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Electrochemical CO₂ Reduction at Glassy Carbon Electrodes Functionalized by Mn(I) and Re(I) Organometallic Complexes

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Abstract

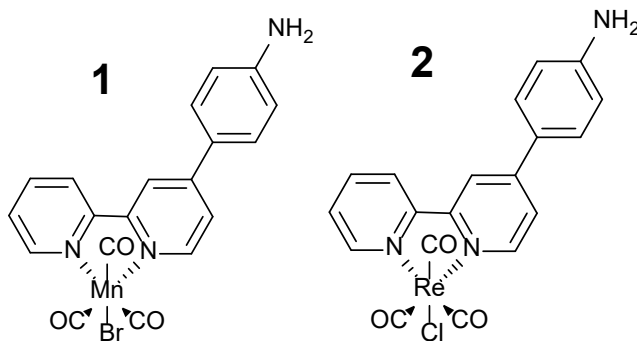
The catalytic activities towards electrochemical CO₂ reduction of two new rhenium and manganese complexes, namely *fac*-Mn(apbpy)(CO)₃Br (**1**) and *fac*-Re(apbpy)(CO)₃Cl (**2**) (apbpy = 4-(4-aminophenyl)-2,2'-bipyridine), in both homogeneous and heterogeneous phases are compared. Glassy Carbon Electrode (GCE) surface has been functionalized with complexes **1** and **2** by two approaches: a) direct electrochemical oxidation of the amino group with formation of C–N bonds, and b) electrochemical reduction of the corresponding diazonium salts with formation of C–C bonds. The chemically modified GCEs show efficient conversion of CO₂ into CO with turnover numbers (TONs) about 60 times higher than those of the corresponding catalysts in homogeneous solutions, and in a much shorter time.

Introduction

Catalytic reduction of CO₂ is a great challenge for clean energy and environment. The reduction of greenhouse gas (e.g. CO₂) emissions and the quest for new energy sources are currently among the world top research priorities.^[1] Therefore, CO₂ reduction by renewable energies (artificial photosynthesis) to useful chemicals and fuels such as CO, HCOOH, CH₃OH and CH₄ is a perfect combination that would give substantial contributions to both fields.

The selective conversion of CO₂ into CO catalyzed by Re(bpy)(CO)₃Cl takes place via photochemical activation followed by reductive quenching.^[2] Such a mechanism is very close to the electrochemical one,^[3] since in both cases the active catalyst is the 1e⁻ reduced species. The direct electrochemical reduction of CO₂ is an interesting, convenient and clean approach, because the role of the sacrificial reagent in the photocatalytic process is replaced by electrons. However, for kinetic reasons, the direct electrochemical reduction of CO₂ is a highly unfavorable process that requires a very negative reduction potential (-1.9 V vs. SHE in water^[1, 4]), thus the use of a suitable catalyst is mandatory.^[4]

In this context, organometallic Re^[2, 5] and Mn^[5b-d, 6] complexes carrying bipyridyl ligand have been employed as photo- and electro-active catalysts towards the reduction of CO₂ in homogeneous phase. A promising alternative is the hybrid homogeneous-heterogeneous approach,^[7] consisting in bonding an intact organometallic fragment (the catalysts) onto the electrode surface for electrocatalytic CO₂ reduction. Herein we extended this method employing organometallic Re and Mn complexes (see Scheme 1). While there are several procedures to obtain electrode functionalization,^[7a] two approaches^[7c] drawn our attention for functionalizing glassy carbon electrodes by intact organometallic fragments: the first consists in the oxidation of a terminal amino group, leading to the formation of a C-N bond, the second is based on the reduction of a diazonium salt that leads to the formation of a strong C-C bond.^[8] Herein we will compare and discuss the properties of these two kinds of functionalization.



Scheme 1. The synthesized complexes.

Experimental Section

Materials and Reagents. Reagents were purchased from Alfa Aesar and Aldrich and used without further purification. Acetonitrile was distilled over calcium hydride just before use. Materials for electrochemistry were prepared as described elsewhere.^[9] 4-(4-aminophenyl)-2,2'-bipyridine was synthesized according to published procedures.^[10] Re and Mn carbonyl complexes **1** and **2** were synthesized reacting 4-(4-aminophenyl)-2,2'-bipyridine with the corresponding precursor, Re(CO)₅Cl or the Mn(CO)₅Br, following a similar synthetic approach as previously reported.^[5e-i, 11]

Complex 1: ¹H NMR (200 MHz, acetone-*d*⁶): δ = 9.31 (d, 1H, J = 4.0 Hz), 9.11 (d, 1H, J = 6.0 Hz), 8.73~8.79 (m, 2H), 8.22 (t, 1H, J = 8.0 Hz), 7.91~7.70 (m, 4H), 6.85 (d, 2H, J = 10.0 Hz), 5.31 (s, 2H) ppm. ATR-IR (selected): 3408 m, 3321 m, 3203 w, 2016 s, 1914 s, 1895 s, 1593 m, 1479, 1441, 829, 188, 686, 632 cm⁻¹.

Complex **2**: ^1H NMR (400 MHz, $\text{dms}\text{-}d^6$): $\delta = 9.02\text{--}9.00$ (m, 2H), 8.84 (d, 1H, $J = 1.6$ Hz), 8.78 (d, 1H, $J = 6.2$ Hz), 8.34 (td, 1H, $J = 7.9$ Hz, $J = 1.4$ Hz), 7.91~7.86 (m, 3H), 7.75 (t, 1H, $J = 6.9$ Hz), 6.73 (d, 2H, $J = 8.6$ Hz), 5.93 (s, 2H). ATR-IR (selected): 3423 m, 3320 m, 3201 w, 2015 s, 1892 s, 1596 m, 1442, 1253, 1200, 828, 188, 482 cm^{-1} . The corresponding diazonium salt chlorides of **1** and **2** were synthesized by ordinary procedure. The appropriate complex is solubilized into a 37% HCl solution, cooled at -5 °C by salt ice bath, and an aqueous solution of NaNO_2 (1.01 molar ratio) is added over 40 min to the mixture, with a continuous vigorous stirring for further 5 h. The starting yellow color changes to brown and the resulting solid is washed twice with 37% HCl, then with ethanol and diethyl ether, and finally dried under vacuum.

Diazonium salt of complex **1** ATR-IR (selected): 3350 plateau, 2264 m, 2024 s, 1907 s, 1612 m, 1581 m, 1476, 1440, 1396, 826, 789, 680, 628 cm^{-1} .

Diazonium salt of complex **2** ATR-IR (selected): 3386 plateau, 2272 m, 2294 m, 2014 s, 188 3s, 1604, 1475, 1441, 191, 167 cm^{-1} .

Electrochemistry. Electrochemical experiments were carried out in freshly distilled acetonitrile 0.1 M TBAPF₆ solutions, in the usual conditions^[9] employing an Autolab PGSTAT302N electrochemical analyzer. Glassy Carbon Electrode (GCE) was used as working electrode, Ag wire as pseudo reference and Pt wire as counter electrode; all the potentials are reported against ferrocene/ferrocinium (Fc/Fc^+) redox couple.

General procedure for electrode functionalization. Two approaches have been adopted for electrode functionalization: the first is based on the oxidation of the amino moiety to get a C–N bond, the second consists in the reduction of the diazonium salt to get a C–C bond. Before every experiment, the working electrode was polished on alumina nano-powder suspended in deionised water, and rinsed with water and acetone. Background current was registered in a solution containing only the supporting electrolyte. The functionalization was accomplished by Cyclic Voltammetry (CV) in a 1 mM acetonitrile solution of the selected complex, using TBAPF₆ 0.1 M as supporting electrolyte. For amino-containing complexes (**1** and **2**) the switching potential was selected to be more positive than the oxidation peak of the amino group. On the contrary, functionalizations leading to the formation of C–C bonds on the electrode surface were obtained by selecting a switching potential more negative than the reduction of the corresponding diazonium salts. The formation of C–N bond via oxidative pathway was obtained from solutions containing collidine (2,4,6-trimethylpyridine), which helps the functionalization by favouring the radical cation deprotonation, as previously described.^[7c, 12] After each functionalization cycle the electrode was rinsed with solvent and sonicated for 2 min in distilled acetonitrile, to remove physisorbed molecules. The presence of the covalently bound complexes was evaluated electrochemically in a solution containing the supporting electrolyte only, which generated reversible redox signals characteristic of the chemically bonded species. Electrodes area were assessed by chronoamperometric measurements of a ferrocene solution at a known concentration, in a similar way as previously described.^[7c]

Results and Discussion

Figure 1 shows the CVs of complexes **1** and **2** in acetonitrile solution under Ar. The electrochemical behavior of **1** and **2** is similar to that of analogue derivatives extensively investigated.^[6b, 10a, 13] Details are listed and compared in Table 1.

Table 1. Half wave and peak potentials for **1** and **2** and for similar complexes (in V vs. Fc/Fc⁺).

