Synthetic efforts to investigate the effect of planarizing the triarylsamine geometry in dyes for dye-sensitized solar cells.

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Experimental

Synthesis. All reactions were performed under inert N$_2$-atmosphere.

Analytical instruments. $^1$H and $^{13}$C NMR was performed using either a BRUKER 400 MHz or 600 MHz magnet, the spectra obtained are calibrated against residual solvent peak of CDCl$_3$ (7.26/77.16 ppm), CD$_2$Cl$_2$ (5.32/53.84 ppm), DMSO-$d_6$ (2.50/39.52 ppm), Acetone-$d_6$ (2.05/29.84 ppm) or THF-$d_8$ (1.72/25.31 ppm). The IR-spectra are obtained using a BRUKER Alpha Eco-ATR FTIR spectrometer, the data is reported with wavenumber and intensity of the signal. Mass determination was performed by MS-analysis in positive ionization mode on a Synapt G2-S Q-TOF-instrument for Waters, the samples were ionized by an ASAP-probe (APCI) without prior chromatographic separation. UV-Vis spectroscopy was performed using a Hitachi U-1900 spectrometer, and photoluminescence characterization was carried out on an Edinburgh Instruments FS5-spectrofluorometer.

5-(4-(bis(2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)amino)phenyl)thiophene-2-carbaldehyde (2)

The triaryl bromide 1 (101 mg, 0.115 mmol), 5-formylthiophen-2-yl-boronic acid (28.9 mg, 0.185 mmol), XPhos Pd G3 (7.0 mg, 8.27 × 10$^{-3}$ mmol) and K$_3$PO$_4$ (85.5 mg, 0.403 mmol) were mixed in a Schlenk-tube, before the reaction system was evacuated and filled with dry nitrogen gas. THF (2 mL) and water (4 mL) were degassed and added to the mixture. The reaction mixture was stirred at 40 °C for 4 h before cooling to 22 °C. Water (10 mL) and Et$_2$O (10 mL) were then added, and the aqueous and organic phases were separated. The aqueous phase was extracted with more Et$_2$O (3 × 10 mL). The combined organic phases were dried with anhydrous Na$_2$SO$_4$, filtered and the solvents removed in vacuo. The crude product (59.9 mg) was purified by silica-gel column chromatography (gradient: start: CH$_2$Cl$_2$/n-pentane, 1:3, $R_f$= 0.29, end: CH$_2$Cl$_2$) to yield 2 as yellow resin (41.8 mg, 0.0460 mmol, 40%). $^1$H NMR (600 MHz, CDCl$_3$) δ: 9.85 (s, 1H), 7.70 (d, $J = 3.9$ Hz, 1H), 7.54-7.51 (m, 2H), 7.49-7.46 (m, 4H), 7.30 (d, $J = 3.9$ Hz, 1H), 7.27-7.25 (m, 2H), 5.32-5.31 (m, 2H), 5.05-5.04 (m, 2H), 4.89-4.88 (m, 2H), 4.76-4.75 (m, 2H), 4.62-4.61 (m, 2H), 4.50-4.49 (m, 2H), 4.38-4.37 (m, 2H), 4.23-4.22 (m, 2H), 4.10-4.09 (m, 2H), 3.97-3.96 (m, 2H), 3.85-3.84 (m, 2H), 3.73-3.72 (m, 2H), 3.61-3.60 (m, 2H), 3.49-3.48 (m, 2H), 3.37-3.36 (m, 2H), 3.25-3.24 (m, 2H), 3.13-3.12 (m, 2H), 3.01-3.00 (m, 2H), 2.90-2.89 (m, 2H), 2.78-2.77 (m, 2H), 2.66-2.65 (m, 2H), 2.54-2.53 (m, 2H), 2.43-2.42 (m, 2H), 2.32-2.31 (m, 2H), 2.20-2.19 (m, 2H), 2.09-2.08 (m, 2H), 1.97-1.96 (m, 2H), 1.85-1.84 (m, 2H), 1.73-1.72 (m, 2H), 1.62-1.61 (m, 2H), 1.51-1.50 (m, 2H), 1.40-1.39 (m, 2H), 1.20-1.19 (m, 2H), 1.10-1.09 (m, 2H), 0.88-0.87 (m, 2H), 0.76-0.75 (m, 2H), 0.64-0.63 (m, 2H), 0.52-0.51 (m, 2H), 0.39-0.38 (m, 2H), 0.28-0.27 (m, 2H), 0.17-0.16 (m, 2H), 0.06-0.05 (m, 2H).
2H), 7.19-7.14 (m, 6H), 6.56-6.52 (m, 4H), 3.99 (t, J = 6.6 Hz, 4H), 3.96 (t, J = 6.5 Hz, 4H), 1.83-1.71 (m, 8H), 1.52-1.23 (m, 24H), 0.92 (t, J = 7.0 Hz, 6H), 0.87 (t, J = 7.0 Hz, 6H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\): 182.6, 159.7 (2C), 157.0 (2C), 154.8, 149.3, 145.0 (2C), 141.2, 137.7, 134.1 (2C), 130.9 (2C), 130.4 (4C), 127.2 (2C), 125.8, 124.5 (4C), 122.8 (2C), 122.7, 122.3 (2C), 105.4 (2C), 100.4 (2C), 68.4 (2C), 68.1 (2C), 31.6 (2C), 31.5 (2C), 29.3 (2C), 29.1 (2C), 25.78 (2C), 25.76 (2C), 22.63 (2C), 22.58 (2C), 14.1 (2C), 14.0 (2C); IR (EtOAc, cm\(^{-1}\)): 3354 (w), 3313 (w), 2924 (s), 2854 (s), 2655 (m), 2325 (m), 1665 (s), 1597 (s), 1444 (s), 1291 (m), 1271 (m), 1181 (s), 1051 (s), 828 (m), 530 (s), 505 (s); HRMS (ASAP+, m/z): found 907.5206, calcd. for C\(_{59}\)H\(_{73}\)NO\(_5\)S [M\(^{+}\)]\(^{+}\) 907.5209.

**5-(4-(bis(2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)amino)phenyl)furan-2-carbaldehyde (3)**

The synthesis of 3 was performed as described for compound 2 using 5-formylfuran-2-yl-boronic acid (27.7 mg, 0.198 mmol). Silica-gel column chromatography (gradient: start: CH\(_2\)Cl\(_2\)/n-pentane, 1:3, \(R_f\) = 0.26, end: CH\(_2\)Cl\(_2\)) gave (57.0 mg, 0.0639 mmol, 56%) of 3 as a yellow resin.

\(^{1}\)H NMR (600 MHz, CDCl\(_3\)) \(\delta\): 9.59 (s, 1H), 7.69-7.65 (m, 2H), 7.51-7.45 (m, 4H), 7.30 (d, J = 3.7 Hz, 1H), 7.27-7.25 (m, 2H), 7.17 (d, J = 8.6 Hz, 6H), 6.70 (d, J = 3.7 Hz, 1H), 6.56-6.52 (m, 4H), 3.99 (t, J = 6.6 Hz, 4H), 3.96 (t, J = 6.4 Hz, 4H), 1.84-1.71 (m, 8H), 1.51-1.22 (m, 24H), 0.92 (t, J = 7.0 Hz, 6H), 0.87 (t, J = 7.0 Hz, 6H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta\): 176.7, 160.1, 159.7 (2C), 157.0 (3C), 151.6, 149.5, 145.0 (2C), 134.1 (2C), 130.9 (2C), 130.4 (4C), 126.3 (2C), 124.6 (4C), 122.8 (2C), 122.1 (2C), 121.7, 106.3, 105.4 (2C), 100.2 (2C), 68.4 (2C), 68.1 (2C), 31.6 (2C), 31.5 (2C), 29.3 (2C), 29.1 (2C), 25.8 (4C), 22.63 (2C), 22.59 (2C), 14.1 (2C), 14.0 (2C); IR (EtOAc, cm\(^{-1}\)): 2954 (s), 2926 (s), 2857 (s), 2662 (m), 1674 (s), 1601 (s), 1474 (s), 1323 (m), 1271 (m), 1182 (s), 1027 (m), 1003 (m), 835 (m), 518 (m); HRMS (ASAP+, m/z): found 892.5507, calcd. for C\(_{59}\)H\(_{74}\)NO\(_6\) [M+H]\(^{+}\) 892.5516.

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(E)-3-(5-(4-(bis(2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)amino)phenyl)thiophen-2-yl)-2-cyanoacrylic acid (TAA-Th)

Compound 2 (36 mg, 0.0396 mmol) and cyanoacetic acid (79 mg, 0.926 mmol) were dissolved in degassed MeCN (15 mL) under nitrogen atmosphere. Piperidine (60.0 μL, 51.7 mg, 0.607 mmol) was added to the mixture, and the reaction was stirred at 80 °C for 1.5 h before cooling to 22 °C. The reaction mixture was then quenched in aqueous HCl (4M, 25 mL). CH₂Cl₂ (100 mL) was added and the organic phase was washed with water (6 × 100 mL), then dried over anhydrous Na₂SO₄, filtered and the solvents were removed in vacuo. The crude product (44.8 mg) was purified by silica-gel column chromatography (gradient: 0-20% MeOH in CH₂Cl₂, Rf = 0.00 in CH₂Cl₂). The dye-containing fractions were washed with HCl (1M, 2 × 20 mL), dried over anhydrous Na₂SO₄ and filtered to obtain (37 mg, 0.0383 mmol, 95%) of TAA-Th as a dark purple solid, mp. 62.1-67.5 °C. ¹H NMR (600 MHz, CDCl₃) δ: 8.32 (s, 1H), 7.78 (d, J = 4.0 Hz, 1H), 7.56 (d, J = 8.5 Hz, 2H), 7.49 (d, J = 8.6 Hz, 4H), 7.34 (d, J = 4.0 Hz, 1H), 7.28-7.24 (m, 2H), 7.18 (d, J = 8.6 Hz, 4H), 7.15 (d, J = 8.8 Hz, 2H), 6.57-6.52 (m, 4H), 3.99 (t, J = 6.5 Hz, 4H), 3.97 (t, J = 6.4 Hz, 4H), 1.84-1.71 (m, 8H), 1.52-1.22 (m, 24H), 0.92 (t, J = 7.0 Hz, 6H), 0.87 (t, J = 7.0 Hz, 6H); ¹³C NMR (150 MHz, CDCl₃) δ: 168.1, 159.7 (2C), 157.0 (2C), 156.9, 149.8, 147.9, 144.8 (2C), 140.5, 134.3 (2C), 133.5, 130.9 (2C), 130.4 (4C), 127.4 (2C), 125.1, 124.7 (4C), 123.3, 122.7 (2C), 121.9 (2C), 115.9, 105.4 (2C), 100.4 (2C), 95.2, 68.4 (2C), 68.1 (2C), 31.6 (2C), 31.5 (2C), 29.3 (2C), 29.1 (2C), 25.78 (2C), 25.76 (2C), 22.62 (2C), 22.59 (2C), 14.0 (4C); IR (EtOAc, cm⁻¹): 2954 (m), 2928 (s), 2857 (m), 2321 (w), 2217 (w), 2069 (w), 1686 (m), 1576 (s), 1493 (s), 1412 (s), 1323 (m), 1281 (s), 1222 (m), 1183 (s), 1063 (m), 599 (m), 480 (m); HRMS (ASAP+, m/z): found 975.5330, calcd. for C₆₂H₇₅N₂O₆S [M+H]⁺ 975.5346.
(E)-3-(5-(4-(bis(2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)amino)phenyl)furan-2-yl)-2-cyanoacrylic acid (TAA-Fu)

