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

Electronic Supplementary Information

Cooperative Enhancement versus Additivity of Two-Photon-Absorption Cross Sections in Linear and Branched Squaraine Superchromophores

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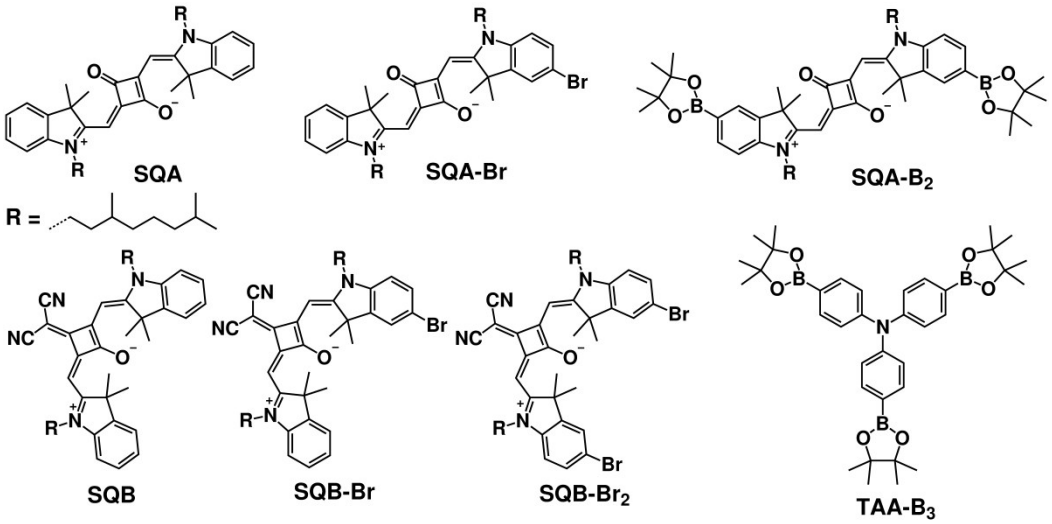
Synthetic procedures

All synthetic preparations were performed in standard glassware. The chemicals were obtained from commercial suppliers and used without further purification. Reactions under nitrogen atmosphere were performed in flame dried glassware. The nitrogen was dried over Sicapent from Merck and oxygen was removed by copper catalyst R3-11 from BASF. The solvents were dried according to standard literature procedures and stored under nitrogen. Silica gel 32-64 µm from Merck was used for flash chromatography.

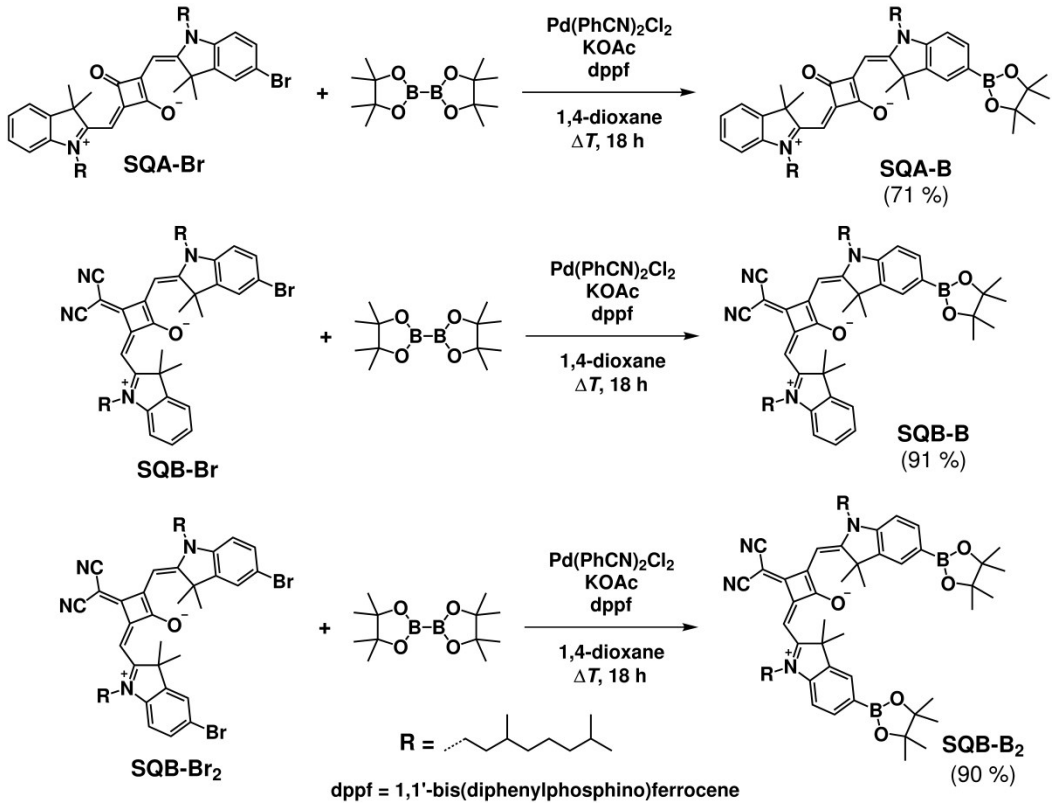


Scheme S1: Precursors **SQA-Br**, **SQA-B_2**, **SQB-Br**, **SQB-Br_2** and **TAA-B_3** and the monomeric squaraines **SQA** and **SQB**.

Compounds **SQA**[1], **SQA-Br**[2], **SQA-B_2**[1], **SQB**[3], **SQB-Br**[2], **SQB-Br_2**[3] and **TAA-B_3**[4] were synthesized according to the given literature.

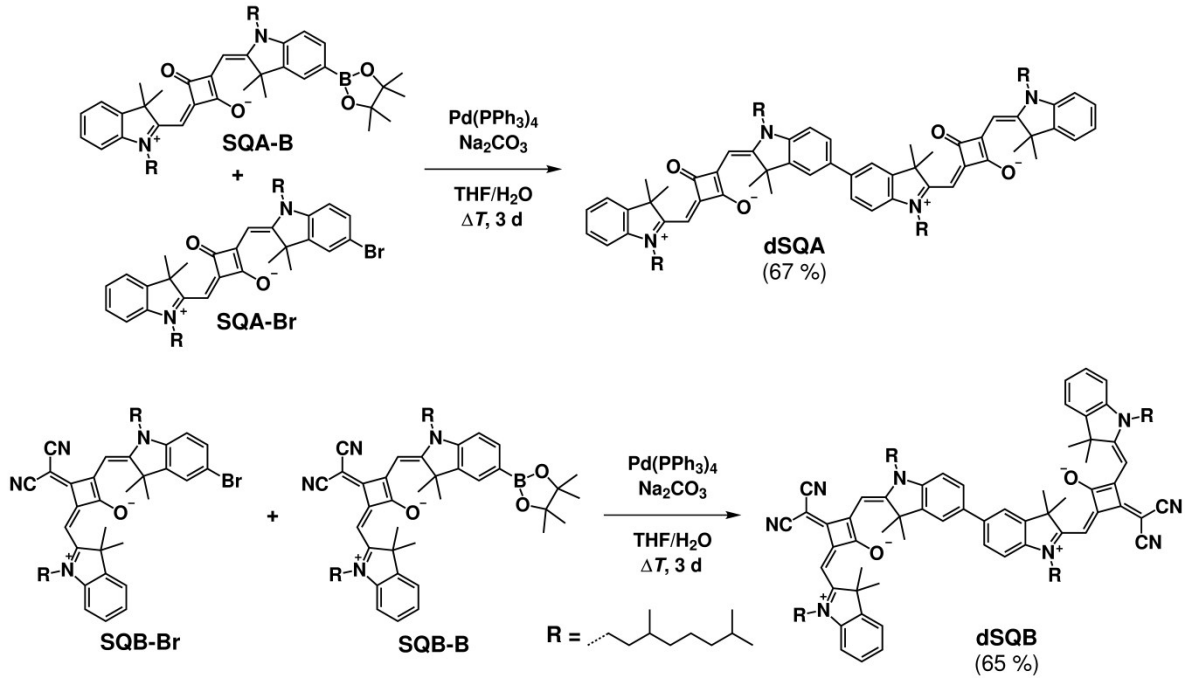
NMR-Spectra were recorded on either a Bruker Avance III HD 400 or a Bruker Avance III HD 600 FT-spectrometer. The chemical shifts are relative to the internal standard tetramethylsilane and are given in ppm. The coupling constants are given in Hz. Abbreviations used for the spin multiplicities or for C-atom descriptions are: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, dd = doublet of doublet, ddd = doublet of doublet of doublet; prim. = primary, sec. = secondary, tert. = tertiary, quart. = quaternary. Multiplet signals or overlapping signals in proton NMR spectra that could not be assigned to first order couplings are given as (-).

High resolution mass spectrometry was performed on a Bruker Daltonics microTOF focus (ESI).

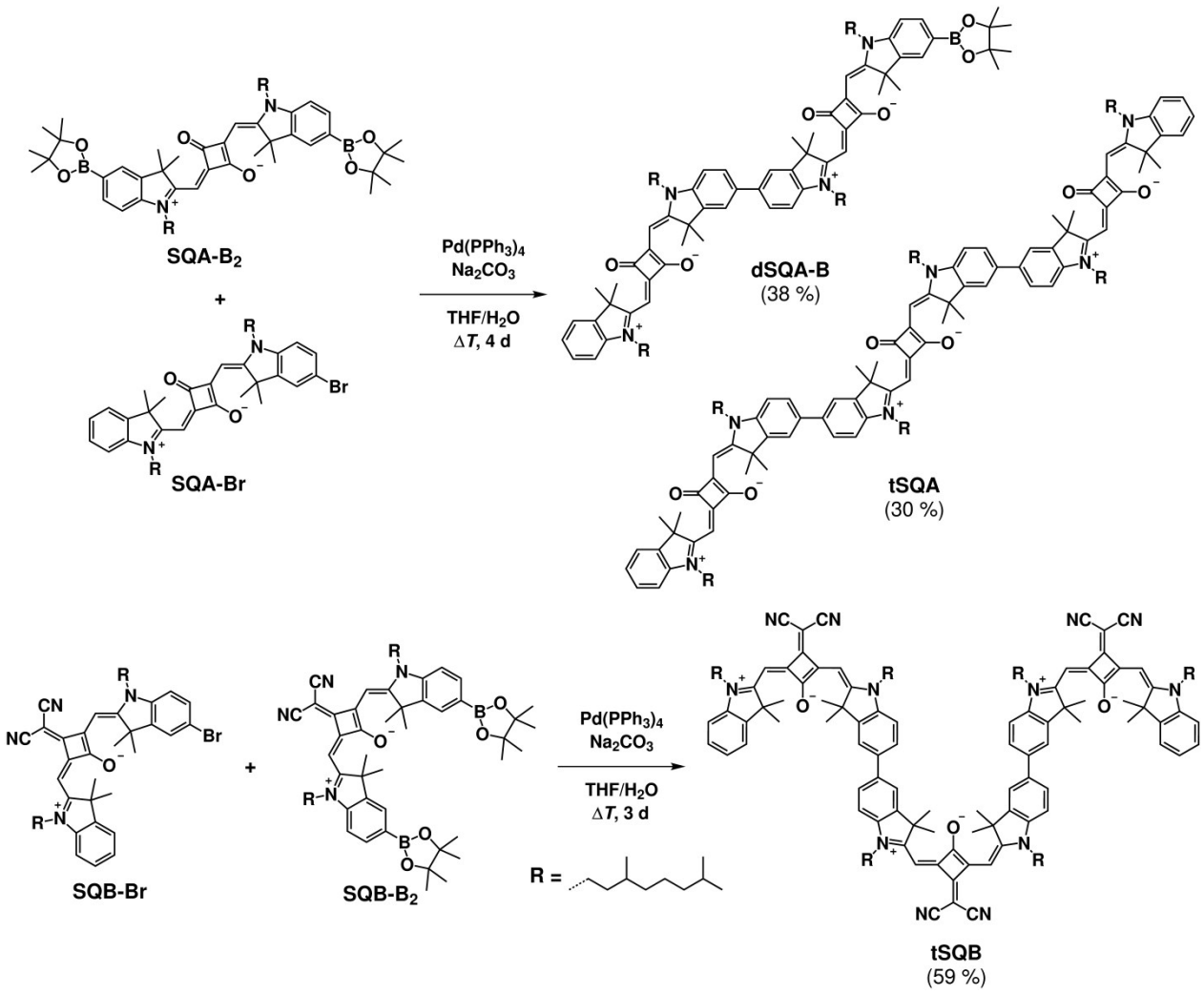


Scheme S2: Synthesis of the precursors **SQA-B**, **SQB-B** and **SQB-B$_2$**.

The precursors **SQA-B**, **SQB-B** and **SQB-B$_2$** were synthesised by a Pd-catalysed *Miyaura* borylation reaction of their brominated analogues with 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane).

