

Two-photon states in squaraine monomers and oligomers

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Dedicated to Prof. Dr. Walter Grahn

Abstract

The excited states of novel monomeric and oligomeric squaraines of the indole series were studied by two-photon fluorescence (TPF). Two-photon excitation scans have been performed in an energy range from 1.75 to 3.2 eV by linearly and circularly polarized light. In addition, results from linear absorption and fluorescence measurements are presented. For the monomers a two-photon transition into the first excited state (B_u -symmetry) allowed by vibronic coupling was found. The interpretation of this transition is different to results of other groups. A second transition to an electronic state in an energy range of 2.5–3.5 eV was observed experimentally for the first time. The optical properties of this $2A_g$ state strongly depend on the molecular structure. The experimental results are compared to a four-state model. It is shown theoretically and experimentally that both, the linear absorption and the two-photon spectra of squaraine oligomers can be explained by a state interaction between excitons localized at the monomeric subunits (exciton coupling theory). © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Two-photon absorption; Two-photon fluorescence; Two-photon states; Vibronic coupling; Squaraines; Oligomers; Structure–property relationships; Exciton coupling

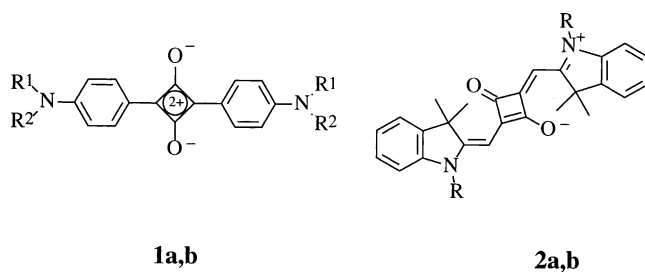
1. Introduction

Squaraines (or squarylium dyes) like **1** and **2** (see Scheme 1) consist of two electron donating endgroups (D) and a central electron withdrawing 1,3-disubstituted C_4O_2 -unit (A) forming a donor–

acceptor–donor (D–A–D) alignment. They exhibit very sharp and intense absorption bands in the long-wavelength range of the visible spectrum and in the near-IR region. Their electronic ground state structure is commonly described in form of two mesomeric forms: a cyclobutenediylum (exemplified in **1**) or a dipolar cyanine structure (exemplified in **2**) [1]. As expected for cyanine-like molecules squaraines of the type considered in this work exhibit reduced bond-length alternation

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¹ Prof. Dr. W. Grahn deceased on 15 August 2001.



1				2	
	X	R ₁	R ₂		R
a	H	Me	Me	ISQ	a H
b	OH	Et	C ₁₈ H ₃₇	C16-ISQ	b C ₁₆ H ₃₃

Scheme 1. Monomeric squaraines **1** and **2**, displayed in two commonly used mesomeric forms (left: cyclobutenediylum structure; right: dipolar cyanine structure).

(BLA) within the conjugated C—C double and single bonds between the heterocyclic endgroups and the central four-membered ring, which has been proved by X-ray crystallographic studies [2,3]. Squaraines are used in a broad variety of applications (e.g. as fluorescence labels or electroconductive materials [4,5]). Within the past decade their large nonlinear optical properties have been the subject of several studies [6–15].

For potential applications in various fields such as all-optical switching, optical data storage and two-photon technology, it is important to know the spectral dependence of the real part and the imaginary part of the third-order polarizability. The spectral dependence of the real part and the imaginary part in the optical spectrum are determined by the energies of the electronic states and their transition dipole moments.

Several theoretical and experimental investigations have shown that for developing structure–property relationship models for the third-order nonlinearity only a few essential states are necessary [16–21]. For simple donor–acceptor molecules the two-state models are commonly used [22,23]. For squaraines the two-state model is inadequate and contributions from additional excited states must be included. This behavior has been found in several theoretical and experimental studies. The dominating excited states are the low lying one-photon state and several additional two-photon states [6,8,9,11]. However, comparison of theoret-

ical and experimental works shows partial deviations and not all two-photon transitions which have been determined experimentally could be predicted from theory. Bigelow and Freund calculated (MNDO) for bis(4-dimethylaminophenyl)squaraine **1a** 2.033 eV for the one-photon state and 2.875 eV for the lowest two-photon state; their results are based on linear absorption measurements [6]. More current calculations by Zhou et al. [7] gave 2.02 and 2.54 eV for these states.

However, a two-photon state at an energy of 2.05 eV was determined experimentally for ISQ **2a** by third-harmonic generation (THG) by Andrews et al. [13], which is only 0.154 eV above the first odd one-photon state. A similarly small energy difference of 0.15 eV between the one-photon state and the first two-photon state was observed for C16-ISQ **2b**.

In addition, a two-photon transition 0.15 eV above the B_u like one-photon state in cyanines and merocyanines was observed by Feldner et al. [24] using two-photon fluorescence (TPF).

These general experimental results do not correspond to the theoretical results cited above and a reason for this discrepancy is missing. The present work will explain the nature of this two-photon transition.

The calculated energies of the higher lying two-photon states spread between 2.5 and 5 eV [6,7]. Andrews postulated two-photon states for squaraines in an energy range of 3.3–5 eV from the

results of THG-measurements and predicted a four-state model for these molecules, but no experimental data were given in this energy range [13]. Unfortunately, only little experimental data covering this energy range are available: a two-photon transition at 4.45 eV was found for **1b** by excited-state absorption measurements [9].

In order to get further insight into the structure–property relationships of squaraines, we investigated the influence of substitution and oligomerisation. Based upon the monomeric chromophore C2-ISQ **2** (a squaraine with indole-based endgroups) a homologous series of oligomers up to and including the pentamer was designed and synthesized (**14c**, **15–17**) in which the monomeric subunits are linked by thienyl spacers via the five-positions of the indole moiety. Thiophene was chosen as linkage to render a conjugative interaction between adjacent chromophores within the oligomers (“ π -bridge”). In order to estimate the effect of the thienyl group as a substituent to the chromophores within the oligomers and of the resulting asymmetry two substituted monomers (TpISQ **13d** and Tp₂ISQ **13e**) as well as a squaraine bearing one indole and one benzothiazole endgroup (ISQ–ThSQ **13f**) were synthesized as model compounds.² In contrast to other oligomeric and polymeric squaraines that have been reported [25,26] our derivatives are distinguished by their defined length and their structural uniformity. The absence of any 1,2-disubstituted isomeric moieties within the oligomers is clearly indicated by the absence of the typical absorption at ca. 1745 cm⁻¹ in the IR (C=O) and at ca. 500 nm in the UV/Vis spectra [27]. All our oligomers exhibit an IR absorption band in the range 1599–1605 cm⁻¹ which is attributed to the conjugated C=C double bond within the central four membered ring [28].

² The synonyms for the new squaraines were based upon those for similar compounds used in the literature [13]. Though the squaraines synthesized in this work are drawn assuming a dipolar cyanine structure, they were denominated as “cyclobutenidylilium diolates” within Appendix A for the sake of simplicity. Systematic nomenclature was not extended to the di- and oligomers.

In this paper, we will show results of TPF measurements of four different squaraine monomers **13a,d–f** and of four oligomers **14c,15–17** (see Schemes 3–5). In addition, we will present results from linear absorption and fluorescence measurements. The two-photon excitation scans have been performed in an energy range from 1.75 to 3.2 eV (excitation energy 0.875 to 1.6 eV) by linearly and circularly polarized light and the two-photon absorption cross-sections have been determined for both light polarizations. We will compare these results for our monomers with the above mentioned results obtained by Andrews et al. [13]. The TPF-technique represents a simple method to determine the spectral dispersion of the imaginary part of the third-order polarizability γ . A further advantage of the TPF is the possibility to get information about symmetry classes of electronic wave functions of excited states and information about the isomers being present in solution. We explain the influence of the molecular symmetry and the chromophore length on the two-photon states.

We further explore the change of the electronic properties of the molecules upon oligomerisation. The interaction of monomeric chromophore subunits within the oligomers and its influence on the TPF spectra is explained in the framework of exciton coupling theory.

Experimental and theoretical investigations of two-photon states of oligomeric squaraines are reported in this work for the first time.

2. Synthesis and experimental methods

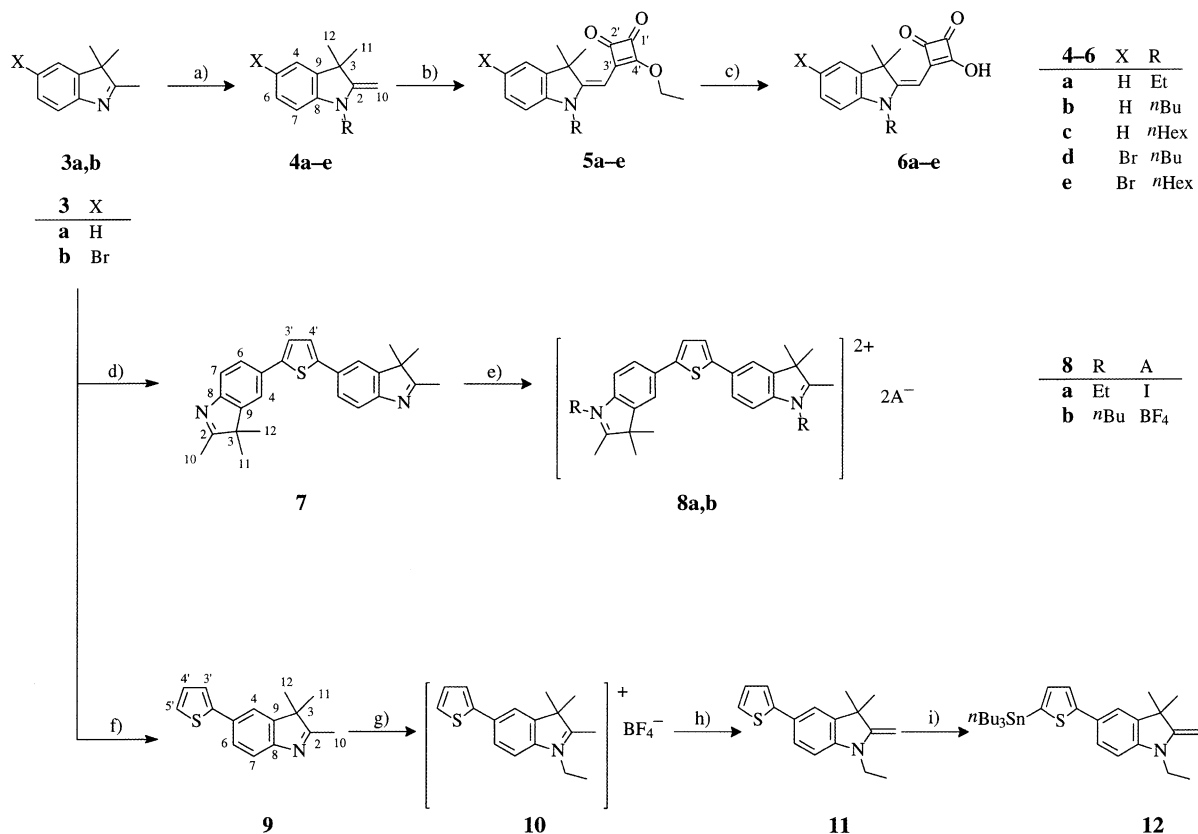
2.1. Synthesis

The straightforward synthesis of the monomeric and oligomeric squaraines is mainly based upon two types of reactions: the well established formation of the symmetric or asymmetric squaraine chromophore by condensation of the precursors of the heterocyclic endgroups (methylenbases or corresponding quaternary salts) with squaric acid or substituted hydroxycyclobut-3-ene-1,2-diones, respectively [4,29,30], and the introduction of the thienyl group to the endgroups (as substituent or

as linkage) by Stille-type coupling of the appropriate tri-*n*-butylstannylthiophene derivative and a brominated endgroup [31].

The synthesis of the end group precursors (see Scheme 2) starts from the commercially available 2,3,3-trimethyl(3*H*)indole **3a** or the corresponding 5-bromo derivative **3b** [32]. *N*-alkylation according to known procedures [33] and subsequent deprotonation of the quaternary salts by 2 N NaOH yields the methylenebases **4a–e** in very good yields (62–79%; **4a–c** have already been reported [34–36]). Condensation with squaric acid diethylester in ethanol in the presence of triethylamine affords the substituted ethoxycyclobut-3-ene-1,2-diones **5a–e** (27–35% yield of material with sufficient pu-

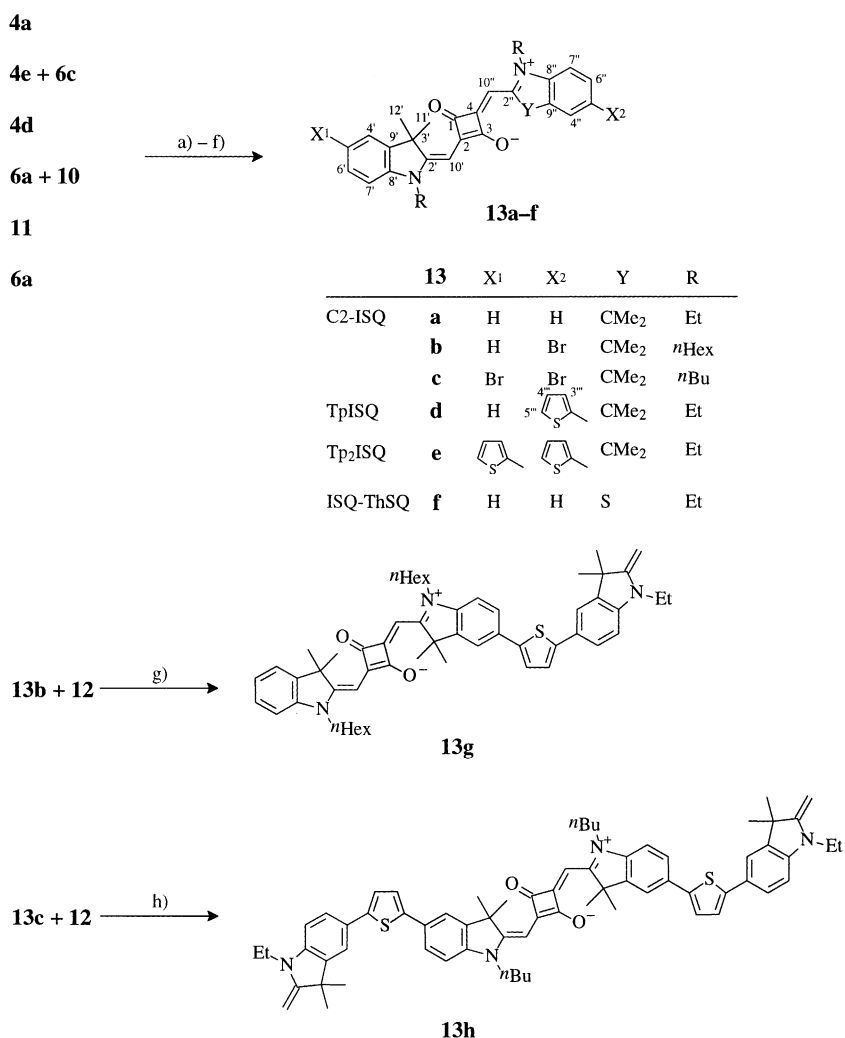
urity for synthetic purposes), which can be saponified in refluxing acetone by 2 N HCl to the corresponding hydroxy compounds **6a–e** (78–92% yield of crude product, which is used without further purification [4]). X-ray crystallographic studies of **5a** and **6a** have already been reported by us [37]. The dimerised end group precursor **7** containing the thiophene linkage is obtained in moderate yield (32%) by Pd-catalysed cross coupling reaction of **3b** and 2,5-bis(tri-*n*-butylstannyl)thiophene [38] (0.5 eq) using 1% (Ph₃P)₄Pd in DMF [31], *N*-alkylation (vide supra) affords the quaternary salts **8a,b** (ca. 82% and 36% yield, resp.). The bifunctional intermediate **12** contains the methylenebase as endgroup precursor as well



Scheme 2. Syntheses of the precursors **3–12**: (a) 1. alkyl iodide, MeNO₂, reflux, 2. 2 N NaOH; (b) 3,4-diethoxycyclobut-3-ene-1,2-dione, Et₃N, EtOH, 60 °C; (c) 2 N HCl, acetone, reflux; (d) 2,5-bis(tri-*n*-butylstannyl)thiophene, (Ph₃P)₄Pd, DMF, 110 °C; (e) 1. alkyl iodide, MeNO₂, reflux, (2. NaBF₄); (f) 2-tri-*n*-butylstannylthiophene, (Ph₃P)₄Pd, DMF, 110 °C; (g) Et₃OBF₄, CH₂Cl₂, 0 °C; (h) 2 N NaOH; (i) 1. *n*-BuLi, diethylether, reflux, 2. tri-*n*-butylstannylchloride, 80 °C; the numbering of the carbon atoms was chosen to render comparability of the NMR data and does not correspond to systematic nomenclature.

as the thiophene linkage and is stepwise prepared by cross-coupling (vide supra) of the bromo compound **3b** with 2-tri-*n*-butylstannylthiophene to give **9** (32%) that is further transformed by *N*-alkylation [39] and deprotonation to the methylenebase **11** (55% overall yield). The tri-*n*-butylstannyl group is achieved by lithiation and quenching with tri-*n*-butylstannyl chloride in diethyl ether (reflux and $-80\text{ }^{\circ}\text{C}$, resp.) **12** is obtained in ca. 59% yield with sufficient purity for further reactions.

