Gating the Conductance of Single - Molecule Junction with Ion-π Interaction

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Materials and instruments

Unless otherwise stated, all the chemicals were obtained from a commercial supplier (Adamas) and used without further purification. The NMR spectra were obtained using Bruker AVANCE III 600 MHz NMR instruments. The HRMS was carried out on a Waters Xevo G2-XS Tof mass spectrometer. Single molecule conductance measurements were carried out using Xtech STM-BJ instrument, and the data was analyzed using XMe open-source code.

VSMe and PA[5] were synthesized according to reported literatures.[1, 2]

Conductance measurement of single-molecule junctions

The single molecular conductance of compounds was measured under an applied bias of 100 mV in propylene carbonate (PC) solvent. The concentration of VSMe was 0.1 mM. As for VSMe -PA[5] complex, PA[5] was added excessively to the solution of VSMe to ensure the complete complexation of VSMe. The STM tip (0.25 mm diameter, 99.99%) was etched electrochemically at a constant bias of 5 V and coated with Apiezon wax to suppress the background conductance of the PC solvent. The Au substrates were prepared by slow evaporation of ~20/200 nm Cr/Au at 1 Å s^{-1} onto a silicon wafer.

In STM-BJ measurement, the Au tip was controlled firstly by a stepper motor to obtain the approximate position to contact the substrate (less than 1 μm); thereafter the tip is

controlled by a piezo stack under the voltage of 0.1 V, with the approach/retract speed of 15 nm/s. During breaking and forming junctions process, the bias is kept at 100 mV, the real-time conductance is recorded using a custom-built I-V converter with a sampling rate of 20 *k*Hz. During the test process, the contact between Au STM tip and Au substrate was repeatedly formed and broken. With the tip retraction, the Au-Au point contact formed initially. Upon the rupture of the contact, the target molecule bound to the electrodes and Au-molecule-Au junction formed. Figure 2a in manuscript shows the conductance-displacement of the target molecules, where the conductance quantum G_0 ($2e^2/h$ = 77.5 μS) represents the formation of Au-Au point contact. After the breaking of Au-Au point contact, a plateau under G_0 is observed, which indicates the formation of the molecular junction.

