Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Supporting Information

Exciton Coupling Effects on the Two–Photon Absorption of Squaraine Homodimers with Varying Bridge Units.

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Contents

1 Synthetic Procedures

Compounds **SQA**[1], **dSQA-1**[2], **dSQA-2**[3], **dSQA-6**[4] and precursor **SQA-Br**[1] were synthesized as described in the given literature.

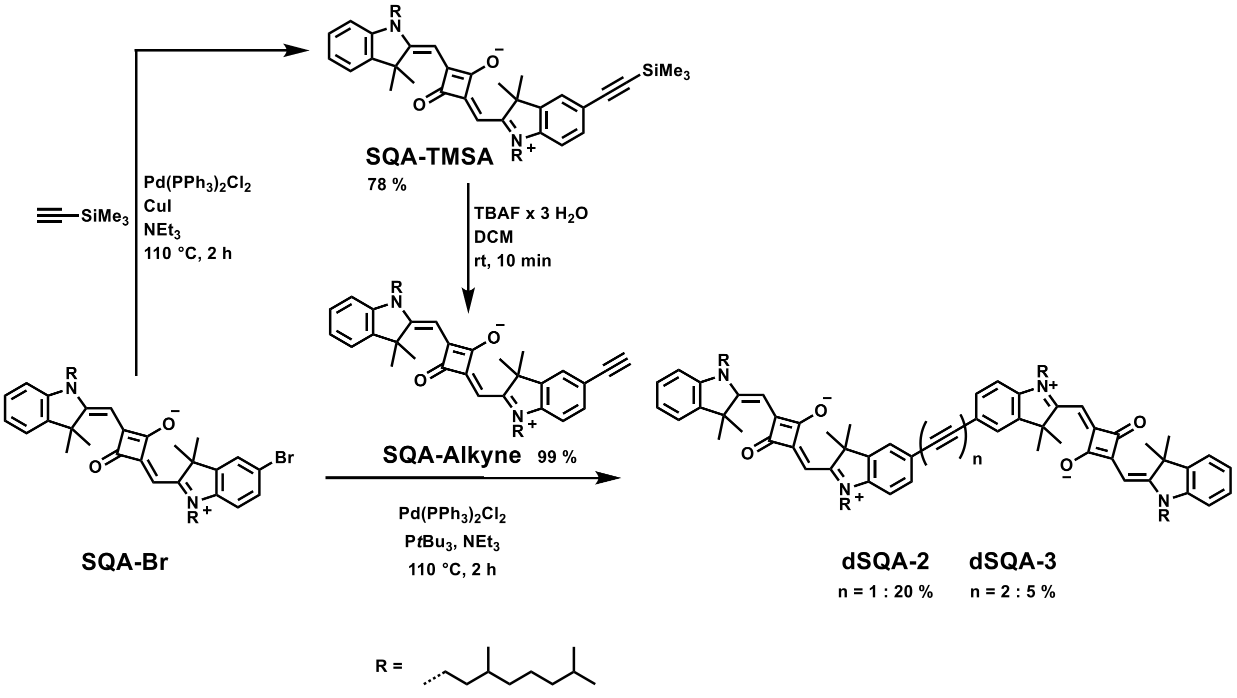


Figure S1. Synthesis of squaraine dimers **dSQA-2** and **dSQA-3**.

The terminal alkyne squaraine **SQA-Alkyne** was coupled with the brominated squaraine **SQA-Br** in a modified copper-free Sonogashira coupling reaction using Pd(PPh$_3$)Cl$_2$ and P*t*Bu$_3$ to favour the formation of **dSQA-2** as outlined in Figure S1.[5] In addition, the alkyne derivative was added dropwise to the reaction mixture over a long period of time (~ 45 min) in a highly diluted manner. Separation of **dSQA-2** and the Glaser coupling byproduct **dSQA-3** was not feasible by flash column chromatography. Yet, it could effectively be separated by preparative GPC.

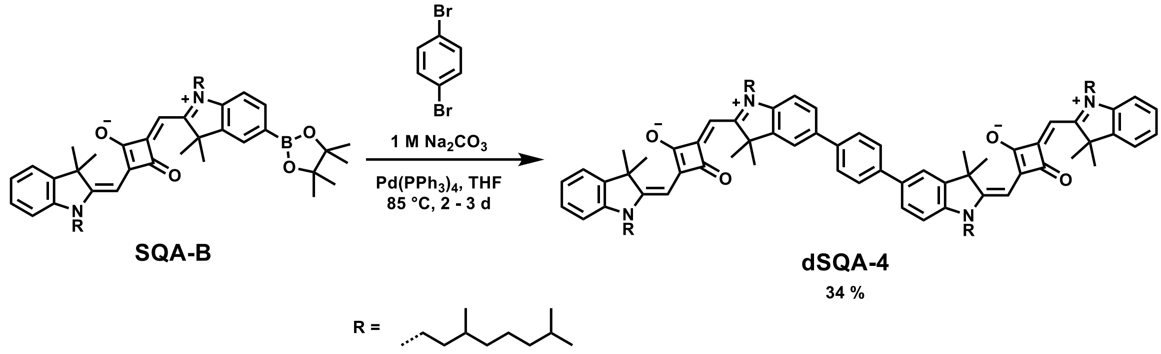


Figure S2: Synthesis of squaraine dimer **dSQA-4**.

Commercial 1,4-dibromobenzene was coupled with the boronic ester derivative **SQA-B** to give the homodimer **dSQA-4** in 34 % yield (Figure S2).

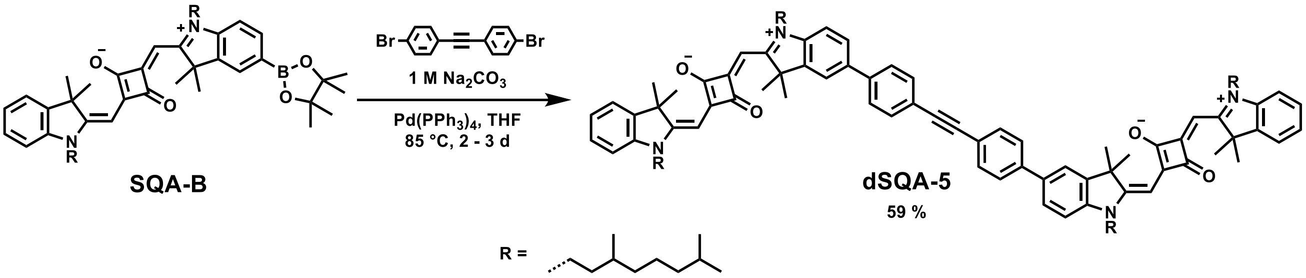


Figure S3: Synthesis of squaraine dimer **dSQA-5**.

The Suzuki coupling reaction of commercially available 1,2-bis(4-bromophenyl)ethyne as spacer substrate was performed under aqueous conditions in THF using a slight excess of borylated squaraine **SQA-B** (Figure S3). By this means, the homodimer **dSQA-5** was obtained in good yields of almost 60 %.

1.1 Experimental Section

NMR-Spectroscopy

- Avance III HD 400 FT-Spectrometer (^{1}H: 400.13 MHz, ^{13}C: 100.61 MHz) with a Bruker Ultrashield magnet
- Avance III HD 400 FT-Spectrometer (^{1}H: 400.03 MHz, ^{13}C: 100.59 MHz) with a Bruker Ascend magnet
- Avance III HD 600 FT-Spectrometer (^{1}H: 600.13 MHz, ^{13}C: 150.90 MHz) with an Oxford Instrument magnet
- Avance III HD 600 FT-Spectrometer (^{1}H: 600.43 MHz, ^{13}C: 150.98 MHz) with a Bruker Ascend magnet

^{1}H and ^{13}C spectra were recorded with one of the spectrometers listed above using high sample concentration of > 0.1 mM in CD_2Cl_2. The deuterated solvent was used without further purification. ^{1}H chemical shifts are indicated in ppm relative to the residual non-deuterated solvent signal (^{1}H: CH_2Cl_2: δ 5.32 ppm; ^{13}C: CH_2Cl_2: δ 53.84 ppm).[6] The abbreviations used for the spin multiplicities and C-atom descriptions are: s = singlet, d =doublet, m = multiplet, dd = doublet of doublet, ddd = doublet of doublet of doublet; prim = primary, sec =secondary, tert =tertiary, quart =quaternary. Multiplet signals or overlapping multiplet signals in ^{1}H-NMR spectra which could not be assigned to first order couplings are indicated as (-). The coupling constants are given in Hertz (Hz). Order of description for ^{1}H-NMR spectra: chemical shift (spin multiplicity, coupling constant, number of protons, assignment).

