

Bis-, Tris-, and Tetrakis(squaraines) Linked by Stilbenoid Scaffolds

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Dedicated to Professor Leopold Horner on the occasion of his 90th birthday

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The oligosquaraines **1–5**, with stilbenoid scaffolds, were prepared by multistep syntheses in which the final steps consisted of condensation reactions between the semisquaric acid **21** and multiple resorcinols **12b–15b** and **17b**. The target compounds exhibit intense ($\epsilon > 250\,000 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$) and sharp absorption bands with maxima between 687 to 778 nm,

depending on the conjugation in the stilbenoid scaffold. Comparison with the monosquaraine **6** as a model compound reveals intramolecular interactions between different donor–acceptor–donor moieties, which give rise to increased absorption intensities.

Introduction

Since their discovery by Treibs and Jacob in 1965, squaraines have attracted considerable attention.^[1] They possess semiconductor and photoconductor properties and have been investigated for a variety of technological applications, such as in xerographic photoreceptors, organic solar cells, and optical recording media.^[2] Squaraines show aggregation in the solid state and in LB films and have therefore been extensively studied in the field of nonlinear optics.^[3] Their absorptions and emissions in the Vis and NIR regions, combined with their narrow bands ($\Delta\nu_{1/2} < 1000 \text{ cm}^{-1}$) and high molar absorption coefficients ($\epsilon_{\text{max}} > 10^5 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$), also make them attractive in the area of biolabeling.^[4] Stilbenoid compounds, on the other hand, have interesting photophysical and photochemical properties and are used in, for example, light-emitting diodes or nonlinear optical devices.^[5]

In previous reports we showed that the combination of these two structural principles – squaraines and stilbenes – resulted in NIR dyes with long-wavelength absorption maxima of up to 900 nm and more.^[6] The aim of this work was to generate a new class of “multi-arm” squarylium compounds with stilbenoid scaffolds – dyes with high chromophore densities.

Results and Discussion

Scheme 1 provides an overview of the two-, three-, and fourfold squaraines **1–5** described here, together with the model compound **6**. The bis(squaraines) **1** and **2** have linear

structures, and are conjugated through a stilbene and a 1,4-distyrylbenzene unit, respectively. The tris(squaraine) **3** has a tristyrylbenzene core and, thanks to the 1,3,5-trisubstitution, no possible linear conjugation pathway through the central benzene ring. In contrast to **3**, the tetrakis(squaraine) **4** is a conjugated system, although steric hindrance prevents a completely planar arrangement. The central saturated carbon atom in the tetrakis(squaraine) **5** blocks conjugation completely. As a simple model compound, we also synthesized the monosquaraine **6**. All of the squaraines prepared in this work bear 4-(dialkylamino)phenyl groups with two 2-hexyloctyl chains, to increase the solubility of the compounds and strengthen the terminal donor activity.

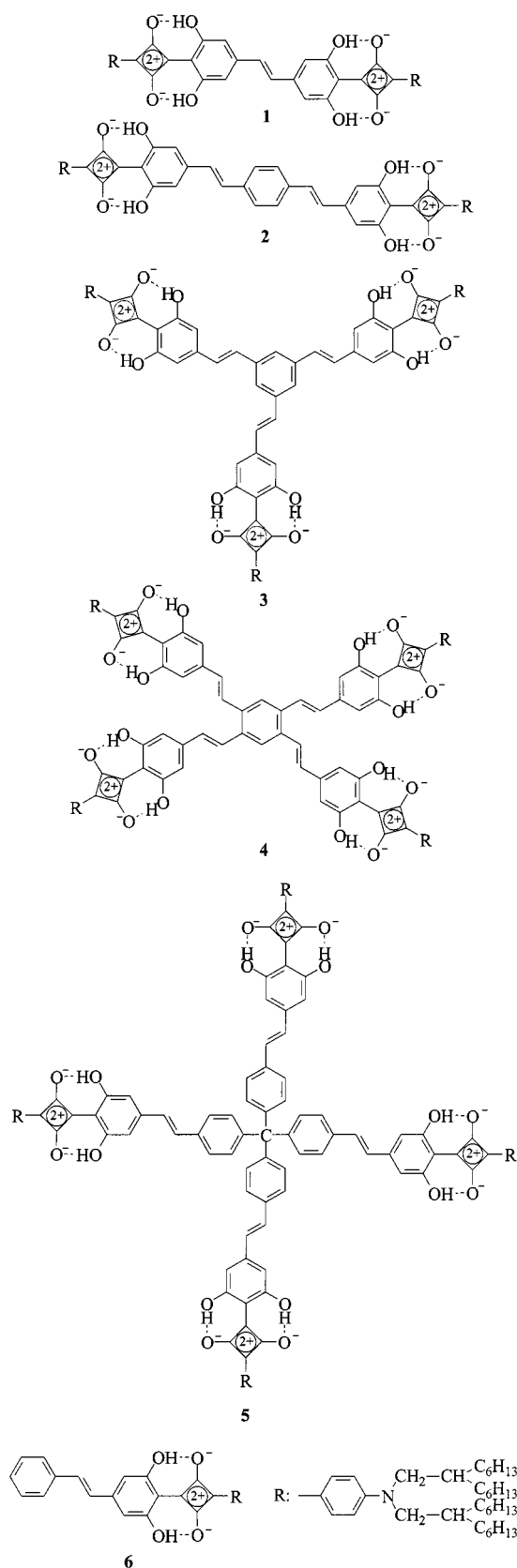
The synthetic procedure for the squaraines **1–6** is based on the preparation of the corresponding stilbenoid resorcinols. The olefinic double bonds could easily be produced by means of Wittig–Horner reactions. Scheme 2 summarizes the preparation of the phosphonates **7c–10c**, which were obtained by Wohl–Ziegler brominations of the hydrocarbons **7a–10a** and Arbusov rearrangements. The bromomethyl compounds **7b–10b** were treated in situ with triethyl phosphite; the yields given in Scheme 2 refer to the transformations **a** $\rightarrow$ **c**.

As shown in Scheme 3, the phosphonates **7c–10c** served as components for Wittig–Horner treatment with the aldehydes **11** and **16**. Subsequent deprotection with boron tribromide afforded the resorcinols (**12a–15a**, **17a** $\rightarrow$ **12b–15b**, **17b**). The total yields of these two steps amounted to 27–54%. The protection of the hydroxy groups proved to be necessary, since free phenols give only very poor yields in Wittig–Horner reactions.

