Supporting information

Dipolar 3-methoxychromones as bright and highly solvatochromic fluorescent dyes

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Spectroscopic characterization of compounds 1-3

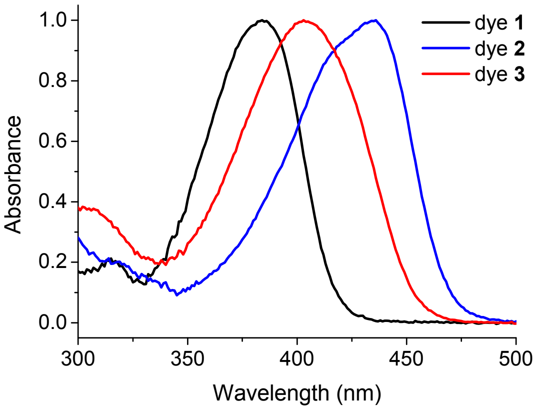

Figure S1. Normalized absorption spectra of compounds **1-3** in toluene.

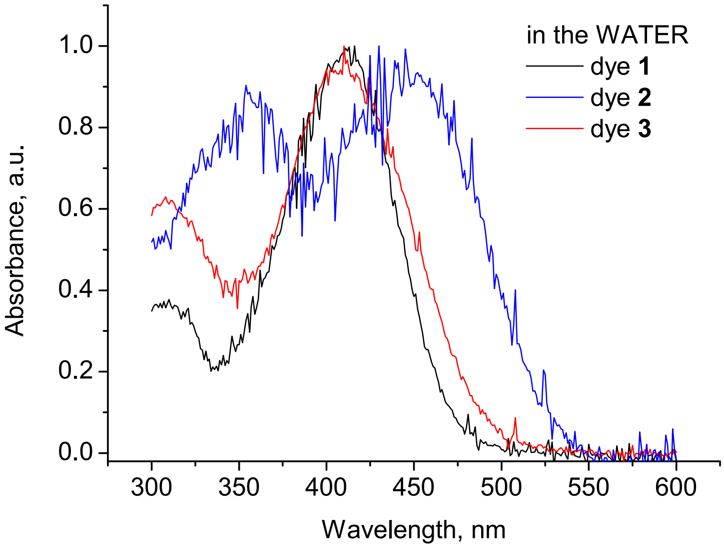

Figure S2. Normalized absorption spectra of compounds **1-3** in water. The spectra are noisy because of low dyes concentration (0.5 µM) used due to solubility problems.

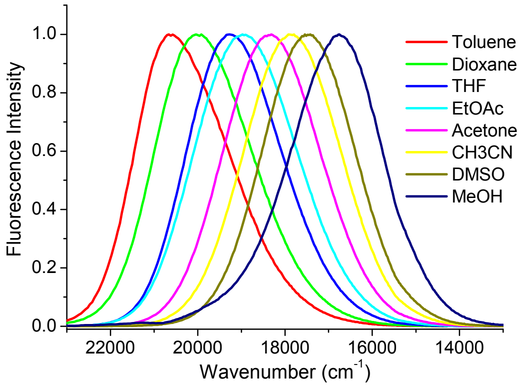

Figure S3. Fluorescence spectra of dye **2**, presented in a wavenumber scale. The spectra were obtained by conversion of wavelengths into wavenumbers without additional corrections.

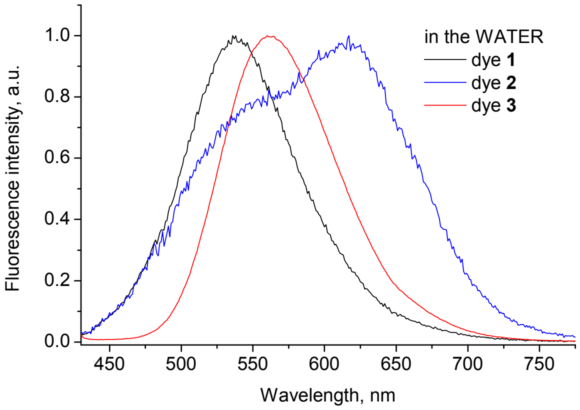

Figure S4. Normalized fluorescence spectra of dyes **1-3** in water.

