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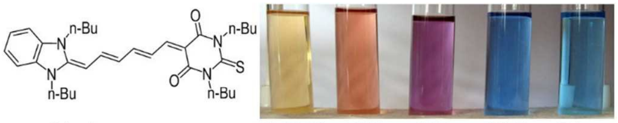
Scope of negative solvatochromism and solvatofluorochromism of merocyanines



Solvent	CF_3CH_2OH	EtOH	DMF	CH_2Cl_2	Toluene
Fluor. quantum yield (%)	2.3	7.4	12.7	26.6	73.0

Can negatively solvatochromic merocyanines retain their generic characteristic in the full range of solvent polarities including low-polar alkanes? To find the answer, the solvatochromism of a vinylogous series of tailored highly dipolar merocyanines was thoroughly investigated both experimentally and theoretically.

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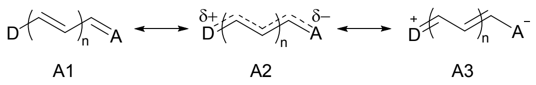
A vinylogous series of highly dipolar merocyanines was designed to study their solvatochromism in a wide range of solvents including low-polar alkanes. It has been revealed that the lower vinylogues indeed have negative solvatochromism in the full range of solvent polarities starting from n-hexane, while the hexamethinemerocyanine exhibits reversed solvatochromism. With the extreme ranges of solvatochromism, the studied dyes possess a 5-7 times weaker solvatofluorochromism, which can be rationalized via their decreased dipolarity in the fluorescent state. They also demonstrate an inverse dependence of their fluorescent quantum yields on solvent polarity and have near-record Stoke's shifts in high-polar media. The experimental data are supplemented by the results of DFT quantum chemical analysis of dye electronic structures in both the ground and excited states with PCM solvent field simulation.

Introduction

Merocyanines – the donor-acceptor substituted neutral polymethine dyes – are most notable for their pronounced solvatochromism,[1-4] which stems from the peculiarities of their electronic structure. Having the so-called push-pull D−π−A chromophore, upon electronic excitation merocyanines undergo both charge resonance between the adjacent positions of the polymethine chain, in common with the symmetrical cationic or anionic cyanine dyes, and light induced charge transfer from donor to acceptor terminal group.[5,6] The relative contributions of these two possible responses depend upon the ground state electronic structure of a merocyanine molecule. To simplify depiction of the latter, the graphical scheme of superposition of the three limiting structures was proposed by Dähne.[5]



These structures correspond to the neutral polyene (A1), the ideal polymethine (A2), and the dipolar polyene (A3) – three fictitious states which can be achieved (as well as any intermediate one) depending on the donor-acceptor properties of D and A, the polymethine chain length, and the solvent polarity.

The π-electrons are appreciably localized in A1 and A3 and maximally delocalized in A2, what has been proven via determination of the solvent dependence of the specific polarizability of polymethines.[7] Besides, the A2 state along with a "symmetrical" π-electron distribution has maximum π-charges alternation between odd and even positions along the polymethine chain, which is not explicit within the given conventionalized scheme, prompting its abandoning now and then for the sake of the more meticulous multi-state model.[8] The long-wavelength $\pi\pi^*$-transition, which is $S_1^{FC} \leftarrow S_0$ mostly, is accompanied by an increase of the dipole moment for the A1-to-A2 structures and by its decrease for the A2-to-A3 structures due to the light induced intramolecular charge transfer.[5,6] But in the ideal state A2 the molecular dipole moment changes only slightly upon excitation, the latter results in the chromophore unique π-charges reversal or charge resonance according to Mulliken's nomenclature.[7] Since the long-wavelength electronic transition in the state A2 is accompanied by the least change of the chromophore π-bond orders, the vibronic interactions (VI) in it are weaker than in A1 or A3. This results in narrowing of the spectral bands and growing of their peak intensity (extinction) and favours the fluorescence quantum yield increase.[3] The most remarkable feature of the ideal polymethine state A2 is the least excitation energy to the first excited singlet state, which reveals itself in the long-wavelength shift of an absorption (and fluorescence) maximum comparative to A1 or A3. Probably, this only fact could vindicate an addition of the non-classical limiting structure.

The electronic structure of most of merocyanines falls into the interval A1–A2, i.e. they possess positive solvatochromism. Indeed, the sound charge separation, characteristic of the A2–A3 suite, is considered energetically unfavourable. Both, higher electron-donating ability of the donor group and electron-withdrawing ability of the acceptor group facilitate

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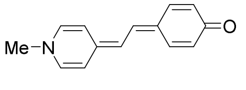
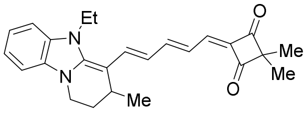
charge separation. Are these two factors sufficient to achieve the A2 or an even more dipolar state without some help from solvation, thus providing negative solvatochromism in the full range of solvent polarities? In the case of Brooker's merocyanine, which was reckoned negatively solvatochromic formerly, more thorough investigations of its spectral behaviour in low-polar solvents as well as quantum chemical calculations have revealed that actually its solvatochromism is reversed.[9] This result implies pivotal impact of solvation upon stabilization of merocyanine's dipolar structure, even in the case when many structural factors favour charge separation. Another noteworthy negatively solvatochromic merocyanine was used by Brooker as a solvent polarity indicator for his χ_B scale.[10] Because of its insolubility in low-polar solvents, toluene and 2,6-lutidine were the least polar solvents applied, the question of its absolute negative solvatochromism is abeyant.



