**Supplementary Information to:**

# Electronic transport properties of individual 4,4'-bis(mercaptoalkyl)-biphenyl derivatives measured in STM-based break junctions

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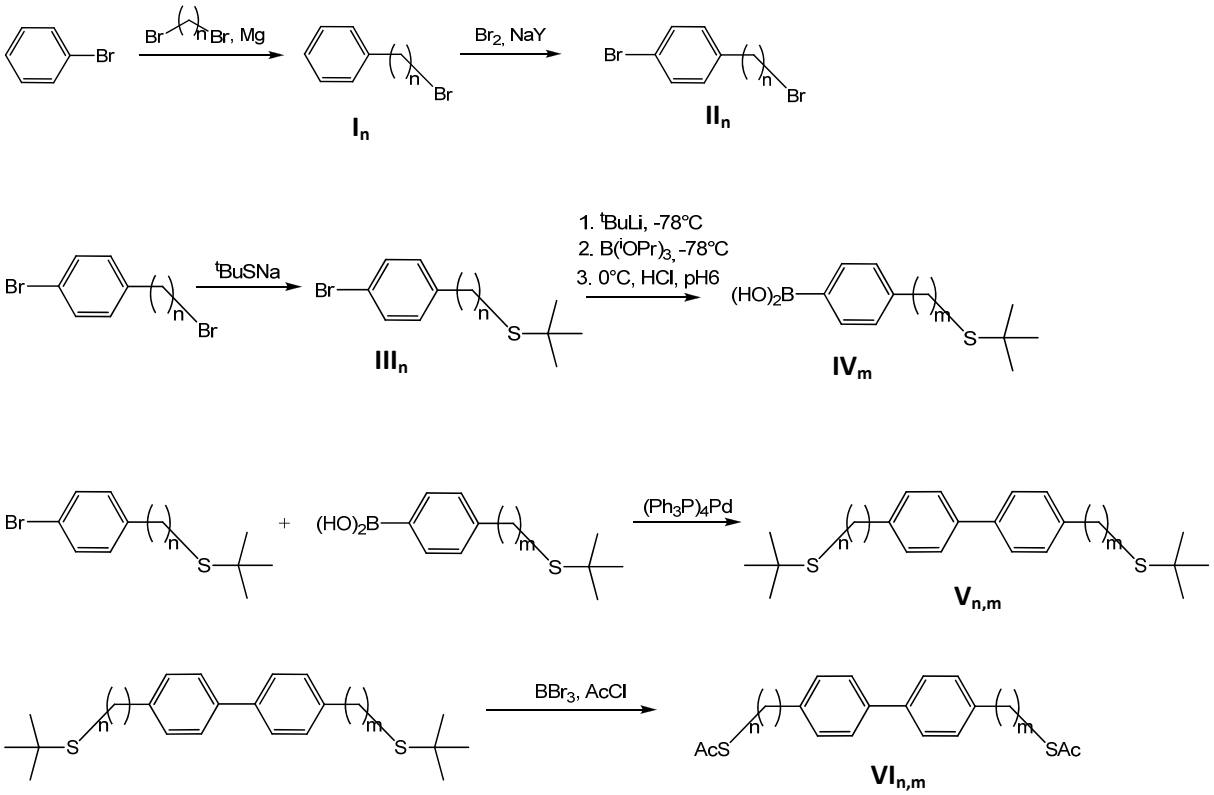
## Preparation of acetyl protected 4,4'-bis(mercaptoalkyl)-biphenyl derivatives

### General Reaction Scheme for the preparation of mBPn:




### General

Solvents were purchased from Aldrich and if necessary purified and dried by standard laboratory techniques. The following chemicals were used as purchased from Aldrich without further purification: bromobenzene, 1,7-dibromoheptane, 1,9-dibromonone, 3-bromopropybenzene, 5-bromopentylbenzene, 1-bromo-4-(bromomethyl)benzene, bromine, sodium 2-methyl-2-propanethiolate, acetylchloride, acetic acid, Na*S*t*Bu*, *t*-BuLi (1.7 mol/L in hexane), NaY. The following chemicals were purchased from Strem: CuBr, LiBr, Mg turnings, $(i\text{PrO})_3\text{B}$, $(\text{Ph}_3\text{P})_4\text{Pd}$. NMR spectra were obtained using following instruments: Varian Mercury 200 ($^1$H: 200.389 MHz), Varian Mercury 300 ($^1$H: MHz); Bruker 400 ($^1$H: 400.13 MHz, $^{13}$C: 100,6 MHz) and Varian Unity 500 ($^1$H: 499.843 MHz, $^{13}$C: 125.697 MHz; $^{11}$B: 160.346 MHz). Mass spectra were recorded with the following machine:

Finnigan MAT-95. Elemental analysis was performed with the following instrument: Vario EL Elemental Analyzer.

