

# Effect of bulky substituents in the donor and acceptor terminal groups on solvatochromism of Brooker's merocyanine

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**Cartesian atomic coordinates** (in Å) for the optimized ground-state geometries of dyes BM, BM1, BM2, and BM3 from (PCM-)DFT/B3LYP/6-31G(d,p) calculations are given in a separate ZIP-archive as XYZ files. The files are named as follows: **dye code-medium.xyz** where medium is either vacuum or solvent.

### Additional details about the UV-Vis and fluorescence spectral measurements and data treatment.

Solutions of new dyes BM2 and BM3 were confirmed to obey the Lambert–Beer law in the concentration range  $1 \times 10^{-6}$ – $8 \times 10^{-5}$  M in DCM, pyridine, DMF, acetonitrile and methanol. For BM3 the same study was performed in toluene up to concentration  $2.5 \times 10^{-5}$  M. Dye BM2 has very low solubility in toluene. It was heated for 5 min at 80 °C with the solvent and filtered off to give the solution with the absorbance of nearly 0.08 in maximum at 588 nm. However, comparison of its absorption spectrum with the spectra of dyes BM1 and BM3 in toluene gave no evidence of its aggregation in this solvent.

All values given in wavenumber are rounded up to  $10 \text{ cm}^{-1}$ .

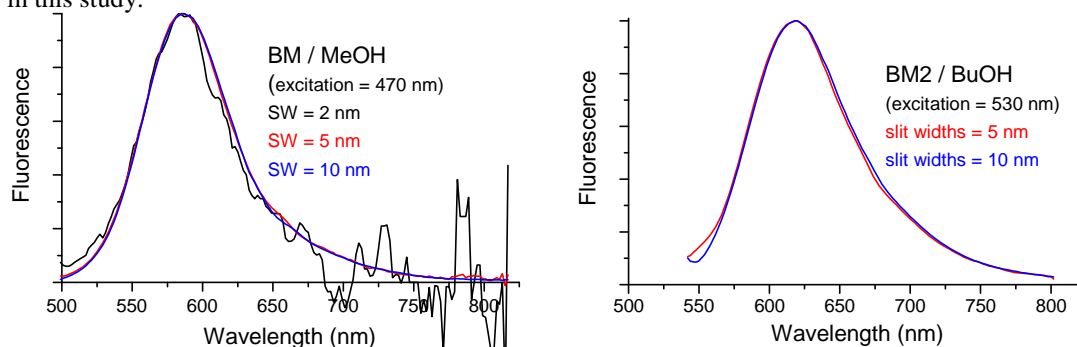
The fluorescence spectra of the stilbazolium merocyanines in DMF and methanol were measured with the same instrumental settings as that of reper dyes (Rhodamine 6G and Nile blue). However, in other solvents, to increase the signal intensity, the slit widths of the spectrofluorimeter were increased to 10 nm, which was not possible because of overswing in the case of highly fluorescent reper compounds. Therefore, the fluorescence quantum yields in other solvents were measured relative to that in DMF and methanol (the fluorescence in these solvents was registered with the slit widths of 10 nm as well). Considering this and very weak fluorescence of the studied dyes (which increase the possible error due to stray signals), we can roughly evaluate the relative error of the derived  $\Phi_f$  values as  $\pm 30\%$ .

The fluorescence quantum yields were calculated using the following equation:

$$\Phi = \Phi_r \frac{S_f}{S_r} \frac{(1-10^{-A_r})}{(1-10^{-A})} \left( \frac{n_D}{n_r} \right)^2 \left( \frac{D_r}{D} \right)$$

where  $S_f$  is the intensity (area) of the fluorescence band,  $A$  is the absorbance at the excitation wavelength,  $n_D$  is the refractive index of a solvent, and the index 'r' denotes the parameters relating to a reper dye.

We compared the fluorescence bands of dyes BM and BM2 in polar solvents, in which they had greater fluorescence quantum yields, at slit widths of 5 nm and 10 nm (at SW of 2 nm fluorescence was too weak even in methanol; see figures below — they are also included in Supplementary). It was found that their maxima were unaffected at greater slit widths but their bandwidth increased slightly. That was an additional reason why we did not discuss the fluorescence bandwidths in this study.