Synthesis and purification of TAA-Fu were performed as described for TAA-Th starting with intermediate 3 (52.6 mg, 0.059 mmol). This gave 42.3 mg (0.0441 mmol, 75%), of a dark purple solid, mp. 62.4-68.9 °C. $^1$H NMR (600 MHz, CDCl$_3$) δ: 7.95 (s, 1H), 7.73 (d, $J$ = 8.9 Hz, 2H), 7.51-7.47 (m, 4H), 7.28-7.24 (m, 2H), 7.21-7.16 (m, 6H), 6.81 (d, $J$ = 3.9 Hz, 1H), 6.57-6.52 (m, 4H), 3.99 (t, $J$ = 6.7, 4H), 3.97 (t, $J$ = 6.6 Hz, 4H), 1.82-1.71 (m, 8H), 1.52-1.22 (m, 24H), 0.92 (t, $J$ = 7.0 Hz, 6H), 0.86 (t, $J$ = 7.0 Hz, 6H); $^{13}$C NMR (150 MHz, CDCl$_3$) δ: 168.5, 161.8, 159.7 (2C), 157.0 (2C), 150.0, 147.2, 144.7 (2C), 138.6, 134.4 (2C), 130.9 (2C), 130.5 (4C), 126.8 (2C), 124.9 (4C), 122.8 (2C), 121.6 (2C), 120.8 (2C), 115.9, 108.2, 105.4 (2C), 100.4 (2C), 93.6, 68.4 (2C), 68.1 (2C), 31.6 (2C), 31.4 (2C), 29.3 (2C), 29.1 (2C), 25.77 (2C), 25.75 (2C), 22.62 (2C), 22.58 (2C), 14.1 (2C), 14.0 (2C); IR (EtOAc, cm$^{-1}$): 3270 (w), 3239 (w), 3087 (w), 3087 (w), 2956 (s), 2930 (s), 2860 (m), 1591 (s), 1494 (s), 1470 (s), 1268 (m), 1182 (m), 824 (m), 792 (m); HRMS (ASAP+, m/z): found 957.5399, calcd. for C$_{62}$H$_{73}$N$_2$O$_7$ [M-H]$^+$ 957.5418.

1-(3,7-dibromo-10H-phenothiazin-10-yl)ethan-1-one (5)

3,7-Dibromo-10H-phenothiazine (4) (1.05 g, 2.94 mmol) was suspended in dry toluene (30 mL). Acetyl chloride (0.461 g, 5.88 mmol) was added under a nitrogen atmosphere and the reaction mixture was then stirred for 3 h at reflux. The solvent was removed and the crude product washed with cold hexane to give 5 as a green powder (1.01 g, 2.52 mmol, 83%), mp. 138.5 °C. $^1$H NMR (400 MHz, DMSO-d$_6$) δ: 7.83 (d, $J$=2.0 Hz, 2H), 7.60 (dd, $J$ = 8.5, 2.1 Hz, 2H), 7.56 (d, $J$ = 8.5
Hz, 2H), 2.13 (s, 3H); $^1$H NMR (100 MHz, DMSO-$d_6$) δ: 168.8, 138.2 (2C), 134.4 (2C), 130.2 (2C), 139.6 (2C), 129.5 (2C), 119.9 (2C), 23.1; IR (neat, cm$^{-1}$): 3026, 1683, 1568, 1459, 1356, 1301, 1253, 1018 and 818; HRMS (ASAP+, m/z): found 399.8834, calcd. for C$_{14}$H$_{10}$NO$_8$S$_1$Br$_2$ [M+H]$^+$ 399.8829.

1-(3,7-bis(2,4-bis(hexyloxy)phenyl)-10$H$-phenothiazin-10-yl)ethan-1-one (7)

**Formation of pinacol borane:** A mixture of 1-bromo-2,4-bis(hexyloxy)benzene (2.67 mg, 7.52 mmol mmol), PdCl$_2$(CH$_3$CN)$_2$ (67.3 mg, 259 µmol) and SPhos (199 mg, 485 µmol) was evacuated before a nitrogen atmosphere was established. Degassed and dry 1,4-dioxane (23 mL) was then added and the reaction mixture was stirred for 20 min. Then dry triethylamine (2.46 g, 24.4 mmol) and 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (1.92 mg, 15.0 mmol were added and the reaction mixture stirred at 105 °C for 90 min. The reaction mixture was then cooled down and filtered through Celite, before the solvents were removed *in vacuo* to give crude 2-(2,4-bis(hexyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane as a yellow oil, which was then used directly in the Suzuki cross-coupling reaction.

**Suzuki cross-coupling:** Crude 6 (1.19 g, 2.98 mmol), Pd(OAc)$_2$ (35.0 mg, 160 µmol), SPhos (126 mg, 307 µmol) and K$_2$CO$_3$ (2.06 g, 14.9 mmol) were mixed with 2-(2,4-bis(hexyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane from above, before the mixture was evacuated and a nitrogen atmosphere established. Degassed H$_2$O (20 mL) and 1,4-dioxane (20 mL) were added under a nitrogen atmosphere. This mixture was stirred at 80 °C for 6 h. After the mixture was cooled down to rt, H$_2$O (75 mL) was added and the aqueous phase extracted with CH$_2$Cl$_2$ (4 × 75 mL). The combined organic phase was washed with H$_2$O (2 × 50 mL), dried over Na$_2$SO$_4$ before the solvents were removed in vacuo. The crude product was purified twice with column chromatography ($n$-pentane/EtOAc, 17:3, $R_f = 0.25$) to yield 7 (1.54 g, 1.93 mmol, 65%) as an orange oil. $^1$H NMR (600 MHz, DMSO-$d_6$, 80 °C) δ: 7.65-7.59 (m, 4H), 7.45 (dd, $J = 2.0, 8.4$ Hz, 2H), 7.26 (d, $J = 8.4$ Hz, 2H), 6.62 (d, $J = 2.4$ Hz, 2H), 6.60 (dd, $J = 8.5, 2.3$ Hz, 2H), 4.02-3.94
(m, 8H), 2.19 (s, 3H), 1.77-1.70 (m, 4H), 1.67-1.61 (m, 4H), 1.47-1.39 (m, 4H), 1.39-1.27 (m, 12H), 1.27-1.18 (m, 8H), 0.88 (t, \( J = 6.7 \) Hz, 6H), 0.77 (t, \( J = 6.7 \) Hz, 6H); \(^{13}\)C NMR (150 MHz, DMSO-\(d_6\), 80 °C) \( \delta \): 168.0, 159.6 (2C), 156.4 (2C), 136.4 (2C), 136.5 (2C), 131.1 (2C), 130.3 (2C), 127.6 (2C), 127.3 (2C), 126.2 (2C), 120.8 (2C), 106.3 (2C), 100.4 (2C), 68.0 (2C), 67.5 (2C), 30.50 (2C), 30.45 (2C), 28.29 (2C), 28.20 (2C), 24.9 (2C), 24.7 (2C), 22.1, 21.49 (2C), 21.45 (2C), 13.2 (2C), 13.1 (2C); IR (CH\(_2\)Cl\(_2\), cm\(^{-1}\)): 2928, 2857, 1682, 1608, 1499, 1301, 1277, 1181; HRMS (ASAP+, m/z): found 794.4808, calcd. for C\(_{50}\)H\(_{68}\)NO\(_5\)S [M+H]\(^+\) 794.4818.

3,7-bis(2,4-bis(hexyloxy)phenyl)-10H-phenothiazine (8)

Compound 7 (1.52 g, 1.91 mmol) was dissolved in THF (8 mL) and MeOH (20 mL), before this solution was degassed and added under a nitrogen atmosphere to a flask containing NaOH (319 mg, 7.98 mmol). This mixture was then stirred for 2 h at 60 °C, before being cooled down to 22 °C. Water (50 mL) was added and the aqueous phase extracted with CH\(_2\)Cl\(_2\) (4 × 50 mL). The organic phases were combined and washed with saturated NaHCO\(_3\) (3 × 50 mL) and H\(_2\)O (4 × 50 mL) before being dried over Na\(_2\)SO\(_4\). The solvents were removed in vacuo to give 8 (1.34 g, 1.78 mmol, 93%) as a green solid; mp. 85-89 °C. \(^1\)H NMR (600 MHz, DMSO-\(d_6\)) \( \delta \): 8.62 (s, 1H), 7.13 (d, \( J = 8.2 \) Hz, 2H), 7.08-7.05 (m, 2H), 7.05-7.01 (m, 2H), 6.69 (d, \( J = 8.2 \) Hz, 2H), 6.58-6.54 (m, 2H), 6.54-6.49 (m, 2H), 4.00-3.88 (m, 8H), 1.73-1.66 (m, 4H), 1.66-1.58 (m, 4H), 1.46-1.34 (m, 8H), 1.34-1.00 (m, 16H), 0.88 (t, \( J = 6.7 \) Hz, 6H), 0.84 (t, \( J = 6.7 \) Hz, 6H); \(^{13}\)C NMR (150 MHz, DMSO-\(d_6\)) \( \delta \): 159.0 (2C), 156.3 (2C), 140.2 (2C), 131.5 (2C), 130.0 (2C), 128.0 (2C), 126.7 (2C), 121.4 (2C), 115.6 (2C), 113.9 (2C), 105.8 (2C), 100.1 (2C), 67.7 (2C), 67.5 (2C), 31.00 (2C), 30.97 (2C), 28.7 (2C), 28.6 (2C), 25.4 (2C), 25.2 (2C), 22.10 (2C), 22.06 (2C), 13.88 (2C), 13.86 (2C); IR (CH\(_2\)Cl\(_2\), cm\(^{-1}\)): 3374 (w), 2954 (m), 2931 (m), 2867 (m), 1604 (m), 1576 (w), 1487 (m), 1287 (m), 1269 (m), 1257 (m), 1184 (m), 1040 (w), 1019 (w), 819 (m); HRMS (ASAP+, m/z): found 752.4700, calcd. for C\(_{48}\)H\(_{66}\)NO\(_4\)S, [M+H]\(^+\) 752.4713.
3,7-bis(2,4-bis(hexyloxy)phenyl)-10-(4-(trimethylsilyl)phenyl)-10H-phenothiazine (9)

