Electronic Supplementary Information

Localised and Delocalised Excitons in Star-like Squaraine Homo- and Heterotrimers

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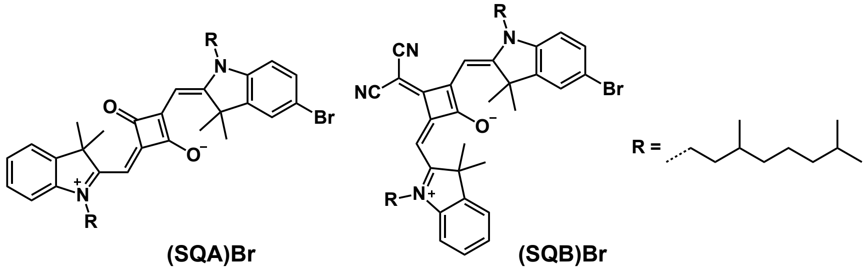
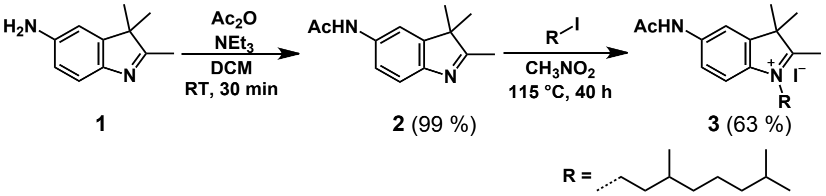
Compounds **1**[1], **4**[2] and **(SQA)Br**[3] were synthesized according to the given literature. Semisquaraine **5**[2] and **(SQB)Br**[2] were synthesized analogue to the given literature.

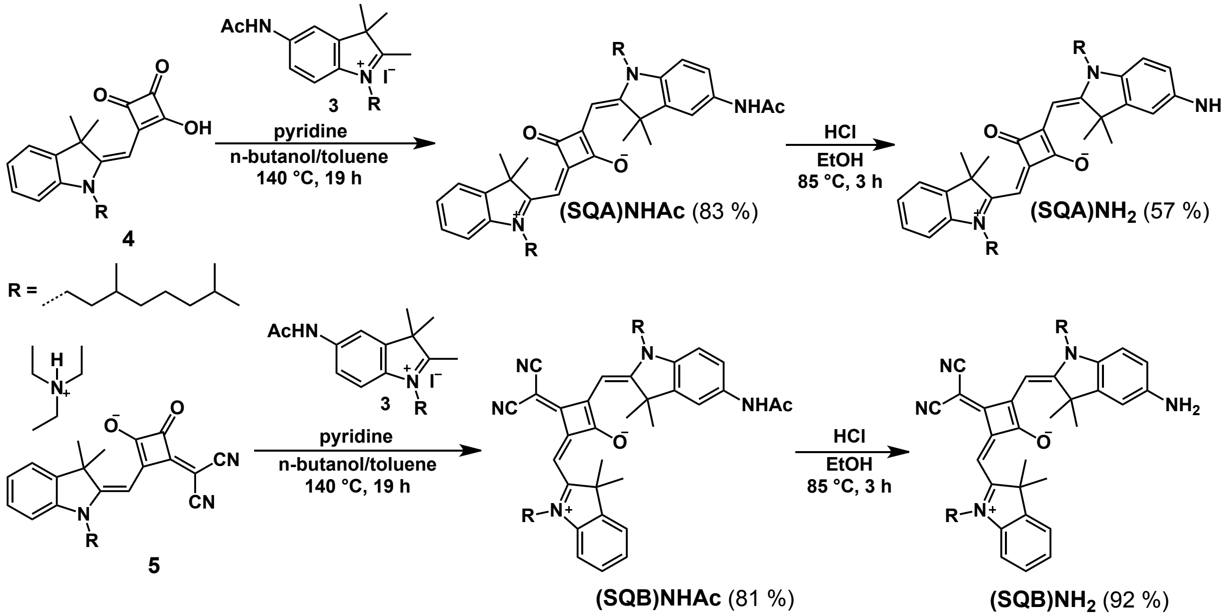


Scheme 1: Unsymmetrical Squaraines **(SQA)Br** and **(SQB)Br**



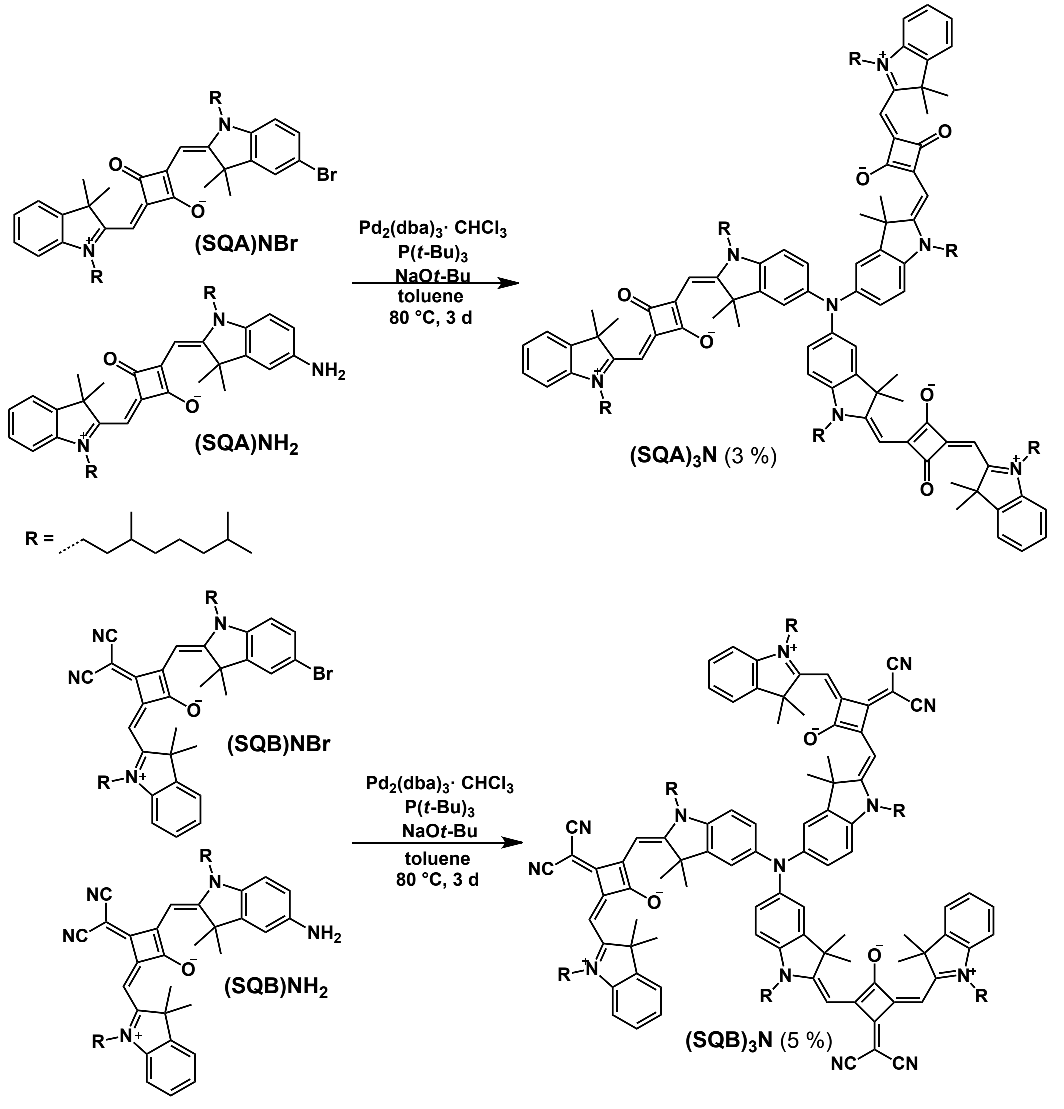
Scheme 2: Synthesis of the quaternary indolenine salt **3**

The amine functionality of **1** was protected with acetic anhydride prior to the alkylation of the indolenine.

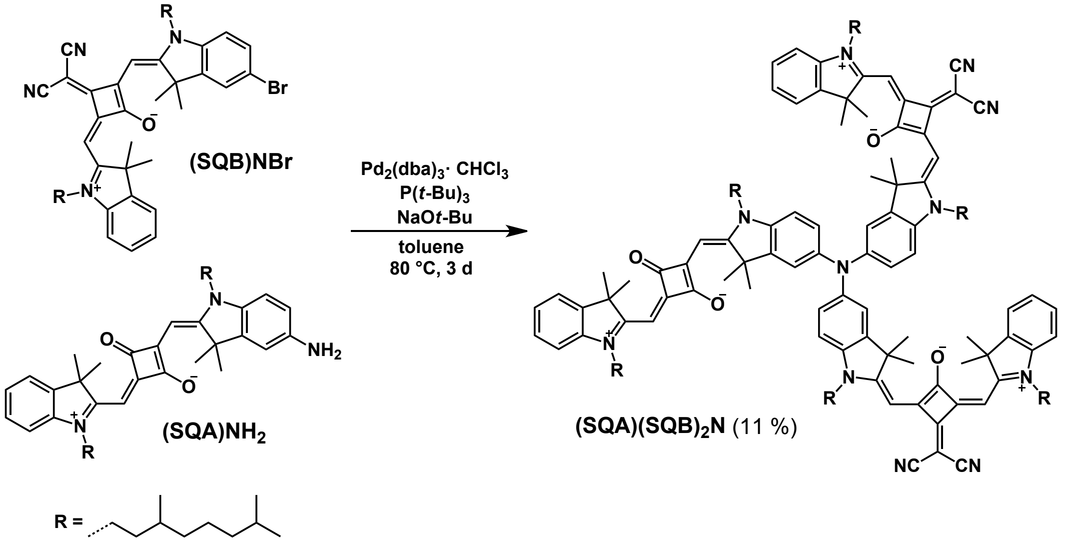


Scheme 3: Synthesis of **(SQA)NH$_2$** and **(SQB)NH$_2$**

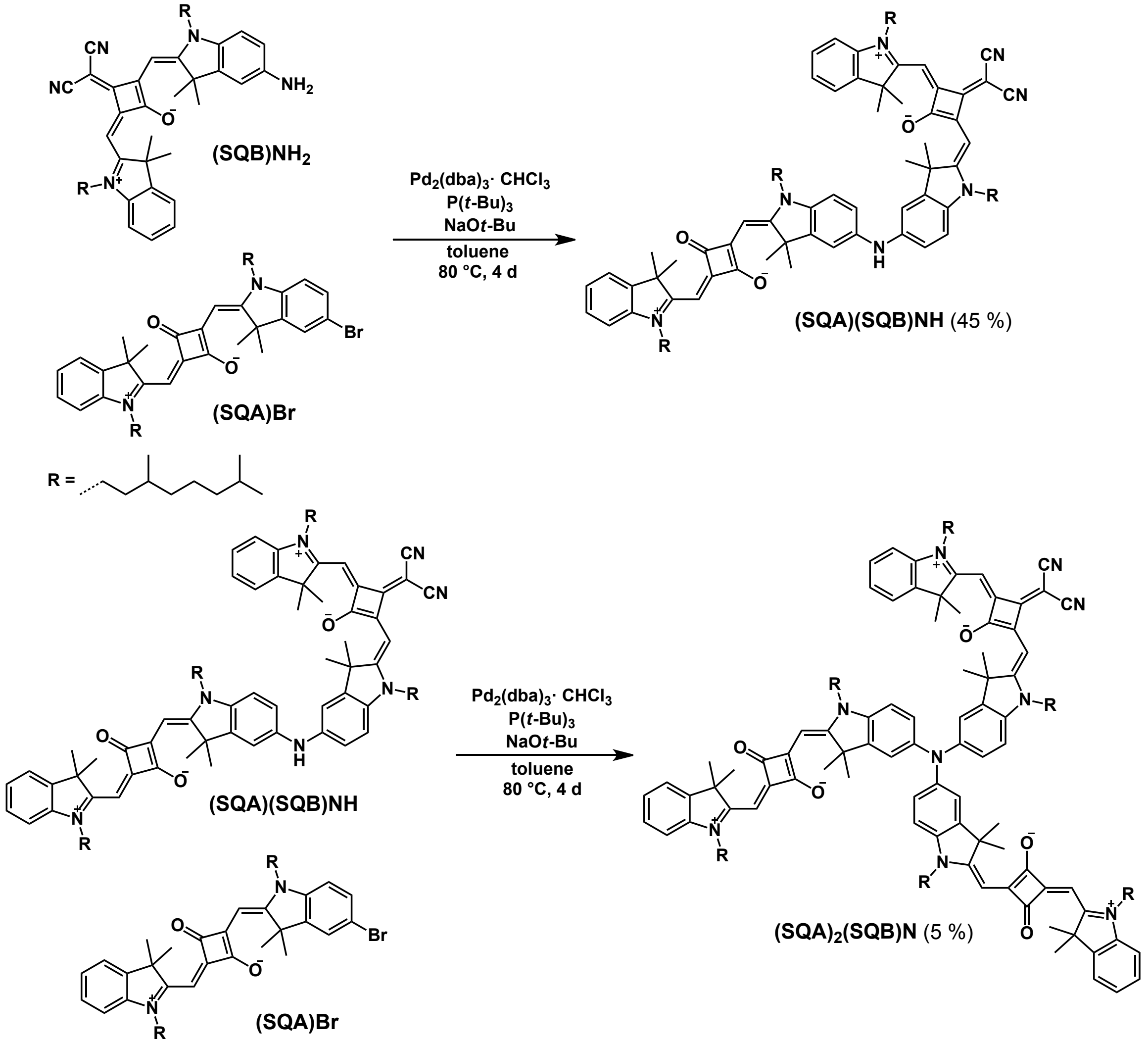
The reference compounds **(SQA)NHAc** and **(SQB)NHAc** were synthesized in a condensation reaction of the quaternary indolenine salt **3** with the corresponding semisquaraines **4** and **5**. The deprotection of the amine functionality was achieved with HCl in ethanol.



Scheme 4: Synthesis of the symmetrical trimers **(SQA)$_3$N** and **(SQB)$_3$N**



Scheme 5: Synthesis of the unsymmetrical trimer **(SQA)(SQB)$_2$N**

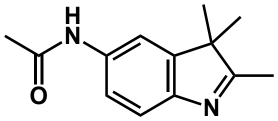


Scheme 6: Synthesis of the dimer **(SQA)(SQB)NH** and the unsymmetrical trimer **(SQA)$_2$(SQB)N**

The trimerisation of the squaraines was achieved by a palladium catalysed *Buchwald-Hartwig*-coupling reaction of one equivalent of the aminated and two equivalents of the brominated unsymmetrical squaraines. In the case of the unsymmetrical trimer **(SQA)$_2$(SQB)N** the *Buchwald-Hartwig* reaction of the monomeric squaraines only yielded the dimer **(SQA)(SQB)NH**. An additional *Buchwald-Hartwig* reaction of the dimer with one equivalent of the brominated squaraine resulted in the desired trimer.

Synthesis

N-(2,3,3-trimethyl-3H-indol-5-yl)acetamide (2)

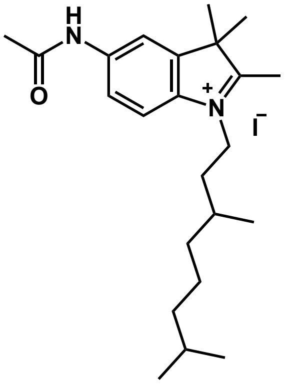


6-Amino-2,3,3-trimethylindole **1** (1.00 g, 5.74 mmol) was dissolved in dry DCM (20 ml). Acetic anhydride (514 µl, 5.45 mmol) and N,N,N-triethylamine (756 µl, 5.45 mmol) were added and the mixture stirred for 30 min at rt. The solvent was removed and the residue purified by flash-chromatography (eluent: EA).

Yield: 1.17 g (5.41 mmol; **99 %**) of a light brown solid
$C_{13}H_{16}N_2O$ [216.28]

^{1}H-NMR (400 MHz, $CDCl_3$, 300 K):
δ[ppm] = 7.75 (d, ^4J = 2.0 Hz, 1H, -C$\underline{H}$-), 7.44 (d, ^3J = 8.0 Hz, 1H, -C$\underline{H}$-), 7.35 (s, 1H -N$\underline{H}$-), 7.15 (dd, ^3J = 8.4 Hz, ^4J = 2.0 Hz, 1H, -C$\underline{H}$-), 2.26 (s, 3H, -COC$\underline{H_3}$), 2.18 (s, 3H, -CC$\underline{H_3}$), 1.29 (s, 6H, -C(C$\underline{H_3}$)$_2$).