Mass Spectroscopy

- Bruker Daltonics microTOF focus (ESI)
- Bruker Daltonics autoflex II (MALDI)

Mass spectra were recorded with a Bruker Daltonics autoflex II (MALDI) in positive mode (POS) utilizing a DCTB (*trans*-2-[3-(4-*tert*-butylphenyl)-2-methyl-2-propenyl-idene]malononitrile) matrix. High resolution mass spectrometry was performed on a Bruker Daltonic microTOF focus (ESI). All mass spectrometry peaks are reported as m/z. For calculation of the respective mass values of the isotopic distribution, the software Compass 1.1 from Bruker Daltonics GmbH (Bremen, Germany) was used. Calculated (calc.) and measured (found) peak values always refer to the most intense peak of the isotopic distribution.

Recycling Gel Permeation Chromatography (GPC)

Shimadzu GPC System

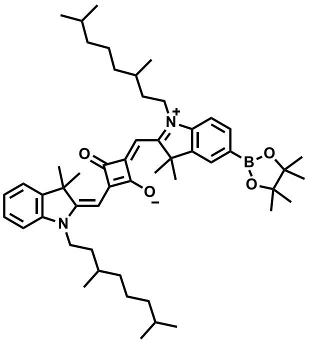
- Model SPD-M20A diode array detector
- CBM-20A system controller
- LC-20AD solvent delivery unit
- DGU 20A9 online degasser

Gel permeation chromatography (GPC) was carried out at 293 K in chloroform (HPLC grade). Preparative chromatography was performed in recycling mode on two consecutive SDV columns (PSS preparative 50 Å and 500 Å, dimensions 20 × 600 mm) from PSS (Mainz, Germany) with a flow rate of 1 and 4 ml min^{-1}.

1.2 Synthesis

All reactions were carried out in standard glassware and chemicals purchased from commercial suppliers were used without further purification. All reactions being conducted under nitrogen atmosphere were performed in oven-dried vessels. The solvents were dried according to standard literature procedures and stored under nitrogen atmosphere. The nitrogen was dried over Sicapent® from Merck and oxygen was removed by copper oxide catalyst R3-11 from BASF. Flash column chromatography was carried out on silica gel (60 Å, 40 - 63 µm, Macherey-Nagel “Silica 60 M”) in glass columns.

SQA-B



Synthesis based on literature.[1]

Under a nitrogen atmosphere squaraine **SQA-Br** (810 mg, 1.07 mmol), bis(pinacolato)diboron (381 mg, 1.50 mmol) and KOAc (335 mg, 3.41 mmol) were suspended in dry 1,4-dioxane (15 ml). The mixture was purged in a gentle stream of nitrogen for 15 min. $Pd(PhCN)_2Cl_2$ (21.0 mg, 54.7 µmol) and 1,1´-bis(diphenylphosphino)ferrocene (dppf) (30.0 mg, 54.1 µmol) were added and the reaction was continuously heated at 85 °C in a sealed tube for 18 h. The solvent was removed *in vacuo* and the residue purified by flash chromatography (PE/EA 1:1). The crude product was dissolved in a small amount of DCM and dripped into an excess of *n*-hexane. The mixture was allowed to stand at 4 °C in the refrigerator overnight. The precipitate formed was separated by filtration and dried under high vacuum.

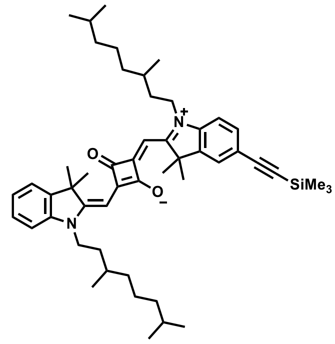
Yield: 773 mg (963 µmol, 90 %) of a blue solid.
$C_{52}H_{75}BN_2O_4$ [802.98]

^{1}H-NMR (400.1 MHz, CD_2Cl_2):
δ [ppm] = 7.78 (dd, ^3J = 8.0 Hz, ^4J = 1.2 Hz, 1H, C*H*), 7.76-7.73 (m, 1H, C*H*), 7.36 (dd, ^3J = 7.7 Hz, ^4J = 0.9 Hz, 1H, C*H*), 7.31 (ddd, ^3J = 7.7 Hz, ^3J = 7.7 Hz, ^4J = 1.0 Hz, 1H, C*H*), 7.15 (ddd, ^3J = 7.5 Hz, ^3J = 7.5 Hz, ^4J = 0.7 Hz, 1H, C*H*), 6.97 (d, ^3J = 8.3 Hz, 1H, C*H*), 6.93 (d, ^3J = 8.3 Hz, 1H, C*H*), 5.98 (s, 1H, C*H*), 5.96 (s, 1H, C*H*), 4.07-3.92 (-, 4H, 2 × NCH_2), 2.08-1.89 (-, 2H, 2 × NCH_2CH), 1.85-1.46 (-, 18H, 2 × NCH_2CH, 4 × C*H*, 4 × CH_3), 1.36 (s, 12H, 4 × CH_3), 1.42-1.10 (-, 12H, 6 × CH_2), 1.05 (d, ^3J = 5.7 Hz, 3H, CH_3), 1.03 (d, ^3J = 5.7 Hz, 3H, CH_3), 0.87 (d, ^3J = 6.4 Hz, 6H, 2 × CH_3), 0.86 (d, ^3J = 6.4 Hz, 6H, 2 × CH_3).

^{13}C-NMR (100.6 MHz, CD_2Cl_2):
δ [ppm] = 182.0 (2 × quart), 181.8 (quart), 180.1 (quart), 170.7 (quart), 169.4 (quart), 145.5 (quart), 142.73 (quart), 142.70 (quart), 141.8 (quart), 135.3 (tert), 128.4 (tert), 128.2 (tert), 124.2 (tert), 124.0 (quart), 122.6 (tert), 109.9 (tert), 109.0 (tert), 87.2 (tert), 87.0 (tert), 84.2 (quart), 49.7 (quart), 49.2 (quart), 42.5 (sec), 42.3 (sec), 39.5 (2 × sec), 37.5 (2 × sec), 34.1 (sec), 34.0 (sec), 31.50 (tert), 31.48 (tert), 28.4 (2 × tert), 27.2 (prim), 27.0 (prim), 25.08 (2 × sec), 25.06 (prim), 22.8 (prim), 22.7 (prim), 19.78 (prim), 19.77 (prim).

MALDI-MS pos: $[M^{\cdot+}]$
calc.: 802.976 m/z
found: 802.625 m/z

SQA-TMSA



Synthesis based on literature.[7]

Under a nitrogen atmosphere squaraine **SQA-Br** (364 mg, 482 µmol) was dissolved in dry NEt_3 (15 ml). The deep blue solution was degassed in a gentle stream of nitrogen for 20 min. CuI (2.76 mg, 14.5 µmol), $Pd(PPh_3)_2Cl_2$ (10.2 mg, 14.5 µmol), and trimethylsilylacetylene (267 µl, 1.92 mmol) were subsequently added and the reaction mixture was heated under reflux for 2 h. After cooling to room temperature the solvent was removed *in vacuo* and the residue was subjected to a rapid silica filtration (DCM/MeOH = 99:1).

Yield: 290 mg (375 µmol, 78 %) of a blue solid.
$C_{51}H_{72}N_2O_2Si$ [773.22]

^{1}H-NMR (400.1 MHz, CD_2Cl_2):

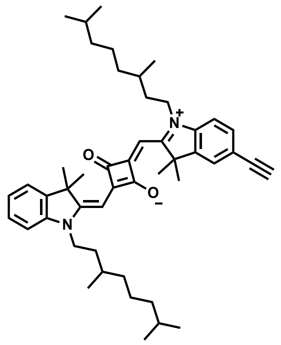
δ [ppm] = 7.45-7.36 (-, 3H, 3 × C*H*), 7.33 (ddd, ^3J = 7.7 Hz, ^3J = 7.7 Hz, ^4J = 1.2 Hz, 1H, C*H*), 7.18 (ddd, ^3J = 7.4 Hz, ^3J = 7.4 Hz, ^4J = 0.8 Hz, 1H, C*H*), 7.04 (d, ^3J = 7.9 Hz 1H, C*H*), 6.90 (dd, ^3J = 8.6 Hz, ^4J = 0.6 Hz, 1H, C*H*), 5.96 (s, 1H, C*H*), 5.90 (s, 1H, C*H*), 4.13-4.00 (m, 2H, NCH_2), 4.00-3.80 (m, 2H, NCH_2), 1.88-1.69 (-, 14H, 2 × NCH_2CH, 4 × CH_3), 1.69-1.59 (-, 4H, 2 × NCH_2CH, 2 × C*H*), 1.59-1.48 (-, 2H, 2 × C*H*), 1.45-1.13 (-, 12H, 6 × CH_2), 1.09-1.02 (-, 6H, 2 × CH_3), 0.90-0.82 (-, 12H, 4 × CH_3), 0.25 (s, 9H, $Si(CH_3)_3$).

