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## Highly-selective electrocatalytic reduction of CO<sub>2</sub> in neutral water by a C-functionalized Ni-cyclam complex grafted onto carbon

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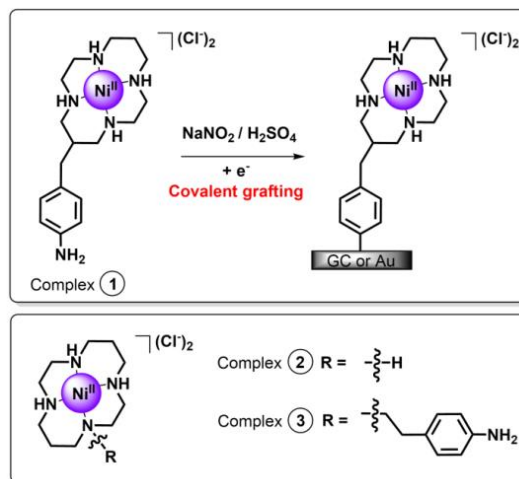
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**We present here a novel strategy based on the C-functionalization of the well-known Ni-cyclam complex to afford heterogeneous electrocatalytic CO<sub>2</sub> reduction in neutral water at low overpotential (-1.2 V vs. Ag/AgCl), with high turnover number (TON = 564), high selectivity (85 % CO produced) and good faradic efficiency (56% for CO<sub>2</sub> to CO conversion).**

The continuous growing of carbon dioxide content in atmospheric and marine media has become one of the main human's concerns for the last years, due to the environmental and societal consequences associated with the greenhouse effect. Hence, cheap and environment-friendly catalytic devices, which can effectively and selectively reduce CO<sub>2</sub> into industrial feedstocks (CO, HCO<sub>2</sub>H, CH<sub>3</sub>OH) are highly sought.<sup>1-4</sup> So far, many metal-based molecular catalysts have been developed for more than thirty years as both homogenous and heterogeneous catalysts.<sup>5-7</sup> Nevertheless, activation of CO<sub>2</sub> by molecular-based heterogeneous catalysts has remained less investigated, despite being very challenging. One main reason is the difficulty to design a catalyst, which displays a sufficiently low overpotential value, such that it does not deactivate upon CO<sub>2</sub> reduction in aqueous media. Moreover, the heterogeneous catalyst must be selective, not only against the hydrogen evolution reaction, but also against the formation of various CO<sub>2</sub>-related by-products. Several recent works have shown the possible immobilization of metal-based catalysts onto various surfaces.<sup>7, 8</sup> Inspired by the seminal works of Sauvage *et al.* on Ni-cyclam complexes (cyclam = 1,4,8,11-tetraazacyclotetradecane),<sup>9-11</sup> Neri *et al.* have attached these derivatives onto TiO<sub>2</sub> nanoparticles.<sup>12</sup> More recently, Kubiak *et al.* reported the grafting of *N*-alkynyl-terminated Ni<sup>II</sup> cyclam complexes onto glassy carbon (GC) surfaces,<sup>13</sup> whereas Fontecave and co-workers described the electrocatalytic CO<sub>2</sub> reduction by *N*-functionalized Ni cyclam complexes immobilized onto multi-walled carbon nanotubes (MWCNTs).<sup>14</sup>

Considering this, we found interesting to develop devices based on the Ni-cyclam complex, since it is an effective and selective catalyst for CO<sub>2</sub> reduction, which would display all the following features: (i) covalent grafting of the electrode surface to stabilize the catalyst; (ii) C-functionalization (meaning *via* a carbon atom of the macrocyclic skeleton)<sup>15</sup> of the anchoring group on the cyclam for a better control of the metal-ion coordination sphere; (iii) easy procedure of immobilization involving soft conditions. For such purpose, we have based our device on a newly synthesized cyclam ligand which is functionalized by a 4-aminobenzyl (BnNH<sub>2</sub>) group in a β-C position of the macrocycle, as shown in Scheme 1 (complex 1).<sup>16-18</sup> In suitable conditions, the aromatic group can be converted into a diazonium moiety, which itself can be electrochemically reduced to allow covalent binding.<sup>19-21</sup> This procedure was previously reported for the direct grafting of *N*-functionalized cyclam ligands.<sup>22</sup>



**Scheme 1** Covalent grafting of complex **1** onto Au or GC electrode (top) and chemical representation of complexes **2** and **3** (bottom).

