Extension of the Squaraine Chromophore in Symmetrical Bis(stilbenyl)squaraines

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Received February 14, 1997[⊗]

The bis(stilbenyl)squaraines **6d**−**j,d′,j′** represent a novel class of NIR pigments. Their synthesis was performed by the regioselective 2-fold condensation of highly nucleophilic 3,5-dihydroxystilbenes **4d**−**j,d′,j′** with squaric acid (**5**). Depending on the substitution with alkoxy groups, the absorption maxima range in solution from 680 to 735 nm. Reflexion measurements in the solid state reveal an exciton splitting with maxima at about 670 and 1000 nm.

Introduction

1,3-Disubstituted squaric acid derivatives, which are often intensively colored, constitute the class of the squaraines that has been known for more than 30 years.[1−5] The remarkable activity for the generation of new derivatives is due to the considerable industrial interest in developing suitable squaraines for technical applications such as electrophotography,[3] solar energy conversion,[6] optical data storage,[7] nonlinear optics,[8−10] fluorescent labels,[11] etc. Like the squaraines, stilbenoid compounds qualify for the application in materials science as optical brighteners, laser dyes, photoconductors, photoresists, light emitting diodes, materials for nonlinear optics, optical recording media, etc. owing to their extraordinary optical and optoelectronic characteristics.[12] A combination of these two building blocks—squaraine and stilbene—should originate very interesting new materials.

The introduction of stilbene units with the accompanying extension of conjugation in comparison to the known diphenylsquaraines should lead to a bathochromic shift of the vis absorption into the NIR region which would be very useful for the applicability of GaAs diode lasers. We reported recently on the synthesis of the first bis(stilbenyl)squaraines.[13]

Results and Discussion

The condensation of squaric acid with 2 equiv of electron rich aromatic compounds represents the original procedure[14] for the synthesis of symmetrical squaraines. Resultant water of the reaction can be removed by an azeotropic distillation.

In the first instance stilbenes had to be developed which are capable of reacting with squaric acid in the described manner. The Wittig−Horner olefination provides a convenient route. The benzyl bromides **1** were treated with triethyl phosphite at 160 °C. The phosphonates generated in the Arbuzov rearrangement could be applied without further purification. The addition of the substituted benzaldehydes **2** led in the presence of NaH/DME or $NaOCH_3$/DMF to the stilbenes **3a**−**j**. Chromatography on silica gel afforded the pure (*E*)-configurations. The yield varied between 64 and 95% and decreased to 39% when 3-hydroxybenzaldehyde with an unprotected hydroxy group was used.

It turned out that the nucleophilicity of C-4 in **3a,b** was too low for an attack on squaric acid. Therefore a hydroxy group was placed in C-3; however, stilbene **3c** still did not react. A second activating hydroxy group in position C-5 had to be introduced.[15] In order to enhance the yields of the Witting−Horner reaction we started with 1-(bromomethyl)-3,5-dimethoxybenzene. The selective deprotection **3d**−**j** → **4d**−**j** was achieved by the action of lithium diphenylphosphide whereas boron tribromide cleaved all alkoxy groups present in **3d** (Scheme 1).

Compound **3j** with three neighboring hexyloxy substituents represented the most difficult case. The reaction time had to be carefully optimized, otherwise the central hexyloxy group was cleaved, too (**3j** → **4j′**). The 2-fold condensation reactions of **4d**−**j,d′,j** and squaric acid (**5**) afforded the desired squaraines, **6d**−**j,d′,j**. The yields were moderate, but the selectivity of the 1,3-attack on **5** was perfect (Scheme 2).

The squaraine pigments **6** form small blue crystals with a metallic lustre. Their solubility in organic solvents is very low, it just allows the determination of the vis absorption. The narrow bands have a half-width of 60−100 nm; the λ_{max} values in chloroform are listed in Scheme 2.[16] Due to the low double-bond character of the carbonyl groups in the 4-membered ring the CO stretching bands appear at 1600−1620 cm^{-1} in KBr. The low solubility of the bis(stilbenyl)squaraines **6** did not permit

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1997.

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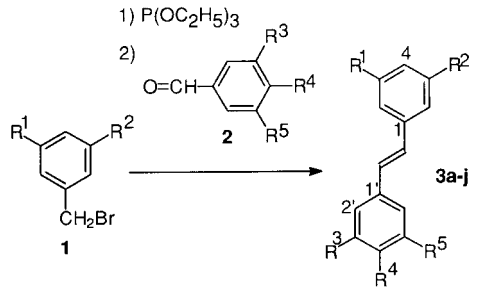
(15) The substitution pattern 3-OH/5-OCH_3 works, too; however, the yield of the condensation reaction is not satisfying.
(16) The extremely low solubility did not permit an exact determination of the ϵ values; log ϵ is in the range of 5.

S0022-3263(97)00284-3 CCC: $14.00

Scheme 1

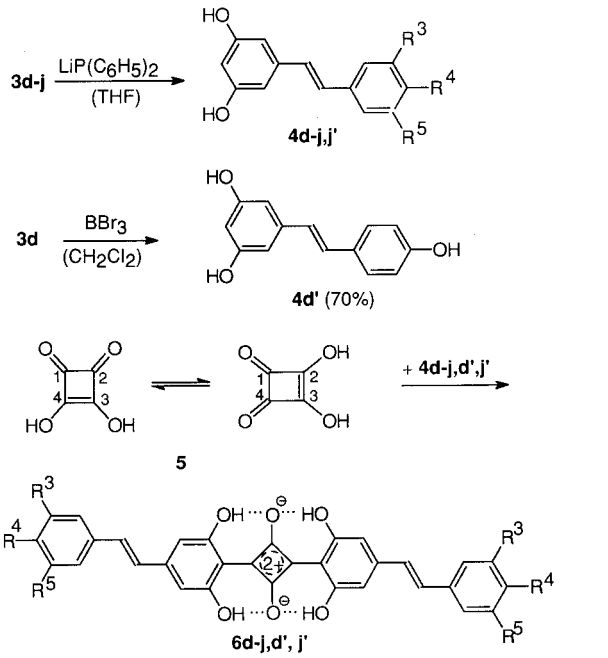


3	R^1	R^2	R^3	R^4	R^5	Yield [%]
a	H	H	H	OC_6H_{13}	H	64
b	H	H	$OC_{12}H_{25}$	$OC_{12}H_{25}$	$OC_{12}H_{25}$	81
c	H	OH	H	OC_6H_{13}	H	39
d	OCH_3	OCH_3	H	OC_6H_{13}	H	87
e	OCH_3	OCH_3	H	OC_8H_{17}	H	81
f	OCH_3	OCH_3	H	$OC_{10}H_{21}$	H	95
g	OCH_3	OCH_3	H	$OC_{12}H_{25}$	H	86
h	OCH_3	OCH_3	OC_6H_{13}	OC_6H_{13}	H	76
i	OCH_3	OCH_3	OC_6H_{13}	H	OC_6H_{13}	88
j	OCH_3	OCH_3	OC_6H_{13}	OC_6H_{13}	OC_6H_{13}	84

