

Chemical control of double barrier tunnelling in α,ω -dithiaalkane molecular wires.

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Supplementary Information

	Page	
S1	Syntheses	
	Compound 1	S2-3
	Compound 2	S3-4
	Compound 3	S4-5
	Compound 4	S5-6
S2	Additional details of $I(s)$ and $I(t)$ experimental methods.	S6-S8

S1. Syntheses

Reagents were purchased from the Aldrich Chemical Company and used as received, except where otherwise stated. Solvents were dried by standard laboratory procedures and distilled under nitrogen or argon before use in the coupling reactions. Proton, ^{13}C and $^{13}\text{C}\{\text{H}\}$ NMR spectra were recorded using a Bruker Avance 400 MHz spectrometer, and were referenced to internal TMS. Mass spectra were recorded in CI positive ion mode using NH_3 .

1,4-Bis-(6-chloro-hexyl)-benzene: A mixture of 1,4-diodobenzene (3.22 g, 9.75 mmol), $[\text{PdCl}_2(\text{MeCN})_2]$ (0.13 g, 5 mol%), PPh_3 (0.256 g, 10 mol %) and CuI (0.056 g, 3 mol %) in iPr_2NH (50 cm 3) was degassed for 20 min. by Ar bubbling. The 6-chloro-hex-1-yne (3.07 g, 26.3 mmol) was added, and the mixture was refluxed for 5 h under N_2 . It was allowed to cool to room temperature and then filtered, the precipitate was washed with CH_2Cl_2 (30 cm 3) and the combined solutions were evaporated to dryness. The residue was extracted with hexanes and filtered. The solution was evaporated to dryness, yielding the crude product. Since ^1H and ^{13}C NMR spectra and CIMS indicated the presence of some 1,12-dichloro-dodeca-5,7-diyne (from oxidative dimerisation of 6-chloro-hex-1-yne), and this proved impossible to remove using chromatography, the crude product (2.236 g, 7.28 mmol) was dissolved in EtOAc (60 cm 3), treated with 10% Pd on charcoal (1.01 g) and stirred for 24 h under H_2 (8 bar) at room temperature. The solution was filtered, the solids were washed with EtOAc (3×50 cm 3) and the solvent was evaporated under reduced pressure. The product was purified by column chromatography (95:5 hexanes: EtOAc) to remove 1,12-dichlorododecane, and afford the product (1.44 g, 47%). CI MS (NH_3): m/z: 332 [$\text{M}+\text{NH}_4$] $^+$, 314 [M] $^+$. ^1H NMR data (CDCl_3) δ = 1.43, 1.77 (q's, 16H in total, $-\text{CH}_2\text{CH}_2-$), 2.58 (t, 4H, ^3J 7.7 Hz, Ar- CH_2), 3.52 (t, 4H, ^3J 6.7 Hz, - CH_2Cl), 7.08 (s, 4H, C_6H_4).

Thioacetic acid S-[6-{4-(6-acetylsulfanyl-hexyl)-phenyl}-hexyl] ester, 1: 1,4-Bis-(6-chloro-hexyl)-benzene (1.38 g, 4.44 mmol) was treated with 20 eq. NaI (13.3 g) in refluxing acetone (60 cm 3) for 24 h. The solvent was removed in *vacuo* and the product was extracted into diethyl ether (100 cm 3), filtered from sodium salts and evaporated to dryness. Crude yield 2.00 g, 91 %. This was recrystallised from hexane (1.27 g, 58 %). A portion (1.05 g, 2.13 mmol) of the recrystallised di-iodide was added to a solution of

KSAc (0.728 g, 6.39 mmol) in acetone (100 cm^3) and brought to reflux for 24 h, then allowed to cool to room temperature. The solution was filtered, the solvent was removed in *vacuo* and the crude product was recrystallised from hexane. Yield 0.661 g, 80 % (based on di-iodo compound). Elemental analysis: found; C, 66.92; H, 8.72 %. $\text{C}_{22}\text{H}_{34}\text{O}_2\text{S}_2$ requires C, 66.96; H, 8.68 %. CI MS (NH₃): m/z: 412 [M+NH₄]⁺, 395 [M+H]⁺. ¹H NMR data (CDCl₃) δ = 1.39 (m, 8H, $-\text{CH}_2-$), 1.57 (m, 8H, $-\text{CH}_2-$), 2.32 (s, 6H, $-\text{C}(\text{O})\text{CH}_3$), 2.56 (t, 4H, ³J 7.7 Hz, ArCH₂-), 2.85 (t, 4H, ³J 7.3 Hz, $-\text{CH}_2\text{S}$), 7.07 (s, 4H, C₆H₄). ¹³C NMR data (CDCl₃) δ = 29.08, 29.20, 29.54, 29.84, 31.06, 31.77, 35.83, 128.65, 140.29, 196.46.