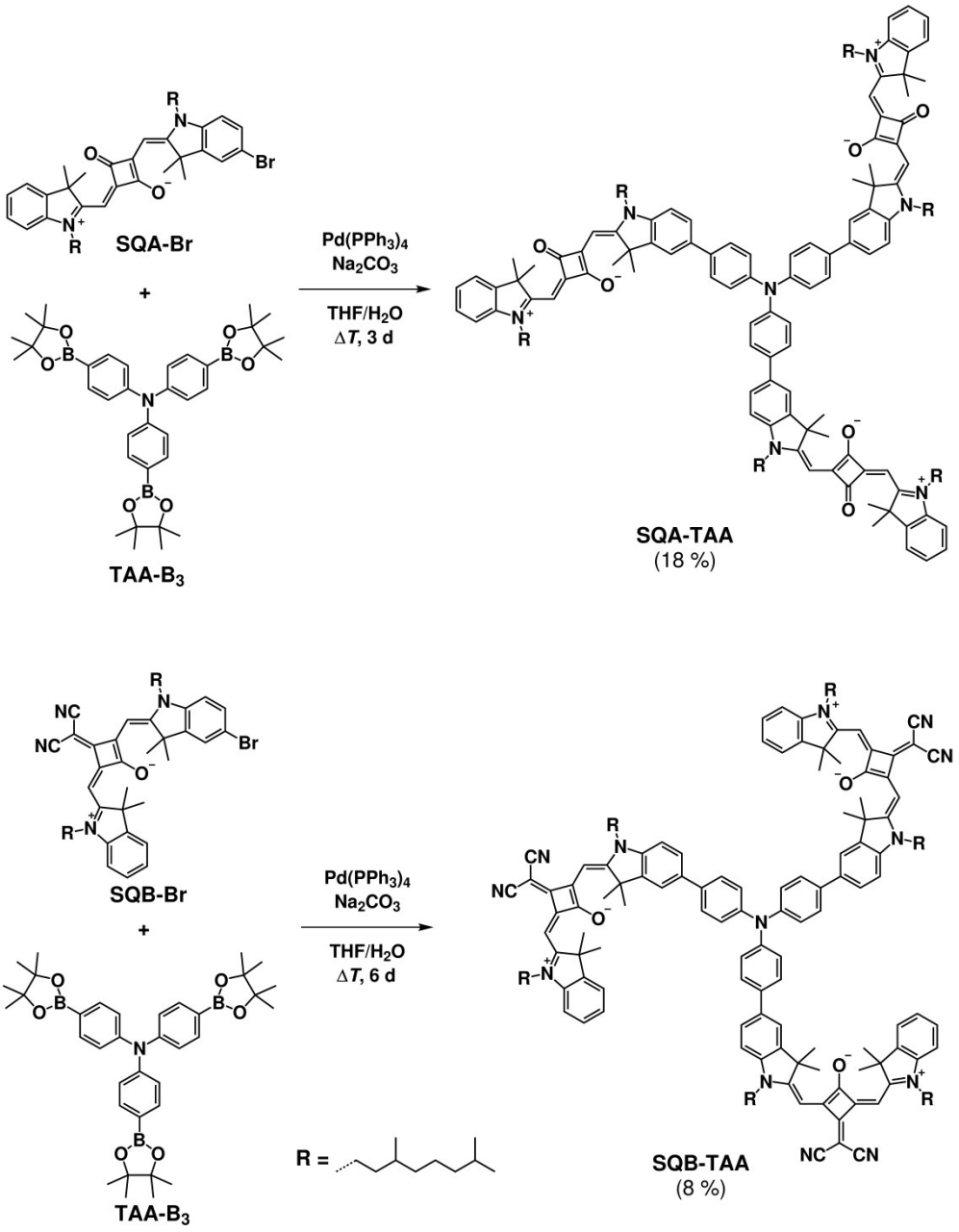


Scheme S3: Synthesis of the dimers **dSQA** and **dSQB**.

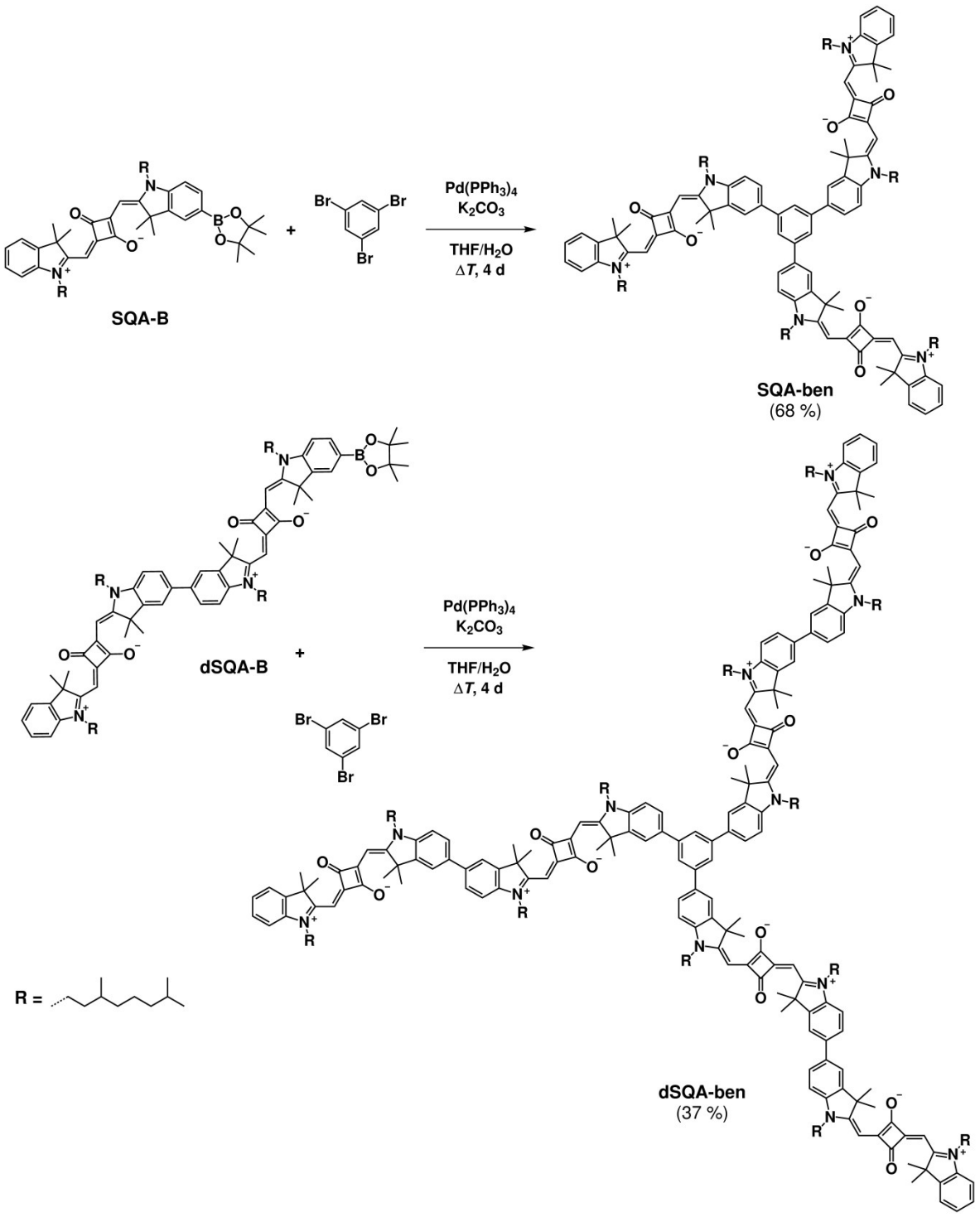


Scheme S4: Synthesis of the trimers **tSQA** and **tSQB** and the functionalized dimer **dSQA-B**.

The dimers **dSQA** and **dSQB** and the trimers **tSQA** and **tSQB** were synthesised by Pd-catalysed *Suzuki* coupling reactions. In the case of the transoid **tSQA** the reaction educts were used in a 1:1 ratio in order to isolate the borylated dimer **dSQA-B** as well. For the cisoid **tSQB** the ratios were 2:1, therefore almost no dimer formation was observed.



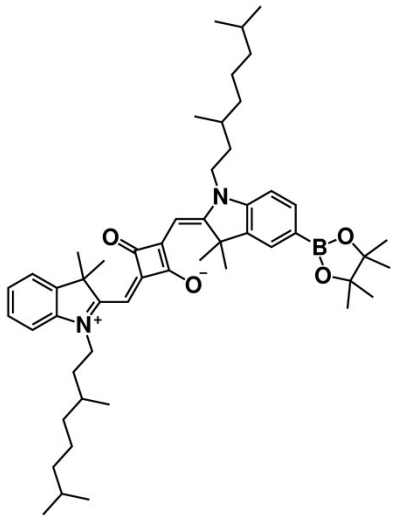
Scheme S5: Synthesis of the star shaped trimers **SQA-TAA** and **SQB-TAA**.



Scheme S6: Synthesis of the star shaped trimers **SQA-ben** and **dSQA-ben**.

The star shaped trimers **SQA-TAA**, **SQB-TAA**, **SQA-ben** and **dSQA-ben** were synthesised via Pd-catalysed *Suzuki* coupling reactions. In the case of the TAA core the brominated monomer squaraines **SQA-Br** or **SQB-Br** and the borylated **TAA-B$_3$** were used. For the trimers with benzene as core the borylated squaraines **SQA-B** or **dSQA-B** and 1,3,5-tribrombenzene were used.

SQA-B



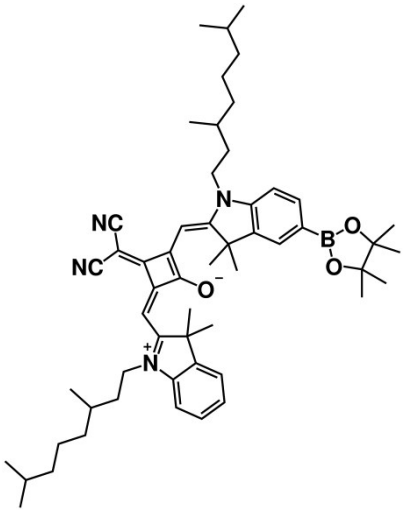
Under nitrogen atmosphere **SQA-Br** (500 mg, 661 µmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (168 mg, 662 µmol) and KOAc (64.9 mg, 661 µmol) were dissolved in dry 1,4-dioxane (10 ml). The solution was degassed for 10 min. Then $Pd(PhCN)_2Cl_2$ (12.7 mg, 33.1 µmol) and 1,1'-bis(diphenylphosphino)ferrocene (18.3 mg, 33.0 µmol) were added and the blue solution was refluxed under exclusion of light for 18 h. The solvent was removed *in vacuo* and the blue residue was purified by flash-chromatography (eluent: PE/EA 1:1 → DCM/EA 1:1). Finally the crude product was dissolved in a small amount of DCM and dropped into an excess of *n*-hexane. The resulting precipitate was filtered off and dried under high vacuum.

Yield: 377 mg (470 µmol; **71 %**) of a blue powder

$C_{52}H_{75}BN_2O_4$ [802.98]

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K):
δ [ppm] = 7.78 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, -CH-), 7.76 – 7.73 (m, 1H, -CH-), 7.36 (dd, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 0.9 Hz, 1H, -CH-), 7.31 (ddd, $^3J_{HH}$ = 7.7 Hz, $^3J_{HH}$ = 7.7 Hz, $^4J_{HH}$ = 1.0 Hz, 1H, -CH-), 7.15 (ddd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 0.7 Hz, 1H, -CH-), 6.97 (d, $^3J_{HH}$ = 8.3 Hz, 1H, -CH-), 6.93 (d, $^3J_{HH}$ = 8.3 Hz, 1H, -CH-), 5.98 (s, 1H, -CCHC-), 5.96 (s, 1H, -CCHC-), 4.07 – 3.92 (-, 4H, 2x -NCH_2-), 2.08 – 1.89 (-, 2H, 2x -NCH_2CH_2-), 1.85 – 1.46 (-, 18H, 2x -NCH_2CH_2-, 2x -$CHCH_3$, 2x -$CH(CH_3)_2$, 2x -$C(CH_3)_2$), 1.36 (s, 12H, 2x –$OC(CH_3)_2$), 1.42 – 1.10 (-, 12H, 2x -$CH_2CH_2CH_2$-), 1.05 (d, $^3J_{HH}$ = 5.7 Hz, 3H, -$CHCH_3$), 1.03 (d, $^3J_{HH}$ = 5.7 Hz, 3H, -$CHCH_3$), 0.87 (d, $^3J_{HH}$ = 6.4 Hz, 6H, -$CH(CH_3)_2$), 0.86 (d, $^3J_{HH}$ = 6.4 Hz, 6H, -$CH(CH_3)_2$).

