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Introduction

The photoelectrochemical conversion of CO$_2$ into valuable chemicals/fuels is an ideal approach for the contemporary challenges of greenhouse emission and energy shortage. However, the knowledge and technology are still in their infancy, when compared to the water splitting ones.$^{5-6}$\footnote{Department of Chemistry, NIS and CIRCC (Ban), University of Torino via P. Giuria 7, 10125 Torino, Italy. Email: carlo.nervi@unito.it.} Over the last decades, many organometallic catalysts were explored for efficient and selective electrochemical CO$_2$ conversion.$^{7-15}$\footnote{School of Mechanical Engineering, Korea University, Seoul 136-713, Republic of Korea.} Rhenium chlorotricarbonyl complexes bearing bipyridyl ligands introduced by Lehn$^{16}$\footnote{Electronic Supplementary Information (ESI) available: Detailed syntheses of the ligands T, TT and ETT, CV of 1, 2 and 3 at first and second reduction, plot of the peak current vs. square root of the scan rate, HOMO-1, HOMO and LUMO pictures, electro-polymerization data and stability under CO$_2$ for complex 3. See DOI: 10.1039/x0xx00000x} are among the most studied, robust and higher selective catalysts for the electrochemical reduction of CO$_2$ to CO.$^{17-19}$\footnote{Sam S. Yoon, Roberto Gobetto$^a$ and Carlo Nervi$^a$*} The effects of several type of substituted bipyridines$^{20-23}$ were tested, and the photochemical and electrochemical mechanism leading to CO thoroughly explored (see$^{14,23}$ for a recent brief synopsis).

Most of the published papers focused on homogeneous catalysis, mainly because the design, fine-tuning and the synthesis of catalysts are more straightforward and simple. On the other hand, large-scale applications of heterogeneous catalytic systems are widespread due to their advantages in terms of operation, cost, durability and easier recovering procedure. The combination of the two approaches could make the heterogeneous CO$_2$ conversion by green energy (i.e. solar energy) more industrially feasible and appealing.$^{18,24}$

Not many papers$^{18,25-34}$ deal with electrode modified by Re-bipyridine complexes, meanwhile immobilization of intact organometallic catalysts on a surface$^{35}$ is a challenging opportunity$^{36-37}$ because of potential improved stability, durability, handling and reactivity in electrochemical and photoelectrochemical cells.$^5$ Cyclic Voltammetry (CV) can quickly test the catalyst activity, simply comparing the cathodic peak currents with and without CO$_2$ atmosphere. However, the evaluation of durability is time and material consuming, usually requiring exhaustive electrolysis. Herein we suggest that one or few molecular layers of catalyst deposited on the electrode surface would dramatically reduce both the required amount of catalyst and time for durability tests, since the bulk of the solution no longer renew the catalyst produced on the electrode surface by diffusion.$^7$

Direct functionalization of the electrode surface by intact organometallic fragments can be realized by oxidation$^{35}$ or reduction$^{40}$ of a complex containing amino or diazonium groups, respectively. An alternative approach is to resort to a suitable polymer as solid support for Re catalysts. In such a case, the polymer must allow the transport of electrons from the electrode surface to the polymer-bound Re centres in contact with the solution. Thiophene and polythiophene have drawn a lot of attention for their high stability and good electron conducting properties.$^{41-45}$ Besides thiophene, 3'-substituted terthiophene, used as polymer backbone, shows some advantages,$^{46,47}$ such as less steric hindrance and higher conductivity.

In this work, bipyridines modified at 4-position with thiophene (T), 2,2':5',2''-terthiophene (TT) and 3'-ethynyl 2,2':5',2''-terthiophene (ETT) were synthesized, the corresponding new Re complexes (T)Re(CO)$_3$Cl (1), (TT)Re(CO)$_3$Cl (2) and (ETT)Re(CO)$_3$Cl (3) obtained (see Scheme 1), and their electrochemical behaviour in homogeneous solutions studied. We evaluated the catalytic properties of the electron-conducting polymer films. Complexes 2 and 3, bearing...
terthiophene units were successfully electropolymerized on the electrode surface by oxidation and their catalytic activity towards CO$_2$ reduction compared. We thought that the active metal centre in 2 could be hindered by the organic moiety during the polymerization process, so that 3 was synthesized in order to evaluate the effect of a C≡C triple bond (an electron-conducting rigid spacer) on the overall catalytic performance.

Results and Discussion

Homogeneous solution.