Complex	E _{1/2} (0/1 ⁻)	E _p (1 ⁻ /2 ⁻)	E _p (1 ⁻ /0)	E _p (0/1 ⁺)	Ref
1	-1.52 ^a	-1.76	-1.42	-0.61	This work
2	-1.70	-2.12	-1.57	-0.49	This work
Mn(bpy)(CO) ₃ Br	-1.64 ^a	-1.88 ^a	-1.47	-0.59	[5b]
Mn(dmbpy)(CO) ₃ Br	-1.72 ^a	-1.97	-1.56	-0.63	[5b]
Mn(bpy- ^t Bu)(CO) ₃ Br	-1.77 ^a	-1.95	-0.68		[6b]
Re(bpy)(CO) ₃ Cl	-1.72	-2.11			[14]
Re(dmbpy)(CO) ₃ Cl	-1.81	-2.15			[14a]
Re(bpy- ^t Bu)(CO) ₃ Cl	-1.83	-2.21			[14a]

^a E_p for irreversible processes. ^b two electron reduction.

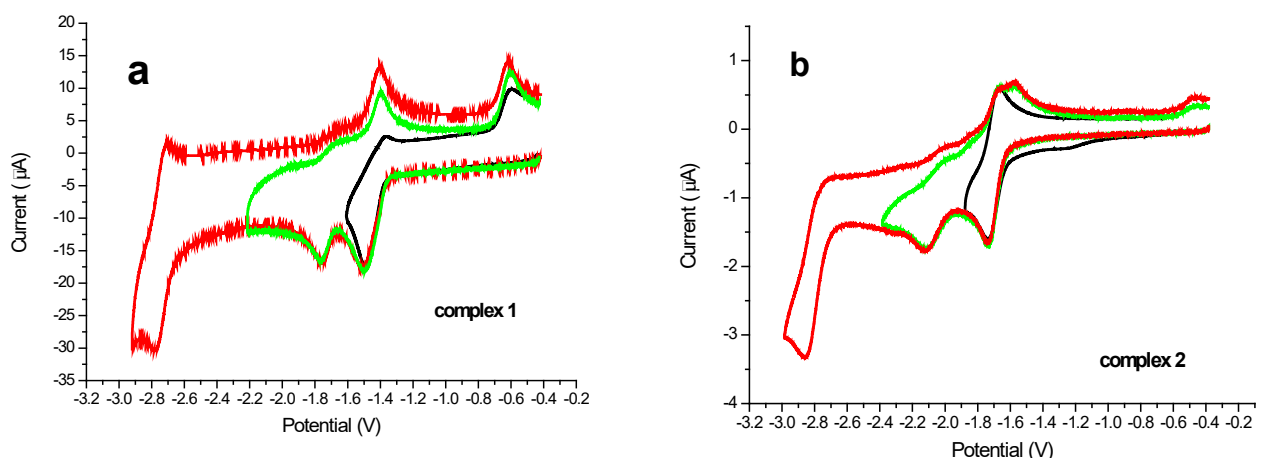


Fig. 1. a) CVs of a 1 mM solution of **1** in acetonitrile (GCE \varnothing 3 mm), and b) CVs of a 1 mM solution of **2** in acetonitrile (GCE \varnothing 1 mm) at scan rate of 0.2 V/s.

The electrochemical behavior of complex **1** is similar to that of the parent compound Mn(bpy)(CO)₃Br.^[5b] After the first irreversible reduction (E_p = -1.52 V) the Br⁻ is quickly released. The remaining fragment dimerizes, forming the neutral Mn dimer that is reduced at -1.76 V vs. Fc/Fc⁺. The reoxidation of the radical anion and the dimer can be observed at -1.42 V and -0.61 V, respectively.

The CV of complex **2** shows the classical first reversible or quasi-reversible reduction (E_{1/2} = -1.70 V vs. Fc/Fc⁺) and a second irreversible reduction at more negative potential (E_p = -2.12 V vs. Fc/Fc⁺) followed by the release of Cl⁻.^[15] Although the radical anions of bipyridyl Re analogues are generally stable at low temperatures, they could still lose Cl⁻ at r.t.,^[13b] whereas in the absence of a coordinating solvent they can dimerize.^[14b] The peaks at -1.57 and -0.49 V are due to the reoxidation of **2** (where Cl⁻ is replaced by the solvent) and of the dimer, respectively.^[16] Complexes **1** and **2** show a further reduction process at more negative potential that will not be discussed here. The Randles-Sevcik analysis (plot of peak currents vs. square root of the scan rate) is linear, indicating that the electrochemical behavior of these complexes is diffusion-controlled (Figure S1).

Since the Mn complex **1** does not have local proton sources, under CO₂-saturated solution (~0.28 M^[6b, 17]) it does not show any catalytic activity (Figure 2a).^[5b, 5c] The progressive addition of a Brønsted acid (water or methanol) results in a dramatic increase of current after the second reduction. The maximum peak current was obtained with the addition of 8% (v/v) water or 4% (v/v) methanol (Figure 2 and Table 2). Higher quantities had limited effects on the observed catalytic current peak.

Complex **2** shows an evident catalytic reduction of CO₂ already after the second reduction process (with E_p = -2.15 V, see Figure 3), even in the absence of Brønsted acids.

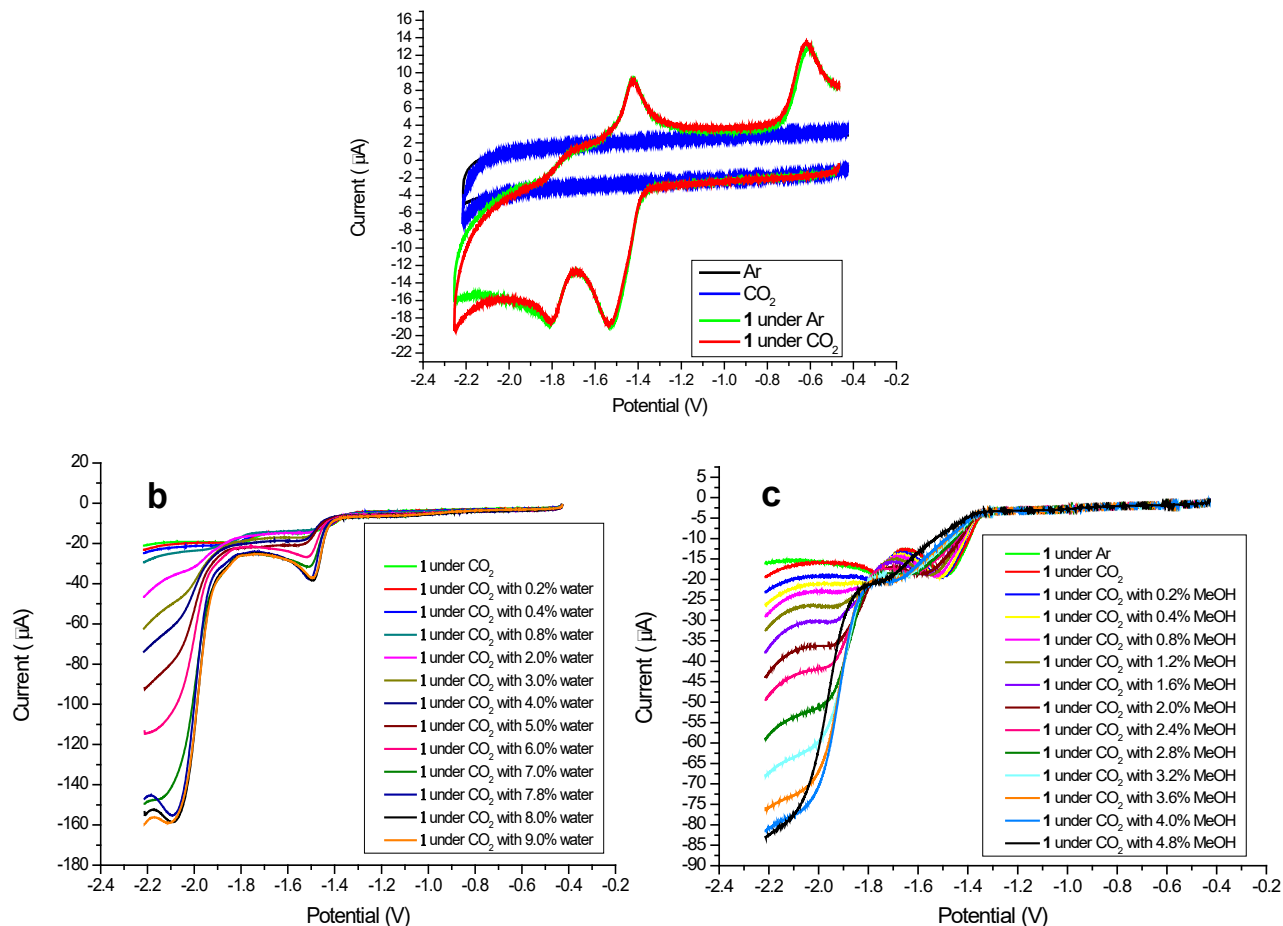


Fig. 2. CVs of **1** in acetonitrile solutions (a), with added water (b), and with added methanol (c) at scan rate of 0.2 V/s.

