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Supporting information

Conjugated 12 nm long oligomers as molecular wires in nanoelectronics

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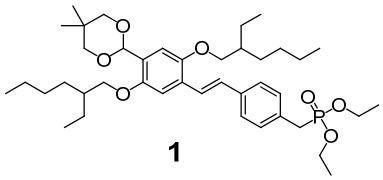
Synthesis:

General. Purification by column chromatography was performed by conventional dry column vacuum chromatography[1] or 'flash' column chromatography using Merck Silica Gel 60 (15–40 μm) (column height 5-7 cm) and suction to drive the mobile phase. Size exclusion chromatography (SEC) was performed in chloroform using either of two preparative Knauer systems employing two gel columns in succession with respectively pore diameters of 100 Å and 1000 Å. The gel columns had dimensions of 25 mmØ x 600 mm.

(E)-diethyl4-(4-(5,5-dimethyl-1,3-dioxan-2-yl)-2,5-bis(2-ethylhexyloxy)-styryl)-benzylphosphonate (**1**) was prepared in a 6 step synthesis as described in the literature.[2]

Methyl-*p*-tolyl sulfide was commercially available.



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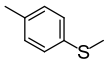
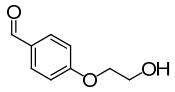
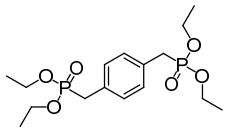




4-(2-hydroxyethoxy)benzaldehyde (2). 2-Chloro-ethanol (12.0 g, 149 mmol), 4-hydroxybenzaldehyde (10.0 g, 81.9 mmol) and K_2CO_3 (15.0 g, 109 mmol) was dissolved in DMF (100 ml) and refluxed for 6 hours. Water (50 ml) was added and the mixture was extracted with ethyl acetate (3 × 50 ml). The combined organic phases were washed (saturated aqueous Na_2CO_3, water and brine) and dried over $MgSO_4$. A crude yield (11.6 g) containing small impurities was isolated upon evaporation of the solvent. Purification by dry column chromatography (heptane/AcOEt, 5% steps) gave a total yield of 9.93 g (73%) of pure compound.

^{1}H NMR (500 MHz, $CDCl_3$) δ 9.88 (s, 1H), 7.83 (d, 2H, J = 8.8), 7.02 (d, 2H, J = 8.7), 4.17 (m, 2H), 4.01 (m, 2H), 2.04 (s, 1H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 190.94, 163.79, 132.15, 130.35, 114.94, 69.68, 61.31.

Mass ($M + Na^+$): 189.0529 Da (measured), 189.0528 Da (theoretical).

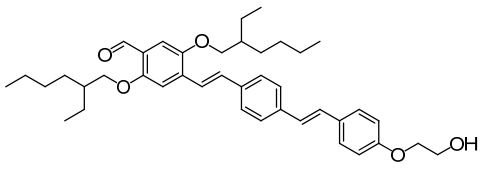


***p*-xylylene-bis-phosphonic acid tetraethyl ester (3).** A mixture of α,α'-dichloro-*p*-xylene (50.0 g, 0.286 mol) and triethyl phosphate (100.0 g, 0.601 mol) were heated until ethylchloride evolution had ceased. The hot mixture was poured into cold hexane (0 °C; 1 L) while stirring vigorously. After collection of the precipitate this was reheated and the precipitation procedure in hexane was repeated yielding a slightly waxy white granulate (98.3 g, 91%).

^{1}H NMR (250 MHz, $CDCl_3$) δ 7.23 (s, 4H), 3.99 (p, 8H, J = 7.1), 3.11 (d, 4H, J = 20.2), 1.22 (t, 11H, J = 7.1). ^{13}C NMR (125 MHz, $CDCl_3$) δ 130.31, 129.99, 62.13, 33.99, 32.89, 16.42.

Mass ($M + Na^+$): 401.1255 Da (measured), 401.1259 Da (theoretical).

General procedure (A): Step wise elongation of the OPV7 and OPV8. Deviations from the procedure will be noted for the specific compounds:



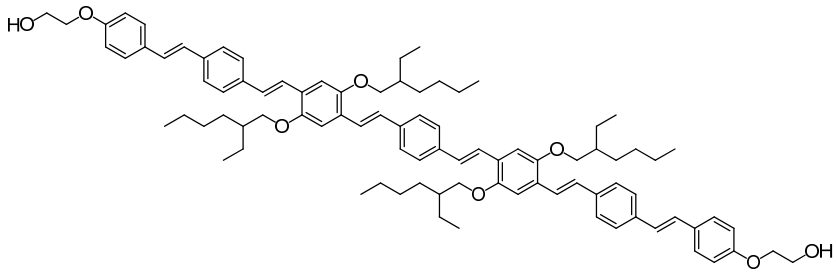
OPV7-monomer-OH (4). Compound **2** (1.43 g, 8.61 mmol, 1.2 eq.) and compound **1** (5.00 g, 7.28 mmol) in THF (120 ml) under argon was cooled on acetone/dry ice. KO^tBu (2.32 g, 21 mmol, 2.9 eq.) was added in one portion while stirring. After 30 min. THF (100 ml) was added where after a precooled mixture of H_2O/H_2SO_4 (1:4, 120 ml) in THF (120 ml) was added slowly and the temperature was allowed to reach room temperature. After end hydrolysis ice water (100 ml) was added and the mixture was extracted with ether. Saturated aq. $NaHCO_3$ was then added to the ethereal solution until neutral pH was achieved (emulsion). The organic solvent was removed *in vacuo* yielding a thick oil and an aqueous phase. The aqueous phase was removed by decantation and the oil was washed with water which was again removed. The last traces of water were then removed *in vacuo* and the resulting oil was dissolved in dichloromethane and dried over $MgSO_4$. (When dealing with solids, these were isolated by filtration and washed with excess of water. The filtrate was then dried in a vacuum oven at 45 ºC). Evaporation of the solvent gave a crude yield of 4.53 g. Purification was performed by 1) dry column vacuum chromatography (AcOEt/heptane, 5 % steps) and 2) treatment with heptane. The final product (2.55 g, 57 %) was isolated as orange/yellow solid (mp: 86.5-88 °C).

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.47 (s, 1H), 7.58 - 6.85 (m, 14H), 4.12 (t, 2H, *J* = 4.5 Hz), 4.03 (m, 2H), 3.99 (m, 2H), 3.94 (d, 2H, *J* = 5.6 Hz), 2.09 (s, 1H), 1.82 (m, 2H), 1.54 (m, 8H), 1.37 (m, 8H), 0.98 (t, 6H, *J* = 7.4 Hz), 0.93 (m, 6H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.18, 158.64, 156.57, 151.09, 137.78, 136.45, 134.59, 132.05, 130.71,

128.59, 127.99, 127.33, 126.82, 126.51, 124.41, 122.75, 115.03, 110.48, 110.20, 71.79, 71.64, 69.48, 61.63, 39.82, 39.76, 31.08, 30.87, 29.35, 29.33, 24.42, 24.25, 23.22, 23.17, 14.21, 11.41, 11.39.

Mass ($M + Na^+$): 649.3860 Da (measured), 649.3869 Da (theoretical).

General procedure (B): Coupling of the OPV7 and OPV8 with a di-phosphonate. Deviations from the procedure will be noted for the specific compounds:

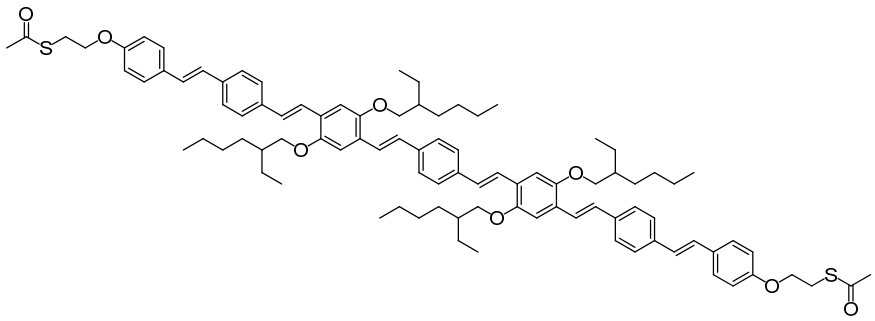


OPV7-rod-dimer-OH (5). Compound **4** (0.50 g, 7.99 mmol, 2.4 eq) dissolved in dry THF (20 ml) under argon was cooled on acetone/dry ice after which KO^tBu (0.24 g, 2.1 mmol, 6.4 eq) was added. Compound **3** (0.13 g, 0.32 mmol) in dry THF (10 ml) was then added drop wise after which the mixture was allowed to reach room temperature while monitoring by TLC. Ice (50 g) was added followed by saturated $NaHCO_3$ until neutral pH. The organic solvent was removed *in vacuo* and the organic precipitate was filtered off, washed with water, dissolved in dichloromethane and dried over $MgSO_4$. Evaporation of the solvent gave a crude (0.74 g) which was purified by dry column vacuum chromatography (AcOEt/heptane, 5% steps) yielding the pure product (328 mg, 74%) as a yellow/orange solid.