**Table 1** Spectroscopic and electrochemical data for complexes **1**, **2** and **3**.

	<b>1</b>	<b>2</b>	<b>3</b>
$\lambda_{\text{max}}/\text{nm}$ ( $\epsilon_{\text{max}}/\text{M}^{-1}\text{cm}^{-1}$ )	439 (22) <sup>a</sup>	450 (36) <sup>a</sup>	461 (13) <sup>a</sup>
$E_{1/2}(\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}})/\text{V}$ ( $\Delta E_p/\text{mV}$ )	-1.41 (100) <sup>b</sup>	-1.40 (100) <sup>b</sup>	-1.30 (100) <sup>b</sup>
$E_{1/2}(\text{Ni}^{\text{III}}/\text{Ni}^{\text{I}})/\text{V}$ ( $\Delta E_p/\text{mV}$ )	0.67 <sup>b,c</sup>	0.78 (140) <sup>b</sup>	0.89 <sup>b,c</sup>
$j_{\text{pc}}(\text{CO}_2)/j_{\text{pc}}(\text{Ar})$	3.3 <sup>d</sup>	3.4 <sup>d</sup>	2.1 <sup>d</sup>

<sup>a</sup> In H<sub>2</sub>O. <sup>b</sup> In H<sub>2</sub>O:CH<sub>3</sub>CN (1:4)/NBu<sub>4</sub>PF<sub>6</sub> 0.1 M,  $E/\text{V}$  vs. Ag/AgCl/NaCl 3M. <sup>c</sup> Irreversible anodic peak. <sup>d</sup> Determined from the ratio of peak current densities under CO<sub>2</sub> and Ar from CVs obtained in H<sub>2</sub>O:CH<sub>3</sub>CN (1:4)/NBu<sub>4</sub>PF<sub>6</sub> 0.1 M ( $\nu = 0.1\text{ V}\cdot\text{s}^{-1}$ ,  $C = 1\text{ mM}$ ) (see Fig. S10).

The C-functionalized *p*-H<sub>2</sub>N-Bn-cyclam was synthesized through one-step reaction<sup>23, 24</sup> starting from the previously-reported di-*N*-benzylcyclam-BnNO<sub>2</sub> compound<sup>25</sup> (Ligand **L1**, Scheme S1 and details in ESI). The new *N*-functionalized analogue *N*-(*p*-H<sub>2</sub>N-Ph-(CH<sub>2</sub>)<sub>2</sub>)-cyclam was prepared from cyclamPO<sup>26</sup> (Ligand **L3**, Scheme S2). The complex **1** was then synthesized from the stoichiometric reaction between NiCl<sub>2</sub> and the ligand (see SI for details). The resulting beige-brown solid was analyzed by UV-Vis spectroscopy, high-resolution mass spectrometry, and cyclic voltammetry (CV) (Fig.s S11, S14-S17). Spectroscopic and electrochemical data are gathered in Table 1 and compared to those obtained from the parent complex [Ni(cyclam)]Cl<sub>2</sub> (**2**) and the *N*-functionalized analogue (**3**) in the same conditions (Scheme 1). For all complexes, UV-Vis data are consistent with a Ni(II) complex in a square planar geometry featuring a weak absorption d-d band in the 430-460 nm wavelength range.<sup>27</sup> CV of **1** at a GC electrode ( $\nu = 0.1\text{ V}\cdot\text{s}^{-1}$ ) displayed a diffusion-controlled reversible system at  $E_{1/2} = -1.41\text{ V}$  vs. Ag/AgCl in H<sub>2</sub>O/CH<sub>3</sub>CN (1:4) as well as an irreversible oxidation peak at  $E_{\text{pc}} = 0.67\text{ V}$  (Fig.s S15 and S17). These processes are ascribed to the Ni<sup>III</sup>/Ni<sup>II</sup> and Ni<sup>II</sup>/Ni<sup>I</sup> redox couples, respectively, by analogy with complex **2** and from previous studies.<sup>12, 13, 28</sup> When the solution was saturated with CO<sub>2</sub>, a significant increase of the current density was observed for **1**, as shown by the ratio  $j_{\text{pc}}(\text{CO}_2)/j_{\text{pc}}(\text{Ar}) = 3.3$  (Table 1), consistent with an electrocatalytic reduction of CO<sub>2</sub> by the complex **1** (Fig. S16-A). For comparison (Table 1), the complex **2** displayed a similar enhancement of the current density (Fig. S16-B) under the same experimental conditions, whereas it was found to be smaller for **3** (Fig. S16-C).