The squaraine monomers **13a–f** (see Scheme 3) were obtained by the above mentioned condensation reactions (in refluxing toluene/*n*-BuOH (1:1) with azeotropic removal of water using a Dean–Stark trap) in moderate to excellent yields (30–83%) after chromatography and extraction of the resulting solid with a boiling solvent as microcrystals or powder. (Symmetric and asymmetric squaraine monomers similar to **13a–c,f** can be found in several works [4,29,40–42].) Pd-catalyzed coupling of the thienyl-substituted endgroup pre-

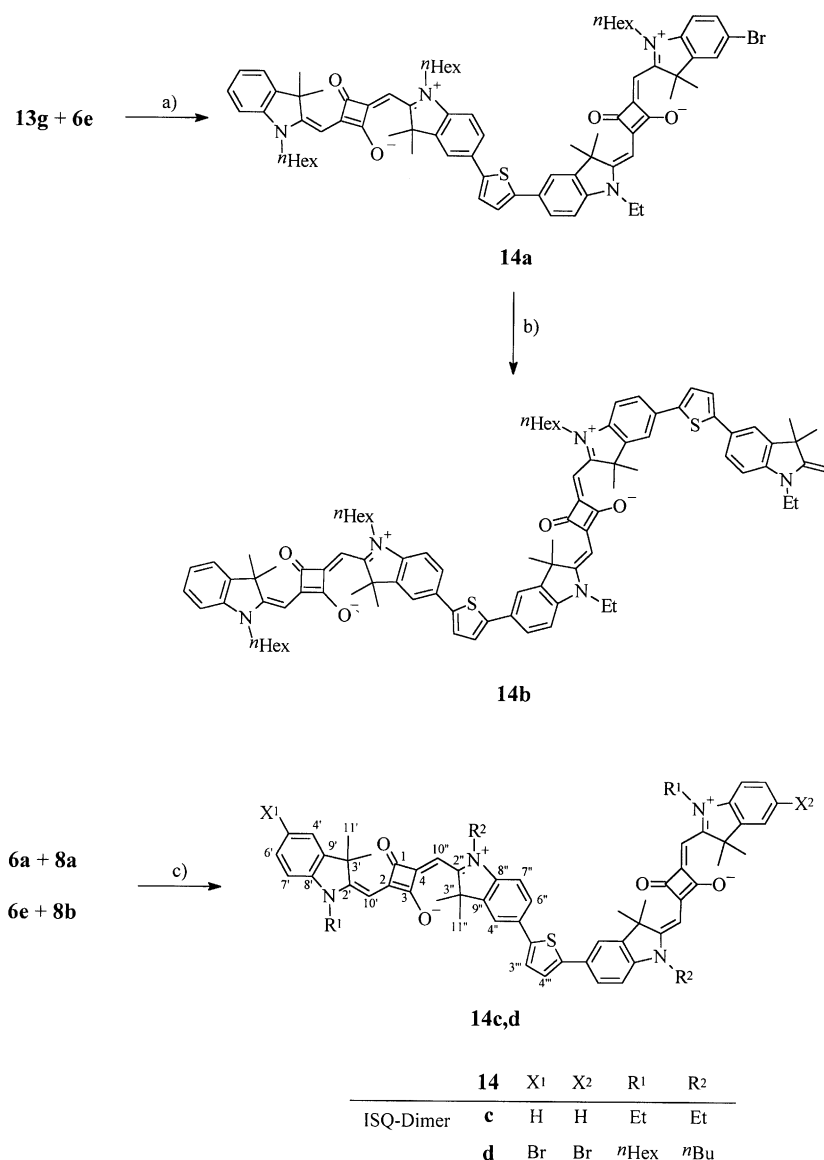


Scheme 3. Synthesis of the monomeric squaraines **13a–h**: (a), (c) and (e) 3,4-dihydroxycyclobut-3-en-1,2-dione, *n*-BuOH/toluene 1:1, reflux; (b) and (d) quinoline, *n*-BuOH/toluene 1:1, reflux; (f) 3-ethyl-2-methylbenzothiazolium tetrafluoroborate, quinoline, *n*-BuOH/toluene 1:1, reflux; (g) and (h) $(\text{Ph}_3\text{P})_4\text{Pd}$, DMF, $110\text{ }^{\circ}\text{C}$.

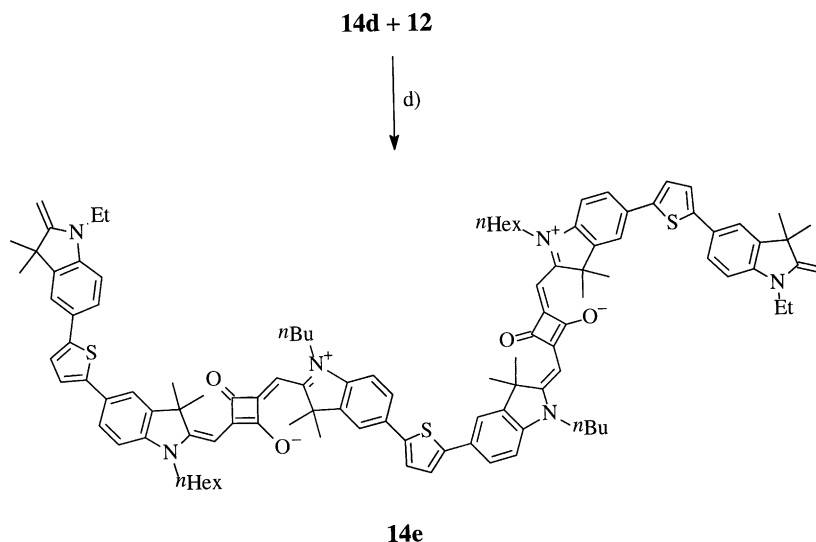
cursor **12** to the mono-brominated monomer **13b** afforded the intermediate **13g** in ca. 67% yield. Though **13g** could not be completely purified even by repeated chromatography (probably due to the reactivity of the methylenebase moiety), the proposed structure was confirmed by its ^1H , ^{13}C NMR and mass spectra. For these reasons, the analogous

bis-substituted compound **13h** was used as crude product (ca. 75%) for further reactions.

The dimers **14a,c,d** (see Scheme 4) were prepared analogously in ca. 36–54% yield. The intermediates **14b** (ca. 56%) and **14e** were purified to a similar extent as described for **13g**. From the crude monomeric squaraine intermediate **13h** the trimer



Scheme 4. Synthesis of the dimeric squaraines **14a–e**: (a) *n*-BuOH/toluene 1:1, reflux; (b) **12**, $(\text{Ph}_3\text{P})_4\text{Pd}$, DMF, 110 °C; (c) quinoline, *n*-BuOH/toluene 1:1, reflux; (d) $(\text{Ph}_3\text{P})_4\text{Pd}$, DMF, 110 °C.



Scheme 4. (continued)

15 (see Scheme 5) was obtained in 16% yield (with respect to **13c**, vide supra). The tetramer **16** (11% with respect to **14d**, vide supra) and the pentamer **17** (ca. 15% with respect to **14a**, vide supra) were prepared in the same manner from **14e** and **14b**, but had to be purified by preparative TLC.

We assume that the *N*-alkyl substituted squaraines of the indole series adopt a *trans*-conformation with respect to the endgroups (C_{2h} -symmetry) as is displayed in the schemes: the ^1H and ^{13}C NMR spectra gave only one set of signals for the endgroups and two signals were observed within the ^{13}C NMR spectra for the carbon atoms of the four membered ring within the symmetric monomers.

All oligomers are thermally stable up to temperatures above 200 °C. Beginning decomposition was observed by DSC at temperatures ranging from 233 °C (ISQ-pentamer) to 279 °C (ISQ-dimer).

2.2. Absorption and fluorescence measurements

All investigations were carried out in chloroform solution. Absorption spectra were recorded in fused silica cells (1 mm, $C = 10^{-5} \text{ mol l}^{-1}$) with a Perkin Elmer Lambda 2 UV/Vis spectrometer.

Fluorescence spectra were recorded with a LS 50B Perkin Elmer fluorescence spectrometer

($C = 10^{-5} \text{ mol l}^{-1}$ and $C = 10^{-4} \text{ mol l}^{-1}$). Fluorescence quantum yields η_1 were determined relative to that of rhodamine 700 ($\eta_r = 0.36$) for both concentrations [43].

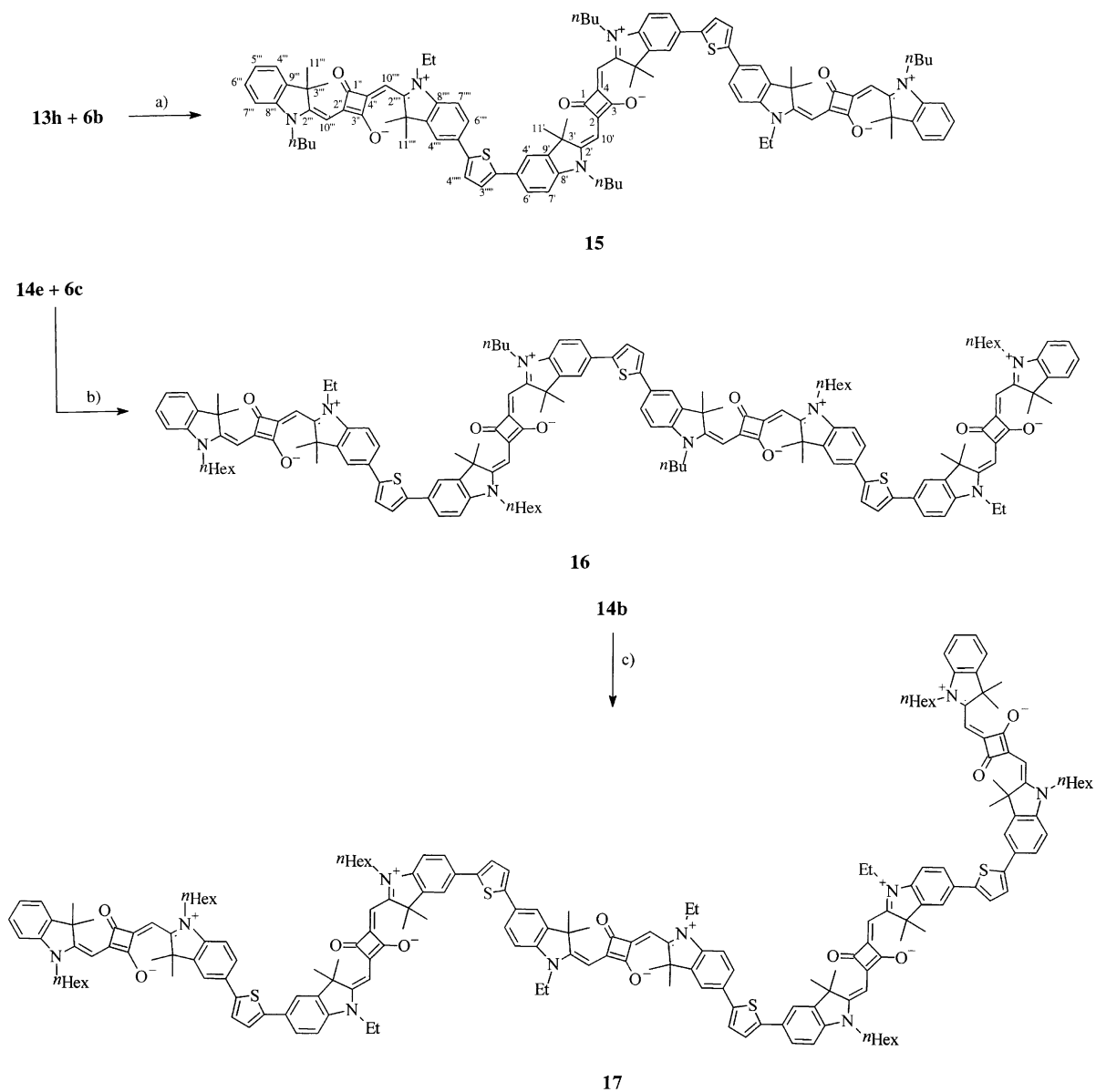
2.3. Two-photon fluorescence measurements

The TPF scans were recorded in a wavelength range of 750–1500 nm. A tripled Nd:YAG nanosecond laser ($\lambda = 355 \text{ nm}$, 2.5 ns pulse duration, 10 Hz repetition rate) pumps an optical parametric oscillator (OPO) and the outcoming light (pulse energy $\sim 50 \mu\text{J}$, spectral bandwidth $\sim 2 \text{ nm}$) was focused in the dye solutions. The fluorescence emitted from the sample is collected at an angle of 90° relative to the exciting beam. As the optimal concentration for the measurements we found $C = 10^{-4} \text{ mol l}^{-1}$.

The measured fluorescence signal I_F is proportional to the square of the incoming photon flux or to the incoming intensity I_0

$$I_{\text{fl}} \propto \eta_2 \delta \cdot I_0^2, \quad (1)$$

where η_2 is the fluorescence quantum yield after a two-photon excitation and δ the two-photon absorption cross-section. The fluorescence emission spectra under one-photon and two-photon excitations are identical for all molecules and we as-



Scheme 5. Synthesis of the trimer **15**, tetramer **16**, and the pentamer **17**: (a) and (b) *n*-BuOH/toluene 1:1, reflux; (c) 3,4-dihydroxycyclobut-3-ene-1,2-dione, *n*-BuOH/toluene, reflux.

sume that $\eta_1 = \eta_2$ is constant over the entire spectral range [44,45]. Finally, the absolute values for two-photon cross-sections were obtained by comparison with the value of fluorescein: $\delta = 38 \times 10^{-50} \text{ cm}^4 \text{ s}$ per photon and per molecule, $\eta = 0.9$ [44].

The experimental accuracy ranges between 10% and 15%. The two-photon absorption cross-section depends on the polarization of the exciting light. For randomly oriented molecules, the polarization ratio $\Omega = \delta_{\text{cir}}/\delta_{\text{lin}}$ gives information about the symmetry classes of the excited states [46–49],

where δ_{cir} and δ_{lin} are the cross-sections under circular and linear polarization. Ω was determined within a wavelength range of 750–1500 nm.

3. Results

3.1. Absorption and fluorescence

The absorption spectra of the monomers are shown in Fig. 1(a) and are typical for cyanine like molecules in solution: the spectra exhibit large oscillator strengths at the 0–0 transition (see Table 1) and small vibronic shoulders and are inhomogeneously broadened by the solvent [50]. The absorption maxima of the mono- and bis-thienyl substituted molecules TpISQ **13d** and Tp₂ISQ **13e**

are red shifted by 17 and 34 nm, respectively, relative to the parent chromophore C2-ISQ **13a**. The effect of mono-substitution is comparable to that of the introduction of the more “basic” (= electron donating) benzothiazole endgroup in ISQ–ThSQ **13f**, which is clearly asymmetric in the sense of Brooker [4,51].

The spectra of the oligomers are much more complex (see Fig. 1(b)). The spectrum of each higher oligomer covers the one of the lower oligomer and is slightly red shifted. The oscillator strengths increase with the number of monomer units (see Table 1). However, the normalized oscillator strength divided by the number of monomer subunits N reveals a ca. 50% increase compared to an additive behavior for the trimer. For explaining the red shift of the absorption

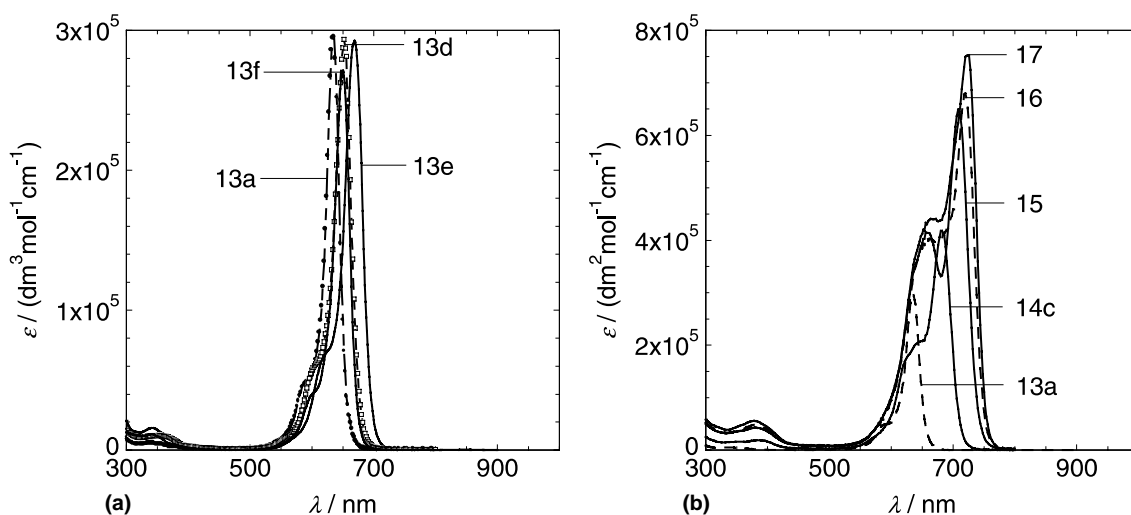


Fig. 1. Linear absorption spectra: (a) of the monomers **13a** and **13d–13f**; (b) of the oligomers **14c**, **15–17** and monomer **13a**.

