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Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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

Heorhii V. Humeniuk, Nadezhda A. Derevyanko, Alexander A. Ishchenko and Andrii V. Kulinich\*

Vinylogous series of merocyanines have been synthesized with indole, benzimidazole, and benzo[*cd*]indole as the donor termini and 1,2-diphenyl-3,5-pyrazolidinedione as the acceptor terminal group. Their absorption and fluorescence spectra have been studied in different polarity solvents. From the analysis of their solvatochromism, vinylene shifts, Brooker's deviations, and spectral band shape, the effects of structural modifications, *viz*. the donor group strength and the polymethine chain length, on their electronic structure have been revealed. Based on the obtained data, the acceptor strength of the 1,2-diphenyl-3,5-pyrazolidinedione residue has been re-evaluated, showing – contrary to the literature data – it not being a record-strong acceptor. The (TD)-DFT/B3LYP calculations of the studied dyes have been performed in three different solvents using the PCM solvation model. From the analysis of TD-B3LYP electronic transitions, the low fluorescence of the studied dyes has been explained by the fast competitive unimolecular non-radiative decay associated with the low-lying non-fluorescent  $\pi\pi^*$ -excited state involving the molecular orbital localized on the acceptor terminal group.

# 1. Introduction

Merocyanines - donor-acceptor polymethine dyes - are one of the most versatile functional compounds. They are widely used as colorimetric sensors and fluorescent probes sensitive to environmental polarity and viscosity in physicochemical and biomedical studies,<sup>1-4</sup> as well as in various technologies related cells,5-7 to light–energy conversion such as solar electroluminescent materials,<sup>8</sup> nonlinear optics,<sup>9,10</sup> and information recording.<sup>11,12</sup> The reason for such versatility is that their photophysical properties can be tuned in the very wide range depending on the polymethine chain length and the chromophore electronic structure, the latter varying from the nonpolar polyene A1 to the ideal polymethine A2 and further to the dipolar polyene A3 (Scheme 1).13

Merocyanines are well-known for their pronounced solvatochromism, which is attributable to the fact that solvent polarity is one of the factors determining the alteration of their electronic structure within the A1–A2–A3 range.<sup>2</sup> However, the main factor, which predetermines the solvatochromism as well, is the donor–acceptor properties of the terminal groups D and A. There is a huge range of available donor (electron donating) groups in the polymethine dye chemistry like alkyl and arylaminos, alkylamino and arylaminoarenes (both carbo- and

heterocyclic), nitrogen-, oxygen-, and sulphur-containing heterocycles, even organometallic compounds, which give rise to the hundreds of structures with varying electronic properties.<sup>2,9,14,15</sup> On the contrary, the number of acceptor (electron withdrawing) terminal groups used in the synthesis of merocyanines is rather limited (see fundamental review 16 by D. M. Sturmer and D. W. Heseltine from Eastman Kodak Co.) and has increased just slightly over the past four decades. Only a few of them are characterized by extremely strong electronwithdrawing properties, required for creation of donoracceptor dyes, whose electronic structure in polar solvents approaches the dipolar polyene structure A3.<sup>9,17–19</sup> Among the strong acceptor groups, the derivatives of barbituric and thiobarbituric acids have been studied most extensively; for example, the fluorescent probe Merocyanine-540. Other strong acceptors have found lesser attention from researchers.

Besides barbiturates, the list of the most acidic (acceptor) terminal groups in ref. 16 includes some imidazolones and the residue of 1,2-diphenyl-3,5pyrazolidinediones. pyrazolidinedione being estimated as the strongest noncharged acceptor. To the best of our knowledge, merocyanines comprising this acceptor can be found in patents mainly, only in some of them their spectral properties being briefly reported.<sup>20,21</sup> In a few journal articles, several styryl dyes,<sup>22,23</sup> an indole-based dimethinemerocyanine,<sup>24</sup> five tetramethinemerocyanines with different donor groups,<sup>25</sup> and one dye of the D– $\pi$ –A– $\pi$ –D structure,<sup>26</sup> which can be tentatively classified as bis-merocyanine, are described. Their solvatochromism, electronic structure, and fluorescent properties have not been studied in detail, although it is noted in ref. 25 that such dyes are characterized by low fluorescence brightness along with comparatively high photochemical stability. Hence, the main goal of this work was to examine spectral properties and electronic structure of merocyanines based on 1,2-diphenyl-3,5-pyrazolidinedione in a set of solvents of different polarity.

View Article Online DOI: 10.1039/C9NJ03275D

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Electronic Supplementary Information (ESI) available. See DOI: 10.1039/x0xx00000x

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# 2. Experimental section

The UV-Vis absorption spectra were recorded using a Shimadzu UV-3100 spectrophotometer (Japan). The fluorescence spectra were measured using a Solar CM2203 spectrofluorimeter (Belarus) and corrected by the instrument sensitivity. The fluorescence quantum yields (FQY;  $\Phi_{\rm f}$ ) were determined relative to those of Rhodamine 6G in ethanol ( $\Phi_{\rm f}$  = 95%<sup>27</sup>), Nile blue in methanol ( $\Phi_{\rm f}$  = 27%<sup>28</sup>), and indotricarbocyanine dye (C7) in ethanol ( $\Phi_{\rm f}$  = 28%<sup>29</sup>) and corrected taking into account solvents' refractive indices. The long-wavelength absorption and fluorescence bands of the studied dyes in the "mirror" coordinates  $\varepsilon(v)/v - v$  and  $F(v)/v^4 - v$ , suggested by B. I. Stepanov,<sup>30</sup> were analysed by the method of moments<sup>29</sup> to calculate their gravity centres ( $M^{-1} = 10^7/v$ , where v is the band mean position in wavenumber) and the deviations from the band gravity centre ( $\sigma$ ) – the characteristic of bandwidth, which in the case of the "ideal" Gauss, Poisson or Gaussian curves is equal to a half of their full width at half-maximum. The parameter  $M^{-1}$  can be used to characterize relative positions of the spectral bands of different shapes, which is often the case of merocyanines. The value  $\sigma$  allows comparing bandwidth of spectral bands of different shapes. <sup>1</sup>H NMR spectra were measured with a Varian VXR-300 or Varian VXR-400 instruments; the residual solvent peaks of [D<sub>6</sub>]DMSO ( $\delta_{\rm H}$  = 2.50 ppm) and CDCl<sub>3</sub> ( $\delta_{\rm H}$  = 7.26 ppm) were used as an internal standard.

DFT/TD-DFT calculations were performed with the Gaussian 09 program suite using the hybrid B3LYP functional and the double- $\zeta$  basis set 6-31G(d,p).<sup>31</sup> The solvent effect was accounted for by the integral equation formalism polarizable continuum model (IEFPCM).<sup>32</sup> The ground-state geometry optimizations (the convergence criterion on the residual forces was set to  $1 \times 10^{-5}$  Hartree-Bohr<sup>-1</sup> or Hartree-Rad<sup>-1</sup>) were followed by frequency calculations to verify that the found stationary points were true minima. In the case of fast absorption processes (Franck–Condon principle), the nuclear relaxation was avoided by employing state-specific solvation calculations in terms of fast electronic cloud reorganizations and slow solvent and solute nuclear motions.<sup>33</sup> The NBO atomic charges were obtained using the embedded in Gaussian-09 algorithm.<sup>34</sup>

Solvents for spectral measurements were purified by the methods given in ref. **35**. Column chromatography was performed on Silica gel 60 (Merck). The purity of dyes **1–11** was checked by TLC (Silufol UV-254, CH<sub>2</sub>Cl<sub>2</sub> as an eluent). Melting (decomposition) points were measured using the open capillary method and are not corrected.

## 2.1.Synthetic procedures

Merocyanines **1**, **2** and anionic dyes **10**, **11** were described elsewhere before;<sup>20,24,25</sup> they were synthesized and purified according to the known procedures and characterized only by melting points and <sup>1</sup>H NMR spectra. The intermediate hemicyanines were mostly used in the following synthetic stages without further purification.

## 4-[(dimethylamino)methylene]-1,2-diphenyl-3,5-

pyrazolidinedione (12): 1,2-diphenyl-3,5-pyrazolidinedione

(0.5 g, 2 mmol) was dissolved in a mixture of acetic anhydride (3 mL) and DMF (2 mL), and the solution Was heated at 1235 °C for 2 h. After cooling, the reaction mixture was diluted with brine. The crude product was filtered out, washed with water, dried, and chromatographed on silica gel (CH<sub>2</sub>Cl<sub>2</sub>) to afford **12** as a white solid; yield: 0.32 g, 52%. <sup>1</sup>H NMR:  $\delta_{\rm H}$  (300 MHz; CDCl<sub>3</sub>) 7.58 (1H, s), 7.45-7.33 (4H, m), 7.33-7.23 (4H, m), 7.15-7.05 (2H, m), 3.83 (3H, s), 3.35 (3H, s).

