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Synthesis of new squaraine dyes for optical switches

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Abstract

This work describes the synthesis of new, highly soluble squaraine dyes, which have absorption maxima over 900 nm in solution. The absorption spectra of their spin-coated films show broad absorption bands, which are caused by aggregation phenomena. The absorption bands in the solid phase are red-shifted compared to those in solution. Because of these characteristics and nonlinear optical data which were obtained by Z-scan measurements, the new substances are principally useful for optical switches.

Keywords: Squaraine dyes; Extended conjugation; J-Aggregates; Nonlinear optical properties; Z-Scan measurements; Optical switches

1. Introduction

Squaraines, 1,3-disubstituted derivates of squaric acid, display strong absorption in the visible and near infrared regions; this group of dyes also show photoconductivity and high fluorescence quantum yields. Because of these properties, squaraines are suited for application in optical data storage, xerography and lasers [1–6].

The aggregation behavior of squaraines has attracted much interest [7]. Recently, it was shown [8], that J-aggregates have an ultrafast optical response and exhibit large optical nonlinearity. The absorption spectra of bis(*p*-(dialkylamino)-phenyl)squaraines in spin-coated films display aggregation in which absorption maxima reach 780 nm [8]. The wavelength of optical pulses used in telecommunication should be 1.3 or 1.55 μm because of the high transmittance of optical fibers at these wavelengths. Thus, optical switching compounds that exhibit a fast optical response at 1.55 μm are of great interest.

The extension of the π-conjugation within molecules is one possibility for shifting the absorption to longer wavelengths. The introduction of two styryl units in bis(*p*-(dialkylamino)-phenyl)squaraines leads to amino-substituted bis(stilbenyl)squaraines, which have absorption maxima in solution at about 900 nm; further extension of the conjugation of these molecules results in a hypsochromic shift [9].

To obtain a further redshift, one can enhance the strength of the donor groups. The introduction of two more dialkylamino groups (compound **1**) or two alkoxy chains (compound **2**), as practised in this work, does not only result in a bathochromic shift, but also leads to higher solubility. High solubility is necessary for the preparation of solution-coated films. For example,

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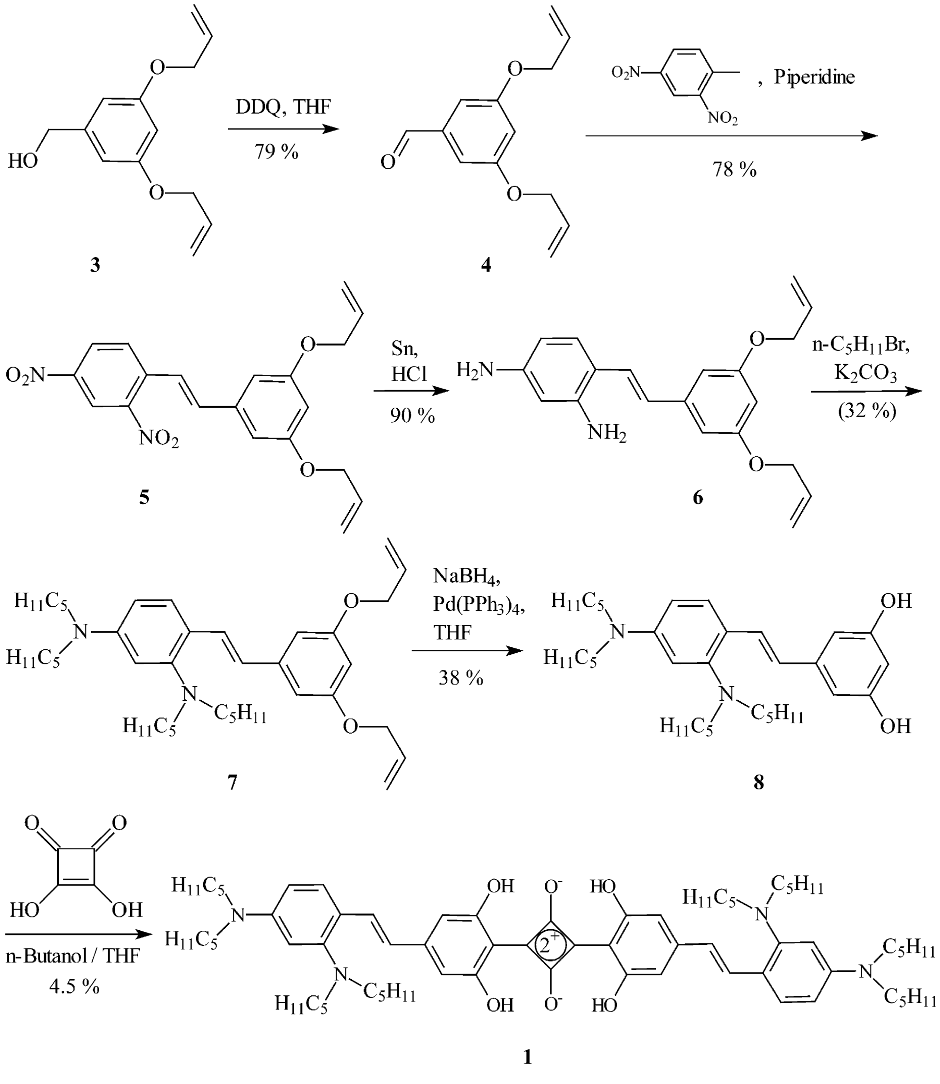
for the preparation of solid films from a dye solution using spin-coating, solubility of at least 10^{-3} M is essential, and solubility greater than 10^{-2} M is strongly preferred in order to achieve sufficient optical density for optical characterization.

In this paper, we report the synthesis of squaraine compounds with extended π-conjugation and enhanced solubility. The aggregation and preliminary nonlinear optical properties of their solution-coated thin-films are also reported.

2. Results and discussion

The starting compound of the synthesis of compound **1** (Scheme 1) was the alcohol **3** [9,10]. Oxidation with DDQ gave aldehyde **4**, which was used for the condensation reaction with 3,5-dinitrotoluene. Thereafter, the two nitro groups of the resulting dinitrostilbene **5** were reduced using Sn/HCl. The yields of the first steps were between 78 and 90%.



