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### Strategies and investigations on bridging squaraine dye units

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### ABSTRACT

Synthetic strategies and basic molecular principles were investigated in order to achieve chromophores absorbing light in the far red or even near infrared region. Therefore, a comprehensive series of new squaraine dyes were synthesized and characterized. Beside monomeric unsymmetrical and symmetrical squaraine dyes, also squaraine dye dimers and oligomers bridged with phenylene, fluorene, *iso*-octyloxy phenylene and tetrafluoro phenylene moieties or directly coupled via condensation reaction were obtained. The influence of the various molecular dye structures to their absorption properties was studied with UV–vis measurements supported by theoretical investigations applying Kiprianov's theory of coupled dyes. With regard to Meyer's theory of the limiting values, the effective number of repeating units for dye series for the highest possible absorption maximum was determined. Observed trends and limiting values for electrochemical potentials and electrical band gaps of the dyes are in agreement with the UV–vis investigations. Finally, calculated molecular structures and frontier orbitals of dimers verify the results of the optophysical and electrochemical studies.

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### 1. Introduction

In the last decade, organic dyes, especially near infrared (NIR) absorber, have increasingly gained in importance [1-6] mainly for diverse applications e.g. bio markers [7,8], sensitizers in solar cells [9-14] or detector materials in fibre optics [15]. To arrive at far red or even NIR absorption properties, synthetic strategies and basic molecular principles were followed. One well known strategy is the elongation of the  $\pi$ -electron system of polymethine dyes by increasing the number of the methine units in order to achieve a bathochromic shift of the absorption towards the NIR regime [16]. A similar approach with oligometric push-pull systems including an enhanced conjugated  $\pi$ electron system between donor (D) and acceptor (A) functional groups were described by Meier et al. [17–22]. This D- $(\pi$ -)<sub>n</sub>-A approach opened different modification possibilities as e.g.  $D-(\pi-A)_n$  or  $(D-\pi-)_n$ -A. Very recently, the former modification was used to develop linearly  $\pi$ -electron system extended NIR absorbing oligometric squaraine dyes [23]. As logical consequence, a further strategy is the polymerization of fully conjugated structures like thiophenes, phenylen vinylenes or imines to their corresponding NIR absorbing polymers [24,25]. With this principle nearly infinite elongated  $\pi$ -system can be realized.

One sophisticated strategy was reported for cyanine dyes by Kiprianov [26]. In contrast to the above mentioned systems the chromophoric unit in cyanine dyes is a "real world" example for the electron in a box model [27]. Kiprianov demonstrated that in special cases the absorption maximum ( $\lambda_{max}$ ) of cyanine dye dimers and oligomers connected over a conjugated bridge could be positioned at higher wavelength [26]. He related the spherical orientation of the dye units on the one hand, and under the orientation of the transition dipole moments of each dye unit on the other hand to the position of the absorption band [26]. Linearly bridging of dye units with similar orientated transition dipole moments result in the highest possible bathochromic shift of the  $\lambda_{max}$  value. The communication of each individual dye system over its potential walls via a conjugated bridge influences the optical properties of the molecules and Kiprianov called this the coupling of the dye units [26]. By adapting this strategy, several low band gap oligomeric as well as polymeric cyanine and also squaraine dyes were synthesized by Geiger et al. [28], Ajayaghosh et al. [29-34] and Havinga et al. [35-38]. Especially, cyanine dye polymers absorb up to 180 nm towards higher wavelengths by bridging the monomeric dye unit with planar and fully conjugated bis-indole derivative in comparison to their monomer unit [28].

Although a skillful bridging of dye units leads to a remarkable bathochromic shift resulting absorption in the NIR, little is known about the structure property relation of conjugated bridges of dye dimers, oligomers or polymers. So the major questions we have





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asked were: What is the influence of a conjugated system on a squaraine dye? And how a conjugated bridge should be configured to maximize the coupling of the dye units?

In this respect, we report on the investigation of the structure property relation of different squaraine dyes joined by conjugated aromatic synthons. Therefore, *mono-squaraines* (MSQ), *bis-squaraines* (BSQ) and *tris-to-tetra-squaraines* (TSQ) with different phenylene, fluorene, alkoxy phenylene, tetrafluoro phenylene and naphthalene synthons were synthesized (Schemes 1–4). The optical and the electrochemical parameters of all dyes were determined and related to their calculated molecular structure. The influence of the aromatic bridges, their electronic nature, length and molecular structure on the chromophore was studied. In addition, limiting values were determined according to the theory of Meier [17].

### 2. Experimental

### 2.1. General information

Unless otherwise stated, the reactions were run under an argon atmosphere. The analytical thin-layer chromatography (TLC) was performed on glass-baked silica gel with fluorescent indicator 254 nm from Fluka and RediSep TM. TLCs were controlled by naked-eye, under UV (254 or 365 nm) or stained either with aqueous cobalt thiocyanate or aqueous alkaline potassium permanganate solution. Flash chromatography was performed on a CombyFlash TeledyneISCO system from Companion using RediSep Normal Phase Disposable Columns. Ultraviolet and visible (UV-vis) spectra of dye solutions were recorded on a Varian Cary 50 Scan spectrometer in suitable dilution in a 1.0 cm optical glass cuvette. Thermogravimetric analysis (TGA) was performed using a Netzsch TG 209 F1 and differential scanning calorimetry (DSC) was performed using a Perkin Elmer DSC-7 in order to determine the melting (m.p.) and decomposition (d.p.) points. Nuclear magnetic resonance (NMR) spectra were recorded at 297 K in a 5 mm broadband inverse probe on a Bruker 400 MHz spectrometer. Matrix-assisted laser

desorption/ionization (MALDI) spectra were performed on an IonSpec Varian Ultima-MALDI-FTICR-MS or on a Bruker UltraFlex II - MALDI-TOF (MALDI-TOF). MALDI spectra of small organic molecules were usually measured in a matrix of 3-hydroxypicolinic acid (3-HPA). MALDI-TOF was measured in a matrix of 2-[(2E)-3-(4-tert-butylphenyl)-2-methylprop-2-enylidenelmalononitrile sodium salt (DCTB + Na). Calculated masses were based on average isotope composition or on single isotope masses for high resolution spectra. Data are reported as follows: isotopic mass in atomic mass units, relative intensity in percent written in parenthesis and if possible the identification is given in squared brackets. Cyclic voltammetry measurements were recorded on a PGStat 30 potentiostat (Autolab) using a three-cell electrode system with a rotating glassy carbon working electrode, a platinum counter electrode and an Ag/AgCl  $(0.1 \text{ mol } L^{-1} \text{ tetrabutyl ammonium chloride in dimethylformamide})$ (DMF)) reference electrode. All prepared dyes were measured in DMF using 0.1 mol L<sup>-1</sup> tetrabutyl ammonium perchlorate (TBAP) as supporting electrolyte. Exception: MSQ 3 was measured in chloroform with the same electrolyte system. The ferrocene/ferrocenium couple (Fc/Fc<sup>+</sup>) was used as internal reference. The scanning rate was 100 mV s<sup>-1</sup> and rotation speed of the working electrode was set to 50 rpm. All potentials were referenced to NHE, by adopting a potential of +0.72 V vs. NHE for Fc/Fc<sup>+</sup> in DMF [39] and +0.25 V vs. NHE in chloroform. Fluorescence spectroscopy was carried out on a Fluorolog from Horbia Jobin Yvon with UV-vis detector. The averaged degree of polymerization  $(X_n)$  was calculated from the weighted masses from the MALDI-TOF measurements.

### 2.2. Synthesis

2.2.1. 4-((3,3-Dimethyl-1-octyl-3H-indolium-2-yl)methylene)-2-((3,3-dimethyl-1-octyl-indolin-2-ylidene)methyl)-3-oxocyclobut-1enolate (**MSO 1**)

In a Dean–Stark apparatus, the alkylated indole **2** (15.0 g, 40.3 mmol, Supplemental Information), squaric acid (2.24 g,



Scheme 1. Preparation of mono squaraines MSQ 1, 2, 3, 4 and 5.



Scheme 2. Preparation of the core part 29, 30, 31, 32 and 33.

19.7 mmol, OChem Inc.), toluene (60 mL), 1-butanol (120 mL) and quinoline (10 mL) were heated to reflux overnight. After reaction, the solution was concentrated to the half of its volume under reduced pressure. The ensuing residue was poured into aqueous citric acid solution (1.5 L, 5%) under continuous stirring until golden-green crystals precipitates. The precipitate was filtered and finally recrystallized from boiling ethanol (500 mL) to yield the dye **MSQ 1** (9.4 g, 15 mmol, 76%). m.p. 155–160 °C. d.p. 290 °C. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz, ppm):  $\delta$  7.34 (d, <sup>3</sup>*J* = 7.4 Hz, 2H, H-4"), 7.29 (ddd,  ${}^{3}J = 7.8$  Hz, 7.6 Hz,  ${}^{4}J = 1.0$  Hz, 2H, H-6"), 7.12 (dd,  ${}^{3}J = 7.4$  Hz, 7.6 Hz, 2H, H-5"), 6.96 (d,  ${}^{3}J = 7.8$  Hz, 2H, H-7"), 5.95 (s, 2H, H-1'), 4.1-3.8 (br, 4H, H-1\*\*), 1.8-1.7 (m, 16H, H-1\*, H-2\*\*), 1.4-1.2 (m, 10H, H-3<sup>\*\*</sup>, H-4<sup>\*\*</sup>, H-5<sup>\*\*</sup>, H-6<sup>\*\*</sup>, H-7<sup>\*\*</sup>), 0.86 (t,  ${}^{3}J$  = 6.9 Hz, 6H, H-8\*\*). For numeration see Supplemental Information. <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 100 MHz, ppm): δ 182.25, 179.42, 169.92, 142.41, 142.17, 127.66, 123.55, 122.20, 109.27, 86.48, 49.20, 43.66, 31.66, 29.25, 29.08, 27.01, 26.98, 22.52, 14.00. MS (MALDI): m/z 621 (100)  $[M + H]^+$ , 620 (100)  $[M]^+$ , 605 (7)  $[M - CH_3]^+$ , 364 (7)  $[C_{24}H_{30}NO_2]^+$ , 310.7 (5)  $[M + H]^{++}$ , 310.2 (4)  $[M]^{++}$ 207.1 (1)  $[M + H]^{3+}$ , 155.4 (2)  $[M + H]^{4+}$ , 103.6 (1)  $[M + H]^{6+}$ . HR-MS (MALDI): m/z calculated for  $C_{42}H_{56}N_2O_2$  [M]<sup>+</sup>: 620.4336; found: 620.4410. Elemental analysis: calculated for C<sub>42</sub>H<sub>56</sub>N<sub>2</sub>O<sub>2</sub>: C, 81.24; H, 9.09; N, 4.51; O, 5.15. Found: C, 81.14; H, 9.10; N, 4.50; O, 5.23.