^{13}C-NMR (100.6 MHz, CD_2Cl_2):

δ [ppm] = 181.9 (2 × quart), 181.8 (quart), 179.4 (quart), 171.3 (quart), 168.8 (quart), 144.2 (quart), 143.2 (quart), 142.8 (quart), 142.6 (quart), 132.3 (tert), 128.2 (tert), 126.1 (tert), 124.5 (tert), 122.6 (tert), 117.9 (quart), 110.1 (tert), 109.3 (tert), 105.5 (quart), 94.2 (quart), 87.3 (2 × tert), 49.9 (quart), 49.1 (quart), 42.6 (sec), 42.4 (sec), 39.5 (2 × sec), 37.5 (2 × sec), 34.2 (sec), 34.0 (sec), 31.49 (tert), 31.47 (tert), 28.4 (2 × tert), 27.2 (prim), 27.0 (prim), 25.1 (2 × sec) 22.8 (prim), 22.7 (prim), 19.8 (2 × prim), 0.04 (prim).

MALDI pos: $[M^{\cdot+}]$
calc.: 773.536 m/z
found: 772.549 m/z

SQA-Alkyne



Synthesis based on literature.[8]

A mixture of squaraine **SQA-TMSA** (290 mg, 375 mmol) and tetrabutylammonium fluoride trihydrate (829 mg, 2.63 mmol) in DCM (15 ml) was stirred at ambient temperature for 10 min. The reaction was diluted with DCM (20 ml) and washed with H_2O (2 × 20 ml). The organic phase was dried over $MgSO_4$ and evaporated under reduced pressure. The crude product was used without further purification.

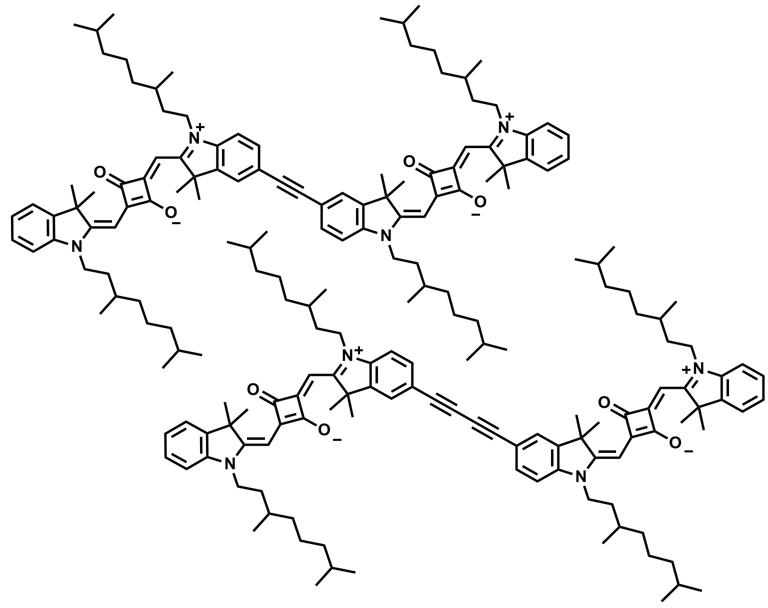
Yield: 261 mg (372 mmol, 99%) of a blue solid.
$C_{48}H_{64}N_2O_2$ [701.04]

^{1}H-NMR (400.1 MHz, $CDCl_3$):
δ [ppm] = 7.46-7.41 (-, 2H, 2 × C*H*), 7.37 (dd, ^3J = 7.4 Hz, ^4J = 0.8 Hz, 1H, C*H*), 7.33 (ddd, ^3J = 7.7 Hz, ^3J = 7.7 Hz, ^4J = 1.2 Hz, 1H, C*H*), 7.17 (ddd, ^3J = 7.5 Hz, ^3J = 7.5 Hz, ^4J = 0.7 Hz, 1H, C*H*), 7.00 (d, ^3J = 7.8 Hz, 1H, C*H*), 6.86 (d, ^3J = 8.6 Hz, 1H, C*H*), 6.00 (s, 1H, C*H*), 5.95 (s, 1H, C*H*), 4.15-3.83 (-, 4H, 2 × NC*H*$_2$), 3.10 (s, 1H, ≡C*H*), 1.85-1.69 (-, 12H, 4 × C*H*$_3$), 1.68-1.56 (-, 6H, 2 × NCH$_2$C*H*$_2$, 2 × C*H*), 1.55-1.44 (-, 2H, 2 × C*H*), 1.44-1.11 (-, 12H, 6 × C*H*$_2$), 1.08-1.00 (-, 6H, 2 × C*H*$_3$), 0.89-0.83 (-, 12H, 4 × C*H*$_3$).

^{13}C-NMR (100.6 MHz, CD_2Cl_2):
δ [ppm] = 182.2 (2 × quart), 182.1 (quart), 179.6 (quart), 171.2 (quart), 168.5 (quart), 143. 5 (quart), 142.8 (quart), 142.6 (quart), 142.5 (quart), 132.6 (tert), 128.2 (tert), 126.3 (tert), 124.4 (tert), 122.6 (tert), 116.6 (quart), 110.1 (tert), 109.2 (tert), 87.3 (tert), 87.2 (tert), 84.1 (tert), 77.0 (quart), 49.9 (quart), 49.0 (quart), 42.6 (sec), 42.3 (sec), 39.5 (2 × sec), 37.4 (2 × sec), 34.2 (sec), 34.0 (sec), 31.50 (tert), 31.47 (tert), 28.4 (2 × tert), 27.2 (prim), 27.0 (prim), 25.1 (2 × sec), 22.8 (prim), 22.7 (prim), 19.7 (2 × prim).

MALDI-MS pos: [$M^{\cdot+}$]
calc.: 700.036 m/z
found: 700.488 m/z

dSQA-2 and dSQA-3



Under a nitrogen atmosphere functionalized squaraine dye **SQA-Br** (623 mg, 824 µmol) was dissolved in dry NEt_3 (25 ml). The deep blue solution was degassed in a gentle stream of nitrogen for 20 min. P*t*Bu_3 (1 M in solution, 35.3 µl, 35.3 µmol) and $Pd(PPh_3)_2Cl_2$ (24.8 mg, 35.3 µmol) were subsequently added and the mixture was heated to 60 °C. A degassed solution of **SQA-Alkyne** (413 mg, 589 µmol) in dry NEt_3 (30 ml) was carefully added dropwise over a period of 45 min. After complete addition, the reaction mixture was heated to reflux for 2 h. The solvent was removed *in vacuo* and the residue purified by flash chromatography (DCM/MeOH = 99:1). Preparative recycling GPC ($CHCl_3$) was used to separate both compounds **dSQA-2** and **dSQA-3**. Each batch was finally recrystallized from *n*-hexane.

dSQA-2:

<u>Yield</u>: 163 mg (118 µmol, 20 %) of a blue powder.
$C_{94}H_{126}N_4O_4$ [1376.03]

^{1}H-NMR (600.1 MHz, CD_2Cl_2):

δ [ppm] = 7.53-7.46 (-, 4H, 4 × C*H*), 7.39 (d, ^3J = 7.4 Hz, 2H, 2 × C*H*), 7.36-7.30 (m, 2H, 2 × C*H*), 7.22-7.13 (m, 2H, 2 × C*H*), 7.04 (d, ^3J = 7.3 Hz, 2H, C*H*), 6.96 (d, ^3J = 7.3 Hz, 2H, 2 × C*H*), 5.96 (s, 2H, 2 × C*H*), 5.91 (s, 2H, 2 × C*H*), 4.23-3.80 (-, 8H, 4 × NCH_2), 1.85-1.71 (-, 28H, 4 × NCH$_2$C*H*, 8 × CH_3), 1.68-1.57 (-, 8H, 4 × NCH$_2$C*H*, 4 × C*H*), 1.57-1.49 (-, 4H, 4 × C*H*), 1.44-1.13 (-, 24H, 12 × CH_2), 1.10-1.03 (-, 12H, 4 × CH_3), 0.87 (d, ^3J = 6.6 Hz, 12H, 4 × CH_3), 0.86 (d, ^3J = 6.7 Hz, 12H, 4 × CH_3).