^{1}H and ^{13}C NMR measurements in solution. In order to characterize the structures by spectroscopic methods other than UV/vis/NIR and IR, we performed a solid state ^{13}C NMR spectrum of compound **6d**. Figure 1 shows the normal CPMAS spectrum and additionally a section of it that was measured with a different cross-polarization. Thus quarternary carbon atoms could be distinguished from aromatic or olefinic CH groups. The low-field signals at 180 and 169 ppm belong to the 4-membered ring. In comparison to the stilbene precursor **4d**, many signals of **6d** exhibit a downfield shift. (See Experimental Section.) We attribute this effect to a partial delocalization of the positive charge;[17] however, one should not disregard the influence of the neighbor molecules in solid state NMR.

The most important property of the squaraines **6** concerns the absorption and the fluorescence. According to the theory of Bigelow and Freund,[18] the $S_0 \rightarrow S_1$ transition is largely localized on the central 4-membered ring. Consequently a significant bathochromic shift of the absorption provoked by the extension of the conjugation could not be expected.[19] Nevertheless, we recorded such an effect by replacing the aryl substituents in 1,3-position by stilbenyl groups. The λ_{max} values listed in Scheme 2 are between 680 and 735 nm. The comparison of **6d** and **6h/6j** reveals that the electron-donating alkoxy substituents enhance the charge transfer from the stilbene moieties to the central ring. The ground state S_0 as well as the first excited singlet state S_1 represents intramolecular charge transfer states of the type D−A−D (donor−acceptor−donor). Normal diarylsquaraines have absorption maxima around 570 nm, i.e., the bathochromic effect observed for the novelly prepared bis(stilbenyl) systems amounts to $\Delta\lambda = 165$ nm! Therefore a strongly localized electron transition can be ruled out. The narrow absorption band, which is characteristic for all squaraines,

Scheme 2



	R^3	R^4	R^5	4 Yield[%]	6 Yield[%]	6 λ_{max}[nm]
d	H	OC_6H_{13}	H	50	33	714
d'	H	OH	H	70	49	696
e	H	OC_8H_{17}	H	47	23	721
f	H	$OC_{10}H_{21}$	H	11	9	717
g	H	$OC_{12}H_{25}$	H	58	8	719
h	OC_6H_{13}	OC_6H_{13}	H	48	28	730
i	OC_6H_{13}	H	OC_6H_{13}	42	16	680
j	OC_6H_{13}	OC_6H_{13}	OC_6H_{13}	20	20	727
j'	OC_6H_{13}	OH	OC_6H_{13}	8	21	735

seems to be a consequence of the rigid skeleton which causes small Franck−Condon factors for higher vibrational states.

Concerning the applications of the squaraine pigments, the absorption in solid state is even more important. Figure 2 shows a comparison of the absorption of **6h** dissolved in chloroform and as a dispersion, which was spin-coated in a silane matrix. The exciton splitting leads to a broad band with two maxima, one at $\lambda = 670$ nm and the other at $\lambda = 1000$ nm. Thus, the bis(stilbenyl)squaraines **6** represent new, interesting NIR pigments.

Whereas a strong fluorescence is unfavorable for some applications like the photoconductivity, it is a precondition for the use of the compounds as fluorescence markers. The dotted line in Figure 2 shows the fluorescence of **6h** in arbitrary units. The comparison of the λ_{max} values of the fluorescence bands of **6d**, **6h**, and **6j** (752, 787, and 777 nm, respectively) reveals again the influence of the alkoxy groups. A red shift (induced by an enhanced charge transfer) can be observed by going from **6d** to **6h**; however, the third alkoxy group in **6j** reduces the effect—probably due to steric reasons.

Finally we should mention that the squaraines **6** are completely stable on irradiation in the range of the intense long-wavelength absorption. In contrast to this experiment we measured a fast degradation of the chromophore when we used UV light (254 nm).[20,21]

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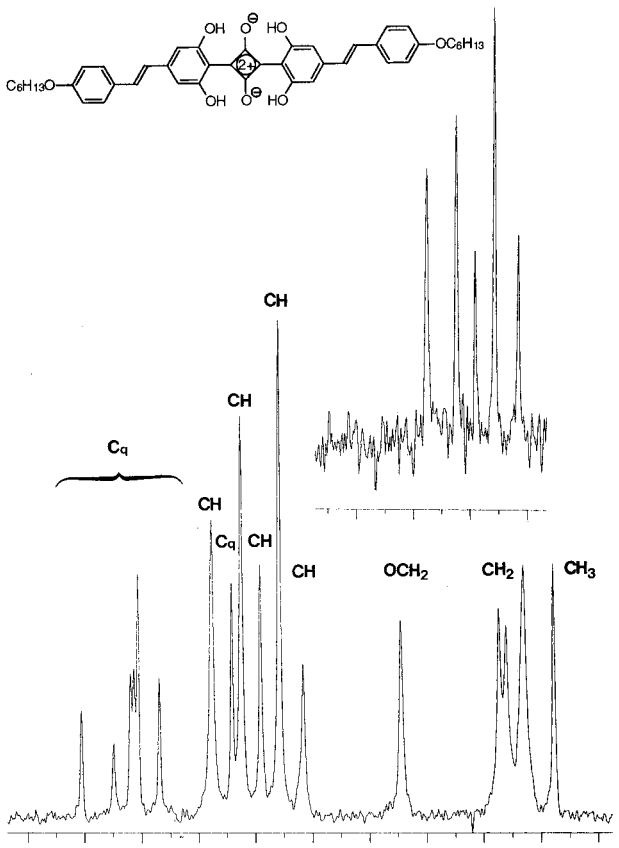

Figure 1. Solid state NMR spectrum (CPMAS) of squaraine **6d**. (Measurement at $\nu_r = 12\,000$ Hz, cross-polarization CP at 2000 μs for the lower spectrum and at 10 μs for the upper section of the spectrum, which does no longer contain the quarternary carbon atoms.)