^1H NMR (500 MHz, CDCl3) δ 7.63 - 6.61 (m, 36H), 4.13 (t, 4H, J = 4.5 Hz), 3.99 (m, 12H), 2.06 (s, 2H), 1.86 (m, 4H), 1.71 - 1.25 (m, 32H), 1.03 (t, 12H, J = 7.4 Hz), 0.96 (m, 12H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.47, 151.42, 137.37, 137.28, 136.88, 130.85, 128.51, 128.47, 127.98, 127.91, 127.07, 127.05, 126.95, 126.93, 126.75,

123.43, 114.97, 110.42, 72.03, 72.00, 69.42, 61.65, 39.98, 31.14, 29.46, 24.44, 23.29,

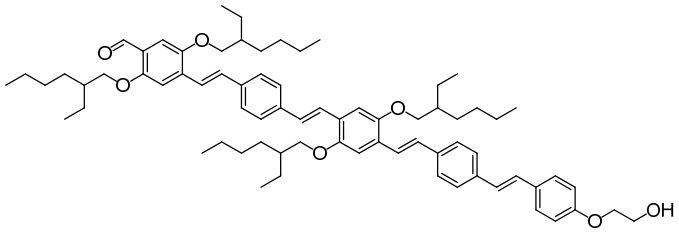
14.29, 11.51. Mass ($M^{+\bullet}$): 1322.7835 Da (measured), 1322.8514 Da (theoretical).



OPV7-rod-dimer-SAc (20). Compound **5** (42.0 mg, 31.7 μmol) and 2,4,6-collidine (50.2 μL, 46 mg, 0.38 mmol, 12 eq.) in $CHCl_3$ (2.5 ml) was placed under argon on a acetone/ice bath (approx -10 °C) while stirring. Trifluoromethanesulfonic anhydride (53.7 mg, 0.19 mmol, 6 eq.) in $CHCl_3$ (0.6 ml) was added in 4 portions over 3 hours while monitoring the reaction by TLC. The mixture was then flushed though a short silica column to remove excess anhydride and salts using $CHCl_3$ as eluent. After removal of the solvent the crude was dissolved in dry THF (2.5 ml) under argon and potassium thioacetate (14.5 mg, 0.127 mmol, 4 eq.) was added. The mixture was left stirring over night. After removal of the solvent, the crude was purified by flash chromatography (heptane/$CHCl_3$ 20:80). Yield: 76% (38.1 mg).

^{1}H NMR (500 MHz, CDCl3) δ 7.6-6.85 (m, 36H), 4.15 (t, 3H, *J* = 6.5 Hz), 3.99 (d, 8H, *J* = 5.5 Hz), 3.31 (t, 4H, *J* = 6.5 Hz), 2.40 (s, 6H), 1.86 (m, 4H), 1.53 (m, 32H), 0.97 (m, 24H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.50, 170.62, 158.23, 153.11, 151.43, 141.12, 137.38, 137.28, 136.91, 130.85, 128.52, 128.49, 128.03, 127.90, 127.07, 126.95, 126.93, 126.75, 126.71, 123.51, 123.44, 123.40, 115.04, 110.43, 72.01, 66.77, 39.99, 31.14, 30.72, 29.46, 28.65, 24.45, 23.29, 14.28, 11.51.

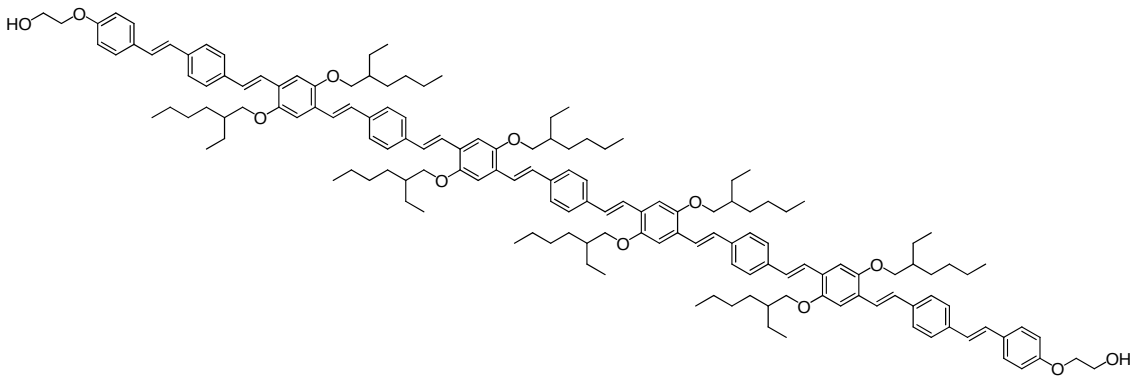
Mass ($M^{+\bullet}$): 1438.7612 Da (measured), 1438.8268 Da (theoretical).



OPV7-dimer-OH (6). General procedure **(A)**: Reaction of compound **4** (2.54 g, 4.05 mmol), KO^{t}Bu (1.15 g, 10.2 mmol, 3.2 eq) and compound **1** (3.36 g, 4.79 mmol, 1.2 eq.) in THF (40 ml) followed by hydrolysis of the acetal and initial workup yielded a crude (5.45 g) which upon purification by 1) dry column vacuum chromatography (AcOEt/heptane, 5% steps) and 2) treatment with heptane gave the desired compound (3.72 g, 84%) as an orange solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.48 (s, 1H), 7.62 - 6.87 (m, 24H), 4.14 (t, 2H, J = 4.5 Hz), 4.02 - 3.92 (m, 10H), 2.05 (s, 1H), 1.84 (m, 4H), 1.70 - 1.20 (m, 32H), 0.96 (m, 24H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.19, 158.54, 158.52, 156.58, 156.58, 151.52, 151.44, 151.11, 138.29, 137.26, 136.96, 136.54, 134.63, 132.11, 130.89,128.63, 128.29, 128.05, 127.92,127.36, 127.32, 127.01, 126.95, 126.76, 124.42, 124.08, 123.39, 122.77, 115.02, 110.55, 110.49, 110.22, 72.08, 71.83, 71.65, 69.48, 61.66, 40.01, 39.83, 39.78, 32.03, 31.15, 31.10, 30.88, 29.47, 29.37, 29.33, 24.46, 24.43, 24.26, 23.28, 23.23, 23.18, 22.83, 14.26, 14.21, 11.50, 11.41, 11.40.

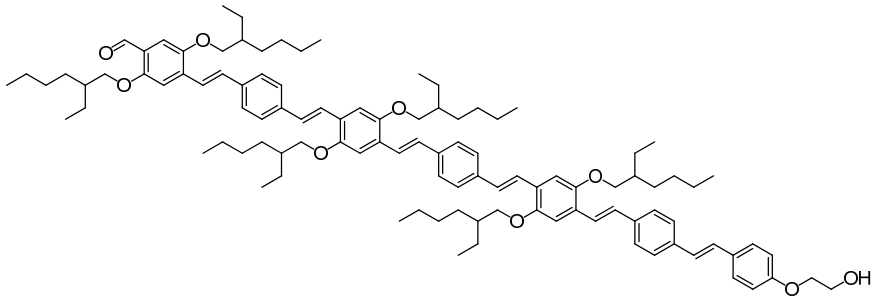
Mass ($M^{+\bullet}$): 1086.6579 Da (measured), 1086.7313 Da (theoretical).



OPV7-rod-tetramer-OH (7). General procedure **(B)**: The reaction of compound **6** (611 mg, 0.56 mmol, 2.3 eq) and KO^{t}Bu (0.18 g, 1.59 mmol, 6.5 eq) in dry THF (40 ml) and compound **3** (92.1 mg, 0.24 mmol) in dry THF (15 ml) yielded a crude (0.76 g) which upon purification by 1) forced precipitation with heptane from a saturated dichloromethane solution and 2) 'flash' column chromatography ($CHCl_3$ + 4% THF) yielded the pure product as an orange solid (392 mg, 72 %).

^{1}H NMR (500 MHz, CDCl3) δ 7.65 - 6,70 (m, 56H), 4.12 (t, 4H, *J* = 4.4 Hz), 3.98 (m, 20H), 2.01 (s, 2H), 1.85 (m, 8H), 1.70 - 1,25 (m, 64H), 1.02 (t, 24H, *J* = 7.2 Hz), 0.95 (m, 24H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.47, 151.42, 137.37, 137.28, 136.88, 130.85, 128.51, 128.47, 127.98, 127.91, 127.07, 127.05, 126.95, 126.93, 126.75, 123.43, 114.97, 110.42, 72.03, 72.00, 69.42, 61.65, 39.98, 31.14, 29.46, 24.44, 23.29, 14.29, 11.51.

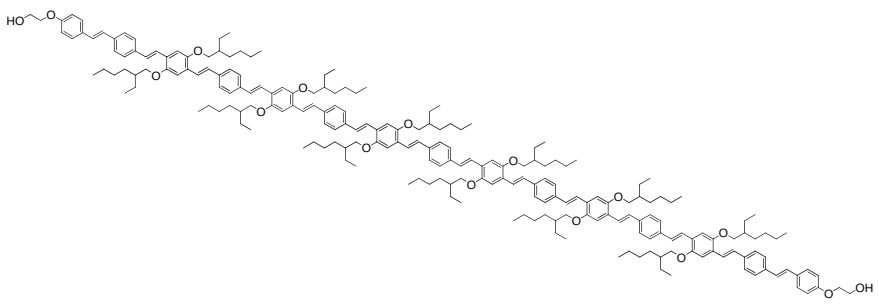
Mass ($M^{+\bullet}$): 2243.4118 Da (measured), 2243.5196 Da (theoretical).



