Charge transport mediated by d-orbitals in transition metal complexes.

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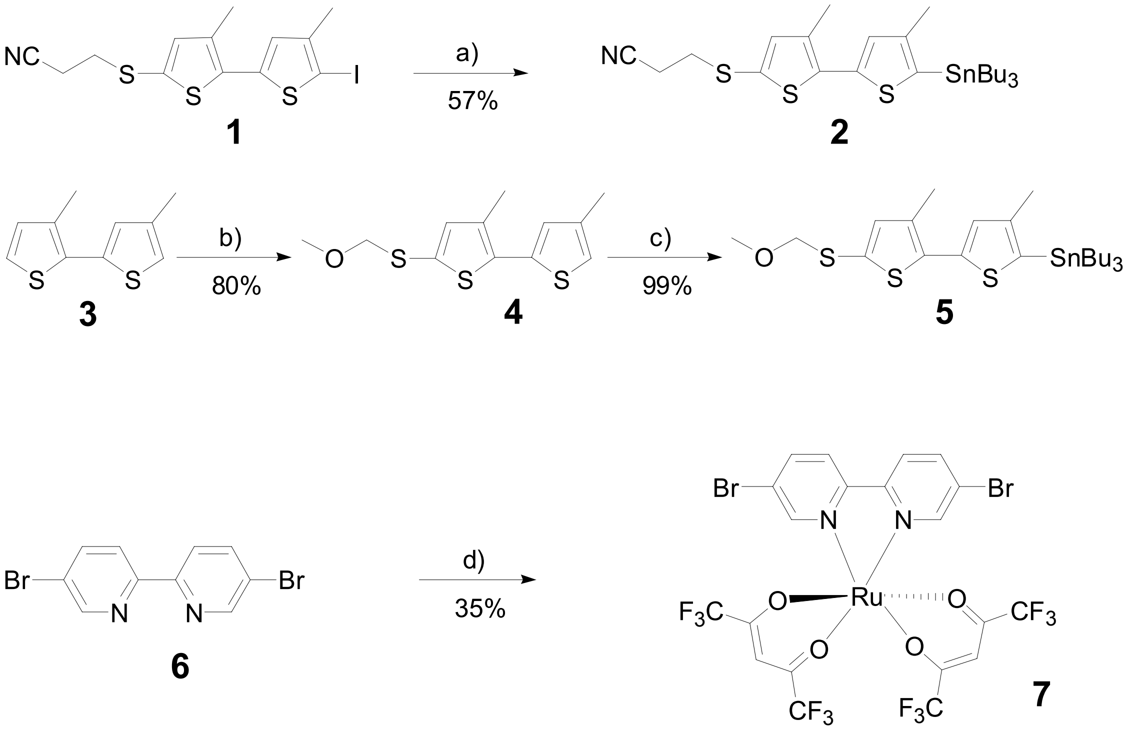
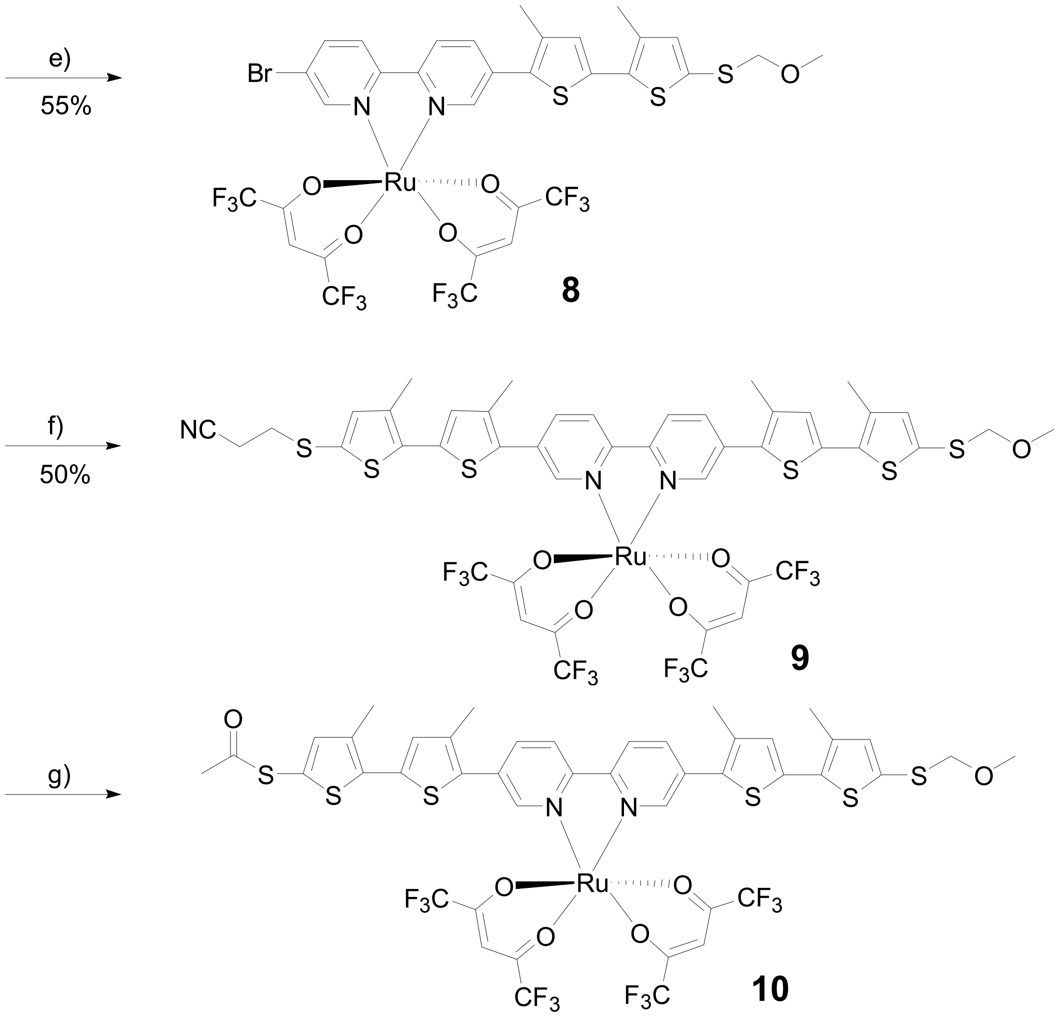
Synthesis