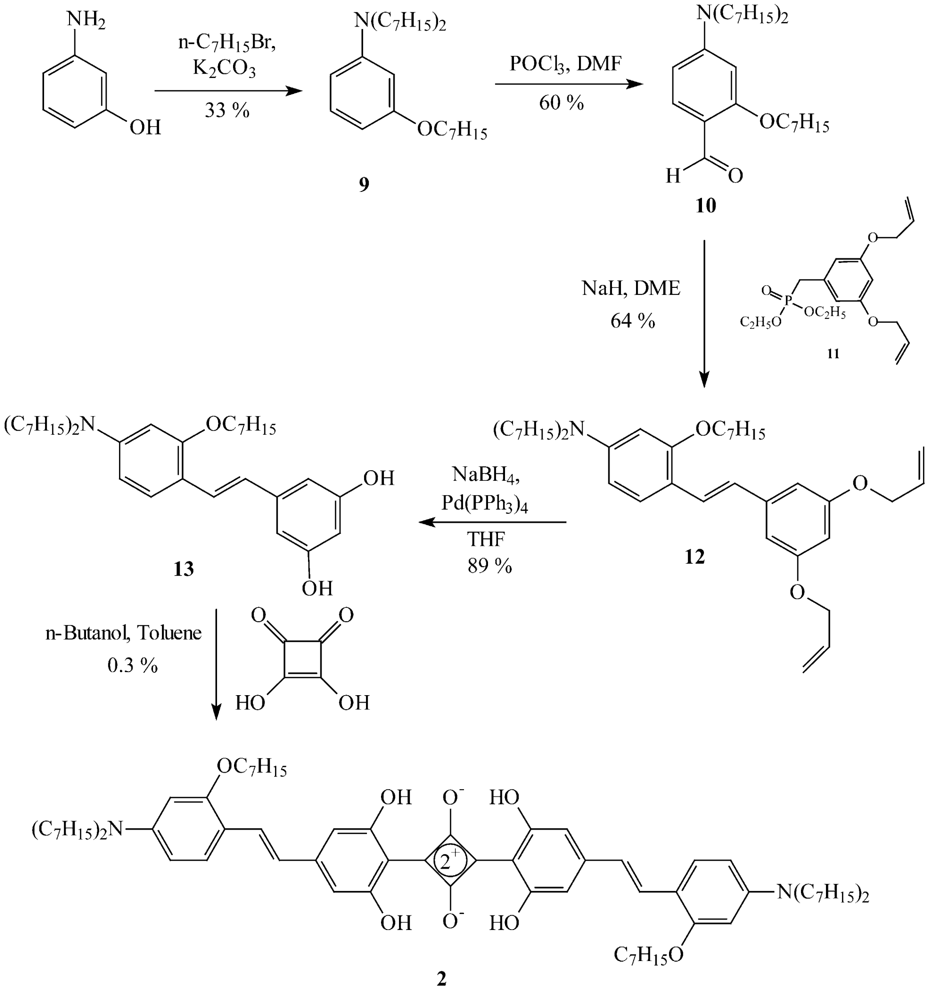
Scheme 1.

The alkylation of the two amino groups with pentyl bromide then followed. The resulting stilbene was obtained in only 32% yield; the low yield may be due to the low stability of the diaminostilbene and the difficult conditions that were needed for the introduction of the four alkyl groups.

Deprotection with $NaBH_4/Pd(PPh_3)_4$ gave the unstable diol **8**, which was immediately used for the following condensation reaction. The yield of compound **1** was 4.5%, a usual value for the condensation reaction of these compounds [9,10].

The first step of the synthesis of compound **2** (Scheme 2) was the alkylation of *m*-aminophenol (15%) followed by the Vilsmeier-reaction (73%). The Horner-reaction of the resulting aldehyde **10** with the phosphonate **11** [9–11] gave the stilbene **12** in 64% yield.

The selective deprotection (alkoxy vs. allyloxy) of **11** was affected with $NaBH_4/Pd(PPh_3)_4$ (89%). The resulting diol **13** was unstable and was used immediately after preparation for the condensation reaction (as written for compound **8**). The yield was only 0.3% because many byproducts were formed (some byproducts were observed by absorption measurements and by NMR-measurements).



Scheme 2.