### 2.2.2. 4-((3,3-Dimethyl-1-octyl-3H-indolium-2-yl)methylene)-2-((1-ethyl-3,3-dimethyl-5-phenylindolin-2-ylidene)methyl)-3oxocyclobut-1-enolate (**MSQ 2**)

In a 50 mL Schlenk tube the functionalized asymmetric dye **10** (1.00 g, 1.51 mmol, Supplemental Information), bromobenzene (0.355 g, 2.26 mmol), potassium acetate (0.445 g, 4.53 mmol), dichloro[1,1'-bis(diphenylphosphino)-ferrocen]-palladium(II) (50 mg, 56  $\mu$ mol, CombiPhos Catalysts Inc.) and dioxane (20 mL) were suspended and stirred at 80 °C for 4 d. Subsequently, the

solvent was evaporated under vacuum and the residue was dissolved in chloroform (50 mL). The solution was filtered through a silica gel bed (3 cm) which, subsequently, was extracted with chloroform twice (2  $\times$  40 mL). The solvent of the filtrate was removed under reduced pressure in order to obtain the crude dye MSQ 2 which was further purified by column chromatography in chloroform yielding a golden crystalline powder (0.42 g, 0.60 mmol, 40%). d.p. 283 °C. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz, ppm): δ 7.85 (d, <sup>4</sup>J = 1.7 Hz, 1H, H-4<sup>\*</sup>), 7.71 (dd, <sup>3</sup>J = 7.4 Hz, <sup>4</sup>J = 1.2 Hz, 2H, H-2§), 7.64 (dd,  ${}^{3}J = 8.3$  Hz,  ${}^{4}J = 1.8$  Hz, 1H, H-6\*), 7.51 (d,  ${}^{3}J = 7.3$  Hz, 1H, H-4<sup>\*\*</sup>), 7.46 (dd,  ${}^{3}J =$  7.9 Hz, 7.4 Hz, 2H, H-3§), 7.39 (d,  ${}^{3}I = 8.4$  Hz, 1H, H-7<sup>\*</sup>), 7.37–7.29 (m, 3H, H-6<sup>\*\*</sup>, H-7<sup>\*\*</sup>, H-4§), 7.16 (ddd,  ${}^{3}J = 8.2$  Hz, 7.3 Hz,  ${}^{4}J = 1.8$  Hz, 1H, H-5\*\*), 5.80 (m, 2H, H-1', H-1''), 4.15 (q,  ${}^{3}J = 6.7$  Hz, 2H, H-1‡), 4.07 (t,  ${}^{3}J = 6.2$  Hz, 2H, H-1‡‡), 1.77-1.65 (m, 14H, H-1<sup>+</sup>, H-1<sup>+</sup>, H-2<sup>+</sup>), 1.4-1.2 (m, 13H, H-3<sup>+</sup>, H-4 $\ddagger$ t, H-5 $\ddagger$ t, H-6 $\ddagger$ t, H-7 $\ddagger$ t, H-2 $\ddagger$ ), 0.81 (t, <sup>3</sup>*J* = 6.8 Hz, 3H, H-8 $\ddagger$ t). For numeration see Supplemental Information. <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 100 MHz, ppm): δ 180.65, 178.90, 178.45, 169.11, 168.34, 142.38, 142.21, 141.43, 141.30, 139.93, 135.89, 128.89, 127.96, 127.10, 126.59, 126.52, 123.69, 122.25, 120.76, 110.34, 86.15, 86.02, 48.80, 48.73, 42.92, 38.06, 31.14, 28.66, 28.58, 26.51, 26.50, 26.47, 26.19, 25.49, 22.04, 13.93, 11.78. MS(MALDI): 613 (99) [M + H]<sup>+</sup>, 612 (100) [M]<sup>+</sup>, 597 (21)  $[M - CH_3]^+$ , 583 (2)  $[M - C_2H_5]^+$ , 499 (1)  $[M - C_8H_{17}]^+$ , 364 (11) [C<sub>24</sub>H<sub>30</sub>NO<sub>2</sub>]<sup>+</sup>, 356 (13) [C<sub>24</sub>H<sub>22</sub>NO<sub>2</sub>]<sup>+</sup>, 306 (9) [M]<sup>++</sup>, 153 (2)  $[M]^{4+}$ . HR-MS(MALDI): calculated for  $C_{42}H_{48}N_2O_2$   $[M]^+$ : 612.3710. Found: 612.3589.

# 2.2.3. 4-((3,3-Dimethyl-1-octyl-5-phenyl-3H-indolium-2-yl) methylene)-2-((3,3-dimethyl-1-octyl-5-phenylindolin-2-ylidene) methyl)-3-oxocyclobut-1-enolate (**MSQ 3**)

Dye **13** (3.00 g, 3.44 mmol, Supplemental Information), bromobenzene (1.62 g, 10.32 mmol), potassium acetate (2.02 g, 20.6 mmol), dichloro[1,1'-bis(diphenylphosphino)-ferrocen]-palladium(II)



Scheme 3. Preparation of bis squaraines BSQ 1, 2, 3, 4 and 5.

(200 mg, 250 µmol, CombiPhos Catalysts Inc.) and dioxane (50 mL) were suspended in a 100 mL Schlenk tube and heated to 80 °C for 4 d. The product precipitated during the reaction. After reaction, the reaction mixture was cooled to room temperature and the crude product was filtered. The filtration residue was recrystallized from hot dimethyl sulfoxide (600 mL at 120 °C). The crystals were filtered and washed with cold ethanol (3 × 10 mL) and dried to yield **MSQ 3** (1.9 g, 2.5 mmol, 71%) as golden needle like crystals. d.p. 304 °C. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz, ppm):  $\delta$  7.86 (d, <sup>4</sup>*J* = 1.5 Hz, 2H, H-4"), 7.72 (d, <sup>3</sup>*J* = 7.7 Hz, 4H, H-2†), 7.66 (dd, <sup>3</sup>*J* = 8.4 Hz, <sup>4</sup>*J* = 1.5 Hz, 2H, H-6"), 7.47 (dd, <sup>3</sup>*J* = 7.5 Hz, 2H, H-4†), 5.83 (s, 2H, H-1'), 4.12 (br, 4H, H-1\*\*), 1.8–1.6 (m, 16H, H-1\*, H-2\*\*), 1.5–1.2 (m, 20H, H-3\*\*, H-4\*\*, H-5\*\*, H-6\*\*, H-7\*\*), 0.85 (t, <sup>3</sup>*J* = 6.8 Hz, 6H, H-8\*\*). For numeration see

 $\begin{array}{l} \mbox{Supplemental Information. MS(MALDI): 774 (100) [M + H]^+, 772 \\ (97) [M]^+, 757 (21) [M - CH_3]^+, 660 (2) [M + H - C_8 H_{17}]^+, 440 (10) \\ [C_{30} H_{34} NO_2]^+, 386 (3) [M]^{++}, 193 (1) [M]^{4+}. HR-MS(MALDI): calculated for C_{54} H_{64} N_2 O_2 [M]^+: 772.4962. Found: 772.4974. \end{array}$ 

2.2.4. 2-((3-Ethyl-1,1-dimethyl-1H-benzo[e]indol-2(3H)-ylidene) methyl)-4-((1-ethyl-3,3-dimethyl-3H-indolium-2-yl)methylene)-3oxocyclobut-1-enolate (**MSQ 4**)

Half dye **15** (6.85 g, 20.5 mmol, Supplemental Information), indolium derivative **14** (6.80 g, 21.6 mmol, Supplemental Information) were dissolved in a mixture of toluene (50 mL), 1-butanol (100 mL) and quinoline (10 mL). The condensation proceeded for 15 h at reflux temperature in a Dean–Stark apparatus. Subsequently, the reaction mixture was concentrated under



Scheme 4. Preparation of tris and tetra squaraines TSQ 1, 2, 3, 4, 5 and 6.

vacuum and the bluish-black oily residue was diluted in ethanol (50 mL). Under vigorously stirring, the solution was poured into an aqueous citric acid solution (800 mL, 5%). The green precipitate was filtered off and the crude dye was recrystallized from boiling methanol (120 mL) to yield MSQ 4 (3.8 g, 7.6 mmol, 37%) as golden crystals. d.p. 288 °C. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz, ppm):  $\delta$  8.23 (dd,  ${}^{3}I = 8.4 \text{ Hz}, {}^{4}I = 0.8 \text{ Hz}, 1\text{H}, \text{H}-9''), 8.03 (\text{d}, {}^{3}I = 8.8 \text{ Hz}, 1\text{H}, \text{H}-5''), 8.01$  $(dd, {}^{3}J = 8.0 \text{ Hz}, {}^{4}J = 1.3 \text{ Hz}, 1\text{H}, \text{H}-6''), 7.71 (d, {}^{3}J = 8.8 \text{ Hz}, 1\text{H}, \text{H}-4''),$ 7.62 (ddd,  ${}^{3}J = 8.4$  Hz, 7.0 Hz,  ${}^{4}J = 1.3$  Hz, 1H, H-8"), 7.53 (dd,  ${}^{3}J$  = 7.2 Hz,  ${}^{4}J$  = 1.3 Hz, 1H, H-7<sup>†</sup><sup>†</sup>), 7.45 (ddd,  ${}^{3}J$  = 8.0 Hz, 7.0 Hz,  ${}^{4}J$  = 0.8 Hz, 1H, H-7"), 7.35 (dd,  ${}^{3}J$  = 7.2 Hz, 7.2 Hz,  ${}^{4}J$  = 0.8 Hz, 1H, H-6<sup>††</sup>), 7.31 (dd,  ${}^{3}J$  = 7.2 Hz,  ${}^{4}J$  = 0.8 Hz, 1H, H-4<sup>††</sup>)), 7.16 (dd,  ${}^{3}J = 7.2$  Hz, 7.2 Hz,  ${}^{4}J = 1.3$  Hz, 1H, H-5††), 5.86 (s, 1H, H-1'), 5.80 (s, 1H, H-1†), 4.27 (q,  ${}^{3}J = 7.1$  Hz, 2H, H-1\*\*), 4.12 (q,  ${}^{3}J = 6.9$  Hz, 2H, H-1‡), 1.95 (s, 6H, H-1\*), 1.70 (s, 6H, H-1‡‡), 1.34 (t, <sup>3</sup>*J* = 7.1 Hz, 3H, H- $2^{**}$ ), 1.29 (t,  ${}^{3}J = 6.9$  Hz, 3H, H-2†). For numeration see Supplemental Information. <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 100 MHz, ppm): δ 180.72, 178.36, 177.91, 170.24, 168.18, 141.77, 141.51, 139.24, 133.31, 130.91, 129.83, 129.73, 127.99, 127.95, 127.44, 124.22, 123.53, 122.29, 122.25, 111.15, 109.96, 85.66, 85.58, 50.62, 48.63, 38.22, 37.89, 26.50, 26.10, 12.09, 11.72. MS(MALDI): 525 (2)  $[M + Na]^+$ , 503 (100)  $[M + H]^+$ , 502 (97)  $[M]^+$ , 487 (5)  $[M - CH_3]^+$ , 473 (1)  $[M - C_2H_5]^+$ , 330 (6) [C<sub>22</sub>H<sub>20</sub>NO<sub>2</sub>]<sup>+</sup>, 280 (8) [C<sub>18</sub>H<sub>18</sub>NO<sub>2</sub>]<sup>+</sup>, 276 (7) [C<sub>19</sub>H<sub>18</sub>NO]<sup>+</sup>, 252 (7)  $[M + H]^{2+}$ , 251 (7)  $[M]^{2+}$ , 168 (1)  $[M + H]^{3+}$ , 126 (3)  $[M + H]^{4+}$ , 101 (1)  $[M + H]^{5+}$ , 84 (1)  $[M + H]^{6+}$ , 72 (1)  $[M + H]^{7+}$ , 63 (1)  $[M + H]^{8+}$ . HR-MS(MALDI): calculated for  $C_{34}H_{35}N_2O_2 [M + H]^+$ : 503.2693. Found: 503.2696.

