Electrografted Monolayer Based on a Naphthalene Diimide-Ruthenium Terpyridine Complex Dyad: Efficient Creation of Large-area Molecular Junctions with High Current Densities

Denis Frath, Van Quyen Nguyen, Frédéric Lafolet, Pascal Martin, Jean-Christophe Lacroix

Supporting informations

General considerations. Reagent-grade solvents and reagents were used as received from commercial sources unless specified otherwise. $tpyPhNH_2$ and $Ru(tpy)_2PhNH_2$ were synthesized according to literature.[1,2] Reactions were monitored by thin-layer chromatography (TLC silica gel 60 F_{254}). Column chromatography was performed using silica gel 40-63 µm and eluent mixtures are reported as volume ratio (v/v). ^1H and ^{13}C NMR spectra were recorded on a Bruker AC400. ^1H and ^{13}C chemical shifts are reported in parts per million (ppm) referenced to the residual non-deuterated solvent peak. This work has benefited from the facilities of the Small Molecule Mass Spectrometry platform of ICSN (www.icsn.cnrs-gif.fr) for HRMS analyses.

Synthesis of $Ru[tpyPhNH_2]Cl_3$. A solution containing $tpyPhNH_2$ (110 mg) and $RuCl_3.xH_2O$ (91 mg) in EtOH (20 mL) was refluxed for two hours. After the mixture was cooled down to room temperature, the precipitate was filtered and washed successively with ethanol and diethyl ether to afford a dark brown solid. Yield: 77% (140 mg).

Synthesis of 1. 1,4:5,8-Naphthalenetetracarboxylic dianhydride (4.36 g, 16.3 mmol) was dissolved in dry dimethylformamide (40 mL) and the solution was heated to 140°C under argon. Then, *n*-hexylamine (1.72 mL, 13.0 mmol) in dry dimethylformamide (3 mL) was added dropwise, and the solution was further heated for 16 h. The reaction mixture was cooled in a fridge for two hours and the resulting precipitate was filtered. The filtrate was evaporated, dissolved in 50 ml of acetone, cooled in a fridge overnight and the resulting precipitate was filtered. The filtrate was evaporated and the residue was purified by silica gel chromatography eluted with dichloromethane. Light-yellow solid. Yield: 40% (1.83 g). ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.81 (4H, s, CH Arom), 4.21-4.18 (2H, m, CH_2 Hexyl), 1.76-1.70 (2H, m, CH_2 Hexyl), 1.45-1.41 (2H, m, CH_2 Hexyl), 1.37-1.32 (4H, m, CH_2 Hexyl), 0.91-0.87 (3H, m, CH_3 Hexyl); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 162.4, 159.0, 133.3, 131.3, 129.0, 128.1, 127.0, 123.0, 41.4, 31.6, 28.1, 26.9, 22.7, 14.2; HRMS (ESI-TOF) m/z: $[M + H + MeOH]^+$ calcd for $C_{21}H_{22}NO_6$ 384.1447; found 384.1435.

Synthesis of 2. A solution of **1** (324 mg, 0.62 mmol), tpyPhNH_2 (200 mg, 0.62 mmol) and isoquinoline (2 droplets) in *m*-cresol (4 mL) was heated progressively from 80°C to 200°C and then stirred for 24h. The reaction mixture was cooled to room temperature, diluted with ethanol and filtered. The brown precipitate was washed with boiling ethanol. Quant. Yield: 74% (300 mg). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.78-8.72 (8H, m, CH Arom), 8.64 (2H, d, J = 8.0 Hz, CH Arom), 8.08 (2H, d, J = 8.4 Hz, CH Arom), 7.88 (2H, td, ^3J = 7.8 Hz, ^4J = 1.7 Hz, CH Arom), 7.48 (2H, d, J = 8.4 Hz, CH Arom), 7.37-7.34 (2H, m, CH Arom), 4.19 (2H, t, J = 7.6 Hz, CH_2 Hexyl), 1.78-1.72 (2H, m, CH_2 Hexyl), 1.54 (9H, s, CH_3 Boc) 1.47-1.42 (2H, m, CH_2 Hexyl), 1.37-1.35 (4H, m, CH_2 Hexyl), 0.93-0.89 (3H, m, CH_3 Hexyl); ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 163.0, 162.8, 156.1, 149.3, 139.5, 137.0, 135.4, 131.5, 131.1, 129.3, 128.6, 127.12, 127.06, 126.9, 126.7, 124.0, 121.4, 119.1 41.2, 31.6, 28.1, 26.9, 22.7, 14.1; HRMS (ESI-TOF) m/z: $[M + H]^+$: calcd for $C_{41}H_{32}N_5O_4$ 658.2449; found 658.2454.