OPV7-trimer-OH (8). General procedure **(A)**: Reaction of compound **6** (4.30 g, 3.95 mmol), compound **1** (3.33 g, 4.75 mmol, 1.2 eq) and KO^{t}Bu (1.77 g, 15.5 mmol, 4 eq) in dry THF (60 ml) followed by hydrolysis of the acetal and initial workup gave a crude (7.05 g) which was purified by 1) forced precipitation from a saturated dichloromethane solution with heptane and 2) 'flash' column chromatography yielding the desired compound as a red/orange solid (5.60 g, 92 %).

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.47 (s, 1H), 7.75 - 6.82 (m, 34H), 4.13 (t, 2H, J = 4.5 Hz), 4.03 (m, 14H), 2.01 (s, 1H), 1.84 (m, 6H), 1.50 (m, 48H), 0.96 (m, 36H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.23, 158.50, 158.48, 156.58, 151.50, 151.43, 151.09, 138.28, 137.44, 137.34, 137.30, 136.90, 136.52, 134.61, 132.10, 130.89, 128.67, 128.50, 128.28, 128.01, 127.92, 127.37, 127.31, 127.08, 127.07, 127.01, 126.96, 126.94, 126.87, 126.76, 124.37, 124.05, 123.48, 123.42, 123.38, 122.75, 115.00, 110.51, 110.44, 110.17, 72.04, 71.79, 71.60, 69.45, 61.67, 40.00, 39.81, 39.76, 32.04, 31.16, 31.09, 30.88, 29.47, 29.36, 29.33, 29.17, 24.45, 24.42, 24.25, 23.29, 23.24, 23.19, 22.85, 14.28, 14.23, 11.51, 11.41.

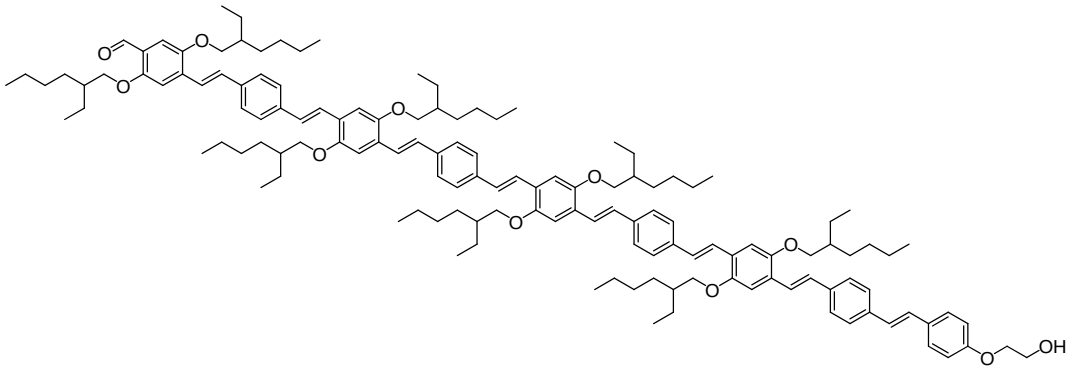
Mass ($M^{+\bullet}$): 1547.0137 Da (measured), 1547.0654 Da (theoretical).



OPV7-rod-hexamer-OH (9). General procedure **(B)**: Compound **8** (3.00 g, 1.92 mmol, 2.3 eq) and KO^{t}Bu (662 mg, 5.90 mmol, 7 eq) in dry THF (120 ml) was reacted with compound **3** (319 mg, 0.84 mmol) in dry THF (30 ml). After initial workup the filtrated organic precipitate was dried in a vacuum oven (45 °C) and then dissolved in $CHCl_3$ and filtered through cellite. Evaporation of the solvent gave a crude (3.1 g) as a red sticky solid. Purification was performed by 1) forced precipitation from saturated $CHCl_3$ solution with heptane 2) 'flash' column chromatography ($CHCl_3$ + 1% THF) yielding the pure compound (1.66 g, 27%) as a red solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 - 6.85 (m, 72H), 4.10 (t, 4H, J = 4.5 Hz), 4.00 (m, 28H), 2.12 (s, 2H), 1.87 (m, 12H), 1.56 (m, 102H), 1.01 (m, 72H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 158.46, 151.41, 137.35, 137.24, 136.86, 130.79, 128.48, 127.96, 127.88, 127.05, 126.93, 126.73, 126.67, 123.40, 114.93, 110.40, 72.01, 71.97, 69.40, 61.59, 39.96, 31.13, 29.45, 24.42, 23.28, 14.27, 11.50.

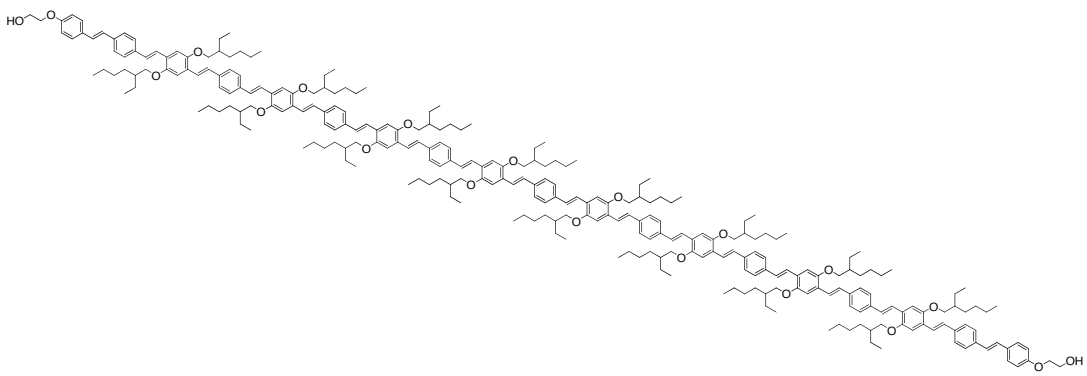
Mass ($M^{+\bullet}$): 3164.1780 Da (measured), 3164.1879 Da (theoretical).



OPV7-tetramer-OH (10). General procedure **(A)**: Reaction of compound **8** (2.40 g, 1.55 mmol), compound **1** (1.31 g, 1.88 mmol, 1.2 eq) and KO^{t}Bu (0.702 g, 6.23 mmol, 4 eq) in dry THF (60 ml) followed by hydrolysis of the acetal and initial workup. The filtrated organic precipitate was dried in a vacuum oven (45 °C) and then dissolved in $CHCl_3$ and filtered through cellite. Evaporation of the solvent gave a red crude solid which upon purification by 1) forced precipitation from a saturated chloroform solution with heptane (200 ml) (performed twice) and 2) 'flash' column chromatography ($CHCl_3$) yielded the desired compound (1.82 g, 58%) as a red solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.48 (s, 1H), 7.65 - 6.83 (m, 44H), 4.12 (t, 2H, *J* = 4.6 Hz), 4.03 (m, 18H), 2.05 (t, 1H, *J* = 6.3 Hz), 1.84 (m, 8H, *J* = 6.1, 12.9 Hz), 1.70 - 1.32 (m, 64H), 0.99 (m, 48H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.22, 158.47, 156.56, 151.48, 151.41, 151.06, 138.26, 137.43, 137.37, 137.36, 137.32, 137.27, 136.88, 136.51, 134.60, 132.08, 130.85, 128.65, 128.52, 128.49, 128.46, 128.26, 127.98, 127.91, 127.36, 127.29, 127.09, 127.05, 127.00, 126.95, 126.92, 126.85, 126.75, 126.72, 124.34, 124.03, 123.47, 123.42, 123.40, 123.36, 122.72, 114.97, 110.48, 110.41, 110.14, 72.02, 71.76, 71.56, 69.42, 61.64, 39.98, 39.79, 39.74, 31.14, 31.08, 30.86, 29.46, 29.35, 29.32, 24.44, 24.40, 24.23, 23.28, 23.24, 23.18, 14.28, 14.23, 11.51, 11.41, 11.40

Mass ($M^{+\bullet}$): 2007.3046 Da (measured), 2007.3995 Da (theoretical).

