

Merocyanines based on 1,2-diphenyl-3,5-pyrazolidinedione

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UV-Vis absorption spectra

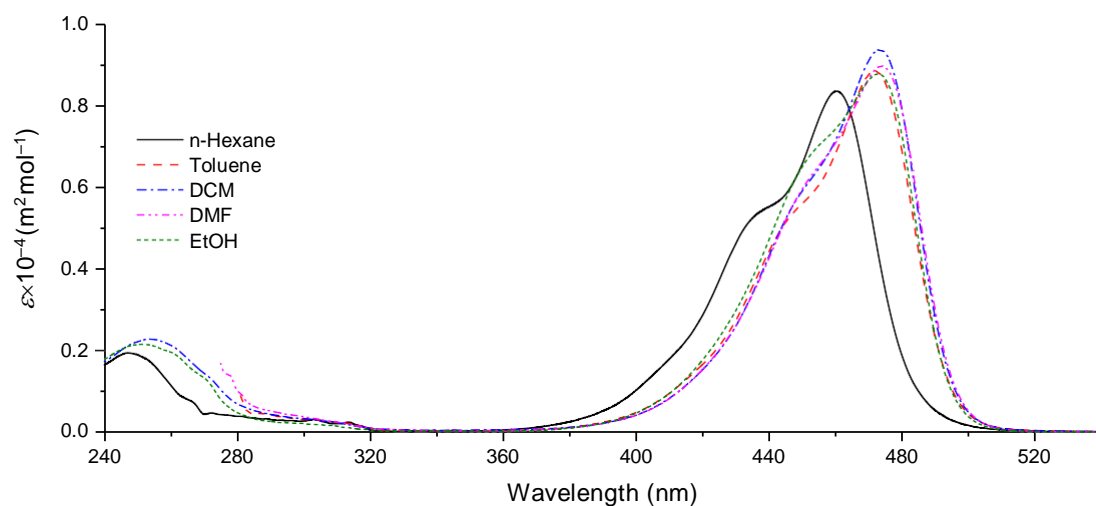


Fig. S1. Absorption spectra of dye 1 in solvents of different polarities.

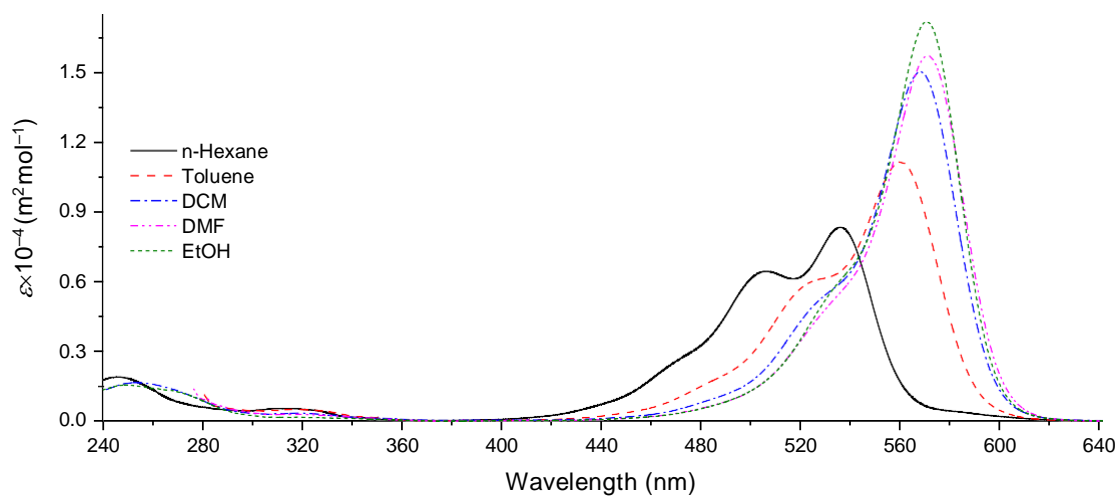


Fig. S2. Absorption spectra of dye 2 in solvents of different polarities.

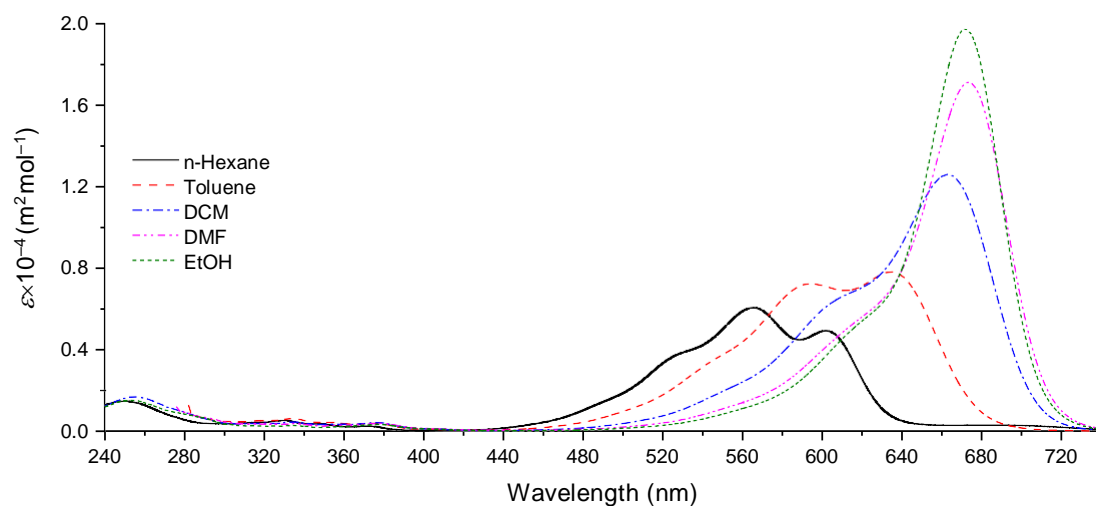


Fig. S3. Absorption spectra of dye 3 in solvents of different polarities.

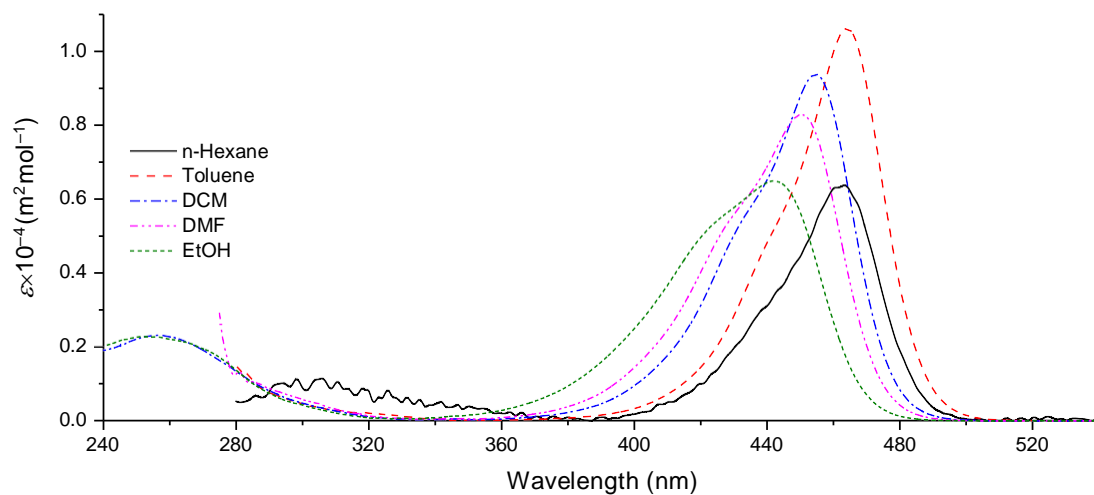


Fig. S4. Absorption spectra of dye **4** in solvents of different polarities (spectrum in *n*-hexane is the actual absorbance spectrum multiplied 20 times, not quantitative).

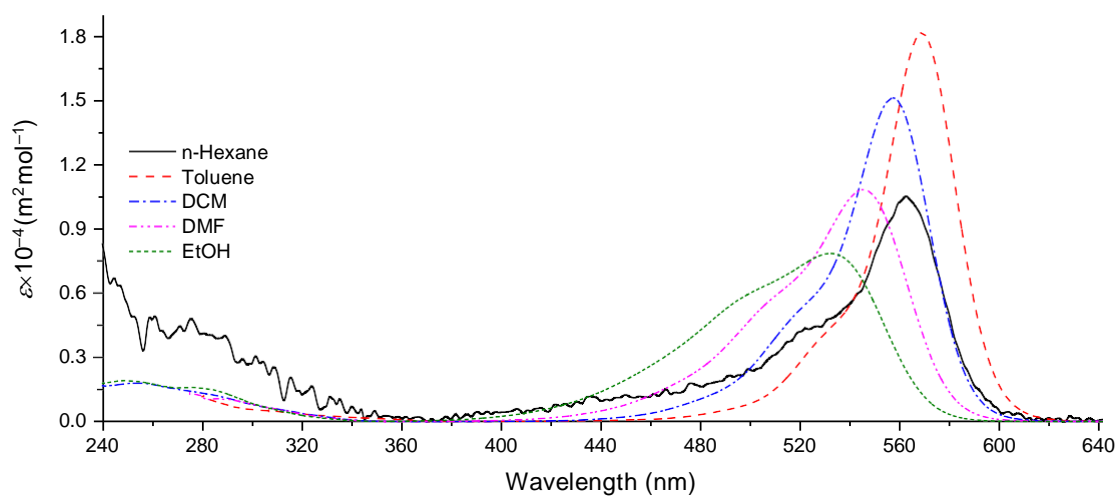


Fig. S5. Absorption spectra of dye **5** in solvents of different polarities (spectrum in *n*-hexane is the actual absorbance spectrum multiplied 50 times, not quantitative).

