Supporting Information for:

Probing Charge Transport of Ruthenium-Complex-Based Molecular Wires at the Single-Molecule Level

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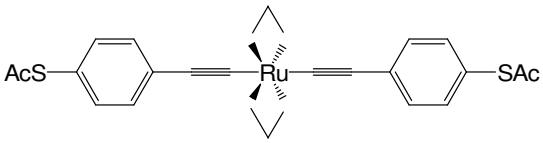
Synthesis

^{1}H NMR spectra were recorded on a Bruker Avance 400 or Varian Unity 400 spectrometer. Proton chemical shifts (δ) were obtained in ppm downfield from tetramethylsilane (TMS). Mass spectroscopy was performed on VG-Qauttro and LCQ Finnigion Mat. Tetrahydrofuran (THF) was distilled under nitrogen over sodium

benzophenone ketyl. Diisopropylethylamine (*i*-Pr_2NEt) and CH_2Cl_2 were distilled over CaH_2 under nitrogen. THF and *i*-Pr_2NEt was degassed with argon stream for 1 h before used in the Castro-Stephens-Sonogashira coupling reaction. Flash chromatography was carried out using silica gel and neutral alumina (230-400 mesh). Thin layer chromatography (TLC) was performed on silica gel coated aluminum foils (Merck alumina foils 60F254). Beilstein Autonom was used to name the new compounds.



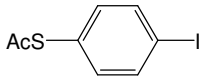
Bis-alkynyl ruthenium(II) complex (1). An oven-dried flask equipped with a magnetic stir bar was charged with **3** (0.470g, 0.5mmol), $NaPF_6$ (0.252g, 1.50mmol) and dichloromethane (25mL). The mixture was stirred for 1 day in the absence of light with **6** (0.264g, 1.50mmol), *i*-Pr_2NEt (0.70mL) and dichloromethane (25mL). 1,8-diazabicyclo[5.4.0]-undec-7-ene (0.15mL, 1.0mmol) was added and the mixture was stirred for an additional 2h, filtered through Al_2O_3 and the solvent was removed under reduced pressure to afford crude product. The crude product was purified by column chromatography (neutral Al_2O_3, petroleum ester/dichloromethane from 6:1 to 3:2 as eluent) to provide 0.41g of green yellow solid product (67%). ^1H NMR ($CDCl_3$, 400MHz): δ 7.48(br s, 16H), 7.29-7.23(m, 8H), 7.17-7.08(m, 16H), 6.96(d, 4H), 6.23(d, 4H), 4.82(s, 4H), 2.43(s, 6H). ES-MS(m/z):1221$[M]^+$.

Thioacetic acid S-{4-[4-(4-acetylsulfanyl-phenylethynyl)-phenylethynyl]-phenyl} ester (2). All of the reagents were thoroughly dried and flushed with argon before use. To a flame-dried vessel were added **4** (0.310g, 1.10mmol), **8** (0.070g, 0.55mmol), $Pd(dba)_2$ (0.0317g, 0.055mmol), PPh_3 (0.0721g, 0.28mmol), CuI (0.0209g, 0.055mmol), well-degassed *i*-Pr_2NEt (1mL) and THF (4mL). The vessel was sealed and allowed to stir at 50ºC for 1 day. The reaction mixture was then poured into water,

and the aqueous layer was extracted three times with dichloromethane. After drying the combined organic layers over magnesium sulfate, the solvent was removed in vacuum to afford a crude product. The crude product was purified by column chromatography (silica gel, petroleum ester/THF 4:1 as eluent) to provide 0.20g of white solid product (86%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ 7.56 (d, 4H), 7.52 (s, 4H), 7.41 (d, 4H), 2.44(s, 6H). EI-MS(m/z): 426 (M^+).

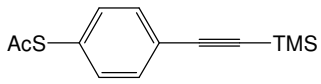
Cis-Ru(dppm)$_2$Cl$_2$ (3). An oven-dried flask equipped with a magnetic stir bar was charged with bis(diphenylphosphino)methane (3.38g, 8.8mmol) and ethanol (240mL). The mixture was refluxed at 90ºC for 2h with solution of ruthenium(III) chloride (0.84g, 4.2mmol) in water (25mL). Water (200mL) was added and the mixture was extracted with chloroform, dried over magnesium sulfate and recrystallized in dichloromethane/ethanol to provide 2.71g trans-Ru(dppm)$_2$Cl$_2$ of orange yellow solid product (65%).

An oven-dried flask equipped with a magnetic stir bar was charged with trans-Ru(dppm)$_2$Cl$_2$ (1.41g, 1.4mmol) and 1,2-dichloroethane (100mL). The mixture was refluxed for 1 day, cooled to room temperature, poured into pentane (400mL) and filtered to provide 1.13g of yellow solid product (80%).

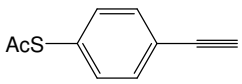


Thioacetic acid S-(4-iodo-phenyl) ester (4). An oven-dried flask equipped with a magnetic stir bar was charged with Zn powder (4.55g, 70.0mmol) and dichlorodimethylsilane (8.49mL, 70.0mmol) in dry 1,2-dichloroethane (160mL). 4-Iodo-benzenesulfonyl chloride (6.05g, 20.0mmol) and N,N-Dimethyl-acetamide (5.60mL, 60.0mmol) in dry 1,2-dichloroethane (160mL) was added dropwise and the solution was stirred at 75ºC for 4h. The mixture was stirred at 75□ for an additional 30min after the addition of potassium carbonate (1.52g, 11.0mmol). The mixture was cooled to room temperature and acetyl chloride (5.68mL, 80.0mmol) was added. The mixture was stirred overnight and filtered. The resulting solution was diluted with

80mL dichloromethane, washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure. The resulting solid was purified by column chromatography (silica gel, petroleum ester as eluent) to provide 4.62g of white solid product (83%). ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.742(d, 2H), 7.128(d, 2H), 2.425(s, 3H).



