

Supplement Information

Measurements of Contact Specific Low-bias Negative Differential Resistance of Single Metalorganic Molecular Junction

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SI-1 Synthesize the terpyridine molecules with or without Ruthenium metal ion

Experimental Section.

Synthesis.

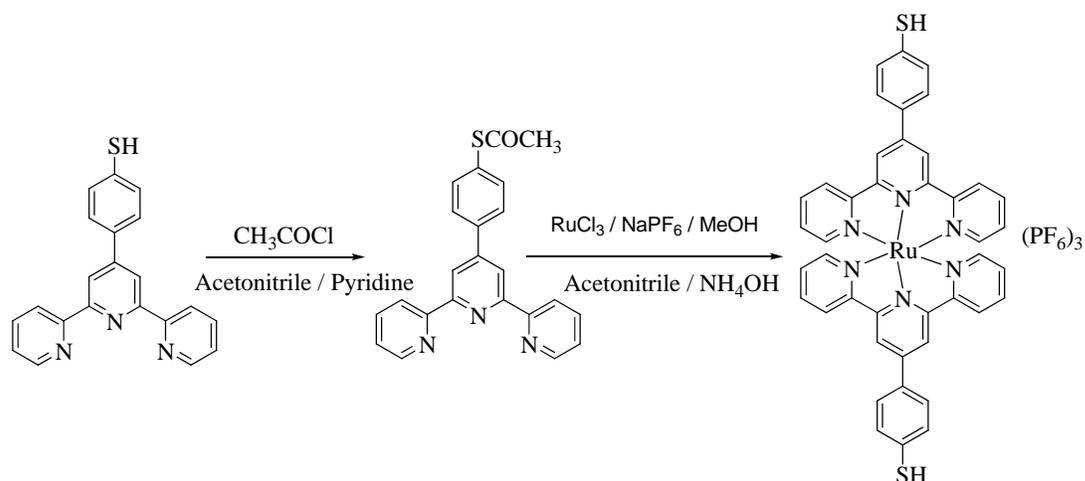
Materials. Ruthenium(III)Cl₃ (Aldrich), Acetylchloride (EMD Chemical), sodium hexafluorophosphate (Alfa Aesar), and ammonium hydroxide (VWR) were used as received. Mercaptophenyl terpyridine (MPTP) was synthesized based on known literature procedures.¹

4'-(4-Acetylmercaptophenyl)-2,2':6,2'-terpyridine (tpySCOMe): To a suspension of mercaptophenylterpyridine (MPTP) (0.34 g, 1 mmol) in acetonitrile (20 ml) was added 0.096 g (1.2 mmol) of pyridine. To this reaction mixture 0.11 g (1.4 mmol) acetylchloride was added dropwise and stirred at room temperature for two hours. The mixture was concentrated to dryness using rotary evaporation. The solid residue was dissolved in 50 ml of DCM and washed with water (3 × 100 ml). The DCM solution was dried with anhydrous sodium sulfate, concentrate to dryness. Finally, the product was purified using a neutral alumina column with hexane /ethylacetate (4:1) solvent mixture. Yield: 0.29 g (76 %). ¹H NMR (300 MHz, CDCl₃) δ (ppm): 8.73 (m, 2H); 8.72 (s, 2H); 8.67 (d, J = 8.1 Hz, 2H); 7.93-7.84 (m, 4H); 7.38-7.33 (m, 4H); 2.54 (s, 3H). ¹³C NMR (300 MHz, CDCl₃) δ (ppm): 155.26, 154.93, 148.13, 148.07, 135.83, 135.82, 133.80, 126.57, 125.48, 122.27, 120.32, 177.84, 117.36, 28.65.

[Ru^{III}(tpySH)₂](PF₆)₂ : RuCl₃ (0.104 g, 0.5 mmol) was added to a methanolic (15 ml) solution of 4'-(4-Acetylmercaptophenyl)-2,2':6,2'-terpyridine (tpySCOMe) (0.191 g, 0.5 mmol) and stirred at room temperature for 1 hr. During the reaction, the metal complex precipitated as the chloride salt. Sodium hexafluorophosphate (0.101 g, 0.6 mmol) was added

and stirred for an additional 1 hour. The solution was filtered and concentrated to dryness under rotary evaporation. The solid material was dissolved in acetonitrile and NH_4OH (1 ml) was added and stirred for 30 minutes. The mixture was concentrated to dryness, and the resulting orange-red solid was crystallized from methanol. Yield: 0.256 g (51 %). ^1H NMR (300 MHz, CDCl_3) δ (ppm): 8.73 (m, 2H); 8.71 (s, 2H); 8.65 (d, $J = 7.2$ Hz, 2H); 7.90-7.84 (m, 4H); 7.67 (d, $J = 9.0$ Hz, 2H); 7.36-7.33 (m, 2H). MS (MALDI) m/z 784.