4-(3-Acetanilidoallylidene)-1,2-diphenyl-3,5-

**pyrazolidinedione** (13): 1,2-diphenyl-3,5-pyrazolidinedione (0.5 g, 2 mmol) and N-(3-phenyliminopropenyl)aniline hydrochloride (0.51 g, 2 mmol) were heated under reflux in acetic anhydride (6 mL) for 5 min. After cooling, the solution was diluted with diethyl ether (15-20 mL) and left in the fridge overnight. The precipitate was filtered out, washed with diethyl ether, and dried to afford 13 as a dark-yellow solid; yield: 0.62 g, 73%. <sup>1</sup>H NMR: δ<sub>H</sub> (300 MHz; CDCl<sub>3</sub>) 8.49 (1H, d, *J* = 13.7 Hz), 7.83 (1H, d, *J* = 12.4 Hz), 7.61-7.52 (3H, m), 7.37-7.19 (10H, m), 7.15-7.06 (2H, m), 6.64 (1H, dd, *J* = 13.7, 12.4 Hz), 2.00 (3H, s). **4-(5-Acetanilido-2,4-pentadienylidene)-1,2-diphenyl-3,5-**

**pyrazolidinedione** (14):<sup>20</sup> from 1,2-diphenyl-3,5pyrazolidinedione (0.5 g, 2 mmol) and N-(5-phenylimino-1,3pentadienyl)aniline hydrochloride (0.57 g, 2 mmol). Crude dye 14 was obtained as a red solid; yield: 0.58 g, 63%. <sup>1</sup>H NMR:  $\delta_{\rm H}$ (300 MHz; CDCl<sub>3</sub>) 8.15 (1H, d, *J* = 13.8 Hz), 7.69 (1H, d, *J* = 12.4 Hz), 7.61-7.46 (4H, m), 7.40-7.24 (9H, m), 7.22-7.09 (4H, m), 5.34 (1H, dd, *J* = 13.8, 11.4 Hz), 1.97 (3H, s).

### 1,2-Diphenyl-4-[(2E)-2-(1,3,3-trimethyl-2-

indolinylidene)ethylidene]-3,5-pyrazolidinedione (1):<sup>24</sup> orange crystals; yield: 66 mg, 76%; mp 258-259 °C (from ethanol). <sup>1</sup>H NMR:  $\delta_{\rm H}$  (300 MHz; CDCl<sub>3</sub>) 8.25 (1H, d, *J* = 14.3 Hz), 7.50-7.40 (4H, m), 7.40-7.27 (7H, m), 7.20 (1H, t, *J* = 7.7 Hz), 7.16-7.05 (2H, m), 7.02 (1H, d, *J* = 7.9 Hz), 3.51 (3H, s), 1.71 (6H, s).

# 1,2-Diphenyl-4-[(2E,4E)-4-(1,3,3-trimethyl-2-indolinylidene)-

**2-butenylidene]-3,5-pyrazolidinedione** (2):<sup>25</sup> a dark-green solid; yield: 47 mg, 51%; mp 182-184 °C (from ethanol). <sup>1</sup>H NMR:  $\delta_{\rm H}$  (300 MHz; CDCl<sub>3</sub>) 7.78 (1H, t, *J* = 13.1 Hz), 7.73 (1H, d, *J* = 12.8 Hz), 7.57 (1H, t, *J* = 13.1 Hz), 7.47-7.40 (4H, m), 7.34-7.25 (6H, m), 7.16-7.06 (3H, m), 6.92 (1H, d, *J* = 7.9 Hz), 5.87 (1H, d, *J* = 12.9 Hz), 3.36 (3H, s), 1.65 (6H, s).

1,2-Diphenyl-4-[(2E,4E,6E)-6-(1,3,3-trimethyl-2-

## indolinylidene)-2,4-hexadienylidene]-3,5-pyrazolidinedione

(3): 2-(6-acetanilido-1,3,5-hexatrienyl)-1,3,3-trimethyl-3Hindolium tetrafluoroborate<sup>36</sup> (92 mg, 0.2 mmol) and 1,2diphenyl-3,5-pyrazolidinedione (55 mg, 0.22 mmol) were dissolved in CH<sub>2</sub>Cl<sub>2</sub>. Anhydrous potassium carbonate (200 mg, 1.45 mmol) was added, and the solution was stirred at room temp. for 3 h, filtered, chromatographed on silica gel (CH<sub>2</sub>Cl<sub>2</sub>), and crystallized from ethanol to afford **3** as a peacock green solid; yield: 27 mg, 28%; mp 159-160 °C (decomp.). Calcd. for C<sub>32</sub>H<sub>29</sub>N<sub>3</sub>O<sub>2</sub> (487.60): C 78.82, H 6.00, N 8.62; found: C 78.74, H 6.07, N 8.49. <sup>1</sup>H NMR:  $\delta_{\rm H}$  (300 MHz; CDCl<sub>3</sub>) 7.70 (1H, d, J = 12.3 Hz), 7.63 (1H, t, J = 12.6 Hz), 7.49-7.38 (5H, m), 7.35-7.19 (7H, m), 7.15-7.07 (2H, m), 7.03 (1H, t, J = 7.5 Hz), 6.83 (1H, d, J = 7.8 Hz), 6.37 (1H, t, J = 12.7 Hz), 5.66 (1H, d, J = 12.7 Hz), 3.30 (3H, s), 1.63 (6H, s). <sup>1</sup>H NMR:  $\delta_{\rm H}$  (300 MHz; [D<sub>6</sub>]-DMSO) 7.87 (1H, t, J = 13.0 Hz), 7.70 (1H, t, J = 12.5 Hz), 7.51 (1H, d, J = 7.4 Hz), 7.47-

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7.23 (12H, m), 7.16-7.07 (3H, m), 6.46 (1H, t, J = 12.6 Hz), 6.12 (1H, d, J = 13.4 Hz), 3.48 (3H, s), 1.60 (6H, s).

4-[2-(1,3-Diphenyl-2-benzoimidazolylidene)ethylidene]-1,2-

diphenyl-3,5-pyrazolidinedione (4): a solution of 2-methyl-1,3diphenylbenzoimidazolium chloride (80 mg, 0.25 mmol) and hemicyanine 12 (77 mg, 0.25 mmol) in pyridine (4 mL) was heated under reflux for 2 h. The crude product was precipitated with water, filtered out, and chromatographed on silica gel (CH<sub>2</sub>Cl<sub>2</sub>) to afford **4** as a bright-yellow solid; yield: 38 mg, 28%; mp >270 °C. Calcd. for C<sub>36</sub>H<sub>26</sub>N<sub>4</sub>O<sub>2</sub> (546.63): C 79.10, H 4.79, N 10.25; found: C 78.98, H 4.89, N 10.13. <sup>1</sup>H NMR: δ<sub>H</sub> (300 MHz; CDCl<sub>3</sub>) 6.88 (1H, d, J = 15.0 Hz), 6.92-7.07 (5H, m), 7.11-7.23 (4H, m), 7.23-7.36 (6H, m), 7.52-7.60 (4H, m), 7.65-7.78 (6H, m). <sup>1</sup>H NMR: δ<sub>H</sub> (300 MHz, [D<sub>6</sub>]-DMSO) 7.84-7.70 (10H, m), 7.44-7.37 (2H, m), 7.24-7.06 (10H, m), 7.04-6.96 (2H, m), 6.72 (1H, d, J = 15.3 Hz), 6.69 (1H, d, J = 15.3 Hz).

## 4-[(2E)-4-(1,3-Diphenyl-2-benzoimidazolylidene)-2-

butenylidene]-1,2-diphenyl-3,5-pyrazolidinedione (5): а solution of 2-methyl-1,3-diphenylbenzoimidazolium chloride (80 mg, 0.25 mmol), hemicyanine 13 (106 mg, 0.25 mmol), and triethylamine (50 mg, 0.5 mmol) in pyridine (3 mL) was heated for 5 min under reflux. Upon cooling, water (10-12 mL) was added to the mixture that was then left at room temp. overnight. The precipitate was filtered out and crystallized from methanol to give 5 as an ashy-pink solid; yield: 60 mg, 42%; mp >270 °C. Calcd. for C<sub>38</sub>H<sub>28</sub>N<sub>4</sub>O<sub>2</sub> (572.67): C 79.70, H 4.93, N, 9.78; found: C 79.58, H 4.81, N, 9.63. <sup>1</sup>H NMR:  $\delta_{\rm H}$  (300 MHz; CDCl<sub>3</sub>) 7.78-7.68 (6H, m), 7.57-7.49 (4H, m), 7.44-7.35 (4H, m), 7.33-7.16 (6H, m), 7.12-6.95 (5H, m), 6.84 (1H, d, J = 13.8 Hz), 6.51 (1H, dd, J = 14.3, 12.1 Hz), 5.48 (1H, d, J = 14.3 Hz).