^{13}C-NMR (150.9 MHz, CD_2Cl_2):

δ [ppm] = 182.0 (2 × quart), 181.6 (quart), 179.6 (quart), 171.0 (quart), 168.5 (quart), 143.1 (quart), 142.8 (quart), 142.7 (quart), 142.3 (quart), 131.8 (quart), 128.1 (tert), 125.6 (tert), 124.3 (tert), 122.7 (tert), 122.5 (tert), 110.0 (tert), 109.5 (tert), 90.0 (quart), 87.4 (tert), 87.2 (tert), 49.8 (quart), 49.1 (quart), 42.6 (2 × sec), 39.5 (2 × sec), 37.5 (2 × sec), 34.1 (2 × sec), 31.5 (2 × tert), 28.4 (2 × tert), 27.2 (2 × prim), 27.0 (2 × prim), 25.1 (2 × sec), 22.8 (2 × prim), 22.7 (2 × prim), 19.8 (2 × prim).

ESI-MS pos (high resolution): $[MH^{\cdot+}]$

calc.: 1376.9885 m/z

found: 1376.9904 m/z *Δ* = 1.38 ppm

dSQA-3:

Yield: 44.0 mg (31.4 µmol, 5 %) of a blue powder.

$C_{94}H_{126}N_4O_4$ [1400.06]

^{1}H-NMR (600.1 MHz, CD_2Cl_2):

δ [ppm] = 7.52-7.46 (-, 4H, 4 × C*H*), 7.40 (dd, ^3J = 7.4 Hz, ^4J = 0.6 Hz, 2H, 2 × C*H*), 7.34 (ddd, ^3J = 7.7 Hz, ^3J = 7.7 Hz, ^4J = 1.2 Hz, 2H, 2 × C*H*), 7.19 (ddd, ^3J = 7.4 Hz, ^3J = 7.7 Hz, ^4J = 0.7 Hz, 2H, 2 × C*H*), 7.06 (d, ^3J = 8.0 Hz, 2H, 2 × C*H*), 6.92 (d, ^3J = 8.2 Hz, 2H, 2 × C*H*), 5.98 (s, 2H, 2 × C*H*), 5.91 (s, 2H, 2 × C*H*), 4.15-4.00 (m, 4H, 2 × NCH_2), 4.00-3.86 (m, 4H, 2 × NCH_2), 1.87-1.70 (-, 28H, 4 × NCH_2CH, 8 × CH_3), 1.68-1.58 (-, 8H, 4 × NCH_2CH, 4 × C*H*), 1.56-1.50 (-, 4H, 4 × C*H*), 1.45-1.13 (-, 24H, 12 × CH_2), 1.10-1.02 (-, 12H, 4 × CH_3), 0.87 (d, ^3J = 6.6 Hz, 12H, 4 × CH_3), 0.86 (d, ^3J = 6.6 Hz, 12H, 4 × CH_3).

^{13}C-NMR (150.9 MHz, CD_2Cl_2):

δ [ppm] = 181.9 (2 × quart), 179.2 (quart), 171.5 (quart), 167.9 (quart), 143.9 (quart), 142.82 (quart), 142.77 (quart), 142.6 (quart), 133.2 (tert), 128.2 (tert), 126.5 (tert), 124.5 (tert), 122.7 (tert), 116.0 (quart), 110.2 (tert), 109.3 (tert), 87.6 (tert), 87.4 (tert), 82.8 (quart), 74.2 (quart), 50.0 (quart), 48.9 (quart), 42.7 (sec), 42.3 (sec), 39.52 (sec), 39.51 (sec), 37.5 (sec), 37.4 (sec), 34.2 (sec), 34.0 (sec), 31.50 (tert), 31.47 (tert), 28.4 (2 × tert), 27.3 (prim), 26.93 (prim)*, 26.92 (prim)*, 25.08 (sec), 25.07 (sec), 22.82 (prim)*, 22.81 (prim)*, 22.72 (prim), 19.8 (prim), 19.7 (prim).

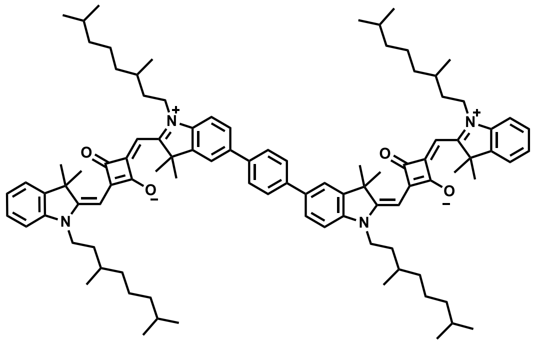
* The signal of the primary C-atoms splits into two signals of equal intensity.

ESI-MS pos (high resolution): $[M^{\cdot+}]$

calc.: 1399.98067 m/z

found: 1399.97979 m/z *Δ* = 0.63 ppm

dSQA-4



Functionalized squaraine dye **SQA-B** (100 mg, 125 µmol) and 1,4-dibromobenzene (13.0 mg, 55.1 µmol) were dissolved in peroxide-free THF (8 ml) under a nitrogen atmosphere. An aqueous solution of Na_2CO_3 (1 M, 336 µl, 336 µmol) was added and the mixture was purged in a gentle stream of nitrogen for 15 min. $Pd(PPh_3)_4$ (6.54 mg, 5.66 µmol) was added and the reaction was heated at 85 °C in a sealed tube for 2 d. The solvent was removed *in vacuo* and the residue purified by flash chromatography (DCM/MeOH = 99:1) and subsequent preparative recycling GPC ($CHCl_3$). Finally, the product was dissolved in a small amount of DCM and dripped into an excess of *n*-hexane. The mixture was allowed to stand in the refrigerator at 4 °C overnight. The precipitate formed was filtered off and dried under high vacuum.

Yield: 27.0 mg (18.9 µmol, 34 %) of a blue powder.
$C_{98}H_{130}N_4O_4$ [1428.11]

^{1}H-NMR (600.1 MHz, CD_2Cl_2):

δ [ppm] = 7.73-7.72 (m, 4H, 4 × C*H*), 7.65 (d, ^4J = 1.6 Hz, 2H, 2 × C*H*), 7.63 (dd, ^3J = 8.2 Hz, ^4J = 1.8 Hz 2H, 2 × C*H*), 7.38 (dd, ^3J = 7.4 Hz, ^4J = 0.6 Hz, 2H, 2 × C*H*), 7.34 (ddd, ^3J = 7.7 Hz, ^3J = 7.7 Hz, ^4J = 1.1 Hz, 2H, 2 × C*H*), 7.20-7.13 (m, 2H, 2 × C*H*), 7.09 (d, ^3J = 8.2 Hz, 2H, 2 × C*H*), 7.02 (d, ^3J = 7.9 Hz, 2H, 2 × C*H*), 6.07-5.80 (-, 4H, 4 × C*H*), 4.21-3.84 (-, 8H, 4 × NCH_2), 1.89-1.73 (-, 28H, 4 × NCH_2CH, 8 × CH_3), 1.69-1.60 (-, 8H, 4 × C*H*, 4 × NCH_2CH), 1.57-1.49 (-, 4H, 4 × C*H*), 1.46-1.14 (-, 24H, 12 × CH_2), 1.09 (d, ^3J = 6.3 Hz, 6H, 2 × CH_3), 1.07 (d, ^3J = 6.3 Hz, 6H, 2 × CH_3), 0.88 (d, ^3J = 6.6 Hz, 12H, 4 × CH_3), 0.87 (d, ^3J = 6.7 Hz, 12H, 4 × CH_3).

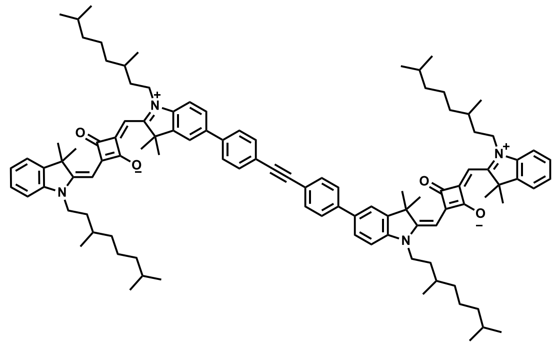
^{13}C-NMR (150.9 MHz, CD_2Cl_2):

δ [ppm] = 182.0 (2 × quart), 180.9 (quart), 180.0 (quart), 170.2 (quart), 169.5 (quart), 143.4 (quart), 142.8 (quart), 142.6 (quart), 142.5 (quart), 139.8 (quart), 136.4 (quart), 128.1 (tert), 127.6 (tert), 126.9 (tert), 124.0 (tert), 122.6 (tert), 121.2 (tert), 109.9 (tert), 109.8 (tert), 87.1 (tert), 86.9 (tert), 49.64 (quart), 49.57 (quart), 42.51 (sec), 42.45 (sec), 39.54 (sec), 39.53 (sec), 37.49 (sec), 37.47 (sec), 34.14 (sec), 34.11 (sec), 31.5 (2 × tert), 28.38 (tert), 28.37 (tert), 27.3 (prim), 27.1 (prim), 25.10 (sec), 25.08 (sec), 22.83 (prim)*, 22.82 (prim)*, 22.74 (prim)*, 22.73 (prim)*, 19.80 (prim), 19.76 (prim).

