Supplementary Information

# Stepwise fabrication of donor/acceptor thin films with a charge-transfer molecular wire motif

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## **Experimental Section**

## Preparation of powder sample of 1

DMDCNQI (38 mg, 0.206 mmol) was added to a solution of  $[Ru_2(o-ClPhCO_2)_4(THF)_2]$  (200 mg, 0.206 mmol) in THF (30 mL) and the dark blue suspension was refluxed for 24 h under a N<sub>2</sub> atmosphere. The resulting dark blue precipitate was separated from the solution by centrifuge, washed with THF (20 mL), and dried in vacuo. Yeild 54%. IR (KBr):  $\nu$ (C=N), 2115 cm<sup>-1</sup>; $\nu$ (C=O), 1460, 1399 cm<sup>-1</sup>.

#### **XPS, FT-IR, and AFM Measurements**

The indium-tin oxide (ITO) electrode, purchased from Geomatec co. Ltd., was cleaned by sonication in a mixture of  $H_2O-H_2O_2-NH_4OH = 5:1:1$  (v/v/v), washed with methanol and then water (Clean-ITO). Absorption spectra were measured using a JASCO V-770 UV-Visible/NIR spectrophotometer. XPS spectra were measured using an AXIS Ultra DLD system from Shimadzu-Kratos Analytical Ltd. using a focused monochromatic Al Ka X-ray source (1486.6 eV). In the present study, the binding energy was calibrated using the C(1s) binding energy of 284.8 eV for contaminated carbon species on the bare ITO surface. The X-ray power, spot size, and pass energy of the analyzer were set at 150 W (15 kV, 10 mA), 300 x 700 µm, and 40 eV. FT-IR RAS was conducted by using a JASCO FT/IR-6300V equipped with RAS attachment, RAS PRO-410-B. AFM images were obtained using a JEOL JSPM-5200 unit using a NSC35/Ti-Pt/15 cantilever (Mikromash). We used a Shimadzu SPM-9700 unit for scratching the film to estimate the film thickness. A Shimadzu SPM-9700 scanning probe microscope was used in contact (DC) mode using a standard Si<sub>3</sub>N<sub>4</sub> cantilever (24 kHz, 0.15 N m<sup>-1</sup>). SEM images were obtained using JSM-7500F (JEOL). Magnetic susceptibility measurements were performed using a Quantum Design SQUID magnetometer (MPMS-XL). Dc measurements were conducted over the temperature range 1.8–300 K. The measurements were performed on powder samples restrained by Nujol. Diamagnetic contributions were corrected for the sample holder, Nujol, and for the sample using Pascal's constants.<sup>1</sup>



Fig. S1. Temperature dependence of  $\chi T$  for 1 (bulk sample) measured applying a DC field of 1 kOe, where the inset is a close-up view for the temperature range of 100–300 K. The data were simulated in the temperature range of 120–300 K using an alternating chain model with  $S_i = 3/2$  and  $S_{i+1} = 1/2$  in the Hamiltonian  $H = -2J \sum_{i=1}^{N} \vec{S_i} \cdot \vec{S_{i+1}}^2$  and an adequate parameter set was obtained as  $g_{\text{Ru}} = 2.04$ ,  $g_{\text{Rad}} = 2.0$  (fix), and  $J/k_{\text{B}} = -102.6$  K. These data indicate that a strong antiferromagnetic exchange is present between  $[\text{Ru}_2^{\text{II,III}}]^+$  and DMDCNQI<sup>-</sup>, as was observed in the previous D<sup>+</sup>A<sup>-</sup> chain compounds.<sup>3,4</sup>



**Fig. S2**. Time course of XPS signal intensity of (a) Ru 3d and (b) Cl 2p by immersion of PPA-ITO into  $[Ru_2^{II,II}(o-ClPhCO_2)_4(THF)_2]$  solution. The data indicates that the changes in the increase of the peak intensity were saturated after a 3 h immersion.



**Fig. S3**. Cl 2p XPS spectra before (top, PPA-ITO) and after (bottom, Ru-ITO) immersion of the ITO substrate into a  $[Ru_2^{II,II}(o-ClPhCO_2)_4(THF)_2]$  solution for 3 h.



Fig. S4. (a) In 3d and (b) Sn 3d XPS spectra of a thin film of [{Ru<sub>2</sub>}DMDCNQI]<sub>n</sub>.



**Fig. S5.** (a) Survey XPS spectra of the thin film of  $[\{Rh_2\}DMDCNQI]_n$ . (b) Cycle number dependent coverage of atoms of Rh 3d and Cl 2p estimated by XPS spectra for a thin film of  $[\{Rh_2\}DMDCNQI]_n$ .



Fig. S6. Absorption spectra of 1 (black) and the thin film of  $[{Ru_2}DMDCNQI]_{20}$  (purple).



**Fig. S7**. AFM images of (a) PPAITO, and  $[{Ru_2}DMDCNQI]_n$  in (b) n = 5, (c) 10, (d) 15, (e) 20, respectively.



Fig. S8. Side view SEM image of [{Ru<sub>2</sub>}DMDCNQI]<sub>20</sub>.

#### **References in ESI**

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