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Near infrared dyes by combination of squaraine and ferrocene chromophores

Herbert Meier* and Ralf Petermann

Institute of Organic Chemistry, University of Mainz, Duesbergweg 10-14, D-55099 Mainz, Germany

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Abstract

Squaraines represent a class of compounds which attracts a lot of attention in materials science. A synthetic sequence for the preparation of the symmetrical squaraines **12a**,**b**, which contain ferrocene units as electron donors, is described. The compounds exhibit, in dichloromethane or chloroform, two intense absorption bands. One of them is located at 641/650 nm—a normal region for squaraines; however, the other band is strongly shifted to long wavelengths and has its maximum at 921/961 nm. Alkyl sidechains enhance the solubility of **12a**,**b**, which represent a new type of NIR dyes. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: oxocarbon acids and derivatives; ferrocenes; dyes.

Squaraines, 1,3-diaryl substituted derivatives of squaric acid[1] attract technical interest in electrophotography,[2] optical data storage,[3] non-linear optics,[4,5] conversion of solar energy[6] and as fluorescence markers.[7] Some time ago we prepared a series of squaraines, whose chromophores were extended by stilbene units.[8–10] It turned out that the extension of the conjugation leads first to a strong bathochromic effect,[8,9] but surprisingly the further extension of the conjugation causes a hypsochromic effect.[10] In order to come to NIR dyes, we replaced the dialkylamino or alkoxy substituted stilbene units by building blocks, which contain ferrocenes as electron donors. Compound **12** visualises such a target molecule. The four hydroxy groups guarantee an enhanced stability.[8,9] Moreover, alkyl side chains attached on the ferrocene moieties should increase the solubility. The synthetic sequence was started with ferrocene (**1**). Alkylation with 3-bromomethylheptane yielded the rearranged substitution product **2** which contains the highly branched 1-ethyl-1-methylpentyl sidechain. An alternate twofold substitution of ferrocene was performed according to the method described by Vogel et al.[11] The Friedel–Crafts acylation **1**→**3** was followed by a Clemmensen reduction **3**→**4**. Both alkylated ferrocenes were subjected to a Vilsmeier formylation which yielded the aldehydes **5**[12] and **6**.[13] The resorcinol derivatives **7a**,**b** with protected

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* Corresponding author. Fax: 49 (0)6131 3925396; e-mail: hmeier@mail.uni-mainz.de

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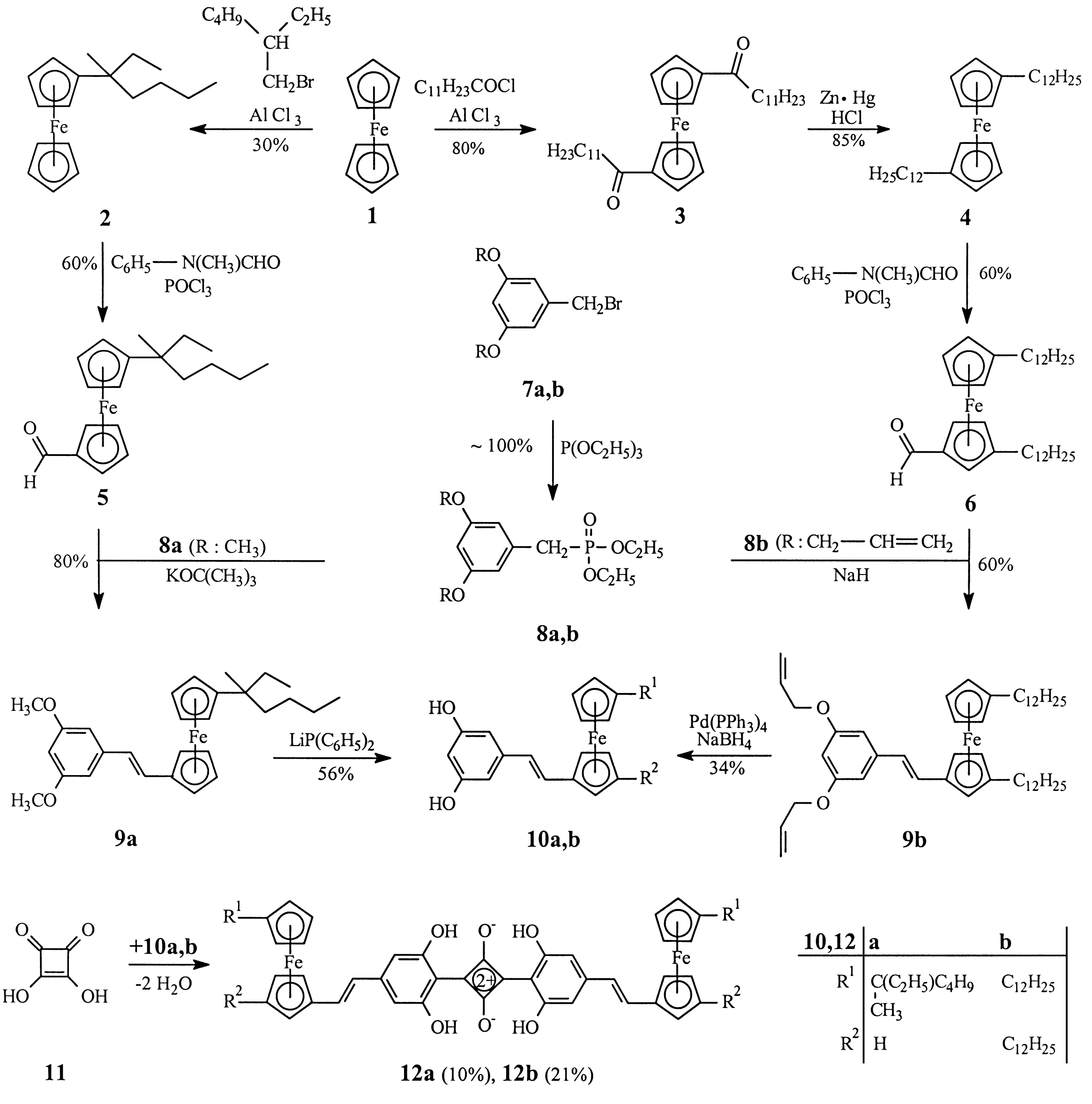
hydroxy functions were transformed by quantitative Arbusov reactions to the phosphonates **8a**,**b**. Wittig–Horner reactions of **8a** and **5** and **8b** and **6** furnished the compounds **9a**[14] and **9b**[15] with high *trans* selectivity. Deprotection of **9a** was achieved by the cleavage of the methyl ethers with lithium diphenylphosphide; the allyl ether groups in **9b** were split with sodium borohydride in the presence of tetrakis(triphenylphosphine)palladium. The methyl ether cleavage proved to be the better and easier variant. The final step consisted of the condensation of squaric acid (**11**) with the resorcinols **10a**,**b**. Although the generated water was continuously removed by azeotropic distillation (*n*-butanol/toluene), the yields of the products **12a**,**b**[16,17] remained moderate (Scheme 1).