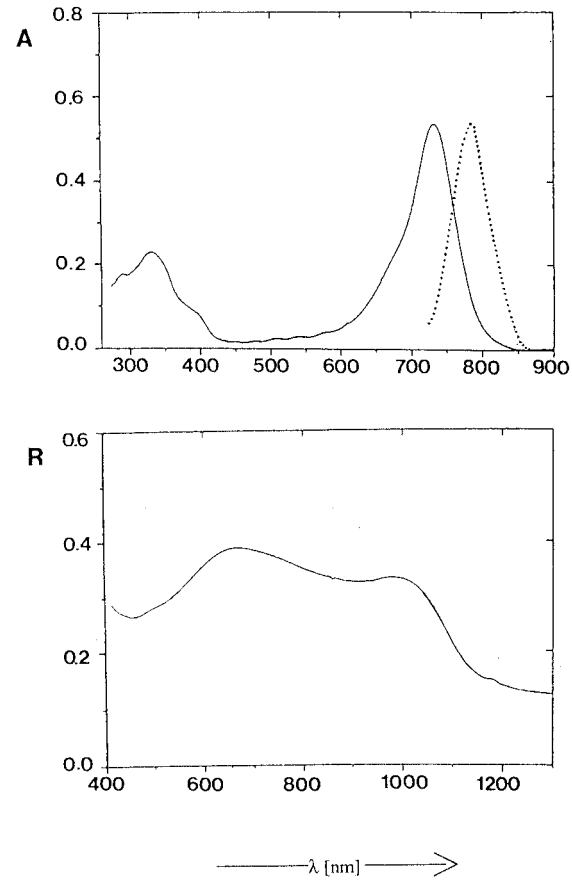

Figure 2. Absorption (−) and fluorescence (···) of squaraine **6h** in solution in chloroform (upper part) and solid state reflection spectrum of **6h** in a silane matrix (lower part).

Summary and Conclusion

A series of symmetrical bis(stilbenyl)squaraines has been synthesized by a 2-fold condensation reaction in the 1,3-position of squaric acid with highly nucleophilic 3,5-dihydroxystilbenes bearing alkoxy side chains. The absorption maxima in solution and in solid state (reflexion measurement) as well as the fluorescence maxima show a very strong bathochromic shift in comparison to normal diarylsquaraines. Thus, these new NIR pigments are highly interesting compounds for applications in materials science. The introduction of dendrimeric side chains should lead to an enhanced solubility and should therefore enable also an application as fluorescence marker.

Experimental Section

General. Melting points are uncorrected. ^{1}H and ^{13}C NMR spectra in solution (in $CDCL_3$ or solvent indicated) were obtained at 400 and 100 MHz, respectively, and ^{13}C NMR spectra in solid state at 75 MHz. Fluorescence excitation and emission spectra are not corrected. The solvents were dried using standard methods.

Starting Compounds. 1, 2: benzyl bromide (**1a**) is commercially available. 3-(Bromomethyl)phenol,[22] 1-(bromomethyl)-3,5-dimethoxybenzene,[11,23] 4-(hexyloxy)benzaldehyde (**2a**),[24] 3,4,5-tris(dodecyloxy)benzaldehyde,[25] 4-(octyloxy)benzaldehyde,[26] 4-(decyloxy)benzaldehyde,[27] 4-(dodecyloxy)benzaldehyde,[27] 3,4-bis(hexyloxy)benzaldehyde,[25] and 3,4,5-tris(hexyloxy)benzaldehyde[28] were prepared from the references cited.

3,5-Bis(hexyloxy)benzaldehyde. The preparation was performed as described for 3,5-bis(dodecyloxy)benzaldehyde.[29] Methyl 3,5-dihydroxybenzoate was transformed in the first step into methyl 3,5-bis(hexyloxy)benzoate: yield 71%, oil; ^{1}H NMR δ 7.12 (d, 2 H), 6.60 (t, 1 H), 3.92 (t, 4 H), 3.85 (s, 3 H), 1.73 (m, 4 H), 1.45−1.23 (m, 12 H), 0.87 (t, 6 H); ^{13}C NMR δ 166.8, 160.1 (2 C), 131.7, 107.5 (2 C), 106.4, 68.2 (2 C), 52.0, 31.5 (2 C), 29.1 (2 C), 25.7 (2 C), 22.6 (2 C), 14.0 (2 C); MS (EI) *m*/*e* (relative intensity) [$M^{+\bullet}$] 336 (39), 168 (100). Anal. Calcd for $C_{20}H_{32}O_4$ (336.5): C, 71.39; H 9.59. Found: C, 71.42; H 9.66. The reduction with $LiAlH_4$ led to 3,5-bis(hexyloxy)benzyl alcohol: yield 80%, oil; ^{1}H NMR δ 6.45 (d, 2 H), 6.34 (t, 1 H), 4.52 (s, 2 H), 3.88 (t, 4 H), 2.89 (s, 1 H), 1.74 (m, 4 H), 1.50−1.22 (m, 12 H), 0.91 (t, 6 H); ^{13}C NMR δ 160.4 (2 C), 143.3, 104.9 (2 C), 100.4, 68.0 (2 C), 65.0, 31.6 (2 C), 29.2 (2 C), 25.7 (2 C), 22.6 (2 C), 14.0 (2 C); MS (EI) *m*/*e* (relative intensity) [$M^{+\bullet}$] 308 (1), 56 (100). Anal. Calcd for $C_{19}H_{32}O_3$ (308.5): C, 73.98; H 10.46. Found: C, 73.95; H, 10.27. Finally the primary alcohol was oxidized with DDQ to yield 82% of 3,5-bis(hexyloxy)benzaldehyde as a colorless oil: ^{1}H NMR δ 9.84

(20) The photochemistry of the squaraines will be published elsewhere.
(21) See also: Das, S.; Thomas, K. G.; Kamat, P. V.; George, M. V. *J. Phys. Chem*. **1994**, *98*, 9291.
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(30) The bis(stilbenyl)squaraine crystals usually contain up to 1% H_2O. Extensive drying at temperatures close to the melting point does not increase the purity.

(s, 1 H), 6.94 (d, 2 H), 6.64 (t, 1 H), 3.93 (t, 4 H), 1.72 (m, 4 H), 1.51-1.19 (m, 12 H), 0.87 (t, 6 H); ^{13}C NMR δ 192.1, 162.5 (2 C), 138.0, 108.0, 107.6 (2 C), 68.4 (2 C), 31.5 (2 C), 29.1 (2 C), 25.6 (2 C), 22.6 (2 C), 14.0 (2 C); MS (EI) *m/e* (relative intensity) [M$^{+\bullet}$] 306 (7), 138 (30), 43 (100). Anal. Calcd for $C_{19}H_{30}O_3$ (306.5): C, 74.47; H, 9.87. Found: C, 74.35; H, 9.83.