Synthesis of 3. A schlenck containing triethylamine (0.6 ml) and ethanol (120 ml) was degased by bubling argon through the solution. Ru[tpyPhNH_2]Cl_3 (300 mg, 0.56 mmol) and **2** (365 mg, 0.55 mmol) were added. The resulting mixture was stirred under argon at 85°C during four days. The solvent was evaporated and the residue was purified by silica gel chromatography eluted with MeCN/MeOH/H_2O/$NaCl_{sat.}$ (4/1/1/1). The solid was diluted in the minimum amount of methanol, excess of salts were removed by filtration and the filtrate was added to a saturated solution of KPF_6. The precipitate was washed with water, diethyl ether and dichloromethane. Dark red solid. Yield, 18% (100 mg). ^{1}H NMR (400 MHz, Acetone-d_6) δ (ppm): 9.49 (2H, d, J = 11.5 Hz, CH Arom), 9.27 (2H, d, J = 11.5 Hz, CH Arom), 9.07 (2H, br t, CH Arom), 8.99 (2H, br t, CH Arom), 8.87-8.82 (4H, m, CH Arom), 8.49 (2H, br t, CH Arom), 8.15-8.02 (6H, m, CH Arom), 7.86-7-84 (4H, m, CH Arom), 7.77 (2H, br d, CH Arom), 7.38-7.29 (4H, m, CH Arom), 6.99-6-97 (2H, m, CH Arom), 5.43 (2H, br s, NH_2), 4.21-4.17 (2H, m, CH_2 Hexyl), 1.78-1.74 (2H, m, CH_2 Hexyl), 1.41-1.38 (6H, m, CH_2 Hexyl), 0.92-0.87 (3H, m, CH_3 Hexyl); ^{13}C NMR: Solubility is too low; ESI-HRMS (ESI-TOF) m/z: $[M – PF_6]^+$: calcd for $C_{62}H_{47}F_6N_9O_4P$ 1228.2442; found 1228.2448.

In-situ Preparation of Diazonium Cation. The in-situ formation of the diazonium cation from aminophenyl was performed in the electrochemical cell using tert-butyl nitrite (tBuO-NO).[3] An acetonitrile solution containing amino compound (0.5 mM) and Bu_4NPF_6 (0.1 M) as supporting electrolyte was prepared and degassed for at least ten min. Following that, 15 eq. of tBuO-NO were added and the solution was degased for at least five more min. Working electrodes were immersed prior to electro-grafting of the resulting diazonium cation.

Electrochemical Experiments. Electrochemical experiments were performed in a conventional three-electrode configuration. Three types of working electrodes were used, namely glassy carbon (GC, 3 mm diameter), gold electrodes (ca. 50 nm thick on Si/SiO_2) and gold μ-electode (ca. 20 μm x 2 cm large and 50 nm thick on Si/SiO_2) for junctions preparation. A saturated calomel electrode (SCE) and a stainless steel grid were used as reference and counter-electrode respectively.