**Fig. S1.** Fluorescence spectra of dyes BM and BM2 at different slit width.

**Table S1.** Some characteristics of the solvents used in the study.

Solvent	$\epsilon_D$	$n_D$	$E_T^N$	$\alpha$	$\beta$	$\pi^*$	SPP	$\eta$ (cP)
Toluene	2.38	1.497	0.099	0.00	0.11	0.54	0.655	0.59
DCM	8.93	1.424	0.309	0.13	0.10	0.82	0.875	0.44
Pyridine	12.4	1.510	0.302	0.00	0.64	0.87	0.930	0.95
MeCN	37.5	1.344	0.460	0.19	0.40	0.75	0.895	0.38
DMF	36.7	1.431	0.386	0.00	0.69	0.88	0.954	0.92
MeOH	32.7	1.329	0.762	0.98	0.66	0.60	0.857	0.59
H <sub>2</sub> O	80.1	1.333	1.000	1.17	0.47	1.09	0.962	1.00
EtOAc	6.02	1.372	0.228	0.00	0.45	0.55	0.795	0.45
PC	64.9	1.421	0.472	0.00	0.40	0.83	0.930	2.50
<i>n</i> -BuOH	17.5	1.399	0.586	0.84	0.84	0.47	0.837	2.98
EtOH	24.6	1.361	0.654	0.86	0.75	0.54	0.853	1.10
1-Br-Naph	5.06	1.658						4.98

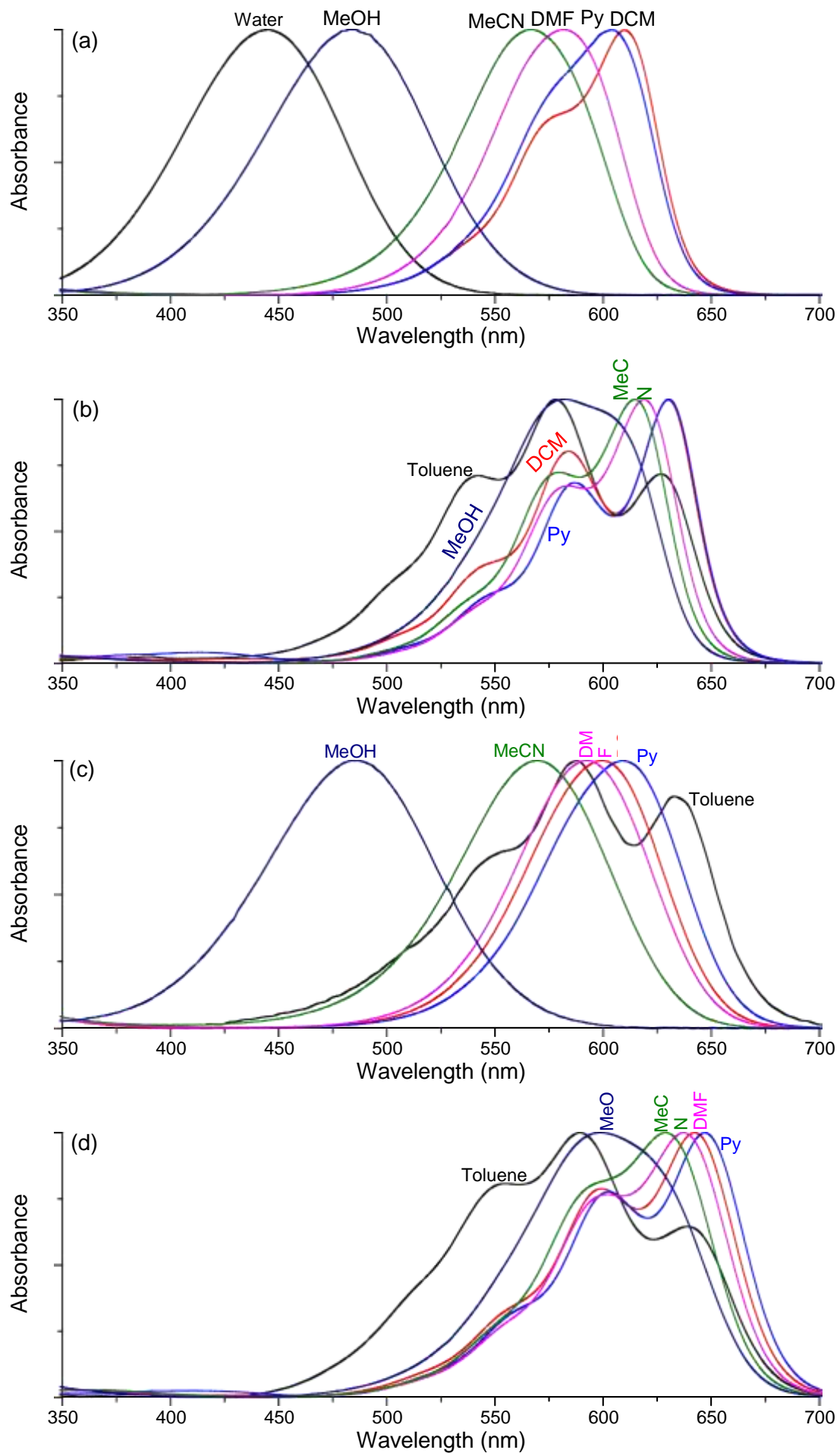
Here:  $\epsilon_D$ , relative permittivity (dielectric constant);  $n_D$ , refractive index;  $E_T^N$ , normalized Dimroth–Reichardt solvent polarity parameter;  $\alpha$ ,  $\beta$ ,  $\pi^*$ , Kamlet–Taft solvent parameters, which measure the hydrogen bond donor ( $\alpha$ ), hydrogen bond acceptor ( $\beta$ ), and dipolarity/polarizability ( $\pi^*$ ) properties of solvents; SPP, empirical parameter of solvent dipolarity/polarizability, based on the  $\pi \rightarrow \pi^*$ -absorption of substituted 7-nitrofluorenes (Catalán);  $\eta$ , viscosity. The parameters are given for 20 °C or 25 °C (in case if the parameter at 20 °C was not found).