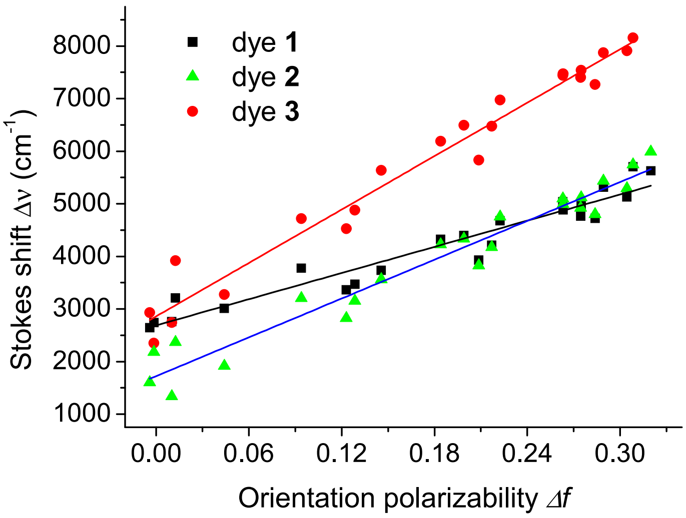

Figure S5. Dependence of the Stokes shifts ($\Delta\nu$) of dyes **1-3** as a function of the Lippert parameter (Δf). Results of the linear fits are: dye **1** $\Delta\nu = 2688+8300*\Delta f$, $r^2 = 0.927$, dye **2** $\Delta\nu = 1721+12310*\Delta f$, $r^2 = 0.950$, dye **3** $\Delta\nu = 2859+16935*\Delta f$, $r^2 = 0.967$, where the r^2 value represents goodness of fit.

Plotting the Stokes shift $\Delta\nu$ versus the Lippert parameter Δf (Fig. S3) and using the Lippert-Mataga equation,[1,2] we estimated the dipole moment difference $\Delta\mu$ to be equal to 8.4±0.5 D (a=4.4Å), 13.1±0.5 D (a=5.2Å) and 20.0±0.5 D (a=6.2Å) for compounds **1, 2** and **3,** respectively. The cavity radius (a) was determined from their chemical structure (through the distance between donating Nitrogen atom and accepting Oxygen) using a chemical modeling software.

Photostability of compounds 1-3

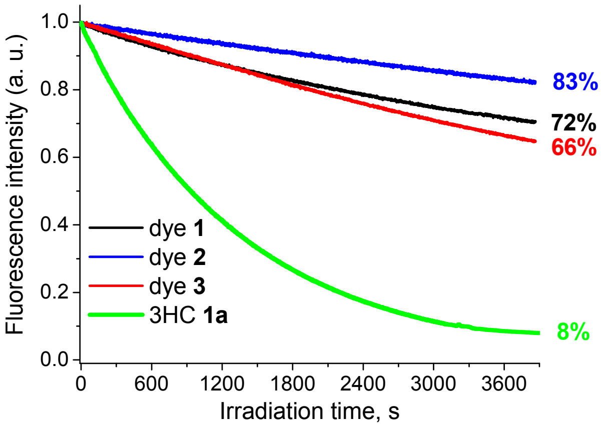

Figure S6. Photodegradation of dyes **1-3** in DMF in comparison to that of 3HC analogue **1a**. The fluorescence intensity of the dyes was recorded as a function of the irradiation time. For comparison, the curves were normalized to the same initial intensity. Numbers (%) correspond to residual fluorescence intensity after 1h of irradiation. Concentration of the dyes was 1µM. Excitation wavelength was 400 nm for **1** and **1a**, 430 nm for **2** and **3**. The absorption coefficient of **1** and **1a** at 400 nm was *ca* 30000 $M^{-1}cm^{-1}$, while for **2** and **3** at 430 nm it was *ca* 28000 and 26000 $M^{-1}cm^{-1}$, respectively.

Table S1. Photostability of compounds **1-3** in different solvents[a].