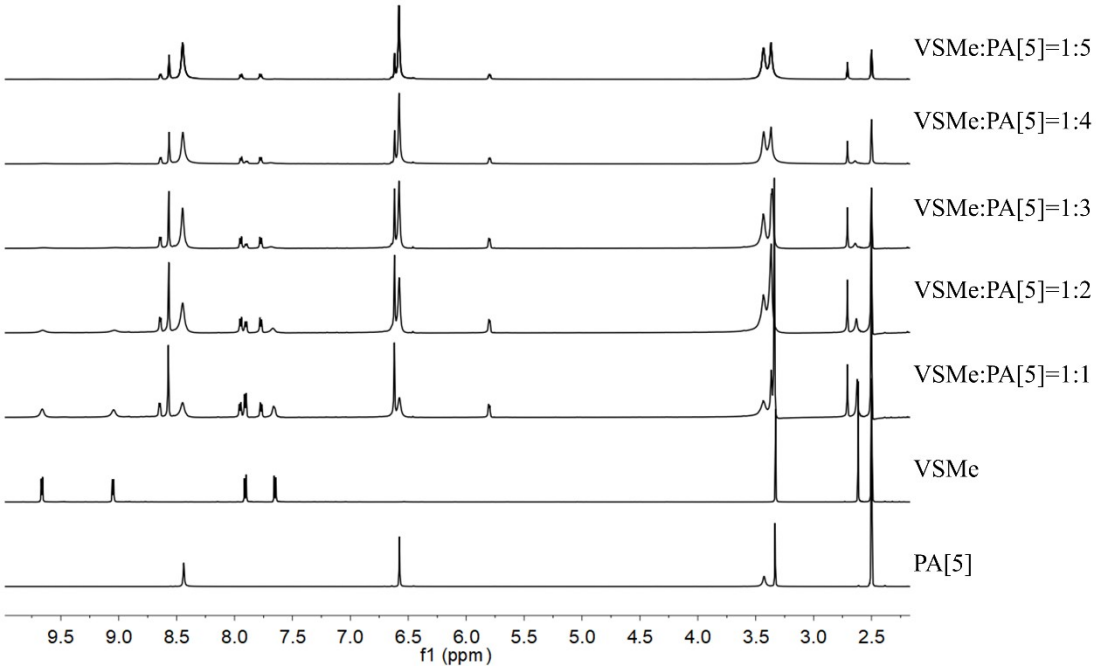

Fig. S1 ^{1}H NMR spectra (600 MHz, d_6-DMSO, 298 K) of VSMe titrated with PA[5] from 0 to 5.0 equivalents.

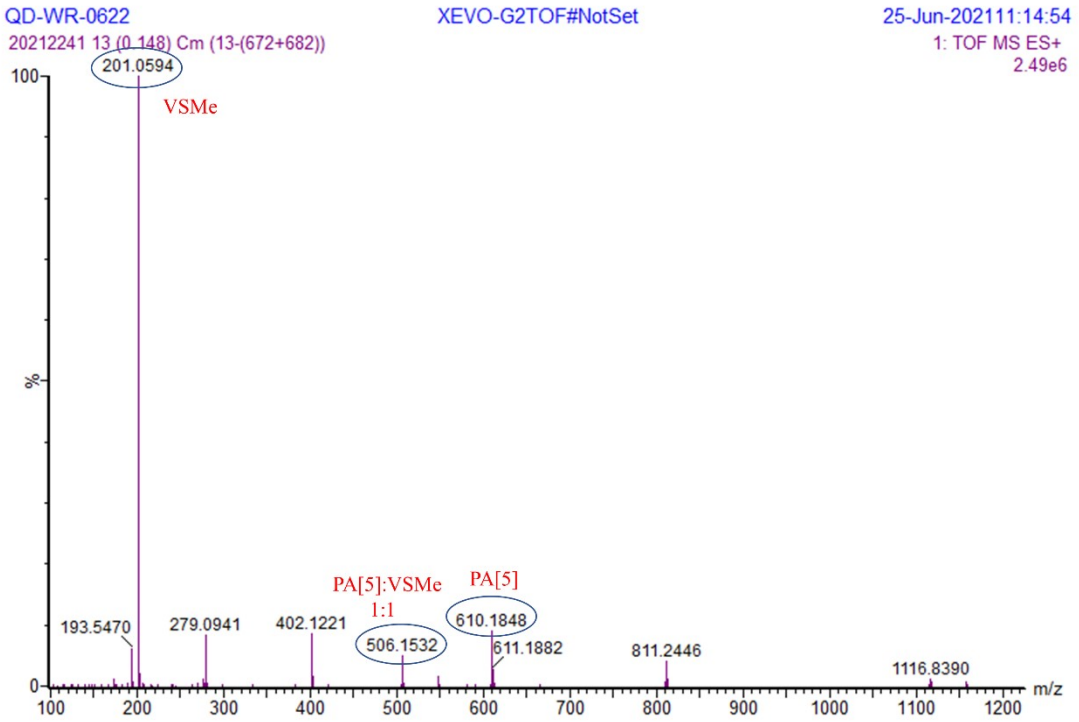

Fig. S2 Electrospray ionization mass spectrometry of a mixture with equimolar of VSMe and PA[5].

