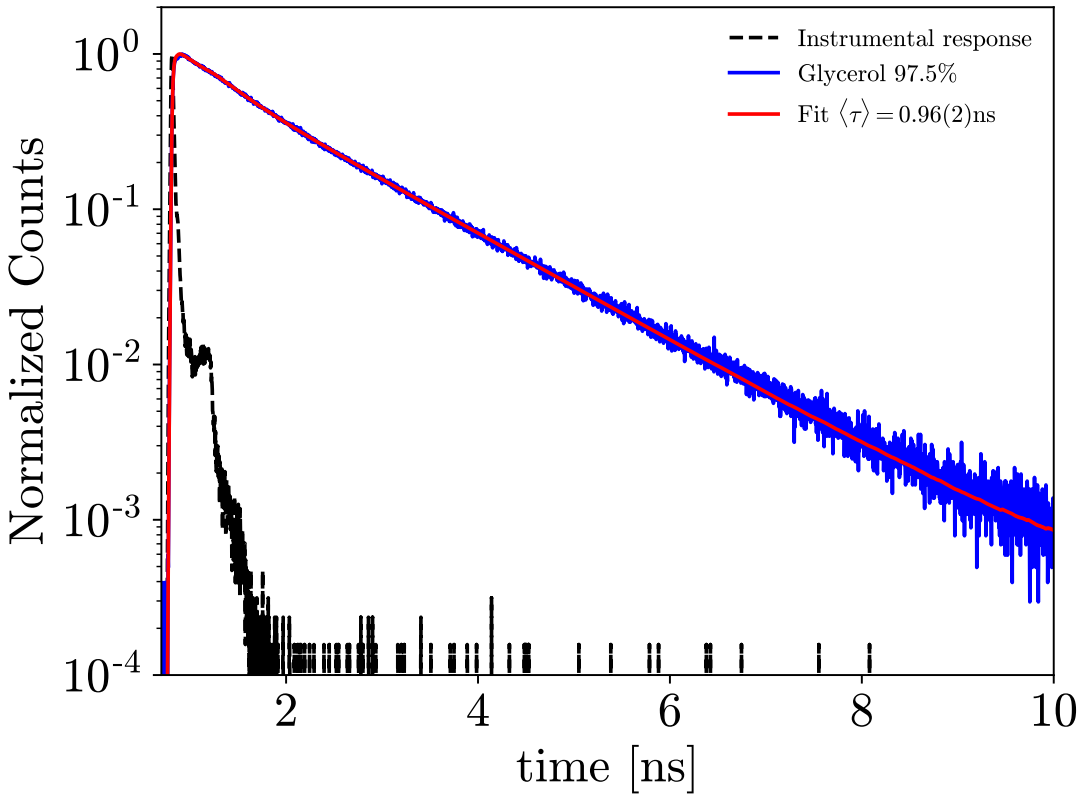

FIG. S3. Fluorescence decay of 4-DASPI glycerol (97.5%wt) excited at λ_{exc} = 490 nm and probed at 600 nm. The black,blue and red lines represent the instrument response function (FWHM$\simeq$ 24 ps), the experimental data, and the curve obtained from fitting the data with a bi-exponential decay, respectively.

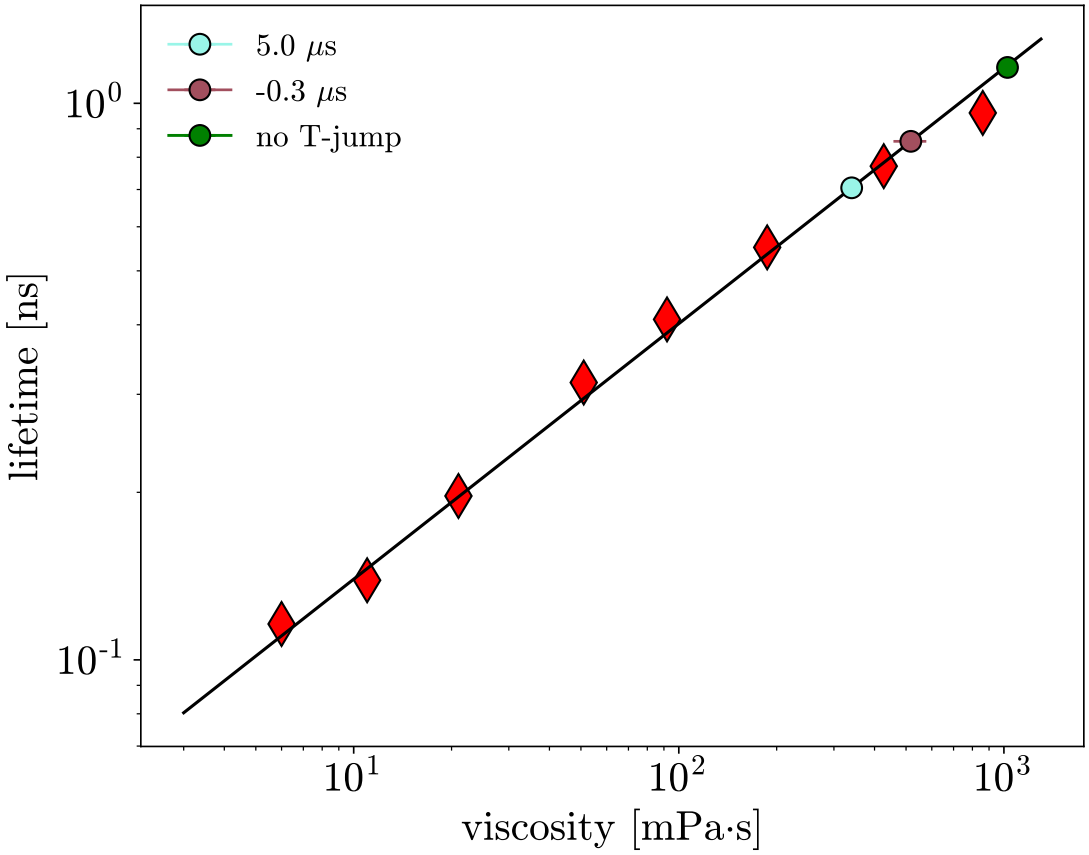

FIG. S4. Fluorescence lifetime as a function of viscosity of 4-DASPI in aqueous solutions of glycerol with different molar fractions of water. The macroscopic viscosities are measured by conventional rheology. The solid line is obtained by fitting the Föster-Hoffman equation to the experimental data. The green, cyan and brown circles with errorbars reports the viscosity of glycerol measured without, 5μs after and 300ns before the T-jump, respectively.

REFERENCES

[S1]Förster, T.; Hoffmann, G. Zeitschrift für Physikalische Chemie 1971,75, 63–76

[S2]T. Suhina, S. Amirjalayer, B. Mennucci, S. Woutersen, M. Hilbers, D. Bonn and A. M. Brouwer, J. Phys. Chem. Lett., 2016, 7, 4285;