Fig. 1 shows the CVs of complexes 1-3 in acetonitrile under Ar and in saturated CO$_2$ solutions on Glassy Carbon Electrode (GCE). These CVs can be compared afterward with those of the corresponding heterogeneous phases (see below). The electrochemical behaviour of this class of complexes under inert atmosphere is well known. Normally, to a first reversible or quasi-reversible 1e ligand-centred reduction follows a second chemical irreversible reduction. Cl$^-$ can be released after both reductions. For all complexes, HOMO-1 orbitals are centred on the metal.

Chemical irreversible oxidations occur between 0.75 and 1.03 V (Table 1). These processes are expected to involve the thiophene moieties, inducing their polymerization on the electrode surface. We used DFT calculations to shed light on the nature of the redox processes.

For all complexes, HOMO-1 orbitals are centred on the metal. In the case of 1 the HOMO (involved in the oxidation) is mainly metal-centred, while in 2 and in 3 the HOMOs are centred on the thiophene moieties (Fig. S4). Thus, electro-polymerization after the first oxidation is expected to occur on 2 and 3, but not on 1, because in the latter complex the metal-centred oxidation avoids the thiophene activation towards the polymerization. Furthermore, a rough estimation of the redox potentials could be done by DFT methods, based on the calculation of the free energy with respect that of ferrocene. The overall agreement is reasonably good (Table 1), with the understandable exception of the oxidation peak potentials that are not reversible.

![Scheme 1. The synthesized ligands and complexes.](image)

![Figure 1. CV of complexes 1, 2 and 3 in MeCN.](image)

<table>
<thead>
<tr>
<th>Complex</th>
<th>$E_{1/2}$ 1$^{st}$ red.</th>
<th>$E_p$ 2$^{nd}$ red.</th>
<th>$E_s$ 1$^{st}$ ox.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-1.62 (-1.70)</td>
<td>-1.94</td>
<td>+1.03 (+1.02)</td>
</tr>
<tr>
<td>2</td>
<td>-1.67 (-1.64)</td>
<td>-1.98</td>
<td>+0.88 (+0.67)</td>
</tr>
<tr>
<td>3</td>
<td>-1.51 (-1.43)</td>
<td>-1.84</td>
<td>+0.75 (+0.58)</td>
</tr>
<tr>
<td>(bpy)Re(CO)$_3$Cl$_3$</td>
<td>-1.72 (-1.73)</td>
<td>-2.11</td>
<td>(+1.11)</td>
</tr>
<tr>
<td>(Bu-bpy)Re(CO)$_3$Cl$_3$</td>
<td>-1.83</td>
<td>-2.21</td>
<td></td>
</tr>
</tbody>
</table>

Please do not adjust margins
In a CO$_2$-saturated solution (~0.28 M), the current of the second reduction markedly increased, and its magnitude is related to the activity of the catalyst in the CO$_2$ reduction process. An electrochemical method to evaluate the homogeneous catalytic rate constant ($k$) from CV data has been proposed by Savéant and co-workers.$^{38,39}$ We adopted a similar method,$^{38,39}$ herein briefly reviewed. For a reversible electron-transfer process followed by a fast catalytic reaction, the catalytic current ($i_c$) is given by equation (1). The peak current ($i_p$) of a reversible electron transfer process with no following reactions can be expressed by the Randles-Sevčík equation (2). Thus, a very rough estimation of $k$ can be obtained by the $i_c$ to $i_p$ ratio (eq. 3),

$$i_c = nFA_{cat}\sqrt{Dk[Q]}$$

(1)

$$i_p = 0.4463 \cdot n^{1/2}FA_{cat}\sqrt{DFv/R}$$

(2)

$$i_c/i_p = \frac{1}{0.4463} \frac{RT}{nF} \sqrt{\frac{k[Q]}{v}}$$

(3)

where $n$ is the number of electrons involved in the catalyst reduction, $F$ the Faraday constant, $A$ the electrode area, $[cat]$ the catalyst concentration, $D$ the diffusion coefficient of the active catalyst, $[Q]$ the concentration of the substrate (in this case CO$_2$), $y$ the kinetic order of the reaction involving the substrate, and $v$ is the scan rate. Assuming a pseudo first order kinetic and a large concentration of the substrate in comparison with that of the catalyst, $y=1$.$^{17,28,29}$ We are aware that this is a very rough method for rate constants evaluation. However, the computed $k$ values for reduction of CO$_2$ (see Table 2) are comparable to those found for (bpy)Re(CO)$_3$Cl.$^{14,17,28,29}$

