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Supporting Information

fs-ps Exciton dynamics in a stretched tetraphenylsquaraine polymer

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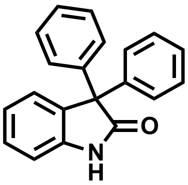
Synthesis

3,3-diphenylindolin-2-one (2a)



CAS: 1922-79-8

Synthesis based on given literature.[1]

Under a nitrogen atmosphere indoline-2,3-dione (500 mg, 3.40 mmol) was dissolved in TfOH (10.0 ml, 113 mmol) and benzene (5.00 ml, 55.7 mmol) was subsequently added dropwise over a period of 5 min. The resulting mixture was stirred at ambient temperature for 18 h. The reaction was poured on ice (100 g) and extracted with $CHCl_3$ (3 × 50 ml). The organic layer was washed with H_2O (50 ml) and saturated NaCl-solution (50 ml). The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (DCM/EA = 20:1).

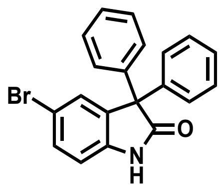
Yield: 950 mg (3.33 mmol, 98 %) of a colourless solid.

$C_{20}H_{15}NO$ [285.34]

^{1}H-NMR (400.1 MHz, $CDCl_3$):

δ [ppm] = 7.61 (s, 1H, N*H*), 7.35-7.21 (-, 12H, 12 × C*H*), 7.07 (dd, ^3J = 6.6 Hz, ^4J = 1.0 Hz, 1H, C*H*), 6.95 (m, 1H, C*H*).

5-bromo-3,3-diphenylindolin-2-one (2b)



CAS: 63483-15-8

Synthesis based on given literature.[1]

Under a nitrogen atmosphere 5-bromoindoline-2,3-dione (154 mg, 681 µmol) was dissolved in TfOH (2.00 ml, 22.5 mmol) and benzene (1.00 ml, 11.1 mmol) was subsequently added dropwise. The resulting mixture was stirred at rt for 18 h. The reaction was poured on ice (25 g) and extracted with $CHCl_3$ (3 × 50 ml). The organic layer was washed with H_2O (50 ml) and saturated NaCl-solution (50 ml). The combined organic phases were dried over $MgSO_4$ and the solvent was removed under reduced pressure. The crude product was purified by flash chromatography (DCM/EA = 20:1).

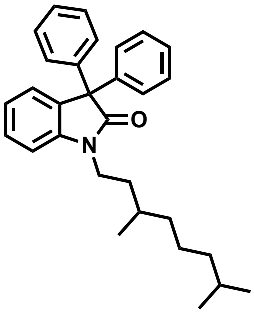
Yield: 236 mg (648 µmol, 95 %) of a colourless solid.

$C_{20}H_{14}BrNO$ [364.24]

^{1}H-NMR (400.1 MHz, $CDCl_3$):

δ [ppm] = 7.52 (s, 1H, N*H*), 7.39 (dd, ^3J = 8.2 Hz, ^4J = 1.9 Hz, 1H, C*H*), 7.36-7.22 (-, 11H, 11 × C*H*), 6.58 (d, ^3J = 8.3 Hz, 1H, C*H*).

1-(3,7-dimethyloctyl)-3,3-diphenylindolin-2-one (3a)



Synthesis based on given literature.[2]

Under a nitrogen atmosphere 3,3-diphenylindolin-2-one (950 mg, 3.33 mmol) and oven-dried anhydrous K_2CO_3 (4.60 g, 33.3 mmol) were suspended in dry DMF (10 ml) and stirred at ambient temperature for 30 min. Racemic 1-Iodo-3,7-dimethyloctane (1.79 g, 8.09 mmol) was subsequently added and the reaction was heated at 60 °C in a sealed tube for 18 h. The cooled reaction was quenched with H_2O (50 ml) and extracted with $CHCl_3$ (3 × 50 ml). The organic layer was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography (PE/EA = 20:1).

Yield: 826 mg (1.94 mmol, 58 %) of a colourless oil.

$C_{30}H_{35}NO$ [425.61]

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

δ [ppm] = 7.32 (dd, ^3J = 7.8 Hz, 1H, C*H*), 7.31-7.19 (-, 11H, 11 × C*H*), 7.07 (dd, ^3J = 7.6 Hz, ^4J = 1.0 Hz, 1H, C*H*), 6.96 (d, ^3J = 7.9 Hz, 1H, C*H*), 3.87-3.70 (m, 2H, NCH_2), 1,79-1.66 (m, 1H, NCH_2C*H*), 1.53-1.42 (-, 3H, 2 × C*H*, NCH_2C*H*), 1.38- 1.08 (-, 6H, 3 × CH_2), 0.97 (d, ^3J = 6.4 Hz, 3H, CH_3), 0.85 (d, ^3J = 6.6 Hz, 6H, 2 × CH_3).

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

δ [ppm] = 177.3 (quart), 143.0 (quart), 142.55 (quart)*, 142.50 (quart)*, 133.4 (quart), 128.79 (tert)*, 128.77 (tert)*, 128.73 (tert)*, 128.72 (tert)*, 128.70 (tert), 127.6 (tert), 126.4 (tert), 122.8 (tert), 109.3 (tert), 62.7 (quart), 39.5 (sec), 39.0 (sec), 37.4 (sec), 34.7 (sec), 31.1 (tert), 28.4 (tert), 25.0 (sec), 22.83 (prim)*, 22.75 (prim)*, 19.6 (prim).

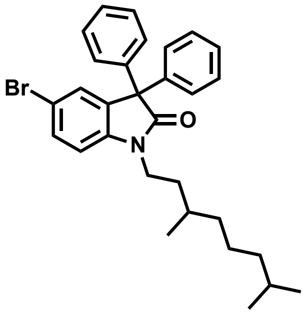
* Because of diastereomers signals marked by * split into a pair of two signals of equal intensity which belong to one C-atom.

MALDI-MS pos: [$M^{\cdot+}$]

calc.: 425.271 m/z

found: 425.228 m/z

5-bromo-1-(3,7-dimethyloctyl)-3,3-diphenylindolin-2-one (3b)



Synthesis based on given literature.[2]

Under a nitrogen atmosphere 5-bromo-3,3-diphenylindolin-2-one (3.35 g, 9.19 mmol) and oven-dried anhydrous K_2CO_3 (12.7 g, 91.9 mmol) were suspended in dry DMF (25 ml) and stirred at rt for 30 min. Racemic 1-Iodo-3,7-dimethyloctane (4.93 g, 18.4 mmol) was subsequently added and the reaction was heated at 60 °C in a sealed tube for 18 h. The cooled reaction was quenched with H_2O (100 ml) and extracted with $CHCl_3$ (3 × 50 ml). The organic layer was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography (PE/EA = 20:1).

Yield: 3.36 g (6.66 mmol, 72 %) of a colourless oil.

$C_{30}H_{34}BrNO$ [504.50]

^{1}H-NMR (400.1 MHz, $CDCl_3$):

δ [ppm] = 7.40 (dd, ^3J = 8.3 Hz, ^4J = 2.0 Hz, 1H, CH), 7.32 (d, ^4J = 2.0 Hz, 1H, CH), 7.32-7.31 (-, 10H, 10 × CH), 6.78 (d, ^3J = 8.3 Hz, 1H, CH), 3.84-3.65 (m, 2H, NCH_2), 1.75-1.61 (m, 1H, NCH$_2$CH), 1.54-1.40 (-, 3H, NCH$_2$CH, 2 × CH), 1.34-1.04 (-, 6H, 3 × CH_2), 0.93 (d, ^3J = 6.2 Hz, 3H, CH_3), 0.82 (d, ^3J = 6.6 Hz, 6H, 2 × CH_3).

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

δ [ppm] = 176.9 (quart), 142.1 (quart)*, 141.83 (quart)*, 141.77 (quart), 135.5 (quart), 131.6 (tert), 129.4 (tert), 128.88 (tert)*, 128.87 (tert)*, 128.72 (tert)*, 128.70 (tert)*, 127.9 (tert), 115.3 (quart), 110.9 (tert), 62.8 (quart), 39.5 (sec), 39.1 (sec), 37.4 (sec), 34.5 (sec), 31.1 (tert), 28.3 (tert), 25.0 (sec), 22.8 (prim)*, 22.7 (prim)*, 19.6 (prim).