Data for Table 1 were taken from:

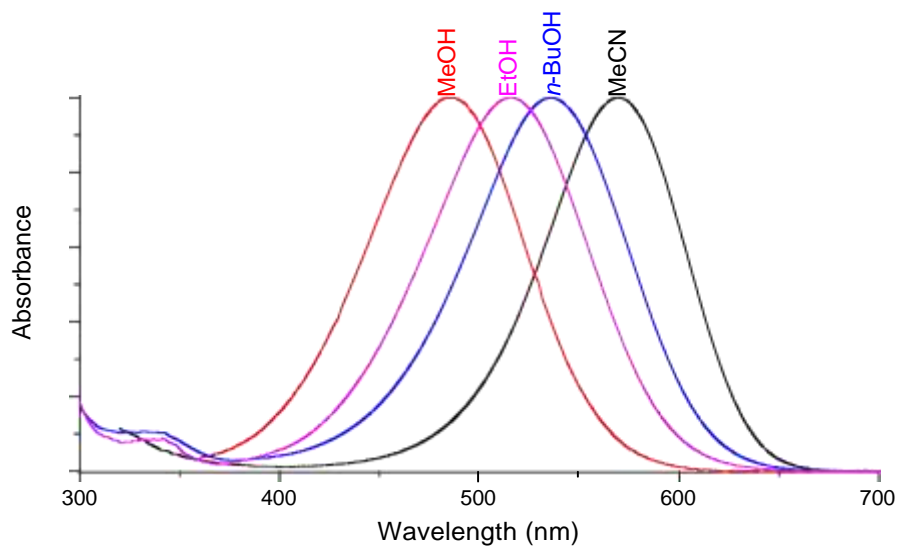
[S1] C. Reichardt and T. Welton, *Solvents and Solvent Effects in Organic Chemistry (4th edn)*, Wiley-VCH, Weinheim, 2010.

[S2] M. J. Kamlet, J.-L. M. Abboud, M. H. Abraham, R. W. Taft, *J. Org. Chem.*, 1983, **48**, 2877. (Kamlet–Taft solvent parameters  $\alpha$ ,  $\beta$ ,  $\pi^*$ ).

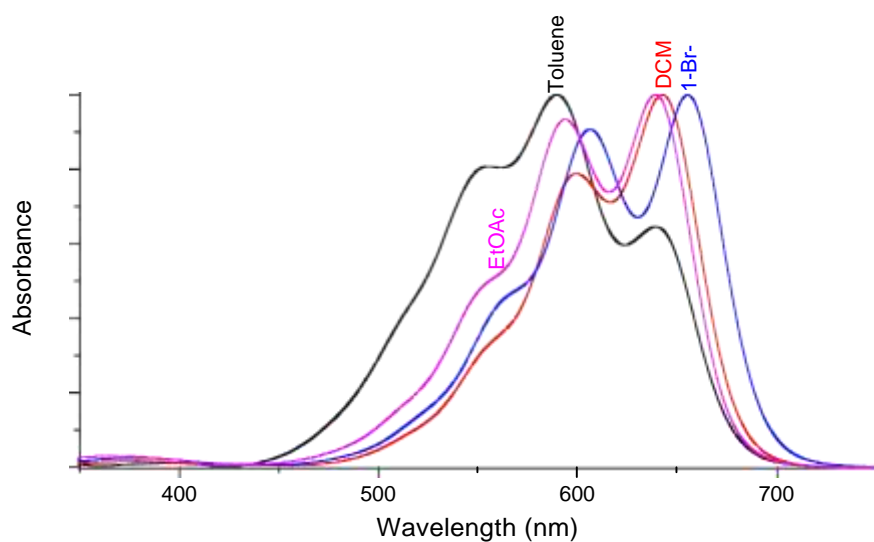
[S3] *Pure Organic Liquids C10: Datasheet from Landolt-Börnstein - Group IV Physical Chemistry*, Volume 18B: “Pure Organic Liquids” in SpringerMaterials: [https://dx.doi.org/10.1007/10639283\\_11](https://dx.doi.org/10.1007/10639283_11) (viscosity of 1-bromonaphthalene at 20 °C).