## 4-[(2E,4E)-6-(1,3-Diphenyl-2-benzoimidazolylidene)-2,4-

hexadienylidene]-1,2-diphenyl-3,5-pyrazolidinedione (6): the synthesis is analogous to that of dye 5 (only with hemicyanine 14). Because of very low solubility, the proper crystallization of 6 was not performed. Instead, the precipitated dye was washed with hot ethanol (3×5 mL) and then with CH<sub>2</sub>Cl<sub>2</sub> (2×5 mL). A greenish dark-gray solid; yield: 38 mg, 25%; mp 228-229 °C. Calcd. for  $C_{40}H_{30}N_4O_2$  (598.71): C 80.25, H 5.05, N 9.36; found: C 80.31, H 4.93, N 9.23. <sup>1</sup>H NMR: δ<sub>H</sub> (300 MHz; [D<sub>6</sub>]-DMSO) 7.87-7.74 (10H, m), 7.54-7.46 (2H, m), 7.31-7.16 (10H, m), 7.03-6.94 (2H, m), 6.81 (1H, t, J = 12.8 Hz), 6.67 (1H, d, J = 13.8 Hz, 1H), 6.36-6.21 (2H, m), 6.00 (1H, dd, J = 14.0, 10.9 Hz), 5.78 (1H, d, J = 14.5 Hz).

### 4-[(2E)-2-(1-benzyl-2-benzo[cd]indolylidene)ethylidene]-1,2-

46 diphenyl-3,5-pyrazolidinedione (7): a solution of 1-benzyl-2-[2-47 (dimethylamino)vinyl]benzo[cd]indolium tetrafluoroborate<sup>37</sup> 48 (80 mg, 0.2 mmol) and 1,2-diphenyl-3,5-pyrazolidinedione (50 49 mg, 0.2 mmol) in pyridine (3 mL) was heated for 30 min under 50 reflux. Upon cooling, water-ethanol (1:1) (10 mL) was added 51 dropwise with stirring and the mixture was put for 2 h in a 52 fridge. The obtained dye was filtered out, washed with cold 53 ethanol and dried to afford a green-gray solid with metallic 54 shine; yield: 76 mg, 73%; mp 253-254 °C. Calcd. for C<sub>35</sub>H<sub>25</sub>N<sub>3</sub>O<sub>2</sub> 55 (519.60): C 80.90, H 4.85, N 8.09; found: C 80.72, H 4.80, N 8.20. 56 <sup>1</sup>H NMR:  $\delta_{\rm H}$  (300 MHz; CDCl<sub>3</sub>) 8.76 (1H, d, J = 13.8 Hz), 8.48 (1H, 57 d, J = 7.3 Hz), 8.02 (1H, d, J = 8.1 Hz), 7.78 (1H, d, J = 13.8 Hz), 58 7.76 (1H, t, J = 7.7 Hz), 7.56 (1H, d, J = 8.3 Hz), 7.51-7.41 (5H, m), 59

4-[(2E,4E)-4-(1-benzyl-2-benzo[cd]indolylidene)-2-

# butenylidene]-1,2-diphenyl-3,5-pyrazolidinedione

(8): а 1-benzyl-2-methylbenzo[cd]indolium solution of tetrafluoroborate (69 mg, 0.2 mmol) and hemicyanine 13 (85 mg, 0.2 mmol) in pyridine (3 mL) was heated for 5 min under reflux. The product was precipitated with water, filtered out, dried, and chromatographed on silica gel (CH<sub>2</sub>Cl<sub>2</sub>). After solvent removal, methanol (7 mL) was added to the residue and the mixture was heated under reflux for 3-5 min, cooled, and the dye was filtered out and dried. A green-gray solid; yield: 46 mg, 42%; mp 246-247 °C. Calcd. for C<sub>37</sub>H<sub>27</sub>N<sub>3</sub>O<sub>2</sub> (545.64): C 81.45, H 4.99, N 7.70; found: C 81.34, H 5.07, N 7.67. <sup>1</sup>H NMR:  $\delta_{
m H}$ (300 MHz; [D<sub>6</sub>]-DMSO) 8.80 (1H, d, J = 7.4 Hz), 8.62 (1H, t, J = 13.2 Hz), 8.12 (1H, d, J = 7.8 Hz), 8.11 (1H, d, J = 13.3 Hz), 7.82 (1H, t, J = 7.8 Hz), 7.67-7.51 (3H, m), 7.40-7.25 (14H, m), 7.17-7.10 (2H, m), 6.65 (1H, d, J = 13.1 Hz), 5.48 (2H, s).

# 4-[(2E,4E,6E)-6-(1-benzyl-2-benzo[cd]indolylidene)-2,4-

hexadienylidene]-1,2-diphenyl-3,5-pyrazolidinedione (9): a 1-benzyl-2-methylbenzo[cd]indolium solution of tetrafluoroborate (69 mg, 0.2 mmol) and hemicyanine 14 (90 mg, 0.2 mmol) in acetonitrile (4 mL) was heated for 10 min under reflux in the presence of sodium acetate (250 mg, 3 mmol). The crude product was precipitated with water, filtered out, dried, chromatographed twice on silica gel (CH<sub>2</sub>Cl<sub>2</sub> with 0.5to-2.0 v.v. % of MeOH), and crystallized from acetonitrilemethanol (1:2) to afford 9 as a dark green solid; yield: 16 mg, 14%; mp 190-191 °C. Calcd. for C<sub>39</sub>H<sub>29</sub>N<sub>3</sub>O<sub>2</sub> (571.68): C 81.94, H 5.11, N 7.35; found: C 81.88, H 5.06, N 7.30. <sup>1</sup>H NMR:  $\delta_{\rm H}$ (400 MHz; CDCl<sub>3</sub>) 8.04 (1H, d, J = 7.3 Hz), 7.85 (1H, d, J = 8.1 Hz), 7.78 (1H, dd, J = 13.8, 12.5 Hz), 7.76-7.66 (3H, m), 7.44-7.33 (8H, m), 7.33-7.28 (6H, m), 7.25-7.21 (2H, m), 7.17-7.09 (2H, m), 6.74 (1H, dd, J = 6.8, 1.0 Hz), 6.52 (1H, dd, J = 13.8, 11.7 Hz), 6.08 (1H, d, J = 12.5 Hz), 5.15 (2H, s). <sup>1</sup>H NMR:  $\delta_{\rm H}$  (400 MHz; [D<sub>6</sub>]-DMSO) 8.42 (1H, d, J = 7.4 Hz), 8.11 (1H, t, J = 12.9 Hz), 8.00 (1H, d, J = 8.1 Hz), 7.83-7.73 (2H, m), 7.61 (1H, d, J = 12.8 Hz), 7.57-7.45 (3H, m), 7.40-7.30 (11H, m), 7.29-7.22 (3H, m), 7.19-7.12 (3H, m), 6.70 (1H, t, J = 12.7 Hz), 6.70 (1H, t, J = 12.7 Hz), 6.50 (1H, d, J = 12.7 Hz), 5.35 (2H, s).

Triethylammonium (E)-4-(3-(3,5-dioxo-1,2-diphenyl-4pyrazolidinylidene)-1-propenyl)-5-oxo-1,2-diphenylpyrazol-3olate (10):<sup>20</sup> a dark-orange solid; yield: 33 mg, 26%; mp 230-231 °C (from methanol, decomp.) (lit. mp 233-235 °C). <sup>1</sup>H NMR:  $\delta_{\rm H}$ (300 MHz; CDCl<sub>3</sub>) 9.40 (1H, br.s), 8.20 (1H, t, J = 13.7 Hz), 7.75 (2H, d, J = 13.7 Hz), 7.44-7.35 (8H, m), 7.32-7.21 (8H, m), 7.15-7.02 (4H, m), 2.93 (6H, q, J = 7.4 Hz), 1.08 (9H, t, J = 7.4 Hz). <sup>1</sup>H NMR:  $\delta_{\rm H}$  (300 MHz; [D<sub>6</sub>]-DMSO) 8.91 (1H, br.s), 8.15 (1H, t, J = 13.7 Hz), 7.52 (2H, d, J = 13.7 Hz), 7.39-7.24 (16H, m), 7.14-7.03 (4H, m), 1.16 (9H, t, J = 7.2 Hz).

#### Triethylammonium 4-((1E,3E)-5-(3,5-dioxo-1,2-diphenyl-4pyrazolidinylidene)-1,3-pentadienyl)-5-oxo-1,2-

diphenylpyrazol-3-olate (11):<sup>20</sup> a dark-bronze solid; yield: 14 mg, 10%; mp 125-126 °C. <sup>1</sup>H NMR:  $\delta_{\rm H}$  (300 MHz; CDCl<sub>3</sub>) 9.64

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(1H, br.s), 7.54-7.19 (21H, m), 7.14-7.02 (4H, m), 2.73 (6H, q, *J* = 7.1 Hz), 1.11 (9H, t, *J* = 7.1 Hz).