* The signals of the primary C-atoms split into two signals of equal intensity.

ESI-MS pos (high resolution): $[M^{\cdot+}]$
calc.: 1428.0120 m/z
found: 1428.0111 m/z *Δ* = 0.63 ppm

dSQA-5



Under a nitrogen atmosphere functionalized squaraine dye **SQ-B** (205 mg, 255 µmol) and 1,2-bis(4-bromophenyl)ethyne (43.0 mg, 128 µmol) were dissolved in peroxide-free THF (8 ml). An aqueous solution of Na_2CO_3 (1 M, 758 µl, 758 µmol) was added and the mixture was purged in a gentle stream of nitrogen for 15 min. $Pd(PPh_3)_4$ (15.0 mg, 13.0 µmol) was added and the reaction was heated at 85 °C in a sealed tube for 2 d. The solvent was removed *in vacuo* and the residue purified by flash chromatography (DCM/MeOH = 99:1) and subsequent preparative recycling GPC ($CHCl_3$). Finally, the product was dissolved in a small amount of DCM and dripped into an excess of *n*-hexane. The mixture was allowed to stand in the refrigerator at 4 °C overnight. The precipitate formed was filtered off and dried under high vacuum.

Yield: 116 mg (75.9 µmol, 59 %) of a shiny purple solid.
$C_{106}H_{134}N_4O_4$ [1528.23]

^{1}H-NMR (600.1 MHz, CD_2Cl_2):
δ [ppm] = 7.68-7.57 (-, 12H, 12 × C*H*), 7.38 (d, ^3J = 7.1 Hz, 2H, 2 × C*H*), 7.36-7.30 (m, 2H, 2 × C*H*), 7.22-7.12 (m, 2H, 2 × C*H*), 7.08 (d, ^3J = 6.7 Hz, 2H, 2 × C*H*), 7.02 (d, ^3J = 6.7 Hz, 2H, 2 × C*H*), 6.10-5.72 (-, 4H, 4 × C*H*), 4.50-3.70 (-, 8H, 4 × NCH_2), 1.92-1.70 (-, 28H, 4 × NCH_2CH, 8 × CH_3), 1.69-1.60 (-, 8H, 4 × NCH_2CH, 4 × C*H*), 1.57-1.48 (-,4H, 4 × C*H*), 1.45-1.15 (-, 24H, 12 × CH_2), 1.11-1.04 (-, 12H, 4 × CH_3), 0.87 (d, ^3J = 6.6 Hz, 12H, 4 × CH_3), 0.86 (d, ^3J = 6.6 Hz, 12H, 4 × CH_3).

^{13}C-NMR (150.9 MHz, CD_2Cl_2):
δ [ppm] = 182.0 (2 × quart), 181.4 (quart), 180.1 (quart), 170.4 (quart), 169.3 (quart), 143.4 (quart), 142.78 (2 × quart), 142.77 (quart), 141.0 (quart), 136.0 (quart), 132.4 (2 × tert), 128.1 (tert), 127.1 (2 × tert), 127.0 (tert), 124.1 (tert), 122.6 (tert), 122.2 (quart), 121.2 (tert), 109.9 (2 × tert), 90.4 (quart), 87.2 (tert), 87.0 (tert), 49.7 (quart), 49.5 (quart), 42.5 (2 × sec), 39.5 (2 × sec), 37.5 (2 × sec), 34.1 (2 × sec), 31.5 (2 × tert), 29.380 (tert), 29.377 (tert), 27.3 (prim), 27.1 (prim), 25.1 (2 × sec), 22.8 (prim), 22.7 (prim), 19.80 (prim), 19.77 (prim).

ESI-MS pos (high resolution): [$M^{\cdot+}$]
calc.: 1528.0433 m/z
found: 1528.0447 m/z Δ = 0.92 ppm

2 Linear Optical Spectroscopy

2.1 Steady–State UV/vis Absorption Spectroscopy

All squaraine dyes were dissolved in toluene (Uvasol from Merck, solvent for spectroscopic studies) and all measurements were performed in 10 mm standard quartz cuvettes. The UV/vis absorption spectra were measured using a Jasco V670 UV/vis/NIR spectrometer and an Agilent Technologies Cary 5000 UV/vis/NIR spectrometer.

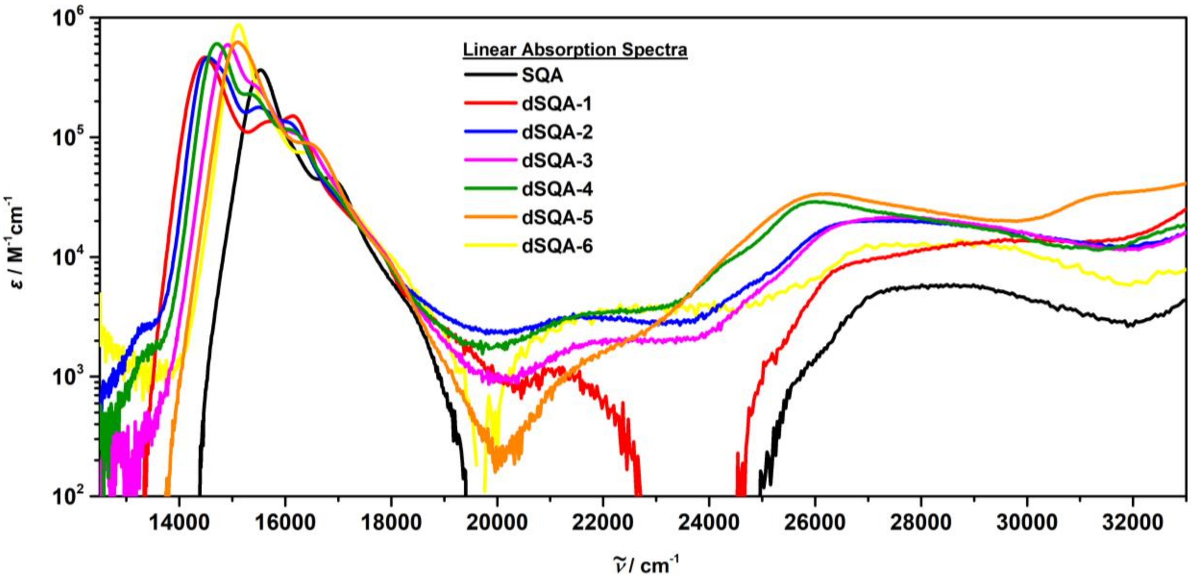


Figure S4. Extended linear absorption spectra of monomer **SQA** and of homodimers **dSQA-1** – **dSQA-6** in toluene.

2.2 Steady-State and Time Resolved Fluorescence Spectroscopy

The steady–state and time dependent fluorescence emission measurements were performed with an Edinburgh Instruments FLS980 spectrometer. The samples were strongly diluted (OD < 0.05 @ $\lambda_{\max}$) in order to prevent self-absorption in 10 mm standard quartz cuvettes.

For the steady–state fluorescence measurements a 450 W Xenon lamp was used as excitation source and a R928P PMT cooled detector. Time-correlated single photon counting was used in order to measure the fluorescence lifetimes of the dimers. The samples were excited by pulsed laser diodes at 15200 cm^{-1} and 12800 cm^{-1} under magic angle conditions. The fluorescence was detected with a H10720 high-speed PMT detector. The instrument response function was determined by using a scattering solution consisting of colloidal silicon in deionized water (LUDOX). Lifetimes were determined using the FAST software (version 3.4.2) by fitting with an (multi-)exponential decay function. The resulting expectation value is:

$$\bar{\tau}_{\mathrm{fl}} = \frac{a_1\tau_1^2 + a_2\tau_2^2}{a_1\tau_1 + a_2\tau_2} \qquad \textbf{(S1)}$$

where a_n are the amplitudes and the corresponding lifetimes τ_n. The time constants from biexponential fit with the relative amplitudes, the average fluorescence lifetimes, and the square of the fluorescence transition moments of parent squaraine **SQA** and squaraine dimers are summarized in Table S1.