### Heterogeneous measurements

Upon thiophene-centred oxidation at a moderate positive potential (around 1 V, Table 1), the formation of a conductive film via electro-polymerization of the complexe is expected. The films deposited on the electrode surface were obtained going towards positive potentials by repeated CV scans (Fig. 2) at 0.2 V/s. The CV switching potentials are 0.1 V more positive than the peak potentials at 1.03, 0.88 and 0.75 V vs. Fc/Fc$^+$ for complexes 1, 2 and 3, respectively. The CV of a solution of 1 is almost unchanged after several cycles (Fig. 2a). As predicted by DFT calculations, the oxidation of 1 is metal-centred and does not involve the thiophene moiety, thus no film is formed. The CV of a solution of 2 (and 3) shows an increment of the anodic peak current at increasing number of CV cycles, indicating the formation and grow of a polymer. A new oxidation peak, assigned to a redox process of the polymer,$^{27,47,57}$ appears at less positive potentials.

After the polymerization of 2 (and 3), the modified electrode was washed with CH$_3$CN and sonicated for 3 min to release unbounded molecules. Both surface-bounded polymers produced from solutions of 2 and 3 appear to be rather stable, since they do not change their electrochemical properties even after 12h in acetonitrile. CVs of the modified electrodes in solutions containing the supporting electrolyte only, and the homogeneous solutions show quite similar responses.

### Table 2. Catalytic current measured at –2.16 V and corresponding computed $k$ and TOF values.

<table>
<thead>
<tr>
<th>Complex</th>
<th>$i_c/i_p$</th>
<th>$k$ (M$^{-1}$ s$^{-1}$)</th>
<th>TOF (s$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>6.0</td>
<td>398.3</td>
<td>111.5</td>
</tr>
<tr>
<td>2</td>
<td>4.5</td>
<td>259.6</td>
<td>62.7</td>
</tr>
<tr>
<td>3</td>
<td>7.8</td>
<td>673.9</td>
<td>188.7</td>
</tr>
</tbody>
</table>

*This journal is © The Royal Society of Chemistry 20xx J. Name., 2013, 00, 1-3 | 3*
Compound 2 and 3 behave in a similar way, so the rest of the discussion will be focused on the electro-polymerized film obtained from complex 2 with five CV oxidation cycles (see SI for 3).

The GCE functionalized with 2 by this method shows at the first CV cycle three peaks, two reductions and one reoxidation, at –1.70 V, –2.00 V and –1.65 respectively (Fig. 3). These values are approximately the same as those observed in the corresponding homogeneous solutions. The first reduction peak, not discussed in the former works, vanished in the following cycles, and probably is associated either to the release of Cl\textsuperscript{–}, or to the neutralization of the polymer film after its electro-oxidation. The small cathodic peak around –1.2 V is assigned to trapped charges in the layer, or to the corresponding cationic complex in which Cl\textsuperscript{–} is replaced by MeCN\textsuperscript{56,57}.

From the second/third CV cycle, the surface-modified electrode reach a steady state, showing a stable and broad peak (green curve in Fig. 3). At higher CV scan rates two reversible processes (at –1.70 and –2.05 V) become evident (Fig. 4; note the same values of cathodic and anodic peaks due to the absence of diffusion). Apparently, the surface-modified electrode not only retains a very similar electrochemical behaviour of the corresponding homogeneous solution, but it seems more reversible, probably due to the effect of immobilization. Similar stabilization effect has been already observed in the case of vinylterpyridinyl complex of cobalt.\textsuperscript{58}

Actually, the plot of peak current versus the CV scan rate is linear (Fig. 5), strongly suggesting that the redox process is no longer diffusion controlled, but it is associated to a bound species on the electrode surface. Dahms\textsuperscript{59} and Ruff\textsuperscript{60,62} showed that the diffusion coefficient in polymeric films has two main contributions, one arising from the physical diffusion of the species and a second due to electron self-exchange. However, in modified electrodes the latter term should be dominant. Since the thickness of the film in our case is very thin, the CV should be as that of an adsorbed species on the electrode surface, with the peak current given by:\textsuperscript{53}

\begin{align}
  i_p &= \frac{n^2 F^2 \nu AT}{4RT} \Gamma \quad \text{(a)} \\
  i_p &= \frac{\alpha F^2}{2.718RT} \nu AT \Gamma \quad \text{(b)}
\end{align}