# 3. Results and discussion

In order to track the regularities connecting the properties of such merocyanines with the structural parameters such as the donor strength of the group D and the polymethine chain length, three vinylogous series of dyes - derived from medium electron-donating indole (1-3), strongly electron-donating benzimidazole (4–6), and weakly electron-donating benzo[cd]indole (7-9) (Scheme 2) - have been synthesized and their spectral-fluorescence properties have been studied in solvents of different polarities (Table 1, Fig. S1-S9, S13-S21 in ESI). In order to calculate Brooker's deviations<sup>36</sup> of merocyanines' spectral bands, parent anionic dyes 10, 11 (Scheme 3) have also been obtained (Table 1, Fig. S10, S11, S22, S23 in ESI). The spectral data for the parent cationic dyes are taken from ref. 28.

Judging by the vicinal spin-spin coupling constants for the polymethine chain H-atoms, which are close to or exceed 12 Hz, the all-trans conformation dominate for molecules 1-9 in the solutions in both low-polarity CDCl<sub>3</sub> and high-polarity (CD<sub>3</sub>)<sub>2</sub>SO. The Bouguer–Lambert–Beer law holds for merocyanines 1-9 in the concentration range from 1×10<sup>-6</sup> to 5×10<sup>-5</sup> mol/L in dichloromethane (DCM), DMF, and ethanol; for compounds 1-3, 7, 9 also in toluene. In *n*-hexane, and in toluene for dyes 4–6, 8, the concentration-dependence study has not been performed because of the low solubility. Still, their aggregation in the solutions has not been observed, although there were signs of adsorption of some compounds on the cuvette walls (see ESI, Fig. S12). For anionic dyes 10, 11, the absorption bands in DCM at a concentration of 10<sup>-5</sup> mol/L are broadened as compared to those in high-polarity solvents (Table 1), which can be explained by the beginning of ion-pair formation.<sup>38</sup>

# 3.1. Electronic structure and solvatochromism

For merocyanines **1–3**, with the medium electron-donating indole residue, an increase in the solvent polarity results in

bathochromic shifts of the absorption bands  $by_{v}both_{i}\lambda_{a}$  and  $M_a^{-1}$ , their narrowing (a decrease in  $\sigma_a$ ), and growing of motar absorption (Table 1, Fig. S1–S3 in ESI). The deviations Da, an important characteristic of the electronic asymmetry of merocyanines,<sup>36</sup> decrease for them going from medium-polarity DCM to DMF and ethanol as the solvent. The degree of electronic asymmetry can also be estimated by a vinylene shift (VS): it is close to 100 nm for symmetric polymethine dyes and decreases with a deviation from the ideal polymethine structure A2.<sup>10,13,39</sup>. For merocyanines **1–3**, the VS values approach 100 nm only in DMF and ethanol and decrease going to less polar solvents. In the latter, a decrease in VS with the polymethine chain lengthening is also observed. For example, for the pairs of vinylogues 1 - 2 and 2 - 3 in toluene, the VS is equal to 88 nm (81.1 nm by band centres  $M_a^{-1}$ ) and 74 nm (54.2 nm), respectively.



Fig. 1. Absorption spectra of dyes 1–3 in *n*-hexane (blue solid) and ethanol (red dash).



Scheme 3. Molecular structures of anionic dyes 10 (n = 1) and 11 (n = 2).





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 Table 1. Characteristics<sup>[a]</sup> of the UV-Vis absorption and steady-state fluorescence bands of dyes 1–11 at 20°C

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Dye	Solvent	$\lambda_{a}$	ε×10⁻³	Da	$M_{a}^{-1}$	$\sigma_{a}$	$\lambda_{ m f}$	$arPsi_{ m f}$	Df	$M_{\rm f}^{-1}$ $\sigma_{\rm f}$ $\Delta v_{\rm s}$		
		(nm)	(m²/mol)	(nm)	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	(nm)	(%)	(nm)	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )	(cm <sup>-1</sup> )
1	<i>n</i> -Hexane	460	5.67	_	444.0	1240	475	0.005	_	501.2	1540	690
	Toluene	472	8.85	_	455.3	1170	487	0.009	_	510.4	1420	650
	DCM	473	9.38	_	457.0	1130	488	0.023	_	510.7	1210	650
	DMF	474	8.97	-	457.0	1130	492	0.071	-	518.5	1280	770
	EtOH	473	8.77	-	455.2	1120	493	0.073	-	521.0	1330	860
2	n-Hexane	536; 506	8.48; 6.55	-	507.1	1280	565	0.005	-	616.5	1510	960
	Toluene	560	11.1	-	536.4	1210	590	0.059	-	628.3	1120	910
	DCM	568	15.0	9.0	549.9	1050	592	0.22	6.50	614.7	930	710
	DMF	571	15.7	0.5	554.8	980	595	0.64	-0.50	613.8	910	710
	EtOH	570	17.2	-1.0	554.5	940	592	1.42	1.00	615.2	960	650
3	<i>n</i> -Hexane	601; 565	4.92; 6.05	-	552.3	1460	627; 678	0.003	-	717.4	1730	2950
	Toluene	634; 594	7.80; 7.22	-	590.6	1410	683	0.09	-	732.8	1360	1130
	DCM	662	12.6	18	626.3	1290	700	2.8	6.5	722.4	830	820
	DMF	673	17.1	2.5	644.6	1150	702	8.2	2.0	720.6	740	610
	EtOH	671	19.7	0	648.1	1030	698	16.5	1.5	715.0	710	580
4	<i>n</i> -Hexane	463	[b]	—	452.4	960	498	0.12	—	528.0	1850	1520
	Toluene	464	10.6	—	453.6	990	498	0.37	—	526.1	1660	1470
	DCM	455	9.37	—	441.6	1120	493	0.31	—	513.4	1460	1690
	DMF	450	8.29	—	435.8	1220	487	0.38	—	509.4	1550	1690
	EtOH	442	6.49	—	424.2	1480	486	0.26	—	508.4	1620	2050
5	n-Hexane	563	[b]	-	[b]	[b]	586	1.3	-	608.5	990	700
	Toluene	569	18.1	-	558.1	830	596	7.2	-	614.8	890	800
	DCM	557	15.1	6.5	541.6	1010	587	13.8	7.0	604.7	910	920
	DMF	545	10.8	15.5	523	1290	583	6.2	7.5	603.2	960	1200
	EtOH	532	7.85	25	502.6	1590	578	4.1	11.0	598.2	1030	1500
6	n-Hexane	658	[b]	_	[b]	[b]	683	2.8	_	713.2	890	560
	Toluene	680	20.3	—	661.8	950	706	49.0	—	718.3	810	540
	DCM	660	16.4	6	635.3	1140	696	58.5	4.0	712.5	760	780
	DMF	641	8.82	19	596.9	1600	693	44.0	6.0	710.0	790	1170
	EtOH	592	5.73	68	557.4	1990	686	25.7	9.0	705.3	890	2310
7	n-Hexane	579; 540	4.88; 4.58	_	539.8	1390	[C]	-	_	-	_	_
	Toluene	593; 551	5.79; 4.89	_	554.5	1300	[c]	_	_	_	_	_
	DCM	593; 551	6.69; 5.22	—	555.9	1260	611; 655	0.009	—	661.8	1250	500
	DMF	595; 553	6.52; 5.08	_	558.6	1250	614	0.018	_	663.1	1230	520
	EtOH	593; 551	7.87; 5.56	-	558.2	1220	607; 652	0.037	-	647.1	1170	390
8	<i>n</i> -Hexane	633; 596	[D]	_	582.1	1430	_[C]	_	-	_	_	_
	Toluene	665; 621	5.05; 6.63	_	610.7	1350	700	0.03	_	793.5	1540	750
	DCM	675; 627	6.73; 7.11	13	623.2	1330	707; 769	0.03	_	767.4	1210	670
	DMF	684; 633	7.57; 6.96	3.5	632.3	1310	711; 774	0.11	-	765.6	1080	560
	EtOH	685; 634	10.9; 7.41	-4.5	641.9	1200	705	0.17	_	759.2	1070	410
9	<i>n</i> -Hexane	635; 603	7.37; 7.14	_	603.4	1550	[C]	_	_	_	_	_
	Toluene	664	7.66	-	636.5	1570	[c]	_	_	_	_	_
	DCM	686	7.52	110.5	662.7	1600	_[c]	_	_	_	_	_
	DMF	704	7.37	93	681.6	1610	826	0.160	_	893.5	1010	2100
	EtOH	/80; 714	/./1; 8.10	/4	697.9	1520	818	0.091	_	868.7	890	600
10	DCM	502	13.0	_	491.3	970	526	0.11	_	545.4	1060	910
	DMF	501	14.7	_	492.7	840	519	0.14	_	540.8	1060	690
	EtOH	498	15.1	_	489	900	519	0.10	_	538.5	980	810
11	DCM	602	12.6	-	578.6	1260	630	5.3	-	647.4	750	740
	DMF	605	18.1	-	595	800	630	5.0	-	644.6	700	660
	EtOH	600	17.9	—	585.3	970	624	4.1	—	640.2	710	640

 $^{[a]}\lambda_a$  and  $\lambda_f$ , band maxima;  $D_a$  and  $D_f$ , Brooker's deviations;  $\Delta v_s$ , Stokes shift;  $\varepsilon$ , molar absorption; indexes "a" and "f" denote characteristics of absorption and fluorescence bands, respectively.  $^{[b]}$  Not determined because of low solubility.  $^{[c]}$  Below the detection limit.