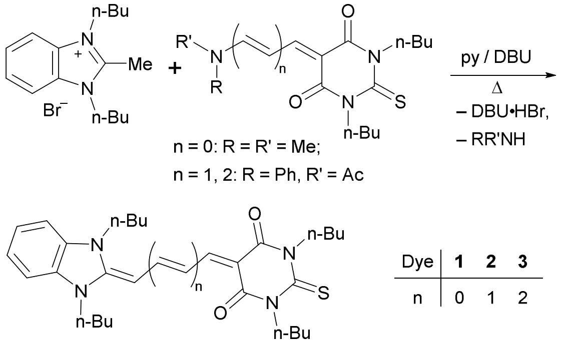
Brooker's merocyanine



Merocyanine of the χ_B scale

Solvatochromism and electronic structure of many series of merocyanines based on 1,3-diphenylbenzimidazole have been investigated in detail earlier (see rev. [3] and refs. therein). In most cases, when such inspection had not been prevented by the dyes' insolubility, it was observed that their "negative" solvatochromism was in fact reversed. Therefore, in pursuit for highly dipolar merocyanines, the 1,3-dibutylbenzimidazole terminus was chosen in the present work as a donor. First and foremost, its electron-donating ability is increased relative to the 1,3-diphenyl-substituted one. In addition, there was a fancy that n-butyl substituents would provide a fair solubility to the resulting merocyanines in low-polar media. The 1,3-dibutylthiobarbituric acid residue, one of the strongest electron-acceptor group,[11,12] was also believed of avail for both solubility and dipolarity.

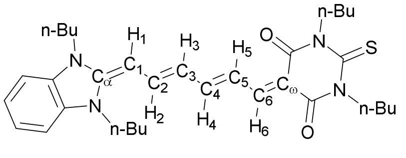
Experimental Section



Dye	1	2	3
n	0	1	2

Because of weakened acidity of the required quaternary heterocyclic salt, strong bases should be used in the cyanine condensation Merocyanines **1–3** were synthesized by heating equivalent amounts of 1,3-dibutyl-2-methyl-benzimidazolium bromide [13] and the corresponding hemicyanine [1,14] in pyridine for 10-30 min in the presence of a twofold excess of DBU (1,8-diazabicycloundec-7-ene). The reaction mixture was diluted with water and the resulting precipitate was filtered off, dried, and refined by column chromatography on neutral alumina-80 with chloroform as an eluent. After solvent removal under reduced pressure, the resulting product was crystallized from anhydrous ethanol. Special attention was paid to the purification of dye **3**. Its R_f value in chloroform is rather close to that of merocyanine **2**, which is among the major impurities in crude **3**, and all pursuits of a better chromatography system were of no avail. Due to the extreme solvatochromism of these dyes, spectral control is possible only in low-polar toluene – even in chloroform their long-wavelength absorption bands are very broad and overlap largely. However, in toluene dye **3** forms an aggregate whose absorption maximum (λ^{a}_{max}) well-nigh coincides with the λ^{a}_{max} of merocyanine **2**. Therefore, the purity of dye **3** was controlled by using synchronous luminescent spectroscopy technique (toluene, $\Delta\lambda$ = 30 nm).

Melting points were measured in an open capillary and were not corrected. n-Hexane, toluene, chloroform, dichloromethane (DCM), DMF, ethanol (96%), and other solvents used for study of solvatochromism of dyes **1–3** were refined according to the methods given in.[15] The UV/Vis absorption spectra were recorded with a spectrophotometer Shimadzu UV-3100. Solutions of merocyanines **1–3** were confirmed to obey the Lambert–Beer law in the concentration range of 1×10^{-6} – 5×10^{-5} M in DCM, DMF, and ethanol. For toluene as a solvent it holds true for dyes **1** and **2** but not for **3**. Because of limited solubility of the studied dyes in n-hexane, the corresponding analysis was not carried out in this solvent. However, no sign of aggregation in n-hexane was traced in the absorption spectra of vinylogue **1**. The fluorescence spectra were measured with a spectrofluorometer CM2203 ("Solar", Belarus, wavelength scale 220-900 nm). Solutions of merocyanines were not degassed since the fluorescent characteristics for degassed and non-degassed solutions were found to be identical. The fluorescence quantum yields (Φ_f) of merocyanine **1** were measured in relation to Coumarin 1 in ethanol (Φ_f = 73% [16]), of dye **2** – in relation to Rhodamine 6G in ethanol (Φ_f = 95% [17]), of dye **3** — in relation to Nile blue in methanol (Φ_f = 27% [18]). The optical densities of solutions for fluorescent measurements were kept below 0.1 to avoid inner filter effects. The values of Φ_f were corrected taking into account refractive indices of the solvents. ^{1}H NMR spectra were measured on the spectrometer Varian VXR-300 (299.943 MHz for H-atoms) in $CDCl_3$ or $(CD_3)_2SO$ with TMS as an internal standard. The polymethine chain atom labelling used in the discussion is shown below.



The long-wavelength absorption and fluorescence bands of merocyanines **1**–**3** were analysed by the method of moments which allows the quantitative characterization of their position and shape.[19] Three parameters gained by this way are discussed alongside with the band maxima (λ_{max}) and the molar extinctions (ε): M^{-1} is the centre of gravity of a band in the scale of wavenumbers ($M^{-1} = 10^7/\nu$, where ν is wavenumber); the value of σ characterizes the deviation of a spectral band from its gravity centre and is similar to the widely used full width at half maximum (FWHM); f is the oscillator strength of the long-wavelength absorption transition ($f = 4.317\times10^{-9} \int\varepsilon_\nu d\nu$). All the parameters relative to absorption are marked with an index 'a', those relative to fluorescence with an index 'f'. The moments of the absorption and fluorescence bands were determined accordingly in coordinates $I_a(\nu)/\nu$ and $I_f(\nu)/\nu^4$ (where I_f and I_a are intensities of absorption and fluorescence) in which the mirror symmetry rule is most rigorously obeyed.[19] The deviations by maxima (D^a_λ) of the absorption bands of merocyanines **1**–**3** were calculated using the spectral data of the corresponding cationic and anionic dyes. The Stokes shifts were calculated both by the band maxima (SS_λ) and by the band centres (SS_M).

Results and Discussion

Spectral characteristics of merocyanines **1**–**3** are collected in Table 1.

Merocyanine **1** was found to be extremely photosensitive; its absorption spectra changed dramatically even upon a short (some 20-30 seconds) exposure to the direct sunlight and within minutes under natural lighting in the lab (Figure 1).