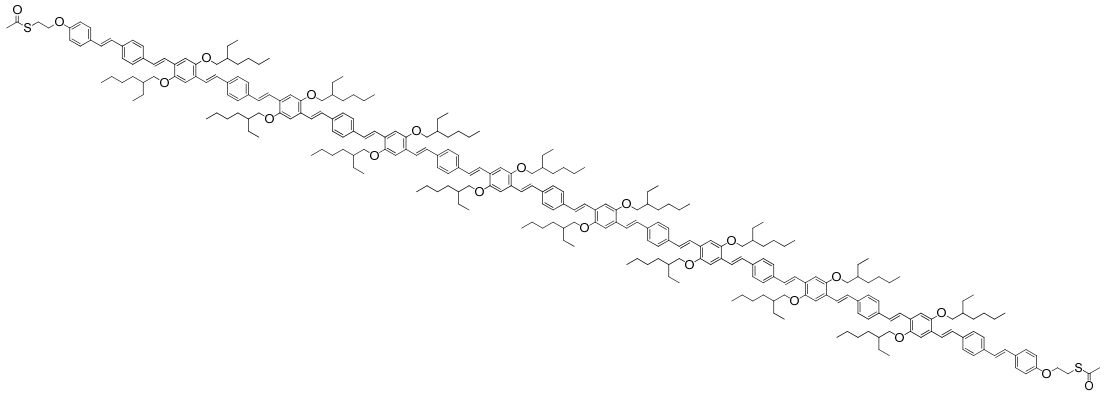


OPV7-rod-octamer-OH (11). General procedure **(B)**: Compound **10** (1.72 g, 0.856 mmol, 2.2 eq) and KO^{t}Bu (0.35 g, 3.11 mmol, 8 eq) in dry THF (120 ml) was reacted with compound **3** (147 mg, 0.389 mmol) in dry THF (40 ml). The filtrated organic precipitate was dried in a vacuum oven (45 °C) and then dissolved in $CHCl_3$ and filtered through cellite. Evaporation of the solvent gave a crude (1.72 g) as a red sticky solid. Purification was performed as 1) forced precipitation from saturated $CHCl_3$ solution with ethyl acetate 2) 'flash' column chromatography ($CHCl_3$ + 0.5% THF) yielding the pure compound (1.07 g, 67%) as a red solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 - 6.80 (m, 96H), 4.12 (t, 4H, *J* = 4.5 Hz), 3.95 (m, 36H), 2.09 (s, 2H), 1.82 (m, 16H), 1.70 - 1.35 (m, 128H), 1.04 (m, 48H), 0.97 (m, 48H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 158.46, 151.41, 137.35, 137.24, 136.86, 130.79, 128.48, 127.96, 127.88, 127.05, 126.93, 126.73, 126.67, 123.40, 114.93, 110.40, 72.01, 71.97, 69.40, 61.59, 39.96, 31.13, 29.45, 24.42, 23.28, 14.27, 11.50.

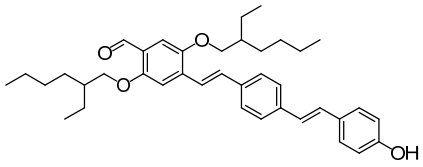
Mass ($M^{+\bullet}$): 4084.86058 Da (measured), 4084.85615 Da (theoretical).



OPV7-rod-octamer-SAc (21). Compound **11** (39.70 mg, 9.71 µmol), 2,4,6-collidin (20,7 µL, d=0.917, 0.157 mmol, 16 eq) in $CHCl_3$ (1.4 ml) under argon, was cooled on an acetone/ice bath (approx -10 ºC) while stirring. Trifluoromethanesulfonic anhydride (44.3 mg, 0.157 mmol, 16 eq.) in $CHCl_3$ (0.6 ml) was then added in four portions over 3 hours while monitoring the reaction by TLC. The mixture was then flushed through a short silica column to remove excess anhydride and salts using $CHCl_3$ as the eluent. After removal of the solvent the crude was dissolved in dry THF (2.6 ml) under argon and potassium thioacetate (13 mg, 0.114 mmol, 12 eq) was added. The mixture was left stirring over night. After removal of the solvent the crude was purified by 'flash' chromatography (heptane:$CHCl_3$ – 30:70). Yield 76 % (38.1 mg)

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.75 – 6.84 (m, 96H), 4.13 (t, *J* = 6.4, 4H), 3.98 (t, *J* = 10.7, 32H), 3.29 (t, *J* = 6.4, 4H), 2.39 (s, 6H), 1.92 – 1.76 (m, 16H), 1.72 – 1.34 (m, 128H), 1.03 (m, 48H), 0.95 (m, 48H). ^{13}C NMR (126 MHz, $CDCl_3$) δ 195.54, 158.19, 151.40, 137.35, 137.23, 130.79, 129.65, 128.49, 128.00, 127.89, 127.04, 126.94, 126.74, 126.66, 123.39, 114.99, 110.37, 71.98, 66.72, 39.96, 31.14, 30.73, 29.46, 28.63, 24.42, 23.29, 14.30, 11.51.

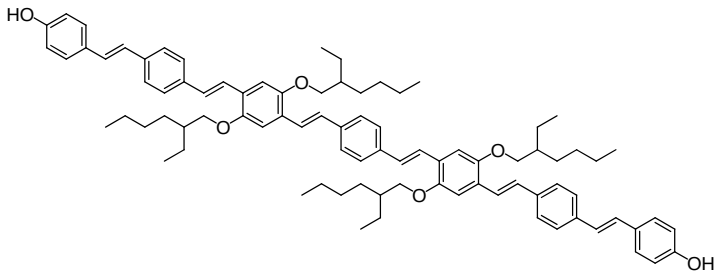
Mass ($M^{+\bullet}$): 4200.8195 Da (measured), 4200.8316 Da (theoretical).



OPV8-monomer-OH (12). General procedure **(A)**: The reaction of 4-hydroxybenzaldehyde (0.84 g, 6.85 mmol, 1.2 eq), compound **1** (4.02 g, 5.71 mmol) and KO^{t}Bu (2.53 g, 22.8 mmol, 4 eq) in dry THF (100 ml) followed by hydrolysis of the acetal gave an orange solid crude (2.15 g) which was purified by 1) dry column chromatography and 2) treatment with heptane yielding the desired pure product (1.97 g, 59%).

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.46 (s, 1H), 7.55 - 6,82 (m, 14H), 4.98 (s, 1H), 4.02 (m, 2H), 3.93 (d, 2H, *J* = 5.6 Hz), 1.81 (m, 2H), 1.48 (m, 16H), 0.97 (2×t, 6H, *J* = 7.5 Hz), 0.92 (2×t, 6H, *J* = 7.1 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.32, 156.60, 155.59, 151.07, 137.81, 136.40, 134.65, 132.09, 130.44, 128.65, 128.15, 127.34, 126.81, 126.30, 124.33, 122.69, 115.84, 110.42, 110.15, 71.74, 71.58, 39.80, 39.74, 31.07, 30.87, 29.35, 29.33, 24.41, 24.24, 23.24, 23.18, 14.23, 11.42, 11.41.

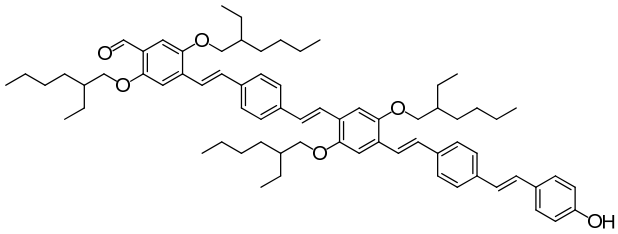
Mass (M + Na^+): 605.3625 Da (measured), 605.36068 Da (theoretical).



OPV8-rod-dimer-OH (13). General procedure **(B)**: The reaction of compound **12** (200 mg, 0.34 mmol, 2.3 eq) and KO^{t}Bu (134 mg, 1.2 mmol, 8 eq) in dry THF (30 ml) with and compound **3** (92.1 mg, 0.24 mmol) in dry THF (10 ml) yielded a crude (322 mg) which was purified by 1) 'flash' column chromatography ($CHCl_3$ + 2.5% THF) and 2) forced precipitation from saturated dichloromethane with heptane giving the by TLC pure compound (145 mg, 78%) as a red solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.62 - 6.75 (m, 36H), 4.78 (s, 2H), 3.98 (d, 8H, *J* = 5.5), 1.85 (m, 4H), 1.67 - 1.30 (m, 32H), 1.01 (t, 12H, J = 7.5 Hz), 0.94 (2×t, 12H, *J* = 7.0 Hz). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.25, 151.32, 137.26, 137.16, 136.79, 130.56, 128.41, 128.37, 127.91, 127.00, 126.98, 126.79, 126.77, 126.58, 126.47, 123.35, 123.31, 115.65, 110.41, 72.00, 71.97, 39.88, 31.01, 29.31, 24.31, 23.11, 14.08, 11.33.

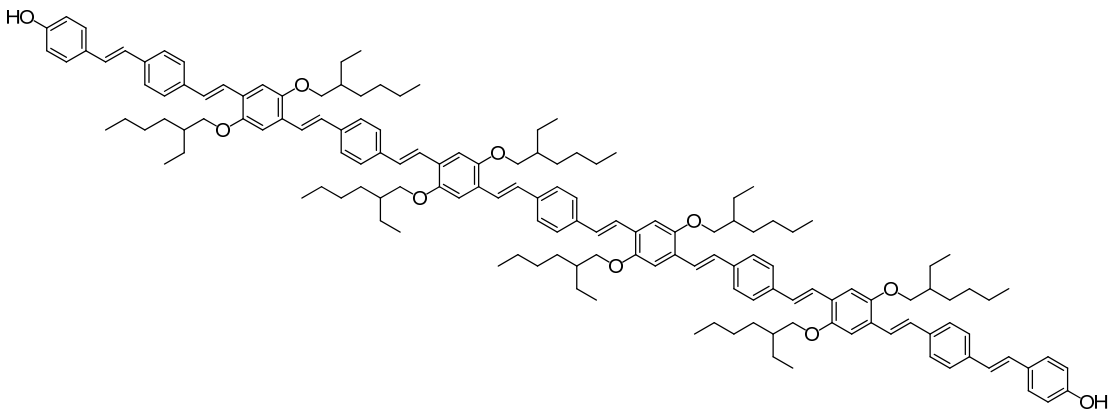
Mass ($M^{+\bullet}$): 1234.7665 Da (measured), 1234.7989 Da (theoretical).