The polymethine chain lengthening in the series 1-3 is accompanied by a noticeable broadening of the long-wavelength absorption bands in low-polarity *n*-hexane and toluene, caused by an increase in the relative intensity at the short-wavelength

edge of the band due to an increase in probability of higher vibronic transitions (Table 1, Fig. 1). In more polar solvents, the transition from 1 to 2 results in a decrease of  $\sigma_a$ , but when going from 2 to 3, the bandwidth increases even in ethanol.

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Based on their solvatochromism and trends in  $\sigma_a$ ,  $D_a$ , and VS, it can be concluded that the electronic structure of merocyanines **1–3** in the ground state S<sub>0</sub> varies within the A1–A2 range, approaching the structure A2 in high-polarity solvents. In addition, the  $\sigma_a$ ,  $D_a$ , and VS variations indicate that the contribution of the nonpolar polyene structure A1 increases for dyes **1–3** with the polymethine chain lengthening, at least in low- and medium-polarity solvents.

For imidazole-based merocyanine 4, a bathochromic shift by 1 nm (by both  $\lambda_a$  and  $M_a^{-1}$ ) is observed going from *n*-hexane to toluene as the solvent (Table 1). However, since toluene has much greater refractive index (1.497) as compared to that of nhexane (1.375), this shift must be explained by the Bayliss refractive index function,<sup>1</sup> not by an approach of dye's electronic structure to the ideal polymethine A2 in toluene. This assumption is justified by the smaller bandwidth ( $\sigma_a$ ) of **4** in *n*hexane, since  $\sigma$  does not depend on  $n_{\rm D}$ .<sup>29</sup> For higher vinylogues 5 and 6, the *n*-hexane-toluene bathochromic shifts are much greater: 6 nm (190 cm<sup>-1</sup>) and 22 nm (490 cm<sup>-1</sup>) by  $\lambda_a$ , respectively. For all three dyes 4-6, a further increase in the solvent polarity results in hypsochromic shifts of the absorption bands, their broadening, growing of deviations, and reducing of vinylene shifts (Table 1, Fig. S4-S6 in ESI). Hence, dye 4 has negative solvatochromism, while its vinylogues 5 and 6 have reverse solvatochromism in the chosen range of solvent polarities. Consequently, the electronic structures of molecules 5 and 6 are close to the ideal polymethine structure A2 in toluene, vary within the A2-A3 range in more polar solvents, and shift to the A1–A2 range in *n*-hexane.

Similarly to indole-based merocyanines 1-3, benzo[cd]indole derivatives 7-9 demonstrate positive solvatochromism. However, for the latter a noticeable structuring of the absorption bands due to an increase in the intensity of higher vibronic transitions is observed even for dimethinemerocyanine 7 (Fig. S7 in ESI). The absorption bands of dye 8 in low-polarity n-hexane and toluene are already similar in shape to those of carotenoids (Fig. S8). For higher vinylogue 9, the band is carotenoid-like even in high-polarity DMF (Fig. 2). Furthermore, the bandwidths ( $\sigma_a$ ) and deviations ( $D_a$ ) of absorption bands of dye 9 are much greater than those of its indole analogue 3, while the vinylene shifts by  $M_a^{-1}$  – it is incorrect to calculate VS by  $\lambda_a$  in this case, since the bandshape changes significantly and the maxima can correspond to different vibronic transitions are equal to only 21-56 nm in the pair 8 - 9. Hence, one can conclude that the contribution of the nonpolar-polyene structure A1 to the electronic structure of merocyanines 7-9 is higher than for indole-based dyes 1-3.

Note, that for dye 9, unlike to vinylogues 7 and 8, the long-50 wavelength absorption band broadens in the series n-hexane-51 toluene–DCM–DMF, its  $\sigma_a$  value decreases only when going to 52 ethanol as the solvent (Table 1). The maxima of the long-53 wavelength absorption band of merocyanine **9** in *n*-hexane are 54 distanced by 830 cm<sup>-1</sup>, while typically the vibronic sub-bands in 55 polymethines are distanced by 1050–1370 cm<sup>-1</sup>, which is 56 attributable to the symmetric carbon-carbon valence vibration 57 of the polymethine chain.<sup>39</sup> A possible explanation of this could 58 be the presence of several isomeric forms of dye 9 in low-59

polarity solvents. However, its <sup>1</sup>H NMR spectra in both CDCla and in [D6]-DMSO contain one set of signals, attributable to the polymethine chain H-atoms. Taking into account that for lessdipolar merocyanines timescale of thermal isomerization is in the range of seconds,<sup>40</sup> this indicates the great prevalence of the *all-trans* isomer of dye **9** in the solution. The deconvolution of the absorption bands of dye 9 in *n*-hexane and ethanol shows that they both can be fitted by a set of Gaussian components separated by 1040-1060 cm<sup>-1</sup> from each other (see ESI, Fig. S26, Table S1). The relative height of higher "vibronic" components is smaller in polar ethanol, reflecting a greater contribution of the ideal polymethine structure A2 in it. On the other hand, the bandwidths of "vibronic" components increase substantially in the polar solvent (Fig. S26), which can be indicative of an enhancement in solute-solvent interactions. It can be assumed therefore, that irregular changes of the absorption bandwidth for merocyanine 9 are determined by variable contributions from the vibronic and solute-solvent interactions.



Fig. 2. Absorption spectra of dye 9 in solvents of different polarities: *n*-hexane (black solid), toluene (red dash), DCM (blue dash-dot), DMF (magenta short-dash), and ethanol (olive dash-dot-dot).

Comparison of deviations ( $D_a$ ), VS, and bandwidths ( $\sigma_a$ ) of dyes **1–9** (Table 1) with those of their analogues comprising other strong acceptor groups, such as 1,3-dimethylbarbituric<sup>41</sup> and 1,3-diethylthiobarbituric,<sup>42</sup> reveals that the acceptor strength of 1,2-diphenyl-3,5-pyrazolidinedione residue is much lower than that of the 1,3-diethylthiorbarbituric residue, contrary to the data in ref. **16**. The same conclusion can also be made upon comparison of the shape of the absorption bands of dyeanalogues in the same solvent (Fig. 3, Fig. S27 in ESI).



**Fig. 3.** Normalized absorption spectra of dye **3** (black solid) and its analogues with the 1,3-dimethylbarbituric (blue dash) and 1,3-diethylthiobarbituric (red dash-dot) acceptor groups in *n*-hexane.

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The relative intensity of the maxima corresponding to the longest-wavelength (0-0) and higher (0-1, 0-2) vibronic transitions can be used as the characteristic of electronic asymmetry in this case. If the donor group remains the same, this asymmetry will be a criterion for the strength of the acceptor. Estimated in such a way electron-withdrawing abilities of the acceptor groups roughly correlate with the  $pK_a$  of the corresponding CH-acids (see ESI, Table S2).

Why does the order of the acceptor strength (acidity) presented in ref. 16 differ from that found in this study? Earlier, L.G.S. Brooker suggested using the deviation  $D_a$  of styryl dyes as a criterion for donor-acceptor properties of the terminal groups, since 4-dimethylaminophenyl was one of the least electron-donating ("weakly basic") residues.<sup>36</sup> There are typically two methine groups in the cationic styryl dyes used to evaluate the strength of donor groups and three methine groups in the corresponding parent dyes. Spatial hindrances in such molecules are insignificant and cannot affect position of the spectral band. On the contrary, in the case of the acceptor groups, both the styryls and parent anionic dyes contain only one methine group (Scheme 4). Spectral properties of such dyes should be determined not only by the donor-acceptor properties of the terminal groups, but also by the steric hindrances which cause a violation of the chromophore planarity and a distortion of the valence angles in it.



Scheme 4. Molecular structures of some styryl dyes (15, 16) and parent anionic dyes (17, 18; without counterions) used by L.G.S. Brooker and other authors to evaluate the strength of acceptor residues.