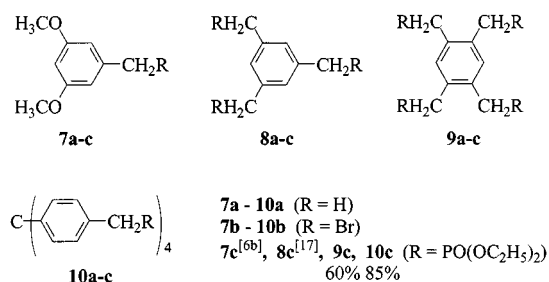
The final reaction sequence for the preparation of the squaraines **1–6** is illustrated in Scheme 4. The coupling process applied to squaric acid was originally developed by West and co-workers^[7] and improved by Law, Whitten, et al.^[8] Squaric acid dichloride **18** reacted under Friedel–Crafts alkylation conditions with 1 equiv. of *N,N*-

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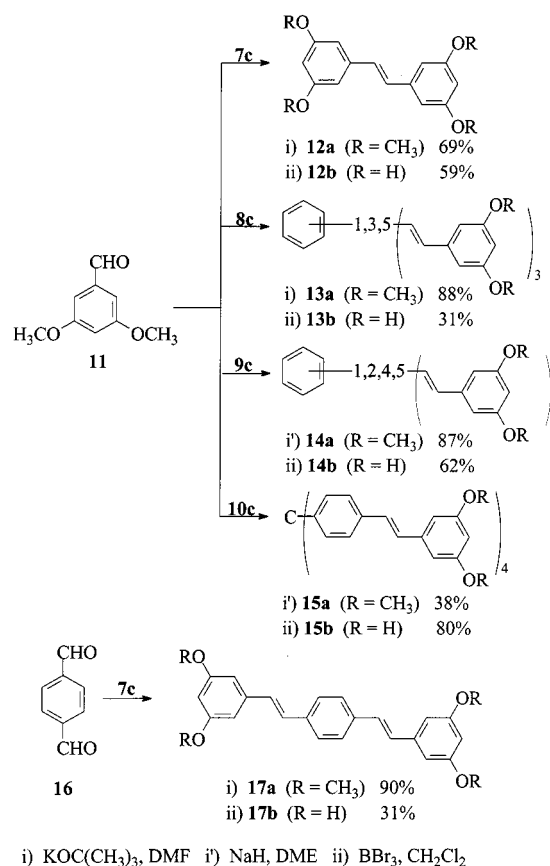
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Scheme 1. Target compounds: multiple squaraines **1–5** and model compound **6**



Scheme 2. Preparation of the phosphonates **7c–10c**; the corresponding methyl compounds **7a–10a** were brominated with NBS and the crude bromo compounds **7b–10b** heated to 160 °C with excess triethyl phosphite in order to obtain the phosphonates **7c–10c**

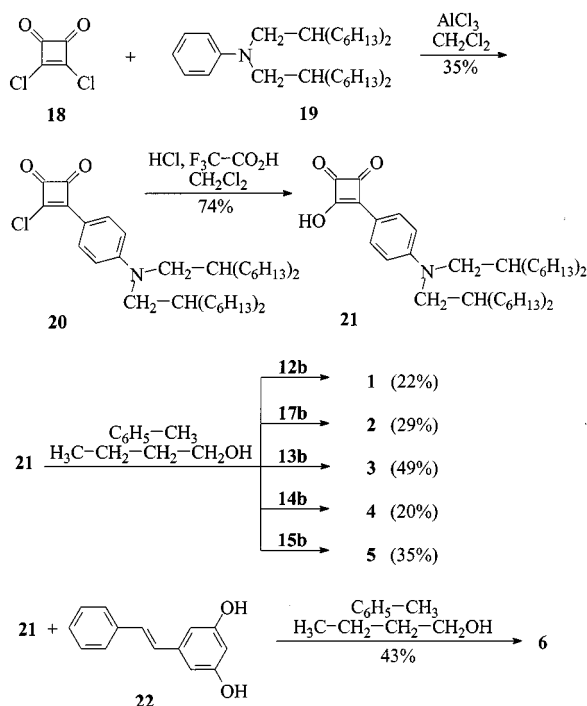


Scheme 3. Preparation of the multiple resorcinols **12b–15b** and **17b**

bis(2-hexyloctyl)aniline (**19**) to give compound **20**, which was hydrolyzed to the semisquaric acid **21** by treatment with hydrochloric acid and trifluoroacetic acid. Two-, three-, and fourfold condensation reactions between **21** and the corresponding diols **12b–15b** and **17b**, in refluxing toluene/1-butanol mixtures (3:1), afforded the desired squaraines **1–5** in reasonable yields. The water generated in the condensation reactions was removed by azeotropic distillation. The model compound **6** was prepared in an analogous electrophilic substitution (**21** + **22**^[9] → **6**).

The isolated squaraines **1–5** are blue to violet, crystalline compounds with metallic lusters. The monosquaraine **6** forms bronze, metal-like crystals. The compounds **1–6** are

reasonably soluble in organic solvents such as chloroform, and could be completely characterized by their NMR and mass spectra.^[10] Even ¹³C NMR spectra could be obtained,



Scheme 4. Preparation of the multiple squaraines 1–5 and the model squaraine 6

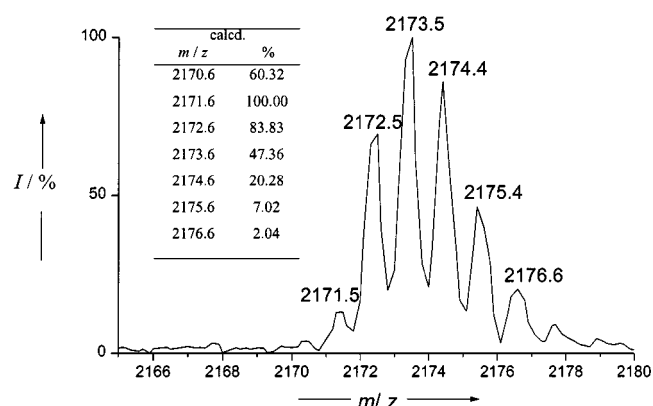


Figure 1. MALDI-TOF spectrum of 3 in dithranol

with the exception of 5. As an example, Figure 1 shows the MALDI-TOF spectrum of 3, with the typical molecular ion peak group $[M + n H]^+$ ($n = 0, 1, 2, 3, \dots$), where $n = 2$ represents the maximum.

We also performed condensation reactions between 13b, 14b, and 15b and a semisquaric acid^[11] lacking the dialkylamino group present in 21. The reaction, carried out in tributyl orthoformate as a water-removing agent, gave excellent yields (70–93%), but the resulting dark pigments were totally insoluble in organic solvents, and so we refrained from their structural characterization.