Compound 8 (764 mg, 1.06 mmol), NaO-tBu (137 mg, 1.42 mmol), XPhos (48.4 mg, 102 mmol) and Pd(OAc)$_2$ (11.4 mg, 50.8 mmol) were mixed and degassed 1,4-dioxane (5 mL) was added under nitrogen atmosphere, before this mixture was left for stirring at rt for a couple of minutes. 1-Bromo-4(trimethylsilyl)benzene (704 mg, 3.07 mmol) was then added, and the reaction mixture was heated to 110 °C and left stirring for 15 h. The reaction mixture was then cooled down to rt, H$_2$O (100 mL) was added and the crude product extracted with CH$_2$Cl$_2$ (4 × 75 mL). The organic phases were combined, washed with H$_2$O (2 × 100 mL), dried over Na$_2$SO$_4$ and filtrated before the solvents were removed in vacuo. Purification by silica-gel column chromatography (n-pentane/CH$_2$Cl$_2$, 1:3, R$_f$ = 0.20) gave 9 (828 mg, 0.920 mmol, 87%) as a green oil. $^1$H NMR (600 MHz, CD$_2$Cl$_2$) δ: 7.78 (d, $J = 8.0$ Hz, 2H), 7.40 (d, $J = 8.1$ Hz, 2H), 7.22 (d, $J = 1.9$ Hz, 2H), 7.15 (d, $J = 8.1$ Hz, 2H), 7.02 (dd, $J = 8.4$, 1.9 Hz, 2H), 6.52-6.48 (m, 4H), 6.24 (d, $J = 8.6$ Hz, 2H), 3.96 (t, $J = 6.7$ Hz, 4H), 3.93 (t, $J = 6.4$ Hz, 4H), 1.81-1.69 (m, 8H), 1.50-1.40 (m, 8H), 1.40-1.28 (m, 16H), 0.93 (t, $J = 6.9$ Hz, 6H), 0.88 (t, $J = 6.8$ Hz, 6H), 0.36 (s, 9H); $^{13}$C NMR (150 MHz, CD$_2$Cl$_2$) δ: 160.1 (2C), 157.3 (2C), 142.8 (2C), 142.2, 141.0, 136.1 (2C), 133.3 (2C), 130.8 (2C), 129.8 (2C), 128.1 (2C), 127.8 (2C), 122.3 (2C), 120.2 (2C), 116.2 (2C), 105.8 (2C), 100.5 (2C), 68.8 (2C), 68.6 (2C), 32.03 (2C), 31.97 (2C), 29.7 (2C), 29.6 (2C), 26.3 (2C), 26.1 (2C), 23.0 (4C), 14.3 (2C), 14.2 (2C), -1.0 (3C); IR (CH$_2$Cl$_2$, cm$^{-1}$): 2954, 2930, 2859, 1608, 1466, 1297, 1248, 1179, 1135, 1077, 1017, 832, 662, 602, 537; HRMS (ASAP+, m/z): found 899.5332, calcd. for C$_{57}$H$_{77}$NO$_4$SiS, [M$^+$]$^+$ 899.5343.
3,7-bis(2,4-bis(hexyloxy)phenyl)-10-(4-iodophenyl)-10H-phenothiazine (10)

Compound 9 (693 mg, 0.770 mmol) was dissolved in dry CH₂Cl₂ (16 mL) and dry acetonitrile (16 mL) and left stirring at 0 °C for 5 min. Then a solution of ICl in CH₂Cl₂ (1.88 mL, 0.6 M) was added at 0 °C and the reaction was left stirring at 22°C for 20 h. The reaction was then quenched with an aqueous solution of Na₂S₂O₃ (5 wt%, 40 mL) and the mixture was extracted with CH₂Cl₂ (2 × 60 mL). The combined organic phases were washed with H₂O (30 mL), dried over Na₂SO₄, filtered and the solvents removed in vacuo. The product was purified by silica-gel column chromatography (n-pentane/acetone, 20:1, R_f = 0.15) to yield 10 (137 mg, 0.144 mmol, 19%) as a yellow oil. ¹H NMR (600 MHz, acetone-d₆) δ: 8.01 (d, J = 8.6 Hz, 2H), 7.30 (d, J = 2.0 Hz, 2H), 7.26 (d, J = 8.5 Hz, 2H), 7.18 (d, J = 8.4 Hz, 2H), 7.10 (dd, J = 8.5, 2.0 Hz, 2H), 6.59 (d, J = 2.2 Hz, 2H), 6.54 (dd, J = 8.5, 2.3 Hz, 2H), 6.33 (d, J = 8.5 Hz, 2H), 4.02-3.96 (m, 8H), 1.81-1.67 (m, 8H), 1.52-1.42 (m, 8H), 1.40-1.27 (m, 16H), 0.90 (t, J = 7.1 Hz, 6H), 0.87 (t, J = 6.9 Hz, 6H); ¹³C NMR (150 MHz, acetone-d₆) δ: 160.9 (2C), 157.8 (2C), 142.7 (2C), 142.5, 140.9 (2C), 134.5 (2C), 132.9 (2C), 131.2 (2C), 128.7 (2C), 128.5 (2C), 122.5 (2C), 121.4 (2C), 117.4 (2C), 106.7 (2C), 101.0 (2C), 93.2, 69.0 (2C), 68.6 (2C), 32.4 (4C), 30.04 (2C), 30.00 (2C), 26.8 (2C), 26.5 (2C), 23.4 (2C), 23.3 (2C), 14.4 (2C), 14.3 (2C); IR (CH₂Cl₂, cm⁻¹): 2953, 2929, 2868, 2858, 1608, 1455, 1388, 1298, 1181, 1135, 1053, 1010, 833, 816, 602, 532; HRMS (ASAP+, m/z): found 953.3906, calcd. for C₅₄H₆₈NO₄SI, [M⁺]⁺ 953.3914.

3,7-bis(2,4-bis(hexyloxy)-5-iodophenyl)-10-(4-iodophenyl)-10H-phenothiazine (10-by)
The tri-iodinated by-product 10-by was isolated in a synthesis as described for compound 10, but starting with 9 (897 mg, 0.996 mmol) and more ICl (485 mg, 2.99 mmol). Two purifications using silica-gel column chromatography (n-pentane/CH₂Cl₂, 1:2, Rf = 0.35) gave 10-by (193 mg, 0.160 mmol, 16%) as a yellow solid, mp. 145 °C. ¹H NMR (600 MHz, CD₂Cl₂) δ: 7.95 (d, J = 8.5 Hz, 2H), 7.60 (s, 2H), 7.23-7.16 (m, 4H), 7.00 (br.d, J = 5.2 Hz, 2H), 6.47 (s, 2H), 6.25 (br.d, J = 5.8 Hz, 2H), 4.03 (t, J = 6.5 Hz, 4H), 3.95 (t, J = 6.4 Hz, 4H), 1.87-1.79 (m, 4H), 1.76-1.68 (m, 4H), 1.58-1.50 (m, 4H), 1.46-1.28 (m, 20H), 0.92 (t, J = 7.2 Hz, 6H), 0.88 (t, J = 7.0 Hz, 6H); ¹³C NMR (150 MHz, CD₂Cl₂) δ: 158.3 (2C), 157.8 (2C), 140.5 (2C), 139.59 (2C), 139.57, 132.6 (2C), 128.1 (2C), 127.8 (2C), 124.3 (2C), 116.4 (2C), 115.8 (2C), 98.7 (2C), 93.3, 75.3 (2C), 70.0 (2C), 69.2 (2C), 31.92 (2C), 31.90 (2C), 29.51 (2C), 29.50 (2C), 26.23 (2C), 26.13 (2C), 14.25 (2C), 14.22 (2C); IR (CH₂Cl₂, cm⁻¹): 2950, 2925, 2867, 2856, 1590, 1460, 1359, 1302, 1244, 1187, 1040, 1009, 814, 538; HRMS (ASAP+, m/z): found 1205.1830 calc for C₅₄H₆₆I₃NO₄S, [M⁺]* 1205.1847.