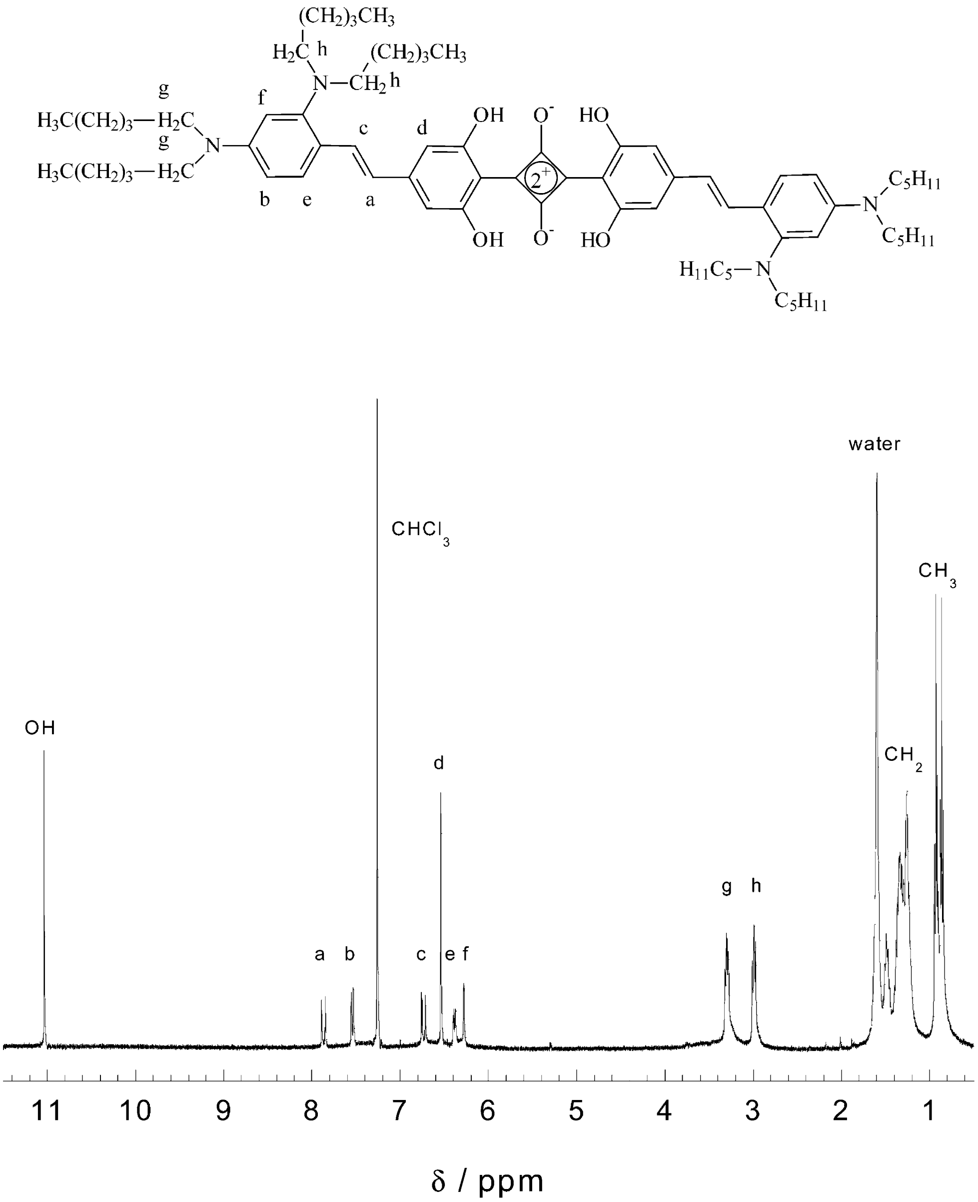


Fig. 1. ^{1}H-NMR spectrum of **1** measured in $CDCl_3$.

As the solubility of compounds **1** and **2** was very good, ^{1}H-NMR spectra could be obtained (Figs. 1 and 2). Compared to the solubility of their analogue (*E*,*E*)-bis{4-{2-[4-(dihexylamino)phenyl]ethenyl}-2,6-dihydroxyphenyl}squaraine [10], the solubility of dyes **1** and **2** was enhanced by at least three times. Due to their good solubility, preparation of spin-coated films was possible.

The UV/vis/NIR absorption spectrum of compound **1** (Fig. 3) measured in chloroform showed

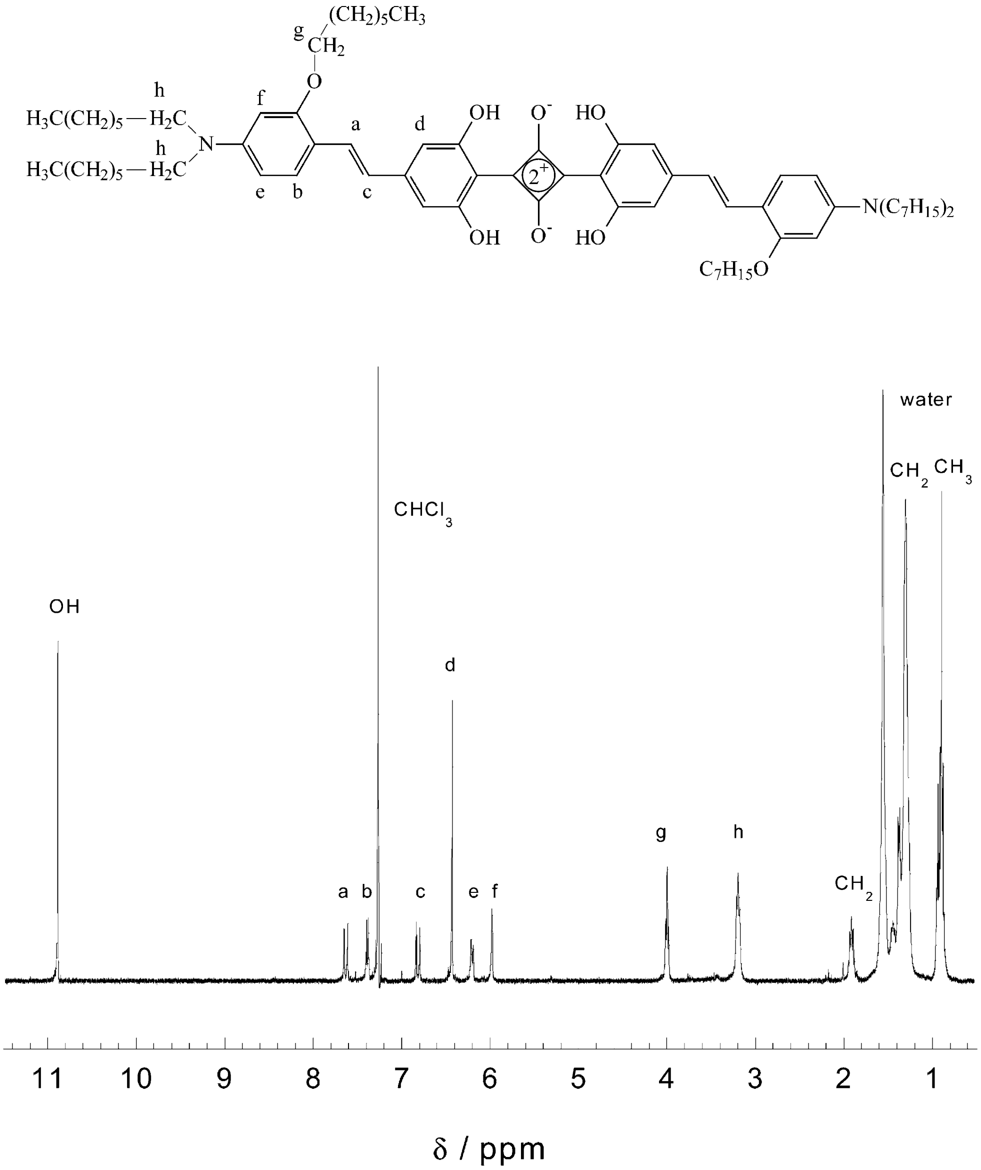


Fig. 2. ^{1}H-NMR spectrum of **2** measured in $CDCl_3$.

an absorption maximum at 942 nm ($\varepsilon = 59{,}500$ l mol^{-1} cm^{-1}). The spectrum of compound **2** also measured in chloroform (Fig. 4) was characterized by an intensive absorption at 924 nm ($\varepsilon = 93{,}800$ l mol^{-1} cm^{-1}). The absorption maximum of the spin-coated film of **1** (Fig. 5) was located at about 830 nm. The broad absorption band had a shoulder at 1030 nm; the onset of the band was 1300 nm.