### 2.2.5. 2-((3-Ethyl-1,1-dimethyl-1H-benzo[e]indol-2(3H)-ylidene) methyl)-4-((3-ethyl-1,1-dimethyl-1H-benzo[e]indolium-2-yl) methylene)-3-oxocyclobut-1-enolate (**MSQ 5**)

In a Dean–Stark apparatus the benzindolium derivative **16** (15.4 g, 42.1 mmol, Supplemental Information), squaric acid (2.34 g, 20.5 mmol, OChem Inc.), toluene (50 mL), 1-butanol (100 mL) and quinoline (10 mL) were mixed and heated to reflux for 36 h. Thereafter, the reaction mixture was concentrated under reduced

pressure and the oily residue was dissolved in ethanol (100 mL). Under vigorously stirring, the solution was added drop wise to an aqueous citric acid solution (1 L, 5%). After 30 min, the precipitate was filtered and subsequent recrystallization of the remnant from boiling methanol (750 mL) yielded MSQ 5 as golden-green shiny crystals (6.6 g, 12 mmol, 58%). d.p. 318 °C. <sup>1</sup>H NMR (DMSO-d<sub>6</sub>, 400 MHz, ppm):  $\delta$  8.23 (dd,  ${}^{3}I = 8.3$  Hz,  ${}^{4}I = 0.9$  Hz, 2H, H-9"), 8.03  $(d, {}^{3}J = 8.9 \text{ Hz}, 2\text{H}, \text{H-5''}), 8.02 (dd, {}^{3}J = 7.9 \text{ Hz}, {}^{4}J = 1.4 \text{ Hz}, 2\text{H}, \text{H-6''}),$ 7.71 (d,  ${}^{3}J = 8.9$  Hz, 2H, H-4″), 7.62 (ddd,  ${}^{3}J = 8.3$  Hz, 6.9 Hz,  ${}^{4}J = 1.4$  Hz, 2H, H-8″), 7.45 (ddd,  ${}^{3}J = 7.9$  Hz, 6.9 Hz,  ${}^{4}J = 0.9$  Hz, 2H, H-7"), 5.87 (s, 2H, H-1'), 4.27 (q,  ${}^{3}J = 7.1$  Hz, 4H, H-1\*\*), 1.97 (s, 12H, H-1\*), 1.35 (t,  ${}^{3}J = 7.1$  Hz, 6H, H-2\*\*). For numeration see Supplemental Information. <sup>13</sup>C NMR (DMSO-d<sub>6</sub>, 100 MHz, ppm):  $\delta$  184.74, 177.51, 169.85, 138.91, 133.18, 130.86, 129.82, 129.75, 127.99, 127.45, 124.18, 122.24, 111.12, 85.54, 50.55, 38.18, 26.16, 12.08. MS(MALDI): 575 (2)  $[M + Na]^+$ , 552 (100)  $[M]^+$ , 537 (5)  $[M - CH_3]^+, 523 (2) [M - C_2H_5]^+, 330 (18) [C_{22}H_{20}NO_2]^+, 276 (7)$  $[M]^{++}, 184 (1) [M]^{3+}, 138 (1) [M]^{4+}, 110 (1) [M]^{5+}, 92 (1) [M]^{6+}, 79$ (1)  $[M]^{7+}$ . HR-MS(MALDI): calculated for  $C_{38}H_{36}N_2O_2$   $[M]^+$ : 552.2771. Found: 552.2779.

2.2.6. 2,2'-(5,5'-(1,4-Phenylene)bis(1,3,3-trimethyl-indoline-5-yl-2ylidene))bis(methan-1-yl-1-ylidene)bis(4-((1,1-dimethyl-3-octyl-1H-benzo[e]indolium-2-yl)methylene)-3-oxocyclobut-1-enolate) (**BSQ 1**)

Half dye **34** (1.36 g, 3.27 mmol, Supplemental Information), phenylene bridge **29** (1.00 g, 1.31 mmol, Supplemental Information) were dissolved in a mixture of toluene (10 mL), 1-butanol (20 mL) and quinoline (5 mL) and heated to reflux for 60 h in a Dean–Stark apparatus. Afterwards, the reaction mixture was concentrated under reduced pressure. The residue was diluted with ethanol (50 mL) and, under vigorously steering for 15 min, added drop wise to cold aqueous citric acid solution (600 mL, 10% w/v). The suspension was filtered and the crude dye was digested in saturated potassium carbonate solution (100 mL) and, subsequently, washed with water thrice. Further purification by column

chromatography (chloroform) yielded BSQ 1 (1.1 g, 0.85 mmol, 65%). d.p. 300 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  8.18 (d,  ${}^{3}J = 8.5$  Hz, 2H, H-9\*), 7.86 (d,  ${}^{3}J = 8.1$  Hz, 2H, H-6\*), 8.84 (d, J = 0.5 Hz, 2H, H $\cdot$ 5 ), 7.66 (s, 4H, H $\cdot$ 2§), 7.6-7.5 (m, 6H, H $\cdot$ 8\*, H $\cdot$ 4††, H-6††), 7.38 (dd,  ${}^{3}J$  = 8.1 Hz, 7.5 Hz, 2H, H-7\*), 7.27 (d,  ${}^{3}J$  = 8.8 Hz, 2H, H-4<sup>\*</sup>), 7.03 (d,  ${}^{3}J$  = 8.2 Hz, 2H, H-7<sup>††</sup>), 6.04 (s, 2H, H-1"), 5.95 (s, 2H, H-1'), 4.10 (br, 4H, H-1†), 3.52 (br, 6H, H-1‡‡), 2.06 (s, 12H, H-1\*\*), 2.0–1.8 (m, 16H, H-1<sup>+</sup>, H-2<sup>+</sup>), 1.5–1.2 (m, 20H, H-3<sup>+</sup>, H-4<sup>+</sup>, H-5<sup>+</sup>, H-6<sup>†</sup>, H-7<sup>†</sup>), 0.84 (t,  ${}^{3}I = 6.8$  Hz, 6H, H-8<sup>†</sup>). For numeration see Supplemental Information. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm): δ 182.27, 179.74, 177.49, 172.13, 169.24, 142.55, 142.45, 139.26, 135.93, 134.50, 131.15, 129.53, 128.41, 127.18, 127.14, 126.43, 124.29, 122.40, 120.59, 110.05, 109.04, 86.84, 86.48, 51.22, 48.79, 43.78, 31.51, 29.12, 28.94, 27.25, 27.14, 26.83, 26.50, 22.39, 13.90. MS(MALDI): 1220 (100)  $[M + H]^+$ , 1219 (82)  $[M]^+$ , 1205 (24)  $[M + H - CH_3]^+$ , 1190 (10)  $[M + H - 2xCH_3]^+$ , 912 (16)  $[C_{62}H_{62}N_3O_4]^+$ , 805 (11)  $[C_{56}H_{59}N_3O_2]^+$ , 790 (6)  $[C_{55}H_{56}N_3O_2]^+$ , 609.8 (4)  $[M + H]^{++}$ , 609.3 (3)  $[M]^{++}$ , 414 (12)  $[C_{28}H_{32}NO_2]^{+}$ . HR-MS(MALDI): calculated for C<sub>84</sub>H<sub>90</sub>N<sub>4</sub>O<sub>4</sub> [M]<sup>+</sup>: 1218.6957. Found: 1218.6980. Elemental analysis: calculated for C<sub>84</sub>H<sub>90</sub>N<sub>4</sub>O<sub>4</sub>: C, 82.72; H, 7.44; N, 4.59; O, 5.25. Found: C, 82.45; H, 7.50; N, 4.65; O, 5.45.

### 2.2.7. 2,2'-(5,5'-(9,9-Bis(2-ethylhexyl)-9H-fluorene-2,7-diyl) bis(1,3,3-trimethyl-indoline-5-yl-2-ylidene))bis(methan-1-yl-1ylidene)bis(4-((1,1-dimethyl-3-octyl-1H-benzo[e]indolium-2-yl) methylene)-3-oxocyclobut-1-enolate) (**BSQ 2**)

Fluorene bridge 30 (1.00 g, 0.928 mmol, Supplemental Information), half dye 34 (1.02 g, 2.32 mmol, Supplemental Information) were dissolved in toluene (10 mL). 1-butanol (10 mL) and 1-methyl-2-pyrrolidinone (10 mL) and heated to reflux for 2 d. Afterwards, the solvent was removed under vacuum and the concentrate was dissolved in ethanol (25 mL). This solution was poured into ice-water (1 L) under vigorously stirring. After 1 h, the precipitate was filtered off and dissolved in chloroform (200 mL). The organic phase was extracted with saturated citric acid (2  $\times$  150 mL), water (4  $\times$  150 mL) and brine (150 mL). After evaporating the solvent under reduced pressure, the remnant was suspended in diethyl ether (2  $\times$  50 mL) to dissolve the intermediates and side products. After filtration and drying in a vacuum oven BSQ 2 (1.2 g, 0.76 mmol, 82%) was isolated as a dark blue amorphous powder. d.p. 283 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  8.21  $(d, {}^{3}J = 8.4 \text{ Hz}, 2H, H-9^{*}), 7.91 (d, {}^{3}J = 8.0 \text{ Hz}, 2H, H-6^{*}), 7.88 (d,$  ${}^{3}J = 9.2$  Hz, 2H, H-5\*), 7.78 (d,  ${}^{3}J = 8.1$  Hz, 2H, H-4§), 7.65–7.55 (m, 10H, H-8<sup>\*</sup>, H-4<sup>††</sup>, H-6<sup>††</sup>, H-1<sup>§</sup>, H-3<sup>§</sup>), 7.43 (ddd,  ${}^{3}J = 8.0$  Hz, 7.0 Hz,  ${}^{4}J = 0.8$  Hz, 2H, H-7\*), 7.31 (d,  ${}^{3}J = 9.2$  Hz, 2H, H-4\*), 7.05 (d,  ${}^{3}J = 8.5$  Hz, 2H, H-7<sup>†</sup>, 6.15–5.9 (m, 4H, H-1′, H-1″), 4.2–4.0 (m, 4H, H-1†), 3.7-3.5 (br, 6H, H-1‡‡), 2.2-2.0 (m, 16H, H-1§§, H-1\*\*), 2.0-1.7 (m, 16H, H-1<sup>‡</sup>, H-2<sup>†</sup>), 1.5-1.2 (m, 24H, alkyl chain), 1.0-0.7 (m, 20H, alkyl chain), 0.65–0.5 (m, 10H, alkyl chain). MS(MALDI): 1532 (100)  $[M + H]^+$ , 1517 (14)  $[M + H-CH_3]^+$ , 1225 (4)  $[C_{85}H_{99}N_3O_4]^+$ , 1118 (2)  $[C_{79}H_{95}N_3O_2]^+$ , 766 (1)  $[M + H]^{++}$ . HR-MS(MALDI): calculated for  $C_{107}H_{127}N_4O_4 [M + H]^+$ : 1531.9852. Found: 1531.9823.

