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Exciton Coupling Effects in Polymeric *cis*-Indolenine Squaraine Dyes

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ABSTRACT: Dicyanovinylene-substituted *cis*-indolenine squaraines were polymerized by a Ni-mediated *Yamamoto* homocoupling reaction. Preparative recycling GPC was used to obtain polymer fractions with different molecular weight distributions in order to investigate the influence of molecular weight on the optical properties. In this attempt, conjugated cyclic trimers could also be isolated that are, to the best of our knowledge, the first of their kind. These trimers and the squaraine polymers were investigated by cyclic voltammetry, absorption spectroscopy, and static and time-resolved fluorescence bands with, for squaraines, an exceptional huge Stokes' shift, the polymers show broad absorption in the red to



near infrared (NIR) region with narrow fluorescence and only the common minor Stokes' shift. The spectral features of the squaraines were interpreted to be caused by excitonic coupling. By comparison of experimental and computed (CNDO/S2 CIS) spectra detailed, structural models of the polymers were derived that consist of helix (H-aggregate behavior) and zigzag motifs (J-aggregate behavior).

KEYWORDS: squaraine dye, polymer, exciton coupling, time-resolved fluorescence spectroscopy

INTRODUCTION

The goal of this work is to synthesize polysquaraine dyes that are based on dicyanovinylene indolenine squaraine monomers and to study their optical and electrochemical properties. Squaraines (Scheme 1) are intensely colored dyes that are generated by 1,3-dicondensation reactions of nucleophilic compounds such as heterocycles or other electron-rich aromatics with squaric acid. This results in a donor– acceptor–donor structure with a strong and narrow cyanine-

Scheme 1. Different Types of Squaraine Dyes



cis-indolenine squaraine

like absorption ($\varepsilon > 10^5 \text{ M}^{-1} \text{ cm}^{-1}$) and fluorescence in the red to near-infrared (NIR) region. These unique absorption and fluorescence properties make squaraines suitable for a variety of applications in nonlinear optics,^{1–7} data imaging,⁸ organic photovoltaics,^{9–17} or as fluorescence labels^{18–21} and sensors for anions,²² cations,^{23–27} and neutral molecules.^{28,29} There are several highly recommended reviews that give more-detailed insight into this remarkable class of dye.^{30–33}

The absorption maximum of squaraine dyes can be influenced by the nucleophilic component (e.g., anilines, pyrroles, indolenines and its heteroatom analogues), by replacing one oxygen of squaric carbonyl group by, e.g., sulfur^{34,35} or methylene active moieties, such as dicyanomethylene^{9,34,36} or barbituric acid,³⁴ and finally by adding electron-donating substituents to the nucleophilic (hetero)cycle component. We recently investigated the latter aspect, using triarylamine substituents attached to a series of indolenine squaraine dyes.³⁷ These triarylamine-squaraine conjugates display a bathochromic shift of the absorption maximum and versatile redox behavior. A totally different way to shift the absorption of squaraine dyes is to synthesize oligomers or polymers that then show band shifts and broadenings due to excitonic coupling of localized squaraine states. In this context, we recently prepared polymers based on indolenine squaraine dyes, and their optical and redox properties were inves-

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Scheme 2. Yamamoto Polycondensation of trans-Dibromoindolenine Squaraine to Give a Polysquaraine



tigated.^{1,11} These polymers indeed show a bathochromic shift of the absorption maximum but also a weaker band at higher energy. This observation can be explained by a mixture of Hand J-type alignment of chromophores, which then display hypsochromic (H) and bathochromic (J) shifts.

Concerning the synthesis of polysquaraines, there have been various approaches since Treibs and Jacob discovered the formation of insoluble colored compounds upon the reaction of pyrrole derivatives with squaric acid.³⁸⁻⁴⁰ Low solubility and the formation of 1,2-dicondensation products were the issues that arose from early attempts of making carbazole-squaraine polymers using either polyphosphoric acid or dimethylsulfoxide (DMSO) as solvent.⁴¹ Later, it was Havinga et al. who suggested that, by alternation of conjugated electron-donor and electron-acceptor moieties, small-band-gap polymers could be obtained.⁴²⁻⁴⁴ This idea was also supported by theoretical considerations of Brocks et al., who proposed low band gaps in polysquaraines.⁴⁵ Havinga et al. proved this concept, using benzo(1,2-4,5)-di(1-alkyl-2-methylene-3,3-dimethylpyrroline), benzo(1,2-4,5)-di(3-alkyl-2-methylenethiazole), or terthiophene units as donors in the reaction with squaric acid to yield polymers with band gaps of $\sim 1 \text{ eV.}^{42-44}$ However, especially in the field of pyrrole-derived squaraine dyes, there is an ongoing effort to decrease the band gap, using variously substituted pyrrole derivatives.^{46–48} Those studies have further been extended, using electron-donating bridging units such as 2,5-divinylthiophene between the squaraine dyes, thus forming copolymers.⁴⁹ Even more popular is the use of 1,4dialkoxydivinylbenzene bridging units. Low-band-gap polymers $(\sim 1 \text{ eV})$ with a strong and broad absorption in the NIR region near ~1000 nm were obtained, showing intrinsic conductivities of ~10⁻⁵ S cm^{-1,50,51} Furthermore, dialkyl-substituted fluorene was used as the bridge between pyrrole-squaraine, resulting in polymers with high polydispersity and broad absorption.52 Instead of an electron donor as the bridge between squaraine dyes, an electron acceptor (pyridopyrazine) was recently used, giving a low-band-gap polymer that exhibits strong two-photon absorption behaviors.³ Hecht et al. produced a series of nonconjugated polysquaraines via a two-step one-pot synthesis where isolated 2,4-dihydroxybenzene-squaraines are linked by various amine bridges.⁵³ These authors also attempted to synthesize polysquaraines with different topologies, such as helical, rodlike, or cyclic structures by polycondensation of phenylenediamines with squaric acid. Unfortunately this approach failed due to an exceeding low reactivity of the intermediate semisquaraine.⁵⁴ All those polymers mentioned so far were obtained by polycondensation reaction of bifunctional electron donors with squaric acid. This reaction usually is performed in a solvent mixture of n-butanol and toluene (or benzene) for almost no 1,2-dicondensation products are formed in this mixture. However, traces of 1,2-dicondensation

moieties cannot always completely be ruled out. Another synthetic approach to polysquaraines is to use metal-catalyzed or metal-promoted C–C cross coupling reactions of squaraine dye monomers in the final polycondensation step. Here, the formation of unwanted 1,2-dicondensation products in the polymer strand can be excluded by thorough purification of the squaraine precursor monomer. This approach was successfully used when dibrominated 1,4-dialkoxydivinylbenzene–pyrrole– squaraine was coupled with either *N*-alkyl-2,7-diethynylcarbazole, dialkoxy-diethynylbenzene or 2,5-diethynyl-thiophene derivatives using the *Sonogashira* cross coupling reaction. ^{55,56} However, a major drawback of the *Sonogashira* reaction is the risk of homocouplings of the terminal alkyne compounds.

In our recent work,¹¹ we synthesized a squaraine homopolymer without any bridges using a Ni-promoted Yamamoto coupling from monomeric dibromoindolenine squaraine (Scheme 2). In the present work, we use a cisindolenine squaraine in which one central oxygen atom of the squaric ring is replaced by a dicyanovinylene moiety (see Scheme 1). This results in a stronger central acceptor moiety and induces a bathochromic shifted absorption as outlined previously. Even more important, because of steric reasons, a cis conformation, instead of the usually found trans conformation, of the monomeric indolenine squaraine is induced.^{9,34,36,37,57} The goal of the present work is to use the highly bent *cis* isomer for the Yamamoto polycondensation reaction, which should lead to a pronounced zigzag structure or even helical structures of the resulting polymer. Because of this zigzag motif, we expect strongly modified optical properties, compared to the more elongated structure of trans-indolenine squaraine polymers. In order to modify solubility, we prepared two different squaraine monomers: one with hexadecyl chains attached to the indolenine nitrogen and one with 3,7-dimethyloctyl chains.