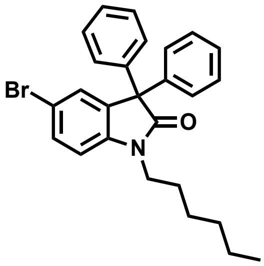
* Because of diastereomers signals marked by * split into a pair of two signals of equal intensity which belong to one C-atom.

MALDI-MS pos: [$M^{\cdot+}$]

calc.: 505.180 m/z

found: 505.170 m/z

5-bromo-1-hexyl-3,3-diphenylindolin-2-one (3c)



Synthesis based on given literature.[2]

Under a nitrogen atmosphere 5-bromo-3,3-diphenylindolin-2-one (1.00 g, 2.75 mmol) and oven-dried anhydrous K_2CO_3 (3.79 g, 27.4 mmol) were suspended in dry DMF (25 ml) and stirred at ambient temperature for 30 min. 1-Iodohexane (1.79 g, 8.44 mmol) was subsequently added and the reaction was heated at 60 °C in a sealed tube for 18 h. The cooled reaction was quenched with H_2O (100 ml) and extracted with $CHCl_3$ (3 × 50 ml). The organic layer was dried over Na_2SO_4 and the solvent was evaporated under reduced pressure. The crude product was purified by flash chromatography (PE/EA = 20:1).

Yield: 764 mg (1.70 mmol, 62 %) of a colourless solid.

$C_{26}H_{26}NOBr$ [448.40]

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

δ [ppm] = 7.45 (dd, ^3J = 8.3 Hz, ^4J = 2.0 Hz, 1H, C*H*), 7.35 (dd, ^4J = 2.0 Hz, ^5J = 0.3 Hz, 1H, C*H*), 7.34-7.26 (-, 6H, 6 × C*H*), 7.24-7.14 (-, 4H, 4 × C*H*), 6.86 (d, ^3J = 8.3 Hz, 1H, C*H*), 3.74 (t, ^3J = 7.3 Hz, 2H, NCH_2), 1.69 (m, 2H, NCH_2CH_2), 1.37-1.20 (-, 6H, 3 × CH_2), 0.85 (t, ^3J = 7.0 Hz, 3H, CH_3).

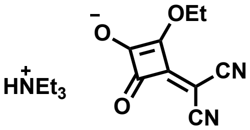
^{13}C-NMR (100.6 MHz, CD_2Cl_2):

δ [ppm] = 177.0 (quart), 142.2 (quart), 141.8 (quart), 135.5 (quart), 131.5 (tert), 129.4 (tert), 128.9 (tert), 128.7 (tert), 127.9 (tert), 115.3 (quart), 110.9 (tert), 62.8 (quart), 40.8 (sec), 31.7 (sec), 27.6 (sec), 26.8 (sec), 22.9 (sec), 14.1 (prim).

MALDI-MS pos: [$M^{\cdot+}$]

calc.:	449.118 m/z
found:	449.150 m/z

CN



CAS: 1788877-12-2

Synthesis according to given literature.[3]

Malononitrile (382 mg, 5.78 mmol) was dissolved in benzene (30 ml) and 3,4-diethoxycyclobut-3-ene-1,2-dione (1.00 g, 5.88 mmol), and triethylamine (792 ml, 5.68 mmol) were consecutively added dropwise over a period of 5 min, respectively. The reaction was stirred at ambient temperature for 10 min and allowed to stand in the freezer at -25 °C overnight. The resulting solid was filtered off and dried under high vacuum.

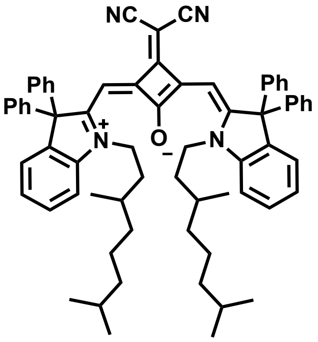
Yield: 1.57 g (5.39 mmol, 95 %) of a light yellow solid.

$C_{15}H_{21}N_3O_3$ [291.35]

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

δ [ppm] = 8.83 (s, 1H, NH), 4.61 (q, ^3J = 7.1 Hz, 2H, OCH_2CH$_3$), 3.10 (q, ^3J = 7.2 Hz, 6H, 3 × HNCH_2CH$_3$), 1.34 (t, ^3J = 7.1 Hz, 3H, OCH$_2$CH_3), 1.18 (t, ^3J = 7.2 Hz, 9H, 3 × HNCH$_2$CH_3).

TP-SQB



Under a nitrogen atmosphere MeMgBr (5.24 ml, 7.34 mmol, 1.4 M in 3:1 toluene/THF) was added dropwise to 1-(3,7-dimethyloctyl)-3,3-diphenylindolin-2-one (780 mg, 1.83 mmol) in dry THF (10 ml), and the reaction was heated to 60 °C for 2.5 h. The reaction was allowed to cool. MeOH (10 ml) was subsequently added and the reaction was concentrated under reduced pressure. The resulting residue was treated with HCl (3 M, 30 ml) and extracted with DCM (3 × 50 ml). The combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure to yield crude 1-(3,7-dimethyloctyl)-2-methyl-3,3-diphenyl-3*H*-indol-1-ium chloride as a green foam (759 mg, 1.65 mmol, 90 %), which was used without further purification due to rapid decomposition when exposed to moist air.

1-(3,7-Dimethyloctyl)-2-methyl-3,3-diphenyl-3*H*-indol-1-ium chloride (759 mg, 1.65 mmol) and dicyanovinylene salt **CN** (200 mg, 686 µmol) were suspended in pyridine (3 ml) and a mixture of toluene and 1-butanol (1:1, 50 ml) and heated under reflux for 18 h using a *Dean-Stark* trap. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (DCM). The crude product was recrystallized from *n*-hexane.

Yield: 321 mg (330 µmol, 48 %) of a green solid.

$C_{69}H_{72}N_4O$ [973.34]

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

δ [ppm] = 7.38 (dd, ^3J = 8.0 Hz, ^4J = 1.2 Hz, 2H, 2 × C*H*), 7.33-7.27 (-, 12H, 12 × C*H*), 7.26-7.12 (-, 14H, 14 × C*H*), 6.06 (s, 2H, 2 × C*H*), 4.69-4.19 (m, 4H, 2 × NCH_2), 1.76-1.64 (m, 2H, 2 × NCH_2CH), 1.52-1.43 (-, 4H, 2 × CH, 2 × NCH_2CH), 1.43-1.32 (m, 2H, 2 × C*H*), 1.31-1.19 (-, 4H, 2 × CH_2), 1.16-1.03 (-, 8H, 4 × CH_2), 0.88 (d, ^3J = 6.5 Hz, 6H, 2 × CH_3), 0.84 (d, ^3J = 6.7 Hz, 12H, 4 × CH_3).

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

δ [ppm] = 175.2 (quart), 170.9 (quart), 166.15 (quart), 166.07 (quart), 143.6 (quart), 142.05 (quart)*, 141.99 (quart)*, 139.8 (quart), 129.1 (tert), 129.0 (tert), 128.0 (2 × tert), 125.9 (tert), 125.5 (tert), 118.3 (quart), 112.2 (tert), 92.5 (tert), 68.5 (quart), 45.4 (sec), 41.7 (quart), 39.6 (sec), 37.44 (sec)*, 37.42 (sec)*, 34.6 (sec), 31.0 (tert), 28.4 (tert), 24.99 (sec)*, 24.98 (sec)*, 22.8 (prim)*, 22.7 (prim)*, 19.7 (prim).

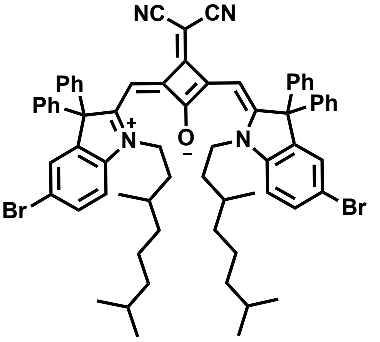
* Because of diastereomers (the 3,6-dimethyloctyl chain was used as a racemate) the signals marked by * split into a pair of two signals of equal intensity which belong to one C-atom.