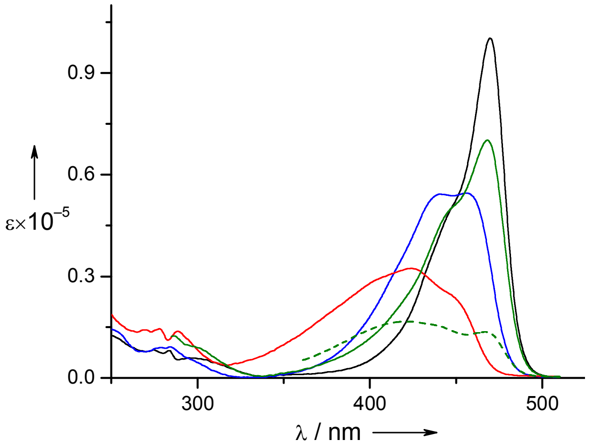
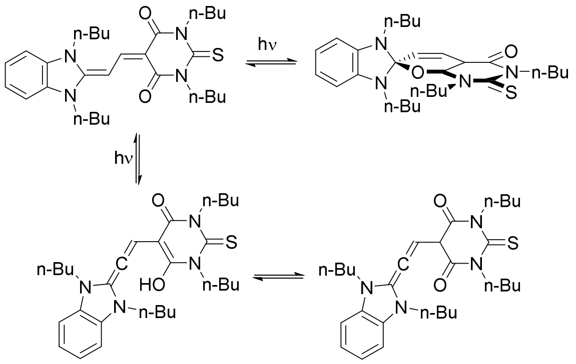


Figure 1. UV/Vis absorption spectra of dye **1** in n-hexane (black), toluene (olive), DCM (blue), and ethanol (red). Spectrum in toluene after exposure to sunlight is given as dash-line.

The photo-durability of merocyanines tends to decline with an increase of the electron-donating ability of a donor terminal group as well as with the polymethine-chain lengthening,[20] and dyes **2** and **3** were found even less stable under irradiation than the derivatives of 1,3-diphenylbenzimidazole. To prevent photodestruction, all spectral solutions were prepared and kept in amber glass volumetric flasks. Withal, it was utterly unexpected that compound **1** would be far more photoactive than its higher vinylogues. Further, the primary UV/Vis spectrum of dye **1** in toluene solution recovered almost completely after its keeping in a dark box for 24 hrs. Hence, the one-way photochemical processes, e.g. photooxidation, can be dismissed as irrelevant. There is a well-known group of dimethinemerocyanine dyes apt to reversible photo or thermal isomerisation, to wit, spiropyrans.[2] Indeed, dye **1** comprises the essential fragment of a spiropyran while its high dipolarity can well facilitate isomerisation into the spiro-form. But so far there are only scarce samples of spiropyrans with heterocyclic acceptor groups, e.g. with the coumarin terminus instead of the *ortho*-phenolate one.[21] Benzimidazole-based spiropyrans are also pretty rare. Another possible way of reversible photoisomerisation of **1** is the [1,5]-sigmatropic shift of the H_1-hydrogen leading to the corresponding allene. Although strongly disfavoured thermodynamically such an isomerisation can indeed take place under photochemical conditions.[22]



Scheme 1. Possible ways of photoisomerisation of dye 1.

To check these hypotheses, a solution of merocyanine **1** in $CDCl_3$ in a NMR-tube was exposed to the sunlight for 20 min and then its ^1H NMR spectrum was promptly registered. The only easily traced changes in the spectrum were the weak multiplet signals at 4.56 ppm and 1.95 ppm, which can be attributed to the N-C$\underline{H}_2$-C$\underline{H}_2$-Et fragments of the thiobarbiturate in some photoproduct, but they do not give evidence of its structure. In order to minimize the photoconversion of dye **1** in the course of spectral measurements, 2,6-di-*tert*-butylphenol, a common UV-stabilizer, was added to all dye and blank solutions (10 mg per 100 ml). In addition, the optical densities of the working solutions nearby their absorption maxima were checked before and after the measurements to verify their steadiness.

As follows from the data of Table 1, merocyanine **1** possesses a distinct negative solvatochromism. A hypsochromic shift both by λ^a_{max} and by M_a^{-1} is observed even in going from low-polar n-hexane to toluene as solvent, in spite of the much greater refractive index of the latter, which by itself should cause a red-shift of the spectral band according to Bayliss' law.[4] Increase of solvent polarity is accompanied also with a drastic decrease of the molar extinction (ε), while an integral intensity of the spectral band (f), does not change noticeably (Table 1).

Indeed, reduction in peak intensity is counterpoised with a major broadening of the long-wavelength spectral band in polar solvents. The band shape gradually changes from a "cyanine-like" (characteristic of typical symmetric polymethine dyes narrow band with a short-wavelength shoulder) in n-hexane to a bell-like form in ethanol (Figure 1). It can be deduced from these data that merocyanine's **1** ground-state electronic structure is highly dipolar, close to the cyanine limit A2 even in low-polar n-hexane and varies within the A2–A3 range in more polar media.

The polymethine chain lengthening in going from dye **1** to the higher vinylogue **2** resulted in a substantial decrease of the dye's solubility in n-hexane. There is also an additional blue-shifted spectral band in the absorption spectrum of merocyanine **2** in n-hexane (Table 1). Aggregation is the most obvious explanation of the case although, because of the limited solubility, we could not study thoroughly the effect of concentration variations onto the spectrum appearance. Nevertheless, the suggestion that the maximum at 510 nm corresponds to a short-wavelength aggregate (dimer or H-aggregate) was confirmed via detection of the correspondent fluorescence band, broad and of very low intensity, and red-shifted relative to the "normal" fluorescence.

Since overlapping of bands obstructs the application of the method of moments, the corresponding data have not been gained here as well as in other similar cases.

The absorption maximum of dye **2** in toluene is 1 nm red-shifted versus that in n-hexane. Considering the much lesser n_D value of the latter solvent, this shift should be explained by the Bayliss refractive index function. The increase of solvent polarity in going from toluene to chloroform is accompanied by a substantial hypsochromic shift of the long-wavelength band: $\Delta\lambda^a_{max}$ = 16 nm (500 cm^{-1}), ΔM_a^{-1} = 40.9 nm (1420 cm^{-1}). Even more material changes take place in going from DCM to highly-polar DMF and then to ethanol (Table 1). The effect of solvent polarity on the band peak intensity and bandwidth is even more profound than for dye **1** (Table 1); the value of the molar extinction dwindles 5.3 times in going from toluene to ethanol. Insomuch as the juxtaposition cannot be done for n-hexane because of aggregation of vinylogue **2**, only in toluene its absorption band is narrower than that of merocyanine **1**, in more polar solvents the opposite change of σ^a values is observed. It testifies to a weakening of VI in toluene for the higher vinylogue, which is characteristic of polymethines whose electronic structure is close to A2. In more polar media the dye's electronic structure deviates from A2 toward A3 and the augmented polarizability of the longer chromophore favours an increase of SSI. In sum, these data reveal that vinylogue **2** possess a negative solvatochromism as well, and its electronic structure falls within the range A2–A3.

