Supplementary Material (ESI) for Photochemical & Photobiological Sciences

A push-pull aromatic chromophore with a touch of merocyanine

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Supplementary Information

Dielectric properties of liquid 2-methyltetrahydrofuran as a function of temperature

The experimental densities of MTHF[1] depend linearly on the temperature according to eq. S1.

$$\rho = 1.12 - 9.2 \times 10^{-4} T \qquad \text{(S1)}$$

The refractive index can be calculated from its relationship with the density of the solvent, as expressed by the Lorentz-Lorenz equation (eq. S2).[2, 3] It is assumed that the molecular polarizibility (α) is independent of the temperature.

$$\left(\frac{n^2 - 1}{n^2 + 2}\right)\frac{M}{\rho} = \frac{N_A \alpha}{3\varepsilon_0} \qquad \text{(S2)}$$

In this equation n is the refractive index of the medium, M the molecular weight, ρ the density, N_A Avogadro's number and ε_0 the vacuum permittivity. The molecular polarizability α of MTHF was calculated from the literature value of the refractive index n = 1.406 at 293 K.[4]

To describe the temperature dependence of the static dielectric constant of a solvent it is common practice to fit a series of values at different temperatures with a polynomial:

$$\varepsilon_r(T) = a + bT + cT^2 + dT^3 \qquad \text{(S3)}$$

In this way values at temperatures for which measured data are not available can be interpolated or extrapolated. The dielectric constants of MTHF between 180 and 300 K[1, 5] are well fitted with a 2nd order polynomial of which the coefficients are: a = 25.94, b = -0.11, c = 1.52 × 10^{-4}.

In Table 1 the refractive indices and the dielectric constants of MTHF are given at the temperatures at which the spectroscopic measurements were performed. Values at temperatures outside the range 180-300 K were extrapolated according to Equation S3, with the coefficients given above.

Table S1 Calculated dielectric constants and refractive indices of liquid 2-methyltetrahydrofuran (MTHF) at various temperatures.

Temperature (K)	MTHF[a] ε	n	$\Delta f^{\,b}$
298	6.24	1.402	0.386
283	6.63	1.410	0.393
273	6.92	1.415	0.398
263	7.22	1.419	0.402
253	7.55	1.424	0.407
243	7.91	1.429	0.412
233	8.30	1.435	0.416
223	8.72	1.440	0.420
213	9.19	1.445	0.425
203	9.70	1.450	0.430
198	9.97	1.452	0.432
193	10.43[c)]	1.454	0.437
183	10.96[c)]	1.459	0.440
173	11.51[c)]	1.464	0.443
163	12.10[c)]	1.469	0.445
153	12.72[c)]	1.475	0.447
143	13.36[c)]	1.480	0.450

[a)] Glass transition temperature = 137 K ,
[b)] Defined as $\Delta f = f(\varepsilon) - f(n^2)$ with $f(\varepsilon) = 2(\varepsilon-1)/(2\varepsilon+1)$ and $f(n^2) = 2(n^2-1)/(2n^2+1)$
[c)] Values at T >193 K are extrapolated from eq. S3, others are literature values.[1, 5]

With the calculated dielectric constants and refractive indices from Table S1 it is possible to relate the temperature with the polarity of the solvent. In Fig. S1 the values of the polarity functions $f(\varepsilon)$, $f(n^2)$ and $f(\varepsilon)$-$f(n^2)$ as function of the temperature are shown. The polarity increases with lowering the temperature.

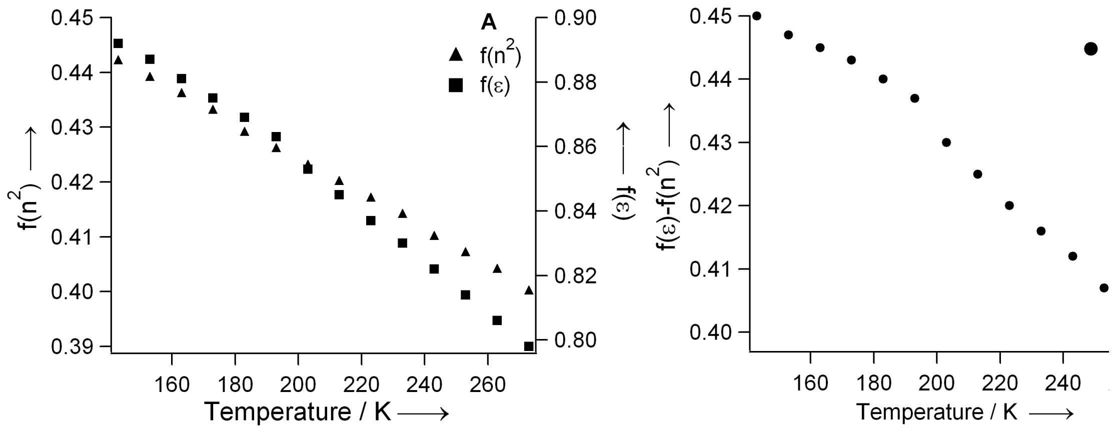

Fig. S1 The effect of temperature on the solvent polarity functions of liquid MTHF: A, *f(ε)* at the right vertical axis and $f(n^2)$ versus the left vertical axis. B) $f(\varepsilon)$-$f(n^2)$, as calculated with the data from Table S1.

References

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