**Preparation of the precursors (In, IIn, IIIn, IVm)**

**n-Bromoalkylbenzene ($I_n$, n = 7, 9)**

The synthesis of the n-bromoalkylbenzene derivatives (n= 7, 9) was performed according to a procedure published by Rong et al.[1] The reactions were carried out in a nitrogen atmosphere utilizing conventional *Schlenk*-technique. This scheme also worked for the preparation of the n = 3, 5 derivatives, which have also been obtained commercially.

Catalyst preparation: For a typical run 5 ml thf are added to 2.5 mmol (0.36 g) CuBr and 5 mmol of anhydrous LiBr (0.43 g), previously heated in high vacuum ($10^{-2}$ mbar) at 60-70°C for about 2h. This mixture is stirred for further 2h at ambient temperature giving a homogeneous green solution. This catalyst solution is used for the further alkylation steps.

Alkylation: For the preparation of the Grignard reagent a solution of bromobenzene (48.5 mmol, 1 eq.) in 90 ml thf is slowly added to metallic magnesium (49.9 mmol, 1.03 eq.) in thf, activated with 1-2 drops of dichloroethane. After addition is completed the reaction mixture is refluxed for about 1 h and filtered into a dropping funnel as soon as ambient temperature is achieved.

The thus obtained Grignard reagent is dropwise added at 0°C to a solution containing 90 ml thf, 1,3-dibromoalkane (193 mmol, 4 eq.) and 7 ml of the catalyst solution. After complete addition the reaction mixture is allowed to warm up to room temperature over night while stirring. Following this, saturated $NH_4Cl$ is added and the n-bromoalkylbenzene is extracted with 2x30 ml $Et_2O$, washed with water and brine, and dried over $Na_2SO_4$. The n-bromoalkylbenzene derivatives are obtained as colorless oils (typical yields: 45% - 60%). Purification is achieved by high vacuum short path distillation with liquid $N_2$ cooling of the distillate flask.

**7-Bromoheptylbenzene ($I_7$):** $^1$H-NMR (200 MHz, $C_6D_6$) $\delta$ = 0.94 – 1.20 (m, 6 H, $CH_2$); 1.30 – 1.50 (m, 4 H, $CH_2$); 2.42 (t, 2 H, $C_{benzene}CH_2$); 2.90 (t, 2 H, $CH_2Br$); 7.01-7.19 (m, 5H, $C_{benzene}H$) ppm. **9-Bromononylbenzene ($I_9$):** $^1$H-NMR (300 MHz, $C_6D_6$) $\delta$ = ): 0.89 – 1.20 (m, 10 H, $CH_2$); 1.37 – 1.58 (m, 4 H, $CH_2$); 2.44 (t, 2 H, $C_{benzene}CH_2$); 2.91 (t, 2 H, $CH_2Br$); 7.00-7.19 (m, 5H, $C_{benzene}H$) ppm.

**1-bromo-4-(n-bromoalkyl)benzene ($II_n$, n = 3, 5, 7, 9)**

Selective *para*-bromination of the n-bromoalkylbenzene was achieved by applying a procedure published by K. Smith et al.[2]. For a typical run 35g Zeolith NaY (calcinated at 550°C for 24h) is suspended in 250 ml $CH_2Cl_2$ and 50 mmol (1eq.) 3-bromoalkylbenzene is added. This suspension is stirred for 10 min in the dark. Afterwards this suspension is treated dropwise with a solution of 55 mmol (1.1 eq.) bromine in 60 ml $CH_2Cl_2$ while rapid stirring. After the addition is completed the mixture was further stirred over night in the dark at room temperature. The suspension is then filtered and the zeolith is washed three times with 60 ml $CH_2Cl_2$. The combined filtrates are evaporated in high vacuum yielding 1-bromo-4-(n-bromoalkyl)benzene as a pale yellow liquids. The products were analyzed by $^1$H-NMR spectroscopy, and used as obtained for the further reaction steps. Typical yields are 85 - 95%. Especially in the case of the 1-bromo-4-(9-bromononyl)benzene

purification via high vacuum short path distillation with liquid $N_2$ cooling of the distillate flask was necessary, yielding colorless liquids.