5-(4-(3,7-bis(2,4-bis(hexyloxy)phenyl)-10H-phenothiazin-10-yl)phenyl)furan-2-carbaldehyde (11)

(5-Formylfuran-2-yl)boronic acid (31.0 mg, 0.221 mmol, 1.6 equiv), K₃PO₄ (59.0 mg, 0.278 mmol), and XPhos Pd G3 (2.30 mg, 2.73 μmol) were mixed in a Schlenk tube. Then compound 10 (132 mg, 0.138 mmol) was dissolved in degassed THF (2.5 mL) and added to the mixture, followed by degassed H₂O (5 mL). The reaction mixture was stirred at 40 °C for 23 h before being cooled down to rt, followed by addition of H₂O (20 mL). The mixture was then extracted using CH₂Cl₂ (4 × 20 mL), and the organic phases washed with H₂O (40 mL). After drying over Na₂SO₄, and concentration in vacuo, the material was purified by silica-gel column chromatography (n-pentane/acetone, 1:8, Rf = 0.15) to yield 11 (55.0 mg, 0.0596 mmol, 43%) as a yellow oil. ¹H NMR (600 MHz, acetone-d₆) δ: 9.70 (s, 1H), 8.13-8.11 (m, 2H), 7.56 (d, J = 3.7 Hz, 1H), 7.56-7.53 (m, 2H), 7.37 (d, J = 2.1 Hz, 2H), 7.24 (d, J = 3.8 Hz, 1H), 7.20 (d, J = 8.4 Hz, 2H), 7.16 (dd, J = 8.5, 2.1 Hz, 2H), 6.61 (d, J = 2.2 Hz, 2H), 6.57-6.52 (m, 4H), 4.03-3.98 (m, 8H), 1.80-1.68 (m, 8H),
1.57-1.43 (m, 8H), 1.38-1.27 (m, 16H), 0.90 (t, \(J = 7.1\) Hz, 6H), 0.86 (t, \(J = 7.0\) Hz, 6H); \(^{13}\)C NMR (150 MHz, acetone-\(d_6\)) \(\delta:\) 178.0, 160.9 (2C), 158.9, 157.9 (2C), 153.5, 144.1, 142.5 (2C), 134.9 (2C), 131.3 (2C), 129.5 (2C), 128.76 (2C), 128.71, 128.60 (2C), 128.23 (2C), 124.8, 122.94 (2C), 122.45 (2C), 118.6 (2C), 109.3, 106.7 (2C), 101.0 (2C), 69.0 (2C), 68.6 (2C), 32.4 (4C), 30.0 (4C)*, 26.8 (2C), 26.5 (2C), 23.35 (2C), 23.30 (2C), 14.40 (2C), 14.32 (2C); IR (CH\(_2\)Cl\(_2\), cm\(^{-1}\)):

2954, 2930, 2867, 2856, 1679, 1608, 1467, 1158, 1137, 1121, 1077, 1016, 822, 625, 603, 512;
HRMS (ASAP+, m/z): found 921.4983, calcd. for C\(_{59}\)H\(_{71}\)NO\(_6\)S, [M\(^+\)]\(^+\) 921.5002. *Signal found using \(^1\)H-\(^{13}\)C HSQC NMR due to overlap with solvent residual signal.

\((E)\)-3-(5-(4-(3,7-bis(2,4-bis(hexyloxy)phenyl)-10\(^{10}\)H-phenothiazin-10-yl)phenyl)furan-2-yl)-2-cyanoacrylic acid (10\(^{10}\)H-PTZ-Fu)

10\(^{10}\)H-PTZ-Fu was prepared as described for TAA-Th starting with the aldehyde 11 (54.0 mg, 58.6 \(\mu\)mol) and reacting for 1.5 h. Purification by silica-gel column chromatography (0-10% MeOH in CH\(_2\)Cl\(_2\)) gave 10\(^{10}\)H-PTZ-Fu (49.5 mg, 50.0 \(\mu\)mol, 85%) as a red solid, mp. 173-178 °C. \(^1\)H NMR (600 MHz, CDCl\(_3\)) \(\delta:\) 11.11 (s, 1H), 8.03 (s, 1H), 7.95 (br.d, \(J = 6.3\) Hz, 2H), 7.46-7.35 (m, 5H), 7.23-7.15 (m, 4H), 6.90 (s, 1H), 6.68 (d, \(J = 8.1\) Hz, 2H), 6.53-6.49 (m, 4H), 4.00-3.90 (m, 8H), 1.83-1.68 (m, 8H), 1.52-1.23 (m, 24H), 0.92 (t, \(J = 7.0\) Hz, 6H), 0.86 (t, \(J = 6.7\) Hz, 6H); \(^{13}\)C NMR (150 MHz, CDCl\(_3\)) \(\delta:\) 168.3, 160.7, 159.9 (2C), 157.1 (2C), 147.9, 144.9, 141.2 (2C), 140.2, 139.1, 134.5 (2C), 130.8 (2C), 128.6 (2C), 128.1 (2C), 127.6 (2C), 126.7, 125.8 (2C), 125.5, 125.2 (2C), 122.2 (2C), 119.6 (2C), 115.9, 109.3, 105.4 (2C), 100.5 (2C), 68.5 (2C), 68.3 (2C), 31.74 (2C), 31.64 (2C), 29.4 (2C), 29.2 (2C), 26.0 (2C), 25.9 (2C), 22.8 (4C), 14.2 (4C); IR (CH\(_2\)Cl\(_2\), cm\(^{-1}\)): 2954, 2926, 2855, 1609, 1579, 1467, 1390, 1297, 1260, 1248, 1182, 1135, 1030, 797; HRMS (ASAP+, m/z): found 989.5113, calcd. for C\(_{62}\)H\(_{72}\)N\(_2\)O\(_7\)S, [M\(^+\)]\(^+\) 989.5138.
1-(3-(2,4-bis(hexyloxy)phenyl)-7-bromo-10H-phenothiazin-10-yl)ethan-1-one (12)

The compound 12 was prepared as described for compound 7 starting with the building block 5 (1.20 g, 3.01 mmol), except this time with a halved amount of 1-bromo-2,4-bis(hexyloxy)benzene (682 mg, 3.61 mmol) was used. The crude product was purified with column chromatography (n-pentane/EtOAc, 6:1, Rf = 0.26) to yield 12 as a colorless oil (800 mg, 1.34 mmol, 45%). \[^1\text{H} \text{NMR} \text{(600 MHz, DMSO-d}_6 \text{)} \delta: 7.80 \text{ (d, } J = 1.8 \text{ Hz, 1H)}, 7.65-7.54 \text{ (m, 4H), 7.46 (dd, } J = 2.0 \text{ Hz, 8.3 Hz, 1H), 7.26 (d, } J = 8.5 \text{ Hz, 1H), 6.63 (d, } J = 2.4 \text{ Hz, 1H), 6.59 (dd, } J = 2.0 \text{ Hz, 8.3 Hz, 1H)}, 4.03-3.94 \text{ (m, 4H), 2.16 (s, 3H), 1.71 (q, } J = 7.7 \text{ Hz, 2H), 1.65-1.58 \text{ (m, 2H), 1.46-1.39 (m, 2H), 1.36-1.28 (m, 6H), 1.25-1.17 (m, 4H), 0.88 (t, } J = 7.7 \text{ Hz, 3H), 0.79 (t, } J = 7.7 \text{ Hz, 3H); } ^{13}\text{C NMR (150 MHz, DMSO-d}_6 \text{)} \delta: 168.4, 159.9, 156.5, 138.0, 137.0, 136.5, 134.6, 130.9, 130.6, 130.0 (2C), 129.0, 128.2, 128.1, 126.7, 120.5, 119.1, 106.1, 100.1, 67.9, 67.6, 31.0, 30.9, 28.6, 28.5, 25.4, 25.2, 22.6, 22.07, 22.05, 13.9, 13.8; IR (CH$_2$Cl$_2$, cm$^{-1}$): 2927 (m), 2856 (m), 1684 (s), 1607 (s), 1480 (m), 1300 (m), 1269 (s), 1180 (m), 1012 (m); HRMS (ASAP+, m/z): found 596.1836, calcd. for C$_{32}$H$_{39}$NO$_3$SBr [M+H]$^+$ 596.1834.

1-(3-(2,4-bis(hexyloxy)phenyl)-7-(furan-2-yl)-10H-phenothiazin-10-yl)ethan-1-one (13)

Compound 12 (475 mg, 0.80 mmol), PdCl$_2$(dppf) (30.7 mg, 42 μmol), and K$_2$CO$_3$ (463 mg, 3.35 mmol) were mixed with 2-furanylboronic acid (141 mg, 1.26 mmol), before the mixture was evacuated and a nitrogen atmosphere established. Degassed H$_2$O (7 mL) and 1,4-dioxane (7 mL) were added under a nitrogen atmosphere. This mixture was stirred at 80 °C for 1.5 h. After the mixture was cooled down to rt, H$_2$O (75 mL) was added, and the aqueous phase extracted with ethyl acetate (3 × 50 mL). The combined organic phase was washed with H$_2$O (2 × 50 mL), dried over Na$_2$SO$_4$ before the solvents were removed in vacuo. The crude product was purified with
column chromatography (CH$_2$Cl$_2$, R$_f$ = 0.16) to yield 13 as a light-orange oil (298 mg, 0.51 mmol, 64%). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 7.85 (d, $J = 2.0$ Hz, 1H), 7.78 (d, $J = 2.0$ Hz, 1H), 7.74-7.65 (m, 2H), 7.65-7.59 (m, 2H), 7.45 (dd, $J = 2.0$ Hz, 8.3 Hz, 1H), 7.26 (d, $J = 8.6$ Hz, 1H), 7.06 (d, $J = 3.3$ Hz, 1H), 6.65-6.56 (m, 3H), 4.03-3.94 (m, 4H), 2.18 (s, 3H), 1.76-1.67 (m, 2H), 1.66-1.57 (m, 2H), 1.47-1.38 (m, 2H), 1.37-1.27 (m, 6H), 1.26-1.19 (m, 4H), 0.88 (t, $J = 6.5$ Hz, 3H), 0.78 (t, $J = 6.7$ Hz, 3H); $^{13}$C NMR (150 MHz, DMSO-$d_6$) $\delta$: 168.5, 159.8, 156.5, 151.6, 143.5, 137.5, 136.8, 136.6, 130.9 (2C), 128.9, 128.1, 127.7 (2C), 126.7, 122.3, 122.1, 120.6, 112.3, 107.1, 106.1, 100.1, 97.2, 67.9, 67.6, 30.99, 30.95, 28.7, 28.5, 25.4, 25.2, 25.1, 22.07, 22.05, 13.9, 13.8; IR (CH$_2$Cl$_2$, cm$^{-1}$): 2928 (m), 2857 (m), 1682 (s), 1607 (s), 1464 (s), 1372 (s), 1274 (s), 1180 (m) 1101 (m); HRMS (ASAP+, m/z): found 584.2830, calcd. for C$_{36}$H$_{42}$NO$_4$S [M+H]$^+$ 584.2835.