SQB-B



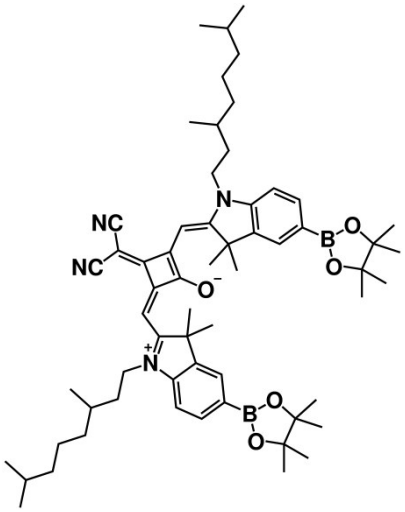
Under nitrogen atmosphere **SQB-Br** (1.58 g, 1.97 mmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (700 mg, 2.76 mmol), and KOAc (615 mg, 6.27 mmol) were dissolved in dry 1,4-dioxane (20 ml). The solution was degassed for 15 min. Then $Pd(PhCN)_2Cl_2$ (38.0 mg, 99.1 µmol) and dppf (54.0 mg, 97.4 µmol) were added and the green solution was refluxed under exclusion of light for 18 h. The solvent was removed *in vacuo* and the green residue was purified by flash chromatography (eluent: DCM→ PE/EA 1:1). Finally the crude product was dissolved in a small amount of DCM and dropped into an excess of *n*-hexane. The resulting precipitate was filtered off and dried under high vacuum.

Yield: 1.52 g (1.79 mmol, **91 %**) of a shiny red powder

$C_{55}H_{75}BN_4O_3$ [851.02]

^{1}H-NMR (400 MHz, CD_2Cl_2, 300 K):
δ [ppm] = 7.77 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, -CH-), 7.75 (s, 1H, -CH-), 7.41 (dd, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 0.8 Hz, 1H, -CH-), 7.36 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, -CH-), 7.24 (ddd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 0.8 Hz, 1H, -CH-), 7.09 (d, $^3J_{HH}$ = 8.0 Hz, 1H, -CH-), 7.04 (d, $^3J_{HH}$ = 8.0 Hz, 1H, -CH-), 6.51 (s, 1H, -CCHC-), 6.46 (s, 1H, -CCHC-), 4.12 – 3.94 (-, 4H, 2x -NCH_2-), 1.85 – 1.71 (-, 14H, 2x -NCH_2CH_2-, 2x -$C(CH_3)_2$), 1.69 – 1.56 (-, 4H, 2x -NCH_2CH_2-, 2x -$CHCH_3$), 1.45 – 1.11 (-, 26H, 2x -$CH(CH_3)_2$, 2x -$CH_2CH_2CH_2$-, 2x -$OC(CH_3)_2$), 1.03 (d, $^3J_{HH}$ = 6.2 Hz, 3H, -$CHCH_3$), 1.02 (d, $^3J_{HH}$ = 6.2 Hz, 3H, -$CHCH_3$), 0.87 (d, $^3J_{HH}$ = 6.8 Hz, 6H, -$CH(CH_3)_2$), 0.86 (d, $^3J_{HH}$ = 6.8 Hz, 6H, -$CH(CH_3)_2$).

SQB-B_2



Under nitrogen atmosphere **SQB-Br_2** (700 mg, 793 µmol), 4,4,4',4',5,5,5',5'-octamethyl-2,2'-bi(1,3,2-dioxaborolane) (562 mg, 2.21 mmol), and KOAc (248 mg, 2.53 mmol) were dissolved in dry 1,4-dioxane (15 ml). The solution was degassed for 15 min. Then $Pd(PhCN)_2Cl_2$ (15.0 mg, 39.1 µmol) and dppf (22.0 mg, 39.7 µmol) were added and the green solution was refluxed under exclusion of light for 18 h. The solvent was removed *in vacuo* and the green residue was purified by flash chromatography (eluent: PE/EA 1:1). Finally the crude product was dissolved in a small amount of DCM and dropped into an excess of *n*-hexane. The resulting precipitate was filtered off and dried under high vacuum.

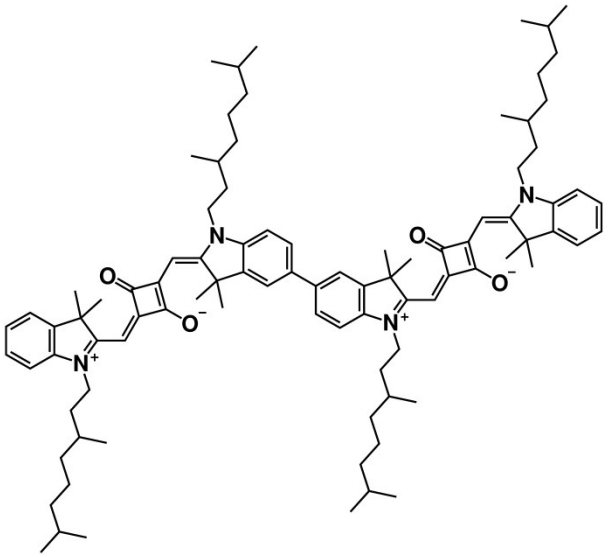
Yield: 700 mg (716 µmol, **90 %**) of a shiny red powder

$C_{61}H_{86}B_2N_4O_5$ [976.98]

^{1}H-NMR (600 MHz, CD_2Cl_2, 293.5 K):
δ [ppm] = 7.78 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz, 2H, 2x -CH-), 7.76 (s, 2H, 2x -CH-), 7.07 (d, $^3J_{HH}$ = 7.8 Hz, 2H, 2x -CH-), 6.49 (s, 2H, 2x -CH-), 4.09 – 3.98 (m, 4H, 2x -NCH_2-), 1.82 – 1.70 (-, 14H, 2x -NCH_2CH_2-, 2x -$C(CH_3)_2$), 1.62 – 1.55 (-, 4H, 2x -NCH_2CH_2-, 2x -$CHCH_3$), 1.54 – 1.46 (-, 2H, 2x -$CH(CH_3)_2$), 1.41 – 1.12 (-, 36H, 2x -$CH_2CH_2CH_2$-, 4x -$OC(CH_3)_2$), 1.01 (d, $^3J_{HH}$ = 6.5 Hz, 6H, 2x -$CHCH_3$), 0.86 (d, $^3J_{HH}$ = 6.6 Hz, 12H, 2x -$CH(CH_3)_2$).

^{13}C-NMR (151 MHz, CD_2Cl_2, 293.5 K):
δ [ppm] = 173.3 (quart.), 172.4 (quart.), 168.0 (quart.), 167.3 (quart.), 144.8 (quart.), 142.1 (quart.), 135.4 (tert.), 128.4 (tert.), 125.4 (quart.), 119.0 (quart.), 109.9 (tert.), 89.9 (tert.), 84.3 (quart.), 49.6 (quart.), 43.3 (sec.), 40.8 (quart.), 39.5 (sec.), 37.4 (sec.), 34.3 (sec.), 31.3 (tert.), 28.4 (tert.), 26.72 (prim.), 26.70 (prim.), 25.04 (prim.), 25.00 (sec.), 22.8 (prim.), 22.7 (prim.), 19.8 (prim.).

dSQA



Under nitrogen atmosphere **SQA-Br** (37.0 mg, 48.9 µmol) and **SQA-B** (33.0 mg, 41.1 µmol) were dissolved in peroxide-free THF (8 ml). A saturated solution of Na_2CO_3 (2 ml) was added and the solution was degassed for 15 min. Then $Pd(PPh_3)_4$ (4.75 mg, 4.11 µmol) was added and the blue solution was refluxed under exclusion of light for 3 d. The solvent was removed *in vacuo* and the blue residue was purified by flash chromatography (eluent: DCM/MeOH 99:1 → 98:2). The main fraction was purified by GPC ($CHCl_3$). Finally the crude product was dissolved in a small amount of DCM and dropped into an excess of *n*-hexane. The resulting precipitate was filtered off and dried under high vacuum.

Yield: 37.0 mg (27.4 µmol, **67 %**) of a blue powder

$C_{92}H_{126}N_4O_4$ [1352.01]

^{1}H-NMR (600 MHz, CD_2Cl_2, 293.5 K):
δ [ppm] = 7.55 – 7.50 (-, 4H, 4x -CH-), 7.36 (d, $^3J_{HH}$ = 7.2 Hz, 2H, 2x -CH-), 7.34 – 7.28 (m, 2H, 2x -CH-), 7.15 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 7.2 Hz, 2H, 2x -CH-), 7.02 (d, $^3J_{HH}$ = 8.4 Hz, 2H, 2x -CH-), 6.67 (d, $^3J_{HH}$ = 7.8 Hz, 2H, 2x -CH-), 6.03 – 5.94 (-, 4H, 4x -CH-), 4.17 – 3.88 (-, 8H, 4x -NCH_2-), 1.85 (s, 12H, 2x -$C(CH_3)_2$), 1.80 (s, 12H, 2x -$C(CH_3)_2$), 1.71 – 1.57 (-, 8H, 4x -NCH_2CH_2-, 4x -$CHCH_3$), 1.57 – 1.47 (-, 4H, 4x -NCH_2CH_2-), 1.45 – 1.10 (-, 28H, 4x -$CH_2CH_2CH_2$-, 4x -$CH(CH_3)_2$), 1.07 (d, $^3J_{HH}$ = 6.0 Hz, 6H, 2x -$CHCH_3$), 1.05 (d, $^3J_{HH}$ = 6.0 Hz, 6H, 2x -$CHCH_3$), 0.872 (d, $^3J_{HH}$ = 6.6 Hz, 12H, 2x -$CH(CH_3)_2$), 0.868 (d, $^3J_{HH}$ = 6.6 Hz, 12H, 2x -$CH(CH_3)_2$).

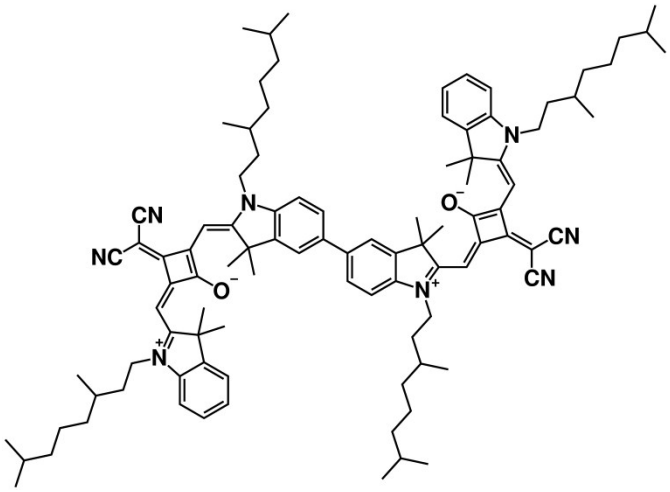
^{13}C-NMR (151 MHz, CD_2Cl_2, 293.5 K):
δ [ppm] = 182.5 (2x quart.), 180.2 (quart.), 179.3 (quart.), 170.3 (quart.), 169.4 (quart.), 143.3 (quart.), 142.5 (2x quart.), 141.9 (quart.), 136.8 (quart.), 127.9 (tert.), 126.8 (tert.), 123.9 (tert.),

122.5 (tert.), 121.0 (tert.), 109.6 (tert.), 109.4 (tert.), 87.0 (tert.), 86.8 (tert.), 49.5 (quart.), 49.4 (quart.), 42.3 (2x sec.), 39.32 (sec.), 39.31 (sec.), 37.29 (sec.), 37.26 (sec.), 34.0 (2x sec.), 31.4 (2x tert.), 28.1 (2x tert.), 27.4 (2x prim.), 27.1 (2x prim.), 24.83 (sec.), 24.81 (sec.), 22.848 (prim.), 22.836 (prim.), 22.74 (prim.), 22.73 (prim.), 19.78 (prim.), 19.74 (prim.).

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

calc.: 1350.97736 m/z
found: 1350.97682 m/z Δ: 0.40 ppm

dSQB



Under nitrogen atmosphere **SQB-Br** (46.0 mg, 57.2 µmol) and **SQB-B** (41.0 mg, 48.2 µmol) were dissolved in peroxide-free THF (8 ml). 2 ml of a saturated solution of Na_2CO_3 (2 ml) was added and the solution was degassed for 15 min. Then $Pd(PPh_3)_4$ (5.57 mg, 4.82 µmol) was added and the green solution was refluxed under exclusion of light for 3 d. The solvent was removed *in vacuo* and the green residue was purified by flash chromatography (eluent: DCM → DCM/MeOH 99.5:0.5 → 99:1). The main fraction was purified by GPC ($CHCl_3$). Finally the crude product was dissolved in a small amount of DCM and dropped into an excess of *n*-hexane. The resulting precipitate was filtered off and dried under high vacuum.