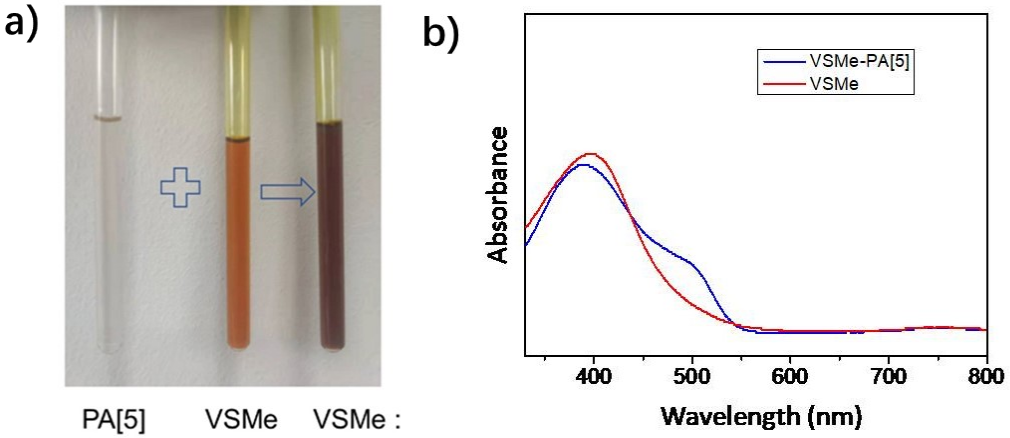

Fig. S3 a) The solution color of PA[5], VSMe and VSMe-PA[5] complex; b) The absorption spectra of VSMe and VSMe-PA[5] in DMSO solution. VSMe-PA[5] was prepared *in situ* by mixing the same equivalence of VSMe and PA[5].

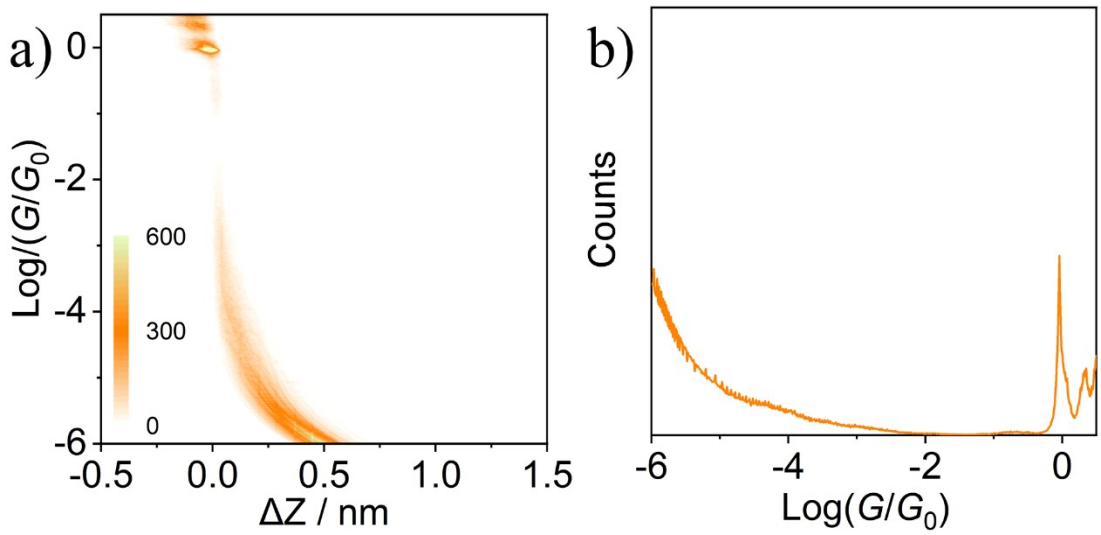

Fig. S4 (a) Two-dimensional (2D) conductance-displacement histogram and (b) One-dimensional (1D) conductance histograms for PA[5].

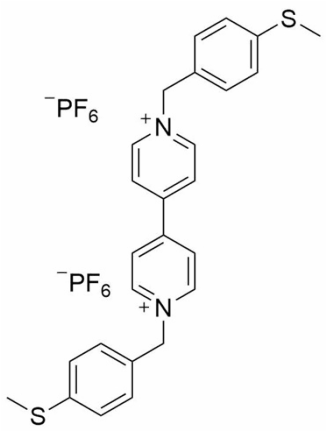

Fig. S5 The molecular structure of BIPY-SMeBn.

References

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