# Electrocatalytic Transformation of Carbon Dioxide into Low Carbon Compounds on Conducting Polymers Derived from Multimetallic Porphyrins

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The electrochemical reduction of carbon dioxide is studied herein by using conducting polymers based on metallotetraruthenated porphyrins (MTRPs). The polymers on glassy carbon electrodes were obtained by electropolymerization processes of the monomeric MTRP. The linear sweep voltammetry technique resulted in polymeric films that showed electrocatalytic activity toward carbon dioxide reduction with an onset potential of -0.70 V. The reduction products obtained were hydrogen, formic acid, formaldehyde, and methanol, with a tendency

### Introduction

A considerable portion of the solar radiation that falls on the earth's surface is re-emitted as thermal radiation.<sup>[1]</sup> This energy is retained by atmospheric gases (CO<sub>2</sub>, N<sub>2</sub>O, CH<sub>4</sub>, among others); a phenomenon that is called the Greenhouse Effect.<sup>[1]</sup> The concentration of these gases has been increasing since the Industrial Revolution due to human economic activities, such as the use of fossil fuels (petroleum, natural gas, and coal) and deforestation processes.<sup>[2]</sup> The increase of these gasses, mainly carbon dioxide, has generated dramatic weather perturbations and changed the global average temperature of the earth's atmosphere and oceans.<sup>[3,4]</sup> In this context, CO<sub>2</sub> conversion into species that are harmless to the environment or that can be useful as fuels appears to be a feasible alternative to decrease the concentration of this gas.<sup>[5-7]</sup> The electrochemical reduction of CO<sub>2</sub> is a promising process for this aim and, depending on the number of electrons transferred, it is possible to obtain several reduction products, the most interesting of which are those that involve the transfer of more than two electrons, for example, methane, methanol, and ethanol.<sup>[8,9]</sup> To obtain these products, electrocatalysts based on transitionmetal complexes containing multiple metal centers have been utilized to achieve multielectron transfers.<sup>[10,11]</sup>

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for a high production of methanol with a maximum value of turnover frequency equal to 15.07 when using a zinc(II) polymeric surface. Studies of the morphology (AFM) and electrochemical impedance spectroscopy results provide an adequate background to explain that the electrochemical reduction is governed by the roughness of the polymer, for which the possible mechanism involves a series of one-electron reduction reactions.

There have been diverse studies on the electrocatalytic reduction of CO<sub>2</sub> by using macrocycles with transition metals as electrocatalysts.<sup>[12–16]</sup> One of the first studies showed that films of cobalt and nickel phthalocyanines deposited onto electrode surfaces were active catalysts for the reduction of CO<sub>2</sub> in water.<sup>[12]</sup> Also, cobalt(II) macrocyclic complexes<sup>[13,14]</sup> and *meso*-cobalt(I) tetracarboxyphenylporphyrins have been used as homogeneous electrocatalysts, with which formic acid was the main product.<sup>[15,16]</sup> In the case of Fe<sup>0</sup> porphyrins, CO production was verified in DMF at  $-1.80 V^{[17]}$  and weak Brønsted acids at  $-1.50 V.^{[18]}$  Recently, a lower reduction potential has been obtained (-0.80 V) by using a conducting polymer of cobalt 5,10,15,20-tetrakis(4-aminophenyl)porphyrin on an indium tin oxide (ITO) electrode with an ionic liquid as the reaction medium.<sup>[19,20]</sup>

Tetraruthenated porphyrin (TRP) consists of a tetrapyridylporphyrin (TPyP) coordinated to four ruthenium(II) complexes on the periphery of the macrocycle. These macrocycles are particularly attractive because they display unusual electrocatalytic,<sup>[21]</sup> electroanalytical,<sup>[22,23]</sup> photophysics,<sup>[24]</sup> and photoelectrochemical<sup>[25-27]</sup> properties. In particular, these porphyrins have been used in the electroanalytical detection of S<sup>IV</sup> oxoanions<sup>[28-30]</sup> and electrocatalytic reduction processes of O<sub>2</sub><sup>[31]</sup> NO<sub>2</sub><sup>-</sup>,<sup>[32,33]</sup> and CO<sub>2</sub>.<sup>[34,35]</sup> In all cases, multielectron transfer is essential to enhance catalytic activity, which is observed by changes to current density associated with each process.<sup>[31–35]</sup> In addition, reduction products that involve the transfer of more than one electron are obtained,<sup>[32,33]</sup> therefore, these TRPs can be considered as catalysts able to orient reaction selectivity toward one particular product.