3-(2,4-bis(hexyloxy)phenyl)-7-(furan-2-yl)-10H-phenothiazine (14)

The compound 14 was prepared as described for compound 8 starting with the compound 13 (260 mg, 0.45 mmol). This produced 14 as a red resin (205 mg, 0.38 mmol, 85%). $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$: 8.76 (s, 1H), 7.65 (d, $J = 1.3$ Hz, 1H), 7.32 (dd, $J = 2.1$ Hz, 8.5 Hz, 1H), 7.23 (d, $J = 2.1$ Hz, 1H), 7.14 (d, $J = 8.5$ Hz, 1H), 7.07 (dd, $J = 2.0$ Hz, 8.2 Hz, 1H), 7.04 (d, $J = 2.0$ Hz, 1H), 6.74 (dd, $J = 0.8$ Hz, 3.4 Hz, 1H), 6.71 (d, $J = 8.4$ Hz, 1H), 6.68 (d, $J = 8.2$ Hz, 1H), 6.57 (d, $J = 2.4$ Hz, 1H), 6.55-6.51 (m, 2H), 4.00-3.91 (m, 4H), 1.70 (q, $J = 8.0$ Hz, 2H), 1.64 (q, $J = 8.5$ Hz, 2H), 1.46-1.35 (m, 4H), 1.35-1.21 (m, 8H), 0.91-0.83 (m, 6H); $^{13}$C NMR (150 MHz, DMSO-$d_6$) $\delta$: 159.1, 156.3, 152.5, 142.0, 141.1, 139.6, 131.8, 130.0, 128.2, 126.7, 124.3, 122.9, 121.4, 121.2, 116.9, 115.2, 114.5, 114.0, 111.9, 105.8, 104.0, 100.1, 67.7, 67.5, 31.00, 30.98, 28.7, 28.6, 25.4, 25.2, 22.12, 22.07, 13.91 (2C); IR (CH$_2$Cl$_2$, cm$^{-1}$): 3399 (w), 2954 (m), 2927 (m), 2857 (m), 1607 (m), 1488 (s), 1296 (m), 1271 (m), 1177 (m), 1010(m); HRMS (ASAP+, m/z): found 541.2644, calcd. for C$_{34}$H$_{39}$NO$_3$S [M+H]$^+$ 541.2651.
4'-bromo-2,4-bis(hexyloxy)-1,1'-biphenyl (16)

Compound 16 was prepared following a modified procedure reported by Seo et al.[1] 1-Bromo-4-iodobenzene 15 (200 mg, 0.71 mmol), Pd(PPh$_3$)$_4$ (40.9 mg, 35 μmol), and K$_2$CO$_3$ (391 mg, 2.83 mmol) were mixed with crude 2-(2,4-bis(hexyloxy)phenyl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane 6 (343 mg, 0.85 mmol), before the mixture was evacuated and a nitrogen atmosphere established. Degassed H$_2$O (7 mL) and 1,4-dioxane (7 mL) were added under a nitrogen atmosphere. This mixture was stirred at 80 °C for 1 h. After the mixture was cooled down to rt, H$_2$O (75 mL) was added and the aqueous phase extracted with ethyl acetate (3 × 50 mL). The combined organic phase was washed with H$_2$O (50 mL), dried over Na$_2$SO$_4$ before the solvents were removed in vacuo. The crude product was purified with column chromatography (n-pentane/CH$_2$Cl$_2$, 5:1, R$_f$ = 0.16) to yield 16 as a yellow oil (189 mg, 0.44 mmol, 62%). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 7.53 (d, $J$ = 9.0 Hz, 2H), 7.39 (d, $J$ = 9.0 Hz, 2H), 7.19, (d, $J$ = 8.0 Hz, 1H), 6.62 (d, $J$ = 2.5 Hz, 1H), 6.57 (dd, $J$ = 2.5 Hz, 8.0 Hz, 1H), 4.02-3.92 (m, 4H), 1.71 (q, $J$ = 7.7 Hz, 2H), 1.62 (q, $J$ = 7.8 Hz, 2H), 1.47-1.37 (m, 2H), 1.37-1.27 (m, 6H) 1.27-1.18 (m, 4H), 0.88 (t, $J$ = 7.8 Hz, 3H), 0.83 (t, $J$ = 7.7 Hz, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$: 159.7, 156.4, 137.3, 131.1 (2C), 130.68, 130.66 (2C), 121.0, 119.4, 106.0, 100.1, 67.9, 67.5, 31.0, 30.8, 28.7, 28.5, 25.20, 25.16, 22.1, 22.0, 13.9, 13.8.

10-(2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)-3-(2,4-bis(hexyloxy)phenyl)-7-(furan-2-yl)-10H-phenothiazine (17)

The compound 17 was prepared as described for compound 9 starting with the compound 14 (140 mg, 0.26 mmol) and compound 16 (135 mg, 0.31 mmol). The crude product was purified with column chromatography (n-pentane/CH$_2$Cl$_2$, 2:1, R$_f$ = 0.68) to yield 17 as an orange wax (154 mg, 0.17 mmol, 65%). $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$: 7.77 (d, $J$ = 8.6 Hz, 2H), 7.68 (d, $J$ = 1.7 Hz,
1H), 7.44 (d, J = 8.6 Hz, 2H), 7.41 (d, J = 2.1 Hz, 1H), 7.36 (d, J = 8.6 Hz, 1H), 7.26 (dd, J = 2.2 Hz, 8.7 Hz, 1H), 7.22 (d, J = 2.1 Hz, 1H), 7.15 (d, J = 8.5 Hz, 1H), 7.03 (dd, J = 2.1 Hz, 8.6 Hz, 1H), 6.81 (d, J = 3.3 Hz, 1H), 6.68 (d, J = 2.3 Hz, 1H), 6.64 (dd, 2.3 Hz, 8.5 Hz, 1H), 6.59 (d, J = 2.2 Hz, 1H), 6.56-6.53 (m, 2H), 6.25 (d, J = 8.7 Hz, 1H), 6.21 (d, J = 8.5 Hz, 1H), 4.06-3.99 (m, 4H), 3.99-3.91 (m, 4H), 1.78-1.60 (m, 8H), 1.48-1.19 (m, 24H), 0.93-0.85 (m, 6H), 0.85-0.76 (m, 6H); 13C NMR (150 MHz, DMSO-d6) δ: 159.8, 159.3, 156.6, 156.4, 152.0, 142.7, 142.4, 141.5, 138.4, 138.0, 132.7, 131.6 (2C), 130.9, 130.1 (2C), 129.7, 129.1, 127.7, 127.0, 125.1, 122.3, 121.3, 120.8, 119.8, 117.9, 115.9, 115.5, 112.0, 106.1, 105.9, 104.8, 100.2, 100.1, 67.9, 67.8, 67.6, 67.5, 31.01, 30.99 (2C), 30.8, 28.69, 28.65, 28.6, 28.5, 25.4, 25.22 (2C), 25.19, 22.09 (2C), 22.07, 22.0, 13.92, 13.90, 13.85, 13.8; IR (CH2Cl2, cm⁻¹): 2926 (m), 2857 (m), 1607 (m), 1492 (s), 1296 (s), 1274 (s), 1178 (s), 1011 (m); HRMS (ASAP+, m/z): found 893.5048, calcd. for C58H71NO5S [M*]+ 893.5053.

5-(10-(2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)-7-(2,4-bis(hexyloxy)phenyl)-10H-phenothiazin-3-yl)furan-2-carbaldehyde (18)

[Chemical structure image]

Compound 17 (130 mg, 0.15 mmol) was dissolved in anhydrous THF (4 mL) and cooled to -78 °C, a solution of n-BuLi in hexanes (1.4 M, 160 µL, 0.22 mmol) was added to this over 5 minutes. The reaction mixture was then stirred for 15 minutes before DMF (40 µL, 0.51 mmol) was added. After 15 more minutes of stirring, the reaction vessel was removed from the cooling mixture and left to reach r.t over 45 minutes. The reaction was quenched by addition of aqueous HCl (2 M, 4 mL), the aqueous phase was extracted with ethyl acetate (3 x 15 mL). The combined organic phase was washed with H2O (15 mL), dried over Na2SO4 before the solvents were removed in vacuo. The crude product was purified with column chromatography (CH2Cl2, Rf = 0.58) to yield 18 as a red wax (46 mg, 50 µmol, 34%). 1H NMR (600 MHz, CD2Cl2) δ: 9.55 (s, 1H), 7.81 (d, J = 8.8 Hz, 2H), 7.46 (d, J = 2.0 Hz, 1H), 7.41 (d, J = 8.8 Hz, 2H), 7.35, (d, J = 9.0 Hz, 1H), 7.30-7.26 (m, 2H), 7.22 (d, J = 2.0 Hz, 1H), 7.14 (d, J = 8.1 Hz, 1H), 7.02 (dd, J = 1.9 Hz, 8.7 Hz, 1H), 6.69 (d,
$J = 4.1 \text{ Hz, } 1\text{H}), 6.62-6.59 (m, 2\text{H}), 6.52-6.48 (m, 2\text{H}), 6.32 (d, J = 9.0 \text{ Hz, } 1\text{H}), 6.27 (d, J = 9.0 \text{ Hz, } 1\text{H}), 4.02 \text{ (app. t, } J = 6.2 \text{ Hz, } 4\text{H}), 3.96 \text{ (t, } J = 6.7 \text{ Hz, } 2\text{H}), 3.94 \text{ (t, } J = 6.7 \text{ Hz, } 2\text{H}), 4.02 \text{ (app. t, } J = 6.2 \text{ Hz, } 4\text{H}), 3.96 \text{ (t, } J = 6.7 \text{ Hz, } 2\text{H}), 3.94 \text{ (t, } J = 6.7 \text{ Hz, } 2\text{H}), 1.84-1.69 (m, 8\text{H}), 1.52-1.41 (m, 8\text{H}), 1.40-1.28 (m, 16\text{H}), 0.96-0.84 (m, 12\text{H}); ^{13}\text{C NMR (150 MHz, CD}_2\text{Cl}_2) \delta: 177.0, 160.8, 160.3, 159.2, 157.5, 157.3, 152.2, 145.9, 142.1, 139.6, 138.7, 133.9, 132.3 (3\text{C}), 131.5 (2\text{C}), 130.7, 130.5, 128.3, 127.8, 124.5, 123.5, 123.5, 122.4, 122.1, 121.0, 118.7, 116.2 (2\text{C}), 106.9, 106.0, 105.8, 100.64, 100.55, 68.9, 68.8, 68.64, 68.57, 32.04, 32.02, 31.99, 31.9, 29.71, 29.69, 29.6, 29.5, 26.3, 26.21, 26.15, 26.1, 23.1 (2\text{C}), 23.04, 23.02, 14.3, 14.24, 14.22 (2\text{C}); \text{IR (CH}_2\text{Cl}_2, \text{cm}^{-1}): 2953 (m), 2929 (m), 2858 (m), 1675 (m), 1609 (m), 1460 (s), 1298 (m), 1265 (m), 1182 (m); \text{HRMS (ASAP+, m/z): found 921.4994, calcd. for C}_{59}\text{H}_{71}\text{NO}_6\text{S [M]*} + 921.5002.$

$(E)-3$-(5-(10-(2',4'-bis(hexyloxy)-[1,1'-biphenyl]-4-yl)-7-(2,4-bis(hexyloxy)phenyl)-10H-phenotheniazin-3-yl)furan-2-yl)-2-cyanoacrylic acid (3,7-PTZ-Fu)