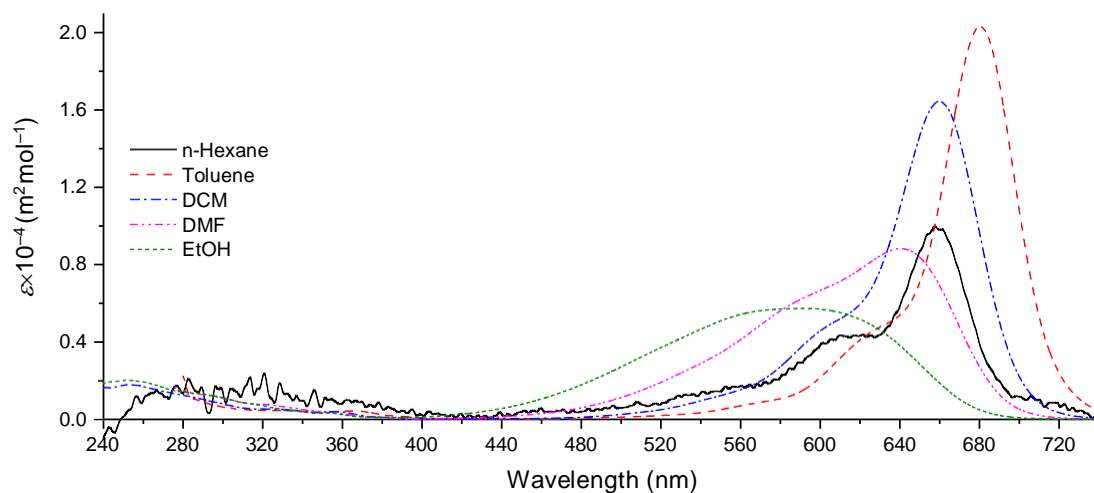


Fig. S6. Absorption spectra of dye **6** in solvents of different polarities (spectrum in *n*-hexane is the actual absorbance spectrum multiplied 50 times, not quantitative).

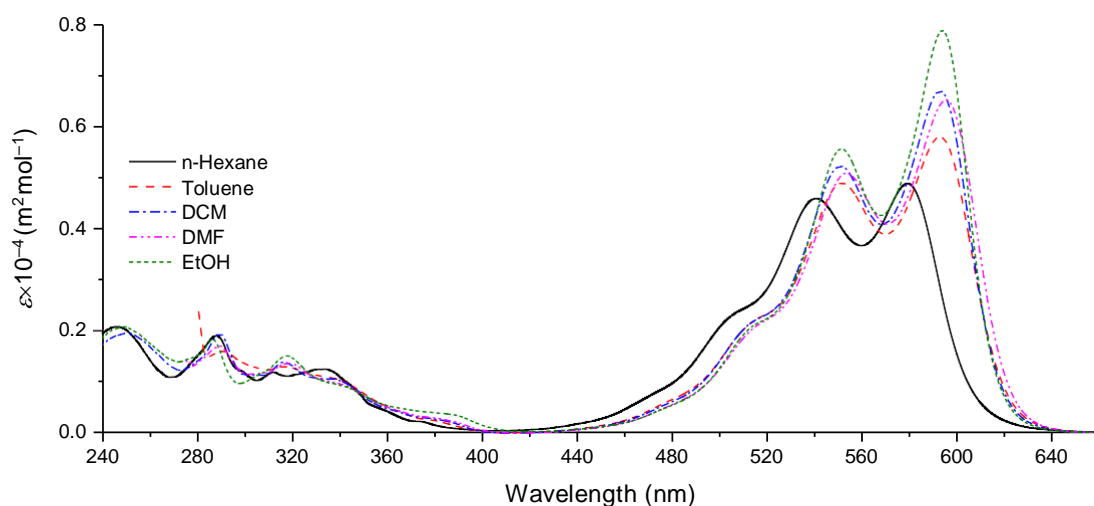


Fig. S7. Absorption spectra of dye **7** in solvents of different polarities.

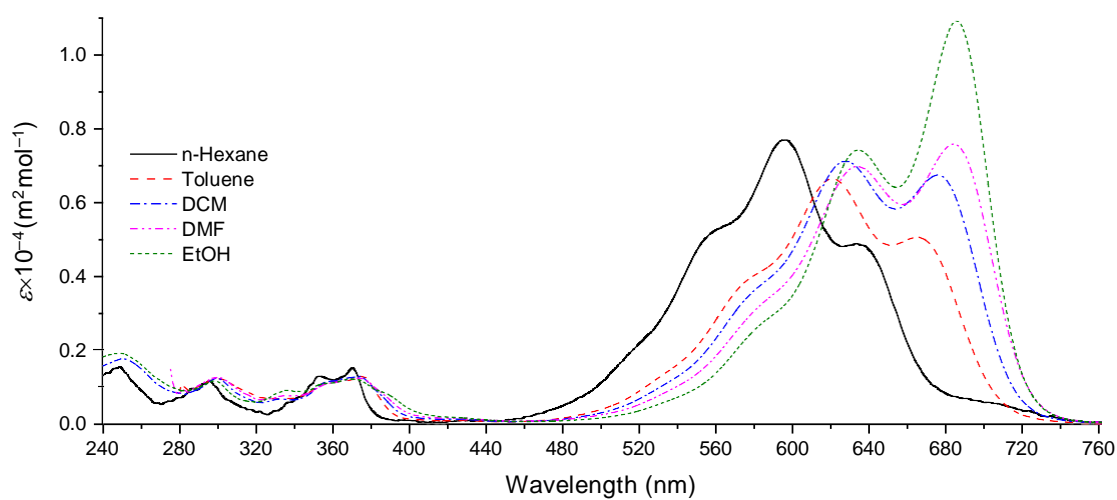


Fig. S8. Absorption spectra of dye **8** in solvents of different polarities (spectrum in *n*-hexane is the actual absorbance spectrum multiplied 5 times, not quantitative).

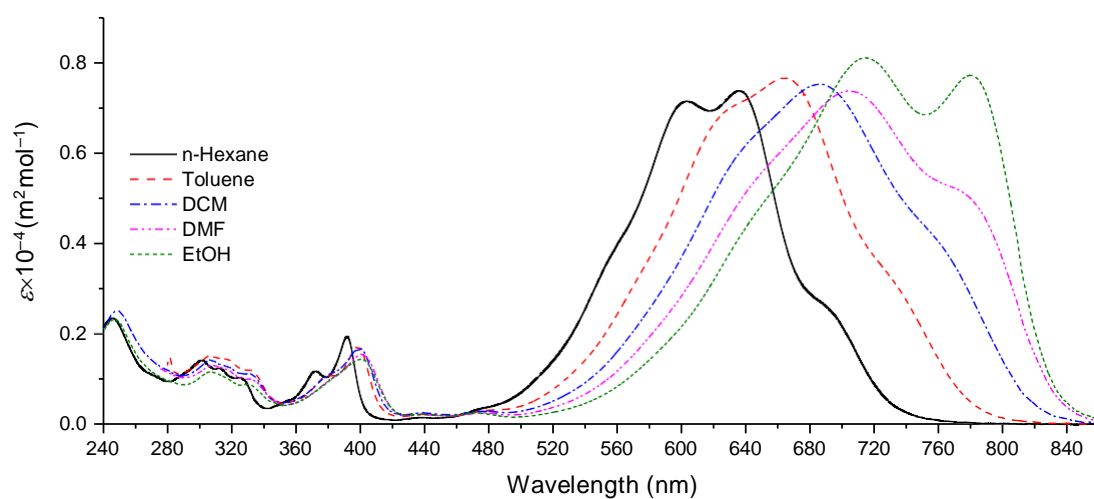


Fig. S9. Absorption spectra of dye **9** in solvents of different polarities (the short-wavelength range of these spectra is not shown in Fig. 2).

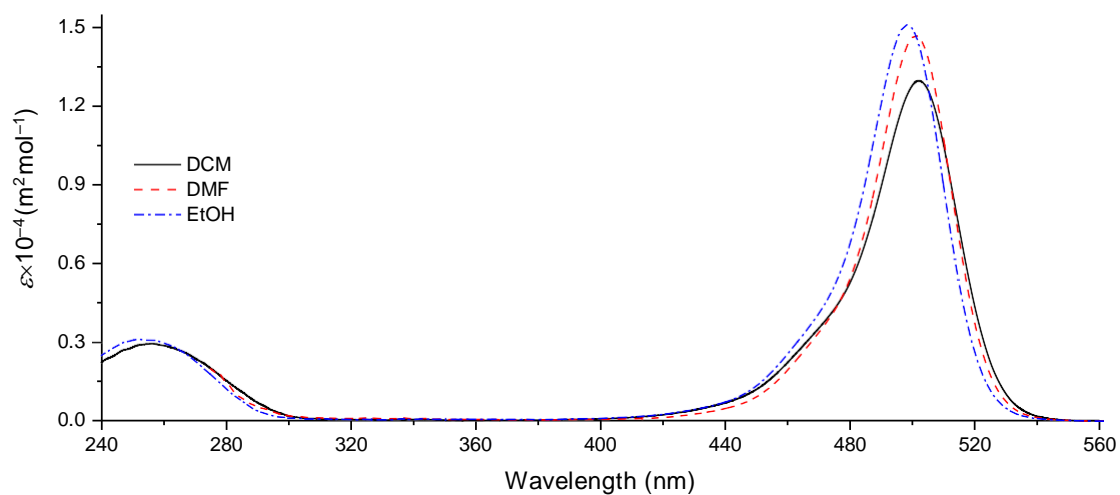


Fig. S10. Absorption spectra of anionic dye **10** in solvents of different polarities.