for a reversible (a) or irreversible (b) chemical reaction. \( \Gamma \) is the surface coverage, i.e. the number of molecules bound to the surface, and \( \nu \) is the CV scan rate. The apparent area of the electrode \( A \) was estimated to be 6.24 mm\textsuperscript{2} by chronocompartmentometric measurements of a ferrocene solution at known concentration, in a similar way as previously described.\textsuperscript{35} We will use this value thoroughly. From the slope of the linear regression of \( i_p \) vs. \( \nu \), \( \Gamma \) values of 4.6×10\textsuperscript{-10} and 6.2×10\textsuperscript{-10} mol cm\textsuperscript{2} for the reversible and irreversible cases, respectively, can be roughly estimated. This surface coverage is slightly larger, but of the same order of magnitude (3.43×10\textsuperscript{-10} mol cm\textsuperscript{2}), than that observed for a monolayer of organometallic derivative of similar dimensions.\textsuperscript{35} Thus, these data suggest that a preparative five CV oxidation cycles at 0.2 V/s creates few film layers on the electrode surface.

\( \Gamma \) could be assessed\textsuperscript{35,64} also by means of the formula \( \Gamma=Q/FA \), where \( Q \) is the charge that reduces or oxidizes the organometallic complexes on the electrode surface, evaluated by integration of the background-corrected CV response. \( \Gamma \)

![Figure 3](image-url) First and steady state CVs of the electrode modified with complex 2 at scan rate 0.2 V/s, with \( \Gamma = 7.74 \times 10^{-10} \) mol/cm\textsuperscript{2}.

![Figure 4](image-url) CVs (scan rate 2.0 V/s) of the steady-state electrode modified by complex 2, with \( \Gamma = 7.74 \times 10^{-10} \) mol/cm\textsuperscript{2}. 

\[ y = 24.69 x - 2.712 \quad R^2 = 0.99947 \]

\[ y = -28.85 x - 8.866 \quad R^2 = 0.99031 \]
value computed on the CV performed at 0.2 V/s gave $7.74 \times 10^{-10}$ mol/cm$^2$, which is in reasonable good agreement with the above $\Gamma$ value estimated from the peak current vs. scan rate. Following the same experimental procedure, a series of modified electrodes were prepared by applying an increasing number of CV oxidation cycles. In this case the formation of multilayers and the random polymerization process does not allow a precise evaluation of the catalyst distribution on the surface. However, the measure of the total charge $Q$ allows guessing the amount of the deposited reducible organometallic complex (either on the surface or embedded in the polymeric structure). As expected, the amount of the Re electro-active species deposited on the electrode surface increases by increasing the number of CV cycles (Table 3). For example, after fifteen CV oxidation cycles the electrode surface holds $35.30 \times 10^{-10}$ mol cm$^{-2}$ of electro-active catalyst. CV of the modified electrode shows in saturated CO$_2$ solutions a dramatic enhancement of the catalytic current. It increases by increasing the number of CV cycles used for functionalization (Table 3); instead, the $i_c/i_p$ ratio decreases. This is reasonable since only the Re centres on the surface are in direct contact with the solution, and thus able to fully act as catalyst. In particular, the electrode obtained after 15 CV oxidation cycles ($\Gamma = 35.30 \times 10^{-10}$ mol cm$^{-2}$), shows in saturated CO$_2$ solutions a catalytic current 93.2 times higher than that measured under Ar (Fig. 6). Similar results are obtained for 3, where the $i_c/i_p$ ratio is about 89 (Fig. S6).

However, we observed a current decrease during the subsequent CV cycles (Fig. 7), and after hundred CV cycles, almost no catalytic current is observed. Slightly worse results were obtained for 3 (Fig. S6), where the catalyst was completely deactivated after sixty CV cycles. This is the opposite of the expected effect. Since the alkyne unit in 3 usually does not interrupt the molecular electronic communication, probably the rigid C≡C spacer either reacts with CO$_2$ or push away the metal centre from the solid polymer towards the solution, making its behaviour and stability more similar to a situation of the homogeneous solution where less stability is observed.