Yield: 45.0 mg (31.1 µmol, **65 %**) of a green powder

$C_{98}H_{126}N_8O_2$ [1448.11]

^{1}H-NMR (600 MHz, CD_2Cl_2, 293.5 K):
δ [ppm] = 7.62 – 7.58 (-, 4H, 4x -CH-), 7.41 (dd, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 0.6 Hz, 2H, 2x -CH-), 7.39 – 7.34 (m, 2H, 2x -CH-), 7.26 – 7.20 (m, 2H, 2x -CH-), 7.14 (d, $^3J_{HH}$ = 8.4 Hz, 2H, 2x -CH-),

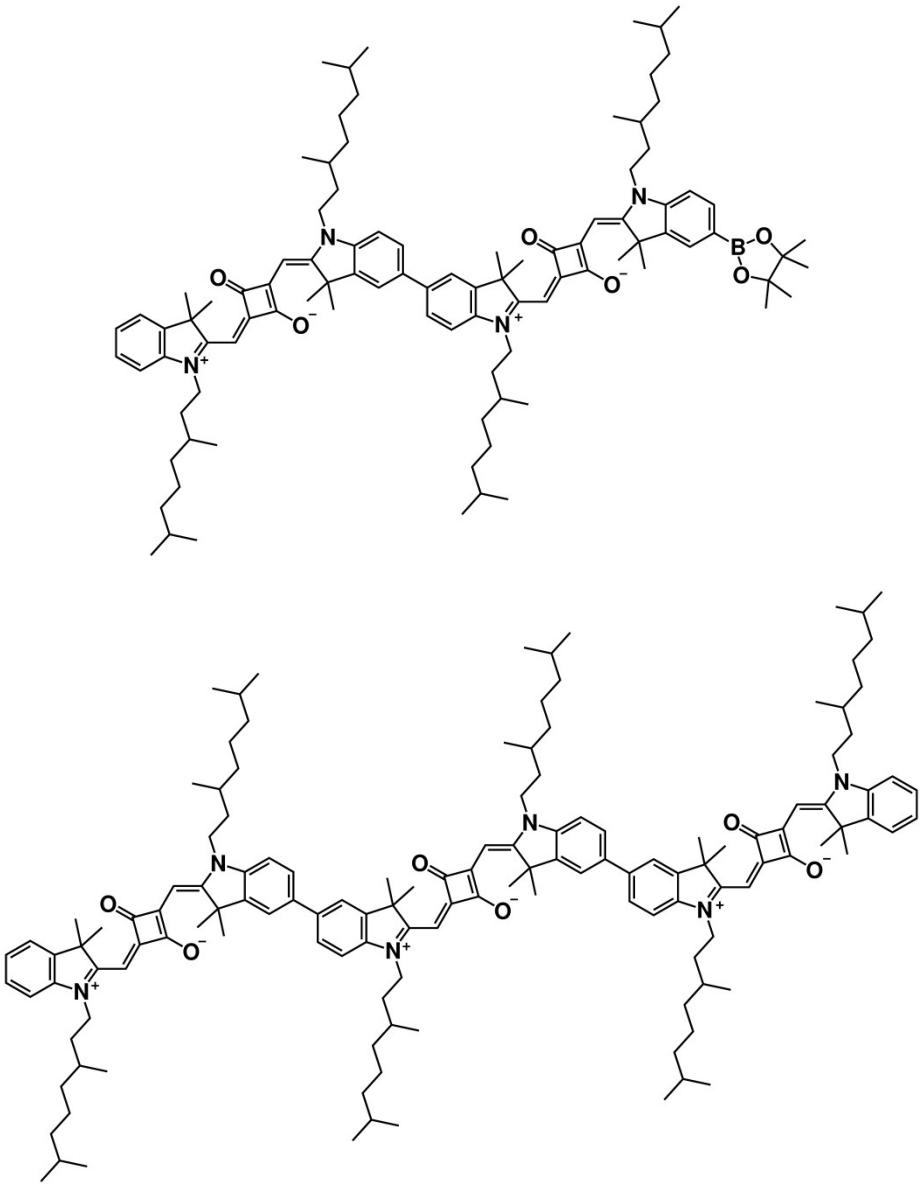
7.09 (d, $^{3}J_{HH}$ = 7.8 Hz, 2H, 2x -C<u>H</u>-), 6.495 (s, 2H, 2x -C<u>H</u>-), 6.489 (s, 2H, 2x -C<u>H</u>-), 4.16 – 3.97 (-, 8H, 4x -NC<u>H$_2$</u>-), 1.86 – 1.72 (-, 28H, 4x -NCH$_2$C<u>H$_2$</u>-, 4x -C(C<u>H$_3$</u>)<u>$_2$</u>), 1.71 – 1.47 (-, 12H, 4x -NCH$_2$C<u>H$_2$</u>-, 4x -C<u>H</u>CH$_3$, 4x -C<u>H</u>(CH$_3$)$_2$), 1.46 – 1.14 (-, 24H, 4x -C<u>H$_2$</u>C<u>H$_2$</u>C<u>H$_2$</u>-), 1.05 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, 2x -CHC<u>H$_3$</u>), 1.03 (d, $^{3}J_{HH}$ = 6.6 Hz, 6H, 2x -CHC<u>H$_3$</u>), 0.87 (d, $^{3}J_{HH}$ = 6.6 Hz, 12H, 2x -CH(C<u>H$_3$</u>)<u>$_2$</u>), 0.86 (d, $^{3}J_{HH}$ = 6.6 Hz, 12H, 2x -CH(C<u>H$_3$</u>)<u>$_2$</u>).

^{13}C-NMR (151 MHz, CD_2Cl_2, 293.5 K):
δ [ppm] = 173.5 (quart.), 172.4 (quart.), 171.4 (quart.), 167.9 (quart.), 166.2 (quart.) 143.7 (quart.), 142.9 (quart.), 142.3 (quart.), 141.9 (quart.), 137.5 (quart.), 128.4 (tert.), 127.2 (tert.), 125.0 (tert.), 122.6 (tert.), 121.1 (tert.), 119.14 (quart.), 119.12 (quart.), 110.7 (tert.), 110.6 (tert.), 89.55 (tert.), 89.51 (tert.), 49.9 (quart.), 49.8 (quart.), 43.4 (2x sec.), 40.6 (2x quart.), 39.52 (sec.), 39.51 (sec.), 37.48 (sec.), 37.46 (sec.), 34.4 (2x sec.), 31.3 (2x tert.), 28.39 (tert.), 28.38 (tert.), 26.87 (prim.), 26.83 (prim.), 26.61 (prim.), 26.60 (prim.), 25.04 (sec.), 25.01 (sec.), 22.82 (prim.), 22.81 (prim.), 22.73 (prim.), 22.72 (prim.), 19.82 (prim.), 19.77 (prim.).

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

calc.: 1448.00305 m/z
found: 1448.00449 m/z Δ: 0.99 ppm

dSQA-B and tSQA



Under nitrogen atmosphere **SQA-Br** (332 mg, 439 µmol) and **SQA-B$_2$** (429 mg, 462 µmol) were dissolved in peroxide-free THF (10 ml). A saturated solution of Na_2CO_3 (3 ml) was added and the solution was degassed for 15 min. Then $Pd(PPh_3)_4$ (25.4 mg, 22.0 µmol) was added and the blue solution was refluxed under exclusion of light for 4 d. The solvent was removed *in vacuo* and the green residue was purified by flash chromatography (eluent: DCM/MeOH 99:1 → 98:2). The main fraction was purified by GPC ($CHCl_3$) and **dSQA-B** and **tSQA** could be separated. Finally the crude products were dissolved in a small amount of DCM and dropped into an excess of *n*-hexane. The resulting precipitates were filtered off and dried under high vacuum.

dSQA-B:

Yield: 249 mg (168 µmol, **38 %**) of a blue powder

$C_{98}H_{137}BN_4O_6$ [1477.97]

^{1}H-NMR (600 MHz, CD_2Cl_2, 293.5 K):
δ [ppm] = 7.75 – 7.72 (-, 2H, 2x -CH-), 7.59 – 7.56 (-, 4H, 4x -CH-), 7.38 (dd, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 0.6 Hz, 1H, -CH-), 7.32 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.2 Hz, 1H, -CH-), 7.16 (ddd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 0.6 Hz, 1H, -CH-), 7.10 (d, $^3J_{HH}$ = 8.4 Hz, 1H, -CH-), 7.07 (d, $^3J_{HH}$ = 8.4 Hz, 1H, -CH-), 7.02 (d, $^3J_{HH}$ = 7.8 Hz, 1H, -CH-), 7.00 (d, $^3J_{HH}$ = 8.4 Hz, 1H, -CH-), 5.97 (s, 1H, -CH-), 5.93 (-, 3H, 3x -CH-), 4.15 – 3.92 (-, 8H, 4x -NCH_2-), 1.89 – 1.70 (-, 28H, 4x -NCH$_2$CH_2-, 4x -C(CH_3)$_2$), 1.63 – 1.59 (-, 8H, 4x -NCH$_2$CH_2-, 4x -CHCH_3), 1.58 – 1.49 (-, 4H, 4x -CH(CH_3)$_2$), 1.46 – 1.14 (-, 36H, 4x -CH_2CH_2CH_2-, 2x -OC(CH_3)$_2$), 1.084 (d, $^3J_{HH}$ = 6.0 Hz, 3H, -CHCH_3), 1.082 (d, $^3J_{HH}$ = 6.0 Hz, 3H, -CHCH_3), 1.07 (d, $^3J_{HH}$ = 6.0 Hz, 3H, -CHCH_3), 1.06 (d, $^3J_{HH}$ = 6.0 Hz, 3H, -CHCH_3), 0.874 (-, 12H, 2x -CH(CH_3)$_2$), 0.869 (d, $^3J_{HH}$ = 6.6 Hz, 6H, -CH(CH_3)$_2$), 0.866 (d, $^3J_{HH}$ = 6.6 Hz, 6H, -CH(CH_3)$_2$).

^{13}C-NMR (151 MHz, CD_2Cl_2, 293.5 K):
δ [ppm] = 182.04 (4x quart.), 181.35 (quart.), 181.0 (quart.), 180.4 (quart.), 180.1 (quart.), 170.2 (quart.), 170.1 (quart.), 169.6 (quart.), 169.4 (quart.), 145.5 (quart.), 143.5 (2x quart.), 142.8 (quart.), 142.6 (quart.), 142.3 (quart.), 142.1 (quart.), 141.8 (quart.), 137.1 (quart.), 136.7 (quart.), 135.3 (tert.), 128.4 (tert.), 128.1 (tert.), 126.9 (2x tert.), 124.1 (quart.), 124.0 (tert.), 122.6 (tert.), 121.1 (2x tert.), 110.1 (tert.), 109.9 (tert.), 109.8 (tert.), 109.0 (tert.), 87.4 (2x tert.), 87.1 (tert.), 86.9 (tert.), 84.2 (quart.), 49.8 (quart.), 49.63 (quart.), 49.57 (quart.), 49.2 (quart.), 42.6 (sec.), 42.5 (sec.), 42.43 (sec.), 42.35 (sec.), 39.5 (4x sec.), 37.48 (sec.), 37.47 (sec.), 34.46 (2x sec.), 34.2 (sec.), 34.12 (sec.), 34.09 (sec.), 34.06 (sec.), 31.5 (4x tert.), 28.37 (2x tert.), 28.36 (2x tert.), 27.28 (prim.), 27.27 (prim.), 27.20 (2x prim.), 27.19 (2x prim.), 27.07 (prim.), 27.06 (prim.), 25.10 (2x sec.), 25.07 (2x sec.), 25.05 (prim.), 22.82 (2x prim.), 22.81 (2x prim.), 22.73 (2x prim.), 22.72 (2x prim.), 19.79 (2x prim.), 19.76 (prim.), 19.75 (prim.).

tSQA:

Yield: 133 mg (65.6 µmol, **30 %**) of a blue powder

$C_{138}H_{188}N_6O_6$ [2027.01]

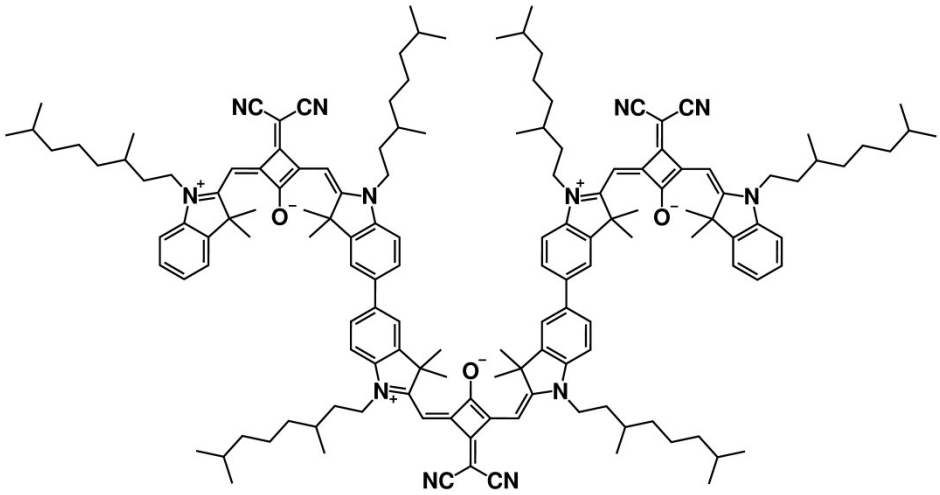
^{1}H-NMR (600 MHz, CD_2Cl_2, 293.5 K):
δ [ppm] = 7.60 – 7.57 (-, 6H, 6x -CH-), 7.56 (dd, $^4J_{HH}$ = 1.8 Hz, $^4J_{HH}$ = 1.8 Hz, 2H, 2x -CH-), 7.38 (d, $^3J_{HH}$ = 7.2 Hz, 2H, 2x -CH-), 7.33 (ddd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 0.6 Hz, 2H, 2x -CH-), 7.16 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 7.2 Hz, 2H, 2x -CH-), 7.08 (dd, $^3J_{HH}$ = 7.2 Hz, $^3J_{HH}$ = 7.2 Hz, 4H, 4x -CH-), 7.02 (d, $^3J_{HH}$ = 7.8 Hz, 2H, 2x -CH-), 6.00 – 5.88 (-, 6H, 6x -CH-), 4.14 – 3.94 (-, 12H, 6x -NCH_2-), 1.83 – 1.76 (-, 42H, 6x -NCH_2CH_2-, 6x -$C(CH_3)_2$), 1.70 – 1.59 (-, 12H, 6x -NCH_2CH_2-, 6x -$CHCH_3$), 1.56 – 1.51 (-, 6H, 6x -$CH(CH_3)_2$), 1.47 – 1.12 (-, 36H, 6x -$CH_2CH_2CH_2$-), 1.09 (d, $^3J_{HH}$ = 6.0 Hz, 6H, 2x -$CHCH_3$), 1.08 (d, $^3J_{HH}$ = 6.0 Hz, 6H, 2x -$CHCH_3$), 1.07 (d, $^3J_{HH}$ = 6.0 Hz, 6H, 2x -$CHCH_3$), 0.880 (d, $^3J_{HH}$ = 6.6 Hz, 12H, 2x -$CH(CH_3)_2$), 0.876 (d, $^3J_{HH}$ = 6.6 Hz, 12H, 2x -$CH(CH_3)_2$), 0.87 (d, $^3J_{HH}$ = 6.6 Hz, 12H, 2x -$CH(CH_3)_2$).