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

calc.: 972.57006 m/z

found: 972.57101 m/z Δ = 0.98 ppm

TP-SQB-1-Br$_2$



Under a nitrogen atmosphere MeMgBr (15.3 ml, 21.4 mmol, 1.4 M in 3:1 toluene/THF) was added dropwise to 5-bromo-1-(3,7-dimethyloctyl)-3,3-diphenylindolin-2-one (2.69 g, 5.34 mmol) in dry THF (85 ml), and the reaction was heated to 60 °C for 2.5 h. The reaction was allowed to cool. MeOH (12 ml) was subsequently added and the reaction was concentrated under reduced pressure. The resulting residue was treated with HCl (3 M, 80 ml) and extracted with DCM (3 × 50 ml). The combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure to yield crude 5-bromo-1-(3,7-dimethyloctyl)-2-methyl-3,3-diphenyl-3*H*-indol-1-ium chloride as a green foam (2.73 g, 5.07 mmol, 95 %) which was used without further purification since it readily decomposes when exposed to moist air.

Under a nitrogen atmosphere 5-bromo-1-(3,7-dimethyloctyl)-2-methyl-3,3-diphenyl-3*H*-indol-1-ium chloride (200 mg, 371 µmol) and dicyanovinylene salt **CN** (51.0 mg, 175 µmol) were suspended in pyridine (1 ml) and a mixture of toluene and 1-butanol (1:1, 10 ml). The suspension was degassed in a gentle stream of nitrogen for 15 min. The reaction was heated at 130 °C for 3 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (DCM). The crude product was recrystallized from *n*-hexane.

Yield: 64.0 mg (56.6 µmol, 32 %) of dark green crystals.

$C_{69}H_{70}Br_2N_4O$ [1131.13]

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

δ [ppm] = 7.50 (dd, ^3J = 8.4 Hz, ^4J = 1.8 Hz, 2H, 2 × C*H*), 7.37-7.14 (-, 22H, 22 × C*H*), 7.04 (d, ^3J = 8.5 Hz, 2H, 2 × C*H*), 6.07 (s, 2H, 2 × C*H*), 4.60-4.16 (m, 4H, 2 × NCH_2), 1.74-1.61 (m, 2H, 2 × NCH$_2$C*H*), 1.52-1.05 (-, 18H, 2 × NCH$_2$C*H*, 6 × CH_2, 4 × C*H*), 0.87 (d, ^3J = 6.2 Hz, 6H, 2 × CH_3), 0.83 (d, ^3J = 6.6 Hz, 12H, 4 × CH_3).

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

δ [ppm] = 175.0 (quart), 170.5 (quart), 166.6 (quart), 166.2 (quart), 142.7 (quart), 141.9 (quart), 141.4 (quart)*, 141.3 (quart)*, 132.1 (tert), 129.3 (tert), 129.0 (2 × tert), 128.3 (tert), 118.5 (quart), 118.0 (quart), 113.5 (tert), 93.0 (tert), 68.3 (quart), 45.6 (sec), 42.2 (quart), 39.6 (sec), 37.40 (sec)*, 37.39 (sec)*, 34.5 (sec), 31.0 (tert), 28.4 (tert), 24.98 (sec)*, 24.97 (sec)*, 22.8 (prim)*, 22.7 (prim)*, 19.7 (prim).

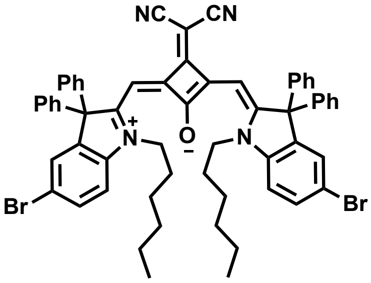
* Because of diastereomers signals marked by * split into a pair of two signals of equal intensity which belong to one C-atom.

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

calc.: 1130.39017 m/z

found: 1130.38998 m/z Δ = 0.17 ppm

TP-SQB-2-Br$_2$



Under a nitrogen atmosphere MeMgBr (4.80 ml, 6.72 mmol, 1.4 M in 3:1 toluene/THF) was added dropwise to 5-bromo-1-hexyl-3,3-diphenylindolin-2-one (754 mg, 1.68 mmol) in dry THF (15 ml), and the reaction was heated to 60 °C for 2.5 h. The reaction was allowed to cool. MeOH (5 ml) was subsequently added and the reaction was concentrated under reduced pressure. The resulting residue was treated with HCl (3 M, 30 ml) and extracted with DCM (3 × 50 ml). The combined organic phases were dried over Na_2SO_4 and the solvent was removed under reduced pressure to yield crude 5-bromo-1-hexyl-2-methyl-3,3-diphenyl-3*H*-indol-1-ium chloride as a green foam (812 mg, 1.68 mmol, 99 %) which was used without further purification since it readily decomposes when exposed to moist air.

Under a nitrogen atmosphere 5-bromo-1-hexyl-2-methyl-3,3-diphenyl-3*H*-indol-1-ium chloride (812 mg, 1.68 mmol) and dicyanovinylene salt **CN** (254 mg, 872 µmol) were suspended in pyridine (2 ml) and a mixture of toluene and 1-butanol (1:1, 20 ml). The suspension was degassed in a gentle stream of nitrogen for 15 min. The reaction was heated at 130 °C for 3.5 h. The solvent was removed under reduced pressure and the residue was purified by flash chromatography (DCM). The crude product was recrystallized from *n*-hexane.

Yield: 230 mg (226 µmol, 26 %) of dark green crystals.

$C_{61}H_{54}Br_2N_4O$ [1018.92]

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

δ [ppm] = 7.50 (dd, ^3J = 8.5 Hz, ^4J = 1.9 Hz, 2H, 2 × C*H*), 7.35-7.30 (-, 14H, 14 × C*H*), 7.27- 7.15 (-, 8H, 8 × C*H*), 7.05 (d, ^3J = 8.5 Hz, 2H, 2 × C*H*), 6.08 (s, 2H, 2 × C*H*), 4.56-4.13 (m, 4H, 2 × NCH_2), 1.78-1.61 (m, 4H, 2 × NCH_2CH_2), 1.27-1.20 (-, 12H, 6 × CH_2), 0.83 (t, ^3J = 6.9 Hz, 6H, 2 × CH_3).

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

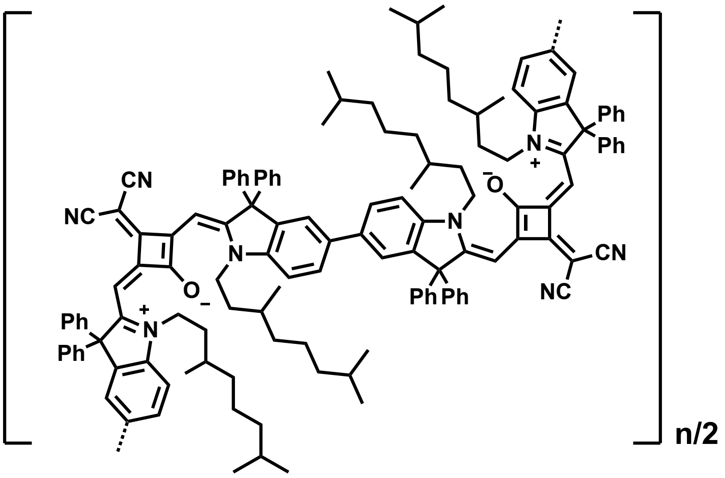
δ [ppm] = 174.6 (quart), 170.0 (quart), 166.7 (quart), 166.3 (quart), 142.8 (quart), 141.8 (quart), 141.4 (quart), 132.1 (tert), 129.3 (tert), 129.02 (tert), 128.96 (tert), 128.2 (tert), 118.4 (quart), 118.1 (quart), 113.5 (tert), 93.0 (tert), 68.3 (quart), 47.05 (sec), 41.9 (quart), 31.8 (sec), 27.5 (sec), 26.7 (sec), 22.8 (sec), 14.1 (prim).