Solvent	**Dye 1**		**Dye 2**		**Dye 3**	
	τ_d, min	***R*, %**	**τ_d, min**	***R*, %**	**τ_d, min**	***R*, %**
EtOH	215	75	2445	97	>10000	99
DMF	185	72	335	83	145	66

[a] τ_d is the time constant of photodegradation; *R* is residual fluorescence intensity after 60 min of irradiation.

Table S2. Physical parameters of solvents used in our studied.

№	**Solvent**	**Refractive index $n_{20°C}$** [a]	**Dielectric constant ε** [a]	**Δf** [b]	**$E_T(30)$** [c]
1	CS_2	1.6319	2.61	-0.0040	32.8
2	Hexane	1.3749	1.88	-0.0014	31.0
3	CCl_4	1.4601	2.23	0.0102	32.4
4	Toluene	1.4961	2.37	0.0126	33.9
5	Dioxane	1.4224	2.21	0.0205	36.0
6	Et_3N	1.4010	2.38	0.0441	32.1
7	n-Bu_2O	1.3992	3.05	0.0939	33.0
8	iPr_2O	1.3679	3.38	0.1230	34.1
9	PhBr	1.5597	5.4	0.1286	36.6
10	$CHCl_3$	1.4459	4.71	0.1456	39.1
11	*Tert*-pentanol	1.4050	5.8	0.1841	41.0
12	EtOAc	1.3723	5.99	0.1991	38.1
13	THF	1.405	7.43	0.2086	37.4
14	CH_2Cl_2	1.4242	8.93	0.2171	40.7
15	1-Octanol	1.4295	9.86	0.2225	48.1
16	1-Butanol	1.3993	17.3	0.2630	49.7
17	DMSO	1.4790	46.8	0.2632	45.1
18	DMF	1.4305	37.2	0.2746	43.2
19	2-Propanol	1.3776	19.3	0.2749	48.4
20	Acetone	1.3588	20.5	0.2839	42.2
21	EtOH	1.3611	24.9	0.2893	51.9
22	CH_3CN	1.3442	35.7	0.3044	45.6
23	MeOH	1.3288	32.6	0.3084	55.4
24	Water	1.3328	78.4	0.3200	63.1

[a] refractive index and dielectric constant are from Ref. 3.

[b] Δf is Lippert orientation polarizability function, $\Delta f = (\varepsilon-1)/(2\varepsilon+1) - (n^2-1)/(2n^2+1)$, where ε is dielectric constant, n is refractive index

[c] E_T30 values are from ref 4.