To shed light on the mechanism of surface catalyst depletion, we prepared another electrode functionalized with 2 (five CV cycles), and tested its stability at constant potentials under CO$_2$. With an applied potential of $-2.1$ V vs. Fc (Fig. 8) the modified electrode shows an initial high current which slowly decreases, and in 75 min the catalytic activity on the surface is totally lost. This value is very similar to the lifetime that can be extrapolated from the 100 CV cycles above outlined, and similar also to that obtained from the exhaustive electrolysis of a homogeneous solution of (bpy)Re(CO)$_3$Cl in the same conditions. If one consider that few molecular layers of catalyst have the same lifetime of a whole homogeneous solution with a much higher amount of catalyst (continuously renewed by diffusion), these results strongly suggest that functionalization of the electrode surface greatly enhances the catalyst stability during CO$_2$ electrochemical reduction.

GC measurements.

We collected Gas Chromatographic data with the aim to evaluate the amount of CO and H$_2$ produced during exhaustive electrolysis. Our experimental setup consists in applying a potential of $-2.10$ V vs. Fc/Fc$^+$ with a CO$_2$ constant flow of 40
Figure 8. Chronoamperometry of electrode functionalized by complex 2 under Ar and CO$_2$ with $\Gamma = 9.55 \times 10^{-10}$ mol/cm$^2$.

ml/min, and sampling the gas in the electrochemical cell at regular intervals for 60 min. At non-modified GCE and in homogeneous solutions, complexes 1, 2, and 3 show different degree of selectivity towards CO with a CO/H$_2$ ratio of 44, 11 and 8, respectively. The faradic efficiencies $\eta_{\text{CO}}$ are 97.5%, 35.4% and 46.4%, while TON$_{\text{CO}}$ after 60 min are 3.8, 1.7 and 3.9 for the complexes 1, 2 and 3, respectively (Table 4). These values are worse than the Lehn’s catalyst (bpy)Re(CO)$_3$Cl in the same conditions. Another unexpected feature of the homogeneous solution is that all the catalysts apparently suffer of rapid deactivation in relative short time.

However, if after 60 min the GCE is sonicated, the catalytic current is reactivated. Moreover, compounds 2 and 3 have a low $\eta_{\text{CO}}$. We suppose that the products of CO$_2$ reduction and thiophene units, especially for 2 and 3, might interact with GCE and undergo in long time scale physical adsorption, altering the nature of the catalytic specie. The absorption on the surface of these reaction products probably reduce $\eta_{\text{CO}}$ and the apparent catalyst lifetimes. The variation of $\eta_{\text{CO}}$ during the exhaustive electrolysis is particular evident for complex 3 (see Fig. S7). We cannot exclude, also, that chemical reactions with CO$_2$ occur at thiophene moiety, or at the C≡C triple bond of 3 where the contributions of sp carbon atoms to the LUMO appear to be relevant (Fig. S4).

On the other hand, TON$_{\text{CO}}$ of the electrodes modified with 2 and 3 show significant improvements (Table 4). Surprisingly,

**Table 4. Comparison of selected modified electrode performances (obtained from the corresponding monomers) for catalytic CO$_2$ electrochemical reductions in MeCN solutions (0.1 M TBAPF$_6$).** Potentials are in V vs. Fc/Fc$^+$. 

<table>
<thead>
<tr>
<th>Monomer</th>
<th>E (V)</th>
<th>$\eta_{\text{CO}}$ (%)</th>
<th>TON$_{\text{CO}}$</th>
<th>Time (min)</th>
<th>Ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (GCE in solution)</td>
<td>$-2.23$</td>
<td>98</td>
<td>118</td>
<td>120</td>
<td>11</td>
</tr>
<tr>
<td>2 (GCE in solution)</td>
<td>$-2.23$</td>
<td>2</td>
<td>120</td>
<td>11</td>
<td></td>
</tr>
<tr>
<td>2</td>
<td>$-1.98$</td>
<td>15.4</td>
<td>155</td>
<td>120</td>
<td>14</td>
</tr>
<tr>
<td>3 (GCE in solution)</td>
<td>$-2.23$</td>
<td>69</td>
<td>34</td>
<td>120</td>
<td>13</td>
</tr>
<tr>
<td>3</td>
<td>$-2.23$</td>
<td>33</td>
<td>60</td>
<td>25</td>
<td></td>
</tr>
</tbody>
</table>