**1-bromo-4-(3-bromopropyl)benzene ($II_3$)**: $^1$H-NMR (200 MHz, $C_6D_6$) $\delta$ = 1.56 (quint, *J* = 6.8 Hz, 2H, m, $CH_2$); 2.20 (2H, t, *J* = 7.0 Hz, $C_{benzene}CH_2$); 2.80 (2H, t; *J* = 6.6 Hz, $CH_2Br$); 6.52 (2H, *pseudo*-d, $C_{benzene}H$); 7.19 (2H, *pseudo*-d, $C_{benzene}H$) ppm. **1-bromo-4-(5-bromopentyl)benzene ($II_5$)**: $^1$H-NMR (200 MHz, $C_6D_6$) $\delta$ = 0.94 -1.23 (4 H, m, $CH_2$); 1.40 (2 H, quint, *J* = 7.1 Hz, $CH_{2CH2Br}$); 2.11 (2 H, t, *J* = 7.1 Hz, $C_{benzene}CH_2$); 2.89 (2H, t; *J* = 6.6 Hz, $CH_2Br$); 6.60 (2H, *pseudo*-d, $C_{benzene}H$); 7.25 (2H, *pseudo*-d, $C_{benzene}H$). **1-bromo-4-(7-bromoheptyl)benzene ($II_7$):** $^1$H-NMR (200 MHz, $C_6D_6$) $\delta$ = 0.90 - 1.19 (6 H, m, $CH_2$); 1.21 – 1.38 (m, 2H, $CH_2$); 1.47 (2 H, quint, J ≈ 7.0 Hz, $CH_{2CH2Br}$); 2.22 (2H, t, *J* ≈ 7.0 Hz, $C_{benzene}CH_2$); 2.95 (2H, t; *J* = 6.6 Hz, $CH_2Br$); 6.68 (2H, *pseudo*-d, $C_{benzene}H$); 7.27 (2H, *pseudo*-d, $C_{benzene}H$) ppm. **1-bromo-4-(9-bromononyl)benzene ($II_9$)**: $^1$H-NMR (200 MHz, $C_6D_6$) $\delta$ = 0.93- 1.20 (10 H, m, $CH_2$); 1.24 – 1.60 (m, 4H, $CH_2$); 2.29 (2H, t, *J* ≈ 7 Hz, $C_{benzene}CH_2$); 2.99 (2H, t; *J* = 6.6 Hz, $CH_2Br$); 6.69 (2H, *pseudo*-d, $C_{benzene}H$); 7.29 (2H, *pseudo*-d, $C_{benzene}H$).

**(*n*-(4-Bromophenyl)alkyl)(*tert*-butyl)sulfane ($III_n$, n= 1, 3, 5, 7, 9)**

Conversion of the bromo-substituent into the *tert*-butylthioether group was achieved adopting a procedure published by A. Blaszczyk et al. [3]. For a typical run 11 mmol (1 eq.) of 1-bromo-4-(n-alkyl)benzene dissolved in 50 ml dry thf are treated portionwise with 22 mmol (2eq.) sodium 2-methyl-2-pronaethiolate. This reaction mixture was refluxed for about 16 h. Afterwards the mixture was poured into saturated NaCl-solution, the organic products were extracted with $CH_2Cl_2$, washed with water and dried over $Na_2SO_4$. After evaporation of the solvent the (n-(4-bromophenyl)alkyl)(*tert*-butyl)sulfane derivatives were obtained nearly quantitavely as colorless oily liquids. In some cases purification utilizing high vacuum short path distillation with liquid $N_2$ cooling of the distillate flask was necessary.