### 2.2.8. 2,2'-(5,5'-(2,5-Bis(2-ethylhexyloxy)-1,4-phenylene)bis(1,3,3trimethyl-indoline-5-yl-2-ylidene))bis(methan-1-yl-1-ylidene) bis(4-((1,1-dimethyl-3-octyl-1H-benzo[e]indolium-2-yl) methylene)-3-oxocyclobut-1-enolate) (**BSQ 3**)

In a Dean–Stark apparatus half dye **34** (1.25 g, 2.85 mmol, Supplemental Information), alkoxyphenylene bridge **31** (1.00 g, 1.14 mmol, Supplemental Information), toluene (5 mL), 1-butanol (5 mL) and 1-methyl-2-pyrrolidinone (5 mL) were mixed and heated to reflux for 2 d. According to UV–vis measurements the reaction proceeded slowly and the pH changed from 6 to 7.5. In order to acidify the reaction mixture, aqueous hydrochloric acid

(2 mL, 1 N) was added. The reaction was completed by refluxing for an additional day. Subsequently, the solvent was removed under reduced pressure. The concentrate was diluted with ethanol (10 mL) and poured into water (250 mL). The suspension was stirred for 30 min and the precipitate was filtered. The residue was digested with diethyl ether several times. Subsequent purification by column chromatography (chloroform) vielded BSQ 3 (0.48 g. 0.33 mmol, 29%). d.p. 287 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  8.21 (dd,  ${}^{3}J = 8.4$  Hz,  ${}^{4}J = 1.0$  Hz, 2H, H-9\*), 7.90 (dd,  ${}^{3}J = 8.0$  Hz,  ${}^{4}J = 1.2$  Hz, 2H, H-6\*), 7.88 (d,  ${}^{3}J = 9.0$  Hz, 2H, H-5\*), 7.66 (d,  ${}^{4}J = 1.5$  Hz, 2H, H-4††), 7.58 (dd,  ${}^{3}J = 8.4$  Hz, 7.0 Hz,  ${}^{4}J = 1.2$  Hz, 2H, H-8\*), 7.51 (dd,  ${}^{3}J = 8.2$  Hz,  ${}^{4}J = 1.5$  Hz, 2H, H-6††), 7.42 (ddd,  ${}^{3}J = 8.0$  Hz, 7.0 Hz,  ${}^{4}J = 1.0$  Hz, 2H, H-7\*), 7.31 (d,  ${}^{3}J = 9.0$  Hz, 2H, H-4\*), 7.05 (d,  ${}^{3}J = 8.2$  Hz, 2H, H-7††), 6.99 (s, 2H, H-3§), 6.1–5.8 (m, 4H, H-1', H-1"), 4.2-4.0 (m, 4H, H-1<sup>+</sup>), 4.0-3.7 (m, 4H, H-1<sub>§§</sub>), 3.7–3.5 (br, 6H, H-1‡‡), 2.07 (s, 12H, H-1\*\*), 2.0–1.7 (m, 16H, H-1±, H-2<sup>†</sup>), 1.7–1.5 (m, 4H, H-2<sub>§§</sub>), 1.5–1.1 (m, 36H, H-3<sup>†</sup>, H-4<sup>†</sup>, H-5<sup>†</sup>, H-6†, H-7†, H-3§§, H-4§§, H-5§§, H-1#), 0.86 (m, 18H, H-8†, H-6§§, H-2#). For numeration see Supplemental Information. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm):  $\delta$  182.43, 178.68, 177.47, 172.13, 170.04, 166.59, 150.35, 141.45 139.46, 134.63, 134.07, 131.28, 130.14, 129.67, 129.65, 128.86, 128.60, 127.31, 124.39, 123.86, 122.59, 120.27, 115.54, 110.18, 108.47, 86.88, 86.54, 71.61, 51.32, 49.06, 43.95, 39.59, 31.72, 31.69, 30.40, 29.30, 29.11, 28.97, 27.40, 27.21, 27.01, 26.66, 23.88, 22.95, 22.55, 14.03, 11.01. MS(MALDI): 1498 (3) [M + Na]<sup>+</sup>, 1476 (100) [M + H]<sup>+</sup>, 1475 (55) [M]<sup>+</sup>, 1461 (11) [M + H–CH<sub>3</sub>]<sup>+</sup>, 1446 (2)  $[M - C_2H_5]^+$ , 1169 (6)  $[C_{78}H_{94}N_3O_6]^+$ , 1077 (12)  $[C_{73}H_{94}N_3O_4]^+$ , 1062 (7)  $[C_{72}H_{91}N_3O_4]^+$ , 738 (1)  $[M + H]^{++}$ . HR-MS(MALDI): calculated for  $C_{100}H_{123}O_6N_4$  [M + H]<sup>+</sup>: 1475.9437. Found: 1475.9468.

### 2.2.9. 2,2'-(5,5'-(Perfluoro-1,4-phenylene)bis(1,3,3-trimethyl-indoline-5-yl-2-ylidene))bis(methan-1-yl-1-ylidene)bis(4-((1,1-dimethyl-3octyl-1H-benzo[e]indolium-2-yl)methylene)-3-oxocyclobut-1-enolate) (**BSQ 4**)

In a Dean-Stark apparatus half dye 34 (474 mg, 1.08 mmol, Supplemental Information), tetrafluoro phenylene bridge 32 (300 mg, 0.433 mmol, Supplemental Information), toluene (5 mL), 1-butanol (5 mL) and 1-methyl-2-pyrrolidinone (5 mL) were combined to generate **BSQ04** within 7 d at 120 °C. Due to a change of the pH value to about 7.5, the reaction preceded very slowly which was controlled by UV-vis measurements. Therefore, aqueous hydrochloric acid (2 mL, 1 N) was added and the reaction mixture was heated for an additional 2 d. Then, the reaction mixture was concentrated under reduced pressure and the remnant was dissolved in ethanol (10 mL). Under vigorously stirring, the solution was added drop wise to water (1 L). After 30 min, the suspension was filtered and the residue was digested in diethyl ether several times to yield BSQ 4 (0.39 g, 0.30 mmol, 69%). d.p. 283 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  8.21 (d, <sup>3</sup>J = 8.5 Hz, 2H, H-9<sup>\*</sup>), 7.91 (d,  ${}^{3}J = 8.3$  Hz, 2H, H-6<sup>\*</sup>), 7.89 (d,  ${}^{3}J = 8.6$  Hz, 2H, H-5<sup>\*</sup>), 7.59  $(dd, {}^{3}J = 8.5 Hz, 7.0 Hz, 2H, H-8^{*}), 7.5-7.4 (m, 6H, H-4^{\dagger}, H-6^{\dagger}, H-$ 7\*), 7.32 (d,  ${}^{3}J = 8.6$  Hz, 2H, H-4\*), 7.05 (d,  ${}^{3}J = 8.4$  Hz, 2H, H-7††), 6.12 (br, 2H, H-1"), 6.00 (br, 2H, H-1'), 4.18 (m, 4H, H-1†), 3.56 (br, 6H, H-1<sup>‡‡</sup>), 2.07 (s, 12H, H-1<sup>\*\*</sup>), 2.0–1.7 (m, 16H, H-1<sup>‡</sup>, H-2<sup>†</sup>), 1.5–1.2  $(m, 20H, H-3\dagger, H-4\dagger, H-5\dagger, H-6\dagger, H-7\dagger), 0.87 (t, {}^{3}J = 6.5 Hz, 6H, H-8\dagger).$ For numeration see Supplemental Information. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm): δ 182.44, 178.68, 177.47, 173.36, 170.04, 168.89, 145.49, 143.84, 142.86, 142.25, 139.23, 135.10, 131.51, 130.70, 130.02, 129.80, 129.70, 128.53, 127.44, 124.70, 124.05, 122.66, 121.99, 110.28, 108.71, 87.32, 87.07, 51.64, 48.69, 44.18, 31.69, 30.43, 29.29, 29.10, 27.51, 27.22, 27.00, 26.56, 22.55, 14.03. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 376 MHz, ppm):  $\delta - 144.4$  (s, 4F, F-2§). MS(MALDI): 1314 (2) [M + Na]<sup>+</sup>, 1292  $(100) [M + H]^+, 1277 (16) [M + H - CH_3]^+, 1262 (7) [M - C_2H_5]^+, 984$ (5)  $[C_{62}H_{58}F_4N_3O_4]^+$ , 877 (4)  $[C_{56}H_{55}F_4N_3O_2]^+$ , 720 (8)  $[C_{45}H_{44}F_4N_2O_2]^+,\ 646\ (4)\ [M\ +\ H]^{++},\ 414\ (4)\ [C_{28}H_{32}NO_2]^+.\ HR-MS(MALDI):\ calculated\ for\ C_{84}H_{87}F_4N_4O4\ [M\ +\ H]^+:\ 1291.6658.$  Found: 1291.6634.

# 2.2.10. 2,2'-(1,1,3,6,6,8-Hexamethyl-indolo[7,6-g]indole-2,7-(1H,3H,6H,8H)-diylidene)bis(methan-1-yl-1-ylidene)bis(4-((1,1-dimethyl-3-octyl-1H-benzo[e]indolium-2-yl)methylene)-3-oxocvclobut-1-enolate) (**BSO 5**)

Half dye 34 (1.36 g, 3.27 mmol, Supplemental Information), condensed middle part **33** (1.00 g, 1.31 mmol [28]), toluene (10 mL), 1-butanol (20 mL) and guinoline (5 mL) were combined and heated to reflux for 60 h in a Dean-Stark apparatus. Subsequently, the reaction mixture was concentrated under reduced pressure. The residue was dissolved in ethanol (50 mL) and added drop wise to cold aqueous citric acid solution (600 mL, 10% w/v) as it was stirred vigorously for 15 min. The suspension was filtered and the residue was digested in saturated potassium carbonate solution (100 mL) and, afterwards, washed with water four times. Subsequent purification by column chromatography (chloroform) yielded BSQ5 (1.1 g, 0.85 mmol, 65%) and dye 36 (used for the production of TSQ 6, Scheme 4) d.p. 317 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 8.25–8.15  $(m, 2H, H-4\dagger\dagger), 8.21 (dd, {}^{3}J = 8.6 Hz, {}^{4}J = 0.8 Hz, 2H, H-9^{*}), 7.90 (dd, J)$  ${}^{3}J = 7.8$  Hz,  ${}^{4}J = 1.1$  Hz, 2H, H-6\*), 7.88 (d,  ${}^{3}J = 8.7$  Hz, 2H, H-5\*), 7.58  $(ddd, {}^{3}J = 8.6 \text{ Hz}, 7.0 \text{ Hz}, {}^{4}J = 1.1 \text{ Hz}, 2\text{H}, \text{H}-8^{*}), 7.55-7.45 \text{ (m, 2H, H}-8^{*}), 7.55-7.55 \text{ (m, 2H, H}-8^{*}), 7.55-7.55$ 5<sup>††</sup>), 7.43 (ddd,  ${}^{3}J$  = 7.8 Hz, 7.0 Hz,  ${}^{4}J$  = 0.8 Hz, 2H, H-7<sup>\*</sup>), 7.31 (d,  $^{3}I = 8.7 \text{ Hz}, 2\text{H}, \text{H}-4^{*}), 6.2-6.0 \text{ (m, 4H, H}-1', \text{H}-1''), 4.5-4.0 \text{ (m, 10H, H}-1')$ 1<sup>†</sup>, H-1<sup>‡‡</sup>), 2.08 (s, 12H, H-1<sup>\*\*</sup>), 1.95–1.15 (m, 36H, H-1<sup>‡</sup>, H-2<sup>†</sup>, H-3<sup>†</sup>, H- $4^{\dagger}$ , H-5<sup>{\dagger}</sup>, H-6<sup>{\dagger}</sup>, H-7<sup>{\dagger}</sup>), 0.86 (t,  ${}^{3}I = 6.9$  Hz, 6H, H-8<sup>{\dagger}</sup>). For numeration see Supplemental Information. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm): δ 182.43, 180.19, 177.13 (2C), 172.72, 171.12, 139.31, 138.93, 138.42, 134.86, 131.39, 129.72, 129.67, 128.54, 127.36, 124.54, 122.60, 122.33, 119.43, 117.89, 110.21, 88.08, 86.87, 51.50, 49.35, 48.62, 44.03, 31.66, 29.64, 29.28, 29.08, 27.45, 26.98, 26.59, 22.53, 14.01. MS(MALDI): 1140 (2) [M + Na]<sup>+</sup>, 1118 (100) [M + H]<sup>+</sup>, 1117 (65) [M]<sup>+</sup>, 1103 (17)  $[M + H - CH_3]^+$ , 1088 (7)  $[M + H - 2 \times CH_3]^+$ , 1062 (2)  $[C_{72}H_{77}N_4O_4]^+$ , 1006 (4)  $[C_{68}H_{69}N_4O_4]^+$ , 810 (5)  $[C_{54}H_{56}N_3O_4]^+$ , 718 (10)  $[C_{49}H_{56}N_3O_2]^+$ , 704 (6)  $[C_{48}H_{54}N_3O_2]^+$ , 558.8 (4)  $[M + H]^{++}$ , 414 (3)  $[C_{28}H_{32}NO_2]^+$ , 279 (2)  $[M + H]^{4+}$ . HR-MS(MALDI): calculated for C<sub>76</sub>H<sub>85</sub>N<sub>4</sub>O<sub>4</sub> [M + H]<sup>+</sup>: 1117.6565. Found: 1117.6590.