According to the PCM<sub>DCM</sub>/DFT/B3LYP/6-31G(d,p) calculations, the angle between the mean planes of the terminal heterocycles in molecules 17 and 18 is equal to 32° and 34° respectively (see ESI, Fig. S28), i.e. their non-planar distortions are nearly the same. The valence angle distortions in them are also very close, for example, the CCC-angle at the central methine atom of dyes 17 and 18 is equal to 132° and 133° respectively. It can be assumed therefore that the error in estimating the relative acceptor strength of 1,2-diphenyl-3,5pyrazolidinedione and 1,3-dimethyl-barbituric residues is caused by the different degrees of distortion of chromophores 15 and 16. Their PCM<sub>DCM</sub>/DFT/B3LYP/6-31G(d,p) geometry optimization results in nearly planar structures stabilized by the intramolecular CH---O hydrogen bond. Note that the calculated structure of **16** is very close to its X-ray data,<sup>43</sup> which testifies in favour of the chosen calculation method. The main difference between **15** and **16** lies in the chromophore valence angles, which are more distorted in the latter; for AMPR, the Methine CCC-angle is equal to 135° and 139° in **15** and **16** respectively. It should be assumed therefore that such distortions cause the additional hypsochromic shift of the absorption band, which should obviously be greater in **16**, resulting in an increase of its deviation and, hence, comparative underestimation of the barbituric residue acceptor strength.

# 3.2. Electronic structure and fluorescent properties

The signs of solvatofluorochromism of merocyanines **1–3** and **4–6** coincide with the signs of their solvatochromism (Table 1). At that, the ranges of solvatofluorochromic shifts are smaller. This is especially noticeable for negatively solvatochromic benzimidazole derivatives **4–6** in the series DCM–DMF–ethanol. Indeed, for polymethine dyes the solute–solvent interactions are usually diminished in the state S<sub>1</sub>, most probably due to the reduction of charge alternation in the chromophore.<sup>44</sup> For negatively solvatochromic merocyanines **4–6**, the dipolarity should decrease in the excited state as well, so the solute–solvent interactions abate even more. As a result, the Stokes shifts decrease for positively solvatochromic indole-based dyes **1–3** and increase for dyes **4–6** as the solvent polarity rises.

Growth of the VS and decrease of Brooker's deviations of the fluorescence bands of merocyanines **4–6** in comparison with those parameters of their absorption bands (Table 1) indicate that in the fluorescent state  $S_1$  their electronic structure becomes more symmetrical, i.e. the contribution of the ideal structure A2 increases. This tendency is also visible from TD-DFT calculations, which reveal greater electronic symmetry for the  $S_1^{FC}$  excited state of merocyanines.

Note, however, that in the pair **4** - **5** the fluorescence VS are smaller than the absorption VS in low- and medium-polarity solvents. Probably, this is caused by an additional bathochromic shift of the fluorescence bands of merocyanine **4** due to a greater distortion of its chromophore planarity in the state S<sub>1</sub>. This assumption is supported by the considerable broadening of the fluorescence bands of dye **4** compared to its absorption bands (cf. the  $\sigma_a$  and  $\sigma_f$  values in Table 1). For its indole analogue **1** the absorption and fluorescence bandwidths are rather close while for higher vinylogues **2**, **3**, **5**, **6** the fluorescence become narrower than the absorption (Table 1, Fig. 4).



Fig. 4. Absorption (solid) and fluorescence (dash) spectra of dyes 4-6 in DCM.

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Benzo[*cd*]indole derivatives **7–9** have very low FQY, so their fluorescence spectra were not detected in all solvents (ESI, Fig. S19–S21). It is found that solvatofluorochromism of dyes **7–9** is also weakened as compared to their solvatochromism. At that, in the pair DMF–ethanol, their solvatofluorochromic shifts apparently depend mostly on the solvent refractive index (Table 1). The fluorescence VS are much higher than the absorption VS; for example, in DMF for the pair **8** - **9** they are equal to 115 nm and 20 nm respectively. The fluorescence bands are narrower than the corresponding absorption bands, at least for vinylogues **8** and **9** (Table 1). Hence, it can be deduced that the contribution of the structure A2 increases significantly for merocyanines **7–9** in the fluorescent state S<sub>1</sub>.

The FQYs of positively solvatochromic dyes 1-3 and 7-9 increase significantly upon the solvent polarity growth. For negatively/reversely solvatochromic benzimidazole derivatives **4–6**, the maximum  $\Phi_{\rm f}$  values are reached in toluene or DCM and then decrease in high-polarity DMF and ethanol (Table 1). The FQYs increase also upon the polymethine chain lengthening. This regularity is however violated for the pair 8 - 9, whose fluorescence bands lie in the longest-wavelength spectral range among the studied dyes. In accordance with the energy gap law, the nonradiative fluorescent-state energy dissipation via internal conversion should be enhanced for them. Another irregularity is observed in the series 1-3 in n-hexane, in which, as shown above, the contribution of the non-polar polyene structure A1 increases drastically going from dye 1 to vinylogues 2 and 3. An electronic asymmetry increase for positively solvatochromic merocyanines with the polymethine chain lengthening is most pronounced in low-polarity solvents. This results in a greater dependence of FQY on the solvent polarity for higher vinylogues. For example, going from *n*-hexane to ethanol as the solvent, the  $\Phi_{\rm f}$  value increases 14 times for dye 1, 280 times for 2, and 5400 times for 3.

The obtained data are consistent with the regularities revealed in our previous works, *viz*. the FQY of merocyanines increases when their electronic structure approaches the structure A2, which can be explained by both a decrease in vibronic interactions and an increase in the oscillator strength of the long-wavelength polymethine transition.<sup>2</sup>

. 1 ∰ 1 42 Comparing the FQYs of dyes 1-9 and their analogues based on 43 1,3-dimethylbarbituric and 1,3-diethylthiorbarbarituric 44 acids,45,46 one can notice that for positively solvatochromic 45 merocyanines **1–3** and **7–9** the  $\Phi_f$  values are much lower than 46 the corresponding (thio)barbiturates. 47 those for As abovementioned, the low fluorescence "brightness" of 1,2-48 diphenyl-3,5-pyrazolidinedione derivatives was observed in ref. 49 25, however an explanation was not suggested for this effect. 50

The major competitive channels for fluorescence decay in 51 merocyanine dyes are: (i) electron-vibrational relaxation of the 52 polymethine excited state; (ii) twisting and trans-cis 53 photoisomerization around the polymethine chain bonds;<sup>40</sup> (iii) 54 formation of the twisted intramolecular charge transfer (TICT) 55 states;<sup>47</sup> (*iv*) spin–orbital coupling (heavy atom) effects;<sup>48</sup> (v) 56 low-lying non-fluorescent  $n\pi^*$ -states associated with the lone 57 electron pairs on heteroatoms in the acceptor group, the 58 presence of which enhances internal conversion.<sup>49</sup> There are 59

also some singular cases of the enhancement of competitive non-radiative relaxation of the excited state  $10407 \times 1000$  for 1,3-indanedione derivatives, whose FQY decrease sharply in protic solvents, the mechanism of the fast non-radiative decay is proposed, based on the TD-DFT calculations, associated with the low-lying non-fluorescent  $\pi\pi^*$ -state, which mainly has HOMO->LUMO+1 character with the LUMO+1 localized at the 1,3-indanedione residue.<sup>50</sup>

In the present case, reasons i-iv can be ruled out. Thus, as shown hereinabove, the electronic structure of dyes 1-9 is rather close on the A1–A2–A3 scale to that of the corresponding 1,3-dimethylbarbituric derivatives, hence, vibronic interactions should be comparable for them. The hydrodynamic volume of the 1,2-diphenyl-3,5-pyrazolidinedione residue is not smaller than those of the (thio)barbituric residues, i.e. there is no evident reason for enhancing trans-cis photoisomerization of merocyanines based on the former. In addition, spectralfluorescent properties of dye 2 has been studied in highly viscous ethylene glycol as the solvent (Fig. S24, S25). Going from ethanol to ethylene glycol, the FQY of dye 2 increases from 1.4% to 4.0%. For comparison, the 1,3-dimethylbarbituric and 1,3diethylthiobarbituric analogues of **2** have the FQY of 14% and 16% in ethanol, respectively.<sup>45,46</sup> Hence, in the present case should be other fast competitive processes besides isomerization, absent for the dyes with, e.g., the barbituric acceptor groups. Then, molecules 1-9 do not comprise a common TICT-active group or a heavy spin-active atom. Therefore, to identify the cause(s) of their fast non-radiative decay, the TD-DFT calculations were performed.

## 3.3. Quantum-chemical calculations

The *all-trans* conformation of the polymethine chain was chosen as the initial geometry for optimization of molecules **1–9**. It is consistent with both their <sup>1</sup>H NMR spectra and the X-ray structural data for similar merocyanines.<sup>51</sup> According to the PCM/DFT-B3LYP/6-31G(d,p) calculations, the chromophores of dyes **1–9** are essentially planar in the ground state S<sub>0</sub>. The maximum planarity violation is observed for benzimidazole derivatives **4–6**, owing mainly to a torsion around the bond connecting the donor residue and the polymethine chain, which still does not exceed 3°.