5-Acetamido-1(3-7-dimethyloctyl)-2,3,3-trimethyl-3H-indol-1-ium iodide (3)



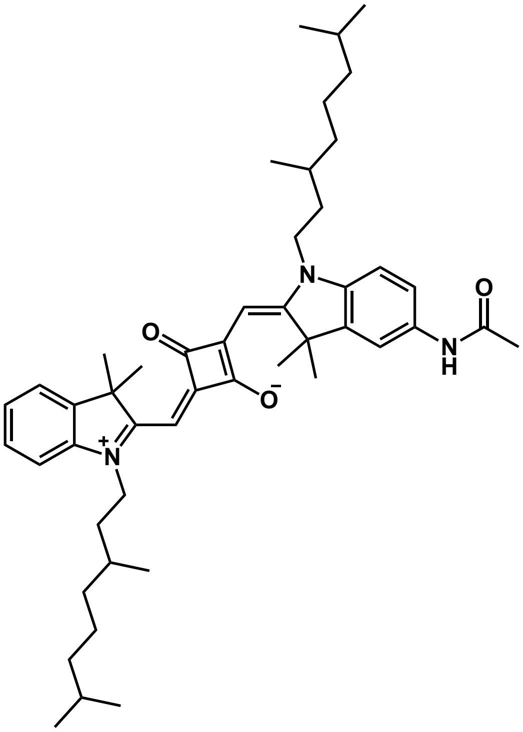
The indolenine derivative **2** (5.73 g, 26.5 mmol) was dissolved in nitromethane (30 ml). 1-Iodo-3,7-dimethyloctane (8.53 g, 31.8 mmol) was added and the solution was refluxed for 18 h. After cooling the solution was concentrated *in vacuo*. Et_2O and Acetone (20:1) were added to the residue und the solution was left at -30 °C for 2 h. The resulting precipitate was filtered, washed with Et_2O and dried under high vacuum.

Yield: 8.03 g (16.6 mmol; **63 %**) of a yellow green solid
$C_{23}H_{37}IN_2O$ [484.46]

^{1}H-NMR (400 MHz, DMSO, 300 K):
δ [ppm] = 10.32 (s, 1H, -N$\underline{H}$-), 8.05 (d, ^4J = 0.8 Hz, 1H, -C$\underline{H}$-), 7.83 (d, ^3J = 8.8 Hz, 1H, -C$\underline{H}$-), 7.66 (dd, ^3J = 8.8 Hz, ^4J = 2.0 Hz, 1H, -C$\underline{H}$-), 4.43 – 4.34 (-, 2H, -NC$\underline{H_2}$-), 3.38 (s, 3H, -COC$\underline{H_3}$),

2.79 (s, 3H, -C(C$\underline{H_3}$)-), 1.88 – 1.76 (m, 1H, -C$\underline{H}$(CH$_3$)-), 1.70 – 1.57 (m, 2H, -NCH$_2$C$\underline{H_2}$-), 1.50 (s, 6H, -C(C$\underline{H_3}$)$_{\underline{2}}$-), 1.56 – 1.44 (m, 1H, -C$\underline{H}$(CH$_3$)$_2$-), 1.40 – 1.06 (-, 6H, -C$\underline{H_2}$C$\underline{H_2}$C$\underline{H_2}$-), 1.0 (d, ^3J = 6.0 Hz, 3H, -CHC$\underline{H_3}$-), 0.848 (d, ^3J = 6.6 Hz, 3H, -CH(C$\underline{H_3}$)$_2$), 0.846 (d, ^3J = 6.6 Hz, 3H, -CH(C$\underline{H_3}$)$_2$).

(SQA)NHAc



The semisquaric acid **4** (156 mg, 394 µmol) and the quaternary salt **3** (191 mg, 394 µmol) were dissolved in a 6/4 mixture of *n*-butanol/toluene (100 ml). Pyridine (3 ml) was added and the mixture was refluxed for 20 h using a Dean-Stark trap. The solvent was removed *in vacuo* and the residue was purified by flash-chromatography (eluent: DCM/MeOH 99:1). 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.

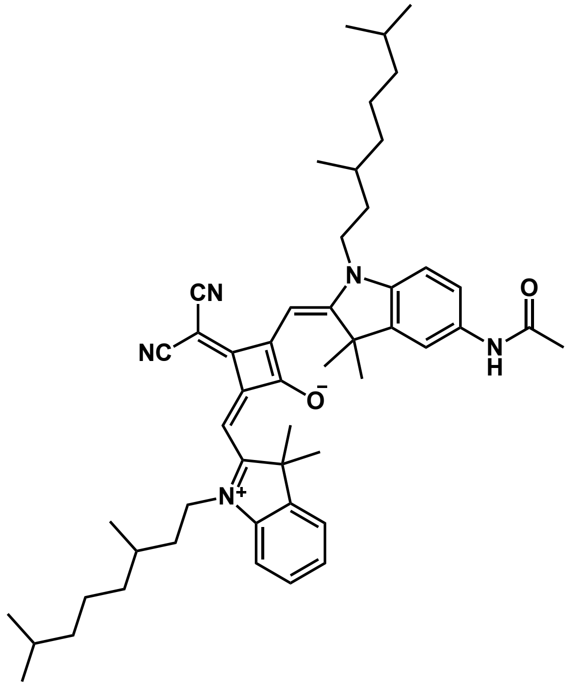
Yield: 240 mg (327 µmol; **83 %**) of a blue powder
$C_{48}H_{67}N_3O_3$ [734.07]

^{1}H-NMR (600 MHz, CDCl$_3$, 303.6 K):
δ [ppm] = 7.67 (s, 1H, -N$\underline{H}$-), 7.54 (d, ^4J = 2.0 Hz, 1H, -C$\underline{H}$-), 7.51 (dd, ^3J = 8.4 Hz, ^4J = 2.0 Hz, 1H, -C$\underline{H}$-), 7.36 (dd, ^3J = 7.5 Hz, ^4J = 0.6 Hz, 1H, -C$\underline{H}$-), 7.31 (ddd, ^3J = 7.7 Hz, ^3J = 7.7 Hz, ^4J = 1.2 Hz, 1H, -C$\underline{H}$-), 7.13 (ddd, ^3J = 7.5 Hz, ^3J = 7.5 Hz, ^4J = 0.5 Hz, 1H, -C$\underline{H}$-), 6.99 (d, ^3J = 8.0 Hz, 1H, -C$\underline{H}$-), 6.93 (d, ^3J = 8.5 Hz, 1H, -C$\underline{H}$-), 5.88 (s, 1H, -CC$\underline{H}$C-), 5.87 (s, 1H, -CC$\underline{H}$C-), 4.04 – 3.87 (-, 4H, 2x -NC$\underline{H_2}$-), 2.15 (s, 3H, -NHCC$\underline{H_3}$), 1.82 – 1.77 (-, 2H, 2x

-NCH$_2$C$\underline{H}_{\underline{2}}$-), 1.76 – 1.74 (-, 12H, 2x -C(C$\underline{H}_{\underline{3}}$)$_{\underline{2}}$), 1.64 – 1.48 (-, 6H, 2x –NCH$_2$C$\underline{H}_{\underline{2}}$-, 2x -C$\underline{H}CH_3$, 2x -C$\underline{H}$(CH$_3$)$_2$), 1.42 – 1.12 (-, 12H, 2x -C$\underline{H}_{\underline{2}}C\underline{H}_{\underline{2}}C\underline{H}_{\underline{2}}$-), 1.04 (d, ^3J = 6.2 Hz, 3H, -CHC$\underline{H}_{\underline{3}}$), 1.03 (d, ^3J = 6.0 Hz, 3H, -CHC$\underline{H}_{\underline{3}}$), 0.87 – 0.85 (-, 12H, 2x -CH(C$\underline{H}_{\underline{3}}$)$_{\underline{2}}$).

^{13}C-NMR (151 MHz, CD$_2$Cl$_2$, 303.6 K):
δ [ppm] 182.1 (2x quart.), 180.1 (quart.), 179.8 (quart.), 169.72 (quart.), 169.67 (quart.), 168.5 (quart.), 143.3 (quart.), 142.9 (quart.), 142.5 (quart.),139.0 (quart.), 135.1 (quart.), 128.1 (tert.), 123.8 (tert.), 122.5 (tert.), 119.9 (tert.), 115.0 (tert.), 109.8 (tert.), 109.6 (tert.), 86.7 (tert.), 86.6 (tert.), 49.8 (quart.), 49.5 (quart.), 42.5 (sec.), 42.3 (sec.), 39.5 (2x sec.), 37.4 (2x sec.), 34.1 (sec.), 34.0 (sec.), 31.46 (tert.), 31.45 (tert.), 28.4 (tert.), 28.3 (tert.), 27.09 (2x prim.), 27.07 (2x prim.), 25.06 (sec.), 25.05 (sec.), 24.7 (prim.), 22.8 (2x prim.), 22.7 (2x prim.), 19.73 (prim.), 19.71 (prim.).

(SQB)NHAc



The semisquaric acid **5** (700 mg, 1.28 mmol) and the quaternary salt **3** (623 mg, 1.29 mmol) were dissolved in a 6/4 mixture of *n*-butanol/toluene (100 ml). Pyridine (5 ml) was added and the mixture was refluxed for 20 h using a Dean-Stark trap. The solvent was removed *in vacuo* and the residue was purified by flash-chromatography (eluent: DCM/MeOH 99:1). 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: 816 mg (1.04 mmol; **81 %**) of a dark green powder
$C_{51}H_{67}N_5O_2$ [782.11]

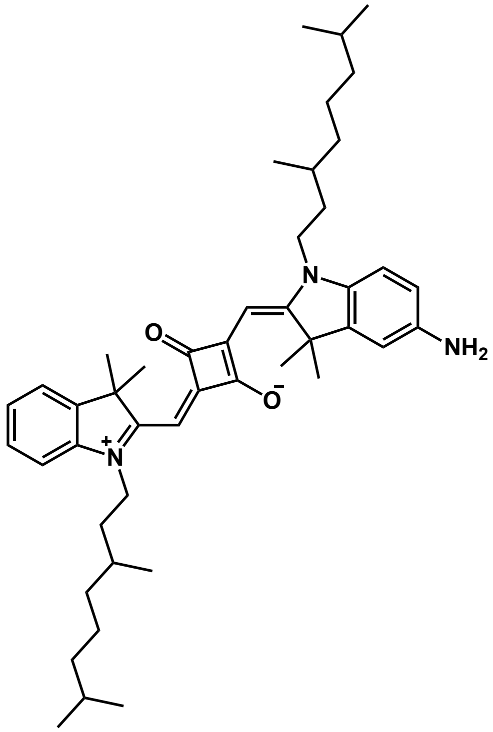
^{1}H-NMR (600 MHz, CDCl$_3$, 303.6 K):

δ [ppm] = 7.60 (d, ^4J = 1.8 Hz, 1H, -C$\underline{H}$-), 7.44 (dd, ^3J = 9.0 Hz, ^4J = 1.8 Hz, 1H, -C$\underline{H}$-), 7.37 – 7.32 (-, 3H, 2x -C$\underline{H}$-, -N$\underline{H}$-), 7.20 (dd, ^3J = 7.4 Hz, ^3J = 7.4 Hz, 1H, -C$\underline{H}$-), 7.02 (d, ^3J = 7.8 Hz, 1H, -C$\underline{H}$-), 6.93 (d, ^3J = 8.4 Hz, 1H, -C$\underline{H}$-), 6.48 (s, 1H, -CC$\underline{H}$C-), 6.45 (s, 1H, -CC$\underline{H}$C-), 4.89 – 3.90 (-, 4H, 2x –NC$\underline{H_2}$-), 2.21 (s, 3H, -CC$\underline{H_3}$), 1.81 – 1.69 (-, 2H, 2x -NCH$_2$C$\underline{H_2}$-), 1.763 (s, 6H, -C(C$\underline{H_3}$)$_{\underline{2}}$), 1.759 (s, 6H, -C(C$\underline{H_3}$)$_{\underline{2}}$), 1.68 – 1.56 (-, 4H, 2x -NCH$_2$C$\underline{H_2}$-, 2x -C$\underline{H}$CH$_3$-), 1.55 – 1.48 (-, ^3J = 6.6 Hz, 2H, 2x -C$\underline{H}$(CH$_3$)$_2$), 1.41 – 1.11 (-, 12H, 2x -C$\underline{H_2}$C$\underline{H_2}$C$\underline{H_2}$-), 1.02 (d, ^3J = 6.6 Hz, 3H, -CHC$\underline{H_3}$), 1.01 (d, ^3J = 6.6 Hz, 3H, -CHC$\underline{H_3}$), 0.857 (d, ^3J = 6.6 Hz, 6H, -CH(C$\underline{H_3}$)$_{\underline{2}}$), 0.856 (d, ^3J = 6.6 Hz, 6H, -CH(C$\underline{H_3}$)$_{\underline{2}}$).

^{13}C-NMR (151 MHz, CDCl$_3$, 303.6 K):

δ [ppm] = 173.4 (quart.), 171.8 (quart.), 171.5 (quart.), 168.4 (quart.), 167.8 (quart.), 166.5 (quart.), 166.4 (quart.), 143.5 (quart.), 142.6 (quart.), 142.1 (quart.), 138.5 (quart.), 135.2 (quart.), 128.1 (tert.), 124.6 (tert.), 122.4 (tert.), 119.9 (tert.), 119.14 (quart.), 119.07 (quart.), 114.9 (tert.), 110.2 (tert.), 110.1 (tert.), 89.2 (tert.), 89.1 (tert.), 49.8 (quart.), 49.6 (quart.), 43.1 (sec.), 43.0 (sec.), 40.9 (quart.), 39.30 (sec.), 39.29 (sec.), 37.28 (sec.), 37.25 (sec.), 34.21 (sec.), 34.20 (sec.), 31.1 (tert.), 31.0 (tert.), 28.120 (tert.), 28.116 (tert.), 26.76 (prim.), 26.72 (2 x prim.), 26.70 (prim.), 24.76 (sec.), 24.75 (sec.), 24.70 (prim.), 22.84 (prim.), 22.83 (prim.), 22.7 (2 x prim), 19.83 (prim.), 19.80 (prim.).

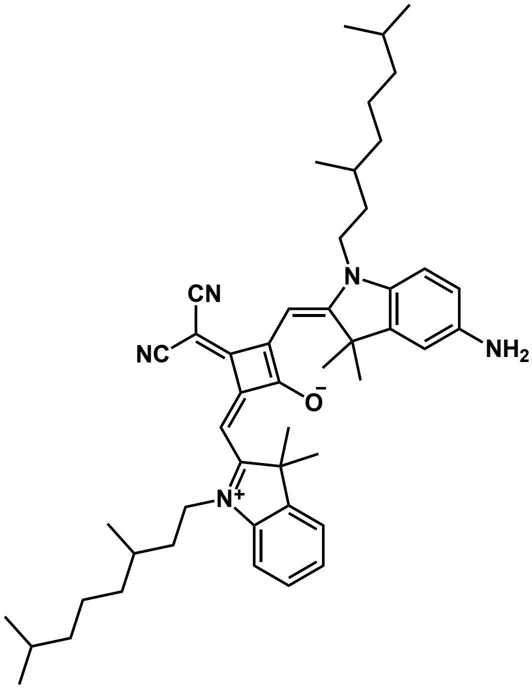
(SQA)NH$_2$



(SQA)NHAc (467 mg, 636 µmol) was dissolved in Ethanol (100 ml).HCl (20 ml 2N) was added and the solution was heated to 85 °C. After 2 h the reaction mixture was allowed to cool to RT, neutralized with a 10 % solution of K_2CO_3 and extracted with DCM (3x 50 ml). The solvent was removed and the residue purified by flash-chromatography (eluent: DCM/MeOH 99:1).