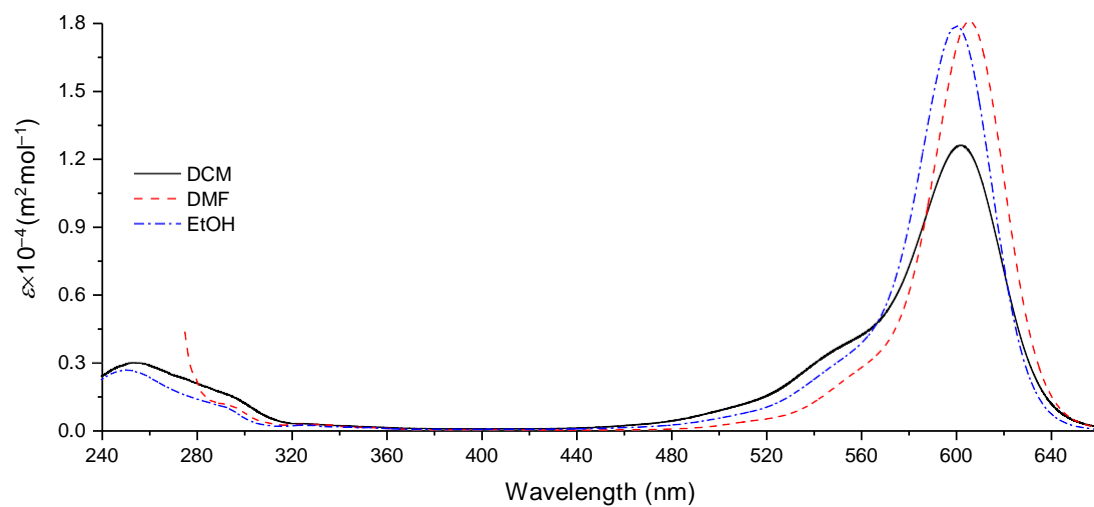


Fig. S11. Absorption spectra of anionic dye **11** in solvents of different polarities.

About the cuvette-wall adsorption of some dyes in *n*-hexane

It is mentioned in the main part of the paper that in *n*-hexane there were signs of adsorption of some compounds on the cuvette walls. Such signs are the long-wavelength “shoulders” of the long-wavelength absorption bands, which were observed for dyes **2**, **3**, **6**, and **8**. There are several reasons to attribute them to the adsorbed form of a dye: (a) their intensity increases with time, (b) their intensity increases further if the cuvette is emptied out and then filled with the fresh solution from the volumetric flask; (c) if the cuvette is emptied out and then filled with the pure solvent (*n*-hexane), the initial relative intensity of the long-wavelength shoulder is much greater (than that of the original solution) and decreases very slowly with time; (d) if the content of the cuvette from clause (c) is poured into a clean quartz cuvette the long-wavelength shoulder becomes much smaller. Such tests were carried out for dyes **2**, **3** and **8** (the solubility of dye **6** is far too small to perform the operations). They are illustrated below for dye **3**.

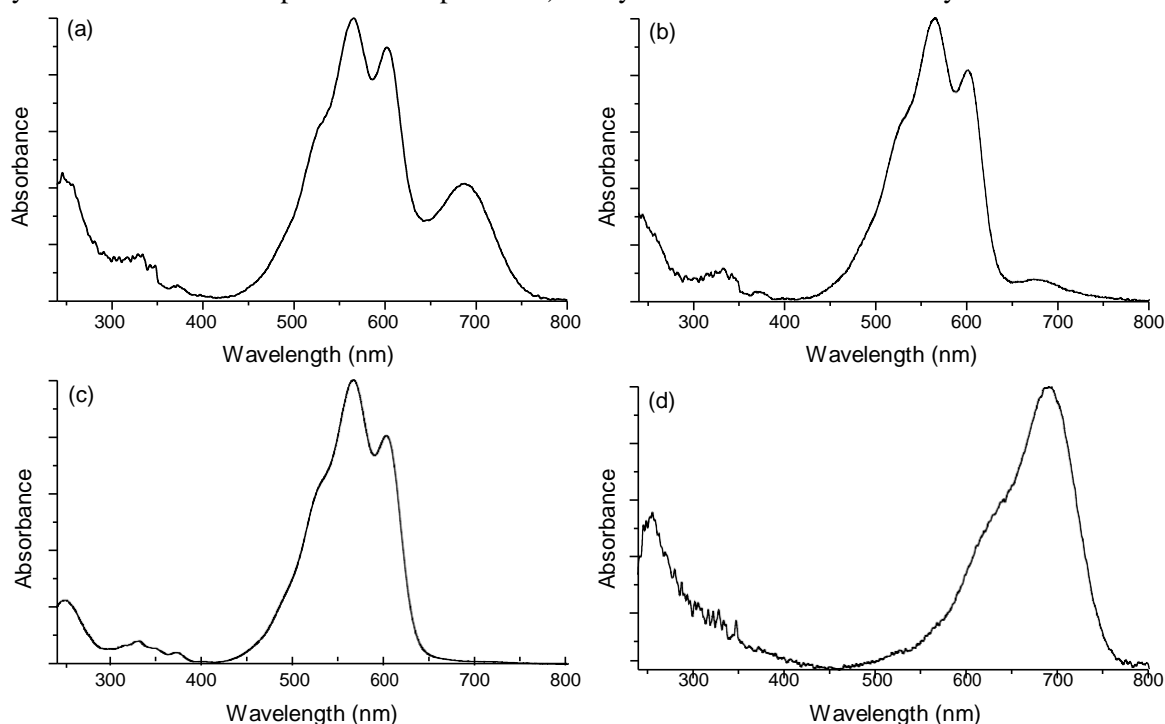


Fig. S12. Normalized absorption spectra of dye **3** in *n*-hexane:

- (a) the cuvette was emptied out and then filled with *n*-hexane;
- (b) the obtained solution was poured into a clean quartz cuvette;
- (c) “pure” spectrum of dye **3** in *n*-hexane, obtained via normalized subtraction of curve (a) from curve (b);
- (d) “pure” spectrum of the adsorbed form of dye **3**, obtained via normalized subtraction of curve (b) from curve (a).

Note that the shape of band (d) is similar to the shapes of absorption bands of dye **3** in high-polarity solvents, while its maximum (690 nm) is even more bathochromic than the maxima in DMF or ethanol (Table 1). Possibly, this shift is caused by a greater local refractive index of the medium (refractive index of quartz is equal to 1.54-1.56). There might also occur formation of some long-wavelength aggregate on the cuvette surface.

Fluorescence spectra

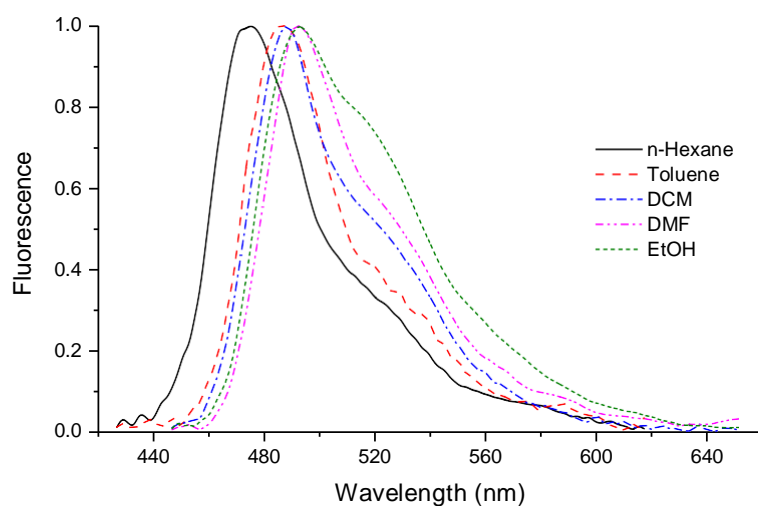


Fig. S13. Normalized fluorescence spectra of dye 1 in solvents of different polarities.

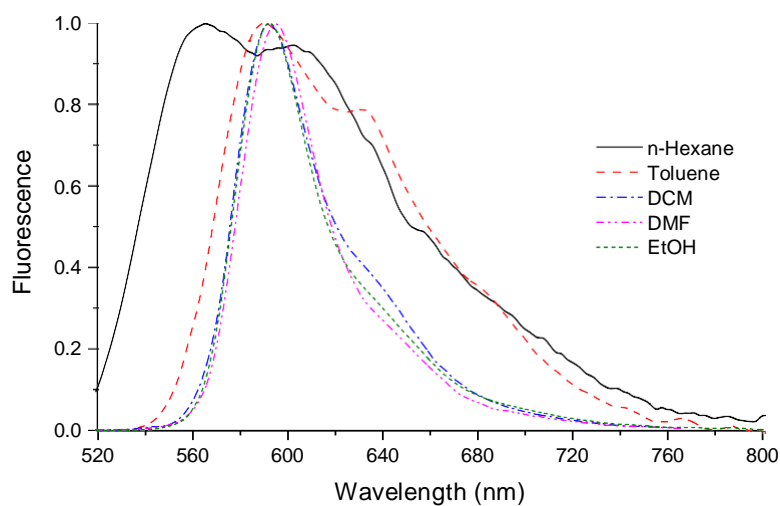


Fig. S14. Normalized fluorescence spectra of dye 2 in solvents of different polarities.