^{13}C-NMR (151 MHz, CD_2Cl_2, 293.5 K):
δ [ppm] = 182.1 (3x quart.), 181.0 (quart.), 180.4 (quart.), 180.2 (quart.), 170.2 (quart.), 169.6 (quart.), 169.4 (quart.), 143.5 (2x quart.), 142.8 (quart.), 142.7 (quart.), 142.31 (quart.), 142.26 (quart.), 136.9 (quart.), 136.8 (quart.), 128.1 (tert.), 126.9 (2x tert.), 124.0 (tert.), 122.6 (tert.), 121.1 (2x tert.), 110.04 (tert.), 109.95 (tert.), 109.8 (tert.), 87.3 (tert.), 87.1 (tert.), 86.9 (tert.), 49.68 (quart.), 49.65 (quart.), 49.6 (quart.), 42.52 (2x sec.), 42.45 (sec.), 39.6 (2x sec.), 39.5 (sec.), 37.50 (2x sec.), 37.48 (sec.), 34.19 (sec.), 34.15 (sec.), 34.1 (sec.), 31.5 (3x tert.), 28.39 (2x tert.), 28.38 (tert.), 27.3 (4x prim.), 27.1 (2x prim.), 25.11 (2x sec.), 25.09 (sec.), 22.84 (2x prim.), 22.83 (prim.), 22.75 (2x prim.), 22.74 (prim.), 19.81 (2x prim.), 19.77 (prim.).

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

calc.: 2026.46180 m/z
found.: 2026.46389 m/z Δ: 1.03 ppm

tSQB



Under nitrogen atmosphere **SQB-B$_2$** (100 mg, 102 µmol) and **SQB-Br** (181 mg, 225 µmol) were dissolved in peroxide-free THF (8 ml). A saturated solution of Na_2CO_3 (3 ml) was added and the mixture was degassed 15 min. Then $Pd(PPh_3)_4$ (9.11 mg, 7.88 µmol) was added and the green solution was refluxed under exclusion of light for 3 d. The solvent was removed *in vacuo* and the residue was purified by flash chromatography (eluent: DCM/MeOH 99:1). The main fraction was purified by GPC ($CHCl_3$). Finally the crude product was dissolved in a small amount of DCM and dropped into an excess of *n*-hexane. The resulting precipitate was filtered off and dried under high vacuum.

Yield: 130 mg (59.9 µmol, **59 %**) of a green powder

$C_{147}H_{188}N_{12}O_3$ [2171.15]

^{1}H-NMR (600 MHz, CD_2Cl_2, 293.5 K):
δ [ppm] = 7.62 – 7.59 (-, 8H, 8x -C<u>H</u>-), 7.41 (d, $^3J_{HH}$ = 7.2 Hz, 2H, 2x -C<u>H</u>-), 7.37 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.0 Hz, 2H, 2x -C<u>H</u>-), 7.25 – 7.20 (m, 2H, 2x -C<u>H</u>-), 7.18 – 7.13 (-, 4H, 4x -C<u>H</u>-), 7.09 (d, $^3J_{HH}$ = 8.0 Hz, 2H, 2x -C<u>H</u>-), 6.52 – 6.49 (-, 6H, 6x -C<u>H</u>-), 4.16 – 3.99 (-, 12H, 6x -NC<u>H$_2$</u>-), 1.88 – 1.75 (-, 42H, 6x -NCH$_2$C<u>H$_2$</u>-, 6x -C(C<u>H$_3$</u>)$_2$), 1.72 – 1.57 (-, 12H, 6x -NCH$_2$C<u>H$_2$</u>-, 6x -C<u>H</u>CH$_3$), 1.57 – 1.49 (-, 6H, 6x -C<u>H</u>(CH$_3$)$_2$), 1.44 – 1.19 (-, 36H, 6x -C<u>H$_2$</u>C<u>H$_2$</u>C<u>H$_2$</u>-), 1.07 – 1.02 (-, 18H, 6x -CHC<u>H$_3$</u>), 0.89 – 0.85 (-, 36H, 6x -CH(C<u>H$_3$</u>)$_2$).

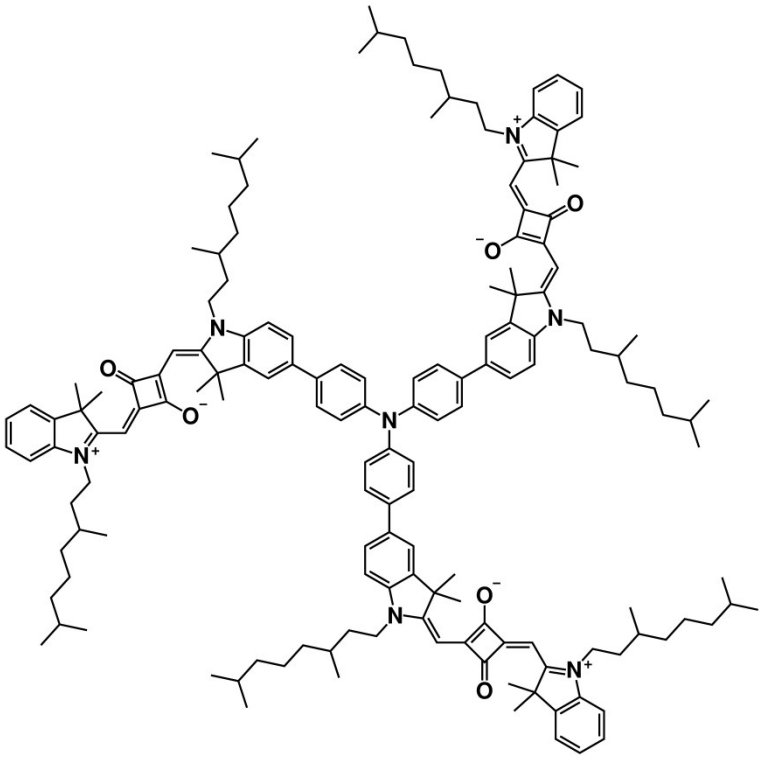
^{13}C-NMR (151 MHz, CD_2Cl_2, 293.5 K):
δ [ppm] = 173.54 (quart.), 173.50 (quart.), 172.4 (quart.), 171.7 (quart.), 171.4 (quart.), 168.0 (quart.), 167.9 (quart.), 167.1 (quart.), 166.5 (quart.), 166.2 (quart.), 143.8 (quart.), 143.7 (quart.), 142.9 (quart.), 142.3 (quart.), 141.9 (quart.), 141.8 (quart.), 137.7 (quart.), 137.4 (quart.), 128.4 (tert.), 127.3 (2x tert.), 125.0 (tert.), 122.6 (2x tert.), 121.2 (tert.), 119.1 (2x quart.), 110.9 (tert.), 110.7 (tert.), 110.6 (tert.), 89.8 (tert.), 89.6 (2x tert.), 49.92 (quart.), 49.91 (quart.), 49.8 (quart.), 43.47 (sec.), 43.37 (2x sec.), 40.75 (quart.), 40.66 (quart.), 39.53 (2x sec.), 39.52

(sec.), 37.49 (2x sec.), 37.47 (sec.), 34.45 (sec.), 34.40 (2x sec.), 31.3 (2x tert.), 28.40 (2x tert.), 28.39 (2x tert.), 26.89 (prim.), 26.85 (2x prim.), 26.81 (prim.), 26.62 (prim.), 26.59 (prim.), 25.05 (2x sec.) 25.02 (sec.), 22.83 (2x prim.), 22.82 (prim.), 22.74 (2x prim.), 22.73 (prim.), 19.83 (2x prim.), 19.78 (prim.).

ESI-MS pos (high resolution): $[M^{\cdot 2+}]$

calc.: 1085.24743 m/z
found: 1085.24770 m/z Δ: 0.25 ppm

SQA-TAA



Under nitrogen atmosphere **SQA-Br** (340 mg, 450 µmol) and **TAA-B$_3$** (80.0 mg, 128 µmol) were dissolved in peroxide-free THF (12 ml). A saturated solution of K_2CO_3 (2 ml) was added and the mixture was degassed for 15 min. Then $Pd(PPh_3)_4$ (7.42 mg, 6.42 µmol) was added and the blue solution was refluxed under exclusion of light for 3 d. The solvent was removed *in vacuo* and the residue was purified by flash chromatography (eluent: DCM/MeOH 99.5:0.5 → 99:1 → 98:2). Finally the crude product was dissolved in a small amount of DCM and dropped into an excess of *n*-hexane. The resulting precipitate was filtered off and dried under high vacuum.

Yield: 51.0 mg (22.5 µmol; **18 %**) of a blue powder

$C_{156}H_{201}N_7O_6$ [2270.31]

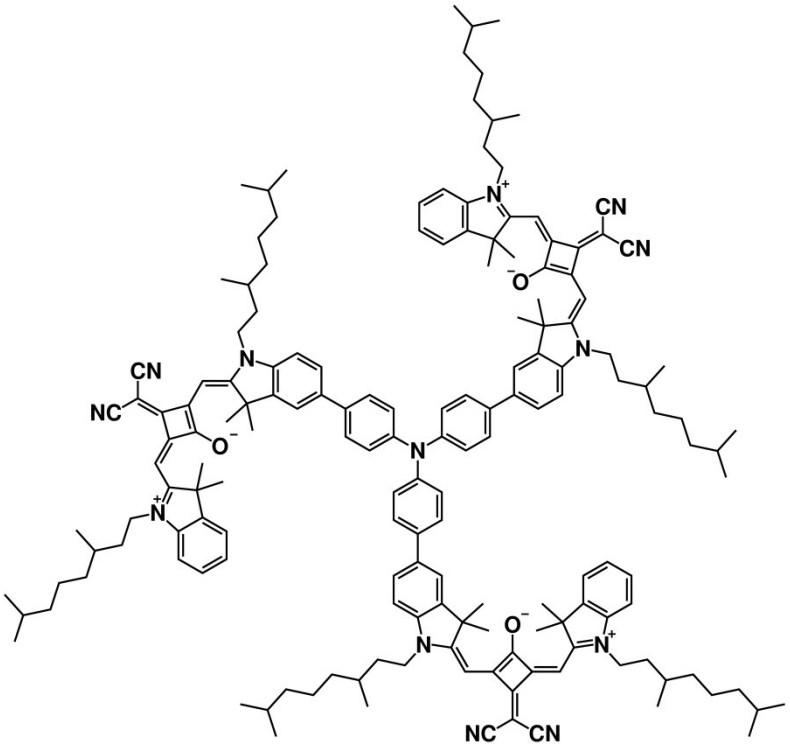
^{1}H-NMR (600 MHz, CD_2Cl_2, 293.5 K):
δ [ppm] = 7.60 – 7.57 (-, 12H, 12x -CH-), 7.37 (dd, $^3J_{HH}$ = 7.2 Hz, $^4J_{HH}$ = 1.1 Hz, 3H, 3x -CH-), 7.32 (ddd, $^3J_{HH}$ = 7.8 Hz, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.1 Hz, 3H, 3x -CH-), 7.29 – 7.22 (-, 6H, 6x -CH-), 7.15 (ddd, $^3J_{HH}$ = 7.5 Hz, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 0.5 Hz, 3H, 3x -CH-), 7.07 (d, $^3J_{HH}$ = 8.3 Hz, 3H, 3x -CH-), 7.01 (d, $^3J_{HH}$ = 8.0 Hz, 3H, 3x -CH-), 5.93 (s, 3H, 3x -CCHC-), 5.92 (s, 3H, 3x -CCHC-), 4.12 – 3.95 (-, 12H, 6x -NCH$_2$-), 1.88 – 1.73 (-, 6H, 6x -NCH$_2$CH$_2$-), 1.82 (s, 18H, 3x -C(CH$_3$)$_2$), 1.76 (s, 18H, 3x -C(CH$_3$)$_2$), 1.70 – 1.59 (-, 12H, 6x -NCH$_2$CH$_2$-, 6x -CHCH$_3$), 1.58 – 1.48 (-, 6H, 6x -CH(CH$_3$)$_2$), 1.46 – 1.14 (-, 36H, 6x -CH$_2$CH$_2$CH$_2$-), 1.08 (d, $^3J_{HH}$ = 6.0 Hz, 9H, 3x -CHCH$_3$), 1.06 (d, $^3J_{HH}$ = 6.6 Hz, 9H, 3x -CHCH$_3$), 0.87 (d, $^3J_{HH}$ = 6.6 Hz, 18H, 3x -CH(CH$_3$)$_2$), ,0.86 (d, $^3J_{HH}$ = 6.6 Hz, 18H, 3x -CH(CH$_3$)$_2$).

