Electronic Supplementary Material (ESI) for ChemComm.

Supporting Information

Versatile functionalization of carbon electrodes with a polypyridine ligand: metallation and electrocatalytic H^+ and CO_2 reduction

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Index *Page*

Experimental section

General considerations

Unless otherwise noted, all solvents and reagents were purchased from Sigma-Aldrich at ACS reagent grade or higher and used as received. Annealed platinum wire was purchased from Alfa Aesar and Nickel(II) chloride, dimethoxyethane adduct from Strem. All electrochemical data were recorded using a Bio-Logic SP 300 or a Princeton Applied Research 263A potentiostat and the IUPAC convention was used to report current. Chemical analyses of CO and H_2 were performed following previously reported procedures.[1] All solutions were thoroughly degassed and saturated with inert gas or CO_2 before electrochemical measurements.

Electrochemical measurements

The glassy carbon electrodes were polished with 800/2400 and 1200/4000 grit silicon carbide paper, followed by a 1 µm diamond suspension. The electrodes were then rinsed with water before drying in air.

All cyclic voltammetry experiments were carried out in a 3 mL single-compartment cell using a 1.5 mm diameter glassy carbon electrode (from Bio-Logic). A Pt wire counter electrode was used, with a Ag/AgCl reference electrode (RE-1B from Bio-Logic) separated from the solution by a Vycor tip.

Bulk electrolysis experiments were carried out in a custom made two-compartment cell, schematically depicted bellow (a). The working electrode used was a 1.4 cm diameter glassy carbon pellet, separated from the coiled annealed platinum wire counter electrode by a porous 4 frit, and the Ag/AgCl, 3M NaCl reference electrode was separated from the solution by a Vycor tip. The typical volume of solution used in the working compartment of the cell is 30 mL, and the typical headspace volume is 29 mL. Bulk electrolysis solutions were stirred throughout bulk electrolysis experiments.

General procedure for electrode modification

A polished glassy carbon electrode is immersed in a solution of [tpy-Ph-N_2]BF_4 (2.8 mg for 3 mL of solvent) in MeCN with 0.1 M of $TBAPF_6$ as supporting electrolyte under Ar and shielded from light. A Cyclic Voltammetry experiment is conducted at 50 mV/s from +0.8 to –0.4 V *vs.* Ag/AgCl for 10 cycles. The modified electrode is rinsed by immersion in DMF and H_2O for 10 minutes each. A typical metallation procedure calls for soaking of the modified electrode in a DMF solution of 75 mM of metal salt for 3 to 10 hours, followed by rinsing in H_2O for 10 minutes.

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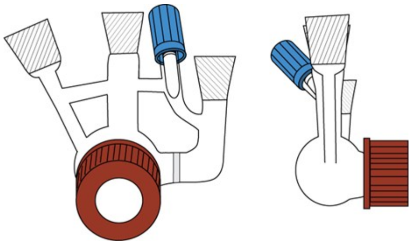
[1] N. Elgrishi, M. B. Chambers and M. Fontecave, *submitted.*

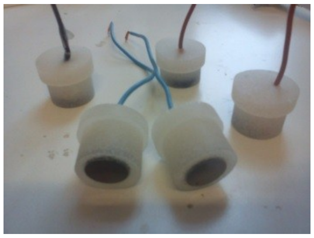
Electrode manufacturing for bulk electrolyses

A 1.4 cm diameter glassy carbon pellet is connected to a copper wire with carbon tape and coated with a cold mounting KM-U resin purchased from Presi in a 30 mm diameter rubber mold. After drying and unmolding, the resin around the electrode is carved to the appropriate shape (b).

a)



b)



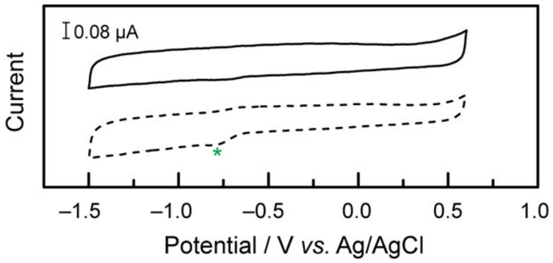


Figure S1. Cyclic voltammograms under Ar in DMF, $TBAPF_6$ 0.1M, of a bare (top, — solid black line) and a modified (bottom, --- dashed black line, the green star * indicates residual O_2) glassy carbon electrode at 100 mV/s.

