Supporting Information

for

Conformational Gating of Single-Molecule Conductance in Crown Ether Junctions by Li^+ Coordination

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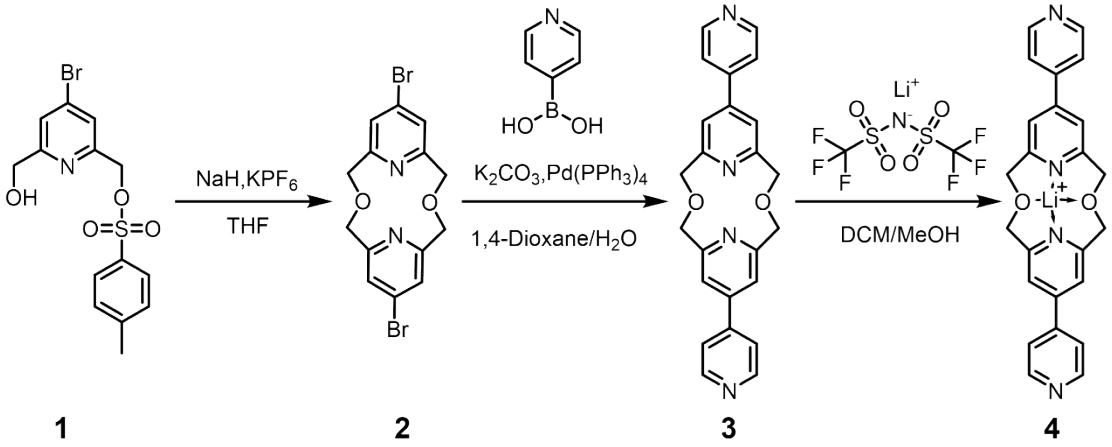
1. Instrumentation and Materials

All reactions were carried out under nitrogen atmosphere and anhydrous conditions unless otherwise indicated. The commercial reagents were purchased from Adamas-beta China and were used as received. Precursor **1** was prepared following the reported procedure.[1] Reactions were monitored by thin-layer chromatography (TLC) carried out on silica gel plates using UV light as the visualizing agent. NMR spectra were recorded using a Bruker AVANCE III HD 600 MHz spectrometers. Mass spectra were recorded on a BRUKER microflex LRF MALDI TOF model using positive or negative mode and an AB SCIEX TripleTOF™ 5600+ using positive or negative mode.

2. Experimental Section



Scheme S1. Synthesis of **3** and **4**.

Synthesis of 2: To a mixture of KPF_6 (608 mg, 3.3 mmol) and anhydrous tetrahydrofuran (4 mL), sodium hydride (60%, 110 mg, 4.58 mmol) was added slowly under N_2 atmosphere. Upon stirring for 30 min, **1** (400 mg, 108 mmol) in anhydrous tetrahydrofuran (2 mL) was added dropwise to the system. After the mixture was stirred at 30 ℃ for 24 h, the reaction was quenched by adding 5 mL of saturated (aq.) NH_4Cl. Removal of solvents under reduced pressure gave the crude product which was further purified by GPC (polystyrene；eluent: THF) to afford the pure **2** as a white solid. (26 mg, 0.065 mmol, 12%).^{1}H NMR (600 MHz, $CDCl_3$) δ 7.13 (s, 4H), 4.82 (s, 8H).^{13}C NMR (600 MHz, CDCl3) δ 158.52, 126.48, 76.28. HRMS: m/z calcd for $C_{14}H_{12}Br_2N_2O_2$ $[M+H]^+$, 398.9338, found 398.9336.

Synthesis of 3: 2 (65 mg, 10.1625 mmol), Pyridine-4-boronic acid (55 mg, 0.48 mmol), K_2CO_3 (132 mg, 0.95 mmol), and $Pd(PPh_3)_4$ (56 mg, 0.048 mmol) were added to a two-necked flask. A mixture of 1,4-dioxane (4 mL) and H_2O (1 mL) was degassed and then added to the reaction flask under N_2 atmosphere. The reaction mixture was heated to reflux at 90 °C for 72 h. After the solvent was taken off under reduced pressure, the crude product was purified by GPC (polystyrene；eluent: THF) to afford the pure **3** as a white solid. (22 mg, 0.055 mmol, 33%).^{1}H NMR (600 MHz, Acetone) δ 8.63 (d, J = 6 Hz, 4H), 7.70 (s, 4H), 7.65 (d, J = 6 Hz, 4H), 4.72 (s, 8H).^{13}C NMR (600 MHz, Acetone) δ 159.97, 151.48, 122.14, 119.21, 74.09. HRMS: m/z calcd for $C_{24}H_{20}N_4O_2$ $[M+H]^+$, 397.1659, found 397.1641.