All solvents were HPLC grade. Tetrahydrofuran (THF) was distilled from sodium benzophenone ketyl under an argon atmosphere prior to use. Absolute ethyl alcohol (200 proof) was purchase from Aaper alcohol and chemical Co. Flash chromatography was carried using EM science Kieselgel 60(230-400) mesh. All reagents were purchase from Sigma-Aldrich, Acros, and Strem and used as received. All reactions were carried out under nitrogen atmosphere. ^{1}H NMR spectra were recorded at 400MHz or 500MHz (^{13}C NMR, at 100MHz or 125MHz) on Bruker DRX-400 or DRX-500 spectrometers, respectively. $CDCl_3$ was used as NMR solvent for all samples.

Scheme 1. Synthesis of the ruthenium(II) Complex **10**





a) $Bu_3SnSnBu_3$ (1eq), $Pd(PPh_3)_4$ (5mol%), Toluene, reflux, 24hr; b) i) n-BuLi (1.2eq), THF, -78°C, then warm to RT for 25min; ii) S8 (1.3eq), -78°C, then warm to 0Oc for 30min; iii) ClCH2OCH3 (1.5eq), -78°C, then warm to RT for 5h; c) n-BuLi (1.2eq), THF, -78°C, then warm to RT for 25min; ii) Bu3SnCl(1.3eq), -78°C, then warm to RT overnight; d) i) RuCl3 xH2O (2eq), CHCl3/EtOH (2:1), 60°C, 4h; ii) mixture of hexafluoropentanedione (4eq) and KOH (4eq) in EtOH, Triethylamine (4eq), THF, 60°C, 3h; e) **5** (1eq), $Pd(PPh_3)_4$ (5mol%), Toluene, reflux, 24h; f) 2 (1.2eq), $Pd(PPh_3)_4$ (10mol%), Toluene, reflux, overnight; g) NaOEt in EtOH (1eq), THF, 20 sec, then quenched with AcCl and Ac_2O (both largely excess, 40eq).

Compound **1** and **3** were synthesized according to the procedure reported by Ng and Lee.[1] Compound **6** was synthesized using the method reported by Bai and co-workers,[2] about 40% pure product was obtained.

Synthesis of 5-Cyanoethylthio-3,4'-dimethyl-5'-tribuyltin-2,2'-bithiophene (2) 0.406g (1.0mmol) of **1** and 0.058g (0.05mmol) of $Pd(PPh_3)_4$ was added to a flame dried round bottom flask equipped with a stir bar and a condenser. The flask was evacuated and nitrogen was filled. Then 0.70mL (1.3mmol) of Bis(tributyltin) was added by a syringe, and 10mL degassed anhydrous toluene was transferred to the flask. The mixture was refluxed at 125°C for 24 hours. Then the reaction mixture was filtered through a pad of celite, washed with ethyl ether, the solution was concentrated in vacuum to give orange oil. The crude product was purified on basic alumina gel using Hexane-Ethyl acetate (10:1 gradient to 5:1 v/v) as eluent to afford 0.3255g (57%) of **2** as yellow oil. ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm): 0.91 (m, 9H, CH_3), 1.15 (m, 6H, CH_2), 1.36 (m, 6H, CH_2), 1.56 (m, 6H, CH_2), 2.30 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 2.65 (t, J=7.2Hz, 2H, CH_2), 2.96 (t, J=7.2Hz, 2H, CH_2), 6.98 (s, 1H, Ar-H), 7.08 (s, 1H, Ar-H). ^{13}C NMR (100MHz, $CDCl_3$): δ (ppm): 10.82, 13.68, 15.51, 17.88, 18.24, 27.26, 29.04, 33.64, 117.93, 127.23, 129.43, 133.23, 133.71, 137.21, 139.87, 140.61, 145.43.

