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Synthesis and ion-selective properties of an amphiphilic butadienyl dye

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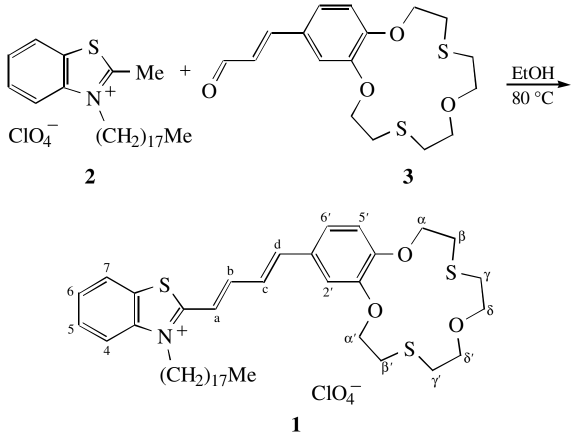
The synthesised amphiphilic benzodithia-15-crown-5 butadienyl dye forms stable monolayers on distilled water (up to 47 mN m^{-1}) and undergoes specific interactions (complex formation) with Hg^{2+} or non-specific interactions with K$^+$, as follows from surface pressure – and surface potential – molecular area isotherms.

Among numerous studies of various crown ether derivatives,[1] only a few were devoted to photosensitive amphiphilic crown ether dyes with azobenzene[2–5] or –C=C– groups.[5–10] These compounds are particularly useful for the construction of various supramolecular systems[1,5,11,12] and promising for future applications as sensitive components for ion sensors and materials for the recording, storage and proceeding of optical information and for the photocontrolled extraction of metal cations.

Our recent studies[6–11] on the monolayers of amphiphilic crown-ether styryl dyes demonstrated the possibility of preparing photosensitive films with the ability to selectively bind particular heavy metal cations. These monolayers can serve as unique models for studying molecular recognition and interaction phenomena at interfaces that can be considered as fundamental features of biological membranes.

Here, we report on the synthesis and ion-selective properties of an amphiphilic benzodithia-15-crown-5 butadienyl dye in monolayers.

Amphiphilic benzodithia-15-crown-5 ether butadienyl dye **1** was prepared in a moderate yield by the condensation of 2-methyl-3-octadecylbenzothiazolium perchlorate **2** with dithia-15-crown-5 ether cinnamaldehyde **3** (Scheme 1).[†] The syntheses of heterocyclic salt **2**[13] and cinnamaldehyde **3**[14] were described earlier. Dye **1** was characterised by ^{1}H NMR spectroscopy, including COSY spectra, and elemental analysis. According to the NMR spectra, dye **1** exhibited the *E,E*-configuration [$^3J_{\mathrm{H(a),H(b)}}$ = 14.4 Hz and $^3J_{\mathrm{H(c),H(d)}}$ = 15.3 Hz] and the *s-trans*-conformation [$^3J_{\mathrm{H(b),H(c)}}$ = 11.1 Hz].



Scheme 1

Dye **1** forms stable insoluble monolayers on distilled water and various aqueous salt subphases. The collapse pressure of dye **1** monolayers, according to π/*A* isotherms, is about 47.0 mN m^{-1} on distilled water, which is much higher than that for 18-crown-6 styryl dye (25.5 mN m^{-1}) or 15-crown-5 styryl dye (34.5 mN m^{-1}).[6–10] A comparison of the π/*A* isotherms for

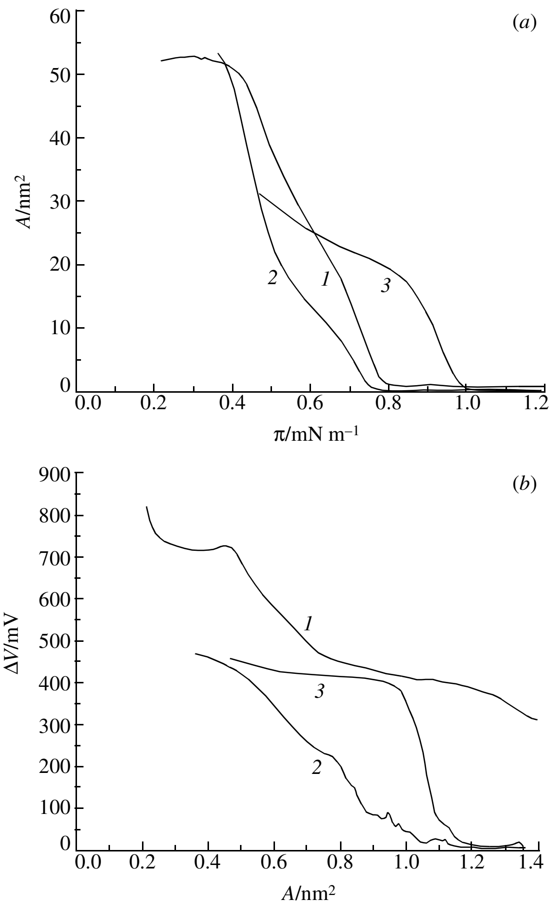


Figure 1 (*a*) Surface pressure–molecular area isotherms and (*b*) surface potential–molecular area isotherms of dye **1** monolayers on (*1*) distilled water and 1 mM aqueous solutions of (*2*) $KClO_4$ and (*3*) $Hg(ClO_4)_2$ at 20 °C.

dye **1** on water and 1 mM $KClO_4$ shows a pronounced contraction in the presence of $KClO_4$ [Figure 1(*a*)]. Since no complex formation of this macrocyclic dye with K^+ was found in solution, the differences are attributed to the non-specific interaction of dye **1** with the cation.