Yield: 249 mg (360 µmol; **57 %**) of a blue solid
$C_{46}H_{65}N_3O_2$ [692.03]
^{1}H-NMR (400 MHz, $CDCl_3$, 300 K):
δ [ppm] = 7.32 (d, ^3J = 7.6 Hz, 1H, -C$\underline{H}$-), 7.27 (ddd, ^3J = 7.7 Hz, ^3J = 7.7 Hz, ^4J = 1.2 Hz, 1H, -C$\underline{H}$-), 7.08 (ddd, ^3J = 7.5 Hz, ^3J = 7.5 Hz, ^4J = 0.6 Hz, 1H, -C$\underline{H}$-), 6.89 (d, ^3J = 7.9 Hz, 1H, -C$\underline{H}$-), 6.78 (d, ^3J = 8.4 Hz, 1H, -C$\underline{H}$-), 6.72 (d, ^4J = 2.0 Hz, 1H, -C$\underline{H}$-), 6.62 (dd, ^3J = 8.4 Hz, ^4J = 2.0 Hz, 1H, -C$\underline{H}$-), 5.90 (s, 1H, -CC$\underline{H}$C-), 5.88 (s, 1H, -CC$\underline{H}$C-), 4.04 – 3.85 (-, 4H, 2x -NC$\underline{H}_2$-), 3.81 – 3.62 (m, 2H, -N$\underline{H}_2$), 1.77 (s, 6H, -C(C$\underline{H}_3$)$_2$), 1.76 (s, 6H, -C(C$\underline{H}_3$)$_2$), 1.84 – 1.71 (-, 2H, 2x -$NH_2CH_2C\underline{H}_2$-), 1.65 – 1.45 (-, 6H, 2x -$NH_2CH_2C\underline{H}_2$-, 2x –C$\underline{H}$CH$_3$, 2x -C$\underline{H}$(CH$_3$)$_2$), 1.41 – 1.11 (-, 12H, 2x -C$\underline{H}_2$C$\underline{H}_2$C$\underline{H}_2$-), 1.04 (d, ^3J = 6.0 Hz, 3H, -CHC$\underline{H}_3$),1.03 (d, ^3J = 6.0 Hz, 3H, -CHC$\underline{H}_3$), 0.88 – 0.84 (-, 12H, 2x -CH(C$\underline{H}_3$)$_2$).

(SQB)NH$_2$

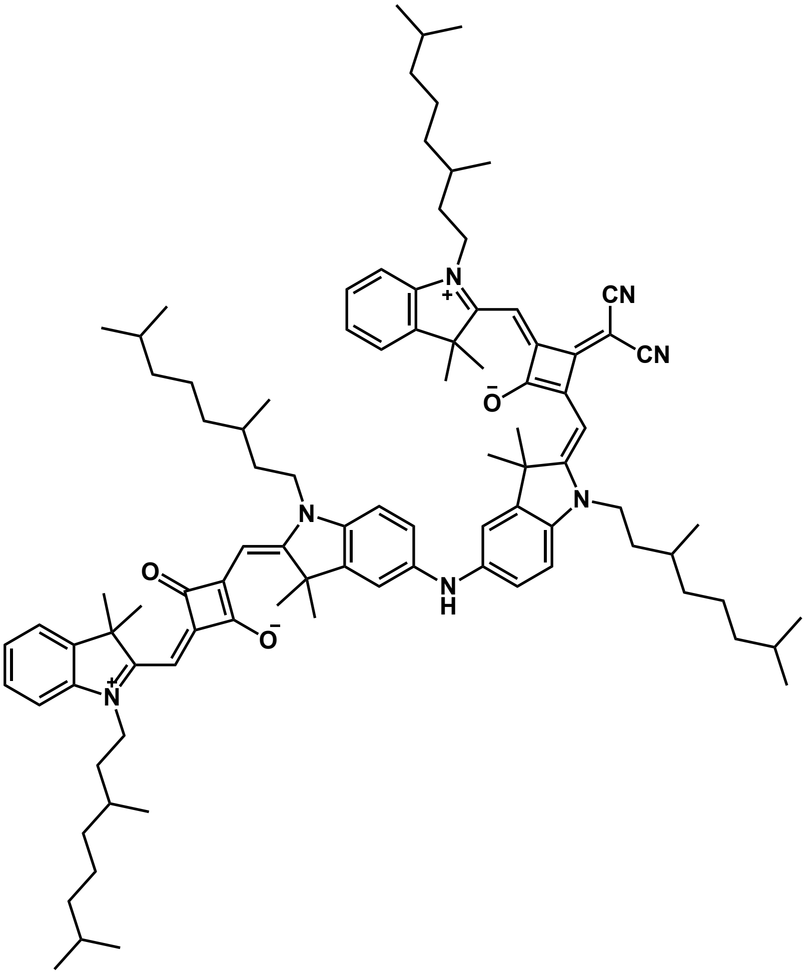


(SQB)NHAc (816 mg, 1.04 mmol) was dissolved in Ethanol (100 ml).HCl (40 ml 2N) was added and the solution was heated to 85 °C. After 3 h the reaction mixture was allowed to cool to rt, neutralized with a 10 % solution of K_2CO_3 and extracted with DCM (3x 50 ml). The solvent was removed and the residue purified by flash-chromatography (eluent: DCM/MeOH 99:1).

<u>Yield</u>: 709 mg (958 µmol; **92 %**) of a green solid
$C_{49}H_{65}N_5O_2$ [740.08]

^{1}H-NMR (400 MHz, $CDCl_3$, 300.0 K):
δ [ppm] = 7.33 – 7.28 (-, 2H, 2x -C$\underline{H}$-), 7.14 (ddd, ^3J = 7.6 Hz, ^3J = 7.6 Hz, ^4J = 0.6 Hz, 1H, -C$\underline{H}$-), 6.96 (d, ^3J = 8.0 Hz, 1H, -C$\underline{H}$-), 6.87 (d, ^3J = 8.4 Hz, 1H, -C$\underline{H}$-), 6.70 (d, ^4J = 2.0 Hz, 1H, -C$\underline{H}$-), 6.64 (dd, ^3J = 8.0 Hz, ^4J = 2.0 Hz, 1H, -C$\underline{H}$-), 6.46 (s, 1H, -CC$\underline{H}$C-), 6.39 (s, 1H, -CC$\underline{H}$C-), 4.89 – 3.92 (-, 4H, 2x –NC$\underline{H_2}$-), 3.80 (s, 2H, -N$\underline{H_2}$), 1.81 – 1.71 (-, 2H, 2x -NCH$_2$C$\underline{H_2}$-), 1.75 (s, 6H, -C(C$\underline{H_3}$)$_{\underline{2}}$), 1.74 (s, 6H, -C(C$\underline{H_3}$)$_{\underline{2}}$), 1.69 – 1.10 (-, 18H, 2x -NCH$_2$C$\underline{H_2}$-, 2x -C$\underline{H}$CH$_3$-, 2x -C$\underline{H}$(CH$_3$)$_2$, 2x -C$\underline{H_2}$C$\underline{H_2}$C$\underline{H_2}$-), 1.02 (d, ^3J = 6.6 Hz, 3H, -CHC$\underline{H_3}$), 1.01 (d, ^3J = 6.6 Hz, 3H, -CHC$\underline{H_3}$), 0.88 – 0.84 (-, 12H, 2x -CH(C$\underline{H_3}$)$_{\underline{2}}$).

Squaraine Dimer **(SQA)(SQB)NH**



Under nitrogen atmosphere **(SQB)NH$_2$** (300 mg, 405 µmol), **(SQA)Br** (919 mg, 1.22 mmol), NaO*t*-Bu (117 mg, 1.22 mmol) and P(*t*-Bu)$_3$ (20.3 µl, 1.00 M in toluene, 20.3 µmol) were dissolved in dry toluene (20 ml). The solution was degassed for 10 min. Then Pd$_2$(dba)$_3$ · CHCl$_3$ (21.0 mg, 20.3 µmol) was added and the blue solution was stirred at 100 °C under exclusion of light for 4 d. The solution was cooled to rt and the solvent was evaporated *in vacuo*. The blue residue was dissolved in DCM (100 ml) and water (100 ml). The organic layer was separated and the aqueous layer was extracted with DCM (2x 100 ml). The combined organic layers were dried over Na$_2$SO$_4$ and the solvent was evaporated. The blue residue was purified by flash-chromatography (eluent: DCM/MeOH 99:1). 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.

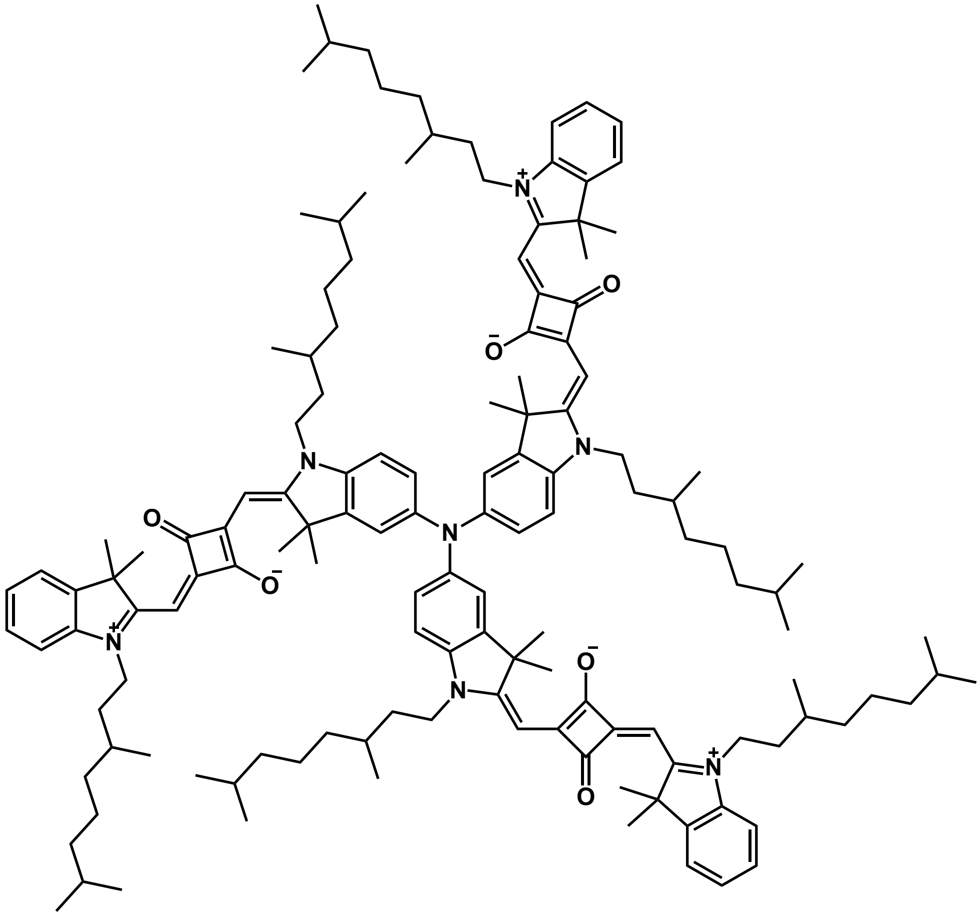
Yield: 260 mg (184 µmol, **45 %**) of a blue powder
$C_{95}H_{127}N_7O_3$ [1415.07]

^{1}H-NMR (600 MHz, CD_2Cl_2, 293.5 K):
δ [ppm] = 7.41 – 7.29 (-, 8H, 8x $-C\underline{H}-$), 7.20 – 7.12 (-, 2H, 2x $-C\underline{H}-$), 7.06 – 6.97 (-, 4H, 4x $-C\underline{H}-$), 6.57 – 6.28 (-, 2H, 2x $-CC\underline{H}C-$), 6.07 – 5.67 (-, 2H, 2x $-CC\underline{H}C-$), 4.43 – 3.64 (-, 8H, 4x $-NC\underline{H_2}-$), 1.84 – 1.70 (-, 16H, 4x $-NCH_2C\underline{H_2}-$, 2x $-C(C\underline{H_3})_{\underline{2}}$), 1.76 (s, 6H, 2x $-C(C\underline{H_3})_2$), 1.73 (s, 6H, $-C(C\underline{H_3})_{\underline{2}}$), 1.69 – 1.47 (-, 12H , 4x $-NCH_2C\underline{H_2}-$, 4x $-C\underline{H}CH_3$, 4x $-C\underline{H}(CH_3)_2$), 1.45 – 1.11 (-, 24H, 4x $-C\underline{H_2}C\underline{H_2}C\underline{H_2}-$), 1.07 (d, ^3J = 6.5 Hz, 3H, $-CHC\underline{H_3}$), 1.05 (d, ^3J = 6.5 Hz, 3H, $-CHC\underline{H_3}$), 1.03 (d, ^3J = 6.6 Hz, 3H, $-CHC\underline{H_3}$), 1.02 (d, ^3J = 6.6 Hz, 3H, $-CHC\underline{H_3}$), 0.88 (d, ^3J = 6.7 Hz, 6H, $-CH(C\underline{H_3})_{\underline{2}}$), 0.87 (d, ^3J = 6.8 Hz, 6H, $-CH(C\underline{H_3})_{\underline{2}}$), 0.86 (d, ^3J = 6.7 Hz, 6H, $-CH(C\underline{H_3})_{\underline{2}}$), 0.85 (d, ^3J = 6.7 Hz, 6H, $-CH(C\underline{H_3})_{\underline{2}}$).
The signal for the $-CN\underline{H}C-$ is missing.

^{13}C-NMR (151 MHz, CD_2Cl_2, 293.5 K):
δ [ppm] = 182.1 (4x quart.), 173.7 (quart.), 170.7 (4x quart.), 167.8 (2x quart.), 165.0 (quart.), 144.5 (2x quart.), 142.7 (8x quart.), 128.2 (4x tert.), 124.3 (2x tert.), 122.5 (4x tert.), 119.3 (2x quart.), 110.1 (4x tert.), 88.9 (2x tert.), 86.9 (tert.), 86.7 (tert.), 50.2 (quart.), 49.8 (quart.), 49.4 (2x quart.), 43.0 (4x sec.), 40.4 (quart.), 39.5 (4x sec.), 37.5 (4x sec.), 34.3 (4x sec.), 31.5 (2x tert.), 31.3 (2x tert.), 28.4 (4x tert.), 27.8 (4x prim), 26.6 (4x prim.), 25.1 (2x sec.), 25.0 (2x sec.), 22.8 (4x prim.), 22.7 (4x prim.), 19.8 (2x prim.), 19.7 (2x prim.).

ESI-MS ($M^{\cdot+}$, high resolution):
calc.: 1415.00274 m/z
found: 1415.00304 m/z delta: 0.21 ppm

Squaraine Trimer **(SQA)₃N**



Under nitrogen atmosphere **(SQA)NH₂** (95.0 mg, 137 µmol), **(SQA)Br** (228 mg, 302 µmol), NaO*t*-Bu (33.0 mg, 343 µmol) and P(*t*-Bu)$_3$ (6.86 µl, 1.00 M in toluene, 6.86 µmol) were dissolved in dry toluene (10 ml). The solution was degassed for 10 min. Then Pd$_2$(dba)$_3$ · CHCl$_3$ (7.10 mg, 6.86 µmol) was added and the blue solution was stirred at 80 °C under exclusion of light for 3 d. The solution was cooled to rt and the solvent was evaporated *in vacuo*. The blue residue was dissolved in DCM (100 ml) and water (100 ml). The organic layer was separated and the aqueous layer was extracted with DCM (2x 100 ml). The combined organic layers were dried over Na$_2$SO$_4$ and the solvent was evaporated. The blue residue was purified by flash-chromatography (eluent: DCM/MeOH 99:1). The main fraction contained additional to the desired trimer some dimer. This fraction was purified by another flash-chromatography. The ratio of MeOH in the eluent (DCM) was raised in 0.1‰ steps from 0‰ to 7.0‰. 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: 9.00 mg (4.41 µmol, **3 %**) of a blue powder

$C_{138}H_{189}N_7O_6$ [2042.03]