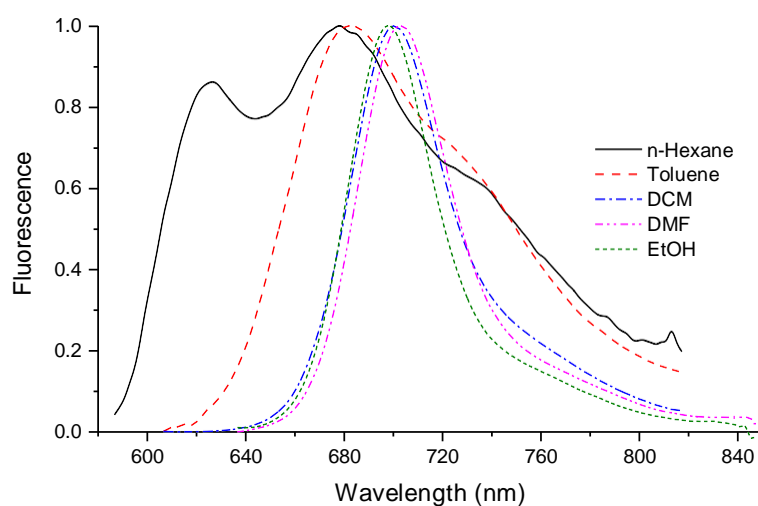


Fig. S15. Normalized fluorescence spectra of dye 3 in solvents of different polarities.

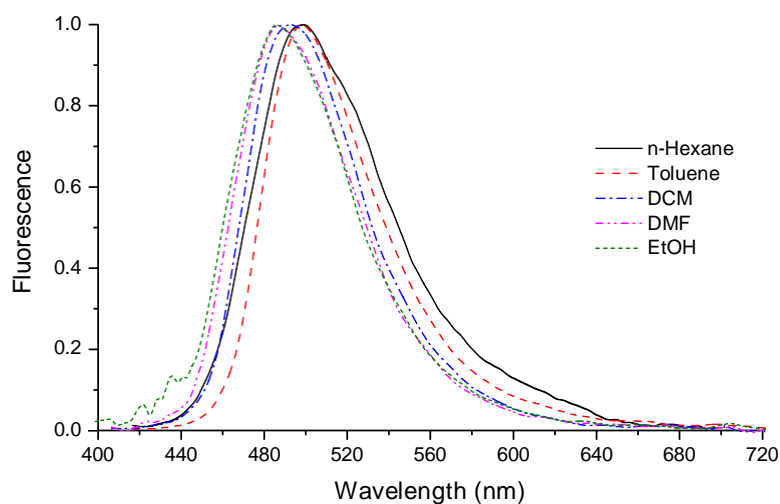


Fig. S16. Normalized fluorescence spectra of dye **4** in solvents of different polarities.

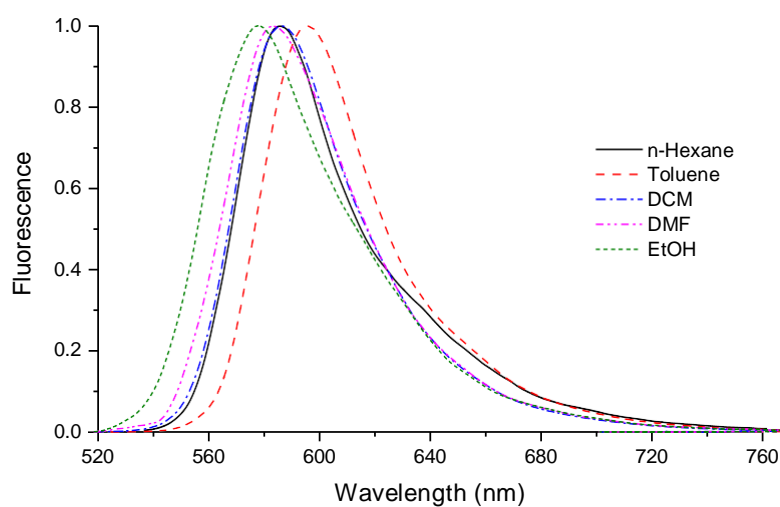


Fig. S17. Normalized fluorescence spectra of dye **5** in solvents of different polarities.

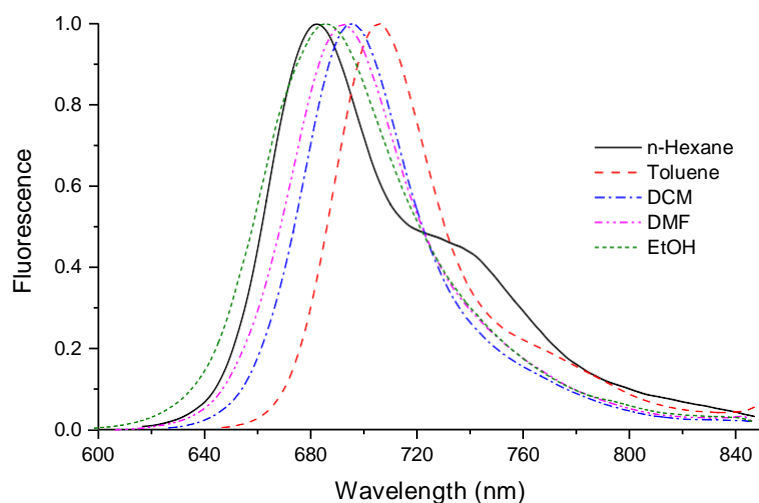


Fig. S18. Normalized fluorescence spectra of dye **6** in solvents of different polarities.

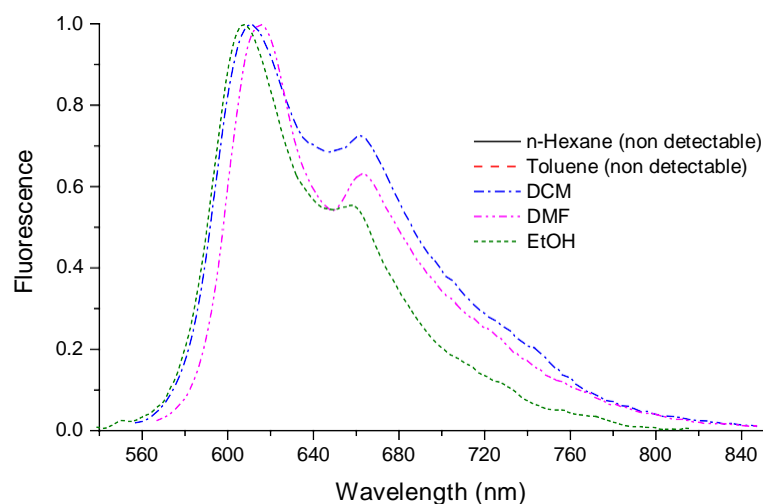


Fig. S19. Normalized fluorescence spectra of dye **7** in solvents of different polarities.

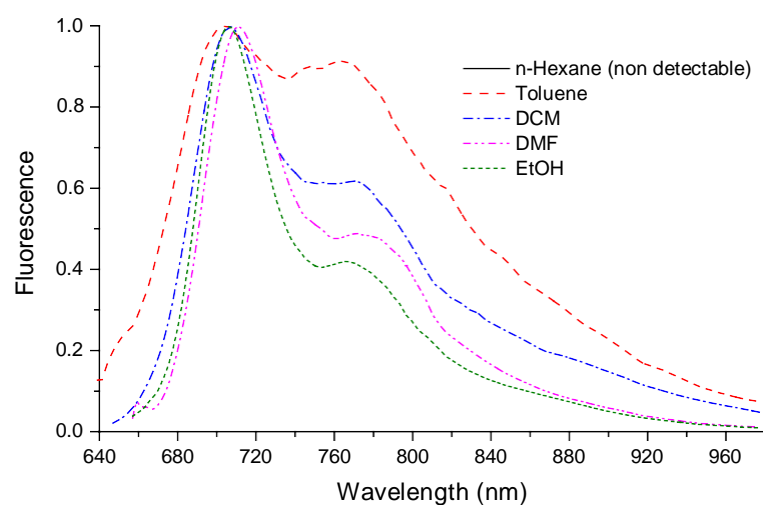


Fig. S20. Normalized fluorescence spectra of dye **8** in solvents of different polarities.

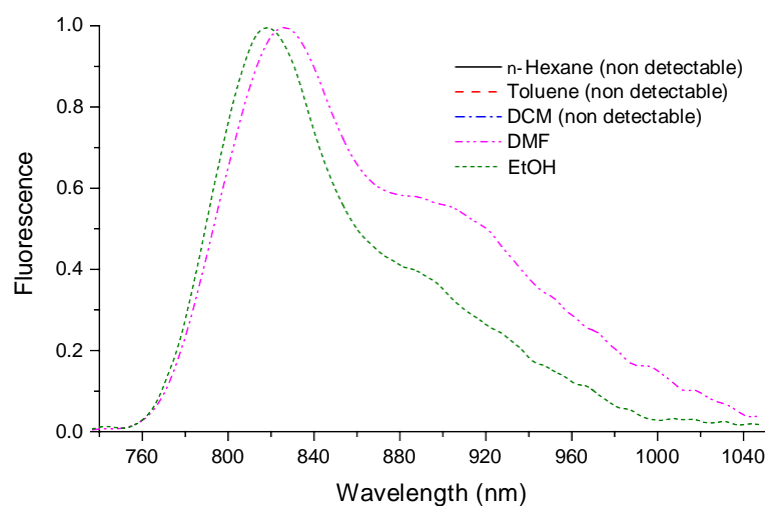


Fig. S21. Normalized fluorescence spectra of dye **9** in solvents of different polarities (these spectra were detected with the slitwidths of 20-nm).

