Supplementary Information

Add a Third Hook: S-Acetyl Protected Oligophenylene Pyridine Dithiols as Advanced Precursors for Self-Assembled Monolayers

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S1. General Methods - Used Reagent, Solvents and Analytical Devices

All commercially available starting materials were of reagent grade and used as received. Absolute tetrahydrofuran (THF) was purchased from *Fluka*, stored over 4 Å molecular sieves, and handled under Argon. Dichloromethane and all other used solvents were of technical grade and distilled prior to use. For microwave reactions a *Biotage Initiator 8* was used. Column chromatography purifications were carried out on *silica gel 60* (particle size 40-63 μm) from *Fluka*. Deuterated solvents were purchased from *Cambridge Isotope Laboratories*. ^{1}H and ^{13}C NMR spectra were recorded with a *Bruker DMX 400* instrument (^{1}H resonance 400 MHz) or a *Bruker DRX 500* instrument (^{1}H resonance 500 MHz) at 298 K. Electron Impact (EI) mass spectra were recorded on a *Finnigan MAT 95Q* by H. Nadig. Elemental analyses were performed by W. Kirsch on a *Perkin-Elmer Analysator 240*.

S2. Synthesis Procedures and Analytical Data for the OPBs 1 - 3 and OPPs 4 - 6

General Procedure for 1 and 4

The reactions were carried out in 3 mmol scale. The corresponding dibromide (1 eq.) was dissolved in 10 mL degassed THF and 3 eq. potassium thoiacetate were added. The mixture was stirred under argon over night. After quenching the reaction with 20 mL water the mixture was extracted three times with 20 mL dichlormethan and the combined organic phases were dried over $MgSO_4$. After removing the solvent in vacuum the product was purified by column chromatography (silica, 6:1, c-hexane:ethyl acetate). The products were yielded as colorless solids.

1 S,S'-(1,3-phenylenebis(methylene)) diethanethioate

Yield: 98%

^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.25-7.16 (m, 4H, arom-*H*); 4.09 (s, 4H, benz-*H*); 2.35 (s, 6H, C*H*$_3$)

^{13}C-NMR (100MHz, $CDCl_3$) δ = 195.0; 138.0; 129.2; 129.0; 127.8; 33.2; 30.3

MS EI(m/z (%)): 254 (30)[M^+], 211 (95)[M^+-Ac), 179(100) (M^+-SAc)

EA calc C=56.66, H=5.55, N=0.0; found: C=56.68, H=5.65, N=0.0

4 S,S'-(pyridine-2,6-diylbis(methylene)) diethanethioate

Yield: 96%

^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.56(t, $^3J_{HH}$=7.7 Hz, 1H, arom*H*); 7.21(d, $^3J_{HH}$=7.7 Hz, 2H, arom*H*); 4.22 (s, 4H, benz-*H*); 2.36(s, 6H, C*H*$_3$)

^{13}C-NMR (100MHz, $CDCl_3$) δ = 209.0; 157.2; 137.5; 121.7; 35.3; 30.3

MS EI(m/z (%)): 255 (1)[M^+], 213 (100)[M^+-Ac), 170 (47)(M^+-Ac_2)

EA calc: C=51.74; H=5.13; N=5.49; found: C=51.77; H=5.12; N=5.49

General Procedure for Suzuki coupling:

The reactions were carried out in 1 mmol scale. A microwave tube containing a magnetic stirrer and purged with argon was charged with phenylboronic acid (1.5 eq.), freshly grounded anhydrous K_3PO_4 (2.0 eq.), and **10**; S,S'-((5-bromo-1,3-phenylene)bis(methylene)) diethanethioate or **16**; (((4-bromopyridine-2,6-diyl)bis(methylene)) diethanethioate) and 2-dicyclohexyl phosphino-2',6'-dimethoxybiphenyl (S-Phos) (12.5 mol%). 5 mL dry toluene were added and the reaction mixture was degassed with argon for 10 min. After adding $Pd(OAc)_2$ (10 mol%) the reaction vessel was closed and the mixture was heat to 180 °C under microwave irradiation for 1.5 hours. After cooling down to room temperature the reaction mixture was filtered through thin silica pad elucidate with ethyl acetate (EE), concentrate under vacuum. The compounds were purified by column chromatography (silica, 6:1, c-hexane:ethyl acetate) and the products yielded as colorless solids.