1,4-Bis-(6-chloro-hex-1-ynyl)-2,3,5,6-tetrafluoro-benzene: A mixture of 1,4-dibromo-2,3,5,6-tetrafluoro-benzene (3.00 g, 9.74 mmol), [PdCl₂(MeCN)₂] (0.13 g, 5 mol %), PPh₃ (0.256 g, 10 mol %) and CuI (0.056 g, 3 mol %) in ⁱPr₂NH (50 cm³) was degassed for 30 min. by Ar bubbling. The 6-chloro-hex-1-yne (3.07 g, 26.3 mmol) was added, and the mixture was refluxed for 5 h under N₂. It was allowed to cool to room temperature, then filtered, the precipitate was washed with CH₂Cl₂ (30 cm³) and the combined solutions were evaporated to dryness. The residue was extracted with hexanes and filtered. The solution was evaporated to one third volume and the precipitated product was filtered off. The mother liquor was evaporated to dryness, taken up in the minimum of hot hexane and cooled to -10 °C. The product was filtered off. Combined yield 1.39 g, 38 %. Elemental analysis: found; C, 57.12; H, 4.34 %. C₁₈H₁₆F₄Cl₂ requires C, 57.01; H, 4.25 %. CI MS (NH₃): m/z: 378 [M]⁺. ¹H NMR (CDCl₃) δ = 1.81, 1.97 (m's, 8H, $-\text{CH}_2\text{CH}_2-$), 2.57 (t, 4H, ³J 6.9 Hz, C≡CCH₂), 3.60 (t, 4H, ³J 6.4 Hz, $-\text{CH}_2\text{Cl}$). ¹³C NMR data (CDCl₃) δ = 19.6, 25.7, 31.8, 44.7, 67.2, 94.3; other resonances not resolved owing to ¹⁹F-¹³C coupling.

1,4-Bis-(6-chloro-hexyl)-2,3,5,6-tetrafluoro-benzene: 1,4-Bis-(6-chloro-hex-1-ynyl)-2,3,5,6-tetrafluoro-benzene (1.14 g, 3.01 mmol) was subjected to hydrogenation (60 cm³ EtOAc, 0.52 g 10 % Pd/C, 8 bar H₂, 24 h, room temperature). The catalyst was filtered off and the solvent was removed in *vacuo*. The product was pure enough to use in the next step. Yield 1.06 g, 92 %. CI MS (NH₃): m/z: 404 [M+NH₄]⁺, 386 [M]⁺. ¹H NMR data (CDCl₃) δ = 1.38, 1.48 (m's, 8H, $-\text{CH}_2\text{CH}_2-$), 1.61 (m, 4H, $-\text{CH}_2-$), 1.78 (m, 4H, $-\text{CH}_2-$), 2.70 (t, 4H, ³J 7.6 Hz, Ar-CH₂), 3.52 (t, 4H, ³J 6.6 Hz, $-\text{CH}_2\text{Cl}$). ¹³C NMR data

(CDCl₃) δ = 22.9, 26.9, 28.8, 29.5, 32.8, 45.3, 100.0; other resonances not resolved owing to ¹⁹F-¹³C coupling.