Table 1

Results of linear optical measurements the monomers **13a–f** and the oligomers **14c**, **15–17**: maximum absorption wavelength λ_{abs} , molar extinction coefficient η , maximum emission wavelength λ_{fl} , quantum yield η_1 , oscillator strengths f and normalized oscillator strengths $f/(f(\mathbf{13a})N)$

	13a	13d	13e	13f	14c	15	16	17
λ_{abs} (nm)	635	652	669	649	681	708	720	725
ϵ ($\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$)	295,000	294,000	293,000	271,000	418,000	649,000	680,000	752,000
λ_{fl} (nm)	645	664	683	662	701	731	739	739
η_1	0.44	0.56	0.67	0.65	0.42	0.59	0.63	0.64
f	1.18	1.37	1.41	1.13	2.71	5.18	5.60	6.30
$f/(f(\mathbf{13a})N)$	1	1.16	1.19	0.96	1.15	1.46	1.19	1.07

maxima, we used the exciton coupling theory [52,53]. In this theory dipolar coupling of excitons localized on monomers within a chromophore aggregate or oligomer leads to a manifold of excited states describing the excited state properties of the whole chromophore aggregate. The energy eigenstates can be calculated by solving the secular determinant (given here for the trimer)

$$\begin{vmatrix} H_{11} - \varepsilon & V_{12} & 0 \\ V_{12} & H_{22} - \varepsilon & V_{23} \\ 0 & V_{23} & H_{33} - \varepsilon \end{vmatrix} = 0, \quad (2)$$

where

$$H_{11} = \langle \varphi_1^* \varphi_2 \varphi_3 | \hat{h}_1 + \hat{h}_2 + \hat{h}_3 | \varphi_1^* \varphi_2 \varphi_3 \rangle = H_{22} = H_{33}$$

and

$$V_{12} = \langle \varphi_1^* \varphi_2 \varphi_3 | \hat{V} | \varphi_1 \varphi_2^* \varphi_3 \rangle = V_{23}.$$

φ_n and φ_n^* denote the localized ground state and excited state wavefunction, respectively, of monomer n , \hat{h}_n is the Hamiltonian acting on centre n only and \hat{V} is the coupling operator. The eigenstate solutions for the trimer are $\varepsilon_1 = H_{11} + \sqrt{2}V$, $\varepsilon_2 = H_{11}$ and $\varepsilon_3 = H_{11} - \sqrt{2}V$. In Fig. 2, the relative energy shift of the experimental absorption

maxima is plotted vs. the relative lowest eigenstate solution $\varepsilon_1(\text{oligomer}) - \varepsilon_1(\text{monomer})$ (in units of V). From the slope of a linear correlation we obtained $V_{12} = 1130 \pm 30 \text{ cm}^{-1}$. The fact that the correlation is excellent ($R = 0.9992$) and that the correlation line goes through the origin supports the application of exciton coupling theory and shows that there is no significant ground state interaction between the monomeric subunits, i.e., the thienyl-unit acts in these cases as an insulating spacer and not as a conjugative π -bridge. For a hypothetical polymer the lowest eigenstate solution is $\varepsilon_1(\text{oligomer}) - \varepsilon_1(\text{monomer}) = 2V$ [52,53]. This corresponds to an absorption maximum of 1.67 eV. Thus, the pentamer ($E_1 = 1.71 \text{ eV}$) is already quite close to the polymer absorption.

The very broad high energy absorption band may be explained by a manifold of vibronic side bands of each of the above mentioned exciton states. Additionally, a lot of rotamers have to be assumed due to the unhindered C—C single bonds connecting the indole endgroups and the thiophene linkage, though the monomeric squaraine subunits within the oligomers are expected to adopt the *trans*-conformation (vide supra).

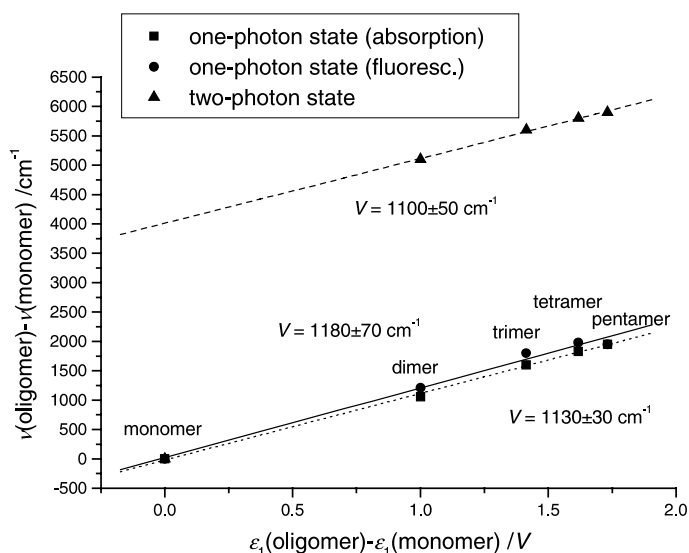


Fig. 2. The relative energy shifts $\varepsilon(\text{oligomer}) - \varepsilon(\text{monomer})$ of the experimental absorption maxima (squares), of the fluorescence maxima (circles) and two-photon fluorescence maxima E_3 (triangles) plotted versus the relative lowest eigenstate solution $\varepsilon_1(\text{oligomer}) - \varepsilon_1(\text{monomer})$ (in units of V).

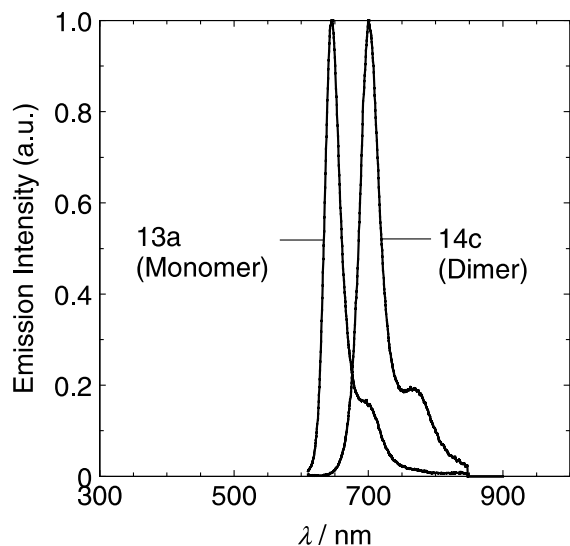


Fig. 3. Fluorescence spectra of the monomer **13a** and the dimer **14c** after one-photon excitation.

The main conclusion is that there is no conjugation over the thiophene bridge and the thiophene group can be understood as a simple spacer.

The emission spectra of the monomer C2-ISQ **13a** and the ISQ-dimer **14c** are shown in Fig. 3. It is typical of cyanine-like dyes that the monomer emission spectra are symmetrical to the absorption spectra and only small Stokes shift are observed. Contrary to the absorption spectra the emission spectra of the oligomers are quite narrow and are not the mirror image of the absorption spectra. This is because the emission occurs from the lowest energy exciton state only. Again, a correlation of the fluorescence maxima $\varepsilon_1(\text{oligomer}) - \varepsilon_1(\text{monomer})$ vs. the lowest eigenstate solution is linear (see Fig. 2) with $V_{12} = 1180 \pm 70 \text{ cm}^{-1}$ in excellent agreement with the coupling obtained from the absorption data.

No dependence of the quantum yields on the degree of oligomerisation could be observed (see Table 1).

3.2. Two-photon fluorescence

3.2.1. Monomers

In Section 2, it has been demonstrated that only the *trans*-isomers of monomers C2-ISQ **13a** and

Tp₂ISQ **13e** (see Scheme 3) with C_{2h} symmetry are present in solution. For these centrosymmetric molecules rigorous selection rules exist for the optical transitions: from the electronic ground state (A_g) only the transition into the (lowest) excited B_u state is allowed by a one-photon process while the higher excited A_g states can only be reached by two-photon processes. We assume the validity of the Born–Oppenheimer and the Condon approximations, where state wavefunctions are products of electronic and vibrational wavefunctions and the electronic transition moment is only dependent on the coordinates of all electrons r , but is not dependent on the internuclear distance R (see Eq. (3)).

$$\Psi = \varphi_{\text{el}}(r; R)\phi_{\text{vib}}(R). \quad (3)$$

The results of TPF measurements are shown in Table 2.

The two-photon excitation scans (dots) and the linear absorption (line) for **13a,e** are shown in Figs. 4(a) and (b) (see also Fig. 5). The normalized fluorescence emission signal I_{fl} (see Eq. (1)) is plotted against the doubled excitation energy. We can interpret E_1 as the first odd excited state (B_u) and we first pay attention to the two-photon transition at E_2 . As one can see for all four monomers E_2 lies quite close in energy to the one-photon state E_1 ($E_2 - E_1 = 0.15 \text{ eV}$, or 1210 cm^{-1}) and exactly at the same energy as the vibronic shoulder of the absorption band. This behavior can be observed for all but very different kinds of cyanines or cyanine-like molecules (fluoresceine and rhodamine B), independent of their molecular structure and length [24,44].

Note that 0–0 transitions for **13a,e** are not observed. This is further evidence for the assumed *trans*-conformation.

For molecules with slightly (TpISQ **13d**) or markedly broken symmetry (ISQ–ThSQ **13f**) the selection rules are less rigorous and weak 0–0 transitions into the one-photon states at E_1 induced by two-photon processes can also be observed (see Figs. 4(c) and (d)).

Exactly the same energies for the B_u state and for this two-photon state of **13a** were obtained by Andrews et al. [13] by THG measurements for C16-ISQ **2b**, but the interpretation of the origin of

Table 2
Summary of two-photon fluorescence measurements and fit results for the monomers **13a–f**

	13a	13d	13e	13f	2b^a
E_1 (eV)	1.95	1.90	1.85	1.91	1.95
Γ_1 (meV)	37	43	48	40	33
μ_{01} (10^{-30} cm)	42.0	46.0	47.3	41.6	41.0
$\Delta\mu_{01}$ (10^{-30} cm)	1.0	3.3	0	7.3	0
E_2 (eV)	2.10	2.06	2.0	2.06	2.10
Γ_2 (meV)	55	55	50	55	46
μ_{12} (10^{-30} cm)	12.7	17.2	18.3	15.2	20.0
$\delta(\omega_2)$ (10^{50} cm ⁴ s)	202	399	483	231	–
Ω	0.74	0.68	0.69	0.66	–
E_3 eV	3.02	2.86	2.76	(3.39)	5.00
Γ_3 (meV)	100	100	70	100	370
μ_{13} (10^{-30} cm)	6.0	11.0	29.3	–	40.7
$\delta(\omega_3)$ (10^{50} cm ⁴ s)	326	967	5065	–	–
Ω	0.73	0.75	0.62	–	–

Energy E_1 , FWHM Γ_1 and transition dipole moment μ_{01} are obtained by linear absorption measurements; energy E_2 , E_3 , two-photon absorption cross-section δ and polarization ratio Ω derived from two-photon fluorescence measurements; photo-induced change of dipole moment $\Delta\mu_{01}$, transition dipole moment μ_{12} , μ_{13} and FWHM Γ_2 , Γ_3 are parameters of fit-equation (4). The value in parentheses was obtained by fitting the experimental data.

^a Ref. [13].

this two-photon transition is different to ours. Andrews et al. understood this transition as a two-photon process into a $2A_g$ state.

We interpret the two-photon transition to the B_u state at E_2 to be allowed by vibronic coupling. This was already assumed for fluoresceine and rhodamine by Xu and Webb [44]. The excited states are inhomogeneously broadened and, therefore, so are the vibronic states. From that we can interpret the two-photon band at E_2 ($E_2 - E_1 = 1210$ cm⁻¹) as an average over one or more vibronically coupled transitions. Such strong odd vibrations were obtained by infrared spectroscopy in an energy range 800–1800 cm⁻¹.

Our assumption can be based on the following arguments:

1. Theoretical works predict for squaraines the first strong two-photon state at markedly higher energies, as mentioned in Section 1. A general result of theoretical works for cyanines and cyanine-like molecules is, that the energy difference between the first two-photon state and the first one-photon state strongly depends on the molecular structure, molecular length and symmetry and is generally larger than 0.15 eV [16,18]. This apparent discrepancy between cal-

culations and experiments cannot be explained by the approximation used in these calculations.

2. The linear absorption spectra and two-photon excitation spectra are complementary in the energy band of the S_1 state ($1B_u$ state). For all cyanines and cyanine-like molecules (merocyanines, fluoresceine, rhodamine B and rhodamine 6G, vide supra) the two-photon transition is exactly located at the vibronic shoulder of the absorption band [24,44].

The Condon approximation breaks down in this case, because the electronic transition moment is also dependent on R . The theory of vibronic coupling was developed by Herzberg and Teller [54] in 1936. In 1966 Honig et al. [55] developed a theoretical description of vibronic coupling of two-photon transitions.

Our third argument is that transitions allowed by vibronic coupling are well-known from several theoretical and experimental investigations on benzene [47,55–59]. Friedrich and McClain [47] determined and characterized all vibronically induced transitions of benzene vapor by circularly and linearly polarized two-photon absorption measurements. There is no reason why such

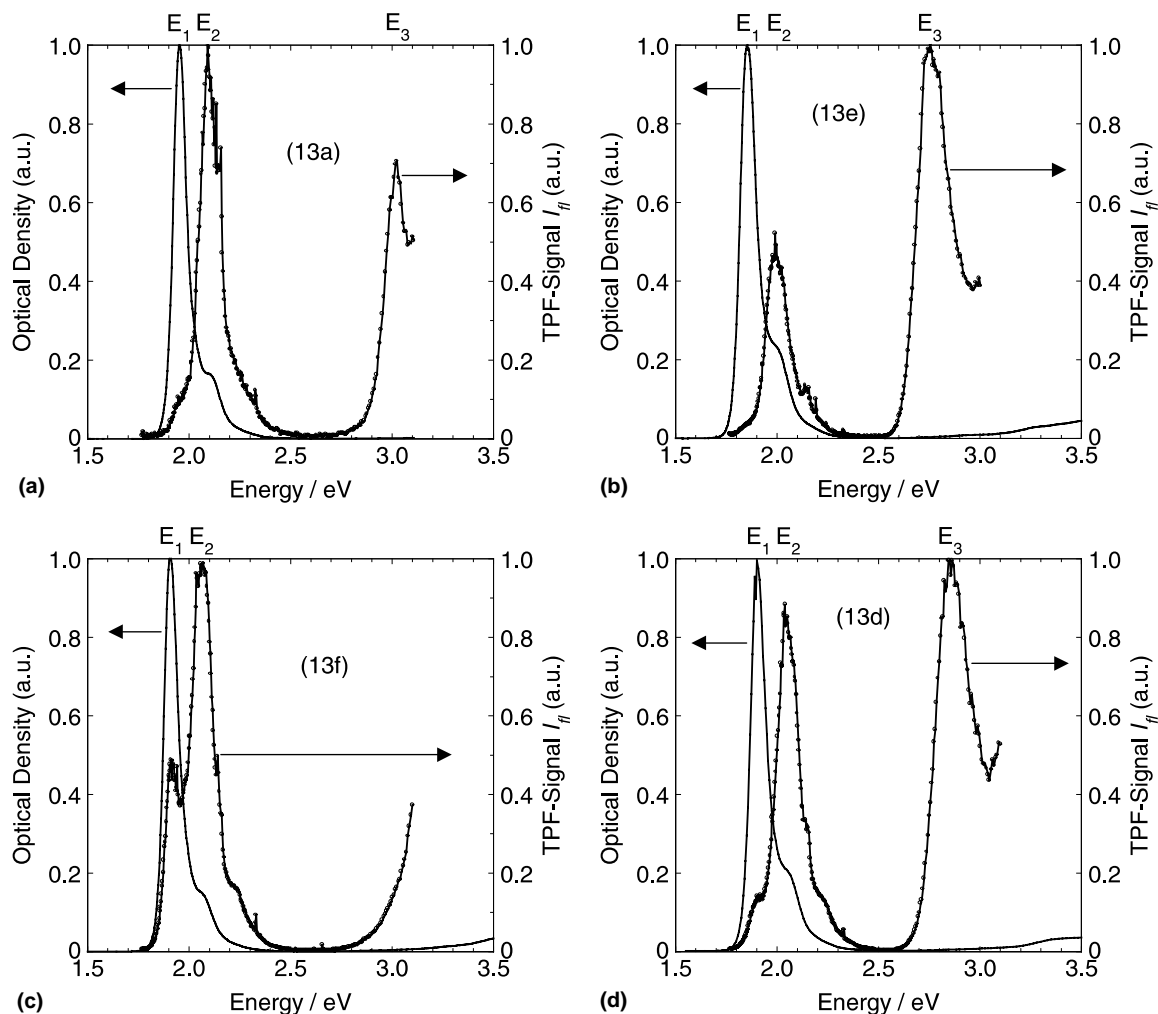


Fig. 4. Two-photon excitation scans (dots) and linear absorption spectra (line) for centrosymmetric monomers **13a**, **13e** and monomers with broken symmetry **13d**, **13f**. The normalized fluorescence emission signal $I_{||}$ is plotted versus the doubled excitation energy. One-photon transition to the odd state $1B_u$ at energy E_1 ; by vibronic coupling allowed two-photon transition at energy E_2 ; two-photon transition to the even state $2A_g$ at energy E_3 .

vibronic coupling should not occur in such cyanines.

A direct experimental evidence could be obtained by circularly and linearly polarized two-photon absorption measurements on this squaraines in the gas phase. In the liquid phase this is not possible.

The experimentally observed two-photon transitions induced by vibronic coupling are remarkably strong. In general the Herzberg–Teller theory

does not quantitatively explain the transition intensities accurately [48].

We have investigated the transition at E_2 by excitation with circularly and linearly polarized light. For centrosymmetrical molecules like C2-ISQ **13a** and Tp_2 ISQ **13e** only two kinds of two-photon transitions are theoretically possible: $A_g \rightarrow A_g$ and $A_g \rightarrow B_g$, where the selection rules refer to the total wave function $\psi = \varphi_{el} \times \varphi_{vib}$.

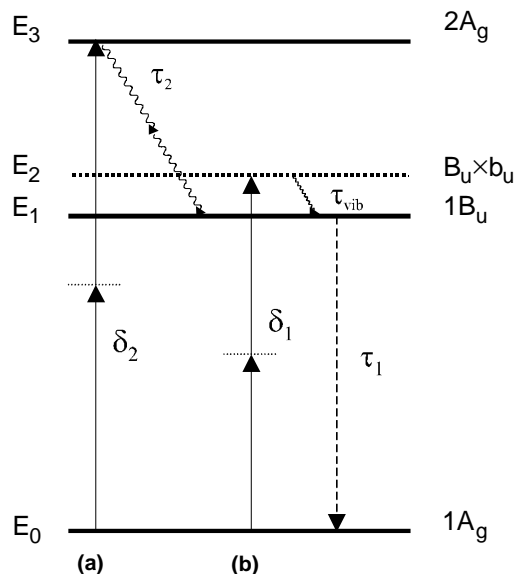


Fig. 5. Two-photon processes in monomeric squaraines: (a) two-photon transition (δ_2) in the second excited singlet $2A_g$ state (E_3) and fast relaxation (τ_2) in the $1B_u$ state; (b) two-photon transition (δ_1) (by vibronic coupling) in a high lying vibrational state (b_u symmetry) (E_2) of the first excited singlet $1B_u$ -state (E_1) and fast relaxation (τ_{vib}). In both case, subsequent fluorescence from the $1B_u$ state (τ_1).