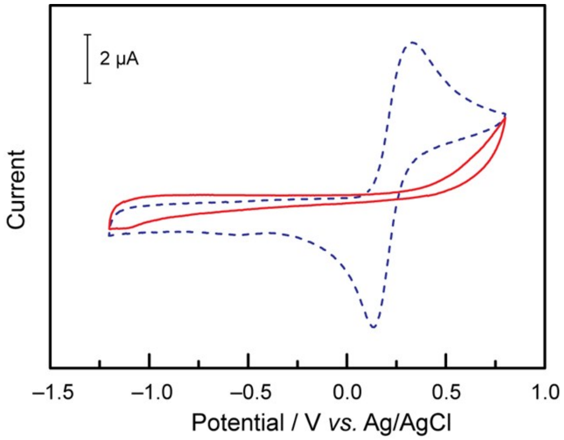


Figure S2. Cyclic voltammograms under Ar at 100 mV/s in a 0.1 M KCl solution of 5 mM of $K_4[Fe(CN)_6]$ on: a bare polished glassy carbon electrode (----blue) and a tpy-modified glassy carbon electrode (—red).

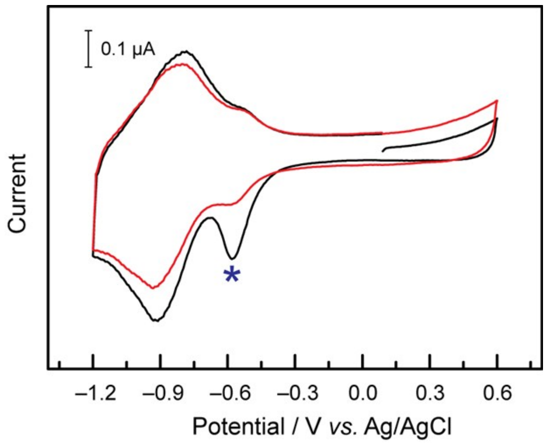


Figure S3. Cycles 1 (black) and 2 (red) of the cyclic voltammograms under Ar at 100 mV/s in DMF, TBAPF$_6$ 0.1 M of a modified glassy carbon electrode after metallation by CoCl$_2$ and rinsing in DMF (but not water) showing the feature attributed to chloride liberation (* blue star).

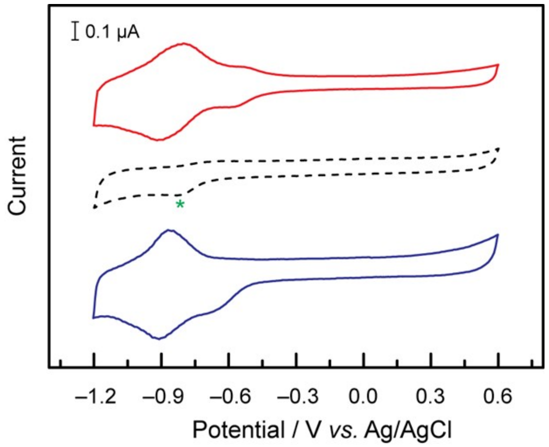


Figure S4. Cyclic voltammograms at 100 mV/s under Ar in DMF, TBAPF$_6$ 0.1M, of a tpy-modified glassy carbon electrode and freshly metallated with CoCl$_2$ and rinsed (— red). The same electrode after immersion in a solution of 50 mM ethylenediaminetetraacetic acid solution in water at pH 10 for 3 h (--- black, the green star * indicates residual O$_2$) and after re-metallation with CoCl$_2$ and rinsing (— blue).

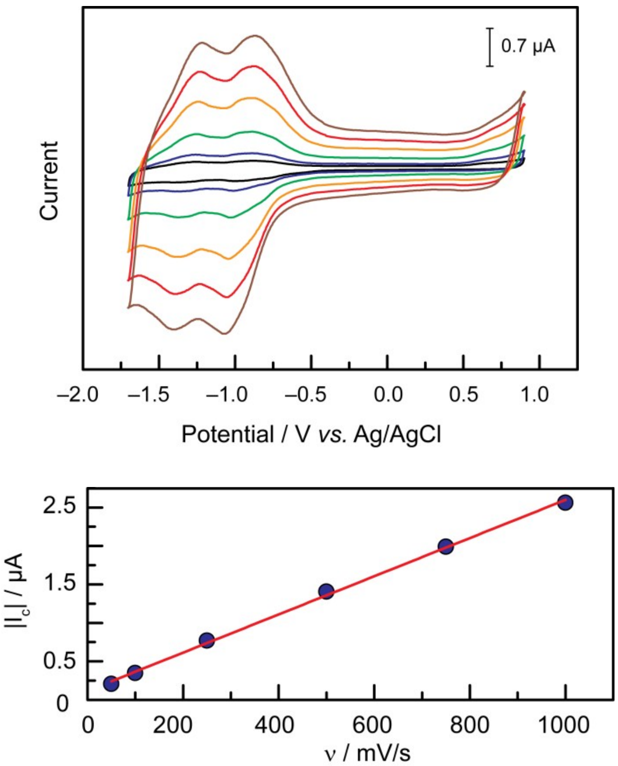


Figure S5. Top: Cyclic voltammograms under Ar in DMF, TBAPF$_6$ 0.1M, of a glassy carbon electrode modified with the tpy ligand and freshly metallated with NiCl$_2$ and rinsed at 50 (— black), 100 (— blue), 250 (— green), 500 (— orange), 750 (— red) and 1000 (— brown) mV/s. Bottom: Absolute value of the cathodic current observed on the peak at –1.07 V and its linear evolution with scan rate (correlation coefficient: 0.998).

