Supporting Information for

The Single-Molecule Electrical Conductance of a Rotaxane-Hexayne Supramolecular Assembly

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1. Binding distance of Rotaxane and Dumbbell on a gold surface

To calculate the optimum binding distance for 3 and 3-M1 between two Au(111) surfaces we use DFT and the counterpoise method, which removes basis set superposition errors (BSSE). The binding distance \( d \) is defined as the distance between the gold surface and the nitrogen atom of the pyridyl group. Here molecule 3-M1 or 3 are defined as entity A and the gold electrodes as entity B.

The ground state energy of the total system is calculated using SIESTA and is denoted \( E_{AB}^{AB} \), with the DFT parameters defined as those in the method section of the main text. Here the gold leads consist of 3 layers of 25 atoms. The energy of each entity is then calculated in a fixed basis, which is achieved through the use of ghost atoms in SIESTA. Hence the energy of the individual 3-M1 or 3 molecules in the presence of the fixed basis is defined as \( E_{A}^{AB} \) and for the gold as \( E_{B}^{AB} \). The binding energy is then calculated using the following equation:

\[
\text{Binding Energy} = E_{AB}^{AB} - E_{A}^{AB} - E_{B}^{AB}
\]  

(S1)

Fig. S1 shows that for the optimum binding distance \( d \) is 2.4 Å for both molecules and the binding energy is approximately 0.35 eV.

![Figure S1](image_url)

**Figure S1.** Binding energy of 3-M1 and 3 on a gold surface. Right panel: Orientation of 3 with respect to the gold leads.
2. Transmission coefficient as a function of macrocycle position and orientation along the dumbbell

We next investigate the effect of the position and orientation of the rotaxane ring along the axis. Fig. S2 shows the effect of shifting the macrocycle along the length of 3, starting from one end and progressively moving to the other, (i.e., from $z = +3$ Å to $-3$ Å along 3, where $z = 0$ corresponds to half way along the oligoyne chain). The transmission curves show that there is a strong interaction between the 2,6-phenyl substituents of the pyridyl groups and the macrocycle only at $z = \pm 3$ Å (i.e., where the transmission curves are significantly altered). This only changes the transmission close to the HOMO resonances, which is well away from the Fermi energy.

Figure S2. Transmission coefficient as a function of shifting the 3·M1 ring along the 3. Transmission curves, $T(E)$, for seven different positions (ends when the ring is close to the anchor groups, 0 when the ring in the middle).

Figure S3 shows the effect of shifting the orientation of the macrocycle around 3 for $\theta = 0^\circ$ and $300^\circ$ at $z = 0$, and it can be seen that there is no effect due to the rotation.
Figure S3. Transmission coefficient as a function of orientation. Zero bias transmission coefficient $T(E)$ versus electron energy $E$ for rotation angles $\theta$ between $0^\circ$ and $300^\circ$ of the the rotaxane ring with respect to the 3.

3. Frontier Orbitals

Plots of the frontier orbitals of 3 and 3-M1 are shown in Figures S4 and S5. The results show that for 3-M1, orbitals from HOMO to HOMO-4 inclusive are localised on the ring, while the HOMO-5 orbital has a similar energy to the HOMO of isolated 3 and is localised along the oligoyne backbone.

Figure S4. HOMO and LUMO orbitals of (left) 3 and (right) 3-M1.
Figure S5. HOMO orbitals of the 3·M1.
4. Synthesis and characterization

**General procedures and methods:**
Reagent grade chemicals were purchased from commercial suppliers and used without further purification. THF was distilled from sodium/benzophenone. CH$_3$CN and CH$_2$Cl$_2$ were distilled from CaH$_2$. MgSO$_4$ was used as the drying reagent after aqueous workup. $^1$H and $^{13}$C NMR spectra were recorded on a Bruker AVII 500 at 500 MHz ($^1$H NMR) and 126 MHz ($^{13}$C NMR). NMR spectra were referenced to the residual solvent signal ($^1$H CD$_2$Cl$_2$: 5.32 ppm; $^{13}$C CD$_2$Cl$_2$: 53.8 ppm) and recorded at ambient probe temperature. For simplicity, the coupling constants of the aryl protons for para-substituted aryl groups have been reported as pseudo first-order (i.e., doublets), even though they are second-order (AA'XX') spin systems. UV-vis measurements were carried out on a Varian Cary 5000 UV-Vis-NIR spectrophotometer at rt. Mass spectra were obtained from a Bruker maxis 4G. IR spectra were recorded on a Varian 660-IR spectrometer as solids in ATR-mode. Differential scanning calorimetry (DSC) measurements were made on a Mettler Toledo TGA/STDA 851e/1100/SF. Melting points were measured with an Electrothermal 9100 instrument. TLC analyses were carried out on TLC plates from Macherey-Nagel (ALUGRAM® SIL G/UV254) and visualized via UV-light (264/364 nm) or standard coloring reagents. Column chromatography was performed using Silica Gel 60M (Merck).