On the other hand, with the aim of obtaining stable electrochemical sensors and electrocatalysts, transition-metal complexes can be incorporated into electrode surfaces by different procedures, such as absorbed monolayers,<sup>[36-39]</sup> polymeric



membranes,<sup>[40–43]</sup> and conducting polymers.<sup>[44–46]</sup> Some electropolymerizable functional groups found in polypyridyl and macrocyclic complexes are 5-NH<sub>2</sub>-phen (phen: phenanthroline),<sup>[47]</sup> 5,6-NH<sub>2</sub>-phen,<sup>[48]</sup> and 5,5'-NH<sub>2</sub>-bpy (bpy: bipyridine).<sup>[49]</sup> Also, the role of nitro groups as precursors in the electropolymerization process has been reported in coordination compounds containing transition metals.<sup>[50]</sup>

Herein, we describe electrocatalytic reduction of carbon dioxide by using conducting polymers derived from metallotetraruthenated porphyrins (MTRPs). In particular, electrocatalysts of TPyP (containing Ni<sup>II</sup>, Zn<sup>II</sup>, or metal free) with four [Ru(5-NO<sub>2</sub>phen)<sub>2</sub>Cl]<sup>+</sup> moieties coordinated to the periphery of the macrocycle.

The conducting polymers were obtained by electropolymerization on the surface of a glassy carbon (GC) or ITO electrode. The catalytic activity was evaluated by linear sweep voltammetry (LSV) analysis, that is, *j* versus *E* curves. The reduction products were obtained by means of potential-controlled bulk electrolysis (PCBE) experiments. The correlation between the morphology and product distribution was studied based on AFM measurements of the polymeric surfaces. Finally, electrochemical impedance spectroscopy (EIS) was carried out to understand the relationship between electrical behavior, catalytic activity, and morphology of the modified electrodes.

These studies allow us to suggest that electrocatalysts are efficient for methanol generation, and the roughness of the polymer surface utilized determines the amount of methanol produced.

### **Results and Discussion**

The general structure of the electrocatalysts studied is shown in Figure 1, in which TPyP (containing Ni<sup>II</sup>, Zn<sup>II</sup>, or metal-free macrocycle) coordinated to four  $[Ru(5-NO_2-phen)_2CI]^+$  units on the periphery of macrocycle can be seen.

### **Electropolymerization process**

The modified electrodes were prepared according to a previously reported electropolymerization process.<sup>[50]</sup> Briefly, electropolymerization takes place by continuous cyclic voltammetry between -1.2 and 1.45 V versus Ag/AgCl in organic solution with a fast scan rate (at least 500 mV s<sup>-1</sup>). It has been demonstrated that at this scan rate radical species form after the reduction of nitro groups, which are present in the phenanthroline ligands, and can be coupled in the reverse scan.<sup>[50]</sup> In every cycle, an electrodeposit of conducting material is accumulated on the electrode surface. This deposit exhibits characteristics of a conducting polymer and maintains spectroscopic and electrochemical properties of the whole macrocycle. Figure 2A displays a representative example of this electrochemical procedure. An ITO surface was used as the working electrode with the ZnTRP macrocycle. An increase in current with an increasing number of cycles indicates film growth.<sup>[51]</sup> Figure 2B displays UV/Vis characterization results for Poly-ZnTRP and Poly-NiTRP on modified ITO electrodes. Both electrodes show similar patterns. In the case of the Poly-ZnTRP-ITO elec-

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Figure 1. Structure of the  $[MTPyP{Ru(5-NO_2-phen)_2Cl}_4]^{4+}$  complex.



**Figure 2.** Modification of an ITO electrode with MTRP. A) Electropolymerization of 1 mm ZnTRP/DMF/0.1 m tetraethylammonium perchlorate (TEACIO<sub>4</sub>), 500 mV s<sup>-1</sup> (first cycle is shown by the red solid line). B) UV/Vis spectra of Poly-NiTRP-ITO (black) and Poly-ZnTRP-ITO (red).

trode, a well-defined set of absorptions bands centered at  $\lambda = 275$ , 440, 570, and 618 nm are observed and assigned as follows:  $\pi \rightarrow \pi^*$  NO<sub>2</sub>-phen, Soret Band  $\pi \rightarrow \pi^*$ , Q band  $\pi \rightarrow \pi^*$ , and Q band  $\pi \rightarrow \pi^*$ , respectively. It has been largely recognized that when a metal center ion is coordinated in an N-4 porphyrin core, the distribution of Q bands changes from four to two because of changes in the symmetry from  $D_{2h}$  (in H<sub>2</sub>TRP) to  $D_{4h}$  (MTRP).<sup>[52]</sup> For the Poly-NiTRP-ITO electrode, an analogous case is observed, for which the Q bands change from four to one as a consequence of the Ni<sup>2+</sup> ion in the porphyrin core. These facts provide evidence that zinc or nickel atoms are still coordinated to the N-4 porphyrin core after the electropolymerization process.



