

Supporting Information to:

**Impact of device design on the electronic and optoelectronic properties of
integrated Ru-terpyridine complexes**

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1. Chemical compounds

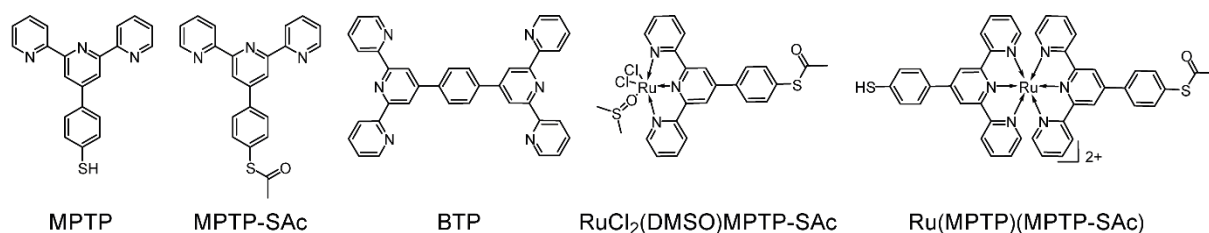


Figure S1. Chemical formulas of the substances used for synthesis: 4'-Mercaptophenyl-2,2':6',2''-terpyridine (MPTP), 4'-[4-(acetylthio)phenyl]-2,2':6',2''-terpyridine (MPTP-SAc), 1,4-bis(2,2':6',2''-terpyridine-4-yl)benzene (BTP), the Ru-complexes RuCl₂(DMSO)MPTP-SAc and Ru(MPTP)(MPTP-SAc).

2. SEM image of Ru(MPTP)₂-AuNP

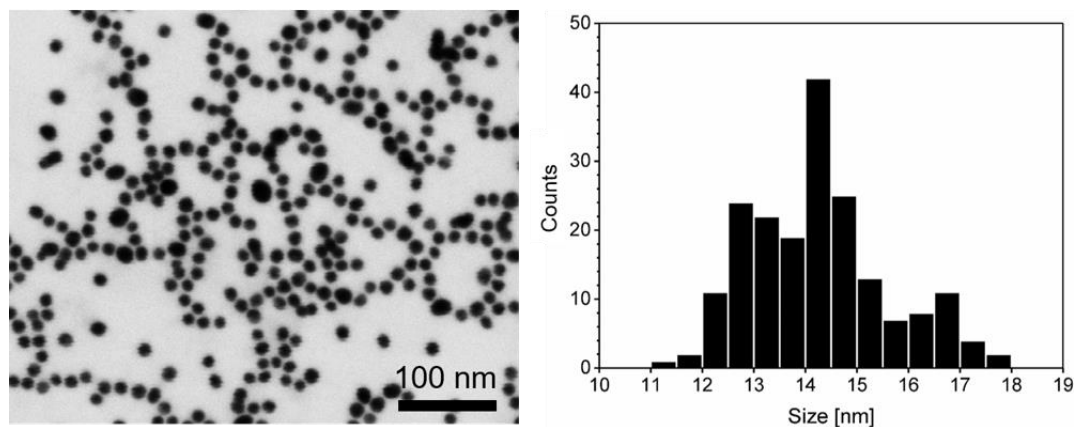


Figure S2. SEM image and corresponding histogram representing the size distribution of Ru(MPTP)₂-AuNP.