The absorption spectrum of the spin-coated film of **2** (Fig. 6) showed two maxima in the NIR-region, one at 827 nm and the other at 1128 nm;

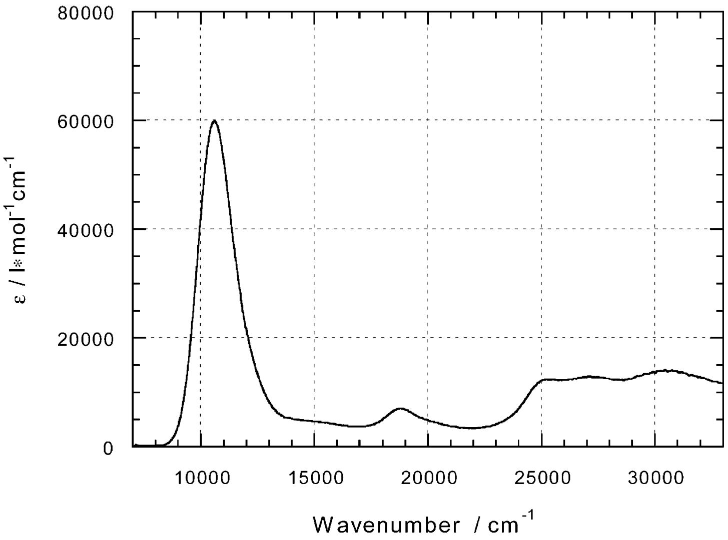


Fig. 3. UV/vis/NIR spectrum of **1** recorded in chloroform.

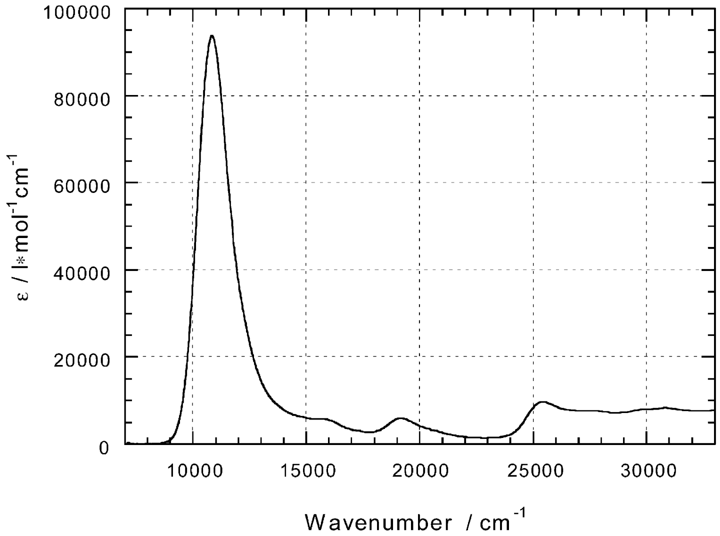


Fig. 4. UV/vis/NIR spectrum of **2** recorded in chloroform.

the onset of the band continued until 1400 nm. The largest amount of red-shifted, J-like aggregates was observed by the absorption measurement of a film that was obtained by casting a hot toluene solution of the dye. In this case the two maxima were located at 830 nm and 1168 nm (Fig. 6) and the onset of the band at 1168 nm continued until 1600 nm. Because of these results, this film was suitable for nonlinear optical measurements, which are described in the following section.

The nonlinear optical property of dye **2** was examined using the Z-scan technique [12]. Typical

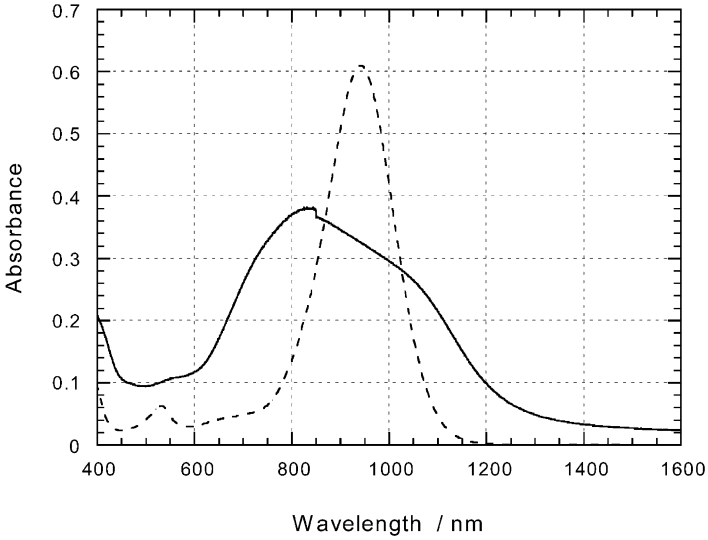


Fig. 5. Measurement of **1** in chloroform (dashed line), measurement as a spin-coated film (solid line).

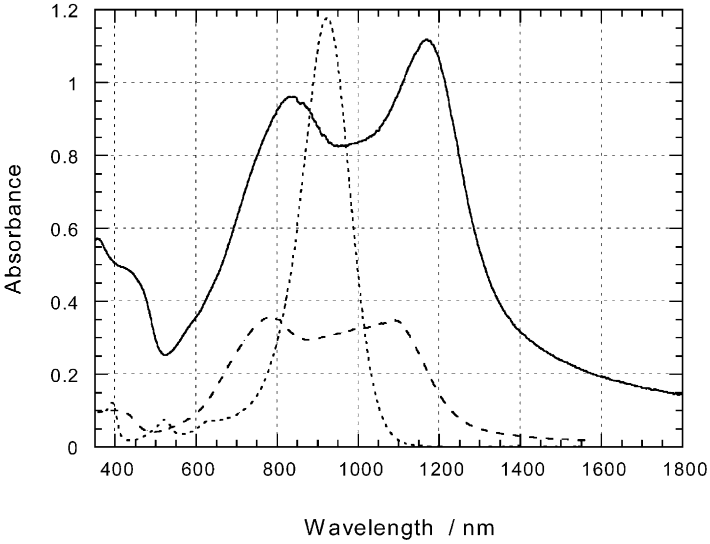


Fig. 6. Measurement of **2** in chloroform (····), measurement of a spin-coated film of **2** (- - - -) and of a film cast from a hot toluene solution (solid line).