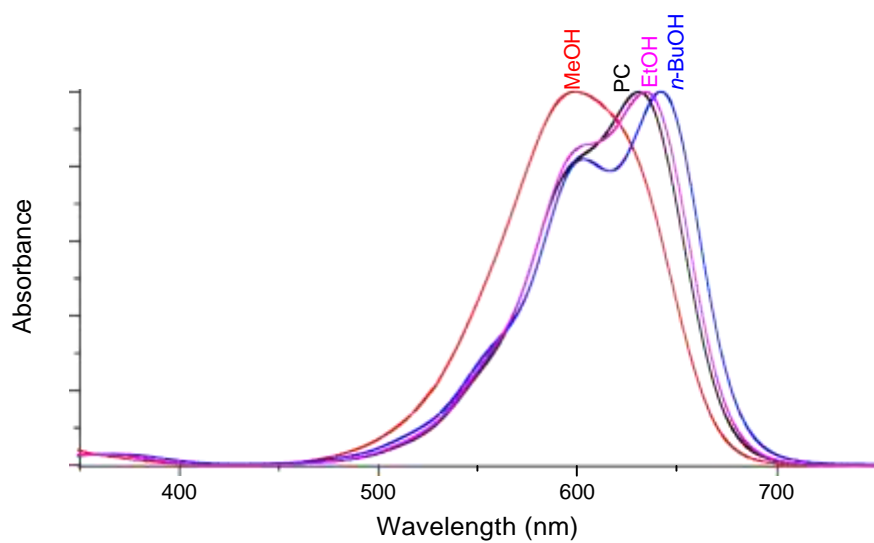
**Fig. S2** Normalized absorption spectra of dyes BM (a), BM1 (b), BM2 (c), and BM3 (d) in solvents of various polarity.



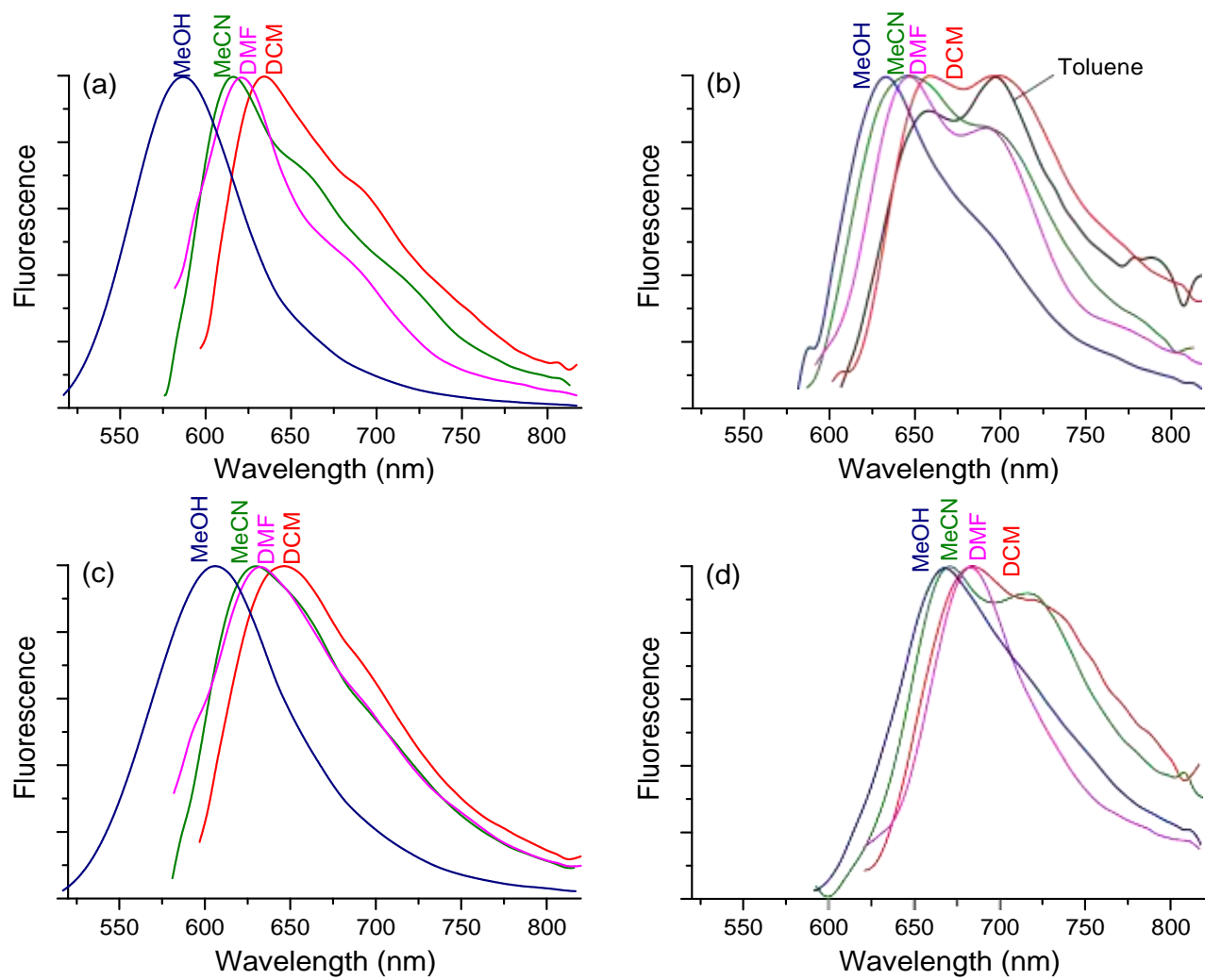
**Fig. S3** Normalized absorption spectra of dye BM2 in acetonitrile and alcohols.