General Procedure for the Preparation of the Stilbenes 3a−j. The corresponding benzyl bromide (**1**) (0.1 mol) was dissolved in excess triethyl phosphite (34.2 g, 0.2 mol), and the solution was heated to 160 °C for 3 h. The ethyl bromide resulting from the Arbuzov reaction was distilled continuously through a to 60 °C tempered reflux condenser. The surplus triethyl phosphite was removed under high vacuum (0.1 Torr), and the remaining colorless phosphonate was used without further purification. The following Horner olefination was carried out either with NaH/dimethoxyethane (method A) or with NaOMe/DMF (method B). **(A)** A solution of the phosphonate in dry dimethoxyethane (DME) was added dropwise to a suspension of 3.0 equiv of NaH (80% in paraffin) in the same solvent. After 15 min of stirring at room temperature, a solution of the corresponding benzaldehyde **2** (0.1 mol) in DME was added. The reaction mixture was heated under reflux for 2 h, carefully quenched with methanol/water, and extracted with ethyl acetate. The combined organic phases were washed with brine, dried over $MgSO_4$, and concentrated to leave a residue which was purified chromatographically (silica gel, toluene). **(B)** A solution of the phosphonate in DMF was treated with 3.5 equiv of NaOMe and cooled to 0 °C prior to the addition of the corresponding benzaldehyde **2**. After the reaction mixture was heated to 100 °C for 5 h and the reaction quenched with methanol/water, the precipitated crystals were filtered off and washed with water. Chromatography (silica gel, toluene) afforded the pure (*E*)-stilbene **3**.

(*E*)-1-[4-(Hexyloxy)phenyl]-2-phenylethene (3a): yield 64% (method A); mp 110 °C; IR (KBr, cm^{-1}) 1600, 1500, 960; ^{1}H NMR δ 7.51 (d, 2 H), 7.46 (d, 2 H), 7.36 (t, 2 H), 7.25 (t, 1 H), 7.09 (d, ^3J = 16.3 Hz, 1 H), 6.99 (d, ^3J = 16.3 Hz, 1 H), 6.91 (d, 2 H), 3.97 (t, 2 H), 1.82 (m, 2 H), 1.50−1.30 (m, 6 H), 0.91 (t, 3 H); ^{13}C NMR ($CDCl_3$) δ 158.9, 137.7, 130.0, 128.6 (2 C), 128.3, 127.7 (2 C), 127.1, 126.5, 126.2 (2 C), 114.7 (2 C), 68.1, 31.6, 29.2, 25.7, 22.6, 14.0; MS (EI) *m/e* (relative intensity) [M$^{+\bullet}$] 280 (53), 196 (100). Anal. Calcd for $C_{20}H_{24}O$ (280.41): C, 85.67; H, 8.63. Found: C, 85.39; H, 8.80.

(*E*)-1-[3,4,5-Tris(dodecyloxy)phenyl]-2-phenylethene (3b): yield 81% (method A); mp 45 °C; IR (KBr, cm^{-1}) 1570, 1500, 955; ^{1}H NMR δ 7.49 (d, 2 H), 7.34 (t, 2 H), 7.25 (m, 1 H), 7.01 (d, ^3J = 16.3 Hz, 1 H), 6.96 (d, ^3J = 16.3 Hz, 1 H), 6.71 (s, 2 H), 4.02 (t, 4 H), 3.97 (t, 2 H), 1.83 (m, 4 H),1.76 (m, 2 H), 1.49 (m, 6 H), 1.27 (m, 48 H), 0.89 (t, 9 H); ^{13}C NMR δ 153.4 (2 C), 138.7, 137.5, 132.6, 128.6 (2 C), 129.0, 127.7, 127.4, 126.4 (2 C), 105.6 (2 C), 73.5, 69.3 (2 C), 31.9−22.7 (30 C), 14.1 (3 C); MS (EI) *m/e* (relative intensity) [M$^{+\bullet}$] 733 (100), 565 (18). Anal. Calcd for $C_{50}H_{84}O_3$ (733.22): C, 81.91; H, 11.55. Found: C, 81.76; H, 11.54.

(*E*)-1-[4-(Hexyloxy)phenyl]-2-(3-hydroxyphenyl)ethene (3c): yield 39% (method A); mp 131 °C; IR (KBr, cm^{-1}) 3460, 3400, 1600, 1505, 970; ^{1}H NMR δ 7.40 (d, 2 H), 7.20 (t, 1 H), 7.06 (d, 1 H), 6.98 (d, ^3J = 16.4 Hz, 1 H), 6.97 (d, 1 H), 6.87 (d, 2 H), 6.87 (d, ^3J = 16.4 Hz, 1 H), 6.70 (dd, 1 H), 5.12 (s, 1 H), 3.96 (t, 2 H), 1.87 (m, 2 H), 1.49−1.29 (m, 6 H), 0.90 (t, 3 H); ^{13}C NMR δ 159.1, 155.9, 139.6, 130.0, 129.8, 128.9, 126.2, 119.3, 127.8 (2 C), 114.9 (2 C), 114.3, 112.8, 68.3, 31.6, 29.3, 25.7, 22.6, 13.9; MS (EI) *m/e* (relative intensity) [M$^{+\bullet}$] 296 (89), 212 (100). Anal. Calcd for $C_{20}H_{24}O_2$ (296.41): C, 81.04; H, 8.16. Found: C, 80.99; H, 8.11.

(*E*)-1-[4-(Hexyloxy)phenyl]-2-(3,5-dimethoxyphenyl)ethene (3d): yield 87% (method B); mp 62 °C; IR (KBr, cm^{-1}) 1590, 1505, 955; ^{1}H NMR δ 7.44 (d, 2 H), 7.04 (d, ^3J = 16.3 Hz, 1 H), 6.90 (d, ^3J = 16.3 Hz, 1 H), 6.89 (d, 2 H), 6.66 (d, 2 H), 6.38 (t, 1 H), 3.97 (t, 2 H), 3.83 (s, 6 H), 1.79 (m, 2 H), 1.47−1.32 (m, 6 H), 0.92 (t, 3 H); ^{13}C NMR δ 160.9 (2 C), 158.9, 139.7, 129.6, 128.8, 127.7 (2 C), 126.3, 114.6 (2 C), 104.2 (2 C), 99.5, 68.0, 55.3 (2 C), 31.6, 29.2, 25.7, 22.6, 14.0; MS (EI) *m/e* (relative intensity) [M$^{+\bullet}$] 340 (100), 256 (82). Anal. Calcd for $C_{22}H_{28}O_3$ (340.46): C, 77.61; H, 8.29. Found: C, 77.41; H, 8.22.

