Supporting Information

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Stepwise Formation of Ruthenium(II) Complexes by Direct Reaction on Organized Assemblies of Thiol-Terpyridine Species on Gold: a Surface Study.

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Material and Methods.

All available chemicals were purchased from commercial sources and were used without any further purification. Solvents were purified by using standard methods and dried if necessary. Air- and moisture-sensitive reactions were performed under usual inert atmosphere techniques. Thin layer chromatography (TLC) was conducted on plates precoated with silica gel Si 60-F$_{254}$ (Merck, Darmstadt, Germany) and detected by UV light. Column chromatography was conducted by using silica gel Si 60, mesh size 0.040-0.063 mm (Merck, Darmstadt, Germany). Melting points have been obtained by a Büchi 535 instrument and are uncorrected. NMR spectra were recorded on a Bruker Avance 400 referenced as following: $^1$H (400 MHz), internal SiMe$_4$ at $\delta$ 0.00 ppm and $^{13}$C (100.6 MHz), solvent carbon resonance (CDCl$_3$ = 77.23 ppm, CD$_3$CN = 1.3 ppm). Protons and carbon assignments were achieved by $^1$H-$^1$H COSY and $^1$H-$^{13}$C heteronuclear correlation experiments.

4’-[4-(Methylthio)phenyl]-2,2’;6’,2’’-terpyridine (2). 2-Acetylpyridine (2.66 g, 22 mmol) was added to a stirred solution of 1BuOK (3.70 g, 33 mmol) in anhydrous THF (50 mL). The mixture was stirred at room temperature, in an inert atmosphere, for 2h then a solution of 4-(methylthio)benzaldehyde (1.52 g, 10 mmol) in anhydrous THF (10 mL) was added via sringe and the reaction mixture was stirred overnight. During this time a dark red color developed. Ammonium acetate (26 g, 337 mmol) and EtOH (180 mL) were added sequentially and the
mixture was heated to reflux for 4 h. The solvent was concentrated to 1/3 of the volume with formation of a yellow solid precipitate which was separated by filtration on a fritted glass and crystallized with EtOH to afford 1.34 g (35%) of 2 as yellow powder. m.p. 173-174 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 2.55 \) [s, 3H; SCH\(_3\)], 7.35 [bd, \(^3\)J (H,H)= 7.4 Hz, \(^3\)J (H,H)= 5.0 Hz, 2H; tpySCH\(_3\)(5,5\(\text{II}\))], 7.38 [d, \(^3\)J (H,H)= 8.5 Hz, 2H; Ph(3,5)], 7.86 [d, \(^3\)J (H,H)= 8.5 Hz, 2H; Ph(2,6)], 7.88 [ddd, \(^3\)J (H,H)= 7.9 Hz, \(^4\)J (H,H)= 1.7 Hz, 2H; tpySCH\(_3\)(4,4\(\text{II}\))], 8.67 [d, \(^3\)J (H,H)= 7.9 Hz, 2H; tpySCH\(_3\)(3,3\(\text{II}\))], 8.73 [s, 2H; tpySCH\(_3\)(3,5\(\text{II}\))], 8.80 [bd, \(^3\)J (H,H)= 5.0 Hz, 2H; tpySCH\(_3\)(6,6\(\text{II}\))]. \(^13\)C NMR (100.6 MHz, CDCl\(_3\)): \(\delta = 15.5 \) [CH; tpySCH\(_3\)(3,5\(\text{II}\))], 121.4 [CH; tpySCH\(_3\)(3,3\(\text{II}\))], 123.8 [CH; tpySCH\(_3\)(5,5\(\text{II}\))], 126.5 [CH; Ph(3,5)], 127.6 [CH; Ph(2,6), tpy(5,5\(\text{II}\))], 134.9 (C), 136.8 [CH; tpySCH\(_3\)(4,4\(\text{II}\))], 140.1 (C), 149.1 [CH; tpySCH\(_3\)(6,6\(\text{II}\))], 149.5 (C), 156.0 (C), 156.2 (C).