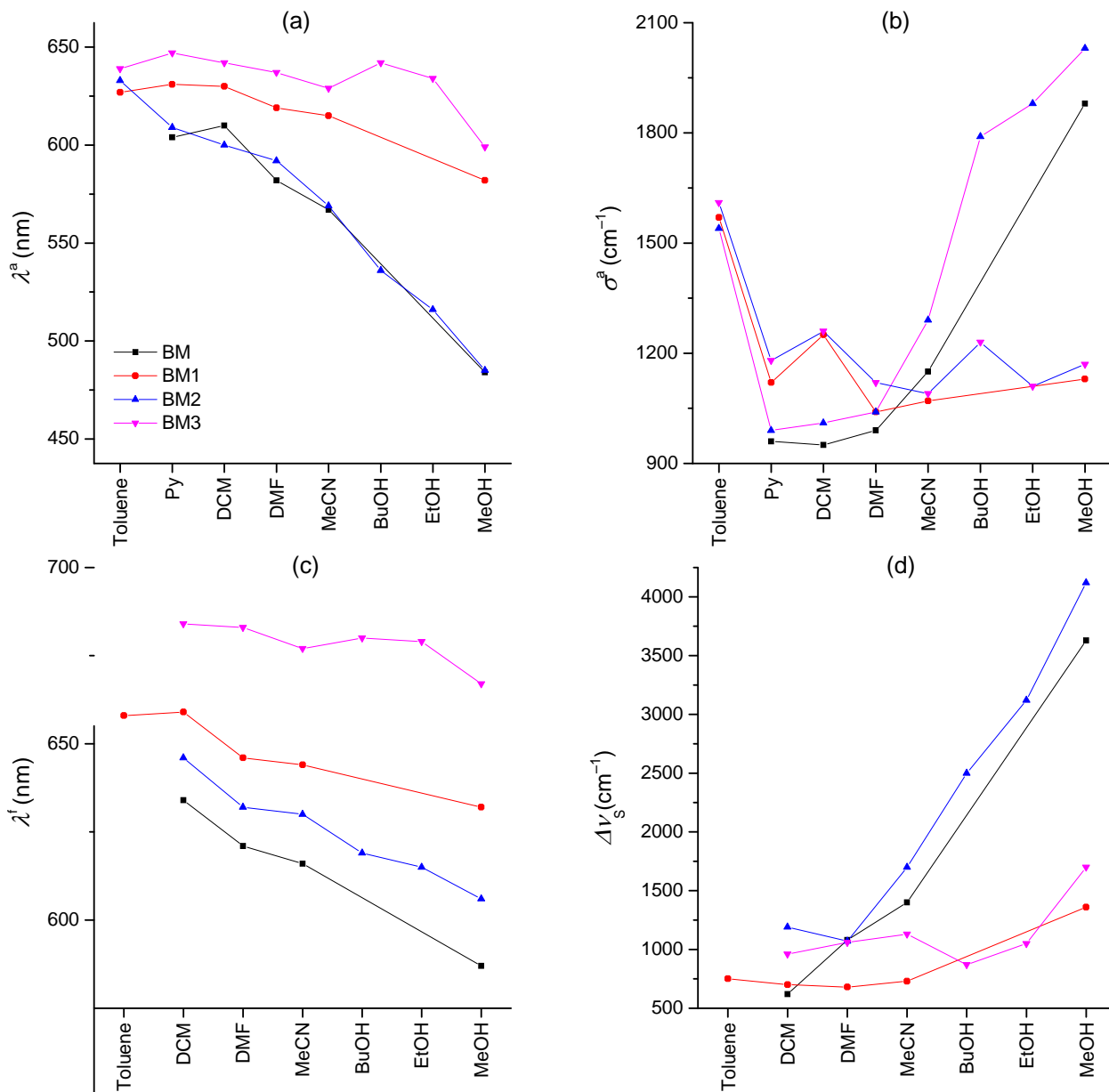
**Fig. S4** Normalized absorption spectra of dye BM3 in less-polarity solvents.