Z-scan data for a 1-μm-thick cast film measured with open aperture are shown in Fig. 7. The Z-scan data were obtained using femtosecond pulses of wavelength 1190 nm and a peak irradiance of 4.8 GW cm^{-2}. The finding that transmittance was increased indicates the bleached absorption of the film. Each mark in Fig. 7 corresponds to a different scan. The low scattering suggests high reversibility and repeatability of the bleached absorption. The nonlinear absorption coefficient β was

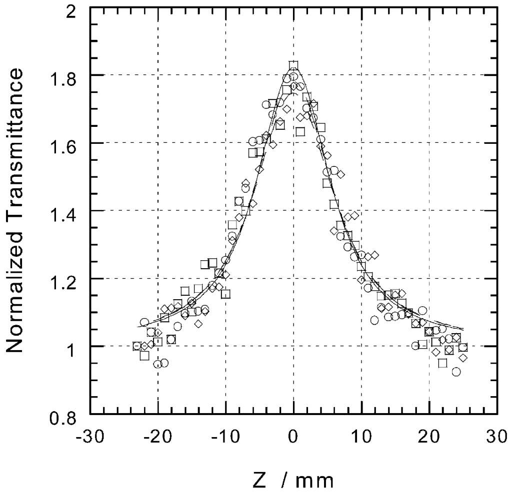


Fig. 7. Three Z-scan measurements of a cast film of **2** and the belonging curve fits (lines).

approximately 1×10^{-7} m W^{-1}, which indicates a good applicability of dye **2** to optical switches working in the infrared region.

3. Conclusions

In the present work, we synthesized some new, highly soluble squaraine dyes of extended conjugation. Both dyes in solution displayed absorption maxima located above 900 nm. The absorption spectra of spin-coated films showed red-shifted absorption bands belonging to J-like aggregates. The nonlinear optical measurements of one dye indicated that this type of colorant was potentially useful for application in optical switches operating in the infrared region.

4. Experimental

The starting materials for the synthesis were obtained from Kanto Chemical Co., Wako Pure Chemical Industries, Tokyo Kasei Kogyo and Aldrich. NMR spectra were recorded on a JEOL JNM-AL400 Fourier transform nuclear magnetic resonance spectrometer (400 MHz) using TMS as an internal standard. The absorption measurements were recorded on a Hitachi U-4100 spectrophotometer.

*4.1. 3,5-bis(Allyloxy)benzaldehyde **4** [13]*

3,5-bis(Allyloxy)benzyl alcohol (14.5 g, 66 mmol) [9–11] and 15.0 g (66 mmol) of DDQ were dissolved in 60 ml of THF and stirred for 20 h. After the solvent was removed by evaporation, the substance was purified by column filtration (ϕ6×12 cm) with hexane/acetone (5:1) as eluent. Yield: 11.3 g (78.6%). IR (KBr): ν_{max}/cm^{-1} 2930, 2864, 2818, 1688, 1594, 1451, 1389, 1297, 1170, 1054, 930. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ =4.53 (d, 4 H, CH_2), 5.28 (dd, 2H, olefinic H, $^3J=10.5$ Hz), 5.40 (dd, 2 H, olefinic H, $^3J=17.1$ Hz), 6.01 (m, 2 H, olefinic H), 6.70 (t, 1 H, aromatic H), 6.98 (d, 2 H, aromatic H), 9.85 (s, 1 H, CHO). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ =68.9 (2 C, CH_2), 107.8, 108.2 (3 C, aromatic CH), 117.8, 132.4 (4 C, olefinic CH), 138.1, 159.9 (3 C, aromatic C_q), 191.4 (1 C, CHO).

*4.2. (E)-1-(3,5-bis(Allyloxyphenyl)-2-(2,4-dinitrophenyl)ethene **5***

3,5-bis(Allyloxy)benzaldehyde (5.7 g, 26 mmol), 5.6 g (31 mmol) of 2,4-dinitrotoluene and 0.1 ml of piperidine were stirred at 100 °C for 5 h. Purification of the resulting oil was carried out by column filtration (ϕ10×12 cm) with a mixture of hexane and chloroform (2:1) as eluent. Yield : 8 g (78%); mp: 87 C. IR (KBr): ν_{max}/cm^{-1} 3094, 2902, 2864, 1601, 1527, 1410, 1344, 1181, 952, 830. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ =4.54 (d, 4 H, CH_2), 5.30 (dd, 2H, olefinic H, $^3J=10.5$ Hz), 5.42 (dd, 2H, olefinic H, $^3J=17.2$ Hz), 6.05 (m, 2 H, olefinic H), 6.51 (t, 1 H, aromatic H), 6.70 (d, 2 H, aromatic H), 7.15, 7.56 (AB, 2 H, olefinic H, $^3J=16.1$ Hz), 7.95 (d, 1 H, aromatic H, $^3J=8.8$ Hz), 8.42 (dd, 1 H, aromatic H), 8.81 (d, 1 H, aromatic H, $^3J=2.4$ Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ =68.6 (2 C, CH_2), 103.1, 106.3, 120.4, 121.5, 128.7 (6 C, aromatic CH), 117.7, 132.6, 137.0, 138.3 (6 C, olefinic CH), 126.7, 137.6, 145.9, 147.1, 159.7 (6 C, aromatic C_q). FD–MS (relative intensity): m/z 382 (100%, M^+).