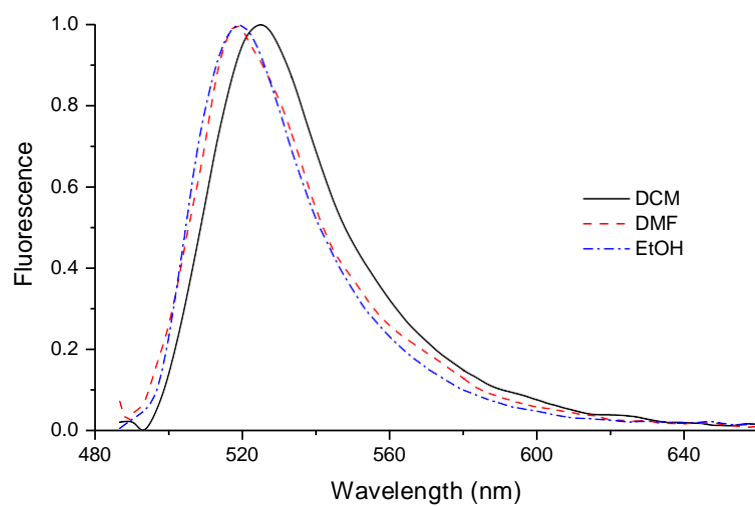


Fig. S22. Normalized fluorescence spectra of anionic dye **10** in solvents of different polarities.

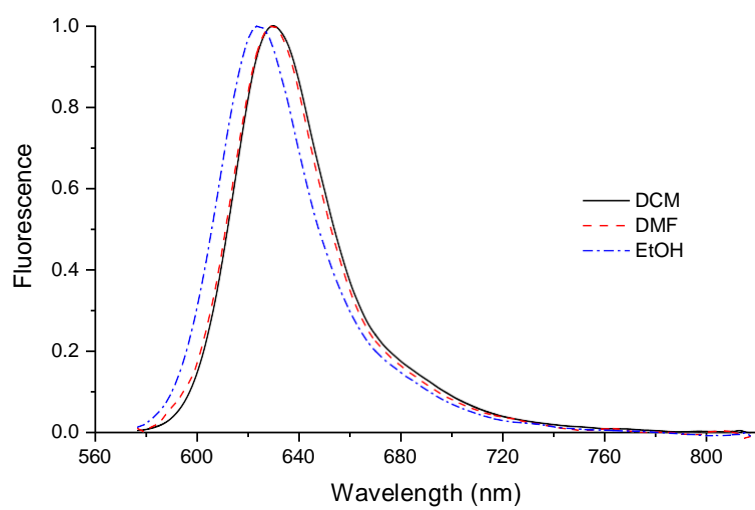


Fig. S23. Normalized fluorescence spectra of anionic dye **11** in solvents of different polarities.

Absorption and fluorescence spectra of dye 2 in ethylene glycol

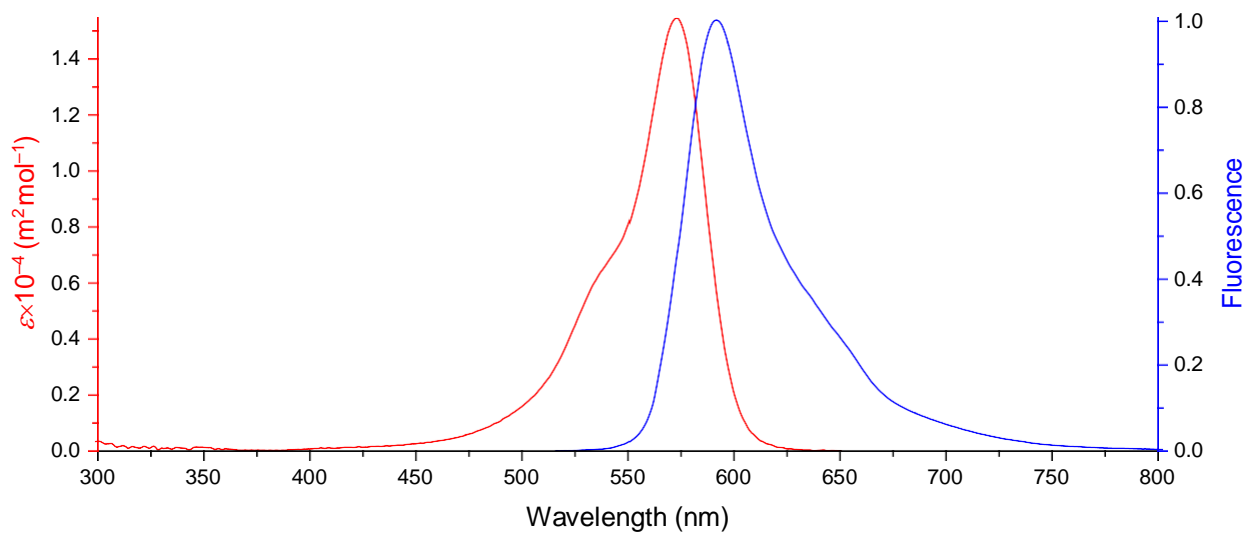


Fig. S24. Absorption and normalized fluorescence spectra of dye 2 in ethylene glycol.

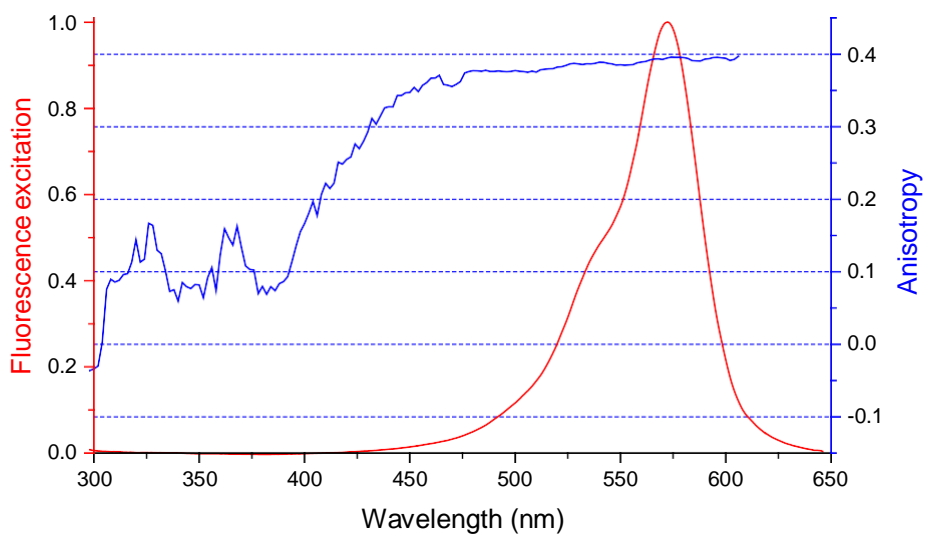


Fig. S25. Normalized fluorescence excitation and anisotropy of dye 2 in ethylene glycol.

Gaussian deconvolution of the spectral bands of dye **9**

The deconvolution of the absorption spectral bands of dye **9** in *n*-hexane and ethanol into Gaussian components was performed using the free Fityk-1.3.1 software (<http://fityk.nieto.pl/>).

It is known that the main vibronic components of the spectral bands of polymethine dyes are distanced by 1050-1300 cm^{-1} . The long-wavelength absorption bands of dye **9** were transposed into coordinates $\varepsilon(\nu)/\nu - \nu$, roughly divided into Gaussian components distanced by ca. 1150 cm^{-1} , and fitted. For the band in ethanol, the fitting was straightforward. For the band in *n*-hexane, the positions of higher three components were determined from straightforward deconvolution. The distance between them was then used to adjust the positions of the 0–3 and 0–4 vibronic bands.

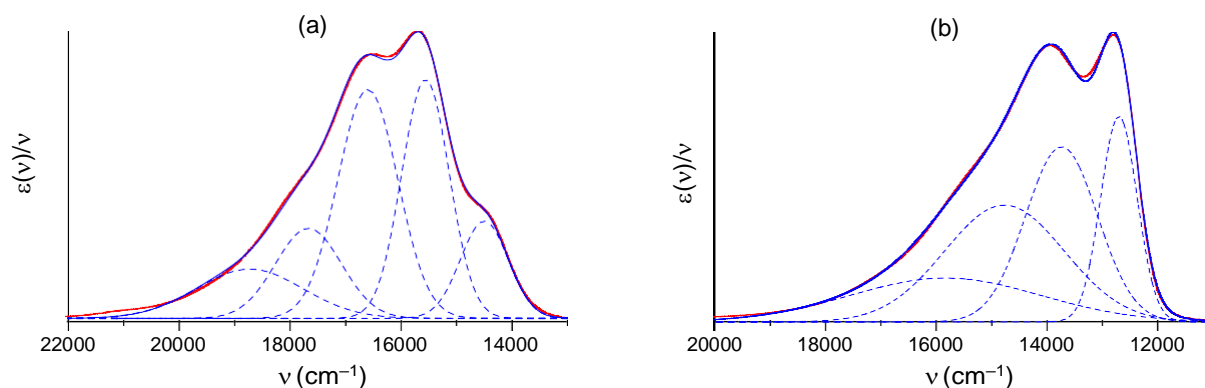


Fig. S26. Deconvolution of the absorption bands of dye **9** in *n*-hexane (a) and ethanol (b); experimental spectra are shown as red lines, deconvolution bands as blue solid integral curve and blue dash Gaussian components.

