

Phys. Chem. Chem. Phys.

**Polar solvation dynamics in water and methanol:
search for molecularity**

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Supporting Information

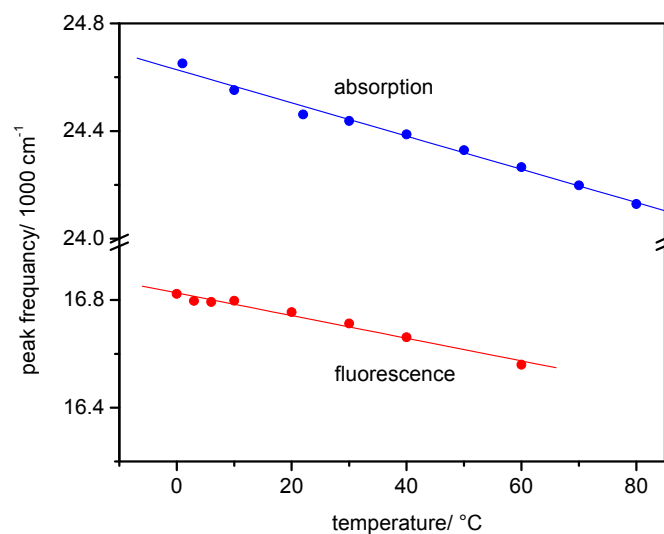


Fig. S1 Thermochromism of MQ in water. Absorption and fluorescence bands of MQ shift to the red when the temperature is increased. Since the dipole moment decreases $8\text{ D} \leftarrow 10\text{ D}$ upon excitation $S_1 \leftarrow S_0$, this red shift is consistent with the reverse solvatochromism of MQ. [4]

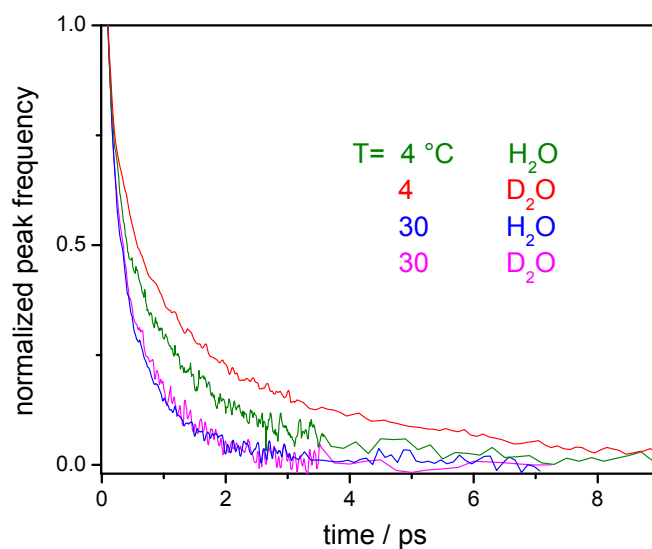


Fig. S2 Peak frequency evolution of MQ in H₂O and D₂O at 30°C and 4°C. Data were set to 1 and 0 at 100 fs and 10 ps, respectively.

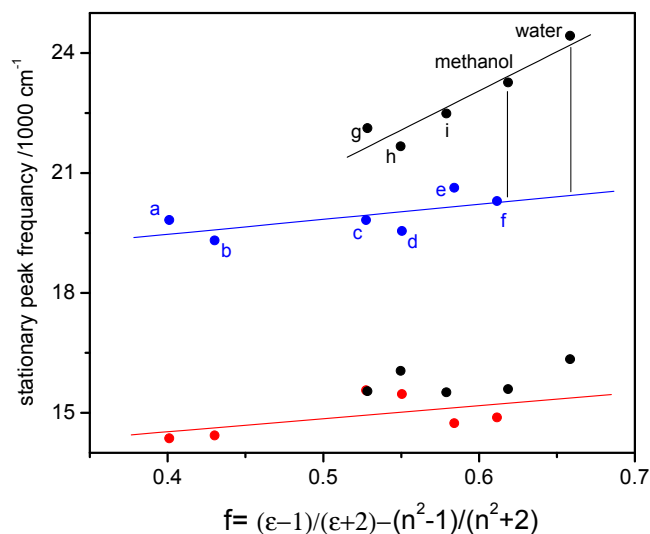


Fig. S3

Solvatochromism of MQ: peak position of absorption and fluorescence line shapes against polarity f . a-i: ethylacetate, methylacetate, dimethyl sulfoxide, dimethyl formamide, propionitrile, acetonitrile, n-butanol, n-propanol, and ethanol. Regression lines for subsets are also shown. Vertical lines mark the deviation of MQ in methanol and water from regression line for nonspecific polar behavior.