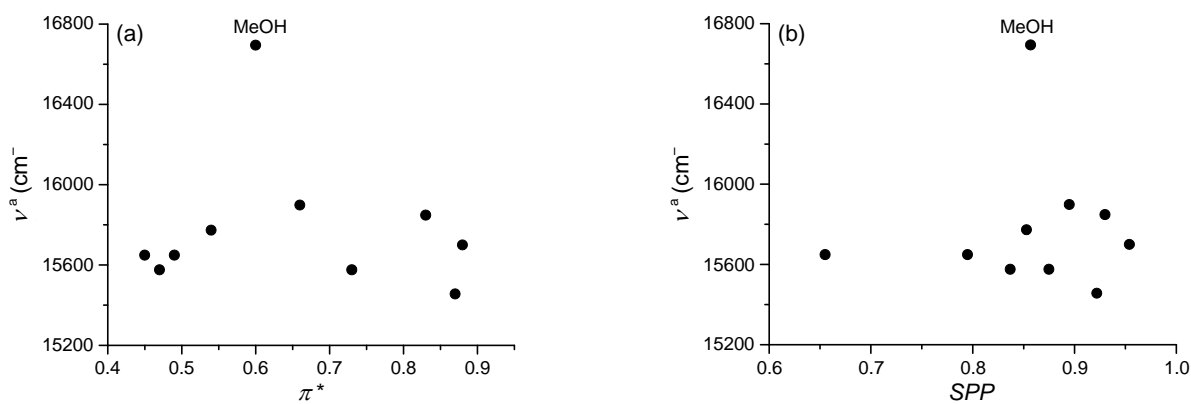
**Fig. S5** Normalized absorption spectra of dye BM3 in propylene carbonate (PC) and alcohols.



**Fig. S6** Normalized fluorescence spectra of dyes BM (a), BM1 (b), BM2 (c), and BM3 (d) in solvents of various polarity. The presented spectra are registered at slit widths of 10 nm.



**Fig. S7** Dependences of the absorption maxima (a), absorption bandwidths (b), fluorescence maxima (c), and Stokes shifts (d) on the solvent.



**Fig. S8** Dependence of the absorption maximum of dye BM3 on the empirical parameters of nonspecific solvent polarity/polarizability by Kamlet-Taft (a) and Catalán (b).