10,12	a	b
R^1	$C(C_2H_5)C_4H_9$ CH_3	$C_{12}H_{25}$
R^2	H	$C_{12}H_{25}$

Scheme 1.

Diaryl squaraines exhibit, normally in dichloromethane or chloroform, a narrow but intense absorption band with a maximum between 510 and 670 nm.[2] The compounds **12a**,**b** show a narrow band in this region and additionally a broad absorption in the near infrared (NIR): **12a** ($CHCl_3$), λ_{max}/ $\log_{\varepsilon}$: 641/4.90 nm and 921/4.65 nm; **12b** (CH_2Cl_2), λ_{max}/ $\log_{\varepsilon}$: 650/4.92 nm and 961/4.66 nm.

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12. **5**: Red oil; ^{1}H NMR ($CDCl_3$): δ 0.72 (t, 3H, CH_3), 0.85 (t, 3H, CH_3), 1.16 (s, 3H, CH_3), 1.2–1.6 (m, 8H, CH_2), 4.08, 4.20 (AA′BB′, 4H, ferrocene), 4.56, 4.74, (AA′BB′, 4H, ferrocene), 9.93 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$): δ 8.5, 14.1, 25.1 (CH_3), 23.4, 26.1, 32.7, 39.8 (CH_2), 35.6 (C_q), 67.4, 68.3, 69.9, 73.6 (CH, ferrocene), 79.2, 103.0 (C_q, ferrocene), 193.5 (CHO); despite the chiral centre, the molecule shows C_s symmetry; MS (FD): m/z 326 (100%), [$M^{+\bullet}$].
13. **6**: Red oil; ^{1}H NMR ($CDCl_3$): δ 0.84 (m, 6H, CH_3), 1.23 (m, 36H, CH_2), 1.40 (m, 2H, β-CH_2), 1.50 (m, 2H, β-CH_2), 2.20 (m, 2H, α-CH_2), 2.33 (m, 2H, α-CH_2), 4.05 (m, 4H, ferrocene), 4.40 (s, 1H, ferrocene), 4.57 (m, 2H, ferrocene), 9.84 (s, 1H, CHO); ^{13}C NMR ($CDCl_3$): δ 14.0 (CH_3), 22.6 (CH_2), 28.8–31.8 (CH_2, superimposed), 69.3, 69.4, 69.6, 69.7, 70.2, 70.2, 74.1 (CH, ferrocene), 78.8, 91.5, 95.1 (C_q, ferrocene), 193.6 (CHO); MS (FD): m/z 550 (100%), [$M^{+\bullet}$].
14. **9a**: Red oil; ^{1}H NMR ($CDCl_3$): δ 0.72 (t, 3H, CH_3), 0.85 (t, 3H, CH_3), 1.20 (s, 3H, CH_3), 1.22–1.60 (m, 8H, CH_2), 3.80 (s, 6H, OCH_3), 3.93, 4.04 (AA′BB′, 4H, ferrocene), 4.25, 4.41 (AA′BB′, 4H, ferrocene), 6.35 (t, 1H, benzene), 6.57 (d, 2H, benzene), 6.59, 6.83 (AB, ^3J = 16.1 Hz, 2H, olefin. H); ^{13}C NMR ($CDCl_3$): δ 8.6, 14.2, 25.3 (CH_3), 23.6, 26.3, 33.0, 40.0 (CH_2), 35.8 (C_q), 67.1, 67.3, 68.2, 69.7 (CH, ferrocene), 82.8, 101.5 (C_q, ferrocene), 99.1, 103.9 (CH, benzene), 125.8, 127.8 (olefin. CH), 140.1, 161.0 (C_q, benzene); MS (FD): m/z 460 (100%), [$M^{+\bullet}$].