#### **AFM characterization**

AFM measurements were carried out on the conducting polymers attached to ITO electrodes. The images obtained are presented in Figure 3 A and histograms that represent the average size of the conglomerates shown in Figure 3 A are depicted in Figure 3 B. The images of the three modified electrodes show a random distribution of conglomerates in a pseudospherical shape. These images are completely different to the morphology of the bare ITO surface (see Figure S1 in the Supporting Information), which confirms that the electrodes are totally modified during the electropolymerization process. The images show that Poly-NiTRP is smaller and thinner than the other conducting polymers. The latter is also reflected in the histograms, in which the average sizes of conglomerates are 60, 37, and 90 nm for Poly-H<sub>2</sub>TRP, Poly-NiTRP, and Poly-ZnTRP, respectively.

Also, for Poly- $H_2$ TRP and Poly-ZnTRP, the Z-axis magnitudes (absolute value) are higher than that for Poly-NiTRP. These characteristics can be related to the presence of a more homogenous and compact polymer in the case of Poly-NiTRP.

On the other hand, the average roughness parameter (Ra) was determined, and the values for Poly- $H_2$ TRP, Poly-NiTRP, and Poly-ZnTRP were 11.7, 7.81, and 17.2 nm respectively.

In summary, Poly-ZnTRP appears to have a more voluminous and rougher surface, with a larger area and bigger conglomerates. In contrast, Poly-NiTRP is a more compact film, as corroborated by its smaller Z value and the diameter of conglomerates. Poly-H<sub>2</sub>TRP appears to be an intermediate case, in which the Z magnitude, conglomerate size, and Ra value are between those of Poly-NiTRP and Poly-ZnTRP.

### **Electrocatalytic activity**

Figure 4 shows *j* versus *E* curves of the Poly-MTRP-GC electrodes recorded in 0.1 M NaClO<sub>4</sub> at  $5 \text{ mV s}^{-1}$ . Figure 4A shows



**Figure 4.** A) Electrochemical behavior of the modified electrodes measured by LSV in 0.1  $\,$  MaClO<sub>4</sub> at 5 mV s<sup>-1</sup> under N<sub>2</sub> (dashed lines) and CO<sub>2</sub> (solid lines). Inset: Magnification of the linear sweep voltammogram under a N<sub>2</sub> atmosphere. B) Cyclic voltammogram of the Poly-H<sub>2</sub>TRP-GC electrode in 0.1  $\,$ M NaClO<sub>4</sub> at 100 mV s<sup>-1</sup> before (black solid line) and after (red solid line) electrolysis under a CO<sub>2</sub> atmosphere.

a comparative plot for Poly-MTRP-GC modified electrodes under N<sub>2</sub> and CO<sub>2</sub> atmospheres. Under a N<sub>2</sub> atmosphere (Figure 4, inset), a low current density at -0.6 V is observed, which is probably related to a redox process occurring in the



conducting polymer frame or H<sub>2</sub> generation with a maximum current density for poly-H<sub>2</sub>TRP of 5  $\mu$ A cm<sup>-2</sup>. Under the CO<sub>2</sub> atmosphere, for all modified electrodes it is possible to observe an irreversible electrochemical process without diffusion control. However, a considerable change in the cathodic current density with an onset potential of -0.7 V versus Ag/AgCl is evident. This change in the current density can be associated with the CO<sub>2</sub> reduction process, as described in the literature for similar electrocatalysts.[35] The Tafel slope was evaluated in the low polarization regime for the three modified electrodes and showed values near to 200 mV dec<sup>-1</sup>, which indicated that there was a chemical pathway as a rate-determining step multiple electrochemical for steps.[53]

Figure 3. A) AFM images of the modified electrodes studied, and B) relative conglomerate sizes are presented in histograms.