Synthesis of 5-methoxymethylenethio-3,4'-dimethyl-2,2'bithiophene (4) 0.723g (3.72mmol) of **3** was added to a flame dried round bottom flask equipped with a stir bar. The flask was evacuated and nitrogen was filled. Then anhydrous THF (10mL) was added and the solution was cooled to -78°C. 1.6mL (3.9mmol) of n-Butyllithium (2.5M in hexanes) was added via a syringe. The reaction mixture was warmed to room temperature for 20 minutes and cooled to -78°C again. And 0.144g (4.5mmol) Sulfur (S_8) was added in one portion, and the reaction mixture was warmed to 0°C for 30 min and cooled to -78°C, followed by addition of 0.42mL (5.58mmol) of chloromethyl methyl ether, the dry ice bath was removed and stirring continued for 5 hours. The resulting mixture was washed with water and extracted by ethyl ether, combined organic solution was dried by anhydrous sodium sulfate, and the solvent was removed. 0.8g (80%) compound **4** was obtained after purification using silica gel column. ^{1}H NMR (500MHz, $CDCl_3$): δ (ppm): 2.27 (d, J=0.8Hz, 3H, CH_3), 2.33 (s, 3H, CH_3), 3.48 (s, 3H, CH_3), 4.81 (s, 2H, CH_2), 6.87 (s, 1H, Ar-H), 6.92 (d, J=0.8Hz, 1H, Ar-H), 6.93 (s, 1H, Ar-H). ^{13}C NMR (100MHz, $CDCl_3$): δ (ppm): 15.42, 15.75, 56.21, 80.81, 120.83, 127.89, 129.98, 133.95, 135.33, 135.75, 137.81, 138.04.

Synthesis of 5-methoxymethylenethio-3,4'-dimethyl-5'-tributyltin-2,2'bithiophene (5) 0.591g (2.18mmol) of **4** was added to a flame dried round bottom flask equipped with a stir bar. The flask was evacuated and nitrogen was filled. Then anhydrous THF (10mL) was added and the solution was cooled to -78°C. 0.96mL (2.4mmol) of n-Butyllithium (2.5M in hexanes) was added via a syringe. The reaction mixture was warmed to room temperature for 25 minutes and cooled to -78°C, followed by addition of 0.71mL (2.62mmol) of tributyltin chloride, and the dry ice bath was removed and stirring continued for another 7 hours. The resulting mixture was washed with water and extracted by ethyl ether, combined organic solution was washed again with brine and then dried by anhydrous sodium sulfate, and the solvent was removed to obtain the desired compound **5** (yellow oil) in almost quantitative yield base on ^{1}H NMR.

Synthesis of [Ruthenium (II) (5,5'-dibromo-2,2'-bipyridine)] diketonate (7) (Modified from the literature procedures. [3, 4]) 0.2975g (0.95mmol) of 5,5'-dibromo-2,2'-bipyridine and 0.393g (1.895mmol) of hydrated ruthenium trichloride was dissolved in a mixture solvent of $CHCl_3$ (10mL) and ethanol (5mL) in a round bottom flask. The reaction mixture was heated at 60°C for 4 hours, and then the solvent was evaporated in vacuum. To the above reaction mixture 10mL anhydrous THF was added, followed by adding 5mL ethanol solution mixture of 0.213g (3.8mmol) of KOH and 0.54mL (3.8mmol) of 1,1,1,5,5,5-Hexafluoro-2,4-pentanediketone under nitrogen, and then added 0.53mL (3.8mmol) of triethylammine. The resulting mixture was heated at 60°C for 3 hours. Then the solvent was evaporated in vacuum, and 50mL methylene chloride was added to dissolve the remaining solid, and washed once with water. The organic layer was separated, dried over sodium sulfate, and concentrated for flash chromatography. Basic alumina gel was packed in a short column, hexane/methylene chloride(2:1) was used as eluent. 0.27g (35%) of the title compound **7** was obtained as dark purple solid. ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm): 6.16 (s, 2H, CH), 7.96 (dd, J=8.6Hz, J=1.9Hz, 2H, Ar-H), 8.00 (d, J=8.6Hz, 2H, Ar-H), 8.64 (d, J=1.35Hz, 2H, Ar-H).