OPV8-dimer-OH (14). General procedure **(A)**: Reaction of compound **12** (1.60 g, 2.75 mmol), compound **1** (2.35 g, 3.35 mmol, 1,2 eq) and KO^tBu (1.28 g, 11.4 mmol, 4.15 eq) in dry THF (50 ml) followed by hydrolysis of the acetal yielded a crude (3.3 g) which was purified by 1) forced precipitation from saturated dichloromethane with heptane 2) 'flash' column chromatography ($CHCl_3$ + 1% THF). The final product (2.55 g, 89%) was an orange-red solid, was pure by TLC.

^{1}H NMR (250 MHz, $CDCl_3$) δ 10.46 (s, 1H), 7.70 - 6.75 (m, 24H), 3.99 (m, 8H), 1.82 (m, 4H), 1.67 - 1.25 (m, 32H), 0.98 (m, 24H). ^{13}C NMR (63 MHz, $CDCl_3$) δ 189.3, 156.6, 155.5, 151.5, 151.4, 151.1, 138.3, 137.2, 137.0, 136.5, 134.7, 132.2, 130.6, 128.6, 128.3, 128.1, 128.0, 127.4, 127.3, 127.0, 126.9, 126.85, 126.7, 126.5, 124.4, 124.1, 123.3, 122.7, 117.9, 115.8, 110.5, 110.45, 110.2, 72.0, 71.8, 71.6, 40.0, 39.8, 39.75, 31.2, 31.1, 30.9, 29.5, 29.35, 29.3, 24.45, 24.40, 24.3, 23.3, 23.25, 23.20, 14.27, 14.23, 11.5, 11.4.

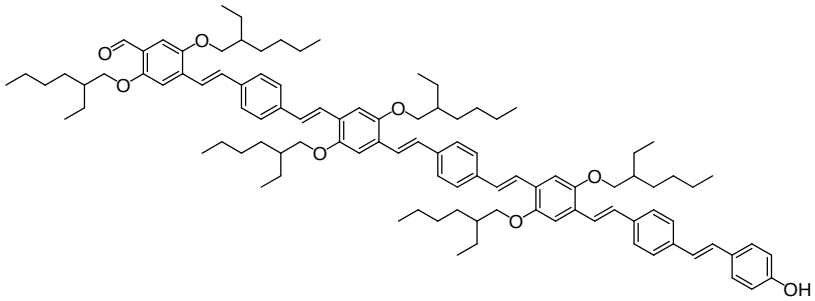
Mass ($M^{+\bullet}$): 1042.6459 Da (measured), 1042.7050 Da (theoretical).



OPV8-rod-tetramer-OH (15). General procedure **(B)**: Reaction of compound **14** (746 mg, 0.72 mmol, 2.2 eq) and KO^{t}Bu (293 mg, 2.60 mmol, 8 eq) in dry THF (60 ml) with compound **3** (123 mg, 0.33 mmol) in dry THF (20 ml). After separation of the organic fraction this was dried in a vacuum oven (45 °C), then diluted in $CHCl_3$ and the solution was filtered trough cellite followed by removal of the solvent. Purification was done by 1) 'flash' column chromatography ($CHCl_3$ + 2% THF) and 2) 'flash' column chromatography ($CHCl_3$ + 1.5% THF) yielding the by TLC pure compound (456 mg, 65%) as a red solid.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 - 6.8 (m, 56H), 4.98 (s, 2H), 4.00 (m, 16H), 1.87 (m, 8H), 1.54 (m, 64H), 1.04 (m, 24H), 0.97 (m, 24H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.31, 151.30, 137.25, 137.12, 136.79, 130.46, 128.39, 128.35, 127.93, 126.95, 126.93, 126.83, 126.61, 126.40, 123.30, 123.24, 115.68, 110.30, 71.91, 71.88, 39.85, 31.02, 29.34, 24.31, 23.16, 14.16, 11.38.

Mass ($M^{+\bullet}$): 2155.3733 Da (measured), 2155.4672 Da (theoretical).

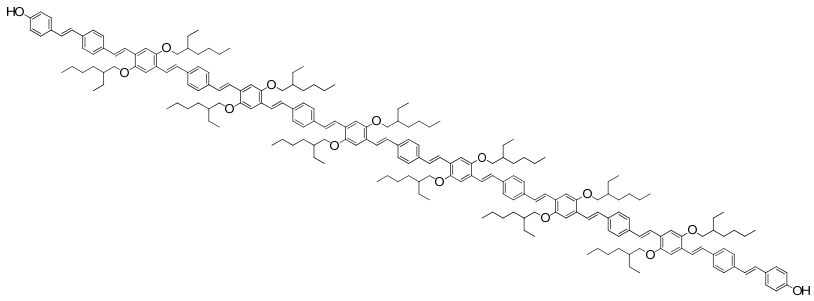


OPV8-trimer-OH (16). General procedure **(A)**: Reaction of compound **14** (2.24 g, 2.15 mmol), compound **1** (1.85 g, 2.58 mmol, 1.2 eq) and KO^{t}Bu (0.96 g, 8.57 mmol, 4 eq) in dry THF (50 ml) followed by hydrolysis of the acetal. The filtrated organic precipitate was dried in a vacuum oven (45 °C) and then dissolved in $CHCl_3$ and filtered through cellite. Evaporation of the solvent gave a red crude which upon purification yielded a crude (3.5 g) which was purified by 'flash' column chromatography ($CHCl_3$) (performed twice). The final product (2.37 g, 73%), a red solid, was pure by TLC.

^{1}H NMR (500 MHz, CDCl3) δ 10.47 (s, 1H), 7.60 - 6.80 (m, 34H), 5.03 (s, 1H), 4.03 (dd, 2H, *J* = 2.2, 5.4 Hz), 3.97 (m, 10H), 1.84 (m, 6H), 1.48 (m, 34H), 0.98 (m, 36H).

^{13}C NMR (125 MHz, $CDCl_3$) δ 189.21, 156.48, 155.35, 151.36, 151.28, 150.95, 138.15, 137.30, 137.19, 137.10, 136.80, 136.37, 134.55, 132.00, 130.44, 128.53, 128.37, 128.14, 127.93, 127.24, 127.18, 126.96, 126.91, 126.88, 126.83, 126.80, 126.73, 126.60, 126.38, 124.18, 123.92, 123.35, 123.23, 122.59, 115.68, 110.37, 110.29, 110.03, 71.93, 71.89, 71.64, 71.45, 39.85, 39.67, 39.61, 31.02, 30.96, 30.73, 29.33, 29.23, 29.20, 24.31, 24.28, 24.11, 23.16, 23.11, 23.06, 14.15, 14.11, 11.38, 11.29, 11.28.

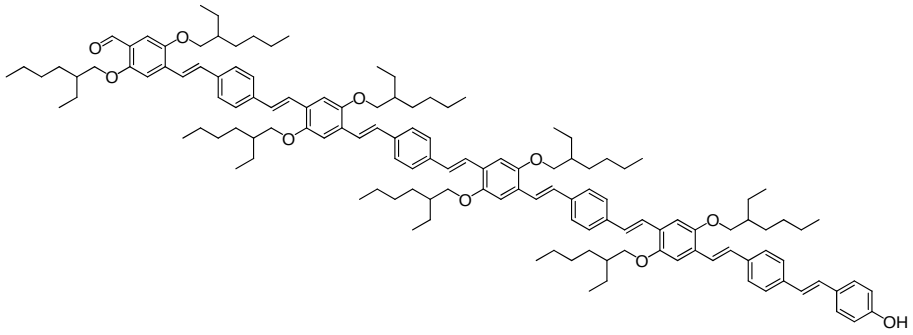
Mass ($M^{+\bullet}$): 1503.0048 Da (measured), 1503.0392 Da (theoretical).



OPV8-rod-hexamer-OH (17). General procedure **(B)**: Reaction of compound **16** (1.00 g, 0.665 mmol. 2.2 eq) and KO^{t}Bu (273 mg, 2.41 mmol, 8 eq) in THF (100 ml) with compound **3** (114 mg, 0.302 mmol) in dry THF (25 ml). After separation of the organic fraction this was dried in a vacuum oven (45 °C), then diluted in $CHCl_3$ and the solution was filtered trough cellite. Removal of the solvent *in vacuo* gave a crude (1.01 g) which was purified by 1) 'flash' column chromatography ($CHCl_3$) and 2) 'flash' column chromatography ($CHCl_3$ + 0.5% THF) yielding the by TLC pure compound (417 mg, 45%) as a dark red solid. Length ~ 9 nm.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.70 - 6.75 (m, 76H), 5.11 (s, 2H), 4.00 (m, 24H), 1.88 (m, 12H), 1.70 - 1.25 (m, 96H), 1.10 - 0.87 (m, 72H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.48, 151.42, 137.37, 137.21, 136.91, 130.51, 128.51, 128.04, 127.08, 126.95, 126.91, 126.72, 126.46, 123.42, 123.35, 115.80, 110.44, 72.04, 72.01, 39.97, 31.14, 29.46, 24.43, 23.28, 14.28, 11.51.