Merocyanine **3** was found insoluble in n-hexane. Therefore, the analogous dye with the 1,3-didodecylbenzimidazole terminus was synthesized to circumvent this obstacle. Even this tailored compound turned out to be nearly insoluble in pure n-hexane. To obtain the most coveted spectrum, it was dissolved in toluene and then diluted with lukewarm (40 °C) n-hexane at a ratio of 1 to 100, and the absorption was registered forthwith, since even on these premises quick discoloration of the solution was observed. The resulting spectrum is similar to that of dye **2**, with the long-wavelength band of the monomer and the red-shifted dimer/aggregate band. The aggregation of dye **3** can be better traced in n-hexane–acetone mixtures (Figure 2).

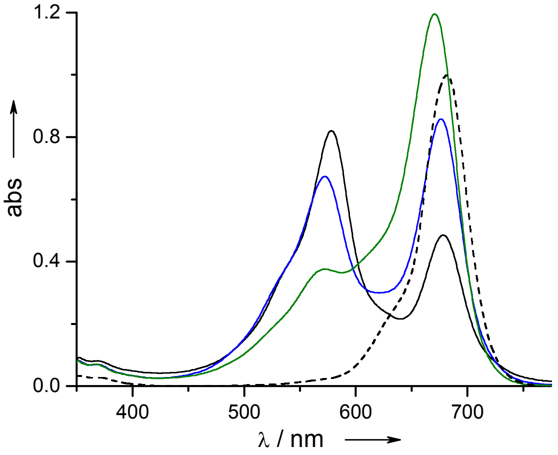


Figure 2. Vis absorption spectra of 1×10^{-5} M solutions of dye **3** in n-hexane–acetone mixtures: 98 : 2 – black, 95 : 5 – blue, 90 :10 – olive; for comparison the normalized spectrum of the fluorescence excitation in a 98 : 2 mixture is given in black dash.

In toluene, as it was mentioned above, dye **3** also forms an aggregate whose short-wavelength band virtually disappears upon dilution. Thus, for a 1.19×10^{-5} M solution of merocyanine **3** in an 1-cm cuvette the optical densities at 689 and 578 nm were 1.449 and 0.314 correspondingly (D_{689}/D_{578} = 4.6). The fluorescence spectra of dye **3** in toluene were recorded after 15-fold dilution of the starting solution (C = 7.93×10^{-7} M), and no discernible absorption maximum at 578 nm could be traced (D_{689}/D_{578} = 19.7). Nevertheless, it was found that the fluorescence quantum yield of dye **3** in toluene under 580-nm excitation amounts to only 31% instead of 70-73% under 600-650-nm excitation. Hence, some quantity of the dim-fluorescent aggregate is "hidden" under the vibronic shoulder of the long-wavelength band of the monomer (yet the values of M_a^{-1} and σ^a have been calculated for the band as it appears in the diluted solution).

In going from n-hexane to toluene the long-wavelength maximum of merocyanine **3** is shifted by $\Delta\lambda^a_{max}$ = 11 nm (240 cm^{-1}) bathochromically, a much greater effect compared to that for vinylogue **2**. Therefore, it should not be explained by mere refraction index change. Heretofore it has been shown by many examples that the polymethine chain lengthening in merocyanines is usually accompanied with an increase of the relative share of the non-polar structure A1 in low-polar solvents.[3] We suppose that this is the case here, i.e., that dye **3** in n-hexane is less dipolar than vinylogues **1** and **2** and does not reach the A2 limit in this solvent. In more polar toluene its electronic structure becomes more dipolar, attaining A2 or perhaps deviating slightly to A3. Anyway, this result manifests once again that even in the case of extreme donor/acceptor abilities of the terminal groups there exists a delimiter – chain length – which curbs the dipolarity level of long-chain merocyanines that can be attained without some assistance of SSI.[3,23] Further increase of solvent polarity results in hypsochromic shifts of the absorption band of merocyanine **3**, a decrease of its peak intensity, and band broadening (Table 1). For every pair of solvents both $\Delta\lambda^{a}_{max}$ and ΔM_{a}^{-1} values are greater than those of dye **2**, according to the increased polarizability of the former, although the bandwidth decreases in all media in going from **2** to **3**.

Vinylogue **3**, having the broadest range of solvatochromism in the series, was additionally studied in acetonitrile, methanol, 2,2,2-trifluoroethanol (TFE), and in DMF-water mixtures. In acetonitrile its absorption maximum, molar extinction, band centre, and bandwidth fell in between the correspondent values in DMF and ethanol. Taking into account that acetonitrile and DMF have close dielectric constants, the effect should be explained by a greater electrophilicity of acetonitrile. In going from ethanol to methanol only small changes in the absorption band position and shape take place. But in TFE, one of the most electrophilic alcohols, considerable bathochromic shift and further broadening of the absorption band takes place (Table 1). Thus, the established solvatochromic range of merocyanine **3** is equal to $\Delta\lambda^{a}_{max}$ = 225 nm (7040 cm^{-1}). It is comparable to that of Brooker's χ_{B}-merocyanine (9500 cm^{-1} in going from toluene to water as solvent) or of Reichardt's betaine dye (9730 cm^{-1} between diphenyl ether and water).

In the DMF-water mixture with 10% of water by volume the absorption maximum shifts hypsochromically relative to its position in DMF to 526 nm ($\Delta\lambda^{a}_{max}$ = 23 nm) and some broadening of the spectral band is observed. Increase of the water content to 20% causes an additional minor blue-shift of the spectral band to 522 nm. Further increase of the water content results in a red-shift of the spectral band (λ^{a}_{max} = 535 nm at 50% of water) and a considerable change of its form. The solutions of dye **3** in DMF-water mixtures with high water percentages have visible opalescence, probably due to incipient precipitation of the dye. Therefore, we suppose that the spectral changes observed in solutions with 50 and higher % of water are caused by aggregation of dye **3**.

