Electronic Supplementary Information to

On the Tuning of Electric Conductance of Extended-Metal-Atom-Chains via Axial Ligands for $[Ru_3(\mu_3\text{-dpa})_4(X)_2]^{0/+}$ ($X = NCS^-, CN^-$)

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Synthetic procedures of $[Ru_3(\mu_3\text{-dpa})_4(NCS)_2]$.

To a 100-mL round bottom flask, Hdpa (171 mg, 1 mmol), $Ru_2(OAc)_4Cl$ (354 mg, 0.75 mmol), and LiCl (100 mg) were dissolved in melted naphthalene (20 g). The mixture was heated to ~160 °C for 20 min and then raised to ~220 °C. *t*-BuOK (112 mg, 1 mmol, in *n*-BuOH) was added dropwise into the mixture and the reaction temperature was maintained at ~220 °C for another 1.5 hr. 200-mg NaNCS was then added to this solution to replace the axial ligand. After 30 min, this solution was cooled to ~50 °C and 100-mL hexane was added. After filtration, the crude was washed 3 times with the same amount of hexane to remove naphthalene. 100-mL CH_2Cl_2 was added to extract the product. After filtration, 130-mg dark brown crystals were formed by layering the solution with ether (yield 42%). FAB-MS(m/z): 1100 $[M+H]^+$. IR(KBr, cm^{-1}): 3070 w ($\upsilon_{\mathrm{CH,\ arom}}$), 2030 ($\upsilon_{C\equiv N}$, NCS), 1603, 1592 s ($\upsilon_{C=C}$, $\upsilon_{C=N}$), 1460 s, 1425 m, 1362 m, 1311 m, 1156 s, 1025 m, 754 w, 736 m.

Instrumentation of X-ray crystallographic characterization for $[Ru_3(\mu_3\text{-dpa})_4(NCS)_2]$.

Data collection was carried out on a NONIUS Kappa CCD diffractometer with Mo K_α radiation (λ = 0.71073 Å). Cell parameters were retrieved and refined using HKL Scalepack software on all observed reflections. Data reduction was performed with the HKL Denzo and Scalepack software.[S1] An empirical absorption was based on the symmetry-equivalent reflections, and absorption corrections were applied with the SORTAV program.[S2] All the structures were solved using SHELXS-97[S3] and refined with SHELXL-97[S4] by full-matrix least-squares methods on F^2 values. Hydrogen atoms were fixed at calculated positions and refined using a riding mode.

Table S1. Summary of selected bond distances (Å) for $[Ru_3(\mu_3\text{-dpa})_4(NCS)_2]$ and $[Ru_3(\mu_3\text{-dpa})_4(CN)_2]$.

	crystallographic results		simulated results[a]	
distance	$[Ru_3(\mu_3\text{-dpa})_4(NCS)_2]$	$[Ru_3(\mu_3\text{-dpa})_4(CN)_2]$[b]	$[Ru_3(\mu_3\text{-dpa})_4(NCS)_2]$	$[Ru_3(\mu_3\text{-dpa})_4(CN)_2]$
Ru(1)–Ru(2)	2.264(5)	2.3738(5)	2.3325	2.3943
Ru(2)–Ru(3)	2.30(2)	2.3794(5)	2.3325	2.3943
Ru(1)–X	2.22(2)	2.053(5)	2.177	2.016
Ru(3)–X	2.26(2)	2.061(5)	2.177	2.016
Ru(1)–N	2.08(8)	2.105(4)	2.133	2.161
Ru(2)–N	2.12(9)	2.041(4)	2.089	2.089
Ru(3)–N	2.08(10)	2.120(4)	2.133	2.161

a. This study. The calculations were optimised based on a D_4 symmetry for both compounds.

b. C.-K. Kuo, I. P.-C. Liu, C.-Y. Yeh, C.-H. Chou, T.-B. Tsao, G.-H. Lee and S.-M. Peng, *Chem.−Eur. J.*, 2007, **13**, 1442-1451.

Experimental procedures for STM break junction.