Thioacetic acid S-(4-trimethylsilanylethynyl-phenyl) ester (5). All of the reagents were thoroughly dried and flushed with argon before use. To a flame-dried vessel were added the trimethylsilylacetylene (2.8mL, 20.0mmol), **4** (4.17g, 15.0mmol), $Pd(PPh_3)Cl_2$ (0.525g, 0.75mmol), CuI (0.143g, 0.75mmol), well-degassed *i*-Pr_2NEt (5.3mL) and THF (24mL). The vessel was sealed and allowed to stir at 50ºC for 1 day. The reaction mixture was then poured into water, and the aqueous layer was extracted three times with dichloromethane. After drying the combined organic layers over magnesium sulfate, the solvent was removed in vacuum to afford a crude product. The crude product was purified by column chromatography (silica gel, petroleum ester and petroleum ester/dichloromethane 4:1 as eluent) to provide 3.46g of light yellow solid product (93%). ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.48□d, 2H□, 7.34 (d, 2H), 2.43 (s, 3H), 0.25(s, 9H).

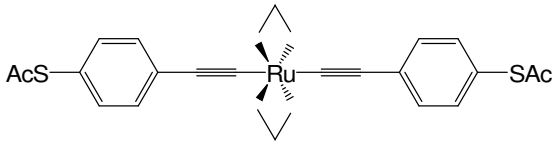


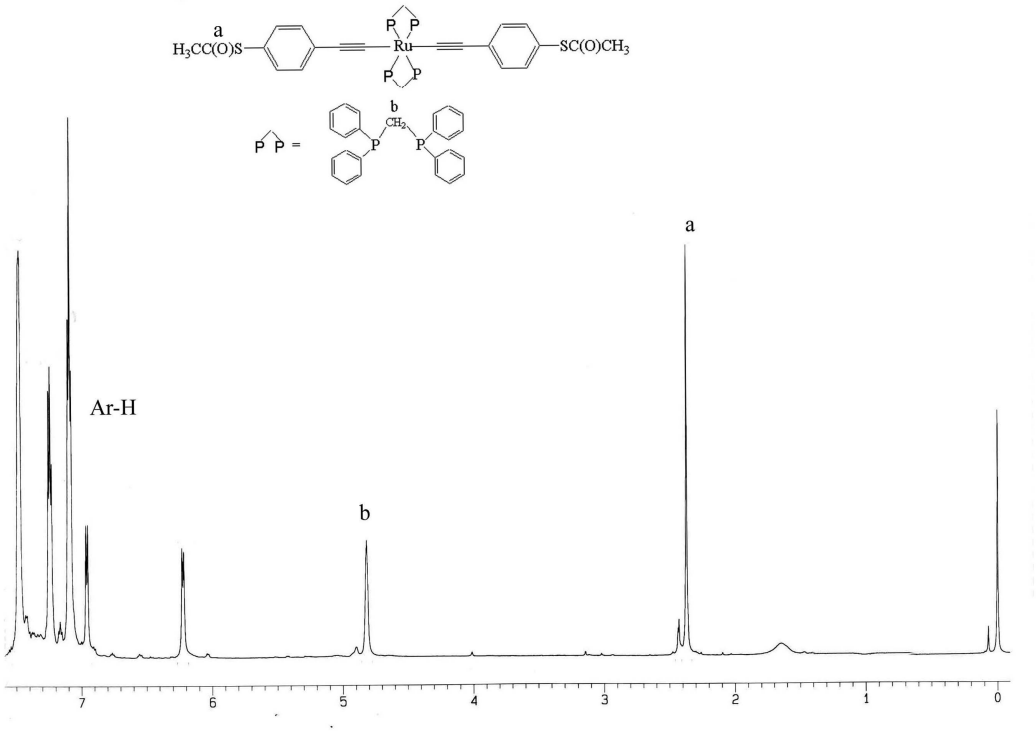
Thioacetic acid S-(4-ethynyl-phenyl) ester (6). The **5** (1.87g, 7.53mmol) was dissolved in THF in a plastic vessel. A mixed solution of acetic anhydride/acetic acid (4.8mL:4.8mL) and 1.0M tetrabutylammonium fluoride (2.59g, 8.21mmol) in THF (10mL) was added dropwise at -15ºC. The solution was stirred for 15 min and quenched with silica gel. The mixture was poured into water and extracted with diethyl ether. The extract was washed with brine and dried over magnesium sulfate. After filtration the solvent was evaporated in vacuo. The crude product was purified by a flash chromatography (silica gel, petroleum ester/dichloromethane from 5:1 to

1:1 as eluent) to provide 1.30g of light yellow liquid product (95%). ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.52(d, 2H), 7.37(d, 2H), 3.16(s, 1H), 2.43(s, 3H).

1,4-Bis-trimethylsilanylethynyl-benzene (7). All of the reagents were thoroughly dried and flushed with argon before use. To a flame-dried vessel were added 1,4-diiodobenzene (1.24g, 3.75mmol), $Pd(PPh_3)Cl_2$ (0.263g, 0.375mmol), CuI (0.143g, 0.375mmol), trimethylsilylacetylene (1.4mL, 9.90mmol), well-degassed *i*-Pr_2NEt (2.5mL) and THF (5mL). The vessel was sealed and allowed to stir at room temperature for 1 day. The reaction mixture was then poured into water, and the aqueous layer was extracted three times with dichloromethane. After drying the combined organic layers over magnesium sulfate, the solvent was removed in vacuum to afford a crude product. The crude product was purified by column chromatography (silica gel, petroleum ester as eluent) to provide 0.84g of white solid product (83%). ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.39(s, 4H), 0.25(s, 18H).

