[5] The structure of resin **2** was confirmed by acidolytic cleavage from the support and analysis of the crude product by HPLC and LCMS.
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[7] The loading of resin **1a** was as indicated by the manufacturer. The loading of resin **1b** was determined by acylation with 4-fluoro-3-nitrobenzoic acid, cleavage from the support, and yield determination of the monoacylated piperazine by ^{1}H NMR spectroscopy.

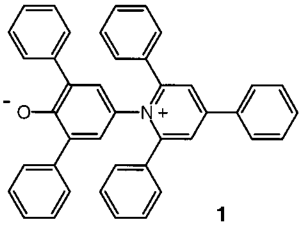
New Solvatochromic Dyes of the 5-Dimethylamino-5′nitro-2,2′-bithiophene Type[**]

Horst Hartmann,[*] Katrin Eckert, and Anke Schröder

Dedicated to Professor Christian Reichardt
on the occasion of his 65th birthday

Solvatochromic dyes are suitable as probes for the determination of solvent polarity.[1] Pyridinium betaines **1**, whose long-wavelength absorption is shifted towards shorter wavelengths by more than 9700 cm^{-1} (negative solvatochromism) on changing from a nonpolar to a polar solvent, have proved to be particularly suitable for this purpose.[2] However, probe dyes **1** suffer from the defect that in acidic solvents they can lose their solvent sensitivity in part or totally by protonation. This disadvantage is not displayed by the positive solvatochromic 2,2′-bithiophene dye **2a** described recently by Effenberger and Würthner.[3] It can therefore also be used to advantage for the determination of the solvent polarity of protic solvents. More recently the polarity of solid surfaces was also determined with this dye.[4] However, in comparison to **1**, **2a** exhibits a significantly lower solvent sensitivity of about 4700 cm^{-1}, which is only about half the value for the pyridinium betaine dye.

In the synthesis of 5-dimethylamino-5′-nitro-substituted 2,2′-bithiophene **2a**, use was made of a heteroaryl–heteroaryl coupling mediated by organometallic intermediates. This method is also suitable for the preparation of other 5-donor-5′acceptor-substituted 2,2′-bithiophenes.[3] Until now, however, it has not been suitable for the synthesis of compounds of analogous structure in which, for example the thiophene fragment is replaced by ring systems with equal numbers of π electrons. Consequently, nothing is known of the suitability of such compounds for the determination of solvent polarity.



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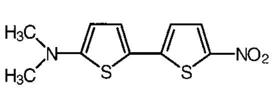
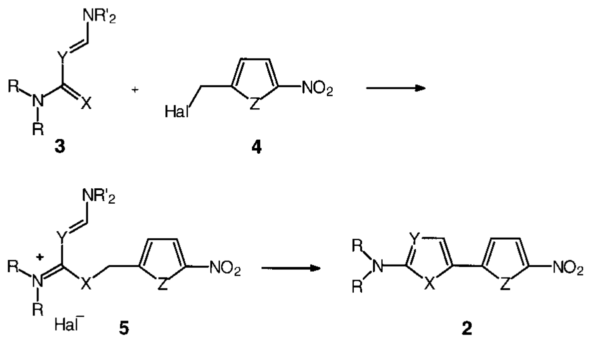


2a



We describe now an alternative route for the preparation of **2a** that is also suitable for the synthesis of other compounds of structure **2** in which the dimethylamino and the nitro groups may be replaced by other substituents with electron-donor or electron-acceptor properties and the thiophene rings may be replaced by other ring systems of similar electronic structure. The principle features of this route were developed initially by Rajappa in the 1970s[5] and later expanded by, in particular, Liebscher and ourselves. [6] It consists of the reaction of a compound of the general formula **3**[7, 8] with a halomethyl compound **4** with formation of iminium salts of type **5**. These are then transformed into the respective target compounds of type **2** by treatment with a suitable auxiliary base.

Table 1 illustrates a number of the compounds of the general type **2** which we have been prepared. Their structures were confirmed by elemental analysis and by spectrographic methods.[9] Characteristic compound data are summarized in Table 2.

The compounds described are highly crystalline, air-stable but light-sensitive solids. Their color is highly dependent upon

Table 1. Selected compound data of compounds of type **2**.[a,b]

2b: M.p. 160–162 °C; ^{1}H NMR (CDCl$_3$): $\delta = 3.23$ (t, 4H, NCH$_2$), 3.74 (t, 4H, OCH$_2$), 6.28 (d, 1H, CH), 7.09 (d, 1H, CH), 7.45 (d, 1H, CH), 7.97 (d, 1H, CH)

2c: M.p. 142–143 °C; ^{1}H NMR (CDCl$_3$): $\delta = 6.51$ (d, 1H, CH), 6.85 (d, 1H, CH), 7.12–7.17 (m, 3H, CH), 7.20–7.23 (m, 4H, CH), 7.30–7.36 (m, 4H, CH), 7.78 (d, 1H, CH)