EXPERIMENTAL SECTION

UV/vis/NIR. Ultraviolet-visible light-near-infrared (UV/vis/NIR) spectra were measured in 1 cm quartz cuvettes, using a JASCO Model V-670 spectrometer. The substances were dissolved in Uvasol solvents from Merck, and the pure solvent was used as a reference. Absorption spectra were recorded within a concentration range from 1×10^{-5} M to 1×10^{-7} M.

Spectra of films of the polymers were prepared by spin-casting of a concentrated dye solution (2.5 mg mL⁻¹ at 2000 rpm) in the appropriate solvent onto a flat glass substrate (20 mm × 20 mm × 1 mm). UV/vis/NIR spectra of these samples were then measured using a Carey Model 5000 UV/vis/NIR spectrometer with an integrating sphere ($\phi = 15$ cm).

Fluorescence. Fluorescence measurements were performed with a Photon Technology International (PTI) QM fluorescence spectrometer with a cooled photomultiplier (Model R928P) or an InGaAs detector. Standard 1-cm cuvettes were used and spectra were recorded in Uvasol solvents from Merck after purging the samples for 10 min with argon gas. As a fluorescence standard, oxazine 1 in ethanol (Φ_{fl} =

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0.11) was used and the following equation was applied to determine the quantum yields: $^{\rm S8}$

$$\Phi_{\rm f} = \Phi_{\rm f,Ref} \left(\frac{I(\tilde{\nu}) \times \rm OD_{Ref} \times (n_{\rm D}^{20})^2}{I(\tilde{\nu})_{Ref} \times \rm OD \times (n_{\rm D}^{20})_{Ref}^2} \right)$$

where $\Phi_{\rm f}$ is the quantum yield of the sample, $I(\tilde{\nu})$ the integrated emission band, OD the optical density of the absorption band at the excitation wavelength, and $n_{\rm D}^{20}$ the refraction index of the solvent.

Fluorescence Lifetimes. Fluorescence lifetimes were measured with a PTI TM fluorescence lifetime spectrometer with a 650-nm laser-diode for excitation. Colloidal silica in deionized water was used as scatter solution to determine the instrument response. Lifetimes were determined by fitting the decay curves with exponential decay functions. Solvents and cuvette were used as in the steady-state fluorescence experiments.

Cyclic Voltammetry. Cyclic voltammetry was performed for all squaraine dyes using a BAS CV-50 W electrochemical workstation in DCM and tetrabutylammonium hexafluorophosphate (TBAH ≈ 0.2 M) as supporting electrolyte. In our three electrode setup, a platinum working electrode (1 mm in diameter), a helical platinum counter electrode and a platinum pseudo-reference electrode were used in a completely sealed and with argon flushed glass vessel. DCM was dried over CaH₂. Prior to use, the solvent was filtered over an activated neutral aluminum oxide column under argon atmosphere for further drying. All potentials were measured against the redox couple of decamethylferrocene and its cation. The redox potential was then calculated, relative to the ferrocene/ferrocenium (Fc/Fc⁺) redox couple.⁵⁹

NMR. Nuclear magnetic resonance (NMR) spectra were recorded on either a Bruker Avance 400 or a Bruker Avance DMX 600 Fouriertransform spectrometer. The chemical shifts are given in ppm, relative to the internal standard tetramethylsilane (TMS). The coupling constants are given in Hertz and the following abbreviations were used for the spin multiplicities or for C-atom descriptions: s = singlet, d =doublet, t = triplet, q = quartet, dd=doublet of doublet, m = multiplet; prim=primary, sec=secondary, tert=tertiary, quart=quaternary.

Mass Spectrometry. Mass spectrometry was performed on a Bruker Daltonik micrOTOF focus (ESI) system.

Gel Permeation Chromatography (GPC). Gel permeation chromatography (GPC) was performed at 20 °C in chloroform with a Shimadzu instrument (including a diode array detector (Model SPD-M20A), system controller (Model CBM-20A), solvent delivery unit (Model LC-20AD), and online degasser (Model DGU 20A9)). Preparative chromatography was carried out in recycling mode on two consecutive SDV columns (PSS SDV preparative 50 Å and 500 Å, dimension: 20 × 600 mm, particle size: 10 μ m) from PSS/Mainz, Germany. Analytical chromatography was measured on a SDV column (PSS SDV analytical linear S mixed bed, dimension: 8 × 300 mm, particle size: 5 μ m) from PSS/Mainz, Germany with polystyrene as a standard.

Synthetic Procedures. Synthetic procedures were performed in standard glassware.

Materials. The chemicals used were purchased from commercial suppliers and used without further purification. Reactions under nitrogen (dried over Sicapent from Merck; oxygen was removed by copper catalyst R3–11 from BASF) were performed in flame-dried glass ware with solvents that were dried according to literature procedures and stored under nitrogen. For flash chromatography, Merck silica gel 32–63 μ m was used. 5-Brom-2,3,3-trimethyl-3*H*-indole,¹¹ triethylammonium 2-butoxy-3-(dicyanomethylene)-4-oxocy-clobut-1-enolate (CN),⁶⁰ 3,7-dimethyloctyl tosylate,⁶¹ 2,¹¹ and mSQ2³⁷ were synthesized according to the given literature.

1-(3,7-Dimethyloctyl)-2,3,3-trimethyl-3*H*-indol-1-ium tosylate (1). 2,3,3-Trimethyl-3*H*-indole (2.00 g, 12.6 mmol) and 3,7dimethyloctyl tosylate (2.75 g, 8.79 mmol) were refluxed in MeNO₂ for 17 h. The solvent and remaining indole were removed under reduced pressure. The residue was digested with Et₂O several times to obtain a wine red solid (2.76 g, 5.80 mmol, 66%). ¹H NMR (600 MHz, CDCl₃): δ [ppm] = 7.64–7.60 (AA', 2H), 7.56–7.49 (4 H), 7.05–7.01 (BB', 2H), 4.73–4.62 (m, 2H, NCH₂), 2.99 (s, 3H, CH₃), 2.29 (s, 3H, O₃SC₆H₄CH₃), 1.85–1.77 (m, 1H, CH), 1.66–1.58 (8H, CH₃, CH₂), 1.54–1.46 (m, 1H, CH), 1.38–1.28 (m, 2H, CH₂), 1.25–1.17 (m, 2H, CH₂), 1.17–1.09 (m, 2H, CH₂), 1.04 (d, ³*J* = 6.0 Hz, 3H, CH₃), 0.86 (d, ³*J* = 6.5 Hz, 3H, CH₃), 0.85 (d, ³*J* = 6.6 Hz, 3H, CH₃); ¹³C NMR (150 MHz, CDCl₃): δ [ppm] = 195.7 (quart), 143.7 (quart), 141.8 (quart), 141.2 (quart), 138.8 (quart), 129.7 (tert), 129.2 (tert), 128.4 (tert), 125.9 (tert), 123.1 (tert), 115.0 (tert), 54.4 (quart), 47.4 (sec), 23.0 (sec), 36.9 (sec), 35.0 (sec), 31.0 (tert), 27.9 (tert), 24.6 (sec), 23.0 (prim), 22.9 (prim), 22.6 (prim), 22.5 (prim), 21.2 (prim), 19.5 (prim), 14.9 (prim); ESI-MS pos (high resolution): [M-OTos⁻]⁺ calcd: 300.26858 *m/z*, found: 300.26840 *m/z*, Δ = 0.58 ppm.