Thioacetic acid S-[6-(6-acetylsulfanyl-hexyl)-2,3,5,6-tetrafluoro-phenyl]-hexyl ester, 2: 1,4-Bis-(6-chloro-hexyl)-2,3,5,6-tetrafluoro-benzene (0.95 g, 2.48 mmol) was treated with 20 eq. NaI (7.44 g) in refluxing acetone (60 cm³) for 24 h. The solvent was removed in *vacuo* and the product was extracted into diethyl ether (2 × 100 cm³), shaken with solid sodium thiosulfate, and evaporated to dryness. Crude yield 1.173 g, 84 %. It was added to a solution of KSAc (0.71 g, 6.2 mmol) in acetone (100 cm³) and brought to reflux for 24 h, then allowed to cool to room temperature. The solution was filtered, the solvent was removed in *vacuo* and the crude product (0.911 g, 96 %) was recrystallised from hexane. Elemental analysis: found; C, 56.81; H, 6.53 %. C₂₂H₃₀F₄O₂S₂ requires C, 56.63; H, 6.48 %. CI MS (NH₃): m/z: 410 [M]⁺. ¹H NMR data (CDCl₃) δ = 1.38 (m, 8H, -CH₂-), 1.57 (m, 8H, -CH₂-), 2.32 (s, 6H, -C(O)CH₃), 2.68 (t, ³J 7.7 Hz, ArCH₂-), 2.86 (t, ³J 7.2 Hz, -CH₂S). ¹³C NMR data (CDCl₃) δ = 22.9, 28.8, 29.0, 29.4, 29.7, 31.0, 196.3; other resonances not resolved owing to ¹⁹F-¹³C coupling.

1,4-Bis-(6-chloro-hex-1-ynyl)-2,5-dimethoxy-benzene: A mixture of 1,4-dibromo-2,5-dimethoxy-benzene (2.88 g, 9.75 mmol), [PdCl₂(MeCN)₂] (0.13 g, 5 mol%), PPh₃ (0.256 g, 10 mol %) and CuI (0.056 g, 3 mol %) in ⁱPr₂NH (40 cm³) was degassed for 30 min. by Ar bubbling. The 6-chloro-hex-1-yne (3.07 g, 26.3 mmol) was added, and the mixture was refluxed for 24 h under N₂. It was allowed to cool to room temperature and then filtered, the precipitate was washed with CH₂Cl₂ (20 cm³) and the combined solutions were evaporated to dryness. The residue was taken up in the minimum hot CH₂Cl₂:hexane (20:80) and cooled in the freezer (-20 °C). The product was filtered off. Yield 1.37 g, 39 %. Elemental analysis: found; C, 65.30; H, 6.62 %. C₂₀H₂₄Cl₂O₂ requires C, 65.40; H, 6.59 %. CI MS (NH₃): m/z: 384 [M+NH₃]⁺, 367 [M]⁺. ¹H NMR (CDCl₃) δ = 1.79, 1.99 (m's, 8H, -CH₂CH₂-), 2.53 (t, 4H, ³J 6.9 Hz, C≡CCH₂), 3.61 (t, 4H, ³J 6.6 Hz, -CH₂Cl), 3.82 (s, 6H, OMe), 6.85 (s, 2H, aromatic H). ¹³C NMR data (CDCl₃) δ = 19.5, 26.3, 32.1, 44.9, 56.8, 95.3, 113.6, 116.2, 154.3.

Thioacetic acid S-[6-(6-acetylsulfanyl-hexyl)-2,5-dimethoxy-phenyl]-hexyl ester, 3: 1,4-Bis-(6-chloro-hex-1-ynyl)-2,5-dimethoxy-benzene (0.721 g, 2.15 mmol) was

subjected to hydrogenation (40 cm³ EtOAc, 0.287 g 10 % Pd/C, 8 bar H₂, 24 h, room temperature). The catalyst was filtered off and the solvent was removed in *vacuo*. The product was purified by column chromatography (hexane), and used directly. Yield 0.553 g, 75 %. A 0.50 g portion (1.36 mmol) was dissolved in acetone (50 cm³), and treated with a mixture of KSAc (0.47 g, 4.1 mmol) and catalytic NaI (0.02 g). The mixture was refluxed for 48 h, cooled to room temperature and evaporated to dryness. The residue was extracted with Et₂O (3 × 20 cm³). The combined extracts were evaporated to dryness. Purification by chromatography (hexane) yielded the product (0.37 g, 61 %). Elemental analysis: found; C, 65.30; H, 9.42 %. C₂₄H₃₈O₄S₂·0.5 hexane requires C, 65.15; H, 9.11 %. ES MS (MeOH, 10 V): m/z: found 477.2109. Calc for [M+²³Na]⁺ 477.2109. ¹H NMR (CDCl₃) δ = 1.40, 1.58 (m's, 16H, -CH₂CH₂-), 2.31 (s, 6H, -C(O)CH₃), 2.55 (t, 4H, ³J 7.7 Hz, -CH₂Ar), 2.86 (t, 4H, ³J 7.3 Hz, -CH₂S), 3.77 (s, 6H, OMe), 6.63 (s, 2H, aromatic H). ¹³C NMR data (CDCl₃) δ = 29.1, 29.4, 29.6, 29.9, 30.4, 30.5, 31.0, 56.6, 113.5, 129.5, 151.7, 196.3.