15. **9b**: Red oil; ^{1}H NMR ($CDCl_3$): δ 0.86 (m, 6H, CH_3), 1.25 (m, 36H, CH_2), 1.42 (m, 2H, β-CH_2), 1.48 (m, 2H, β-CH_2), 2.22 (m, 2H, α-CH_2), 2.30 (m, 2H, α-CH_2), 3.90 (m, 4H, ferrocene), 4.10, 4.24 (AB, 2H, ferrocene), 4.26 (s, 1H, ferrocene), 4.53 (m, 4H, OCH_2), 5.29, 5.42, 6.06 (m, 6H, olefin. H, allyloxy), 6.37 (t, 1H, benzene), 6.52, 6.74 (AB, ^3J = 16.1 Hz, 2H, olefin. H), 6.58 (d, 2H, benzene); ^{13}C NMR ($CDCl_3$): δ 14.0 (CH_3), 22.6 (CH_2), 28.9–31.9 (CH_2), 66.7, 67.7, 68.8, 68.9, 69.3, 69.8, 70.8 (CH, ferrocene), 68.9 (OCH_2), 82.4, 90.4, 91.0 (C_q, ferrocene), 100.5, 105.0 (CH, benzene), 117.5 (CH_2, allyloxy), 133.4 (CH, allyloxy), 125.4, 128.0 (olefin. CH), 140.2, 160.0 (C_q, benzene); MS (FD): m/z 736 (100%), [$M^{+\bullet}$].
16. **12a**: Green, metallic crystals which start to decompose at 200°C; ^{1}H NMR ($C_2D_2Cl_4$): δ 0.65 (t, 6H, CH_3), 0.79 (t, 6H, CH_3), 1.12 (s, 6H, CH_3), 1.14–1.40 (m, 16H, CH_2), 3.94 (m, 4H, ferrocene), 4.05 (m, 4H, ferrocene), 4.50 (m,

8H, ferrocene), 6.39 (s, 4H, benzene), 6.41, 7.23 (AB, $^3J = 16.1$ Hz, 4H, olefin. H), 10.97 (s, 4H, OH); MS (FD): *m*/*z* 942 (100%), [$M^{+\bullet}$].

17. **12b**: Green, metallic crystals, m.p. 141°C; ^{1}H NMR ($CDCl_3$): δ 0.83 (m, 12H, CH_3), 1.23 (m, 72H, CH_2), 1.39 (m, 4H, β-CH_2), 1.50 (m, 4H, β-CH_2), 2.13 (m, 4H, α-CH_2), 2.31 (m, 4H, α-CH_2), 3.95 (m, 8H, ferrocene), 4.36 (m, 6H, ferrocene), 6.37, 7.15 (AB, $^3J = 16.1$ Hz, 4H, olefin. H), 6.38 (s, 4H, benzene), 11.02 (s, 4H, OH); ^{13}C NMR ($CDCl_3$): δ 14.1 (CH_3), 22.7 (CH_2), 28.8–32.0 (CH_2, superimposed), 68.6, 69.1, 69.6, 70.3, 70.6, 70.8, 72.6 (CH, ferrocene), 81.0, 91.6, 93.2, (C_q, ferrocene), 107.1 (CH, benzene), 124.0, 139.4 (olefin. CH), 110.8, 153.1, 162.6, 167.4, 182.3 (C_q); MS (FD): *m*/*z* 696 (100%), [M^{2+}], 1392 (30%), [$M^{+\bullet}$].