Synthesis of 4: 3 (15 mg, 0.038 mmol) was dissolved in dichloromethane solution (5 ml), and a solution of lithium bis(trifluoromethanesulfonimide) (10.86 mg, 0.038 mmol) in methanol (5 mL) was slowly added dropwise with stirring at room temperature. After stirring at room temperature was continued for 3 h, the solution was concentrated under reduced pressure and subsequently purified by washing with dichloromethane as eluent to give **4** as a yellow oil (14.55 mg, 0.036 mmol, yield 95%).^{1}H NMR (600

MHz, DMSO) δ 8.62 (d, J = 5.4 Hz, 4H), 7.72 (s, 4H), 7.69 (d, J = 6 Hz, 4H), 4.67 (s, 8H).^{13}C NMR (600 MHz, DMSO) δ 158.94, 150.89, 123.14, 121.72, 121.00, 118.87, 73.26, 74.09.^{7}Li NMR (600 MHz, DMSO) δ -1.18.HRMS: m/z calcd for $C_{24}H_{20}LiN_4O_2^+$ $[M-Li+H]^+$, 397.1659, found 397.1655.

3. NMR Spectra

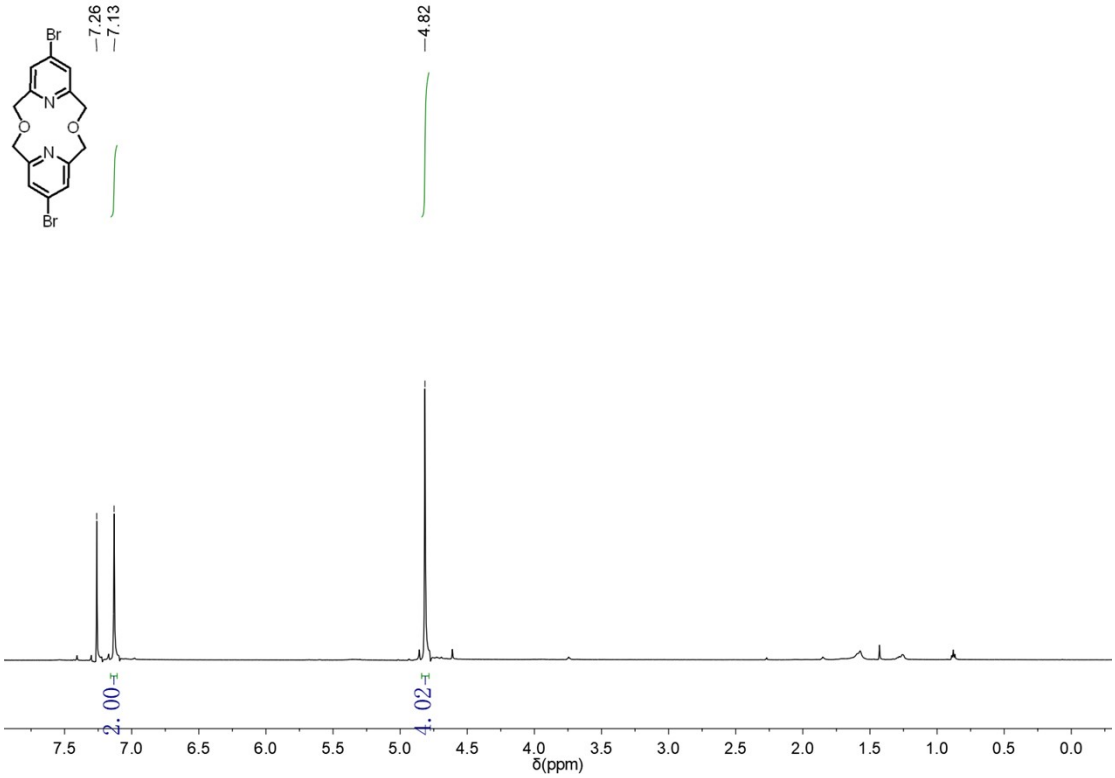


Figure S1. ^{1}H NMR-spectrum (600 MHz, $CDCl_3$) of **2**.