Table S1. The fluorescence lifetimes τ_{fl} with the relative amplitudes in parentheses, the average fluorescence lifetimes values $\bar{\tau}_{\mathrm{fl}}$ and the square of the fluorescence transition moments μ_{fl}^2 of **SQA** and squaraine dimers in toluene.

	$\boldsymbol{\tau_{\mathrm{fl}}}$ / ns (a_n)	$\boldsymbol{\bar{\tau}_{\mathrm{fl}}}$ / ns	$\boldsymbol{\mu_{\mathrm{fl}}^2}$ / D^2
SQA	0.25 (0.09) 1.71 (0.91)	1.69	114
dSQA-1	1.22 (0.53) 2.14 (0.47)	1.78	172
dSQA-2	0.80 (0.22) 1.84 (0.78)	1.73	168
dSQA-3	0.63 (0.06) 1.61 (0.94)	1.59	168
dSQA-4	0.57 (0.13) 1.70 (0.87)	1.64	164
dSQA-5	0.27 (0.07) 1.66 (0.93)	1.64	147
dSQA-6	0.37 (0.02) 1.34 (0.98)	1.33	177

2.3 Fluorescence Quantum Yields

The fluorescence quantum yields were measured using an integrating sphere combined with the FLS980 spectrometer applying the method of Bardeen et al.[9] The observed photoluminescence quantum yield Φ_{obs}, corrected for self-absorption by using the equation:

$$\Phi_{fl}=\frac{\Phi_{obs}}{1 - \alpha + (\alpha\Phi_{obs})} \qquad (\mathbf{S2})$$

where α is the probability of self-absorption of an emitted photon and is dependent on the overlap of the absorption and emission spectra.

2.4 One-Photon Fluorescence Excitation Anisotropy (1P-FEA)

The fluorescence excitation anisotropy measurements with FLS980 spectrometer were conducted using two motorized polarisers for excitation and detection. The compounds were dissolved in highly viscus polyTHF (M_n~650) in 10 mm standard quartz cuvettes. The anisotropy values r_{1PA} are defined by[10].

$$r_{1PA}=\frac{I_{VV}\text{-}GI_{VH}}{I_{VV}+2GI_{VH}}=\frac{2}{5}\left(\frac{3\cos^2(\theta_{01})\text{ -1}}{2}\right) \qquad (\mathbf{S3})$$

Where I_{VV} and I_{VH} are the detection fluorescence intensities with excitation polariser aligned vertically and the detection polariser vertically or horizontally, respectively. G is the grating factor which is the instrument sensitivity ratio of vertically and horizontally polarised light. The r_{1PA} values range from $-0.2 \le r_{1PA} \le 0.4$ and depend on the angle θ_{01} between the absorption and emission transition dipole moments, $90° \le \theta_{01} \le 0°$. The anisotropy spectra are given in Figure S6. For the sake of comparison, the linear and two-photon spectra of all the compounds in toluene are also depicted.

3 Non-Linear Optical spectroscopy

3.1 Two-Photon Induced Fluorescence Spectroscopy

The 2PA cross-section of the chromophores was determined by the two-photon induced fluorescence technique (2PIF). It is based on relative measurements of an unknown compound (sample) with respect to a reference with well characterized 2PA cross section spectrum. A critical prerequisite is that both sample and reference are measured under identical experimental conditions. Thus, a comparison between the two samples yields the 2PA cross-section spectrum of the unknown compound free of any experimental parameters. The 2PA cross-section as a function of energy can be determined using the following equation:

$$[\sigma^{2PA}(\tilde{\nu})]_S=[\sigma^{2PA}(\tilde{\nu})]_R\frac{[\Phi(\tilde{\nu}_{em.})]_R}{[\Phi(\tilde{\nu}_{em.})]_S}\left(\frac{C_R}{C_S}\right)\frac{[I^{(2PA)}(\tilde{\nu}_{em.})]_S}{[I^{(2PA)}(\tilde{\nu}_{em.})]_R} \qquad (\mathbf{S4})$$

where indices S and R denote the sample compound and reference compound, respectively. C is the compound`s concentration and $\Phi(\tilde{\nu}_{em.})$ is the fluorescence quantum efficiency which related to the ratio between the fluorescence quantum yields of reference and sample as determined through the 2PIF apparatus. The latter helps avoiding errors due to the detection spectral response as the sample`s and reference`s emission are not always spectrally overlapping. Our experimental apparatus consists of a Solstice amplified Ti: sapphire laser from Newport Spectra-Physics operating at 1 KHz repetition rate, delivering 100 fs pulses at 800 nm. 70 % of the available energy seeds a tunable computer-driven optical parametric amplifier (TOPAS-C, Light Conversion) which produces the excitation pulses in the range of 290 – 2600 nm. A parabolic mirror with 15 cm focal length was used in order to focus the vertically polarised light ca. 10mm before the sample, while upon each acquisition the excitation energy was varied between 0.2-3 μJ. The excitation polarization and energy were controlled by using a series of three thin broadband polarisers (ColorPol® IR 1300 BC5, CODIXX AG) and a mechanical rotation mount (PR50PP, Newport). Maintenance of identical excitation conditions for both samples and the reference standard was achieved using a high precision motorized rotation stage (URS75BPP, Newport). The excitation pulse’s average power was monitored during acquisition using an IR photodetector (PD300-IR, Ophir) coupled to an optical power meter (StarLite, Ophir). The emitted fluorescence signal was collected at 90° using an achromatic lens and then direct to a compact CCD spectrometer (QE65000, Ocean Optics) for detection. Verification of the quadratic dependence between the excitation power and emitted fluorescence is shown in Figure S5. The differential quantum efficiency was obtained by the emission spectra for reference standards and samples in one-photon excitation in the two-photon spectrometer. LDS698 and Styryl 9M in $CHCl_3$ were used as reference compounds.[11, 12] All samples were placed in10 mm quartz cuvettes and the molecular concentration was in the range $10^{-5} – 10^{-6}$ M.

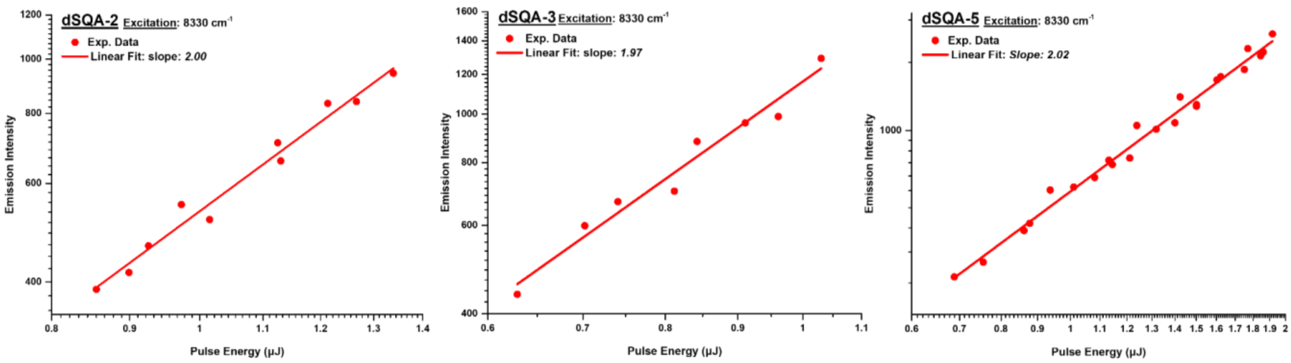


Figure S5. Power dependence of fluorescence signal in the 2PA cross-section measurments of homodimers **dSQA-2**, **dSQA-3**, and **dSQA-5** at 8330 cm^{-1}.