2e: M.p. 233–234 °C; ^{1}H NMR (CDCl$_3$): $\delta = 3.51$ (t, 4H, NCH$_2$), 3.79 (t, 4H, OCH$_2$), 7.18 (d, 1H, CH), 7.85 (s, 1H, CH), 8.02 (d, 1H, CH)

2g: M.p. 206–207 °C; ^{1}H NMR (CDCl$_3$): $\delta = 3.04$ (s, 3H, CH$_3$), 5.79 (d, 1H, CH), 6.66 (d, 1H, CH), 7.32 (d, 1H, CH), 7.76 (d, 1H, CH)

2h: M.p. 210–212 °C; ^{1}H NMR (CDCl$_3$): $\delta = 3.20$ (m, 4H, NCH$_2$), 3.85 (m, 4H, OCH$_2$), 6.08 (d, 1H, CH), 6.74 (d, 1H, CH), 7.30 (d, 1H, CH), 7.78 (d, 1H, CH)

2i: M.p. 220–221 °C; ^{1}H NMR (CDCl$_3$): $\delta = 3.04$ (s, 6H, CH$_3$), 5.86 (d, 1H, CH), 7.38 (d, 1H, CH), 7.43 (d, 2H, CH), 8.10 (d, 2H, CH)

2j: M.p. 200–201 °C; ^{1}H NMR (CDCl$_3$): $\delta = 3.21$ (m, 4H, NCH$_2$), 3.85 (m, 4H, OCH$_2$), 6.16 (d, 1H, CH), 7.40 (d, 1H, CH), 7.48 (d, 2H, CH), 8.14 (d, 2H, CH)

2k: M.p. 260–262 °C; ^{1}H NMR (CDCl$_3$): $\delta = 3.54$ (m, 4H, NCH$_2$), 3.82 (m, 4H, OCH$_2$), 6.79 (d, 1H, CH), 7.44 (s, 1H, CH), 7.79 (d, 1H, CH)

2l: M.p. 226–228 °C; ^{1}H NMR (CDCl$_3$): $\delta = 3.83$ (m, 4H, NCH$_2$), 3.81 (m, 4H, OCH$_2$), 7.43 (d, 2H, CH), 7.51 (s, 1H, CH), 8.15 (d, 2H, CH)

2m: M.p. 122–125 °C; ^{1}H NMR ([D$_6$]DMSO): $\delta = 2.95$ (s, 6H, CH$_3$), 5.92 (d, 1H, CH), 7.04 (d, 1H, CH), 7.21 (d, 1H, CH), 7.74 (d, 1H, CH)

2n: M.p. 147–148 °C; ^{1}H NMR ([D$_6$]DMSO): $\delta = 3.17$ (t, 4H, NCH$_2$), 3.74 (t, 4H, OCH$_2$), 6.20 (d, 1H, CH), 7.12 (d, 1H, CH), 7.24 (d, 1H, CH), 7.77 (d, 1H, CH)

[a] For the substitution pattern, see Table 2. [b] **2a**: ref. [3], **2d**: ref. [6d], **2f** and **2o**: ref. [6e], **2p** and **2q**: ref. [11b].

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Table 2. Absorption and solvatochromism data for 5-donor–5′-acceptor-substituted 2,2′-bithiophenes of type **2**.

Compd	R_2N	X	Y	Z	Acceptor	λ_{max} ($\lg\varepsilon$)[a]	*a*	*b*	*r*
2a	Me_2N	S	CH	S	NO_2	537 (4.36)	21.150	– 3.33	– 0.9906
2b	morpholino	S	CH	S	NO_2	501 (4.31)	22.246	– 3.13	– 0.9945
2c	$(C_6H_5)_2N$	S	CH	S	NO_2	507 (4.28)	21.399	– 2.08	– 0.9831
2d	morpholino	S	CH	CH=CH	NO_2	437 (4.36)	24.480	– 2.26	– 0.9907
2e	morpholino	S	N	S	NO_2	456 (4.30)	23.453	– 2.19	– 0.9673
2f	morpholino	S	N	CH=CH	NO_2	406 (4.30)	25.716	– 1.55	– 0.9851
2g	Me_2N	Se	CH	S	NO_2	544 (4.26)	20.918	– 3.47	– 0.9868
2h	morpholino	Se	CH	S	NO_2	505 (4.19)	21.876	– 3.06	– 0.9798
2i	Me_2N	Se	CH	CH=CH	NO_2	474 (4.30)	22.956	– 2.53	– 0.9898
2j	morpholino	Se	CH	CH=CH	NO_2	445 (4.23)	24.059	– 2.26	– 0.9806
2k	morpholino	Se	N	S	NO_2	462 (4.22)	23.332	– 2.40	– 0.9798
2l	morpholino	Se	N	CH=CH	NO_2	409 (4.18)	25.516	– 1.56	– 0.9045
2m	Me_2N	S	CH	S	CN	417 (4.34)	25.124	– 1.59	– 0.9857
2n	morpholino	S	CH	S	CN	397 (4.41)	26.041	– 1.33	– 0.9783
2o	morpholino	S	CH	CH=CH	CN	378 (4.41)	27.186	– 1.18	– 0.9650
2p	morpholino	S	CH	S	$CH{=}C(CN)_2$	536 (4.54)	19.866	– 1.65	– 0.9883
2q	morpholino	S	CH	S	$C(CN){=}C(CN)_2$	681 (4.69)	16.826	– 2.61	– 0.9229