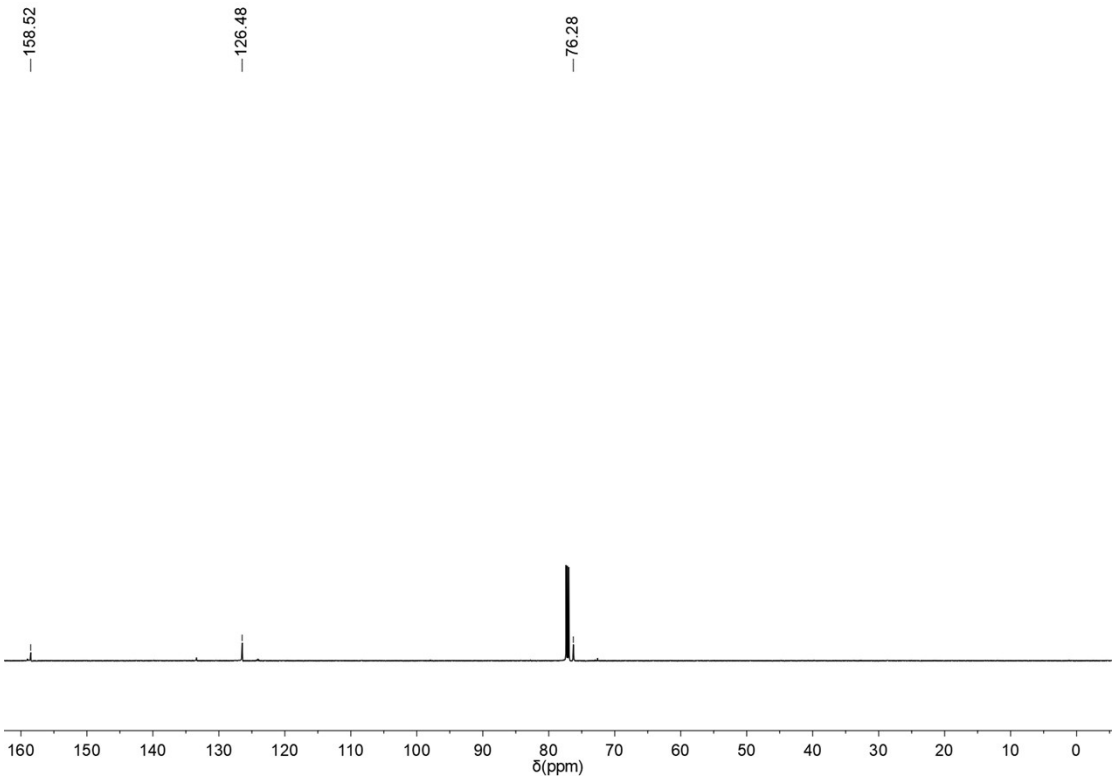


Figure S2. ^{13}C NMR-spectrum (600 MHz, $CDCl_3$) of **2**.

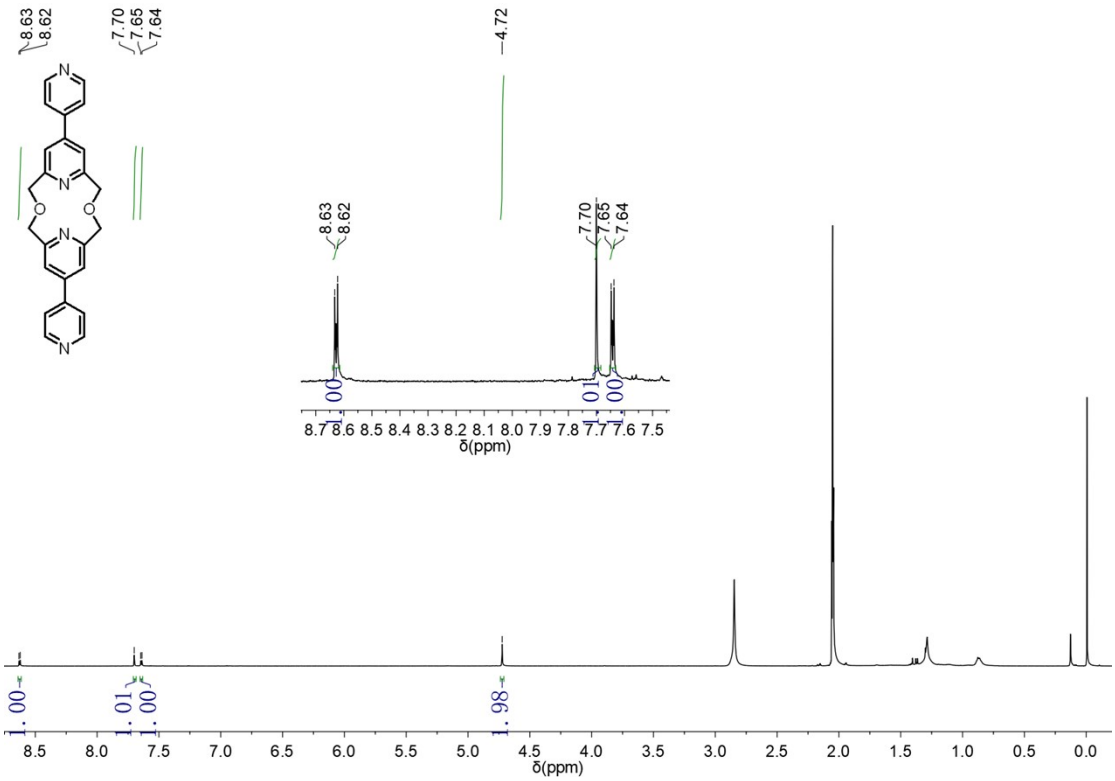


Figure S3. ^{1}H NMR-spectrum (600 MHz, Acetone-d6) of **3**.