Scheme 1.



Results and discussions

The synthetic strategy for ruthenium-terpyridine complex is outlined in Scheme 1. The reactive thiol group was protected by conversion to an acetyl group before complex formation. The acetyl derivative of terpyridine was isolated as light yellow solid, in good yield (78 %) by a condensation reaction between terpyridine thiol and acetylchloride in acetonitrile at room temperature. We prepared the Ru complex with PF_6 counter ion by reacting metal chloride with acetyl substituted terpyridine followed by ion exchange with NaPF_6 and finally deprotection with NH_4OH . We exchanged the counter anion to achieve for solubility reasons. The PF_6 salt was purified as orange-red crystals by recrystallization from

methanol.

References:

- (1) Auditore, A.; Tuccitto, N.; Marzanni, G.; Quici, S.; Puntoriero, F.; Campagna, S.; Licciardello, A. *Chem. Commun.* **2003**, 2494-2495.

SI-2. STM image of Ru(tpy-SH)₂ Self-Assembled Monolayers (SAMs)

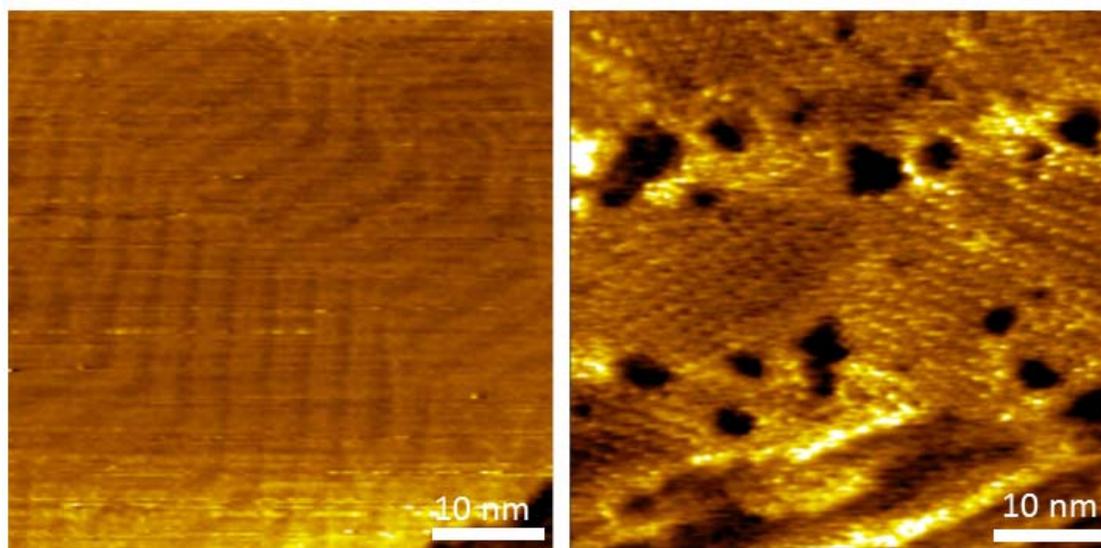


Figure SI-1. STM high-resolution images of Au (1,1,1) (left) and Ru(tpy-SH)₂ SAMs (right).

SI-3. Conductance histograms and IV-curves for multiple single molecular conductance sets of Ru(tpy-SH)₂ molecular junctions