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Table 1. Product distribution for carbon dioxide reduction at various electrodes.										
Property	Bare GC	Poly-H <sub>2</sub> TRP-GC	Poly-NiTRP-GC	Poly-ZnTRP-GC						
amount formed	H <sub>2</sub>	1.81	-	_	2.26					
[µmol]	HCOOH	1.17	0.46	-	-					
	HCHO	2.52	-	-	3.26					
	CH₃OH	1.03	13.3	25.0	71.6					
TOF	H <sub>2</sub>	-	-	-	0.476					
[s <sup>-1</sup> ]	HCOOH	-	0.029	-	-					
	HCHO	-	-	-	0.680					
	CH₃OH	-	0.842	4.526	15.07					
faradaic efficiency	H <sub>2</sub>	2.5	-	-	1.8					
[%]	HCOOH	1.6	0.42	-	-					
	HCHO	3.4	-	-	2.6					
	CH₃OH	1.4	12.2	55	56					

Because the experiments are carried out aqueous media, possible interference from solvent reduction can occur; hence, PCBE experiments (see Table 1) were carried out at -0.8 V versus Ag/AgCl. At this potential, all modified electrodes show a considerable difference between CO<sub>2</sub> and N<sub>2</sub> atmospheres, whereas H<sub>2</sub> production from proton reduction is sluggish.

To verify stability or activity loss of these modified electrodes, Figure 4B displays cyclic voltammetry results for the Poly-H<sub>2</sub>TRP-GC electrode in aqueous medium before and after the PCBE experiment (see the Experimental Section and Table 1) under a CO<sub>2</sub> atmosphere. The cyclic voltammogram of the modified electrode after electrolysis shows a reversible redox couple at  $E_{1/2} = 0.71$  V versus Ag/AgCl, which is associated with the Ru<sup>III</sup>/Ru<sup>II</sup> redox process of ruthenium complexes on the periphery of the macrocycle. According to previous work, this process is a simultaneous four-electron process.<sup>[50]</sup> After the PCBE experiments, the cyclic voltammogram remains unchanged, with only a decrease in charge of 4.96% under the voltammetric peak of the Ru<sup>III</sup>/Ru<sup>II</sup> redox couple. Results obtained from the above-described experiments show that the conducting polymer does not suffer from any transformation that is detectable by cyclic voltammetry; hence, no redoxactive compounds are coordinated or adsorbed on the polymeric matrix. The same behavior was observed with the other modified electrodes (see Figure S2 in the Supporting Information).

### **PCBE** experiments

The products of electrochemical reduction of  $CO_2$  at the Poly-MTRP-GC electrodes were determined after PCBE, which was carried out as indicated in the Experimental Section. The quantified products were hydrogen, carbon monoxide, formic acid, formaldehyde, and methanol, which corresponded to the transfer of two, four, or six electrons [see Eqs. (1)–(5)].

$$2 H^+ + 2 e^- \rightarrow H_2 \tag{1}$$

 $CO_2 + 2 H^+ + 2 e^- \rightarrow CO + H_2O$  (2)

$$CO_2 + 2 H^+ + 2 e^- \rightarrow HCOOH$$
(3)

$\mathrm{CO}_2 + 4\mathrm{H}^+ + 4\mathrm{e}^- \rightarrow \mathrm{HCHO} + \mathrm{H_2O}$	(4)
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$$\mathrm{CO}_2 + 6\,\mathrm{H}^+ + 6\,\mathrm{e}^- \to \mathrm{CH}_3\mathrm{OH} + \mathrm{H}_2\mathrm{O} \tag{5}$$

Table 1 collects the concentration distribution of these products, along with turnover frequency (TOF) values and faradaic efficiencies. In all experiments, carbon monoxide is below the detection limit.

Bare GC produces a wide distribution of products with poor selectivity and catalytic activity (Table 1).<sup>[54]</sup> In the case of the Poly-H<sub>2</sub>TRP-GC electrode, hydrogen and formaldehyde are not produced. For Poly-NiTRP-GC, the only product obtained is methanol. Finally, in the case of Poly-ZnTRP-GC, formic acid is not produced. The predominance of methanol is clear in all cases; Poly-ZnTRP-GC is the most efficient electro-