![Chemical structure of 3,7-PTZ-Fu](image)

3,7-PTZ-Fu was prepared as described for TAA-Th starting with the aldehyde 18 (45.0 mg, 48.8 \mu\text{mol}) and reacting for 1.5 h. Purification by silica-gel column chromatography (0-10% MeOH in CH2Cl2) gave 3,7-PTZ-Fu as a red solid (31.2 mg, 31.5 \mu\text{mol, } 65%), mp. 74.1-75.8 °C. $^1\text{H NMR (600 MHz, acetone-}d_6) \delta: 8.01 (s, 1\text{H}), 7.86 (d, J = 8.3 \text{ Hz, } 2\text{H}), 7.64 (d, J = 2.1 \text{ Hz, } 1\text{H}), 7.51 (dd, J = 2.1 \text{ Hz, } 8.9 \text{ Hz, } 1\text{H}), 7.49 (d, J = 4.2 \text{ Hz, } 1\text{H}), 7.46 (d, J = 8.3 \text{ Hz, } 2\text{H}), 7.38 (d, J = 8.5 \text{ Hz, } 1\text{H}), 7.26 (d, J = 2.1 \text{ Hz, } 1\text{H}), 7.18 (d, J = 8.5 \text{ Hz, } 1\text{H}), 7.10 (d, J = 3.6 \text{ Hz, } 1\text{H}), 7.05 (dd, J = 2.1 \text{ Hz, } 8.9 \text{ Hz, } 1\text{H}), 6.69 (d, J = 2.5 \text{ Hz, } 1\text{H}), 6.64 (dd, J = 2.5 \text{ Hz, } 8.4 \text{ Hz, } 1\text{H}), 6.60 (d, J = 2.5 \text{ Hz, } 1\text{H}), 6.54 (dd, J = 2.5 \text{ Hz, } 8.2 \text{ Hz, } 1\text{H}), 6.33 (d, J = 8.7 \text{ Hz, } 1\text{H}), 6.27 (d, J = 8.7 \text{ Hz, } 1\text{H}), 4.09-4.04 (m, 4\text{H}), 4.02-3.97 (m, 4\text{H}), 1.84-1.68 (m, 8\text{H}), 1.54-1.43 (m, 8\text{H}), 1.41-1.24 (m, 16\text{H}), 0.95-0.81 (m, 12\text{H}); ^{13}\text{C NMR (150 MHz, Acetone-}d_6) \delta: 164.3, 161.4, 160.9, 159.9, 158.1, 157.9, 148.5, 146.3, 142.3, 140.4, 139.1, 138.5, 134.7, 132.9 (2\text{C}), 132.0, 131.2, 130.9 (2\text{C}), 128.8, 128.2, 127.0, 125.3, 124.02 (2\text{C}), 122.8, 122.3, 121.4, 118.9, 117.0, 116.7, 116.7, 109.3, 106.9, 106.7, 101.1, 101.0, 97.1, 69.1, 69.0, 68.7, 68.6, 32.38, 32.36 (2\text{C}), 32.2, 29.9 (4\text{C}*), 26.7, 26.6, 26.53,
26.51, 23.4, 23.33, 23.30 (2C), 14.43, 14.37, 14.34, 14.32; IR (CH$_2$Cl$_2$, cm$^{-1}$): 2953 (m), 2937 (m), 2869 (m), 2337 (w), 1686 (m), 1608 (m), 1493 (s), 1299 (m), 1263 (m), 1182 (m); HRMS (ASAP+, m/z): found 988.5042, calcd. for C$_62$H$_72$N$_2$O$_7$S [M$^+$] 988.5060. *Signal found using $^1$H-$^{13}$C HSQC NMR due to overlap with solvent residual signal.

**2,2′-((2-nitro-1,3-phenylene)bis(oxy))bis(bromobenzene) (21)**

![Image of compound 21](image)

Sodium hydride (103 mg, 4.30 mmol) and 2-bromophenol 19 (0.3 mL, 2.60 mmol) was dissolved in DMSO (2 mL) before being heated to 50 °C. The reaction mixture was stirred for 15 minutes before 1,3-dichloro-2-nitrobenzene (100 mg, 0.52 mmol) was added, then the reaction was left stirring for 24 hours. Upon cooling to room temperature H$_2$O (10 mL) was added, and the aqueous phase was extracted using diethyl ether (3 x 25 mL). The combined organic phases were washed with water (3 x 25 mL), before being dried with brine and over Na$_2$SO$_4$. The crude product was concentrated in vacuo and purified by silica gel column chromatography ($n$-pentane/CH$_2$Cl$_2$, 10:1, R$_f$ = 0.08) to give compound 21 as a yellow solid (136 mg, 0.29 mmol, 56%), mp. 128.4-129.6 °C. $^1$H NMR (600 MHz, DMSO-$d_6$) $\delta$: 7.81 (dd, $J = 1.7$ Hz, 8.1 Hz, 2H), 7.51 (td, $J = 1.7$ Hz, 8.2 Hz, 2H), 7.44 (t, $J = 8.7$ Hz, 1H), 7.35 (dd, $J = 1.4$ Hz, 8.2 Hz, 2H), 7.28 (td, $J = 1.4$ Hz, 7.9 Hz, 2H), 6.60 (d, $J = 8.7$ Hz, 2H); $^{13}$C NMR (150 MHz, DMSO-$d_6$) $\delta$: 150.7, 148.9, 134.1, 132.8, 132.6, 129.9, 127.7, 122.2, 114.5, 111.3; IR (CH$_2$Cl$_2$, cm$^{-1}$): 2895 (w), 1608 (m), 1464 (s), 1307 (m), 1244 (s), 1121 (s); HRMS (ASAP+, m/z): found 463.9138, calcd. for C$_{18}$H$_{12}$NO$_4$Br$_2$ [M+H]$^+$ 463.9133.

**2,6-bis(2-bromophenoxy)aniline (22)**

![Image of compound 22](image)

Compound 21 (100 mg, 0.22 mmol) was mixed with NH$_4$Cl (104 g, 1.94 mmol) and iron powder (36 mg, 0.65 mmol), before EtOH (2 mL) and water (0.5 mL) were added under nitrogen atmosphere. The reaction mixture was stirred at 78 °C for 4 h, cooled to rt, filtered through celite using ethyl acetate as eluent, and concentrated. This provided 22 as a colorless wax that was carried forward without further purification.
Benzo[5,6][1,4]oxazino[2,3,4-kl]phenoxazine (23)

![Chemical structure of compound 23](23)

Compound 22 (94 mg, 0.22 mmol), Pd(OAc)$_2$ (2.4 mg, 11 µmol), XPhos (10 mg, 22 µmol), and sodium tert-butoxide (42 mg, 0.43 mmol) was added to a Schlenk tube, and nitrogen atmosphere was established. Dry 1,4-dioxane (2 mL) was added under nitrogen and the reaction mixture was heated to 110 °C, the reaction was stirred for 18 hours. Upon cooling down to room temperature, an aqueous solution of NH$_4$Cl was added (saturated, 5 mL). The aqueous phase was extracted with ethyl acetate (3 x 25 mL), and the combined organic phase was dried with brine and over Na$_2$SO$_4$. The solvents were removed in vacuo, and the crude product was purified by silica gel column chromatography (n-pentane/CH$_2$Cl$_2$, 1:1, $R_f = 0.66$) to give compound 23 as a white solid (26 mg, 0.11 mmol, 50% over two steps from 21), mp. 163.7-164.8 °C (lit. 165 °C).[2] $^1$H NMR (600 MHz, DMSO-$_d$6) $\delta$: 7.37 (d, $J = 8.2$ Hz, 2H), 7.08-6.95 (m, 6H), 6.87 (t, $J = 8.3$ Hz, 1H), 6.64 (d, $J = 8.3$ Hz, 2H); $^{13}$C NMR (150 MHz, DMSO-$_d$6) $\delta$: 146.0, 144.6, 128.3, 124.3, 124.2, 123.9, 120.2, 117.3, 114.8, 111.2; IR (CH$_2$Cl$_2$, cm$^{-1}$): 3425 (w), 2922 (w), 2850 (w), 1618 (m), 1468 (s), 1306 (m), 1281 (s), 1112 (m), 738 (s); HRMS (ASAP+, m/z): found 274.0867, calcd. for C$_{18}$H$_{12}$NO$_2$ [M+H]$^+$ 274.0868. $^1$H NMR spectrum is in accordance with previously reported data.[2]

7-bromobenzo[5,6][1,4]oxazino[2,3,4-kl]phenoxazine (24)

![Chemical structure of compound 24](24)

The synthesis of 7-bromobenzo[5,6][1,4]oxazino[2,3,4-kl]phenoxazine, 24, was attempted through the following two procedures [3,4] with slight modifications. In our hands the resulting product mixture proved impossible to purify by column chromatography or recrystallization.

NBS-procedure: A solution of compound 23 (20 mg, 0.073 mmol) in chloroform (4 mL) is mixed with N-bromosuccinimide (11.7 g, 0.066 mmol) at 0 °C under exclusion of light, and the mixture was stirred at this temperature for 2 h. The reaction was quenched by addition of sodium sulfite solution (5w%, 10 mL), and the mixture was stirred at room temperature for a further 30 min. After phase separation, the organic phase was washed with water (20 mL), and the aqueous phase was extracted with dichloromethane (3 x 20 mL).
The combined organic phases were dried over sodium sulfate and concentrated in vacuum. The residue was dissolved in ethyl acetate and filtered over silica gel. The crude product was subsequently recrystallized from hexane.

**Br$_2$-Procedure:**

A stirred solution of compound 23 (50 mg, 0.18 mmol) in acetic acid (2 mL) was flushed with nitrogen then a solution of bromine (1 M, 0.20 mL, 1 mmol) in acetic acid was added dropwise, and stirring was continued overnight. The reaction was quenched by addition of sodium sulfite (5w%, 20 mL) solution, and the mixture was stirred at room temperature for a further 30 min. After phase separation, the organic phase was washed with water (20 mL), and the aqueous phase was extracted with dichloromethane (3 x 20 mL). The combined organic phases were dried over sodium sulfate and concentrated in vacuum. The crude product was subjected to silica gel column chromatography ($n$-pentane/CH$_2$Cl$_2$, 1:3, $R_f = 0.30$).