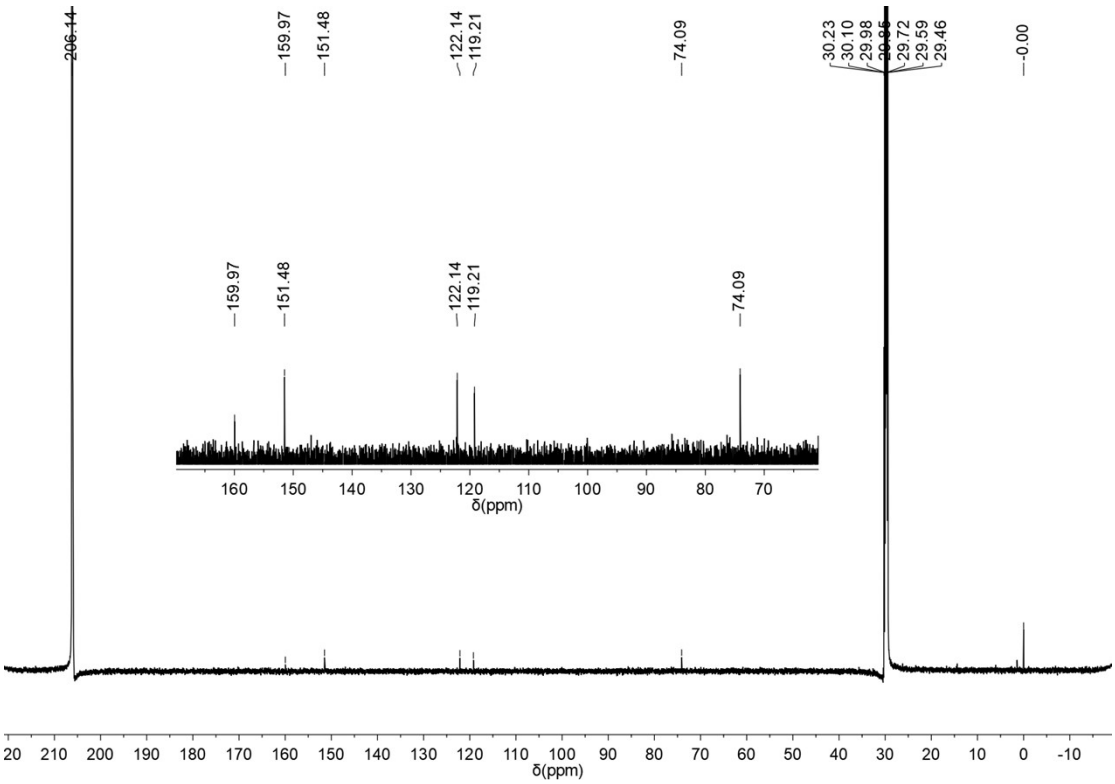


Figure S4. ^{13}C NMR-spectrum (600 MHz, Acetone-d6) of **3**.

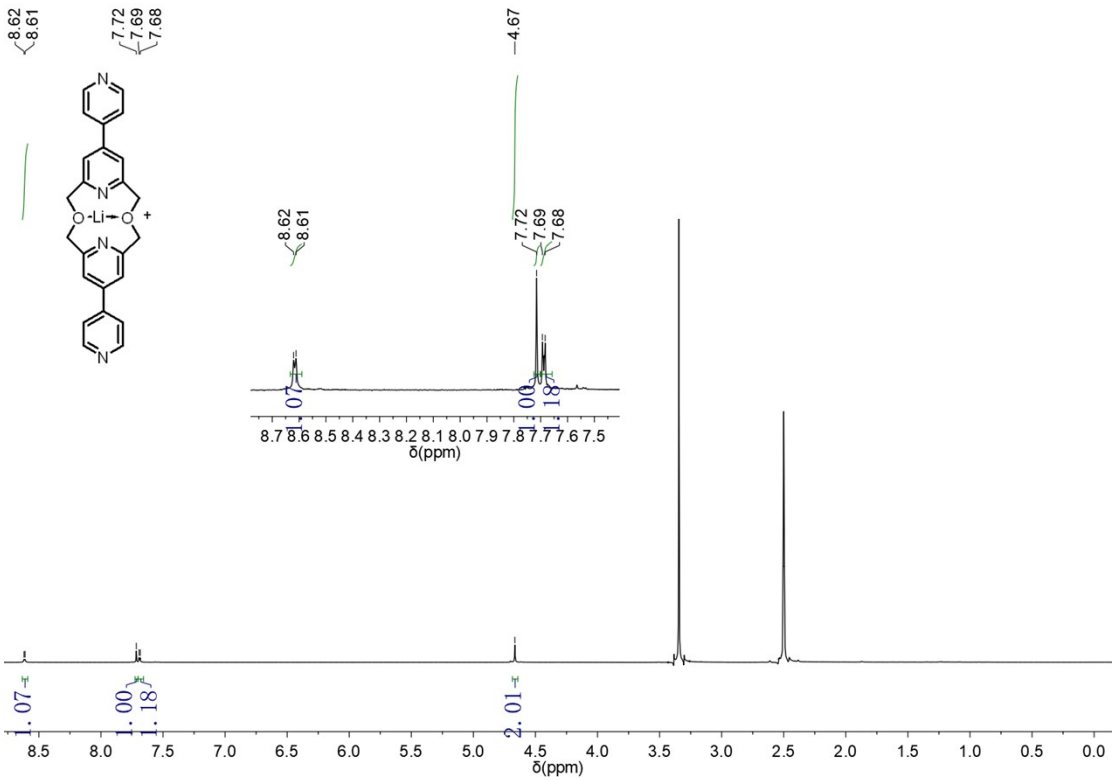


Figure S5. ^{1}H NMR-spectrum (600 MHz, DMSO-d6) of **4**.