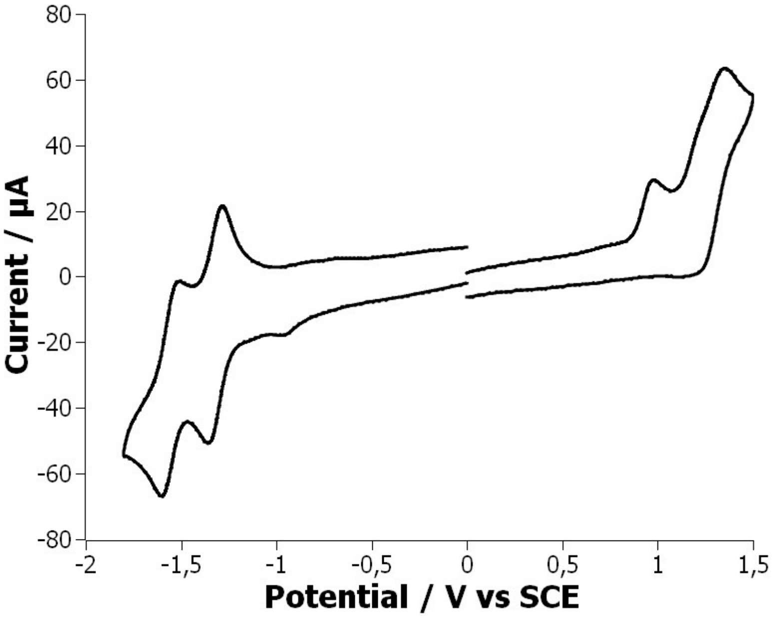

Figure S1. Cyclic voltammetry of $Ru(tpy)_2PhNH_2$ in MeCN (1 mM), $TBAPF_6$ 0.1M on GC at 0.1 V/s

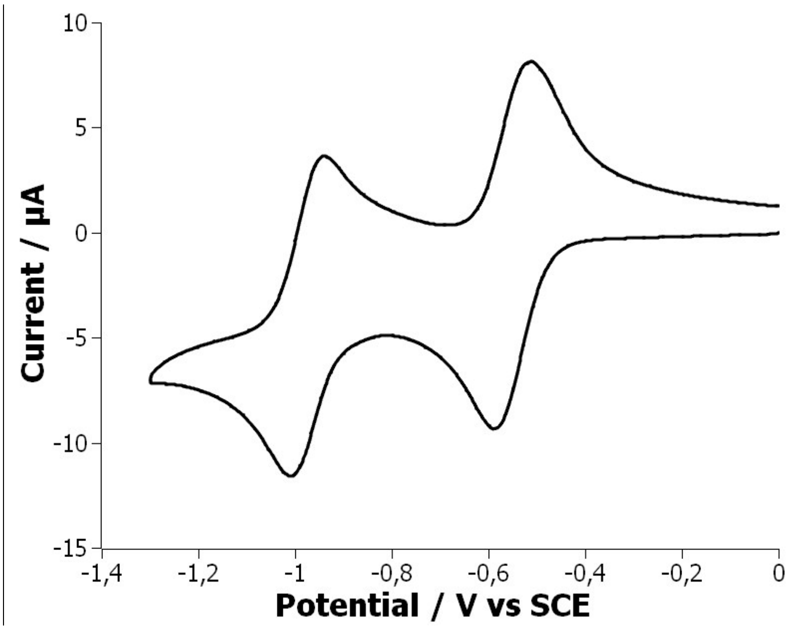

Figure S2. Cyclic voltammetry of compound **2** in MeCN (0.5 mM), $TBAPF_6$ 0.1M on GC at 0.1 V/s