# 2.2.11. (p-Phenylene-(4-((3,3-dimethyl-1-octyl-3H-indolium-2,5-diyl)methylene)-2-((3,3-dimethyl-1-octyl-indolin-2-ylidene-5-yl) methyl)-3-oxocyclobut-1-enolate))\_{3-4} (**TSQ 1**)

All solvents and solutions were degassed by freeze-pump-thaw cycles. Dye 12 (200 mg, 257 µmol, Supplemental Information), benzene diboronic acid ester 35 (63.2 mg, 257 µmol, Supplemental Information) and the palladium catalyst (2.0 mg, 1.8 µmol, Supplemental Information) were placed in a 25 mL round bottom flask and fitted with a septum. Subsequently, 1-methyl-2-pyrrolidone (5 mL), tetrahydrofuran (3 mL) and an aqueous saturated sodium hydrogen carbonate solution (2 mL) were added via syringe. The reaction mixture was heated to 80 °C for 7 d while an intensively coloured powder precipitated. After reaction, the solvent was completely removed under vacuum and the residue was dissolved in chloroform (100 mL). This organic layer was washed with water (2  $\times$  50 mL) and brine (50 mL). The dried organic layer was concentrated under reduced pressure to 2-5 mL and, subsequently, added drop wise to ethanol (250 mL) under vigorously stirring. A very fine crystalline powder precipitated and was filtered. TSQ 1 (0.12 g, 0.17 mmol per formal unit, 67%) was obtained after drying at 40 °C under reduced pressure. d.p. 288 °C. MS (MALDI-TOF): 4254 (2) [6 dye units and 5 bridges], 3559 (10) [5 dye units and 5 bridges], 3132 (4) [4 dye units and 5 bridges], 2864 (42) [4 dye units and 3 bridges], 2437 (13) [3 dye units and 4 bridges], 2168 (100) [3 dye units and 2 bridges], 1742 (10) [2 dye units and 3 bridges], 1047 (7) [1 dye unit and 2 bridges].  $X_n$ : 3–4.

2.2.12. (9,9-Bis(2-ethylhexyl)-9H-2,7-fluorenylene-(4-((3,3dimethyl-1-octyl-3H-indolium-2,5-diyl)methylene)-2-((3,3dimethyl 1 octyl indolin 2 ylidene 5 yl)methyl 2 overydebyt 1

### dimethyl-1-octyl-indolin-2-ylidene-5-yl)methyl)-3-oxocyclobut-1enolate))<sub>3-4</sub> (**TSQ 2**)

All solvents and solutions were degassed by freeze-pump-thaw cycles. Dye 13 (200 mg, 229 umol, Supplemental Information), 2.7dibromo-9.9-bis(2-ethylhexyl)-9H-fluorene **19** (126 mg, 229 umol) and the palladium catalyst (1.9 mg, 1.6 umol, Supplemental Information) were combined in a 25 mL round bottom flask and fitted with a septum. Then 1-methyl-2-pyrrolidone (5 mL), tetrahydrofuran (3 mL) and an aqueous saturated sodium hydrogen carbonate solution (2 mL) were added via syringe. The reaction mixture was heated to 80 °C for 7 d while an intensively coloured powder precipitated. After reaction, the solvent was completely removed under vacuum and the residue was dissolved in chloroform (100 mL). This organic layer was washed with water  $(2 \times 50 \text{ mL})$  and brine (50 mL). The dried organic layer was concentrated under reduced pressure to 2-5 mL which was then added drop wise to ethanol (250 mL) under vigorously stirring. A very fine crystalline powder precipitated and was filtered. TSQ 2 (150 mg, 0.15 mmol per formal unit, 64%) was obtained after drying at 40 °C under reduced pressure. d.p. 296 °C. MS (MALDI-TOF): 6595 (3) [6 dve units and 7 bridges], 5587 (10) [5 dye units and 6 bridges], 4578 (34) [4 dye units and 5 bridges], 4186 (8) [4 dye units and 4 bridges], 3764 (15) [4 dye units and 3 bridges], 3571 (77) [3 dye units and 4 bridges], 3180 (11) [3 dye units and 3 bridges], 2756 (21) [3 dye units and 2 bridges], 2563 (24) [2 dye units and 3 bridges], 1748 (41) [2 dye units and 1 bridge], 933 (55). X<sub>n</sub>: 3–4.

# 2.2.13. (2,5-Bis(2-ethylhexyloxy)-p-phenylene-(4-((3,3-dimethyl-1-octyl-3H-indolium-2,5-diyl)methylene)-2-((3,3-dimethyl-1-octyl-indolin-2-ylidene-5-yl)methyl)-3-oxocyclobut-1-enolate))<sub>3-4</sub> (**TSQ 3**)

All solvents and solutions were degassed by freeze-pump-thaw cycles. Dye 13 (200 mg, 229 µmol, Supplemental Information), compound 24 (113 mg, 229 µmol, Supplemental Information) and the palladium catalyst (1.9 mg, 1.6 μmol, Supplemental Information) were placed in a 25 mL round bottom flask and fitted with a septum. Then 1-methyl-2-pyrrolidone (5 mL), tetrahydrofuran (3 mL) and an aqueous saturated sodium hydrogen carbonate solution (2 mL) were added via syringe. The reaction mixture was heated to 80 °C for 7 d while an intensively coloured powder precipitated. After reaction, the solvent was completely removed under vacuum and the residue was dissolved in chloroform (100 mL). This organic layer was washed with water  $(2 \times 50 \text{ mL})$  and brine (50 mL). The dried organic layer was concentrated under reduced pressure to 2-5 mL which was then dripped into ethanol (250 mL) under vigorously stirring. A very fine dark powder precipitated and was filtered. According to UV-vis measurements the residue showed a more red shifted  $\lambda_{max}$  then the filtrate, therefore it was assumed that some of the lower molecular weight component could be washed out by this precipitation. TSQ 3 (80 mg, 84 µmol per formal unit, 37%) was obtained after drying at 40 °C under reduced pressure. d.p. 344 °C. MS (MALDI-TOF): 8106 (2) [8 dye units and 9 bridges], 7153 (3) [7 dye units and 8 bridges], 6202 (12) [6 dye units and 7 bridges], 5250 (34) [5 dye units and 6 bridges], 4854(9)[5 dye units and 5 bridges], 4298 (100) [4 dye units and 5 bridges], 3903 (23) [4 dye units and 4 bridges], 3347 (80) [3 dye units and 4 bridges], 2588 (8) [3 dye units and 2 bridges], 1636 (16) [2 dye units and 1 bridge]. X<sub>n</sub>: 3–4.

### 2.2.14. (2,3,5,6-Tetrafluoro-phenylene-(4-((3,3-dimethyl-1-octyl-3H-indolium-2,5-diyl)methylene)-2-((3,3-dimethyl-1-octyl-indolin-2-ylidene-5-yl)methyl)-3-oxocyclobut-1-enolate))<sub>3-4</sub> (**TSQ 4**)

All solvents and solutions were degassed by freeze-pump-thaw cycles. Dye **13** (200 mg, 229  $\mu$ mol, Supplemental Information), 1,4-dibromotetrafluorobenzene **26** (70.5 mg, 229  $\mu$ mol, ABCR) and the

palladium catalyst (1.9 mg, 1.6 µmol, Supplemental Information) were placed in a 25 mL round bottom flask and fitted with a septum. Then 1-methyl-2-pyrrolidone (5 mL), tetrahydrofuran (3 mL) and an aqueous saturated sodium hydrogen carbonate solution (2 mL) were added via syringe. The reaction mixture was heated to 80 °C for 7 d, while a very dark powder started to precipitate. After reaction, the solvent was completely removed under vacuum and the residue was dissolved in chloroform (100 mL). This organic layer was washed with water (2x50 mL) and brine (50 mL). The dried organic layer was concentrated under reduced pressure to about 2-5 mL which was added drop wise to ethanol (250 mL) under vigorously stirring. A very fine crystalline powder precipitated and was filtered. TSQ 4 (70 mg, 91 µmol per formal unit, 40%) was obtained after drying at 40 °C under reduced pressure. d.p. 345 °C. MS (MALDI-TOF): 4682 (1) [6 dye units and 5 bridges], 4064 (4) [5 dye units and 5 bridges], 3837 (3) [5 dye units and 4 bridges], 3297 (8) [4 dye units and 4 bridges], 832 (13) [1 dye unit]. X<sub>n</sub>: 3–4.