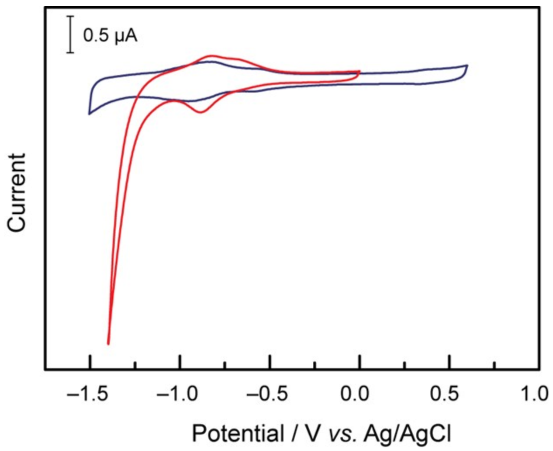


Figure S6. Cyclic voltammograms in DMF, $TBAPF_6$ 0.1M, of a glassy carbon electrode modified with the tpy ligand freshly metallated with $CoCl_2$ under Ar (— blue) and with added 4.3 mM acetic acid (— red), at 100 mV/s.

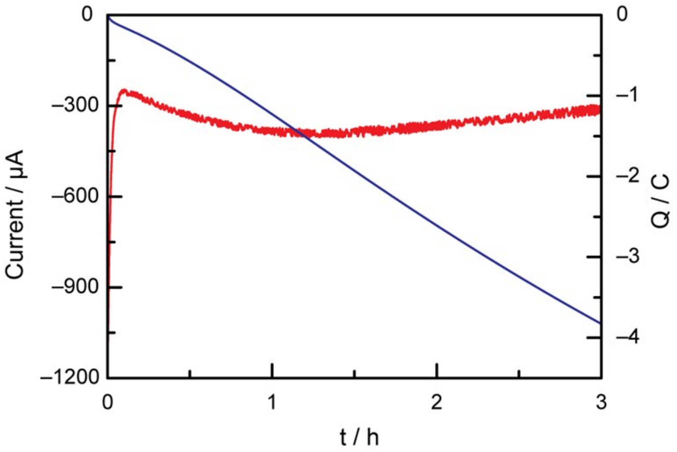


Figure S7. Current (red) and charge (blue) measured during a controlled-potential electrolysis of cobalt-metallated tpy-modified glassy carbon electrode in DMF at –1.50 V *vs.* Ag/AgCl, in the presence of 0.1M acetic acid and 0.1M $TBPF_6$ as supporting electrolyte. The solution was N_2-saturated prior to electrolysis, and the electrode and cell are described in the Experimental section. Data was recorded every 0.02 s and the current intensity data was smoothed using an adjacent-averaging method over 10 s.