The electronic properties of a series of nonconjugated bis(squaraines) have already been described in the literature.^[12] A cationic bis(squaraine) with extended conjugation was described by Nakazumi et al.^[13] and displayed a strong pH dependence in its absorption spectra. Oligosquaraines with molecular masses of about 2000 and some polysquaraines have been investigated by different groups.^[14,15]

The electronic spectroscopic data (in chloroform) of the oligosquaraines 1–5 and the model squaraine 6 are summarized in Table 1. The absorption maxima vary from 674 to 778 nm, depending on the stilbenoid scaffold. Figure 2 shows a comparison of the absorption and emission of 1 and the model compound 6.

In both cases, the absorption consists of two close-lying bands.^[16] However, the absorption of the conjugated bis(squaraine) 1, a donor–acceptor–donor–donor–acceptor–donor system, is bathochromically shifted by 104 nm relative to that of the donor–acceptor–donor system of model compound 6. The tetrakis(squaraine) 5, with isolated chromophores, resembles that of 6 in its absorption characteristics. The cross-conjugated tris(squaraine) 3, the tetrakis(squaraine) 4 with sterically hindered conjugation, and the linearly conjugated bis(squaraine) 2 exhibit increasing red shifts, but do not reach the $\lambda_{\max}$ value of 1. The half-widths b of the absorption bands of the squaraines 1, 2, 3, and 5 are all in the range of $610 \pm 80 \text{ cm}^{-1}$, but the half-width of the band of 4, at 1334 cm^{-1} , is more than twice as large. Squaraine 4 is the only example in which intramolecular *steric interaction* between squaraine moieties is possible.

The intensities S of the absorption bands grow with increasing numbers of squaraine units, but they do so more than proportionally. The largest excess was found for the

Table 1. Absorption and fluorescence data of the multiple squaraines 1–5 and the model squaraine 6 in chloroform

Compound	Absorption $\lambda_{\max}$ [nm]	$\epsilon_{\max}$ [$10^8 \text{ cm}^2 \cdot \text{mol}^{-1}$]	Half-width b [cm^{-1}]	Intensity ^[a] S [$10^{11} \text{ cm}^2 \cdot \text{mol}^{-1}$]	Intensity per squaraine unit [$10^{11} \text{ cm}^2 \cdot \text{mol}^{-1}$]	Emission $\lambda_{\max}$ [nm]
1	778	2.58	552	1.42	0.71	798
2	724	4.56	689	3.14	1.57	750
3	693	8.11	532	4.32	1.44	714
4	707	3.93	1334	5.24	1.31	753
5	687	7.23	662	4.79	1.20	707
6	674	2.70	323	0.87	0.87	702

^[a] $S = b \cdot \epsilon_{\max}$

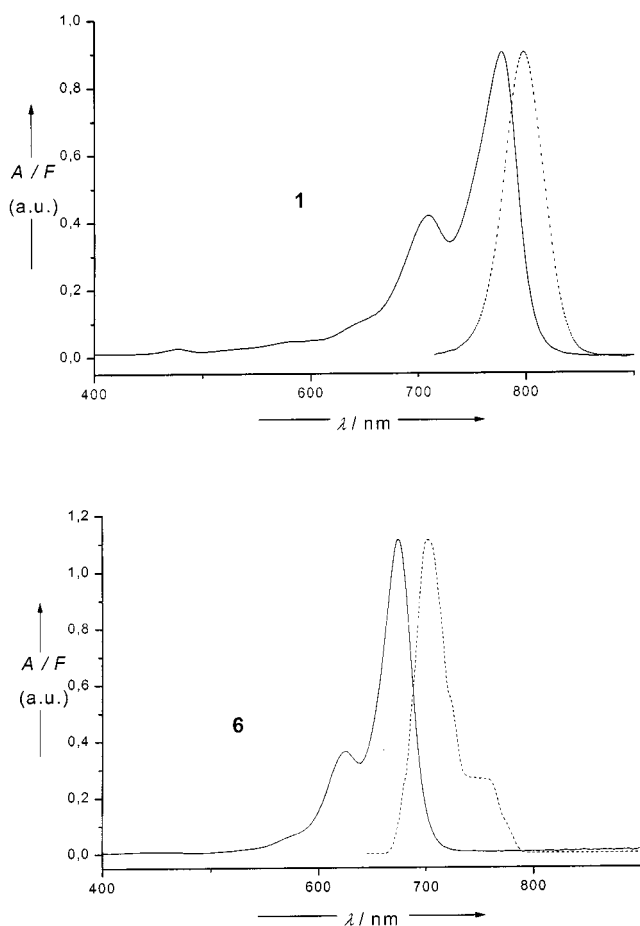


Figure 2. Absorption and normalized emission spectra of the squaraines **1** and **6** in chloroform; the emission spectra are uncorrected, concentration-independent, and also independent of the wavelength of excitation

bis(squaraine) **2**, the *S* value of which is more than three times higher than that of the model compound **6**. Obviously, there is intramolecular *electronic interaction* present (between the different donor–acceptor–donor moieties of **2–5**), which enhances the absorption intensity.

The squaraines **1–6**, when dissolved in chloroform, exhibit fluorescence. The fluorescence band of **6** is a mirror image of the absorption band (Figure 2). The emission at long wavelengths appears as a shoulder on the intense band in the spectra of **2–6**; only in **1** is such a shoulder not visible, perhaps because superimposed over by the strong emission at 800 nm.

Interestingly, protonation by addition of trifluoroacetic acid to a chloroform solution of the squaraines affected only the absorption behavior of the bis(squaraine) **1**. Its absorption maximum was blue-shifted, indicating that the D–A–D character of the compound had decreased on protonation. The maxima of the other squaraines were slightly red-shifted, due to positive solvatochromism arising from the enhanced polarity of the solvent. Solvatochromism and lessening of the D–A–D character by protic solvents cause opposite effects, so no quantitative conclusions can be drawn.

Conclusions

Two-, three-, and fourfold squaraines **1–5**, linked by stilbenoid scaffolds, have been produced by condensation reactions between the semisquaric acid **21** and the corresponding resorcinols **12b–15b** and **17b**. Reasonably good solubility of the dyes in organic solvents such as chloroform was guaranteed by the terminal bis(2-hexyloctyl)amino groups. Depending on the conjugation of the systems – fully present, sterically hindered, or totally absent – the absorption bands exhibit maxima between 778 and 687 nm. The fluorescence bands are situated at the Vis/NIR border. Apart from the high density of the chromophores both in the blue, metal-like crystals and in solution, the absorption intensity per squaraine unit in **2–5** – relative to that in the model squaraine **6** – is increased thanks to intramolecular interactions of the charge-transfer moieties.