In the case of Hg^{2+}, the monolayer of dye **1** has two states (lower and higher than π of about 20 mN m^{-1}) [Figure 1(*a*)]. A significant difference between the dye π/A isotherm on $Hg(ClO_4)_2$ and that on other salts, as well as on distilled water, is evidence for the specific interaction (complex formation) between the macrocyclic dye and Hg^{2+}. This complex formation and further repulsion of the positively charged molecules in this monolayer is a reasonable explanation of the pronounced 'enlargement' (about 35%) of area per dye molecule at low pressures in the presence of Hg^{2+} as compared to other salts or water.

The potential values ($\Delta V/A$ isotherm) for a dye monolayer on water increased gradually over the entire range of dye monolayer compressions [Figure 1(*b*)] due to a continuous chromophore tilting upon dye monolayer compression. By contrast, in the presence of any salt, a significant and sharp increase of the potential values for dye **1** monolayer was observed clearly. Moreover, the $\Delta V/A$ isotherm on an Hg^{2+} salt solution with a sharp increase of about 400 mV [Figure 1(*b*)] differs considerably from that of water (gradual increase by about 410 mV) or $KClO_4$ (sharp increase by about 580 mV) providing evidence for the specific complex formation with Hg^{2+}. These π/A and $\Delta V/A$ isotherm features prove the existence of a special type of monolayer structures (due to the complex formation of dye **1** with Hg^{2+}), as compared to distilled water.

These results are indicative of the pronounced ion-selective properties of dye **1** in monolayers, which can be useful for the construction of functional supramolecular systems and their further applications.

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† *3-Octadecyl-2-[(1*E*,3*E*)-4-(2,3,5,6,8,9,11,12-octahydro-1,7,13,4,10-benzotrioxadithiacyclopentadecin-15-yl)-1,3-butadienyl]-1,3-benzothiazol-3-ium perchlorate* **1**. A solution of 2-methyl-3-octadecylbenzothiazolium perchlorate **2** (56 mg, 0.11 mmol) and dithia-15-crown-5 ether cinnamaldehyde **3** (47 mg, 0.13 mmol) in anhydrous ethanol (7 ml) was refluxed for 100 h and then cooled to 5 °C. The precipitate formed was filtered off, washed with cold ethanol (2×3 ml) and recrystallised from ethanol (15 ml) to give dye **1** as reddish-brown powder (29 mg, 31%), mp 141–143 °C. ^{1}H NMR (Bruker DRX500 spectrometer, $CDCl_3$, 25 °C) δ: 0.89 (t, 3H, Me, *J* 6.8 Hz), 1.19–1.37 (m, 28H, 14CH_2), 1.49 (m, 2H, $CH_2CH_2CH_2N$), 1.87 (m, 2H, CH_2CH_2N), 2.98 and 3.02 (2t, 4H, γ- and γ'-CH_2S, *J* 6.5 Hz, *J* 6.9 Hz), 3.11 (br. t, 4H, β- and β'-CH_2S), 3.84 and 3.86 (2t, 4H, δ- and δ'-CH_2O, *J* 6.9 Hz, *J* 6.5 Hz), 4.12 (m, 2H, α-CH_2O), 4.32 (m, 2H, α'-CH_2O), 4.60 (m, 2H, CH_2N), 6.52 [d, 1H, H(5′), *J* 8.3 Hz], 6.95 [br. d, 1H, H(6′), *J* 8.3 Hz], 7.17 [br. s, 1H, H(2′)], 7.26 [d, 1H, H(d), *J* 15.3 Hz], 7.48 [dd, 1H, H(c), *J* 15.3 Hz, *J* 11.1 Hz], 7.50 [d, 1H, H(a), *J* 14.4 Hz], 7.61 [d, 1H, H(4), *J* 8.4 Hz], 7.64 [m, 1H, H(6)], 7.72 [m, 1H, H(5)], 7.89 [dd, 1H, H(b), *J* 14.4 Hz, *J* 11.1 Hz], 7.95 [d, 1H, H(7), *J* 8.0 Hz]. Found (%): C, 62.13; H, 7.70; N, 1.65. Calc. for $C_{43}H_{64}ClNO_7S_3$ (838.6) (%): C, 61.58; H, 7.69; N, 1.67.

The $KClO_4$ (99+%) and $Hg(ClO_4)_2$ (98%) salts (Aldrich) were dissolved in distilled water (cleaned with a Milli-Q filtration unit from Millipore).

The surface pressure (π)–molecular area (*A*) and surface potential (ΔV)–molecular area (*A*) isotherms of dye monolayers were recorded on a rectangular trough (11 cm×38 cm×0.8 cm) provided with a 2 cm wide filter paper Wilhelmy balance and a vibrating plate condenser.[7] An 1 mM solution of dye **1** (35 μl) was spread onto water or various 1 mM aqueous salt solutions (20 °C), and the monolayers were compressed by moving a barrier with a constant speed of about 16.1 cm^2 min^{-1}.[7]