5-Bromo-1-(3,7-dimethyloctyl)-2,3,3-trimethyl-3H-indol-1ium tosylate (3). 5-Bromo-2,3,3-trimethyl-3H-indole (1.01 g, 4.23 mmol) and 3,7-dimethyloctyl tosylate (1.78 g, 5.69 mmol) were dissolved in MeNO₂ under nitrogen atmosphere and refluxed for 17 h. After cooling to room temperature, $\text{Et}_2O\ (40\text{ mL})$ was added and the product crystallized within 1 h. The precipitate was filtered off and washed with Et₂O to give a light brown solid (955 mg, 1.73 mmol, 41%). ¹H NMR (600 MHz, CDCl₃): δ [ppm] = 7.64 (dd, ³J = 8.5 Hz, ${}^{4}J = 1.6$ Hz, 1H, H-6), 7.62 (d, ${}^{4}J = 1.6$ Hz, 1H, H-4), 7.59–7.54 (AA', 2H), 7.42 (d, ³*J* = 8.6 Hz, 1H, H-7), 7.04–7.00 (BB', 2H), 4.70–4.55 (m, 2H, NCH₂), 2.94 (s, 3H, CH₃), 2.29 (s, 3H, O₃SC₆H₄CH₃), 1.81-1.74 (m, 1H, CH), 1.65-1.54 (8H, CH₃, CH₂), 1.54-1.45 (m, 1H, CH), 1.36–1.25 (m, 2H, CH₂), 1.24–1.16 (m, 2H, CH₂), 1.15– 1.07 (m, 2H, CH₂), 1.01 (d, ${}^{3}J = 6.2$ Hz, 3H, CH₃), 0.85 (d, ${}^{3}J = 6.6$ Hz, 6H, CH₃); ¹³C NMR (150 MHz, CDCl₃): δ [ppm] = 195.7 (quart), 143.6 (quart), 143.5 (quart), 140.3 (quart), 138.9 (quart), 132.5 (tert), 128.4 (tert), 126.6 (tert), 125.8 (tert), 124.1 (quart), 116.6 (tert), 54.5 (quart), 47.7 (sec), 39.0 (sec), 36.8 (sec), 34.9 (sec), 31.0 (tert), 27.9 (tert), 24.6 (sec), 22.90 (prim), 22.85 (prim), 22.6 (prim), 22.5 (prim), 21.3 (prim), 19.5 (prim), 15.0 (prim); ESI-MS pos (high resolution): $[M-OTos^-]^+$ calcd: 378.17909 m/z, found: 378.17910 m/z, $\Delta = 0.03$ ppm.

mSQ1. Compound 1 (2.10 g, 424 µmol), **CN** (64.5 mg, 202 µmol), and pyridine (7.5 mL) were refluxed in a mixture of toluene and 1butanol (1:1, 16 mL) for 17 h. The solvent was evaporated under reduced pressure and the residue purified by flash chromatography (eluent: DCM) and dried in vacuo. The residue was crystallized from hexane to give green crystals (100 mg, 138 μ mol, 68%). ¹H NMR (600 MHz, $CDCl_3$): δ [ppm] = 7.38–7.32 (4H, CH), 7.22–7.18 (m, 2H, CH), 7.03 (d, ³J = 7.9 Hz, 2H, CH), 6.49 (s, 2H, CH), 4.10-3.98 (m, 4H, NCH₂), 1.82-1.74 (14H, CH₃, CH), 1.70-1.58 (m, 4H, CH₂), 1.55-1.48 (m, 2H, CH), 1.42-1.29 (m, 4H, CH₂), 1.29-1.18 (m, 4H, CH_2), 1.18–1.11 (m, 4H, CH_2), 1.03 (d, ³J = 6.5 Hz, 6H, CH_3), 0.86 $(d, {}^{3}J = 6.6 \text{ Hz}, 12\text{H}, CH_{3}); {}^{13}C \text{ NMR} (150 \text{ MHz}, CDCl_{3}): \delta [ppm] =$ 173.2 (quart), 171.7 (quart), 167.7 (quart), 166.6 (quart), 142.5 (quart), 141.9 (quart), 128.0 (tert), 124.5 (tert), 122.3 (tert), 118.9 (quart), 109.9 (tert), 89.0 (tert), 49.4 (quart), 42.9 (sec), 40.8 (quart), 39.1 (sec), 37.1 (sec), 34.1 (sec), 30.9 (tert), 28.0 (tert), 26.55 (prim), 26.53 (prim), 24.6 (sec), 22.7 (prim), 22.6 (prim), 19.7 (prim); ESI-MS pos (high resolution): $[M^+]$ calcd: 724.50746 m/z, found: 724.50728 m/z, $\Delta = 0.25$ ppm.

mSQ3. To a solution of 3 (1.12 g, 2.03 mmol) in pyridine (7.5 mL), CN (325 mg, 1.02 mmol) dissolved in a mixture of toluene and 1-butanol (1:1, 40 mL) was added. The mixture was refluxed for 17 h using a Dean-Stark trap. The solvent was evaporated under reduced pressure, and the residue was purified by flash chromatography (eluent: DCM \rightarrow DCM/EA 40:1 \rightarrow 30:1 \rightarrow 25:1) and dried in vacuo to give a red violet shining solid (737 mg, 835 μ mol, 82%). ¹H NMR (600 MHz, CD_2Cl_2): δ [ppm] = 7.50 (d, ⁴J = 1.9 Hz, 2H, H-4), 7.48 $(dd, {}^{3}J = 8.3 Hz, {}^{4}J = 1.9 Hz, 2H, H-6), 6.96 (d, {}^{3}J = 8.4 Hz, 2H, H-7),$ 6.46 (s, 2H, CH), 4.06-3.93 (m, 4H, NCH₂), 1.80-1.71 (14H, CH₃, CH), 1.67-1.55 (m, 4H, CH₂), 1.55-1.47 (m, 2H, CH), 1.41-1.30 (m, 4H, CH_2), 1.29–1.10 (8H, CH_2), 1.01 (d, ${}^{3}J$ = 6.5 Hz, 6H, CH_3), 0.86 (d, ${}^{3}J$ = 6.6 Hz, 12H, CH₃); ${}^{13}C$ NMR (150 MHz, CD₂Cl₂): δ [ppm] = 173.2 (quart), 171.6 (quart), 167.9 (quart), 167.2 (quart), 144.8 (quart), 141.4 (quart), 131.2 (tert), 126.0 (tert), 118.9 (quart), 117.7 (quart), 111.8 (tert), 89.7 (tert), 49.8 (quart), 43.4 (sec), 40.9

Scheme 3. Synthetic Pathway to the Polysquaraines and the Cyclic Trimers



(quart), 39.4 (sec), 37.4 (sec), 34.2 (sec), 31.20 (tert), 28.3 (tert), 26.61 (prim), 26.57 (prim), 25.0 (sec), 22.8 (prim), 22.7 (prim), 19.7 (prim); ESI-MS pos (high resolution): $[M^+]$ calcd: 880.32849 m/z, found: 880.32851 m/z, $\Delta = -0.02$ ppm.

pSQ2. A mixture of Ni(COD)₂ (152 mg, 571 μ mol), 2,2'-bipyridine (89.0 mg, 571 μmol), 1,5-cyclooctadiene (62.0 mg, 571 μmol), degassed toluene (1 mL) and degassed DMF (2 mL) was stirred at room temperature (rt) under a nitrogen atmosphere for 30 min. A solution of mSQ2 (250 mg, 238 µmol) in degassed toluene (4.5 mL) and degassed DMF (3.5 mL) was added and the resulting mixture was stirred at rt for 6 d. The reaction mixture was poured into MeOH/HCl (20%) (4:1) (500 mL) and stirred for 90 min. The purple precipitate was filtered off and washed consecutively with hexane and MeOH using a Soxhlet extractor. Each washing ran overnight. The remaining solid was dissolved in CHCl3 (30 mL) and poured into MeOH/HCl (20%) (4:1) (500 mL). The resulting precipitate was filtered off and dried under high vacuum. The product was obtained as purple solid (167 mg, 78%). Preparative GPC was used to separate the product into two batches of different molecular weight and to isolate the cyclic trimer:

pSQ2-1: 61 mg, **pSQ2-2**: 40 mg, **tSQ2**: 13 mg (4.86 μmol, 6%). **pSQ2-1**, **pSQ2-2**: ¹H NMR (400 MHz, CDCl₃): δ [ppm] = 7.66– 7.44 (CH), 7.20–7.06 (CH), 6.66–6.46 (CH), 4.20–3.80 (CH₂), 1.92–1.74 (CH₃), 1.54–1.42 (CH₂), 1.42–1.33 (CH₂), 1.33–1.12 (CH₂), 0.90–0.81 (CH₃). **tSQ2**: ¹H NMR (600 MHz, CDCl₃): δ [ppm] = 7.75 (dd, ³J = 8.3 Hz, ⁴J = 1.4 Hz, 6H, H-6), 7.57 (d, ⁴J = 1.1 Hz, 6H, H-4), 7.17 (d, ³J = 8.3 Hz, 6H, H-7), 6.66 (s, 6H, CH), 4.12– 4.04 (m, 12H, NCH₂), 1.93–1.85 (m, 12H, CH₂), 1.83 (s, 36H, CH₃), 1.54–1.45 (m, 12H, CH₂), 1.42–1.34 (m, 12H, CH₂), 1.34–1.19 (132H, CH₂), 0.87 (t, ³J = 6.9 Hz, 18H, CH₃); ¹³C NMR (150 MHz, CDCl₃): δ [ppm] = 173.0 (quart), 171.3 (quart), 167.9 (quart), 166.4 (quart), 143.8 (quart), 141.5 (quart), 135.8 (quart), 125.8 (tert), 119.7 (tert), 118.9 (quart), 110.6 (tert), 89.7 (tert), 49.2 (quart), 44.6 (sec), 41.2 (quart), 31.9 (sec), 29.69 (sec), 29.684 (sec), 29.681 (sec), 29.66 (sec), 29.65 (sec), 29.62 (sec), 29.57 (sec), 29.45 (sec), 29.42 (sec), 29.3 (sec), 27.5 (sec), 26.8 (sec), 26.7 (prim), 22.7 (sec), 14.1 (prim); ESI-MS pos (high resolution): $[M^{+2}]$ calcd: 1336.01970 *m/z*, found: 1336.01980 *m/z*, $\Delta = 0.08$ ppm.

pSQ3. A mixture of Ni(COD)₂ (224 mg, 816 μ mol), 2,2'-bipyridine (127 mg, 816 µmol), 1,5-cyclooctadiene (88.0 mg, 816 µmol), degassed toluene (2 mL), and degassed DMF (2 mL) was stirred at 65 °C under nitrogen atmosphere for 30 min. A solution of mSQ3 (300 mg, 340 μ mol) in degassed toluene (4 mL) and degassed DMF (4 mL) was added and the resulting mixture was stirred at 65 °C for 6 d. The reaction mixture was poured into MeOH/HCl (20%) (4:1) (500 mL) and stirred for 5 h. The purple precipitate was filtered off and washed consecutively with hexane, MeOH and acetone using a Soxhlet extractor. Each washing ran overnight. The major part remained in the acetone fraction (192 mg, 77%) with very little solid that remained insoluble in acetone. Preparative GPC was used to separate the acetone fraction into two batches of different molecular weight and to isolate the cyclic trimer: pSQ3-1: 58 mg, pSQ3-2: 53 mg, tSQ3: 14 mg (6.80 μmol, 6%). **pSQ3-1**, **pSQ3-2**: ¹H NMR (400 MHz, CDCl₃): δ [ppm] = 7.64–7.44 (CH), 7.18–7.04 (CH), 6.62–6.44 (CH), 4.23– 3.87 (CH₂), 1.92-1.58 (CH, CH₂, CH₃), 1.58-1.46 (CH), 1.46-1.10 (CH_2) , 1.10–0.98 (CH_3) , 0.92–0.76 (CH_3) . tSQ3: ¹H NMR (600 MHz, CDCl₃): δ [ppm] = 7.74 (dd, ³J = 8.3 Hz, ⁴J = 1.6 Hz, 6 H, H-6), 7.56 (d, ${}^{4}J$ = 1.4 Hz, 6H, H-4), 7.15 (d, ${}^{3}J$ = 8.3 Hz, 6H, H-7), 6.64 (s, 6H, CH), 4.17-4.04 (m, 12H, NCH₂), 1.90-1.81 (42H, CH₃, CH), 1.74–1.63 (m, 12H, CH₂), 1.56–1.50 (m, 6H, CH), 1.45–1.33 (12H, CH₂), 1.32–1.22 (12H, CH₂), 1.20–1.15 (12H, CH₂), 1.07 (d, $^{3}J = 6.3$ Hz, 18H, CH₃), 0.89–0.86 (36H, CH₃); 13 C NMR (150 MHz, $CDCl_3$: δ [ppm] = 174.3 (quart), 171.2 (quart), 167.8 (quart), 166.3 (quart), 143.8 (quart), 141.4 (quart), 135.9 (quart), 125.8 (tert), 119.7



Figure 1. (Left) Chromatograms of three preparative recycling GPC runs of pSQ3 with separation into three fractions indicated by vertical dotted lines. (Right) Analytical GPC run (detection at 400 nm) of the separated fractions with different molecular weight of pSQ3 in CHCl₃.

(tert), 118.8 (quart), 110.4 (tert), 89.6 (tert), 49.3 (quart), 43.1 (sec), 41.2 (quart), 39.2 (sec), 37.2 (sec), 34.3 (sec), 31.0 (tert), 28.0 (tert), 26.70 (prim), 26.67 (prim), 24.6 (sec), 22.7 (prim), 22.6 (prim), 19.7 (prim); ESI-MS pos (high resolution): $[M^{+2}]$ calcd: 1083.73800 *m/z* found: 1083.73987 *m/z*, $\Delta = 1.73$ ppm.

RESULTS

Synthesis. The synthesis of polymeric squaraines followed a straightforward route, analogous to the one recently published by our group.¹¹ 5-Bromo-2,3,3-trimethyl-3H-indole, which was synthesized via Fischer-Indole synthesis from p-bromophenylhydrazine hydrochloride, according to literature procedures, and commercially available 2,3,3-trimethyl-3H-indole were alkylated with either 1-iodohexadecane or 3,7-dimethyloctyl tosylate in MeNO₂ to yield the quaternary salts 1-3. The dicondensation reactions to the dicyanovinylene-substituted squaraines mSQ1-mSQ3 were carried out with 1-3, respectively, and triethylammonium 2-butoxy-3-(dicyanomethylene)-4-oxocyclobut-1-enolate (CN) in a solvent mixture of toluene and 1-butanol (1:1) and pyridine as a base at high temperatures. The Ni-mediated Yamamoto homocoupling reaction was chosen for the final polycondensation step of the bromine substituted squaraines mSQ2 and mSQ3. This reaction was performed under inert gas atmosphere with Ni(COD)₂, 1,5-cyclooctadiene, and 2,2'-bipyridine in a solvent mixture of deaerated toluene and DMF (1:1) at either room temperature (pSQ2) or 65 °C (pSQ3) for several days.