^{13}C-NMR (151 MHz, CD_2Cl_2, 293.5 K):
δ [ppm] = 182.0 (2x quart.), 180.6 (quart.), 180.1 (quart.), 170.0 (quart.), 169.5 (quart.), 147.0 (quart.), 143.6 (quart.), 142.8 (quart.), 142.6 (quart.), 142.1 (quart.), 136.6 (quart.), 135.7 (quart.), 128.1 (tert.), 128.0 (2x tert.), 126.6 (tert.), 124.9 (2x tert.), 123.9 (tert.), 122.6 (tert.), 120.9 (tert.), 109.9 (tert.), 109.7 (tert.), 87.0 (tert.), 86.8 (tert.), 49.58 (quart.), 49.58 (quart.), 42.5 (sec.), 42.4 (sec.), 39.52 (sec.), 39.51 (sec.), 37.47 (sec.), 37.45 (sec.), 34.14 (sec.), 34.07 (sec.), 31.50 (prim.), 31.49 (prim.), 28.37 (prim.), 28.36 (prim.), 27.25 (tert.), 27.23 (tert.), 27.08 (tert.), 27.07 (tert.), 25.09 (sec.), 25.07 (sec.), 22.82 (prim.), 22.81 (prim), 22.73 (prim.), 22.72 (prim.), 19.8 (prim.), 19.7 (prim.).

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

calc.: 2269.56659 m/z
found: 2269.56774 m/z Δ: 0.51 ppm

SQB-TAA



Under nitrogen atmosphere **SQB-Br** (226 mg, 281 µmol) and **TAA-B$_3$** (50.0 mg, 80.2 µmol) were dissolved in peroxide-free THF (10 ml). A saturated solution of K_2CO_3 (2 ml) was added and the mixture was degassed for 15 min. Then $Pd(PPh_3)_4$ (4.64 mg, 4.02 µmol) was added and the green solution was refluxed under exclusion of light for 6 d. The solvent was removed *in vacuo* and the residue was purified by flash chromatography (eluent: DCM/MeOH 99:1 → 98:2 → 97:3). The main fraction was purified by GPC ($CHCl_3$). Finally the crude product was dissolved in a small amount of DCM and dropped into an excess of *n*-hexane. The resulting precipitate was filtered off and dried under high vacuum.

Yield: 16.0 mg (6.63 µmol; **8 %**) of a green powder

$C_{165}H_{201}N_{13}O_3$ [2414.45]

^{1}H-NMR (600 MHz, CD_2Cl_2, .293.5 K):
δ [ppm] = 7.61 – 7.58 (-, 12H, 12x -CH-), 7.40 (d, $^3J_{HH}$ = 7.5 Hz, 3H, 3x -CH-), 7.36 (ddd, $^3J_{HH}$ = 7.9 Hz, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 0.8 Hz, 3H, 3x -CH-), 7.29 – 7.25 (-, 6H, 6x -CH-), 7.22 (ddd, $^3J_{HH}$ = 7.6 Hz, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 0.6 Hz, 3H, 3x -CH-), 7.14 (d, $^3J_{HH}$ = 9.0 Hz, 3H, 3x -CH-), 7.08 (d, $^3J_{HH}$ = 8.0 Hz, 3H, 3x -CH-), 6.49 (s, 3H, 3x -CCHC-), 6.48 (s, 3H, 3x -CCHC-), 4.14 – 3.98 (-, 12H, 6x -NCH$_2$-), 1.87 – 1.73 (-, 6H, 6x -NCH$_2$CH$_2$-), 1.81 (s, 18H, 3x -C(CH$_3$)$_2$), 1.76 (s, 18H, 3x -C(CH$_3$)$_2$), 1.71 – 1.57 (-, 12H, 6x -NCH$_2$CH$_2$-, 6x -CHCH$_3$), 1.57 – 1.48 (-, 6H, 6x -CH(CH$_3$)$_2$), 1.46 – 1.13 (-, 36H, 6x -CH$_2$CH$_2$CH$_2$-), 1.05 (d, $^3J_{HH}$ = 6.4 Hz, 9H, 3x -CHCH$_3$),

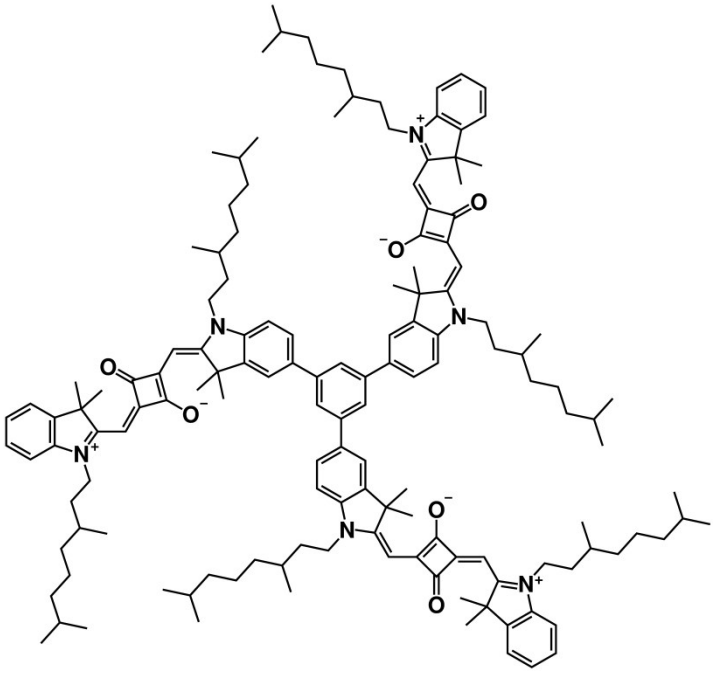
1.03 (d, $^{3}J_{HH}$ = 6.5 Hz, 9H, 3x -CHC$\underline{H_3}$), 0.87 (d, $^{3}J_{HH}$ = 6.6 Hz, 18H, 3x -CH(C$\underline{H_3}$)$_{\underline{2}}$), 0.86 (d, $^{3}J_{HH}$ = 6.6 Hz, 18H, 3x -CH(C$\underline{H_3}$)$_{\underline{2}}$).

^{13}C-NMR (151 MHz, CD_2Cl_2, 293.5 K):
δ [ppm] = 173.5 (quart.), 172.2 (quart.), 171.6 (quart.), 167.9 (quart.), 166.8 (quart.), 166.3 (quart.), 147.1 (quart.), 143.7 (quart.), 142.9 (quart.), 142.3 (quart.), 141.6 (quart.), 137.5 (quart.), 135.5 (quart.), 128.4 (tert.), 128.2 (2x tert.), 126.8 (tert.), 124.9 (3x tert.), 122.6 (tert.), 120.9 (tert.), 119.17 (quart.), 119.14 (quart.), 110.7 (tert.), 110.5 (tert.), 89.5 (tert.), 89.4 (tert.), 49.8 (2x quart.), 43.4 (sec.), 43.3 (sec.), 40.6 (quart.), 39.54 (sec.), 39.52 (sec.), 37.49 (sec.), 37.47 (sec.), 34.42 (sec.), 34.37 (sec.), 31.3 (tert.), 31.0 (tert.), 28.40 (tert.), 28.39 (tert.), 26.9 (prim.), 26.8 (prim.), 26.7 (prim.), 26.6 (prim.), 25.04 (sec.), 25.02 (sec.), 22.83 (prim.), 22.82 (prim.), 22.74 (prim.), 22.73 (prim.), 19.82 (prim.), 19.78 (prim.).

ESI-MS pos (high resolution): [$M^{\cdot 2+}$]

calc.: 1206.79983 m/z
found.: 1206.80119 m/z Δ: 1.13 ppm

SQA-ben



Under nitrogen atmosphere **SQA-B** (150 mg, 187 µmol) and 1,3,5-tribromobenzene (17.8 mg, 56.5 µmol) were dissolved in peroxide-free THF (12 ml). A saturated aqueous solution of K_2CO_3 (2 ml) was added and the mixture was degassed for 15 min. Then $Pd(PPh_3)_4$ (3.27 mg, 2.83 µmol) was added and the solution was refluxed under exclusion of light for 4 d. The solvent was removed *in vacuo* and the residue was purified by flash chromatography (eluent: DCM/MeOH 99.5:0.5 → 99:1 → 98:2). Finally the crude product was dissolved in a small amount of DCM and dropped into an excess of *n*-hexane. The resulting precipitate was filtered off and dried under high vacuum.

Yield: 81.0 mg (38.5 *µ*mol; **68 %**) of a blue powder

$C_{144}H_{192}N_6O_6$ [2103.11]

^{1}H-NMR (600 MHz, $CDCl_3$, 303.6 K):
δ [ppm] = 7.70 (s, 3H, 3x -CH-), 7.65 (dd, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.6 Hz, 3H, 3x -CH-), 7.63 (d, $^4J_{HH}$ = 1.5 Hz, 3H, 3x -CH-), 7.36 (d, $^3J_{HH}$ = 7.3 Hz, 3H, 3x -CH-), 7.31 (ddd, $^3J_{HH}$ = 8.1 Hz, $^3J_{HH}$ = 8.1 Hz, $^4J_{HH}$ = 1.2 Hz, 3H, 3x -CH-), 7.16 (dd, $^3J_{HH}$ = 7.3 Hz, $^3J_{HH}$ = 7.3 Hz, 3H, 3x -CH-), 7.08 (d, $^3J_{HH}$ = 8.1 Hz, 3H, 3x -CH-), 6.97 (d, $^3J_{HH}$ = 8.0 Hz, 3H, 3x -CH-), 6.00 (s, 3H, 3x -CCHC-), 5.99 (s, 3H, 3x -CCHC-), 4.16 – 3.91 (-, 12H, 6x -NCH_2-), 1.94 – 1.73 (-, 6H, 6x -NCH_2CH_2-), 1.87 (s, 18H, 3x -$C(CH_3)_2$), 1.80 (s, 18H, 3x -$C(CH_3)_2$), 1.71 – 1.57 (-, 12H, 6x -NCH_2CH_2-, 6x -$CHCH_3$), 1.57 – 1.48 (-, 6H, 6x -$CH(CH_3)_2$), 1.45 – 1.11 (-, 36H, 6x -$CH_2CH_2CH_2$), 1.08 (d, $^3J_{HH}$ = 6.0 Hz, 9H, 3x -$CHCH_3$), 1.04 (d, $^3J_{HH}$ = 6.2 Hz, 9H, 3x -$CHCH_3$), 0.88 (d, $^3J_{HH}$ = 6.6 Hz, 18H, 3x -$CH(CH_3)_2$), 0.86 (d, $^3J_{HH}$ = 6.7 Hz, 18H, 3x -$CH(CH_3)_2$).