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

calc.: 1018.26474 m/z

found: 1018.26305 m/z Δ = 1.66 ppm

[TP-PhSQB]$_n$



A mixture of Ni(COD)$_2$ (138 mg, 502 µmol), 2,2'-bipyridine (99.0 mg, 634 µmol), 1,5-cyclooctadiene (78.0 mg, 721 µmol), degassed toluene (2 ml), and degassed DMF (2 ml) was stirred at 65°C under nitrogen atmosphere for 30 min. A solution of squaraine **TP-SQB-Br$_2$** (145 mg, 128 µmol) in degassed toluene (5 ml) and degassed DMF (5 ml) was added dropwise and the reaction mixture was continuously heated at 65 °C for 6 d under exclusion of light. The cooled reaction mixture was poured into MeOH/HCl (20%) (4:1, 500 ml) and stirred for 2 h. The resulting green precipitate was filtered off and washed consecutively with *n*-hexane, MeOH and acetone using a *Soxhlet* extractor, until no colouring of the solvent could be observed anymore, respectively. The *n*-hexane and MeOH-fraction were both discarded. The acetone-fraction was dissolved in a small amount of DCM and dripped into an excess of MeOH/HCl (5 %, 4:1). The green precipitate was filtered off and washed with MeOH.

Yield: 60.0 mg (~ 61.8 µmol, 48 %) of a green solid.

$(C_{69}H_{70}N_4O)_n$ $[971.32]_n$

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

δ [ppm] = 7.49-6.91 (26H, 26 × C*H*), 6.04 (2H, 2 × C*H*), 4.83-4.04 (4H, 2 × NC*H*$_2$), 1.77-1.60 (2H, 2 × NCH$_2$C*H*), 1.51-1.31 (6H, 2 × NCH$_2$C*H*, 4 × C*H*), 1.31-1.00 (12H, 6 × C*H*$_2$), 0.92-0.76 (18H, 6 × C*H*$_3$).

GPC analysis of the [TP-PhSQB]$_n$ polymer

Shimadzu GPC System

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

Gel permeation chromatography (GPC) was carried out at 293 K in chloroform (HPLC grade). Preparative chromatography was performed in recycling mode on two consecutive SDV columns (PSS preparative 50 Å and 500 Å, dimensions 20×600 mm) from PSS (Mainz, Germany) with a flow rate of 1 and 4 ml min^{-1}. Analytical chromatography was performed with a SDV column (mixed bed, "Linear S", 5 µm particle size, 8×300 nm) from PSS. Polystyrene solutions of different molecular weight (~ 1 mg ml^{-1}) were used as calibration standard.

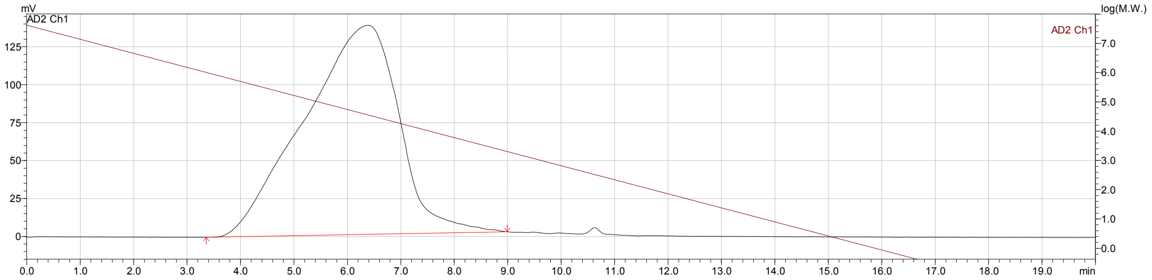


Fig. S1. GPC profile and calibration curve of **[TP-PhSQB]$_n$** polymer.

X-ray Structure

Single crystal X-ray diffraction data for compound **TP-SQB-2-Br$_2$** were collected at 100 K on a Bruker D8 Quest Kappa Diffractometer with a Photon100 CMOS detector and multi-layered mirror monochromated CuK$_\alpha$ radiation. Single crystals suitable for X-ray diffraction analysis were grown from a highly concentrated DCM solution by layering with hexane. The structure was solved using direct methods, expanded with Fourier techniques and refined with the Shelx software package.[4] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the structure factor calculation on geometrically idealized positions. Crystallographic data have been deposited with the Cambrige Crystallographic Data Center as supplementary publication no. CCDC 1916888 (**TP-SQB-2-Br$_2$**). These data can be obtained free of charge from The Cambrige Crystallographic Data Center *via* www.ccdc.ac.uk/data.request/cif.

Table S1: Bond lengths for the polymethine chain for squaraines **SQB**[b] and **TP-SQB-2-Br$_2$** according to single crystal X-ray analysis.[c]

	N1-C1 / Å	C1-C2 / Å	C2-C3 / Å	C3-C4 / Å	C4-C5 / Å	C5-C6 / Å	C6-C7 / Å	N2-C7 / Å
SQB[a,b]	1.351	1.389	1.386	1.439	1.433	1.399	1.379	1.360
TP-SQB-2-Br$_2$	1.303	1.429	1.365	1.435	1.424	1.396	1.395	1.339

[a]Crystallographic data taken from literature.[5] [b]**SQB** with a *n*-butyl alkyl chain. [c]Atoms of polymethine chain are labelled from left to right as indicated in **Fehler! Verweisquelle konnte nicht gefunden werden.**1..

Crystal data for **TP-SQB-2-Br$_2$** ($C_{61}H_{54}Br_2N_4O$ • 1.71 CH_2Cl_2): *M*r = 1164.48, 0.230x0.124x0.037 mm^3, monoclinic space group P21/n, *a* = 12.3578(5) Å, α = 90°, *b* = 19.6171(8) Å, β = 93.8074(18)° *c* = 24.1612(9) Å, γ = 90°, *V* = 5844.3(4) Å^3, *Z* = 4, ρ(*calcd)* = 1.323 g·cm^{-3}, μ = 3.535 mm^{-1}, $F_{(000)}$ = 2392, *GooF*(F^2) = 1.144, R_1 = 0.0395, wR^2 = 0. 1133 for *I* > 2sigma(*I*), R_1 = 0.0413, wR^2 = 0. 1147 for all data, 11929 unique reflections [θ = 67.679°] with a completeness of 99.5% and 683 parameters, 5 restraints.

Table S2: Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters (Å2 × 10^3) for twin crystal. U(eq) is definded as one third of the trace of the orthogonalised U_{ij} tensor.

	x	y	z	*U*(eq)
Br(1)	4371(1)	921(1)	22(1)	22(1)

Br(2)	4483(1)	986(1)	24(1)	24(1)
O(1)	6174(2)	2175(1)	22(1)	22(1)
N(1)	6881(3)	2125(2)	16(1)	16(1)
N(2)	6595(3)	2078(2)	16(1)	16(1)
N(3)	8151(4)	4994(2)	33(1)	33(1)
N(4)	7482(4)	5034(2)	30(1)	30(1)
C(1)	6346(3)	1755(2)	16(1)	16(1)
C(2)	6331(3)	1057(2)	18(1)	18(1)
C(3)	5728(3)	823(2)	18(1)	18(1)
C(4)	5182(3)	1271(2)	17(1)	17(1)
C(5)	5190(3)	1973(2)	17(1)	17(1)
C(6)	5787(3)	2206(2)	14(1)	14(1)
C(7)	5886(3)	2918(2)	14(1)	14(1)
C(8)	6654(3)	2788(2)	16(1)	16(1)
C(9)	6984(3)	3307(2)	16(1)	16(1)
C(10)	7042(3)	3234(2)	15(1)	15(1)
C(11)	7232(3)	3698(2)	16(1)	16(1)
C(12)	6891(3)	3209(2)	16(1)	16(1)
C(13)	6635(3)	2726(2)	16(1)	16(1)
C(14)	6664(3)	3267(2)	16(1)	16(1)
C(15)	6387(3)	2761(2)	15(1)	15(1)
C(16)	5738(3)	2917(2)	16(1)	16(1)
C(17)	5660(3)	2210(2)	16(1)	16(1)
C(18)	5162(3)	1998(2)	18(1)	18(1)
C(19)	5162(3)	1305(2)	18(1)	18(1)
C(20)	5637(3)	833(2)	18(1)	18(1)
C(21)	6145(3)	1044(2)	18(1)	18(1)
C(22)	6145(3)	1742(2)	16(1)	16(1)
C(23)	7540(3)	4380(2)	18(1)	18(1)
C(24)	7865(3)	4727(2)	21(1)	21(1)
C(25)	7527(3)	4746(2)	20(1)	20(1)
C(31)	6378(3)	3454(2)	16(1)	16(1)
C(32)	7021(3)	3249(2)	21(1)	21(1)
C(33)	7511(4)	3728(2)	28(1)	28(1)