(*E*)-1-(3,5-Dimethoxyphenyl)-2-[4-(octyloxy)phenyl]ethene (3e): yield 81% (method B); mp 67 °C; IR (KBr, cm^{-1}) 1590, 1510, 955; ^{1}H NMR δ 7.44 (d, 2 H), 7.06 (d, ^3J = 16.3 Hz, 1 H), 6.90 (d, ^3J = 16.3 Hz, 1 H), 6.89 (d, 2 H), 6.66 (d, 2 H), 6.39 (t, 1 H), 3.97 (t, 2 H), 3.83 (s, 6 H), 1.80 (m, 2 H), 1.50−1.31 (m, 10 H), 0.91 (t, 3 H); ^{13}C NMR δ 161.0 (2 C), 159.1, 139.8, 129.7, 128.9, 127.8 (2 C), 126.4, 114.7 (2 C), 104.3 (2 C), 99.6, 68.1, 55.4 (2 C), 31.9, 29.4, 29.3 (2 C), 26.1, 22.7, 14.2; MS (EI) *m/e* (relative intensity) [M$^{+\bullet}$] 368 (100), 256 (45). Anal. Calcd for $C_{24}H_{32}O_3$ (368.52): C, 78.22; H, 8.75. Found: C, 78.26; H, 8.68.

(*E*)-1-[4-(Decyloxy)phenyl]-2-(3,5-dimethoxyphenyl)ethene (3f): yield 95% (method B); mp 69 °C; IR (KBr, cm^{-1}) 1590, 1510, 955; ^{1}H NMR δ 7.43 (d, 2 H), 7.05 (d, ^3J = 16.3 Hz, 1 H), 6.89 (d, ^3J = 16.3 Hz, 1 H), 6.88 (d, 2 H), 6.66 (d, 2 H), 6.38 (t, 1 H), 3.96 (t, 2 H), 3.82 (s, 6 H), 1.79 (m, 2 H), 1.50−1.25 (m, 14 H), 0.90 (t, 3 H); ^{13}C NMR δ 160.9 (2 C), 158.9, 139.7, 129.6, 128.8, 127.7 (2 C), 126.3, 114.6 (2 C), 104.2 (2 C), 99.5, 68.0, 55.3 (2 C), 31.9, 29.5 (2 C), 29.4, 29.3, 29.2, 26.0, 22.6, 14.1; MS (EI) *m/e* (relative intensity) [M$^{+\bullet}$] 396 (100), 256 (67). Anal. Calcd for $C_{26}H_{36}O_3$ (396.57): C, 78.75; H, 9.15. Found: C, 78.77; H, 9.25.

(*E*)-1-[4-(Dodecyloxy)phenyl]-2-(3,5-dimethoxyphenyl)ethene (3g): yield 86% (method B); mp 67 °C; IR (KBr, cm^{-1}) 1585, 1500, 950; ^{1}H NMR δ 7.43 (d, 2 H), 7.05 (d, ^3J = 16.2 Hz, 1 H), 6.89 (d, ^3J = 16.2 Hz, 1 H), 6.88 (d, 2 H), 6.65 (d, 2 H), 6.38 (t, 1 H), 3.96 (t, 2 H), 3.82 (s, 6 H), 1.79 (m, 2 H), 1.45−1.21 (m, 18 H), 0.90 (t, 3 H); ^{13}C NMR δ 161.1 (2 C), 159.1, 139.8, 129.8, 128.9, 127.8 (2 C), 126.5, 114.8 (2 C), 104.5 (2 C), 99.7, 68.2, 55.3 (2 C), 32.0−22.7, (10 C) 14.1; MS (EI) *m/e* (relative intensity) [M$^{+\bullet}$] 424 (100), 256 (21). Anal. Calcd for $C_{28}H_{40}O_3$ (424.62): C, 79.20; H, 9.49. Found: C, 79.01; H, 9.48.

(*E*)-1-[3,4-Bis(hexyloxy)phenyl]-2-(3,5-dimethoxyphenyl)ethene (3h): yield 76% (method B); mp 54 °C; IR (KBr, cm^{-1}) 1590, 1510, 955; ^{1}H NMR δ 7.07 (d, 1 H), 7.01 (d, ^3J = 16.2 Hz, 1 H), 7.01 (dd, 1 H), 6.88 (d, ^3J = 16.2 Hz, 1 H), 6.84 (d, 1 H), 6.65 (d, 2 H), 6.37 (t, 1 H), 4.04 (t, 2 H), 4.00 (t, 2 H), 3.81 (s, 6 H), 1.83 (m, 4 H), 1.54−1.32 (m, 12 H), 0.92 (t, 3 H), 0.91 (t, 3 H); ^{13}C NMR δ 160.9 (2 C), 149.2 (2 C), 139.6, 130.2, 129.1, 126.5, 120.1, 113.6, 111.5, 104.2 (2 C), 99.6, 69.3, 69.2, 55.2 (2 C), 31.6 (2 C), 29.3, 29.2, 25.7 (2 C), 22.6 (2 C), 14.0 (2 C); MS (EI) *m/e* (relative intensity) [M$^{+\bullet}$] 440 (100), 356 (23), 272 (33). Anal. Calcd for $C_{28}H_{40}O_4$ (440.62): C, 76.33; H, 9.15. Found: C, 76.54; H, 9.05.

(*E*)-1-[3,5-Bis(hexyloxy)phenyl]-2-(3,5-dimethoxyphenyl)ethene (3i): yield 88% (method B); mp 41 °C; IR (KBr, cm^{-1}) 1590, 1450, 960; ^{1}H NMR δ 6.98 (s, 2 H), 6.63 (2 d, 4 H), 6.37 (2 t, 2 H), 3.97 (t, 4 H), 3.81 (s, 6 H), 1.80 (m, 4 H), 1.48−1.34 (m, 12 H), 0.93 (t, 6 H); ^{13}C NMR δ 161.0 (2 C), 160.6 (2 C), 139.3, 139.0, 129.4, 129.0, 105.3 (2 C), 104.7 (2 C), 101.2, 100.1, 68.1 (2 C), 55.2 (2 C), 31.6 (2 C), 29.3 (2 C), 25.7 (2 C), 22.6 (2 C), 14.0 (2 C); MS (EI) *m/e* (relative intensity) [M$^{+\bullet}$] 440 (79), 44 (100). Anal. Calcd for $C_{28}H_{40}O_4$ (440.62): C, 76.33; H, 9.15. Found: C, 76.40; H, 9.17.