[a] In [nm], measured in dichloromethane.

the acceptor substituent, but less so upon the ring substituents X, Y, and Z. Whereas the cyano-substituted compounds **2m**–**2o** are yellow, the nitro-substituted derivatives **2a**–**2l** are mostly dark red. The dicyanovinyl-substituted compound **2p** is violet, and the tricyanovinyl compound **2q** deep blue.

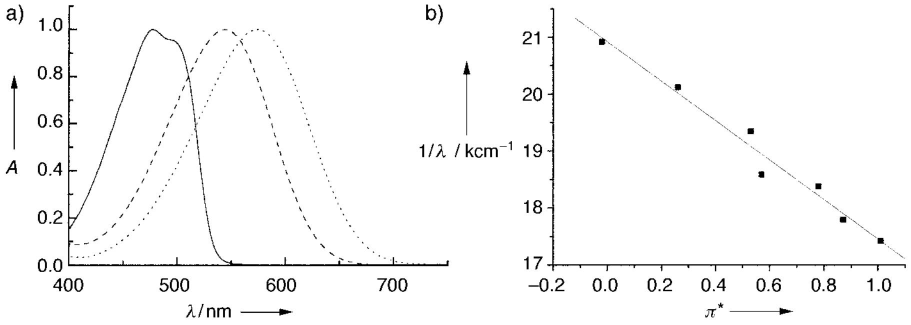

Figure 1. a) Normalized absorption spectra of **2g** in cyclohexane (——), dichloromethane (– – –), and DMSO (••••); b) correlation of the measured λ_{max} values of **2g** with the π^* values of different solvents calculated with Equation (1).

To determine the suitability of the described dyes for the determination of solvent polarity their absorption spectra were measured in a range of solvents of different polarity. The most intense long-wave absorption maxima were compared with the solvent specific π^* values introduced by Kamlet and Taft[10] and modified by Effenberger, Würthener, and Steybe with polarization terms[3b] (Figure 1). The correlation parameters *a*, *b*, and *r* obtained with Equation (1) for all compounds investigated are shown in Table 2.

$$1/\lambda_{max} = a + b\pi^* \quad (1)$$

Whereas parameter *r* is a measure of the quality of the relevant correlation, parameter *b* reflects the solvent sensitivity of the respective dye. Its negative sign indicates a positive solvatochromism. Parameter *a* shows the absorption wavelength in units of 10^{-5} cm of the respective dye in a nonpolar solvent of polarity index $\pi^* = 0$.

As can be seen, the donor–acceptor-substituted 2,2′-bithiophene dye **2a** exhibits almost the greatest solvent dependency of its long-wavelength absorption band. Neither the replacement of the dimethylamino group by other donor groups (for example, by a morpholino group or diphenylamino group) nor the replacement of the nitro group by another acceptor group (for example, a dicyano- or tricyanovinyl group) nor the exchange of one of the two thiophene rings by other ring systems (for example, by a thiazole, selenazole, or phenyl moiety) leads to a marked increase in the solvent sensitivity of the relevant absorption band of the respective compound. However, a slight increase in solvent dependency was measured with **2g**, in which the dimethylamino-substituted thiophene ring was replaced by a selenophene ring. With a *b* value of –3.47 this compound exhibits the greatest solvent dependency yet measured for a compound of structure **2**, and thus for a positive solvatochromic compound. To illustrate this fact the corrsponding spectroscopic data and the correlation data determined for **2g** are shown graphically in Figure 1.

The statements expressed here remain valid, in principle, if other solvent parameters are used for a quantitative description of the solvent dependency of the absorption spectra of the compounds investigated, or if the range of solvents used is significantly extended (see the Supporting Information).

Because of the structural similarity of all the compounds investigated, it would be reasonable to expect that in each case the difference in dipole moment between the ground state and the first excited state would be responsible for the solvent dependency of the absorption bands.[15] That would mean that this difference is particularly large in **2g**, followed by the difference in **2a**. However, attempts to support this suggestion by appropriate MO calculations, for example in the framework of the known PPP formalism with optimized molecular geometry, have been unsuccessful until now. Thus, within the investigated series of compounds **2** no proportionality between measured solvent sensitivity, quantified by the corresponding *b* value, and calculated dipole moment change could be established.

