Supporting Information

Nano-junction of self-assembled mixed-metal-centre molecular wires on transparent conductive oxides

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NMR and ESI-MS data for RuDT$_2$

^{1}H NMR (DMSO-d$_6$, 400 MHz, 330 K): δ 9.14 (s, 4H), 8.94 (s, 4H), 8.77-8.70 (m, 12H), 8.45-8.43 (d, J = 7.9Hz, 4H), 8.35-8.33 (d, J = 8.0Hz, 4H), 8.06-8.02 (t, J = 8.5Hz, 4H), 8.00-7.96 (t, J = 7.6Hz, 4H), 7.54-7.47 (m, 8H), 7.23-7.20 (t, J = 6.5Hz, 4H). ^{13}C NMR (DMSO-d$_6$, 100 MHz, 330 K): δ 157.9, 155.6, 155.1, 154.6, 152.2, 149.4, 148.9, 146.1, 139.2, 138.0, 137.7, 137.1, 128.6, 128.0, 127.7, 124.9, 124.7, 121.2, 118.4, 118.0. High Resolution ESI-MS (CH_3CN): $[M]^{2+}$ = 591.16090 m/z (theoretical = 591.15883 m/z).

Table S1. UV-Vis spectroscopy and photophysical data for the Ru(II) complexes in deaerated CH_3CN solutions.

	Absorption	Emission	Lifetime	Quantum yield
Compound	λ_{max}, nm (ε, x10^{-4} M^{-1}cm^{-1})	λ_{max}, nm	τ,ns	Φ
Ru(ttpy)$_2$$^{2+}$ [a]	284 (6.80), 310 (7.58), 490 (2.93)	640 (293 K)	0.95	3.2 x 10^{-5}
RuDT$_2$	295 (7.3), 310 (8.4), 330 (7.0), 455 (1.4), 493 (3.0)	645 (293 K)	2.6	6 x 10^{-5}

[a] ttpy = 4′-tolyl-2,2′:6′,2″-terpyridine. From [1].

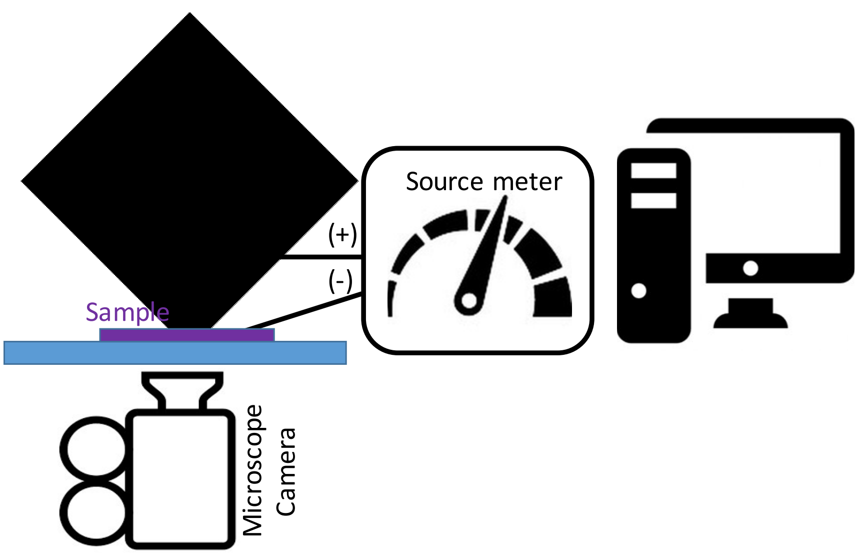

Figure S1: Experimental set-up for EGaIn junction measurement.

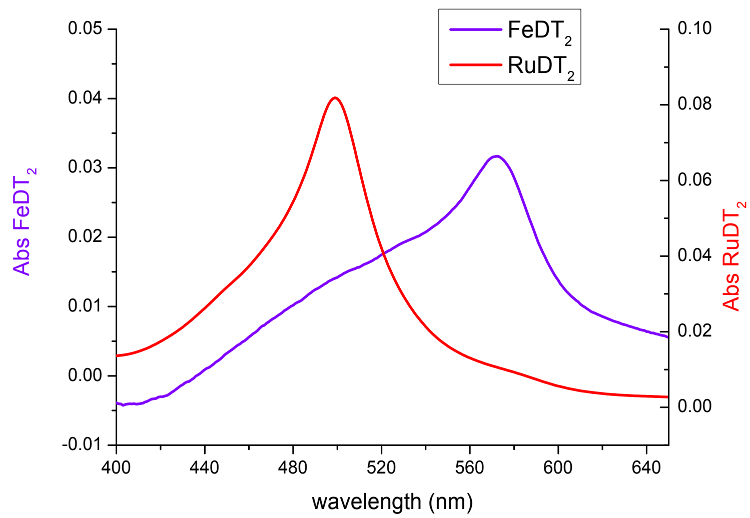

Figure S2: absorption spectra of $RuDT_2$ and $FeDT_2$ solutions (~10^{-4} M) in, respectively, acetonitrile and $CHCl_3$.