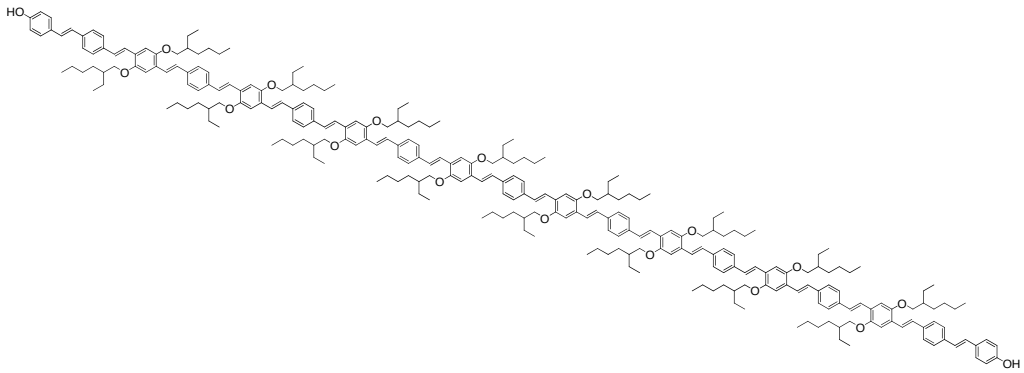
Mass ($M^{+\bullet}$): 3076.1386 Da (measured), 3076.1355 Da (theoretical).



OPV8-tetramer-OH (18). General procedure **(A)**: Reaction of compound **16** (1.07 g, 0.711 mmol), compound **1** (604 mg, 0.86 mmol, 1.2 eq) and KO^tBu (325 mg, 2.90 mmol, 4 eq) in dry THF (60 ml) followed by hydrolysis of the acetal. The filtrated organic precipitate was dried in a vacuum oven (45 °C) and then dissolved in $CHCl_3$ and filtered through cellite. Evaporation of the solvent gave a dark red crude which upon purification yielded a crude (2.5 g) which was purified by 1) 'flash' column chromatography ($CHCl_3$) and 2) 'flash' column chromatography ($CHCl_3$ + 0.5% THF). The final product (1.28 g, 92%), a red solid, was pure by TLC.

^{1}H NMR (500 MHz, $CDCl_3$) δ 10.49 (s, 1H), 7.67 - 6.80 (m, 44H), 5.21 (s, 1H), 4.01 (m, 16H), 1.86 (m, 8H), 1.70 - 1.30 (m, 64H), 1.10 - 0.90 (m, 48H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 189.38, 156.61, 155.54, 151.48, 151.42, 151.06, 138.27, 137.42, 137.38, 137.31, 137.21, 136.93, 136.49, 134.70, 132.14, 130.49, 128.65, 128.53, 128.48, 128.25, 128.08, 128.04, 127.36, 127.30, 127.10, 127.07, 127.04, 127.00, 126.95, 126.91, 126.84, 126.72, 126.44, 124.28, 124.04, 123.46, 123.43, 123.41, 123.35, 122.70, 115.81, 110.49, 110.41, 110.14, 72.03, 71.75, 71.56, 39.97, 39.78, 39.73, 31.14, 31.07, 30.85, 29.46, 29.35, 29.31, 24.43, 24.39, 24.23, 23.28, 23.23, 23.18, 14.28, 14.23, 11.50, 11.41, 11.39.

Mass ($M^{+\bullet}$): 1963.2920 Da (measured), 1963.3733 Da (theoretical).

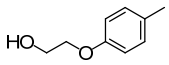


OPV8-rod-octamer-OH (19). General procedure **(B)**: Reaction of compound **18** (1.15 g, 0.59 mmol. 2.2 eq) and KO^{t}Bu (240 mg, 2.13 mmol, 8 eq) in THF (160 ml) with compound **3** (101 mg, 0.27 mmol) in dry THF (25 ml). After separation of the organic fraction this was dried in a vacuum oven (45 °C), then diluted in $CHCl_3$ and the solution was filtered trough cellite. Removal of the solvent *in vacuo* gave a crude (1.2 g) which was purified by 1) 'flash' column chromatography ($CHCl_3$) and 2) 'flash' column chromatography ($CHCl_3$ + 1% THF) yielding the by TLC pure compound (823 mg, 77%) as a dark red solid. Length ~ 11 nm.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.65 - 6.80 (m, 96H), 5.01 (s, 2H), 4.00 (m, 32H), 1.87 (m, 16H), 1.70 - 1.33 (m, 128H), 1.04 (m, 48H), 0.96 (m, 48H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 155.47, 151.43, 137.38, 137.23, 136.92, 130.55, 128.52, 128.05, 127.35, 127.08, 126.95, 126.73, 126.49, 123.43, 123.36, 115.80, 110.44, 72.04, 72.01, 68.12, 39.98, 31.15, 29.46, 29.17, 24.44, 23.29, 14.29, 11.51, 11.41. .

Mass ($M^{+\bullet}$): 3996.8157 Da (measured), 3996.8037 Da (theoretical).

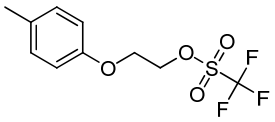
Test compound for gold attachment experiments



2-(p-tolyloxy)ethanol (22). *p*-Cresol (4.40 g, 40.7 mmol), 2-chloro-ethanol (8.5 g, 106 mmol) and K_2CO_3 (10.5 g, 76 mmol) in DMF (50 ml) were refluxed for 6 hours. Water (50 ml) was added and the mixture was extracted with EtOAc. The organic phase was washed with saturated K_2CO_3 and brine, dried over $MgSO_4$ and the solvent was evaporated. Workup by dry column chromatography (heptane/EtOAc, 5% steps) yielded the desired product (4.50 g, 73 %) as white crystals.

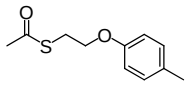
^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (d, 2H, J = 8.2 Hz), 6.82 (d, 2H, J = 8.2 Hz), 4.06 (t, 2H, J = 4.5 Hz), 3.94 (t, 2H, J = 4.5 Hz), 2.29 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 156.66, 130.55, 130.11, 114.62, 69.45, 61.71, 20.60.

Mass ($M + Na^+$): 175.0756 Da (measured), 175.0735 Da (theoretical).



2-(p-tolyloxy)ethyl trifluoromethanesulfonate (23): 2-(p-tolyloxy)ethanol (27.5 mg, 0.1783 mmol) was reacted with trifluoromethanesulfonic anhydride (100.6 mg, 0.36 mmol, 2 eq.). The reaction was filtered through a short column of Kieselgel flushing with CH_2Cl_2. Evaporation of the solvent gave a crude (43 mg) which was used in the next step without further purification.

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, 2H, J = 8.4 Hz), 6.81 (d, 2H, J = 8.4 Hz), 4.80 (m, 2H), 4.26 (m, 2H), 2.30 (s, 3H).



S-2-(p-tolyloxy)ethyl ethanethioate (**24).** Compound **23** (43 mg, 0.15 mmol) and potassium thioacetate (41 mg, 0.36 mmol, 2 eq) was dissolved in dry THF (2 ml) and the mixture was whil stirring overnight. The reaction mixture was purified by flash column chromatography ($CHCl_3$) yielding the pure compound as a slightly brown thin oil (25.9 mg, 69% yield from 2-(p-tolyloxy)ethanol).

^{1}H NMR (500 MHz, $CDCl_3$) δ 7.09 (d, 2H, J = 8.6 Hz), 6.82 (d, 2H, J = 8.6 Hz), 4.08 (t, 2H, J = 6.4 Hz), 3.27 (t, 2H, J = 6.4 Hz), 2.37 (s, 3H), 2.30 (s, 3H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 195.36, 156.36, 130.44, 130.02, 114.66, 66.75, 30.60, 28.67, 20.54.

Mass ($M + Na^+$): 233.0665 Da (measured), 233.0612 Da (theoretical).

Control of purity by Size exclusion chromatography (SEC):

All final compounds were subjected to SEC analysis in order to control the purity of the compounds. The UV-curves of the final compounds **5**, **7**, **9** and **11** as well as **13**, **15**, **17** and **19** are shown in Figure S1. As can be seen the compounds **5**, **7**, **9** and **11** are very pure but the compounds **13**, **15**, **17** and **19** contains various impurities. Some tailing is observed for the phenol compounds. This is probably due to the fact that the chloroform eluent contains 0.5 % of triethylamine that can interact with the phenol groups. An UV-curve for the SEC-purified compound **19** is also added.