a) coated with Nafion membrane; b) $\eta_{\text{H}_2}$; c) calculated from the corresponding reference; d) 0.1 M TBAPF$_6$/TBAClO$_4$ as electrolyte; e) Phosphate aqueous buffer (pH=7); f) TON$_{\text{HCOOH}}$ g) R=phenylethynyl
GCE modified with 2 has a much higher \( \eta_{\text{CO}} \) (84.7\%) than its homogeneous solution counterpart (35.4\%), whereas \( \eta_{\text{CO}} \) of 3 is almost unvaried. It is interesting to note that both electrodes modified with monomer containing C≡C triple bond, 5,5’-bis-(phenylethynyl)-2,2’-bipyridine and 3, shows low similar \( \eta_{\text{CO}} \) values. It should be mentioned that in only 10 minutes of the catalytic activity of our surface-modified GCE with 2 and 3, the overall TON\(_{\text{CO}}\) of 201 and 288 are already achieved, respectively. The final TON\(_{\text{CO}}\) of 489 and 519 of complexes 2 and 3 for 40 min, are among the best values reported in the literature for analogues surface-modified electrodes.

**Conclusions**

We reported novel bipyridine ligands carrying thiophene (T), 2,2’:5’,2’’-terthiophene (TT) and 3’-ethynyl 2,2’:5’,2’’-terthiophene (ETT), and synthesized their corresponding tricarbonyl chlororhenium complexes. Their electrochemical oxidation on GCE allows depositing stable electron conducting films that carry rhenium complexes. These chemical modified electrodes were used to investigate the electrocatalytic reduction of CO\(_2\). This approach may represent an alternative pathway to support the desired intact organometallic catalyst on an electrode surface.

A relative comparison outlines that activity and lifetime of the solid-supported catalysts are greatly enhanced with respect the corresponding homogeneous counterparts. A rough estimation of the TOFs (both in homogeneous and in heterogeneous phase) and their lifetimes can be obtained by CVs and repeated CV scans or by chronoamperometric measurements, respectively. Electro-polymerized (TT)Re(CO)\(_3\)Cl (2) and (ETT)Re(CO)\(_3\)Cl (3) show a relative higher stability towards their reduction than the corresponding homogeneous solutions, similarly as observed for a vinyterpyridinyl complex of cobalt.\(^{29}\) This suggests that the proximity with the surface may protect the active form of the catalysts against its decomposition, which is higher in homogeneous solution. The film of 3 is slightly less stable than that of 2, while their catalytic activities are almost equivalent. A change of selectivity is observed for 3, apparently due to the C≡C triple bond. Thus, this observation may suggests that either the reduced ethynyl group reacts with CO\(_2\) and/or pushes the rhenium center of the electro-polymerized 3 towards the solution, making it more exposed to the effect of the solution. Unfortunately our attempts to use the OTTLE spectroelectrochemical cell to investigate the deactivation process did not resulted in any useful data, probably because Pt-S interactions on the Pt minigrid electrode.

Larger film thickness gave higher catalytic current, but lower \( i_{\text{L}}/i_{\text{R}} \) ratio, suggesting that only the rhenium metal centres on the top of the electrodeposited polymer surface are catalytically active. Although no final conclusions can be extrapolated from the data reported in Table 4, it seems that the insertion of functional groups like CO\(_2\) or C≡C decreases the selectivity of CO\(_2\) reduction to CO, probably because increased local electron density and hence localized reactivity towards the weak electrophile CO\(_2\). This observation should be taken in account for the design of new generation of electrode-modified catalysts, where the electron conduction properties of the employed polymers appear to be somewhat beneficial, but it should be carefully selected. Finally, the applied potential for the reduction of CO\(_2\) to CO for 2 and 3 in acetonitrile is comparable with other monomers reported in Table 4 (between \(-1.9\) and \(-2.2\) V vs. Fe\(^{0/+}\)), being those typical of Re(bpy)-type 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. All reactions were performed under inert atmosphere. Microwave (MW) reactions were carried out in single-mode Biotage Initiator 2.5. Column chromatography was done on a Biotage Isolera flash purification system. Mass spectra were recorded with an XCT PLUS electrospray ionization ion trap (ESIT) mass spectrometer (Agilent Italy, Milan). Samples were dissolved in methanol. The samples for microanalyses were dried under vacuum to constant weight (25 °C, ca. 0.1 torr). Elemental analyses (C, H, N, S) were performed in-house with a Fisons 1108 CHNS-O elemental analyzer. Infrared spectra were recorded as powder ATR with a Bruker Equinox 55 FTIR spectrophotometer with a resolution of 1 cm\(^{-1}\) and an accumulation of 64 scans. NMR spectra were recorded with a Bruker Avance 200 and a JEOL EX 400 spectrometer (1H operating frequency 400 MHz) at 298 K. \(^1\)H chemical shifts are relative to TMS (δ = 0 ppm) and referenced against solvent residual peaks. Electrochemical experiments were carried out in freshly distilled acetonitrile with TBAPF\(_6\) 0.1 M as supporting electrolyte, in the usual conditions employing an Autolab PGSTAT302N electrochemical analyzer controlled by a PC. A pure silver wire was used as pseudo reference, platinum wire as counter electrode and Glassy Carbon Electrode (GCE) as working electrode. Under our experimental conditions, all the potential are shown versus the half-wave potential of the ferrocene redox couple (Fc/Fc\(^+\)). The ferrocene diffusion coefficient is taken from the literature: \( D_{\text{Fc}} = \) 2.24×10\(^{-5}\) cm\(^2\)/s.\(^{66, 67}\)