C(34)	7375(4)	4421(2)	28(1)	28(1)
C(35)	6747(4)	4625(2)	27(1)	27(1)
C(36)	6263(3)	4148(2)	21(1)	21(1)
C(41)	4750(3)	3098(2)	18(1)	18(1)
C(42)	4017(3)	3464(2)	21(1)	21(1)
C(43)	2969(3)	3569(2)	27(1)	27(1)
C(44)	2632(3)	3310(2)	30(1)	30(1)
C(45)	3358(4)	2942(2)	29(1)	29(1)
C(46)	4410(3)	2833(2)	23(1)	23(1)
C(51)	6355(3)	3438(2)	17(1)	17(1)
C(52)	6198(3)	4137(2)	20(1)	20(1)
C(53)	6806(4)	4603(2)	25(1)	25(1)
C(54)	7572(4)	4380(2)	27(1)	27(1)
C(55)	7746(4)	3687(2)	26(1)	26(1)
C(56)	7146(3)	3217(2)	21(1)	21(1)
C(61)	4568(3)	3128(2)	19(1)	19(1)
C(62)	4102(3)	2924(2)	26(1)	26(1)
C(63)	3015(4)	3052(3)	34(1)	34(1)
C(64)	2384(3)	3390(2)	34(1)	34(1)
C(65)	2849(4)	3596(2)	29(1)	29(1)
C(66)	3924(3)	3457(2)	23(1)	23(1)
C(71)	7471(3)	1764(2)	16(1)	16(1)
C(72)	8572(3)	1942(2)	27(1)	27(1)
C(73)	9508(4)	1599(2)	32(1)	32(1)
C(74)	9619(3)	837(2)	30(1)	30(1)
C(75)	10427(5)	499(3)	39(1)	39(1)
C(76)	10505(5)	-263(3)	46(1)	46(1)
C(81)	7732(3)	1802(2)	19(1)	19(1)
C(82)	8735(4)	1649(3)	32(1)	32(1)
C(83)	9568(4)	1277(3)	34(1)	34(1)
C(84)	10490(20)	951(17)	47(3)	47(3)
C(85)	11230(20)	514(19)	62(4)	62(4)
C(86)	10750(30)	-187(17)	63(4)	63(4)
C(83B)	9568(4)	1277(3)	34(1)	34(1)

C(84B)	10660(8)	1199(8)	47(3)	47(3)
C(85B)	11433(10)	720(9)	62(4)	62(4)
C(86B)	11103(13)	-33(7)	63(4)	63(4)
C(101)	264(6)	5935(4)	60(2)	60(2)
Cl(1)	195(2)	5641(1)	78(1)	78(1)
Cl(2)	1511(2)	6291(2)	120(1)	120(1)
C(102)	309(8)	3854(4)	71(2)	71(2)
Cl(3)	188(3)	3002(1)	131(2)	131(2)
Cl(4)	1552(2)	4134(1)	71(1)	71(1)

TableS3: Anisotropic displacement parameters (Å2 × 10^3) for twin crystal.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Br(1)	25(1)	21(1)	20(1)	-5(1)	-3(1)	-4(1)
Br(2)	27(1)	25(1)	20(1)	4(1)	9(1)	-6(1)
O(1)	30(2)	16(1)	21(1)	-1(1)	-1(1)	-7(1)
N(1)	21(2)	16(2)	12(1)	1(1)	-1(1)	4(1)
N(2)	20(2)	13(1)	14(1)	-2(1)	6(1)	-1(1)
N(3)	50(2)	21(2)	29(2)	6(2)	12(2)	-2(2)
N(4)	49(2)	17(2)	23(2)	-3(1)	-4(2)	-6(2)
C(1)	18(2)	14(2)	15(2)	0(1)	2(1)	-1(1)
C(2)	23(2)	14(2)	18(2)	3(1)	4(1)	2(2)
C(3)	22(2)	11(2)	21(2)	-1(1)	6(2)	-2(1)
C(4)	16(2)	20(2)	15(2)	-2(1)	2(1)	-3(1)
C(5)	21(2)	15(2)	15(2)	2(1)	0(1)	1(1)
C(6)	17(2)	12(2)	15(2)	0(1)	4(1)	-1(1)
C(7)	20(2)	10(2)	13(2)	0(1)	-1(1)	0(1)
C(8)	18(2)	16(2)	14(2)	2(1)	2(1)	3(1)
C(9)	20(2)	13(2)	15(2)	2(1)	1(1)	2(1)
C(10)	15(2)	13(2)	17(2)	1(1)	3(1)	2(1)
C(11)	18(2)	17(2)	13(2)	1(1)	-1(1)	2(2)
C(12)	18(2)	14(2)	16(2)	3(1)	3(1)	2(1)
C(13)	19(2)	16(2)	14(2)	1(1)	1(1)	0(2)

C(14)	22(2)	12(2)	14(2)	-1(1)	3(1)	-2(1)
C(15)	16(2)	15(2)	14(2)	-1(1)	2(1)	1(1)
C(16)	21(2)	14(2)	15(2)	0(1)	6(1)	-2(1)
C(17)	18(2)	13(2)	17(2)	-1(1)	2(1)	-1(1)
C(18)	17(2)	20(2)	17(2)	-2(1)	5(1)	0(1)
C(19)	17(2)	20(2)	16(2)	3(1)	2(1)	-7(1)
C(20)	20(2)	12(2)	22(2)	1(1)	2(1)	-4(1)
C(21)	21(2)	14(2)	20(2)	-4(1)	4(1)	-2(2)
C(22)	16(2)	16(2)	15(2)	0(1)	1(1)	-1(1)
C(23)	21(2)	15(2)	18(2)	1(1)	0(1)	-2(2)
C(24)	26(2)	15(2)	23(2)	2(2)	2(2)	0(2)
C(25)	24(2)	12(2)	23(2)	4(2)	-2(2)	-3(2)
C(31)	19(2)	14(2)	14(2)	1(1)	-3(1)	0(1)
C(32)	26(2)	20(2)	17(2)	-1(2)	2(2)	1(2)
C(33)	33(2)	31(2)	20(2)	2(2)	5(2)	-3(2)
C(34)	36(2)	25(2)	24(2)	9(2)	0(2)	-7(2)
C(35)	35(2)	16(2)	30(2)	5(2)	-5(2)	-2(2)
C(36)	27(2)	18(2)	19(2)	1(1)	-2(2)	1(2)
C(41)	22(2)	13(2)	19(2)	-4(1)	-2(1)	3(1)
C(42)	24(2)	16(2)	22(2)	-2(1)	-4(2)	2(2)
C(43)	23(2)	23(2)	34(2)	-5(2)	-7(2)	4(2)
C(44)	21(2)	33(2)	35(2)	-9(2)	4(2)	1(2)
C(45)	31(2)	36(2)	22(2)	-2(2)	5(2)	-3(2)
C(46)	24(2)	24(2)	19(2)	2(2)	-1(2)	2(2)
C(51)	24(2)	14(2)	14(2)	-2(1)	8(1)	1(1)
C(52)	26(2)	15(2)	20(2)	-1(1)	8(2)	-1(2)
C(53)	35(2)	14(2)	25(2)	-3(2)	10(2)	-4(2)
C(54)	32(2)	28(2)	23(2)	-8(2)	8(2)	-11(2)
C(55)	28(2)	30(2)	20(2)	-2(2)	7(2)	-2(2)
C(56)	24(2)	18(2)	21(2)	-1(2)	6(2)	0(2)
C(61)	22(2)	14(2)	22(2)	0(1)	6(2)	-2(1)
C(62)	23(2)	28(2)	26(2)	-4(2)	3(2)	2(2)
C(63)	31(2)	40(3)	30(2)	-1(2)	-2(2)	2(2)
C(64)	19(2)	36(2)	46(3)	10(2)	2(2)	6(2)