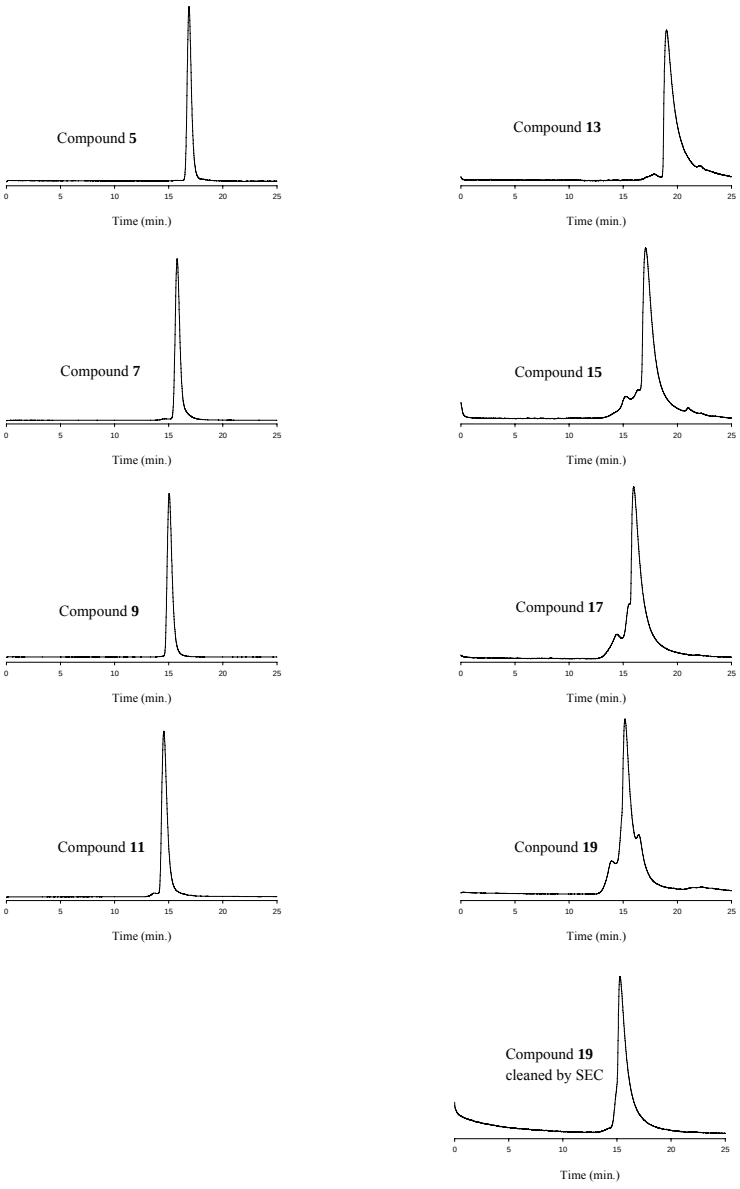


Figure S1: : SEC traces of compound **5**, **7**, **9**, **11**, **13**, **15**, **17** and **19.**

Attachment experiments.

TOF-SIMS analysis on Gold surfaces:

Sample preparation: Gold samples were prepared by thermal evaporation at 5×10^{-5} mBar. A layer of Cr was evaporated before evaporation of gold to ensure attachment to the glass slide. The gold samples were washed with THF and analyzed by time-of-flight secondary ion mass spectrometry (TOF-SIMS).[3] Solutions of compound **24**, commercially available methyl-*p*-tolyl sulfide, compound **20** and compound **21** were prepared (see Table S1) and the gold slides were analyzed by TOF-SIMS after exposure to the solutions for 24 hours.

Table S1: Solutions of compounds for gold attachment experiments.[4]

Sample nr.	Compound	C (mM)	$V_{solution}$ (mL)	V_{HCl} (μL)[a]
1	**24**	43	0.5	-
2	**24**	43	0.5	280
3	Methyl-*p*-tolyl sulfide	43	0.5	-
4	Methyl-*p*-tolyl sulfide	43	0.5	280
5	**20**	1.17	0.3	-
6	**20**	1.17	0.3	4.7
7	**21**	1.17	0.3	-
8	**21**	1.17	0.3	4.7

[a] 40 molal excess of a 3 M HCl solution.

The TOF-SIMS analyses were performed using a TOFSIMS IV (Ion–Tof GmbH, Münster, Germany) operated at a pressure of 4×10^{-9} mbar (with sample). Mass spectra were obtained using 25-ns pulses of 25-keV Bi^+ (primary ions), which were bunched to form ion packets with a nominal temporal extent of <1 ns at a repetition rate of 5 kHz, thus yielding a target current of 0.5 pA. These primary ion conditions were used to scan a 100×100 μm^2 area of the sample for 15 s. Five spots on each sample were measured in order to ensure representative data. Electron bombardment was used to minimize

charge build-up at the surface. Ejected secondary ions were accelerated to 2 keV, mass analyzed in the flight tube, and post-accelerated to 10 keV before detection.

The result is graphically presented in Figure S2a based on the measured signal ratio between sulphur and the gold substrate (S^-/Au^-). It is evident that the thioacetate is more efficiently grafted to the gold substrate compared to the thioether. In addition, the presence of HCl (aq) in the grafting solution clearly improves the grafting efficiency for both compounds. Two oligomers of PPV, compound **20** and compound **21**, were subjected to an equivalent study.

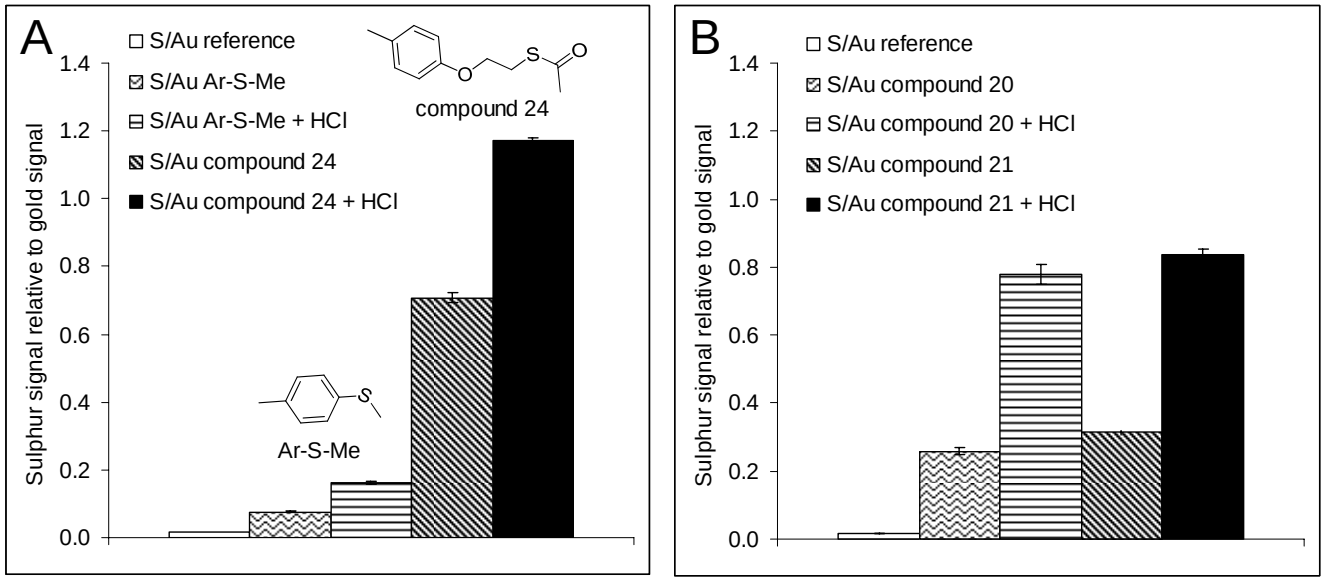


Figure S2. Measured S^-/Au^- intensity ratios obtained from a TOF-SIMS analysis. The following species were grafted onto gold substrates: (A) methyl-*p*-tolyl sulfide (Ar-S-Me), and compound **24**. (B) Compounds **20** and **21**. Each result is the outcome of having analyzed the sample surface at five different locations. An untreated gold substrate constitutes the reference sample.

The result is graphically presented in Figure S2b. The graph (Figure S2b) shows that the compound **20** and compound **21** are grafted to the gold surface with more or less the same efficiency, i.e., apparently independent of the size/length of the oligomers of PPV. The presence of HCl (aq) is, once again, observed to significantly increase the grafting efficiency.

TOF-SIMS analysis on ZnO surfaces:

Sample preparation: ZnO substrates were prepared by spin coating a solution of nanoparticles in chlorobenzene and subsequently heating the substrate samples in a vacuum oven at 200 °C. The resulting ZnO samples were washed with chloroform and analyzed by TOF-SIMS. Solutions of compounds **13** and **19** were prepared (see Table S2) and the ZnO substrates were analyzed by TOF-SIMS after exposure to the solutions for 24 hours.

Table S2. Solutions of compounds for ZnO attachment experiments.

Sample nr.	Compound	C (mM)
1	**13**	4.15
2	**19**	4.15

Compounds **13** and **19** were subjected to an equivalent study, although without the use of HCl (aq) and grafted onto ZnO substrates instead. Due to lack of specific fragment ions during the ionization step of the analysis (like S^- for the thioethers and thioacetates); it is not possible to obtain semi-quantitative information. However, the presence of the molecules on the ZnO substrates can be verified from the fragment ion series typically observed for oligomers and polymers (Figure S3). The material could not be removed from the surface by washing with THF and chloroform. Even after immersion in solvent for 24 hours.