catalyst. This fact is remarkable, especially when considering that methanol is a valuable compound for its use as a liquid fuel. Additionally, two control experiments were carried out, with the purpose of checking the ruthenium moiety contribution and effect of degradation products from the electrocatalysts. In the first case, the [Ru(5-NO2-phen)2Cl2] complex was adsorbed (see the Experimental Section) on the GC electrode and subjected to PCBE for 3 h under the same experimental conditions as those used for the MTRP modified electrodes. The results show no evidence of product formation at that potential. For the second case, Poly-ZnTRP-GC (which was most active for methanol production) was used, but in this case without CO<sub>2</sub> being dissolved in the supporting electrolyte, that is, a N<sub>2</sub>-saturated atmosphere. Again, no products were detected, which indicated that the origin of the reaction products was an electrocatalytic process from the synergism between ruthenium(II) peripheral complexes and the macrocycle ring; thus the reaction products that were quantified were not from degradation of the electrocatalysts. Indeed, it has been demonstrated that porphyrin complexes under heterogeneous electrochemical conditions are mainly active in the production of CO.<sup>[55]</sup> In a few cases, the production of methanol (5% faradaic efficiency) has been reported, for example, a Co<sup>II</sup> phthalocyanine adsorbed on graphite at -1.36 V with 0.1 M KHCO<sub>3</sub> as supporting electrolyte<sup>[55]</sup> On the other hand, methanol production from TRP analogues has been reported for photolysis experiments, in which the TRPs were sensitizers for TiO<sub>2</sub> nanoparticle catalysts<sup>[55]</sup>.The synergism of TRP derivatives has been largely demonstrated from pioneering works by the groups of Anson and Toma, the most significant example is related to the oxygen reduction reaction, for which a four-electron reduction pathway is achieved by using multimetallic macrocycles, compared with two-electron reduction if Co<sup>II</sup>TPyP is used.<sup>[31,56]</sup> The synergistic effect is a combination of back-donation and induced electronic density from the Ru(polypyridyl) moiety to the porphyrin macrocycle center. This effect has also been corroborated by using a layer by layer assembly of [FeTPyP{Cr-(phen)<sub>2</sub>Cl}<sub>4</sub>]<sup>8+</sup>/SiW<sub>12</sub>O<sub>40</sub><sup>4-</sup> on GC.<sup>[57]</sup>

These results seem to be directly related to the intrinsic properties of the conducting polymer. In the case of Poly-NiTRP, the high selectivity toward methanol production can be

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associated with the presence of a very active redox center in the macrocycle core, and also to the formation of a very compact and thin film. These factors suggest that reduction takes place thanks to the possible coordination of carbon dioxide to the reduced metal center in the conducting polymer, which should occur in the conducting polymer/solvent interphase. However, to the best of our knowledge, there are no examples of nickel(II) macrocycles selectively producing methanol. These kinds of compounds are well known as efficient electrocatalysts towards the production of carbon monoxide and formic acid.<sup>[55, 58]</sup> Therefore, the catalytic activity must not only be governed by the coordination property. Other factors must also be involved in assisting this multielectron reduction process.

In the case of Poly-ZnTRP and Poly- $H_2$ TRP, the presence of an inert coordination metal or the absence of a transition metal in the porphyrin core discount the possibility of coordinating carbon dioxide to a reduced metal center. The reduction mechanism must be driven by other phenomena.

One possible explanation could be different rugosities, porosities, and electron densities of the surfaces studied. According to the distribution of products and morphological analysis results, the formation of methanol as the main product is the result of multiple monoelectronic pathways, as reported previously.<sup>[5,59]</sup> Considering that the other products are obtained in lower amounts, they should be participating as precursors for methanol formation, since previously reported CO<sub>2</sub> reduction mechanism on semiconductor surfaces revealed that, after favorable adsorption of CO<sub>2</sub>, different products are released as a consequence of different recombination of radical intermediates, followed by several of these compounds being readsor-

bed to react again and undertake proton-coupled electrontransfer paths.<sup>[59]</sup> Therefore, and owing to similar morphologies, Poly-H<sub>2</sub>TRP-GC and Poly-ZnTRP-GC yield methanol as the main product. The only noticeable difference between the electrodes is a different amount of active sites in the polymeric framework, as evidenced by different roughnesses; this fact allows us to deduce that the active site of the electrocatalyst could be a reduced form of a macrocycle ring, as described previously for nitrite reduction with the same electrocatalysts.[32]

Finally, the insertion of a transition metal into the porphyrin cavity apparently has an important effect on the morphology of the film formed, but it does not have a significant effect on product distribution.

#### UV/Vis spectroelectrochemical measurements

UV/Vis spectroelectrochemistry was carried out to elucidate the electronic structure of the most effective electrocatalyst under the application of an electrochemical potential. Measurements in solution were carried out with a 1 mm solution of ZnTRP in DMF.

Figure 5 shows that ZnTRP suffers from changes to the intensity of Soret and Q bands as long as -1.0 V is applied under a N<sub>2</sub> atmosphere; the effect is most evident in the case of the Soret band. This increase can be explained by the formation of a radical anion, which favors the probability of electronic transitions, particularly the  $\pi \rightarrow \pi^*$  transition associated with the Soret band. The same behavior has been observed in the Soret band of the dimeric cobalt phthalocyanine macrocycle.<sup>[60]</sup>

When ZnTRP was studied at -1.0 V in the presence of CO<sub>2</sub>, a redshift and a decrease in the Soret band could be observed. This behavior can be explained by electron transfer from the reduced macrocycle to CO<sub>2</sub>, which takes place at this potential. The applied potential, along with the presence of CO<sub>2</sub> molecules, promotes the formation of an intermediary species between a porphyrin anion radical and CO<sub>2</sub> with a less energetic and favorable transition to diminish the band gap relative to the original species.