The deviations of the absorption band maxima (a classical measure of the merocyanine electronic asymmetry [1]) of vinylogues **2** and **3** confirm well their high dipolarity. Even in medium-polar DCM they are equal to 25 and 35 nm correspondingly, increasing to whopping 118 and 176 nm in going to ethanol as a solvent.

The solvatochromism of dyes **1–3** reveals their extremely high dipolarity and demonstrates that merocyanines can attain the polymethine-like structure A2 even in low-polar media like n-hexane. Pure negative solvatochromism is observed only for vinylogues **1** and **2**, while dye **3** possesses a reversed solvatochromism, showing a bathochromic shift of the spectral band in going from n-hexane to toluene.

Unlike the absorption, the fluorescence band of merocyanine **1** undergoes a small hypsochromic shift in going from n-hexane to toluene (Table 1), and such a "reversal" of solvatochromism sign can be readily fathomed. Abatement of SSI in the excited state of organic molecule was revealed long ago and was testified by many examples. Thus, it was found that solvatofluorochromism of cationic polymethine dyes is much weaker than their solvatochromism and can be described with high accuracy by the simple Bayliss equation.[19] For positively solvatochromic merocyanines, whose dipole moments increases upon excitation, there are some data in favour of their greater solvatofluorochromism, while other investigations demonstrate that solvent effects on their fluorescence are of the same magnitude as in the absorption spectra or even lesser.[3,4] But for negatively solvatochromic merocyanines, less dipolar in the excited state than in the ground state, solvatofluorochromism is invariably abated in comparison with solvatochromism. In the case of dye **1**, a decrease in solvatochromism in the excited state and a much larger refractive index of toluene result in the red-shift of its fluorescence band in this solvent relative to n-hexane. In going from toluene to more polar solvents the fluorescence band maximum (λ^{f}_{max}) of merocyanine **1** is shifted hypsochromically (it is not the case with the values of M_{f}^{-1}, which are affected by the bandwidth as well). The range of λ^{f}_{max} (510 cm^{-1}) in the used set of solvents is much smaller than that of λ^{a}_{max} (2310 cm^{-1}).

The fluorescence bandwidth σ^{f} of dye **1** is minimal in n-hexane and increases toward high-polar solvents but the influence of solvent polarity onto it (and onto the spectral band shape in general), is considerably weakened in comparison with the absorption spectra (Table 1). One can also note that in n-hexane the value of σ^{f} is greater than σ^{a}, both parameters are very close in toluene, chloroform, and DCM, while in high-polar DMF and ethanol, in which the SSI have the most influence onto absorption bandwidth, $\sigma^{f} << \sigma^{a}$.

The solvatofluorochromism of merocyanines **2** and **3** is very similar to that of the lower vinylogue and their ranges (720 and 610 cm^{-1}) are not considerably greater, in contrast to their relative solvatochromism. Therefore we will not dwell at this point, mentioning only that the increase of Stokes' shifts (SS_{λ} and SS_{M}) of dyes **1–3** with solvent polarity and the polymethine-chain lengthening (Table 1) is determined mainly by their solvatochromism and to a much smaller degree by their solvatofluorochromism.

The decrease of the fluorescence bandwidth in all solvents with the polymethine-chain lengthening (see Table 1) is characteristic of polymethine dyes whose electron structure is rather close to the high-symmetry state A2 – in their molecules the VI as a rule decrease for the higher vinylogues. Also one can see once more that the SSI in the fluorescent transition have a minor influence on the fluorescence band shape of negatively solvatochromic merocyanines. As a consequence, the mirror symmetry rule is violated for them (Figure 3) – the values of σ^{f} for vinylogues **2** and **3** are substantially smaller than those of σ^{a} even in toluene, to say nothing of more polar solvents (Table 1). Very high vinylene shifts ($\Delta\lambda^{f}_{max}$ = 95-107 nm, ΔM_{f}^{-1} = 96.1-102.8 nm for the pair **1** – **2**, $\Delta\lambda^{f}_{max}$ = 112-117 nm, ΔM_{f}^{-1} = 109.1-116.4 nm for the pair **2** – **3**) also testify to high electronic symmetry of the excited state S_1 of dyes **1–3**.

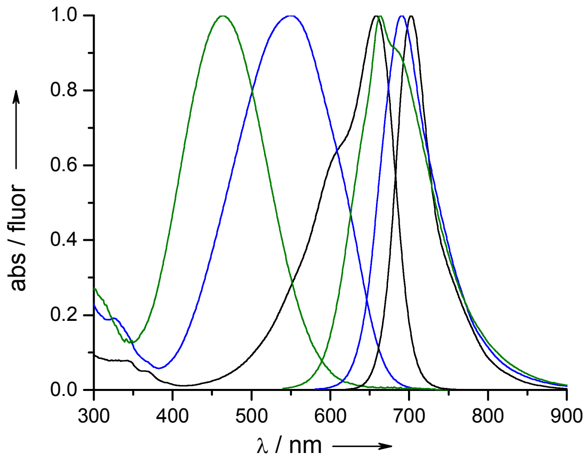


Figure 3. Normalized absorption and fluorescent spectra of dye **3** in chloroform (black), DMF (blue), and TFE (olive).

The tendencies in the fluorescence of merocyanines **1-3** reveal that in the excited state their electronic structure lies near to the ideal polymethine state A2 and is less affected by the solvent polarity than in the ground. Probably, the latter fact is largely related to the light-induced reverse charge transfer in their molecules, which should be especially strong in polar media. As a result, their electronic structure changes from the A2–A3 in the ground state to the less dipolar A1–A2 in the excited state.

The fluorescence quantum yields of dye **1** decrease gradually upon solvent polarity rise (Table 1), in good agreement with the deviation of the dye's electronic structure from the ideal state A2. They are also comparatively low, which is usual for short-chained merocyanines irrespective of their relative position within the A1–A2–A3 scale. Firstly, the VI are maximal for lower vinylogues due to a good share of termini atoms in the absorption and fluorescence transitions. Secondly, close positioning of the terminal groups in such molecules, especially of bulky ones, favours isomerisation or twisting around the polymethine chain. And thirdly, their $\pi\pi^*$-transitions are more proximal by energy to the $n\pi^*$-transitions involving the carbonyl (or thiocarbonyl) groups of the acceptor terminus.[24] The third cause can be effaced here since its effect would be diminished in ethanol due to effective solvation of the (thio)carbonyl groups resulting in an increase of the relative energy of the corresponding $n\pi^*$-transitions and, consequently, an increase of quantum yield in this solvent which is not found in the case of dyes **1–3**.