The experimental procedures and data treatment for STM break-junction studies were documented in detail by the groups of Tao and Lindsay.[S5-S8]

The gold STM tip was freshly prepared by cutting a 0.25 mm gold wire. The substrates were prepared by thermally evaporating 7-nm thick chromium underlayer (99.99 %, Super Conductor Materials, Inc., Suffern, NY) as an adhesive layer on glass slides and subsequently a gold film with another 120 nm in thickness. The glass slides were pre-cleaned with piranha solution, a 1:3 (v/v) mixture of 30% H_2O_2 and concentrated H_2SO_4. *This solution reacts violently with organics and should be handled with great care.* The conductance measurements were performed in a toluene solution (TEDIA) containing 1~5 mM complex. The procedures of tip insulation and ECSTM are referred to the main text.

Histograms for single-molecule conductance. The experiments of single-molecule conductance were carried out in ~100-μL 1,2-dichloroethane containing 0.5-mM triruthenium EMAC and 50-mM TBAP (tetrabutylammonium perchlorate) using scanning tunnelling microscopy break junction (STM-BJ) with a NanoScopeIIIa controller (Veeco, Santa Barbara, CA, USA). The instrument was first operated in imaging mode with a tunnelling current of 1~5 nA. When the images exhibited gold terraces, indicative of smooth surface and a sharp tip, the imaging was discontinued and resumed after filling in toluene containing ~1 mM EMAC. The imaging mode was switched to STS mode (scanning tunnelling spectroscopy) to acquire current-stretching curves (i.e., $I(s)$ or i-s traces). The STM tip was brought onto and pulled out of contact with the substrate (6.0 nm/s, 0.93 Hz) at a fixed E_{bias}. Upon repeated formation of the tip-substrate gap, the headgroups at the termini of the EMACs might bind across two gold electrodes, i.e., the molecular junction. The current, $I(s)$, was recorded by a NanoScope built-in program and exported as ASCII files. In this study, when the tip was pulled away from the substrate, ~20% and ~ 9.2% of the $I(s)$ traces exhibited staircase features for the headgroups of –NCS and –CN, respectively. The magnitudes were orders of magnitude smaller than G_0 (G_0 is the conductance quantum for the cross section of a metallic contact being only that of a single atom; $G_0 = 2\, e^2/h$, ~ 77.5 μS or $(12.9\ \mathrm{k}\Omega)^{-1}$, where e is the electron charge and h is Planck's constant), suggesting the presence of EMACs bridging the tip-electrode junction. Each descent in the $I(s)$ traces implied the loss of a molecule from the junction. More than 500 traces were used to prepare a conductance histogram (Origin, version 6.0, Microcal Software, Inc.) in which local maxima were positioned integer multiples of a fundamental one, suggesting that the number of EMACs in the junctions was one, two, and so forth. The abscissa of the fundamental peak shows the most probable conductance measured by STM-BJ and is reportedly the single-molecule conductance. The histograms were fitted by Gaussian function and the standard deviation of the fitting was used to find the uncertainty for the single-molecule conductance.

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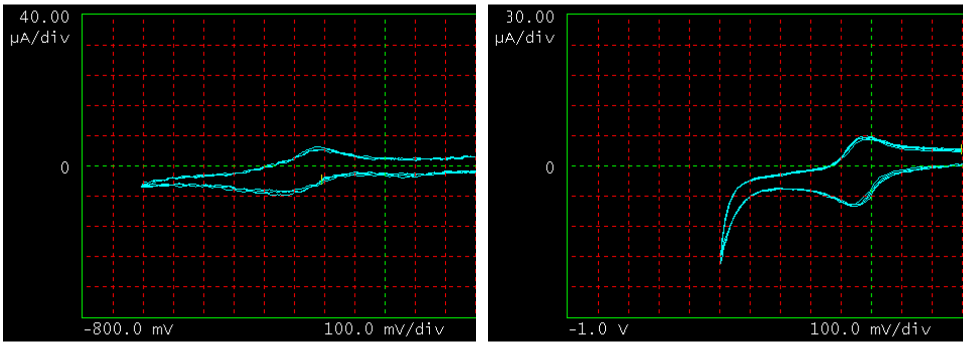