**(4-bromobenzyl)(*tert*-butyl)sulfane ($III_1$):** $^1$H-NMR (200 MHz, $C_6D_6$) $\delta$ = 1.11 (9H, s, $C_{t\mathrm{Bu}}CH_3$); 3.31 (2 H, s, $CH_2$); 6.88 (2H, *pseudo*-d, $C_{benzene}H$); 7.13 (2H, *pseudo*-d, $C_{benzene}H$) ppm. **(3-(4-bromophenyl)propyl)(*tert*-butyl)sulfane ($III_3$):** $^1$H (200 MHz, $C_6D_6$) $\delta$ = 1.18 (9H, s, $C_{t\mathrm{Bu}}CH_3$); 1.60 (2 H, quint, *J* = 7.4 Hz; $CH_2$); 2.20 – 2.40 (4 H, m, $C_{benzene}CH_2CH_2$); 6.63 (2H, *pseudo*-d, $C_{benzene}H$); 7.20 (2H, *pseudo*-d, $C_{benzene}H$) ppm. **(5-(4-bromophenyl)pentyl)(*tert*-butyl)sulfane ($III_5$)**: $^1$H-NMR (200 MHz, $C_6D_6$) $\delta$ = 1.22 (9H, s, $C_{t\mathrm{Bu}}CH_3$); 1.20 – 1.40 (4 H, m, $CH_2$); 1.48 (2 H, quintet, *J* = 7.4 Hz; $C_{benzene}CH_2CH_2$); 2.20 (2 H, t, J = 7.4 Hz, $C_{St\mathrm{Bu}}CH_2$); 2.36 (2 H, t, J = 7.3 Hz, $C_{benzene}CH_2$); 6.65 (2H, *pseudo*-d, $C_{benzene}H$); 7.25 (2H, *pseudo*-d, $C_{benzene}H$) ppm. **(7-(4-bromophenyl)heptyl)(*tert*-butyl)sulfane ($III_7$)**: $^1$H (300 MHz, $C_6D_6$) $\delta$ = 1.21 (9H, s, $C_{t\mathrm{Bu}}CH_3$); 1.01 – 1.37 (8 H, m, $CH_2$); 1.50 (2 H, quint, *J* = 7.5 Hz; $C_{benzene}CH_2CH_2$); 2.20 (2 H, t, J = 7.6 Hz, $C_{St\mathrm{Bu}}CH_2$); 2.39 (2 H, t, J = 7.2 Hz, $C_{benzene}CH_2$); 6.65 (2H, *pseudo*-d, $C_{benzene}H$); 7.22 (2H, *pseudo*-d, $C_{benzene}H$). **(9-(4-bromophenyl)nonyl)(*tert*-butyl)sulfane ($III_9$):** $^1$H-NMR (200 MHz, $C_6D_6$) $\delta$ = 1.24 (9H, s, $C_{t\mathrm{Bu}}CH_3$); 1.09 – 1.40 (12 H, m, $CH_2$); 1.56 (2 H, m; $C_{benzene}CH_2CH_2$); 2.27 (2 H, t, *J* = 7.6 Hz, $C_{StBu}CH_2$); 2.42 (2 H, t, *J* = 7.2 Hz, $C_{benzene}CH_2$); 6.67 (2H, *pseudo*-d, $C_{benzene}H$); 7.20 (2H, *pseudo*-d, $C_{benzene}H$) ppm.

**4-(n-(*tert*-butylthio)alkyl)phenylboronic acid ($IV_m$, m = 1, 3, 5)**

The preparation of the boronic acid ester derivatives has been adopted from [4]. For a typical run 6.0 mmol (1eq.) (n-(4-bromophenyl)alkyl)(tert-butyl)sulfane are solved in 30 ml dry $Et_2O$ and 55.5 ml (1.3 eq.) of 1.7 mol/L *t*-BuLi are added dropwise at -78°C, yielding an orange solution. The reaction was monitored by TLC. After complete reaction of the (n-(4-bromophenyl)alkyl)(tert-butyl)sulfane this solution was slowly added to a solution of 17.4 mmol (2.5 eq.) $B(iOPr)_3$ solved in 20 ml $Et_2O$ at -78°C utilizing commonly *Schlenk* technique. The reaction mixture is stirred for about further 45 min at -78°C (TLC control) and hydrolyzed by pouring the reaction mixture into 25 ml ice water. 2M HCl is added until the pH ≈ 6. The water phase is extracted with $Et_2O$ and the combined organic phases are evaporated in high vacuum for several hours. $^1$H-NMR spectroscopic analysis of the thus obtained colorless solids clearly proofed the existence of the desired boronic acid esters by means of the characteristic *pseudo*-duplets of the $((OH)_2B$-)-substituted benzene-unit at $\delta$ = 7.5 ppm and $\delta$ = 8.3 ppm, though beside the boronic acid esters especially in the case of the 4-(*tert*-butylthiopentyl)phenylboronic acid (**$IV_5$**) up to 50% of not nearer investigated side products were observed. In the case of 4-(tert-butylthiomethyl)phenylboronic recrystallization in a small amount of water yielded the pure derivative. Nevertheless, several Suzuki-coupling reactions performed by us using the solids as obtained in this step, yielded the desired biphenyl derivatives, though in low yields but, after recrystallization or chromatography, as pure products (see below) so that we decided to use the obtained raw products for the next steps.

**4-(*tert*-butylthiomethyl)phenylboronic acid ($IV_1$)**: $^{11}$B(160 MHz, $C_6D_6$): 29.0. **4-(3-(*tert*-butylthio)propyl)phenylboronic acid ($IV_3$):** $^{11}$B-NMR (160 MHz, $C_6D_6$) $\delta$ = 29.2 ppm. **4-(5-(*tert*-butylthio)pentyl)phenylboronic acid ($IV_5$):** $^{11}$B-NMR (160 MHz, $C_6D_6$) $\delta$ = 29.1 ppm.