1,4-Diethynyl-benzene (8). The **7** (0.54g, 2.0mmol) was dissolved in methanol (10mL) and dichloromethane (10mL), and potassium carbonate (1.66g, 12.0mmol) was added. The mixture was stirred at room temperature before being poured into water. The solution was extracted with ether and washed with brine. After drying over magnesium sulfate, the solvent was evaporated in vacuo to afford the 0.23g of white solid product (93%). ^{1}H NMR ($CDCl_3$, 400MHz): δ 7.44 (s, 4H), 3.17 (s, 2H).

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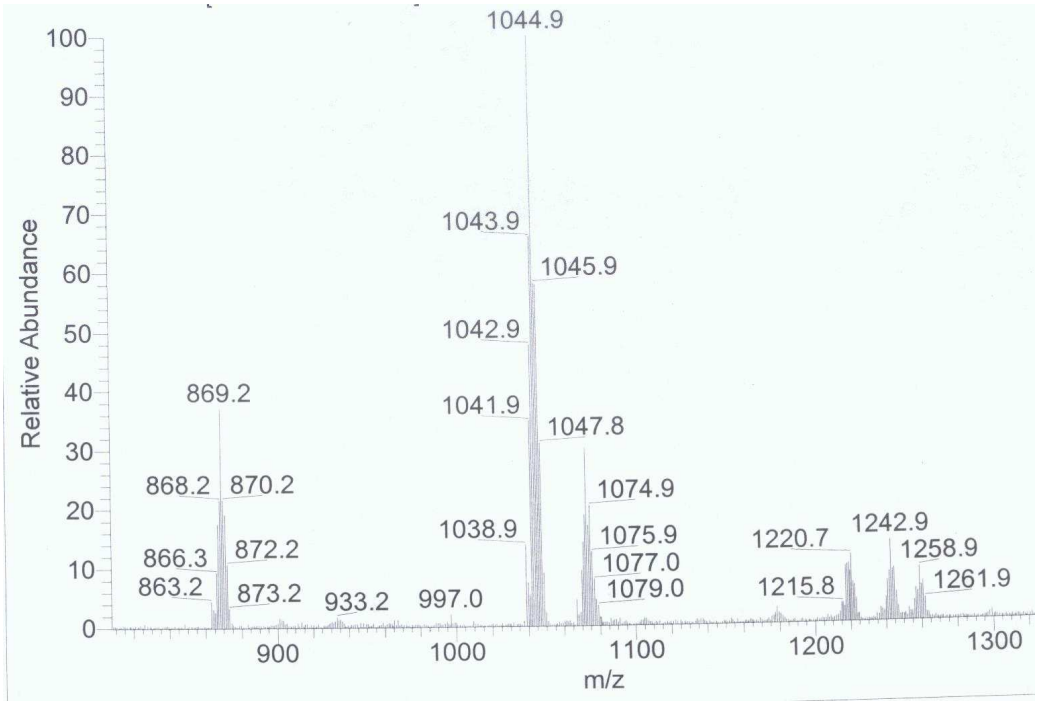