3. SEM images of nanogap devices

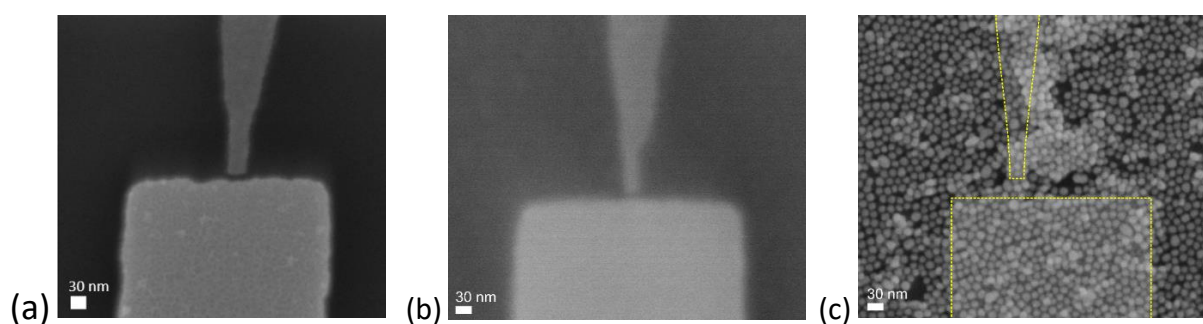


Figure S3. SEM images showing nanogap devices. (a) empty nanogap device; (b) Ru(TP)₂-complex wire device; (c) Ru(MPTP)₂-AuNP device. Scale bars are 30 nm.

4. XPS measurements

XPS measurements have been performed during the first steps of the Ru(TP)₂-complex wire growth to support previously reported IRRAS and Raman spectra [19], since they can provide additional information due to their sensibility towards the oxidation state of ruthenium. Figure S4 shows the C 1s, Ru 3d and O 1s core level spectra. Since the C 1s and Ru 3d core levels, located around 285 eV and 282 eV, respectively, overlap to some extent, we followed the accepted procedure to deconvolute these peaks by fitting the ruthenium contributions first. The Ru 3d peaks are represented by a doublet (3d_{5/2} and 3d_{3/2}) with a separation of 4.17 eV and an area ratio of 3:2 [28]. As the Ru 3d_{5/2} peak is well resolved in most cases we will refer to this peak in the following.

Starting the wire growth with the chemisorption of MPTP on the Au substrate the core level spectrum in the range of 278 eV to 290 eV given in Figure S4a displays two C 1s BE. While the peak with low intensity at 286.7 eV (dashed blue line) corresponds to carbon directly bound to nitrogen, the main C 1s peak appears at 285.5 eV (solid blue line) in accordance with literature and contains contributions of all other carbons in MPTP, that is, the residual carbons in the pyridine rings and the phenyl ring (Table 1) [R1]. In sample (ii), the main C 1s peak shifts by 0.5 eV to lower energies as a result of the first wire growth step, the complexation of MPTP with Ru-PF₆ in ethanol. This significant effect is caused by the fact that in surface sensitive methods like XPS the contribution of the near-surface cores to the total signal intensity is higher compared to low lying cores. In consequence, the main C 1s peak is shifted to a BE of 285.0 eV due to the contribution of the aliphatic carbons terminating the MPTP-Ru growth step while the contribution of aromatic and pyridine carbons is reduced [R2, R3]. The lower intensity C 1s peak, observed at a BE of 286.2 eV, is assigned to the energy of carbon atoms involved in C-O bonds, like in ethanol [R2]. These C 1s core levels of sample (ii) clearly indicate the presence of ethanol and suggest the formation of a Ru(MPTP)(EO)₃-complex (with EO corresponding to an ethoxide anion, CH₃CH₂O⁻). The corresponding Ru 3d_{5/2} peak at 282.1 eV, which can be identified as Ru(III) bound to hydroxide or in this case ethoxide ions, verifies this view (Figure S5b) [28]. In sample (iii), corresponding to MPTP-Ru-BTP wires, and sample (iv), corresponding to MPTP-Ru-BTP-Ru wires, no significant changes of the main C 1s peak can be observed. However, the low intensity C 1s peak shifts alternately between 286.5 eV (C-N) and 286.2 eV (C-O) and strongly alternates in intensity, indicating a termination of the Ru-complex wire by either a TP group or a Ru(TP)(EO)₃-complex, respectively. A minor C 1s component observed in samples (iii) and (iv) at BE of 288.2 eV and 287.9 eV, is assigned to compounds containing C=O double bonds, like HCO₃⁻ species, which may result at Au surfaces due to air exposure [R1-R3].