4.3. *(E)-1-(3,5-bis(Allyloxyphenyl)-2-(2,4-diaminophenyl) ethene **6***

Twenty-five millilitres of concentrated HCl was added dropwise to a mixture of 3.06 g (8 mmol) of (*E*)-1-3,5-bis(allyloxyphenyl)-2-(2,4-dinitrophenyl) ethene and 3.78 g (32 mmol) of tin in 20 ml of ethanol with cooling (water bath) and rapid stirring (mechanical stirrer). The mixture was stirred for 4 h at 60 °C and the resulting solution was cooled to room temperature, 200 ml of water was added and the mixture was neutralised with potassium hydroxide and extracted twice with 200 ml of ethyl acetate. The combined organic phases were dried with magnesium sulfate. After removal of the solvent by evaporation, 2.2 g (85%) of a yellow-brown solid was obtained. IR (KBr): ν_{max}/cm^{-1} 3400, 3370, 2920, 2865, 1595, 1508, 1458, 1288, 1164, 1049, 828. ^{1}H-NMR (CDCl$_3$, 400 MHz): δ =4.52 (d, 4 H, CH$_2$), 5.27 (dd, 2H, olefinic H, ^3J=9.0 Hz), 5.40 (dd, 2 H, olefinic H, ^3J=17.3 Hz), 6.02 (d, 1 H, aromatic H), 6.03 (m, 2 H, olefinic H), 6.15 (dd, 1 H, aromatic H), 6.37 (t, 1 H, aromatic H), 6.62 (d, 2 H, aromatic H), 6.73, 7.02 (AB, 2H, olefinic H, ^3J=15.9 Hz), 7.19 (d, 1 H, aromatic H, ^3J=8.3 Hz). ^{13}C-NMR (CDCl$_3$, 100 MHz): δ =68.7 (2C, CH$_2$), 100.5, 102.0, 104.9, 106.7, 126.3 (6 C, aromatic CH), 117.4, 124.5, 128.2, 132.9 (6 C, olefinic CH), 114.5, 139.9, 144.8, 146.9, 159.4 (6 C, aromatic C$_q$). FD–MS (relative intensity): *m*/*z* 322 (100%, M$^+$).

4.4. *(E)-1-(3,5-bis(Allyloxyphenyl)-2-[2,4-di(dipentylamino)phenyl]ethene 7*

(*E*)-1-3,5-bis(Allyloxyphenyl)-2-(2,4-diaminophenyl)ethene (2.17 g, 6.73 mmol), 100 ml of *n*-bromopentane, 4 g (100 mmol) of potassium hydroxide and 10 g (72 mmol) of potassium carbonate were stirred at 80 °C for 3 h. The temperature was raised to 100 °C and, after stirring for 3 more hours, the mixture was refluxed for 16 h. 100 ml of water was then added and the resulting mixture was extracted thrice with 100 ml of hexane. The combined organic phases were dried with magnesium sulfate and the solvent removed under vacuum. Purification was achieved using column chromatography (ϕ5×15 cm) with a mixture of hexane and acetone (200:1) as eluent. Yield: 1.3 g (32%). IR (KBr): ν_{max}/cm^{-1} 2958, 2925, 2855, 1610, 1509, 1459, 1438, 1261, 1176, 1119, 803. ^{1}H-NMR (CDCl$_3$, 400 MHz): δ =0.82 (m, 12 H, CH$_3$), 1.29 (m, 24 H, CH$_2$), 1.46 (m, 4 H, β-CH$_2$), 1.56 (m, 4 H, β-CH$_2$), 2.93 (t, 4 H, α-CH$_2$), 3.24 (t, 4 H, α-CH$_2$), 4.53 (d, 4 H, CH$_2$), 5.27 (dd, 2 H, olefinic H, ^3J=9.0 Hz), 5.41 (dd, 2 H, olefinic H, ^3J=17.3 Hz), 6.05 (m, 2 H, olefinic H), 6.32 (d, 1 H, aromatic H), 6.34 (t, 1 H, aromatic H), 6.36 (dd, 1 H, aromatic H), 6.66 (d, 2 H, aromatic H), 6.72, 7.44 (AB, 2 H, olefinic H, ^3J=16.4 Hz), 7.44 (d, 1 H, aromatic H, ^3J=8.3 Hz). ^{13}C-NMR (CDCl$_3$, 100 MHz): δ =14.1 (4 C, CH$_3$), 22.5, 22.6, 26.8, 27.1, 29.3, 29.5 (12C, CH$_2$), 51.0, 53.9 (4C, N–CH$_2$), 68.7 (2 C, O–CH$_2$), 99.7, 104.7, 106.8, 107.1, 126.8 (6 C, aromatic CH), 117.4, 122.6, 126.8, 133.0 (6 C, olefinic CH), 117.2, 140.9, 147.8, 150.9, 159.3 (6 C, aromatic C$_q$). FAB–MS (relative intensity): *m*/*z* 604 (12%, (M+H)$^+$).

4.5. *(E)-1-[2,4-Di(dipentylamino)phenyl]-2-(3,5-dihydroxyphenyl)ethene **8***

(*E*)-1-3,5-bis(Allyloxyphenyl)-2-[2,4-di(pentylamino)phenyl]ethene (1.2 g, 2 mmol) was dissolved in 20 ml of THF under nitrogen. Pd(PPh$_3$)$_4$ (1.6 mg, 1.38 mmol) was added to the resulting solution under nitrogen and, after stirring for 10 min, 194 mg (5.12 mmol) of NaBH$_4$ was added. The reaction mixture was stirred for 20 h, then neutralized with 2 N HCl and extracted twice with 100 ml of methylene chloride. The combined organic layers were washed with water and dried with MgSO$_4$. After column filtration (ϕ9×5 cm) with a mixture of hexane and acetone (3:1) as eluent, the deserved compound was obtained. Owing to its low stability, the substance was characterized only per ^{1}H-NMR and IR. It was used immediately for the next step. Yield: 400 mg (38%). IR (KBr): ν_{max}/cm^{-1} 2950, 2930, 2856, 1597, 1508, 1458, 1364, 1163. ^{1}H-NMR (CDCl$_3$, 400 MHz): δ =0.81 (t, 6 H, CH$_3$), 0.90 (t, 6 H, CH$_3$), 1.29 (m, 24 H, CH$_2$), 1.45 (m, 4 H, β-CH$_2$), 1.58 (m, 4 H, β-CH$_2$), 2.93 (t, 4 H, α-CH$_2$), 3.24 (t, 4 H, α-CH$_2$), 6.24 (d, 1 H, aromatic H), 6.32 (t, 1 H, aromatic H), 6.35 (dd, 1 H, aromatic H), 6.53

(d, 2 H, aromatic H), 6.64, 7.40 (AB, 2 H, olefinic H, $^3J = 16.4$ Hz), 7.39 (d, 1 H, aromatic H, $^3J = 8.3$ Hz).