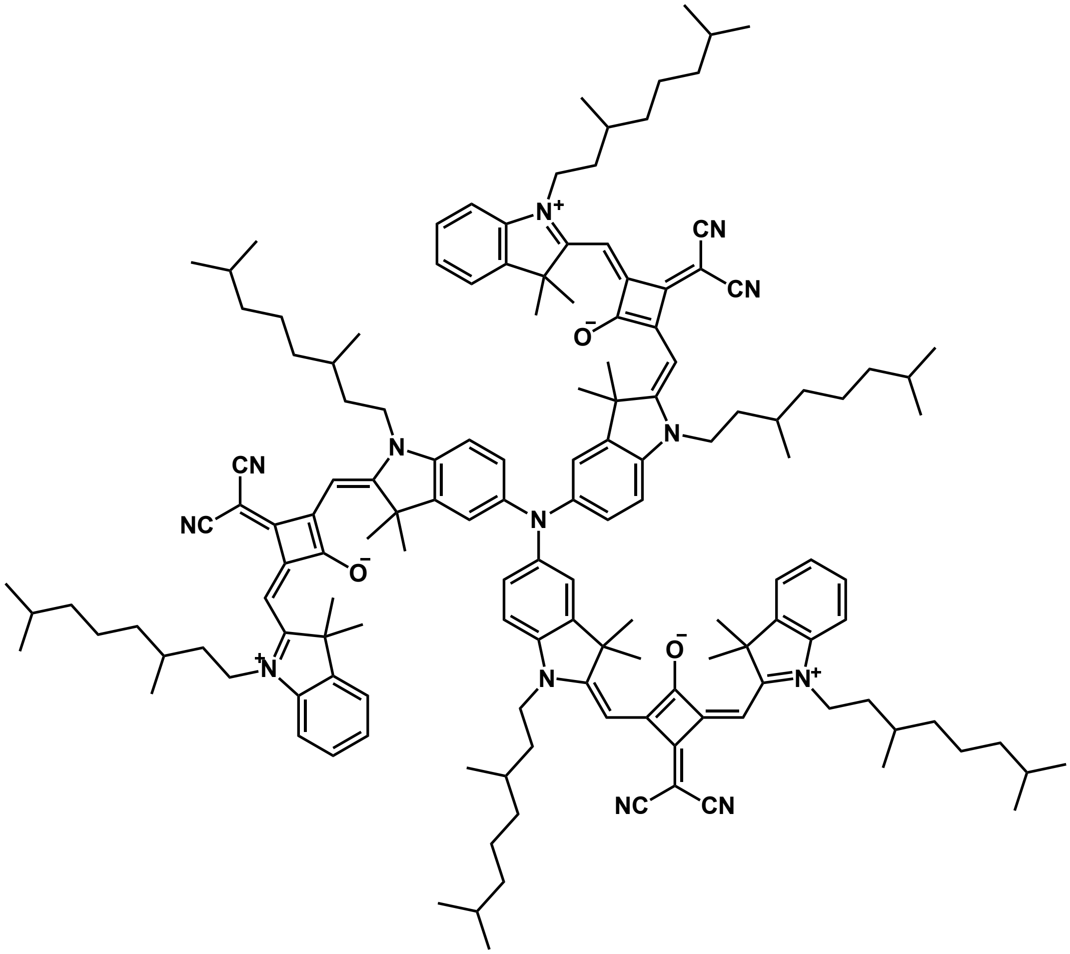
^{1}H-NMR (600 MHz, CD$_2$Cl$_2$, 293.5 K):

δ [ppm] = 7.35 (dd, ^{3}J = 7.5 Hz, ^{4}J = 0.7 Hz, 3H, 3x $\mathrm{-C\underline{H}-}$), 7.30 (ddd, ^{3}J = 7.8 Hz, ^{3}J = 7.8 Hz, ^{4}J = 1.1 Hz, 3H, 3x $\mathrm{-C\underline{H}-}$), 7.15 (d, ^{4}J = 2.0 Hz, 3H, 3x $\mathrm{-C\underline{H}-}$), 7.12 (ddd, ^{3}J = 7.4 Hz, ^{3}J = 7.4 Hz, ^{4}J = 0.6 Hz, 3H, 3x $\mathrm{-C\underline{H}-}$), 7.03 – 6.96 (-, 6H, 6x $\mathrm{-C\underline{H}-}$), 6.89 (d, ^{3}J = 8.7 Hz, 3H, 3x $\mathrm{-C\underline{H}-}$), 5.89 (s, 3H, 3x $\mathrm{-CC\underline{H}C-}$), 5.86 (s, 3H, 3x $\mathrm{-CC\underline{H}C-}$), 4.11 – 3.86 (-, 12H, 6x $\mathrm{-NC\underline{H_2}-}$) 1.85 – 1.76 (-, 6H, 6x $\mathrm{-NCH_2C\underline{H_2}-}$) 1.74 (s, 18H, 3x $\mathrm{-C(C\underline{H_3})_{\underline{2}}}$), 1.70 (s, 18H, 3x $\mathrm{-C(C\underline{H_3})_{\underline{2}}}$), 1.66 – 1.46 (-, 18H, 6x $\mathrm{-NCH_2C\underline{H_2}-}$, 6x $\mathrm{-C\underline{H}CH_3}$, 6x $\mathrm{-C\underline{H}(CH_3)_2}$), 1.45 – 1.11 (-, 36H, 6x $\mathrm{-C\underline{H_2}C\underline{H_2}C\underline{H_2}-}$), 1.06 (d, ^{3}J = 6.4 Hz, 9H, 3x $\mathrm{-CHC\underline{H_3}}$), 1.03 (d, ^{3}J = 6.4 Hz, 9H, 3x $\mathrm{-CHC\underline{H_3}}$), 0.87 (d, ^{3}J = 6.6 Hz, 18H, 3x $\mathrm{-CH(C\underline{H_3})_{\underline{2}}}$), 0.85 (d, ^{3}J = 6.6 Hz, 18H, 3x $\mathrm{-CH(C\underline{H_3})_{\underline{2}}}$).

^{13}C-NMR (151 MHz, $\mathrm{CD_2Cl_2}$, 293.5 K):
δ [ppm] = 182.1 (2x quart.), 180.0 (quart.), 179.4 (quart.), 169.38 (quart.), 169.31 (quart.), 144.7 (quart.), 144.1 (quart.), 142.9 (quart.), 142.5 (quart.), 138.3 (quart.), 128.1 (tert.), 123.7 (tert.), 123.6 (tert.), 122.5 (tert.), 118.6 (tert.), 110.4 (tert.), 109.5 (tert.), 86.8 (tert.), 86.6 (tert.), 49.7 (quart.), 49.4 (quart.), 42.6 (sec.), 42.3 (sec.), 39.51 (sec.), 39.49 (sec.), 37.4 (2x sec.), 34.2 (sec.), 34.0 (sec.), 31.51 (tert.), 31.46 (tert.), 28.37 (tert.), 28.34 (tert.), 27.1 (2x prim.), 27.0 (2x prim.), 25.1 (sec.), 25.0 (sec.), 22.84 (prim.), 22.79 (prim.), 22.74 (prim.), 22.70 (prim.), 19.74 (prim.), 19.73 (prim.).

ESI-MS ($\mathrm{M^{\cdot +}}$, high resolution):
calc.: 2041.47268 m/z
found.: 2041.47634 m/z delta: 1.79 ppm

Squaraine Trimer **(SQB)$_3$N**



Under nitrogen atmosphere **(SQB)NH$_2$** (200 mg, 270 µmol), (**SQB)Br** (478 mg, 595 µmol), NaO*t*-Bu (64.9 mg, 675 µmol) and P(*t*-Bu)$_3$ (13.5 µl, 1.00 M in toluene, 13.5 µmol) were dissolved in dry toluene (20 ml). The solution was degassed for 10 min. Then Pd$_2$(dba)$_3$ · CHCl$_3$ (14.0 mg, 13.5 µmol) was added and the green solution was stirred at 80 °C under exclusion of light for 3 d. The solution was cooled to rt and the solvent was evaporated *in vacuo*. The green residue was dissolved in DCM (100 ml) and water (100 ml). The organic layer was separated and the aqueous layer extracted with DCM (2x 100 ml). The combined organic layers were dried over Na$_2$SO$_4$ and the solvent was evaporated. The blue residue was purified by flash-chromatography (eluent: DCM → DCM/MeOH 99.9:0.1 → 99.5:0.5). The main fraction contained additional to the desired trimer some dimer. This fraction was purified by another flash-chromatography with a gradient of: DCM/MeOH 99.95:0.05 → 99.9:0.1 → 99.8:0.2. 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.

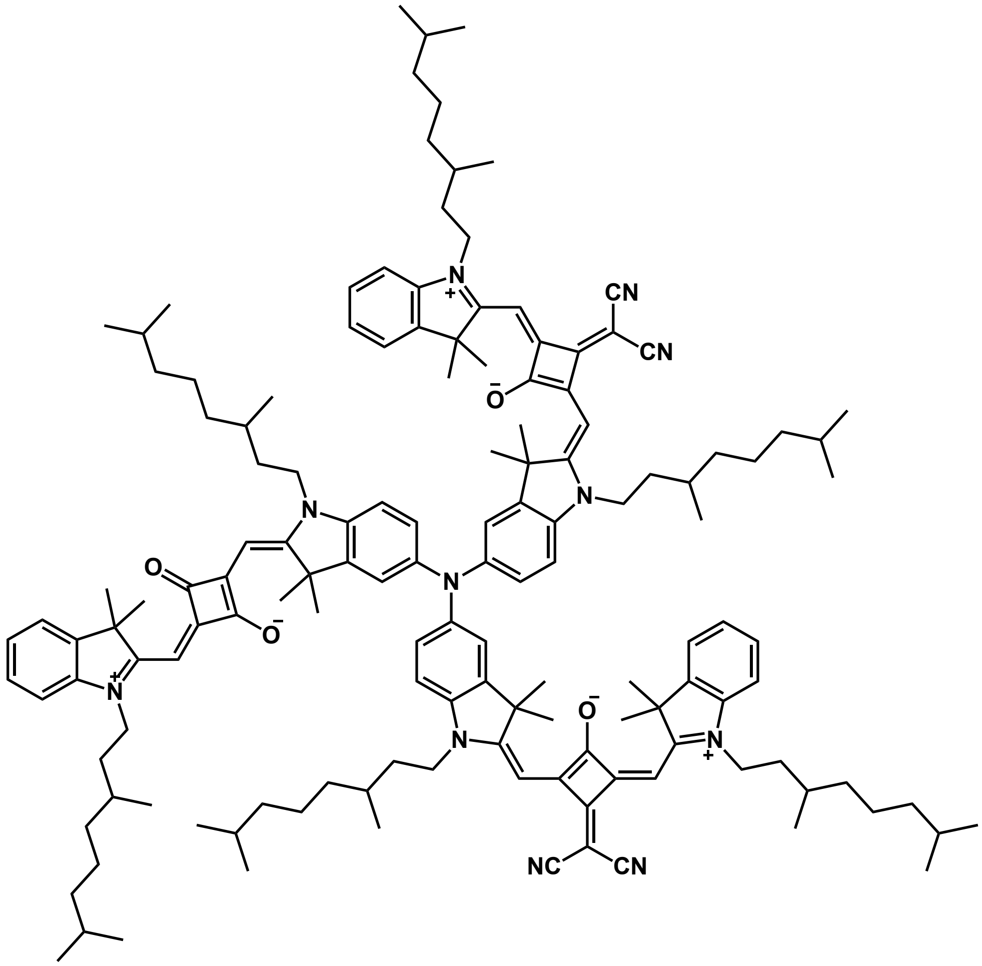
Yield: 27.0 mg (12.4 µmol, **5 %**) of a green powder
$C_{147}H_{189}N_{13}O_3$ [2186.17]

^{1}H-NMR (600 MHz, CD_2Cl_2, 293.5 K):
δ [ppm] = 7.37 – 7.32 (-, 6H, 6x -C$\underline{H}$-), 7.20 – 7.16 (-, 6H, 6x -C$\underline{H}$-), 7.07 – 7.02 (-, 6H, 6x -C$\underline{H}$-), 6.97 (d, ^3J = 8.7 Hz, 3H, 3x -C$\underline{H}$-), 6.46 (s, 3H, 3x -CC$\underline{H}$C-), 6.44 (s, 3H, 3x -CC$\underline{H}$C-), 4.11 – 3.94 (-, 12H, 6x -NC$\underline{H}_{\underline{2}}$-), 1.84 – 1.75 (-, 6H, 6x -NCH_2C$\underline{H}_{\underline{2}}$-), 1.71 (s, 18H, 3x -C(C$\underline{H}_{\underline{3}}$)$_{\underline{2}}$), 1.70 (s, 18H, 3x -C(C$\underline{H}_{\underline{3}}$)$_{\underline{2}}$), 1.73 – 1.48 (-, 18H, 6x -NCH_2C$\underline{H}_{\underline{2}}$-, 6x -C$\underline{H}CH_3$, 6x -C$\underline{H}$(C$H_3$)$_2$), 1.45 – 1.11 (-, 36H, 6x -C$\underline{H}_{\underline{2}}C\underline{H}_{\underline{2}}C\underline{H}_{\underline{2}}$-), 1.04 (d, ^3J = 6.4 Hz, 9H, 3x -CHC$\underline{H}_{\underline{3}}$), 1.02 (d, ^3J = 6.5 Hz, 9H, 3x -CHC$\underline{H}_{\underline{3}}$), 0.87 (d, ^3J = 6.5 Hz, 18H, 3x -CH(C$\underline{H}_{\underline{3}}$)$_{\underline{2}}$), 0.86 (d, ^3J = 6.4 Hz, 18H, 3x -CH(C$\underline{H}_{\underline{3}}$)$_{\underline{2}}$).

^{13}C-NMR (151 MHz, CD_2Cl_2, 293.5 K):
δ [ppm] = 173.6 (quart.), 171.6 (quart.), 171.1 (quart.), 167.9 (quart.), 166.07 (quart.), 166.05 (quart.), 145.1 (quart.), 144.5 (quart.), 142.8 (quart.), 142.4 (quart.), 138.0 (quart.), 128.3 (tert.), 124.7 (tert.), 123.9 (tert.), 122.5 (tert.), 119.23 (quart.), 119.15 (quart.), 118.4 (tert.), 111.3 (tert.), 110.4 (tert.), 89.5 (tert.), 89.2 (tert.), 49.8 (quart.), 49.7 (quart.), 43.5 (sec.), 43.2 (sec.), 40.48 (quart.), 39.53 (sec.), 39.52 (sec.), 37.5 (2x sec.), 34.5 (sec.), 34.3 (sec.), 31.33 (tert.), 31.29 (tert.), 28.40 (tert.), 28.38 (tert.), 26.66 (prim.), 26.63 (prim.), 26.60 (prim.), 26.57 (prim.), 25.04 (sec.), 25.01 (sec.), 22.84 (prim.), 22.81 (prim.), 22.75 (prim.), 22.72 (prim.), 19.79 (prim.), 19.77 (prim.).

ESI-MS ($M^{\cdot +}$, high resolution):
calc.: 2185.50630 m/z
found.: 2185.50695 m/z delta: 0.30 ppm

Squaraine Trimer **(SQA)(SQB)$_2$N**



Under nitrogen atmosphere **(SQA)NH$_2$** (78.0 mg, 113 µmol), **(SQB)Br** (199 mg, 248 µmol), NaO*t*-Bu (27.1 mg, 282 µmol) and P(*t*-Bu)$_3$ (5.64 µl, 1.00 M in toluene, 5.64 µmol) were dissolved in dry toluene (10 ml). The solution was degassed for 10 min. Then Pd$_2$(dba)$_3$ · CHCl$_3$ (5.83 mg, 5.63 µmol) was added and the blue solution was stirred at 80 °C under exclusion of light for 3 d. The solution was cooled to rt and the solvent was evaporated *in vacuo*. The green residue was dissolved in DCM (100 ml) and water (100 ml). The organic layer was separated and the aqueous layer extracted with DCM (2x 100 ml). The combined organic layers were dried over Na$_2$SO$_4$ and the solvent was evaporated. The green residue was purified by flash-chromatography (eluent: DCM → DCM/MeOH 99.9:0.1 → 99.5:0.5). The main fraction contained additional to the desired trimer **(SQA)(SQB)$_2$N** some dimer **(SQA)(SQB)NH**. This fraction was purified by another flash-chromatography. The ratio of MeOH in the eluent (DCM) was raised in 0.1‰ steps from 0‰ to 6.0‰. Finally the crude products were 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.