Various solvents were used for the Soxhlet extractions in order to purify the polymers. The weight-average molecular weights (M_w) of the total crude polycondensation products of pSQ2 and pSQ3 are 13609 and 27258, the polydispersities (PDI) are 2.23 and 3.29, respectively. Since the main part of the polymers was soluble in acetone, this fraction was separated on a preparative recycling GPC to yield batches of polymers of different molecular weight distributions (Figure 1, left). This allows investigation of the influence of molecular weight on the optical properties in those systems. In a first run on the preparative recycling GPC, the fractions pSQ3-1 (pSQ2-1) and pSQ3-2 (pSQ2-2) were separated as indicated by the dotted lines. In this process, an eye-catching peak was observed in the chromatograms of both polycondensation reactions at a similar retention time, which could be isolated in this process. This peak refers to a cyclic trimer whose formation is facilitated by the cis structure of the squaraine monomer was confirmed by mass spectrometry and NMR spectra. These cyclic trimers (tSQ3, tSQ2) could be isolated in 6% yield. The polymeric fractions show relatively small polydispersities (1.2-1.8) due to

the preparative splitting. The M_w values are 27 801 (pSQ2-1) and 46 659 (pSQ3-1) for the heavier molecular weight fractions and 8 264 (pSQ2-2) and 11 941 (pSQ3-2) for the lighter ones (see Table 1). Because the optical properties of the

Table 1. Polymer Characterization^a

	number- average molecular	number-average degree of polymerization,	weight- average molecular	polydispersity,
	weight, M _n	Λ_n	weight, m _w	IVI_w/IVI_n
pSQ2- total	6103	6.8	13609	2.230
pSQ2-1	17543	19.7	27801	1.585
pSQ2-2	6621	7.4	8264	1.248
pSQ3- total	8284	11.4	27258	3.290
pSQ3-1	25639	35.5	46659	1.820
pSQ3-2	8567	11.8	11941	1.394
-				

"Analytical GPC was performed in $CHCl_3$ with polystyrene as a standard. "pSQx-total" assigns polymer batches after Soxhlet extractions but before preparative splitting.

hexadecyl- and dimethyloctyl-substituted squaraines do not differ, we thus can view the four polymers as being a series with an increasing number-average degree of polymerization (X_n) : 7.4 (pSQ2-2), 11.8 (pSQ3-2), 19.7 (pSQ2-1), and 35.5 (pSQ3-1). The polydispersity (PDI) increases as the degree of polymerization increases. All those polymers are quite soluble in solvents such as CHCl₃, DCM, toluene, 1,2-dichlorobenzene, or chlorobenzene.

Cyclic Voltammetry. Electrochemical characterization of the squaraines was done by cyclic voltammetry (CV) in DCM/ 0.2 M TBAH of a monomer, a cyclic trimer and both the highand low-molecular-weight batches of one polymer. The voltammograms are shown in Figure 2, and the redox potentials are listed in Table 2. Since the alkyl side groups only affect the solubility but not the redox potentials, we only give data of the squaraines with dimethyloctyl chains and the monomer with the hexadecyl chain. Each substance shows one reduction wave and two oxidation waves. Compared to the monomer, the waves of the reduction and the first oxidation are broader in case of the cyclic trimer, whereas the second oxidation wave remains remarkably sharp. However, in case of the polymers, this wave also broadens slightly. The first oxidation potentials of the cyclic trimer and the polymers are at 30-40 mV and the reduction potentials at 50-60 mV lower than those of the monomer (207 mV and -1405 mV, respectively) which can be



Figure 2. Cyclic voltammograms of a monomer, a trimer, and two polymers of different molecular weight in DCM/TBAH (\sim 0.2 M) at a scan rate of 250 mV s⁻¹.

explained by the lack of the bromine substituents. In summary, the redox potentials do not differ greatly in this series, which demonstrates weak electronic interaction between the squaraine chromophores in the ground state.

Optical Spectroscopy: UV/vis/NIR Absorption and Fluorescence. Steady-state absorption and fluorescence measurements were carried out in DCM and toluene solutions. The data are summarized in Table 3, and the spectra in toluene are shown in Figure 3.

All squaraine dyes show an intense absorption at ca. 14 000 cm⁻¹. The extinction coefficients of this lowest-energy band range from 51 000 to 61 000 M^{-1} cm⁻¹ (monomer unit)⁻¹ in toluene and 65 000-74 000 M^{-1} cm⁻¹ (monomer unit)⁻¹ in DCM for the polymers and from 194 000 M⁻¹ cm⁻¹ (monomer unit)⁻¹ to $236000 \text{ M}^{-1} \text{ cm}^{-1}$ (monomer unit)⁻¹ in toluene and 220 000-245 000 M⁻¹ cm⁻¹ (monomer unit)⁻¹ in DCM for the monomers and cyclic trimers. The absorption maxima are at somewhat lower energy in toluene than in DCM. For the polymers, this difference is negligible ($<100 \text{ cm}^{-1}$), whereas for the cyclic trimers and the monomers, the energy difference is 300 cm^{-1} . The different alkyl chains do not have any significant impact neither on the energy of the absorption nor on the fluorescence. The monomers show the typical absorption properties of squaraine dyes with a steep rise of the main absorption band at the low energy side with the maximum at 14 300 cm⁻¹ (mSQ1) or 14 100 cm⁻¹ (mSQ2, mSQ3) and a small shoulder on the high energy side. The cyclic trimers again possess this very prominent and sharp absorption at 14300 cm⁻¹ but also a weaker band at 13 600 cm⁻¹ (ε = 50 000 M⁻¹ \mbox{cm}^{-1} (monomer unit) $\mbox{}^{-1}\mbox{)}$ and a very weak shoulder at 12 400 cm^{-1} ($\varepsilon = 4000 M^{-1} cm^{-1} (monomer unit)^{-1}$).

In toluene, the polymers display a very broad absorption in the red-to-NIR region, which covers all the absorption of the trimer (12000-17500 cm⁻¹) but with three almost equally intense maxima at ~12900 cm⁻¹, 13600 cm⁻¹, and 14500 cm⁻¹. The spectra of the polymers are almost identical, irrespective of the molecular weight and alkyl chain substituent. In particular, the transition moments as determined from integration (see eq 1) of the main absorption bands in toluene ranges for all compounds between 8.9 (**pSQ3-1**, **pSQ3-2**), and 10.7 D (**tSQ3**).⁶²

$$\mu_{\rm eg}^2 = \frac{3h\varepsilon\varepsilon_0 \ln 10}{2000\pi^2 N} \left[\frac{9n}{(n^2+2)^2} \right] \int \frac{\varepsilon}{\tilde{\nu}} \,\mathrm{d}\tilde{\nu} \tag{1}$$

Since we noticed a distinct difference of the proportions of the local maxima in the absorption spectra of the polymers in toluene and DCM, we measured the absorption of pSQ3-1 in a series of solvents that differ in polarity, aromatic character, and hydrogen bond donor property (see Figure 4). When we first compare the spectra in CHCl₃, DCM, and toluene, the local maxima are at the same energy but the bands at higher energies increase in relative intensity from CHCl₃ to toluene (Figure 4, left). In PhCN, the three local maxima have almost the same intensity but a weak shoulder, which is due to a fourth band at even higher energy, is visible. In DMF, this shoulder is more pronounced and shifts the maximum of the highest energy band to even higher energies, while the maxima of the other bands at lower energy decrease in intensity. In acetone, this trend increases further: now, the former shoulder at highest energy is the maximum absorption and all other bands show decreasing relative intensities on going to lower energy. The absorption maximum at highest energy shifts hypsochromic, from 14 800 cm^{-1} (PhCN) to 15100 cm^{-1} (DMF) and to 15400 cm^{-1} (acetone). Again, the measured transition moments of the main transitions range between 8.9 (PhCN, toluene) and 9.6 (CHCl₃, DCM).