Nascimento [49] developed the theoretical background for the polarization dependence of two-photon absorption for randomly oriented molecules. For molecules possessing a dominant molecular axis like squaraines values of $\Omega = \delta_{\text{cir}}/\delta_{\text{lin}} = 2/3$ (for the transition $A_g \rightarrow A_g$) and $\Omega = \delta_{\text{cir}}/\delta_{\text{lin}} = 3/2$ (transition $A_g \rightarrow B_g$) have been predicted [49,60–62].

For the squaraines **13a,e** we obtained experimental values of $\Omega = 0.74$ and $\Omega = 0.69$ for the transition at the energy E_2 . As described earlier, we interpret this transition band as an average over one or more vibronically coupled transitions. From this result, we assume that the $A_g \rightarrow A_g = B_u \times b_u$ transitions are the dominant transitions. Obviously, the other possible transition $A_g \rightarrow B_g = B_u \times a_u$ plays no role.

MOPAC-calculations (PM3) show a B_u symmetry for the electronic wave function of the first excited singlet state ϕ_{el} [63], from that b_u symmetry can clearly be deduced for the vibronic wave

function ϕ_{vib} and it is clear, that the 0–0 transition for the two-photon process is not allowed.

In the following, we will discuss the nature of the two-photon transition at E_3 which has been experimentally observed in this study for the first time (see Figs. 4 and 5). We assume that this is the $2A_g$ state, which has been predicted by calculations before [6,7].

Andrews et al. [13] predicted also a two-photon state in the range of 3–5 eV by fitting the experimental data with a four-level model. However, no experimental measurements in this energy range were reported in this study.

We investigated the transition at E_3 by excitation with circularly and linearly polarized light and found values for Ω ranging from 0.62 to 0.75. This ratio confirms a transition $A_g \rightarrow A_g$. The values in Fig. 4 and Table 2 show that the energy (E_3) for these states depend considerably on the molecular structure. Note that this dependence is much stronger than that one for the one-photon states.

Within the substituted molecules TpISQ **13d** and Tp₂ISQ **13e** the $2A_g$ state is slightly red shifted compared to the parent chromophore C2-ISQ **13a** as a result of the extended π -system (see Table 2). The feature that the one- and two-photon states get closer in energy the more extended the π -system is, has been observed in symmetrical α, ω -bis-donor-substituted polyenes [64]. Note that the chromophore of ISQ–ThSQ **13f** is quite different from C2-ISQ **13a** and the $2A_g$ state is extremely blue shifted ($\Delta E_3 \approx 0.37$ eV) whereas the B_u state is red shifted.

3.2.2. Oligomers

The results of the TPF measurements are shown in Table 3 and Fig. 6. For all oligomers two main two-photon absorption bands E_2 and E_3 could be observed in the two-photon excitation scans (dots). We assume that the band E_2 is caused by vibronically induced two-photon transitions. The occurrence of the very broad absorption band may be explained by the manifold of vibronic side bands of each of the excitonic states (B_u) mentioned in Section 3.1. The E_3 two-photon absorption band can be identified as an excitonic state with A_g like symmetry.

Table 3
Summary of two-photon fluorescence measurements for the oligomers **14c**, **15–17**

	14c	15	16	17
E_1 (eV)	1.82	1.75	1.72	1.71
μ_{01} (10^{-30} cm)	66.0	93.0	97.6	103.8
E_3 (eV)	2.39	2.33	2.31	2.30
$\delta(\omega_3)$ (10^{50} cm ⁴ s)	4755	12,945	17,718	24,760

Energy E_1 and transition dipole moment μ_{01} are obtained by linear absorption measurements; energy E_3 and two-photon absorption cross-section δ derived from two-photon fluorescence measurements.

The maximum two-photon absorption cross-sections $\delta(\omega_3)$ at E_3 ($2A_g$ state) increase nonlinearly with the number of the monomeric subunits N , but it seems that the relative increase becomes smaller for $N \geq 4$ (see Fig. 7). This increase is correlated with the increase of the transition moment μ_{01} . From this and from the results for the monomers outlined in Section 3.1. ($\mu_{01} > \mu_{1n}$), we conclude that the transition moment μ_{01} dominates the two-photon absorption processes within this class of molecules.

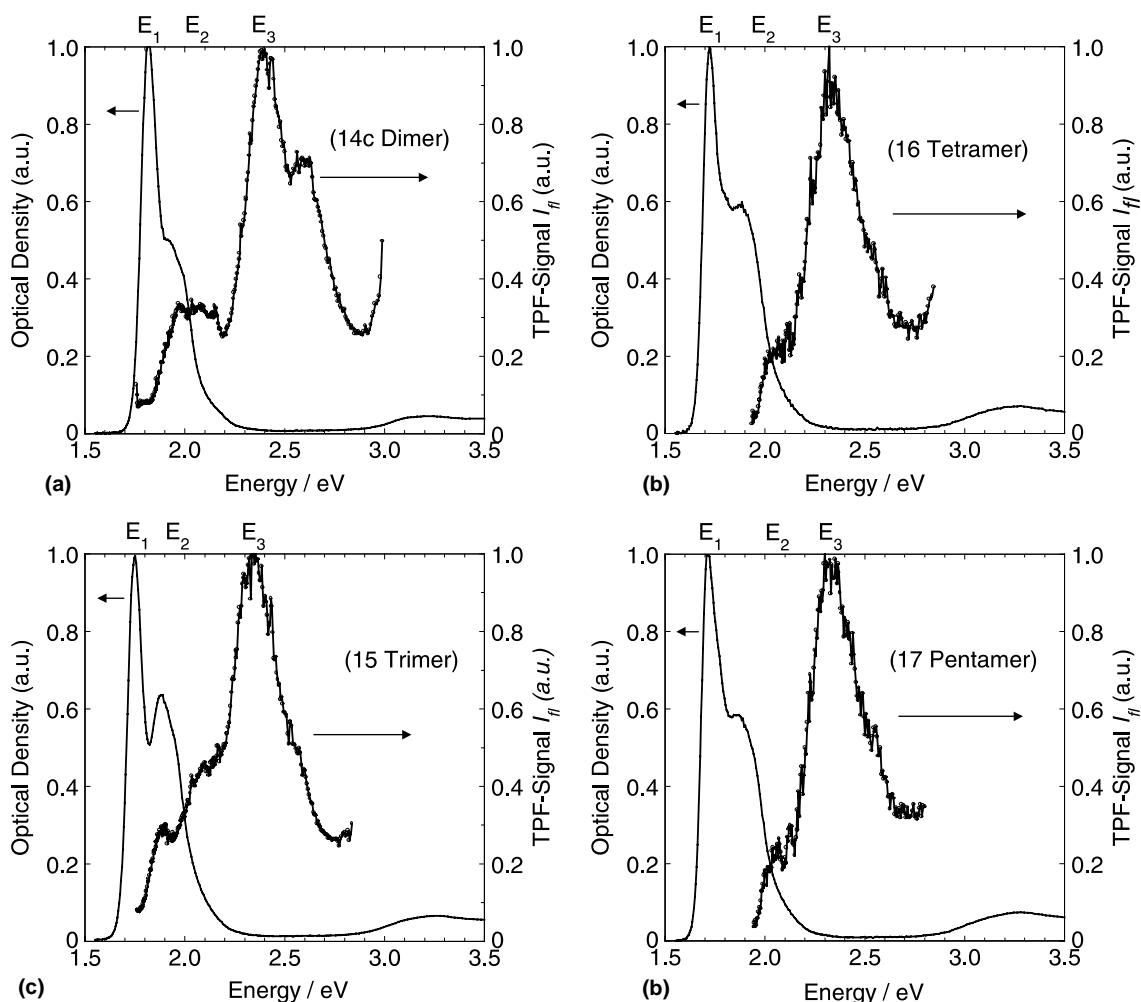


Fig. 6. Two-photon excitation scans (dots) and linear absorption spectra (line) for the oligomers **14c**, **15–17**. The normalized fluorescence emission signal $I_{||}$ is plotted against the doubled excitation energy. One-photon transition to the odd state $1B_u$ at energy E_1 ; by vibronic coupling allowed two-photon transition at energy E_2 ; two-photon transition to the even state $2A_g$ at energy E_3 .

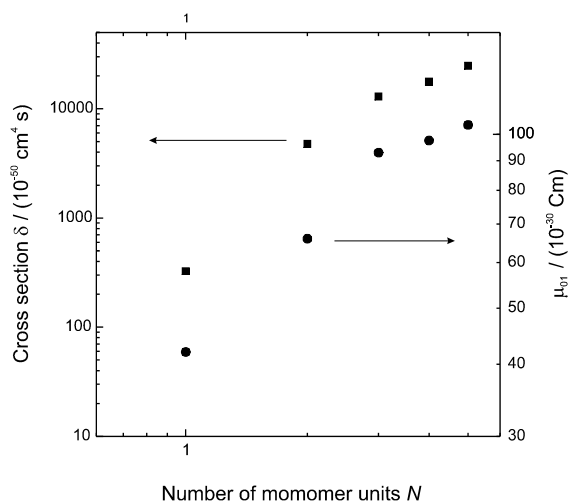


Fig. 7. Plot of the experimental two-photon absorption cross-sections $\delta(\omega_3)$ (squares) at the energy band E_3 ($2A_g$ state) and of the transition dipole moments μ_{01} (circles) of the monomer **13a** and of the oligomers **14c**, **15–17** versus the number of monomeric subunits N .

For the shifts of the two-photon states at E_3 within the oligomer series we used exciton coupling theory again (see Fig. 2). A plot of the relative two-photon energies of the oligomers vs. the eigenvalues ε with $V_{12} = 1100 \pm 50 \text{ cm}^{-1}$ is linear and in excellent agreement with the results from the linear absorption and fluorescence data (see Section 3.1). However, the TPA correlation line is shifted by ca. 4000 cm^{-1} to lower energies compared to the other correlation lines. We interpret this behavior by a different and extended delocalisation within the oligomers at E_3 which is constant for all oligomers and which lowers the energy of these TPA states only. MOPAC-calculations of the electronic orbitals of squaraine monomers give a possible explanation: the electronic wavefunction of the HOMO ($1A_g$ -state) and LUMO ($1B_u$ -state) is restricted to the chromophore unit between both nitrogen atoms. The obvious validity of the model of simple exciton-coupling theory proves that there is no overlap between the electronic wavefunctions in the electronic ground and first excited state of the respective monomers within the thiophene-linked oligomers. In contrast, the wavefunction of the orbital of the $2A_g$ state is spread over the whole molecule including the aromatic moieties of the

heterocyclic endgroups and an overlap between the adjacent subchromophores within the oligomers may occur, which lowers their $2A_g$ states.

3.3. Four-state model for monomeric squaraines

As can be seen in Section 3.2.1, the linear and nonlinear dispersion of squaraines is dominated by the ground state, one one-photon state at E_1 (B_u) and one two-photon state at E_3 ($2A_g$). In addition, a vibronically induced two-photon transition at E_2 (B_u) next to the one-photon state appears which cannot be neglected. The simplest empirically reasonable approach to describe this behavior is to modify the three-state model by the formal insertion of the vibronically induced transition as an additional real two-photon state. In this four-state model, the third-order polarizability γ can be evaluated in a simple expression (see Eq. (4)), using the conventions adopted in [65,66]:

$$\gamma(-\omega; \omega, -\omega, \omega) \propto \frac{\mu_{01}^2 \Delta\mu_{01}^2}{(E_{01} - \hbar\omega - i\Gamma_{01})^2 (E_{01} - 2\hbar\omega - i\Gamma_{01})} + \sum_n \frac{\mu_{01}^2 \Delta\mu_{1n}^2}{(E_{01} - \hbar\omega - i\Gamma_{01})^2 (E_{0n} - 2\hbar\omega - i\Gamma_{0n})} - \frac{\mu_{01}^4}{(E_{01} - \hbar\omega - i\Gamma_{01})^2 (E_{01} + 2\hbar\omega + i\Gamma_{01})}. \quad (4)$$

This expression was developed by Kogej et al. [67] for a two-photon absorption process on an isotropic medium, where $\langle\gamma\rangle$ corresponds to the orientational average of γ ; the summation runs only over two excited states $n = 2, 3$; is the optical frequency; E_{01}, E_{0n} denote transition energies and μ_{01}, μ_{1n} the transition dipole moments between the ground state and the excited states, where Γ_{01} and Γ_{0n} are the corresponding full half-width at half-maximum; $\Delta\mu_{01}$ is the difference between the dipole moments of the ground state and of the excited state; \hbar is Planck's constant divided by 2π . The experimentally determined two-photon cross-section δ is related to the third-order polarizability γ through Eq. (5) (SI units) [68]:

$$\delta = \frac{\hbar\omega^2 L^4}{4\varepsilon_0^2 c^2 n^2} \text{Im}\langle\gamma\rangle, \quad (5)$$

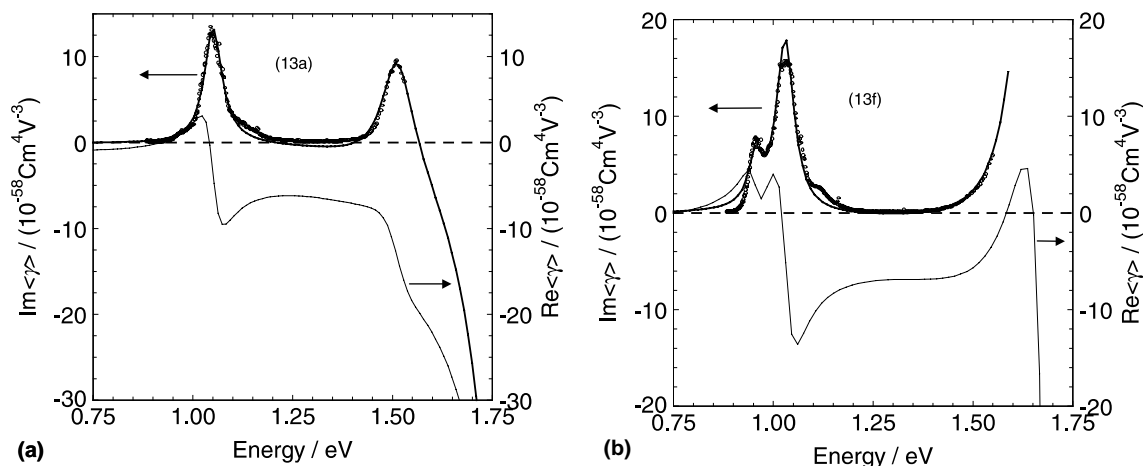


Fig. 8. Measured $\text{Im}\langle\gamma\rangle$ (dots) and results fitted using Eq. (4) (thick line) of the centrosymmetric monomer **13a** and the monomer with broken symmetry **13f**. The $\text{Re}\langle\gamma\rangle$ is obtained by replacing the Im -operator with the Re -operator in Eq. (4).

where L is the local field factor (Lorentz-type local field correction), c is the speed of light and ϵ_0 is the permittivity in vacuum. We determined E_{01}, Γ_{01} from linear absorption spectra and μ_{01} from integrated absorption spectra. The measured excitation scans (linear polarization) were transformed with Eq. (5) in $\text{Im}\langle\gamma\rangle$ and fitted by Eq. (4).

Figs. 8(a) and (b) show the measured $\text{Im}\langle\gamma\rangle$ (dots) and the results fitted using Eq. (4) (thick line) of ISQ–ThSQ **13f** and the centrosymmetrical C2-ISQ **13a**. Note that the measured spectra show Gaussian profile, though a Lorentzian denominator is used in Eq. (4). This approximation leads to slightly different curve shapes for small $\text{Im}\langle\gamma\rangle$ values. Table 2 lists the result obtained from fit with Eq. (4). Using the fitted parameters, we then calculated the real part $\text{Re}\langle\gamma\rangle$ of Eq. (4) (see Fig. 8, thin line). It is remarkable that the $\text{Re}\langle\gamma\rangle$ changes the sign at the vibronically induced two-photon transition. Without this transition the real part would be negative in this energy range. This important fact has to be considered for THG and DFWM-measurements working at a typical operating laser wavelength of 1064 nm. For cyanines with a large optical gap ($E_g > 2.33$ eV) a positive $\text{Re}\langle\gamma\rangle$ would be measured, clearly different from the negative values predicted from theoretical calculations, which neglected vibronic coupling.

A comparison of our results for C2-ISQ **13a** with those of Andrews et al. for the analogous C16-ISQ **2b** is shown in Table 2. As can be seen, there is substantial agreement with respect to the characterization of the energies for the one-photon state and the low-lying two-photon transition. However, Andrews determined larger values for the transition moments μ_{12} and μ_{13} .

Note that in the interpretation of Andrews, the transition moment μ_{12} has the meaning of a transition moment between the electronic states S_1 ($1B_u$) and S_2 ($2A_g$). In our interpretation, μ_{12} describes the strength of the vibronic coupling with the state S_1 ($1B_u$).

The extension of the π -system of C2-ISQ **13a** by substitution with thiophene groups results in slightly increased transition moments μ_{nm} in TpISQ **13d** and Tp₂ISQ **13e**. As a consequence, the two-photon cross-section also increases with the factor $\mu_{01}^2 \times \mu_{1m}^2$. The broken symmetry of TpISQ **13d** and ISQ–ThSQ **13f** is reflected in a non-vanishing difference between the dipole moments in the ground state and the excited state $\Delta\mu_{01}$.

4. Conclusions

We present the synthesis of a homologous series (monomer–pentamer) of oligomeric squaraines

that are linked via the five-positions of their indole-based endgroups to thienyl spacers as well as the one of analogously thienyl-substituted monomers.

It is shown by the results of two-photon fluorescence excitation scans that two-photon transitions have an important influence on the third-order nonlinear susceptibility.

For all monomers a vibronically induced and thereby allowed two-photon transition was found about 0.15 eV higher than the first one-photon state. By polarization measurements, we found a dominant $A_g \rightarrow A_g = B_u \times b_u$ transition. A second transition to an electronic state in an energy range of 2.5–3.5 eV was observed experimentally for the first time. Its $2A_g$ symmetry was confirmed by polarization measurements. The energy of this state depends strongly upon the molecular structure and lies in the energy range, which is predicted by theory. Our new interpretation of the origin of this transition clarifies the present discrepancy between the various theoretical and experimental works.