The grafting of the complex **1** onto gold or glassy carbon electrodes was carried out by *in-situ* generation of the aryl-diazonium moiety from the reaction of complex **1** with sodium nitrite (1.1 equiv.) in diluted acid.<sup>22</sup> XPS analysis of Au wafers functionalized with **1** displayed signals at 400 eV, 855 eV and 872 eV, corresponding to Ni(1s), Ni(2p<sub>3/2</sub>) and Ni(2p<sub>1/2</sub>) respectively, whereas bare Au surfaces yielded no signal (Fig. S18-A). Moreover, the presence of the Ni-cyclam complex on the surface was confirmed by the relative atomic percentage of Ni(2p) (1.6%) vs. N(1s) (8%) (Fig. S18-B). Redox properties of complex **1** grafted onto a glassy carbon electrode (GC-1) were obtained from voltammetric studies in H<sub>2</sub>O/CH<sub>3</sub>CN (1:4) / NBu<sub>4</sub>PF<sub>6</sub> 0.1 M. Under Ar, GC-1 displayed one reversible system upon oxidation at  $E_{1/2} = 0.58\text{ V}$  vs. Ag/AgCl.

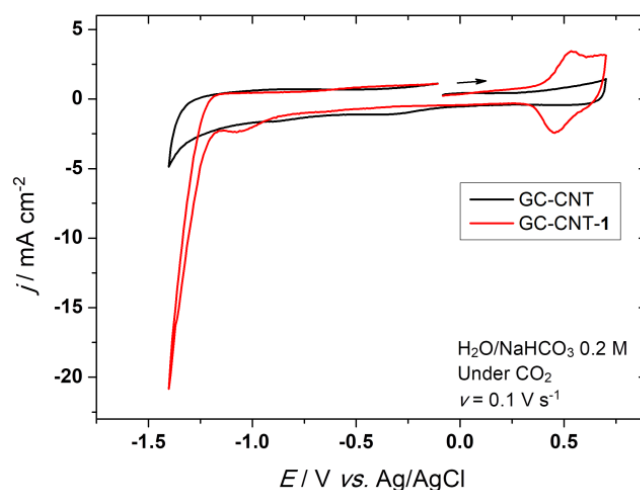


Fig. 1 CVs ( $\nu = 0.1 \text{ V}\cdot\text{s}^{-1}$ ) under  $\text{CO}_2$  of GC-CNT-1 (red) and GC-CNT (black) electrodes in  $\text{NaHCO}_3/\text{H}_2\text{O}$  (pH = 6.8).

Increasing the scan rate ( $0.02 \text{ V}\cdot\text{s}^{-1} < \nu < 5 \text{ V}\cdot\text{s}^{-1}$ ) induced a linear variation of the peak current density  $j$  (Fig. S20-A), in agreement with the expected response for a surface-bound species.<sup>29, 30</sup> Plots of anodic current density  $j_{\text{pa}}$  vs.  $\nu$  (inset, Fig. S20-A) allowed the direct determination of the surface concentration assuming a one-electron oxidation.<sup>29</sup> The resulting value,  $\Gamma = 0.8 \cdot 10^{-10} \text{ mol}\cdot\text{cm}^{-2}$ , is consistent with the grafting of one monolayer of Ni complex on the surface, supposing a compact rearrangement of  $11 \text{ \AA} \times 7 \text{ \AA}$  ellipsoids.<sup>31</sup> Plots of peak potential ( $E_{\text{pa}}$  and  $E_{\text{pc}}$ ) vs.  $\log \nu$  for the GC-1 electrode allowed the determination of the standard electron transfer rate constant  $k^0$  by using Laviron's formalism for non-interacting redox centers (Fig. S22).<sup>32</sup> We found that  $k^0 = 33 \text{ s}^{-1}$ , which indicates a relatively fast electron transfer by comparison with existing data on analogous grafted complexes.<sup>31, 33</sup> Voltammetric studies under  $\text{CO}_2$  showed a significant increase of the current density at  $-1.4 \text{ V}$  by comparison with an unmodified GC electrode (Fig. S20-B). Such a behavior evidences that  $\text{CO}_2$  reduction is mediated by the reduced form of the grafted complex **1**, in agreement with solution studies (*vide infra*, Fig. S16). The same current enhancement was observed in water at neutral pH (Fig. S21).