# 2.2.15. (4-((3,3-Dimethyl-1-octyl-3H-indolium-2,5-diyl) methylene)-2-((3,3-dimethyl-1-octylindolin-2-ylidene-5-yl) methyl)-3-oxocyclobut-1-enolate))<sub>3-4</sub> (**TSQ 5**)

solvents solutions All and were degassed by freeze-pump-thaw cycles. Dye 14 (200 mg, 229 μmol. Supplemental Information), dye 13 (178 mg, 229 μmol. Supplemental Information) and the palladium catalyst (1.9 mg, 1.6 µmol, Supplemental Information) were placed in a 25 mL round bottom flask and fitted with a septum. Then 1-methyl-2pyrrolidone (5 mL), tetrahydrofuran (3 mL) and an aqueous saturated sodium hydrogen carbonate solution (2 mL) were added via syringe. The reaction mixture was heated to 80 °C for 7 d, while an intensively coloured powder precipitated. After reaction, the solvent was completely removed under vacuum and the residue was dissolved in chloroform (100 mL). This organic layer was washed with water (2  $\times$  50 mL) and brine (50 mL), concentrated under reduced pressure to 2-5 mL and added drop wise to ethanol (250 mL) under vigorously stirring. A very fine crystalline powder precipitated and was filtered. TSQ 5 (0.19 g, 0.31 mmol per formal unit, 68%) was obtained after drying at 40 °C under reduced pressure. d.p. 282 °C. MS (MALDI-TOF): 2828 (9) [P-Ligand-(dye unit)4-boronic acid ester + Na], 2572 (12) [H-(dye unit)4-boronic acid ester + Na], 2208 (34) [P-Ligand-(dye unit)3-boronic acid ester + Na], 2145 (13) [boronic acid ester-(dye unit)3-boronic acid ester], 2017 (100) [Br-(dye unit)3-Br], 1890 (62) [H-(dye unit)3-H+Na]. *X*<sub>n</sub>: 3–4.

### 2.2.16. 4-((7-((3-((1,1-Dimethyl-3-octyl-1H-benzo[e]indolium-2yl)-methylene)-2-oxido-4-oxocyclobut-1-enyl)methylene)-1,1,3,6,6,8-hexamethyl-7,8-dihydro-indolo[7,6-g]indol-2-(1H,3H,6H)-ylidene)-methyl)-2-((7-((3-((1,1-dimethyl-3-octyl-1Hbenzo[e]indol-2-(3H)-ylidene)-methyl)-2-oxido-4-oxocyclobut-2enylidene)-methyl)-1,1,3,6,6,8-hexamethyl-1,6-dihydroindolo[7,6-g] indol-3,8-diium-2-yl)-methyl))-3-oxocyclobut-1-enolate (**TSQ 6**)

Dye **36** (115 mg, 141 µmol, see 2.2.10. **BSQ 5**) and squaric acid (7 mg, 61 µmol, OChem Inc.) were suspended in benzene (5 mL), 1-butanol (5 mL), 1-methyl-2-pyrrolidinone (5 mL) and quinoline (0.1 mL) in Dean–Stark apparatus. The reaction mixture was heated to reflux for 7 d before it was poured into an ice-cold aqueous citric acid solution (5%, 250 mL). The precipitate was filtered, and then dissolved in chloroform (250 mL) which was subsequent washed with water (4 × 200 mL) and brine (2 × 200 mL). The dried organic layer was concentrated under reduced pressure to a view millilitre. The product precipitated at room temperature, was filtered and dried under reduced pressure (30 °C, 1 mbar) to yield **TSQ 6** (48 mg, 32 µmol, 52%) as golden shiny crystalline powder. d.p. 302 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  8.3–8.2 (m, 4H, H-4″, H-9″), 8.21 (d,

 ${}^{3}J = 8.3$  Hz, 2H, H-9§§), 7.94 (d,  ${}^{3}J = 7.9$  Hz, 2H, H-6§§), 7.92 (d,  ${}^{3}J = 8.5$  Hz, 2H, H-5§§), 7.62 (dd,  ${}^{3}J = 8.3$  Hz, 7.1 Hz, 2H, H-8§§), 7.55–7.5 (m, 4H, H-5", H-10"), 7.48 (dd,  ${}^{3}J = 7.9$  Hz, 7.1 Hz, 2H, H-7§§), 7.36 (d,  ${}^{3}J = 8.5$  Hz, 2H, H-4§§), 6.6–6.0 (m, 6H, H-1', H-1‡, H-1§), 4.4–4.0 (m, 16H, H-1##, H-1††, H-1\*\*), 2.1–2.0 (m, 16H, H-1#, H-2##), 2.0–1.7 (m, 28H, H-1\*, H-1†, H-3##), 1.55–1.2 (m, 16H, H-4##, H-5##, H-6##, H-7##), 0.87 (t,  ${}^{3}J = 6.8$  Hz, 6H, H-8##). For numeration see Supplemental Information. MS(MALDI): 1514 (100) [M + H]<sup>+</sup>, 1513 (56) [M]<sup>+</sup>, 1499 (14) [M + H–CH<sub>3</sub>]<sup>+</sup>, 1484 (4) [M + H–2 × CH<sub>3</sub>]<sup>+</sup>, 1100 (10) [C<sub>74</sub>H<sub>77</sub>N<sub>5</sub>O<sub>4</sub>]<sup>+</sup>, 414 (6) [C<sub>28</sub>H<sub>32</sub>NO<sub>2</sub>]<sup>+</sup>. HR-MS(MALDI): calculated for C<sub>102</sub>H<sub>108</sub>N<sub>6</sub>O<sub>6</sub> [M]<sup>+</sup>: 1512.8325. Found: 1512.8291.

#### 2.3. Molecular modelling

As a quantum mechanical modelling method, the density functional theory (DFT) was used to investigate the molecular structure and electron density contribution of all BSQs. Therefore, the B3LYP functional and the 6-31G\* basis set were used. The calculations were performed with the NWChem 5.1 program [40,41] installed on the Ipazia computing cluster at Empa [42]. Analysis of NWChem log-files and illustrations of the calculated frontier dye orbitals were performed by the program Jmol, an open-source Java viewer for chemical structures [43], with a cut off value of 0.02 per phase.

### 3. Results and discussion

### 3.1. Synthesis

The synthesis of all symmetric MSQs (Scheme 1) started from a commercial available 3H-indole derivative following the route published by Treibs and Jacob in 1968 [44]. Also others have reported on the synthesis of squaraines [45-47]. For MSQ 1, MSQ 3 and MSQ 5, the corresponding indole heterocycluses were alkylated in order to obtain the imminium derivatives. These active derivatives react with the vinylogue carboxylic acid synthon of the squaric acid under Knoevenagel conditions to the symmetric MSQ dyes. Contrary to the former synthesis, the unsymmetrical dyes, MSQ 2 and MSQ 4, were obtained following and adapting the descriptions published by Terpetschnig et al. [48,49]. Here, the use of squaric acid diethyl ester 6 was particularly advantageous for the stepwise condensation reaction of different imminium derivatives like 2 and 5. In detail, after the first condensation reaction of the indolium derivative 2 and the squaric acid diethyl ester 6, the remaining ester function was cleaved in an additional reaction step. This deprotection allowed the second condensation reaction of the brome indolium derivative 5, which is obtainable via the Fischer indole synthesis of the hydrazine **3**, and the half dye **8** yielding the unsymmetrical dye 9. Subsequent Miyaura borylation reaction followed by a Suzuki cross coupling reaction expanded dye 9 by a phenyl moiety yielding the final unsymmetrical squaraine dye MSQ 2. In analogy, the palladium catalysed derivatisation was also used for the preparation of the said symmetrical dye MSQ 3.

For the synthesis of the dimeric dyes **BSQ 1–5** (Schemes 2 and 3), several homologue half dyes and precursors were used which were exclusively described in the Supplemental Information. The bridges based on phenylene, fluorene, alkoxyphenylene, tetra-fluorphenylene synthons and the formally lateral condensed terminals were individually synthesized. For the phenylene bridge **29** (Scheme 2), the synthesis stared with a double Suzuki cross coupling reaction of benzene diboronic acid **17** and the brom indole derivative **4** to the bis indole derivative **18**. In analogy, fluorene derivative **30**, alkoxyphenylene derivative **31** and tetrafluoro phenylene derivative **32** were obtained from their corresponding

dibromo substituted aromats **19**, **24**, **26**, respectively, and the boronated indole derivative **20** [50] (Scheme 2). The dibromo centre part **24** (Scheme 2) was synthesized according to Aubert et al. [25] and the condensed middle part **33** according to Geiger et al. [28] (Scheme 2). For the final Knoevenagel type condensation reaction, all bis indol derivatives were double alkylated with methyl tosylate in order to obtain their corresponding bis imminium diion cores **29–33** (Schemes 2 and 3). In this particular case and to the best of our knowledge, bis alkylation reactions of such heterocycles with longer alkyl chains using various alkylation agents were not feasible. Subsequent condensation reaction of half dye **34** (structure shown in the Supplemental Information) and the core parts yield the symmetrical dimeric dyes **BSQ 1–5** (Scheme 3).

Elsewhere, we published the poly Knoevenagel type condensation reaction of **33** and an orthoester as well as a dianil in order to obtain oligo trimethine dyes and oligo heptamethine dyes [28]. The analogous poly condensation reaction of the core parts **29–33** and squaric acid resulted in undefined polymeric dyes which could not be characterized. Alternatively, an AA/BB type poly Suzuki cross coupling reaction was applied (Scheme 4) [51]. The functionalized squaraine dyes **12** and **13** could be polymerized among themselves and in skillful combination with the monomers **35**, **19**, **24** and **26** to the corresponding oligomers **TSQ 1–5** (Scheme 4). However, **TSQ 6** was prepared in a Knoevenagel type condensation reaction of the regioselectively produced intermediate **36** and squaric acid.

### 3.2. Optical properties

In the case of polymethine dyes, the absorption maximum  $(\lambda_{max})$  is bathochromically shifted if either the number of the methine units is increased or the  $\pi$ -system of the terminating heterocyclic synthons of the dye is enlarged [16]. Formally, squaraine dyes are a combination of a polymethine structure with amine and imminium terminals and an oxocyclobutenolate core. Therefore, only the extension of their  $\pi$ -electronic system over its terminals is convenient. In this respect, the indole terminals were extended by a benzo or a phenyl moiety in symmetrical and unsymmetrical ways represented by MSQ 1-5 (Scheme 1). The baseline corrected and normalized UV-vis spectra of MSQs 1-5 in chloroform were shown in Fig. 1 and the corresponding data in Table 1. Irrespectively of the heterocyclic end terminal, one narrow, uniform shaped and intense adsorption band with an additional vibronical shoulder at lower wavelength is observable for each dye indicating a non-aggregated state in solution. This was also observed for the solvents: acetone, chlorobenzene, chloroform, decaline, 1,2-dichlorobenzene, dichloromethane, N,N-dimethylformamide, dimethyl sulfoxide, ethanol and toluene as published elsewhere [52] which was also in agreement with the solvatochromic study from a MSQ 1 derivative by Tatikolov et al. [53]. Likewise, typically high values between 300,000 and 400,000 L mol<sup>-1</sup> cm<sup>-1</sup> of the molar absorption coefficient ( $\varepsilon$ ) for MSQ 1–5 were determined. Interestingly, the absorption maxima of the dyes MSQ 2–5 consisting a more extended  $\pi$ -electron system are slightly bathochromic shifted by a maximal value of  $\Delta \lambda = 28$  nm (MSQ 5) in comparison to MSQ 1 as reference dye. Here, the enlargement of a squaraine dye at its heterocyclic terminal is less effective in comparison to the addition of a methine unit to the cyanine dye chromophore core where a bathochromic shift of 100 nm for  $\lambda_{\text{max}}$  could be expected [16].

In order to quantify the influence of additional  $\pi$ -electrons and to get more detailed information about the structure property relation of the monomeric squaraine dyes, the effective total number of  $\pi$ -electron pairs (EP<sub>eff</sub>) outside the chromophore core was calculated. The EP<sub>eff</sub> values were calculated with equation I for the benzo, the phenyl, and the thiophene terminal of a literature



Fig. 1. Baseline corrected and normalized UV–vis spectra of A) MSQ 1, 2, 3, 4 and 5; B) BSQ 1, 2, 3, 4 and 5; C) TSQ 1, 2, 3, 4, 5 and 6 measured in chloroform.