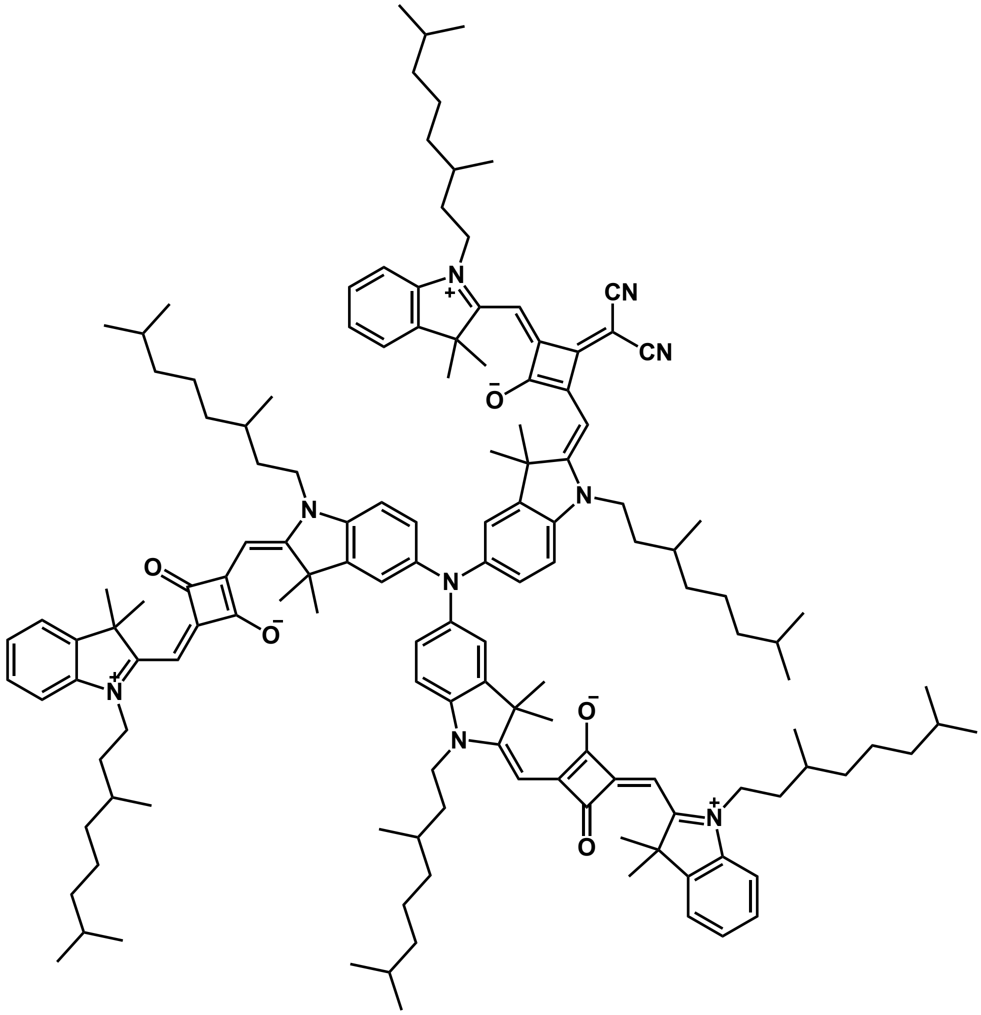
<u>Yield:</u> 25.7 mg (12.0 µmol, **11 %**) of a green powder
$C_{144}H_{189}N_{11}O_4$ [2138.12]

^{1}H-NMR (600 MHz, CD$_2$Cl$_2$, 293.5 K):
δ [ppm] = 7.37 – 7.29 (-, 6H, 6x -C$\underline{H}$-), 7.19 – 7.16 (-, 5H, 5x -C$\underline{H}$-), 7.14 (dd, ^3J = 7.5 Hz, ^3J = 7.5 Hz, ^4J = 0.5 Hz, 1H, -C$\underline{H}$-), 7.06 – 7.01 (-, 5H, 5x -C$\underline{H}$-), 6.99 (d, ^3J = 8.0 Hz, 1H, -C$\underline{H}$-), 6.96 (d, ^3J = 8.6 Hz, 2H, 2x -C$\underline{H}$-), 6.91 (d, ^3J = 8.6 Hz, 1H, -C$\underline{H}$-), 6.46 (s, 2H, 2x -CC$\underline{H}$C-), 6.43 (s, 2H, 2x -CC$\underline{H}$C-), 5.90 (s, 1H, -CC$\underline{H}$C-), 5.88 (s, 1H, -CC$\underline{H}$C-), 4.10 – 3.92 (-, 12H, 6x -NC$\underline{H}_{\underline{2}}$-), 1.85 – 1.46 (-, 42H, 6x -NCH$_2$C$\underline{H}_{\underline{2}}$-, 6x -C$\underline{H}CH_3$, 6x -C$\underline{H}$(CH$_3$)$_2$, 3x -C(C$\underline{H}_{\underline{3}}$)$_{\underline{2}}$), 1.74 (s, 6H, -C(C$\underline{H}_{\underline{3}}$)$_{\underline{2}}$), 1.70 (s, 12H, 2x -C(C$\underline{H}_{\underline{3}}$)$_{\underline{2}}$), 1.44 – 1.11 (-, 36H, 6x -C$\underline{H}_{\underline{2}}C\underline{H}_{\underline{2}}C\underline{H}_{\underline{2}}$-), 1.07 (d, ^3J = 6.3 Hz, 3H, -CHC$\underline{H}_{\underline{3}}$), 1.04 (d, ^3J = 6.4 Hz, 3H, -CHC$\underline{H}_{\underline{3}}$), 1.03 (d, ^3J = 6.5 Hz, 6H, 2x -CHC$\underline{H}_{\underline{3}}$), 1.02 (d, ^3J = 6.5 Hz, 6H, 2x -CHC$\underline{H}_{\underline{3}}$), 0.88 (d, ^3J = 6.7 Hz, 6H, -CH(C$\underline{H}_{\underline{3}}$)$_{\underline{2}}$), 0.87 (d, ^3J = 6.0 Hz, 12H, 2x -CH(C$\underline{H}_{\underline{3}}$)$_{\underline{2}}$), 0.86 (d, ^3J = 6.1 Hz, 12H, 2x -CH(C$\underline{H}_{\underline{3}}$)$_{\underline{2}}$), 0.84 (d, ^3J = 6.7 Hz, 6H, -CH(C$\underline{H}_{\underline{3}}$)$_{\underline{2}}$).

^{13}C-NMR (151 MHz, CD$_2$Cl$_2$, 293.5 K):
δ [ppm] = 182.08 (2x quart.), 179.9 (quart.), 179.7 (quart.), 173.57 (quart.), 171.5 (quart.), 171.2 (quart.), 169.8 (quart.), 169.1 (quart.), 167.8 (quart.), 166.1 (quart.), 165.9 (quart.), 145.4 (quart.), 144.5 (quart.), 144.2 (quart.), 144.1 (quart.), 142.9 (quart.), 142.8 (quart.), 142.6 (quart.), 142.4 (quart.), 138.9 (quart.), 137.7 (quart.), 128.3 (tert.), 128.1 (tert.) 124.6 (tert.), 124.3 (tert.), 123.9 (tert.), 123.5 (tert.), 122.5 (2x tert.), 119.26 (quart.), 119.19 (quart.), 119.14 (tert.), 118.1 (tert.), 111.3 (tert.), 110.4 (tert.), 110.3 (tert.), 109.7 (tert.), 89.5 (tert.), 89.1 (tert.), 86.9 (tert.), 86.7 (tert.), 49.9 (quart.), 49.64 (quart.), 49.57 (quart.), 49.5 (quart.), 43.5 (sec.), 43.2 (sec.), 42.6 (sec.), 42.4 (sec.), 40.4 (quart.), 39.52 (3x sec.), 39.49 (sec.), 37.46 (2x sec.), 37.44 (2x sec.), 34.5 (sec.), 34.3 (sec.), 34.2 (sec.), 34.0 (sec.), 31.52 (tert.), 31.47 (tert.), 31.33 (tert.), 31.29 (tert.), 28.39 (tert.), 28.38 (tert.), 28.37 (tert.), 28.34 (tert.), 27.08 (2x prim.), 27.06 (2x prim.), 26.68 (prim.), 26.65 (prim.), 26.57 (prim.), 26.54 (prim.), 25.09 (sec.), 25.05 (sec.), 25.03 (sec.), 25.01 (sec.), 22.84 (2x prim.), 22.81 (prim.), 22.79 (prim.), 22.75 (2x prim.), 22.72 (prim.), 22.71 (prim.), 19.78 (prim.), 19.77 (prim.), 19.76 (prim.), 19.73 (prim.).

ESI-MS ($M^{\cdot+}$, high resolution):
calc.: 2137.49509 m/z
found.: 2137.49587 m/z delta: 0.36 ppm

Squaraine Trimer **(SQA)₂(SQB)N**



Under nitrogen atmosphere **(SQA)(SQB)HN** (260 mg, 184 µmol), **(SQA)Br** (167 mg, 221 µmol), NaO*t*-Bu (53.0 mg, 552 µmol) and P(*t*-Bu)$_3$ (9.19 µl, 1.00 M in toluene, 9.19 µmol) were dissolved in dry toluene (20 ml). The solution was degassed for 10 min. Then Pd$_2$(dba)$_3$ · CHCl$_3$ (9.51 mg, 9.19 µmol) was added and the blue solution was stirred at 100 °C under exclusion of light for 4 d. The solution was cooled to rt and the solvent was evaporated *in vacuo*. The blue residue was dissolved in DCM (100 ml) and water (100 ml). The organic layer was separated and the aqueous layer extracted with DCM (2x 100 ml). The combined organic layers were dried over Na$_2$SO$_4$ and the solvent was evaporated. The blue residue was purified by flash-chromatography (eluent: DCM/MeOH 99:1). The main fraction was additionally 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: 26.0 mg (11.9 µmol, **6** %) of a blue powder
$C_{141}H_{189}N_9O_5$ [2190.07]

^{1}H-NMR (600 MHz, CD_2Cl_2, 293.5 K):
δ [ppm] = 7.36 – 7.33 (-, 3H, 3x $-C\underline{H}-$), 7.33 – 7.29 (-, 3H, 3x $-C\underline{H}-$), 7.18 – 7.12 (-, 6H, 6x $-C\underline{H}-$), 7.04 – 6.94 (-, 7H 7x $-C\underline{H}-$), 6.90 (d, ^3J = 8.9 Hz, 2H, 2x $-C\underline{H}-$), 6.46 (s, 1H, $-CC\underline{H}C-$), 6.42 (s, 1H, $-CC\underline{H}C-$), 5.90 (s, 2H, 2x $-CC\underline{H}C-$), 5.87 (s, 2H, 2x-$CC\underline{H}C-$), 4.10 – 3.91 (-, 12H, 6x $-NC\underline{H_2}-$), 1.86 – 1.47 (-, 42H, 3x $-C(C\underline{H_3})_2$, 6x $-NCH_2C\underline{H_2}-$, 6x $-C\underline{H}CH_3$, 6x $-C\underline{H}(CH_3)_2$), 1.74 (s, 12H, 2x $-C(C\underline{H_3})_2$), 1.69 (s, 6H, $-C(C\underline{H_3})_2$), 1.46 – 1.11 (-, 36H, 6x $–C\underline{H_2}C\underline{H_2}C\underline{H_2}-$), 1.07 (d, ^3J = 6.2 Hz, 6H, 2x $-CHC\underline{H_3}$), 1.04 (d, ^3J = 6.2 Hz, 6H, 2x $-CHC\underline{H_3}$), 1.03 (d, ^3J = 6.5 Hz, 3H, $-CHC\underline{H_3}$), 1.01 (d, ^3J = 6.6 Hz, 3H, $-CHC\underline{H_3}$), 0.87 (d, ^3J = 6.7 Hz, 12H, 2x $-CH(C\underline{H_3})_2$), 0.86 (d, ^3J = 6.8 Hz, 6H, $-CH(C\underline{H_3})_2$), 0.85 (d, ^3J = 6.6 Hz, 6H, $-CH(C\underline{H_3})_2$), 0.84 (d, ^3J = 6.7 Hz, 12H, 2x $-CH(C\underline{H_3})_2$).

^{13}C-NMR (151 MHz, CD_2Cl_2, 293.5 K):
δ [ppm] = 182.0 (2x quart.), 179.9 (quart.), 179.7 (quart.), 173.6 (quart.), 171.3 (2x quart.), 169.6 (quart.), 169.3 (quart.), 167.8 (quart.), 166.2 (quart.), 165.6 (quart.), 145.8 (quart.), 144.5 (quart.), 144.4 (quart.), 144.2 (quart.), 142.9 (quart.), 142.8 (quart.), 142.5 (quart.), 142.4 (quart.), 138.6 (quart.), 137.4 (quart.), 128.3 (tert.), 128.1 (tert.), 124.5 (tert.), 124.0 (tert.), 123.8 (tert.), 123.1 (tert.), 122.5 (2x tert.), 119.3 (quart.), 119.2 (quart.), 118.9 (tert.), 117.7 (tert.), 111.2 (tert.), 110.4 (tert.), 110.2 (tert.), 109.6 (tert.), 89.5 (tert.), 89.0 (tert.), 86.9 (tert.), 86.7 (tert.), 49.9 (quart.), 49.62 (quart.), 49.58 (quart.), 49.5 (quart.), 43.6 (sec.), 43.1 (sec.), 42.6 (sec.), 42.3 (sec.), 40.4 (quart.), 39.52 (3x sec.), 39.49 (sec.), 37.47 (sec.), 37.45 (2x sec.), 37.44 (sec.), 34.5 (sec.), 34.3 (sec.), 34.2 (sec.), 34.0 (sec.), 31.51 (tert.), 31.47 (tert.), 31.33 (tert.), 31.29 (tert.), 28.39 (tert.), 28.38 (tert.), 28.37 (tert.), 28.34 (tert.), 27.1 (2x prim.), 27.0 (2x prim.), 26.71 (prim.), 26.67 (prim.), 26.53 (prim.), 26.50 (prim.), 25.09 (sec.), 25.05 (sec.), 25.02 (sec.), 25.01 (sec.), 22.84 (2x prim.), 22.81 (prim.), 22.80 (prim.), 22.75 (2x prim.), 22.73 (prim.), 22.71 (prim.), 19.78 (2x prim.), 19.75 (prim.), 19.73 (prim.).

ESI-MS ($M^{\cdot+}$, high resolution):
calc.: 2089.48389 m/z
found.: 2089.48455 m/z delta: 0.32 ppm

Transient absorption spectra

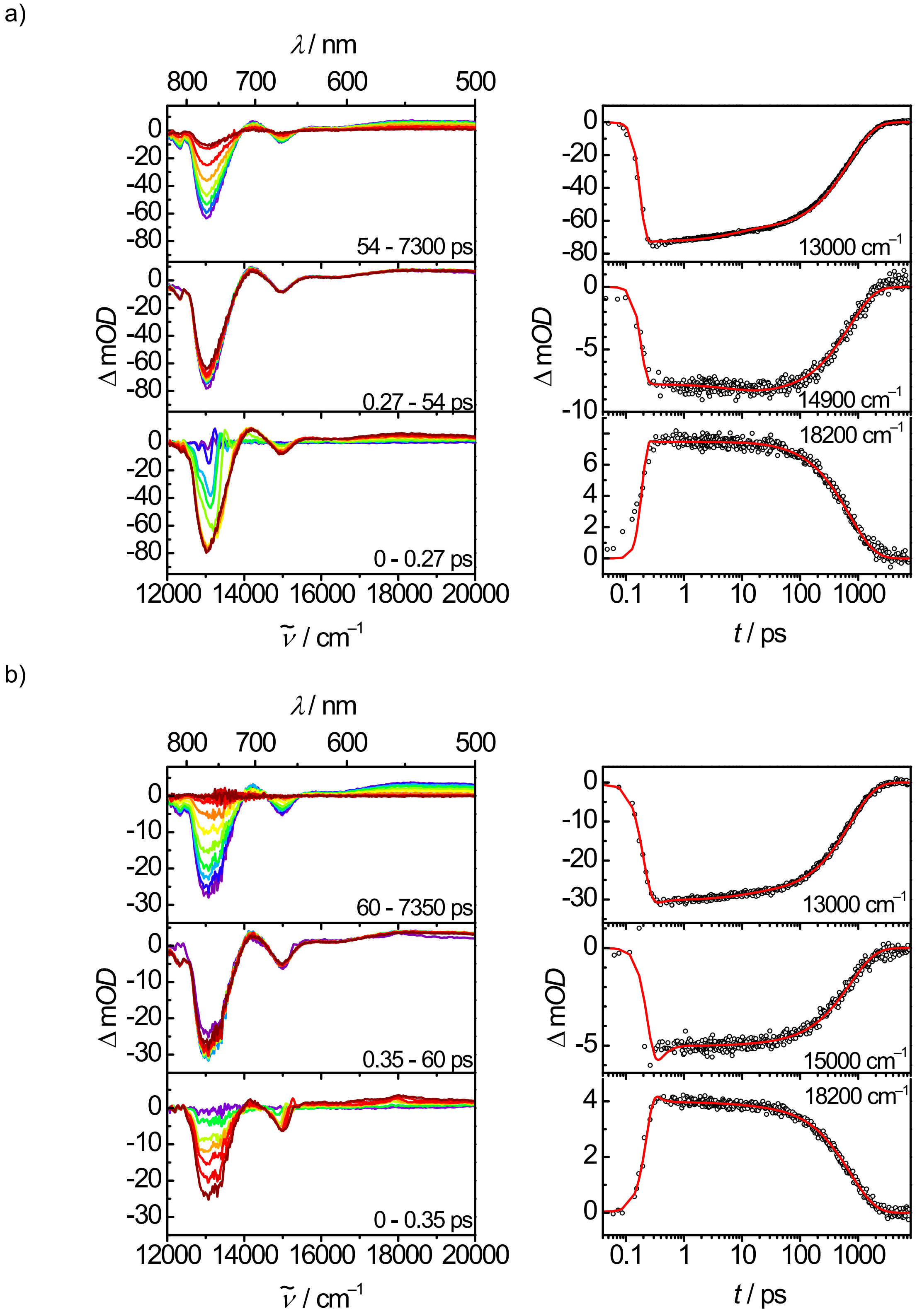


Fig. S1. Transient absorption spectra (stray light and chirp corrected; early spectra are given in blue, later spectra in red) and time scans at selected wavenumbers of **$(SQB)_3N$** in toluene at a) 13200 cm^{-1} pump energy b) 14900 cm^{-1} pump energy.