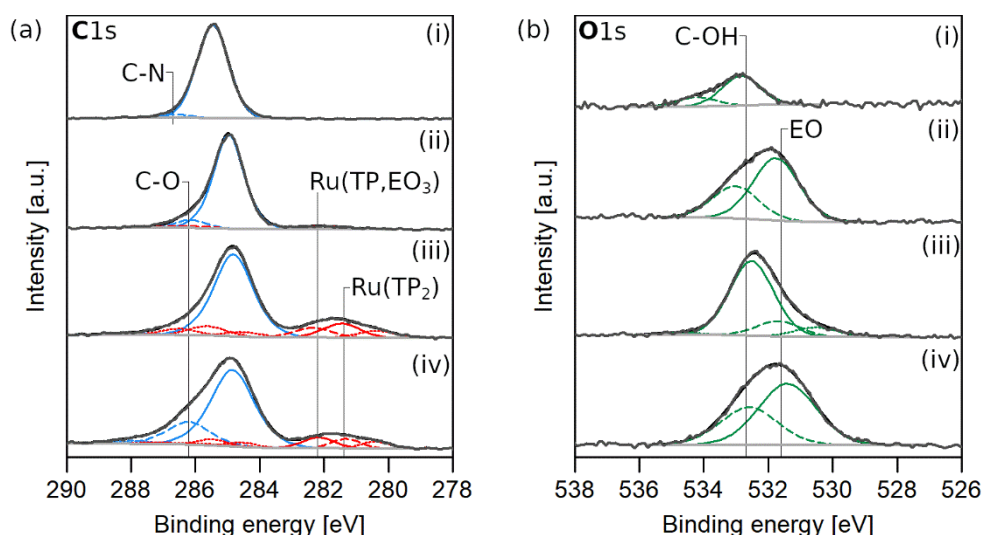


Figure S4. XPS of consecutive wire growth steps. Grey lines correspond to the actual signal while black lines correspond to the envelope of the blue and red fitting curves or the green fitting curves. (a) C 1s (blue) and Ru 3d_{5/2} (red) core level spectra, (b) O 1s core level spectra. (i) MPTP; (ii) MPTP-Ru; (iii) MPTP-Ru-BTP; (iv) MPTP-Ru-BTP-Ru.

The main Ru 3d_{5/2} peak observed during the Ru-complex wire growth from sample (ii) to (iv) tends towards a distinctly higher BE (282.1 eV), when the wire is terminated by the Ru^(III)(TP)(EO)₃-complex (samples (ii) and (iv)) compared to the BE (281.5 eV) attributed to Ru^(III)(TP)₂-complexes (sample (iii)) (Table 1) [28,R1]. For the MPTP-Ru-BTP-Ru wire the contribution of both Ru-complexes to the Ru 3d peak is nearly comparable due to the presence of both Ru-complexes in the wire and the rate of yield of the wire growth steps less than 100% under these mild reaction conditions. An additional Ru 3d_{5/2} peak with lower intensity at a BE of 280.5 eV is obtained in step (iii). This peak corresponds to hydrated ruthenium oxide, like Ru^(IV)O(OH)₂ or Ru^(IV)O(EO)₂, and can be formed due to air exposure. This Ru 3d_{5/2} peak is also observed in the core level spectrum of sample (iv).

In addition, the O 1s peak assignment reveals the alternation of the Ru-complex wire terminating groups, too. The O 1s core level spectrum of sample (i), MPTP chemisorbed on the Au substrate, shows a residual amount of the solvent ethanol adsorbed on the surface indicated by the O 1s BE of 532.9 eV attributed to aliphatic C-O bonds and 534.2 eV corresponding to carbon bound hydroxy groups involved in hydrogen bonds (Figure S5b and Table 1) [29,30]. However, the main O 1s peak in the spectra of sample (ii) and sample (iv) appears at BE of 531.8 eV and 531.4 eV, respectively, and indicates the wire termination by the Ru(TP)(EO)₃-complex as well as the C 1s and Ru 3d_{5/2} spectra [29]. On the other side, mainly the signature of ethanol is found in the O 1s core level spectrum of sample (iii) whose termination can be compared with that of sample (i). Thus, the O 1s BE corresponding to aliphatic C-O bonds alternate with those indicating hydroxide or ethoxide groups and can be attributed to alternating terminations during the Ru(TP)₂-complex wire growth by TP groups

and Ru(TP)(EO)₃-complexes. It should be mentioned that the remaining low intensity O 1s peak at 530.8 eV in sample (iii) is assigned to hydrated ruthenium oxide and thus, complements the low intensity Ru 3d_{5/2} peak [28]. Accordingly, the XP spectra presented here prove, in addition to earlier published results based on by other spectroscopic methods, that the desired wire growth can successfully be conducted [19].