We also measured the solid-state absorption spectra of **pSQ3-1** in a film (see Figure 5) that was formed by spincoating a solution of **pSQ3-1** (2.5 mg mL⁻¹ at 2000 rpm) onto a glass substrate. Taking into account the differences of the absorption spectra in different solvents, we were interested if these properties are maintained in the film when prepared from solutions in different solvents. Thus, we chose three solvents to prepare concentrated solutions for spin-coating: CHCl₃, DMF, and toluene. The spectra of the films were then measured with an integrating sphere. All of these films share the fact that the main absorption band loses its structure with the three local maxima and we observe a slight broadening and bathochromic shift. For films spin-coated from CHCl₃ and toluene, the spectra are almost identical and quite similar to the spectra

Table 2. Oxidation (ox) and Reduction (red) Potentials^{*a*}, Electrochemical Band Gaps^{*b*}, Optical Band Gaps,^{*c*} and Band Gaps Derived from the Intersection of Absorption and Fluorescence^{*d*} of Selected Squaraines

	$E_{1/2}(\text{ox1}) \text{ (mV)}$	$E_{1/2}(\text{ox2}) \text{ (mV)}$	$E_{1/2}(\text{red1}) \text{ (mV)}$	$E_{\rm g}^{ m CV}~({ m eV})$	$E_{\rm g,onset}^{\rm opt}$ (eV)	$E_{g,inter}^{opt}$ (eV)
mSQ2	207	576	-1405	1.61		
tSQ3	167	600	-1456	1.62		
pSQ3-1	175	573	-1465	1.64	1.52 (solution) 1.45 (film)	1.56
pSQ3-2	165	574	-1463	1.63	1.52 (solution) 1.45 (film)	1.56

^{*a*}In DCM/TBAH (~0.2 M) at a scan rate of 250 mV s⁻¹ vs Fc/Fc⁺. ^{*b*}E^{CV}_g = $E_{1/2}(\text{ox1}) - E_{1/2}(\text{red1})$. ^{*c*}E^{opt}_{g,onset} from the onset of the absorption band. ^{*d*}E^{opt}_{e,inter} = energy at the intersection of the normalized absorption and fluorescence spectra

	$X_{\rm n}$	$\tilde{\nu}_{\rm max}~({\rm cm}^{-1})$	$\varepsilon_{\rm max}~({\rm M}^{-1}{\rm cm}^{-1})$	μ (D)	$ ilde{ u}_{ m fl}~(m cm^{-1})$	$\Phi_{\rm f}$	$ au_{\mathrm{f}}^{\ b} \ (\mathrm{ns})$	$\overline{\tau}$ (ns)	$\overline{k}_{\rm f}~(\times~10^8~{\rm s}^{-1})$	$\overline{k}_{\rm nr}~(imes~10^8~{ m s}^{-1})$
mSQ1		14300	236000	10.10	14000	0.41	4.5		0.91	1.31
mSQ2		$14100 \\ (14400)$	194000 (220000)	9.58	13800	0.57	4.1		1.39	1.05
mSQ3		14100	230000	10.37	13800	0.56	4.0		1.39	1.09
tSQ2		14300 (14600)	198000 (245000)	9.86	10800/12100	0.11	6.8		0.16	1.31
tSQ3		$14300 \\ (14600)$	222000 (221000)	10.67	10800/12100	0.08	7.2		0.11	1.27
pSQ2-2	7.4	$13000 \\ (13100)$	61000 (67000)	9.17	12500	0.19	5.4 [0.26] 1.6 [0.74]	3.7	0.52	2.20
pSQ3-2	11.8	13000 (13000)	56000 (74000)	8.95	12400	0.13	5.7 [0.18] 1.8 [0.82]	3.4	0.38	2.53
pSQ2-1	19.7	12900 (12900)	59000 (71000)	9.28	12400	0.10	5.7 [0.16] 1.6 [0.84]	3.2	0.31	2.78
pSQ3-1 toluene	35.5	12900	51000	8.92	12300	0.06	5.6 [0.14] 1.6 [0.86]	3.1	0.19	3.03
DCM		(13000)	(65000)	9.57						
CHCl ₃		12900	71000	9.57						
PhCN		13000	48000	8.94						
DMF		15100	49000	9.02						

 ${}^{a}X_{n}$ = average degree of polymerization, $\tilde{\nu}_{max}$ = absorption maxima, ε_{max} = extinction coefficients (the values are per monomer unit for the trimers and polymers), μ = transition moment, $\tilde{\nu}_{fl}$ = fluorescence maxima, Φ_{f} = quantum yields, τ_{f} = fluorescence lifetimes, $\overline{\tau}$ = average fluorescence lifetime, \overline{k}_{f} = rate constant of the fluorescent decay in toluene, and \overline{k}_{nr} = rate constant of nonradiative decay in toluene. The values shown in parentheses are obtained from measurements in DCM. ^bThe values given in square brackets are relative amplitudes of the different lifetimes.



Figure 3. Complete absorption spectra (top left) and absorption (solid lines) and fluorescence (dotted lines) spectra of a monomer (top right), a trimer (bottom left), and the polymers (bottom right) in toluene. Excitation of the trimer was at 700 nm, of the polymers at 680 nm, and of the monomer at 640 nm.

measured in $CHCl_3$ solution with the maximum at 12 800 cm⁻¹. However, in the case of DMF, the situation is different. Similar to the spectrum in solution, we find the absorption maximum of the film at the high energy side of the

main absorption band with a pronounced bathochromic shift at 14 500 cm⁻¹. Since annealing can lead to a structural reorganization in the films, we recorded absorption spectra after annealing the substrates for 10 and 30 min at 130 $^{\circ}$ C.



Figure 4. (Left) Normalized absorption spectra and (right) complete spectra of pSQ3-1 in various solvents of different polarity. Because of low solubility, the extinction coefficient ε was not determined in acetone.



Figure 5. Absorption spectra of pSQ3-1 in solution and films spin-coated from solutions of different solvents.

While no changes were observed in the films prepared from $CHCl_3$ and toluene, that from DMF shows significant differences upon annealing. As mentioned previously, the maximum is at the high energy side of the main absorption band immediately after film preparation. After 10 min at 130 °C, we find a plateau from 13 500 cm⁻¹ to 14 500 cm⁻¹ and, after 30 min of annealing, the maximum moves to the low-energy side of the absorption band at 13 400 cm⁻¹. Thus, it appears that there is a thermodynamically favored structure which is already present in solutions and in films of CHCl₃ and toluene but not in DMF solution and its pristine film but which is gradually formed upon annealing of the films.

Fluorescence. Fluorescence measurements were carried out in toluene solutions, because, in other solvents (see above),

fluorescence is generally very weak for the chromophores presented here. The fluorescence of mSQ2 in DCM is described in our previous work.³⁷ In toluene, the fluorescence spectra of the monomers are mirror images to the absorption spectra with a small Stokes' shift of 300 cm⁻¹ and the maxima at 14 000 cm⁻¹ (mSQ1) (see Figure 3) or 13 800 cm⁻¹ (mSQ2, mSQ3). The fluorescence spectra of the polymers are similar in shape to the monomers but at significantly lower energy (~12 000 cm⁻¹). Therefore, they are no mirror images to the broad absorption spectra and there exists a Stokes' shift of 500–600 cm⁻¹. As do the absorption properties of the cyclic trimers, the fluorescence properties completely differ from those of the monomers and polymers. Two rather intense fluorescence bands can be observed at 12 100 cm⁻¹ and 10 800

cm⁻¹, with one shoulder at the low-energy side of the latter and a shoulder at ~9500 cm⁻¹. It is noteworthy that, of all compounds investigated here, the absorption maximum of the cyclic trimers is at the highest energy, whereas the fluorescence maximum is, by far, at the lowest energy (apparent Stokes' shift of maxima = 2200 cm⁻¹).

The fluorescence quantum yields of both brominesubstituted monomers are basically the same, with values of ~0.56, while **mSQ1** has a quantum yield of 0.41. The lower quantum yield of the unsubstituted squaraine is in agreement with a recently published work by Würthner et al., where a halogen effect in squaraines was reported, describing the rise of quantum yield in a series of squaraines substituted with H, Cl, Br, and I.⁶³ The quantum yields of the cyclic trimers are 0.11 (tSQ2) and 0.08 (tSQ3), which may be considered to be equal, within experimental error. For the polymers, the fluorescence quantum yields decrease as the degree of polymerization increases, from $\phi_f = 0.19$ ($X_n = 7.4$) to 0.06 ($X_n = 35.5$) (see Table 3).

Fluorescence lifetimes were measured in the nanosecond time regime with a gated detection method at 650 nm excitation with a laser diode. For the monomers and the cyclic trimers, monoexponential decays were observed. The lifetime is 4.5 ns for the monomer **mSQ1** and 7.0 ns for the cyclic trimers. In the case of the polymers, biexponential decays were monitored, with lifetimes of \sim 5.6 and 1.7 ns (see Figure 6).