Triynes 1a and 1b, and macrocycle M1 were synthesized according to literature protocols.\textsuperscript{iii}
3•M1 from triyne 1a. TBAF (1.0 M in THF, 0.12 mL, 0.12 mmol) was added dropwise to a solution of 1a (50 mg, 0.11 mmol) in wet THF (10 mL, and 0.05 mL of H₂O). The mixture was stirred at rt for 10 min, quenched via the addition of satd aq NH₄Cl (10 mL), and extracted with CH₂Cl₂ (2 × 10 mL). The combined organic phases were washed with H₂O (10 mL) and satd aq NaCl (10 mL). The solvent was reduced in vacuo to ca. 5 mL, and the mixture filtered through a plug of Al₂O₃ (EtOAc ca. 150 mL). The solution was concentrated under reduced pressure to ca. 3 mL. THF (5 mL) was added and the solution was concentrated to three mL. This procedure was repeated three times to displace as much of the EtOAc as possible, ultimately giving a solution of terminal triyne in THF (8 mL), which was used without further purification. In a separate flask, CuI (9.5 mg, 0.050 mmol) in CH₃CN (2 mL) was added to a solution of macrocycle M1 (28 mg, 0.050 mmol) in CH₂Cl₂ (2 mL) and the mixture was stirred at rt for 1 h. The solvent was removed in vacuo and the residue dissolved in THF (3 mL). The terminal triyne in THF, as prepared above, K₂CO₃ (27 mg, 0.20 mmol), and I₂ (13 mg, 0.050 mmol) were added to the solution of the Cu-macrocycle complex M1•CuI. The reaction mixture was stirred at 60 °C for 24 h, cooled to rt, and quenched via the addition of CH₂Cl₂ (1 mL), CH₃CN (1 mL), and KCN (20 mg in 1 mL H₂O). After stirring for 2 h, the organic phase was separated, the aqueous phase extracted with CH₂Cl₂ (2 × 10 mL), and the combined organic phases were washed with H₂O (10 mL) and satd aq NaCl (10 mL). The solvent was removed in vacuo and column chromatography (Al₂O₃, hexane/EtOAc 4:1) afforded 3•M1 (1 mg, 2%) as a yellow solid.