Synthesis of methoxymethylenethio functionalized ruthenium complex (8) 0.205mmol of compound **5** and 0.012g (0.01mmol) of $Pd(PPh_3)_4$ were added to a round bottom flask equipped with a stir bar and condenser. Then the flask was evacuated in high vacuum, and filled with nitrogen. A solution of 0.17g (0.205mmol) of compound **7** in degassed anhydrous toluene (15mL) was transferred to the above flask under nitrogen. The reaction mixture was refluxed at 125°C for 24 hours, and allowed to cool to room temperature. Then the reaction mixture was filtered through a pad of celite, concentrated and the resulted dark red solid was dissolved in minimum amount of methylene chloride, then precipitated into large amount of hexane to get crude product for flash chromatography with basic alumina gel, using hexane/methylene chloride as eluent. 0.114g (55%) of the title compound **8** was obtained as brown red solid. ^{1}H NMR (500MHz, $CDCl_3$): δ (ppm): 2.34 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 3.48 (s, 3H, CH_3), 4.83 (s, 2H, CH_2), 6.17 (s, 2H, CH), 6.95 (s, 1H, Ar-H), 6.99 (s, 1H, Ar-H), 7.85 (dd, J=8.5Hz, J=2.0Hz, 1H, Ar-H), 7.91 (dd, J=8.5Hz, J=1.5Hz, 1H, Ar-H), 7.95 (d, J=8.5Hz, 1H, Ar-H), 8.07 (d, J=8.5Hz, 1H, Ar-H), 8.67 (d, J=2.0Hz, 1H, Ar-H), 8.72 (d, J=1.5Hz, 1H, Ar-H).

Synthesis of ruthenium(II) complex (9) 0.105g (0.10mmol) of compound **8**, 0.16mmol of compound **2** and 0.012g (0.01mmol) of $Pd(PPh_3)_4$ were added to a round bottom flask equipped with a stir bar and condenser. Then the flask was evacuated in high vacuum, and filled with nitrogen. Degassed anhydrous toluene (10mL) was transferred to the above flask under nitrogen. The reaction mixture was refluxed at 125°C for 24 hours, and allowed to cool to room temperature. Then the reaction mixture was filtered through a pad of celite, concentrated and the resulted dark red solid was dissolved in minimum amount of methylene chloride, then precipitated into large amount of hexane to afford 0.06g (~50%)of the title compound **8** as brown red solid. ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm): 2.366 (s, 3H, CH_3), 2.373 (s, 3H, CH_3), 2.385 (s, 3H, CH_3), 2.398 (s, 3H, CH_3), 2.69 (t, J=7.2Hz, 2H, CH_2), 3.01 (t, J=7.2Hz, 2H, CH_2), 3.49 (s, 3H, CH_3), 4.83 (s, 2H, CH_2), 6.17 (d, 1H, CH), 6.18 (s, 1H, CH), 6.96 (s, 1H, Ar-H), 7.01 (s, 1H, Ar-H), 7.023 (s, 1H, Ar-H), 7.025 (s, 1H, Ar-H), 7.90 (dd, J=8.4, 2.0Hz, 2H, Ar-H), 8.15 (dd, J=8.2Hz, 1.6Hz, 2H, Ar-H), 8.76 (d, J=1.8Hz, 2H, Ar-H).

Synthesis of ruthenium(II) complex (10) To a solution of 0.020mg (0.0164mmol) compound **9** in anhydrous THF was added dropwise 0.0164mmol of NaOEt in EtOH solution at room temperature, after stirring for about 20 seconds, 0.65mmol of acetyl chloride in THF was added in one portion followed by 0.65mmol of acetic anhydride. The reaction mixture was kept stirring for another 1 h, then THF solvent was evaporated, and small amount of $CHCl_3$ was added to dissolve all the crude solid product. About 50 ml hexane was added to precipitate out the desired product **10**. ^{1}H NMR (400MHz, $CDCl_3$): δ (ppm): 2.37 (s, 6H, CH_3), 2.38 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 3.49 (s, 3H, CH_3), 4.83 (s, 2H, CH_2), 6.17 (s, 2H, CH), 6.96-7.04 (m, 4H, Ar-H), 7.89 (d, J=8.8Hz, 2H, Ar-H), 8.12 (d, J=8.4Hz, 2H, Ar-H), 8.77 (s, 2H, Ar-H).

Characterization Method

General : UV/Vis spectra of ligand and ruthenium(II) complex in THF were recorded on a Shimadzu UV-2401PC UV-visible spectrophotometer. Grazing Incidence FTIR data were recorded under a nitrogen atmosphere in a Nicolet Magna Spectrometer equipped with a FT-85 fixed 85^o grazing angle accessory (Thermo Spectra-Tech). Scanning Tunneling Microscopy (STM) measurements were carried out by utilizing a NanoScope III STM (Digital Instruments) equipped with a low current STM head and Picoamp Boos Box (Digital Instrument). Scanning tunneling spectroscopy (STS) data were acquired using a Nanoscope software version 5.12 (Digital Instrument) working in the I(V) mode.

Substrate Preparation for STM : The gold substrates used in the STM studies were grown by gold(99.999%) deposition from a tungsten boat onto freshly cleaved mica (highest quality V1, Ted Pella, Inc.). Before deposition, the mica was heated at a temperature of ~ 450 ^{o}C overnight under high vacuum. Then, gold film was annealed at ~ 400 ^{o}C for 10h under high vacuum. With exposure to atmospheric air, the surface becomes contaminated by adoption of carbonaceous materials, which are removed by subjecting the gold surface to hydrogen flame annealing until the gold film radiates a dim orange color (in a dark room). Then, the gold film is quenched in pure ethanol saturated with argon.