4-bromo-2',4'-bis(hexyloxy)-[1,1'-biphenyl]-3-ol (26)

![Chemical Structure of 4-bromo-2',4'-bis(hexyloxy)-[1,1'-biphenyl]-3-ol (26)](image)

The compound 26 was prepared as described for compound 16 starting with the building block 6 (1.40 g, 3.45 mmol), except this time with it was coupled with 2-bromo-5-iodophenol 25 (860 mg, 2.88 mmol) in a 3 hour reaction. The crude product was purified with column chromatography ($n$-pentane/EtOAc, 10:1, $R_f = 0.37$) to yield 26 as a colorless oil (663 mg, 1.58 mmol, 51%). $^1$H NMR (400 MHz, DMSO-$d_6$) $\delta$: 10.09 (s, 1H), 7.41 (d, $J = 8.9$ Hz, 1H), 7.14 (d, $J = 8.2$ Hz, 1H), 7.06 (d, $J = 2.0$ Hz, 1H), 6.80 (dd, $J = 2.0$ Hz, 8.9 Hz, 1H), 6.60 (d, $J = 2.5$ Hz, 1H), 6.56 (dd, $J = 2.5$ Hz, 8.2 Hz, 1H), 3.98 (t, $J = 6.6$ Hz, 2H), 3.94 (t, $J = 6.1$ Hz, 2H), 1.71 (q, $J = 6.6$ Hz, 2H), 1.63 (q, $J = 6.1$ Hz, 2H), 1.45-1.38 (m, 2H), 1.36-1.28 (m, 6H), 1.28-1.20 (m, 4H), 0.88 (t, $J = 6.6$ Hz, 3H), 0.83 (t, $J = 6.1$ Hz, 3H); $^{13}$C NMR (100 MHz, DMSO-$d_6$) $\delta$:159.6, 156.4, 153.5, 138.7, 131.9, 130.5, 121.5, 121.4, 117.1, 107.1, 105.9, 100.2, 68.0, 67.5, 31.0, 30.9, 28.7, 28.5, 25.2, 25.1, 22.1, 22.0, 13.9, 13.8; IR (CH$_2$Cl$_2$, cm$^{-1}$): 2928, 2857, 1682, 1608, 1499, 1301, 1277, 1181; HRMS (ASAP+, m/z): found 449.1657, calcd. for C$_{24}$H$_{34}$BrO$_3$ [M+H]$^+$ 449.1691.

**2-(3,5-difluoro-4-nitrophenyl)thiophene (28)**

S23
The compound 28 was prepared as described for compound 2 starting with the building block 5-bromo-1,3-difluoro-2-nitrobenzene 27 (250 mg, 1.05 mmol) and thiophen-2-ylboronic acid (202 mg, 1.58 mmol) The crude product was purified with column chromatography (n-pentane/toluene, 3:1, Rf = 0.28) to yield 28 as a green solid (188 mg, 0.78 mmol, 74%), mp. 96.3-97.1 °C. ¹H NMR (600 MHz, DMSO-d₆) δ: 7.91 (d, J = 4.0 Hz, 1H), 7.86-7.80 (m, 3H), 7.25 (dd, J = 4.0 Hz, 5.0 Hz, 1H); ¹³C NMR (150 MHz, DMSO-d₆) δ: 154.8 (dd, J = 2.2 Hz, 258.7 Hz), 140.1 (t, J = 11.0 Hz), 138.9 (t, J = 2.6 Hz), 130.3 (s), 129.2 (s), 128.5 (s), 126.6 (t, J = 14.2 Hz), 109.7 (dd, J = 3.3 Hz, 21.9 Hz); IR (CH₂Cl₂, cm⁻¹): 3110 (w), 1610 (m), 1478 (m), 1369 (m), 1233 (m), 1083 (m); HRMS (ASAP+, m/z): found 241.0013, calcd. for C₁₀H₅NO₂F₂S [M+H]+ 241.0009.

2-(3,5-bis((4-bromo-2',4'-bis(hexyloxy)-[1,1'-biphenyl]-3-yl)oxy)-4-nitrophenyl)thiophene (29)

Compound 26 (407 mg, 0.91 mmol) and compound 28 (100 mg, 0.41 mmol) were dissolved in DMF (3 mL). K₂CO₃ (378 mg, 2.74 mmol) was added and the mixture was stirred at 100 °C for 4 h. After addition of 1 M HCl aq. (5 mL), the products were extracted with CH₂Cl₂ (3 × 25 mL). The organic phase was dried over Na₂SO₄, filtered off, and concentrated under reduced pressure. The obtained crude product was purified by silica gel column chromatography (CH₂Cl₂, Rf = 0.59) to give compound 29 as a yellow wax (269 mg, 0.24 mmol, 59%). ¹H NMR (400 MHz, DMSO-d₆) δ: 7.80 (d, J = 8.6 Hz, 2H), 7.61 (dd, J = 1.3 Hz, 5.0 Hz, 1H), 7.48 (d, J = 2.0 Hz, 2H), 7.46 (dd, J = 1.2 Hz, 3.8 Hz, 1H), 7.34 (dd, J = 2.3 Hz, 8.6 Hz, 2H), 7.30 (app. d, J = 9.4 Hz, 2H), 7.08 (dd, J = 3.8 Hz, 5.0 Hz, 1H), 6.91 (s, 2H), 6.61-6.57 (m, 4H), 3.99 (t, J = 6.6 Hz, 4H), 3.86 (t, J = 6.6 Hz, 4H), 1.70 (q, J = 7.7 Hz, 4H), 1.46-1.37 (m, 8H), 1.34-1.27 (m, 8H), 1.15-1.09 (m, 4H), 1.07-0.95 (m, 8H), 0.87 (t, J = 7.0 Hz, 6H), 0.67 (t, J = 7.7 Hz, 6H); ¹³C NMR (150 MHz, DMSO-
\(d_6\) \(\delta: 160.1 (2C), 156.4 (2C), 150.4 (2C), 149.5 (2C), 139.7 (3C), 138.0, 133.5 (2C), 132.3, 130.8 (2C), 129.0, 128.6 (2C), 127.6, 126.9, 121.7 (2C), 119.6 (2C), 111.4 (2C), 108.7 (2C), 106.2 (2C), 100.0 (2C), 67.9 (2C), 67.6 (2C), 31.0 (2C), 30.7 (2C), 28.6 (2C), 28.4 (2C), 25.2 (2C), 25.0 (2C), 22.1 (2C), 21.9 (2C), 13.9 (2C), 13.7 (2C); IR (\(\text{CH}_2\text{Cl}_2\), cm\(^{-1}\)): 2928 (m), 2857 (m), 1604 (m), 1509 (m), 1299 (m), 1244 (s), 1180 (s), 700 (m); HRMS (ASAP+, m/z): found 1097.3098, calcd. for \(C_{58}H_{69}NO_8SBr_2\) [M\(^+\)] 1097.3111.

2,6-bis((4-bromo-2',4'-bis(hexyloxy)-[1,1'-biphenyl]-3-yl)oxy)-4-(thiophen-2-yl)aniline (30)

A solution of 29 (250 mg, 0.23 mmol) in acetone (20 mL) was treated with saturated aqueous NH\(_4\)Cl (5 mL), followed by Zn\(^0\) (297 mg, 4.5 mmol). The reaction mixture was stirred at room temperature for 3 h before the reaction mixture was filtered through a plug of Celite (EtOAc). Removal of solvents in vacuo provided 30 as a colorless wax that was carried forward without further purification.

3,11-bis(2,4-bis(hexyloxy)phenyl)-7-(thiophen-2-yl)benzo[5,6][1,4]oxazino[2,3,4-\(k\l\)]phenoxazine (31)

The compound 31 was prepared as described for compound 23 starting with the crude 30 (243 mg, 0.23 mmol). The crude 31 was purified with column chromatography (\(n\)-pentane/CH\(_2\)Cl\(_2\), 10:1, \(R_f = 0.43\)) to yield 31 as a slight green oil (80 mg, 0.09 mmol, 39% over two steps from 29). \(^1\)H NMR (600 MHz, CD\(_2\)Cl\(_2\)) \(\delta: 7.38\) (d, \(J = 7.8\) Hz, 2H), 7.27-7.21 (m, 4H), 7.17-7.12 (m, 4H), 7.05 (dd, \(J = 3.6\) Hz, 5.0 Hz, 1H), 6.80 (s, 2H), 6.57-6.51 (m, 4H), 4.03-3.95 (m, 8H), 1.84-1.74 (m, 8H), 1.53-1.44 (m, 8H), 1.42-1.32 (m, 16H), 0.98-0.88 (m, 12H); \(^{13}\)C NMR (150 MHz, CD\(_2\)Cl\(_2\)) \(\delta: 160.4\) (2C), 157.4 (2C), 146.4 (2C), 145.8 (2C), 143.5, 134.5 (2C), 130.9 (2C), 130.7, 128.4, 127.3 (2C), 124.9 (2C), 124.8, 123.2, 122.2 (2C), 120.6, 118.7 (2C), 114.5 (2C), 108.8 (2C), 105.9 (2C), 100.6
Compound 31 (80 mg, 0.09 mmol) was dissolved in anhydrous THF (2 mL) and cooled to -78 °C, a solution of lithium diisopropylamide in THF (2.0 M, 66 µL, 0.13 mmol) was added to this over 5 minutes. The reaction mixture was then stirred for 15 minutes before DMF (20 µL, 0.26 mmol) was added. After 15 more minutes of stirring, the reaction vessel was removed from the cooling bath and left to reach r.t over 45 minutes. The reaction was quenched by addition of aqueous HCl (2 M, 3 mL), the aqueous phase was extracted with ethyl acetate (3 x 15 mL). The combined organic phase was washed with H$_2$O (15 mL), dried over Na$_2$SO$_4$ before the solvents were removed in vacuo. The crude product was purified with column chromatography (CH$_2$Cl$_2$, R$_f$ = 0.44) to yield 32 as a red wax (40 mg, 43 µmol, 48%). $^1$H NMR (600 MHz, CD$_2$Cl$_2$) δ: 9.83 (s, 1H), 7.69 (d, $J$ = 4.2 Hz, 1H), 7.37 (d, $J$ = 8.9 Hz, 2H), 7.30 (d, $J$ = 4.2 Hz, 1H), 7.22 (d, $J$ = 7.4 Hz, 2H), 7.17-7.12 (m, 4H), 6.84 (s, 2H), 6.56-6.51 (m, 4H), 4.01-3.95 (m, 8H), 1.83-1.73 (m, 8H), 1.52-1.44 (m, 8H), 1.41-1.30 (m, 16H), 0.96-0.87 (m, 12H); $^{13}$C NMR (150 MHz, CD$_2$Cl$_2$) δ: 182.9, 160.4 (2C), 157.4 (2C), 153.0, 146.3 (2C), 145.9 (2C), 142.3 (2C), 137.8, 134.9 (2C), 130.9 (2C), 129.1, 126.9, 125.0 (2C), 124.1, 122.7, 122.1 (2C), 118.7 (2C), 114.6 (2C), 109.5 (2C), 105.9 (2C), 100.6 (2C), 68.9 (2C), 68.6 (2C), 32.1 (2C), 32.0 (2C), 29.7 (2C), 29.6 (2C), 26.3 (2C), 26.2 (2C), 23.07 (2C), 23.06 (2C), 14.3 (2C), 14.2 (2C); IR (CH$_2$Cl$_2$, cm$^{-1}$): 2926 (m), 2857 (m), 1667 (s), 1608 (s), 1491 (s), 1489 (s), 1301 (s), 1277 (s), 1181 (s); HRMS (ASAP+, m/z): found 935.4779, calcd. for C$_{59}$H$_{69}$NO$_7$S $[M^+]$ 935.4795.