4’-[4-(Mercapto)phenyl]-2,2’;6,’2”-terpyridine (3). A sample of potassium ethanthiolate (EtSK) (250 mg, 2.5 mmol) was added to a stirred solution of 2 (457 mg, 1.28 mmol) in anhydrous DMF (5 mL) and the mixture was reacted overnight at reflux under inert atmosphere. After the addition of EtSK the reaction mixture takes a red purple color which remain unchanged during the reaction. The reaction mixture was cooled to room temperature, was diluted with H\(_2\)O (100 mL), heated at 80-85°C and maintained under magnetic stirring and degasing by bubling nitrogen for 1 h. After this time the resulting aqueous suspension was poured in a separatory funnel, diluted with NH\(_4\)Cl saturated aqueous solution (100 mL) and extracted with CH\(_2\)Cl\(_2\) (3 x 100 mL). The organic phase was dried over Na\(_2\)SO\(_4\) and evaporated in vacuo to afford 430 mg of crude yellow powder. This product was crystallized from 40 mL of EtOH to give 380 mg (87%) of pure 3 as pale yellow solid. m.p. 166-168 °C; \(^1\)H NMR (400 MHz, CDCl\(_3\)): \(\delta = 7.23 \) [ddd, \(^3\)J (H,H)= 6.0 Hz, \(^4\)J (H,H)= 4.7 Hz, \(^4\)J (H,H)= 1.1 Hz 2H; tpySH(5,5\(\text{II}\))], 7.28 [d, \(^3\)J (H,H)= 8.3 Hz, 2H; Ph(3,5)], 7.67 [d, \(^3\)J (H,H)= 8.3 Hz, 2H; Ph(2,6)], 7.76 [dt, \(^3\)J (H,H)= 7.8 Hz, \(^4\)J (H,H)= 1.8 Hz, 2H; tpySH (4,4\(\text{II}\))], 8.55 [d, \(^3\)J (H,H)= 7.8 Hz, 2H; tpySH(3,3\(\text{II}\))], 8.58 [s, 2H; tpySH(3,5\(\text{II}\))], 8.61 [bd, \(^3\)J (H,H)= 4.7 Hz, 2H; tpySH(6,6\(\text{II}\))]. \(^13\)C NMR (100.6 MHz, CDCl\(_3\)): \(\delta = 118.4 \) [CH;
{4'-[4-(Mercapto)phenyl]-2,2';6',2''-terpyridine]-[2,2';6',2''-terpyridine] ruthenium (II)-
bis(hexafluorophosphate) [Ru(MPTP)(tpy)²⁺](PF₆)₂ \(\text{1} \). 4'-[4-(mercaptop)phenyl]-2,2';6',2''-
terpyridine (3) (50 mg, 0.146 mmol) was added to a suspension of [Ru(tpy)][Cl]₃ (64 mg, 0.86
mmol) in methanol (15 mL). Few drops of N-ethylmorpholine were added and the mixture was
refluxed for 12 h under magnetic stirring. The deep red mixture was cooled at room temperature
and filtered through a fritted glass. An excess of ammonium hexafluorophosphate dissolved in
water was added in order to precipitate all ruthenium complexes. These were collected by
filtration and sequentially washed with methanol, water and diethyl ether. The product was
purified by column chromatography (silica gel, acetonitrile/0.2M aqueous potassium nitrate
solution 9:1). The second dark red band was evaporated to dryness. The inorganic salts were
eliminated by washing with water and then an excess of aqueous ammonium
hexafluorophosphate solution was added. The precipitate was filtered, washed with water and
diethylether and then dried in vacuo to afford 13 mg (8.9 %) of 1 as ruby red microcrystals. 

\[ \text{1H NMR (400 MHz, CD}_3\text{CN): } \delta = 7.19 \text{ [bt, } ^3J \text{(H,H)= 6.6 Hz, 4H; tpySH(5,5)} \text{H}], 7.37 \text{ [bd,}
\]
\[ ^3J \text{(H,H)= 5.0 Hz, 2H; tpy(6,6)} \text{H]], 7.46 \text{ [bd, } ^3J \text{(H,H)= 5.0 Hz, 2H; tpySH(6,6)} \text{H]], 7.95 \text{ [ddd, } ^3J \text{(H,H)= 7.8 Hz, 4J}
\]
\[ ^3J \text{(H,H)= 8.0 Hz, 4J (H,H)= 1.1 Hz, 4H; tpySH(4,4)} \text{H], tpy(4,4)} \text{H]], 8.03 3d, 3J
\]
\[ ^3J \text{(H,H)= 8.5 Hz, 2H; tpySH(3,3)} \text{H], 8.33 [d, } ^3J \text{(H,H)= 8.5 Hz, 2H; tpySh(3,3)} \text{H], 8.44 [t, } ^3J \text{(H,H)= 8.1 Hz,}
\]
\[ 2H; tpy(4)])], 8.55 [bd, } ^3J \text{(H,H)= 8.0 Hz, 2H; tpySh(3,3)} \text{H], 8.77 [bd, } ^3J \text{(H,H)= 7.8 Hz, 2H;}
\]
\[ tpySH(3,3)} \text{H], 8.81 [d, } ^3J \text{(H,H)= 8.5 Hz, 2H; tpy(3,5)} \text{H], 9.13 [s, } 2H; tpySH(3,3)} \text{H].} \]

\[ \text{13C NMR (100.6 MHz, CD}_3\text{CN): } \delta = 121.1 \text{ [CH; tpySH(3,3)} \text{H)], 123.8 [CH; tpy(3,5)} \text{H], 124.5 [CH; tpy}
\]
\[ (3,3)} \text{H)], 124.7 [CH; tpySh(3,3)} \text{H], 127.4 [CH; tpySH(5,5)} \text{H], tpy(5,5)} \text{H], 128.2 [CH; Ph(3,5),}
\]
\[ 128.9 [CH; Ph(2,6)], 135.8 [CH; tpy(4)} \text{H], 136.1 (C), 138.1 [CH; tpySH(4,4)} \text{H], tpy(4,4)} \text{H], 139.0
\]
Surface characterisation

XPS measurements were performed with a PHI 5500 spectrometer. Spectra were acquired in fixed analyzer transmission mode (pass energy 93.9 eV and 23.5 eV, for survey and detailed scans respectively), using Mg Kα₁,₂ radiation. All spectra were acquired with a take-off angle of 45°. ToF-SIMS spectra were acquired in static mode with a reflector-type spectrometer (ION-TOF TOFSIMS IV), by using a pulsed $^{69}$Ga⁺ primary ion beam (25 keV, ~ 0.1 pA) rastered over a 300 x 300 mm² area. Primary ion fluence was kept < 3 x 10¹¹ ions cm⁻² in order to assure static SIMS conditions. Multivariate analysis was performed by using the MULTI-ION SIMS software (Biophy Research, Aix-en-Provence, France). We created a matrix of data by using 17 characteristic peaks of monolayers from the spectra of 12 samples. For each sample 6 spectra have been acquired, giving a total of 72 objects. The matrix of the data has been mean centred and the values have been scaled in order to give the same statistic importance to all the variables irrespective of the different absolute intensities.

![Figure S1: ToF-SIMS intensities from MB/MPTP monolayers vs time of treatment (ethanol reflux).](image-url)