Experimental Section

The starting materials **3** and **4** used in the preparation of compounds of type **2** were known or could be prepared by literature methods.[7, 8, 11] Previously unknown sulfur- or selenium-containing reagents of type **3** with X = S or Se and Y = CH were obtained by reaction of the corresponding 3-chloro-3-dialkylaminopropeniminium salts[12] with sodium sulfide or selenide[13] in ethanol.[14]

3-Chloro-3-morpholinopropenylidene dimethyliminium perchorate was prepared according to the literature method:[12a] M.p. 177–180°C; ^{1}H NMR (CDCl$_3$): $\delta = 3.20$ (s, 3H, NCH$_3$), 3.41 (s, 3H, NCH$_3$), 3.75 (m, 4H, NCH$_2$), 3.91 (m, 4H, OCH$_2$), 5.84 (d, 1H, CH), 8.23 (d, 1H, CH).

General method for the preparation of **2**: Equivalent amounts of **3** and **4** (each 0.01 mol) were dissolved in methanol (50 mL) or acetonitrile (50 mL) and then heated to boiling for a short time. After the reaction solution had cooled, it was treated with either triethylamine (25 mL) or a 25% sodium methylate solution (50 mL) and then briefly warmed again. After the reaction mixture had once more cooled, it was treated with water (10 mL) and the precipitated solid was filtered off.

In this way, for example, **2a** (m.p. 174–176°C; 176–177°C[3a]) was formed from 1,3-bis(dimethylamino)propene-3-thione **3** (X = S, Y = CH, R$_2$N = NR$'_2$ = (CH$_3$)$_2$N) and 5-chloromethyl-2-nitrothiophene[11c] in 93% yield, and **2g** (m.p. 206–207°C) was prepared from 1,3-bis(dimethylamino)propene-3-selenone **3** (X = Se, Y = CH, R$_2$N = NR$'_2$ = (CH$_3$)$_2$N)) and 5-chloromethyl-2-nitrothiophene in 75% yield.

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[14] 1,3-Bis(dimethylamino)propene-3-selenone **3** (X = Se, Y = CH, R$_2$N = NR$'_2$ = (CH$_3$)$_2$N) was obtained from [3-chloro-3-dimethylaminopropenylidene]dimethylimium perchlorate[12a] and Na$_2$Se: M.p. 120–122°C, ^{1}H NMR (CDCl$_3$): $\delta = 3.06$ (s, 3H, NCH$_3$), 3.16 (s, 3H, NCH$_3$), 3.29 (s, 3H, NCH$_3$), 3.50 (s, 3H, NCH$_3$), 8.77 (s, 1H, CH); 1-dimethylamino-3-morpholinopropene-3-selenone **3** (X = Se, Y = CH, R$_2$N = morpholino, NR$'_2$ = (CH$_3$)$_2$N) was prepared from (3-chloro-3-morpholinopropenylidene)dimethylimium perchlorate and Na$_2$Se in a similar way: M.p. 123–125°C; ^{1}H NMR (CDCl$_3$): $\delta = 2.96$ (s, 4H, NCH$_2$), 4.11 (s, 4H, OCH$_2$), 5.28 (d, 1H, CH), 8.37 (d, 1H, CH).

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Doubly *meso*-*β*-Linked Diporphyrins from Oxidation of 5,10,15-Triaryl-Substituted Ni$^{\text{II}}$– and Pd$^{\text{II}}$ – Porphyrins[**]

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In recent years there has been a considerable upsurge in the synthesis of covalently linked multiporphyrin arrays. These compounds are interesting in light of their unique photoelectronic properties and potential applications as mimics of light-harvesting systems in photosynthesis, and as electron-energy transfer moieties in molecular wires.[1] Among these, fused oligoporphyrins sharing a common extended π-electron network are of particular interest because of their remarkable red-shifted absorption bands as well as their extremely enhanced electronic communications that are favorable for molecular wires.[2, 3] Indeed, several fused diporphyrins and oligoporphyrins exhibit significantly red-shifted Soret bands and intense Q-bands,[2, 3] which demonstrates the promising potential of fused multiporphyrins. Here we report a facile synthesis of other fused diporphyrins that contain two *meso*-*β* direct linkages.

Recently we found that the one-electron oxidation of 5,15-diaryl-substituted metalloporphyrins bearing sterically uncongested *meso*-positions led to the formation of directly linked porphyrin dimers. The Zn$^{\text{II}}$ complex gave a *meso*–*meso*-linked diporphyrin by oxidation with a Ag$^{\text{I}}$ salt or by

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