Table S1. Characteristics of the vibronic bands from the Gaussian deconvolution of the absorption bands of dye **9**.

	<i>n</i> -Hexane					Ethanol			
	0–0	0–1	0–2	0–3	0–4	0–0	0–1	0–2	0–3
$\nu_{\text{max}}, \text{cm}^{-1}$	14500	15560	16600	17670	18730	12702	13738	14770	15835
fwhm, cm^{-1}	1012	1017	1274	1402	2253	778	1532	2548	4048

On the absorption strength of various acceptor groups

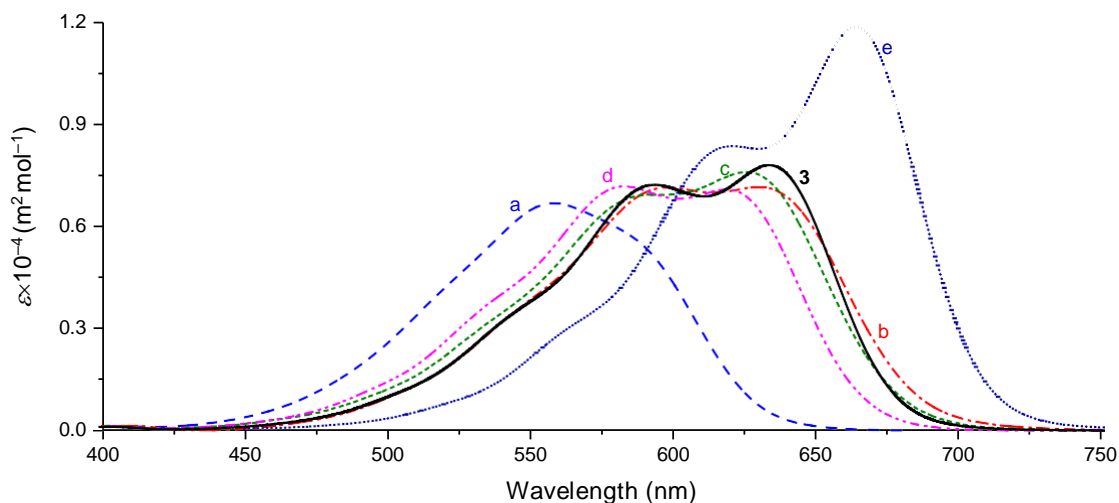


Fig. S27. Absorption spectra of dye **3** and its analogues with other electron-acceptor groups in toluene.

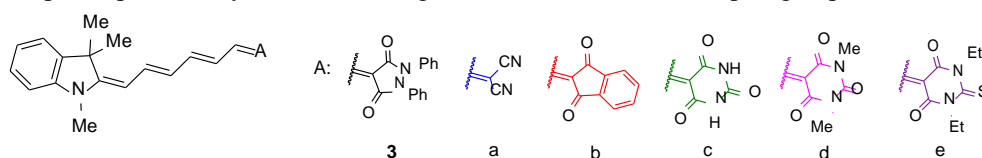


Table S2. The pK_a values* of the CH-acids in water

CH-acid						
pK_a (water)	4.5	11.0-11.4	7.2-7.4	4.68-4.8	4.01-4.09	2.6-3.8

* There are some discrepancies in estimation of pK_a of these compounds. The given values depends on the method of study (photo/colori/metric or titration, for example) and temperature. Therefore, the intervals of values are given in the table. Some references to the data sources are listed below.

- [S1] The Combined Chemical Dictionary, a part of the CHEMnetBASE service: <http://ccd.chemnetbase.com>
- [S2] Serjeant EP, Dempsey B. Ionisation constants of organic acids in aqueous solution. international union of pure and applied chemistry (IUPAC). IUPAC Chemical Data Series No. 23. Oxford–New York: Pergamon Press; 1979.
- [S3] Biggs AI. Thermodynamic ionization constants of barbituric acid and some of its derivatives. J Chem Soc 1596:2485–8. doi:10.1039/jr9560002485.
- [S4] Whitehouse MW, Leader JE. Biochemical properties of anti-inflammatory drugs — IX. Uncoupling of oxidative phosphorylation and inhibition of a thiol enzyme (papain) by some cyclic β -diones and ninhydrin. Biochem Pharmacol 1967;16:537–51. doi:10.1016/0006-2952(67)90101-3.

NB. One can see, comparing Fig. S25 and the data of Table S2 that the shape of the absorption band of indanedione based dye (line b) is rather close to those for the derivatives of barbituric acid or pyrazolidinedione, although the pK_a value of 1,3-indanedione is much greater than those of the latter. On the other hand, the analysis of solvatochromism, especially of band shapes (see refs. [41,45,50]), shows that in high-polarity solvents (DMF, ethanol) the acceptor strength of the 1,3-indanedione residues is indeed lesser than that of the 1,3-dimethylbarbituric residue is.

Some comments about fluorescent lifetimes and bandwidths

Since the studied dyes **1–9** have large extinction coefficients and in some cases very low fluorescence quantum yields, making the lifetimes sub-ps for many of the compounds, their spectral bands could be affected. Therefore, we calculated the theoretical radiative lifetimes of the studied dyes from their absorption spectra using the approximate formula:

$$\tau_r = \frac{1}{3.42 \cdot 10^8 \cdot n^2 \cdot \epsilon(\nu) \cdot \nu}$$

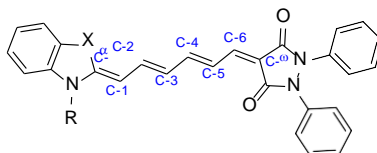
Here n , refractive index of medium; ν , position of the absorption maximum in wavenumbers [cm^{-1}]; ϵ , absorption coefficient.

It has been found that the minimal lifetimes are ca. 100 fs (dyes **1–3** in *n*-hexane). This is equivalent to an additional broadening of the spectral band by 60 cm^{-1} by *fwhm*. Used in this paper parameter σ , the deviations from the band gravity centre, is roughly equal to half of the *fwhm*. So, this effect would have increased the σ value by 30 cm^{-1} at most. For merocyanines **1–3** in *n*-hexane, the σ values exceed 1200 cm^{-1} . Therefore, this effect would not have a significant impact on the bandwidth.

Additional details from quantum chemical calculations

Cartesian atomic coordinates (in Å) for the optimized ground-state geometries of dyes **1–9**, **15–22** PCM_{solvent}/DFT-B3LYP/6-31G(d,p) calculations are given in a separate ZIP-archive as XYZ-files. The files are named as follows: **dye-solvent.xyz**.

Table S3. PCM_{solvent}/(TD)DFT-B3LYP/6-31G(d,p) calculated NBO atomic charges on the polymethine chain of molecules **1–9**.



Dye	Solvent (PCM)	State	NBO atomic charge								$\Sigma q_i $	Σq_i	Δq		
			C- α	C-1	C-2	C-3	C-4	C-5	C-6	C- ω					
1	n-Hexane	S ₀	0.308	-0.099	0.151						-0.296	0.854	0.064		
		S ₁ ^{FC}	0.192	-0.089	-0.001							-0.380	0.662	-0.278	-0.342
	DCM	S ₀	0.323	-0.104	0.153							-0.309	0.889	0.063	
		S ₁ ^{FC}	0.211	-0.002	0.020							-0.233	0.466	-0.004	-0.067
	EtOH	S ₀	0.326	-0.105	0.152							-0.312	0.895	0.061	
		S ₁ ^{FC}	0.214	-0.004	0.021							-0.234	0.473	-0.003	-0.064
2	n-Hexane	S ₀	0.287	-0.110	0.081	-0.035	0.145					-0.287	0.945	0.081	
		S ₁ ^{FC}	0.201	-0.100	-0.027	-0.054	0.039					-0.391	0.812	-0.332	-0.413
	DCM	S ₀	0.306	-0.109	0.097	-0.051	0.143					-0.305	1.011	0.081	
		S ₁ ^{FC}	0.223	-0.025	0.000	0.023	0.049					-0.251	0.571	0.019	-0.062
	EtOH	S ₀	0.311	-0.107	0.101	-0.054	0.142					-0.309	1.024	0.084	
		S ₁ ^{FC}	0.228	-0.027	0.005	0.018	0.049					-0.256	0.583	0.017	-0.067
3	n-Hexane	S ₀	0.276	-0.110	0.061	-0.045	0.073	-0.025	0.145			-0.282	1.017	0.093	
		S ₁ ^{FC}	0.214	-0.029	-0.024	0.029	-0.010	0.035	0.062			-0.248	0.651	0.029	-0.064
	DCM	S ₀	0.297	-0.107	0.08	-0.054	0.086	-0.045	0.14			-0.301	1.110	0.096	
		S ₁ ^{FC}	0.234	-0.035	0.002	0.014	0.012	0.014	0.066			-0.259	0.636	0.048	-0.048
	EtOH	S ₀	0.302	-0.105	0.086	-0.055	0.089	-0.05	0.138			-0.307	1.132	0.098	
		S ₁ ^{FC}	0.239	-0.036	0.009	0.011	0.017	0.009	0.065			-0.262	0.648	0.052	-0.046
4	n-Hexane	S ₀	0.475	-0.128	0.14							-0.320	1.063	0.167	
		S ₁ ^{FC}	0.375	-0.109	-0.009							-0.377	0.87	-0.120	-0.287
	DCM	S ₀	0.487	-0.128	0.145							-0.333	1.093	0.171	
		S ₁ ^{FC}	0.393	-0.004	0.008							-0.219	0.624	0.178	0.007
	EtOH	S ₀	0.490	-0.128	0.143							-0.336	1.097	0.169	
		S ₁ ^{FC}	0.385	-0.109	-0.033							-0.368	0.895	-0.125	-0.294

