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Supporting Information

Unravelling the effect of temperature on viscosity-sensitive fluorescent molecular rotors

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Polarity effect on the photophysics of 1

As could be seen from comparison between Figures 1 and 3 (main text) the overlap between the points (lifetimes and quantum yields) collected for **1** at different temperatures for identical viscosities is not precise, whereas for **3** a perfect overlap is observed (Figure 3b). The lack of overlap at low viscosities is particularly noticeable for the quantum yield measurements of **1**, Figure 1b. We believe that the following reasons could explain this slight spread of data in Figure 1:

1) A smaller dynamic range of lifetimes (260 – 5700 ps) and quantum yields (0.02 - 0.77) in Figure 1 compared to a range of ratios (0.04 – 2.2) in Figure 3b makes the spread in Figure 1 more visible.

2) The photophysics of **1** in low viscosity environments (up to 30 cP) is known to be nominally affected by polarity.[1] The dielectric constant of methanol ranges from 40 to 33 between 0 to 25 ˚C.[2] Furthermore, the dielectric constant of glycerol is 40 at 25 ˚C,[3] which will affect the resulting dielectric constant of methanol/glycerol mixtures. Overall the small variations in the dielectric constant between solutions of identical viscosity may result in less than perfect overlap of curves. The solution polarity appears to have a negligible effect on the photophysics of the porphyrin dimer **3**.

3) Solution polarity can have an effect on both k_{nr} and k_r of rotor **1** and as such the polarity effect on quantum yields may be even more pronounced than that on fluorescence lifetimes. This is indeed seen in Figure 1b, even though we adjusted the quantum yield measurements for variations in the refractive index of methanol/glycerol solutions. However, it is noteworthy that only the fluorescence lifetime is useful as a concentration bias free measurement of viscosity and as such the quantum yield measurements do not affect the usefulness of **1** as a temperature-independent viscosity probe.

In conclusion, we emphasise that the spread seen in Figure 1a is a lot smaller than the spread expected if the photophysics of the dye is affected by temperature, e.g. the data shown in Figures 2b or 3d. Therefore, our conclusion that **1** shows temperature-independent photophysics is valid.

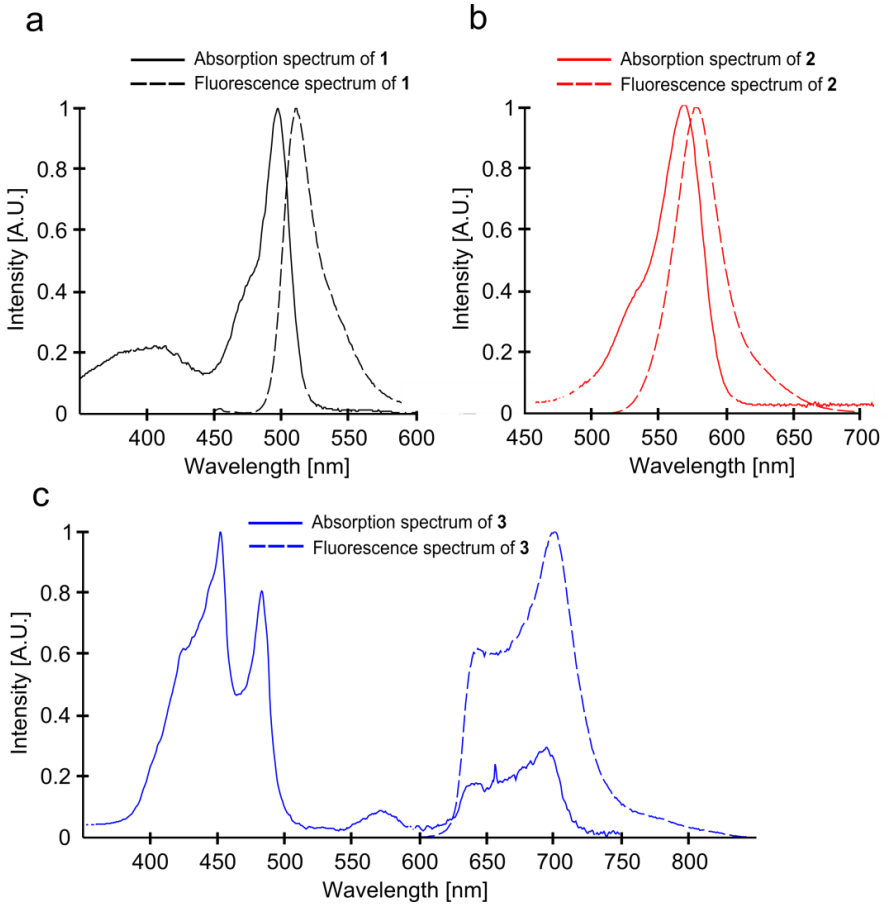

Figure S1. Normalized absorption and fluorescence spectra of dyes **1**(a), **2** (b) and **3** (c) in 50% methanol-glycerol mixture. The excitation wavelengths were 400 nm (for **1**), 500 nm (for **2**) and 453 nm (for **3**).