As a consequence, this result strengthens the idea that the electroreduction of  $CO_2$ , in the case of the macrocycle with an inert coordination metal, is influenced by the electronic density of the macrocycle instead of its specific coordination properties.



Figure 5. Spectroelectrochemical behavior of 1 mm ZnTRP in DMF at -1.0 V.



To relate catalytic activity, morphology, and the electronic behavior of the modified electrodes, EIS experiments were carried out at maximum and minimum TOF values for the production of methanol, that is, by using the Poly-H<sub>2</sub>TRP-GC and Poly-ZnTRP-GC electrodes respectively. The behavior of the electrodes is revealed by Nyquist plots, which are graphic representations of the capacitive impedance  $(Z_{Imaginary})$  versus faradaic impedance (Z<sub>Real</sub>). Figure 6 shows the Nyquist plots of the Poly- $H_2$ TRP-GC and Poly-ZnTRP-GC electrodes at -0.70 and -0.80 V under N<sub>2</sub> and CO<sub>2</sub> atmospheres (see Bode plots in Figures S3 and S4 in the Supporting Information). An imperfect semicircle is observed in all cases; thus a pseudo-Randles equivalent circuit was used, in which a constant phase element was necessary instead of a capacitor.<sup>[61]</sup> This nonideal behavior has been reported in the literature,<sup>[62]</sup> and has been attributed to the roughness of these electrode surfaces.

Relevant data for the electrodes in different media is summarized in Table 2. Both modified electrodes behave similarly when they are immersed in a  $CO_2$ -saturated solution, and show a decrease in the resistance of the solution ( $R_s$ ). This decrease can be roughly explained by the presence of a new



Figure 6. Nyquist plots of Poly-H\_2TRP-GC at A) -0.70 and B) -0.80 V, and Poly-ZnTRP-GC at C) -0.70 and D) -0.80 V.

Table 2. Representative constants obtained from EIS measurements.										
Material	Atmosphere	-0.70 V			-0.80 V					
		$R_{\rm s} \left[\Omega\right]$	Р	$R_{\rm F}  [{\rm k}\Omega]$	$R_{\rm s}\left[\Omega ight]$	Р	$R_{\rm F}$ [k $\Omega$ ]			
	N <sub>2</sub>	201.8	0.904	865.9	206.3	0.915	489.7			
112111	CO <sub>2</sub>	185.1	0.990	513.0	185.2	0.929	64.4			
Zeter	N <sub>2</sub>	175.1	0.840	3572	168.9	0.862	1390			
ZIIIRP	CO <sub>2</sub>	162.0	0.892	3500	160.5	0.918	341			

molecule in the double-layer structure, which gives rise to electrochemical reactions in the film.

As can be seen from the results in Table 2, the resistance to faradaic processes  $(R_{\rm F})$  decreases when the electrode is immersed in a CO<sub>2</sub>-saturated solution. An extreme case is presented at -0.70 V, for which the  $R_{\rm F}$  value remains almost unchanged for both electrodes; this is consistent with the electrochemical behavior presented in Figure 4, in which -0.70 V corresponds to the onset potential of the reduction wave, and hence, the electrochemical reaction is in a low polarization state. At -0.8 V, a decrease in  $R_{\rm F}$  can be seen in both electrodes under a N<sub>2</sub> atmosphere, which indicates that the electrodes are more conductive at this potential, since the polymeric films are in a reduced state. When the solution is saturated with  $CO_2$ , the  $R_F$  values are significantly lower than those in a N<sub>2</sub> atmosphere, which indicates that both surfaces in a reduced state are in the electrocatalytic regime; this is in agreement with results obtained for electrolysis experiments (Table 1).

A comparison between  $R_F$  values and the morphology of the electrodes can shed light on the factors that affect the activity and selectivity of the electrodes.

The Poly-H<sub>2</sub>TRP-GC electrode is a smoother surface with smaller conglomerates. It behaves more like a solid electrode than an amorphous conducting polymer. Due to its density, Poly-H<sub>2</sub>TRP-GC shows a low  $R_{\rm F}$  value under a N<sub>2</sub> atmosphere that changes dramatically when the system is saturated with CO<sub>2</sub> to go from 489 to 64.4 k $\Omega$ ; this value confirms fast electron transfer, which could be used to perform multiple monoe-lectronic reductions, finally ending in the formation of methanol.