(2) S,S'-([1,1'-biphenyl]-3,5-diylbis(methylene)) diethanethioate

Yield: 53%

^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.58-7.56 (m, 2H, arom*H*); 7.46-7.43(m, 2H, arom*H*); 7.41 (m, 2H, arom*H*); 7.38-7.35 (m, 1H, arom*H*); 7.16 (s, 1H), arom*H*); 4.15(s, 4H, benz-*H*); 2.35(s, 6H, C*H*$_3$)

^{13}C-NMR (100MHz, $CDCl_3$) δ = 195.0; 142.1; 140.2; 138.6; 128.7; 128.1; 127.6; 127.2; 126.7; 33.3; 30.37.

MS EI(m/z (%)): 330 (79)[M^+], 255 (100)[M^+-Ac), 212 (71) (M^+-SAc)

EA calc: C=65.42; H=5.49; N=0.0 found: C=66.08; H=5.89; N=0.0

(3) S,S'-([1,1':4',1''-terphenyl]-3,5-diylbis(methylene)) diethanethioate

Yield: 51%

^{1}H-NMR (400 MHz, $CDCl_3$) δ = 7.70 – 7.65 (m, 6H, arom*H*); 7.50 – 7.46 (m, 4H, arom*H*); 7.40 - 7,37 (m, 1H, arom*H*); 7.22 (s, 1H), arom*H*); 4.10 (s, 4H, benz-*H*); 2.40 (s, 6H, C*H*$_3$).

^{13}C-NMR (100MHz, $CDCl_3$) δ = 195.0; 141.6; 140.6; 140.5; 139,3; 138.7; 128.8; 128.2; 127.6; 127.5; 127.4; 127.1; 126.6; 33.3; 30.4.

MS EI(m/z (%)): 406 (100)[M^+], 331 (63)[M^+-Ac), 288 (42) (M^+-SAc)

EA calc: C=70.90; H=5.45; N=0.0 found: C=70.94; H=5.81; N=0.0

(5) S,S'-((4-phenylpyridine-2,6-diyl)bis(methylene)) diethanethioate

Yield: 54%

^{1}H-NMR (400 MHz, $CDCl_3$) δ =7.61-7.60(m, 2H, arom*H*); 7.47-7.44(m, 5H, arom*H*); 4.28(s, 4H, benz-*H*); 2.37(s, 6H, CH_3)

^{13}C-NMR (100MHz, $CDCl_3$) δ = 195.0; 157.7; 150.2; 137.9; 129.2; 129.0; 127.1; 119.8; 35.4; 30.3.

MS ESI (m/z): 354 (M^++Na)

EA calc: C=61.6; H=5.17; N=4.23 found: C=61.55; H=5.37;N=4.17

(6) S,S'-((4-([1,1'-biphenyl]-4-yl)pyridine-2,6-diyl)bis(methylene)) diethanethioate

Yield: 51%

^{1}H-NMR (400 MHz, $CDCl_3$) δ =7.70(m, 4H, arom*H*); 7.65-7.62(m, 2H, arom*H*); 7.49-7.46(m, 4H, arom*H*); 7.40-7.39(m, 1H, arom*H*); 4.30(s, 4H, benz-CH_2); 2.38(s, 6H, CH_3).

^{13}C-NMR (100MHz, $CDCl_3$) δ = 195.0; 157.8; 149.7; 142.1; 140.2; 136.6; 128.9; 127.8; 127.7; 127.5; 127.1; 119.6; 35.5; 30.3

MS ESI m/z: 430 (M^++Na)

EA calc: C=67.78;H=5.17; N=3.44 found: C=67.45; H=5.35; N=3.50

Figure S1: C 1s HRXPS spectra of **1**-**6** on Au acquired at photon energies of 350 eV (left panel) and 580 eV (right panel) along with the corresponding fits by several individual components and a background. For direct comparison, the spectra of DDT/Au (blue) and HDT/Au (red) are included, overlaying with the spectra of **3**/Au and **6**/Au in both panels. DDT/Au and HDT/Au served as references to determine the thickness and effective packing density of **1**-**6** on Au.