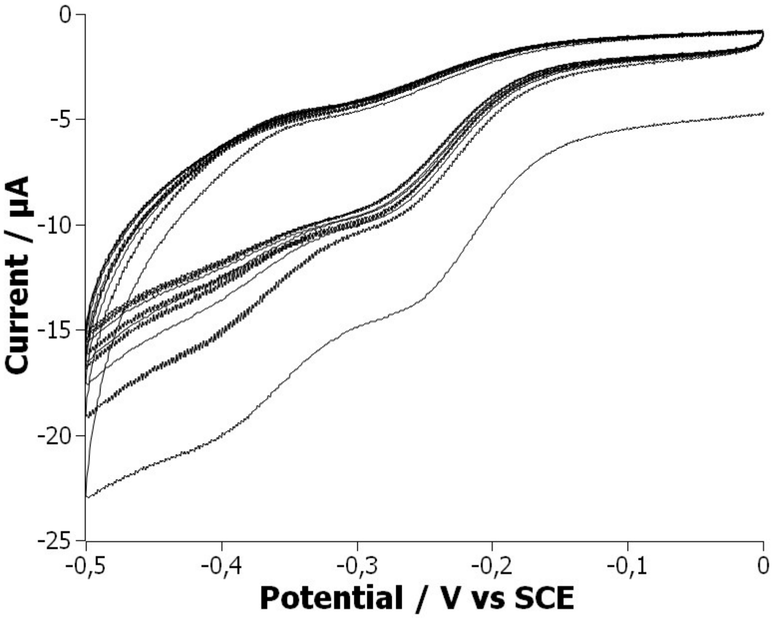

Figure S3. Ten cycle of the electrochemical reduction of the diazonium cation derived from dyad **3** in MeCN, TBAPF$_6$ 0.1M on GC at 0.1 V/s.

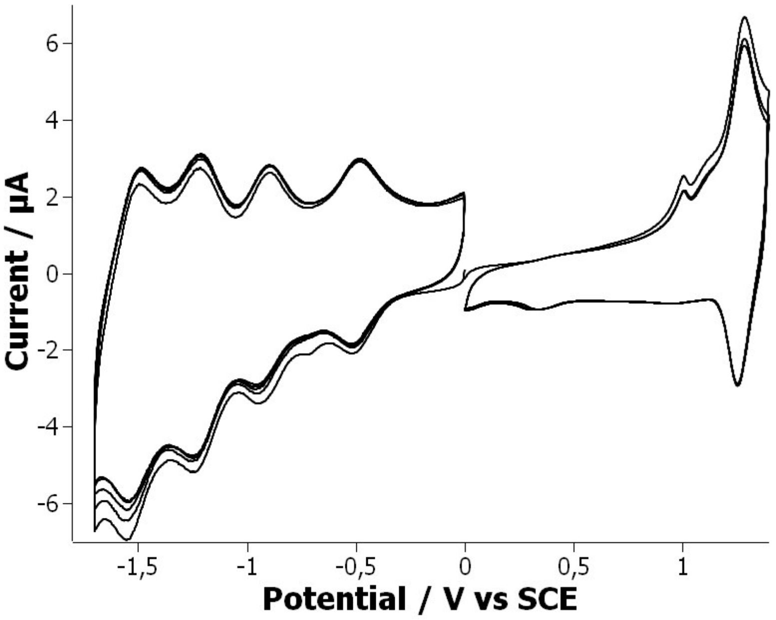

Figure S4. Cyclic voltammetry of dyad **3** grafted layer on GC in MeCN, TBAPF6 0.1M at 0.1 V/s

Table S1. Electrochemical values of reference compounds and Dyad **3** in solution and grafted on GC.

	$^1E_{1/2}$ (V/SCE)	$^2E_{1/2}$ (V/SCE)	$^3E_{1/2}$ (V/SCE)	$^4E_{1/2}$ (V/SCE)	$^5E_{pa}$ (V/SCE)	$^6E_{1/2}$ (V/SCE)
Ru(tpy)$_2$PhNH$_2$	-1.56	-1.32	-	-	0.98	1.28
Compound **2**	-	-	-0.97	-0.55	-	-
Dyad **3** (Solution)	-1.49	-1.30	-0.95	-0.52	1.08	1.32
Dyad **3** (Grafted on GC)	-1.53	-1.24	-0.93	-0.50	-	1.28