A four-state model including the vibronically induced transition provides an easy and reasonable description of the role of excited states in the nonlinear optical response of this class of molecules. From these investigations we conclude that for a sufficient description of the nonlinear response the electron–phonon interaction cannot be neglected.

The shifts of states in the absorption, fluorescence and two-photon spectra of squaraine oligomers could reasonably be explained by exciton coupling theory. Furthermore, high fluorescence quantum yields and large two-photon cross-section were measured for the oligomers.

Acknowledgements

The MALDI/TOF mass spectra were recorded by Anke Waßmann and Dr. Manfred Nimtz at the Gesellschaft für Biotechnologische Forschung mbH, Braunschweig. We thank the Bundesministerium für Bildung und Forschung (BMBF) for generous financial support.

Appendix A

A.1. General remarks

Flash chromatography (FC) was performed using silica gel “Kieselgel 60” (0.040–0.063 mm, Merck). Plates for preparative TLC (ca. $100 \times 30 \text{ cm}^2$, layer thickness 1.5 mm) were prepared using silica gel (“Kieselgel 60PF”, Merck). Melting points were determined on a MEL-Temp II, Laboratory devices, USA or on a Kofler hot stage microscope apparatus, Reichert, Austria and are uncorrected or on a Rheometric Scientific DSC SP differential scanning calorimeter using a heating rate of 10 K min^{-1} . 400 MHz ^1H and 100 MHz ^{13}C NMR spectra were run on Bruker AM 400 and Bruker Avance DRX 400 instruments using CDCl_3 (tetramethylsilane (^1H) or the solvent (^{13}C) as internal standards) or $[\text{D}_6]\text{DMSO}$ (solvent (^1H and ^{13}C) as standard). The degree of substitution of the carbon atoms was determined by DEPT 135° experiments. Further assignments were made with the help of H,H-, C,H-COSY and C,H-COLOC spectra. Additional information was obtained from the literature [69,70]. UV/Vis absorption spectra were measured with a Hewlett Packard diode array spectrophotometer 8452 A using 1 cm cuvettes. Solvents (“Uvasol”, Merck) were used without further purification. Mass spectra were recorded on a Finnigan MAT 8430 spectrometer using either the electron impact (EI) ionisation method (70 eV) or the fast atom bombardment (FAB) method (Xe-atoms, 8 kV; matrix: 3-nitrobenzyl alcohol). The unexpected spectra of the dimeric squaraines obtained under positive FAB conditions (signals corresponding to a $[(\text{M}-\text{H})^+]$) will be discussed in more detail in a future work [71]. Mass spectra of the higher oligomers were achieved using the matrix assisted laser desorption ionisation and the time of flight detection techniques (MALDI/TOF) in a positive mode on a Bruker REFLEXTM spectrometer equipped with a delayed extraction module and a N_2 laser (337 nm) with 3 ns pulse width and 10^7 – 10^8 W cm^{-2} irradiance (matrix: α -cyano-4-hydroxycinnamic acid). The experimentally observed base peak corresponds to the center of gravity of the signal pattern. Elemental analyses

were carried out by the analytical laboratory of the Institute of Pharmaceutical Chemistry, Technical University of Braunschweig.

A.2. General procedure for the synthesis of the ethoxycyclobutene-1,2-diones **5**

An equimolar amount of the methylenbase **4** is added to a solution of squaric acid diethyl ester (diethyl squarate) and triethylamine (Et₃N) in ethanol at 60 °C. After stirring for 1 h and cooling, most of the solvent is removed on a rotary evaporator and the residue is taken up in diethyl ether. After the addition of water and dropwise addition of a sufficient amount of 5 N HCl to obtain phase separation, the aqueous layer is extracted with diethyl ether and the combined organic phases are dried (MgSO₄). Purification is achieved by FC and crystallisation.

A.3. 3-(1-Butyl-3,3-dimethyl-2,3-dihydroindol-2-ylidenemethyl)-4-ethoxycyclobut-3-ene-1,2-dione (**5b**)

0.247 g (4%) analytically pure and 1.986 g (29%) for synthetic purposes from **4b** (4.31 g, 20.0 mmol), diethyl squarate (3.40 g) and Et₃N (4 ml, 29 mmol) in EtOH (20 ml); mp (diethyl ether/ethyl acetate): 120–121 °C; *R*_f = 0.40 (*n*-pentane/diethyl ether 1:1); ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.26–7.30 (m, 2H; 4,6-H), 7.05–7.09 (m, 1H; 5-H), 6.89–6.91 (m, 1H; 7-H), 5.42 (s, 1H; 10-H), 4.99 (q, ³J_{H,H} = 7.1 Hz, 2H; O—CH₂—), 3.83 (t, ³J_{H,H} = 7.5 Hz, 2H; N—CH₂—), 1.71–1.78 (m, 2H; —CH₂—), 1.63 (s, 6H; 11,12-H), 1.55 (t, ³J_{H,H} = 7.1 Hz, 3H; —CH₃), 1.41–1.51 (m, 2H; —CH₂—), 1.00 (t, ³J_{H,H} = 7.3 Hz, 3H; —CH₃); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 192.5 (s, C-2'), 187.4 (2 × s, C-1', 4'), 173.7 (s, C-3'), 168.4 (s, C-2), 142.7 (s, C-8), 140.9 (s, C-9), 127.7 (d, C-6), 122.6 (d, C-5), 121.9 (d, C-4), 108.4 (d, C-7), 81.2 (d, C-10), 69.8 (t, O—CH₂—), 47.9 (s, C-3), 42.8 (t, N—CH₂—), 26.9 (q, C-11,12), 28.5 and 20.3 (2 × t, 2 × —CH₂—), 15.9 and 13.8 (2 × q, 2 × —CH₃); UV/Vis (CHCl₃): λ_{max}(ε) = 426 nm (71,600 dm³ mol⁻¹ cm⁻¹); MS (70 eV, EI): *m/z* (%): 339 (90) [M⁺], 254 (100); C₂₁H₂₅NO₃ (339.43) calcd (%) C 74.31, H 7.42, N 4.13; found C 74.28, H 7.34, N 3.83.

A.4. 4-(1-Hexyl-3,3-dimethyl-2,3-dihydroindol-2-ylidenemethyl)-3-ethoxycyclobut-3-ene-1,2-dione (**5c**)

0.340 g (1%) analytically pure and 9.008 g (32%) for synthetic purposes from **4c** (18.5 g, 76 mmol), diethyl squarate (13 g) and Et₃N (21.0 ml, 150 mmol) in EtOH (100 ml); mp (MeOH): 111 °C; *R*_f = 0.27 (*n*-pentane/diethyl ether 2:1); ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.26–7.29 (m, 2H; 4,6-H), 7.05–7.09 (m, 1H; 5-H), 6.88–6.90 (m, 1H; 7-H), 5.41 (s, 1H; 10-H), 4.89 (q, ³J_{H,H} = 7.1 Hz, 2H; O—CH₂—), 3.82 (broad s, 2H; N—CH₂—), 1.71–1.77 (m, 2H; —CH₂—), 1.62 (s, 6H; 11,12-H), 1.54 (t, ³J_{H,H} = 7.1 Hz, 3H; —CH₃), 1.34–1.42 (m, 6H; —CH₂—), 0.90 (t, ³J_{H,H} = 7.0 Hz, 3H; —CH₃); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 192.5 (s, C-2'), 187.4 (2 × s, C-1', 4'), 173.7 (s, C-3'), 168.4 (s, C-2), 142.6 (s, C-8), 140.9 (s, C-9), 127.7 (d, C-6), 122.6 (d, C-5), 121.9 (d, C-4), 108.4 (d, C-7), 81.2 (d, C-10), 69.8 (t, O—CH₂—), 47.9 (s, C-3), 42.9 (t, N—CH₂—), 26.9 (q, C-11,12), 31.4, 26.6, 26.2 and 22.4 (4 × t, 4 × —CH₂—), 15.9 and 13.9 (2 × q, 2 × —CH₃); UV/Vis (CHCl₃): λ_{max}(ε) = 426 nm (71,100 dm³ mol⁻¹ cm⁻¹); MS (70 eV, EI): *m/z* (%): 367 (94) [M⁺], 282 (100); C₂₃H₂₉NO₃ (367.49) calcd (%) C 75.14, H 7.95, N 3.81; found C 75.23, H 8.09, N 3.68.

A.5. 3-(5-Bromo-1-butyl-3,3-dimethyl-2,3-dihydroindol-2-ylidenemethyl)-4-ethoxycyclobut-3-ene-1,2-dione (**5d**)

0.734 g (15%) analytically pure and 0.578 g (12%) for synthetic purposes from **4d** (3.50 g, 11.9 mmol), diethyl squarate (2.02 g) and Et₃N (2 ml, 14 mmol) in EtOH (15 ml); mp (diethyl ether/ethyl acetate): 126–127 °C; *R*_f = 0.42 (*n*-pentane/diethyl ether 1:1); ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.35–7.38 (m, 2H; 4,6-H), 6.73 (d, ³J_{7,6} = 8.2 Hz, 1H; 7-H), 5.39 (s, 1H; 10-H), 4.90 (q, ³J_{H,H} = 7.1 Hz, 2H; O—CH₂—), 3.78 (t, ³J_{H,H} = 7.5 Hz, 2H; N—CH₂—), 1.64–1.75 (m, 2H; —CH₂—), 1.61 (s, 6H; 11,12-H), 1.53 (t, ³J_{H,H} = 7.1 Hz, 3H; —CH₃), 1.38–1.48 (m, 2H; —CH₂—), 0.99 (t, ³J_{H,H} = 7.3 Hz, 3H; —CH₃); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 192.3 (s, C-2'), 188.0 and 187.8 (2 × s, C-1', 4'), 173.6 (s, C-3'), 167.4 (s, C-2),

143.0 (s, C-9), 141.9 (s, C-8), 130.6 (d, C-4), 125.4 (d, C-6), 115.1 (s, C-5), 109.7 (d, C-7), 81.8 (d, C-10), 70.1 (t, O—CH₂—), 47.9 (s, C-3), 42.9 (t, N—CH₂—), 27.0 (q, C-11,12), 28.4 and 20.3 (2 × t, 2 × —CH₂—), 15.9 and 13.9 (2 × q, 2 × —CH₃); UV/Vis (CHCl₃): λ_{max}(ε) = 428 nm (74,900 dm³ mol⁻¹ cm⁻¹); MS (70 eV, EI): *m/z* (%): 419 (98) [M⁺, ⁸¹Br], 417 (100) [M⁺, ⁷⁹Br], 334 (96), 332 (98); C₂₁H₂₄BrNO₃ (418.33) calcd (%) C 60.29, H 5.78, N 3.35; found C 60.55, H 5.79, N 2.99.

A.6. 3-(5-Bromo-1-hexyl-3,3-dimethyl-2,3-dihydro-indol-2-ylidenemethyl)-4-ethoxycyclobut-3-ene-1,2-dione (5e)

1.840 g (13%) analytically pure and 3.067 g (22%) for synthetic purposes from **4e** (10.0 g, 31 mmol), diethyl squarate (5.28 g) and Et₃N (8.4 ml, 60 mmol) in EtOH (50 ml); mp (MeOH): 140 °C; *R_f* = 0.27 (*n*-pentane/diethyl ether 2:1); ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.35–7.38 (m, 2H; 4,6-H), 6.73 (d, ³*J*_{7,6} = 8.2 Hz, 1H; 7-H), 5.39 (s, 1H; 10-H), 4.90 (q, ³*J*_{H,H} = 7.1 Hz, 2H; O—CH₂—), 3.78 (t, ³*J*_{H,H} = 7.5 Hz, 2H; N—CH₂—), 1.69–1.81 (m, 2H; —CH₂—), 1.61 (s, 6H; 11,12-H), 1.54 (t, ³*J*_{H,H} = 7.1 Hz, 3H; —CH₃), 1.30–1.45 (m, 6H; —CH₂—), 0.90 (t, ³*J*_{H,H} = 6.9 Hz, 3H; —CH₃); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 192.3 (s, C-2'), 188.0 and 187.8 (2 × s, C-1', 4'), 173.6 (s, C-3'), 167.3 (s, C-2), 142.9 (s, C-9), 141.9 (s, C-8), 130.6 (d, C-4), 125.3 (d, C-6), 115.0 (s, C-5), 109.6 (d, C-7), 81.8 (d, C-10), 70.0 (t, O—CH₂—), 47.9 (s, C-3), 43.1 (t, N—CH₂—), 27.0 (q, C-11,12), 31.4, 26.6, 26.2 and 22.4 (4 × t, 4 × —CH₂—), 15.9 and 13.9 (2 × q, 2 × —CH₃); UV/Vis (CHCl₃): λ_{max}(ε) = 428 nm (75,100 dm³ mol⁻¹ cm⁻¹); MS (70 eV, EI): *m/z* (%): 447 (96) [M⁺, ⁸¹Br], 445 (92) [M⁺, ⁷⁹Br], 362 (96), 360 (100); C₂₃H₂₈BrNO₃ (446.38) calcd (%) C 61.89, H 6.32, N 3.14; found C 61.65, H 6.34, N 2.98.

A.7. General procedure for the synthesis of the hydroxycyclobutene-1,2-diones 6

1 mmol of the ethyl ester **5** is dissolved in refluxing acetone (ca. 20 ml) and 2 N HCl (3 ml) is added. When the reaction is complete (TLC monitoring) the solvent is removed. The residue is taken

up in diethyl ether, washed with water and the organic layer is dried. Evaporation of the solvent and drying in vacuo affords dark yellow to brown solids, which are used without further purification.

A.8. General procedure for the Pd-catalysed cross coupling reactions

The brominated compound is dissolved in anhydrous DMF under a nitrogen atmosphere and (Ph₃P)₄Pd (1 mol% per bromine-atom) is added. The mixture is heated to 60 °C and the neat stannane is added. After stirring at 110 °C for 12 h the solvent is removed in vacuo. The residue is dissolved in CH₂Cl₂ and stirred with excess aqueous KF-solution (10%) for several hours. Filtration, phase separation, washing of the organic layer with brine and drying (MgSO₄) affords a crude product, which is further purified by FC using the solvents given with the *R_f*-value.

A.9. 2,5-Bis(2,3,3-trimethyl-3H-indol-5-yl)thiophene (7)

0.596 g (32%) from **3b** (2.200 g, 9.24 mmol), 2,5-bis(tri-*n*-butylstannyl)thiophene (3.060 g, 4.62 mmol), (Ph₃P)₄Pd (0.106 g) in DMF (5 ml); mp after sublimation (215 °C/0.2 mbar): 183–187 °C; *R_f* = 0.30 (toluene/EtOH 10:1); ¹H NMR (400 MHz, [D₆]DMSO, 25 °C): δ = 7.78 (d, ⁴*J*_{4,6} = 1.8 Hz, 2H; 4-H), 7.60 (dd, ³*J*_{6,7} = 8.0, ⁴*J*_{6,4} = 1.8 Hz, 2H; 6-H), 7.53 (s, 2H; 3', 4'-H), 7.45 (d, ³*J*_{7,6} = 8.0 Hz, 2H; 7-H), 2.23 (s, 6H; 10-H), 1.30 (s, 12H; 11,12-H); ¹³C NMR (100 MHz, [D₆]DMSO, 25 °C): δ = 188.4 (s, C-2), 153.3 (s, C-8), 147.0 (s, C-9), 142.6 (s, C-2', 5'), 130.5 (s, C-5), 124.5 (d, C-6, 3', 4'), 119.7 (d, C-7), 118.7 (d, C-4), 53.4 (s, C-3), 22.5 (q, C-11,12), 15.1 (q, C-10); UV/Vis (CHCl₃): λ_{max}(ε) = 356 nm (35,900 dm³ mol⁻¹ cm⁻¹); MS (70 eV, EI): *m/z* (%): 398 (100) [M⁺]; C₂₆H₂₆N₂S (398.57) calcd (%) C 78.35, H 6.57, N 7.03; found C 78.41, H 6.75, N 6.85.

A.10. 5-(2-Thienyl)-2,3,3-trimethyl-3H-indole (9)

1.537 g (32%) from **3b** (4.76 g, 20.0 mmol), 2-(tri-*n*-butylstannyl)thiophene (8.58 g, 23.0 mmol), (Ph₃P)₄Pd (0.231 g) in DMF (7 ml); mp after

sublimation (90–100 °C/0.2 mbar): 81–82 °C; R_f = 0.44 (diethyl ether/ethyl acetate 5:2); ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C): δ = 7.73 (d, $^4J_{4,6}$ = 1.9 Hz, 1H; 4-H), 7.55 (dd, $^3J_{6,7}$ = 8.0, $^4J_{6,4}$ = 1.9 Hz, 1H; 6-H), 7.50 (dd, $^3J_{5',4'}$ = 5.1, $^4J_{5',3'}$ = 1.1 Hz, 1H; 5'-H), 7.48 (dd, $^3J_{3',4'}$ = 3.5, $^4J_{3',5'}$ = 1.0 Hz, 1H; 3'-H), 7.43 (d, $^3J_{7,6}$ = 8.0 Hz, 1H; 7-H), 7.12 (dd, $^3J_{4',5'}$ = 5.1, $^3J_{4',3'}$ = 3.6 Hz, 1H; 4'-H), 2.21 (s, 3H; 10-H), 1.28 (s, 6H; 11,12-H); ^{13}C NMR (100 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C): δ = 188.3 (s, C-2), 153.2 (s, C-8), 146.9 (s, C-9), 143.8 (s, C-2'), 130.7 (s, C-5), 128.4 (d, C-4'), 125.2 (d, C-5'), 124.9 (d, C-6), 123.3 (d, C-3'), 119.6 (d, C-7), 119.0 (d, C-4), 53.4 (s, C-3), 22.5 (q, C-11,12), 15.1 (q, C-10); UV/Vis (CHCl_3): $\lambda_{\text{max}}(\epsilon)$ = 308 nm (19,800 $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$); MS (70 eV, EI): m/z (%): 241 (100) $[\text{M}^+]$; $\text{C}_{15}\text{H}_{15}\text{NS}$ (241.36) calcd (%) C 74.65, H 6.27, N 5.80; found C 74.54, H 6.35, N 5.71.