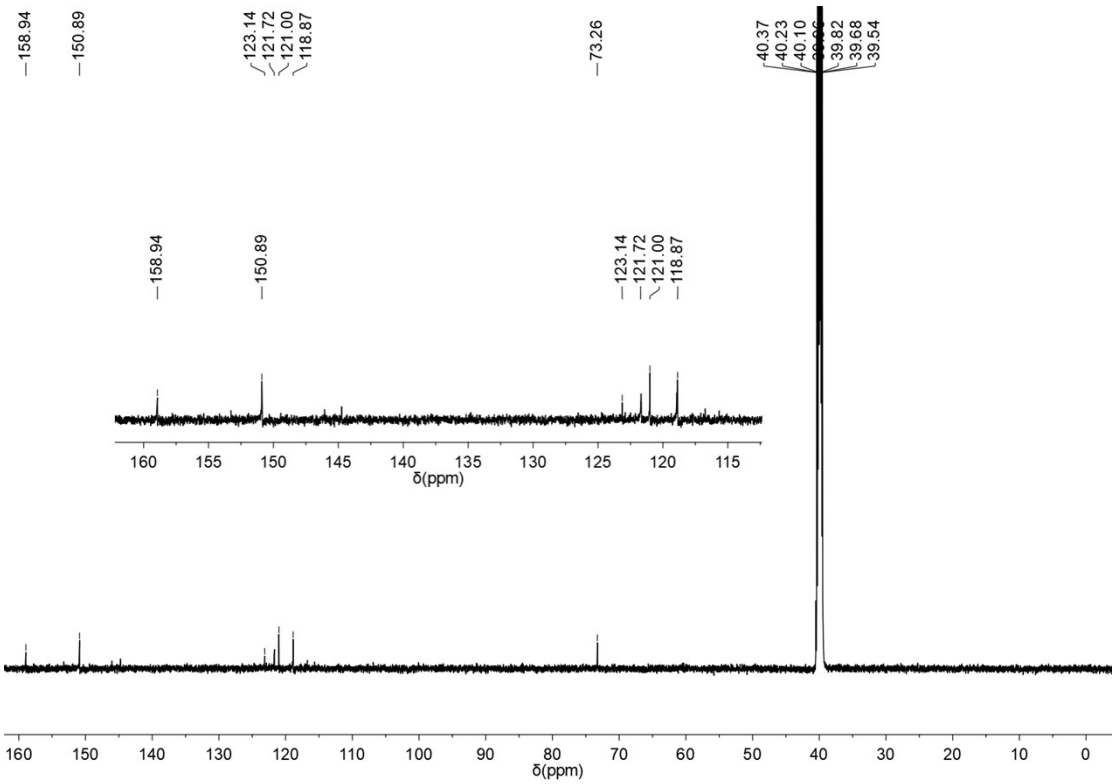


Figure S6. ^{13}C NMR-spectrum (600 MHz, DMSO-d6) of **4**.

