



Synthesis, electronic structure and spectral fluorescent properties of vinylogous merocyanines derived from 1,3-dialkyl-benzimidazole and malononitrile



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ABSTRACT

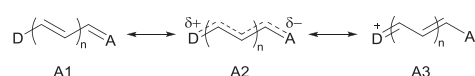
A vinylogous series of merocyanines were synthesized with 1,3-dibutyl-benzimidazole and malononitrile residues as the donor and acceptor terminal groups. These dyes do not comprise carbonyl groups, which are prone to the strong specific solvation by polar solvents up to hydrogen bond formation, and nevertheless they possess distinct reversed solvatochromism, i.e. their molecules have very high dipolarity. At that, they are soluble in a wide range of solvents from *n*-hexane to ethanol and do not aggregate readily. They were studied thoroughly by UV/Vis, fluorescence, IR, and NMR spectroscopy methods. Their structure and spectral properties in the ground and excited fluorescent states were modelled at the DFT level both in vacuum and in solvents of various polarities by using the PCM solvent field simulation. The calculations were performed using several hybrid functionals (B3LYP, CAM-B3LYP, and wb97XD) and the split-valence 6-31G (d,p) basis set.

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1. Introduction

The advent and development of a great deal of modern technologies, such as ink-jet printing, holography, liquid crystal and OLED displays, optical data storage, bio-medical imaging, entailed the ever increasing demand for novel functional dyes to meet the new and challenging criteria [1–4]. Obviously, the tailored design of functional compounds requires revealing the regularities connecting their properties with both their chemical structure and environment. In this respect, the donor-acceptor substituted polymethines, i.e. merocyanines, are among the most suitable objects to study, since their spectral-luminescent and other physical-chemical properties change in a very wide range [5–8]. Depending on the donor-acceptor properties of their terminal groups (D and A), the polymethine chain length, and the solvent polarity, their electronic structure can vary from the neutral polyene (A1), via the ideal polymethine (A2), to the dipolar polyene (A3) – three virtual limiting states suggested by S. Dähne to simplify description of the polymethine dyes; [5] the unconventional limiting structure A2 being commended because of a series of unique characteristics – the minimum excitation energy to the first excited singlet state, narrowing and growing of the peak intensity of the long-wavelength spectral bands due to the least changes of the chromophore π -bond

orders and dipole moment upon electronic excitation, and by the highest fluorescence quantum yield (Φ_f) [6].



Consequently, the deviation from the ideal polymethine state A2 to either side is followed by a hypsochromic shift and broadening of the absorption and fluorescence bands of merocyanines. These changes can be traced most easily by investigation of their solvatochromism and solvatofluorochromism. The chemical structure of dyes is kept constant in this case. Therefore, all the spectral changes observed can be attributed to the electronic structure variations. The reversed solvatochromism is the most interesting situation in this respect, since there can be relatively broad ranges of positive (A1-to-A2) or negative (A2-to-A3) solvatochromism but only a single point in which the solvatochromism reversal takes place.

In addition to physical-chemical methods, the quantum chemistry provides us with ever increasing possibilities to study, predict, and hence to design the properties of novel functional molecules. However, there exist some unsettled issues in application of quantum chemistry for merocyanines. For example, the common ab initio and DFT methods overestimate considerably the energy of the long-wavelength electronic transition in their molecules [9,10], while more sophisticated approaches are too resource consuming. Also, the bulk solvent modelling approaches can be unequal to the task when strong solute-solvent interactions (SSIs) are involved, which is often the case with carbonyl-

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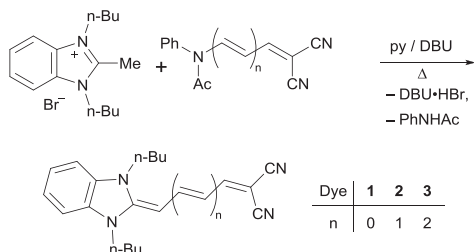
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containing dyes in protic solvents [11,12]. One more issue is the quantum chemical modelling of the excited states of polymethine dyes, which is both resource-intensive and challenging task. Consequently, there is still a demand for some reffer dyes to verify the results of such calculations. Again, merocyanines possessing reversed solvatochromism are probably the most convenient objects in this respect.

Therefore, in the present paper, we designed and studied by using the physical-chemical and quantum-chemical methods the vinylogous series of malononitrile-based merocyanine dyes. The strong electron-donating properties of the 1,3-dialkyl-benzimidazole residue was conjectured to provide high dipolarity of the studied molecules and consequently their reversed solvatochromism. At that, they do not comprise carbonyl groups in their molecules, so the solvent effects can be treated more reliably via the standard PCM approach. The dipolarity of donor-acceptor molecules is known to decrease gradually with the π -conjugated system lengthening [6,12,13]. So, in this case we had at least two criteria to verify the results of the TDDFT calculations – the point of solvatochromism reversal and the change of dyes electronic structure upon the polymethine chain elongation.

2. Materials and methods

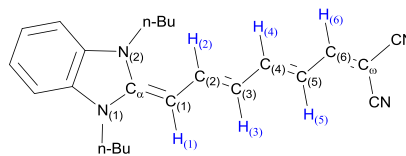
Merocyanines **1–3** were synthesized by heating equal amounts of 1,3-dibutyl-2-methyl-benzimidazolium bromide [14] and the corresponding hemicyanine [15] in pyridine for 30–90 min in the presence of DBU (1,8-diazabicycloundec-7-ene).