***Suzuki* Coupling Reaction ($V_{n,m}$)**

Suzuki-coupling was performed according to Suzuki et al. [5] under nitrogen with slight modifications.

The in the above described step obtained **$IV_m$** raw products (1 eq.) are dissolved in degassed EtOH (approx. 0.5 g/ml EtOH) and added to a solution containing 0.9 eq. **$III_n$**, 0.03 eq. $Pd(Ph_3)_4$ and 2 M $Na_2CO_3$-solution (10 ml per 1 eq.) solved in dry thf (approx. 0.15 g **$III_n$**/ ml). This reaction mixture is refluxed and the proceeding of the reaction is monitored by TLC. After the reaction is completed the organic phase is separated and the solvent is removed in high vaccum. The resulting residue is washed with EtOH several times until the residue remains colorless. For further purification from possible side-products of the Suzuki-coupling reaction the colorless amorphous residue was recrystallized from hexane, yielding the $V_{n,n}$ derivatives as colorless crystals.

**4,4'-bis(5-(*tert*-butylthio)pentyl)biphenyl ($V_{5,5}$)**: $^1$H-NMR ($C_6D_6$, 400 MHz) $\delta$ = 1.32 (18 H, s, *t*-Bu); 1.36 (4 H, m, $CH_2$); 1.72 (8 H, m, *J* = 7.3, $CH_2$); 2.4 (4 H, tr, $C_{StBu}CH_2$); 2.5 (4 H, tr, $C_{benzene}CH_2$); 7.1 (4 H, *pseudo*-d, $C_{benzene}H$); 7.5 (4 H, *pseudo*-d, $C_{benzene}H$) ppm. $^{13}$C-NMR ($C_6D_6$, 100 MHz) $\delta$ = 28.3 ($CH_2$); 29.0 ($CH_2$); 30.0 ($CH_2$); 31.0 ($CH_3$); 31.3 ($CH_2$); 35.6 ($CH_2$); 41.3 ($C_{Me3}$); 127.6 ($C_{benzene}H$); 128.1 ($C_{benzene}H$); 139.1 ($C_{benzene}$); 141.4 ($C_{benzene}$) ppm. MS (EI, PT: 150°C): 470 ($M^+$, 54); 414($M^+$ - *t*Bu, 23); 357 ($M^+$ - 2 *t*bu, 78); 323 ($M^+$- *t*Bu, S*t*Bu, 34); 312 ($M^+$ - $(CH_2)_5$S*t*Bu, 13); 222 (8, biphenyl-$(CH_2)_5$); 88 (16, S*t*Bu).

***tert*-butyl(3-(4'-(7-(tert-butylthio)heptyl)biphenyl-4-yl)propyl)sulfane ($V_{3,7}$):** $^1$H-NMR ($C_6D_6$, 400 MHz) $\delta$ = 1. 23 (9 H, s, *t*Bu); 1.23 – 1.35 (6 H, m, $CH_2$); 1. 28 (9 H, s, *t*Bu); 1.52 (4 H, m, $CH_2$); 1.86 (2 H, m, $CH_2$); 2.42 (4 H, tr, $C_{StBu}CH_2$); 2.49 (2 H, tr, $C_{benzene}CH_2$); 2.60 (2 H, tr, $C_{benzene}CH_2$); 7.1 (4 H, m, $C_{benzene}H$); 7.5 (4 H, m, $C_{benzene}H$) ppm. ***tert*-butyl((4'-(9-(tert-butylthio)nonyl)biphenyl-4-yl)methyl)sulfane ($V_{1,9}$)**: $^1$H-NMR ($C_6D_6$, 200 MHz) $\delta$ = 1. 23 (9 H, s, *t*Bu); 1. 25 (9 H, s, *t*Bu); 1.2 – 1.4 (10 H, m, $CH_2$); 1.58 (4 H, m, $CH_2$); 2.41 (2 H, tr, $C_{StBu}CH_2$); 2.49 (2 H, tr, $C_{benzene}CH_2$); 3.60 (2 H, s, $C_{benzene}CH_2$); 7.34 (4 H, m, $C_{benzene}H$); 7.47 (4 H, m, $C_{benzene}H$) ppm.

**Conversion into the acetyl-protected derivatives ($VI_{n,m}$)**

The conversion of the S*t*Bu moiety into to the SAc group was performed according to [6] with slight modifications.