The parameter of bond length alternation in the polymethine chain (BLA) characterizes the position of merocyanines within the A1–A2–A3 range: it is positive for the A1–A2 region, goes to zero for the ideal polymethine A2, and becomes negative for the A2–A3 region.<sup>52</sup> It is found that the calculated BLA values of molecules 1-9 (Table 2) are in good agreement with the conclusions about their electronic structure inferred from the study of their solvatochromism.

Thus, for positively solvatochromic merocyanines **1–3** and **7–9**, the BLA values are positive, increase with the polymethine chain lengthening, and decrease going from *n*-hexane to DCM and ethanol as the solvent. For dye **4** in *n*-hexane, the parameter BLA is equal to zero and becomes negative in more polar solvents. Then, for its reverse-solvatochromic vinylogues **5** and **6**, the BLA is positive in *n*-hexane and negative in DCM and ethanol. An increase in dipolarity of molecules **1–9** with the

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solvent polarity growth is also reflected in their dipole moments  $(\mu_D)$ . For dyes with the same polymethine chain length, charge alternation in the chromophore in the ground state S<sub>1</sub> should be proportional to the dipolarity. Its magnitude can be estimated as the sum of the absolute values of charges in the polymethine chain  $\Sigma |q_i|$  (see Table S3 in ESI for more detail). The  $\Sigma |q_i|$  values are maximal for benzimidazole merocyanines **4–6** and minimal for weakly electron-donating benzo[*cd*]indole derivatives **7–9** (Table 2). Like dipole moments, they increase in more polar solvents for all dyes **1–9**.

fall within the ranges of -4.6 to -5.6 eV and -1.6 to ric2e.9 neV respectively (Table 2), which are typical for most polyhethine dyes.<sup>54</sup> The highest levels of HOMO and LUMO are observed for the derivatives of strongly electron-donating benzimidazole **4**–**6**. In all three vinylogues series, the values of  $E_{\rm HOMO}$  increase and the values of  $E_{\rm LUMO}$  decrease upon the polymethine chain lengthening (Table 2), which results in a decrease of the energy gaps for higher vinylogues. The solvent dependence of  $E_{\rm HOMO}$  and  $E_{\rm LUMO}$  is most pronounced for highly dipolar merocyanines **4**–**6** and diminishes going to indole and benzo[*cd*]indole based dyes **1–3** and **7–9**, which indicates the stronger solute–solvent interactions for the former.

The energies of frontier molecular orbitals, HOMO and LUMO, are key parameters for organic light energy converters.<sup>53,54</sup> For merocyanines **1–9**, the DFT calculated  $E_{HOMO}$  and  $E_{LUMO}$  values

Dye	PCM solvent	BLA	$\mu_{ extsf{D}}$	$\mu_{D}^{*}$	$\Sigma  q_i $	$\Sigma  q_i ^*$	$\Delta q$	Еномо	Elumo	$\lambda_{calc}$
		(Å)	(D)	(D)				(eV)	(eV)	(nm)
1	n-Hexane	0.023	7.3	10.3	0.854	0.662	-0.342	-5.410	-2.081	492.2
	DCM	0.015	8.8	11.5	0.889	0.466	-0.067	-5.461	-2.150	401.2
	EtOH	0.012	9.2	11.8	0.895	0.473	-0.064	-5.477	-2.168	401.9
	EtOH(2) <sup>[b]</sup>	-0.004	5.6	7.3	0.920	0.491	-0.061	-5.574	-2.268	401.4
2	n-Hexane	0.035	10.3	10.4	0.945	0.812	-0.413	-5.172	-2.342	553.2
	DCM	0.020	13.0	15.8	1.011	0.571	-0.062	-5.196	-2.416	456.5
	EtOH	0.016	13.8	15.7	1.024	0.583	-0.067	-5.207	-2.435	454.9
	EtOH(2)	0.005	11.0	13.0	1.047	0.594	-0.049	-5.294	-2.534	458.5
3	n-Hexane	0.039	12.7	17.3	1.017	0.651	-0.064	-4.990	-2.508	501.9
	DCM	0.023	16.8	20.2	1.110	0.636	-0.048	-4.997	-2.590	512.0
	EtOH	0.018	18.0	21.0	1.132	0.648	-0.046	-5.006	-2.611	512.1
	EtOH(2)	0.008	15.9	18.1	1.162	0.672	-0.046	-5.086	-2.707	511.9
4	n-Hexane	0.000	9.7	9.3	1.063	0.870	-0.287	-5.020	-1.635	452.1
	DCM	-0.016	11.6	9.3	1.093	0.624	0.007	-5.187	-1.740	375.0
	EtOH	-0.020	12.1	7.3	1.097	0.895	-0.294	-5.234	-1.772	389.2
5	n-Hexane	0.011	14.0	13.2	1.193	0.761	0.002	-4.781	-1.955	442.7
	DCM	-0.010	17.7	16.3	1.233	0.756	0.009	-4.922	-2.069	434.3
	EtOH	-0.015	18.6	16.7	1.238	0.755	-0.001	-4.964	-2.096	436.5
6	n-Hexane	0.017	17.7	18.3	1.288	0.820	0.000	-4.615	-2.180	499.6
	DCM	-0.006	23.5	22.6	1.352	0.824	0.004	-4.732	-2.297	491.6
	EtOH	-0.013	22.1	22.4	1.355	0.822	0.001	-4.771	-2.321	493.8
7	n-Hexane	0.025	6.8	15.0	0.749	0.807	-0.262	-5.353	-2.737	658.8
	DCM	0.015	8.4	8.9	0.781	0.554	-0.011	-5.414	-2.798	495.5
	EtOH	0.012	8.7	9.1	0.788	0.561	-0.011	-5.433	-2.816	493.4
8	n-Hexane	0.035	8.9	10.7	0.803	0.579	-0.024	-5.141	-2.806	535.7
	DCM	0.023	11.5	12.7	0.869	0.609	-0.010	-5.175	-2.871	541.0
	EtOH	0.020	12.2	13.5	0.885	0.614	-0.003	-5.188	-2.889	541.8
9	<i>n</i> -Hexane	0.038	10.8	13.7	0.860	0.605	-0.065	-4.987	-2.861	577.0
	DCM	0.027	14.3	16.8	0.951	0.622	-0.029	-5.002	-2.929	588.2
	FtOH	0.023	15 3	174	0 973	0 640	-0.021	-5.011	-2 9/9	580 (

<sup>[a]</sup> BLA, bond length alternation in the polymethine chain;  $\mu_D$ , dipole moment;  $\Sigma |q_i|$ , sum of absolute values of charges in the polymethine chain (see ESI for more detail);  $\Delta q$ , sum of charge alternations in the polymethine chain upon the  $S_1^{FC} \leftarrow S_0$  transition;  $E_{HOMO}$ ,  $E_{LUMO}$ , calculated energy levels of the frontier molecular orbitals;  $\lambda_{calc}$ , calculated wavelength of the  $S_1^{FC} \leftarrow S_0$  transition; the values corresponding to the state  $S_1^{FC}$  are marked with an asterisk. <sup>[b]</sup> Calculations marked as EtOH(2) were performed with ethanol as the PCM solvent and with two molecules of methanol H-bonded to the two carbonyls of the acceptor moiety, the dipole moments  $\mu_D$  for these tasks are characteristics of the whole "cluster", not of an individual merocyanine molecule.

The TD-DFT energy of the long-wavelength electronic transition in polymethine dyes is known to be systematically overestimated.<sup>44,55,56</sup> This is generally explained by the nature of the polymethine  $\pi\pi^*$ -transition, which is accompanied by both the light-induced charge resonance, i.e. the redistribution of electron density between the even and odd positions through the chromophore, and, in the case of asymmetric dyes, the light-induced intramolecular charge transfer.<sup>13,57</sup> A comparison of the experimental absorption maxima  $\lambda_a$  of dyes **1–9** (Table 1) and the PCM/TD-B3LYP calculated energies of the  $S_1^{FC} \leftarrow S_0$  electronic transitions  $\lambda_{calc}$  (Table 2) shows the same issue. There are, however, noticeable irregularities in the  $\lambda_{calc}$  array. The values of  $\lambda_{calc}$  are higher than expected for merocyanines **1**, **2**, **4**, **7** in *n*-hexane and for dye **4** in ethanol. The

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 $\lambda_{\text{calc}}$  of dye **1** in *n*-hexane even exceeds the experimental maximum of its absorption band in this solvent.