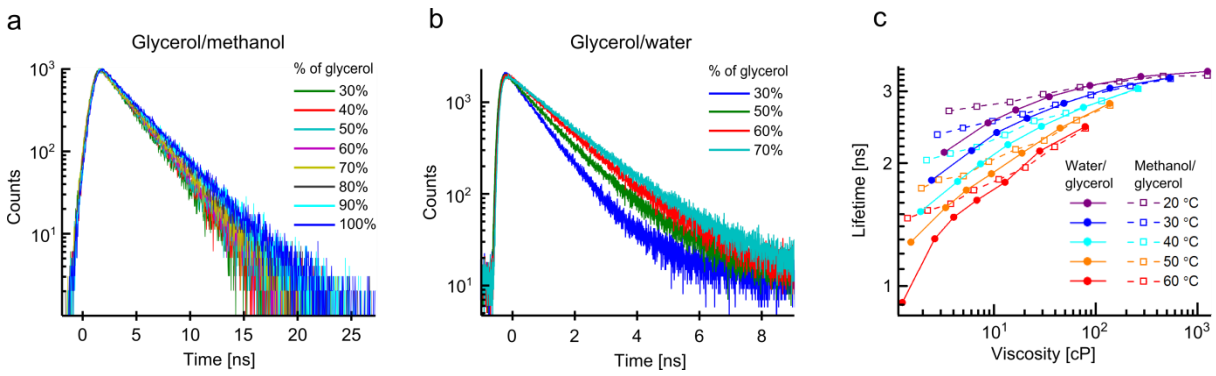

Figure S2. a) Fluorescence decays of **2** in various methanol-glycerol mixtures of increasing viscosity recorded at 20 ˚C with an excitation wavelength of 560 nm. Only a small correlation with the solution viscosity is observed. b) Fluorescence decays of **2** in water-glycerol mixtures at 60 ˚C with an excitation wavelength of 540 nm. Decays show biexponential character at this temperature. c) Lifetimes of **2** in methanol-glycerol (empty squares) and water-glycerol (full circles) mixtures at temperatures ranging from 20 ˚C to 60 ˚C. Intensity-weighted mean lifetimes are shown for biexponential decays.

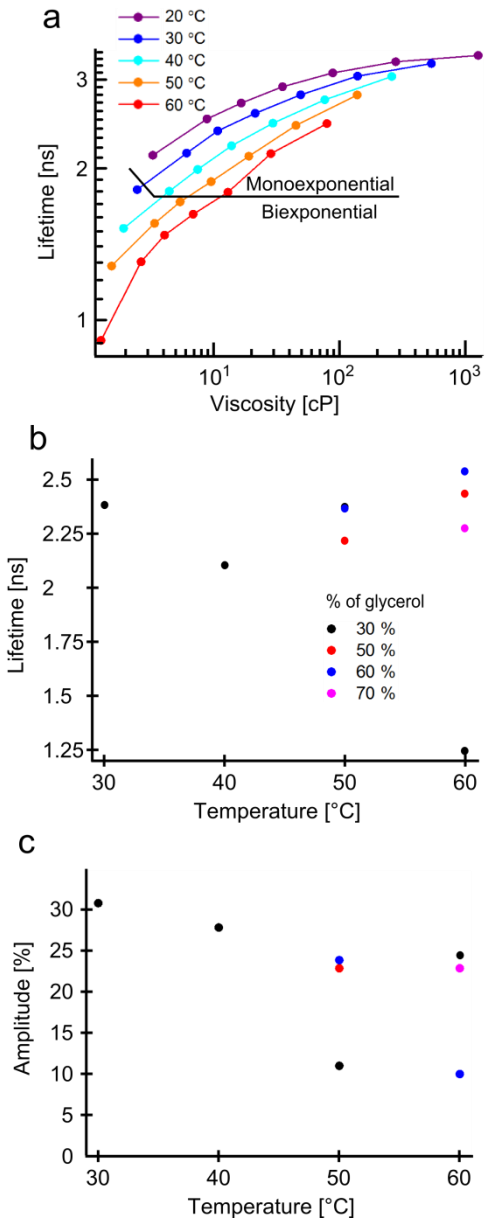

Figure S3. a) Lifetimes of **2** recorded in water-glycerol mixtures at variable temperature.