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1038.9
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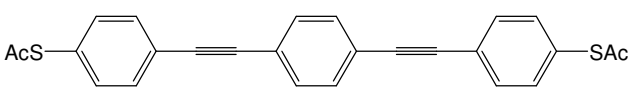
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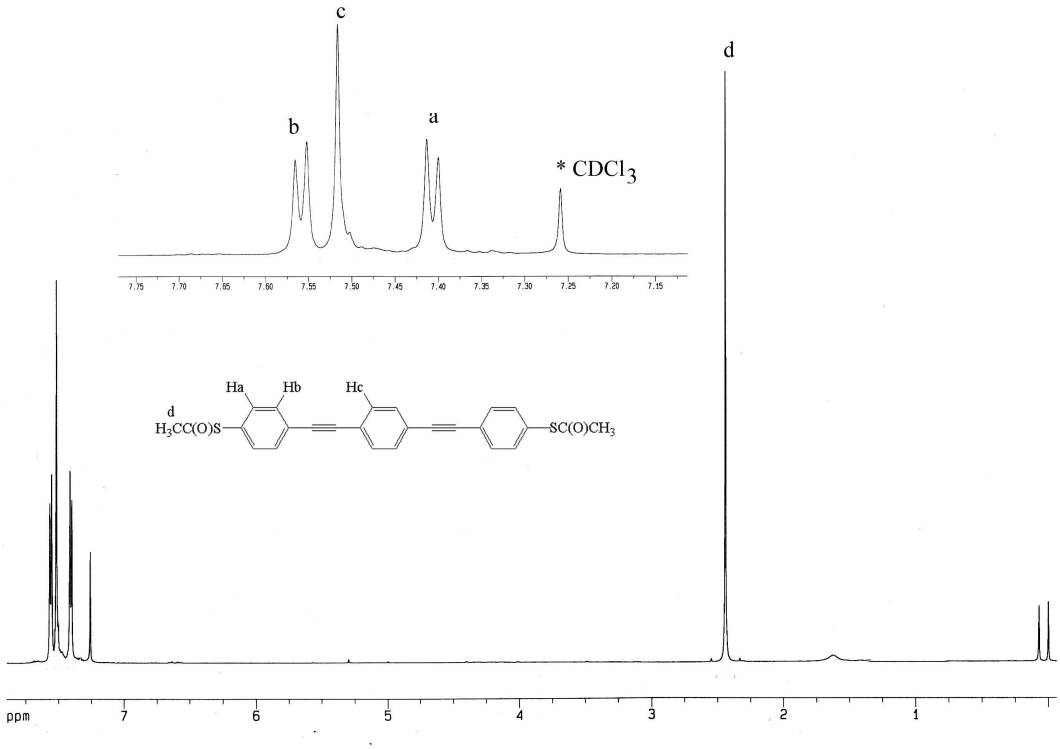
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d
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Hb
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d
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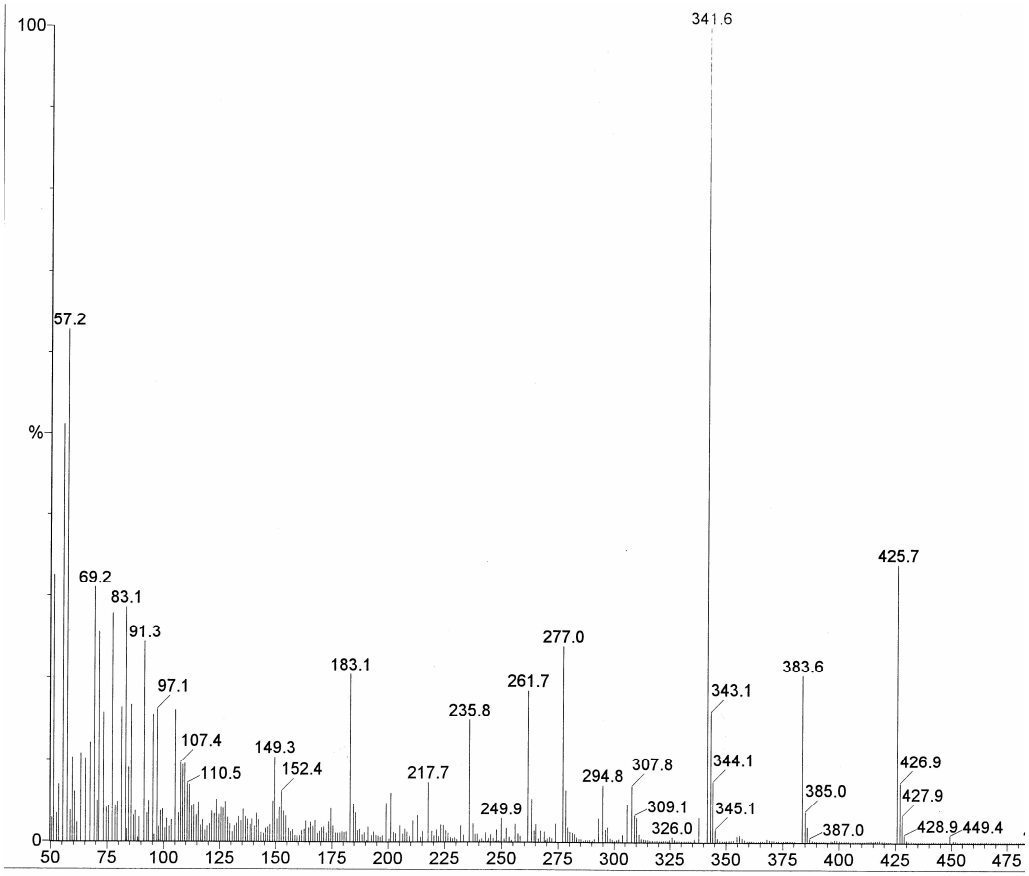
SC(O)CH3
ppm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Stochastic switching of OPERu and OPE