On the other hand, the Poly-ZnTRP-GC electrode produces the largest amount of methanol, as well as having a high TOF value that reaches 15.07 s<sup>-1</sup>. It also presents a high  $R_F$  value, which is in concordance with the morphological properties of the electrode. The presence of H<sub>2</sub> in the reduction product distribution gives an important clue about the possible reduction mechanism of this modified electrode, in which the local proton availability, and hence, morphology, must have an important role in the formation of products that involve multiple coupled electron–proton transfer processes.

 $\begin{array}{c} \operatorname{Poly-MTRP} \xrightarrow{-0.8 \vee /\operatorname{CO}_{2}} \operatorname{Poly-MTRP} / \operatorname{CO}_{2 \text{ (ads)}} \\ \operatorname{Poly-MTRP} / \operatorname{CO}_{2 \text{ (ads)}} \xrightarrow{e^{-}/\operatorname{H}^{+}} \operatorname{Poly-MTRP} / \operatorname{HOCO}^{\bullet}_{\text{ (ads)}} \\ \operatorname{Poly-MTRP} / \operatorname{HOCO}^{\bullet}_{\text{ (ads)}} \xrightarrow{e^{-}/\operatorname{H}^{+}} \operatorname{Poly-MTRP} / \operatorname{HCOOH}_{\text{ (ads)}} \\ \operatorname{Poly-MTRP} / \operatorname{HCOOH}_{\text{ (ads)}} \xrightarrow{e^{-}/\operatorname{H}^{+}} \operatorname{Poly-MTRP} / \operatorname{HC(OH)}_{2}^{\bullet}_{\text{ (ads)}} \\ \operatorname{Poly-MTRP} / \operatorname{HC(OH)}_{2}^{\bullet}_{\text{ (ads)}} \xrightarrow{e^{-}/\operatorname{H}^{+}} \operatorname{Poly-MTRP} / \operatorname{HCHO}_{\text{ (ads)}} + \operatorname{H}_{2}\operatorname{O} \\ \operatorname{Poly-MTRP} / \operatorname{HC(OH)}_{2}^{\bullet}_{\text{ (ads)}} \xrightarrow{e^{-}/\operatorname{H}^{+}} \operatorname{Poly-MTRP} / \operatorname{HCHO}_{\text{ (ads)}} + \operatorname{H}_{2}\operatorname{O} \\ \operatorname{Poly-MTRP} / \operatorname{HCHO}_{\text{ (ads)}} \xrightarrow{e^{-}/\operatorname{H}^{+}} \operatorname{Poly-MTRP} / \operatorname{CH}_{2}\operatorname{OH}^{\bullet}_{\text{ (ads)}} \\ \operatorname{Poly-MTRP} / \operatorname{CH}_{2}\operatorname{OH}^{\bullet}_{\text{ (ads)}} \xrightarrow{e^{-}/\operatorname{H}^{+}} \operatorname{Poly-MTRP} / \operatorname{CH}_{3}\operatorname{OH} \end{array}$ 

Scheme 1. Probable mechanism for the reduction of  $CO_2$  on Poly-MTRPmodified electrodes.



Based on the experimental data above discussed and reports in the literature,  $^{[59,63]}$  a probable mechanism is given in Scheme 1.

The value of the Tafel (chemical electrochemical (CE) mechanism) slope, in accordance with spectroelectrochemical data, account for the first stage in which the conducting polymer is reduced and simultaneous adsorption of  $CO_2$  takes place, followed by several steps that involve monoelectronic reductions with subsequent product release.

### Conclusions

The electrochemical reduction of carbon dioxide by using GC electrodes modified with conducting polymers of TRPs was studied. The electrocatalysts were composed of TPyP (Ni<sup>II</sup>, Zn<sup>II</sup>, or metal free) with four [Ru(5-NO<sub>2</sub>-phen)<sub>2</sub>Cl]<sup>+</sup> moieties coordinated to the periphery of the macrocycle.

The electrocatalytic activity was studied by LSV, which revealed that, at potentials more negative than -0.70 V, the conducting polymers showed activity toward CO<sub>2</sub> reduction. The product obtained by PCBE in higher amounts was methanol; the highest TOF value was recorded for Poly-ZnTRP-GC.

After AFM, spectroelectrochemical/UV/Vis spectroscopy, and EIS measurements, it was possible to confirm that the roughness, and therefore, number of active sites, was the most significant factor in the electrocatalytic activity to obtain methanol as the main product. The previously described characteristics defined the activity of the abovementioned modified electrodes and fit very well with the electrocatalytic performance of Poly-ZnTRP-GC.