In order to increase the number of Ni complexes on the electrode surface for further analysis of the products of the electrocatalytic reaction, we modified the GC surface with MWCNTs prior to Ni-cyclam grafting (see SI for details). The diazonium immobilization of **1** and **3** was then carried out according to the procedure used for GC-1. The resulting electrodes (GC-CNT-1 and GC-CNT-3) were analyzed by CV in water at neutral pH. As shown in Fig. 1 for GC-CNT-1 (red curve), the  $\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}$  redox process was clearly detected upon oxidation, hence evidencing the effective covalent grafting of the complex on MWCNTs. Integration of the peaks for this redox system allowed the determination of the surface concentration ( $1.6 \cdot 10^{-9} \text{ mol}\cdot\text{cm}^{-2}$ ), hence showing a 200-fold increase of the current density compared to GC-1. In reduction, an intense Faradaic signal starting at  $-1.2 \text{ V}$  was obtained compared to that obtained with a GC-CNT modified electrode. The cathodic wave found for GC-CNT-1 under  $\text{CO}_2$  disappeared when CV was performed under argon at neutral pH (Fig. S23). This result clearly evidenced that the catalytic wave under  $\text{CO}_2$  is fully correlated to carbon dioxide rather than proton reduction. Similarly, the *N*-functionalized GC-CNT-3 displayed a current enhancement under  $\text{CO}_2$  as in the homogeneous case (Fig. S24). The stability of the grafted complexes was then examined by CV. Upon cycling at  $\nu = 0.1 \text{ V}\cdot\text{s}^{-1}$ , the voltammetric signal of GC-CNT-1 was shown to be relatively stable (<15 % loss after 5 cycles, Fig. S25-A), whereas GC-CNT-3 displayed no stability (complete loss after 2 cycles) as shown by the  $\text{Ni}^{\text{III}}/\text{Ni}^{\text{II}}$  signal (Fig. S25-B). Clearly, these results demonstrate the superiority of the *C*-functionalized complex for  $\text{CO}_2$  electrocatalytic reduction over the *N*-functionalized one. In order to analyze the reaction products, controlled potential electrolysis was carried out over 1h30 with GC-CNT-1 at  $-1.25 \text{ V}$  vs. Ag/AgCl. The Faradaic current density was found to stabilize at approximately  $0.7 \text{ mA}\cdot\text{cm}^{-2}$  over this time range (Fig. S26). Noteworthy, carbon monoxide was generated as the main product according to GC analysis (Fig. S27 and Table S2) yielding 85%/15%  $\text{CO-H}_2$  ratio with high turnover number (TON = 564) and high faradic efficiency (FE = 56%) for CO production. By comparison, the same experiment with GC-CNT electrodes produced uniquely  $\text{H}_2$  (Fig. S27 and Table S2).

In conclusion, we have successfully performed the synthesis followed by the covalently immobilization of *C*- and *N*-functionalized Ni-cyclam complexes onto electrode surfaces. The grafted *C*-functionalized Ni-cyclam species displays remarkable electrocatalytic properties in aqueous media for the reduction of  $\text{CO}_2$ . These promising results constitute an important first entry in the field of  $\text{CO}_2$  reduction catalysis since it demonstrates that covalent electrode functionalization of molecular complexes can be easily carried out for further use in electrocatalysis.

Furthermore, it evidences the main benefits which can be obtained from the C-functionalization of Ni-cyclam species. This now encourage us to accelerate the development of a new family of C-functionalized cyclam complex catalysts for which various *N*-chelating arms will be introduced on the macrocyclic core in order to decrease the overpotential for CO<sub>2</sub> reduction, as well as to increase of the kinetics for the catalytic reaction.

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## Conflicts of interest

There are no conflicts to declare.

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