Experimental Section

General Methods: The melting points were measured with a Büchi melting point apparatus and are uncorrected. – The ^1H and ^{13}C NMR spectra were recorded with Bruker AM 400 and AC 200 spectrometers with CDCl_3 as solvent unless otherwise noted, using TMS as internal standard. – The FD mass spectra were obtained with a Finnigan Mat 95, the MALDI-TOF mass spectra with a Micromass TOF spec E. A Beckman Acculab 4 spectrometer served for the measurement of the IR spectra. – UV/Vis spectra were taken with a Zeiss MCS 320/340, fluorescence spectra with a Perkin–Elmer LS 50B spectrometer. – Silica gel (E. Merck 60, 70–230 mesh ASTM) was used for column chromatography. – Elemental analyses were performed in the microanalytical laboratory of the Institute of Organic Chemistry at the University of Mainz, Germany.

Preparation of the Phosphonates: The phosphonates **7c**^[6b] and **8c**^[17] were prepared from the corresponding methyl compounds **7a** and **8a** by bromination with NBS and subsequent treatment with triethyl phosphite according to the literature.

Diethyl 2,4,5-Tris[(diethoxyphosphoryl)methyl]benzylphosphonate (9c): 1,2,4,5-Tetramethylbenzene (durene) (**9a**) (20.0 g, 150 mmol), *N*-bromosuccinimide (NBS) (106.0 g, 600 mmol), and catalytic amounts of AIBN (2.0 mg, 0.01 mmol) in 500 mL of dry tetrachloromethane were heated under reflux and irradiation (500-W tungsten lamp) for 20 h. After cooling, the succinimide was filtered off and washed with small amounts of tetrachloromethane. The organic phase was extracted with water and dried with anhydrous Na_2SO_4 . Addition of petroleum ether (40–70 °C) resulted in the precipitation of the crude tetrabromo compound, which was used directly for the following step, in which it was heated in an excess quantity of triethyl phosphite (124.0 g, 750 mmol) for 8 h at 160 °C. The generated bromoethane was distilled off during the reaction and the excess triethyl phosphite was removed at the end. Overall yield 60.7 g (60%), colorless oil. – IR (NaCl): $\tilde{\nu}$ = 2980 cm^{-1} , 2920, 1500, 1470, 1440, 1385, 1230, 1160, 1090, 1025, 960, 880, 850, 790. – ^1H NMR (CDCl_3): δ = 1.15 (t, 24 H, CH_3), 3.28 [d, $^2J(\text{H},\text{P})$ = 19.7 Hz, 8 H, CH_2P], 3.91 (m, 16 H, OCH_2), 7.08 (s, 2 H, arom. H). – ^{13}C NMR (CDCl_3): δ = 16.3 (CH_3), 30.7 (d, $^1J(\text{C},\text{P})$ = 137.5 Hz, CH_2P), 61.9 (OCH_2), 130.0 (aromat. C_q), 134.3 (aromat. CH). – MS (FD): m/z (%) = 678 (100) [M^+]. –

$C_{26}H_{50}O_{12}P_4$ (678.6): calcd. C 46.02, H 7.43; found C 45.85, H 7.36.

Diethyl 4-(Tris{4-[(diethoxyphosphoryl)methyl]phenyl}methyl)benzylphosphonate (10c): Preparation analogous to that of **9c**. Yield 85%, yellowish, resinous substance. – IR (KBr): $\tilde{\nu}$ = 2990 cm^{-1} , 2960, 1630, 1500, 1440, 1410, 1390, 1360, 1240, 1160, 1100, 1020, 910, 860, 800. – 1H NMR ($CDCl_3$): δ = 1.19 (m, 24 H, CH_3), 3.03 [d, $^2J(H,P)$ = 21.5 Hz, 8 H, CH_2P], 3.90 (m, 16 H, OCH_2), 7.01 (AA'BB', 16 H, arom. H). – MS (FD): m/z (%) = 920 (100) [M^+]. – $C_{45}H_{64}O_{12}P_4$ (920.9): calcd. C 58.69, H 7.01; found C 58.51, H 6.88.

Preparation of the Stilbenoid Scaffolds

(E)-3,3',5,5'-Tetramethoxystilbene (12a):^[18] 3,5-Dimethoxybenzaldehyde (**11**)^[19] (1.0 g, 6.0 mmol) and **7c** (1.7 g, 6.0 mmol), dissolved in 50 mL of dry DMF, were added dropwise to a solution of potassium *tert*-butoxide (1.7 g, 15.2 mmol) in 50 mL of dry DMF. The mixture was stirred at room temperature for 1 h and then poured onto 100 g of crushed ice. A precipitate was formed; this was separated by filtration and recrystallized from *n*-hexane/acetone (10:1). Yield 1.25 g (69%), colorless crystals, m.p. 126–128 °C (ref.: 126–128 °C).^[18] – 1H NMR ($CDCl_3$): δ = 3.81 (s, 12 H, OCH_3), 6.39 (t, 2 H, arom. H), 6.65 (d, 4 H, arom. H), 7.00 (s, 2 H, olefin. H).

(E)-3,3',5,5'-Tetrahydroxystilbene (12b):^[20] Compound **12a** (1.0 g, 3.3 mmol) was dissolved in 100 mL of dry dichloromethane and treated dropwise with boron tribromide (22 mL, 22.0 mmol, 1.0 M in *n*-hexane). The reaction mixture was heated under reflux for 7 h and carefully quenched with water. The ochre crystals were separated by filtration and washed several times with water. Yield 0.48 g (59%), m.p. > 300 °C (ref.: 320 °C).^[20] – 1H NMR ($[D_6]$ acetone): δ = 4.96 (s, 4 H, OH), 6.22 (t, 2 H, arom. H), 6.49 (d, 4 H, arom. H), 6.90 (s, 2 H, olefin. H). – MS (FD): m/z (%) = 244 (100) [M^+].

1,3,5-Tris[(E)-2-(3,5-dimethoxyphenyl)ethenyl]benzene (13a): This preparation was performed according to the procedure described for **12a**, using 3 equiv. of compound **11** and with dry THF as solvent in place of DMF. The reaction time was 3 h. Yield 88%, ochre crystals, m.p. 173 °C. – IR (KBr): $\tilde{\nu}$ = 2950 cm^{-1} , 2920, 2830, 1590, 1450, 1200, 1150, 1065, 965. – 1H NMR ($CDCl_3$): δ = 3.83 (s, 18 H, OCH_3), 6.41 (t, 3 H, arom. H), 6.70 (d, 6 H, arom. H), 7.09 (s, 6 H, olefin. H), 7.50 (s, 3 H, arom. H, central ring). – ^{13}C NMR ($CDCl_3$): δ = 55.3 (OCH_3), 100.1, 104.6 (aromat. CH), 124.1 (aromat. CH, central ring), 128.7, 129.2 (olefin. CH), 137.8, 139.2, 161.0 (aromat. C_q). – MS (FD): m/z (%) = 564 (100) [M^+]. – $C_{36}H_{36}O_6$ (564.7): calcd. C 76.57, H 6.43, found C 76.48, H 6.42.