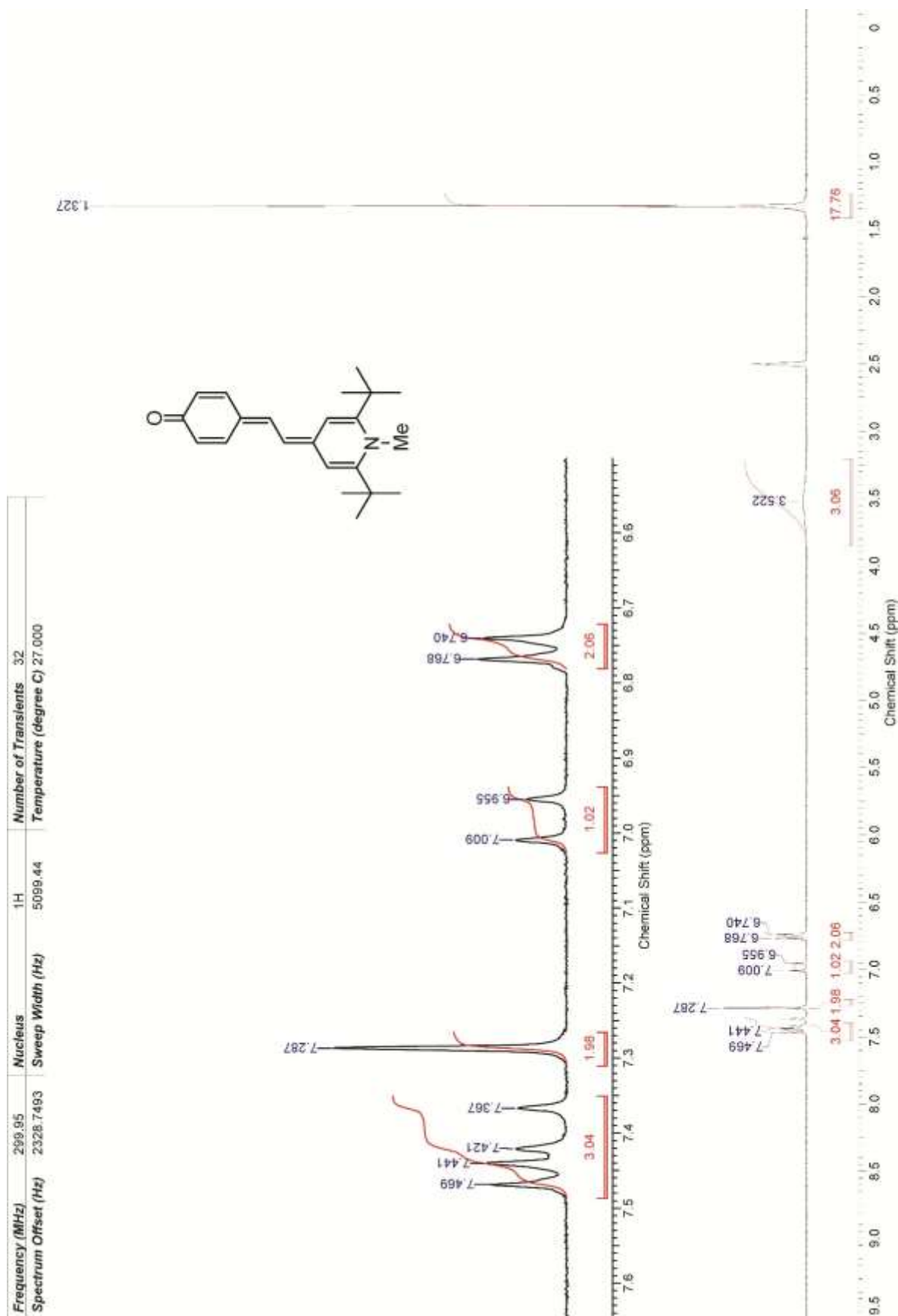


Fig. S9 <sup>1</sup>H NMR spectrum of compound BM2 in [D<sub>6</sub>]DMSO.