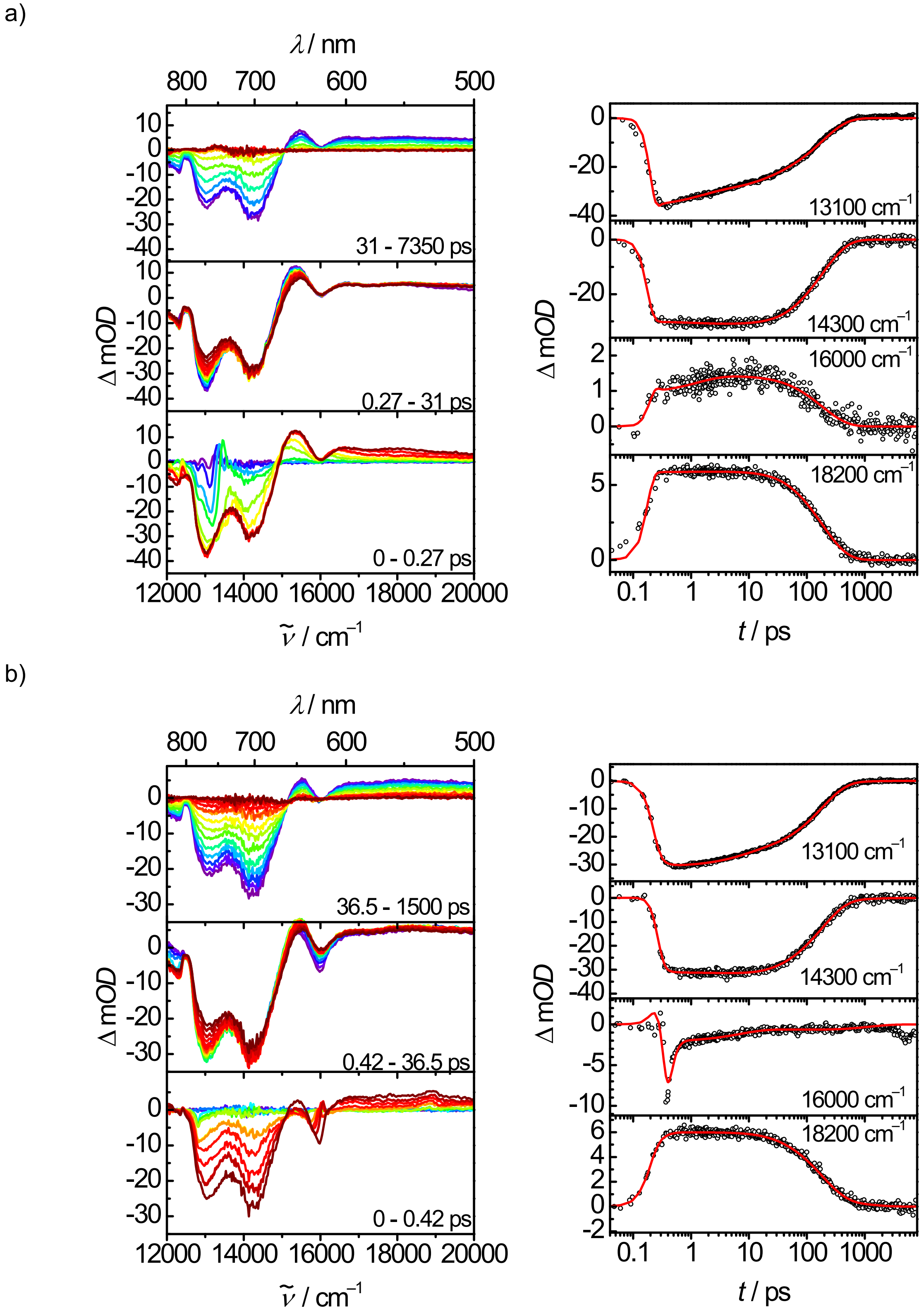


Fig. S2. Transient absorption spectra (stray light and chirp corrected; early spectra are given in blue, later spectra in red) and time scans at selected wavenumbers of **(SQA)$_2$(SQB)N** in toluene at a) 13200 cm^{-1} pump energy b) 15800 cm^{-1} pump energy.

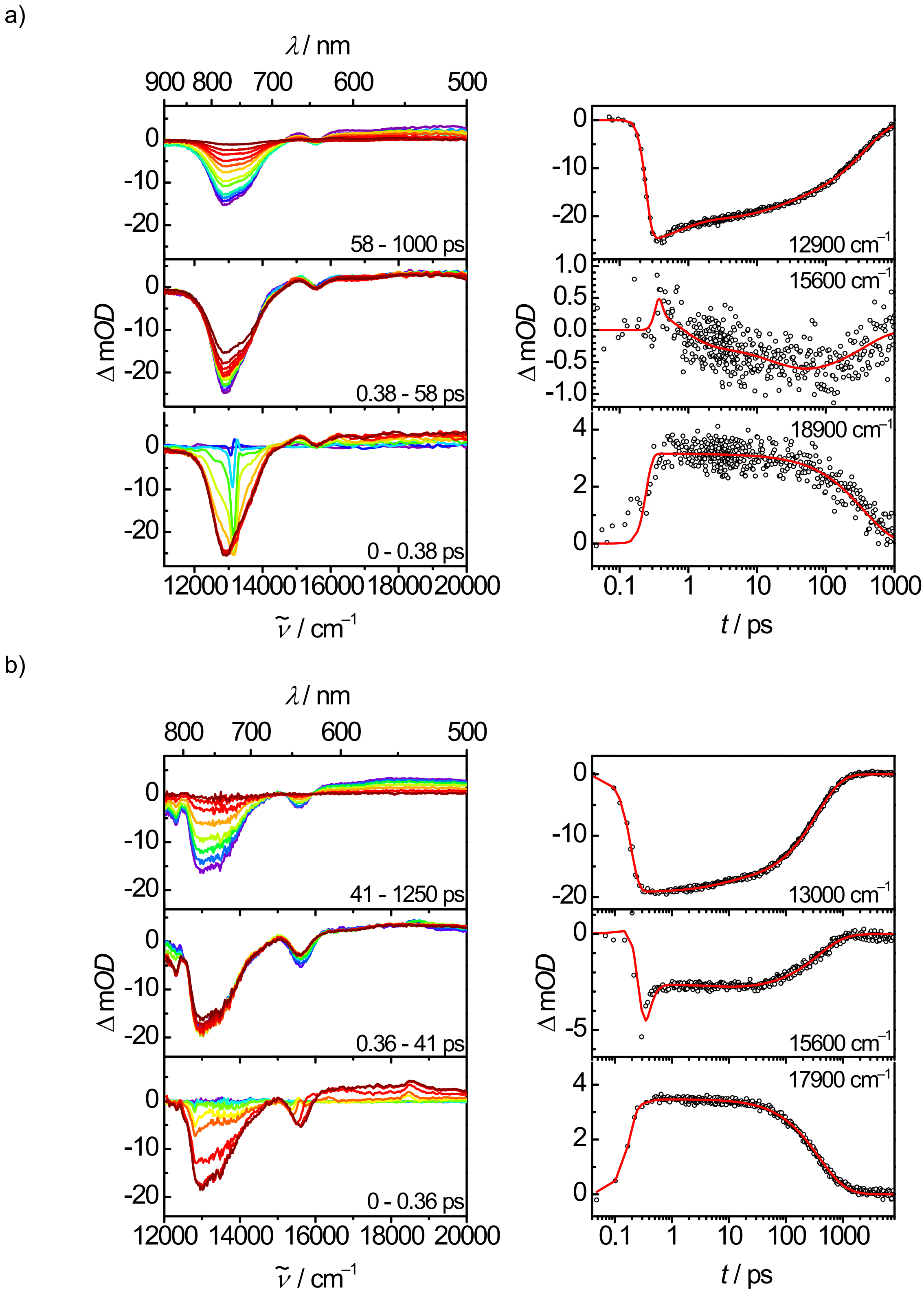


Fig. S3. Transient absorption spectra (stray light and chirp corrected; early spectra are given in blue, later spectra in red) and time scans at selected wavenumbers of **(SQA)(SQB)$_2$N** in toluene at a) 13100 cm^{-1} pump energy b) 15500 cm^{-1} pump energy.

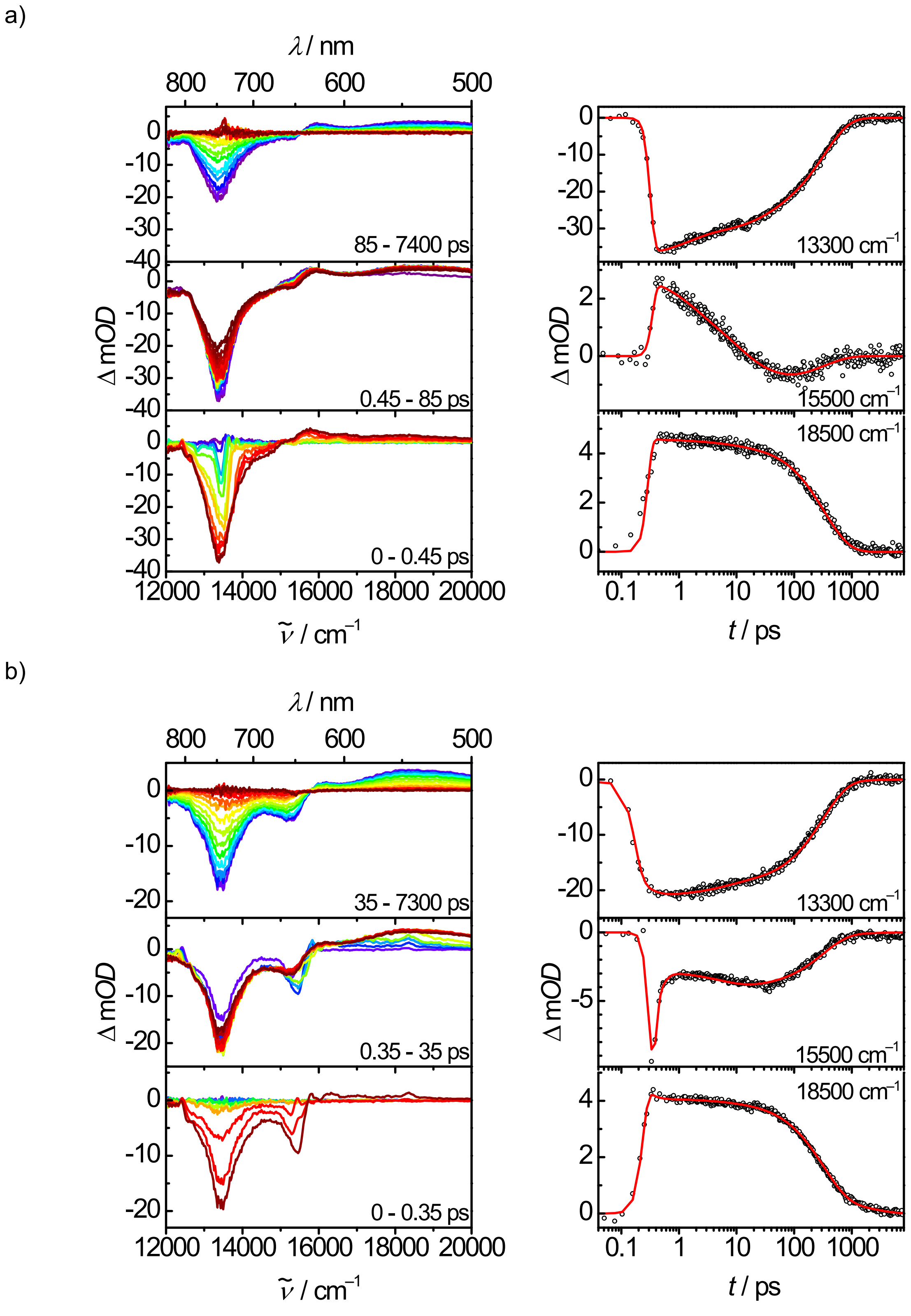


Fig. S4. Transient absorption spectra (stray light and chirp corrected; early spectra are given in blue, later spectra in red) and time scans at selected wavenumbers of **(SQA)(SQB)NH** in toluene at a) 13500 cm^{-1} pump energy b) 15400 cm^{-1} pump energy.

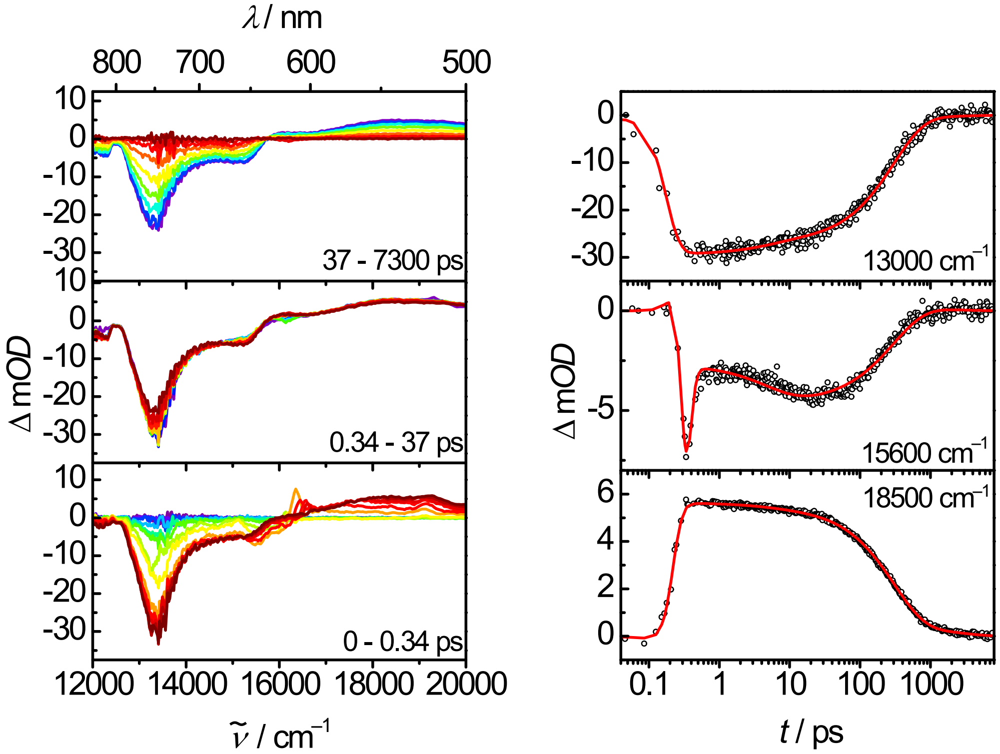


Fig. S5. Transient absorption spectra (stray light and chirp corrected; early spectra are given in blue, later spectra in red) and time scans at selected wavenumbers of **(SQA)(SQB)NH** in toluene at 16100 cm^{-1} pump energy.

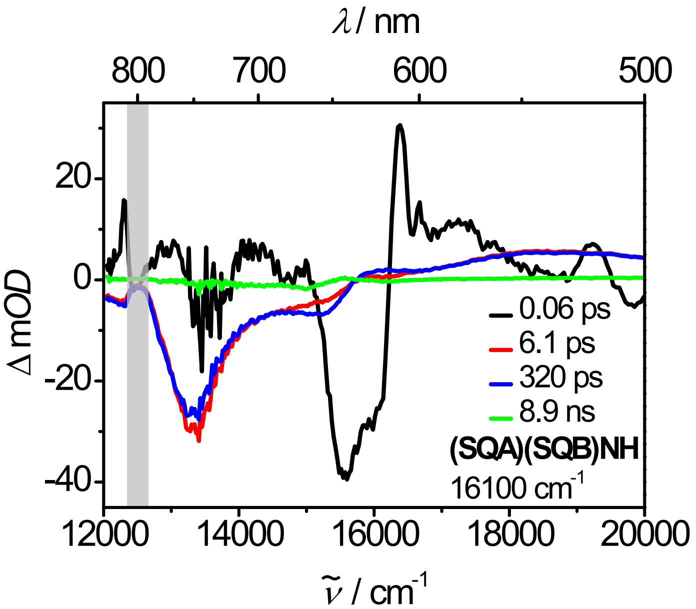


Fig. S6. Species associated difference spectra (SADS) for the excitation of **(SQA)(SQB)NH** in toluene at 16100 cm^{-1} pump energy. The spectra at 12500±200 cm^{-1} (800±10 nm, grey bar) are influenced by the laser fundamental and should be taken with caution.