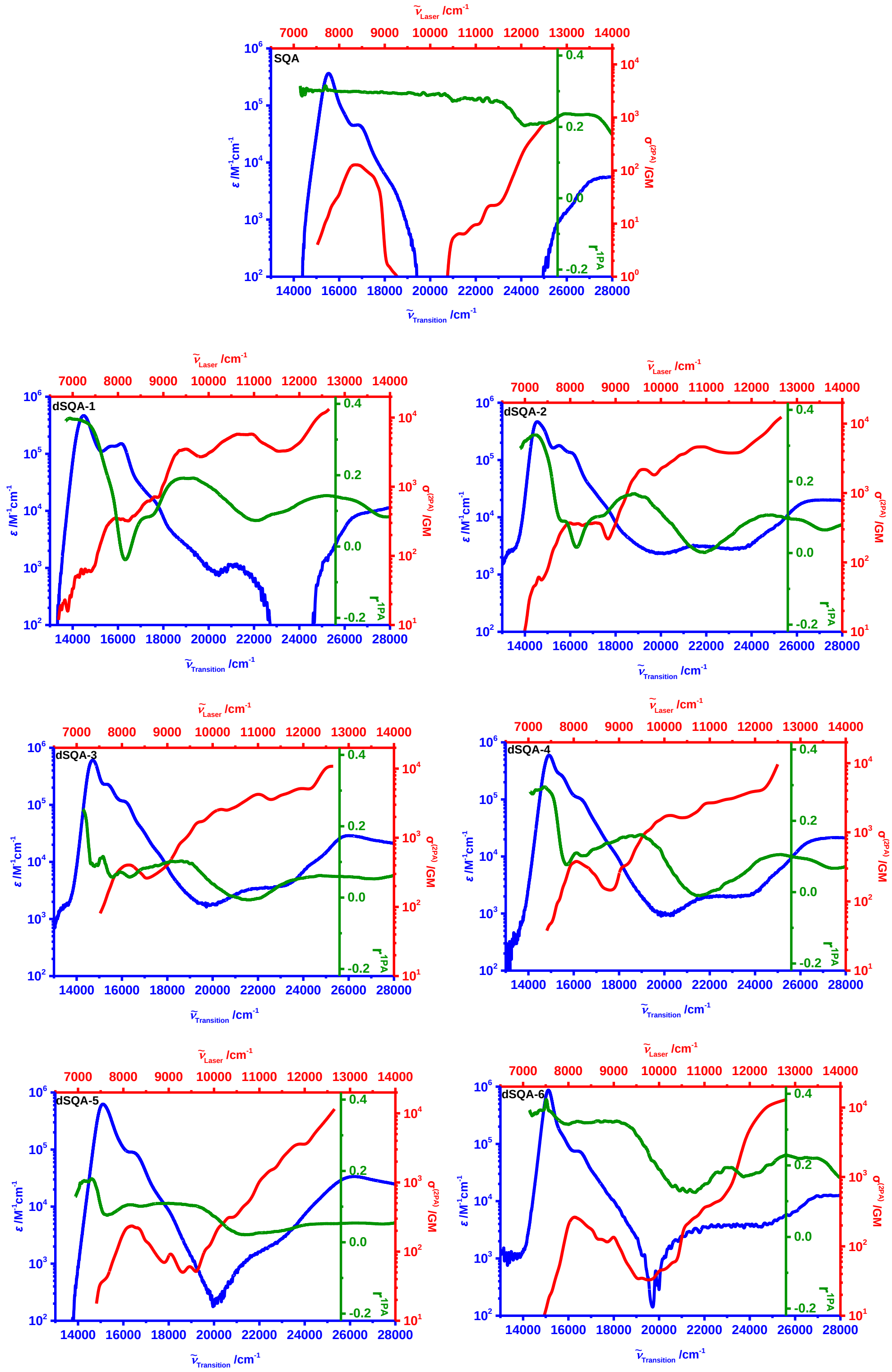


Figure S6. A comparison of the 1PA (blue line), 2PA spectra (red line) and 1P-FEA (green line) of the investigated squaraines in toluene.

3.2 Two-Photon Absorption Polarization Ratio

Additional information can be gained by measuring the two-photon polarization ratio $\left(\Omega^{(2PA)}\right)$ defined as: $\left[I^{(2PA)}(\tilde{\nu}_{em.})\right]_{(cir.)}/\left[I^{(2PA)}(\tilde{\nu}_{em.})\right]_{(lin.)}$. Here, $\left[I^{(2PA)}(\tilde{\nu}_{em.})\right]_{(cir.)}$ and $\left[I^{(2PA)}(\tilde{\nu}_{em.})\right]_{(cir.)}$ are the two-photon induced fluorescence signals recorded for circular and linear excitation beam, respectively, under the identical conditions. Thus, we obtained 2PA polarization dependent measurements in the 2PA induced florescence apparatus by introducing an achromatic quarter–wave plate into the excitation beam, after the focusing mirror. The polarization of the excitation laser beam was adjusted by the combination of the last polariser and the wave-plate. The wavenumber-dependent polarization ratio and the power dependence for selected squaraines can be found in Figures S7 and S8.

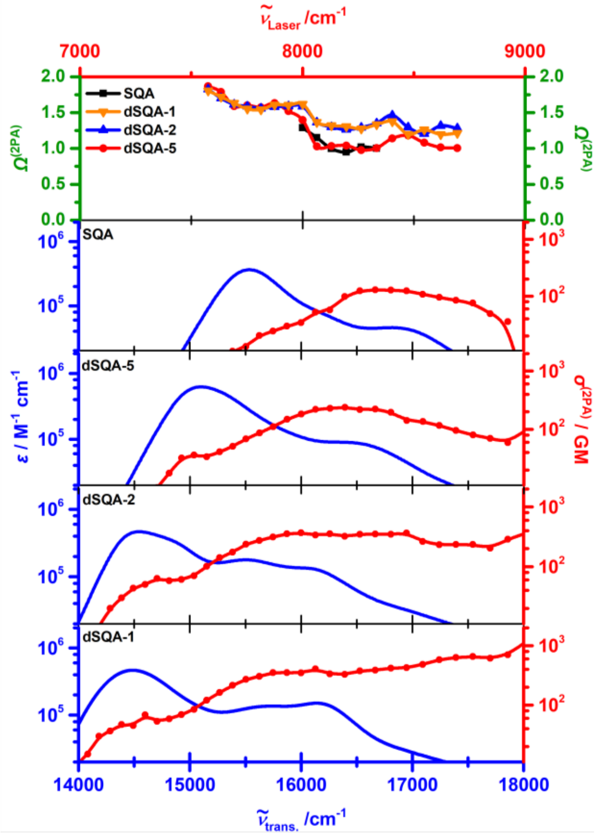


Figure S7. Two-photon absorption polarization ratio of **SQA**, **dSQA-1**, **dSQA-2** and **dSQA-5** in toluene.