A.11. General procedures for the synthesis of the quaternary salts **8**, **10** and the methylenebases **4** and **11**

Method A. The 3H-indole derivatives are heated to reflux with excess alkyl iodide in the presence of nitromethane for 12 h. After cooling the precipitate is filtrated, washed with diethyl ether and crystallized.

Method B. To a solution of the heterocycles in anhydrous CH_2Cl_2 triethyloxonium tetrafluoroborate (1.2–1.3 eq) is added at 0 °C under a nitrogen atmosphere. After stirring for 12 h the excess reagent is hydrolyzed by addition of a few ml of EtOH. (For further workup see Method A.) The methylenebases **4** and **11** are obtained by suspending the salts in a separation funnel in 2 N NaOH, repeated extraction with diethyl ether, drying (MgSO_4) and distillation.

A.12. 5-Bromo-1-butyl-3,3-dimethyl-2-methylene-2,3-dihydroindole (**4d**)

Method A. 3.835 g (62%) from **3b** (5.0 g, 21 mmol), butyl iodide (2.9 ml, 25 mmol) in MeNO_2 (3 ml); bp: 100–110 °C/0.05 mbar; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 7.19 (dd, $^3J_{6,7}$ = 8.3, $^4J_{6,4}$ = 2.0 Hz, 1H; 6-H); 7.13 (d, $^4J_{4,6}$ = 2.0 Hz, 1H; 4-H), 6.37 (d, $^3J_{7,6}$ = 8.3 Hz, 1H;

7-H), 3.88 (d, $^2J_{10(E),10(Z)}$ = 2.0 Hz, 1H; 10-H(E)), 3.84 (d, $^2J_{10(Z),10(E)}$ = 2.0 Hz, 1H; 10-H(Z)), 3.44 (t, $^3J_{\text{H,H}}$ = 7.3 Hz, 2H; N- CH_2 -), 1.55–1.63 (m, 2H; $-\text{CH}_2$ -), 1.31–1.46 (m, 2H; $-\text{CH}_2$ -), 1.30 (s, 6H; 11,12-H), 0.94 (t, $^3J_{\text{H,H}}$ = 7.3 Hz, 3H; $-\text{CH}_3$); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C): δ = 161.0 (s, C-2), 145.1 (s, C-8), 139.9 (s, C-9), 130.1 (d, C-6), 125.1 (d, C-4), 110.0 (s, C-5), 106.4 (d, C-7), 73.9 (t, C-10), 44.3 (s, C-3), 42.9 (t, N- CH_2 -), 30.0 (q, C-11,12), 28.2 and 20.5 ($2 \times \text{t}$, $2 \times -\text{CH}_2$ -), 14.0 (q, $-\text{CH}_3$); MS (70 eV, EI): m/z (%): 297 (88) $[\text{M}^+$, ^{81}Br], 295 (100) $[\text{M}^+$, ^{79}Br]; $\text{C}_{15}\text{H}_{20}\text{NBr}$ (294.33) calcd (%) C 61.23, H 6.85, N 4.76; found C 61.25, H 7.01, N 4.95.

A.13. 5-Bromo-1-hexyl-3,3-dimethyl-2-methylene-2,3-dihydroindole (**4e**)

Method A. 20.38 g (79%) from **3b** (19.00 g, 79.8 mmol), hexyl iodide (14.2 ml, 96 mmol) in MeNO_2 (20 ml); bp: 143 °C/0.5 mbar; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): δ = 7.19 (dd, $^3J_{6,7}$ = 8.3, $^4J_{6,4}$ = 2.0 Hz, 1H; 6-H); 7.13 (d, $^4J_{4,6}$ = 2.0 Hz, 1H; 4-H), 6.37 (d, $^3J_{7,6}$ = 8.3 Hz, 1H; 7-H), 3.88 (d, $^2J_{10(E),10(Z)}$ = 2.0 Hz, 1H; 10-H(E)), 3.84 (d, $^2J_{10(Z),10(E)}$ = 2.0 Hz, 1H; 10-H(Z)), 3.43 (t, $^3J_{\text{H,H}}$ = 7.3 Hz, 2H; N- CH_2 -), 1.58–1.63 (m, 2H; $-\text{CH}_2$ -), 1.27–1.37 (m, 6H; $3 \times -\text{CH}_2$ -), 1.30 (s, 6H; 11,12-H), 0.88 (t, $^3J_{\text{H,H}}$ = 7.0 Hz, 3H; $-\text{CH}_3$); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C): δ = 161.0 (s, C-2), 145.1 (s, C-8), 139.9 (s, C-9), 130.1 (d, C-6), 125.1 (d, C-4), 110.0 (s, C-5), 106.4 (d, C-7), 73.9 (t, C-10), 44.3 (s, C-3), 42.4 (t, N- CH_2 -), 30.0 (q, C-11,12), 31.7, 26.9, 25.9 and 22.6 ($4 \times \text{t}$, $4 \times -\text{CH}_2$ -), 14.0 (q, $-\text{CH}_3$); MS (70 eV, EI): m/z (%): 323 (92) $[\text{M}^+$, ^{81}Br], 321 (90) $[\text{M}^+$, ^{79}Br]; $\text{C}_{17}\text{H}_{24}\text{NBr}$ (322.29) calcd (%) C 63.36, H 7.51, N 4.35; found C 63.63, H 7.78, N 4.46.

A.14. 2,5-Bis(1-ethyl-2,3,3-trimethyl-3H-indol-1-ium-5-yl)thiophene iodide (**8a**)

Method A. 1.466 g (ca. 82%) from **7** (1.00 g, 2.5 mmol), ethyl iodide (7.5 ml, 93 mmol) in MeNO_2 (3 ml); mp (EtOH/ H_2O , DSC): 258–260 °C; ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C): δ = 8.31 (d, $^4J_{4,6}$ = 1.2 Hz, 2H; 4-H), 8.07 (d, $^3J_{7,6}$ = 8.5 Hz, 2H; 7-H), 7.98 (dd, $^3J_{6,7}$ = 8.5, $^4J_{6,4}$ = 1.4 Hz, 2H; 6-H),

7.86 (s, 2H; 3', 4'-H), 4.54 (q, $^3J_{\text{H,H}} = 7.0$ Hz, 4H; $2 \times \text{N}-\underline{\text{CH}_2}-$), 2.88 (s, 6H; 10-H), 1.63 (s, 12H; 11,12-H), 1.49 (t, $^3J_{\text{H,H}} = 7.1$ Hz, 6H; $2 \times -\underline{\text{CH}_3}$); ^{13}C NMR (100 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C): $\delta = 195.9$ (s, C-2), 143.2, 142.3, 140.2 and 134.5 ($4 \times$ s, C-5,8,9,2' (= 5')), 127.1, 125.8, 120.4 and 116.2 ($4 \times$ d, C-4,6,7,3' (= 4')), 54.3 (s, C-3), 43.3 (t, $\text{N}-\underline{\text{CH}_2}-$), 21.9 (q, C-11,12), 14.0 (q, C-10), 12.8 (q, $-\underline{\text{CH}_3}$); UV/Vis (DMF): $\lambda_{\text{max}}(\epsilon) = 394$ nm (ca. $34,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$); MS (FAB, pos.): m/z (%): 455 (100) [$\text{Cat}^{2+}(\text{C}_{30}\text{H}_{36}\text{N}_2\text{S}^{2+}) - \text{H}^+$]; $\text{C}_{30}\text{H}_{36}\text{I}_2\text{N}_2\text{S}$ (710.49): a satisfactory elemental analysis could not be obtained.

A.15. 2,5-Bis(1-butyl-2,3,3-trimethyl-3H-indol-1-ium-5-yl)thiophene tetrafluoroborate (8b)

Method A. 0.613 g (ca. 36%) from **7** (1.00 g, 2.5 mmol), butyl iodide (8.0 ml, 70 mmol) in MeNO_2 (3 ml), anion exchange by dropwise addition of aqueous NaBF_4 -solution (30%) to a hot ethanolic solution (25 ml) of the crude product and filtration of the precipitate; mp (EtOH/ H_2O , DSC): 286 °C; ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C): $\delta = 8.29$ (s, 2H; 4-H), 8.06 (d, $^3J_{7,6} = 8.5$ Hz, 2H; 7-H), 7.98 (d, $^3J_{6,7} = 8.4$ Hz, 2H; 6-H), 7.85 (s, 2H; 3', 4'-H), 4.49 (t, $^3J_{\text{H,H}} = 7.4$ Hz, 4H; $2 \times \text{N}-\underline{\text{CH}_2}-$), 2.87 (s, 6H; 10-H), 1.83–1.91 (m, 4H; $2 \times -\underline{\text{CH}_2}-$), 1.63 (s, 12H; 11,12-H), 1.43–1.52 (m, 4H; $2 \times -\underline{\text{CH}_2}-$), 0.98 (t, $^3J_{\text{H,H}} = 7.4$ Hz, 6H; $2 \times -\underline{\text{CH}_3}$); ^{13}C NMR (100 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C): $\delta = 196.3$ (s, C-2), 143.1, 142.4, 140.5 and 134.6 ($4 \times$ s, C-5,8,9,2' (= 5')), 127.0, 125.8, 120.3 and 116.3 ($4 \times$ d, C-4,6,7,3' (= 4')), 54.3 (s, C-3), 47.6 (t, $\text{N}-\underline{\text{CH}_2}-$), 29.3 and 19.3 ($2 \times$ t, $2 \times -\underline{\text{CH}_2}-$), 22.0 (q, C-11,12), 14.0 (q, C-10), 12.8 (q, $-\underline{\text{CH}_3}$); UV/Vis (DMF): $\lambda_{\text{max}}(\epsilon) = 394$ nm (ca. $38,000 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$); MS (FAB, pos.): m/z (%): 511 (100) [$\text{Cat}^{2+}(\text{C}_{34}\text{H}_{44} \text{N}_2\text{S}^{2+}) - \text{H}^+$]; $\text{C}_{34}\text{H}_{44}\text{B}_2\text{F}_8\text{N}_2\text{S}$ (686.41): a satisfactory elemental analysis could not be obtained.

A.16. 5-(2-Thienyl)-2,3,3-trimethyl-3H-indol-1-ium-tetrafluoroborate (10)

4.122 g (62%) from **9** (4.50 g, 18.6 mmol), triethylxonium tetrafluoroborate (4.60 g, 24.2 mmol) in CH_2Cl_2 (30 ml); mp (EtOH/ H_2O): 272–

275 °C; ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C): $\delta = 8.17$ (d, $^4J_{4,6} = 1.6$ Hz, 1H; 4-H), 7.98 (d, $^3J_{7,6} = 8.5$ Hz, 1H; 7-H), 7.89 (dd, $^3J_{6,7} = 8.4$, $^4J_{6,4} = 1.7$ Hz, 1H; 6-H), 7.70 (dd, $^3J_{3',4'} = 3.6$, $^4J_{3',5'} = 1.0$ Hz, 1H; 3'-H), 7.67 (dd, $^3J_{5',4'} = 5.0$, $^4J_{5',3'} = 0.9$ Hz, 1H; 5'-H), 7.21 (dd, $^3J_{4',5'} = 5.0$, $^3J_{4',3'} = 3.7$ Hz, 1H; 4'-H), 4.49 (q, $^3J_{\text{H,H}} = 7.3$ Hz, 2H; $\text{N}-\underline{\text{CH}_2}-$), 2.82 (s, 3H; 10-H), 1.58 (s, 6H; 11,12-H), 1.46 (t, $^3J_{\text{H,H}} = 7.3$ Hz, 3H; $-\underline{\text{CH}_3}$); ^{13}C NMR (100 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C): $\delta = 195.8$ (s, C-2), 143.1 (s, C-9), 141.8 (s, C-2'), 139.9 (s, C-8), 135.1 (s, C-5), 128.8 (d, C-4'), 127.3 (d, C-5'), 126.0 (d, C-6), 125.5 (d, C-3'), 120.5 (d, C-4), 116.0 (d, C-7), 54.3 (s, C-3), 43.2 (t, $\text{N}-\underline{\text{CH}_2}-$), 21.9 (q, C-11,12), 13.6 (q, C-10), 12.7 (q, $-\underline{\text{CH}_3}$); UV/Vis (DMF): $\lambda_{\text{max}}(\epsilon) = 342$ nm ($24,800 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$); MS (FAB, pos.): m/z (%): 270 (100) [$\text{Cat}^+(\text{C}_{17}\text{H}_{20}\text{NS}^+)]$; $\text{C}_{17}\text{H}_{20}\text{BF}_4\text{NS}$ (357.22) calcd (%) C 57.17, H 5.64, N 3.92; found C 57.17, H 5.76, N 3.79.

A.17. 5-(2-Thienyl)-1-ethyl-3,3-dimethyl-2-methylene-2,3-dihydroindole (11)

4.496 g (88%) from **10** (6.80 g, 18.9 mmol); bp: 162–165 °C/0.5 mbar; ^1H NMR (400 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C): $\delta = 7.45$ (d, $^4J_{4,6} = 1.7$ Hz, 1H; 4-H), 7.36–7.38 (m, 2H; 6,5'-H), 7.31 (d, $^3J_{3',4'} = 3.5$ Hz, 1H; 3'-H), 7.05–7.07 (m, 1H; 4'-H), 6.66 (d, $^3J_{7,6} = 8.1$ Hz, 1H; 7-H), 3.95 (d, $^2J_{10(\text{E}),10(\text{Z})} = 0.9$ Hz, 1H; 10-H(E)), 3.91 (d, $^2J_{10(\text{Z}),10(\text{E})} = 0.9$ Hz, 1H; 10-H(Z)), 3.58 (q, $^3J_{\text{H,H}} = 7.1$ Hz, 2H; $\text{N}-\underline{\text{CH}_2}-$), 1.31 (s, 6H; 11,12-H), 1.08 (t, $^3J_{\text{H,H}} = 7.1$ Hz, 3H; $-\underline{\text{CH}_3}$); ^{13}C NMR (100 MHz, $[\text{D}_6]\text{DMSO}$, 25 °C): $\delta = 159.9$ (s, C-2), 144.7 and 144.6 ($2 \times$ s, C-8,2'), 138.0 (s, C-9), 128.1 (d, C-4'), 125.3 (d, C-6), 124.6 (s, C-5), 123.3 (d, C-5'), 121.3 (d, C-3'), 119.5 (d, C-4), 105.3 (d, C-7), 74.4 (t, C-10), 43.6 (s, C-3), 36.0 (t, $\text{N}-\underline{\text{CH}_2}-$), 29.6 (q, C-11,12), 10.5 (q, $-\underline{\text{CH}_3}$); MS (70 eV, EI): m/z (%): 269 (72) [M^+] 254 (100); $\text{C}_{17}\text{H}_{19}\text{NS}$ (269.41) calcd (%) C 75.79, H 7.11, N 5.20; found C 75.66, H 7.14, N 5.15.

A.18. 5-(5-Tri-butylstannyl-2-thienyl)-1-ethyl-3,3-dimethyl-2-methylene-2,3-dihydroindole (12)

n-BuLi (15% in *n*-hexane, 13.05 ml, 20.8 mmol) is added at 25 °C within 5 min to a solution of **11**

(4.000 g, 14.8 mmol) and TMEDA (3.14 ml) in anhydrous diethyl ether (100 ml). The mixture is heated to reflux for 30 min, cooled to $-75\text{ }^{\circ}\text{C}$ and tri-*n*-butylstannyl chloride (5.87 ml, 20.8 mmol) is added within 30 min. After aqueous workup the crude product is distilled using a 10 cm Vigreux-column. From the fraction obtained at 216–240 $^{\circ}\text{C}/0.25\text{ mbar}$ **12** is obtained by bulb-to-bulb distillation (230 $^{\circ}\text{C}/0.25\text{ mbar}$) as a yellow oil, with sufficient purity for further reactions (4.937 g, ca. 59%); ^1H NMR (400 MHz, CDCl_3 , 25 $^{\circ}\text{C}$, TMS): $\delta = 7.40$ (dd, $^3J_{6,7} = 8.1$, $^4J_{6,4} = 1.8$ Hz, 1H; 6-H), 7.31, (d, $^4J_{4,6} = 1.8$ Hz, 1H; 4-H), 7.27 and 7.09 (2 \times d, $^3J_{\text{H,H}} = 3.3$ Hz, 2 \times 1H; 3', 4'-H), 6.50 (d, $^3J_{7,6} = 8.1$ Hz, 1H; 7-H), 3.90 (d, $^2J_{10(\text{E}),10(\text{Z})} = 1.9$ Hz, 1H; 10-H(E)), 3.86 (d, $^2J_{10(\text{Z}),10(\text{E})} = 1.9$ Hz, 1H; 10-H(Z)), 3.57 (q, $^3J_{\text{H,H}} = 7.1$ Hz, 2H; N- CH_2 -), 1.55–1.68 (m, 6H; 3 \times - CH_2 -), 1.36 (s, 6H; 11, 12-H), 1.33–1.40 (m, 6H; 3 \times - CH_2 -), 1.18 (t, $^3J_{\text{H,H}} = 7.1$ Hz, 3H; - CH_3), 1.091.13 (m, 6H; 3 \times - CH_2 -), 0.91 (t, $^3J_{\text{H,H}} = 7.3$ Hz, 9H; 3 \times - CH_3); ^{13}C NMR (100 MHz, CDCl_3 , 25 $^{\circ}\text{C}$): $\delta = 161.0$ (s, C-2), 151.2, 144.9, 138.3, 134.4 and 125.5 (5 \times s, C-5, 8, 9, 2', 5'), 136.3, 125.7, 122.5 and 120.1 (4 \times d, C-4, 6, 3', 4'), 104.9 (d, C-7), 73.4 (t, C-10), 44.2, (s, C-3), 36.7 (t, N- CH_2 -), 30.0 (q, C-11, 12), 29.0, 27.3 and 10.8 (3 \times t, 3 \times - CH_2 -), 13.7 and 10.7 (2 \times q, 2 \times - CH_3); MS (70 eV, EI): m/z (%): 559 (64) [M^+], 502 (64), 269 (100); $\text{C}_{29}\text{H}_{45}\text{NSSn}$ (558.44).