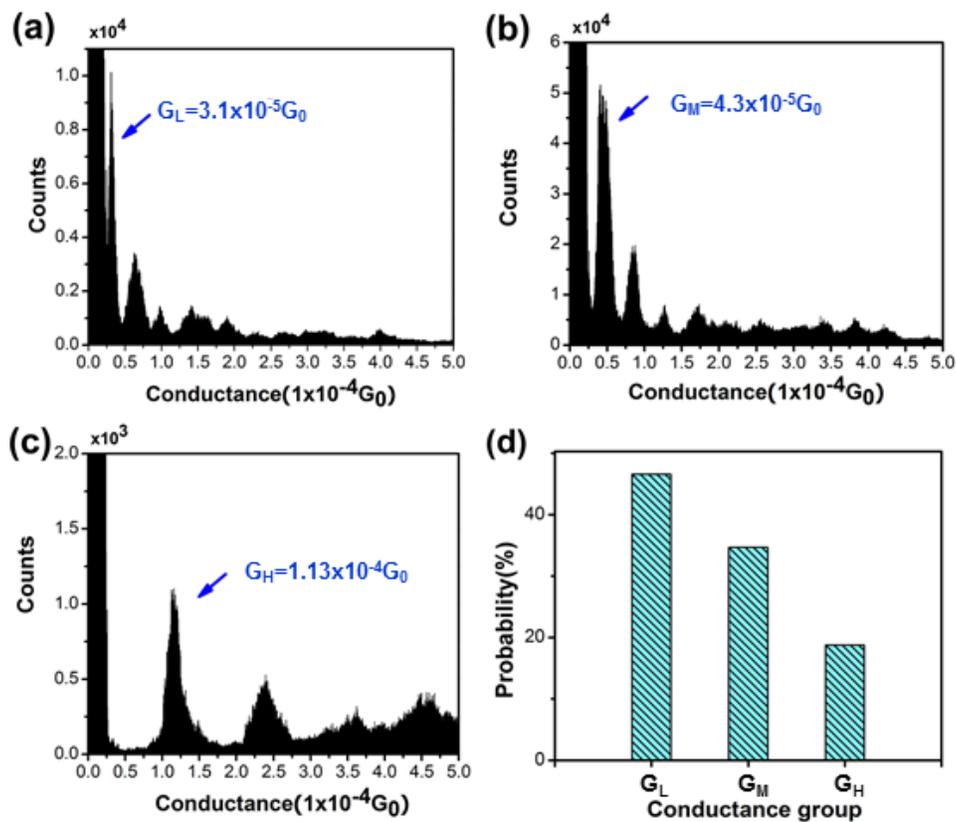


Figure SI-2. Three different single molecular conductance sets for Ru(tpy-SH)₂ molecular junctions measured under the bias of +0.3V (totally 522/~1000 conductance traces with plateaus). (a)-(c) are the conductance histogram for each set, (a) $G_L = 3.1 \times 10^{-5}G_0$, (b) $G_M = 4.3 \times 10^{-5}G_0$, (c) $G_H = 1.13 \times 10^{-4}G_0$. (d) Probability of each conductance set related to specific contact configuration.