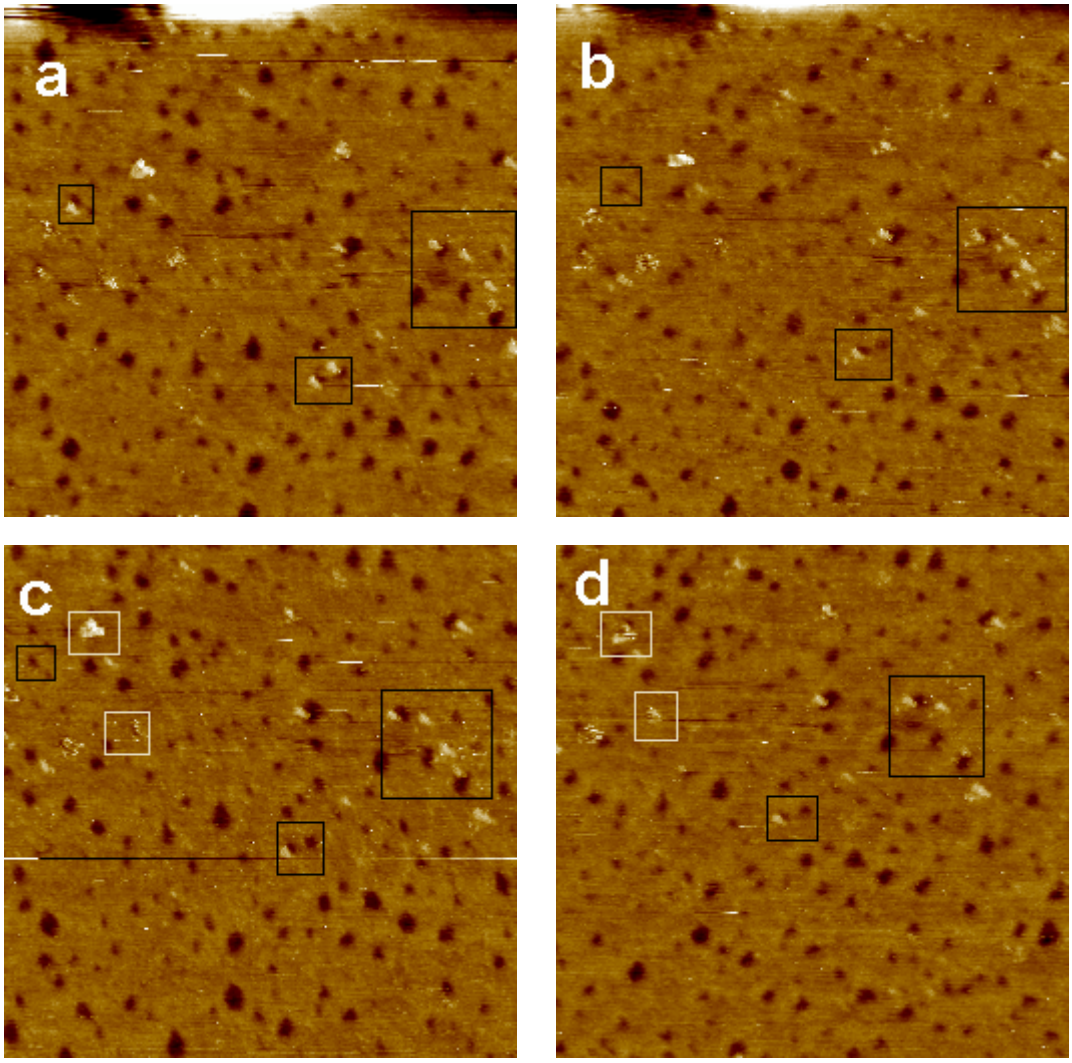


Figure S1. Stochastic switching of **OPERu**, consecutive STM topographies. (a) 0min, (b) 4min, (c) 9min, and (d) 13min. Constant current STM topography (I= 1.5 pA, V= 1.2 