**Computational Details**

All calculations were performed using Gaussian 09 Rev. D.01\(^{68}\) adopting the DFT method, including the solvent effect by the conductor-like polarizable continuum model (CPCM)\(^{69, 70}\) with acetonitrile as solvent. Geometry optimizations were carried out without any constraints by using the B3LYP functional\(^{71, 72}\) employing the optimized def2svp basis set\(^{73, 74}\) with the D3 version of Grimme’s dispersion and applying the Becke-Johnson damping scheme.\(^{75}\) Thermal correction to Gibbs Free Energy has been applied with a scale factor of 0.962 to the IR frequency to take in account the anisotropy. For radical anions, unrestricted Kohn–Sham formalism (UKS) was adopted. The
nature of all stationary points were confirmed by normal-mode analysis (no imaginary frequencies were found). DFT calculation of redox potentials were performed applying the literature method\textsuperscript{51,52,76} that consists in computing the Gibbs free energy in solution of both the oxidized and reduced species with respect that of the reference compound ferrocene.

**Syntheses**

More details and scheme of the syntheses of the organic ligands T, TT and ETT are reported in the ESI material.

**4-(thiophen-3-yl)-2,2'-bipyridine (T):** To 20 ml of DME, previously purged with argon, 4-Bromo-2,2'-bipyridine (0.5 g, 2.13 mmol) and Pd(PPPh\textsubscript{3})\textsubscript{4} (0.246 g, 0.213 mmol, 0.1 eq) were added and further purged with argon for 10 min. Boronic acid (0.299 g, 0.234 mmol, 1.1 eq) was added and purged for 5 min, after which a Na\textsubscript{2}CO\textsubscript{3} solution (2 M, 8.51 mmol, 4 eq) was added and purged for 10 min. The mixture was reacted under MW irradiation for 30 min, filtered to remove the solid and evaporated under reduced pressure. Water was added (10 ml) and the crude product mixture was extracted with diethyl ether (3×10 ml). The organic phase was dried over Na\textsubscript{2}SO\textsubscript{4}, filtered and evaporated under reduced pressure. The product was purified by medium pressure flash chromatography (Biotage) on a 50 g column, with petroleum ether: ethyl acetate (80:20 + 0.05% triethylamine (TEA) as additive. Yield: 80%. 1H NMR (400 MHz, ppm, acetone-d\textsubscript{6}): 8.77 (dd, J=1.8, 0.6 Hz, 1H), 8.71 (dq, J=4.7, 0.9 Hz, 1H), 8.68 (dd, J=5.0, 0.6 Hz, 1H), 8.51 (dt, J=8.2, 1.0 Hz, 1H), 8.16 (dd, J=2.9, 1.5 Hz, 1H), 7.94 (td, J=7.9, 1.8 Hz, 1H), 7.75-7.72 (m, 2H), 7.70-7.68 (m, 1H), 7.42-7.45 (m, 1H). LC-MS (ESI\textsuperscript{+}) calcd. for C\textsubscript{37}H\textsubscript{32}N\textsubscript{8}S\textsubscript{4}[M+H\textsuperscript{+}]: 429.06, found 429.25.

**[2,2':5',2''-terthiophen]-3'-ylboronic acid (TTB, 7, see ESI).** In a Schlenk 20 ml round bottom flask, a solution of 3'-bromotertiophenene (0.668 g, 2.04 mmol) and trimethylborate (0.276g, 0.296 ml, 2.65 mmol) in 8 ml THF was treated with n-BuLi (1.6M in hexanes, 1.658 ml, 2.65 mmol) at –78°C over a period of 20 minutes. The resulting solution was stirred at –78°C for an hour. The solution was then warmed up to –20°C in 1h, quenched slowly using 2N HCl (1.326 ml, 2.65 mmol) and then stirred for 4 h. 2,2'':5',2''-terthiophen-3'-ylboronic acid (TTB, 7) was precipitated out as a white solid, washed with water and dried under reduced pressure. The crude TTB was directly used for the next step.