Usually, the addition of Brønsted acids increases the catalytic current observed employing rhenium bipyridyl derivatives.^[6b, 18] However, in the case of **2**, a small addition of methanol (0.5% v/v) did not alter significantly the catalytic current (Figure 3b), while higher quantities (up to 12.5% v/v) had the effect of increasing the catalytic current in CV, and eventually exceeds the value in the absence of acid.

Normally, turnover frequency (TOF), turnover numbers (TONs), faradic efficiency (FE), selectivity and lifetime parameters are used to evaluate the catalytic activity.^[1, 19]

TOF can be roughly estimated by equation (1)^[6b, 20] at catalyst peak potential from a single CV, as proposed by Savéant and co-workers.^[21]

$$\frac{i_c}{i_p} = \frac{1}{0.4463} \frac{n_c}{n_p^3} \sqrt{\frac{RT}{F}} \sqrt{\frac{(TOF)}{v}} \quad (1)$$

Where i_c and i_p are the catalytic and peak current in the presence and absence of catalysis, respectively; n_c (= 2) and n_p (= 1) are the number of electrons involved in the catalytic and catalyst reduction, respectively, F is the Faraday constant and v is the applied scan rate.

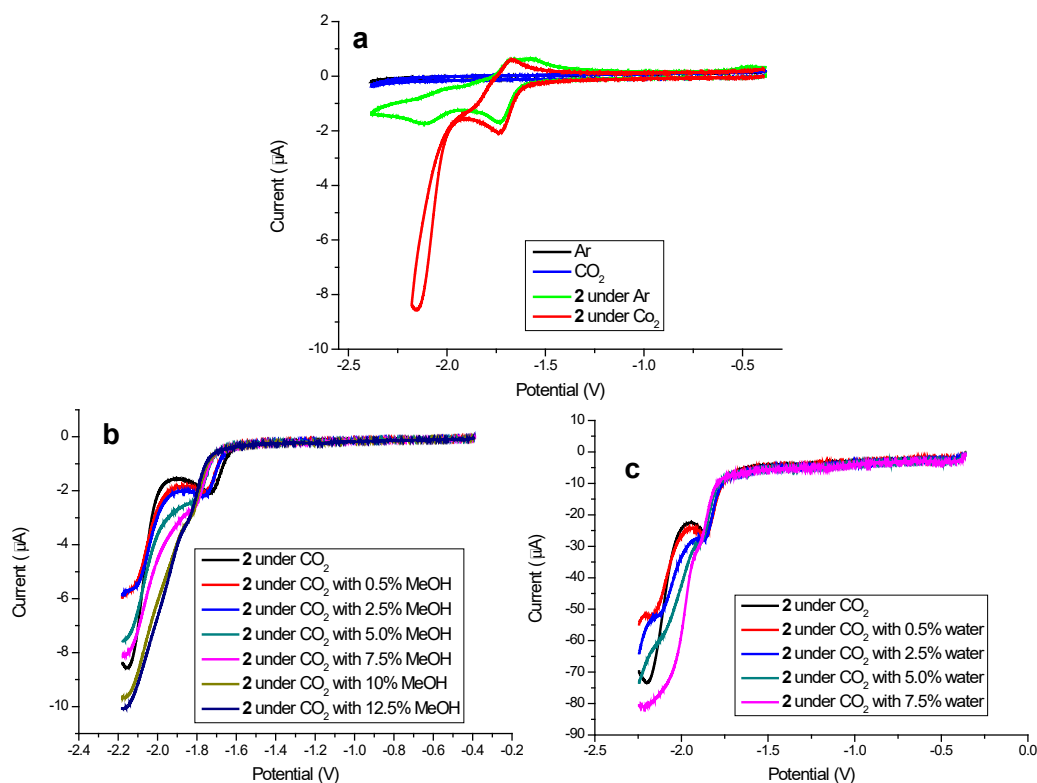


Fig. 3. CVs of **2** in acetonitrile solutions (a), with added methanol (b) and with added water (c) at scan rate of 0.2 V/s.

Table 2 reports the ratio between the catalytic current (i_c) and the current peak (i_p) under Ar with 8% (v/v) water or 4% (v/v) MeOH for **1** and **2** together with analogue compounds. Both complexes **1** and **2** show high TOF at less negative potentials than analogue complexes. For instance, **1** displays TOF comparable with $\text{Mn}(\text{bpy-}^t\text{Bu})(\text{CO})_3\text{Br}$, but at about 200 mV less negative potentials. The effect could be assigned to the electronic properties of the aminophenyl moiety.^[14a] While the CV is suitable for getting a rough estimation of the catalytic process at the very beginning of the cycle, a better overall picture can be guessed from the longer time control potential electrolysis (CPE) experiments (Table 3 and Figures S2 and S3 in SI). From CPE experiment, complex **1** shows much better selectivity with MeOH than water (Figure S2), and it is more stable under lower potential. Complex **2** exhibits ~3 fold TONs of $\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$ in dry MeCN (Table 3 and Figure S3).

Table 2 The catalysis properties.

Complexes	i_c/i_p^a		TOF ^b /s ⁻¹			E_p/V	ref	
	CH ₃ CN	H ₂ O (concentration)	MeOH (concentration)	MeCN	H ₂ O			MeOH
1	1.0	16 (8%)	6 (4%)	0	99	14	-1.76	This work
2	9.7	11.8(8%)	8.3 (4%)	36	54	27	-2.12	This work
$\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}$	3.4	---	---	2.2	---	---	-2.11	[14a]
$\text{Re}(\text{bpy-}^t\text{Bu})(\text{CO})_3\text{Cl}$	18.4	---	---	65	---	---	-2.21	[14a]
$[\text{Re}(\text{bpy-}^t\text{Bu})(\text{CO})_3(\text{MeCN})](\text{OTf})$	3.3	9.0 (10 M)	42 (9.9 M)	2.1	16	340	-2.21	[6b]
$\text{Mn}(\text{bpy})(\text{CO})_3\text{Br}$	1.0	1.6 (2.77 M)	---	0	0.5	---	-1.88	[5b, 22]
$\text{Mn}(\text{bpy-}^t\text{Bu})(\text{CO})_3\text{Br}$	1.0	25 (3.1 M)	26 (5.8 M)	0	120	130	-1.95	[6b]

Whether the CV or the CPE is considered, the catalysis occurs in the reaction layer, involving only the catalyst present near the electrode surface, i.e. a limited quantity if compared with the catalyst present in the bulk of the solution.^[21a] Moreover, electrolysis in homogeneous solution not always gives straightforward real activity and lifetime of a new catalyst, since it can be renewed or consumed by diffusion from the bulk of the solution.^[21] Herein we suggest that one or few molecular layers of catalyst deposited on the electrode surface would offer a faster and reliable way to establish the catalyst properties, overcoming the disadvantages of an homogeneous system. Furthermore, after molecular immobilization, the steric hindrance may only permit the two-electron reduction pathway^[14b, 15, 23] instead of the one-electron reduction pathway^[24].

Oxidative functionalization to form C–N bonds. The first approach adopted to functionalize glassy carbon electrodes consists in the oxidation of a terminal amino group, leading to the formation of a C–N bond in the presence of collidine. Figure 4 shows the oxidation process carried out at a scan rate of 0.2 V/s.

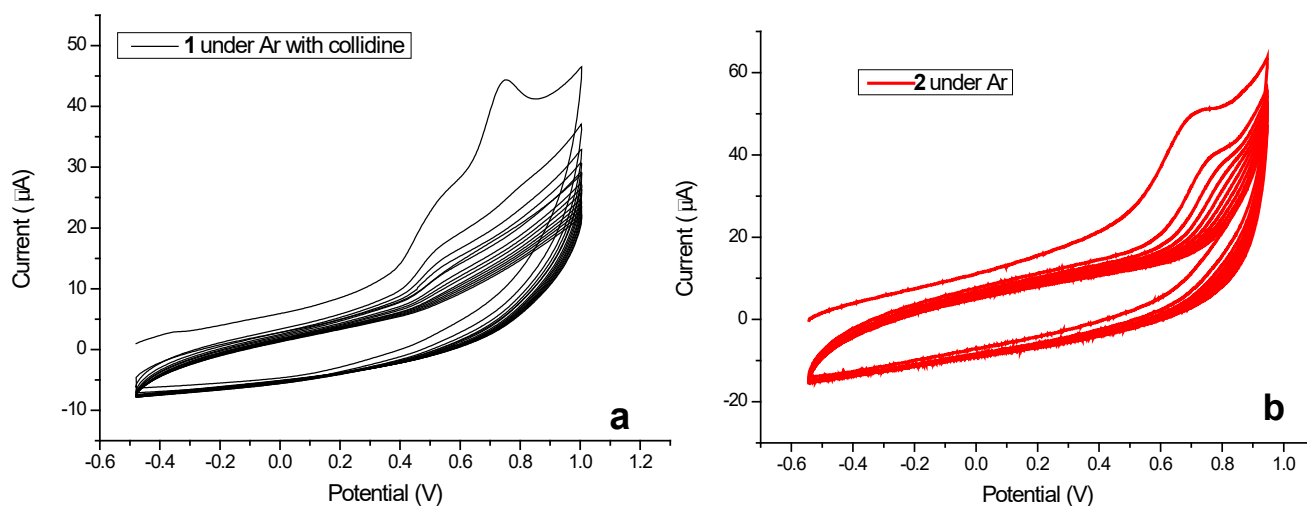


Fig. 4. Oxidation CVs at 0.2 V/s for electrode modification with **1** (a) and **2** (b) in the presence of collidine.