V) of **OPERu** inserted into a decanethiol matrix. The scanning size was 127 × 127 nm^2.

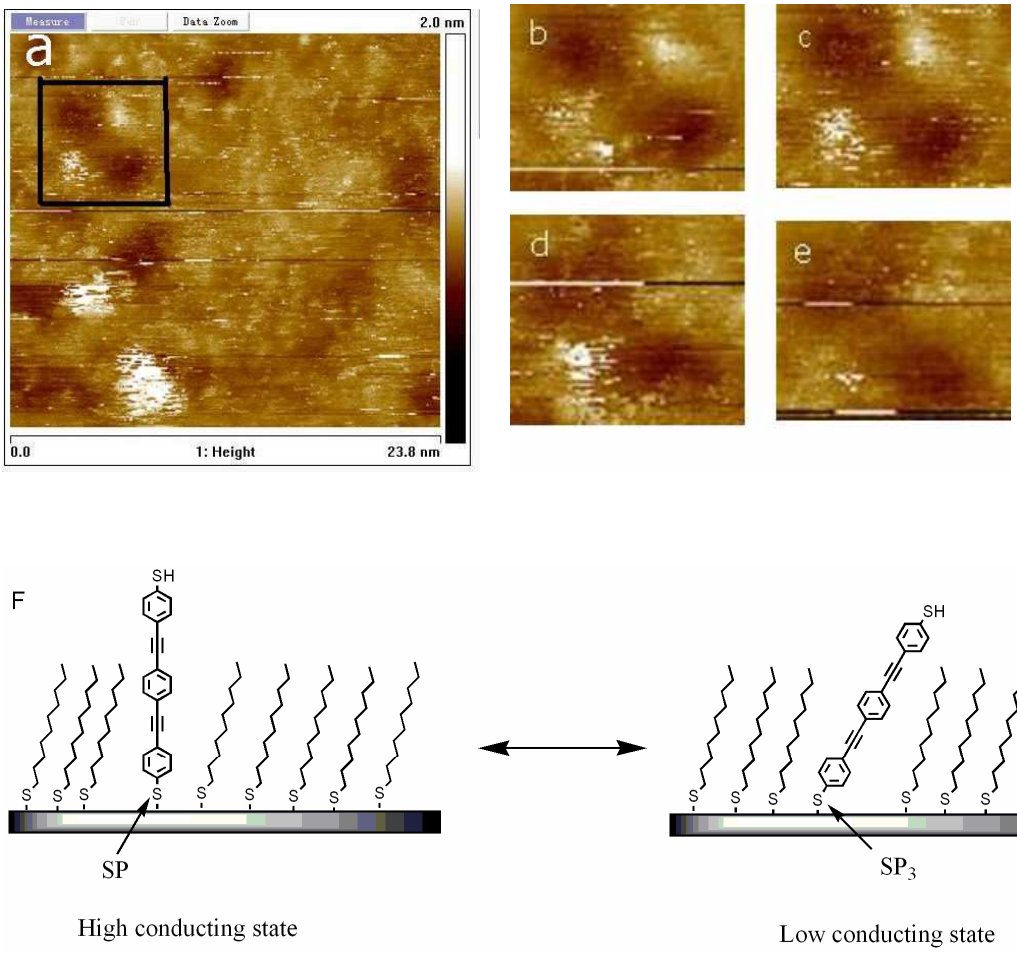
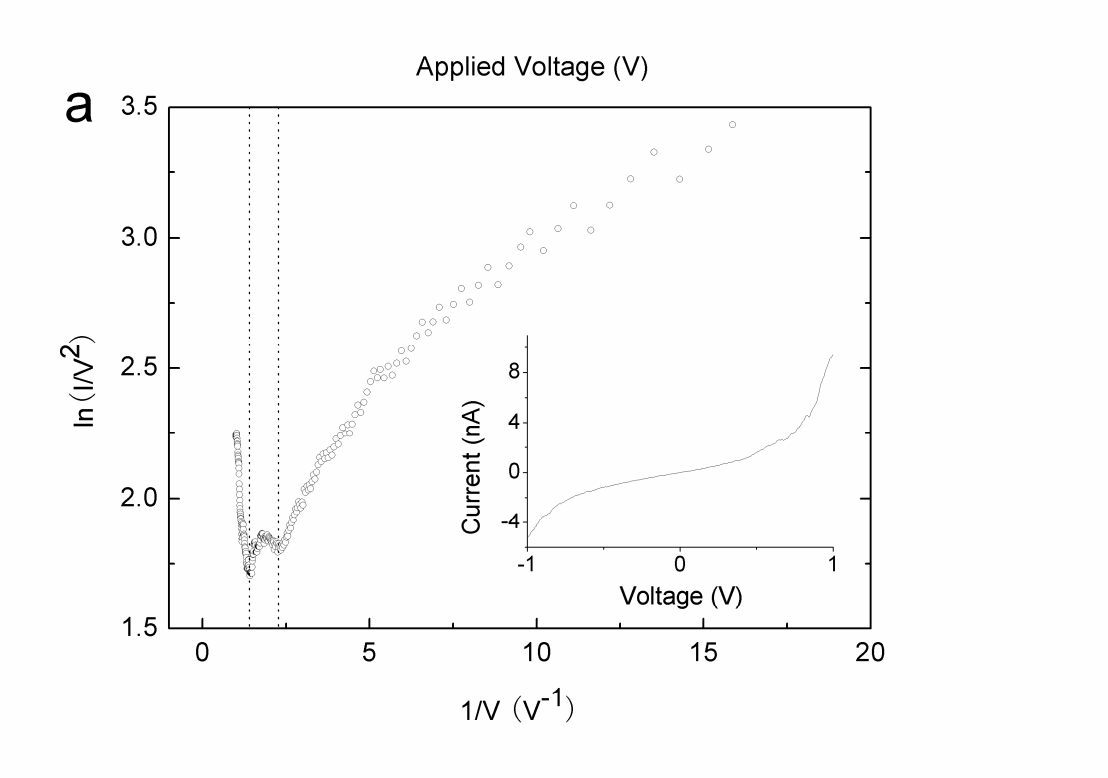
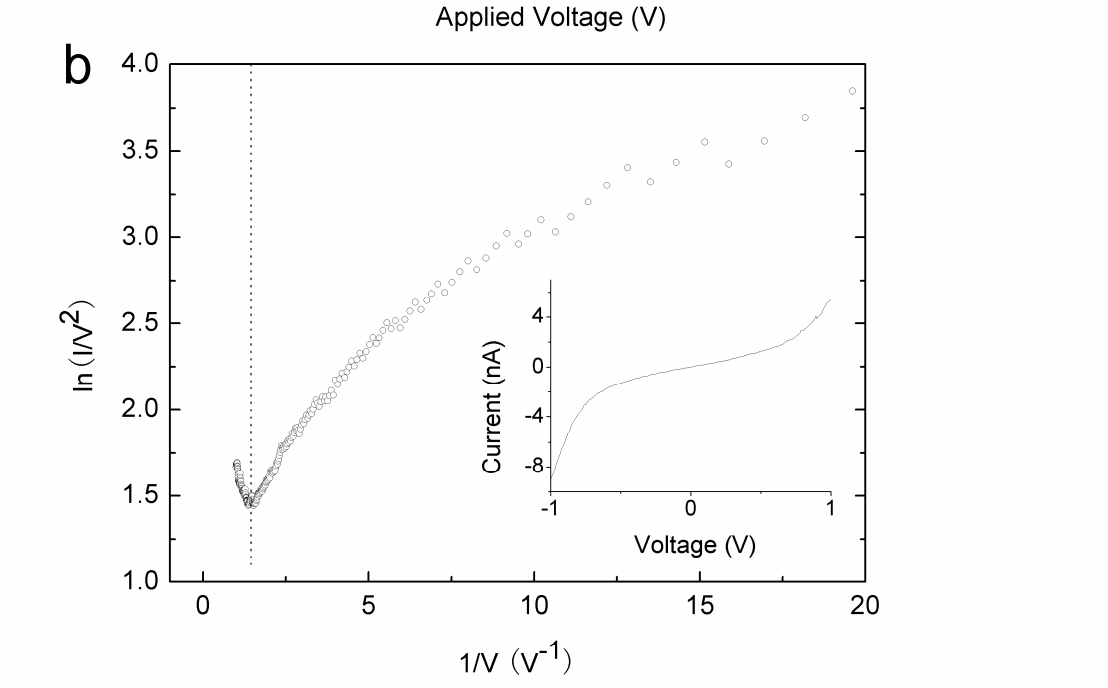