4.6. *(E,E)-bis{4-{2-[2,4-Di(dipentylamino)phenyl]ethenyl}-2,6-dihydroxy-phenyl}squaraine* ***1***

A solution of (*E*)-1-[2,4-di(dipentylamino)phenyl]-2-(3,5-dihydroxyphenyl)ethene (205 mg, 0.39 mmol) and squaric acid (26 mg, 0.20 mmol) in toluene (5 ml) and 1-butanol (2 ml) was heated under reflux for 2 h. The reaction water was removed using sodium sulfate, which was placed in a filter between the flask and the condenser. After the reaction mixture was cooled to room temperature, the solvent was removed under vacuum. The dark brown residue was washed with ethanol and cold hexane, dissolved in chloroform and filtered. After removal of the solvent under vacuum, 10 mg (4.5%) of blue-green metallic crystals were obtained. IR (KBr): ν_{max}/cm^{-1} 2931, 2857, 1615, 1572, 1516, 1499, 1470, 1375, 1231, 1169, 1133, 1055, 957, 842. ^{1}H-NMR (CDCl$_3$, 400 MHz): δ = 0.84 (t, 12 H, CH$_3$), 0.91 (t, 12 H, CH$_3$), 1.3 (m, 48 H, CH$_2$), 1.47 (m, 8 H, β-CH$_2$), 1.58 (m, 8 H, β-CH$_2$), 2.97 (t, 8 H, α-CH$_2$), 3.28 (t, 8 H, α-CH$_2$), 6.26 (d, 2 H, aromatic H), 6.36 (dd, 2 H, aromatic H), 6.52 (s, 4 H, aromatic H), 6.74, 7.87 (AB, 4 H, olefinic H, $^3J = 16.0$ Hz), 7.52 (d, 2 H, aromatic H, $^3J = 9.0$ Hz), 11.02 (s, 4 H, OH). FAB-MS (relative intensity): *m*/*z* 1124 (1.6%, (M+H)$^+$). HR–FAB–MS: calc. (M+H)$^+$: 1123.8190, measured: 1123.8187.

4.7. *N,N-diheptyl-3-heptyloxyaniline* ***9***

m-Aminophenol (5.46 g, 50 mmol), 50 ml (57.0 g, 0.32 mol) of bromoheptane and 20 g (0.15 mol) of potassium carbonate were refluxed for 2 days under nitrogen. After cooling to room temperature, 200 ml of hexane was added and, the mixture was filtered and the solvent removed under vacuum. Column chromatography (ϕ4×12 cm) using a mixture of hexane and ethyl acetate (10:1) as eluent gave a yellow oil. Yield: 3 g (15%). IR (KBr): ν_{max}/cm^{-1} 2931, 2857, 1615, 1572, 1516, 1442, 1265, 1097, 1033, 1097, 809. ^{1}H-NMR (CDCl$_3$, 400 MHz): δ = 0.88 (t, 3 H, CH$_3$), 0.91 (t, 6 H, CH$_3$), 1.3 (m, 28 H, CH$_2$), 1.76 (m, 2 H, β-CH$_2$), 3.22 (t, 4 H, N–CH$_2$), 3.93 (t, 2 H, O–CH$_2$), 6.17 (m, 2 H, aromatic H), 6.24 (dd, 1 H, aromatic H), 7.05 (t, 1 H, aromatic H). ^{13}C-NMR (CDCl$_3$, 100 MHz): δ = 14.1 (3C, CH$_3$), 22.6, 26.0, 27.1, 27.3, 29.0, 29.2, 29.4, 31.8 (15C, CH$_2$), 51.0 (2 C, N–CH$_2$), 67.6 (1 C, O–CH$_2$), 98.6, 100.3, 104.6, 129.4 (4 C, aromatic CH), 146.2, 160.0 (2 C, aromatic C$_q$). EI–MS (relative intensity): *m*/*z* 404 (16%, M$^+$).

4.8. *4-(Diheptylamino)-2-heptyloxybenzaldehyde* ***10***

N,N-diheptyl-3-heptyloxyaniline (3 g, 7.4 mmol) was dissolved in 15 ml (17.0 g, 180 mmol) of DMF. 1.6 ml (2.63 g, 17.2 mmol) of POCl$_3$ was added dropwise to the solution with ice cooling. The solution was then stirred for 4 h at 80 °C and, after cooling to room temperature, the mixture was put on ice and extracted twice with 200 ml of diethyl ether. The combined organic phases were dried with magnesium sulfate and the solvent removed under reduced pressure. Purification was achieved using column filtration (ϕ9×7 cm) with a mixture of hexane and acetone (19:1) as eluent. Yield: 2.35 g (73%) of a yellow oil. IR (KBr): ν_{max}/cm^{-1} 2943, 2859, 1686, 1593, 1507, 1396, 1285, 1163, 1079, 808. ^{1}H-NMR (CDCl$_3$, 400 MHz): δ = 0.87 (t, 3 H, CH$_3$), 0.91 (t, 6 H, CH$_3$), 1.32 (m, 24 H, CH$_2$), 1.59 (m, 4 H, β-CH$_2$), 1.82 (m, 2 H, β-CH$_2$), 3.30 (t, 4 H, N–CH$_2$), 4.00 (t, 2 H, O–CH$_2$), 5.97 (d, 1 H, aromatic H, $^3J = 2.2$ Hz), 6.22 (dd, 1 H, aromatic H), 7.69 (d, 1 H, aromatic H, $^3J = 9.0$ Hz), 10.16 (s, 1H, CHO). ^{13}C-NMR (CDCl$_3$, 100 MHz): δ = 14.0 (3 C, CH$_3$), 22.5, 26.0, 27.0, 27.2, 29.0, 29.1, 29.2, 31.7, 31.7 (15 C, CH$_2$), 51.1 (2 C, N–CH$_2$), 67.8 (1 C, O–CH$_2$), 93.1, 104.1, 129.7 (4 C, aromatic CH), 114.0, 153.8, 163.3 (2 C, aromatic C$_q$), 186.7 (1 C, CHO). EI–MS (relative intensity): *m*/*z* 431 (18%, M$^+$).