Monolayer Preparation : The self-assembled process was carried out at room temperature in under N_2 atmosphere. Immediately after the annealing process, the gold substrates were transferred from the ethanol to a ~1mM ethanol solution of dodecanethiol(DDT). After 14-18 h. the gold substrate was removed from the solution, rinsed five times with pure ethanol and twice with fresh distilled THF. The freshly dodecanethiolated SAM/Au electrode was derivatized using a ~ 10^{-5}M solution prepared from ruthenium(II) complex by using sequential assembly process. The electrode was immersed for 30min in a THF solution of ruthenium(II) complex with 2-3 drops of aq. NH_4OH solution. Then, the electrode was washed consecutively five times with ethanol and THF. This procedure removes acetyl protection group in the molecules leaving the methoxymethyl(MOM) protection group intact. The exposed S^- or SH groups can be covalently bonded to the gold surface. The MOMO protection group was cleaved by dipping the electrode with the modified SAM into conc. trifluoroacetic acid(TFA) for 1h. The resulting sample was rinsed several times with pure THF, ethanol and toluene. Finally the electrode is immersed in a fresh prepared solution of gold nanoparticles(Au NPs) in toluene [6] (absorbance 0.12 at 520 nm) for 1-2 h. and subsequently rinsed with tetraoctylammonium bromide in toluene (several times), then pure toluene, THF and ethanol. The samples were dried with a continuous and gentle flow of argon and immediately used for STM and STS measurements.

Cyclic Voltammetry : Cyclic voltammetry (CV) was performed using a CV-50W Voltammetric Analyzer (Bioanalytical Systems Inc.) in a conventional one compartment three-electrode cell in a solution of methylene chloride (0.1M tetrabutylammonium hexafluorophosphate($TBAPF_6$) as supporting electrolyte) . The electrolyte solution was dried and degassed prior to use. A platinum wire was used as an auxiliary electrode. Ag wire was used as a reference electrode and calibrated against the oxidation of ferrocene. All the measurements were carried out under ambient conditions.

Scanning Tunneling Microscopy (STM) : STM Measurements were carried out by utilizing a NanoScope III (Digital Instrument) equipped with a low current STM head and Picoamp Boost Box (Digital Instrument), which allows STM measurements with tunneling currents in the pA range. The tips used in the measurements were fabricated by electrochemical etching of a Pt/Ir wire (Molecular Imaging, Phoenix, AZ, USA) in aq. 8M NaOH solution. After etching, the tips were rinsed with deionized water, dried, and immediately mounted in the STM converter head. The experiments presented here were performed in atmospheric air at room temperature and the images were recorded in constant current operating mode.

Scanning Tunneling Spectroscopy (STS) : STS data were acquired using a Nanoscope software version 5.12 (Digital Instrument) working in the I(V) mode. This operation mode allows monitoring the variation of the tunneling current (I), due to variations of the bias voltage (V). After the tip is positioned at a specific Au nanoparticle on the Au(111) surface, the feedback is shut off and a spectroscopic plot is acquired (the tunneling current is measured as the sample voltage is ramped at 10 V/s). In all the measurements, the bias potential was applied to the sample with respect to the grounded tip. In this configuration, a positive bias corresponds to an electron flow from the tip to the sample and in the opposite direction for negative bias voltage. The STS data shown here are averaged I(V) curves, measured positioning the STM tip on at least twenty Au nanoparticles attached to the molecules in three samples which were independently prepared. The I(V) data for each Au nanoparticle is the average of about 25 individual I(V) curves, each of which is composed of 256 points.

In order to avoid artifacts, the tips used for the STS measurements were previously examined as follows. : In the alkanethiol region, the tip must be able to produce atomically resolved images with the characteristic (3x3)R 30° layer structure of alkanethiolate SAM on Au(111) surface. Finally, before and after the STS measurement on Au nanoparticle, the I(V) curve the alkanethiolate region should be almost symmetric.