1,4-Bis-(6-chloro-hex-1-ynyl)-2,5-dimethyl-benzene: A mixture of 1,4-dibromo-2,5-dimethyl-benzene (2.57 g, 9.75 mmol), [PdCl₂(MeCN)₂] (0.13 g, 5 mol%), PPh₃ (0.256 g, 10 mol %) and CuI (0.056 g, 3 mol %) in ⁱPr₂NH (40 cm³) was degassed for 30 min. by Ar bubbling. The 6-chloro-hex-1-yne (3.07 g, 26.3 mmol) was added, and the mixture was refluxed for 24 h under N₂. It was allowed to cool to room temperature and then filtered, the precipitate was washed with CH₂Cl₂ (20 cm³) and the combined solutions were evaporated to dryness. The residue was taken up in hexane and purified by column chromatography (hexane). Cream solid. Yield 0.934 g, 29 %. Elemental analysis: found; C, 71.17; H, 7.15 %. C₂₀H₂₄Cl₂ requires C, 71.64; H, 7.21 %. CI MS (NH₃): m/z: 352 [M+NH₃]⁺, 335 [M]⁺. ¹H NMR (CDCl₃) δ = 1.76, 1.98 (m's, 8H, -CH₂CH₂-), 2.32 (s, 6H, ArMe), 2.50 (t, 4H, ³J 7.0 Hz, C≡CCH₂), 3.60 (t, 4H, ³J 6.5 Hz, -CH₂Cl), 7.17 (s, 2H, aromatic H). ¹³C NMR data (CDCl₃) δ = 19.3, 20.35, 26.4, 32.0, 44.9, 80.5, 94.4, 123.3, 133.0, 137.3.

1,4-Bis-(6-chloro-1-hexyl)-2,5-dimethyl-benzene: 1,4-Bis-(6-chloro-hex-1-ynyl)-2,5-dimethyl-benzene (0.62 g, 1.85 mmol) was subjected to hydrogenation (40 cm³ EtOAc, 0.24 g 10 % Pd/C, 8 bar H₂, 24 h, room temperature). The catalyst was filtered off and the solvent was removed in *vacuo*. The product was purified by column chromatography

(hexane). Yield 0.52 g, 82 %. Elemental analysis: found; C, 69.33; H, 9.49 %. $C_{20}H_{32}Cl_2$ requires C, 69.96; H, 9.39 %. CI MS (NH_3): m/z: 360 [$M+NH_4$]⁺, 342 [M]⁺. 1H NMR ($CDCl_3$) δ = 1.40, 1.44, 1.54 (m's, 12H, $-CH_2CH_2CH_2-$), 2.52 (t, 4H, 3J 7.9 Hz, ArCH₂), 3.53 (t, 4H, 3J 6.7 Hz, -CH₂Cl), 6.88 (s, 2H, aromatic H). ^{13}C NMR data ($CDCl_3$) δ = 19.1, 27.2, 29.4, 30.7, 33.0, 33.2, 45.5, 131.1, 133.4, 138.5.

