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Supporting Information for:

The effect of solvent polarity and macromolecular crowding on the viscosity sensitivity of a molecular rotor BODIPY-C_{10}

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Additional data

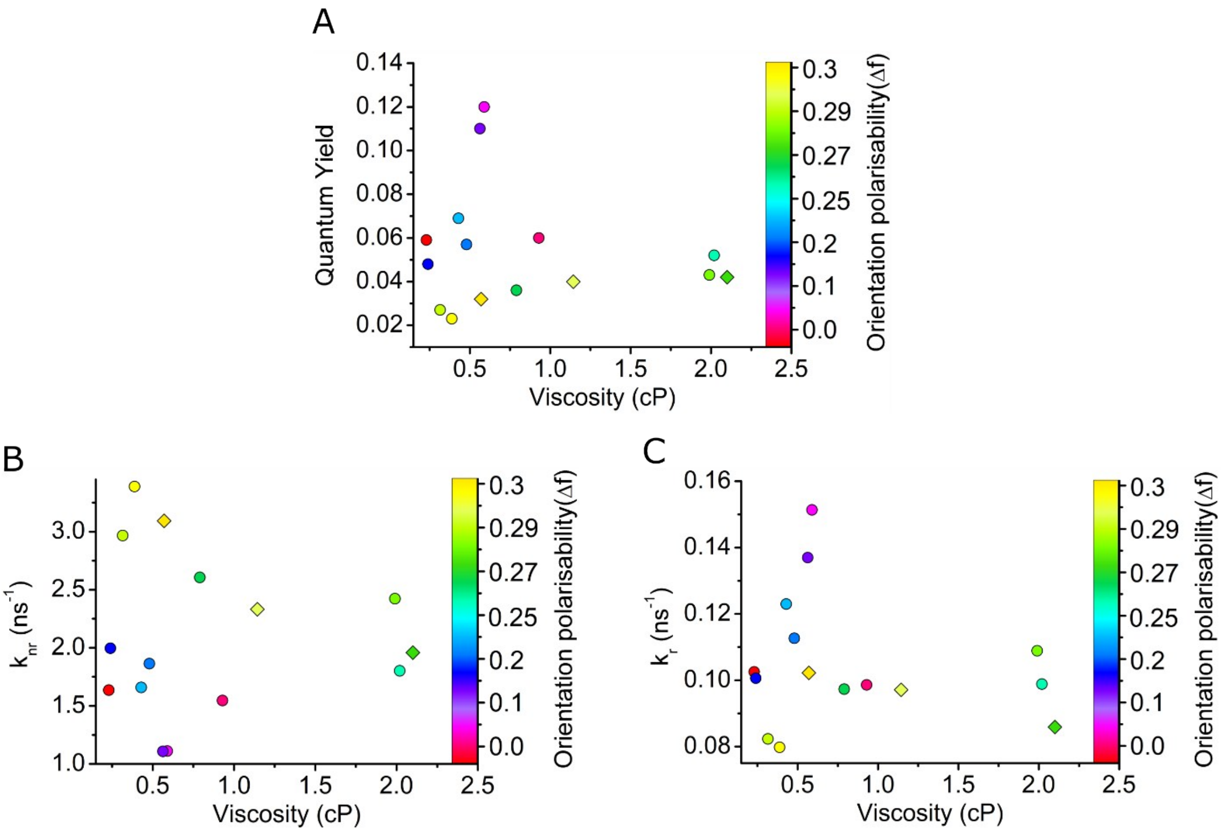

Figure S1. Fluorescence quantum yields (A), non-radiative (B) and radiative (C) decay constants of BODIPY-C_{10} in organic solvents. The data points are coloured according to the orientational polarisability (*Δf*) of solvents, which represents the polarity of a solvent and it is defined in Methods and Materials section, main text. BODIPY-C_{10} has the lowest quantum yields in solvents with high *Δf*, which agrees well with the short fluorescence lifetimes observed in such solvents (Figure 2C, main text). Both short lifetimes and low quantum yields are the result of faster non-radiative decay constants in high *Δf* solvents (C). Since the radiative decay constants are slower by a factor of □20 on average, they have minimal influence in determining the variation of quantum yields and fluorescence lifetimes of BODIPY-C_{10} in different solvents.