Lengthening of the polymethine chain in going to vinylogue **2** and then to **3** is accompanied with a drastic increase of fluorescence quantum yields in all solvents (Table 1). While for the pair **1** - **2** its rise can be explained both by the enlarged distance between the terminal groups and by abated VI, for the pair **2** - **3** only the second factor can play a significant part since the termini in molecule **2** is already remote enough to disregard their interaction. In respect to solvent polarity the fluorescence intensity of higher vinylogues proceeds by the same pattern as that of their short-chain relative, decreasing substantially in going from toluene to more polar solvents, in full compliance with their relative positions on the A1–A2–A3 scale.

It was shown in many works that NMR spectra of merocyanines can be used to study their electronic structure.[8,14,25-27] And while the chemical shifts of H-atoms of the polymethine chain is rendered less informative in the case of dyes **1–3** due to the presence of two magnetically anisotropic carbonyl groups of the thiobarbituric residue, the corresponding vicinal spin-spin coupling constants (SSCC) are independent of such an influence and are known to be proportional to the corresponding bond orders.

In $CDCl_3$ the vicinal SSCC of the methine H-atoms of merocyanine **1** is equal to 15.6 Hz. For reference, in the analogous dye with an indole based donor terminus the corresponding SSCC is equal to 14.6 Hz, in the dye with 1,3-diphenylbenzimidazole as a donor it is 15.3 Hz. Hence, the bond order of the only "single" bond of the polymethine chain in dye **1** is very high, supporting for high dipolarity of its molecule. In vinylogues **2** and **3** there are three and five vicinal SSCC correspondingly, alternation of which conforms to a high-dipolar electronic structure from the interval A2–A3 both in $CDCl_3$ and in $(CD_3)_2SO$ (see Supplementary data). Interestingly, the SSCC alternation in dye **3** does not increase appreciably in going to the high-polar solvent. We presume it is just the case when the simplified A1–A3 scheme is insufficient and a more rigour concept should be applied, accounting the limiting structures with charges on the polymethine chain C-atoms.[8]

Quantum chemical simulation were performed using Gaussian-09 software package.[28] The geometry optimizations of the electronic ground state of dyes **1–3** were carried out at the DFT level, with the hybrid B3LYP exchange-correlation functional and the split-valence 6-31G(d,p) basis set. Then, taking into account some literature data [29,30] that in the case of highly-polarizable molecules application of basis sets with increased Hartree–Fock (HF) exchange shares leads to a better agreement with experimental data than using of B3LYP with just 20% of HF exchange, the same procedure were performed using the CAM-B3LYP functional, which comprises of 0.19 HF plus 0.81 Becke-1988 exchange interaction at short-range, and 0.65 HF plus 0.35 Becke-1988 at long-range. The convergence criterion on the residual forces has been set to 1×10^{-5} Hartree/Bohr or Hartree/Rad. A force constants and vibrational frequencies calculation was performed to verify that the geometry located was a minimum. The vertical excitation energies as well as geometry relaxations in the first singlet excited state have been calculated with the adiabatic approximation of the TDDFT using the same functionals and basis set. The polarisable continuum model (PCM) using the integral equation formalism was applied to model the solvent effects,[31] although this approach lacks to represent properly solvent effects in highly polar, especially in protic solvents.[32] In the case of fast absorption and fluorescence processes (Franck–Condon principle), the inclusion of nuclear relaxations is avoided by employing a state-specific solvation calculation in terms of fast electronic cloud reorganizations and slow solvent and solute nuclear motions.[33] Due to axial symmetry of the terminal groups merocyanine **1** cannot have any isomers. As for the higher vinylogues, their *all-trans* conformation was confirmed by the values of SSCC between the vicinal H-atoms of the polymethine chain in their ^{1}H NMR spectra. Therefore only *all-trans* isomers were considered in the simulation.

It was found that chromophores of all three merocyanines are nearly planar. The maximum distortion from planarity occurs for the bond between the benzimidazole terminus and the polymethine chain: in the ground state the corresponding torsion angle ($N{-}C_{\alpha}{=}C_1{-}C_2$) is equal to ≈15° *in vacuo*, rising to ≈17° in n-hexane and to ≈20° in more polar DCM or ethanol. In the same manner an increase in solvent polarity leads to lengthening of the bond $C_{\alpha}{=}C_1$.

The bond-length alternation (BLA) parameter, which is specified as the difference between the average bond lengths of the formal single and double bonds in the polymethine chain, allows estimation of the relative position of a merocyanine on the A1–A2–A3 scale.[6,34] For merocyanine **1** this parameter has a negative value even *in vacuo* and decreases further when solvent effects are taken into account (Table 2). This result consists with the above conclusions about an extremely high intrinsic dipolarity of molecule **1**, attainment of the A2 or even A2-to-A3 state even in low-polar hexane. Lengthening of the polymethine chain leads to an increase of the BLA values, i.e. the electronic structure of the higher vinylogues indeed shifts towards the A1 state. The BLA value in n-hexane is still negative for dye **2** but changes sign in going to the highest vinylogue **3** (Table 2), the latter indeed possessing a reversed solvatochromism.

The calculations at the TDDFT level indicate the presence of two different long-wavelength transitions for the studied molecules: (i) the dipole allowed polymethine-type $\pi\pi^*$-transition, the dominant configuration of which involves only HOMO and LUMO, (ii) the $n\pi^*$-transition with much smaller oscillator strength which involves mainly HOMO-1, localized on the sulphur atom of the thiobarbiturate residue, and LUMO (Figure 4). Obviously, the optical properties of the studied merocyanines are governed by the allowed polymethine $\pi\pi^*$-transition. But a low-lying $n\pi^*$-state can affect the fluorescent properties of merocyanines contributing to the non-radiative deactivation of the excited state, especially in low-polar solvents.[24] Taking into account the comparatively high fluorescent quantum yield of the studied merocyanines in n-hexane, one could suppose that their first excited state should be of $\pi\pi^*$-nature.