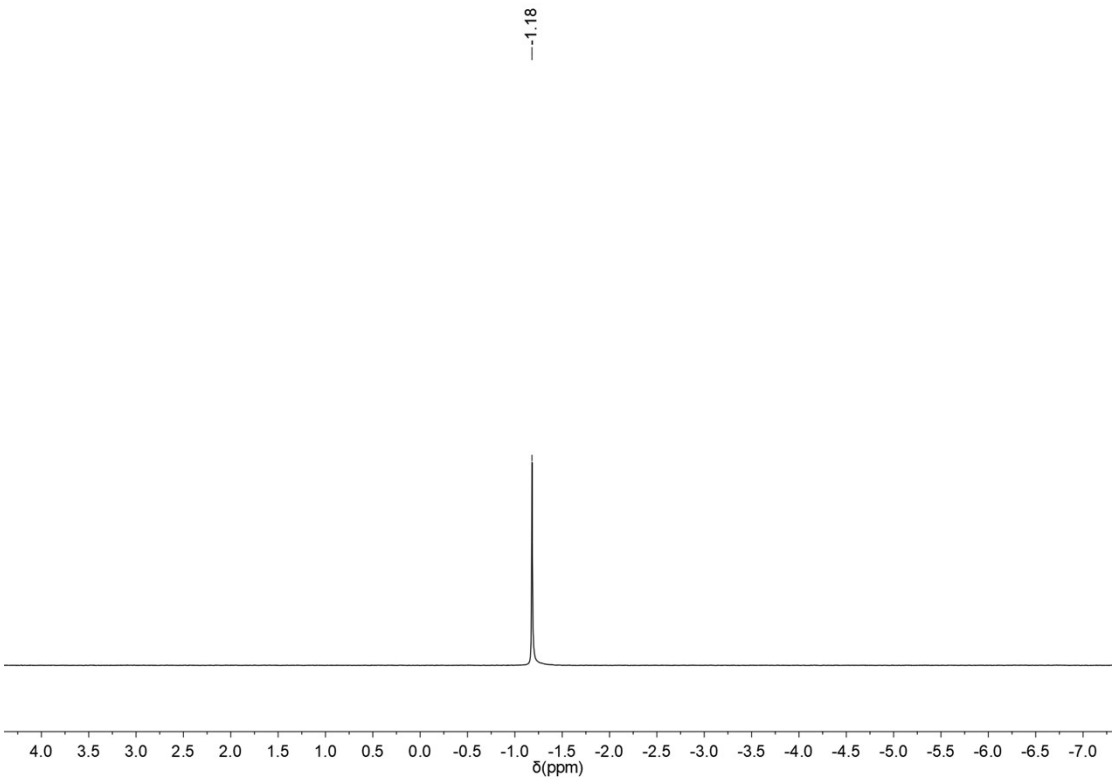


Figure S7. ^{7}Li NMR-spectrum (600 MHz, DMSO-d6) of **4**.

4. Mass Spectra

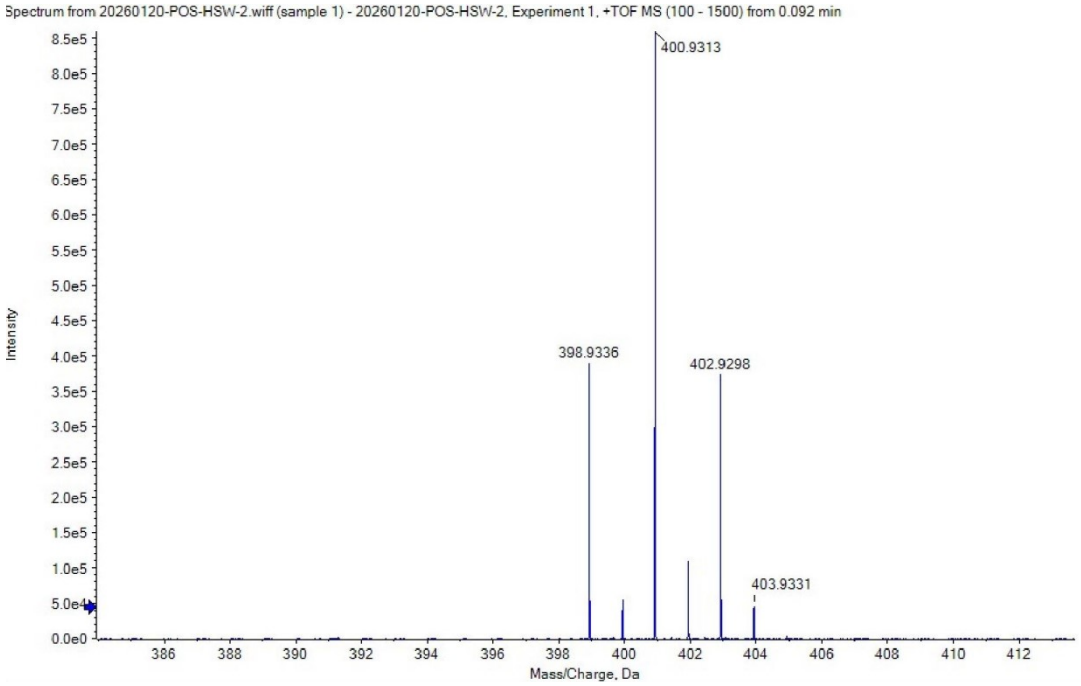


Figure S8. Mass spectrum of **2**.