5. Activation energies of Ru(MPTP)₂-AuNP devices

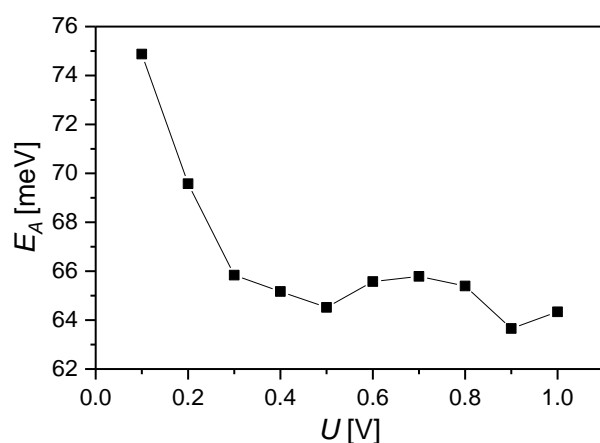


Figure S5. Activation energies, E_A , obtained from linear regressions of Arrhenius plots ($\ln(I)$ vs. $1/T$) given in Figure 4. The curves, $\ln(I)$ vs. $1/T$, were measured for 10 different biases in the range of 0.1 V to 1.0 V. A decline in E_A is determined for increasing bias and indicates a broadening of the electron energy distribution at E_F . This is in line with a tunneling mechanism.

6. Sequential tunneling through Ru(MPTP)₂-AuNP devices

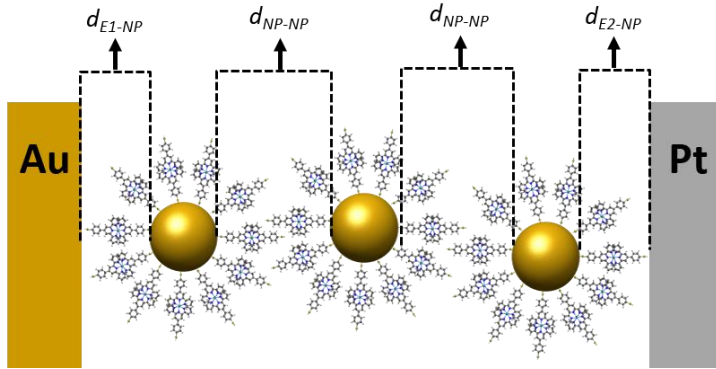


Figure S6. Schematic of three Ru(MPTP)₂-AuNP bridging the gap between heterogeneous nanoelectrodes with a separation of about 50 nm (not to scale).

We assume that transport in a Ru(MPTP)₂-AuNP device is based on tunneling of electrons through multiple small tunneling barriers, between an electrode and a AuNP or between two AuNP, respectively, while a bias voltage is applied between the left and the right electrode. The tunneling barriers are formed by Ru(MPTP)₂-complexes. Considering the junction geometry given in the schematic, the device conductance (G_{dev}) is calculated using the series formula

$$\frac{1}{G_{NPdev}} = \frac{1}{G_{L-NP1}} + \frac{1}{G_{NP1-NP2}} + \frac{1}{G_{NP2-NP3}} + \frac{1}{G_{NP3-R}} \quad (1)$$

with G_{L-NP1} and G_{NP3-R} the conductance values resulting from tunneling through the barrier between the left or the right electrode and the nearest AuNP, respectively, while G_{NP-NP} corresponds to the conductance value through the tunneling barrier between two AuNP.