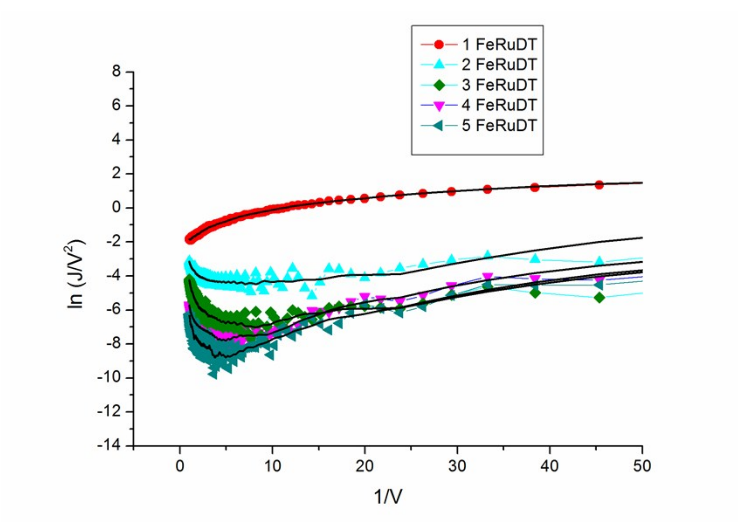

Figure S3: Fowler-Nordheim plot for nFe-$RuDT_2$ systems; the black lines are the result of a smoothing filter applied to the plots.

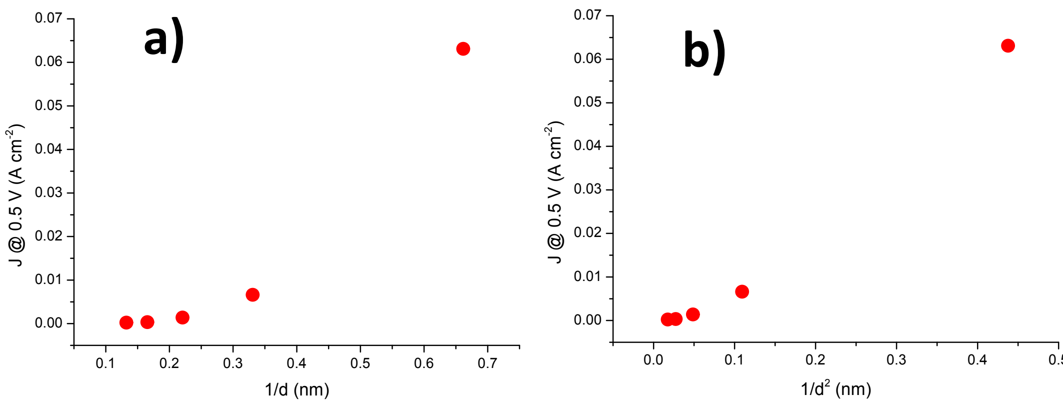

Figure S4: plots showing a non-linear variation of current density as a function of a) 1/d and b) $1/d^2$.

Thickness measurements

The patterning was obtained through Focused Ion Beam (FIB) technique on ZP-SiO_2. A focused bismuth beam (25 keV, 1 nA) was rastered for 2s over 5x5 μm^2 areas of the surface in order to etch the ZP layer and leave bare SiO_2 regions. Irradiation time was optimised to prevent the sputtering of SiO_2 substrate. Fe-RuDT_2 wires of different length were then grown selectively on the ZP portion of the surface. The success of the removal of the ZP layer and the subsequent patterned growth of the wires were confirmed by ToF-SIMS imaging.

The thickness of the organic layer after each step of the molecular wire growth was then measured using a P7 KLA Tencor profilometer. The results of such measurements are reported in Figure S5.

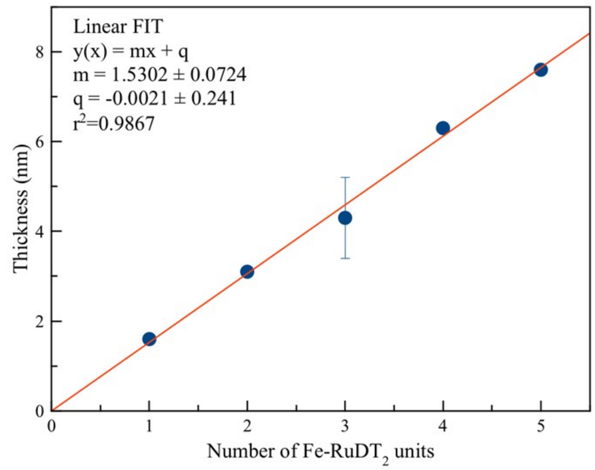

Figure S5: plots showing the film thickness as a function on the number of Fe-RuDT$_2$ units.

By combination of the measured film thickness and molecular dynamic calculations of the molecular structure (3 nm estimated length for Fe-RuDT$_2$ unit), an approximate 60° tilt angle of the wire with respect to the surface was extrapolated. Such value is coherent with tilt angles measured and calculated, by means of various techniques, for other phosphonate-based molecular films on different oxide substrates.[3-6]

References

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