5-[(E)-2-{3,5-Bis[(E)-2-(3,5-dihydroxyphenyl)ethenyl]phenyl}-ethenyl]-1,3-benzenediol (13b): Preparation analogous to that of **12b**. The crude product was purified by column filtration (8 × 10 cm, silica gel, toluene/acetone, 1:1). Yield 93%, ochre crystals, m.p. > 300 °C. – IR (KBr): $\tilde{\nu}$ = 3300 cm^{-1} , 1605, 1580, 1330, 1140, 1000, 955, 845. – 1H NMR ($[D_6]$ acetone): δ = 6.32 (t, 3 H, arom. H), 6.62 (d, 6 H, arom. H), 7.13, 7.24 (AB, 3J = 16.6 Hz, 6 H, olefin. H), 7.69 (s, 3 H, arom. H, central ring), 8.34 (s, 6 H, OH). – ^{13}C NMR ($[D_6]$ acetone): δ = 103.2, 106.0 (aromat. CH), 124.7 (aromat. CH, central ring), 128.9, 130.3 (olefin. CH), 139.1, 140.3, 159.6 (aromat. C_q). – MS (FD): m/z (%) = 480 (100) [M^+]. – $C_{30}H_{24}O_6$ (480.5): calcd. C 74.99, H 5.03; found C 74.75, H 5.12.

1,2,4,5-Tetrakis[(E)-2-(3,5-dimethoxyphenyl)ethenyl]benzene (14a): Tetraphosphonate **9c** (0.6 g, 0.9 mmol) in 100 mL of dry dimethoxy-

ethane (DME) was added dropwise to a suspension of NaH (80% in paraffin, 0.32 g, 10.6 mmol) in the same solvent. After 15 min of stirring at room temperature, a solution of **11** (0.6 g, 3.6 mmol) in DME was added. The reaction mixture was heated under reflux for 3 h and carefully quenched with methanol/water (1:1). The precipitated crystals were separated by filtration and washed with petroleum ether (40–70 °C). Yield 0.5 g (87%), ochre crystals, m.p. 241 °C. – IR (KBr): $\tilde{\nu}$ = 2980 cm^{-1} , 2920, 2820, 1580, 1440, 1415, 1195, 1145, 1050, 940. – 1H NMR ($CDCl_3$): δ = 3.82 (s, 24 H, OCH_3), 6.41 (t, 4 H, arom. H), 6.69 (d, 8 H, arom. H), 7.01, 7.41 (AB, 3J = 16.0 Hz, 8 H, olefin. H), 7.75 (s, 2 H, arom. H, central ring). – ^{13}C NMR ($CDCl_3$): δ = 55.4 (OCH_3), 100.3, 104.9 (aromat. CH), 125.3 (aromat. CH, central ring), 126.9, 131.7 (olefin. CH), 135.6, 139.5, 161.2 (aromat. C_q). – MS (FD): m/z (%) = 726 (100) [M^+]. – $C_{46}H_{46}O_8$ (726.3): calcd. C 76.01, H 6.38; found C 76.07, H 6.26.

5-[(E)-2-{2,4,5-Tris[(E)-2-(3,5-dihydroxyphenyl)ethenyl]phenyl}-ethenyl]-1,3-benzenediol (14b): This preparation was performed according to the procedure described for **12b**. Yield 62%, ochre crystals, m.p. > 300 °C. – IR (KBr): $\tilde{\nu}$ = 3300 cm^{-1} , 1580, 1145, 950. – 1H NMR ($[D_6]$ acetone): δ = 6.32 (t, 4 H, arom. H), 6.68 (d, 8 H, arom. H), 7.11, 7.53 (AB, 3J = 16.0 Hz, 8 H, olefin. H), 7.96 (s, 2 H, arom. H, central ring), 8.43 (s, 8 H, OH). – ^{13}C NMR (methanol- d_4): δ = 103.4, 106.2 (aromat. CH), 125.5 (aromat. CH, central ring), 126.8, 132.6 (olefin. CH), 136.6, 140.7, 159.7 (aromat. C_q). – MS (FD): m/z (%) = 614 (100) [M^+]. – $C_{38}H_{30}O_8$ (614.7): calcd. C 74.26, H 4.92; found C 73.99, H 5.01.

1,3-Dimethoxy-5-[(E)-2-[4-(tris{4-[(E)-2-(3,5-dimethoxyphenyl)ethenyl]phenyl}methyl)phenyl]ethenyl]benzene (15a): This preparation was performed according to the procedure described for **14a**. The reaction time was 6 h. The crude product was dissolved in acetone and precipitated by the addition of a mixture of petroleum ether (40–70 °C)/diethyl ether (1:1). Yield 38%, ochre crystals, m.p. 229 °C. – IR (KBr): $\tilde{\nu}$ = 3000 cm^{-1} , 2920, 2820, 1580, 1445, 1415, 1195, 1140, 1055, 950, 840. – 1H NMR ($CDCl_3$): δ = 3.81 (s, 24 H, OCH_3), 6.39 (t, 4 H, arom. H), 6.66 (d, 8 H, arom. H), 6.99, 7.08 (AB, 3J = 16.6 Hz, 8 H, olefin. H), 7.26, 7.40 (AA'BB', 16 H, arom. H). – ^{13}C NMR ($CDCl_3$): δ = 55.3 (OCH_3), 64.3 (C_q), 99.9, 104.5, 125.9, 131.2 (aromat. CH), 128.6, 128.7 (olefin. CH), 134.8, 139.3, 146.1, 160.9 (aromat. C_q). – MS (FD): m/z (%) = 969 (100) [M^+]. – $C_{65}H_{60}O_8$ (969.2): calcd. C 80.55, H 6.24; found C 80.33, H 6.20.

5-[(E)-2-[4-(Tris{4-[(E)-2-(3,5-dihydroxyphenyl)ethenyl]phenyl}-methyl)phenyl]ethenyl]-1,3-benzenediol (15b): Preparation analogous to that of **12b**. Yield 80%, ochre crystals, m.p. > 300 °C. – IR (KBr): $\tilde{\nu}$ = 3400 cm^{-1} , 1590, 1500, 1150, 960, 830. – 1H NMR ($[D_6]$ DMSO): δ = 5.22 (s, 4 H, arom. H), 5.49 (s, 8 H, arom. H), 6.09 (s, 8 H, olefin. H), 6.26, 6.60 (AA'BB', 8 H, arom. H), 8.37 (br. s, 8 H, OH). – ^{13}C NMR ($[D_4]$ methanol): δ = 65.7 (C_q), 103.0, 106.2, 126.8, 132.4 (aromat. CH), 128.9, 129.9 (olefin. CH), 136.5, 140.7, 147.3, 159.5 (aromat. C_q). – MS (FD): m/z (%) = 857 (100) [M^+]. – $C_{57}H_{44}O_8$ (856.3): calcd. C 79.89, H 5.18; found C 79.75, H 5.26.