Both **1** and **2** behave similarly, displaying an oxidation peak around 0.72 V in the first cycle, due to the oxidation of amino moiety to form the C–N bond.^[7c] After several CV cycles, the current degrades to the background, indicating that the surface has been completely covered with the complexes. The stability of the modified electrodes has been evaluated performing a series of CVs in fresh electrolyte solutions.

The resulting electrode functionalized with **1** proved to be quite instable (Figure 5a). In the first CV cycle, the first peak corresponds to the reduction of **1** followed by the release of the bromide anion. The side and second peaks are assigned to the formation of the dimer and its reduction, respectively. Unexpectedly, the surface quickly decomposes after the reduction and completely loses its functionalization after 4 cycles.

Conversely, complex **2** provided a stable functionalized electrode (Figure 5 b), retaining its properties for 24 h in acetonitrile or for one week when exposed to air.

The surface coverage (Γ) has been assessed by means of the formula:

$$\Gamma = \frac{Q}{FA} \quad (2)^{[7c, 25]}$$

where Q is the charge oxidizing (or reducing) the organometallic complex on the electrode surface evaluated by integration of the background-corrected CVs, F is the Faraday constant and A is the area of the electrode.

In the case of oxidative functionalization with **2**, a value of $\Gamma = 4.3 \times 10^{-10} \text{ mol} \cdot \text{cm}^{-2}$ has been estimated. Meanwhile, the plot of the peak current versus scan rate reveals a linear dependence (Figure 6), indicating that the redox process is no longer diffusion controlled, and the electrochemical behavior is that of an adsorbed species on the electrode surface. Following the same methodology previously discussed,^[7b] the electrode surface coverage can be estimated

from the peak currents using either the equations for reversible or irreversible process. From the slope of the linear regression of i_p vs. v , Γ can be estimated to be $2.3 \times 10^{-10} \text{ mol} \cdot \text{cm}^{-2}$ and $3.4 \times 10^{-10} \text{ mol} \cdot \text{cm}^{-2}$, for the reversible or irreversible cases, respectively. These values are of the same order of magnitude observed for a monolayer of organometallic derivatives of similar dimensions.^[7c]

Table 3. Comparison of the CPE.

Complex	Acid in MeCN	Potential (V)	Time (min)	TON _{CO}	FE _{CO} (%)	Ref
1	No Acid	-1.85	---	---	---	This work
	4% H ₂ O	-1.73	90	12	93	This work
	8% MeOH	-1.85	120	10.9	56.5	This work
2	No Acid	-2.03	120	7.4	100	This work
	8% MeOH	-2.0	120	12	96.4	This work
Mn(CN)(bpy)(CO) ₃	0.5M Phenol	-2.20	---	4	98	[26]
Mn(bpy)(CO) ₃	5% water	-1.78	240	13	100	[5b]
		-1.88	240	13	90	[22]
MnBr(HOPh-bpy)(CO) ₃	5% water	-1.88	240	2.7	76	[22]
Re(bpy)(CO) ₃ Cl	10% water in DMF	-1.88	180	5.1	98	[13a]
	No acid	-2.02	117	2.8	96	This work
FC of 1 diazonium salt	4% H ₂ O	1.75	71	359.6	75	This work
	8% MeOH	1.95	24	145.2	66.1	This work
FC of 2 diazonium salt	No Acid	-2.10	29	402.4	100	This work
FC of 2 oxidation	No Acid	-2.00	20	321.1	100	This work
Re(bpy)(CO) ₃ Br ^a	phosphate buffer (pH ~ 7)	-1.98	143	155	15.4 ^c	[27]
				134 ^b		
Mn(bpy)(CO) ₃ Br ^a	phosphate buffer (pH ~ 7)	-1.92	240	471	51	[28]

^aCoated with Nafion membrane

^bFE_{HCOOH}

^cSelectivity for CO₂/H⁺

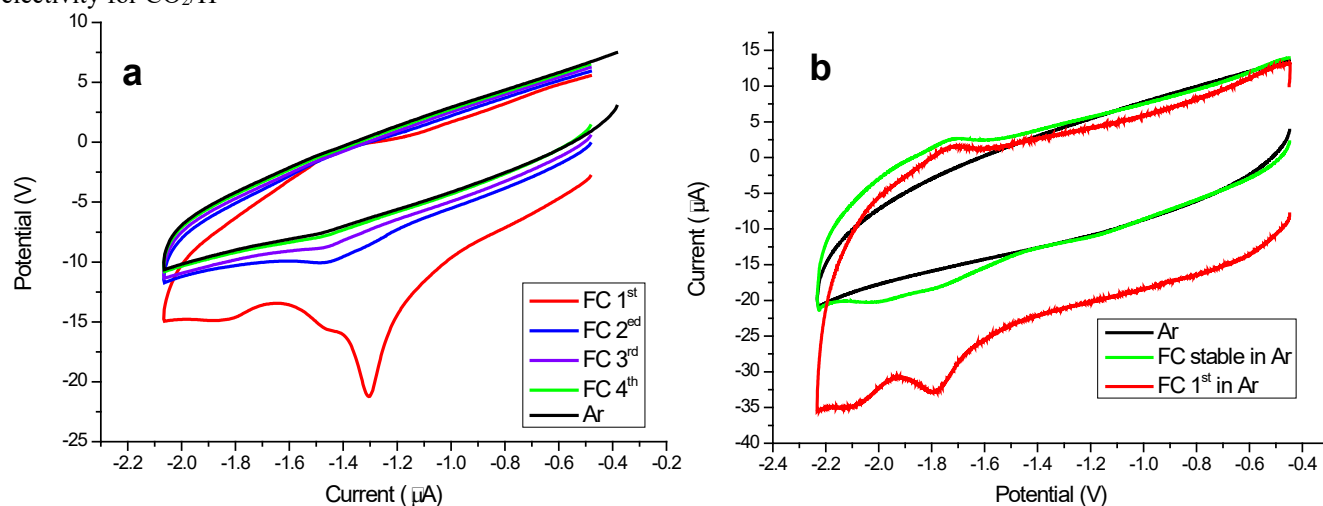


Fig. 5. First and steady state CVs of the electrode modified with complex **1** (a) and **2** (b) at scan rate 0.2 V/s.

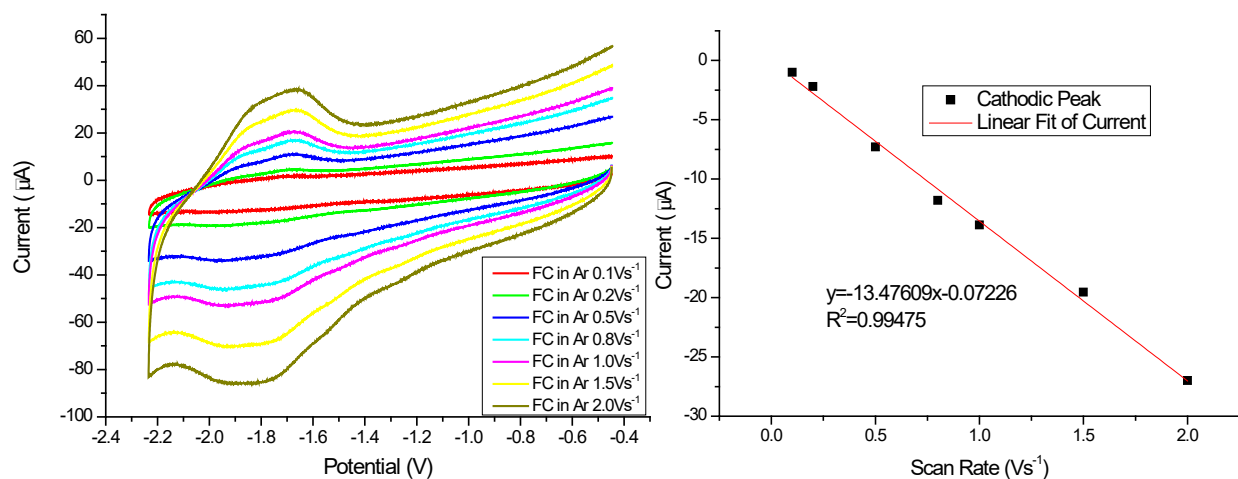


Fig. 6. Plot of the current peak vs. scan rate for electrode surface modified after the oxidation of **2**.

