Supporting Information for Fig. 3

On the basis of the structural data of the Ru\textsuperscript{II}(tpy)(tpy(CH\textsubscript{2})\textsubscript{n}S) molecule, the physical height of the Ru\textsuperscript{II}(tpy)(tpy(CH\textsubscript{2})\textsubscript{7}S) on Au(111) was estimated to be 23.3 Å (the molecular dimensions were estimated according to MM2 calculations in ChemBats3D). This is 12.6 Å longer than that of HT (10.7 Å) on Au(111). However, the apparent STM height of the Ru\textsuperscript{II}(tpy)(tpy(CH\textsubscript{2})\textsubscript{7}S) molecules is found to be approximately 6.0 ± 0.5 Å higher than the HT SAM. This discrepancy between the apparent STM height and the physical height may be a result of the topographic STM image reflecting a combination of the geometric and conductive properties of the substrate. In addition, the apparent STM height of the Ru\textsuperscript{II}(tpy)(tpy(CH\textsubscript{2})\textsubscript{13}S) molecule is found to be approximately 6.0 ± 0.5 Å higher than the DDT SAM. The Ru\textsuperscript{II}(tpy)(tpy(CH\textsubscript{2})\textsubscript{13}S)-incorporated DDT SAM is comparable to the Ru\textsuperscript{II}(tpy)(tpy(CH\textsubscript{2})\textsubscript{7}S)-incorporated HT SAM in that the physical height difference of approximately 12.6 Å between the Ru\textsuperscript{II} terpyridine complexes and alkanethiols in the two SAMs is identical. Thus, the white protrusion indicates the terminal Ru\textsuperscript{II} complex groups in two Ru\textsuperscript{II} terpyridine complexes. A single molecule is defined by a cross-sectional analysis of the STM images.

Supporting Calculation (surface coverage)

Surface coverage for a single monolayer of Ru(tpy)(tpy(CH\textsubscript{2})\textsubscript{n}S): From a STM image (Fig. 3), the redox center (i.e., Ru\textsuperscript{II}(tpy)\textsubscript{2}) was found to be approximately 13-14 Å in diameter, the occupied area of the single molecule is approximately 1.54 x 10\textsuperscript{-14} cm\textsuperscript{2} molecule\textsuperscript{-1} (6.50 x 10\textsuperscript{13} molecules cm\textsuperscript{-2}), and the surface coverage of Ru(tpy)(tpy(CH\textsubscript{2})\textsubscript{n}S) in a fully covered monolayer is theoretically calculated as 1.1 x 10\textsuperscript{-10} mol cm\textsuperscript{-2}. 

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Supporting Figures

Fig. S1. XPS spectra of a Ru$^{II}$(tpy)(tpy(CH$_2$)$_7$S) SAM/Au. (A) Survey scan, (B) C(1s) and Ru(3d) region, and (C) S(2p) region, showing the peak of 162.0 eV respective to the binding energy of a sulfur atom (i.e., 2p$_{3/2}$) to a Au atom (Scienta SES-100 analyzer with an Mg K$_\alpha$ source).

Fig. S2. UV-Vis absorption spectrum of a Ru$^{II}$ terpyridine complex SAM on an ITO substrate in air, indicating the MLCT (metal-to-ligand charge transfer) electronic transition of the molecules. UV-Vis absorption spectroscopy was performed at room temperature (Hitachi, U-3501 UV/VIS/NIR spectrophotometer).
Fig. S3. Cyclic voltammograms of bare ITO and a RuII(tpy)(tpy(CH2)7S) SAM/ITO in 0.1 M NaClO4 at the scan rate of 0.1 V s⁻¹.
Fig. S4. (A) (B) Cyclic voltammograms of Ru(tpy)(tpy(CH$_2$)$_n$S) for $n = 7$ and 13 mixed SAMs with HT and DDT, respectively on ITO electrodes in 0.1 M NaClO$_4$ as a function of the scan rate. The mixed SAMs were prepared in mixed DMF solutions of 1 mM Ru(tpy)(tpy(CH$_2$)$_n$S) and 0.3 mM alkanethiol for 24 hours.

![Cyclic voltammograms](image)

Fig. S5. $I$-$V$ curves obtained with STM in a single molecular junction of a 1-octanedithiol SAM on Au(111). After molecularly resolved imaging the SAM at 20 pA of tunneling current, $I$-$V$ curves were taken at various tunneling set-points. In this experiment, $I$-$V$ curves were taken at various tunneling current set-points in the range of 35 ~ 75 pA. As the tunneling current set-point increases, the tip moves closer to the surface, which compresses the molecules. As the tip closes onto the surface, the measured currents proportionally increase depending on the tunneling current, as shown in the $I$-$V$ curves. The measured $I$-$V$ curves for each tunneling current were reproducible, which indicates that the contacts in the junctions were precisely controlled. Therefore, it is believed that our STM measurements are reliable enough to demonstrate the electrical properties of the molecular junctions.
Fig. S6. $I$-$V$ characteristics of a DDT molecular junction at 300 K

Fig. S7. Low-temperature $I$-$V$ characteristics of a single Ru$^{II}$(tpy)(tpy(CH$_2$)$_7$S) molecular junction at 36 K (circles) and at 46 K (rectangles) in a linear scale. $V_{th}$ indicates the threshold voltage range.
Fig. S8. Cyclic voltammograms of 3 mM Ru$^{II}$(tpy)(tpy(CH$_2$)$_n$S$^{2-}$) $n$ = 7 and 13 solutions in acetonitrile containing 0.1 M TBAPF$_6$ at 0.1 V s$^{-1}$ using a glassy carbon electrode. Cyclic voltammetry was performed at room temperature under a N$_2$ atmosphere. The solution for the voltammetric experiments was degassed with N$_2$ gas.