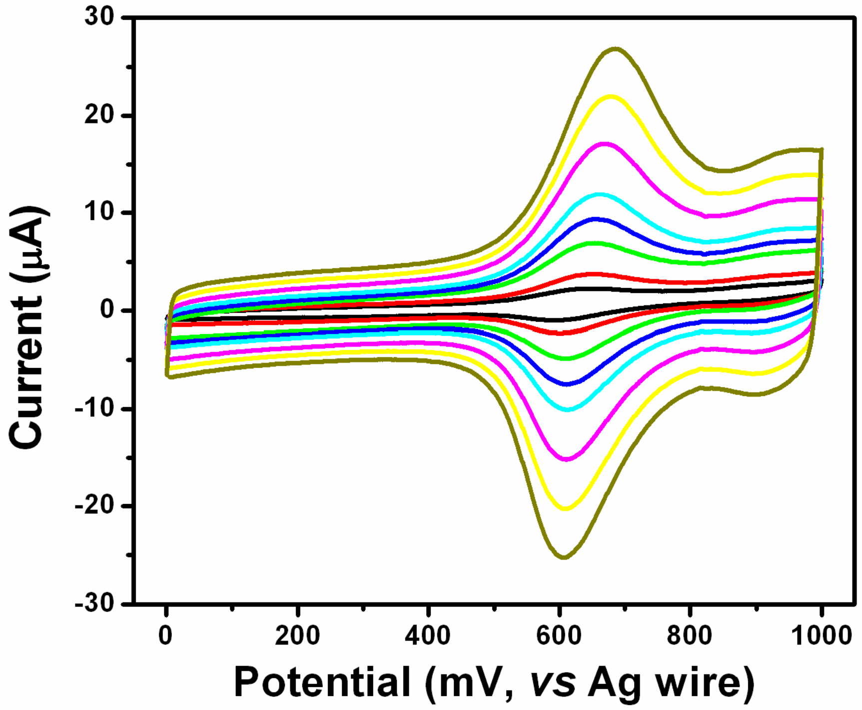


Figure S1. Cyclic voltammogramms of a monolayer of the ruthenium(II) complex on Au(111) substrate. Electrolyte : 0.1 M TBAPF$_6$ in CH$_2$Cl$_2$. Scan rate : 25, 50, 100, 200, 300, 400, and 500 mV/s.

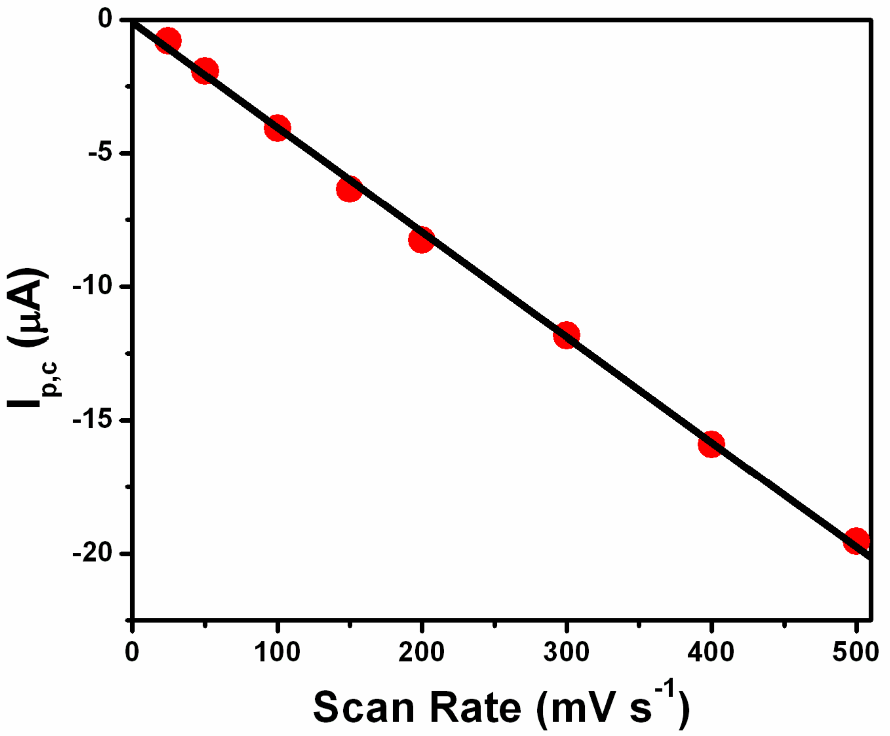


Figure S2. Plot of cathodic peak current density versus scan rate for a monolayer of the ruthenium(II) complex on Au(111) substrate.

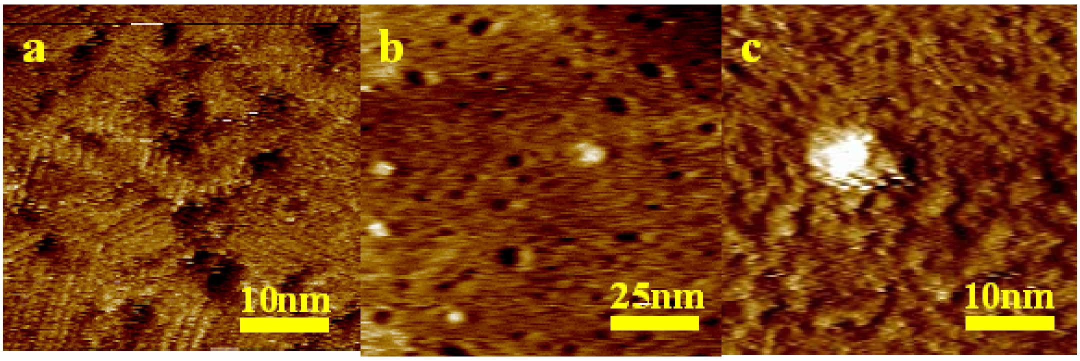


Figure S3. Constant-current STM topography of (a) DDT SAM on Au(111) substrate, before (a) and after (b) the insertion of the ruthenium(II) complex. (c) The image of a Au NP attached to the ruthenium(II) complex. STM imaging condition : V_{bias} = 1.0V, I_t = 1pA