(*E*)-1-[3,4,5-Tris(hexyloxy)phenyl]-2-(3,5-dimethoxyphenyl)ethene (3j): yield 84% (method A); mp 38 °C; IR (KBr, cm^{-1}) 1580, 1490, 950; ^{1}H NMR δ 6.99 (d, ^3J = 16.2 Hz, 1 H), 6.88 (d, ^3J = 16.2 Hz, 1 H), 6.70 (s, 2 H), 6.65 (d, 2 H), 6.38 (t, 1 H), 4.01 (t, 4 H), 3.97 (t, 2 H), 3.81 (s, 6 H), 1.80 (m, 6 H), 1.52−1.26 (m, 18 H), 0.91 (t, 9 H); ^{13}C NMR δ 160.9 (2 C), 153.2 (2 C), 139.4, 138.3, 132.3, 129.3, 127.6, 105.2 (2 C), 104.3 (2 C), 99.8, 73.4, 69.1 (2 C), 55.2 (2 C), 31.7 (2 C), 31.5 (2 C), 30.2 (2 C), 29.3 (2 C), 25.7 (2 C), 22.6 (2 C), 14.0 (3 C); MS (EI) *m/e* (relative intensity) [M$^{+\bullet}$] 540 (100), 456 (29). Anal. Calcd for $C_{34}H_{52}O_5$ (540.78): C, 75.52; H, 9.69. Found: C, 75.52; H, 9.81.

General Procedure for the Preparation of the 3,5-Dihydroxystilbenes 4d−j,j′. To a flame-dried flask equipped with a magnetic stirbar was added under nitrogen a solution of 5 mL (5.4 g, 29.0 mmol) diphenylphosphine in dry THF (20 mL). After the flask was cooled to 0 °C and 19.9 mL (31.9 mmol) of *n*-butyllithium (1.6 M in hexane) was introduced via

a syringe, the red reaction mixture was allowed to warm to room temperature, treated with a solution of the corresponding dimethoxystilbene (**3d**−**j**) in 10 mL of THF, and refluxed for 5 h (unless otherwise stated). After dilution with water, the product was extracted into ethyl acetate and the combined organic phases were washed with brine, dried, and evaporated. The separation of small portions of monodeprotected stilbenes from the 3,5-dihydroxystilbenes was realized chromatographically on silica gel with petroleum ether/ethyl acetate (70:30).

(*E*)-1-[4-(Hexyloxy)phenyl]-2-(3,5-dihydroxyphenyl)-ethene (4d): yield 50%; mp 155 °C; IR (KBr, cm^{-1}) 3380, 3250, 1600, 1575, 1505, 960; ^1H NMR (CD_3OD) δ 7.38 (d, 2 H), 6.98 (d, ^3J = 16.3 Hz 1 H), 6.81 (d, ^3J = 16.3 Hz 1 H), 6.82 (d, 2 H), 6.49 (d, 2 H), 6.22 (t, 1 H), 3.87 (t, 2 H), 1.70 (m, 2 H), 1.45−1.27 (m, 6 H), 0.90 (t, 3 H); ^{13}C NMR (CD_3OD) δ 160.2, 159.6 (2 C), 141.2, 131.2, 129.2, 128.7 (2 C), 127.5, 115.6 (2 C), 105.9 (2 C), 102.7, 69.0, 32.7, 30.3, 26.8, 23.6, 14.4; MS (EI) *m*/*e* (relative intensity) [$M^{+\bullet}$] 312 (86), 228 (100). Anal. Calcd for $C_{20}H_{24}O_3$ (312.41): C, 76.89; H, 7.74. Found: C, 76.85; H, 7.69.

(*E*)-1-(3,5-Dihydroxyphenyl)-2-[4-(octyloxy)phenyl]-ethene (4e): yield 47%; mp 157 °C; IR (KBr, cm^{-1}) 3380, 3225, 1600, 1575, 1500, 960; ^1H NMR (CD_3OD) δ 7.36 (d, 2 H), 6.98 (d, ^3J = 16.2 Hz 1 H), 6.81 (d, ^3J = 16.2 Hz 1 H), 6.81 (d, 2 H), 6.50 (d, 2 H), 6.23 (t, 1 H), 3.84 (t, 2 H), 1.67 (m, 2 H), 1.41−1.26 (m, 10 H), 0.88 (t, 3 H); ^{13}C NMR (CD_3OD) δ 160.3, 159.7 (2 C), 141.3, 131.3, 129.3, 128.8 (2 C), 127.6, 115.8 (2 C), 106.1 (2 C), 102.9, 69.1, 33.1, 30.6, 30.5 (2 C), 27.3, 23.8, 14.6; MS (EI) *m*/*e* (relative intensity) [$M^{+\bullet}$] 340 (73), 228 (100). Anal. Calcd for $C_{22}H_{28}O_3$ (340.46): C, 77.61; H, 8.29. Found: C, 77.59; H, 8.22.

(*E*)-1-[4-(Decyloxy)phenyl]-2-(3,5-dihydroxyphenyl)-ethene (4f): reaction time 3 h; yield 11%; mp 150 °C; IR (KBr, cm^{-1}) 3400, 3250, 1600, 1510, 965; ^1H NMR (CD_3OD) δ 7.41 (d, 2 H), 6.98 (d, ^3J = 16.3 Hz 1 H), 6.86 (d, 2 H), 6.82 (d, ^3J = 16.3 Hz 1 H), 6.47 (d, 2 H), 6.18 (t, 1 H), 3.94 (t, 2 H), 1.75 (m, 2 H), 1.50−1.25 (m, 14 H), 0.90 (t, 3 H); ^{13}C NMR (CD_3OD) δ 160.3, 159.7 (2 C), 141.2, 131.4, 129.2, 128.7 (2 C), 127.7, 115.7 (2 C), 105.9 (2 C), 102.8, 69.1, 33.1, 30.7 (2 C), 30.6, 30.5 (2 C), 27.2, 23.8, 14.5; MS (EI) *m*/*e* (relative intensity) [$M^{+\bullet}$] 368 (79), 228 (100). Anal. Calcd for $C_{24}H_{32}O_3$ (368.52): C, 78.22; H, 8.75. Found: C, 78.33; H, 8.76.

(*E*)-1-[4-(Dodecyloxy)phenyl]-2-(3,5-dihydroxyphenyl)-ethene (4g): yield 58%; mp 148 °C; IR (KBr, cm^{-1}) 3380, 3250, 1600, 1575, 1505, 960; ^1H NMR (CD_3OD) δ 7.40 (d, 2 H), 6.99 (d, ^3J = 16.3 Hz, 1 H), 6.82 (d, 1 H), 6.86 (d, ^3J = 16.3 Hz, 2 H), 6.47 (d, 2 H), 6.19 (t, 1 H), 3.93 (t, 2 H), 1.74 (m, 2 H),1.28 (m, 18 H), 0.89 (t, 3 H); ^{13}C NMR (CD_3OD) δ 160.3, 159.7 (2 C), 141.2, 131.3, 129.2, 128.7 (2 C), 127.7, 115.7 (2 C), 105.9 (2 C), 102.8, 69.1, 33.1−23.8 (10 C), 14.5; MS (EI) *m*/*e* (relative intensity) [$M^{+\bullet}$] 396 (2), 279 (22), 228 (41), 149 (100). Anal. Calcd for $C_{26}H_{36}O_3$ (396.57): C, 78.75; H, 9.15. Found: C, 78.61; H, 9.12.