Note the time resolved decays with average lifetimes shorter than ca 1.8 ns (e.g. those recorded at a temperature between 30-60 ˚C and a viscosity below 10 cP) are best fitted with a biexponential function. b) The second minor (and temperature independent) lifetime component of biexponential decays, plotted against temperature for mixtures of 30-70% glycerol

c) The amplitudes of the second minor lifetime component of biexponential decays.

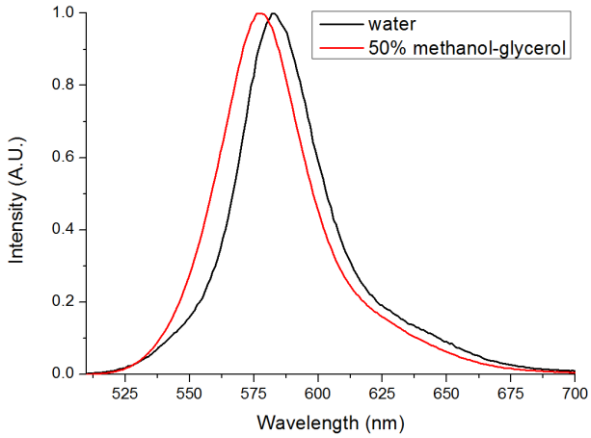

Figure S4. Normalized fluorescence spectra of **2** in 50% methanol-glycerol mixture and in water at room temperature. A small (5 nm) solvatochromic shift between the two curves is visible.

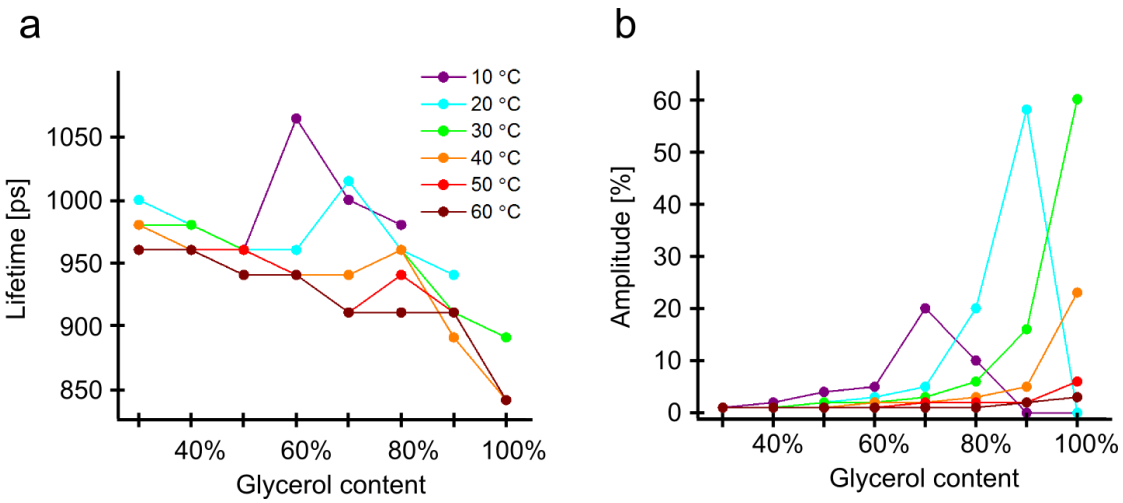

Figure S5. Lifetimes (a) and amplitudes (b) of a minor lifetime component of **3** observed in methanol/glycerol mixtures of varied temperature and viscosity.

We have observed biexponential fluorescence decays of **3**, which is consistent with our previous report.[4] The major component corresponds to the viscosity-sensitive twisted conformer of **3**, whereas the minor component comes from the planar conformer, due to the overlap of the corresponding peaks in the fluorescence spectrum. In most decays, the amplitudes of this minor component are below 5%. Exception to this are decays recorded at high viscosities, where the lifetime of the principal exponential component approaches the lifetime of the minor component. In these cases, the fitting gives unreliable (and high) amplitude values. To determine the lifetime of a principal lifetime component in such cases, we have recalculated the lifetime from the intensity-weighed mean lifetime using fixed amplitudes of 95% and 5% for the principal and minor components respectively. The above mentioned complication affects the following data points:

1) 70% glycerol, 10 ˚C.
2) 80% glycerol, 10 ˚C, 20 ˚C, 30 ˚C.
3) 90 % glycerol, 20 ˚C, 30 ˚C.
4) 100% glycerol, 30 ˚C, 40 ˚C, 50 ˚C.