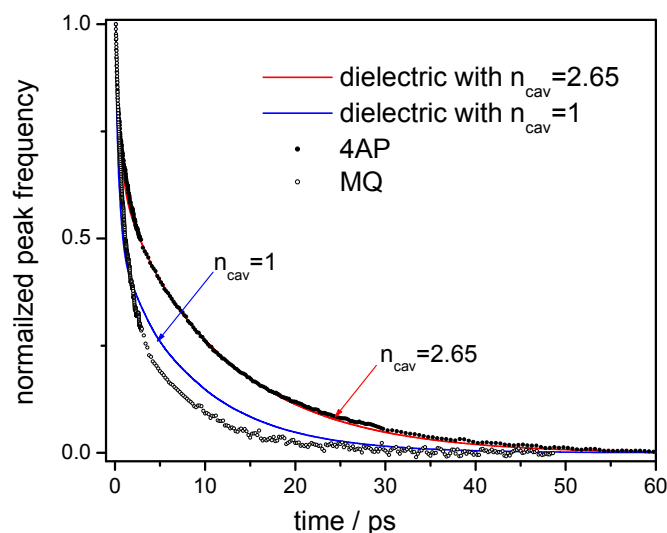


Fig. S4

The dielectric prediction of solvation in methanol (see text) with $n_{\text{cav}} = 2.65$ (red line) matches the observed spectral relaxation function of 4AP in methanol (circles). The same kind of calculation, for example with $n_{\text{cav}} = 1$ (blue line), differs for MQ in methanol (open circles, $T = 22^\circ\text{C}$).

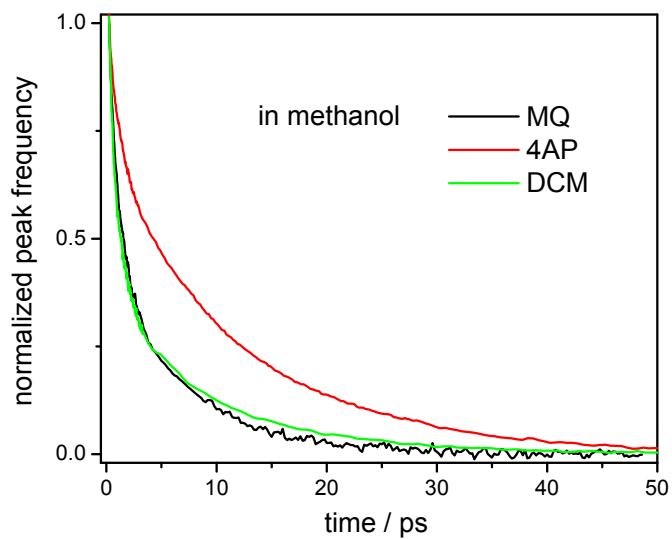


Fig. S5 Normalized peak frequency evolution of DCM (green), MQ (black) and 4AP (red) in methanol (T=22°C). Normalization as in Fig. S2.

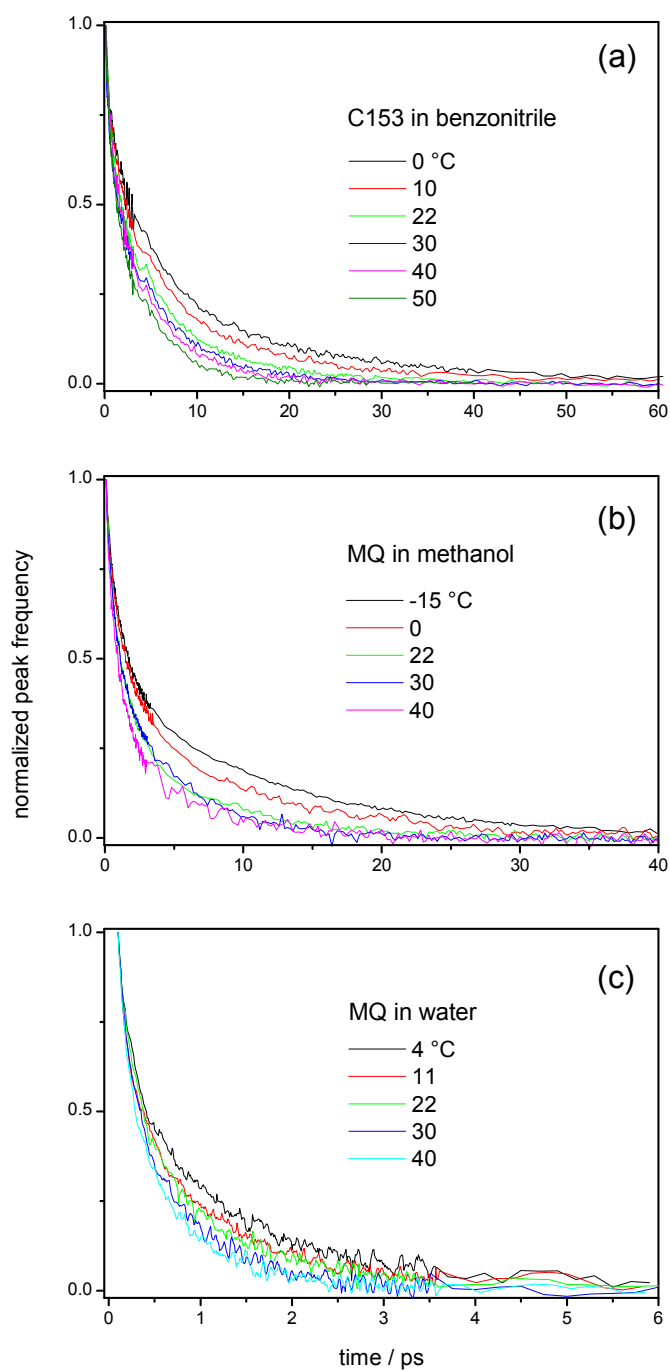


Fig. S6 Normalized peak frequency evolutions (as in Fig. S2) of (a) C153 in benzonitrile, (b) MQ in methanol and (c) in water, at various temperatures.