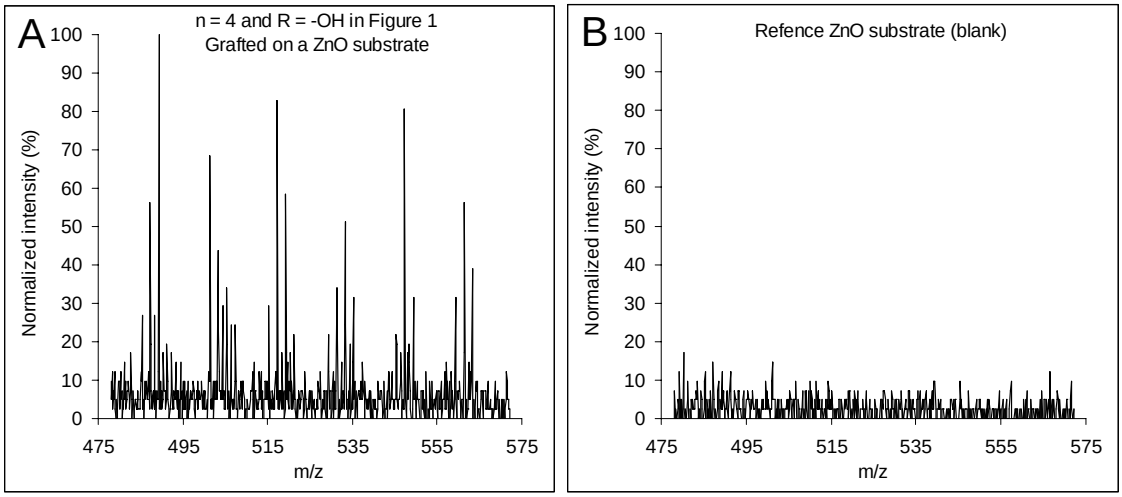


Figure S3. Normalized TOF-SIMS mass spectra analyzed under equivalent conditions and thus normalized with the same factor. (A) Mass spectrum of the compound **19** grafted on a ZnO substrate. (B) A blank (reference) substrate.

XPS analysis

Samples: Two samples were prepared by immersing flat gold into a THF solution of compound **20** and **21** (5 mM) respectively for 16 hours. The samples were then washed extensively with THF and blown dry. Another two samples were prepared by adding a few drops of the solution of compound **20** and **21** respectively onto flat gold surfaces and letting the THF evaporate.

The XPS analyses were performed on a K-Alpha from Thermo Fisher Scientific using a monochromatic Al Kα X-ray source (hν = 1486.6 eV). The binding energy scales were referenced by setting the $Au_{4f7/2}$ binding energy to 84.0 eV. The high-resolution S_{2p} spectra were acquired with an analyzer pass energy of 25 eV. All results were acquired at a nominal photoelectron take off angle of 90º, where the take off angle is defined as the angle between the surface normal and the axis of the analyzer lens. An array of 8×6 points covering an area of 5.88 mm^2 of the sample surface were analyzed using a spot ize of 400 μm. This was done to avoid sample degradation caused by the incident X-rays or the exiting photoelectrons. The S_{2p} spectra were summed in order to increase the spectral signal-to-noise ratio.

Control experiments of the I-V characteristics:

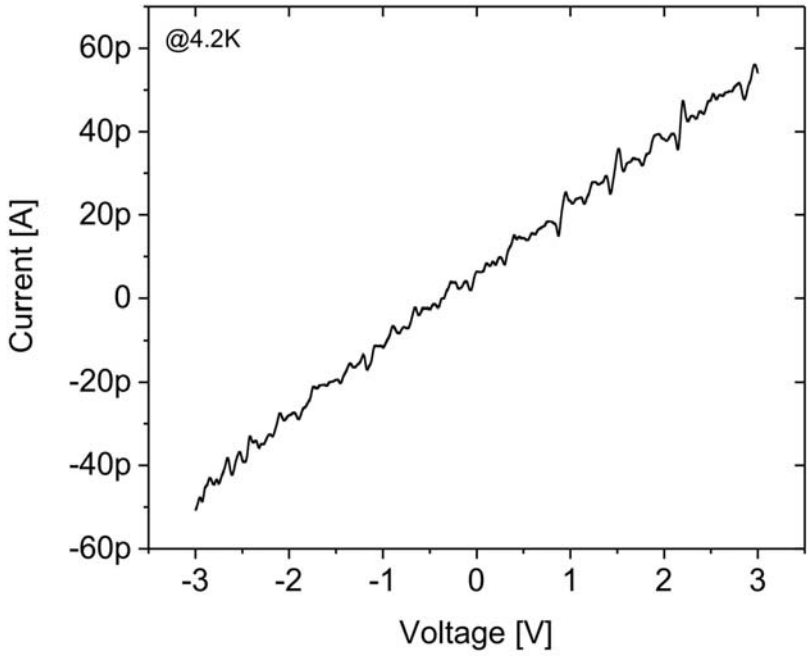


Figure S4: Same I-V characteristic of the device before functionalization with molecules, as presented in Fig. 7. Note the strongly expanded current scale.

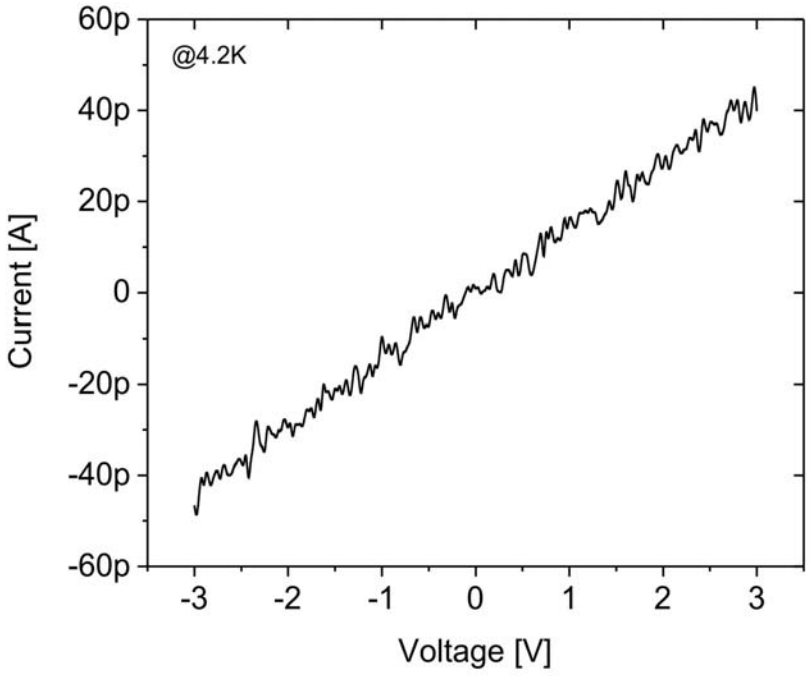


Figure S5: I-V characteristic of the device presented in Fig. 7 after removing all organic surface adsorbates by treatment with 2 x 60s, 75 W, O2-plasma.

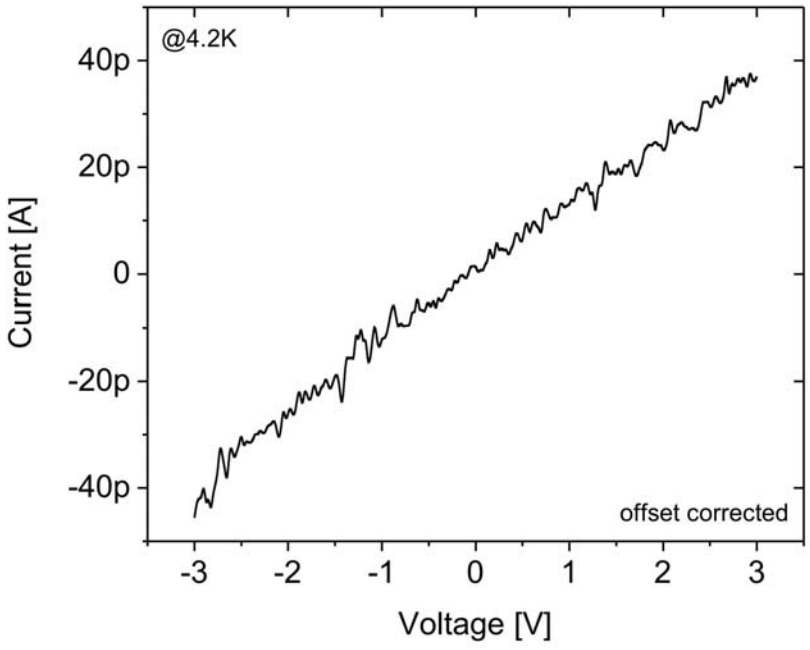


Figure S6: I-V characteristic of a similar, completely independently processed sample having Pt-electrodes, treated with the same functionalization procedure but without molecules. Electrode material: 1.5 nm Ti / 7 nm Pt, evaporated from 65°.

References

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