Table S1. Lifetimes and efficiencies for and between the given states of **(SQA)$_3$N** in toluene at 14200 cm^{-1} pump energy.

	1	2	3	4	5	6	S$_0$
	/ps	/ps	/ps	/ns	/ns	/ns	
1							
2		3.6		90%			10%
3							
4				0.24	80%		20%
5					1.4		100%
6							
S$_0$							

Table S2. Lifetimes and efficiencies for and between the given states of **(SQA)$_3$N** in toluene at 16100 cm^{-1} pump energy.

	1	2	3	4	5	6	S$_0$
	/ps	/ps	/ps	/ns	/ns	/ns	
1	0.08	100%					
2		4.9		95%			5%
3							
4				0.19	80%		20%
5					1.3		100%
6							
S$_0$							

Table S3. Lifetimes and efficiencies for and between the given states of **(SQB)$_3$N** in toluene at 13200 cm^{-1} pump energy.

	1	2	3	4	5	6	S$_0$
	/ps	/ps	/ps	/ns	/ns	/ns	
1							
2		7.3		89%			11%
3							
4				0.71			100%
5							
6							
S$_0$							

Table S4. Lifetimes and efficiencies for and between the given states of **(SQB)$_3$N** in toluene at 14900 cm^{-1} pump energy.

	1	2	3	4	5	6	S$_0$
	/ps	/ps	/ps	/ns	/ns	/ns	
1	0.16		100%				
2							
3			10	93%			7%
4				0.73			100%
5							
6							
S$_0$							

Table S5. Lifetimes and efficiencies for and between the given states of **(SQA)$_2$(SQB)N** in toluene at 13200 cm^{-1} pump energy.

	1	2	3	4	5	6	S$_0$
	/ps	/ps	/ps	/ns	/ns	/ns	
1							
2		1.3	100%				
3			17	100%			
4				0.18			100%
5							
6							
S$_0$							

Table S6. Lifetimes and efficiencies for and between the given states of **(SQA)$_2$(SQB)N** in toluene at 15800 cm^{-1} pump energy.

	1	2	3	4	5	6	S$_0$
	/ps	/ps	/ps	/ns	/ns	/ns	
1	0.09 (90%)	100%					
2		7.2		100%			
3							
4				0.18			100%
5							
6						1.1 (10%)	100%
S$_0$							

Table S7. Lifetimes and efficiencies for and between the given states of **(SQA)(SQB)$_2$N** in toluene at 13100 cm^{-1} pump energy.

	1	2	3	4	5	6	S$_0$
	/ps	/ps	/ps	/ns	/ns	/ns	
1	0.65		100%				
2							
3			20	100%			
4				0.36			100%
5							
6							
S$_0$							

Table S8. Lifetimes and efficiencies for and between the given states of **(SQA)(SQB)$_2$N** in toluene at 15500 cm^{-1} pump energy.

	1	2	3	4	5	6	S_0
	/ps	/ps	/ps	/ns	/ns	/ns	
1	0.11 (85%)	100%					
2		6.7		90%			10%
3							
4				0.35			100%
5							
6						0.77 (15%)	100%
S_0							

Table S9. Lifetimes and efficiencies for and between the given states of **(SQA)(SQB)NH** in toluene at 13500 cm^{-1} pump energy.

	1	2	3	4	5	6	S_0
	/ps	/ps	/ps	/ns	/ns	/ns	
1	1.4	100%					
2		8.4	100%				
3			31	80%			20%
4				0.33			100%
5							
6							
S_0							

Table S10. Lifetimes and efficiencies for and between the given states of **(SQA)(SQB)NH** in toluene at 15400 cm^{-1} pump energy.

	1	2	3	4	5	6	S_0
	/ps	/ps	/ps	/ns	/ns	/ns	
1	0.13 (91%)	100%					
2		5.7		89%			11%
3							
4				0.32			100%
5							
6						2.2 (9%)	100%
S_0							

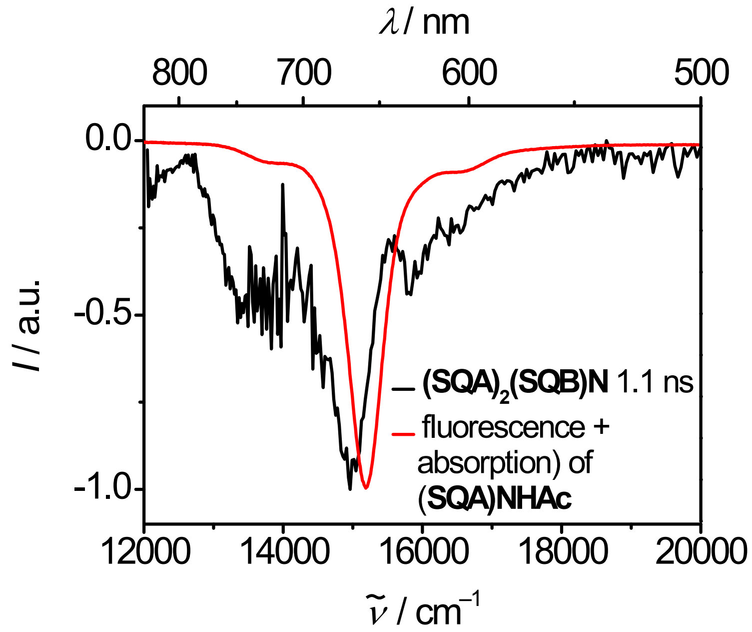


Fig. S7. Species associated difference spectrum of the localised state of **(SQA)$_2$(SQB)N** (black) and negative sum of the normalised fluorescence and absorption spectra of **(SQA)NHAc** (red) in toluene.

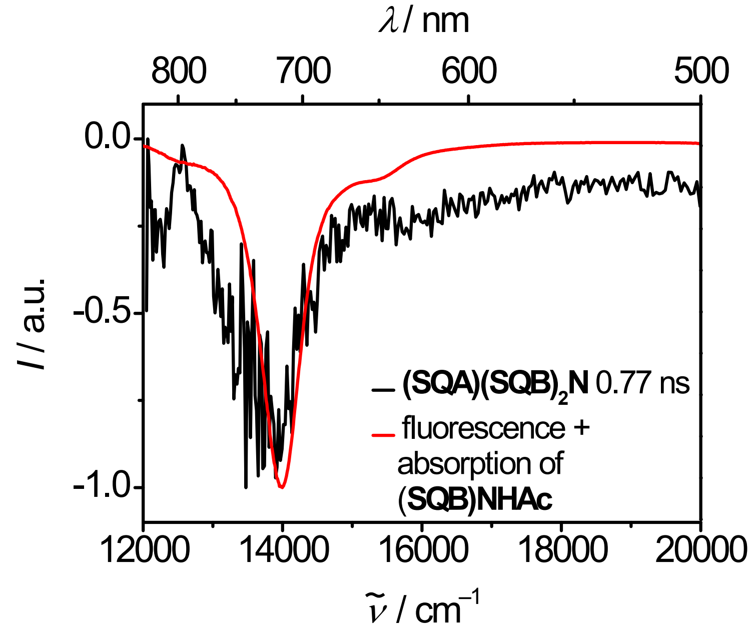


Fig. S8. Species associated difference spectrum of the localised state of **(SQA)(SQB)$_2$N** (black) and negative sum of the normalised fluorescence and absorption spectra of **(SQB)NHAc** (red) in toluene.

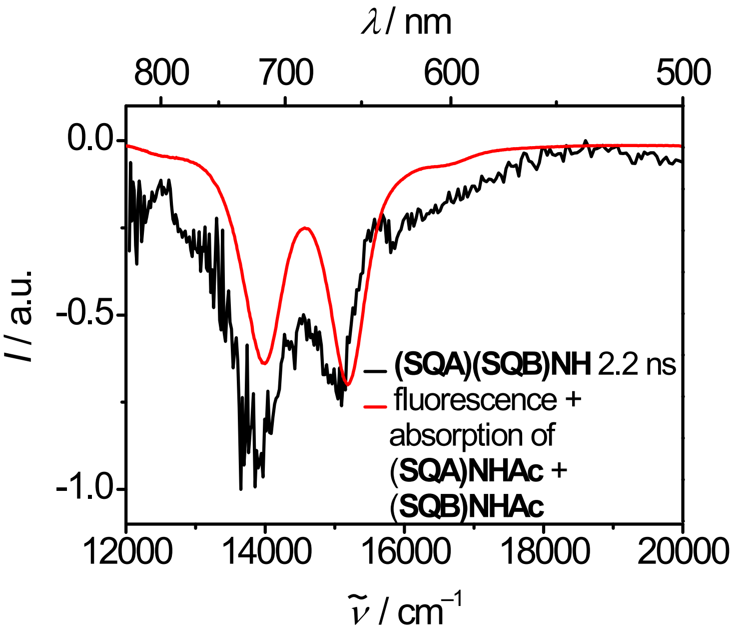


Fig. S9. Species associated difference spectra of the localised state of **(SQA)(SQB)NH** (black) and negative sum of the normalised fluorescence and absorption spectra of **(SQA)NHAc** and **(SQB)NHAc** (red) in toluene.

Fluorescence Lifetimes

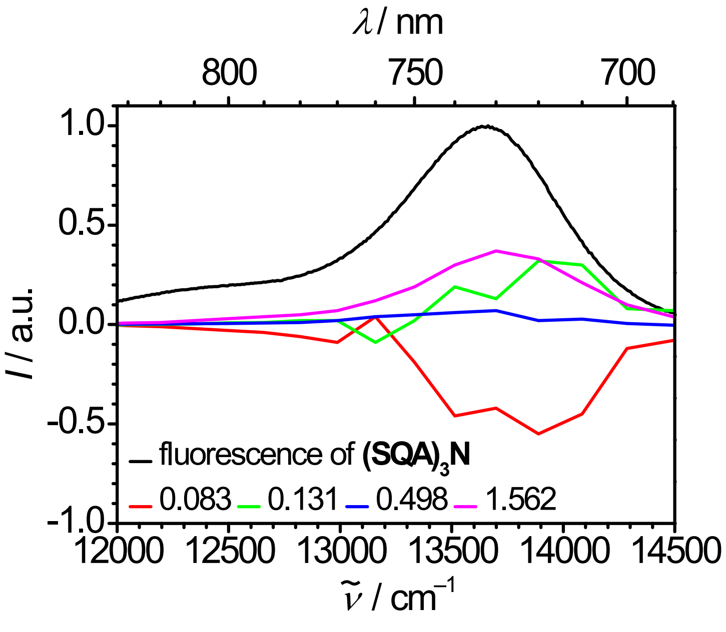


Fig. S10. Fluorescence of **(SQA)$_3$N** and decay associated spectra (parallel model) of the lifetimes in toluene.

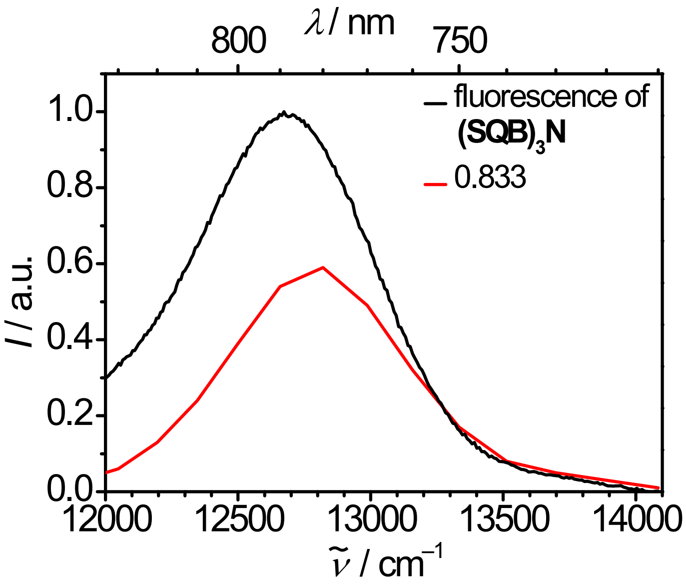


Fig. S11. Fluorescence of **(SQB)$_3$N** and decay associated spectrum of the lifetime in toluene.

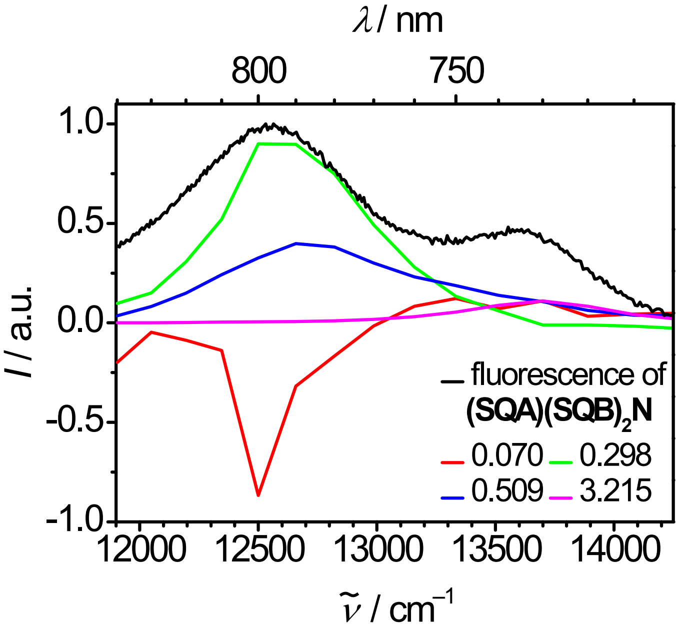


Fig. S12. Fluorescence of **(SQA)(SQB)$_2$N** decay associated spectra (parallel model) of the lifetimes in toluene.

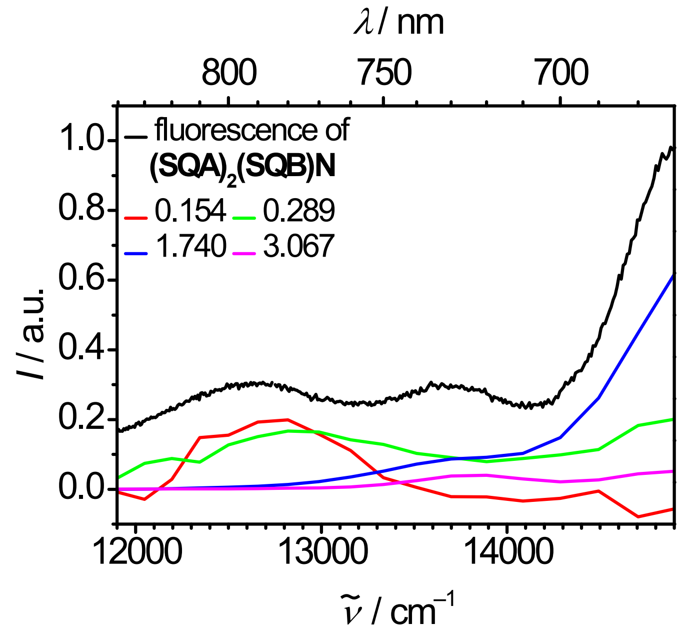


Fig. S13. Fluorescence of **(SQA)$_2$(SQB)N** and decay associated spectra (parallel model) of the lifetimes in toluene.

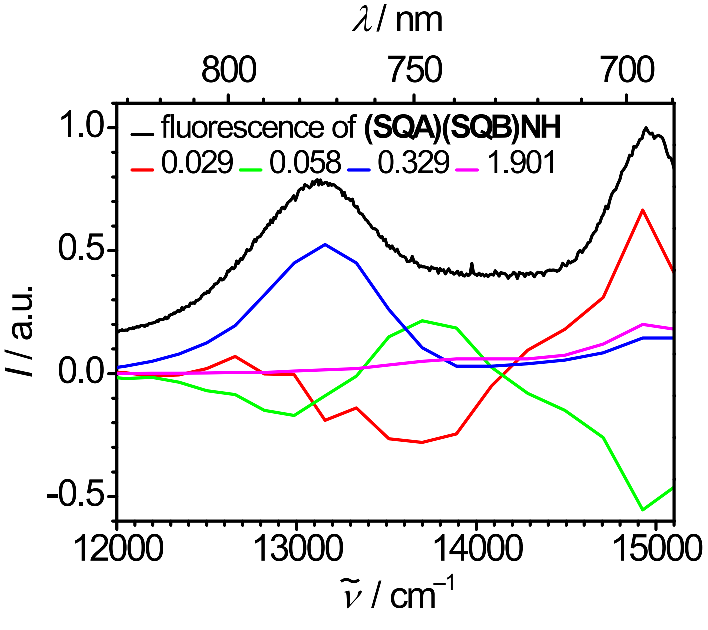


Fig. S14. Fluorescence of **(SQA)(SQB)NH** and decay associated spectra (parallel model) of the lifetimes in toluene.