Figure 6. Fluorescence decay of **pSQ3-1** in toluene. Excitation energy: $\tilde{\nu} = 15 \ 400 \ \text{cm}^{-1} \ (\lambda = 650 \ \text{nm}).$

However, a closer inspection of the biexponential decays revealed an increase of relative amplitude of the shorter component with increasing X_n . The lifetimes are in the same range as those of other molecular squaraine compounds that have been reported in the literature.^{36,37,64–68}

The fluorescence quantum yield (Φ_f) and the fluorescence lifetime (τ_f) were used to calculate the average rate constant of the fluorescent decay (\overline{k}_f) and the nonradiative decay (\overline{k}_{nr}) , using eqs 2 and 3. For the polymers, in these equations, we used the average fluorescence lifetime $(\overline{\tau})$, which was determined by eq 4, to calculate the rate constants.

$$\overline{k}_{\rm f} = \frac{\Phi_{\rm f}}{\tau_{\rm f}} \tag{2}$$

$$\overline{k}_{\rm nr} = \frac{1 - \Phi_{\rm f}}{\tau_{\rm f}} \tag{3}$$

$$\overline{\tau} = \frac{\alpha_1 \tau_1^2 + \alpha_2 \tau_2^2}{\alpha_1 \tau_1 + \alpha_2 \tau_2} \tag{4}$$

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While the excitation wavelength for both static and timeresolved fluorescence measurements was chosen for technical reasons (fixed laser diode wavelength, small Stokes' shift) to be at the high-energy side of the absorption bands, it is unlikely that the emission spectra or the kinetics are influenced by this choice, since we assume fast energy transfer dynamics beyond the time resolution of our setup (ca. 200 ps by deconvolution with IRF).

DISCUSSION

When we compare the pSQ polymers with those of our previous work (trans-indolenine squaraine without dicyanovinylene moiety in the center; see Scheme 2), we see that, although the polymer weights are similar, the lowest-energy absorption band in toluene comprises three almost equally intense features within the 12 000-17 500 cm⁻¹ region, while that of the trans-indolenine-squaraine polymer is highly asymmetric with a very intense band at the lowest-energy side of the band manifold between 13 000 cm⁻¹ and 17 300 cm⁻¹. The spectral features of *trans*-indolenine-squaraine polymer were discussed in terms of exciton coupling of localized squaraine transitions rather than by conjugational effects. This seems also to be reasonable for the tSQ trimers and the pSQ polymers, because the electrochemical characterization indicates weak electronic interactions of the squaraine chromophores. The strong and sharp absorption bands of squaraine dyes should indeed lead to strong exciton coupling due to Coulomb interactions of transition densities. In order to assess these interactions, structural models of the squaraine trimer and the polymers are necessary. Thus, we performed semiempirical AM1 calculations⁶⁹ on the cyclic trimer and some hexamer superstructures for mimicking the polymer: an open loop structure, a helical hexamer, an elongated hexamer with a zigzag structure, and a mixed hexamer in which both features are present. In case of the cyclic trimer, we also optimized the geometry at the density functional theory (DFT) level, using the B3LYP/6-31G* functional/basis set combination.^{70–73} The AM1-optimized structures are depicted in Figure 7.

Because of the bent structure of the cisoid dicyanovinylene squaraine chromophores and the stiff but conformationally flexible biaryl axis, there are different macromolecular superstructures possible for the polymers. The most rigid structure is that of the trimer, which proved to be asymmetric caused by some strain in the ring (see Figure 7). While one squaraine moiety is planar, the other two adopt a bent structure, which deviates from planarity in order to close the cycle. The AM1and DFT-optimized geometries agree very well, which gives confidence that the AM1 computed structures of the polymers are also reasonable. In contrast to the cyclic trimer, the helical hexamer is free of strain and has ca. 2.7 monomer units per helix turn (Figure 7). In the helix motif, the squaraine chromophores possess a tilt and shift π -stack arrangement where the alkyl chains extend radially from the tube formed by the helix (not shown in Figure 7, because the alkyl chains were replaced by methyl groups in the calculations). Alternatively to the helix, an open loop structure can be formed. Furthermore, an elongated structure is conceivable which adopts a zigzag motif with a ca. 114° angle between the centers of the squaric acid ring. In reality, mixtures of the zigzag (or loop) and the



Figure 7. AM1-optimized structures (for simplicity, the long alkyl chains are replaced by methyl groups) of **tSQ**, open loop hexamer, helical hexamer (top view and side view), elongated zigzag hexamer, and mixed zigzag/helical hexamer. The orientation of localized transition moments of the lowest energy squaraine transition is indicated by orange arrows. The phase relation of transition moments, which leads to the lowest energy absorption of the aggregate, is indicated by the direction of the arrows.

Table 4. CNDO/S2 CIS Calculations on AM1 Optimized Cyclic Trimer and Four Different Hexameric Structures

$states (sm^{-1} (sas strength))$	arral tuinn ou	haliaal harraman	alan astad rizzan havenar	anan laan hayamar	mined heremon
states/cm (osc. strength)	cyci. triiner	nencai nexamer	elongated zigzag nexamer	open-loop nexamer	mixed nexamer
1	14800 (0.2)	15300 (0.2)	14700 (7.1)	14700 (1.2)	14700 (2.2)
2	16500 (2.4)	16000 (0.3)	15300 (0.4)	15200 (0.8)	15100 (2.6)
3	17000 (2.0)	16500 (0.1)	15900 (1.2)	15700 (1.9)	15900 (0.6)
4		17200 (0.5)	16400 (0.1)	16500 (5.5)	16700 (0.3)
5		17500 (3.6)	16800 (0.3)	16800 (0.2)	16900 (1.9)
6		18000 (3.9)	16900 (0.4)	17200 (0.8)	17000 (2.2)

helical motif may be present in a polymer strand, as indicated by the mixed zigzag/helical structure in Figure 7.

For the interpretation of the absorption spectra by exciton coupling theory, we must keep in mind that the transition moment of the lowest energy transition of a monomeric squaraine chromophore is polarized along the long molecular axis, i.e., along the N-N vector of the indolenine nitrogen atoms. Because of the C_{2v} symmetry of the monomeric unit, there is also a short-axis polarized transition which is at a significantly higher energy and does not play a role in the discussion here.³⁷ If we assume ideal C_3 symmetry of the tSQ trimer, simple exciton theory predicts an A-symmetric state into which electronic transition is forbidden and which is below two degenerate E states, which are optically allowed.⁷⁴ Because of the asymmetry of the trimer, the degeneracy will be lifted and the selection rules will not strictly apply. Semiempirical CNDO/S2-CIS computations⁷⁵ indeed support this interpretation (see Table 4): although the absolute transition energies are estimated to be too high by ca. 3000 cm^{-1} , these calculations yield two allowed bands (at 17 000 and 16 500 cm⁻¹) and a very weak one (at 14800 cm⁻¹). In fact, we observe two bands at different energy (14 300 and 13 600 cm⁻¹) which are likely the "E-type" bands and a very weak one at lower energy (12400 cm^{-1}) which is supposedly the forbidden A-type band.

For the helix-like arrangement, exciton coupling theory predicts two different excitonic interactions: one H-type behavior (parallel orientation of transition moments) due to the stacked π -systems (see Figure 7) and another interaction that is the consequence of two consecutive chromophores which are arranged in a ca. 70° angle and is analogous to the situation in the trimer. Both excitonic interactions together lead to two allowed transitions into higher lying states, followed by four states that are forbidden (see Table 4). The CNDO/S2 calculations indeed give two strong transitions at 17 800 and 17 500 cm⁻¹ and four very weak lower energy transitions (between 17 200 and 15 300 cm⁻¹). Much in contrast, exciton coupling theory predicts a single intense transition in the case of the elongated zigzag hexamer at low energy and five transitions at higher energy (J-type behavior). This is in agreement with that found by the CNDO/S2 calculations: a strong transition at 14 700 cm^{-1} and five almost-negligible transitions between 15 300 cm⁻¹ and 16 900 cm⁻¹. The openloop hexamer also shows a single very prominent band but at intermediate energy (16 500 cm^{-1}). Interestingly, the individual energies of the six transitions of these three hexamers are very similar and only their associated transition moments vary. Finally, in a mixed zigzag/helical structure, we observed four allowed transitions: two at low energy and two at high energy.