3•M1 from triyne 1b. CsF (34 mg, 0.22 mmol) was added to a solution of 1b (85 mg, 0.20 mmol) in wet THF (10 mL, 0.25 mL H₂O). The mixture was stirred at rt for 30 min, quenched via the addition of satd aq NH₄Cl (10 mL), and extracted with CH₂Cl₂ (2 × 25 mL). The combined organic phases were washed with H₂O (10 mL) and satd aq NaCl (10 mL), and dried (MgSO₄). The solution was concentrated under reduced pressure to ca. 5 mL. THF (10 mL) was added and the solution was concentrated to 5 mL. This procedure was repeated three times to displace as much CH₂Cl₂ as possible, ultimately giving a solution of terminal triyne in THF (10 mL). In a separate flask, CuI (14 mg, 0.072 mmol) in CH₃CN (3 mL) was added to a solution of macrocycle M1 (40 mg, 0.072 mmol) in CH₂Cl₂ (3 mL) and the mixture was stirred at rt for 1 h. The solvent was removed in vacuo and the
residue dissolved in THF (6 mL). The terminal triyne in THF, as prepared above, K$_2$CO$_3$ (40 mg, 0.29 mmol), and I$_2$ (22 mg, 0.086 mmol) were added to the solution of the Cu-macrocycle complex, M1·Cu. The reaction mixture was stirred at 60 °C for 25 h, cooled to rt, and quenched via addition of CH$_2$Cl$_2$ (1 mL), CH$_3$CN (1 mL), and KCN (50 mg in 1 mL H$_2$O). After stirring overnight, the organic phase was separated, the aqueous phase extracted with CH$_2$Cl$_2$ (2 × 20 mL), and the combined organic phases were washed with H$_2$O (10 mL) and satd aq NaCl (10 mL). The solvent was removed in vacuo and column chromatography (silica gel, hexane/EtOAc 10:1, gradient to 1:1) afforded 3•M1 (11 mg, 13%) as a yellow solid. Mp 120–122 °C (decomp). $R_f$ = 0.33 (hexanes/EtOAc 1:1). UV-vis (CH$_2$Cl$_2$) $\lambda_{\text{max}}$ (\(\lambda\)) 478 (6250), 478 (6250), 434 (14000), 438 (12200), 404 (15600), 367 (65500), 351 (83900), 332 (78100), 316 (71600), 302 (59800), 281 (68300), 272 (70900), 259 (65100) nm; UV-vis (CHCl$_3$) $\lambda_{\text{max}}$ 478, 438, 404, 368, 351, 331, 316, 272, 243 nm; UV-vis (toluene) $\lambda_{\text{max}}$ 478, 439, 405, 368, 352, 333, 317, 284 nm; UV-vis (THF) $\lambda_{\text{max}}$ 477, 437, 404, 365, 350, 331, 316, 271 nm; UV-vis (EtOAc) $\lambda_{\text{max}}$ 475, 436, 402, 364, 348, 331, 315, 271 nm; IR (ATR) 3039 (w), 2928 (w), 2158 (w), 2048 (w), 1592 (m), 1489 (m), 1219 (s), 1180 (m) cm$^{-1}$. $^1$H NMR (500 MHz, CD$_2$Cl$_2$) $\delta$ 8.58 (s, 4H), 8.27 (d, $J$ = 8.3 Hz, 2H), 7.89 (d, $J$ = 8.3 Hz, 2H), 7.79 (s, 2H), 7.75 (d, $J$ = 8.7 Hz, 4H), 7.54–7.53 (m, 8H), 7.44–7.38 (m, 12H), 7.05 (d, $J$ = 8.6 Hz, 4H), 7.00 (d, $J$ = 8.6 Hz, 4H), 6.77 (d, $J$ = 8.7 Hz, 4H), 5.20 (s, 4H). $^{13}$C NMR (126 MHz, CD$_2$Cl$_2$) $\delta$ 159.4, 158.3, 158.1, 149.2, 146.8, 140.6, 136.8, 136.5, 134.3, 134.2, 129.9, 129.6, 129.0, 128.9, 127.7, 127.4, 126.0, 125.2, 122.1, 120.8, 116.2, 83.2, 73.7, 70.2, 70.1, 66.5, 64.3, 61.8. APPI HRMS (MeCN/toluene) calcd for C$_{84}$H$_{50}$N$_{4}$O$_{3}$ (M$^+$) 1162.3877, found 1162.3873; calcd for C$_{84}$H$_{51}$N$_{4}$O$_{3}$ ([M + H]$^+$) 1163.3956, found 1163.3944. DSC: Mp = 124 °C; decomposition, 142 °C (onset), 186 °C (peak).
Figure S6. $^1$H NMR spectrum of 3-M1 in CD$_2$Cl$_2$ (500 MHz).

Figure S7. $^{13}$C NMR spectrum of 3-M1 in CD$_2$Cl$_2$ (126 MHz).
Figure S8. Quantitative UV-vis spectra of Dumbbell 3 and Rotaxane 3•M1 in CH₂Cl₂.

Figure S9. Solvent dependent UV-vis absorption spectra of Rotaxane 3•M1.
Figure S10. UV-vis absorption changes upon fully reversible protonation of rotaxane 3•M1 in CH₂Cl₂.

Figure S11. DSC trace of 3•M1.
5. **NMR spectra (1H and 13C) of the naked wire, macrocycle, and rotaxane.**

Figure S12 shows 1H NMR of the naked wire, macrocycle, and rotaxane and Figure S13 shows the corresponding 13C spectra. These confirm that the spectra of the rotaxane are linear combinations of the individual components.

Figure S12. 1H NMR spectral comparison of M1 (green, CD$_2$Cl$_2$), 3 (red, CDCl$_3$), and M1•3 (blue, CD$_2$Cl$_2$). Spectra of M1•3 are essentially a linear combination of the components M1 and 3.
Figure S13. $^{13}$C NMR spectral comparison of M1 (green, CD$_2$Cl$_2$), 3 (red, CDCl$_3$), and M1•3 (blue, CD$_2$Cl$_2$). Spectra of M1•3 are essentially a linear combination of the components M1 and 3.

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