Table 1

Determined optical properties for the MSQ, BSQ, and TSQ series.

Dye	$\lambda_{max}{}^a$	$\log(\varepsilon)^{b}$	$\lambda_{onset}^{c}$	$\Delta E_{\rm opt}^{\rm d}$	$\lambda_{em}^{e}$	$\lambda_s f$	EP <sub>eff</sub> <sup>g</sup>
MSQ1	637.5	5.54	645.5	1.921	644	6.5	6
MSQ2	646.5	5.47	665.5	1.863	656	9.5	7.5
MSQ3	658.5	5.6	680	1.824	667.5	9	9.1
MSQ4	650	5.53	668.5	1.855	657.5	7.5	8
MSQ5	665.5	5.52	684	1.813	672	6.5	10
BSQ1	678	5.68	697.5	1.778	688.5	10.5	10.3
BSQ2	673	5.65	695	1.784	684	11	11.8
BSQ3	672.5	5.67	694.5	1.785	682	9.5	10.3
BSQ4	667	5.62	686	1.808	676	9	10.3
BSQ5	728.5	5.51	754	1.645	739.5	11	10
TSQ1	687.5	5.82	711	1.744	697	9.5	-
TSQ2	683.5	5.96	704	1.761	692	8.5	-
TSQ3	684.5	6.09	706	1.756	691	6.5	-
TSQ4	674	5.26	697	1.779	681	7	-
TSQ6	759.5	5.81	785.5	1.579	771	11.5	_
TSQ5	718	5.77	754.5	1.644	-	-	_

<sup>a</sup> Absorption maximum determined in chloroform.

<sup>b</sup> Molar absorption coefficient determined from the absorbance for a molar concentration (c ~  $10^{-6}$  mol dm<sup>-3</sup>) of the dyes with a path length of 1 cm at  $\lambda_{max}$ .

<sup>c</sup> Onset absorption edge at higher wavelengths determined in chloroform.

<sup>d</sup> Optical band gap  $E_{opt}$  (eV) =  $hc\lambda_{onset}^{-1}$  = 1239.83  $\lambda_{onset}^{-1}$ .

<sup>e</sup> Emission maximum determined in chloroform.

<sup>f</sup> Stockes shift determined in chloroform,  $\lambda_s = \lambda_{em} - \lambda_{max}$ .

<sup>g</sup> Effective total number of  $\pi$ -electron pairs  $E_{\text{eff}}$  (see equation I.).

known dye [54] in order to proof the later correlation. In detail, EP<sub>eff</sub> is the sum of all  $\pi$ -electron pairs ( $E_i$ ) of the entire terminals corrected by the cosine square function ( $\cos^2$ ) of their torsion angle ( $\varphi$ ) relative to the planar chromophore  $\pi$ -electron system [55]. The  $\varphi$  value for the benzo terminal in **MSQs 4** and **5** was set to zero. The  $\varphi$  value of 44.4° for the phenylene terminal in **MSQs 2** and **3** for bisphenyl molecules was assumed.

$$E_{eff} = \sum_{i=1}^{j} E_i \cdot \cos^2\left(\varphi\right)$$

Fig. 2 shows the plot of the seven EP<sub>eff</sub> values of the MSQs against their  $\lambda_{max}$  values demonstrating the strong linear correlation,  $\lambda_{max} = 7 \cdot \text{EP}_{eff} + 595$  nm, with a coefficient of determination ( $R^2$ ) of 0.994. This implies that by simple counting of the electron pairs outside the resonance system between donor and acceptor the  $\lambda_{max}$  value in chloroform of any structural similar squaraine dye could be calculated. In order to validate the correlation,  $\lambda_{max}$  values of both thiophene terminated squaraine dyes (structure shown in Fig. 2) were calculated with  $27^{\circ} \varphi$  value [56] of the thiophene terminal. For squaraine dye with one thiophene terminal:  $E_{eff} = 8.4$  resulting  $\lambda_{max}$ (calculated) = 654 nm, and for squaraine dye with two thiophene terminals:  $E_{eff} = 10.8$  and  $\lambda_{max}$ (calculated) = 671 nm. The calculated values of  $\lambda_{max}$  are in a very good agreement with the reported  $\lambda_{max}$  values, 652 nm and 669 nm, measured in chloroform [54].

The correlation also implies that with decreasing torsion angle the bathochromic shift of the  $\lambda_{max}$  value increases for both hetero and hydrocarbon cyclic terminals. Moreover, the correlation underlines a synthetic strategy towards far red absorbers and tunable  $\lambda_{max}$  values.

Following the strategy of coupled dyes mentioned by Kiprianov [26] in order to achieve far red absorption with dimers, squaraine dye dimers **BSQ 1–5** were synthesized and UV–vis spectra were then recorded in chloroform. Similar to **MSQ 1–5**, again characteristic adsorption bands with high molar extinction coefficients were observed for the dimers **BSQ 1–5** (Fig. 1B and Table 1). In the case of **BSQ 1–4**, the influence of the electronegativity of the distorted bridge between the two chromophore units was also studied and compared with the planar bridge in **BSQ 5**.



**Fig. 2.** Correlation of the  $\lambda_{\text{max}}$  values with the effective total number of  $\pi$ -electron pairs outside the chromophore (EP<sub>eff</sub>) of the **MSQs 1–5(** $\blacksquare$ ) and two published dyes (calculated: $\star$ , measured: $\bullet$ ) [54].

In analogy to the monomeric dyes **MSQ 2–5**, the  $\lambda_{max}$  values of BSQ 1-4 are again slightly bathochromic shifted of around  $\Delta \lambda = 40$  nm with regard to  $\lambda_{max}$  of **MSQ 1**. Here, the influence of the phenylene, fluorene, methoxy phenylene or tetrafluoro phenylene bridge on the bathochromy of the absorption of the whole dimer is almost negligible small. This is reasoned in the distortion of the bridge against the dye units. In contrary,  $\lambda_{max}$  of **BSQ 5** is bathochromical shifted of  $\Delta \lambda = 91$  nm to 730 nm compared to the reference dye MSQ 1 indicating a strong interaction between the dye units. Furthermore, multiple absorption bands at lower wavelength, here,  $\lambda = 730$  nm and 635 nm each with the corresponding vibronical shoulder at 679 nm and 578 nm, respectively, were observed (Fig. 1B). This interaction could be seen as a filled-filled interaction of the two dye units which result in lower and higher energy transition. Such interactions were studied by Kiprianov using cyanine dyes [26]. He reported that a lower energy transition (bathochromic shift of  $\lambda_{max}$ ) dominates for serial linked dimeric dyes and a higher energy transition (hypsochromic shift of  $\lambda_{max}$ ) for parallel linked dimeric dyes. From the molecular structural point of view, BSQ 5 consists of two formally condensed dye units forming a fully planar and conjugated junction with the shortest possible distance in-between. This, in turn, indicates a further synthetic strategy for effective coupling of dye units resulting maximum bathochromy by using planar and conjugated heterocyclic structures.

In general, if oligomeric or polymeric dyes were synthesized an even further red shift of the  $\lambda_{max}$  value based on multiple dye–dye interaction is expected. Although, the chromophores **TSQ 1–4** were supplemented by at least one more dye unit no reasonable additional bathochromic shift (max.  $\Delta \lambda = 50$  nm) of their  $\lambda_{max}$  values with regards to **MSQ 1** was observed. Even here, the effective coupling of these dyes is prevented by the high rotational degree of freedom of the bridge units. If this degree of freedom is reduced, like in **TSQ 5**, a significant red shift of 81 nm to a  $\lambda_{max}$  value of 718 nm in chloroform was observed. Moreover, the specially prepared and flat trimer, **TSQ 6**, showed a near infra-red (NIR) absorption band at 760 nm which is 122 nm red shifted compared to the reference dye (Fig. 1C and Table 1).

At this point the question arose, if a polymeric dye structure would push the absorption maximum further towards higher wavelengths and where are the limitations? According to the theoretical investigations of Meier et al. [17] on D- $(\pi)_n$ -A dye

666

systems, the maximal reachable absorption maximum  $(\lambda_{\infty})$  for structural similar dye series (DS) will be reached after five to ten repeating units. The basis for Meier's investigation was a fitted exponential growth function of which the effective number of repeating units ( $n_{\text{eff}}$ ) was determined according to the following formulae [II. and III.]:

$$\lambda_{\max}(n) = \lambda_{\infty} - (\lambda_{\infty} - \lambda_1) \cdot e^{-b \cdot (n-1)}$$
 II

$$n_{\rm eff} = 1 + \ln(\lambda_{\infty} - \lambda_1)/b$$
 III

In our work, the parameters of the general exponential growth function (II.) were determined by fitting the  $\lambda_{max}$  values, measured in chloroform, of the structure analogue dyes versus the number of dye units (*n*) [57]. For the equation DS1 the phenylene bridged dyes **MSQ 3**, **BSQ 1** and **TSQ 1** were used; for equation DS2 the fluorine bridged dyes **MSQ 3**, **BSQ 2** and **TSQ 2** were used; for equation DS3 the thiophene bridged dyes reported by Scherrer et al. [54] were used, for equation DS4 the direct linked dyes **MSQ 3**, **TSQ 6** and a 43-mer from Völker et al. [58] were used; and for equation DS5 the planar bridged dyes **MSQ 5**, **BSQ 5**, **BSQ 5** and **TSQ 6** were used. The corresponding functions were listed below (IV. to VIII.) and were shown in Fig. 3.

$$DS1 : \lambda_{max}(n) = 696.5 - (696.5 - 658.5) \cdot e^{-0.719 \cdot (n-1)}$$
  
with  $n_{eff} = 6$  IV

DS2 : 
$$\lambda_{max}(n) = 711 - (711 - 658.5) \cdot e^{-0.323 \cdot (n-1)}$$
  
with  $n_{eff} = 13$  V

DS3:
$$\lambda_{\max}(n) = 730 - (730 - 635) \cdot e^{-0.740 \cdot (n-1)}$$
 with  $n_{\text{eff}} = 7$  VI

DS4: 
$$\lambda_{\max}(n) = 738 - (738 - 658.5) \cdot e^{-0.692 \cdot (n-1)}$$
 with  $n_{\text{eff}} = 7$ 

DS5 : 
$$\lambda_{max}(n) = 789.5 - (789.5 - 666.5) \cdot e^{-0.709 \cdot (n-1)}$$
  
with  $n_{eff} = 8$  VIII

At infinite repeating units the theoretical maximal achievable value of the absorption maximum,  $\lambda_{\infty}$ , is at approximately 700 nm for DS1 and DS2 indicating that the two torsions between the dye units with an angle of 44.4° prevent the chromophore interaction

in a similar way. As discussed above, by reducing the torsion angle or the distance between dye units the  $\lambda_{\infty}$  value rose consistently to a maximal value of about 790 nm in the planar bridged case. Furthermore, the thereto determined  $n_{\text{eff}}$  values for DS1–5 were between 6 and 13 repeating units. For DS1–4, where chromophore units are distorted the  $\lambda_{\infty}$  value is smaller than the  $\lambda_{\text{max}}$  value of the planar bridged **TSQ 6**. In other words, "polymerization" of dye units in order to reach a maximal bathochromic shift ( $\Delta\lambda$ ) yielded only a third to a quarter of  $\Delta\lambda$  in comparison to the achievable  $\Delta\lambda$  when changing from dimer to trimer or oligomer. In that context, dimerization reactions of dyes using rigid and planar fully conjugated bridges are to be preferred considering possible issues, e.g. bad solubility of high molecular weight polymers.