X-ray Photoelecron Spectroscopy. XPS analyses were performed on a modified gold substrate using a VG Scientific ESCALAB 250 system equipped with a microfocused monochromatic Al KR X-ray source (1486.6 eV) and a magnetic lens, which increases the electron acceptance angle and hence the sensitivity. The spectra were acquired in the constant analyzer energy mode with pass energies of 150 and 40 eV for the survey and the narrow regions, respectively. Charge compensation was achieved with an electron flood gun combined with an argon ion gun. Software, data processing, calibration, and surface composition determination were described in a previous publication.[4]

Table S2. XPS analysis of the modified gold electrode

Name	Peak BE	FWHM eV	Area (P) CPS.eV	At. %
Au4f [a]	84.04	2.95	658609.21	5.31
C1s A [b]	285.09	1.42	93522	44.63
C1s B [b]	286.29	1.52	38015.97	18.14
C1s C [b]	288.69	1.54	8424.1	4.02
C1s D [b]	292.37	1.54	3524.22	1.68
F1s [a]	686.32	2.91	156195.28	6.05
N1s [a]	400.07	2.94	116413.66	9.82
O1s [a]	532.12	3.23	147611.7	8.05
P2p [a]	135.25	1.88	9934.02	1.17
Ru3d3 [b]	285.41	1.23	12084.85	0
Ru3d5 [b]	281.41	1.23	17511.19	1.13

[a] Integrated from XPS survey [b] Fitted from high-resolution spectra

Fabrication of MJ. The MJ were fabricated using a gold stripe substrate on SiO_2/Si wafers with width of 20 µm and several millimeters long. The gold thickness was 45 nm on a Ti adhesion layer (2 nm). After electrochemical deposition of the organic layer, an electron beam Ti/Gold top contact was deposited as described in detail previously.[5,6] The MJs were thus made by several successive steps of photography/metallic evaporation. As described in figure S5 the first step is the fabrication of nanostructured gold electrodes (20 µm of width for 2 cm of length) by photoligraphy using AZ 5214 resist. After lithography the electrodes are made by e-beam evaporation of 2 nm Ti and 50 nm Au (Ti act as an adhesion layer for gold electrode). Then the electrodes are functionalized by the organometallic layer deposited by electroreduction of the diazonium salts.

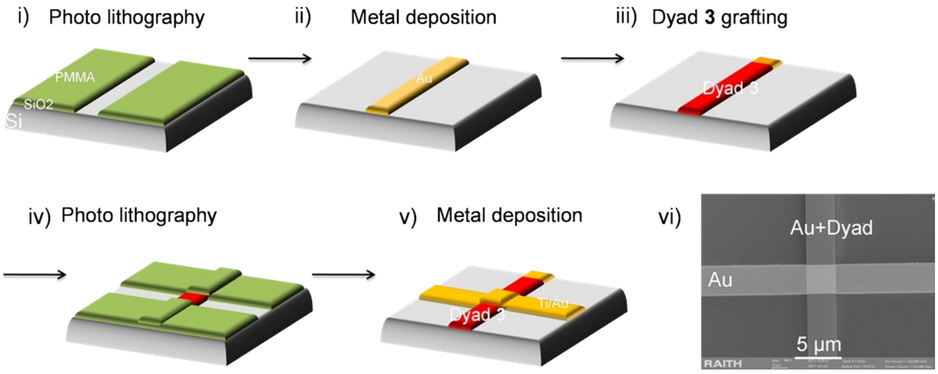

Figure S5. Schematic view of the fabrication of the device (metal/molecule/metal)