The single-channel Landauer formula is applied to determine the theoretical device conductance at ± 1 V according to the method we reported before [15,23,24]. In this model G through Ru(MPTP)₂-complexes forming the tunneling barrier between an electrode and AuNP or two AuNP is given by:

$$G = G_0 T T e^{-\beta d}. \quad (2)$$

The values given in the following are used for the estimation of the device conductance: conductance quantum $G_0 = 77.5 \mu\text{S}$, electronic decay constant for Ru(MPTP)₂-complexes $\beta_{Ru} = 3.1 \text{ nm}^{-1}$, length of the Ru(MPTP)₂-complex $d_{Ru} = d_{E1-NP} = d_{NP-E2} = 2.2 \text{ nm}$, $d_{NP-NP} = 4.0 \text{ nm}$, transmission coefficients $T_{Au-SPhen} = 0.4$, and $T_{Pt-SPhen} = 0.7$ [15].

This procedure leads to a conductance value of $G_{NPdev} = 25 \text{ pS}$ for an Ru(MPTP)₂-AuNP device formed by three functionalized AuNP between a nanoelectrode gap of about 50 nm and an interparticle distance of 4.0 nm as obtained by TEM analysis. This corresponds astonishing well to the median of the experimentally obtained values, $G_{exp} = 16 \text{ pS}$, and confirms the above made assumption that sequential tunneling through the Ru(MPTP)₂-AuNP device is the main transport mechanism.

7. Optical addressing of an empty nanogap

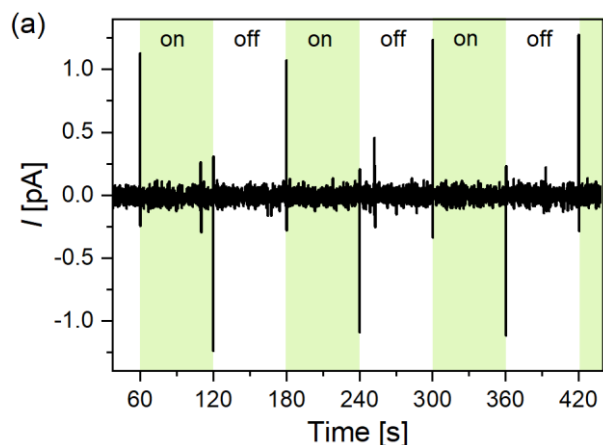


Figure S7. Current *versus* time traces obtained from an empty nanoelectrode gap of 30 nm at 1 V bias irradiated with 530 nm light at a frequency of 60 s. Obviously spikes appear when the light is switched on or off. The same effect was obtained by interrupting the light beam with a sheet of paper manually.

8. On/off ratio of a Ru(TP)₂-complex wire device

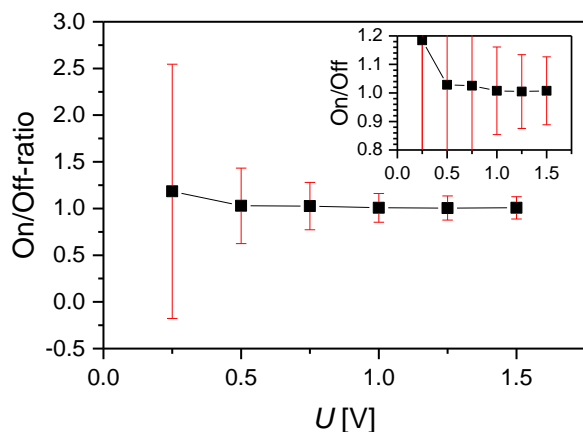


Figure S8. On/off conductance ratio determined between the steady-state currents of a Ru(TP)₂-complex wire device under irradiation and in the dark given for different bias voltages. Red arrow bars correspond to one standard deviation. The inset shows a zoom of the last 5 values. Due to the small conductance values of a Ru(TP)₂-complex wire devices around 1 pS the standard deviation does not allow to determine on/off ratios below 1.1.