Figure S1. Cyclic voltammograms of [$Ru_3(dpa)_4(NCS)_2$] (left) and [$Ru_3(dpa)_4(CN)_2$] (right) in the *in situ* ECSTM cell. These were hardcopy directly from NanoScopeIIIa by using screen-print. The potentials ranged (left panel) from –800 mV to 500 mV and (right panel) from –1.0 V to 300 mV. The solutions were ~100-µL 1,2-dichloroethane containing 0.5-mM triruthenium EMACs and 50-mM TBAP (tetrabutylammonium perchlorate). The working, reference, and counter electrodes were a gold substrate (~0.5 cm^2), a silver wire, and a platinum wire, respectively. Scan rate: 100 mV/s.

Density functional theory calculations.

Calculations and geometry optimizations on the electronic ground state of triruthenium complexes were carried out by using B3LYP density functional theory, implemented in Gaussian03 program package. The Hay-Wadt double-ζ with a Los Alamos relativistic effect core potential basis set, LANL2DZ, was employed for ruthenium. All-electron valence double-ζ basis sets (D95V) were used to describe carbon and hydrogen. Full double-ζ (D95) bases were employed and supplemented with one *d*-type polarization functions for nitrogen and sulfur. The geometries were optimized under constrained D4 point symmetry.

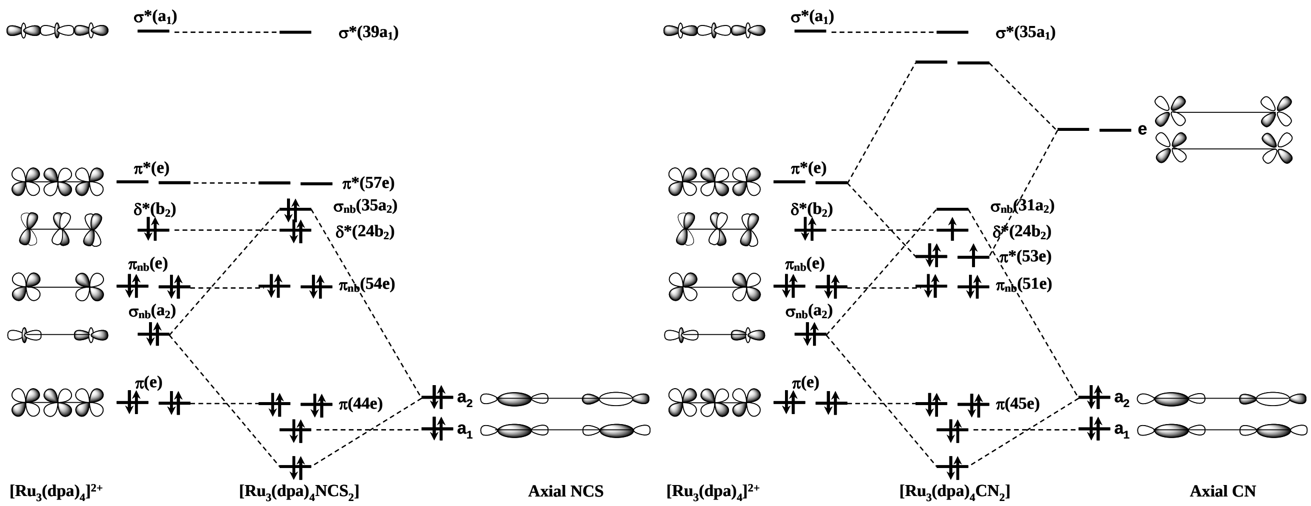

Figure S2. Qualitative molecular orbital energy level correlation diagrams for $[Ru_3(dpa)_4(NCS)_2]$ (left) and $[Ru_3(dpa)_4(CN)_2]$ (right). Orbitals with parentheses were those with significant contributions from metal centres and the others were mainly from ligands. The MOs were derived by unrestricted DFT/B3LYP analysis with Gaussian03w package using LANL2DZ on metal centres, D95V on C, H, and D95* on N, S.