The electrode functionalized with **2** has been tested in the presence of CO₂ (saturated solutions). The functionalization has a dramatic effect, increasing the current by 86-fold in the first cycle, if compared to the argon saturated solution, indicating a strong catalytic activity for **2** anchored on the electrode surface. However, after only 10 CV cycles the functionalized electrode surface loses completely its catalytic activity towards CO₂ reduction (Figure 7).

In homogeneous solutions the catalyst and substrate are mixed thoroughly, so that a 3-D reactivity take place. On the contrary, in heterogeneous condition the catalysis occurs only in 2-D and equation (1) is no longer applicable, even though the ratio of the peak currents is still related to the catalyst activity, and proportional to the TOF.^[22]

The catalytic activity per molecule can be roughly estimated from the CVs via **TON'**, defined as:

$$\mathbf{TON}' = \frac{1}{n_s} \frac{\text{moles of catalytic reduction charges}}{\text{moles of catalysts}} \quad (3)$$

where n_s is the number of electrons needed to reduce one molecule of substrate ($n_s = 2$ for producing H₂, CO or HCOOH). The reduction charges under CO₂ were calculated by charge integration of the CV, adopting the CV background as baseline. By this method a **TON'** of 364 can be estimated.

To identify the products, **CPE** was carried out at -2.03 V under CO₂ with the modified electrode; the amount of catalyst on the surface was calculated by charges integration. Evolution of CO and negligible amounts of H₂ were detected by gas chromatography (GC) within 30 min, when the catalytic current decreased to 10% of the initial value reaching the **GC** detection limit. By this method a **TON** value of 321 was obtained (Figure S2 and Table 3).

TON' (obtained by CV) and **TON** (obtained by CPE) values are in good agreement. Thus we propose to evaluate the catalyst activity simply from the CVs of the surface-modified electrodes, resulting in less complicated, smaller amount and much shorter time experiments.

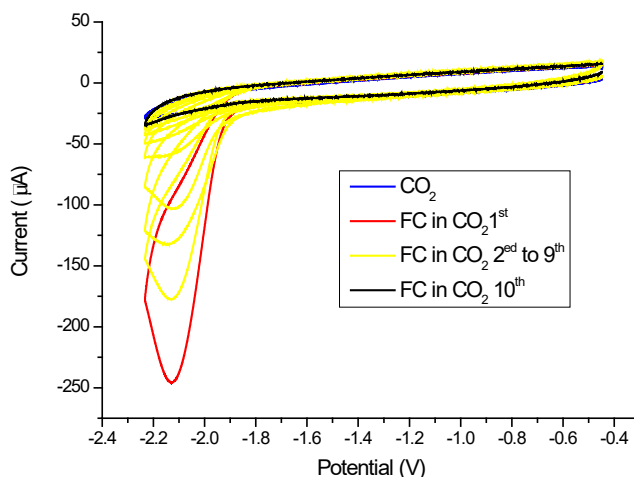


Fig. 7. CVs under CO₂ of the electrode modified by complex **2** at scan rate 0.2 V/s.

Reductive functionalization to form C–C bonds. To increase the stability of the functionalized electrodes, a second approach based on the reduction of diazonium salt has been adopted. This method, which employs the diazonium chlorides of complexes **1** and **2**, leads to the formation of strong C–C bonds between the surface and the catalysts. Figure 8 displays the electrode functionalization by CV scans at reduction potentials. During the first cycle there is no evident current peak, but instead a broad plateau. In the following cycles, a more marked peak appears; the shift of peak position indicates multi-layer formation.

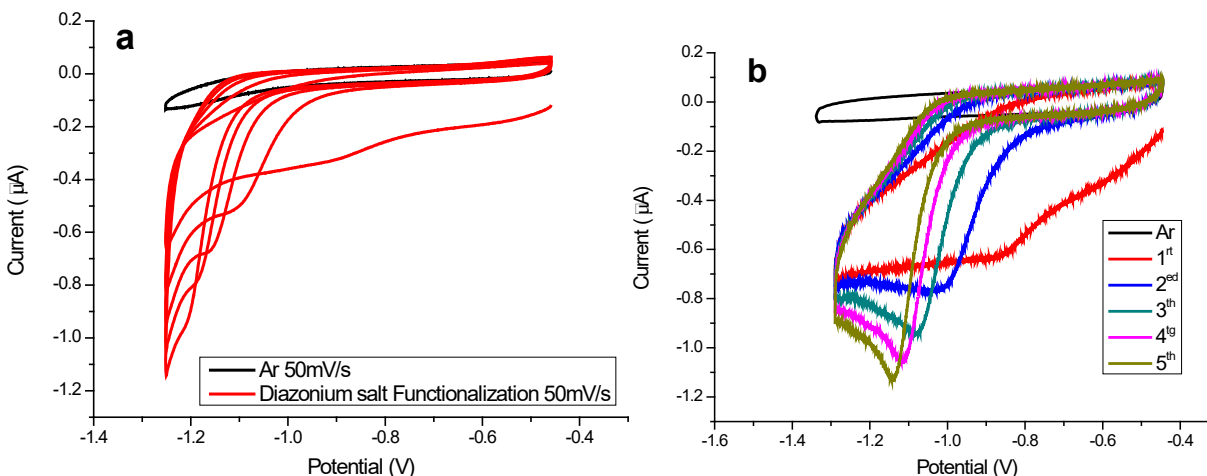


Fig. 8. Electrode functionalization with diazonium salt: a) **1**, b) **2**. Scan rate 50 mV/s.

Both the resulting functionalized electrodes exhibit an evident and sharp reduction peak in the first CV, which vanish in the following cycles (Figure 9). From the analysis and comparison of CVs in homogeneous solutions of **1** and **2**, the peaks around -1.36 V and -1.90 V can be directly assigned to the release of Br⁻ and Cl⁻, respectively. Both surfaces show a non-diffusion controlled electrochemical behavior (Figure 11 for **1** and Figure S5 for **2**) and are stable, displaying limited changes after exposure to the air for one week.

If only one or two CV cycles are applied, a very thin and stable film of complex **1** can be obtained after the release of bromine (Figure 10). CV shows three cathodic (at -1.78 , -1.45 , -1.35 V) and three anodic (at -1.66 , -1.44 , -0.58 V) peaks in a single CV. The peak at -1.35 V can be assigned to the reduction of **1** in which Br⁻ has been substituted by a single acetonitrile molecule. The peak at -1.45 V is assigned to the one electron reduction of the dimer, which is formed by adjacent monomers. The peak at -1.78 V is the reduction of the dimer to get one electron charged

monomer, in a similar fashion as reported in homogeneous solutions.^[6d] Continuous CVs scan from -0.75 to -2.25 V, avoiding the oxidation of the dimer at -0.58 V, show that the peak at -1.35 V vanishes (Figure 10a). When the CV scan is performed starting again from -0.4 V (i.e. the dimer is oxidized), the peak at -1.35 V reappears, restoring the original stable CV. All these data suggests that this peak is associated to the reduction of the solvated complex.

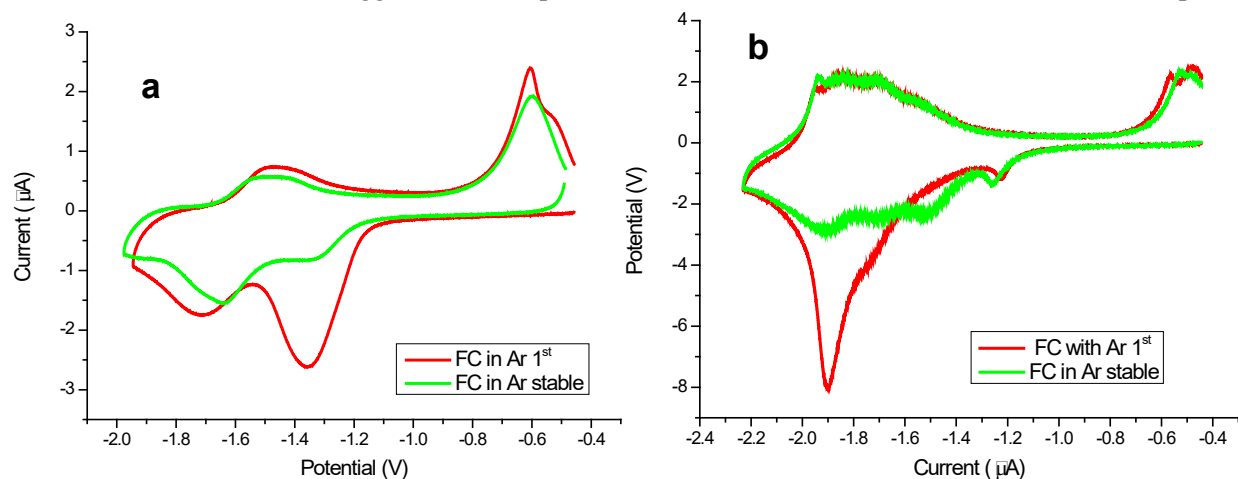


Fig. 9. First and steady state CVs of the electrode modified with diazonium salt of complex **1** (a) and **2** (b).