Preparation of **$VI_{5,5}$**:

To a mixture of **$V_{5,5}$** (1.3 g, 2.76 mmol, 1 eq.) acetyl chloride (3.06 ml) and toluene (12 ml) was added $BBr_3$ (6.8 ml of 1 M $CH_2Cl_2$ solution). This reaction mixture was stirred for about 2h at room temperature. The dark red reaction mixture was poured into ice (60 g), the phases were separated and the water phase was further extracted with a mixture of ether and pentane (1:2). The combined extracts were washed with 40 ml water and dried over $Na_2SO_4$. The solvent amount was reduced in high vacuum and the resulting concentrated liquid was placed in a fridge yielding 0.8 g (66 %) of **$VI_{5,5}$** as colorless crystals.

**S,S'-5,5'-(biphenyl-4,4'-diyl)bis(pentane-5,1-diyl) diethanethioate ($VI_{5,5}$): $^1$H-NMR ($C_6D_6$, 400 MHz)** $\delta$ = 1. 14 – 1.22 (4 H, m, $CH_2$); 1.38 – 1.47 (8 H, m, $CH_2$); 1.87 (6 H, s, $COCH_3$); 2.42 (4 H, tr, $C_{benzene}H_2$); 2.73 (4 H, tr, $SCH_2$); 7.10 (4 H, *pseudo*-d, $C_{benzene}H$); 7.52 (4 H, *pseudo*-d, $C_{benzene}H$). **$^{13}$C-NMR ($C_6D_6$, 100 MHz)** $\delta$ = 28.4 ($CH_2$); 29.0 ($CH_2$); 29.8 ($CH_3$); 30.0 ($CH_2$); 31.0 ($CH_2$); 35.5 ($CH_2$); 127.2 ($C_{benzene}H$); 127.1 ($C_{benzene}H$); 139.0 ($C_{benzene}H$); 139.1 ($C_{benzene}H$); 141.3 ($C_{benzene}H$); 194.2 (CO). **Mass spectrometry (EI)**: 442 ($M^+$, 82); 357 ($M^+$-2$COCH_3$, 100); 298 ($M^+$-C5SAc 60); 180 (BP-C2, 25), 167 (BP-$CH_2$, 66), 101 ($C_5H_{10}S$, 100); 91 ($C_6H_4$-$CH_2$, 20). **Elemental Analysis:** calc.: C: 70.5, H: 7.7; exp.: C: 70.8; H: 7.6.

Preparation of **$VI_{3,7}$**:

To a mixture of **$V_{3,7}$** (1.2g, 2.55 mmol, 1 eq.) acetyl chloride (2.83 ml) and toluene (12 ml) was added $BBr_3$ (6.3 ml of 1 M $CH_2Cl_2$ solution). This reaction mixture was stirred for about 2 h at room temperature. The dark red reaction mixture was poured into ice (55 g), the phases were separated and the water phase was further extracted with a mixture of ether and pentane (1:2). The combined extracts were washed with 40 ml water and dried over $Na_2SO_4$. The solvent amount was reduced in high vacuum and the resulting concentrated liquid was placed in a fridge yielding nearly colorless crystals which were further purified by coloumn chromatography with pentane/$Et_2O$ (5:2).

**S-3-(4'-(7-(acetylthio)heptyl)biphenyl-4-yl)propyl ethanethioate ($VI_{3,7}$): $^1$H-NMR ($C_6D_6$, 400 MHz)** $\delta$ = 1. 10 – 1.23 (6 H, m, $CH_2$); 1.38 – 1.47 (2 H, m, $CH_2$); 1.49 – 1.56 (2 H, m, $CH_2$); 1.71 – 1.81 (2 H, quintett, $CH_2$); 1.88 (3 H, s, $COCH_3$); 1.89 (3 H, s, $COCH_3$); 2.44 – 2.54 (4 H, m, $C_{benzene}H_2$); 2.77 (4 H, tr, $SCH_2$); 7.02 (4 H, *pseudo*-d, $C_{benzene}H$); 7.47 – 7.55 (4 H, m, $C_{benzene}H$) ppm.**$^{13}$C-NMR ($C_6D_6$, 100 MHz)** $\delta$ =