Fluorescence upconversion

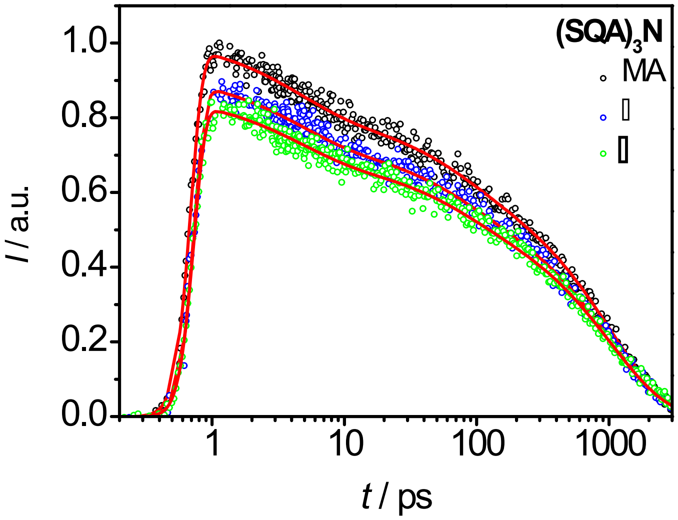


Fig. S15. Fluorescence upconversion measurements in toluene (circles) of **(SQA)$_3$N** (pump at 16100 cm^{-1}, fluorescence at 13600 cm^{-1}) with pump pulse at magic angle (MA), parallel (∥) and perpendicular (⊥) orientation relative to the gate pulse. Global convoluted fit curves (red lines).

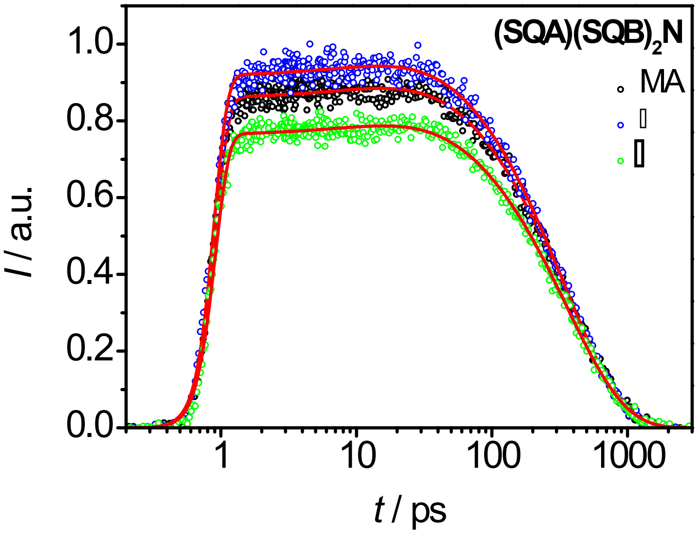


Fig. S16. Fluorescence upconversion measurements in toluene (circles) of **(SQA)(SQB)$_2$N** (pump at 14400 cm^{-1}, fluorescence at 11100 cm^{-1}) with pump pulse at magic angle (MA), parallel (∥) and perpendicular (⊥) orientation relative to the gate pulse. Global convoluted fit curves (red lines).

Exiton Coupling Results:

Exciton coupling of localised states leads to a set of exciton states (exciton manifold) whose eigenvalues ε_i and eigenvectors c_{ij} can be evaluated by solving the appropriate secular determinant. These are given for the homotrimer and the two heterotrimers in Tables S11-S13. In these determinants we assume that the coupling *J* between the localised states are all equal. The transition moments of the exciton states can then be expressed as linear combinations of the localised transition moment vectors μ where the coefficients are those of the normalised eigenvectors

Table S11. Exciton coupling results for **(SQA)$_3$N**.

Secular determinant:
$\begin{vmatrix} -\varepsilon & J & J \\ J & -\varepsilon & J \\ J & J & -\varepsilon \end{vmatrix} = 0$
eigenvalues, normalised eigenvectors, transition moments:
$\varepsilon_3 = 2J$
$c_{31} = \frac{1}{\sqrt{3}}, \quad c_{32} = \frac{1}{\sqrt{3}}, \quad c_{33} = \frac{1}{\sqrt{3}}$
$\boldsymbol{\mu}_3 = c_{31}\boldsymbol{\mu}_{\text{SQA}}\begin{pmatrix} \sin 240° \\ \cos 240° \end{pmatrix} + c_{32}\boldsymbol{\mu}_{\text{SQA}}\begin{pmatrix} \sin 0° \\ \cos 0° \end{pmatrix} + c_{33}\boldsymbol{\mu}_{\text{SQA}}\begin{pmatrix} \sin 120° \\ \cos 120° \end{pmatrix}$
$\varepsilon_2 = -J$
$c_{21} = -\frac{1}{\sqrt{2}}, \quad c_{22} = \frac{1}{\sqrt{2}}, \quad c_{23} = 0$
$\boldsymbol{\mu}_2 = c_{21}\boldsymbol{\mu}_{\text{SQA}}\begin{pmatrix} \sin 240° \\ \cos 240° \end{pmatrix} + c_{22}\boldsymbol{\mu}_{\text{SQA}}\begin{pmatrix} \sin 0° \\ \cos 0° \end{pmatrix} + c_{23}\boldsymbol{\mu}_{\text{SQA}}\begin{pmatrix} \sin 120° \\ \cos 120° \end{pmatrix}$
$\varepsilon_1 = -J$
$c_{11} = -\frac{1}{\sqrt{2}}, \quad c_{12} = 0, \quad c_{13} = \frac{1}{\sqrt{2}}$
$\boldsymbol{\mu}_1 = c_{11}\boldsymbol{\mu}_{\text{SQA}}\begin{pmatrix} \sin 240° \\ \cos 240° \end{pmatrix} + c_{12}\boldsymbol{\mu}_{\text{SQA}}\begin{pmatrix} \sin 0° \\ \cos 0° \end{pmatrix} + c_{13}\boldsymbol{\mu}_{\text{SQA}}\begin{pmatrix} \sin 120° \\ \cos 120° \end{pmatrix}$
splitting between highest and lowest exciton level:
$\delta E_{\text{trimer}} = 3J$

Table S12. Exciton coupling results for **(SQA)$_2$(SQB)N**.

Secular determinant:
$\begin{vmatrix} \Delta E-\varepsilon & J & J \\ J & -\Delta E-\varepsilon & J \\ J & J & \Delta E-\varepsilon \end{vmatrix} = 0$
eigenvalues, normalised eigenvectors, transition moments:
$x = \sqrt{4\Delta E^2 + 4\Delta EJ + 9J^2}$
$\varepsilon_3 = \frac{1}{2}(J+x)$
$c_{31} = \frac{-\frac{2\Delta E - J - x}{2J} + \frac{2\Delta E - 3J - x}{2\Delta E + 3J + x}}{\sqrt{1+\left(\frac{2\Delta E - 3J - x}{2\Delta E + 3J + x}\right)^2 + \left(-\frac{2\Delta E - J - x}{2J} + \frac{2\Delta E - 3J - x}{2\Delta E + 3J + x}\right)^2}},$ $c_{32} = -\frac{2\Delta E - 3J - x}{(2\Delta E + 3J + x)\sqrt{1+\left(\frac{2\Delta E - 3J - x}{2\Delta E + 3J + x}\right)^2 + \left(-\frac{2\Delta E - J - x}{2J} + \frac{2\Delta E - 3J - x}{2\Delta E + 3J + x}\right)^2}},$ $c_{33} = \frac{1}{\sqrt{1+\left(\frac{2\Delta E - 3J - x}{2\Delta E + 3J + x}\right)^2 + \left(\frac{2\Delta E - J - x}{2J} + \frac{2\Delta E - 3J - x}{2\Delta E + 3J + x}\right)^2}}$
$\boldsymbol{\mu}_3 = c_{31}\boldsymbol{\mu}_{\text{SQA}}\begin{pmatrix}\sin 240^\circ \\ \cos 240^\circ\end{pmatrix} + c_{32}\boldsymbol{\mu}_{\text{SQB}}\begin{pmatrix}\sin 0^\circ \\ \cos 0^\circ\end{pmatrix} + c_{33}\boldsymbol{\mu}_{\text{SQA}}\begin{pmatrix}\sin 120^\circ \\ \cos 120^\circ\end{pmatrix}$
$\varepsilon_2 = \Delta E - J$
$c_{21} = -\frac{1}{\sqrt{2}}, \quad c_{22} = 0, \quad c_{23} = \frac{1}{\sqrt{2}}$
$\boldsymbol{\mu}_2 = c_{21}\boldsymbol{\mu}_{\text{SQA}}\begin{pmatrix}\sin 240^\circ \\ \cos 240^\circ\end{pmatrix} + c_{22}\boldsymbol{\mu}_{\text{SQB}}\begin{pmatrix}\sin 0^\circ \\ \cos 0^\circ\end{pmatrix} + c_{23}\boldsymbol{\mu}_{\text{SQA}}\begin{pmatrix}\sin 120^\circ \\ \cos 120^\circ\end{pmatrix}$
$\varepsilon_1 = \frac{1}{2}(J-x)$
$c_{11} = \frac{\frac{-2\Delta E + 3J - x}{-2\Delta E - 3J + x} - \frac{2\Delta E - J + x}{2J}}{\sqrt{1+\left(\frac{-2\Delta E + 3J - x}{-2\Delta E - 3J + x}\right)^2 + \left(\frac{-2\Delta E + 3J - x}{-2\Delta E - 3J + x} - \frac{2\Delta E - J + x}{2J}\right)^2}},$ $c_{11} = -\frac{-2\Delta E + 3J - x}{(-2\Delta E - 3J + x)\sqrt{1+\left(\frac{-2\Delta E + 3J - x}{-2\Delta E - 3J + x}\right)^2 + \left(\frac{-2\Delta E + 3J - x}{-2\Delta E - 3J + x} - \frac{2\Delta E - J + x}{2J}\right)^2}},$ $c_{13} = \frac{1}{\sqrt{1+\left(\frac{-2\Delta E + 3J - x}{-2\Delta E - 3J + x}\right)^2 + \left(\frac{-2\Delta E + 3J - x}{-2\Delta E - 3J + x} - \frac{2\Delta E - J + x}{2J}\right)^2}}$
$\boldsymbol{\mu}_1 = c_{11}\boldsymbol{\mu}_{\text{SQA}}\begin{pmatrix}\sin 240^\circ \\ \cos 240^\circ\end{pmatrix} + c_{12}\boldsymbol{\mu}_{\text{SQB}}\begin{pmatrix}\sin 0^\circ \\ \cos 0^\circ\end{pmatrix} + c_{13}\boldsymbol{\mu}_{\text{SQA}}\begin{pmatrix}\sin 120^\circ \\ \cos 120^\circ\end{pmatrix}$
splitting between highest and lowest exciton level:
$\delta E_{\text{trimer}} = \sqrt{4\Delta E^2 + 4\Delta EJ + 9J^2}$

Table S13. Exciton coupling results for **(SQA)$_2$(SQB)N**.

Secular determinant:
$\begin{vmatrix} -\Delta E-\varepsilon & J & J \\ J & \Delta E-\varepsilon & J \\ J & J & -\Delta E-\varepsilon \end{vmatrix}=0$
eigenvalues, normalised eigenvectors, transition moments:
$x=\sqrt{4\Delta E^2-4\Delta EJ+9J^2}$
$\varepsilon_3=\frac{1}{2}(J+x)$
$c_{31}=\frac{-\frac{-2\Delta E-J-x}{2J}+\frac{-2\Delta E-3J-x}{-2\Delta E+3J+x}}{\sqrt{1+\left(\frac{-2\Delta E-3J-x}{-2\Delta E+3J+x}\right)^2+\left(-\frac{-2\Delta E-J-x}{2J}+\frac{-2\Delta E-3J-x}{-2\Delta E+3J+x}\right)^2}},$ $c_{32}=-\frac{-2\Delta E-3J-x}{(-2\Delta E+3J+x)\sqrt{1+\left(\frac{-2\Delta E-3J-x}{-2\Delta E+3J+x}\right)^2+\left(-\frac{-2\Delta E-J-x}{2J}+\frac{-2\Delta E-3J-x}{-2\Delta E+3J+x}\right)^2}},$ $c_{33}=\frac{1}{\sqrt{1+\left(\frac{-2\Delta E-3J-x}{-2\Delta E+3J+x}\right)^2+\left(\frac{-2\Delta E-J-x}{2J}+\frac{-2\Delta E-3J-x}{-2\Delta E+3J+x}\right)^2}}$
$\boldsymbol{\mu}_3=c_{31}\boldsymbol{\mu}_{\text{SQB}}\begin{pmatrix}\sin 240°\\ \cos 240°\end{pmatrix}+c_{32}\boldsymbol{\mu}_{\text{SQA}}\begin{pmatrix}\sin 0°\\ \cos 0°\end{pmatrix}+c_{33}\boldsymbol{\mu}_{\text{SQB}}\begin{pmatrix}\sin 120°\\ \cos 120°\end{pmatrix}$
$\varepsilon_2=\frac{1}{2}(J-x)$
$c_{21}=\frac{\frac{2\Delta E+3J-x}{2\Delta E-3J+x}-\frac{-2\Delta E-J+x}{2J}}{\sqrt{1+\left(\frac{2\Delta E+3J-x}{2\Delta E-3J+x}\right)^2+\left(\frac{2\Delta E+3J-x}{2\Delta E-3J+x}-\frac{-2\Delta E-J+x}{2J}\right)^2}},$ $c_{22}=-\frac{2\Delta E+3J-x}{(2\Delta E-3J+x)\sqrt{1+\left(\frac{2\Delta E+3J-x}{2\Delta E-3J+x}\right)^2+\left(\frac{2\Delta E+3J-x}{2\Delta E-3J+x}-\frac{-2\Delta E-J+x}{2J}\right)^2}},$ $c_{23}=\frac{1}{\sqrt{1+\left(\frac{2\Delta E+3J-x}{2\Delta E-3J+x}\right)^2+\left(\frac{2\Delta E+3J-x}{2\Delta E-3J+x}-\frac{-2\Delta E-J+x}{2J}\right)^2}}$
$\boldsymbol{\mu}_2=c_{21}\boldsymbol{\mu}_{\text{SQB}}\begin{pmatrix}\sin 240°\\ \cos 240°\end{pmatrix}+c_{22}\boldsymbol{\mu}_{\text{SQA}}\begin{pmatrix}\sin 0°\\ \cos 0°\end{pmatrix}+c_{23}\boldsymbol{\mu}_{\text{SQB}}\begin{pmatrix}\sin 120°\\ \cos 120°\end{pmatrix}$
$\varepsilon_1=-\Delta E-J$
$c_{11}=-\frac{1}{\sqrt{2}},\quad c_{12}=0,\quad c_{13}=\frac{1}{\sqrt{2}}$
$\boldsymbol{\mu}_1=c_{11}\boldsymbol{\mu}_{\text{SQB}}\begin{pmatrix}\sin 240°\\ \cos 240°\end{pmatrix}+c_{12}\boldsymbol{\mu}_{\text{SQA}}\begin{pmatrix}\sin 0°\\ \cos 0°\end{pmatrix}+c_{13}\boldsymbol{\mu}_{\text{SQB}}\begin{pmatrix}\sin 120°\\ \cos 120°\end{pmatrix}$
splitting between highest and lowest exciton level:
$\delta E_{\text{trimer}}=\frac{1}{2}\left(J+\sqrt{4\Delta E^2-4\Delta EJ+9J^2}\right)+\Delta E+J$

1. US 08034626, 2011.
2. U. Mayerhöffer, M. Gsänger, M. Stolte, B. Fimmel and F. Würthner, *Chem.-Eur. J.*, 2013, **19**, 218-232.
3. S. F. Völker and C. Lambert, *Chem. Mat.*, 2012, **24**, 2541-2553.