We assume that the polymers pSQ display in solution both helix-like sequences or loops, as well as elongated structures. Thus, the experimentally observed absorption spectra will show a superposition of the spectral features that are associated with these superstructures, that is, two bands at the high-energy side for the helix sections and one single band at the low-energy side for the elongated sections and one in the middle of the excitonic manifold as being present in the open-loop form. In fact, we observe three bands (see Figure 3) in toluene but four bands in the more-polar solvents (see Figure 4). The fact that these spectral features are clearly visible suggests that, indeed, only a limited number of structures/conformers is present in solution. From the bandwidth $\Delta \tilde{\nu}$ of the excitonic manifold, we estimate the electronic exciton coupling as $V = \Delta \tilde{\nu}/4 \approx 620$ cm⁻¹, which agrees very well with that of the *cis*-indolenine squaraine polymer in Scheme 2 (640 cm⁻¹).⁷⁶

Following Kasha's rule, fluorescence is expected to be emitted from the lowest excited state of the excitonic manifold, irrespective of the energy of excitation into this manifold. Although, for the monomer squaraines, a mirror image fluorescence with very small Stokes' shift is observed, the cyclic trimer displays a very structured fluorescence spectrum with a large Stokes' shift and which extends into the NIR $(>12 \ 000 \ \mathrm{cm}^{-1})$. This somewhat unexpected behavior may be interpreted in two different ways: one possibility is that the strong distortion of two of the three squaraine chromophores leads to a strong vibronic progression in the lowest-energy emitting state. The observation of an almost unperturbed and unshifted narrow absorption band at 14 300 cm⁻¹ for the unperturbed squaraine chromophore but a much broader and weaker band at lower energy (13 600 cm⁻¹) support this interpretation. The other interpretation is that two of the three chromophores behave different and almost independent, which would lead to two different fluorescence emission bands. A similar observation has recently been made for strained small oligothiophene macrocycles,⁷⁷ while Law et al. observed dual or triple fluorescence in squaraine dyes, which these authors interpreted to be caused by conformationally different structures being present in solution or by solute-solvent complexes.⁷⁸⁻⁸¹ However, dual (or triple) fluorescence from a squaraine trimer would require negligible energy transfer within the trimer; otherwise, only a single emission from the lowest of the three excitonic states would be observed. Since this seems unlikely in such a small chromophore arrangement, we prefer the first interpretation. A clarification could be made by measuring the excitation spectra and/or the lifetime of the emission at all wavelengths, neither of which can be done in our laboratory for technical reasons within this particular wavelength region.

Much in contrast to the trimer, the polymers obviously emit from the lowest excited state of the exciton manifold, which can easily be seen from the shape of the fluorescence band, which is a mirror image of the monomer absorption but distinctly shifted to lower energy. The two different time constants of the fluorescence decay may be interpreted as being caused by the two different superstructures (e.g., helical vs elongated zigzag). The lowest-energy state of the helical structure should be a dark state with a small fluorescence rate constant k_f (H-type states with vanishing transition moment should have small fluorescence rate constant k_f according to the Strickler–Berg equation)⁸² while the one with the zigzag structure (J-type band) should be allowed and thus should be associated with a significant k_f value. In the following, we interpret the relative amplitudes of the biexponential decay as the mole fraction x and 1 - x, respectively, of two different superstructures present within one polymer strand. As we will argue below, the shorter lifetime (mole fraction 1 - x) is likely to be associated with the helix or open-loop structures while the long lifetime (mole fraction x) refers to the elongated zigzag chain. A plot of the mole fraction x versus the degree of polymerization X_n (see Figure 8) shows



Figure 8. Plot of the mole fraction of helix structure and of the fluorescence quantum yield versus the degree of polymerization.

that, for increasing chain lengths (X_n) , the fraction of the helix structure also increases and approaches a limiting value of ca. 0.86. This appears to be reasonable as longer chains possess a higher probability to form loops and helix structures than shorter chains. In a reversed trend, the fluorescence quantum yield decreases with the chain length and approaches ca. 0.06. Surprisingly, the absorption spectra in toluene do not reflect this change of mole fraction with increasing degree of polymerization. From these observations and eq 2-4 we derive the following characteristics for purely zigzag ($\tau_{\rm f}$ = 5.6 ns, $\phi_{\rm f}$ = 0.41, $k_f = 1.1 \times 10^8 \text{ s}^{-1}$, $k_{nr} = 7.3 \times 10^7 \text{ s}^{-1}$) and helix structure ($\tau_f = 1.6 \text{ ns}$, $\phi_f = 0$, $k_f = 0 \text{ s}^{-1}$, $k_{nr} = 6.3 \times 10^8 \text{ s}^{-1}$), which are also given in Figure 9. The assignment of the helix-type structure to the short-lifetime component is made because in the limiting case of infinitely long chains this structure must have a vanishing fluorescence rate constant, as required for an H-type superstructure. This model requires that energy transfer between the two different superstructures is slow, relative to the decay rates.



Figure 9. Relaxation pathways depending on helix or zigzag superstructures.

Taking the above outlined structural model into account, we can also explain the solvatochromic behavior of the excitonic manifold (see Figure 4) by a fractional increase of helix or open-loop structures relative to the zigzag chain. While solvents that may form C–H hydrogen bonds to the squaric acid oxygen, such as DCM and chloroform, favor a zigzag chain, more polar solvents (such as DMF or acetone, which are unable to solvate the negative charge of the squaric acid core) induce a folding to yield a more helix-like arrangement.

An interesting point concerns the optical properties of the films: While the films spin-coated from $CHCl_3$ or toluene clearly show a J-type behavior and, consequently, a large mole fraction of zigzag structures, the pristine film formed from DMF clearly displays a more pronounced H-type in the absorption spectra which indicates large fractions of helix or open-loop structures. Obviously, these structural motifs are maintained when spin-coating from solutions in DMF. Annealing then leads to a breakup of these structures to yield more zigzag fractions. This aspect highlights the possibility to induce supramolecular structures by choosing the appropriate solvent for film-forming applications.

Concerning the band gap of the squaraine polymers, we estimate 1.63 eV from the differences of the redox potentials for oxidation and reduction in solution. This is approximately the same as that of the monomer **mSQ2**. The optical band gap from the onset of absorption spectra is dependent neither on the polymer chain length nor on the solvent and is 1.52 eV (in the films prepared from CHCl₃ it is 1.45 eV). From the intersection of absorption and fluorescence, we obtain 1.56 eV. These values are slightly smaller than those from electrochemistry which reflects the exciton binding energy to be on the order of ca. 0.1 eV. The band gap of the polysquaraines derived from *trans*-indolenine is about the same.¹¹

CONCLUSIONS

In conclusion, we successfully synthesized the first dicyanovinylene-substituted polysquaraines by applying the Ni-mediated Yamamoto homocoupling reaction. In this attempt, we were able to isolate conjugated cyclic trimers that, to the best of our knowledge, are the first of their kind and exhibit multiple fluorescence bands with, for squaraines, unusually large Stokes' shift. The polymers show spectroscopic features such as a rather broad absorption in the red-to-NIR region with distinct maxima but a narrow fluorescence, red-shifted relative to the monomer emission. The fluorescence quantum yield decreases as the degree of polymerization increases. These features can best be described by the formation of an excitonic manifold due to at least two different superstructures: a zigzag chain and a helixlike arrangement. While the former shows typical J-type behavior, the latter may be conceived as an H-type aggregate. The fractions to which these structures are formed depend on the chain length and the solvent. Controlling the superstructure will allow one to tune the optical properties, which, in a first attempt, was successfully done in films.

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Notes

The authors declare no competing financial interest.

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