28.6 ($CH_2$); 28.8 ($CH_2$); 29.2 ($CH_2$); 29.3 ($CH_3$); 29.9 ($CH_2$); 30.0 ($CH_2$); 31.5 ($CH_2$); 34.5 ($CH_2$); 35.7 ($CH_2$); 127.1 ($C_{benzene}H$); 127.2 ($C_{benzene}H$); 129.0 ($C_{benzene}H$); 129.1 ($C_{benzene}H$); 138.9 ($C_{benzene}H$); 139.3 ($C_{benzene}H$); 140.1 ($C_{benzene}H$); 141.7 ($C_{benzene}H$); 194.0 (CO); 194.2 (CO).ppm. **Mass spectrometry (EI):** 442 ($M^+$, 60); 262 ($M^+$-2SAc, -2 $CH_2$, 100); 249 (BP-C7, 67); 207 (BP-C4, 88), 193 (BP-C3, 15), 91 ($C_6H_4$-$CH_2$, 30); 77 ($C_6H_4$, 13). **Elemental Analysis:** calc: C: 70.5, H: 7.7 ; exp.: C: 70.8, H: 7.6.

Preparation of **$VI_{1,9}$**:

To a mixture of **$V_{3,7}$** (0.6 g, 1.27 mmol, 1 eq.) acetyl chloride (2.83 ml) and toluene (6 ml) was added $BBr_3$ (6.3 ml of 1 M $CH_2Cl_2$ solution). This reaction mixture was stirred for about 2 h at room temperature. The dark red reaction mixture was poured into ice (55 g), the phases were separated and the water phase was further extracted with a mixture of ether and pentane (1:2). The combined extracts were washed with 40 ml water and dried over $Na_2SO_4$. The solvent amount was reduced in high vacuum and the resulting concentrated liquid was placed in a fridge yielding nearly colourless crystals which were further purified by column chromatography with pentane/$Et_2O$ (5:2).

**S-(4'-(9-(acetylthio)nonyl)biphenyl-4-yl)methyl ethanethioate ($VI_{1,9}$): $^1$H-NMR ($C_6D_6$, 300 MHz)** $\delta$ = 1.10 - 1.25 (8 H, m, $CH_2$); 1.37 - 1.47 (2 H, m, $CH_2$); 1.48 - 1.58 (2 H, m, $CH_2$); 1.71 - 1.81 (2 H, m, $CH_2$); 1.79 (3 H, s, $COCH_3$); 1.85 (3 H, s, $COCH_3$); 2.50 (2 H, *tr*, *J* = 7.6 Hz, $C_{benzene}H_2$); 2.76 (2 H, *tr*, *J* = 7.3 Hz, $SCH_2$); 3.97 (2 H, s, $C_{benzene}CH_2S$); 7.07 – 7.12 (2 H, *pseudo*-d, $C_{benzene}H$); 7.18 (2 H, *pseudo*-d, $C_{benzene}H$ ); 7.35 – 7.44 (4 H, m, $C_{benzene}H$) ppm. **$^{13}$C-NMR ($C_6D_6$, 100)** $\delta$ = 28.9 ($CH_2$); 29.1 ($CH_2$); 29.2 ($CH_2$); 29.4 ($CH_3$); 29.9 ($CH_2$); 29.7 ($CH_2$); 29.9 ($CH_2$); 30.0 ($CH_2$); 31.6 ($CH_2$); 33.2 ($CH_2$); 35.8 ($CH_2$); 127.2 ($C_{benzene}H$); 127.3 ($C_{benzene}H$); 129.0 ($C_{benzene}H$); 129.5 ($C_{benzene}H$); 136.9 ($C_{benzene}H$); 138.6 ($C_{benzene}H$); 140.5 ($C_{benzene}H$); 142.0 ($C_{benzene}H$); 193.5 (CO); 194.1 (CO) ppm. **Mass spectrometry (EI):** 442 ($M^+$, 69); 367 ($M^+$-SAc, 100); 325 ($M^+$-SAc, -Ac, 64); 255 ($M^+$-$C_8H_{16}$SAc, 11), 180(BP-C2, 45), 167 (BP-$CH_2$, 12). **Elemental Analysis:** calc: C: 70.5, H: 7.7; exp.: C: 70.7, H: 7.6.

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## Conductance histogram of 5BP5 constructed from all obtained *I(s)* traces

For the construction of this 'all-data' histogram for the 5BP5 molecule all recorded *I(s)* traces, *i. e.* Type I, Type II, and Type III curves, were used without selection. The histogram exhibits a feature at about 0.1 nA which corresponds to the current value estimated for a single 5BP5 from the histogram constructed only of Type III curves. The quality of the data is comparable to all-data histogram [8].

[8] K. Horiguchi, S. Kurokawa, and A. Sakai, *J. Chem. Phys.* 2009, **131**, 104703.