C(65)	26(2)	21(2)	41(2)	1(2)	14(2)	4(2)
C(66)	25(2)	19(2)	24(2)	1(2)	9(2)	-4(2)
C(71)	22(2)	13(2)	14(2)	-2(1)	6(1)	5(1)
C(72)	25(2)	29(2)	25(2)	-5(2)	-2(2)	0(2)
C(73)	24(2)	35(2)	37(2)	2(2)	4(2)	-1(2)
C(74)	25(2)	35(2)	31(2)	6(2)	7(2)	5(2)
C(75)	45(3)	39(3)	34(2)	8(2)	14(2)	12(2)
C(76)	48(3)	38(3)	54(3)	8(2)	13(3)	18(3)
C(81)	23(2)	18(2)	14(2)	1(1)	-3(1)	5(2)
C(82)	28(2)	48(3)	19(2)	3(2)	1(2)	9(2)
C(83)	28(2)	50(3)	22(2)	1(2)	1(2)	10(2)
C(84)	34(4)	82(9)	26(3)	1(5)	2(3)	13(5)
C(85)	30(5)	130(12)	26(3)	-1(7)	3(4)	29(6)
C(86)	56(9)	87(8)	46(7)	2(5)	6(5)	49(7)
C(83B)	28(2)	50(3)	22(2)	1(2)	1(2)	10(2)
C(84B)	34(4)	82(9)	26(3)	1(5)	2(3)	13(5)
C(85B)	30(5)	130(12)	26(3)	-1(7)	3(4)	29(6)
C(86B)	56(9)	87(8)	46(7)	2(5)	6(5)	49(7)
C(101)	52(4)	37(3)	93(5)	-5(4)	15(4)	5(3)
Cl(1)	71(1)	59(1)	106(2)	17(1)	33(1)	5(1)
Cl(2)	51(1)	142(3)	166(3)	102(2)	4(2)	-7(1)
C(102)	63(5)	78(6)	74(5)	25(4)	8(4)	19(5)
Cl(3)	100(2)	57(1)	226(4)	27(2)	-64(2)	-12(2)
Cl(4)	54(1)	88(2)	70(1)	-10(1)	10(1)	8(1)

Steady-State Absorption Spectroscopy

Solvents for spectroscopic studies were of spectroscopic grade und used as received from Acros Organics. Absorption spectra were measured on a JASCO V670 UV/vis/NIR-Spectrophotometer in quartz cuvettes with path lengths of 0.1-10 mm at 293 K.

Emission Spectroscopy

Steady-state emission spectra were measured on an Edinburgh Instruments FLS980 fluorescence lifetime spectrometer (software F980 version 1.2.2); 450 W Xenon lamp/PMT (R928P). Emission spectra were recorded at 298 K in 10 mm quartz cells from Starna (Pfungstadt, Germany). The emission spectra were measured with strongly diluted samples (λ_{ex} < 0.05 OD) in order to prevent self-absorption. The fluorescence quantum yields were determined with optically dense samples in an integrating sphere. The observed fluorescence quantum yields were afterwards corrected for self-absorption applying the method of Bardeen et al.[6]

The samples for the lifetimes measurements were prepared similarly to the steady-state emission experiments. Fluorescence lifetimes were determined by time-correlated single-photon counting (TCSPC) with the same spectrometer as the steady-state measurements. The samples were excited by a pulsed laser diode (λ_{ex} = 656 nm for the monomer, 783 nm for the polymer) under magic angle conditions and the fluorescence was detected with a high-speed PMT detector (H10720). Deconvolution of the data (4096 channels) was conducted by measuring the instrument response function with a scatterer solution consisting of colloidal silicon in deionised water (LUDOX). The FAST software (version 3.4.2) was used to fit the decay curves with exponential decay functions.

DFT Calculations

Optimizations of the ground states of the expected “normal” configuration and that of the crystal structure (see Fig. 3) in the gas phase were done at the DFT level of theory with the B3LYP functional and 6-31G* basis set using Gaussian09.[7]

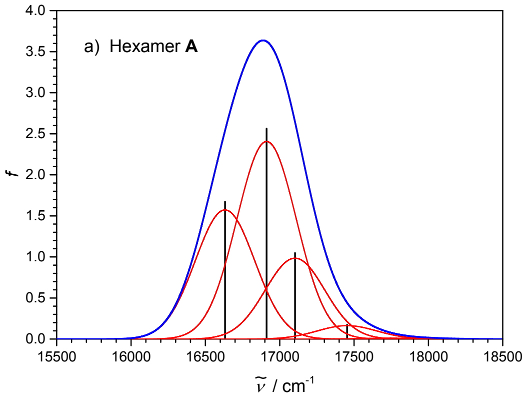
Semiempirical Calculations

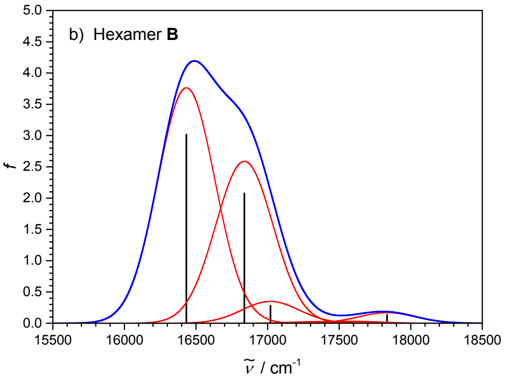
The structures of two model hexamers **[TP-SQB]$_6$** with most different structures A and B (see Fig 4) were first optimized using the AM1 hamiltonian using MOPAC 2016[8] which gives reliable geometries for squaraines.[9] CNDO/S2 calculations[10] were done to get the excited states energies and oscillator strengths using the obtained hexamer structures.

Table S4. CNDO S2 results (wavenumber and oscillator strengths)

Hexamer **A**	Hexamer **B**

$\tilde{v}_{a\ b}$/scm^{-1}	f	$\tilde{v}_{a\ b}$/scm^{-1}	f
16632.293	1.67462	16432.774	3.01877
16911.603	2.56345	16838.135	2.07584
17103.08	1.04851	17020.118	0.28026
17452.921	0.17434	17374.987	0.02160
17747.489	0.01206	17583.963	0.02647
17953.966	0.00968	17834.849	0.13460





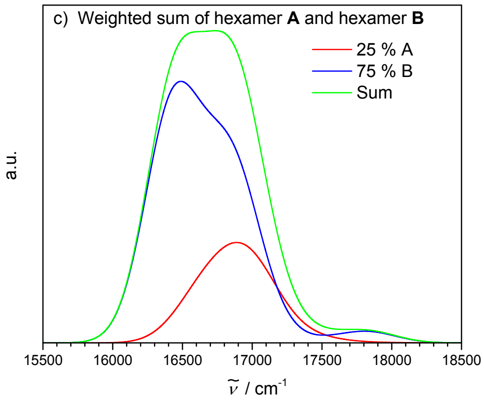


Fig. S2. Simulated absorption spectra of **[TP-SQB]$_6$** based on the CNDO S2 results from Table S1 convoluted with Gaussian function with an estimated half width of 400 cm^{-1} for hexamer **A** (a), hexamer **B** (b) and the weighted sum of both structure **A** and **B** (c).