According to the stable CVs, the coverage calculated by the charge method (eq. 2) is $5.7 \times 10^{-10} \text{ mol cm}^{-2}$. Plotting the peak current versus scan rate, the surface coverage is calculated to be $4.1 \times 10^{-10} \text{ mol cm}^{-2}$ (Figure 11).

Unlike the oxidative functionalization, the reductive approach with diazonium salt provides multilayers by increasing the number of functionalization cycles. For complex **2**, the coverage reached as a function of the number of cycles is listed in Table 4. Thereafter the coverages are evaluated using the charge method (eq. 2).

In the case of the electrode functionalized with complex **2**, the stable surface shows three evident reduction peaks (Figure 10b). The small reduction around -1.2 V is attributed to the opposite charges on the layers,^[29] and the following reductions at -1.5 V, -1.7 V, -1.9 V and the corresponding counter peaks are due to the same process observed in the homogeneous solutions (the reversible redox process at $E_{1/2} = 0$ V is due to the ferrocene, added as internal standard). At -0.5 V, the oxidation peak is due to the overlapped oxidations of the dimer and of the derivative coordinating a solvent molecule (Figure 12), similarly to the case of complex **1**.

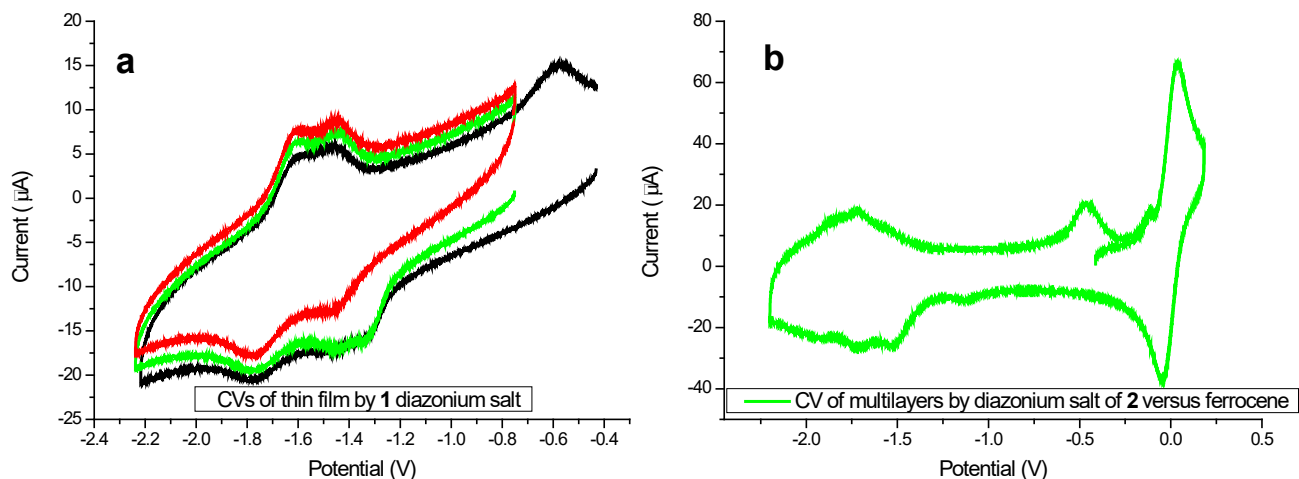


Fig. 10. a) CVs of the electrode functionalized by diazonium salt of **1** (black: origin stable CV by full scan; green: first CV by scan start from -0.75 V; red: stable CV by scan start from -0.75 V continuously). b) CV of the functional electrode by diazonium salt of **2** versus ferrocene.

Employing the electrode functionalized with multilayers of **1** (1 mm diameter GCE, 0.72 mm²) with a coverage of 13.5×10^{-10} mol cm⁻² in a solution saturated with CO₂, no significant difference is observed in the first two reduction peaks, while the addition of methanol induces a dramatic change at the second reduction peak. When the volume of methanol reaches 20%, the current reaches the maximum value (Figure 13). However, it should be recalled that in the presence of multilayers the current ratio $i_p/i_c = 8.5$ underestimate the real activity of the catalysts on the surface.

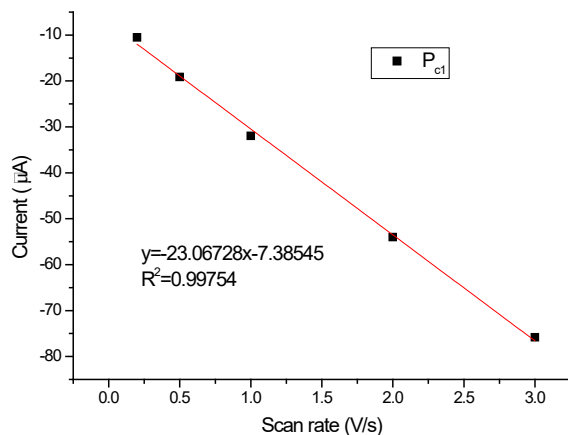


Fig. 11. Plot of the current peak of the first reduction vs. scan rate for functional surface by diazonium salt of **1**.

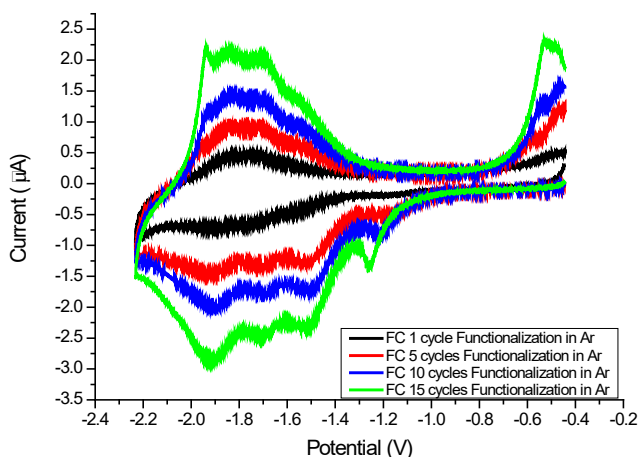


Fig. 12. The CVs of the functional electrode by different cycles (black to green are 1, 5, 10, 15) with diazonium salt of **2**.

Table 4. Functionalized electrode properties of complex **2** (currents in µA).

Cycles	1	5	10	15
Coverage / 10^{-10} mol·cm ⁻²	3.9	17.5	26.5	45.4
i_{CO_2}	30.15	54.66	60.60	84.40
i_{Ar}	0.318	0.87	1.26	2.05
i_{CO_2}/i_{Ar}	97.9	63.1	48.4	41.2

Employing the 6.24 mm² electrode with a coverage of 14.3×10^{-10} mol cm⁻² or of 6.4×10^{-10} mol cm⁻² in a CO₂ saturated solution with 20% methanol, the current ratio is $i_p/i_c = 8.3$ and 24.4, respectively. After addition of the acid, the surface degrades within successive cycles. For the coverage 14.3×10^{-10} mol cm⁻², there is no evidence of residue activity after 60 cycles, when the applied voltage is -2.15 V (Figure 14).

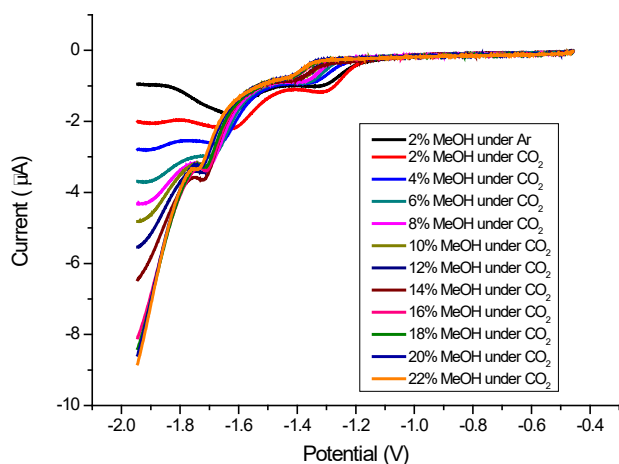


Fig. 13. CO₂ reduction CVs of functional electrode by diazonium salt of complexes **1** with methanol at scan rate 0.2 V/s .

Applying a voltage of -1.9 V with a coverage of 6.4×10^{-10} mol cm⁻², the activity is retained for 100 cycles. To roughly estimate the catalytic activity, TON' were calculated (Figure 14) for three different electrode to be 209, 218 and 201 for coverages of 14.3×10^{-10} , 10.1×10^{-10} , and 6.4×10^{-10} mol cm⁻² and applied potentials of -2.15 , -2.00 and -1.90 V, respectively. These data suggest that there is no effect of the potential applied in the adopted range, and a mean TON' of 209 can be assumed for **1** with methanol.