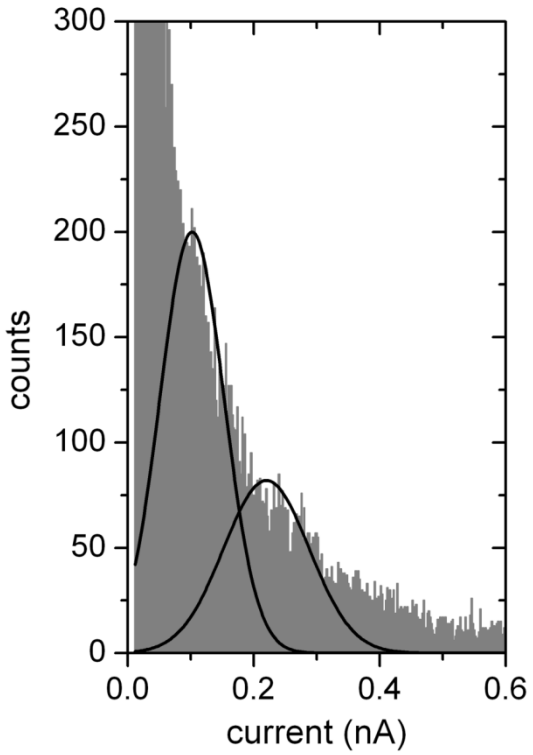


Fig. 1: All-data histogram for 5BP5.

## Statistical analysis of low conductance events for 1BP9

We analyzed the *I(s)* traces of Type III for 1BP9 in the low current region with slightly changed rules for the selection of the current plateaus. *I(s)* traces were taken into account, if they were monotonically non-increasing with respect to the absolute value of the current. A current plateau was added to the histogram if it was maintained for at least 0.1 nm movement of the STM tip during its retraction. In addition only one sharp transition was demanded, *i.e.* from higher current values to the current plateau, while the second edge was allowed to be broadened. With these selection rules additional current plateau values at low currents (below 0.2 nA) were obtained. Taking these new values into account we constructed the histogram for 1BP9 shown in Fig. 2 (bin size: 0.02 nA). The positions of the high conductance peaks did not change compared to Fig. 2c of the main paper, *i. e.* average period current, $I_p$ = 0.26 ± 0.08 nA, single molecule conductance, $G$ = 0.17 ± 0.04 nS, and single molecule resistance, $R$ = 6 ± 1 GΩ.

However, in the low current limit (below 0.2 nA) we analyzed the data also by taking a smaller bin size (0.01 nA), see inset of Fig. 2, and obtained two additional current peaks: at 0.06 nA (FWHM

0.035 nA) and the second at 0.1 nA (FWHM 0.030 nA). These low conductance peaks are assigned to the H-L/L-H contact configuration of 1BP9 resulting in $G_{HL}$(1BP9) = 0.04 ± 0.01 nS and $R_{HL}$(1BP9) = 27 ± 7 GΩ.

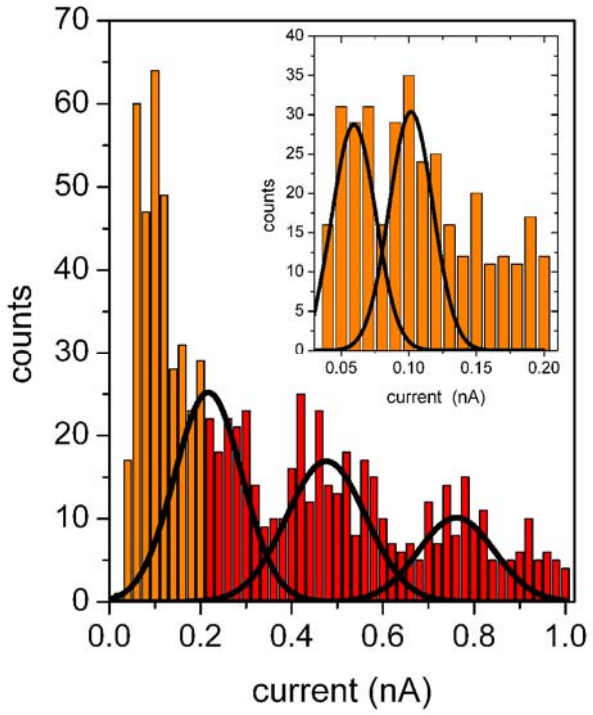


Fig. 2: Current histogram constructed from plateau values of *I(s)* traces for 1BP9 selected with slightly changed rules (see text) (bin size: 0.02 nA). Inset: low conductance events (bin size: 0.01 nA).