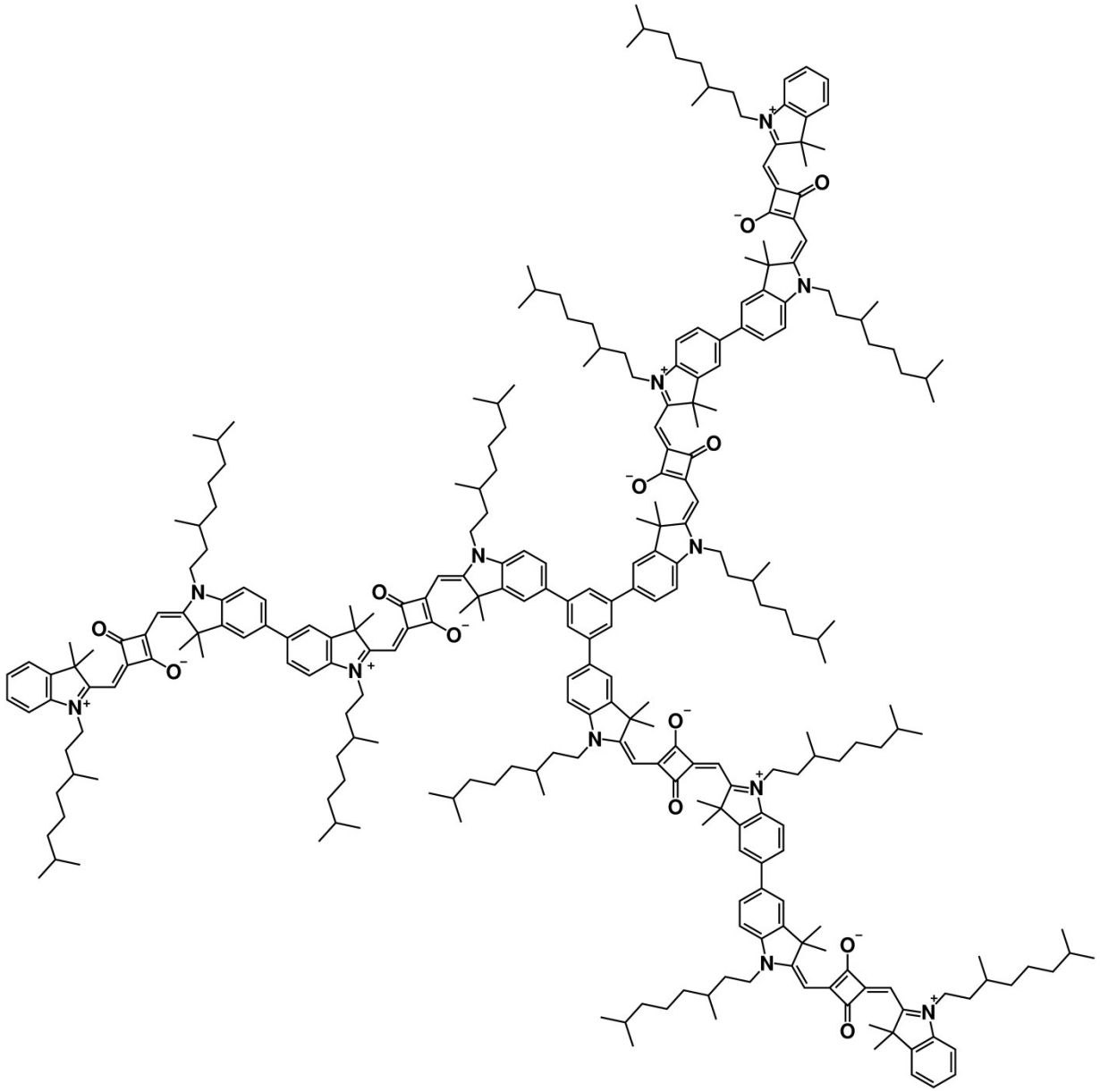
^{13}C-NMR (151 MHz, $CDCl_3$, 303.6 K):

δ [ppm] = 182.5 (2x quart.), 180.4 (quart.), 179.3 (quart.), 170.4 (quart.), 169.4 (quart.), 143.3 (quart.), 142.6 (2x quart.), 142.44 (quart.), 142.39 (quart.), 137.0 (quart.), 127.9 (tert.), 127.3 (tert.), 125.0 (tert.), 124.0 (tert.), 122.5 (tert.), 121.6 (tert.), 109.6 (tert.), 109.5 (tert.), 87.0 (tert.), 86.8 (tert.), 49.6 (quart.), 49.5 (quart.), 42.3 (2x sec.), 39.32 (sec.), 39.30 (sec.), 37.30 (sec.), 37.26 (sec.), 34.0 (2x sec.), 31.37 (prim.), 31.35 (prim.), 28.12 (prim.), 28.10 (prim.), 27.4 (2x tert.), 27.13 (tert.), 27.12 (tert.), 24.84 (sec.), 24,80 (sec.), 22.87 (prim.), 22.84 (prim.), 22.76 (prim.), 22.74 (prim.), 19.8 (prim.), 19.7 (prim.).

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

calc.: 2102.49310 m/z
found.: 2102.49663 m/z Δ: 1.68 ppm

dSQA-ben



Under nitrogen atmosphere **dSQA-B** (150 mg, 101 µmol) and 1,3,5-tribromobenzene (6.26 mg, 19.9 µmol) were dissolved in peroxide-free THF (10 ml). A saturated aqueous solution of K_2CO_3 (2 ml) was added and the mixture was degassed for 15 min. Then $Pd(PPh_3)_4$ (3.45 mg, 2.99 µmol) was added and the solution was refluxed under exclusion of light for 4 d. The solvent was removed *in vacuo* and the residue was purified by flash chromatography (eluent: DCM/MeOH 99:1 → 98:2). The main fraction was purified by GPC ($CHCl_3$). Finally the crude product was dissolved in a small amount of DCM and dropped into an excess of *n*-hexane. The resulting precipitate was filtered off and dried under high vacuum.

Yield: 30.0 mg (7.27 µmol; **37 %**) of a blue powder

$C_{282}H_{378}N_{12}O_{12}$ [4128.10]

^{1}H-NMR (600 MHz, $CDCl_3$, 303.6 K):
δ [ppm] = 7.80 (s, 3H, 3x -CH-), 7.74 – 7.71 (-, 6H, 6x -CH-), 7.59 – 7.56 (-, 12H, 12x -CH-), 7.38 (d, $^{3}J_{HH}$ = 7.8 Hz, 3H, 3x -CH-), 7.32 (ddd, $^{3}J_{HH}$ = 7.3 Hz, $^{3}J_{HH}$ = 7.3 Hz, $^{4}J_{HH}$ = 0.6 Hz, 3H, 3x -CH-), 7.18 – 7.14 (-, 6H, 6x -CH-), 7.10 – 7.06 (-, 6H, 6x -CH-), 7.02 (d, $^{3}J_{HH}$ = 7.8 Hz, 3H, 3x -CH-), 6.01 – 5.91 (-, 12H, 12x -CH-), 4.17 – 3.94 (-, 24H, 12x -NCH_2-), 1.94 – 1.73 (-, 84H, 12x -$C(CH_3)_2$, 12x -NCH_2CH_2-), 1.71 – 1.59 (-, 24H, 12x -NCH_2CH_2-, 12x -$CHCH_3$), 1.59 – 1.48 (-, 12H, 12x -$CH(CH_3)_2$), 1.48 – 1.13 (-, 72H, 12x -$CH_2CH_2CH_2$), 1.12 (d, $^{3}J_{HH}$ = 6.0 Hz, 9H, 3x -$CHCH_3$), 1.11 (d, $^{3}J_{HH}$ = 6.0 Hz, 9H, 3x -$CHCH_3$), 1.09 (d, $^{3}J_{HH}$ = 6.0 Hz, 9H, 3x -$CHCH_3$), 1.07 (d, $^{3}J_{HH}$ = 6.0 Hz, 9H, 3x -$CHCH_3$), 0.89 (d, $^{3}J_{HH}$ = 6.6 Hz, 18H, 3x -$CH(CH_3)_2$), 0.873 (-, 36H, 6x -$CH(CH_3)_2$), 0.869 (d, $^{3}J_{HH}$ = 6.6 Hz, 18H, 3x -$CH(CH_3)_2$).

^{13}C-NMR (151 MHz, $CDCl_3$, 303.6 K):
δ [ppm] = 182.0 (4x quart.), 180.9 (quart.), 180.7 (quart.), 180.3 (quart.), 180.1 (quart.), 170.2 (quart.), 169.8 (quart.), 169.6 (quart.), 169.4 (quart.), 143.5 (3x quart.), 142.8 (quart.), 142.74 (quart.), 142.68 (quart.), 142.6 (quart.), 142.3 (quart.), 142.2 (quart.), 137.00 (quart.), 136.98 (quart.), 136.7 (quart.), 128.1 (tert.), 127.5 (tert.), 126.9 (2x tert.), 124.9 (tert.), 124.0 (tert.), 122.6 (tert.), 121.7 (tert.), 121.1 (2x tert.), 110.1 (tert.), 110.0 (tert.), 109.9 (tert.), 109.8 (tert.), 87.31 (tert.), 87.29 (tert.), 87.1 (tert.), 86.9 (tert.), 49.72 (quart.), 49.68 (quart.), 49.63 (quart.), 49.58 (quart.), 42.59 (sec.), 42.57 (sec.), 42.5 (sec.), 42.4 (sec.), 39.54 (sec.), 39.53 (3x sec.), 37.50 (sec.), 37.48 (2x sec.), 37.46 (sec.), 34.2 (2x sec.), 34.13 (sec.), 34.09 (sec.), 31.53 (prim.), 31.50 (3x prim.), 28.39 (prim.), 28.38 (2x prim.), 28.37 (prim.), 27.31 (2x tert.), 27.28 (tert.), 27.27 (tert.), 27.24 (tert.), 27.23 (tert.), 27.07 (tert.), 27.06 (tert.), 25.12 (sec.), 25.10 (2x sec.), 25.08 (sec.), 22.85 (prim.), 22.83 (2x prim.), 22.82 (prim.), 22.76 (prim.), 22.74 (2x prim.), 22.73 (prim.), 19.82 (prim.), 19.80 (2x prim.), 19.76 (prim.).

ESI-MS pos (high resolution): [$M^{\cdot 2+}$]

calc.: 2063.97126 m/z
found.: 2063.97001 m/z Δ: 0.61 ppm

Lifetime distribution analysis

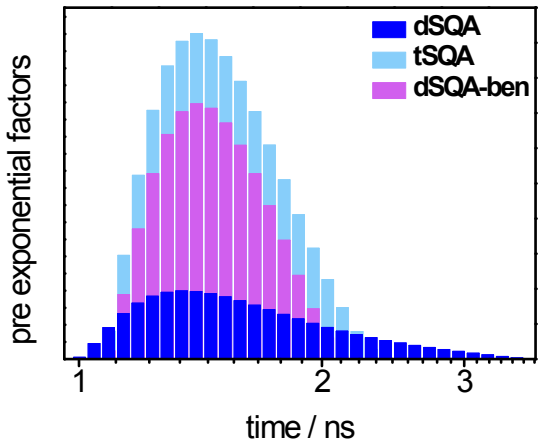


Fig. S1. Lifetime distribution analysis [software: FAST (version 3.4.2)] of the fluorescence spectra of **dSQA**, **tSQA** and **dSQA-ben** measured by TCSPC, excitation at 15200 cm^{-1}.

Fluorescence excitation anisotropy

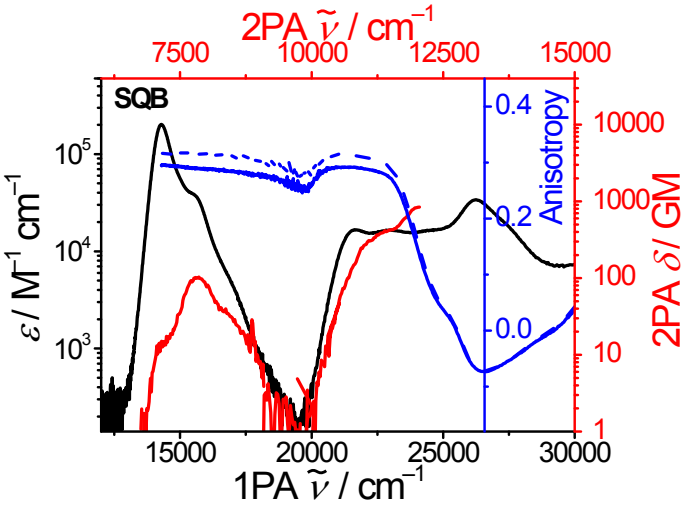


Fig. S2. 1PA (black) and the 2PA (red) spectra of **SQB** in toluene on a logarithmic scale together with the fluorescence excitation anisotropy (FEA) spectrum in polyTHF at 26°C (blue) and at 20°C (dashed blue).