### 3.3. Electrochemical properties

In addition to results of the UV-vis measurements, cyclic voltammetry measurements provide essential information for the structure property relation of the synthesized dyes. Their electrochemical potentials and electrical band gap ( $\Delta E_{el}$ ) correlate directly to their molecular structure. In general, for all dyes, sharp and reversible oxidation and reduction waves within the possible potential range of DMF and CHCl<sub>3</sub>, respectively, were observed. The reversibility was proven by determination of the ratio of each cathodic and anodic peak current  $(i_{pa}/i_{pc})$  which approached mostly unity (data not shown here). For reversible Nernstain waves, the formal electrode potential can be estimated as the averaged cathodic and anodic peak potential ( $E_{pc}$  and  $E_{pa}$ ). The first oxidation  $(E_{\rm ox})$  and reduction potential  $(E_{\rm red})$  of the squaraine dyes were directly influenced by the change of the  $\pi$ -electron system of the chromophore. Enlarging the dye unit itself resulted in a slightly reduction of the  $\Delta E_{el}$  value from 1.62 V to max. 1.58 V for **MSQ 5** (reference **MSQ 1**, Table 2) whereas  $E_{ox}$  was shifted to more negative and  $E_{red}$  to more positive values. Discussing a certain order of  $\Delta E_{el}$  values for the MSQ series distinguishing phenyl and benzindol derivatives is not reasonable.

The electrochemical band gaps of **BSQ 1–4** remain almost unchanged at approx. 1.57 V with regards to **MSQ 5** (Table 2). Here, the effect of all bridges is negligible indicating a nonexistent coupling which is in agreement to the results of the UV–vis measurements. Remarkably, both potentials of **BSQ 4** were shifted towards more positive values (+0.77 V for  $E_{ox}$  and -0.81 V for  $E_{red}$ )



Fig. 3. Calculated growth function based on the absorption maxima from the corresponding dye series DS1 (phenylene bridged), DS2 (fluorene bridged), DS3 (thiophene bridged [54]), DS4 (direct linked) and DS5 (lateral junction).

### Table 2

Determined and calculated electrochemical properties for the reported squaraine dyes.

Dye	Solvent	$E_{\rm ox}^{a}$	$E_{\rm red}^{\rm b,c}$	$\Delta E_{el}^{c}$	$\Delta E_{\rm opt}$
MSQ 1	DMF	0.75	-0.87	1.62	1.88
MSQ 2	DMF	0.75	-0.86	1.61	1.84
MSQ 3	CHCl <sub>3</sub>	0.75	$-0.86^{*}$	1.62*	1.82
MSQ 4	DMF	0.74	-0.86	1.59	1.84
MSQ 5	DMF	0.73	-0.85	1.58	1.80
BSQ 1	DMF	0.73	-0.85	1.57	1.76
BSQ 2	DMF	0.73	-0.84	1.57	1.78
BSQ 3	DMF	0.74	-0.84	1.58	1.77
BSQ 4	DMF	0.77	-0.81	1.58	1.79
BSQ 5	DMF	0.71	-0.82	1.53	1.63
TSQ 1	CHCl <sub>3</sub>	0.80	$-0.82^{*}$	1.54*	1.74
TSQ 2	CHCl <sub>3</sub>	0.78	-0.83*	1.56*	1.76
TSQ 3	CHCl <sub>3</sub>	0.79	$-0.84^{*}$	1.58*	1.78
TSQ 4	CHCl₃	0.92	-0.83*	1.56*	1.76
TSQ 5	CHCl₃	0.82	$-0.77^{*}$	1.59*	1.64
TSQ 6	CHCl <sub>3</sub>	0.80	$-0.74^{*}$	1.38*	1.58

<sup>a</sup> First oxidation potential.

<sup>b</sup> First reduction potential.

<sup>c</sup> Calculated properties marked with an asterisk.

due to the electron withdrawing properties of the fluorine atoms of the bridge. Finally, as it could be expected from UV–vis measurement, a noticeable reduction of the  $\Delta E_{el}$  value to 1.53 V could be observed for the lateral connected **BSQ 5**. The electrochemical band

gap is reduced by 90 mV compared to the band gap of **MSQ 1** again indicating the effective coupling of dye units over planar and conjugated heterocycle.

Due to the reduced potential range of chloroform, only the oxidation potentials of the TSQ series could be determined. Furthermore, beside a linear correlation of the optical and the electrochemical described by Loudfy et al. [59], a linear correlation was found for the oxidation and reduction potential of the MSQ and BSQ series when  $\Delta E_{el}$  was plotted versus their  $E_{red}$  and  $E_{ox}$  values (see also Supplemental Information):

$$E_{\rm ox} = 0.49 \cdot \Delta E_{\rm el} - 0.033 \approx 0.49 \cdot \Delta E_{\rm opt} - 0.131$$
 IX

$$E_{\rm red} = -0.51 \cdot E_{\rm el} - 0.033 \approx -0.51 \cdot E_{\rm opt} + 0.069$$
 X

Applying these correlations of equation IX and X, the missing reduction potentials for the TSQ series could be estimated (Table 2, calculated data were marked with an asterisk). In analogy to the BSQ series, the electrochemical band gaps of the **TSQ 1–4** were narrowed insignificantly indicating again the nonexistent coupling of the bridges. In turn, the influence of the fluorinated bridge of **TSQ 4** caused a more positive oxidation level at 0.92 V. For the fully planar and conjugated trimer **TSQ 6**, the lowest at  $\Delta E_{el}$  at 1.38 V could be estimated following the tendency of **MSQ 5** and **BSQ 5**. In contrast to **BSQ 5**, only the reduction level of **TSQ 6** was lowered and its oxidation level remained unchanged.



Fig. 4. Geometrically optimized molecular structures of BSQ 1-5 (top), the frontier orbital LUMO (middle) and HOMO (down).

668

Additionally, the discussed relation between the electrochemical and the optical properties can be used to estimate the minimal achievable  $\Delta E_{el}$  in a polymeric material with a theoretical maximal achievable value of the absorption maximum ( $\lambda_{max} \sim \lambda_{\infty}$ ). As discussed above,  $\lambda_{\infty}$ , value of the planar bridged DS5 was 790 nm of which  $\Delta E_{opt}$  was estimated to be around 1.52 V. For the theoretical polymeric dye with lateral bridge the electrochemical potentials can be estimated by applying above-mentioned equations resulting  $E_{red} \sim -0.71$  V and  $E_{ox} \sim 0.61$  V with  $\Delta E_{el} \sim 1.32$  V. That implies that only an insignificant narrowing of the electrical band gap of 0.24 V could be expected in a structure analogue polymeric material as **TSQ 6**.

### 3.4. Analysis of the dye structure – molecular modelling

The optical and electrochemical properties of the squaraine dyes originate from their molecular structure and configuration as well as the position of their frontier orbitals. The *in silico* study of the dyes allows obtaining a deeper understanding of the structure property relation. Representatively, the molecular structures of **BSQ1–5** were optimized by adapting the Density Functional Theory (DFT) with B3LYP functional and 6-31G\* as a basis set [12,40,41]. In order to reduce calculation time, long alkyl chains were reduced to methyl groups. Fig. 4 presents one possible optimized conformation of each dye of the BSQ series which will be discussed. The molecules and frontier orbitals were plotted with a cut off value of 0.02 per phase [43].

Generally, all single squaraine dye units exhibit a planar molecular structure with  $\pi$ -electron orbitals mainly located inbetween the amine and imminium terminals at its HOMO and LUMO level. Now, if the dye units are joined together, the  $\pi$ -electron system is influenced depending on the structure of the aromatic moieties and the relative position to the dye units. As it is expected from the results of the UV–vis and cyclic voltammetry measurements, it is distinguished between **BSQ 1–4** and **BSQ 5**. One the one side, phenylene, fluorene, methoxy phenylene and tetrafluoro phenylene bridges (**BSQ 1–4**) are distorted under a certain angle ( $\varphi$ ) against the squaraine units (Table 3). On the other side, the molecular structure of the condensed system, **BSQ 5**, is fully planar over the dye units including the bridge.

Furthermore independently of their molecular structure, there is nearly no electron density contribution at the distorted bridges indicating the absence of a linear combination of the  $\pi$ -orbitals of bridge and dye unit. Therefore, only the individual dye unit itself contributes to the absorption. It could be assumed that this caused the relatively small bathochromic shift of the  $\lambda_{max}$  value and negligible change of the electrochemical potentials.

Contrary, the flat dye, **BSQ 5**, showed a homogenous distribution of the frontier orbitals over the entire molecule at HOMO and LUMO level. The molecule can be considered as one dye with one large  $\pi$ -electron system which is in agreement to the observed

#### Table 3

Torsion angle ( $\varphi$ ) between chromophore and bridge determined from the optimized molecular structure. The  $\varphi$  values are in agreement to the previous assumed value of 44.4° in the calculation with the MSQs.

Dye	$\phi(dye-bridge)$
BSQ1	36°
BSQ2	37°
BSQ3	<b>41</b> °
BSQ4	<b>41</b> °
BSQ5	<b>0</b> °

narrower electrical band gap and bathochromic shift of the absorption maximum.

### 4. Conclusions

Several synthetic strategies and basic molecular principles were followed in order to arrive at dyes with far red or even NIR absorption properties. Finally, we successfully synthesized a comprehensive series of new squaraine dyes. Starting from the origin squaraine dye, **MSQ 1**, the molecular dye structure was expanded stepwise in an unsymmetrical and symmetrical way with either additional benzo or phenyl mojeties resulting in the MSO 1-5 series. As another synthetic strategy, the **BSQ 1–5** series was obtained by bridging the origin squaraine dye with phenylene, fluorene, methoxy phenylene and tetrafluoro phenylene moieties or direct condensation reaction. For the oligomer series TSQ 1–5, an analogous bridging strategy was adapted. To what extend the various molecular dye structures influence their absorption properties was studied with UV-vis measurements. While slightly enlarging of the  $\pi$ -electron system (MSQ 2–4) or dimers/oligomers with distorted bridges (BSQ 1–4, TSQ 1-4) even resulted in minor bathochromic shifts of the absorption maxima of the dyes, fully planar molecular structures (MSQ 5, BSQ 5 and TSQ 6) represented the most effective way in order to reach far red adsorption. Theoretical investigations applying Kiprianov's theory of coupled dyes support the results of the UV-vis measurements. Furthermore, with regard to Meyer's theory of the limiting values, an effective number of repeating units for the TSQ series of six to twelve could be specified where the highest possible absorption maximum could be achieved. For the electrical properties of all dyes, same trends for the electrochemical potentials and electrical band gaps were observed. Here again, the lowest electrical band gaps for the dyes MSQ 5, BSQ 5 and TSQ 6 were determined. Finally, calculated molecular structures and frontier orbitals of exemplarily the BSQ series verify the results of the optophysical and electrochemical studies.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.dyepig.2012.06.017.

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