1-[(E)-2-{4-[(E)-2-(3,5-Dimethoxyphenyl)ethenyl]phenyl}ethenyl]-3,5-dimethoxybenzene (17a): Terephthalaldehyde (**16**) (1.0 g, 7.5 mmol) and phosphonate **7c** (4.3 g, 15.0 mmol), dissolved in 50 mL of dry DMF, were added dropwise to a solution of potassium *tert*-butoxide (4.2 g, 38.0 mmol) in 100 mL of dry DMF. The mixture was stirred at room temperature for 1 h and then poured onto 100 g of crushed ice. A yellowish precipitate was formed; this was separated by filtration and washed with 100 mL of water. Yield

4.18 g (90%), pale yellow crystals, m.p. 162–165 °C. – IR (KBr): $\tilde{\nu}$ = 2950 cm^{-1} , 1590, 1575, 1450, 1430, 1330, 1300, 1260, 1245, 1065, 960, 940, 840, 820. – ^1H NMR (CDCl_3): δ = 3.82 (s, 12 H, OCH_3), 6.39 (t, 2 H, arom. H), 6.67 (d, 4 H, arom. H), 7.06 (s, 4 H, olefin. H), 7.49 (s, 4 H, arom. H, central ring). – ^{13}C NMR (CDCl_3): δ = 55.4 (OCH_3), 100.1, 104.6, 126.9 (arom. CH), 128.6, 128.8 (olefin. CH), 136.6, 139.4, 161.0 (arom. C_q). – MS (FD): m/z (%) = 403 (100) [M^+]. – $\text{C}_{26}\text{H}_{26}\text{O}_4$ (402.5): calcd. C 77.59, H 6.51; found C 77.60, H 6.57.

5-[(E)-2-{4-[(E)-2-(3,5-Dihydroxyphenyl)ethenyl]phenyl}ethenyl]-1,3-benzenediol (17b): Preparation analogous to that of **12b**. The crude product was purified by column filtration (8 × 10 cm, silica gel, acetone) and recrystallized from acetone/chloroform (1:1). Yield 31%, light yellow crystals, m.p. > 300 °C. – IR (KBr): $\tilde{\nu}$ = 3350 cm^{-1} , 1600, 1580, 1340, 1140, 1005, 985, 960, 840. – ^1H NMR ($[\text{D}_6]\text{acetone}$): δ = 6.30 (t, 2 H, arom. H), 6.59 (d, 4 H, arom. H), 7.10 (s, 4 H, olefin. H), 7.56 (s, 4 H, arom. H, central ring), 8.23 (br. s, 4 H, OH). – ^{13}C NMR ($[\text{D}_6]\text{acetone}$): δ = 103.3, 106.1, 127.7 (arom. CH), 128.8, 129.7 (olefin. CH), 137.7, 140.4, 159.6 (arom. C_q). – MS (FD): m/z (%) = 692 (100) [2M^+]; 346 (20) [M^+]. – $\text{C}_{22}\text{H}_{18}\text{O}_4$ (346.4): calcd. C 76.29, H 5.24; found C 76.50, H 5.20.

Synthesis of the Semisquaric Acid 21: 3,4-Dichloro-3-cyclobutene-1,2-dione (squaric acid dichloride) (**18**) was prepared according to the literature.^[1b]

3-{4-[Bis(2-hexyloctyl)amino]phenyl}-4-chloro-3-cyclobutene-1,2-dione (20): A solution of *N,N*-bis(2-hexyloctyl)aniline (**19**)^[6d] (9.7 g, 20.0 mmol) and 3,4-dichloro-3-cyclobutene-1,2-dione (**18**) (3.0 g, 20.0 mmol) in 15 mL of dichloromethane was added dropwise to a boiling suspension of aluminium trichloride (2.7 g, 20.0 mmol) in 30 mL of dichloromethane. The reaction mixture was stirred at reflux for 1 h, allowed to cool to room temperature, and then poured into ice-cold water. The organic layer was separated, washed with water, and dried with MgSO_4 . The solvent was removed, and the residue purified by column chromatography [10 × 35 cm, silica gel, petroleum ether (40–70 °C)]. Yield 4.2 g (35%), red crystals, m.p. 58–62 °C. – IR (KBr): $\tilde{\nu}$ = 2940 cm^{-1} , 2900, 2835, 1785, 1760, 1735, 1590, 1550, 1490, 1470, 1400, 1345, 1320, 1270, 1190, 1120, 1035, 830. – ^1H NMR (CDCl_3): δ = 0.86 (t, 12 H, CH_3), 1.24 (m, 40 H, CH_2), 1.84 (m, 2 H, CH), 3.32 (d, 4 H, NCH_2), 6.71, 8.08 (AA'BB', 4 H, arom. H). – ^{13}C NMR (CDCl_3): δ = 14.1 (CH_3), 22.6, 26.4, 29.7, 31.5, 31.8 (CH_2), 35.9 (CH), 56.7 (NCH_2), 112.4, 131.5 (arom. CH), 113.8, 153.4 (arom. C_q), 171.4, 185.9, 189.9, 196.0 (C_q , four-membered ring). – MS (FD): m/z (%) = 600 (100) [M^+]. – $\text{C}_{38}\text{H}_{62}\text{ClNO}_2$ (600.4): calcd. C 76.02, H 10.41, N 2.33; found C 75.66, H 10.49, N 2.28.