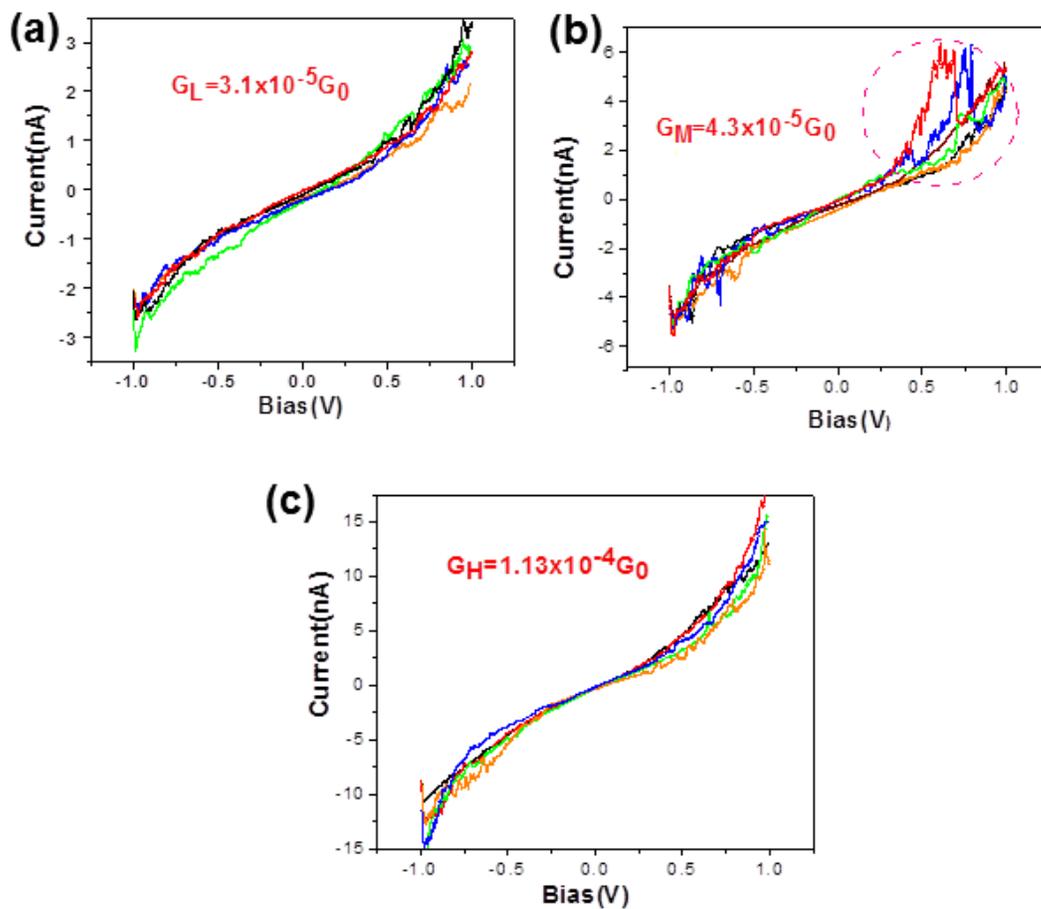


Figure SI-3. Typical I-V curves of Ru(tpy-SH)₂ for the three single molecule conductance sets. (a)

$G_L = 3.1 \times 10^{-5} G_0$, (b) $G_M = 4.3 \times 10^{-5} G_0$, (c) $G_H = 1.13 \times 10^{-4} G_0$.

SI-4. The single molecular I-V curves for all single molecular conductance sets of C8DT

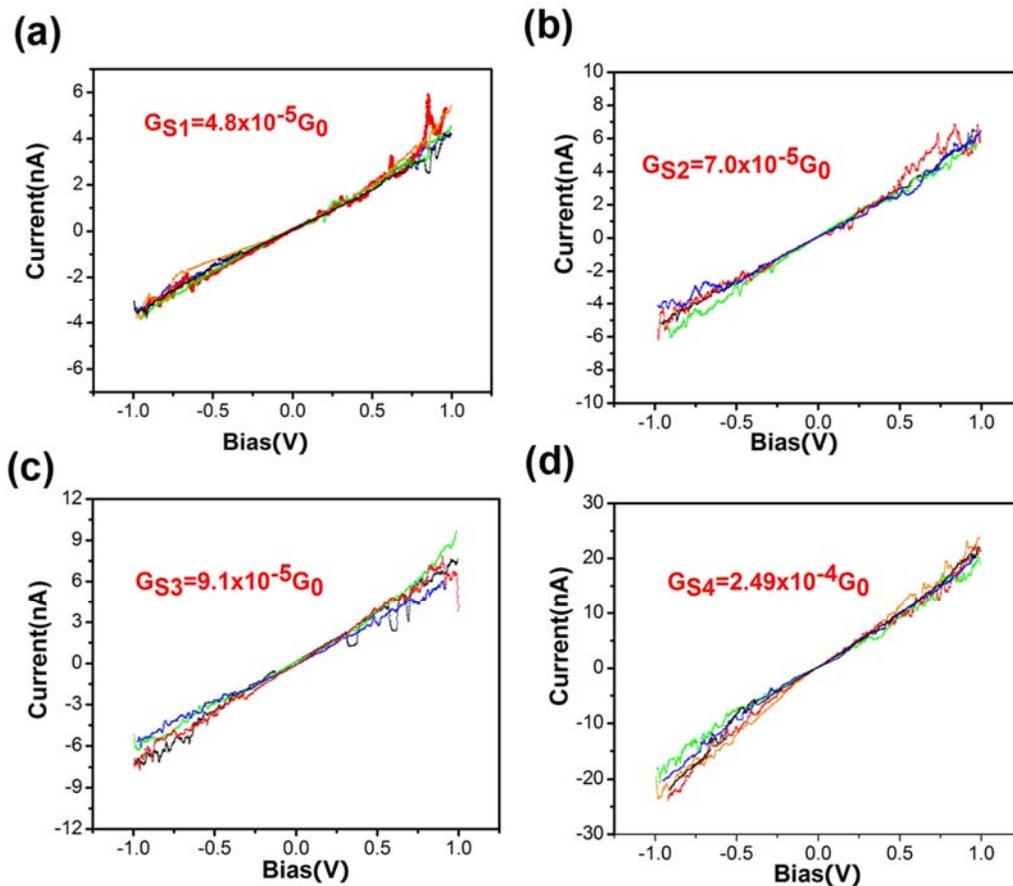


Figure SI-4. The single molecular I-V curves for each single molecular conductance set of C8DT. (a)

$G_{S1} = 4.8 \times 10^{-5} G_0$, (b) $G_{S2} = 7.0 \times 10^{-5} G_0$, (c) $G_{S3} = 9.0 \times 10^{-5} G_0$, and (d) $G_{S4} = 25.9 \times 10^{-5} G_0$.