9. Optical addressing of Ru(MPTP)₂-AuNP devices

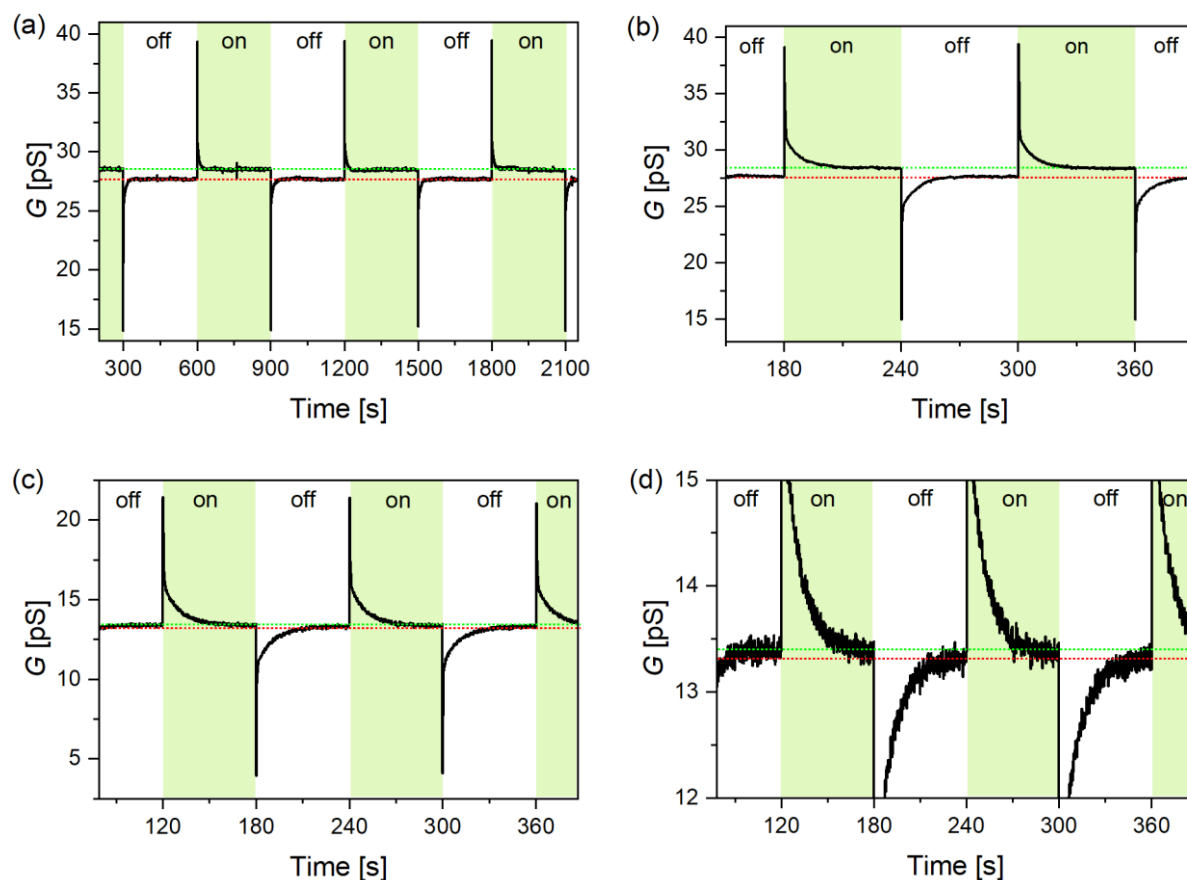


Figure S9. Current *versus* time traces from Ru(MPTP)₂-AuNP devices measured at different experimental conditions (wavelength, bias voltage, frequency). (a) 530 nm, 1 V, 300 s; (b) 530 nm, 1 V, 60 s; (c) 505 nm, 0.5 V, 60 s; (d) 505 nm, 0.5 V, 60 s.

10. References

- (R1) Agnès, C.; Arnault, J.-C.; Omnès, F.; Jusselme, B.; Billon, M.; Bidan, G.; Mailley, P. XPS Study of Ruthenium Tris-Bipyridine Electrografted from Diazonium Salt Derivative on Microcrystalline Boron Doped Diamond. *Phys. Chem. Chem. Phys.* **2009**, *11*, 11647-11654.
- (R2) Beamson, G.; Briggs, D. High Resolution XPS of Organic Polymers – The Scienta ESCA300 Database, Wiley Interscience, **1992**.
- (R3) Naumkin, A. V.; Kraut-Vass, A.; Gaarenstroom, S. W.; Powell, C. J. (Eds.) NIST X-Ray Photoelectron Spectroscopy Database. Version 4.1, National Institute of Standards and Technology, Gaithersburg, **2012**.