3-{4-[Bis(2-hexyloctyl)amino]phenyl}-4-hydroxy-3-cyclobutene-1,2-dione (21): Trifluoroacetic acid (5 mL) and hydrochloric acid (2 mL, 5 mL) were added to compound **20** (2.0 g, 3.3 mmol), dissolved in 20 mL of dichloromethane and 5 mL of acetone. The reaction mixture was refluxed for 2 d. After evaporation of the solvent, yellow crystals remained, and these were washed several times with petroleum ether (40–70 °C). Yield 1.4 g (74%), yellow crystals, m.p. 192–195 °C. – IR (KBr): $\tilde{\nu}$ = 3200 cm^{-1} , 2950, 2920, 2850, 1750, 1695, 1560, 1460, 1415, 1190, 1020. – ^1H NMR ($[\text{D}_6]\text{DMSO}/\text{CDCl}_3$, 3:1): δ = 0.81 (t, 12 H, CH_3), 1.19 (m, 40 H, CH_2), 1.78 (m, 2 H, CH), 3.26 (d, 4 H, NCH_2), 6.72, 7.78 (AA'BB', 4 H, arom. H). – ^{13}C NMR ($[\text{D}_6]\text{DMSO}$): δ = 13.8 (CH_3), 22.0, 25.7, 29.1, 30.7, 31.2 (CH_2), 34.9 (CH), 55.1 (NCH_2), 112.2, 128.0 (arom. CH), 116.0, 150.5 (arom. C_q), 173.4 (aryl-substituted C_q , four-membered ring), 194.3 (3 C_q , four-membered ring, super-

imposed). – MS (FD): m/z (%) = 582 (100) [M^+]. – $\text{C}_{38}\text{H}_{63}\text{NO}_3$ (581.9): calcd. C 78.43, H 10.91, N 2.41; found C 78.56, H 10.80, N 2.37.

General Procedure for the Preparation of the Squaraines 1–6: The corresponding resorcinol (**12b–15b**, **17b**, or **22**) and the appropriate amount of compound **21**, dissolved in toluene/1-butanol (3:1), were refluxed for 4 h (unless otherwise stated). The progress of the reaction was monitored by Vis/NIR spectroscopy every 30 min. Water of condensation was removed by a filter containing anhydrous NaSO_4 between flask and reflux condenser. The reaction mixture was finally allowed to cool to room temperature, the solvent was removed, and the residue treated as described below.

Squaraine 1: The crude product was washed with *n*-hexane and hot acetone. Yield 22%, metal-like, blue crystals, m.p. 220 °C (decomp.). – UV/Vis (CHCl_3): λ_{max} = 778 nm/ ϵ_{max} = $2.58 \cdot 10^8 \text{ cm}^2 \cdot \text{mol}^{-1}$, λ_{max} = 710 nm/ ϵ_{max} = $1.20 \cdot 10^8 \text{ cm}^2 \cdot \text{mol}^{-1}$. – IR (KBr): $\tilde{\nu}$ = 2920 cm^{-1} , 1590, 1425, 1395, 1325, 1185, 1165, 1040, 840, 780. – ^1H NMR (CDCl_3): δ = 0.86 (t, 24 H, CH_3), 1.25 (m, 80 H, CH_2), 1.86 (m, 4 H, CH), 6.52 (s, 4 H, arom. H), 6.81, 8.22 (AA'BB', 8 H, arom. H), 7.05 (s, 2 H, olefin. H), 12.20 (s, 4 H, OH). – ^{13}C NMR (CDCl_3): δ = 13.7 (CH_3), 22.6, 26.4, 29.6, 31.6, 31.7 (CH_2), 37.0 (CH), 57.4 (NCH_2), 107.8, 114.5, 134.9 (arom. CH), 109.7, 118.7, 148.5, 156.1, 163.0 (arom. C_q), 132.8 (olefin. CH), 175.8, 179.7, 182.9 (C_q , four-membered ring). – MS (FD): m/z (%) = 1376 (100) [$\text{M} + 4\text{H}$] $^{4+}$. – $\text{C}_{90}\text{H}_{134}\text{N}_2\text{O}_8$ (1372.1): calcd. C 78.79, H 9.84, N 2.04; found C 78.40, H 9.70, N 2.33.

Squaraine 2: The crude product was washed with *n*-hexane, hot methanol, and acetone. Yield 29%, bronze, metal-like crystals, m.p. > 300 °C. – UV/Vis (CHCl_3): λ_{max} = 724 nm/ ϵ_{max} = $4.56 \cdot 10^8 \text{ cm}^2 \cdot \text{mol}^{-1}$, λ_{max} = 672 nm/ ϵ_{max} = $1.51 \cdot 10^8 \text{ cm}^2 \cdot \text{mol}^{-1}$. – IR (KBr): $\tilde{\nu}$ = 2920 cm^{-1} , 2840, 1590, 1405, 1315, 1290, 1185, 830, 780. – ^1H NMR (CDCl_3): δ = 0.86 (t, 24 H, CH_3), 1.25 (m, 80 H, CH_2), 1.85 (m, 4 H, CH), 3.43 (d, 8 H, NCH_2), 6.51 (s, 4 H, arom. H), 6.79 (d, 4 H, arom. H), 6.94, 7.20 (AB, 3J = 16.1 Hz, 4 H, olefin. H), 7.50 (s, 4 H, arom. H, central ring), 8.20 (d, 4 H, arom. H), 12.22 (s, 4 H, OH). – ^{13}C NMR (CDCl_3): δ = 14.0 (CH_3), 22.6, 26.4, 29.6, 31.6, 31.7 (CH_2), 36.9 (CH), 57.3 (NCH_2), 107.2, 114.4 (arom. CH), 111.5, 118.4 (arom. C_q), 127.8 (arom. CH, central ring), 128.8, 133.5 (olefin. CH), 134.6 (arom. CH), 137.2, 149.6, 155.9, 162.9 (arom. C_q), 174.9, 179.5, 182.9 (C_q , four-membered ring). – MS (FD): m/z (%) = 1477 (100) [$\text{M} + 3\text{H}$] $^{4+}$. – $\text{C}_{98}\text{H}_{140}\text{N}_2\text{O}_8$ (1474.2): calcd. C 79.85, H 9.57, N 1.90; found C 79.83, H 9.58, N 2.00.

Squaraine 3: Reaction time 5 h, the crude product was washed with cold acetone and purified by column filtration (8 × 10 cm, silica gel, chloroform). Yield 49%, violet, metal-like crystals, m.p. 130 °C. – UV/Vis (CHCl_3): λ_{max} = 693 nm/ ϵ_{max} = $8.11 \cdot 10^8 \text{ cm}^2 \cdot \text{mol}^{-1}$, λ_{max} = 638 nm/ ϵ_{max} = $2.26 \cdot 10^8 \text{ cm}^2 \cdot \text{mol}^{-1}$. – IR (KBr): $\tilde{\nu}$ = 2920 cm^{-1} , 2850, 1590, 1405, 1310, 1185, 1035, 780. – ^1H NMR (CDCl_3): δ = 0.86 (t, 36 H, CH_3), 1.25 (m, 120 H, CH_2), 1.86 (m, 6 H, CH), 3.42 (m, 12 H, NCH_2), 6.53 (s, 6 H, arom. H), 6.78 (d, 6 H, arom. H), 6.93, 7.19 (AB, 3J = 16.1 Hz, 6 H, olefin. H), 7.48 (s, 3 H, arom. H, central ring), 8.18 (d, 6 H, arom. H), 12.22 (s, 6 H, OH). – ^{13}C NMR (CDCl_3): δ = 14.0 (CH_3), 22.6, 26.4, 29.6, 31.6, 31.7 (CH_2), 36.9 (CH), 57.3 (NCH_2), 107.3 (arom. CH), 111.6 (arom. C_q), 114.4 (arom. CH), 118.5 (arom. C_q), 126.2 (arom. CH, central ring), 129.0, 133.0 (olefin. CH), 134.6 (arom. CH), 137.4, 149.6, 155.8, 163.2 (arom. C_q), 175.4, 180.3, 182.8 (C_q , four-membered ring). – MS (MALDI-TOF): m/z (%) = 2174 (100) [$(\text{M} + 2\text{H})^+$]. – $\text{C}_{144}\text{H}_{207}\text{N}_3\text{O}_{12}$ (2172.3): calcd. C 79.62, H 9.61, N 1.93; found C 79.44, H 9.70, N 2.11.