Dye	Solvent (PCM)	State	NBO atomic charge								$\Sigma q_i $	Σq_i	Δq	
			C- α	C-1	C-2	C-3	C-4	C-5	C-6	C- ω				
5	n-Hexane	S ₀	0.462	-0.144	0.089	-0.054	0.135				-0.309	1.193	0.179	
		S ₁ ^{FC}	0.397	-0.047	-0.002	0.032	0.042				-0.241	0.761	0.181	0.002
	DCM	S ₀	0.479	-0.134	0.099	-0.069	0.124				-0.328	1.233	0.171	
		S ₁ ^{FC}	0.408	-0.042	0.005	0.023	0.032				-0.246	0.756	0.180	0.009
	EtOH	S ₀	0.483	-0.130	0.101	-0.072	0.120				-0.332	1.238	0.170	
		S ₁ ^{FC}	0.405	-0.043	0.005	0.019	0.033				-0.250	0.755	0.169	-0.001
6	n-Hexane	S ₀	0.456	-0.145	0.073	-0.066	0.070	-0.043	0.134		-0.301	1.288	0.178	
		S ₁ ^{FC}	0.406	-0.068	0.001	0.008	0.000	0.024	0.060		-0.253	0.82	0.178	0
	DCM	S ₀	0.475	-0.131	0.089	-0.072	0.077	-0.063	0.121		-0.324	1.352	0.172	
		S ₁ ^{FC}	0.420	-0.061	0.014	0.001	0.007	0.008	0.050		-0.263	0.824	0.176	0.004
	EtOH	S ₀	0.479	-0.125	0.092	-0.072	0.076	-0.067	0.115		-0.329	1.355	0.169	
		S ₁ ^{FC}	0.417	-0.061	0.013	0.001	0.009	0.003	0.053		-0.265	0.822	0.170	0.001
7	n-Hexane	S ₀	0.260	-0.063	0.146						-0.28	0.749	0.063	
		S ₁ ^{FC}	0.206	-0.107	0.098						-0.396	0.807	-0.199	-0.262
	DCM	S ₀	0.270	-0.070	0.148						-0.293	0.781	0.055	
		S ₁ ^{FC}	0.212	-0.005	0.087						-0.25	0.554	0.044	-0.011
	EtOH	S ₀	0.272	-0.072	0.148						-0.296	0.788	0.052	
		S ₁ ^{FC}	0.213	-0.007	0.088						-0.253	0.561	0.041	-0.011
8	n-Hexane	S ₀	0.238	-0.058	0.075	-0.014	0.142				-0.276	0.803	0.107	
		S ₁ ^{FC}	0.189	0.005	0.020	0.032	0.085				-0.248	0.579	0.083	-0.024
	DCM	S ₀	0.251	-0.063	0.090	-0.031	0.142				-0.292	0.869	0.097	
		S ₁ ^{FC}	0.199	0.001	0.034	0.017	0.097				-0.261	0.609	0.087	-0.01
	EtOH	S ₀	0.254	-0.065	0.093	-0.035	0.142				-0.296	0.885	0.093	
		S ₁ ^{FC}	0.202	0.000	0.039	0.014	0.097				-0.262	0.614	0.09	-0.003
9	n-Hexane	S ₀	0.228	-0.056	0.055	-0.023	0.068	-0.013	0.144		-0.273	0.860	0.130	
		S ₁ ^{FC}	0.182	0.009	-0.002	0.028	-0.014	0.026	0.09		-0.254	0.605	0.065	-0.065
	DCM	S ₀	0.240	-0.059	0.072	-0.032	0.082	-0.032	0.143		-0.291	0.951	0.123	
		S ₁ ^{FC}	0.193	0.005	0.017	0.019	0.031	0.01	0.083		-0.264	0.622	0.094	-0.029
	EtOH	S ₀	0.244	-0.060	0.077	-0.033	0.086	-0.036	0.142		-0.295	0.973	0.125	
		S ₁ ^{FC}	0.197	0.002	0.023	0.016	0.036	0.005	0.093		-0.268	0.640	0.104	-0.021

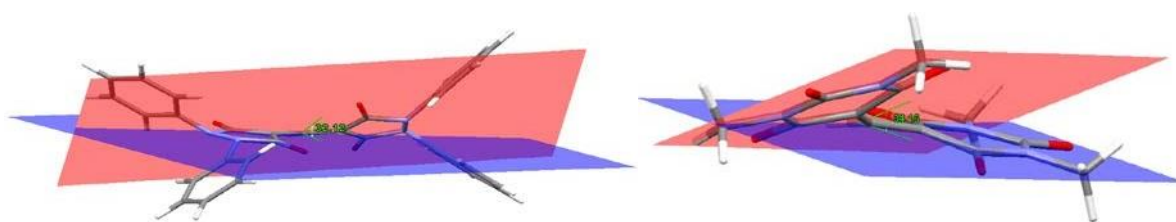


Fig. S28. The angles between the mean planes of the terminal heterocycles of anions **17** and **18** (after their PCM_{CH₂Cl₂}/DFT/B3LYP/6-31G(d,p) geometry optimization) were measured using the “Mercury” program (from Cambridge Crystallographic Data Centre).

Selected molecular orbitals (HOMO-1, HOMO, and LUMO) of merocyanines 2–9 and 19–22

(PCM_{DCM}/DFT/B3LYP/6-31G(d,p), contour value is 0.03 bohr^{-3/2})

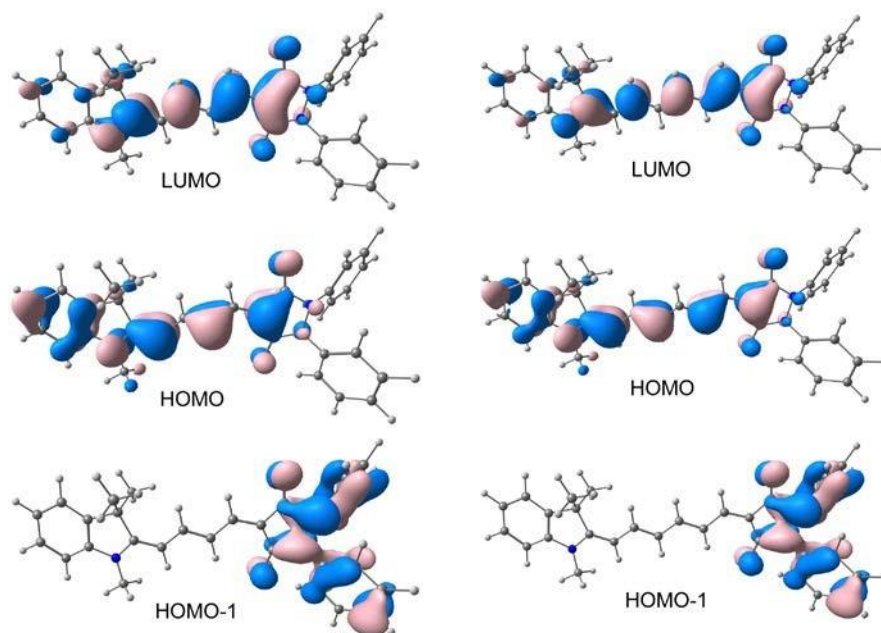


Fig. S29. Molecular orbitals of dyes 2 and 3.

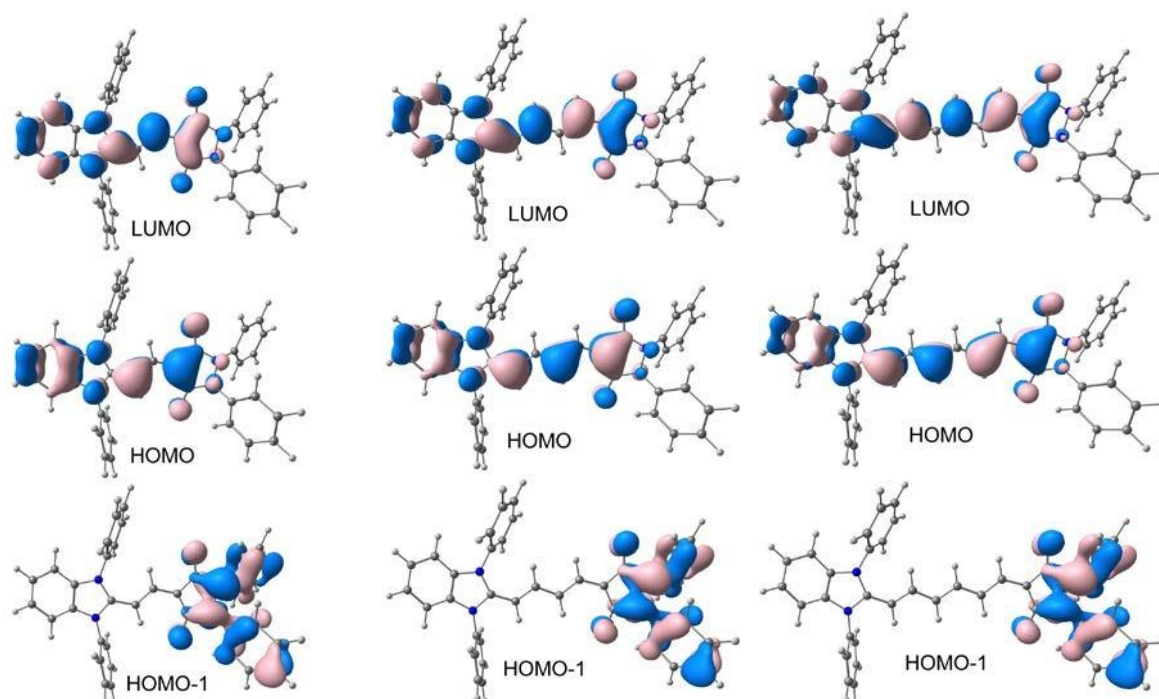


Fig. S30. Molecular orbitals of dyes 4–6.