Power dependence of the fluorescence intensity in 2PA experiments

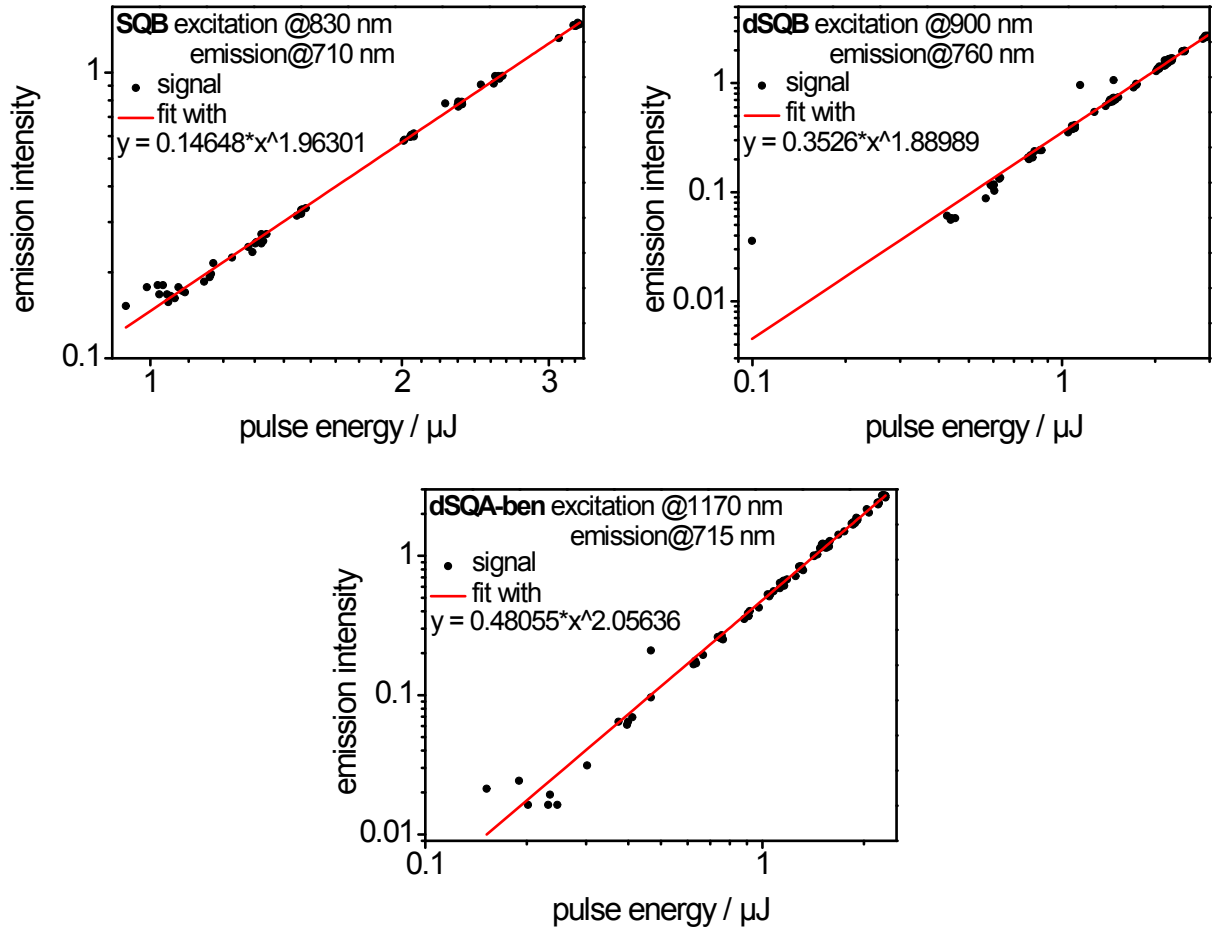


Fig. S3. Power dependence of the fluorescence signal in the 2PA experiments of **SQB**, **dSQB** and **dSQA-ben** at the given excitation wavelengths.

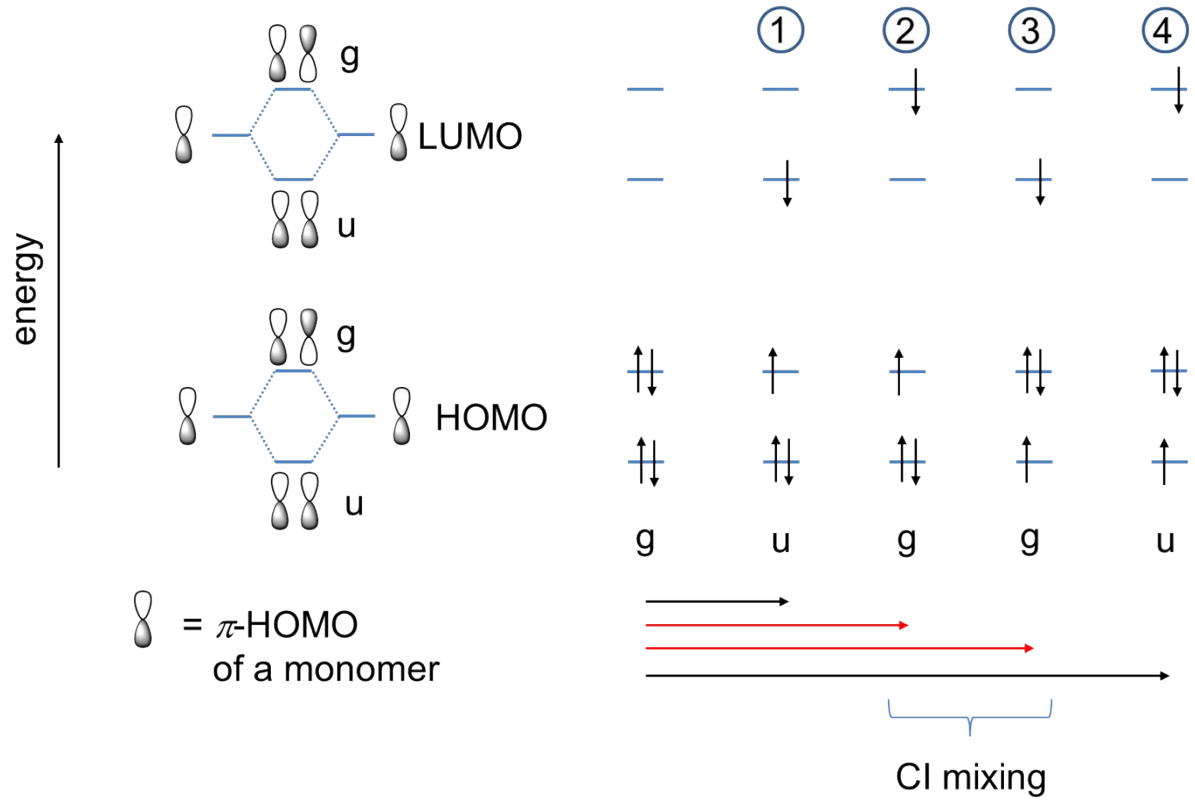


Fig. S4. Orbital state diagram for the interaction of two squaraine dyes in a linear (centrosymmetric) arrangement. Configuration 2 and 3 may undergo CI mixing because of similar energy. The black excitations are 1PA allowed, the red excitations are 2PA allowed.

TD-DFT calculations were performed using Gaussian 09[5]. Here we point out that the results of the quantum chemical calculations of exciton states strongly depend on the functional employed.[6] This is particularly true if CT states are involved. Thus, we consider the presented DFT computations more as an explanation of the findings rather than a confirmation.

Table S1. Excited state of **SQB** (C_{2v} symmetry) from TD-DFT computations at B3LYP/cc-pVTZ//B3LYP/6-31G* level of theory.

Excitation energies and oscillator strengths:

Excited State 1: Singlet-B2 1.9407 eV 638.86 nm f=0.5698 <S**2>=0.000
124 -> 126 0.16413
125 -> 126 0.69114
125 <- 126 -0.10893

Excited State 2: Singlet-B2 2.8668 eV 432.48 nm f=0.8805 <S**2>=0.000
124 -> 126 0.68643
125 -> 126 -0.16850

n-π^*

Excited State 3: Singlet-B1 3.1167 eV 397.80 nm f=0.0000 <S**2>=0.000
122 -> 126 0.70549

Excited State 4: Singlet-A1 3.3428 eV 370.90 nm f=0.0243 <S**2>=0.000
123 -> 126 0.66551
125 -> 128 -0.14424
125 -> 130 -0.15405

Excited State 5: Singlet-A1 3.5429 eV 349.95 nm f=0.2920 <S**2>=0.000
123 -> 126 0.10239
125 -> 127 0.67837
125 -> 128 0.13174

Excited State 6: Singlet-B2 3.7096 eV 334.22 nm f=0.0077 <S**2>=0.000
121 -> 126 0.19082
125 -> 129 0.67505

Excited State 7: Singlet-A1 3.7335 eV 332.08 nm f=0.0301 <S**2>=0.000
120 -> 126 0.14043
125 -> 127 -0.14093
125 -> 128 0.60561
125 -> 130 -0.28127

Excited State 8: Singlet-A1 3.8566 eV 321.48 nm f=0.0438 <S**2>=0.000
120 -> 126 -0.33747
123 -> 126 0.14624
124 -> 127 0.10001
125 -> 128 0.28759
125 -> 130 0.51296

Excited State 9: Singlet-B2 3.9129 eV 316.86 nm f=0.0776 <S**2>=0.000
121 -> 126 0.67062
125 -> 129 -0.19645

Excited State 10: Singlet-A1 3.9624 eV 312.90 nm f=0.0119 <S**2>=0.000
120 -> 126 0.59309
123 -> 126 0.11174
125 -> 130 0.34796

Table S2. Excited state of **SQA** (D_{2h} symmetry) from TD-DFT computations at B3LYP/cc-pVTZ//B3LYP/6-31G* level of theory.

Excitation energies and oscillator strengths:

```
 Excited State   1:      Singlet-BU     2.3071 eV  537.40 nm  f=1.4096  <S**2>=0.000
    113 -> 114        0.71226
    113 <- 114       -0.13147
```

n-π^*

```
 Excited State   2:      Singlet-BG     2.3705 eV  523.02 nm  f=0.0000  <S**2>=0.000
    112 -> 114        0.70517
```

n-π^*

```
 Excited State   3:      Singlet-AU     3.3172 eV  373.76 nm  f=0.0000  <S**2>=0.000
    109 -> 114        0.70524

 Excited State   4:      Singlet-AG     3.4354 eV  360.90 nm  f=0.0000  <S**2>=0.000
    111 -> 114        0.66393
    113 -> 115       -0.12453
    113 -> 117        0.19337

 Excited State   5:      Singlet-BU     3.4944 eV  354.81 nm  f=0.1662  <S**2>=0.000
    110 -> 114        0.70010

 Excited State   6:      Singlet-AG     3.6876 eV  336.22 nm  f=0.0000  <S**2>=0.000
    111 -> 114        0.10036
    113 -> 115        0.68142
    113 -> 117        0.10737

 Excited State   7:      Singlet-BU     3.6996 eV  335.13 nm  f=0.0171  <S**2>=0.000
    107 -> 114       -0.10127
    113 -> 116        0.69411

 Excited State   8:      Singlet-AG     4.0100 eV  309.19 nm  f=0.0000  <S**2>=0.000
    108 -> 114        0.26397
    111 -> 114       -0.17741
    113 -> 115       -0.10182
    113 -> 117        0.61528

 Excited State   9:      Singlet-AG     4.1310 eV  300.13 nm  f=0.0000  <S**2>=0.000
    108 -> 114        0.63864
    113 -> 117       -0.25235

 Excited State  10:      Singlet-BU     4.1319 eV  300.06 nm  f=0.0430  <S**2>=0.000
    107 -> 114        0.68987
    113 -> 116        0.10772
```

Table S3. Excited state of **dSQA** (in C_2 symmetry) from TD-DFT computations at B3LYP/cc-pVTZ(aug at O)//B3LYP/cc-pVDZ level of theory.

Excitation energies and oscillator strengths:

Excited State 1:	Singlet-B	1.9770 eV	627.15 nm	f=1.6513	<S**2>=0.000
224 -> 227	0.10023				
225 -> 226	0.69923				
Excited State 2:	Singlet-A	2.0628 eV	601.05 nm	f=0.0007	<S**2>=0.000
224 -> 226	0.47050				
225 -> 227	0.52664				
Excited State 3:	Singlet-B	2.2744 eV	545.13 nm	f=1.6905	<S**2>=0.000
224 -> 227	0.69670				
Excited State 4:	Singlet-A	2.3581 eV	525.77 nm	f=0.1540	<S**2>=0.000
224 -> 226	0.53186				
225 -> 227	-0.47678				
224 <- 226	-0.10004				
225 <- 227	0.10115				

n-π^*

Excited State 5:	Singlet-A	2.3786 eV	521.26 nm	f=0.0000	<S**2>=0.000
222 -> 227	-0.46476				
223 -> 226	0.52994				

n-π^*

Excited State 6:	Singlet-B	2.3786 eV	521.26 nm	f=0.0000	<S**2>=0.000
222 -> 226	0.52997				
223 -> 227	-0.46483				
Excited State 7:	Singlet-B	3.0941 eV	400.71 nm	f=0.0135	<S**2>=0.000
221 -> 226	0.68279				
225 -> 228	-0.12762				

n-π^*

Excited State 8:	Singlet-B	3.1142 eV	398.13 nm	f=0.0000	<S**2>=0.000
222 -> 226	0.46674				
223 -> 227	0.53061				

n-π^*

Excited State 9:	Singlet-A	3.1142 eV	398.13 nm	f=0.0000	<S**2>=0.000
222 -> 227	0.53065				
223 -> 226	0.46674				
Excited State 10:	Singlet-A	3.1895 eV	388.73 nm	f=0.0002	<S**2>=0.000
221 -> 227	0.68569				
224 -> 228	0.12094				
Excited State 11:	Singlet-B	3.3333 eV	371.95 nm	f=0.0000	<S**2>=0.000
216 -> 227	-0.46096				
217 -> 226	0.53256				
Excited State 12:	Singlet-A	3.3334 eV	371.95 nm	f=0.0000	<S**2>=0.000
216 -> 226	0.53134				
217 -> 227	-0.46199				

Excited State 13:	Singlet-B	3.4505 eV	359.32 nm	f=0.1983	<S**2>=0.000
218 -> 227	0.14807				
219 -> 226	0.51516				
220 -> 227	-0.35877				
225 -> 228	-0.24802				
Excited State 14:	Singlet-A	3.4514 eV	359.23 nm	f=0.0061	<S**2>=0.000
218 -> 226	-0.12075				
219 -> 227	-0.34852				
220 -> 226	0.56535				
224 -> 228	-0.14235				
Excited State 15:	Singlet-B	3.5764 eV	346.67 nm	f=0.0457	<S**2>=0.000
219 -> 226	0.25809				
221 -> 226	0.15091				
225 -> 228	0.62145				

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