Figure S3(a) shows a STM topography of the highly-ordered structure of DDT SAM on Au(111) surface. The bright spots as shown in Figure 3(b), surrounded by DDT SAM, were obtained after the insertion of Ru(II) complexes. Even though the intensity of bright spots varied due to the stochastic behavior of single molecules inserted into SAMs of alkanethiols,[5] the shape and size of the spots are constant during repetitive scans. The average size of the spots is about 2.4 nm. These results indicate that the bright spot is the constant-current STM image of single Ru(II) complex chemisorbed onto the Au(111) surface. Figure 3(c) shows the STM topography of the Au NP bonded to the single Ru(II) complex. The diameter of the Au NPs in STM images ranges from 7 to 10 nm.

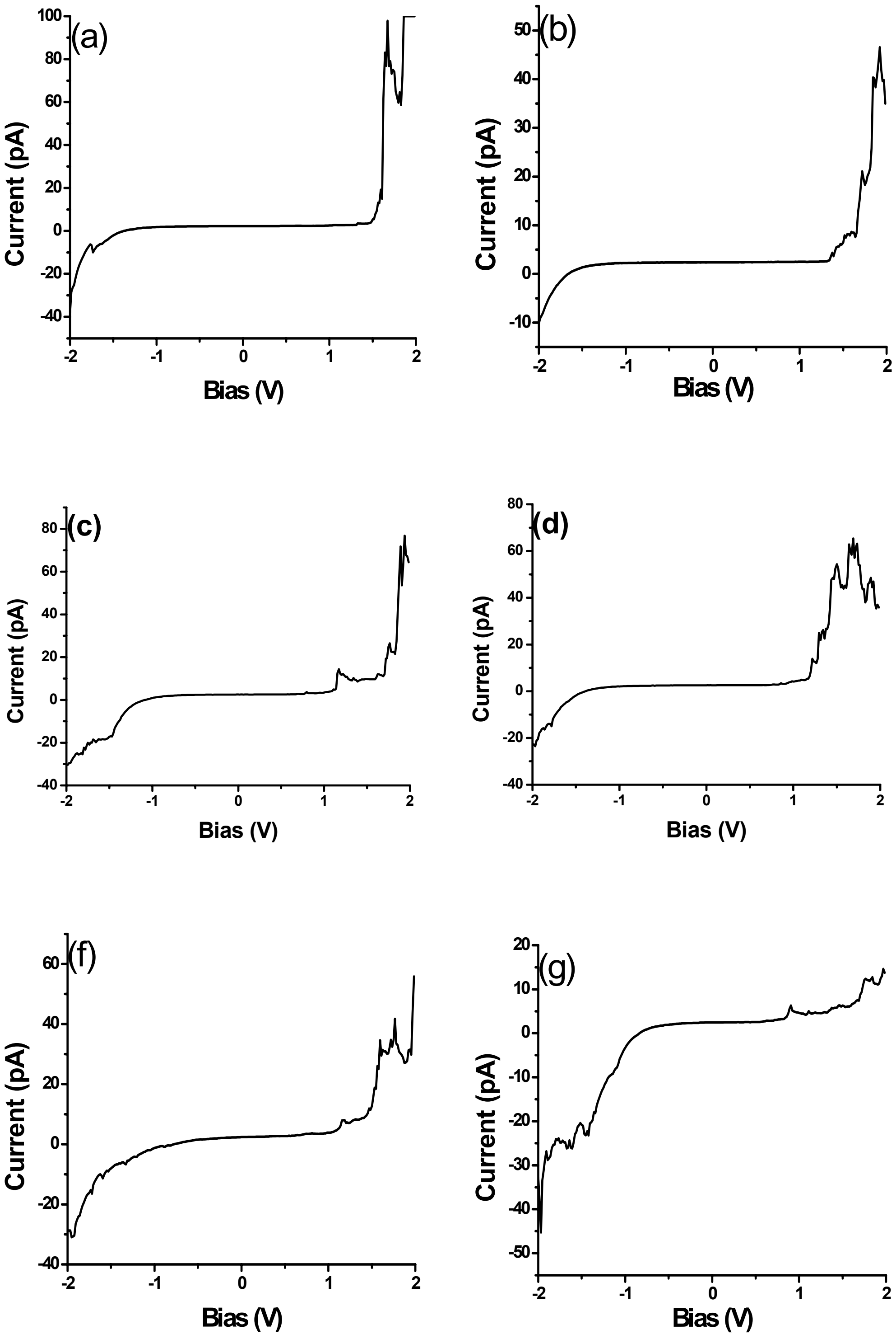


Figure S4. I-V characteristics of the ruthenium(II) complexes. (set point conditions : 1pA and 1000 mV)

Fig. S4 shows six I-V curves of different ruthenium(II) complexes. These I-V curves were obtained under the conditions of set point of 1pA and 1000mV bias voltage. It was found that All I-V curves of the ruthenium(II) complexes were asymmetric and had a few fine NDR features. Five I-V curves (a-f) showed thigher tunneling current at positive bias voltage than at negative bias. However, it was observed that an I-V curve (g) had the opposite rectifying behavior.