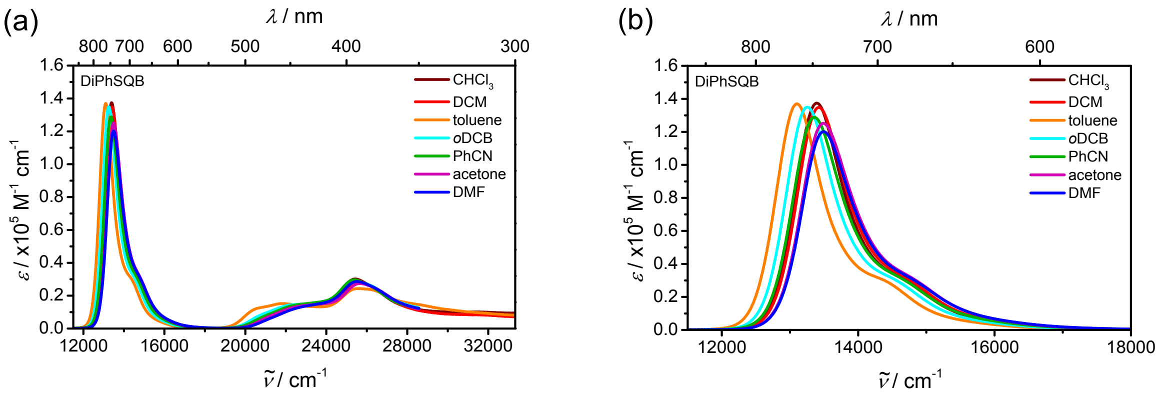
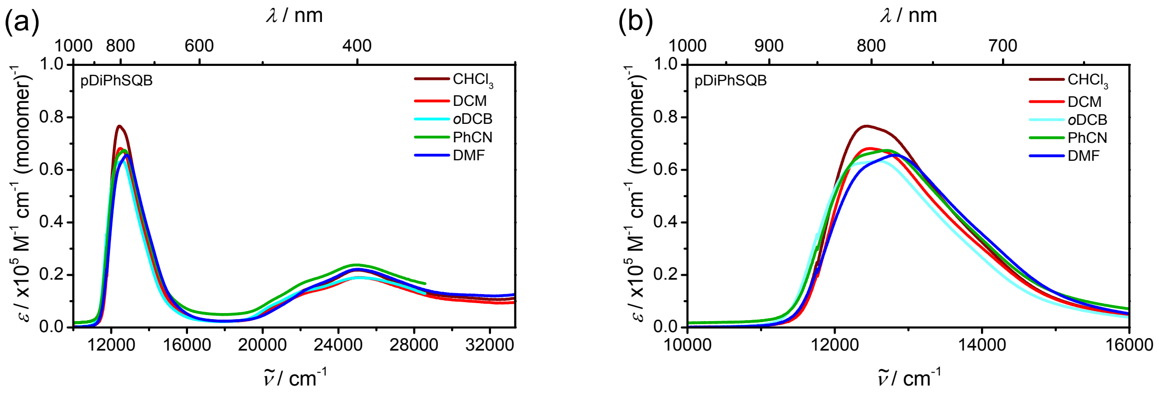


Fig. S3. Absorption spectra of **TP-SQB** in various solvents.



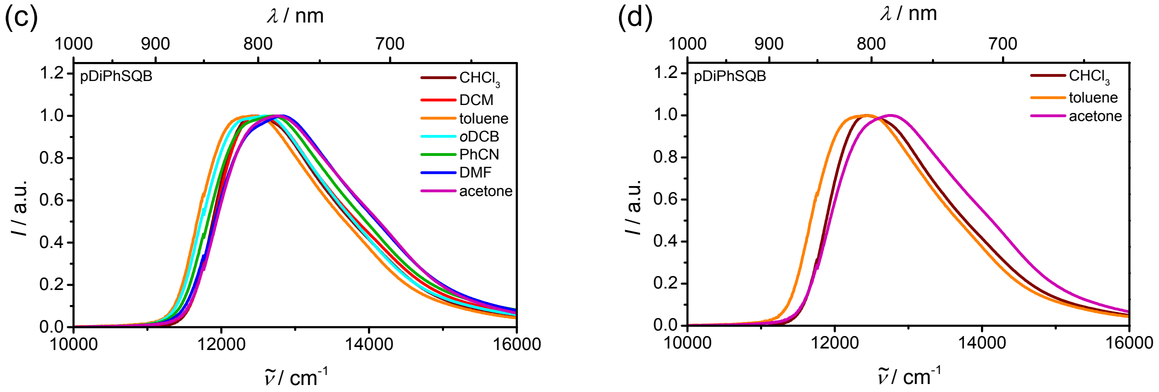
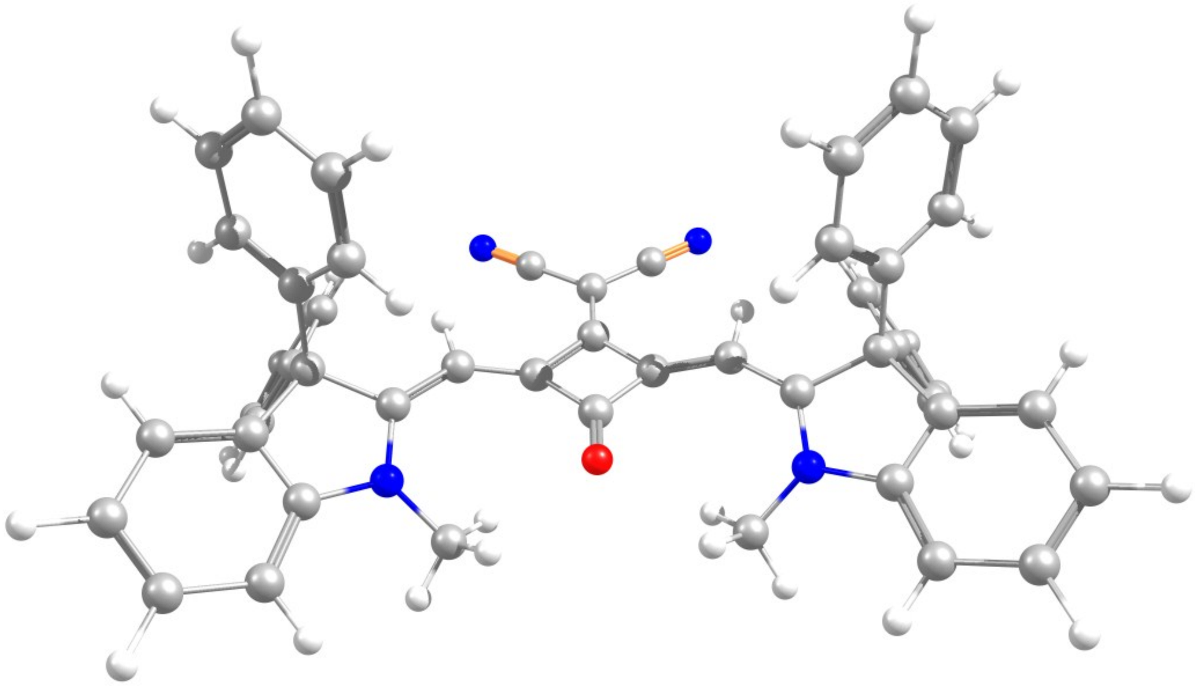


Fig. S4. (a)(b) Complete and (c) normalised absorption spectra of **$[\mathbf{TP\text{-}SQB}]_n$** in various solvents. (d) Normalised absorption spectra of **$[\mathbf{TP\text{-}SQB}]_n$** in $CHCl_3$, toluene, and acetone.