Squaraine 4: The residue was washed with hot *n*-hexane, methanol, and cold acetone, and was further purified by column filtration (8 × 10 cm, silica gel, toluene/ethyl acetate, 30:1). Yield 20%, metal-like, violet crystals, m.p. 143–145 °C. – UV/Vis (CHCl₃): $\lambda_{\max}$ = 707 nm/ $\epsilon_{\max}$ = 3.93·10⁸ cm²·mol^{−1}, shoulder at 652 nm (ϵ = 2.73·10⁸ cm²·mol^{−1}). – IR (KBr): $\tilde{\nu}$ = 2920 cm^{−1}, 1590, 1400, 1315, 1290, 1185, 1035, 780. – ¹H NMR (CDCl₃): δ = 0.86 (t, 48 H, CH₃), 1.25 (m, 160 H, CH₂), 1.86 (m, 8 H, CH), 3.42 (d, 16 H, NCH₂), 6.57 (s, 8 H, aromat. H), 6.79 (d, 8 H, aromat. H), 6.95, 7.56 (AB, ³J = 16.1 Hz, 8 H, olefin. H), 7.79 (s, 2 H, aromat. H, central ring), 8.22 (d, 8 H, aromat. H), 12.24 (s, 8 H, OH). – ¹³C NMR (CDCl₃): δ = 14.0 (CH₃), 22.6, 26.4, 29.7, 31.6, 31.8 (CH₂), 36.9 (CH), 57.3 (NCH₂), 107.6, 114.4, 134.7 (aromat. CH), 130.7, 132.0 (olefin. CH), 111.9, 118.6, 149.7, 155.8, 163.3 (aromat. C_q), 175.5, 180.6, 182.9 (C_q, four-membered ring); the signals of the carbon atoms of the central ring are not detectable. – MS (MALDI-TOF): *m/z* (%) = 2872 (100) [(M + 2H)⁺]. – C₁₉₀H₂₇₄N₄O₁₆ (2870.3): calcd. C 79.51, H 9.62, N 1.95; found C 78.88, H 9.72, N 2.08.

Squaraine 5: The crude product was washed with petroleum ether (40–70 °C), hot methanol, and diethyl ether. Yield 35%, dark violet crystals, m.p. 175 °C (decomp.). – UV/Vis (CHCl₃): $\lambda_{\max}$ = 687 nm/ $\epsilon_{\max}$ = 7.23·10⁸ cm²·mol^{−1}, $\lambda_{\max}$ = 637 nm/ $\epsilon_{\max}$ = 2.96·10⁸ cm²·mol^{−1}. – IR (KBr): $\tilde{\nu}$ = 2920 cm^{−1}, 2850, 1590, 1405, 1325, 1295, 1185, 1035, 830, 780. – ¹H NMR (CDCl₃): 0.86 (t, 48 H, CH₃), 1.25 (m, 160 H, CH₂), 1.87 (m, 8 H, CH), 3.42 (d, 16 H, NCH₂), 6.51 (s, 8 H, aromat. H), 6.79 (d, 8 H, aromat. H), 6.91, 7.22 (AB, ³J = 15.8 Hz, 8 H, olefin. H), 7.23, 7.43 (AA'BB', 16 H, aromat. H), 8.21 (d, 8 H, aromat. H), 12.22 (s, 8 H, OH). – MS (MALDI-TOF): *m/z* (%) = 3115 (100) [(M + 2H)⁺]. – C₂₀₉H₂₈₈N₄O₁₆ (3112.6): calcd. C 80.65, H 9.33, N 1.80; found C 80.41, H 9.22, N 1.90.

Model Squaraine 6: The crude product was washed with hot methanol and hot *n*-hexane. Yield 43%, bronze, metal-like crystals, m.p. 173 °C. – UV/Vis (CHCl₃): $\lambda_{\max}$ = 674 nm/ $\epsilon_{\max}$ = 2.70·10⁸ cm²·mol^{−1}, $\lambda_{\max}$ = 626 nm/ $\epsilon_{\max}$ = 0.88·10⁸ cm²·mol^{−1}. – IR(KBr): $\tilde{\nu}$ = 3400 cm^{−1}, 2920, 2850, 1590, 1550, 1400, 1320, 1285, 1190, 1030, 1000, 960, 840, 780, 750, 690. – ¹H NMR (CDCl₃): δ = 0.86 (t, 12 H, CH₃), 1.25 (m, 40 H, CH₂), 1.86 (m, 2H, CH), 3.43 (d, 4 H, NCH₂), 6.52 (s, 2 H, aromat. H), 6.80 (d, 2 H, aromat. H), 6.92, 7.25 (AB, ³J = 16.6 Hz, 2 H, olefin. H), 7.37–7.51 (m, 5 H, aromat. H), 8.21 (d, 2 H, aromat. H), 12.23 (s, 2 H, OH). – ¹³C NMR (CDCl₃): δ = 14.1 (CH₃), 22.6, 26.4, 29.6, 31.5, 31.8 (CH₂), 36.9 (CH), 57.3 (NCH₂), 107.1, 114.4 (aromat. CH), 111.3, 118.4 (aromat. C_q), 127.3 (aromat. CH), 127.8, 134.0 (olefin. CH), 128.8, 128.8 (aromat. CH), 134.6 (aromat. CH), 136.5, 149.8, 155.7, 163.0 (aromat. C_q), 175.2, 179.8, 182.9 (C_q, four-membered ring). – MS (FD): *m/z* (%) = 779 (100) [(M + 3 H)⁺]. – C₅₂H₇₃NO₄ (776.2): calcd. C 80.47, H 9.48, N 1.80; found C 80.23, H 9.52, N 1.82.

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