**4-[(2,2':5',2''-terthiophen)-3'-yl]-2,2'-bipyridine (TT).** To a degassed solution of 4-bromo-2,2'-bipyridine (0.1772 g, 0.431 mol, 0.9 eq) and Pd(PPPh\textsubscript{3})\textsubscript{4} (55 mg, 0.1284 mmol) in dimethoxyethane (5 ml) 7 ml of a solution of TTB (7) (0.140 g, 0.479 mmol, 1 eq) in dimethoxyethane was added. The reaction mixture was heated at 120 °C for 30 min under MW irradiation. The reaction was controlled by TLC (dichloromethane: ethyl acetate 4:6 + TEA 0.1%) (Rf = 0.26). When the starting material was fully consumed, the solvent was removed at low pressure. Water (5 ml) was added and the product was extracted with ethyl acetate (5×5 ml). The organic phases were collected, dried over Na\textsubscript{2}SO\textsubscript{4}, and filtered.
oxidative cycles starting from the solution of complex experiments with alumina nanopowder, functionalized by CV GCE was carefully polished and cleaned every were dissolved in as many solutions for catalytic test. The column. A thermal conductivity detector was used for CO and analyzed with an Agilent 490 Micro GC gas chromatograph integration of CVs), respectively. The gas sample produced was (2.55 cm high surface area and fast electrochemical conversion, a sampled for 90 s to wash and fill the Micro GC 10 μL sample temperature of 90 °C and at a pressure of 200 kPa. The carrier the analyses. It was possible to determine the amounts of CO concentrations of CO and H ClaindHyGen hydrogen generator. The detection limit s for CO (This journal is © The Royal Society of Chemistry 20xx GC Measurements

The airtight electrochemical cell was equipped with a bubbler that maintained the inner atmosphere but avoided gas overpressure. A Smart Trak 100 (Sierra) mass flow controller C100L was used to measure and control the CO flow during exhaustive electrolysis experiments. A constant CO flow (40 mL min –1 ) was maintained during bulk electrolysis. To ensure high surface area and fast electrochemical conversion, a cylindrical rod (ϕ = 5 mm, length 15 mm) of large surface area (2.55 cm2) was used as GCE. Bulk electrolysis of complex 1, 2 and 3 (4.6, 1.9 and 1.0 μmol in 5 mL of acetonitrile, respectively) were dissolved in as many solutions for catalytic tests. The same GCE was carefully polished and cleaned every experiment with alumina nanopowder, functionalized by 5 CV oxidative cycles starting from the solution of complex 2 and 3, resulting in 21x10 15 and 11x10 15 mol (evaluated by charge integration of CVs), respectively. The gas sample produced was analyzed with an Agilent 490 Micro GC gas chromatograph equipped with a Molsieve column (5 Å) and a CP-Pora PLOT U column. A thermal conductivity detector was used for CO and H2 quantification and the Molsieve column (5 Å) was kept at a temperature of 90 °C and at a pressure of 200 kPa. The carrier gas was argon. The gas inside the measurement cell was sampled for 90 s to wash and fill the Micro GC 10 μL sample loop, and eventually 500 mL were injected into each column for the analyses. It was possible to determine the amounts of CO and H2 produced during the experiment from the concentrations of CO and H2 in the gas samples and knowledge of the gas flow and the cell volume. For the functioning and the calibration of the GC apparatus, Ar, He, N2, O2, CO2 and CO were obtained from Sapios, whereas H2 was produced by a ClaimHyGen hydrogen generator. The detection limits for CO and H2 were 20 and 0.5 ppm (v/v), respectively.

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Notes and references

Synopsis
Electrocatalytic CO₂ reduction at film produced by electropolymerization of thiophene-Re complexes. Three novel thiophene substituted bipyridine ligands and their complexes of rhenium were synthesized and tested for electrochemical CO₂ reduction. Oxidative electropolymerization on GCE gave functionalized electrodes, bearing a combined conductive (polymerized thiophene) and catalytic (Re complexes) parts, showing significant catalytic activity for CO₂ reduction, and a relative higher stability when compared with homogeneous solution counterparts.

Table of Contents Graphics