4.9. *(E)-1-[4-(Diheptylamino)-2-heptyloxyphenyl]-2-(3,5-diallyloxyphenyl) ethene* ***12***

A solution of 1.7 g (5 mmol) of diethyl 3,5-bis(allyloxy)benzylphosphonate [3–5] in 5 ml of dry DME was added to a suspension of 1 g (25 mmol) of NaH (60% in paraffin) in 20 ml of dry

DME. After stirring for 10 min, a solution of 2.15 g (5 mmol) of 4-(diheptylamino)-2-heptyloxybenzaldehyde in 5 ml of dry DME was added dropwise. The reaction mixture was heated under reflux for two hours, carefully quenched using water with ice cooling and extracted twice with 200 ml of hexane. The combined organic phases were dried with magnesium sulfate and the solvent removed under reduced pressure. The product was purified by column chromatography (ϕ18×5 cm) with a mixture of hexane and acetone (200:1) as eluent; 1.94 g (64%) of a yellow oil was obtained. IR (KBr): ν_{max}/cm^{-1} 2950, 2927, 2856, 1594, 1532, 1457, 1373, 1265, 1115, 799. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ =0.87 (m, 9 H, CH_3), 1.32 (m, 24 H, CH_2), 1.54 (m, 4 H, β-CH_2), 1.83 (m, 2 H, β-CH_2), 3.25 (t, 4 H, N–CH_2), 3.97 (t, 2 H, O–CH_2), 4.52 (d, 4 H, CH_2), 5.27 (dd, 2 H, olefinic H, ^3J=10.5 Hz), 5.40 (dd, 2 H, olefinic H, ^3J=17.1 Hz), 6.05 (m, 2 H, olefinic H), 6.12 (d, 1 H, aromatic H), 6.22 (dd, 1 H, aromatic H), 6.33 (t, 1 H, aromatic H), 6.64 (d, 2H, aromatic H), 6.83, 7.31 (AB, 2 H, olefinic H, ^3J=16.4 Hz), 7.37 (d, 1 H, aromatic H, ^3J=8.3 Hz). ^{13}C-NMR ($CDCl_3$, 100 MHz): δ =14.0 (3 C, CH_3), 22.6, 26.2, 27.1, 27.3, 29.1, 29.4, 29, 31.8, 31.7 (15C, CH_2), 51.0 (2C, N–CH_2), 68.2 (1C, O–CH_2), 68.7 (2 C, allyl. O–CH_2), 95.9, 99.9, 104.3, 104.8, 113.7 (6 C, aromatic CH), 117.3, 133.1 (4 C, allyl. C), 124.4, 140.9, 148.7, 157.6, 159.4 (6 C, aromatic C_q). FAB–MS (relative intensity): m/z 618 (84%, $(M+H)^+$).

4.10. (E)-1-[4-(Diheptylamino)-2-heptyloxyphenyl]-2-(3,5-dihydroxyphenyl)-ethene *13*

(*E*)-1-[4-(Diheptylamino)-2-heptyloxyphenyl]-2-(3,5-diallyloxyphenyl)-ethene (1.8 g, 3 mmol) was dissolved in 30 ml of THF under nitrogen. 350 mg (0.3 mmol) of $Pd(PPh_3)_4$ was added to the solution under nitrogen and, after stirring for 10 min, 350 mg (9.2 mmol) of $NaBH_4$ was added. The reaction mixture was stirred for 20 h and, then neutralized with 2 N HCl and extracted twice with 100 ml of methylene chloride. The combined organic layers were washed with water and dried with $MgSO_4$. Column filtration (ϕ9×5 cm), with a mixture of hexane and acetone (3:1) as eluent gave a yield of 1.24 g (79%). Due to its low stability, the product was characterized only per ^{1}H-NMR and was used immediately for the next step. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ =0.90 (m, 9 H, CH_3), 1.30 (m, 24 H, CH_2), 1.55 (m, 4 H, β-CH_2), 1.83 (m, 2 H, β-CH_2), 3.21 (t, 4 H, N–CH_2), 3.95 (t, 2 H, O–CH_2), 6.15 (d, 1 H, aromatic H), 6.28 (dd, 1 H, aromatic H), 6.30 (t, 1 H, aromatic H), 6.55 (d, 2 H, aromatic H), 6.72, 7.31 (AB, 2 H, olefinic H, ^3J=16.4 Hz), 7.37 (d, 1 H, aromatic H, ^3J=8.3 Hz).

4.11. (E,E)-bis{4-{2-[4-(Diheptylamino)-2-heptyloxyphenyl]ethenyl}-2,6-dihydroxyphenyl}squaraine *2*

A solution of (*E*)-1-[4-(diheptylamino)-2-heptyloxyphenyl]-2-(3,5-dihydroxyphenyl)ethene (900 mg, 1.67 mmol) and squaric acid (114 mg, 1 mmol) in toluene (8 ml) and 1-butanol (2.5 ml) was heated under reflux for 2 h. The reaction water was removed by azeotropic distillation with sodium sulfate, which was placed in a filter between the flask and the condenser. After reaction, the mixture was cooled to room temperature and the solvent removed under vacuum. The dark brown residue was washed with ethanol, acetone and cold hexane, dissolved in chloroform and filtered. After removal of the solvent under vacuum there were obtained 3 mg (0.3%) of green metallic crystals. IR (KBr): ν_{max}/cm^{-1} 2955, 2924, 2856, 1612, 1570, 1515, 1467, 1440, 1370, 1260, 1171, 1115, 1023, 806. ^{1}H-NMR ($CDCl_3$, 400 MHz): δ =0.88 (m, 18 H, CH_3), 1.28 (m, 56 H, CH_2), 1.91 (m, 4 H, β-CH_2), 3.20 (t, 8 H, N–CH_2), 3.98 (t, 4 H, O–CH_2), 6.98 (d, 2 H, aromatic H), 6.22 (dd, 2 H, aromatic H), 6.43 (s, 4 H, aromatic H), 6.81, 7.59 (AB, 4 H, olefinic H, ^3J=16.0 Hz), 7.38 (d, 2 H, aromatic H, ^3J=9.0 Hz), 10.89 (s, 4 H, OH). FAB–MS (relative intensity): m/z 1153 (1.2%, $M+H)^+$). HR–FAB–MS: calcd $(M+H)^+$: 1153.8184, measured: 1153.8191.

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