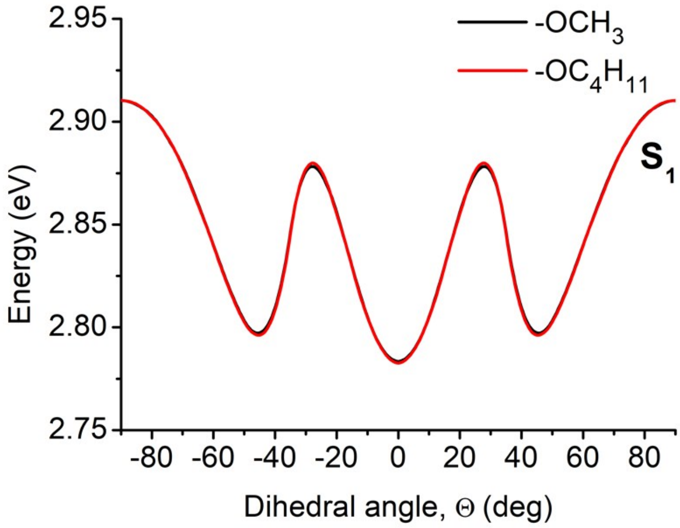

Figure S2. Potential energy curves for the first excited state of BODIPY derivatives calculated by TD-DFT. The results are shown for two shortened variants of BODIPY-C_{10}: with a methyl group, and with an *n*-butyl group instead of the *n*-decane group in BODIPY-C_{10}. The energy curves are almost identical, which means that shortening carbon chain of BODIPY-C_{10} for faster computation does not significantly impact the results.

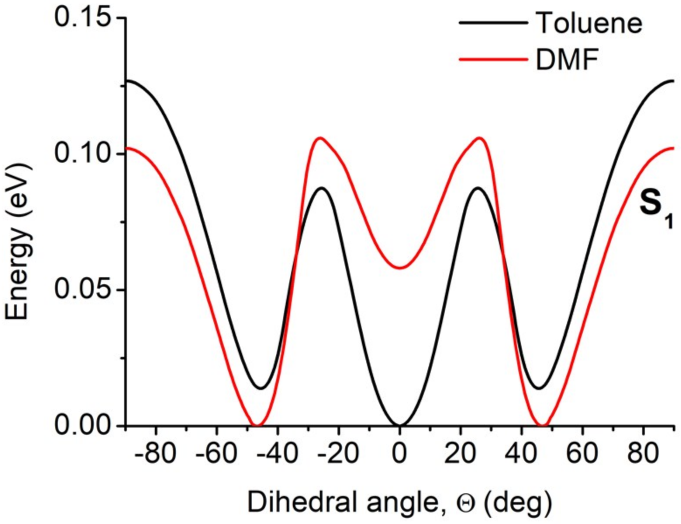

Figure S3. Potential energy curves for the first excited state of BODIPY-C_{10} calculated by TD-DFT. The calculations were performed using solvent models of toluene and DMF. The calculations produce an energy barrier at 25°, which needs to be overcome for the fluorophore to relax non-radiatively. The theoretically obtained energy barrier is greater in the case of DMF, which does not agree well with experimental results: the fluorescence lifetime of BODIPY-C_{10} is significantly lower in DMF, whereas the higher barrier alone would likely produce the opposite. Therefore, the existence of factors not accounted for in this model cannot be ruled out.

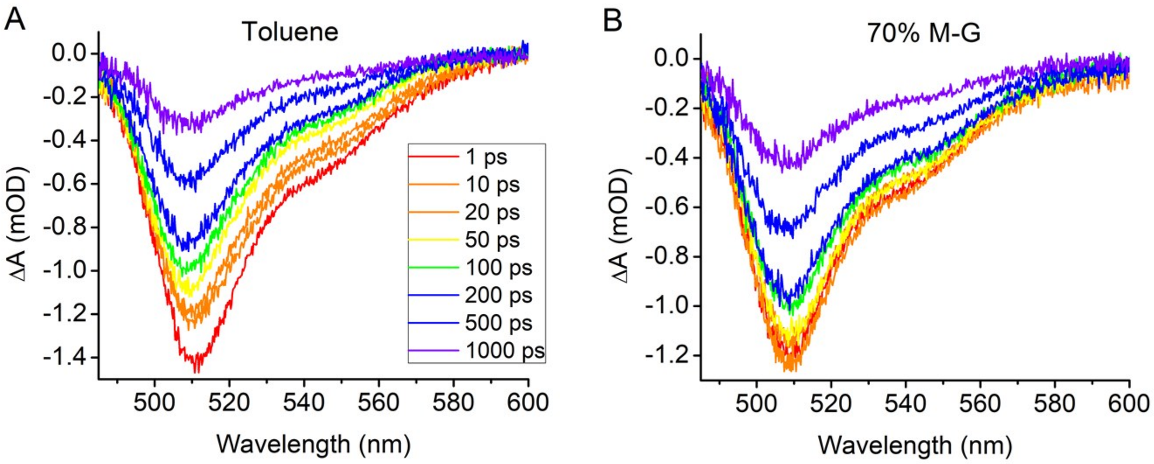

Figure S4. Transient absorption spectra of BODIPY-C_{10} in toluene (A) and 70% glycerol-methanol mixture (v/v%) (B). Compared to data in methanol (Figure 3, main text), spectra in both non-polar (toluene) and viscous (70% glycerol-methanol) solvents decay slower.