NMR spectra of the final compounds

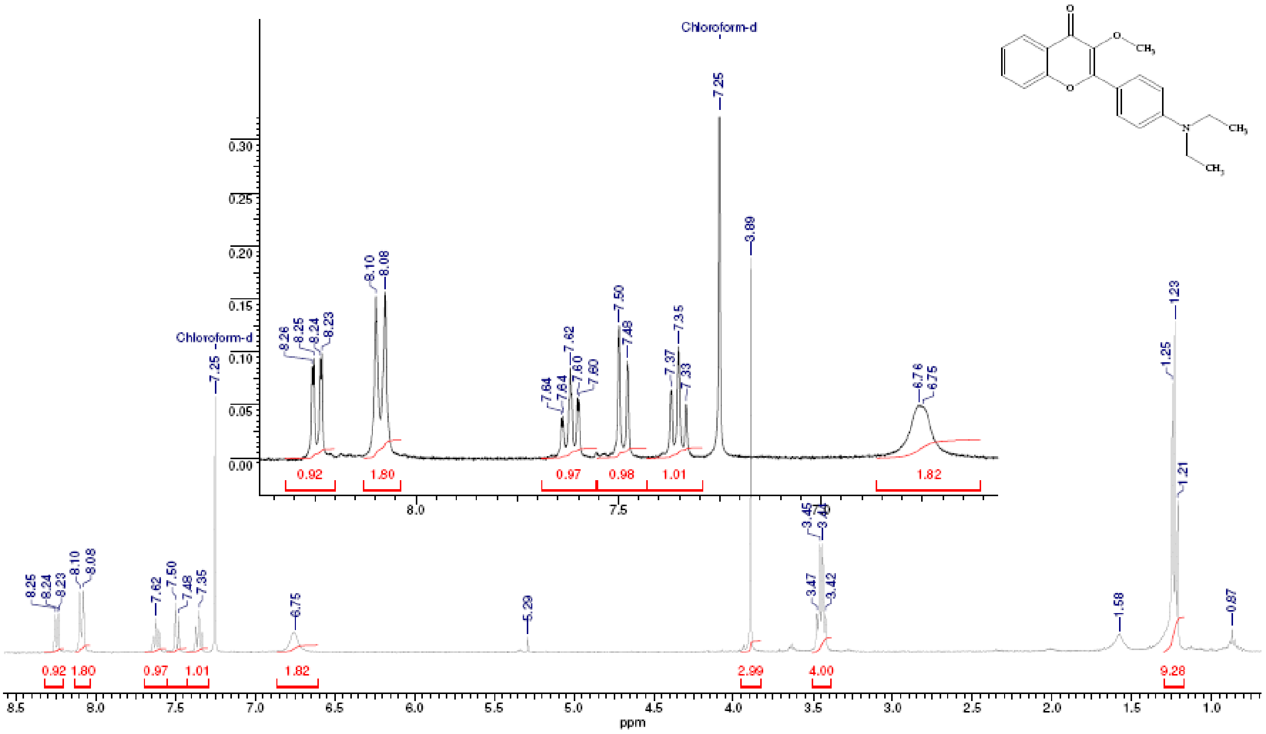

Fig. S7. ^{1}H-NMR spectrum of dye **1.**

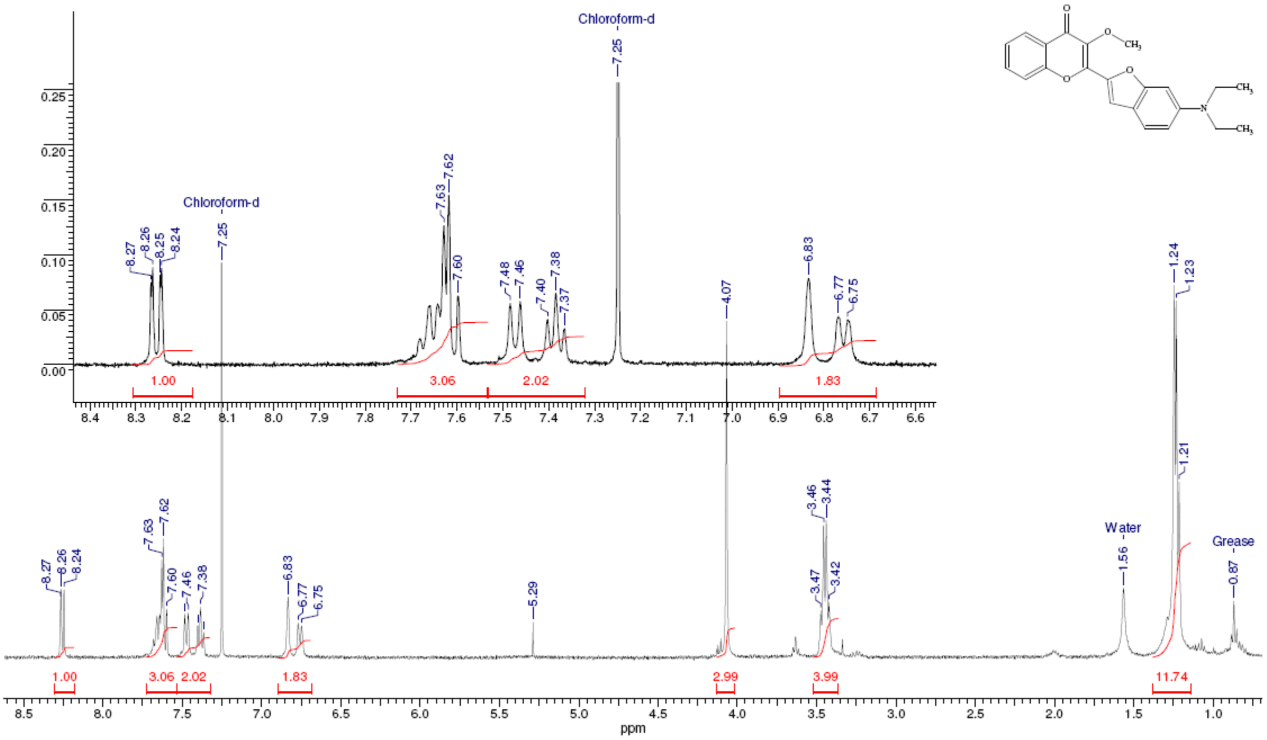

Fig. S8. ^{1}H-NMR spectrum of dye **2.**

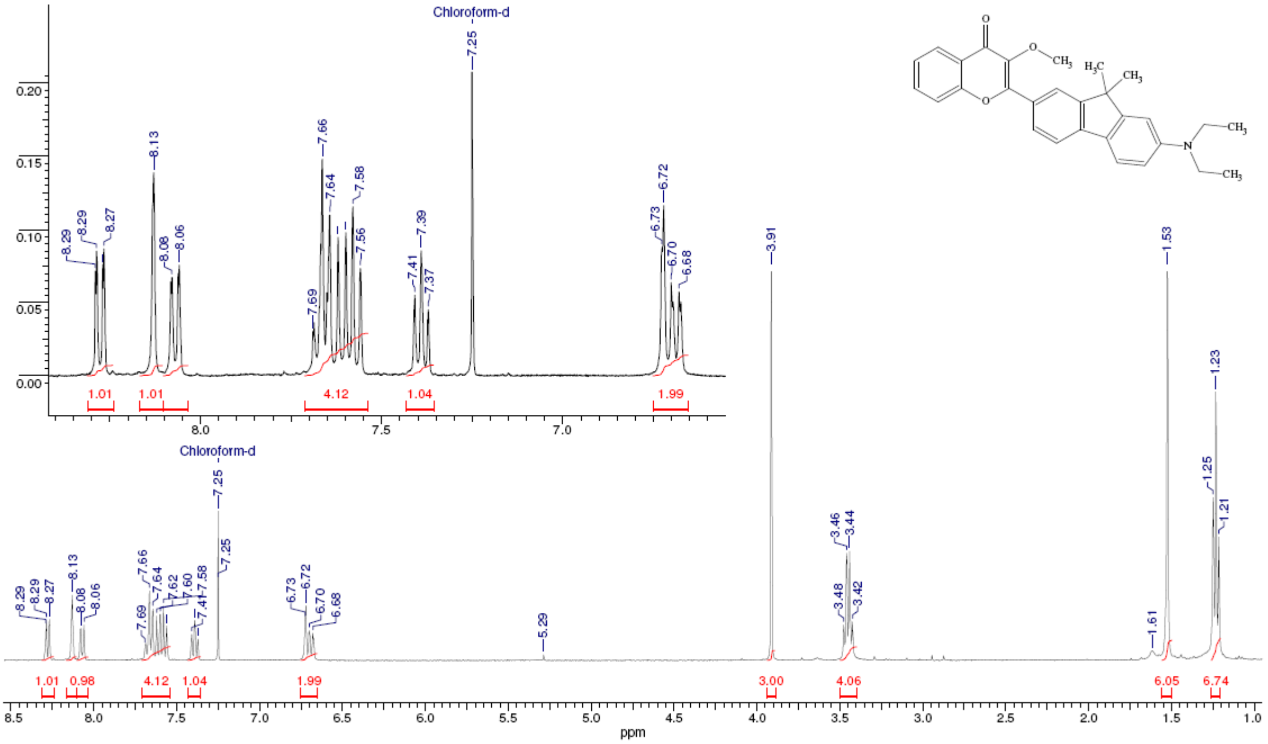

Fig. S9. ^{1}H-NMR spectrum of dye **3.**

References

1. E. L. Lippert, 'Organic molecular photophysics', Wiley-Interscience, 1975.
2. N. Mataga and T. Kubota, 'Molecular interactions and electronic spectra', M. Dekker, 1970.
3. J.-L. M. Abboud, R. Notatio. *Pure Appl. Chem.* 1999, **71**, 645.
4. C. Reichardt, *Chem. Rev.*, 1994, **94**, 2319.