Figure S2. Stochastic switching of **OPE**, consecutive STM topographies. (a) Constant current STM topography (I= 2 pA, V= 1 V) of **OPE** inserted into a decanethiol matrix, the scanning size was 24 × 24 nm^2. (b)-(e) Enlarged images of the blackbox zone in (a), time interval is 4min. (f) The hypothesis of the hybridization change at the molecule-metal interface for the switching phenomena.

Supplemental CP-AFM measurements for OPE and OPERu





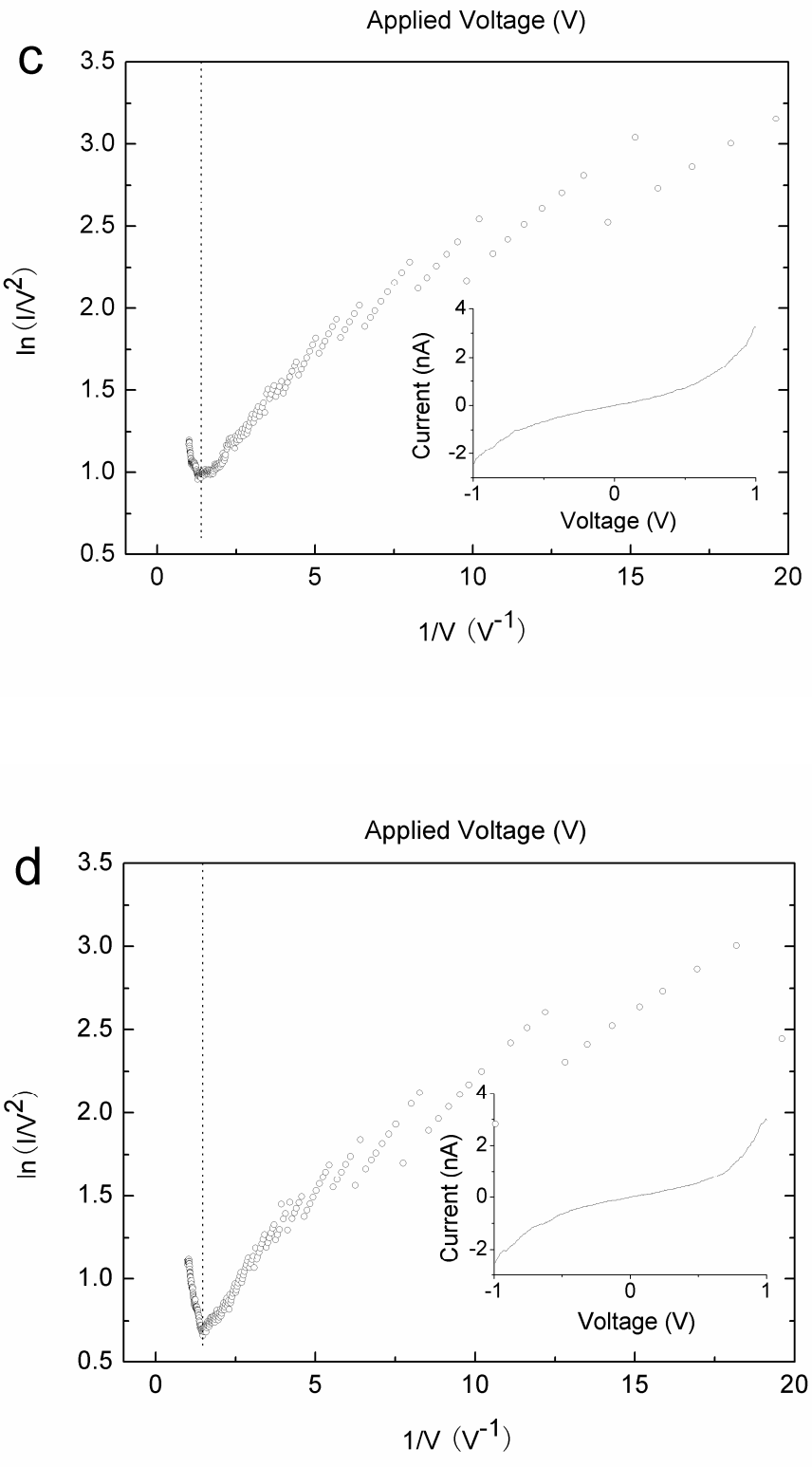
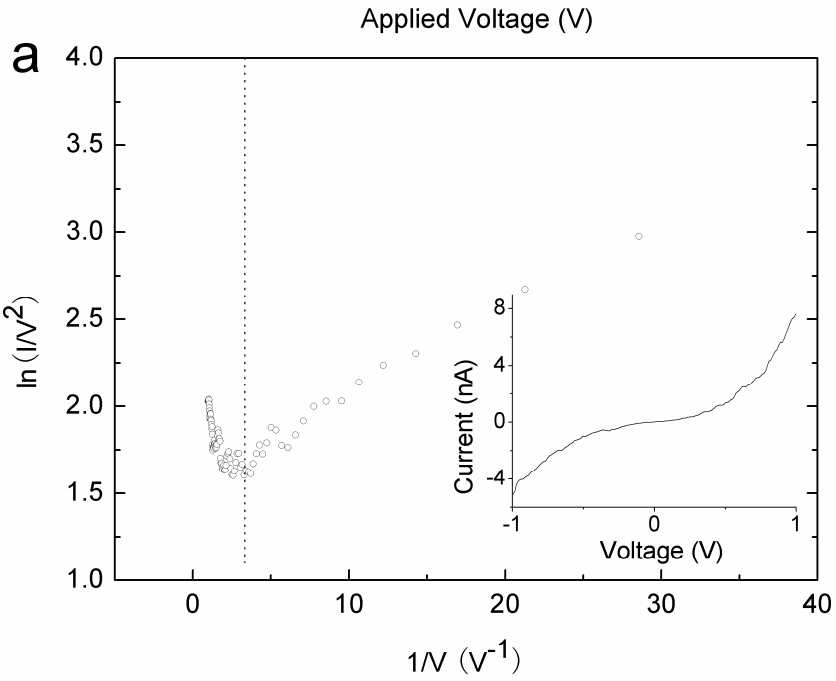


Figure S3. Supplemental CP-AFM measurements for **OPE**. (a)-(d) Circles represent the average of ten current-voltage curves for a Au-**OPE**-PtTi junction measured by CP-AFM. The dashed line corresponds to the voltage at which the tunneling barrier transitions from trapezoidal to triangular (V_{th}). The inset shows current-voltage data.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2.0
1.5
1.0
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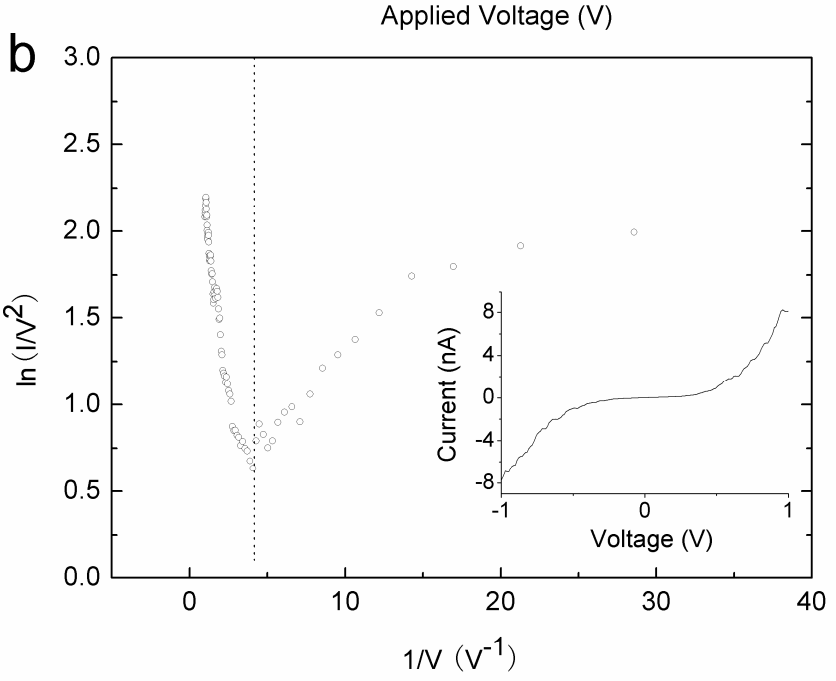
10
20
30
40
1/V (V-1)
8
4
0
-4
Current (nA)
-1
0
1
Voltage (V)