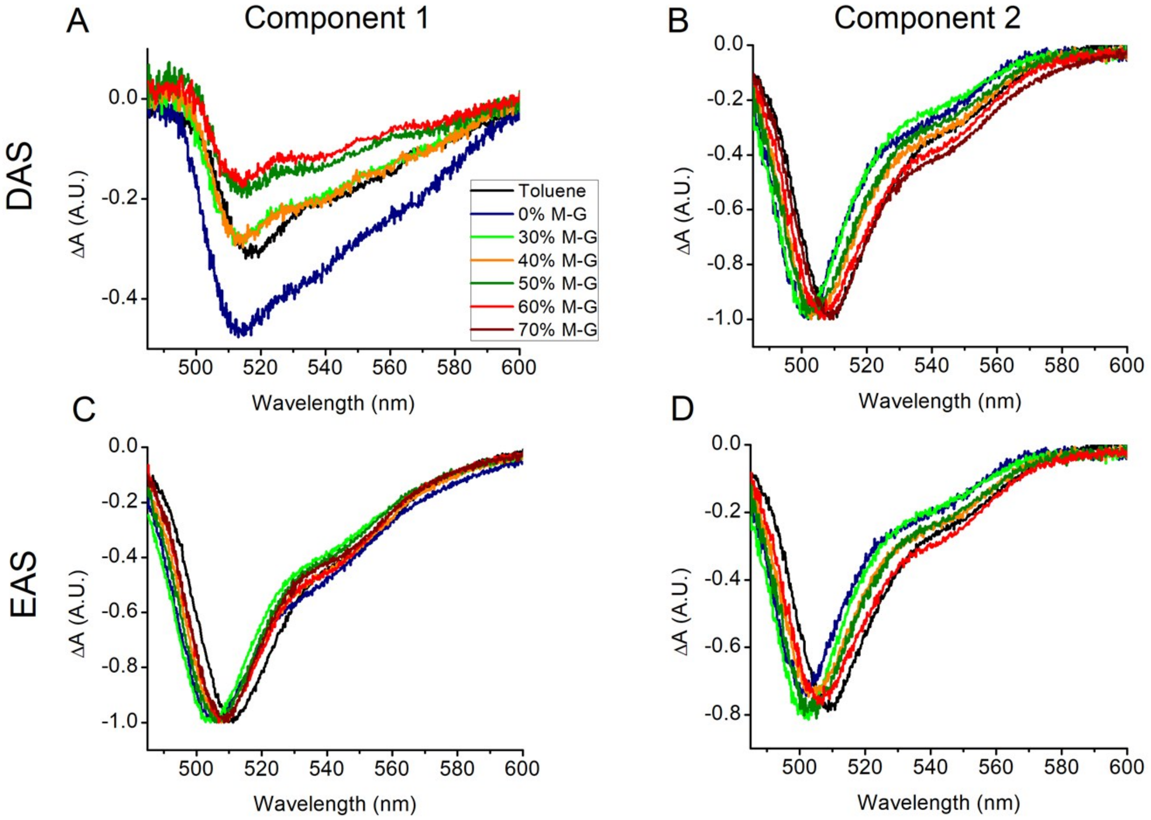

Figure S5. Decay associated (DAS) and evolution associated spectra (EAS) resulting from a global analysis of transient absorption data of BODIPY-C_{10}. The data were fitted using two exponential components except for 70% glycerol-methanol data where a single component was sufficient. DAS shows wavelength-dependence of amplitudes of both exponential components (top panel). Both components were normalized with respect to the intensity of Component 2 to account for the variation of the intensity of the transient absorption signal. The lower panel (C, D) shows EAS, which are the result of the sequential kinetic scheme: $S_0 \xrightarrow{h\upsilon} S'_1 \xrightarrow{\tau_1} S_1 \xrightarrow{\tau_2} S_0$. The first EAS component (C) corresponds to the transient absorption spectra of species in a state S'_1, which is the state the fluorophore is in immediately after excitation. The second EAS component (D) corresponds to the spectra of partially relaxed species S_1, which then decays back to the ground state.