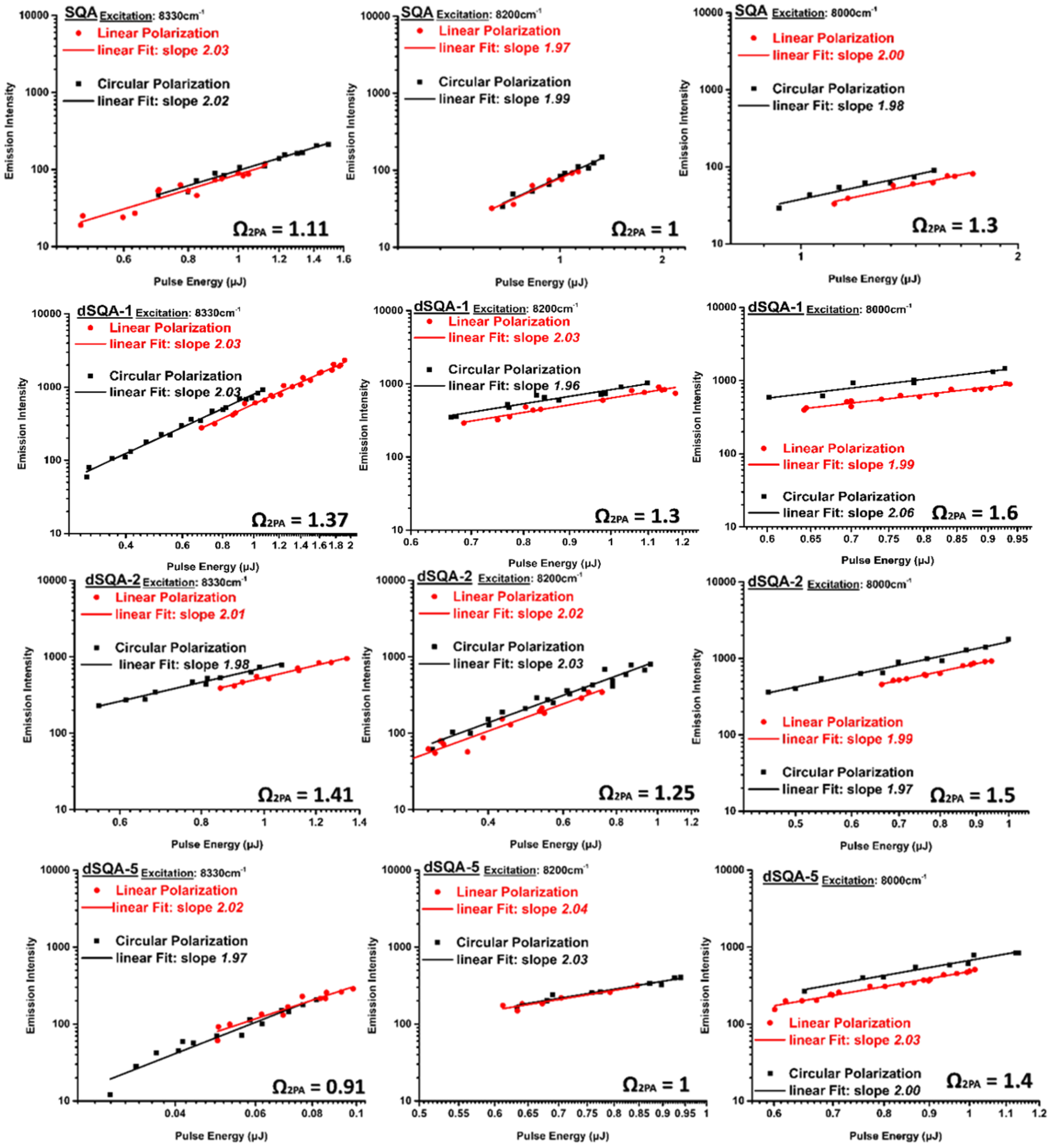


Figure S8. Power-dependent two-photon absorption polarization measurements in toluene.

3.3 Two-Photon Fluorescence Excitation Anisotropy (2P-FEA)

The two-photon excitation anisotropy measurements were recorded by the two-photon induced fluorescence spectrometer, using two thin broadband polarization filters (colorPol® IR 1300BC, CODIXX AG) for excitation and detection. The compounds were dissolved in highly viscus polyTHF (M_n~650) in 10 mm standard quartz cuvettes. The anisotropy values r_{2P} for the three-state model are defined by:

$$r_{2P}=\frac{I_{VV}\text{-}GI_{VH}}{I_{VV}+2GI_{VH}}=\frac{18\cos\left(\frac{\gamma}{2}\text{-}\alpha\right)\cos\left(\frac{\gamma}{2}+\alpha\right)\cos\gamma\text{-}7\cos^2\gamma+1}{7(2\cos^2\gamma+1)} \qquad (\mathbf{S5})$$

which depends on only two angles as depicted in Figure S9. Here γ is the angle between the transition dipole moments μ_{01} and μ_{13}. The angle α is between the bisecting line of the angle γ and the emission dipole μ_{em}.

$$\alpha = \theta_{01}\text{-}\frac{\gamma}{2} \qquad (\mathbf{S6})$$

The r_{2P} values range from $-0.29 \leq r_{2P} \leq 0.57$ and depend on the angle θ_{01} between the absorption and emission transition dipole moments, The anisotropy spectra are given in Figure S9.

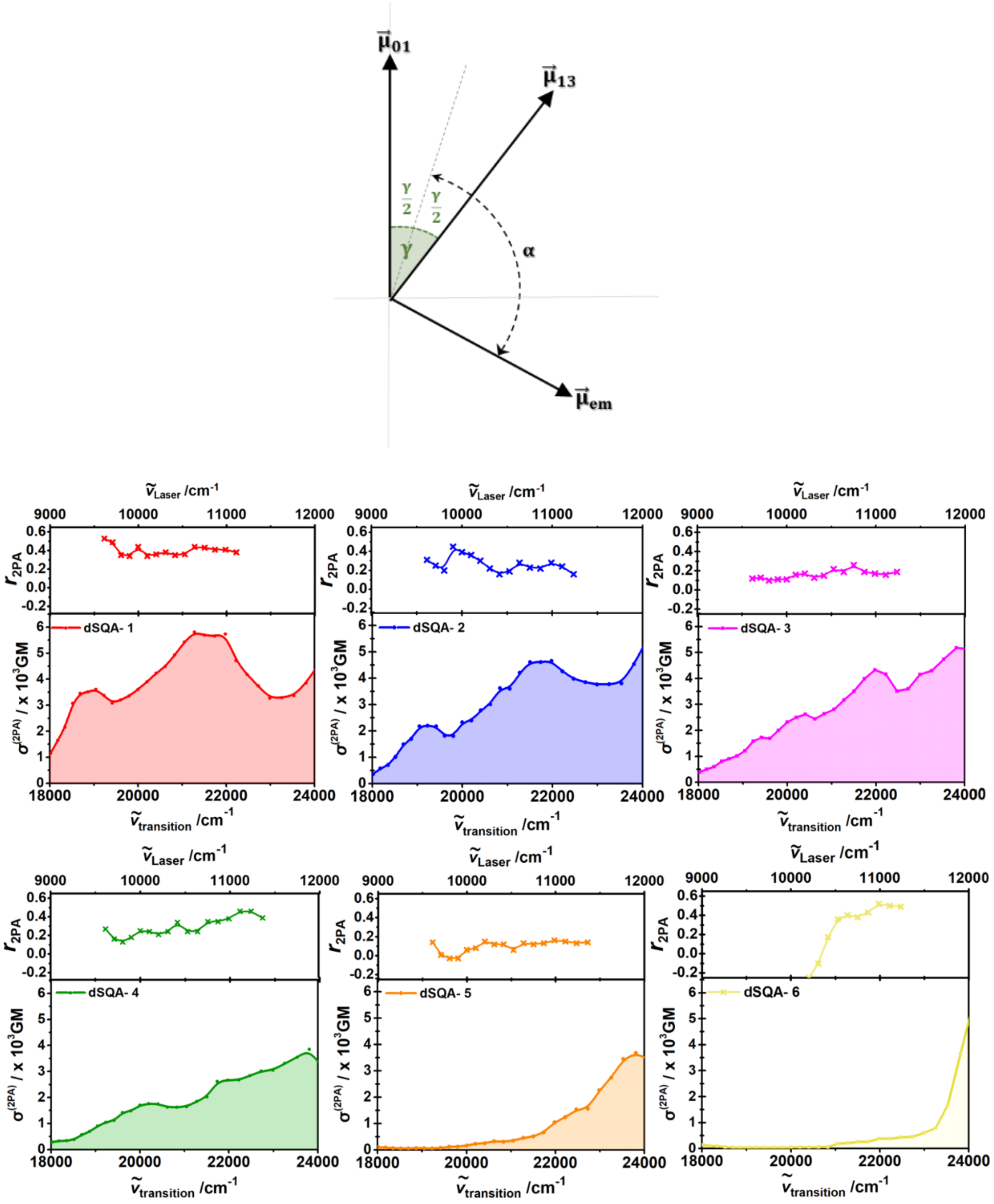


Figure S9. Schematic representation of the transition dipole moment vectors for a three-level model (left) and the two-photon excitation anisotropy spectra together with the 2PA spectra for all squaraine dimers.

4 Transition dipole moment calculations

The squared transition dipole moments μ_{01}^2 between the ground state (S_0) and the first one-photon allowed state (S_1) were obtained using the relation:

$$\mu_{01}^2 = \frac{3hc\varepsilon_0 \ln(10)}{2000\,(\pi^2)\,N_A} \frac{9n}{(n^2+2)^2} \int \frac{\varepsilon_{01}(\tilde{\nu})}{\tilde{\nu}} \mathrm{d}\tilde{\nu} \qquad (\mathbf{S7})$$

where h is the Planck´s constant, c is the speed of light, ε_0 is the vacuum permittivity, n is the refractive index of the medium, N_A is Avogadro´s number and $\varepsilon_{01}(\tilde{\nu})$ the extinction coefficient at the wavenumbers $\tilde{\nu}$. The integral is performed over the $S_1 \leftarrow S_0$ and $S_2 \leftarrow S_0$ low energy absorption bands. The squared fluorescence transition dipole moment μ_{fl}^2 of the squaraines compounds (see Table S1) were obtained by the Stricker – Berg equation[13]

$$k_{fl} = \frac{16 \times 10^6 \pi^3}{3h\varepsilon_0} \frac{n\,(n^2+2)^2}{9} \langle \tilde{\nu}_{fl}^{-3} \rangle_{av}^{-1} \mu_{fl}^2 \qquad (\mathbf{S8})$$

where $\langle \tilde{\nu}_{fl}^{-3} \rangle_{av}^{-1} = \int I_{fl}\,\mathrm{d}\tilde{\nu} / \int \tilde{\nu}_{fl}^{-3} I_{fl}\,\mathrm{d}\tilde{\nu}$ is the average cubic fluorescence energy and k_{fl} is the radiative rate constant $k_{fl} = \Phi_{fl} / \tau_{fl}$ where we used the average lifetimes from Table S1.

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