A.19. General procedures for the synthesis of the monomeric squaraines 13 and the dimers 14c,d

The methylenbases **4** and 0.5 eq of squaric acid (symmetric monomers) or equimolar amounts of the methylenbases **4** and the hydroxycyclobutenediones **6** (asymmetric monomers) or the quaternary salts **8** and 2 eq of the hydroxycyclobutenediones **6** (symmetric dimers) are kept under reflux for 12 h in toluene/*n*-butanol (1:1) in the presence of quinoline using a Dean–Stark trap. After removal of solvent and FC (in some cases pure samples have to be obtained by preparative TLC) a solid is obtained that is either transferred to an extraction thimble and extracted with a boiling solvent and cooled or dissolved in CH_2Cl_2 and precipitated by dropwise addition of *n*-pentane.

The pure products appear as microcrystals or powder.

A.20. 2,4-Bis[(1-ethyl-3,3-dimethyl-2,3-dihydroindol-2-ylidene)methyl]cyclobutenediylum-1,3-diolate (C2-ISQ, 13a)

1.179 g (83%) from **4a** (1.180 g, 6.30 mmol) and squaric acid (0.36 g) in 30 ml of solvent. mp (MeOH, DSC): ca. 290 $^{\circ}\text{C}$ (decomp.); $R_f = 0.44$ ($\text{CHCl}_3/\text{EtOH}$ 20:1); ^1H NMR (400 MHz, CDCl_3 , 25 $^{\circ}\text{C}$, TMS): $\delta = 7.36$ (d, $^3J_{4',5'} = ^3J_{4'',5''} = 7.4$ Hz, 2H; 4', 4''-H), 7.29–7.33 (m, 2H; 6', 6''-H), 7.13–7.17 (m, 2H; 5', 5''-H), 6.99 (d, $^3J_{7',6'} = ^3J_{7'',6''} = 7.9$ Hz, 2H; 7', 7''-H), 5.96 (s, 2H; 10', 10''-H), 4.08 (broad s, 4H; 2 \times N- CH_2 -), 1.79 (s, 12H; 11', 11'', 12', 12''-H), 1.40 (t, $^3J_{\text{H,H}} = 7.2$ Hz, 6H; 2 \times - CH_3); ^{13}C NMR (100 MHz, CDCl_3 , 25 $^{\circ}\text{C}$): $\delta =$ ca. 182.0 (s, C-1,3), 179.7 (s, C-2,4), 169.6 (s, C-2', 2''), 142.3 and 142.0 (2 \times s, C-8', 8'', C-9', 9''), 127.8 (d, C-6', 6''), 123.7 (d, C-5', 5''), 122.3 (d, C-4', 4''), 109.1 (d, C-7', 7''), 86.2 (d, C-10', 10''), 49.3 (s, C-3', 3''), 38.4 (t, N- CH_2 -), 27.0 (q, C-11', 11'', 12', 12''), 12.0 (q, - CH_3); UV/Vis (CHCl_3): see Table 1; MS (FAB, pos.): m/z (%): 452 (100) [M^+]; $\text{C}_{30}\text{H}_{32}\text{N}_2\text{O}_2$ (452.59) calcd (%) C 79.61, H 7.13, N 6.19; found C 79.17, H 7.35, N 6.01.

A.21. 2-(5-Bromo-1-hexyl-3,3-dimethyl-2,3-dihydroindol-2-ylidene)methyl-4-(1-hexyl-3,3-dimethyl-2,3-dihydroindol-2-ylidene)methylcyclobutenediylum-1,3-diolate (13b)

4.530 g (ca. 40%) from **6c** (6.00 g, 17.7 mmol), **4e** (6.27 g, 19.5 mmol) and quinoline (2.55 ml, 21.58 mmol) in 50 ml of solvent after repeated FC ($\text{CH}_2\text{Cl}_2/\text{diethyl ether}$ 40:1, $R_f = 0.13$); an analytical sample was obtained by preparative TLC ($\text{CH}_2\text{Cl}_2/\text{diethyl ether}$ 40:1), extraction with diethyl ether and precipitation from the ethereal solution by the gas diffusion method using *n*-pentane; mp (DSC): 183 $^{\circ}\text{C}$; ^1H NMR (400 MHz, CDCl_3 , 25 $^{\circ}\text{C}$, TMS): $\delta = 7.36$ –7.43 (m, 3H; 4', 4'', 6''-H), 7.30–7.34 (m, 1H; 6'-H), 7.15–7.19 (m, 1H; 5'-H), 7.01 (d, $^3J_{7',6'} = 7.9$ Hz, 1H; 7'-H), 6.81 (d, $^3J_{7'',6''} = 8.3$ Hz, 1H; 7''-H), 6.00 and 5.93 (2 \times s, 2 \times 1H; 10', 10''-H), 4.02 and 3.91

(2 × broad s, 2 × 2H; 2 × N—CH₂—), 1.79–1.85 (m, 16H, 11', 11'', 12', 12''-H, 2 × —CH₂—), 1.32–1.42 (m, 12H; 6 × —CH₂—), 0.87–0.91 (m, 6H; 2 × —CH₃); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 181.1 (s, C-1,3), 178.8 (s, C-2,4), 171.1 (s, C-2'), 168.4 (C-2''), 144.2 (s, C-9''), 142.3 (s, C-8', 9'), 141.7 (s, C-8''), 130.6 (d, C-6''), 127.8 (d, C-6'), 125.6 (d, C-4''), 124.0 (d, C-5'), 122.3 (d, C-4'), 116.0 (s, C-5''), 110.3 (d, C-7''), 109.6 (d, C-7'), 86.9 and 86.8 (2 × d, C-10', 10''), 49.5 and 49.1 (2 × s, C-3', 3''), 43.9 and 43.7 (2 × t, 2 × N—CH₂—), 27.2 (q, C-11'', 12''), 26.9 (q, C-11', 12'), 31.5, 27.1, 26.8, 26.7 and 22.5 (5 × t, 5 × —CH₂—), 13.9 (q, —CH₃); UV/Vis (CHCl₃): λ_{max}(ε) = 640 nm (314,000 dm³ mol⁻¹ cm⁻¹); MS (70 eV, EI): *m/z* (%): 644 (100) [M⁺, ⁸¹Br], 642 (96), [M⁺, ⁷⁹Br]; C₃₈H₄₇BrN₂O₂ (643.71) calcd (%) C 70.91, H 7.36, N 4.35; found C 70.72, H 7.45, N 4.18.

A.22. 2,4-Bis[5-bromo-1-butyl-3,3-dimethyl-2,3-dihydroindol-2-ylidene)methyl]cyclobutenediylum-1,3-diolate (13e)

1.075 g (63%) from **4d** (1.50 g, 5.1 mmol) and squaric acid (0.297 g) in 15 ml of solvent after FC (CHCl₃/ethyl acetate 5:1, *R_f* = 0.27); mp (CH₂Cl₂/*n*-pentane, DSC): 269 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.45 (d, ⁴*J*_{4',6'} = ⁴*J*_{4'',6''} = 1.8 Hz, 2H; 4', 4''-H), 7.41 (dd, ³*J*_{6',7'} = ³*J*_{6'',7''} = 8.3, ⁴*J*_{6',4'} = ⁴*J*_{6'',4''} = 1.9 Hz, 2H; 6', 6''-H), 6.85 (d, ³*J*_{7',6'} = ³*J*_{7'',6''} = 8.3 Hz, 2H; 7', 7''-H), 5.96 (s, 2H; 10', 10''-H), 3.96 (broad s, 4H; 2 × N—CH₂—), 1.74–1.82 (m, 16H; 11', 11'', 12', 12''-H, 2 × —CH₂—), 1.45 (“sext”, ³*J*_{H,H} = 7.5 Hz, 4H; 2 × —CH₂—), 0.99 (t, ³*J*_{H,H} = 7.3 Hz, 6H; 2 × —CH₃); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 182.1 (s, C-1,3), 180.4 (s, C-2,4), 169.5 (s, C-2', 2''), 144.2 (s, C-9', 9''), 141.6 (s, C-8', 8''), 130.7 (d, C-6', 6''), 125.7 (d, C-4', 4''), 116.6 (s, C-5', 5''), 110.7 (d, C-7', 7''), 87.1 (d, C-10', 10''), 49.3 (s, C-3', 3''), 43.7 (t, N—CH₂—), 27.1 (q, C-11', 11'', 12', 12''), 29.0 and 20.3 (2 × t, 2 × —CH₂—), 13.8 (q, —CH₃); UV/Vis (CHCl₃): λ_{max}(ε) = 644 nm (334,000 dm³ mol⁻¹ cm⁻¹); MS (70 eV, EI): *m/z* (%): 668 (56) [M⁺, 2 ⁸¹Br], 666 (100), [M⁺, ⁸¹Br, ⁷⁹Br], 664 (51) [M⁺, 2 ⁷⁹Br]; C₃₄H₃₈Br₂N₂O₂ (666.49) calcd (%) C

61.27, H 5.75, N 4.20; found C 61.15, H 5.77, N 4.06.

A.23. 2-(1-Ethyl-3,3-dimethyl-2,3-dihydroindol-2-ylidene)methyl-4-[5-(2-thienyl)-1-ethyl-3,3-dimethyl-2,3-dihydroindol-2-ylidene]methylcyclobutenediylum-1,3-diolate (TpISQ, 13d)

0.564 g (74%) from **10** (0.500 g, 1.40 mmol) and **6a** (0.400 g, 1.40 mmol) and quinoline (0.17 ml, 1.4 mmol) in 50 ml of solvent after FC (toluene/CHCl₃/ethyl acetate 1:1:1 – to remove apolar by-products – followed by CHCl₃/EtOH 10:1, *R_f* = 0.57 to eluate **13d**); mp (MeOH, DSC): 255 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.54–7.57 (m, 2H; 4'', 6''-H), 7.36 (d, ³*J*_{4',5'} = 7.3 Hz, 1H; 4'-H), 7.26–7.34 (m, 3H; 6', 3''', 5'''-H), 7.14–7.17 (m, 1H; 5'-H), 7.09 (dd, ³*J*_{4'',5''} = 5.1, ³*J*_{4''',3'''} = 3.7 Hz, 1H; 4'''-H), 7.00 (d, ³*J*_{7',6'} = 7.9 Hz, 1H; 7'-H), 6.98 (d, ³*J*_{7'',6''} = 8.7 Hz, 1H; 7''-H), 5.99 (s, 1H; 10'-H), 5.98 (s, 1H; 10''-H), 4.09 (broad s, 4H; 2 × N—CH₂—), 1.83 (s, 6H; 11'', 12''-H), 1.80 (s, 6H; 11', 12'-H), 1.40 (t, ³*J*_{H,H} = 6.6 Hz, 6H; 2 × —CH₃); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 182.3 and 181.4 (2 × s, C-1,3), 180.1 (s, C-2), 179.0 (s, C-4), 170.0 (s, C-2'), 168.8 (s, C-2''), 144.1 (s, C-2'''), 143.0 (s, C-9''), 142.3 and 141.9 (2 × s, C-8', 9'), 141.5 (s, C-8''), 130.3 (s, C-5''), 128.1 (d, C-4'''), 127.8 (d, C-6'), 125.8 (d, C-6''), 124.5 (d, C-5'''), 123.8 (d, C-5'), 122.8 (d, C-3'''), 122.3 (d, C-4'), 120.0 (d, C-4''), 109.3 and 109.2 (2 × d, C-7', 7''), 86.6 (d, C-10''), 86.4 (d, C-10'), 49.4 (s, C-3'), 49.2 (s, C-3''), 38.5 (t, N—CH₂—), 27.1 (q, C-11'', 12''), 26.9 (q, C-11', 12'), 12.0 (q, —CH₃); UV/Vis (CHCl₃): see Table 1; MS (70 eV, EI): *m/z* (%): 534 (100) [M⁺]; C₃₄H₃₄N₂O₂S × 0.5H₂O (543.72) calcd (%) C 75.11, H 6.49, N 5.15; found C 75.05, H 6.45, N 5.10.

A.24. 2,4-Bis[5-(2-thienyl)-1-ethyl-3,3-dimethyl-2,3-dihydroindol-2-ylidene]methylcyclobutenediylum-1,3-diolate (Tp2ISQ, 13e)

0.210 g (30%) from **11** (0.600 g, 1.70 mmol) and squaric acid (0.13 g) in 10 ml of solvent after FC (CHCl₃/EtOH 40:1, *R_f* = 0.27); mp (MeOH, DSC): 293 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.55–7.57 (m, 4H; 4', 4'', 6', 6''-H), 7.30 (dd,

$^3J_{3''',4'''} = 3.6$, $^4J_{3''',5'''} = 1.2$ Hz, 2H; 3'''-H), 7.26 (dd, $^3J_{5''',4'''} = 4.9$, $^4J_{5''',3'''} = 1.0$ Hz, 2H; 5'''-H), 7.09 (dd, $^3J_{4''',5'''} = 5.1$, $^3J_{4''',3'''} = 3.6$ Hz, 2H; 4'''-H), 6.99 (d, $^3J_{7',6'} = ^3J_{7'',6''} = 8.7$ Hz, 2H; 7', 7''-H), 5.99 (s, 2H; 10', 10''-H), 4.09 (broad s, 4H; $2 \times \text{N}-\text{CH}_2-$), 1.83 (s, 12H; 11', 11'', 12', 12''-H), 1.41 (t, $^3J_{\text{H,H}} = 7.2$ Hz, 6H; $2 \times -\text{CH}_3$); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C): $\delta = 182.3$ (s, C-1,3), 179.6 (s, C-2,4), 169.2 (s, C-2', 2''), 144.1 (s, C-2'''), 143.1 (s, C-9', 9''), 141.4 (s, C-8', 8''), 130.5 (s, C-5', 5''), 128.1 (d, C-4'''), 125.8 (d, C-6', 6''), 124.6 (d, C-5'''), 122.9 (d, C-3'''), 120.1 (d, C-4', 4''), 109.4 (d, C-7', 7''), 86.8 (d, C-10', 10''), 49.3 (s, C-3', 3''), 38.6 (t, $\text{N}-\text{CH}_2-$), 27.1 (q, C-11', 11'', 12', 12''), 12.1 (q, $-\text{CH}_3$); UV/Vis (CHCl_3): see Table 1; MS 70 eV, EI): m/z (%): 616 (100) [M^+]; $\text{C}_{38}\text{H}_{36}\text{N}_2\text{O}_2\text{S}_2 \times \text{H}_2\text{O}$ (634.86) calcd (%) C 71.89, H 5.99, N 4.41; found C 72.22, H 5.82, N 4.34.

A.25. 2-(3-Ethyl-2,3-dihydrobenzothiazol-2-ylidene)-methyl-4-(1-ethyl-3,3-dimethyl-2,3-dihydroindol-2-ylidene)methylcyclobutenediylum-1,3-diolate (ISQ-ThSQ, 13f)

0.524 g (50%) from **4a** (0.640 g, 2.26 mmol), 3-ethyl-2-methylbenzothiazolium tetrafluoroborate [72] (0.599 g, 2.26 mmol) and quinoline (0.36 ml, 3.0 mmol) in 20 ml of solvent after FC ($\text{CHCl}_3/\text{EtOH}$ 10:1, $R_f = 0.45$); mp (MeOH, DSC): 275 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.58$ (dd, $^3J_{4',5'} = 7.8$, $^4J_{4',6'} = 0.7$ Hz, 1H; 4'-H), 7.39–7.43 (m, 1H; 6''-H), 7.32 (d, $^3J_{4',5'} = 7.3$ Hz, 1H; 4'-H), 7.21–7.30 (m, 3H; 6', 5'', 7''-H), 7.07–7.11 (m, 1H; 5'-H), 6.94 (d, $^3J_{7',6'} = 7.9$ Hz, 1H; 7'-H), 6.01 (s, 1H; 10''-H), 5.80 (broad s, 1H; 10'-H), 4.22 (q, $^3J_{\text{H,H}} = 7.3$ Hz, 2H; $\text{N}-\text{CH}_2-$), 4.00 (broad s, 2H; $\text{N}-\text{CH}_2-$), 1.78 (s, 6H; 11', 12'-H), 1.44 (t, $^3J_{\text{H,H}} = 7.3$ Hz, 3H; $-\text{CH}_3$), 1.36 (t, $^3J_{\text{H,H}} = 7.2$ Hz, 3H; $-\text{CH}_3$); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C): $\delta = 183.1$ and 180.8 ($2 \times$ s, C-1,3), 179.5 (s, C-4), 175.2 (s, C-2), 167.6 (s, C-2'), 160.8 (s, C-2''), 142.2 (s, C-8'), 142.0 (s, C-9'), 140.4 (s, C-8''), 128.9 (s, C-9''), 127.6 (d, C-6'), 127.3 (d, C-6''), 124.4 (d, C-7''), 122.9 (d, C-5'), 122.3 (d, C-4''), 122.2 (d, C-4'), 111.5 (d, C-5''), 108.5 (d, C-7'), 85.8 (d, C-10'), 85.6 (d, C-10''), 48.7 (s, C-3'), 41.3 and 38.0 ($2 \times$ t, $2 \times \text{N}-\text{CH}_2-$), 27.2 (q, C-11', 12'),

12.4 and 11.8 ($2 \times$ q, $2 \times -\text{CH}_3$); UV/Vis (CHCl_3): $\lambda_{\text{max}}(\epsilon)$: see Table 1; MS (70 eV, EI): m/z (%): 442 (100) [M^+]; $\text{C}_{27}\text{H}_{26}\text{N}_2\text{O}_2\text{S} \times 0.33 \text{ MeOH}$ (463.91) calcd (%) C 72.44, H 6.08, N 6.18; found C 72.42, H 6.01, N 6.14.