The reaction mixture was diluted with water-ethanol (1:1), left overnight, and the resulting precipitate was filtered off, dried and refined by column chromatography on neutral alumina-80 using chloroform as an eluent. The resulting product was then crystallized from ethanol.

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 were refined according to the methods given in ref. [16] The UV/Vis spectra were recorded using a Shimadzu UV-3100 spectrophotometer. 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 toluene, chloroform, DCM, DMF, and ethanol. In *n*-hexane the studied dyes are not soluble enough to carry out the same test. However, no sign of aggregation was traced by their absorption spectra in this solvent. The fluorescence spectra were recorded using a CM2203 spectrofluorometer ("Solar", Belarus, wavelength scale 220–900 nm). Solutions of merocyanines were not degassed since the fluorescent characteristics for degassed and non-degassed solutions were identical. The fluorescence quantum yield of merocyanine **1** was measured in relation to Coumarin 1 in ethanol ($\Phi_f = 73\%$ [17]), of dye **2** – in relation to Rhodamine 6G in ethanol ($\Phi_f = 95\%$ [18]), of dye **3** – in relation to Nile blue in ethanol ($\Phi_f = 27\%$ [19]). 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. The fluorescence excitation spectra have been found to coincide nearly with the absorption spectra of merocyanines **1–3** and to be independent of the emission wavelength, which confirms both the fluorescence purity of the studied dyes and the absence of aggregation in their solutions at the given concentrations.

IR spectra were recorded in KBr pellets using a Bruker Vertex 70/80 FTIR spectrometer. ^1H NMR spectra were registered on a Varian VXR-300 spectrometer (299.943 MHz for H-atoms) in CDCl_3 or $(\text{CD}_3)_2\text{SO}$, ^{13}C NMR spectra with power-gated decoupling, ^{13}C NMR APT spectra with *J*-compensation, HMBC, and HMQC spectra – on a Bruker Avance III spectrometer (100.61 MHz for C-atoms) in CDCl_3 ; TMS was used as an internal standard in both cases. The atom labelling used in the discussion is shown below.



The long-wavelength absorptions and fluorescence bands of merocyanines **1–3** were analysed by the method of moments, which allows the quantitative characterization of their position and shape [20]. Three parameters obtained 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 the 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 ($f = 4.317 \times 10^{-9} f_{\epsilon, d\nu}$). Indices 'a' and 'f' denote the parameters relative to absorption and fluorescence correspondingly. The deviations by maxima (D^{λ}_{a}) 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).

3. Results and discussion

Both ^1H and ^{13}C NMR spectra of compounds **1–3** can be used to evaluate roughly their electronic structure. The most obvious characteristics here are the vicinal spin-spin coupling constants (SSCCs) between the polymethine chain H-atoms, which are known to correlate with the corresponding C–C-bond orders [21–23]. Even in medium-polarity CDCl_3 , the $^3J(\text{H,H})$ SSCCs alternation for dyes **2** and **3** corresponds to the structure from the A2–A3 range. Going from CDCl_3 to $(\text{CD}_3)_2\text{SO}$ as the solvent should naturally enhance dipolarity of dyes **1–3**, which is shown up specifically in the further increase of the polymethine chain $^3J(\text{H,H})$ SSCCs alternation and in the downfield shifts of the NCH_2 , H_{ar} , and $\text{H}_{(1)}$ signals of vinylogue **3**. For comparison, in CDCl_3 the corresponding $^3J(\text{H,H})$ SSCCs values for the relative dyes with 1,3-diphenyl-benzimidazole as the donor terminal group are nearly equalized and only in high-polarity $(\text{CD}_3)_2\text{SO}$ they alternate distinctly [22].

The C_{α} and C_{ω} atoms chemical shifts can also be used to evaluate the merocyanine electronic structure [22]. The C_{ω} signal for merocyanine **3** is shifted upfield by 1.4 ppm relative to that in its *N,N*-diphenyl-analogue, once more confirming the greater dipolarity of *N,N*-dibutyl-benzimidazole based **3**. In the series **1–2–3**, the C_{α} and C_{ω} signals go upfield and downfield correspondingly with the polymethine chain lengthening, thus demonstrating a minor decrease of dipolarity for the higher vinylogues, just as expected.

The characteristic $\text{C}\equiv\text{N}$ frequencies of the malononitrile residue in the IR spectrum should decrease upon growth the electronic density on this group. Malononitrile itself ($\nu_{\text{C}\equiv\text{N}} = 2272 \text{ cm}^{-1}$) and malononitrile anion ($\nu_{\text{C}\equiv\text{N}} = 2158 \text{ cm}^{-1}$) are the two obvious extreme cases. To find the state A2 characteristic frequency of malononitrile-based polymethines, the IR spectra of the three corresponding symmetric anionic dyes (see ESI) were recorded. For all these dyes, an intensive peak of the $\nu_{\text{C}\equiv\text{N}}$ symmetric stretch of the malononitrile residue (the attribution is based on the DFT quantum chemical calculations) lies at 2189–2192 cm^{-1} , with the $\nu_{\text{C}\equiv\text{N}}$ asymmetric stretch shoulder at 2170–

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