An analysis of the electronic transitions in molecules **1–9** has shown that the non-fluorescent  $n\pi^*$ -states are higher than the polymethine  $\pi\pi^*$ -states even in low-polarity *n*-hexane, i.e. they cannot possibly be the cause of their low fluorescence. Indeed, the FQYs of dyes **1–3** are comparatively low even in ethanol, in which the  $n\pi^*$ -excitation should be much suppressed due to the solute–solvent hydrogen bond formation.

However, it has been found that there is a low-lying forbidden  $\pi\pi^*$ -transition in molecules **1–9**, the main contribution to which gives the HOMO-1 $\rightarrow$ LUMO excitation, from the MO located on the acceptor 1,2-diphenyl-3,5-pyrazolidinedione residue (Fig. 5, Fig. S29–S31 in ESI). Since the energy of this transition is very close to the energy of the polymethine  $\pi\pi^*$ -transition, they become vibronically coupled (proximity effect).<sup>[58]</sup> Close excited states of the same spin multiplicity S<sub>1</sub> and S<sub>2</sub> are connected through a nonadiabaticity integral, and internal conversion of the fluorescent state should be noticeably enhanced due to nonadiabatic coupling interactions.



Fig. 5. Molecular orbitals of dye 1 (PCM $_{\text{DCM}}/\text{DFT-B3LYP/6-31G}(d,p),$  contour value is 0.03 bohr=3/2).

The different nature of the long-wavelength transitions in molecules **1–9** can be traced by the charge alternation in the polymethine chain upon the  $S_1^{FC} \leftarrow S_0$  transition. For a polymethine transition, the electron density should increase on the even atoms of the chromophore and decrease on the odd ones (light-induced charge resonance).<sup>13</sup> The PCM/TD-B3LYP calculations are consistent with this rule. As a result, the charge alternation in the polymethine chain decreases in the excited state (cf. the parameters  $\Sigma |q_i|$  and  $\Sigma |q_i|^*$  in Table 2). More significantly, the net charge change in the polymethine chain is very small (see the parameter  $\Delta q$  in Table 2). This regularity is

violated if the transition  $S_1^{FC} \leftarrow S_0$  is not a polymethine-type transition, for example, for dyes **1**, **4**, **7** in P-hexame/C9NJ03275D To study the states  $S_1$  and  $S_2$ , we used the PCM/TD-DFT calculations with a linear-response solvation. According to them, in *n*-hexane for dyes **1**, **2**, **4**, **7** the main contribution to the state  $S_1$  is from the HOMO-1 $\rightarrow$ LUMO excitation. In other cases, the longest-wavelength transition is the polymethine transition and comes mainly from the HOMO $\rightarrow$ LUMO excitation. At that, the separation of the states  $S_1$  and  $S_2$ increases with the polymethine chain lengthening and the solvent polarity growth. The energy difference between these states depends also on the donor group of merocyanines, being the smallest for indole-based merocyanines and the largest for benzimidazole derivatives **5**, **6**.

Since TD-DFT approach has many limitations for large conjugated systems, to verify the TD-DFT results, for merocyanine **2** the excitation energies has been calculated also at the second-order approximate coupled-cluster (CC2) level<sup>59</sup> with the def2-TZVP basis set. This calculation was performed using the Turbomole program version 6.4.<sup>60</sup> The CC2 was shown to give from all second-order methods the smallest mean absolute errors for adiabatic excitation energies.<sup>61</sup>

The molecular geometry of dye **2** was taken from the PCM<sub>DCM</sub>/DFT-B3LYP/6-31G(d,p) optimization. It has been found that the CC2 excitations in molecule **2** are very similar to those, obtained using the TD-DFT. Namely, the CC2 has also shown that the longest-wavelength (2.648 eV, 468 nm) singlet transition in dye **2** is the dipole forbidden  $\pi\pi^*$ -transition, the main contribution to which gives the HOMO-1→LUMO excitation, the same as in the TD-DFT calculation. The polymethine HOMO→LUMO transition (2.687 eV, 461 nm) is the second one. Again, the CC2 calculation shows intermixing of these transitions, with the HOMO→LUMO giving 15.3% contribution to the latter. Hence, our conclusions, based on the TD-DFT calculations are supported by the advanced *ab initio* second-order method.

Thus, the calculations have allowed us to find the probable reason of the fast non-radiative decay in merocyanines based on 1,2-diphenyl-3,5-pyrazolidinedione. Still, since in molecules **1–9** the HOMO-1 is partially localized on the phenyl substituents of the acceptor group (Fig. 5), the questions arise as to what the effect of these substituents is and whether this decay pathway arises if phenyl substituents are introduced into the barbituric acceptor group. In order to clarify these points, the PCM<sub>DCM</sub>/(TD)DFT-B3LYP calculations were carried out for four model molecules comprising the indole donor group and different acceptor groups (Scheme 5, Fig. S32, S33 in ESI).

It is found that disruption of conjugation of the phenyl groups with pyrazolidinedione (structure **19**) or even their replacement with the methyl groups (structure **20**) does not increase substantially the separation of the forbidden HOMO-1 $\rightarrow$ LUMO transition from the polymethine transition. Hence, such chemical modifications should not enhance fluorescence of merocyanines **19** and **20** in comparison with that of dye **2**. For barbituric derivatives **21** and **22**, the next to the polymethine transition is the forbidden n $\pi^*$ -transition, which is separated

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from the former by a more than 1 eV gap and, consequently, should not affects dyes' fluorescence ability. This result suggests that the group responsible for the fluorescence quenching of pyrazolidinedione merocyanines is the fragment (O=C)N-N(C=O) by itself, rather than, for example, the azo-chromophore that can be discerned in molecules 1-9.



# 4. Conclusions

A study of the absorption and fluorescence solvatochromism of the three synthesized vinylogous series of merocyanines comprising the 1,2-diphenyl-3,5-pyrazolidinedione residue as the acceptor group has revealed that the latter, contrary to the literature data,<sup>16</sup> is not a record-strong acceptor. This residue is shown to be comparable by an electron-withdrawing ability to the barbituric or 1,3-dialkylbarbituric one, yielding to the thiobarbituric acceptors. The inaccurate estimation of the relative strength of some acceptor groups in classical studies is rationalized by the steric hindrances in the monomethine anionic dyes and monomethine styryl dyes, UV–Vis maxima of which were used as the key experimental parameters and yet depended unforeseeably on the spatial requirements of an acceptor residue.

ished on US It is found that the fluorescence quantum yields of indole- and benzo[cd]indole-based dyes 1-3 and 7-9 are significantly lower than those of relative merocyanines with the barbituric and thiobarbituric acceptor groups. The PCM/TD-B3LYP calculations ์ 42 have revealed that the probable reason of this is the fast non-43 radiative decay, caused by the presence of the low-lying  $\pi\pi^*$ -44 state, associated with the forbidden transition from the 45 HOMO-1 localized on the acceptor 1,2-diphenyl-3,5-46 pyrazolidinedione fragment. This result has been verified by the 47 second-order approximate coupled-cluster (CC2) calculation performed for dye 2. According to the TD-B3LYP modelling, this 48 49 adverse effect is present even when the phenyl substituents in 50 pyrazolidinedione are replaced with the methyl substituents. 51 Hence, this is an intrinsic "feature" of the pyrazolidinedione 52 acceptor or, possibly, of other acceptor groups with the 53 (O=C)N-N(C=O) conjugated fragment as well. Still some chemical modifications can increase the relative energy of this 54 55 state, making the allowed HOMO $\rightarrow$ LUMO  $\pi\pi^*$ -state the S<sub>1</sub>. In 56 this study, this was the case with merocyanines comprising the 57 highly electron-donating benzimidazole residue.

Rational design of donor–acceptor systems with desirable
 spectral-fluorescent properties is relevant for creation of novel

light conversion materials. Information on the donor acceptor properties of the terminal groups used a intervolver and relative dyes is crucial in that respect. In this paper, we not only have shown that the acceptor strength of one of such groups was estimated erroneously, but also have found the cause of this error. The probable reason of the unexpectedly low fluorescence of the pyrazolidinedione-based merocyanines has also been conjectured from the quantum-chemical calculations. Therefore, the results of this paper should be useful and appealing from both the practical and theoretical perspective.

# **Conflicts of interest**

There are no conflicts to declare.

# Acknowledgements

The quantum-chemical calculations were performed using the computational facilities of the joint computational cluster of State Scientific Institution "Institute for Single Crystals" and Institute for Scintillation Materials of NAS of Ukraine incorporated into the Ukrainian National Grid.

We wish to acknowledge the help by Prof. Alexander B. Rozhenko, who performed the Turbomole ADC(2) calculation.

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

View Article Online DOI: 10.1039/C9NJ03275D



Acceptor strength of the 1,2-diphenyl-3,5-pyrazolidinedione residue is re-evaluated based on the spectral-fluorescent properties of donor–acceptor dyes. The fluorescence of the title merocyanines is shown to be impaired by the low-lying forbidden  $\pi\pi^*$ -state.