Thioacetic acid S-[6-{4-(6-acetylsulfanyl-hexyl)-2,5-dimethyl-phenyl]-hexyl} ester, 4: 1,4-Bis-(6-chloro-1-hexyl)-2,5-dimethyl-benzene (0.50 g, 1.47 mmol) was dissolved in acetone (50 cm³), and treated with a mixture of KSAc (0.50 g, 4.4 mmol) and catalytic NaI (0.02 g). The mixture was refluxed for 48 h, more KSAc (0.3 g) was added, and the mixture was refluxed for a further 16 h. It was then cooled to room temperature and evaporated to dryness. The residue was extracted with Et₂O (3 × 20 cm³). The combined extracts were evaporated to dryness. Purification was by column chromatography (hexanes). Yield 0.405 g, 65 %. Elemental analysis: found; C, 67.80; H, 9.00 %. $C_{24}H_{38}O_2S_2$ requires C, 68.20; H, 9.06 %. CI MS (NH_3): m/z: 440 [$M+NH_4$]⁺, 423 [M]⁺. 1H NMR ($CDCl_3$) δ = 1.41, 1.55 (m's, 16H, $-CH_2CH_2-$), 2.23 (s, 6H, ArCH₃), 2.32 (s, 6H, -C(O)CH₃), 2.50 (t, 4H, 3J 7.8 Hz, -CH₂Ar), 2.87 (t, 4H, 3J 7.3 Hz, -CH₂S), 6.87 (s, 2H, aromatic H). ^{13}C NMR data ($CDCl_3$) δ = 19.1, 29.1, 29.2, 29.6, 29.9, 30.7, 31.0, 131.0, 133.2, 138.5, 196.3.

S2 Additional details of $I(s)$ and $I(t)$ experimental methods and error treatment.

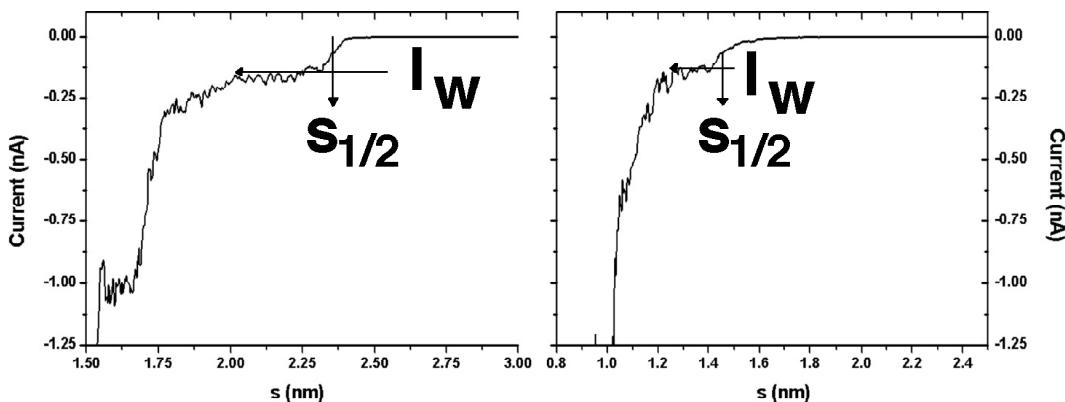


Figure S1 Two typical $I(s)$ curves obtained using molecule **4**, in which molecule(s) have been picked up in the experiment, as is clear from the presence of current plateaux. The values of the current at the plateau (I_w), and the detachment distance $s_{1/2}$ (where the plateau current drops away) are determined in many such experiments, and analysed statistically as described below.

Analyses of histogram data to extract conductance and its standard deviation

The histograms we present are derived from individual molecular events ($I(s)$ and $I(t)$ jumps in the current). We deduce the molecular conductance by first of all looking at the peak at the lowest current (marked J_1 in Figure 2 in the paper), and taking the average of the data between the half maximum for that peak. The quoted error is the standard deviation from the mean for those values. We treat all histograms equally, and the bin size of the histograms is normally chosen as 10-20% of the first peak value.