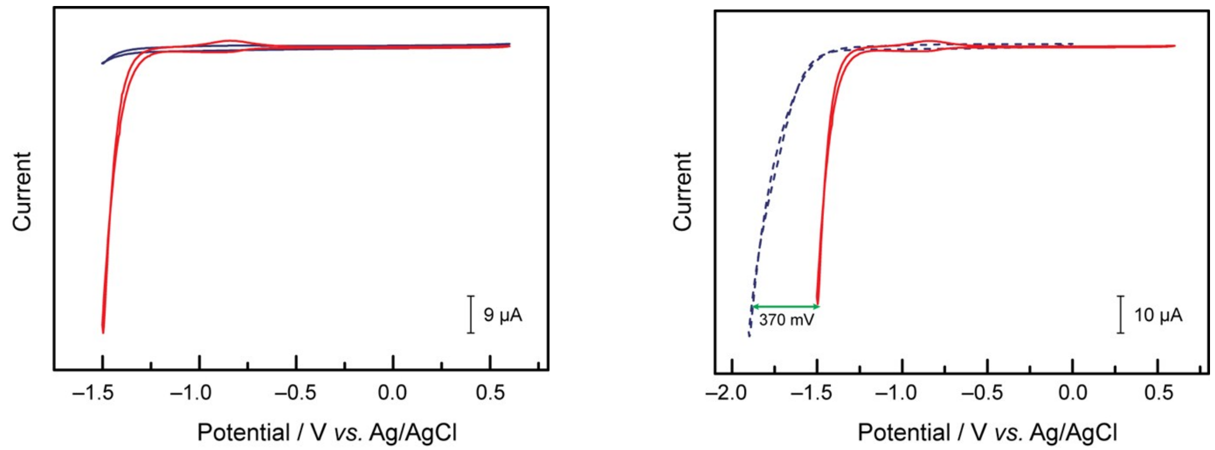


Figure S8. Comparison of the cyclic voltammograms under Ar in water in a phosphate buffer (pH = 7) of a glassy carbon electrode modified with the tpy ligand and metallated with $CoCl_2$ and rinsed (— red) and a polished bare glassy carbon electrode (— blue). The same bare electrode is scanned to more negative potentials (--- blue, right) to reach comparable current intensities to obtain a measure of the diminution of the overpotential due to the modification of the electrode (~ 370 mV).

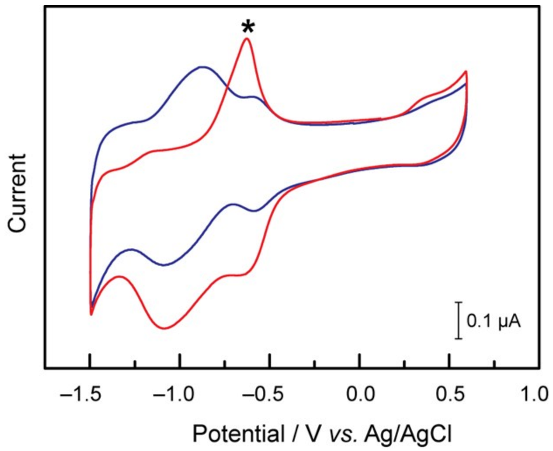


Figure S9. Cyclic voltammograms in DMF, $TBAPF_6$ 0.1M, of a glassy carbon electrode modified with the tpy ligand freshly metallated with $CoCl_2$ under Ar (— blue) and CO (— red) at 100 mV/s showing the new anodic peak at –0.63 V (* black star).

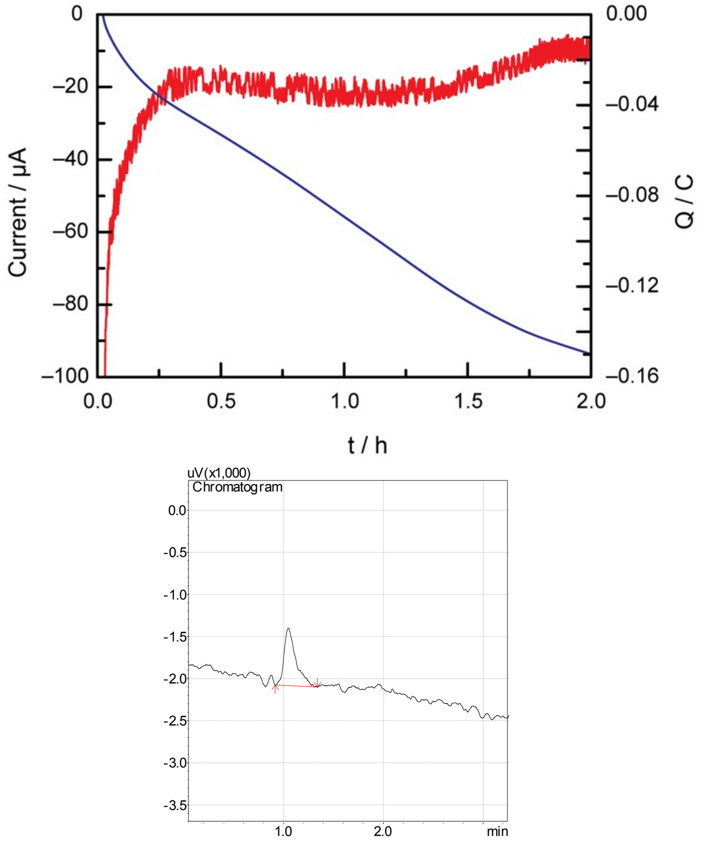


Figure S10. Top: Current (red) and charge (blue) measured during a controlled-potential electrolysis of cobalt-metallated tpy-modified glassy carbon electrode in DMF at −1.50 V *vs.* Ag/AgCl, in the presence of 0.1M $TBPF_6$ as supporting electrolyte. The solution was CO_2-saturated prior to electrolysis, and the electrode and cell are described in the Experimental section. Data was recorded every 0.02 s and the current intensity data was smoothed using an adjacent-averaging method over 10 s. Bottom: First 3 minutes of the chromatogram obtained after a GC injection of 100 μL of headspace after 2h of bulk-electrolysis showing the small CO response peak corresponding to 55 nmoles produced in the bulk electrolysis cell.