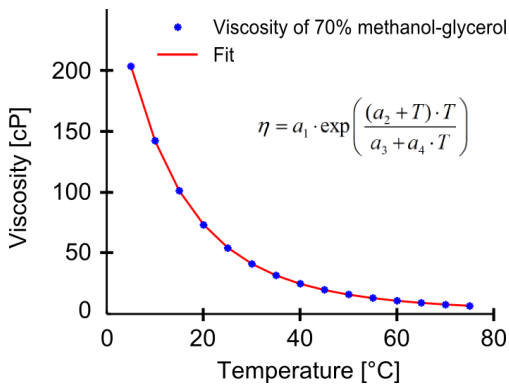

Figure S6. The viscosity-temperature relationship for the 3:7 methanol/glycerol mixture. The viscosity data points (blue circles) were measured in the bulk solution using a viscometer and the temperature dependence was fitted with a function obtained from Cheng *et al* (shown as an insert).[5] This fit was used for calculating predicted temperature maps from viscosity maps.

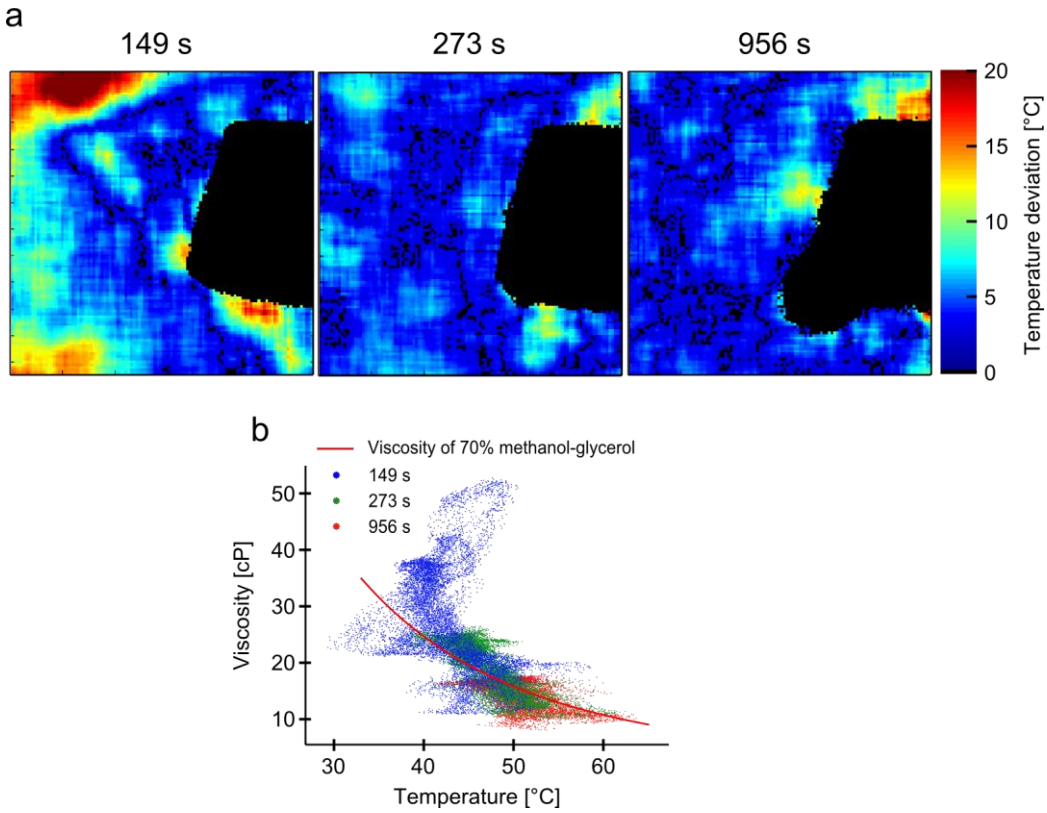

Figure S7. a) The difference between the temperature maps measured with **3** (Figure 5d, main text) and predicted temperature maps calculated from viscosity maps measured with **3** using the viscosity-temperature relationship in Figure S6. b) The plot of pixel viscosity versus pixel temperature as measured in Figure 5, main text, using combined ratiometric and lifetime data collection. The pixels from each image are colour-coded blue (149s), green (273s) and red (956s). The temperature-viscosity curve measured for 70% methanol-glycerol bulk solution (Figure S6) is also shown as a red line.

The data above helps visualise the error of our method for measuring the temperature.

Figure S7a indicates that the error is below 5 ˚C (indicated by a blue colour) in most pixels.

A higher error observed in 149s image might have resulted from rapid initial heating of the sample during the data acquisition periods needed for the acquisition of viscosity and temperature maps (the time needed to measure two images is ca 60 seconds).

References

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