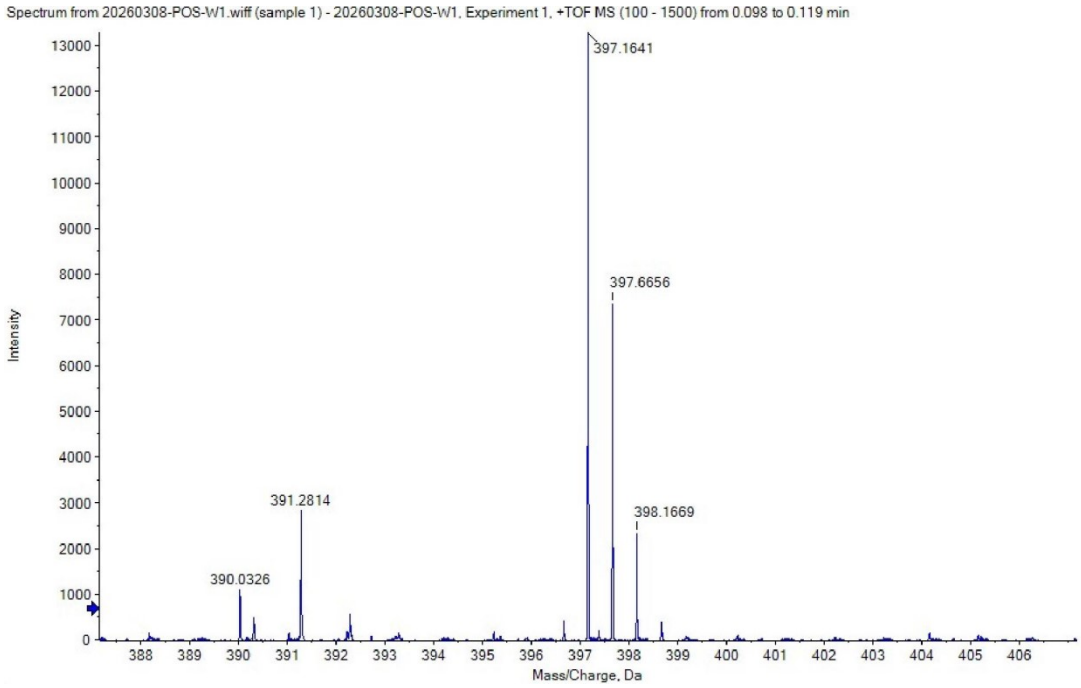


Figure S9. Mass spectrum of **3**.

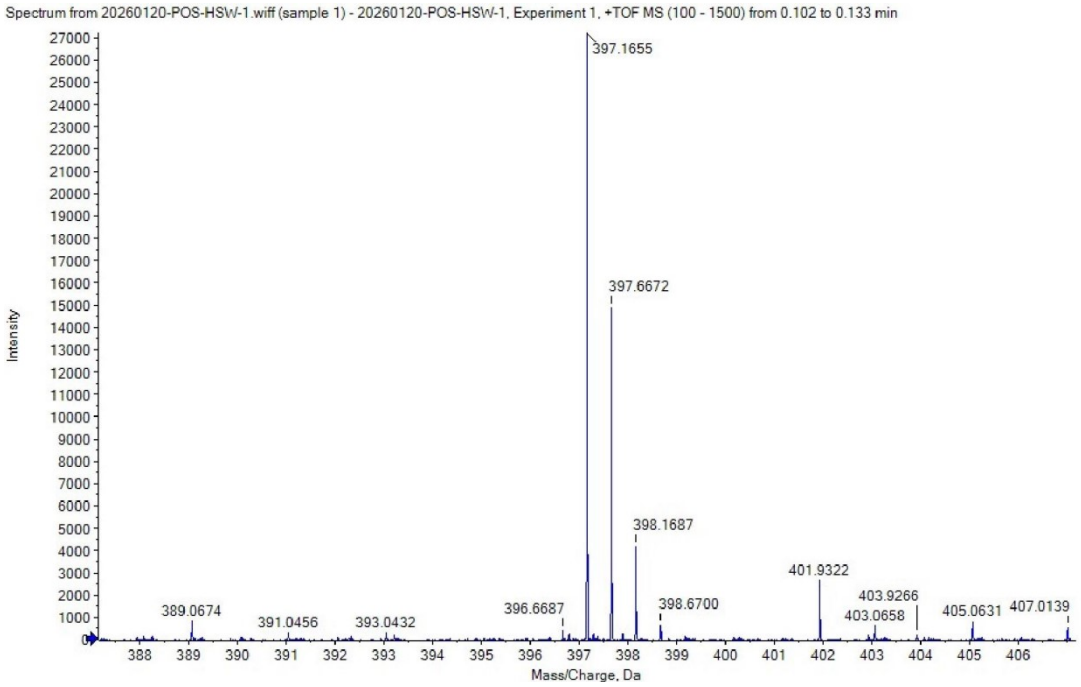


Figure S10. Mass spectrum of **4**.

5. Conductance measurements

The conductance of the single molecules was measured using the STM-controlled break-junction method. In this experiment, the molecules of interest are occasionally trapped between the substrate and an STM tip by periodic modulation of the tip-substrate separation. During this process, the tunneling current is monitored as a function of the tip-substrate distance at a constant bias voltage. The conductance is determined by analysis of the current-distance characteristics. All STM-BJ experiments were conducted at ambient pressure and room temperature in a TCB/THF=4:1 solution (with a molecular concentration of approximately 0.1 mM). During the conductance measurements, a gold tip (99.99% purity, diameter 0.25 μm) and a gold-plated substrate were used as the two electrodes. With a 0.1 V bias applied to the tip, the gold tip was driven to make contact with or detach from the substrate, thereby forming and breaking the molecular junction. During this process, the current was continuously recorded, and the conductivity was calculated using the formula G=I/V. By compiling over 2,000 acquired conductivity curves, one-dimensional and two-dimensional conductivity histograms were constructed.