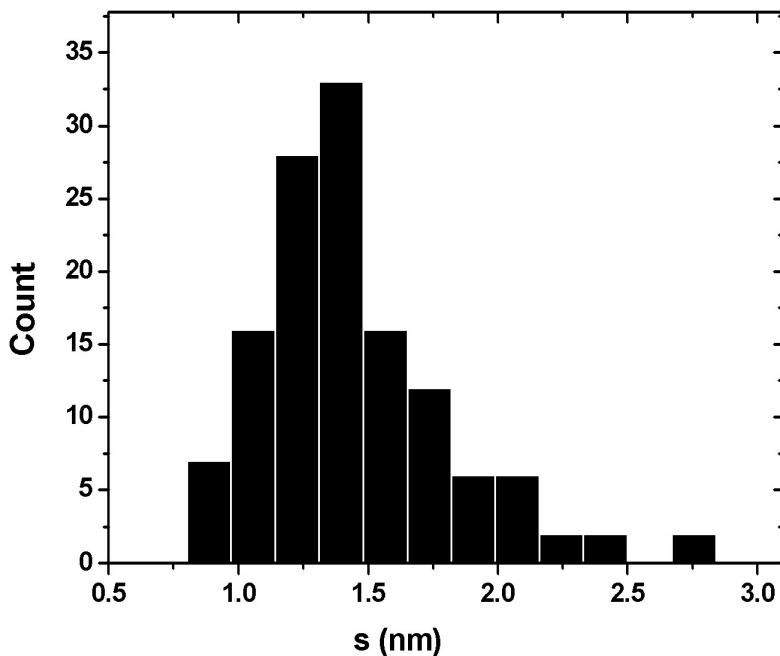


Figure S2 Detachment distance statistics for the $I(s)$ measurements on molecule **4**, corrected from the experimental $s-s_0$ using the method described in the caption to Figure S3.

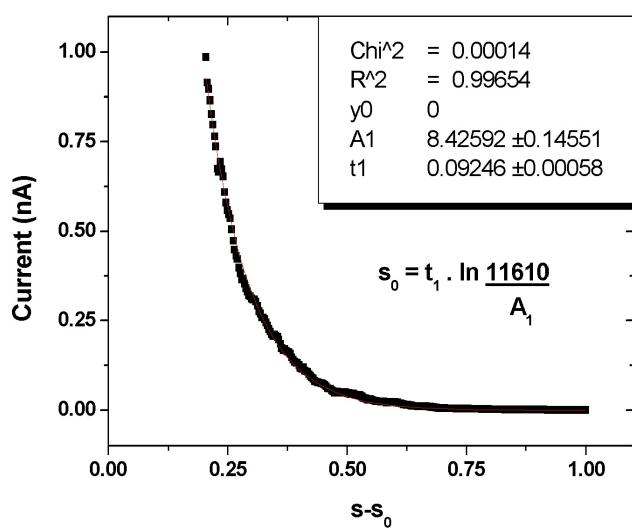


Figure S3 Exponential decay of tunnelling current with distance from $I(s)$ measurements on molecule **4** in which no molecular bridge(s) formed, and hence no current plateaux were observed. Tip bias 0.15 V. Mean of 4 experiments. Since the tip would touch the surface of the substrate at $s = s_0$, the current at this point would be $\geq 77 \mu\text{S}$ (the quantum conductance limit). At a tip bias of 0.15 V, this is therefore $\geq 11610 \text{ nA}$. Therefore, the equation shown is fitted to the observed exponential decay, and parameters t_1 and A_1 are obtained. The values correspond to $s_0 = 0.67 \text{ nm}$.

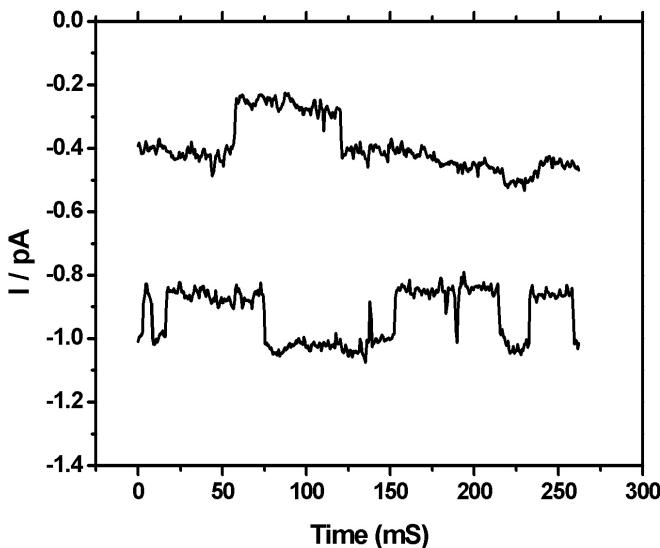


Figure S4 Typical $I(t)$ jumps, observed for molecule **1**. Tip bias +200 mV.