The B3LYP calculation predicts that *in vacuo*, and for vinylogues **1** and **3** in n-hexane as well, the $S_1^{FC}{\leftarrow}S_0$ transition is the $n\pi^*$-one. As solvent polarity increases, both long-wavelength transitions are shifted hypsochromically and reshuffled. One should note also that the polymethine $\pi\pi^*$-transition in molecules **1–3** is accompanied with just a slight decrease of their dipole moments while the $n\pi^*$-transition leads to much greater change of this parameter (Table 2). The energies of the long-wavelength polymethine transitions are in all cases overestimated, which becomes critical in low-polar media leading to entanglement of the $\pi\pi^*$- and $n\pi^*$-transition in vacuum and n-hexane.

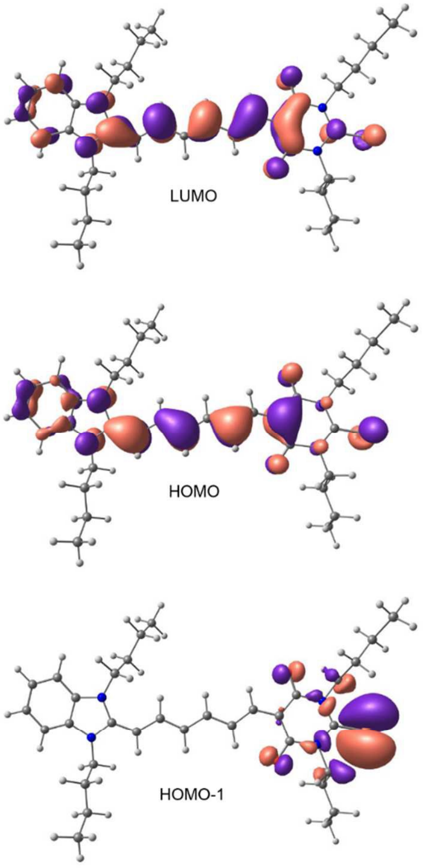


Figure 4. The MOs of dye **3** (B3LYP/6-31G(d,p), contour value is 0.03).

The CAM-B3LYP calculation suggests the $\pi\pi^*$-nature of the $S_1^{FC}{\leftarrow}S_0$ transition in all cases and gives greater solvatochromic shifts, which correlates better with the experimental data. On the other hand, the theoretical energies of the polymethine absorption transitions are here even more overestimated than in the case of B3LYP.

B3LYP geometry optimization of the first excited state S_1 of merocyanines **1–3** *in vacuo* and of vinylogues **1** and **3** in n-hexane results principally in considerable lengthening of the C=S bond of the thiobarbiturate terminus, which is conceivable in view of the predicted by this approac $n\pi^*$-nature of this state. In all other cases the excited state relaxation involves mainly the polymethine chain atoms and leads to levelling of the chromophore bond lengths – a decrease of the absolute BLA* (BLA in the excited fluorescent state) values in comparison with the BLA values (Table 2). The results of this simulation agree totally with the conclusions made from the spectral fluorescent data, viz. that the excited state of dyes **1–3** should lie somewhat nearer to the ideal polymethine A2 and that the VI are weaker in the fluorescent transition (cf. the calculated solvatochromic and solvatofluorochromic shifts). On the other hand, the calculated fluorescent maxima do not correlate always with the negative solvatofluorochromism of the studied merocyanines (in this case CAM-B3LYP again has the upper hand).

Conclusions

It has been shown that merocyanines with extreme donor and acceptor terminal groups can manifest a genuine negative solvatochromism in the whole range of solvent polarities starting from low-polar alkanes, implying that the highly dipolar polymethine-like state A2 can be attained for them without appreciable assistance of solvation. On the other hand, a lengthening of the polymethine chain was shown, by both experimental results and quantum chemical calculations, to curb the charge separation within the merocyanine chromophore. Hence, the electronic structure of the higher vinylogues drifts towards the non-polar polyene A1 in vacuum and low-polar solvents. Highly dipolar merocyanines, in spite of their outstanding solvatochromism, display a rather moderate solvatofluorochromism, which comes from the weakening of solute-solvent interactions in the fluorescent state S_1. Remarkably, in the excited state their electronic structure is close to the ideal polymethine state in the full range of solvent polarities, which is revealed in the high vinylene shifts of their fluorescence bands and their narrowing for the higher vinylogues. The most variable solvatofluorochromic parameter of dyes **1–3** is the fluorescence quantum yield Φ_f, making them promising fluorescent probes for biomedical investigations, provided that their photodurability can be improved. Another shortcoming of negatively solvatochromic merocyanines – their propensity for aggregation both in low-polar and in aqueous media – can be solved via inclusion of bulk substituents into their terminal groups or into the polymethine chain.[35,36]

Since the solvatochromism of highly dipolar merocyanines is governed by the variation of their ground-state electronic structure in the wide range from the polymethine state A2 to the dipolar polyene state A3 while in the fluorescent state S_1 only minor variations near the state A2 takes place, a pronounced violation of the mirror symmetry of the absorption and fluorescence spectral bands of merocyanines **1–3** is observed in medium- and high-polar solvents.

The DFT/B3LYP/6-31G(d,p) level of approximation with the PCM formalism to model solvent effects provides a rather good consistency with the experimental results when dealing with the ground-state structure of the studied dyes and represents properly their negative solvatochromism and higher "electronic symmetry" in the excited state. Nevertheless, CAM-B3LYP approach was more accurate when excited state calculations were involved.

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Table 1. Characteristics of the UV/Vis absorption and steady-state fluorescence bands of dyes **1–3**.