The top electrode is made on top of the organometallic layer by the same approach: photolithography and e-beam evaporation. Each sample allowed the fabrication of 16 molecular junctions with lateral dimensions of 20 by 20 µm (area = 4 x 10^{-6} cm^2). Careful control of the back pressure during Ti deposition was important, as this very reductive metal can easily be oxidized to various conductive titanium oxides.[7–9] A pressure of 10^{-8} torr was used to reduce oxidation from the residual oxygen and water of the vapor deposition systems but since reaction of Ti with the organometallic layer cannot be excluded. The molecule/Ti interface was carefully characterized using X-ray photoelectron spectroscopy (XPS) in a recently accepted paper.[10]

Experimental setup for electrical measurement. Current density vs bias voltage (*JV*) electrical characteristics of molecular junctions were measured in air with a Keithley 2602b source-meter at 1 $V.s^{-1}$ or by dc polarizing the junction while measuring the current with a low-noise current amplifier. In each case a two-probe set-up configuration was used with the top electrode grounded while applying a bias to the bottom electrode.

Statistical analysis of the rectification ratio of the MJ based on Dyad 3 monolayers

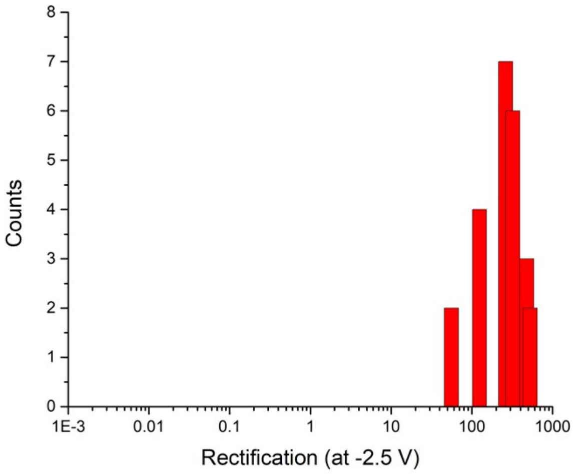

Figure S6: Rectification Ratio (J(-2.5 V)/J(+2.5 V)) histogram for 24 Au/ Dyad **3**/Ti (2nm)/Au junctions

References

[1] W. Y. Ng, X. Gong and W. K. Chan, *Chem. Mater.*, 1999, **11**, 1165–1170.

[2] B. Jousselme, G. Bidan, M. Billon, C. Goyer, Y. Kervella, S. Guillerez, E. A. Hamad, C. Goze-Bac, J.-Y. Mevellec and S. Lefrant, *J. Electroanal. Chem.*, 2008, **621**, 277–285.

[3] V. Stockhausen, G. Trippé-Allard, N. Van Quynh, J. Ghilane and J.-C. Lacroix, *J. Phys. Chem. C*, 2015, **119**, 19218–19227.

[4] V. Stockhausen, J. Ghilane, P. Martin, G. Trippé-Allard, H. Randriamahazaka and J.-C. Lacroix, *J. Am. Chem. Soc.*, 2009, **131**, 14920–14927.

[5] P. Martin, M. L. Della Rocca, A. Anthore, P. Lafarge and J.-C. Lacroix, *J. Am. Chem. Soc*, 2012, **134**, 154–157.

[6] T. Fluteau, C. Bessis, C. Barraud, M. L. Della Rocca, P. Martin, J.-C. Lacroix and P. Lafarge, *J. Appl. Phys.*, 2014, **116**, 114509.

[7] A. M. Nowak and R. L. McCreery, *J. Am. Chem. Soc.*, 2004, **126**, 16621–16631.

[8] R. L. McCreery, J. Wu and R. P. Kalakodimi, *Phys. Chem. Chem. Phys.*, 2006, **8**, 2572–2590.

[9] J. Wu and R. L. McCreery, *J. Electrochem. Soc.*, 2009, **156**, 29–37.

[10].Q. V. Nguyen, P. Martin, D. Frath, M. L. Della Rocca, F. Lafolet, C.Barraud, P. Lafarge, V.Mukundan, D. Jame^c, R. L. McCreery and J.-C Lacroix *J. Am. Chem. Soc*, 2017, in press