### **Experimental Section**

### Reagents

All reagents and solvents were of analytical grade and used without further purification. The [MTPyP{Ru(5-NO<sub>2</sub>-phen)<sub>2</sub>Cl]<sub>4</sub>](PF<sub>6</sub>)<sub>4</sub> (MTRP) coordination compounds were prepared according to procedures reported in the literature.<sup>[32, 50]</sup>

### **Electrochemical measurements**

LSV and EIS were carried out in a CH Instrument 760C potentiostat. PCBE was carried out in a BASI POWER MODULE PWR-3 potentiostat. A GC working electrode (r = 1.5 mm, CH Instruments), a saturated Ag/AgCl reference electrode, and a Pt wire counter electrode were used. All potential values were measured by using an Ag/ AgCl reference electrode. Working electrode modification was carried out by following a description found in the literature.<sup>[32,50]</sup> Modified electrodes were treated in strong acid media and the amount of metal was determine by inductively coupled plasma optical emission spectroscopy (ICP-OES) analysis (Varian Liberty Series II), which showed the following elemental composition: 4.9 and 1.3 nmol cm<sup>-2</sup> for Ru and Zn, respectively, in Poly-ZnTRP. In case of Poly-NiTRP, the composition was 2.9 and 0.78 nmol cm<sup>-2</sup> for Ru and Ni, respectively. The electroactive area of the modified electrodes used for cyclic voltammetry purposes (r = 1.5 mm) was estimated by using the Randles-Sevcik equation to give values of 0.094, 0.090, and 0.1  $\mbox{cm}^2$  for Poly-H\_2TRP, Poly-NiTRP, and Poly-ZnTRP, respectively.

### **Electrocatalytic activity**

The reduction of carbon dioxide was studied by LSV with Poly-MTRP-GC electrodes in 0.1  $\mu$  aqueous solutions of NaClO<sub>4</sub> in CO<sub>2</sub>-saturated media (33 mm),<sup>[64]</sup> between 0.0 and -1.1 V at 5 mV s<sup>-1</sup>.

### **PCBE** analysis

A gas-tight H-type cell and Poly-MTRP-GC plate modified working electrode (area: 1.1  $\rm cm^2)$  were used at -0.80 V for 3 h of electrolysis.

### **Determination of reaction products**

For the determination of H<sub>2</sub>, CO, gas chromatography measurements were carried out by using a DANI MASTERS gas chromatograph: column: Supelco Mol sieve 5 Å (30 m×0.53 mm) coupled with a microthermal conductivity detector ( $\mu$ TCD) by using argon as a gas carrier with an isothermal program (40 °C). Gas samples were directly taken from the electrochemical cell after 3 h of electrolysis by using a gas-tight Hamilton syringe. Formic acid and formaldehyde were determined by UV/Vis spectroscopic methods, as reported in the literature.<sup>[65-68]</sup> Methanol content was determined by using a gas chromatograph coupled with a flame ionization detector (FID), with a Supelcowax 10 ( $30 \text{ m} \times 0.32 \text{ mm} \times$  $0.25 \ \mu m$  film thickness) column. Samples were prepared, after 3 h of electrolysis, with catholyte (3 mL) and propanol as an internal standard. Sealed vials containing the sample were heated at 80 °C for 20 min, and then headspace analysis was carried out. TOF, as an index calculated from the number of moles of product formed per mole of catalyst per unit of time, was evaluated for each product.

#### **AFM measurements**

AFM images were recorded on a Bruker NanoScope Innova AFM, along with NanoDrive v8.01 software. The images of the surfaces were investigated by using tapping mode.

#### UV/Vis spectroelectrochemical measurements

UV/Vis spectroelectrochemical experiments were performed in a one-compartment quartz cuvette containing auxiliary and working Pt electrodes and a Ag/AgCl reference electrode. All spectra were recorded by using 1 mm of MTRP/0.1 m TBAPF<sub>6</sub> in acetonitrile, under an applied voltage of -1.0 V; spectra were recorded every 20 s until 20 spectra were recorded.

#### **EIS** measurements

The EIS measurements were performed by using Poly-MTRP-GC electrodes in 0.1  $\mu$  aqueous solutions of NaClO<sub>4</sub> in CO<sub>2</sub>-saturated media at -0.70 and -0.80 V versus Ag/AgCl, with an amplitude of 5 mV and measured frequencies from  $10^{-2}$  to  $10^{4}$  Hz. Experimental data obtained from the EIS measurements were fitted by using CHI 760C software. All data were fitted within an error of 5%.



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