Dye	Solvent	λ^{a}_{max} nm	$\varepsilon\times10^{-4}$ $L\times mol^{-1}\times cm^{-1}$	λ^{f}_{max} nm	Φ_f %	f	M_a^{-1} nm	σ^a cm^{-1}	M_f^{-1} nm	σ^f cm^{-1}	SS_λ cm^{-1}	SS_M cm^{-1}
1	n-hexane	470	10.04	488	0.33	0.81	452.5	1130	509.9	1240	780	2490
	toluene	468	7.02	490	0.32	0.82	441.4	1400	513.1	1370	960	3170
	$CHCl_3$	461	5.53	489	0.29	0.82	435.7	1480	515.1	1460	1240	3540
	CH_2Cl_2	456	5.45	486	0.17	0.83	432.7	1510	512.3	1470	1350	3590
	DMF	431	4.11	482	0.15	0.83	411.4	2350	507.3	1480	2450	4600
	EtOH	424	3.24	478	0.07	0.82	395.2	2930	505.5	1560	2660	5520
2	n-hexane	574 510	–[a]	595 714	11.5[b]	–	–	–	612.7	820	610	–
	toluene	575	17.23	598	16.8	1.16	556.8	1020	614.5	820	670	1690
	$CHCl_3$	559	7.15	589	4.6	1.02	515.9	1860	611.9	920	910	3040
	CH_2Cl_2	550	6.23	587	3.2	1.03	506.3	1930	610.1	940	1150	3360
	DMF	497	3.87	580	2.3	0.99	464.8	2650	607.0	1080	2880	5040
	EtOH	452	3.10	573	1.3	0.96	437.7	2950	601.6	1120	4670	6220
3	n-hexane	678 585	–[a]	707[c]	17.8[c]	–	–	–	–	–	–	–
	toluene	689 578	–[d]	715	73.0[b]	–	672.9	860	730.9	650	530	1180
	$CHCl_3$	658	10.73	702	36.5	1.32	609.0	1680	722.8	760	950	2590
	CH_2Cl_2	642	8.02	697	26.6	1.32	588.3	1780	718.3	790	1230	3080
	DMF	549	4.88	690	12.7	1.20	524.8	2360	715.4	970	3720	5080
	MeCN	540	4.74	688	9.9	1.22	518.6	2430	712.2	990	3980	5240
	EtOH	492	3.70	685	7.4	1.14	483.6	2830	710.7	1010	5730	6610
	EtOH[e]	494	3.72	685	7.5	1.16	485.4	2830	711.1	1010	5650	6540
	MeOH	483	3.73	682	5.6	1.16	478.3	2860	707.5	1020	6040	6770
	TFE	464	3.82	663	2.3	1.17	457.7	2940	698.5	1200	6470	7530

[a] Low solubility. [b] The fluorescence quantum yield depends on excitation wavelength; the given value is for the solution with the optical density of 0.090 in the maximum and λ_{exc} = 530 nm. [c] These data for an n-hexane–acetone mixture (98 : 2), λ_{exc} = 670 nm. [d] The molar extinction coefficient was not determined because of aggregation. [e] Anhydrous ethanol, to check the influence of water which is present in 96% alcohol.

Table 2. Some results of quantum chemical calculations for dyes **1–3**

Dye	Medium	$\mu(S_0)$ D	$\mu(S_1^{FC})$ D	$\mu(S_1)$ D	$\mu(S_0^{FC})$ D	BLA Å	BLA* Å	λ^{a}_{maxc} nm	f^a	λ^{f}_{maxc} nm	f^f
B3LYP											
1	*vacuo*	11.3	3.2	3.6	15.0	-0.013	-0.056	451.4	0.003	683.0	0.000
	n-hexane	13.6	4.0	3.9	16.5	-0.024	-0.040	468.7	0.038	660.2	0.000
	DCM	17.1	14.3	17.3	15.3	-0.041	0.003	381.5	1.546	424.5	1.179
	EtOH	24.6	23.3	23.6	23.1	-0.044	0.006	367.5	1.576	431.5	1.616
2	*vacuo*	15.1	2.3	1.4	20.4	0.010	-0.052	499.6	0.005	890.2	0.000
	n-hexane	18.6	17.1	17.1	19.0	-0.005	-0.019	451.6	1.984	465.3	1.828
	DCM	24.3	22.0	22.4	22.2	-0.030	-0.006	435.8	2.081	466.4	1.833
	EtOH	24.6	23.3	23.6	23.1	-0.035	-0.003	429.4	1.769	468.2	1.821
3	*vacuo*	18.0	1.7	3.0	24.9	0.019	-0.046	530.4	0.017	1060.1	0.000
	n-hexane	22.7	1.5	2.0	23.5	0.004	-0.011	572.1	0.004	597.0	0.004
	DCM	31.0	28.7	28.3	28.8	-0.024	-0.009	486.8	2.349	514.4	2.405
	EtOH	33.1	30.2	29.6	30.0	-0.031	-0.006	476.5	2.553	513.5	2.399
CAM-B3LYP											
1	*vacuo*	11.8	10.8	10.7	11.2	-0.016	-0.009	373.2	1.284	392.8	1.239
	n-hexane	14.1	12.5	12.6	12.8	-0.029	-0.003	366.2	1.410	389.5	1.245
	DCM	17.7	15.4	15.6	15.1	-0.050	0.006	350.7	1.539	391.3	1.233
	EtOH	18.6	16.3	16.3	15.7	-0.054	0.009	345.9	1.563	392.7	1.226
2	*vacuo*	15.2	16.2	16.3	15.9	0.015	-0.006	429.9	1.927	449.6	1.898
	n-hexane	19.3	18.6	18.5	18.7	-0.007	-0.007	427.6	2.019	447.6	1.882
	DCM	25.9	22.1	21.6	22.0	-0.043	0.001	395.4	2.037	444.2	1.862
	EtOH	27.3	23.0	22.3	22.7	-0.051	0.004	383.0	2.031	443.6	1.857
3	*vacuo*	17.1	20.7	20.8	19.1	0.032	0.001	477.1	2.446	502.3	2.468
	n-hexane	22.7	23.8	23.9	23.5	0.008	-0.006	487.8	2.560	506.0	2.453
	DCM	34.0	28.8	27.5	28.3	-0.042	0.000	436.1	2.487	498.4	2.430
	EtOH	36.5	30.0	28.3	29.2	-0.053	0.003	411.4	2.447	496.4	2.425

$\mu(S_0)$, $\mu(S_1^{FC})$, $\mu(S_1)$, $\mu(S_0^{FC})$ – molecular dipole moments in the ground (S_0), excited Frank-Condon (S_1^{FC}), excited (S_1), and ground Frank-Condon states correspondingly