(*E*)-1-[3,4-Bis(hexyloxy)phenyl]-2-(3,5-dihydroxyphenyl)ethene (4h): reaction time 18 h; yield 48%; mp 114 °C; IR (KBr, cm^{-1}) 3360, 1585, 1500, 955; ^1H NMR (CD_3OD) δ 7.08 (d, 1 H), 6.98 (d, ^3J = 16.3 Hz, 1 H), 6.99 (dd, 1 H), 6.86 (d, ^3J = 16.3 Hz, 1 H), 6.82 (d, 1 H), 6.54 (d, 2 H), 6.26 (t, 1 H), 3.98 (t, 2 H), 3.91 (t, 2 H), 1.75 (m, 4 H), 1.47−1.24 (m, 12 H), 0.92 (t, 6 H); ^{13}C NMR (CD_3OD) δ 159.7 (2 C), 150.5, 150.4, 141.2, 132.1, 129.5, 128.0, 121.4, 115.2, 113.2, 106.1 (2 C), 103.0, 70.6, 70.4, 32.9 (2 C), 30.6, 30.5, 27.0 (2 C), 23.8 (2 C), 14.6 (2 C); MS (EI) *m*/*e* (relative intensity) [$M^{+\bullet}$] 412 (100), 328 (30), 244 (50). Anal. Calcd for $C_{26}H_{36}O_4$ (412.57): C, 75.69; H, 8.80. Found: C, 75.60; H, 8.89.

(*E*)-1-[3,5-Bis(hexyloxy)phenyl]-2-(3,5-dihydroxyphenyl)ethene (4i): reaction time 18 h; yield 42%; oil; IR (neat, cm^{-1}) 3300, 1580, 955; ^1H NMR (CD_3OD) δ 6.94 (s, 2 H), 6.62 (d, 2 H), 6.50 (d, 2 H), 6.34 (t, 1 H), 6.21 (t, 1 H), 3.92 (t, 4 H), 1.74 (m, 4 H), 1.49−1.26 (m, 12 H), 0.92 (t, 6 H); ^{13}C NMR (CD_3OD) δ 161.8 (2 C), 159.7 (2 C), 140.7 (2 C), 130.2, 129.7, 106.2 (2 C), 106.1 (2 C), 103.3, 101.9, 69.1 (2 C), 32.9 (2 C), 30.5 (2 C), 26.9 (2 C), 23.7 (2 C), 14.5 (2 C); MS (FD) *m*/*e* (relative intensity) [$M^{+\bullet}$] 412 (100). Anal. Calcd for $C_{26}H_{36}O_4$ (412.57): C, 75.69; H, 8.80. Found: C, 75.51; H, 8.69.

(*E*)-1-[3,4,5-Tris(hexyloxy)phenyl]-2-(3,5-dihydroxyphenyl)ethene (4j): reaction time 90 min; yield 20%; oil; IR (neat, cm^{-1}) 3300, 1580, 960; ^1H NMR (CD_3OD) δ 6.96 (d, ^3J = 16.3 Hz, 1 H), 6.86 (d, ^3J = 16.3 Hz, 1 H), 6.73 (s, 2 H), 6.50 (d, 2 H), 6.21 (t, 1 H), 3.98 (t, 4 H), 3.95 (t, 2 H), 1.84−1.62 (m, 6 H), 1.50−1.34 (m, 18 H), 0.93 (t, 9 H); ^{13}C NMR (CD_3OD) δ 159.7 (2 C), 154.4 (2 C), 140.8, 139.6, 134.6, 129.7, 129.3, 106.1 (2 C), 105.7 (2 C), 103.1, 74.6, 70.1 (2 C), 33.0−23.8 (12 C), 15.0−14.5 (3 C); MS (EI) *m*/*e* (relative intensity) [$M^{+\bullet}$] 512 (1), 428 (2), 43 (100). Anal. Calcd for $C_{32}H_{48}O_5$ (512.73): C, 74.96; H, 9.44. Found: C, 75.21; H, 9.33.

(*E*)-1-[3,5-Bis(hexyloxy)-4-hydroxyphenyl]-2-(3,5-dihydroxyphenyl)ethene (4j′): reaction time 18 h; yield 8%; mp 60 °C; IR (KBr, cm^{-1}) 3300, 1580, 955; ^1H NMR (CD_3OD) δ 7.00 (d, ^3J = 16.4 Hz, 1 H), 6.86 (d, ^3J = 16.4 Hz, 1 H), 6.82 (s, 2 H), 6.53 (d, 2 H), 6.23 (t, 1 H), 4.10 (t, 4 H), 1.86 (m, 4 H), 1.58−1.33 (m, 12 H), 0.98 (t, 6 H); ^{13}C NMR (CD_3OD) δ 159.6 (2 C), 148.8 (2 C), 141.2, 137.4, 129.9 (2 C), 127.6, 106.3 (2 C), 105.9 (2 C), 102.8, 70.6 (2 C), 32.9 (2 C), 30.4 (2 C), 26.8 (2 C), 23.7 (2 C), 14.5 (2 C); MS (EI) *m*/*e* (relative intensity) [$M^{+\bullet}$] 428 (100), 344 (16), 260 (37). Anal. Calcd for $C_{26}H_{36}O_5$ (428.57): C, 72.87; H, 8.47. Found: C, 73.02; H, 8.54.