Theoretical Calculation : The electronic structure of the ruthenium complex was calculated using B3PW91 hybrid density functional theory (DFT) with the LANL2DZ basis set as implemented in the GAUSSIAN 03 program.

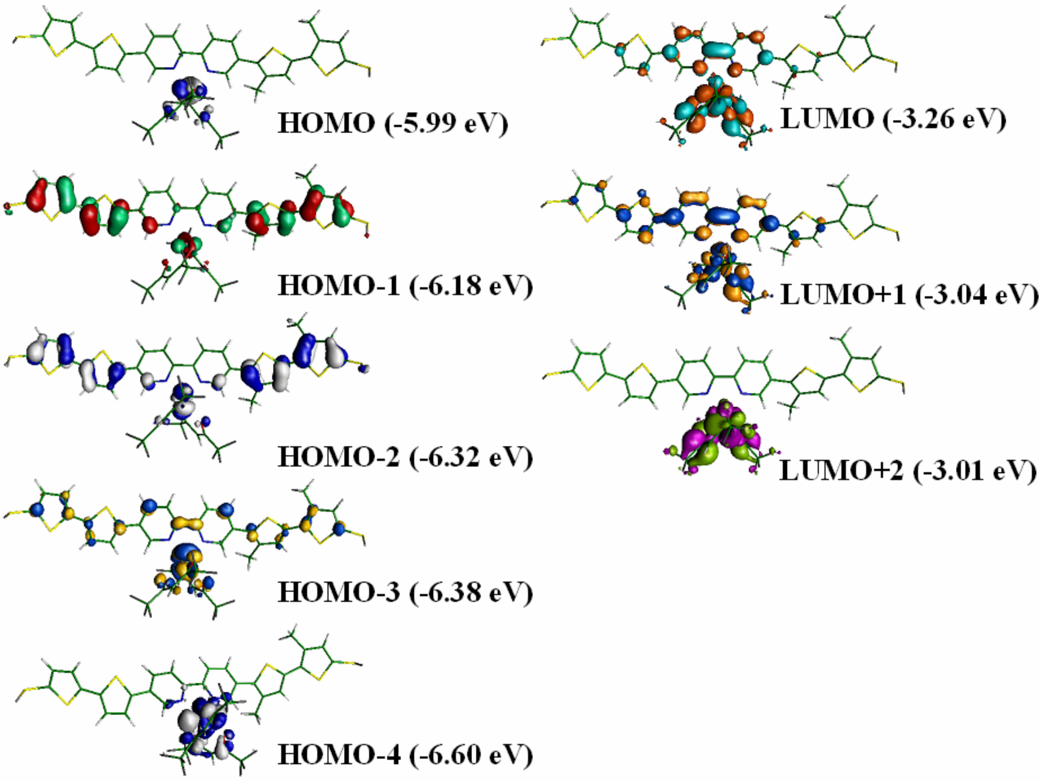


Figure S5. Frontier molecular orbitals of the Ru(II) complex.

Fig. S5 illustrates the charge distribution of five HOMO and three LUMO states of the Ru(II) complex with thiol functional groups at both ends. From these calculations, MO energy level ordering can be deduced as shown in Fig S6. The energy gap deduced from these calculations seems to be consistent with experimental results. This ordering is also consistent from our proposed explanation of the I-V curves of the Ru(II) complex.

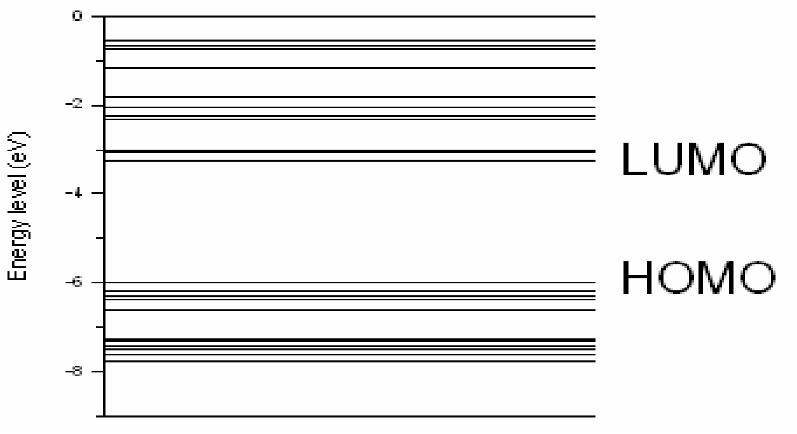


Figure S6. Calculated energy levels ordering of the Ru(II) complex.

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