A.26. ISQ-dimer 14c

0.108 g (ca. 38%) from **8a** (0.200 g, ca. 0.28 mmol), **6a** (0.168 g, 0.59 mmol) and quinoline (0.08 ml, 0.07 mmol) in 20 ml of solvent after repeated FC ($\text{CHCl}_3/\text{EtOH}$ 10:1, $R_f = 0.58$); mp ($\text{CH}_2\text{Cl}_2/n$ -pentane, DSC): 279 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.58$ –7.60 (m, 4H; 4'', 6''-H), 7.38 (d, $^3J_{4',5'} = 7.3$ Hz, 2H; 4'-H), 7.29–7.35 (m, 4H; 6', 3''', 4'''-H), 7.15–7.19 (m, 2H; 5'-H), 6.99–7.03 (m, 4H; 7', 7''-H), 6.00 (s, 2H; 10'-H), 5.99 (s, 2H; 10''-H), 4.10 (broad s, 8H; $4 \times \text{N}-\text{CH}_2-$), 1.85 (s, 12H; 11'', 12''-H), 1.80 (s, 12H; 11', 12'-H), 1.39–1.44 (m, 12H; $4 \times -\text{CH}_3$); ^{13}C NMR (100 MHz, CDCl_3 , 25 °C): $\delta = 182.4$ (s, C-1,3), 180.0 and 178.8 ($2 \times$ s, C-2,4), 170.1 (s, C-2'), 168.7 (s, C-2''), 143.0 (s, C-9'', 2''', 5'''), 142.3 (s, C-9'), 141.9 (s, C-8'), 141.6 (s, C-8''), 130.1 (s, C-5''), 127.8 (d, C-6'), 125.4 (d, C-6''), 123.9 (d, C-5'), 123.8 (d, C-3''', 4'''), 122.4 (d, C-4'), 119.6 (d, C-4''), 2×109.3 ($2 \times$ d, C-7', 7''), 86.7 and 86.5 ($2 \times$ d, C-10', 10''), 49.4 (s, C-3'), 49.2 (s, C-3''), 38.5 (t, $\text{N}-\text{CH}_2-$), 27.2 (q, C-11'', 12''), 26.9 (q, C-11', 12'), 12.1 (q, $-\text{CH}_3$); UV/Vis (CHCl_3): see Table 1; MS (FAB, pos.): m/z (%): 983.7 (100) [($\text{M} - \text{H}$) $^+$]; $\text{C}_{64}\text{H}_{64}\text{N}_4\text{O}_4\text{S} \times 2\text{H}_2\text{O}$ (1021.33) calcd (%) C 75.27, H 6.71, N 5.49; found C 75.13, H 6.61, N 5.74.

A.27. Bisbromodimer 14d

0.032 g analytically pure (ca. 3%) and 0.449 g for synthetic purposes (ca. 36%) from **8b** (0.650 g, ca. 0.95 mmol), **6e** (0.846 g, ca. 1.90 mmol) and quinoline (0.24 ml, 2 mmol) in 20 ml of solvent after repeated FC and preparative TLC ($\text{CHCl}_3/\text{EtOH}$ 40:1, $R_f = 0.25$). mp (MeOH, DSC): 192 °C; ^1H NMR (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.58$ –7.59 (m, 4H; 4'', 6''-H), 7.45 (s, 2H; 4'-H), 7.40 (d, $^3J_{6',7'} = 8.4$ Hz, 2H; 6'-H), 7.31 (s, 2H; 3''', 4'''-H), 7.02 (d, $^3J_{7'',6''} = 8.8$ Hz, 2H; 7''-H), 6.84 (d, $^3J_{7',6'} = 8.8$ Hz, 2H; 7'-H), 6.03 (s, 2H; 10'-H), 5.97

(s, 2H; 10''-H), 4.04 and 3.93 (2 × broad s, 2 × 4H; 4 × N—CH₂—), 1.86 (s, 12H; 11'', 12''-H), 1.79 (s, 12H; 11', 12'-H), 1.79–1.86 (m, 8H; 4 × —CH₂—), 1.26–1.54 (m, 16H; 8 × —CH₂—), 1.01 (t, ³J_{H,H} = 7.3 Hz, 6H; 2 × —CH₃), 0.89 (t, ³J_{H,H} = 6.6 Hz, 6H; 2 × —CH₃); ¹³C NMR (100 MHz, CDCl₃, 25 °C): δ = 182.2 (s, C-1,3), 180.0 (s, C-4), 179.1 (s, C-2), 169.9 (s, C-2''), 168.8 (s, C-2'), 144.1 (s, C-9'), 143.1 (s, C-9''), 142.9 (s, C-2''', 5'''), 141.8 (s, C-8''), 141.6 (s, C-8'), 130.6 (d, C-6''), 130.3 (s, C-5''), 125.6 (d, C-4'), 125.3 (d, C-6'), 123.8 (d, C-3''', 4'''), 119.4 (d, C-4''), 116.3 (s, C-5'), 110.5 (d, C-7'), 109.8 (d, C-7''), 87.3 (d, C-10'), 86.9 (d, C-10''), 49.3 (s, C-3''), 49.1 (s, C-3'), 43.7 (t, N—CH₂—), 27.0 (q, C-11', 11'', 12', 12''), 31.4, 29.1, 26.8, 26.6, 22.4 and 20.3 (6 × t, 6 × —CH₂—), 13.9 and 13.8 (2 × q, 2 × —CH₃); UV/Vis (CHCl₃): λ_{max}(ε) = 690 nm (451,000 dm³ mol⁻¹ cm⁻¹); MS (FAB, pos.): *m/z* (%): 1309.6 (100) [(M, ⁸¹Br, ⁷⁹Br—H)⁺]; C₇₆H₈₆Br₂N₄O₄S (1311.41) calcd (%) C 69.61, H 6.61, N 4.27; found C 69.26, H 6.68, N 4.22.

A.28. Monomeric intermediate **13g**

13b (2.05 g, ca. 3.2 mmol) were reacted with **12** (1.950 g, ca. 3.49 mmol) in the presence of (Ph₃P)₄Pd (0.046 g) in DMF (15 ml) analogously to the general procedure for the coupling reactions. After workup and repeated FC and preparative TLC (CHCl₃/EtOH 40:1, R_f = 0.17) 1.767 g (ca. 67%) of a dark blue sticky solid are obtained, which is not completely pure. ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.54–7.56 (m, 2H), 7.44 (dd, ³J_{H,H} = 8.1, ⁴J_{H,H} = 1.6 Hz, 1H), 7.29–7.34 (m, 3H), 7.24 (d, ³J_{H,H} = 3.0 Hz, 1H), 7.13–7.17 (m, 2H), 6.95–7.00 (m, 2H), 6.54 (d, ³J_{H,H} = 8.2 Hz, 1H), 5.98 and 5.97 (2 × s, 2 × 1H), 3.99, 3.94 and 3.90 (3 × broad s, 3 × 2H), 3.59 (q, ³J_{H,H} = 7.1 Hz, 2H), 1.84 and 1.80 (2 × s, 2 × 9H), 1.32–1.44 (m, 16H), 1.20 (t, ³J_{H,H} = 7.1 Hz, 3H), 0.88–0.91 (m, 6H); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = 182.4, 179.6, 178.8, 170.2, 169.2, 160.8, 145.3, 144.7, 143.0, 142.4, 142.3, 141.7, 141.1, 138.5 and 130.6 (15 × s), 127.8, 125.4 and 125.1 (3 × d), 124.9 (s), 123.7, 123.6, 122.3, 122.0, 119.6, 119.4, 109.6, 109.4, 105.0, 86.9 and 86.7 (11 × d), 73.9 (t, =CH₂), 49.4, 49.2 and 44.2 (3 × s), 43.8, 43.7, 36.7 and 31.5 (4 × t), 30.0 and 27.2 (2 × q), 27.0, 26.8

and 22.5 (3 × t), 14.0 and 10.8 (2 × q); MS (70 eV, EI): *m/z* (%): 832 (100) [M⁺]; C₅₅H₆₅N₃O₂S (832.20).

A.29. Monobromodimer **14a**

1.165 g (ca. 54%) from **13 g** (1.458 g, ca. 1.75 mmol) and **6e** (0.753 g, ca. 1.80 mmol) in toluene/*n*-butanol 1:1 (75 ml) after FC (CHCl₃/EtOH 30:1, R_f = 0.23); mp (MeOH, DSC): 178 °C; ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.57–7.62 (m, 4H), 7.31–7.44 (m, 6H), 7.12–7.20 (m, 1H), 6.95–7.04 (m, 3H), 6.84 (d, ³J_{H,H} = 8.2 Hz, 1H), 2 × 5.99, 5.97 and 5.95 (4 × s, Σ 4H), 4.00 (broad s, 8H), 1.85, 1.80 and 1.79 (3 × broad s, Σ 30H), 1.30–1.42 (m, 21H), 0.89–0.93 (m, 9H); ¹³C NMR (100 MHz, CDCl₃, 25 °C, TMS): δ = ca. 179–182 (4 × s), 170.4, 168.9, 143.1, 142.8 and 142.4 (5 × s), 130.6 (d), 130.4 and 129.9 (2 × s), 127.8, 125.7, 125.4, 125.3, 123.9, 123.7, 122.3, 119.6 and 119.5 (9 × d), 116.3 (s), 2 × 109.5, 86.9 and 86.8 (4 × d), 49.4, 49.2 and 49.1 (3 × s), 43.8 and 31.5 (2 × t), 27.2, 27.1, 27.0 and 26.9 (4 × q), 26.9, 26.7, 26.6 and 22.5 (4 × t), 13.9 and 12.1 (2 × q); UV/Vis (CHCl₃): λ_{max}(ε) = 686 nm (428,000 dm³ mol⁻¹ cm⁻¹); MS (FAB, pos.): *m/z* (%): 1231.6 (100) [(M, ⁸¹Br—H)⁺]; C₇₆H₈₇BrN₄O₄S (1232.49) calcd (%) C 74.06, H 7.11, N 4.55; found C 74.13, H 7.15, N 4.47.

A.30. ISQ-trimer **15**

13c (0.900 g, 1.35 mmol) and **12** (1.66 g, ca. 2.97 mmol) are coupled in the presence of 0.035 g of (Ph₃P)₄Pd in DMF (15 ml). After workup and FC (CHCl₃/EtOH 10:1, R_f = 0.26–0.35) 2.33 g of **13h** are obtained as a dark green sticky solid that is not further purified. 1.4 g of this are reacted with **6b** (0.835 g, ca. 2.68 mmol) in toluene/*n*-butanol 1:1 (30 ml). After repeated FC (CHCl₃/EtOH 40:1, R_f = 0.17) 0.214 g (ca. 16% overall yield) of a dark green powder is obtained; mp (CH₂Cl₂/*n*-pentane, DSC): ca. 246 °C (decomp.); ¹H NMR (400 MHz, CDCl₃, 25 °C, TMS): δ = 7.58–7.60 (m, 8H; 4', 4''', 6', 6''''-H), 7.37 (d, ³J_{4''',5''''} = 7.3 Hz, 2H; 4'''-H), 7.30–7.34 (m, 6H; 6''', 3''''', 4''''''-H), 7.16 (m, 2H; 5'''-H), 6.98–7.02 (m, 6H; 7', 7''', 7''''-H), 6.02, 6.01 and 5.98 (3 × s, 3 × 2H; 10', 10''', 10''''-H), 4.03

(broad s, 12H; $6 \times \text{N}-\text{CH}_2-$), 1.81–1.86 (m, 44H; 11', 11'', 11''', 12', 12'', 12'''-H, $4 \times \text{N}-\text{CH}_2-$), 1.45–1.54 (m, 8H; $4 \times -\text{CH}_2-$), 1.42 (t, ${}^3J_{\text{H,H}} = 7.2$ Hz, 6H; $2 \times -\text{CH}_3$), 0.98–1.04 (m, 12H; $4 \times -\text{CH}_3$); ${}^{13}\text{C}$ NMR (100 MHz, CDCl_3 , 25 °C): $\delta = 182.4$ (s, C-1, 1'', 3, 3''), 180.2 and 2×179.0 ($3 \times$ s, C-2, 2'', 4, 4''), 170.6 (s, C-2'''), 169.4 and 168.5 ($2 \times$ s, C-2', 2'''), 143.1, 142.9, 2×142.4 and 142.0 ($5 \times$ s), 130.2 and 130.0 ($2 \times$ s, C-5', 5'''), 127.8 (d, C-6'''), 125.4 (d, C-6', 6'''), 2×123.8 (d, C-5''', 3''''', 4'''''), 122.3 (d, C-4'''), 2×119.6 ($2 \times$ d, C-4', 4'''), 109.7, 109.5 and 109.3 ($3 \times$ d, C-7', 7''', 7'''''), 3×86.8 ($3 \times$ d, C-10', 10''', 10'''''), 49.4 (s, C-3'''), 49.3 and 49.2 ($2 \times$ s, C-3', 3'''), 43.6 (t, $\text{N}-\text{CH}_2-$), 27.2 (q, C-11', 11''', 12', 12'''), 27.0 (q, C-11''', 12'''), 2×29.1 and 20.4 ($3 \times$ t, $3 \times -\text{CH}_2-$), 13.9, 13.8 and 12.0 ($3 \times$ q, $3 \times -\text{CH}_3$); UV/Vis: see Table 1; MS (MALDI/TOF): m/z (%): 1653 (17) [(M + Na)⁺], 1630 (100) [(M + H)⁺]; $\text{C}_{106}\text{H}_{112}\text{N}_6\text{O}_6\text{S}_2 \times 1.5 \text{H}_2\text{O}$ (1657.24) calcd (%) C 76.82, H 6.99, N 5.07; found C 76.79, H 6.89, N 4.81.

A.31. ISQ-tetramer 16

14d (0.440 g, 0.336 mmol) and **12** (0.413 g, ca. 0.74 mmol) are coupled in the presence of $(\text{Ph}_3\text{P})_4\text{Pd}$ (0.012 g) in DMF (15 ml). From the crude intermediate **14e** the solvent is removed and the residue is taken up in toluene/*n*-butanol 1:1 (20 ml) and heated to reflux with **6c** (0.272 g, ca. 0.80 mmol). Workup (including treatment with aqueous KF-solution), FC and preparative TLC ($\text{CHCl}_3/\text{EtOH}$ 40:1, $R_f = 0.21$) yields 0.088 g of **16** as a dark violett powder (11% overall yield). mp ($\text{CH}_2\text{Cl}_2/n$ -pentane, DSC): ca. 246 °C (decomp.); ${}^1\text{H}$ NMR (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.59$ –7.60 (m, 12H), 7.37 (d, ${}^3J_{\text{H,H}} = 7.3$ Hz, 2H), 7.30–7.34 (m, 8H), 7.15–7.18 (m, 2H), 6.98–7.02 (m, 8H), 5.98, 6.00 and 6.02 ($3 \times$ s, Σ 8H), 4.02 (broad s, 16H), 1.81–1.87 (m, 60H), 1.33–1.51 (m, 34H), 1.02 (t, ${}^3J_{\text{H,H}} = 7.3$ Hz, 6H), 0.88–0.94 (m, 12H); ${}^{13}\text{C}$ NMR (100 MHz, CDCl_3 , 25 °C): $\delta = 182.4$, 180.2, 179.3, 179.2, 178.7, 170.6, 2×169.4 , 168.5, 143.1, 143.0, 142.9, 142.4, 142.0, 141.6, 2×130.2 and 130.0 ($18 \times$ s), 127.8, 125.4, 2×123.8 , 122.3 ($5 \times$ d), 119.6 (s), 119.5, 109.7, 109.5, 109.3, 87.2 and 86.8 ($6 \times$ d), 49.4, 49.3 and 49.1 ($3 \times$ s), 43.8, 31.5, 29.2, 27.1, 27.0, 26.7, 22.5

and 20.4 ($8 \times$ t), 27.2, 27.0, 2×14.0 , 13.9 and 12.0 ($6 \times$ q); UV/Vis: see Table 1; MS (MALDI/TOF): m/z (%): 2355 (17) [(M + Na)⁺], 2331 (100) [(M + H)⁺]; $\text{C}_{152}\text{H}_{168}\text{N}_8\text{O}_8\text{S}_3 \times 2\text{H}_2\text{O}$ (2367.27) calcd (%) C 77.12, H 7.32, N 4.73; found C 76.91, H 7.36, N 4.55.

A.32. ISQ-pentamer 17

14a (0.500 g, 0.406 mmol) and **12** (0.250 g, ca. 0.45 mmol) are coupled in the presence of $(\text{Ph}_3\text{P})_4\text{Pd}$ (0.020g) in DMF (15 ml). After workup and FC ($\text{CHCl}_3/\text{EtOH}$ 30:1, $R_f = 0.19$) 0.326 g of crude **14b** (ca. 56%) are obtained and used without further purification for the reaction with squaric acid (0.013 g, 0.11 mmol) in toluene/*n*-butanol 1:1 (20 ml). After repeated FC ($\text{CHCl}_3/\text{EtOH}$ 30:1, $R_f = 0.27$) and preparative TLC ($\text{CHCl}_3/\text{EtOH}$ 60:1, $R_f = 0.20$) 0.088 g of **17** are obtained as a dark violett solid (ca. 15% overall yield). mp ($\text{CH}_2\text{Cl}_2/n$ -pentane, DSC): ca. 233 °C (decomp.); ${}^1\text{H}$ NMR (400 MHz, CDCl_3 , 25 °C, TMS): $\delta = 7.58$ –7.60 (m, 16H), 7.37 (d, ${}^3J_{\text{H,H}} = 7.2$ Hz, 2H), 7.30–7.34 (m, 10H), 7.14–7.18 (m, 2H), 6.97–7.03 (m, 10H), 5.98, 6.00 and 6.01 ($3 \times$ s, Σ 10H), 4.00 and 4.10 ($2 \times$ broad s, Σ 20H), 1.77–1.86 (m, 72H), 1.30–1.50 (m, 48H), 0.86–0.93 (m, 18H); ${}^{13}\text{C}$ NMR: due to the poor solubility no sufficient data were available; UV/Vis: see Table 1; MS (MALDI/TOF): m/z (%): 2943 (42) [(M + Na)⁺], 2920 (100) [(M + H)⁺]; $\text{C}_{190}\text{H}_{208}\text{N}_{10}\text{O}_{10}\text{S}_4$ (2920.03) a satisfactory elemental analysis could not be obtained.

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