(*E*)-1-(3,5-Dihydroxyphenyl)-2-(4-hydroxyphenyl)-ethene (4d′). Compound **3d** (136 mg, 0.40 mmol) was dissolved in dichloromethane (10 mL), cooled to −78 °C, and treated dropwise with boron tribromide (0.11 mL, 0.30 g, 1.20 mmol). The red reaction mixture was allowed to warm to room temperature, stirred for 4 h, quenched with KOH solution (10%), acidified with HCl, and extracted three times with dichloromethane. The combined organic phases were dried and concentrated prior to purification by chromatography on silica gel (50% ethyl acetate in petrolether). Product **4d′** could be isolated (63 mg, 70%) as colorless crystals: mp 247 °C; IR (KBr, cm^{-1}) 3250, 1600, 1580, 1505, 965; ^1H NMR (CD_3SOCD_3) δ 9.57 (s, 1 H, OH), 9.22 (s, 2 H, OH), 7.36 (d, 2 H), 6.92 (d, ^3J = 16.3 Hz, 1 H), 6.80 (d, ^3J = 16.3 Hz, 1 H), 6.75 (d, 2 H), 6.39 (d, 2 H), 6.12 (t, 1 H); ^{13}C NMR δ 158.5 (2 C), 157.2, 139.2, 128.1, 127.9, 127.8 (2 C), 125.7, 115.5 (2 C), 104.3 (2 C), 101.8; MS (EI) *m*/*e* (relative intensity) [$M^{+\bullet}$] 228 (6), 69 (100). Anal. Calcd for $C_{14}H_{12}O_3$ (228.25): C, 73.67; H, 5.30. Found: C, 73.39; H, 5.48.

General Procedure for the Preparation of Squaraines 6d−j,d′,j′. Squaric acid was added to a solution of 2 equiv of the corresponding dihydroxystilbene **4d**−**j,d′,j′** in toluene/1-butanol (2:1), and the reaction mixture was refluxed for 4 h (unless otherwise stated). Squaric acid should not get in contact with the skin because it is a strong skin irritant. The resultant water of condensation was removed by a filter between flask and reflux condenser containing Na_2SO_4. After the blue reaction mixture was cooled to room temperature, the precipitated blue-green crystals were filtered off and washed with ether.

(*E,E*)-Bis{4-{2-[4-(hexyloxy)phenyl]ethenyl}-2,6-dihydroxyphenyl}squaraine (6d): yield 33%; mp 303 °C; IR (KBr, cm^{-1}) 3500−3200, 1630, 1610, 1590, 1560, 1510, 1410, 965; MS (FAB) *m*/*e* (702) [$M^{+\bullet}$]. Anal. Calcd for $C_{44}H_{46}O_8$ (702.84): C, 75.19; H, 6.60. Found: C, 74.84; H, 6.69.

(*E,E*)-Bis{2,6-dihydroxy-4-[2-(4-hydroxyphenyl)ethenyl]-phenyl}squaraine (6d′): reaction time 2 h; yield 49%; mp 329 °C; IR (KBr, cm^{-1}) 3500−3100, 1630, 1600, 1580, 1500, 1420, 940; MS (FD) *m*/*e* (relative intensity) [M + H^+] 535 (56), [M + 2 H^+] 268.5 (100). Anal. Calcd for $C_{32}H_{22}O_8$ (534.52): C, 71.91; H, 4.15. Found: C, 71.07; H, 4.20.[30]

(*E,E*)-Bis{2,6-dihydroxy-4-{2-[4-(octyloxy)phenyl]-ethenyl}phenyl}squaraine (6e): yield 23%; mp 289 °C; IR (KBr, cm^{-1}) 3400, 1630, 1610, 1590, 1550, 1500, 1410, 960; MS (FAB) *m*/*e* (758) [$M^{+\bullet}$]. Anal. Calcd for $C_{48}H_{54}O_8$ (758.95): C, 75.96; H, 7.17. Found: C, 75.94; H, 7.28.

(*E,E*)-Bis{4-{2-[4-(decyloxy)phenyl]ethenyl}-2,6-dihydroxyphenyl}squaraine (6f): yield 9%; mp 284 °C; IR (KBr, cm^{-1}) 3400, 1630, 1610, 1590, 1560, 1500, 1410, 965.; MS (FAB) *m*/*e* (814) [$M^{+\bullet}$] 815. Anal. Calcd for $C_{52}H_{62}O_8$ (815.06): C, 76.63; H, 7.67. Found: C, 75.94 H, 7.66.

(*E,E*)-Bis{4-{2-[4-(dodecyloxy)phenyl]ethenyl}-2,6-dihydroxyphenyl}squaraine (6g): yield 8%; mp 283 °C; IR (KBr, cm^{-1}) 3400, 1630, 1610, 1590, 1555, 1500, 1410, 960; MS (FAB) *m*/*e* (871) [$M^{+\bullet}$]. Anal. Calcd for $C_{56}H_{70}O_8$ (871.17): C, 77.21; H, 8.10. Found: C, 76.65; H, 8.03.

(*E,E*)-Bis{4-{2-[3,4-bis(hexyloxy)phenyl]ethenyl}-2,6-dihydroxyphenyl}squaraine (6h): reaction time 6 h; yield 27%; mp 295 °C; IR (KBr, cm^{-1}) 3400, 1620, 1600, 1580, 1500, 1410, 950; MS (FAB) *m/e* (903) [$M^{+\bullet}$]. Anal. Calcd for $C_{56}H_{70}O_{10}$ (903.17): C, 74.47; H, 7.81. Found: C, 73.81; H, 7.52.

(*E,E*)-Bis{4-{2-[3,5-bis(hexyloxy)phenyl]ethenyl}-2,6-dihydroxyphenyl}squaraine (6i): reaction time 2 h, yield 16%; mp 245 °C; IR (KBr, cm^{-1}) 3400, 1600, 1435, 960; MS (FAB) *m/e* (903) [$M^{+\bullet}$]. Anal. Calcd for $C_{56}H_{70}O_{10}$ (903.17): C, 74.47; H, 7.81. Found: C, 73.89; H, 7.83.

(*E,E*)-Bis{4-{2-[3,4,5-tris(hexyloxy)phenyl]ethenyl}-2,6-dihydroxyphenyl}squaraine (6j): reaction time 8 h; yield 20%; mp 222 °C; IR (KBr, cm^{-1}) 3400, 1595, 1490, 1405, 950; MS (FD) *m/e* (relative intensity) [M^{2+}] 552 (100). Anal. Calcd for $C_{68}H_{94}O_{12}$ (1103.49): C, 74.02; H, 8.59. Found: C, 73.87; H, 8.51.

(*E,E*)-Bis{4-{2-[3,5-bis(hexyloxy)-4-hydroxyphenyl]-ethenyl}-2,6-dihydroxyphenyl}squaraine (6j′): reaction time 6 h; yield 20%; mp 138 °C; IR (KBr, cm^{-1}) 3400, 1600, 1510, 1410, 960; MS (FAB) *m/e* (935) [$M^{+\bullet}$]. Anal. Calcd for $C_{56}H_{70}O_{12}$ (935.16): C, 71.92; H, 7.54. Found: C, 72.10; H, 7.65.

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie. We thank the MPI für Polymerforschung Mainz for recording solid state CPMAS ^{13}C NMR spectra and solid state UV/vis/NIR spectra.

JO970284E