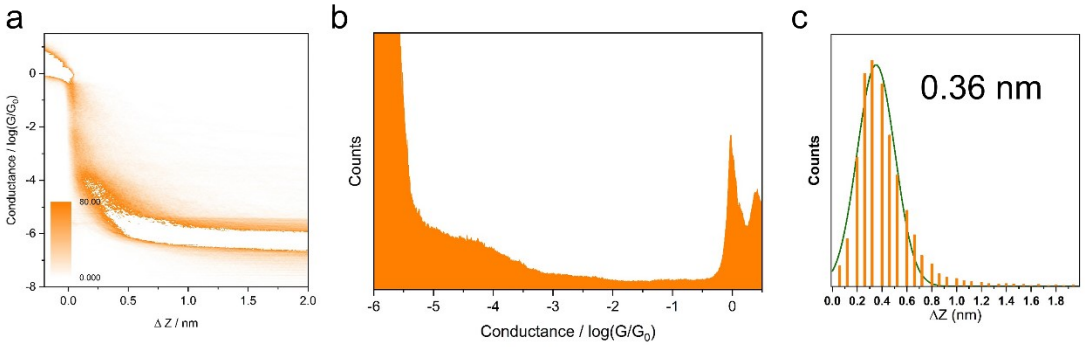


Figure S11. 2D (a) and 1D (b) conductance histogram of background measurement of pure TCB.

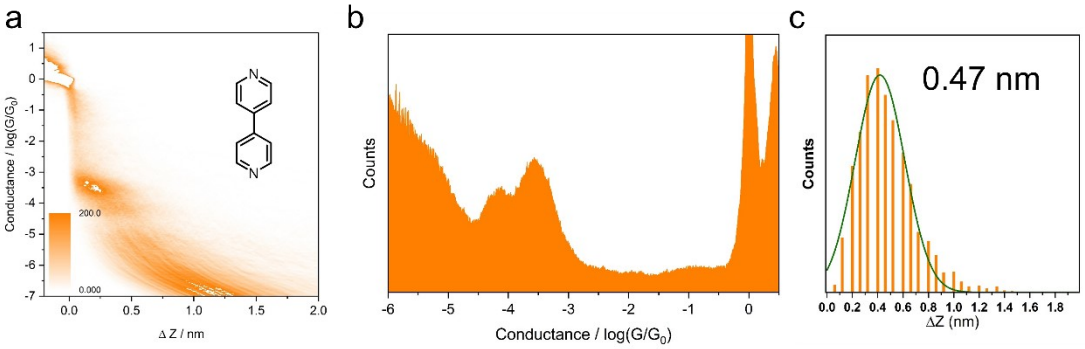


Figure S12. 2D and 1D conductance-displacement histograms for 4,4'-bipyridine.

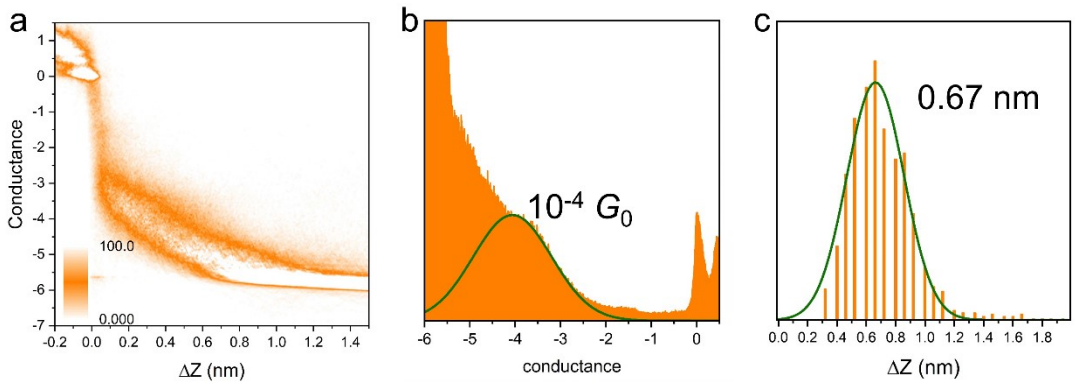


Figure S13. 2D and 1D conductance-displacement histograms for Na^+ coordination.

6. DFT calculation

All molecular geometries were optimized using GAUSSIAN 09,[2] employing the B3LYP functional together with the SDD basis set for lithium. For the remaining atoms, the 6-31G basis set was applied. The global minimum structures were obtained after the optimization process and then the target structures were inserted into the two gold electrodes. The device structures were constructed using QuantumATK-2022.12 software. The interaction between the molecule and electrodes was optimized with GGA-PBE functionals and DZP basis set (with DZ applied to gold atoms). The optimized devices were used for transport calculation with the non-equilibrium Green's function (NEGF) approach combined with density functional theory (DFT)[3, 4], utilizing the PBE functional and a DZP basis set (with DZ applied to gold atoms).

Within the DFT-NEGF framework, the electronic transport characteristics of a single-molecule junction are characterized by the energy-dependent transmission spectrum (T(E)), which represents the likelihood of electrons passing through the junction at a specific energy (E). The transmission coefficient is given by:

$T(E) = Tr[\Gamma_L G^R \Gamma_R G^A]$

where $\Gamma_{L/R}$ quantify how strongly the central scattering region is electronically coupled to the left/right electrodes. They describe the level broadening (finite lifetime) of molecular states induced by hybridization with electrode states：

$\Gamma_{L/R} = i[\Sigma_{L/R} - \Sigma_{L/R}^{\dagger}]$

where $\Sigma_{L/R}$ are the electrode self-energies of the electrodes. And $G^{R/A}$ is the retarded and advanced Green's functions of the device region.

7. Supporting References

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