(E)-3-(5-(3,11-bis(2,4-bis(hexyloxy)phenyl)benzo[5,6][1,4]oxazino[2,3,4-kl]phenoxazin-7-yl)thiophen-2-yl)-2-cyanoacrylic acid (POZPOZ-Th)
POZPOZ-Th was prepared as described for TAA-Th starting with the aldehyde 32 (40.0 mg, 42.7 μmol) and reacting for 2.5 h. Purification by silica-gel column chromatography (0-10% MeOH in CH2Cl2) gave POZPOZ-Th as a dark purple solid (36.2 mg, 36.0 μmol, 84%); mp. 82.4-84.1 °C.  

$^1$H NMR (600 MHz, DMSO-$d_6$) δ: 8.35 (s, 1H), 7.86 (d, $J = 4.2$ Hz, 1H), 7.60 (d, $J = 4.2$ Hz, 1H), 7.23 (d, $J = 8.6$ Hz, 2H), 7.12 (d, $J = 8.4$ Hz, 2H), 7.07-7.00 (m, 4H), 6.89 (s, 2H), 6.55 (s, 2H), 6.47 (d, $J = 8.4$ Hz, 2H), 3.98-3.88 (m, 8H), 1.74-1.61 (m, 8H), 1.43-1.35 (m, 8H), 1.34-1.23 (m, 16H), 0.88 (t, $J = 6.9$ Hz, 6H), 0.83 (t, $J = 6.7$ Hz, 6H);  

$^{13}$C NMR (150 MHz, DMSO-$d_6$) δ: 163.6, 159.4 (2C), 156.4 (2C), 150.6, 145.6, 144.9 (2C), 144.7 (2C), 140.5, 134.3, 134.0 (2C), 130.2 (2C), 128.2, 125.5 (2C), 124.8, 124.3, 121.2 (2C), 120.6 (3C), 117.7 (2C), 116.7, 114.1 (2C), 108.6 (2C), 105.7 (2C), 100.0 (2C), 67.8 (2C), 67.5(2C), 31.04 (2C), 30.98 (2C), 28.7 (2C), 28.6 (2C), 25.4 (2C), 25.2 (2C), 22.1 (4C), 13.9 (2C), 13.8 (2C); IR (CH$_2$Cl$_2$, cm$^{-1}$): 3064 (m), 3041(m), 2928 (m), 2859 (m), 2220 (w), 1692 (m), 1609 (m), 1494 (s), 1300 (m), 1282 (m), 1182 (m); HRMS (ASAP+, m/z): found 1002.4837, calcd. for C$_{62}$H$_{70}$N$_2$O$_8$S [M$^+$] 1002.4853.

References

1. Seo, K. D.; Choi, I. T.; Kim, H. K., D–π–A organic dyes with various bulky amine-typed donor moieties for dye-sensitized solar cells employing the cobalt electrolyte. Org. Electron. 2015, 25, 1-5. DOI:10.1016/j.orgel.2015.06.011

2. Kuratsu, M.; Kozaki, M.; Okada, K., Synthesis, Structure, and Electron-Donating Ability of 2,2′:6′,2″-Dioxatriphenylamine and Its Sulfur Analogue. Chem. Lett. 2004, 33 (9), 1174-1175. DOI:10.1246/cl.2004.1174

3. Brocke, C.; Plumm, C.; Parham, H.A.; Fortte, R., Heteroaromatic compounds and their preparation and use in electronic devices. WO2011107186A2. 2011.

4. Parham, A.; Kroeber, J.; Joosten, D.; Ludemann, A.; Grossmann, T., Bridged triarylamine derivatives, their preparation, use in electronic devices, and the devices. WO2018095839A1. 2018.
**NMR**

Figure S5 $^1$H NMR (600 MHz, CDCl$_3$) of compound 2.

Figure S6 $^{13}$C NMR (150 MHz, CDCl$_3$) of compound 2.
Figure S7 $^1$H NMR (600 MHz, CDCl$_3$) of compound 3.

Figure S8 $^{13}$C NMR (150 MHz, CDCl$_3$) of compound 3.
Figure S9 $^1$H NMR (600 MHz, CDCl$_3$) of dye TAA-Th.

Figure S10 $^{13}$C NMR (150 MHz, CDCl$_3$) of dye TAA-Th.
Figure S11 $^1$H NMR (600 MHz, CDCl$_3$) of dye TAA-Fu.

Figure S12 $^{13}$C NMR (150 MHz, CDCl$_3$) of dye TAA-Fu.
Figure S13 $^1$H NMR (600 MHz, DMSO-$d_6$) of compound 5.

Figure S14 $^{13}$C NMR (150 MHz, DMSO-$d_6$) of compound 5.
Figure S15 $^1$H NMR (600 MHz, DMSO-$d_6$) of compound 7.

Figure S16 $^{13}$C NMR (150 MHz, DMSO-$d_6$) of compound 7.
Figure S17 $^1$H NMR (600 MHz, DMSO-$d_6$) of compound 8.

Figure S18 $^{13}$C NMR (150 MHz, DMSO-$d_6$) of compound 8.
Figure S19 $^1$H NMR (600 MHz, CD$_2$Cl$_2$) of compound 9.

Figure S20 $^{13}$C NMR (150 MHz, CD$_2$Cl$_2$) of compound 9.
Figure S21 $^1$H NMR (600 MHz, acetone-$d_6$) of compound 10.

Figure S22 $^{13}$C NMR (150 MHz, acetone-$d_6$) of compound 10.
**Figure S23** $^1$H NMR (600 MHz, CD$_2$Cl$_2$) of compound 10-by.

**Figure S24** $^{13}$C NMR (150 MHz, CD$_2$Cl$_2$) of compound 10-by.
Figure S25 $^1$H NMR (600 MHz, acetone-$d_6$) of compound 11.

Figure S26 $^{13}$C NMR (150 MHz, acetone-$d_6$) of compound 11.
Figure S27 $^1$H NMR (600 MHz, CDCl$_3$) of dye 10$H$-PTZ-Fu.

Figure S28 $^{13}$C NMR (150 MHz, CDCl$_3$) of dye 10$H$-PTZ-Fu.
Figure S29 $^1$H NMR (600 MHz, DMSO-$d_6$) of compound 12.

Figure S30 $^{13}$C NMR (150 MHz, DMSO-$d_6$) of compound 12.
Figure S31 $^1$H NMR (600 MHz, DMSO-$d_6$) of compound 13.

Figure S32 $^{13}$C NMR (150 MHz, DMSO-$d_6$) of compound 13.
Figure S33 $^1$H NMR (600 MHz, DMSO-$d_6$) of compound 14.

Figure S34 $^{13}$C NMR (150 MHz, DMSO-$d_6$) of compound 14.
Figure S35 $^1$H NMR (600 MHz, DMSO-$d_6$) of compound 16.

Figure S36 $^{13}$C NMR (150 MHz, DMSO-$d_6$) of compound 16.
Figure S37 $^1$H NMR (600 MHz, DMSO-$d_6$) of compound 17.

Figure S38 $^{13}$C NMR (150 MHz, DMSO-$d_6$) of compound 17.
Figure S39 $^{1}$H NMR (600 MHz, CD$_2$Cl$_2$) of compound 18.

Figure S40 $^{13}$C NMR (150 MHz, CD$_2$Cl$_2$) of compound 18.
Figure S41 $^1$H NMR (600 MHz, acetone-$d_6$) of dye 3,7-PTZ-Fu.

Figure S42 $^{13}$C NMR (150 MHz, acetone-$d_6$) of dye 3,7-PTZ-Fu.
Figure S43 $^1$H NMR (600 MHz, DMSO-$d_6$) of compound 21.

Figure S44 $^{13}$C NMR (150 MHz, DMSO-$d_6$) of compound 21.
Figure S45 $^1$H NMR (600 MHz, DMSO-$d_6$) of compound 23.

Figure S46 $^{13}$C NMR (150 MHz, DMSO-$d_6$) of compound 23.
Figure S47 $^1$H NMR (600 MHz, DMSO-$d_6$) of compound 26.

Figure S48 $^{13}$C NMR (150 MHz, DMSO-$d_6$) of compound 26.
Figure S49 $^1$H NMR (600 MHz, DMSO-$d_6$) of compound 28.

Figure S50 $^{13}$C NMR (150 MHz, DMSO-$d_6$) of compound 28.
**Figure S51** $^1$H NMR (600 MHz, DMSO-$d_6$) of compound 29.

**Figure S52** $^{13}$C NMR (150 MHz, DMSO-$d_6$) of compound 29.
Figure S53 $^1$H NMR (600 MHz, CD$_2$Cl$_2$) of compound 31.

Figure S54 $^{13}$C NMR (150 MHz, CD$_2$Cl$_2$) of compound 31.
**Figure S55** $^1$H NMR (600 MHz, CD$_2$Cl$_2$) of compound 32.

**Figure S56** $^{13}$C NMR (150 MHz, CD$_2$Cl$_2$) of compound 32.
Figure S57 $^1$H NMR (600 MHz, DMSO-$d_6$) of compound POZPOZ-Th.

Figure S58 $^{13}$C NMR (150 MHz, DMSO-$d_6$) of compound POZPOZ-Th.