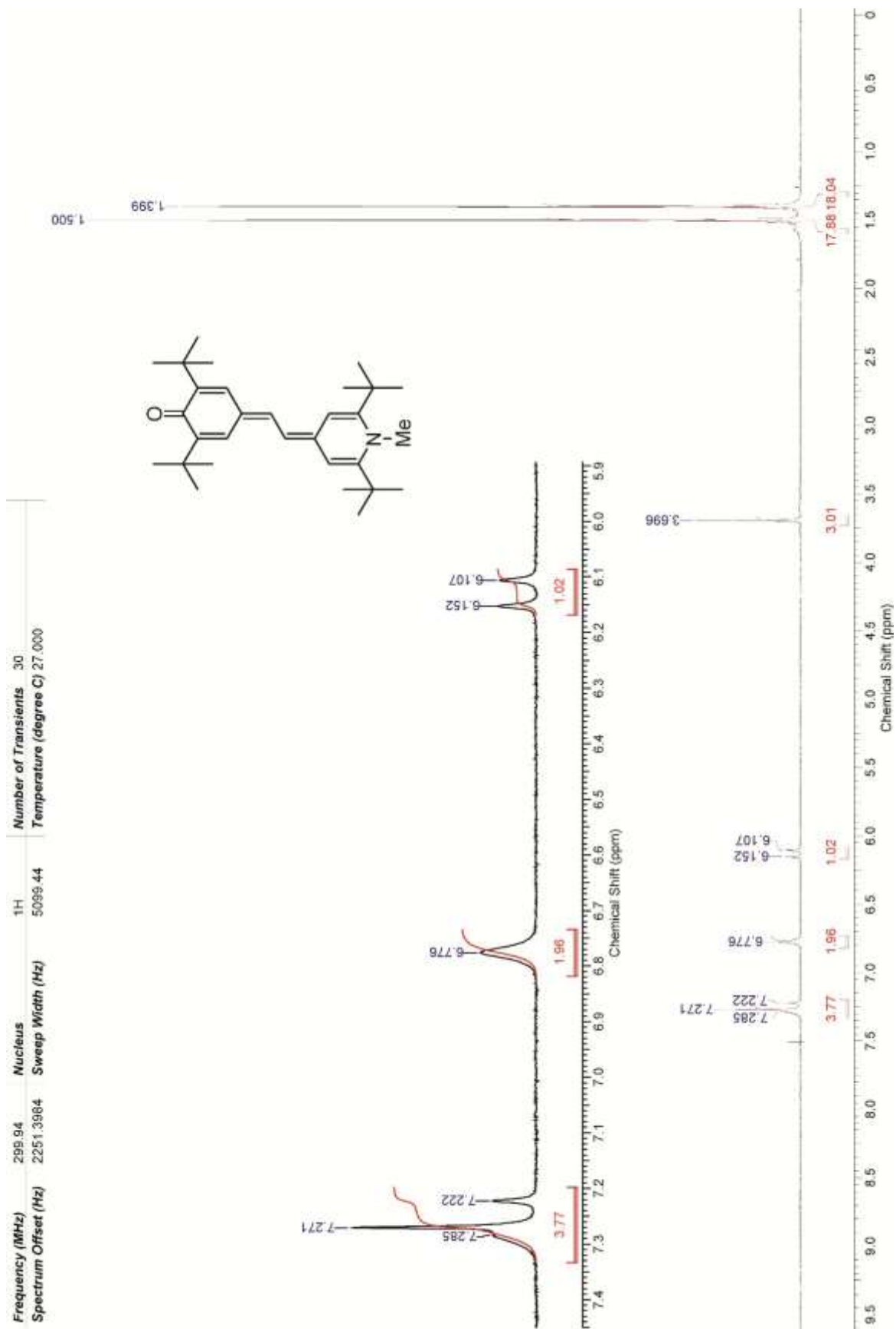
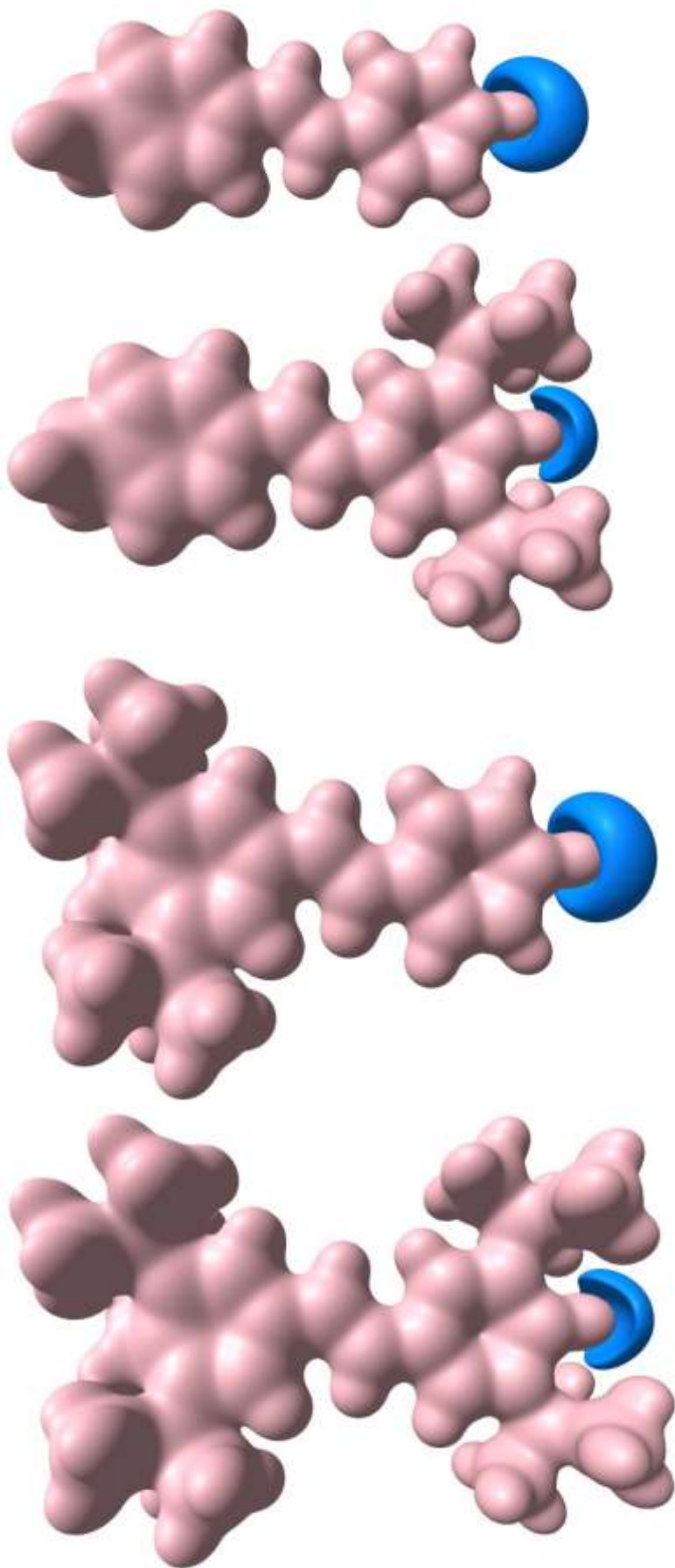


Fig. S10  $^1\text{H}$  NMR spectrum of compound BM3 in  $\text{CDCl}_3$ .



**Fig. S11** The electrostatic potential maps of dyes BM, BM1, BM2, and BM3 (from top to bottom). (PCM<sub>Toluene</sub>/DFT/B3LYP/6-31G(d,p), contour value is 0.1 bohr<sup>-3/2</sup>)