TP-SQB Monomer in the DFT optimized geometry of the X-ray structure (B3LYP/6-31G*) in the gas phase



```
HF=-2259.2379908

                          Standard orientation:
 ---------------------------------------------------------------------
 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
 ---------------------------------------------------------------------
      1          8           0        0.000733   -1.980791   -0.395951
      2          7           0       -2.214317    4.046914   -0.507844
      3          7           0        2.213584    4.047322   -0.507495
      4          7           0       -3.478343   -1.758409   -0.990427
      5          7           0        3.478436   -1.757759   -0.991347
      6          6           0       -4.680037   -2.422882   -0.668734
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     27          6           0       -1.040971    0.297558   -0.622220
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     31          6           0       -0.000240    2.704228   -0.593288
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39	6	0	6.857679	1.536532	-2.681134
40	6	0	6.544723	2.880312	-2.478524
41	6	0	5.711804	3.237051	-1.417102
42	6	0	5.203353	2.259611	-0.562987
43	6	0	4.789394	0.195973	1.622903
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67	1	0	-6.670719	1.730782	4.020230
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74	1	0	7.505832	1.243239	-3.502969
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79	1	0	2.929871	-0.355323	4.427681
80	1	0	4.799494	0.926946	5.458133
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91	1	0	1.783917	-2.945215	-1.429877
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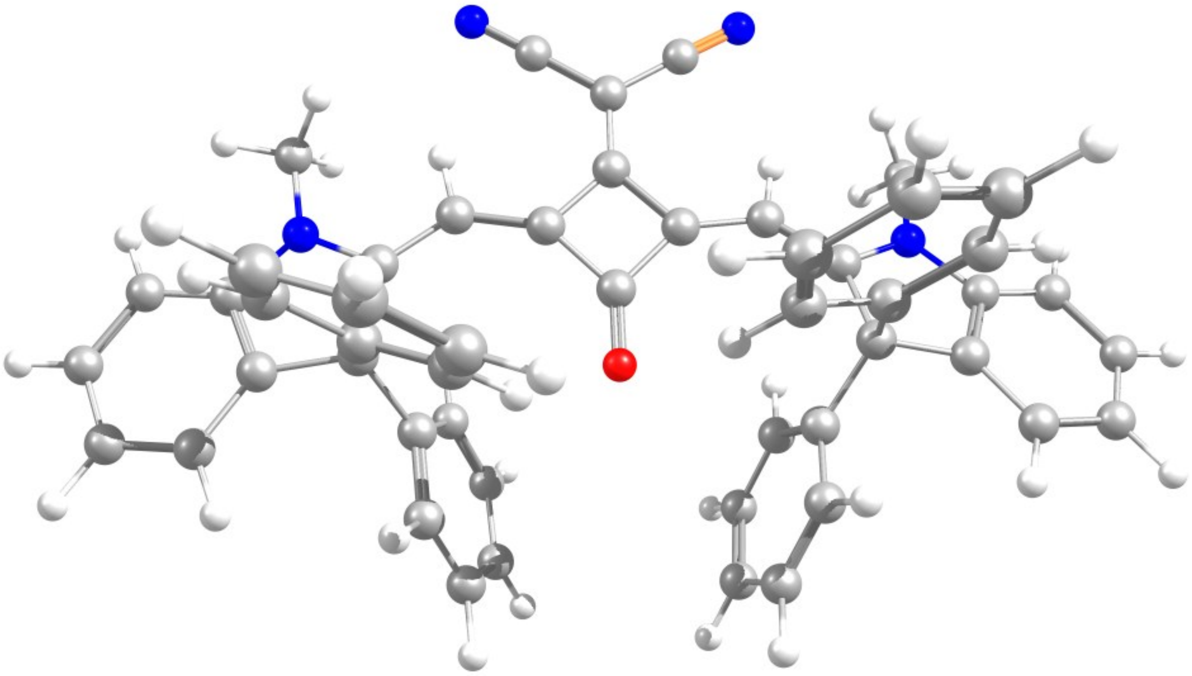
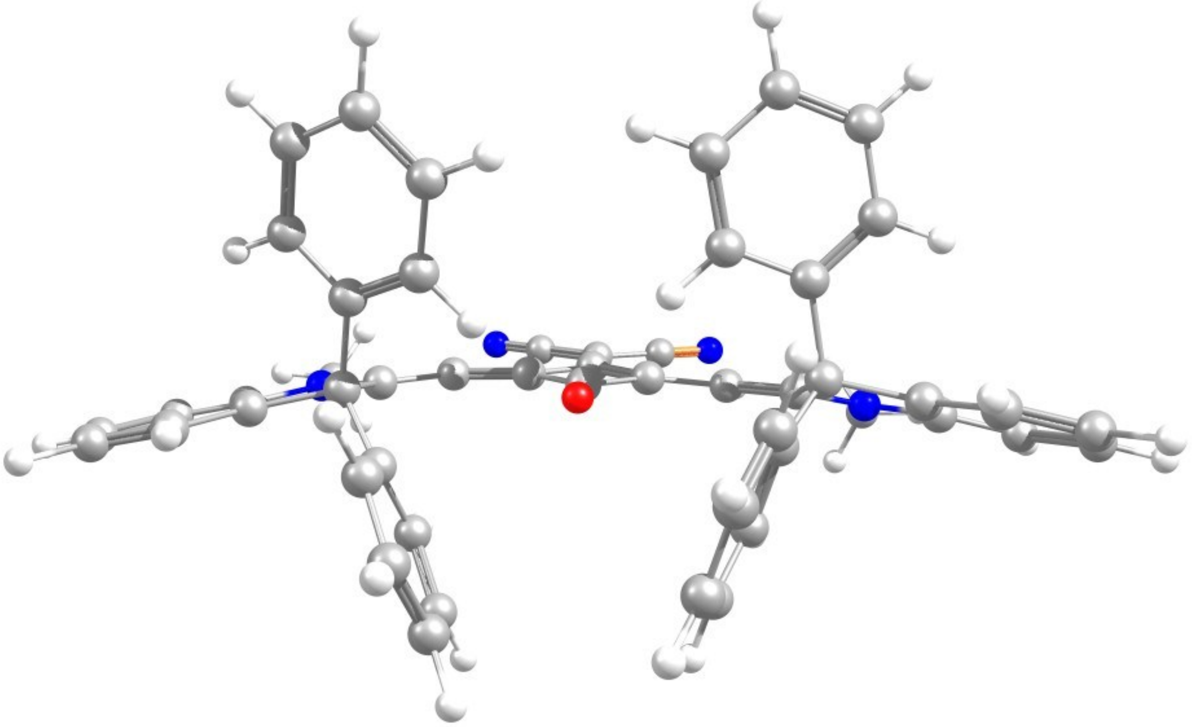
TP-SQB Monomer in the „normal“ optimized squaraine structure (B3LYP/6-31G*) in the gas phase



Top view



Side view

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HF=-2259.2293329
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                         Standard orientation:
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 Center     Atomic      Atomic             Coordinates (Angstroms)
 Number     Number       Type             X           Y           Z
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      1          6           0        1.056711    1.573596   -0.375864
      2          6           0        0.004892    0.526939   -0.212448
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3	6	0	-1.026762	1.603797	-0.275677
4	6	0	0.025655	2.593732	-0.416377
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6	8	0	-0.000856	-0.689904	-0.097970
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8	6	0	-2.408248	1.834704	-0.320178
9	6	0	3.557598	0.945034	-0.492438
10	6	0	-3.548347	1.042221	-0.260351
11	7	0	4.772757	1.449588	-0.880881
12	6	0	5.795849	0.488991	-0.781347
13	6	0	5.270604	-0.680281	-0.227604
14	6	0	3.786298	-0.475146	0.084599
15	6	0	-3.774101	-0.463045	0.027133
16	6	0	-5.279334	-0.586041	-0.237081
17	6	0	-5.809712	0.678477	-0.499936
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19	6	0	7.133955	0.589564	-1.159185
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21	6	0	7.434829	-1.706460	-0.407640
22	6	0	6.085447	-1.786844	-0.040743
23	6	0	-6.106408	-1.698946	-0.234782
24	6	0	-7.472182	-1.530628	-0.496074
25	6	0	-7.990132	-0.259762	-0.757839
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31	6	0	3.075874	-0.042914	4.375355
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38	6	0	-2.391994	-3.660924	-1.582716
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41	6	0	2.004596	-2.510147	-2.639788
42	6	0	1.817401	-3.737894	-2.005601
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45	6	0	3.002460	-1.591517	-0.625112
46	6	0	2.596847	-1.449046	-1.956820
47	6	0	-2.235475	-1.195730	1.967704
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52	6	0	-1.985862	-1.386843	3.328618
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58	1	0	-2.626968	2.883088	-0.480075
59	1	0	7.543027	1.491123	-1.602517
60	1	0	8.994377	-0.479600	-1.246639
61	1	0	8.083389	-2.566002	-0.267251
62	1	0	5.680840	-2.703913	0.376311
63	1	0	-5.699605	-2.686664	-0.041951
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65	1	0	-9.049624	-0.140559	-0.965834
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67	1	0	4.540349	3.542793	-0.732965
68	1	0	6.053029	2.986131	-1.467088
69	1	0	4.533839	2.909417	-2.391644
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71	1	0	-6.049725	3.269603	-0.612080
72	1	0	-4.467359	3.642722	0.090608
73	1	0	1.448368	-0.858682	1.499350
74	1	0	1.033100	-0.557086	3.911437
75	1	0	2.893455	0.087036	5.438800
76	1	0	5.173696	0.443092	4.500768
77	1	0	5.584810	0.153576	2.097485
78	1	0	-2.806496	0.070651	-2.503795
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86        1        0       3.122849   -2.964637    1.034920
87        1        0       2.731929   -0.499424   -2.466124
88        1        0      -1.461601   -1.416502    1.242067
89        1        0      -5.408090    0.000498    2.198393
90        1        0      -4.946288   -0.302270    4.588738
91        1        0      -2.754119   -1.220056    5.339829
92        1        0      -1.026056   -1.792685    3.638564
```

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