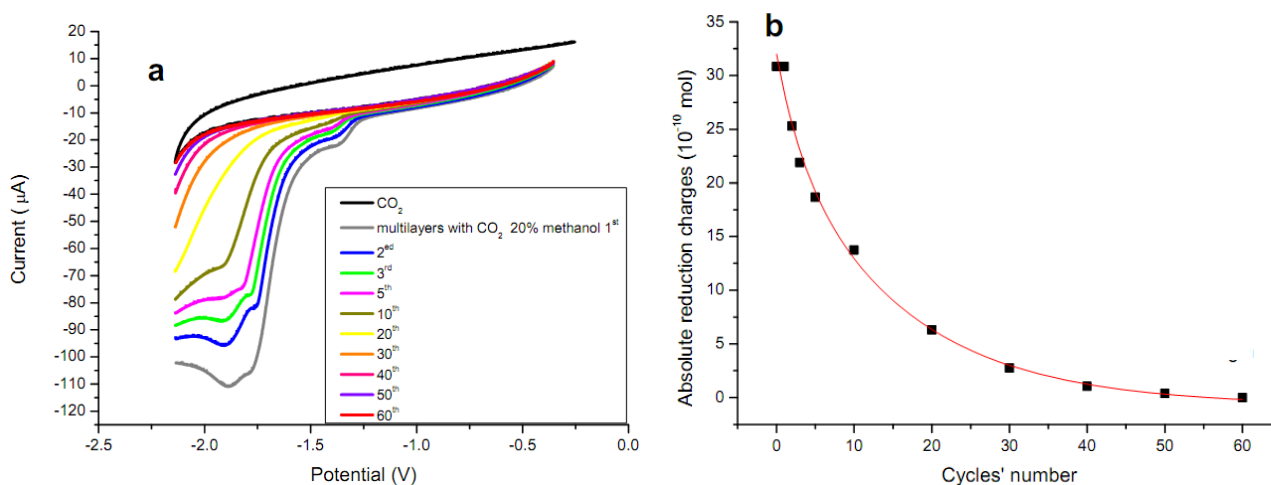


Fig. 14. Properties of electrode decorated by diazonium salt **1** with 20% methanol (a: the decrease of CO₂ reduction; b: the fit plot of the decrease of CO₂ reduction and integrate).

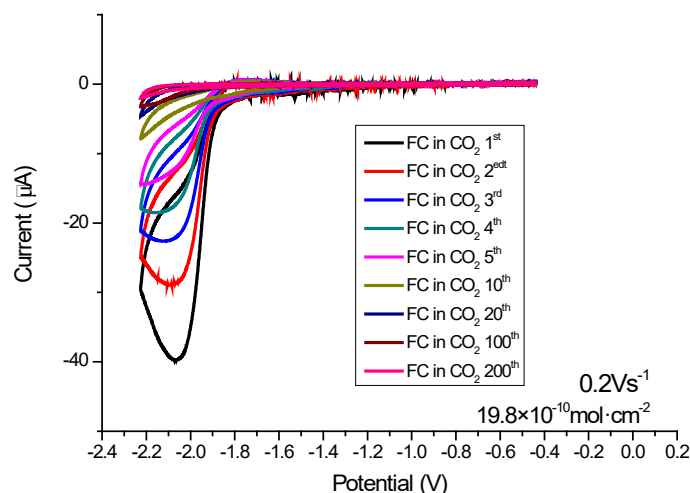


Fig. 15. The CO₂ reduction CVs of electrode decorated by diazonium salt of **2**.

Similarly, to evaluate the properties of complex **2**, CVs of the electrode functionalized with **2** (coverage 19.8×10^{-10} mol·cm⁻² calculated by eq. 2) were recorded under CO₂ atmosphere. The catalytic current decreased progressively cycle after cycle (Figure 15), however the electrode maintained a quite long lifetime if compared with the corresponding electrode modified by oxidative functionalization. The activity lasted for more than 200 cycles when applying a potential of -2.2 V, with a **TON'** value of 377. **TON'** of 387 and 384 were obtained for electrodes with Γ equal to 13.2×10^{-10} and 16.7×10^{-10} mol·cm⁻², respectively, at -2.0 V and at a scan rate of 0.1 V/s.

To check the **TONs**, **CPE** was carried out and the catalytic products were identified by GC (Table 3 and Figure S6–S8). All **TON** and **TON'** values are in very good agreement. This once more confirms that **TON'** is a reliable index to estimate the catalytic activity.

Conclusions

Two new rhenium and manganese complexes, containing a substituted bipyridine ligand bearing an amino group, have been synthesized and their catalytic activities tested towards electrochemical CO₂ reduction.

The behavior of complexes *fac*-Mn(apbpy)(CO)₃Br (**1**) and *fac*-Re(apbpy)(CO)₃Cl (**2**) (apbpy = 4-(4-aminophenyl)-2,2'-bipyridine) has been investigated in both homogeneous and heterogeneous phases.

Two different electrode modification methods have been employed for the functionalization. The complexes with amino terminal group were successfully grafted onto the electrode surface according to an electrochemical oxidation reaction forming C–N bonds. The reduction of the corresponding diazonium salt derivatives provided a grafting based on C–C bonds.

Both complexes exhibit high catalytic activity, reducing CO₂ to CO. The heterogeneous surfaces modified by the catalyst are much more efficient than the corresponding homogeneous solutions. The functionalized electrodes obtained by reducing the diazonium salts display better durability than the ones obtained by oxidizing the amino moiety, this is particularly evident in the case of **1**.

Complex **1**, likewise other typical Mn/Re bipyridyl complexes, accelerates the CO₂ reduction after addition of Brønsted acids. Conversely, complex **2** reveals a hindrance to the catalytic activity for small additions of Brønsted acids, and then increases together with the amount of Brønsted acid.

The functionalization of electrode surface with catalysts by covalent bond could gain most of the advantages of this non-conventional condition. This type of hybrid homogeneous-heterogeneous approach has the advantage of increased performance of the catalysts in terms of **TON**, durability and by far smaller amounts.

Complex **1** is two times more active in water than in methanol, either in homogeneous solutions or on heterogeneous

surfaces. On electrodes functionalized with thin layers of catalyst, complex **1** shows TONs 30–40 fold higher than the homogeneous solution. Although Mn(bpy)(CO)₃Br coated with Nafion membrane showed a slightly higher TON,^[30] this coverage is more expensive than the diazonium salt functionalization.

Complex **2** immobilized on the electrode surface (diazonium salt modification) shows about 60 fold the catalytic activity of homogeneous solution in dry acetonitrile. The catalytic current decreased progressively, however the electrode maintained the activity for more than 200 cycles.