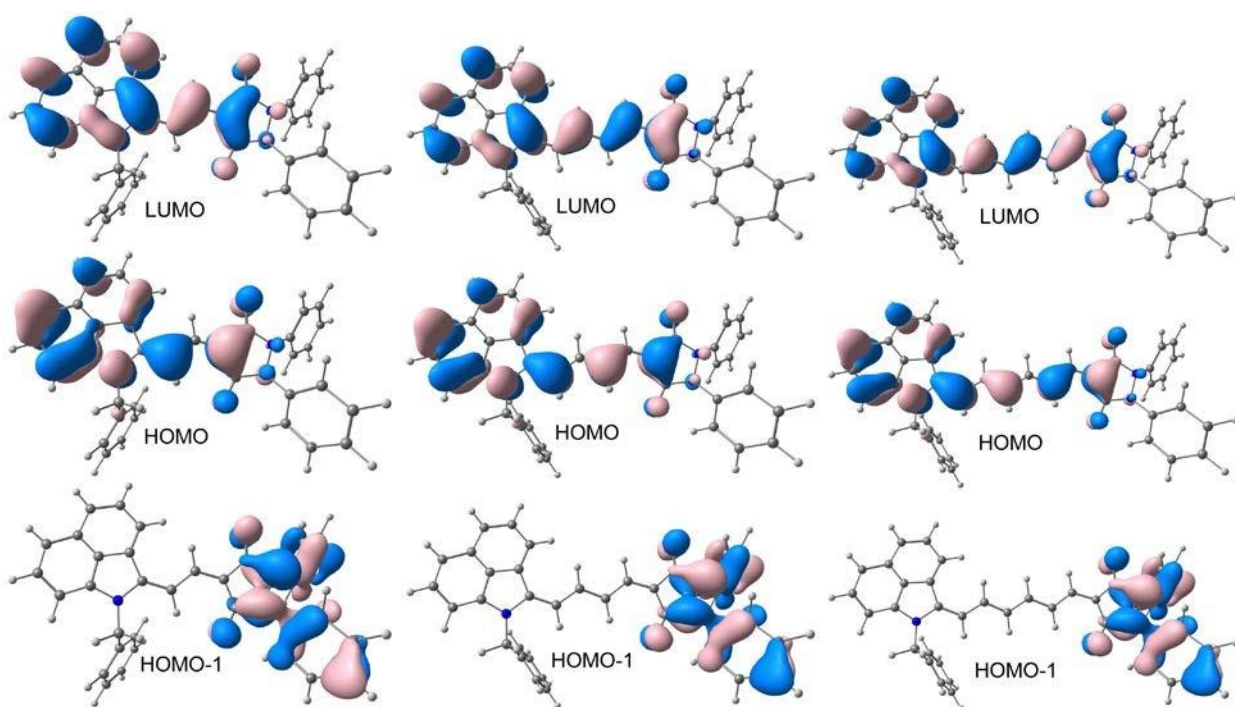


Fig. S31. Molecular orbitals of dyes 7–9.

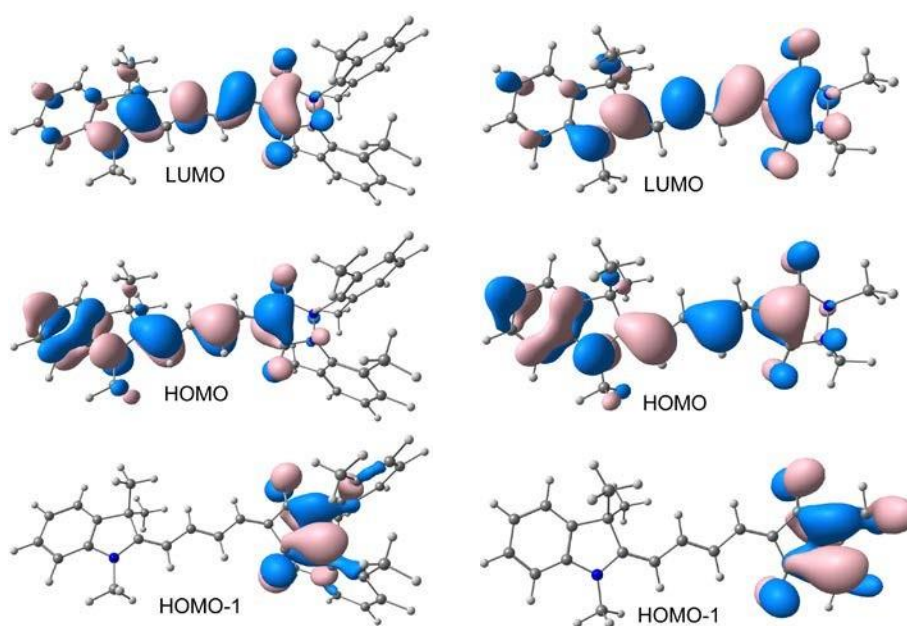


Fig. S32. Molecular orbitals of dyes 19 and 20.

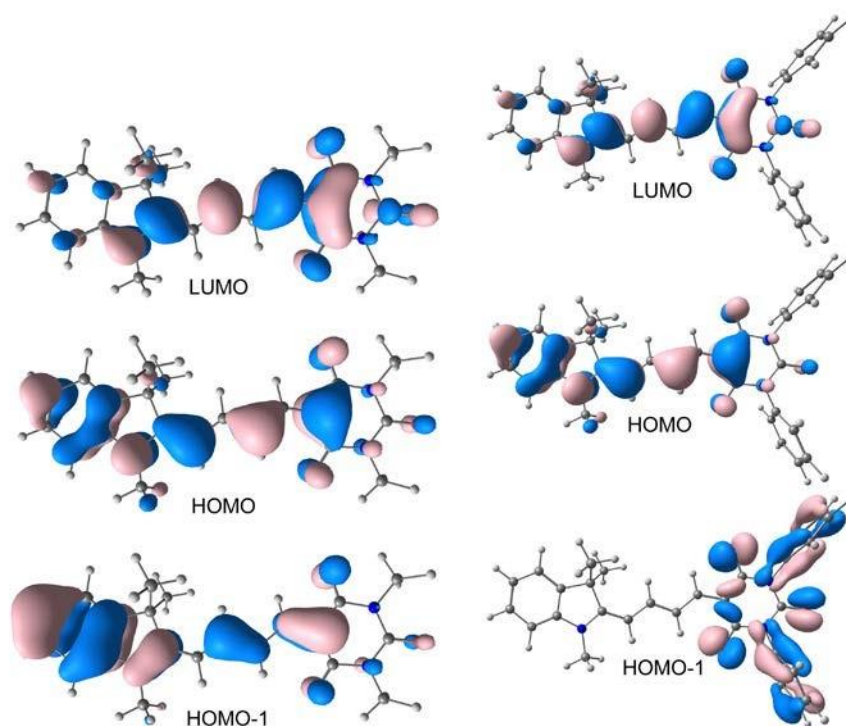


Fig. S33. Molecular orbitals of dyes **21** and **22**.

Selected data from CC2/def2-TZVP calculation of dye 2

```

=====+
| sym | multi | state |      CC2 excitation energies   | ||T1|| | ||T2|| |
| | | | +-----+-----+-----+
| | | | Hartree | eV | cm-1 | % | % |
=====+
| a | 1 | 1 | 0.0973228 | 2.64829 | 21359.895 | 88.83 | 11.17 |
| a | 1 | 2 | 0.0987532 | 2.68721 | 21673.819 | 90.47 | 9.53 |
| a | 1 | 3 | 0.1245045 | 3.38794 | 27325.570 | 89.25 | 10.75 |
=====+

```

```

=====+
| type: RE0          symmetry: a      state: 1 |
+-----+-----+-----+
| occ. orb. index spin | vir. orb. index spin | coeff/|amp|   % |
=====+
| 121 a   121   | 123 a   123   | 0.78861   62.2 |
| 115 a   115   | 123 a   123   | 0.41024   16.8 |
| 122 a   122   | 123 a   123   | -0.39069   15.3 |
| 118 a   118   | 123 a   123   | 0.11168    1.2 |
=====+

```

```

=====+
| type: RE0          symmetry: a      state: 2 |
+-----+-----+-----+
| occ. orb. index spin | vir. orb. index spin | coeff/|amp|   % |
=====+
| 122 a   122   | 123 a   123   | 0.89910   80.8 |
| 121 a   121   | 123 a   123   | 0.32211   10.4 |
| 115 a   115   | 123 a   123   | 0.16245    2.6 |
| 117 a   117   | 125 a   125   | -0.08424    0.7 |
| 111 a   111   | 123 a   123   | -0.06055    0.4 |
| 117 a   117   | 134 a   134   | 0.06030    0.4 |
=====+

```

ONE-PHOTON ABSORPTION STRENGTHS

Transition 1

frequency : 0.0973228428 a.u. 2.64829 e.V. 21359.9 rcm
oscillator strength (length gauge) : 0.30654573

Transition 2

frequency : 0.0987531850 a.u. 2.68721 e.V. 21673.8 rcm
oscillator strength (length gauge) : 1.79063129