b
Applied Voltage (V)
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2.5
2.0
1.5
1.0
0.5
0.0
ln (I/V2)
0
10
20
30
40
1/V (V-1)
8
4
0
-4
-8
Current (nA)
-1
0
1
Voltage (V)

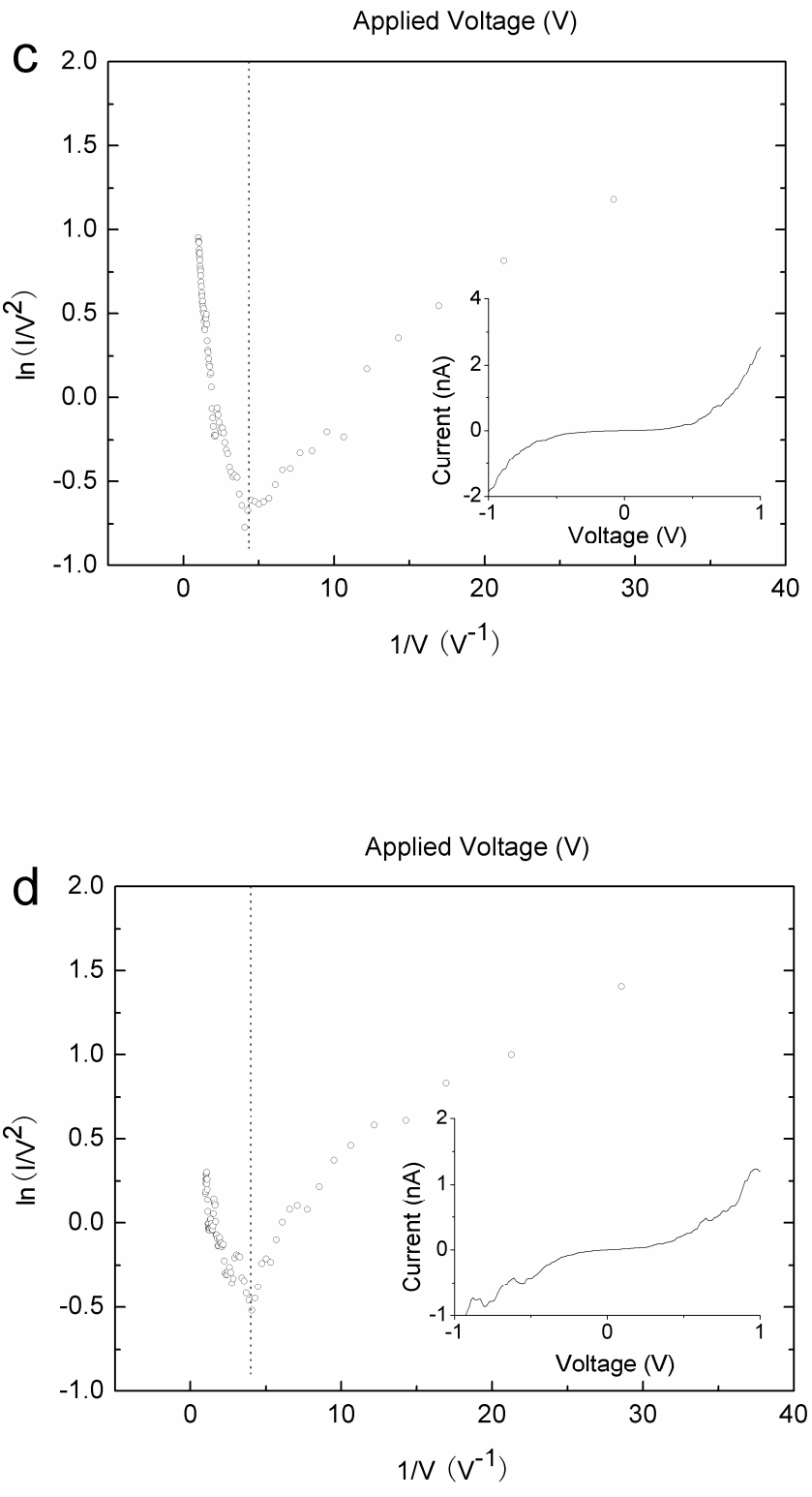

Figure S4. Supplemental CP-AFM measurements for **OPERu**. (a)-(d) Circles represent the average of ten current-voltage curves for a Au-**OPERu**-PtTi junction measured by CP-AFM. The dashed line corresponds to the voltage at which the tunneling barrier transitions from trapezoidal to triangular (V_{th}). The inset shows current-voltage data.

Reference

S1. Frischm M. J.; Trucks, G. W.; H. B. Schlegel, H. B; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery Jr., J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C. *et al.* Gaussian 03 Rev B.03, Gaussian, Inc.: Pittsburgh, PA, 2003.