Notes and references

- [1] J. Ronge, T. Bosserez, D. Martel, C. Nervi, L. Boarino, F. Taulelle, G. Decher, S. Bordiga, J. A. Martens, *Chem. Soc. Rev.* **2014**, *43*, 7963-7981.
- [2] A. J. Morris, G. J. Meyer, E. Fujita, *Acc. Chem. Res.* **2009**, *42*, 1983-1994.
- [3] P. Zanello, C. Nervi, F. Fabrizi De Biani, *Inorganic Electrochemistry. Theory, Practice and Application*, 2nd ed., RSC, Cambridge, **2011**.
- [4] C. Costentin, M. Robert, J.-M. Saveant, *Chem. Soc. Rev.* **2013**, *42*, 2423-2436.
- [5] a) A. M. Appel, J. E. Bercaw, A. B. Bocarsly, H. Dobbek, D. L. DuBois, M. Dupuis, J. G. Ferry, E. Fujita, R. Hille, P. J. A. Kenis, C. A. Kerfeld, R. H. Morris, C. H. F. Peden, A. R. Portis, S. W. Ragsdale, T. B. Rauchfuss, J. N. H. Reek, L. C. Seefeldt, R. K. Thauer, G. L. Waldrop, *Chem. Rev.* **2013**, *113*, 6621-6658; b) M. Bourrez, F. Molton, S. Chardon-Noblat, A. Deronzier, *Angew. Chem. Int. Ed.* **2011**, *50*, 9903-9906; c) F. Franco, C. Cometto, F. Ferrero Vallana, F. Sordello, E. Priola, C. Minero, C. Nervi, R. Gobetto, *Chem. Commun.* **2014**, *50*, 14670-14673; d) H. Takeda, H. Koizumi, K. Okamoto, O. Ishitani, *Chem. Commun.* **2014**, *50*, 1491-1493; e) F. Franco, C. Cometto, C. Garino, C. Minero, F. Sordello, C. Nervi, R. Gobetto, *Eur. J. Inorg. Chem.* **2015**, 296-304; f) C. Garino, S. Ghiani, R. Gobetto, C. Nervi, L. Salassa, G. Croce, M. Milanesio, E. Rosenberg, J. B. A. Ross, *Eur. J. Inorg. Chem.* **2006**, 2885-2893; g) A. Albertino, C. Garino, S. Ghiani, R. Gobetto, C. Nervi, L. Salassa, E. Rosenberg, A. Sharmin, G. Viscardi, R. Buscaino, G. Croce, M. Milanesio, *J. Organomet. Chem.* **2007**, *692*, 1377-1391; h) L. Salassa, C. Garino, A. Albertino, G. Volpi, C. Nervi, R. Gobetto, K. I. Hardcastle, *Organometallics* **2008**, *27*, 1427-1435; i) C. Garino, T. Ruiu, L. Salassa, A. Albertino, G. Volpi, C. Nervi, R. Gobetto, K. I. Hardcastle, *Eur. J. Inorg. Chem.* **2008**, 3587-3591.
- [6] a) M. V. Vollmer, C. W. Machan, M. L. Clark, W. E. Antholine, J. Agarwal, H. F. Schaefer, III, C. P. Kubiak, J. R. Walensky, *Organometallics* **2015**, *34*, 3-12; b) J. M. Smieja, M. D. Sampson, K. A. Grice, E. E. Benson, J. D. Froehlich, C. P. Kubiak, *Inorg. Chem.* **2013**, *52*, 2484-2491; c) M. D. Sampson, A. D. Nguyen, K. A. Grice, C. E. Moore, A. L. Rheingold, C. P. Kubiak, *J. Am. Chem. Soc.* **2014**, *136*, 5460-5471; d) F. Franco, C. Cometto, L. Nencini, C. Barolo, F. Sordello, C. Minero, J. Fiedler, M. Robert, R. Gobetto, C. Nervi, *Chem. Eur. J.* **2017**, *23*, 4782-4793; e) A. Dubey, L. Nencini, R. R. Fayzullin, C. Nervi, J. R. Khusnutdinova, *ACS Catalysis* **2017**, *7*, 3864-3868.
- [7] a) C. Sun, R. Gobetto, C. Nervi, *New J. Chem.* **2016**, *40*, 5656-5661; b) C. Sun, S. Prosperini, P. Quagliotto, G. Viscardi, S. S. Yoon, R. Gobetto, C. Nervi, *Dalton Trans.* **2016**, *45*, 14678-14688; c) M. Sandroni, G. Volpi, J. Fiedler, R. Buscaino, G. Viscardi, L. Milone, R. Gobetto, C. Nervi, *Catal. Today* **2010**, *158*, 22-28; d) J. L. Inglis, B. J. MacLean, M. T. Pryce, J. G. Vos, *Coord. Chem. Rev.* **2012**, *256*, 2571-2600.
- [8] P. Allongue, M. Delamar, B. Desbat, O. Fagebaume, R. Hitmi, J. Pinson, J. M. Saveant, *J. Am. Chem. Soc.* **1997**, *119*, 201-207.
- [9] E. Rosenberg, M. J. Abedin, D. Rokhsana, D. Osella, L. Milone, C. Nervi, J. Fiedler, *Inorg. Chim. Acta* **2000**, *300*, 769-777.
- [10] a) O. Johansson, M. Borgstrom, R. Lomoth, M. Palmblad, J. Bergquist, L. Hammarstrom, L. C. Sun, B. Akermark, *Inorg. Chem.* **2003**, *42*, 2908-2918; b) G. Volpi, C. Garino, C. Nervi, *Dalton Trans.* **2012**, *41*, 7098-7108; c) G. Volpi, C. Garino, E. Breuza, R. Gobetto, C. Nervi, *Dalton Trans.* **2012**, *41*, 1065-1073.
- [11] L. H. Staal, A. Oskam, K. Vrieze, *J. Organomet. Chem.* **1979**, *170*, 235-245.
- [12] O. Buriez, E. Labbé, P. Pigeon, G. Jaouen, C. Amatore, *J. Electroanal. Chem.* **2008**, *619-620*, 169-175.
- [13] a) J. Hawecker, J. M. Lehn, R. Ziessel, *J. Chem. Soc., Chem. Commun.* **1984**, 328-330; b) F. P. A. Johnson, M. W. George, F. Hartl, J. J. Turner, *Organometallics* **1996**, *15*, 3374-3387; c) C. R. Cabrera, H. D. Abruna, *J. Electroanal. Chem.* **1986**, *209*, 101-107; d) T. R. Otoole, L. D. Margerum, T. D. Westmoreland, W. J. Vining, R. W. Murray, T. J. Meyer, *J. Chem. Soc., Chem. Commun.* **1985**, 1416-1417; e) Z. Y. Bian, H. Wang, W. F. Fu, L. Li, A. Z. Ding, *Polyhedron* **2012**, *32*, 78-85; f) C. P. Kubiak, M. D. Sampson, J. M. Smieja, E. E. Benson, I. D. Sharp, K. A. Grice, J. D. Froehlich, *Abstracts of Papers of the American Chemical Society* **2013**, *245*; g) K. A. Grice, C. P. Kubiak, in *Adv. Inorg. Chem., Vol. Volume 66* (Eds.: A. Michele, E. Rudi van), Academic Press, **2014**, pp. 163-188; h) C. Riplinger, M. D. Sampson, A. M. Ritzmann, C. P. Kubiak, E. A. Carter, *J. Am. Chem. Soc.* **2014**, *136*, 16285-16298.
- [14] a) J. M. Smieja, C. P. Kubiak, *Inorg. Chem.* **2010**, *49*, 9283-9289; b) B. P. Sullivan, C. M. Bolinger, D. Conrad, W. J. Vining, T. J. Meyer, *J. Chem. Soc., Chem. Commun.* **1985**, 1414-1415.
- [15] J. A. Keith, K. A. Grice, C. P. Kubiak, E. A. Carter, *J. Am. Chem. Soc.* **2013**, *135*, 15823-15829.
- [16] F. Paolucci, M. Marcaccio, C. Paradisi, S. Roffia, C. A. Bignozzi, C. Amatore, *J. Phys. Chem. B* **1998**, *102*, 4759-4769.

- [17] A. Gennaro, A. A. Isse, E. Vianello, *J. Electroanal. Chem.* **1990**, *289*, 203-215.
- [18] K. Y. Wong, W. H. Chung, C. P. Lau, *J. Electroanal. Chem.* **1998**, *453*, 161-169.
- [19] B. Kumar, M. Llorente, J. Froehlich, T. Dang, A. Sathrum, C. P. Kubiak, *Annu. Rev. Phys. Chem.* **2012**, *63*, 541.
- [20] a) D. L. DuBois, A. Miedaner, R. C. Haltiwanger, *J. Am. Chem. Soc.* **1991**, *113*, 8753-8764; b) A. J. Bard, L. R. Faulkner, *Electrochemical Methods*, 2nd Edition ed., Wiley, New York, **2001**.
- [21] a) C. Costentin, S. Drouet, M. Robert, J. M. Savéant, *J. Am. Chem. Soc.* **2012**, *134*, 11235-11242; b) C. Costentin, S. Drouet, M. Robert, J. M. Savéant, *J. Am. Chem. Soc.* **2012**, *134*, 19949-19950.
- [22] J. Agarwal, T. W. Shaw, H. F. Schaefer, A. B. Bocarsly, *Inorg. Chem.* **2015**, *54*, 5285-5294.
- [23] a) B. P. Sullivan, M. R. M. Bruce, T. R. Otoole, C. M. Bolinger, E. Megehee, H. Thorp, T. J. Meyer, *ACS Symp. Ser.* **1988**, *363*, 52-90; b) T. R. Otoole, B. P. Sullivan, M. R. M. Bruce, L. D. Margerum, R. W. Murray, T. J. Meyer, *J. Electroanal. Chem.* **1989**, *259*, 217-239.
- [24] J. Agarwal, E. Fujita, H. F. Schaefer, J. T. Muckerman, *J. Am. Chem. Soc.* **2012**, *134*, 5180-5186.
- [25] B. Barbier, J. Pinson, G. Desarmot, M. Sanchez, *J. Electrochem. Soc.* **1990**, *137*, 1757-1764.
- [26] C. W. Machan, C. J. Stanton, J. E. Vandezande, G. F. Majetich, H. F. Schaefer, C. P. Kubiak, J. Agarwal, *Inorg. Chem.* **2015**, *54*, 8849-8856.
- [27] T. Yoshida, K. Tsutsumida, S. Teratani, K. Yasufuku, M. Kaneko, *J. Chem. Soc., Chem. Commun.* **1993**, 631-633.
- [28] J. J. Walsh, G. Neri, C. L. Smith, A. J. Cowan, *Chem. Commun.* **2014**, *50*, 12698-12701.
- [29] a) K. Takada, G. D. Storrer, F. Pariente, H. D. Abruna, *J. Phys. Chem. B* **1998**, *102*, 1387-1396; b) B. B. Cui, H. J. Nie, C. J. Yao, J. Y. Shao, S. H. Wu, Y. W. Zhong, *Dalton Trans.* **2013**, *42*, 14125-14133.
- [30] J. J. Walsh, C. L. Smith, G. Neri, G. F. Whitehead, C. M. Robertson, A. J. Cowan, *Faraday Discuss.* **2015**, *183*, 147-160.