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# 1 Immobilization of a molecular Re complex on 2 MOF-derived hierarchical porous carbon for 3 CO<sub>2</sub> electroreduction in water/ionic liquid 4 electrolyte

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23  
24 KEYWORDS: CO<sub>2</sub> electroreduction; catalysis; rhenium complex; heterogenization;  
25 hierarchical porous carbon

26

27 **Abstract**

28 The development of molecular catalysts for CO<sub>2</sub> electroreduction within electrolyzers requests  
29 their immobilization on the electrodes. While a variety of methods have been explored for the  
30 heterogenization of homogeneous complexes, we here report a novel approach using a  
31 hierarchical porous carbon HPC material, derived from a Metal Organic Framework, as a  
32 support for the well-known molecular catalyst [Re(bpy)(CO)<sub>3</sub>Cl] (bpy = 2,2'-bipyridine). This  
33 cathodic hybrid material, named HPC@Re, has been tested for CO<sub>2</sub> electroreduction using a  
34 mixture of an ionic liquid (1-Ethyl-3-methylimidazolium tetrafluoroborate EMIM) and water  
35 as the electrolyte. The present study reveals that HPC@Re is a remarkable catalyst, enjoying  
36 excellent activity (high current densities and high turnover numbers) and good stability.  
37 Interestingly, it catalyzes the conversion of CO<sub>2</sub> into a mixture of carbon monoxide and formic  
38 acid, with a selectivity that depends on the applied potential. These results emphasize the  
39 advantages of integrating molecular catalysts onto such porous carbon materials for developing  
40 novel, stable and efficient, catalysts for CO<sub>2</sub> reduction.

## 41 **Introduction**

42 Carbon dioxide electroreduction into energy-dense carbon-based liquid or gaseous products is  
43 an attractive way to store renewable energies into chemical energy. However, because of the  
44 high stability of CO<sub>2</sub> and the requirement of multiple electron and proton-transfers for its  
45 transformation, catalysts are required to overcome the slow kinetics, minimize overpotentials  
46 and control product selectivity. While heterogeneous catalysts are generally favored due to their  
47 stability as well as facile product and catalyst recovery, homogeneous molecular metal  
48 complexes (coordination and organometallic complexes) have also been developed since the  
49 1980's. In particular, they offer the unique opportunity to tune the coordination environment of  
50 the metal center and its reactivity *via* synthetic modifications of the ligands. The molecular  
51 strategy has been recently described in review articles.<sup>[1,2]</sup>

52 To reconcile these two approaches, homogeneous catalysts have sometimes been immobilized  
53 on heterogeneous conductive supports. However, this strategy has been applied to few  
54 molecular catalysts with limited success so far.<sup>[3-5]</sup> To illustrate the various techniques  
55 developed for providing access to modified electrodes, the case of the prototypical catalyst  
56 [Re(bpy)(CO)<sub>3</sub>Cl] (bpy = 2,2'-bipyridine), highly selective for CO<sub>2</sub> to CO conversion, is  
57 interesting, since its immobilization has been studied using a variety of approaches. The first  
58 attempts to immobilize such complexes were achieved by Meyer and coworkers<sup>[6]</sup> and Abruña  
59 and coworkers<sup>[7]</sup> in 1985 and 1986, respectively, two years after the initial publication by Lehn  
60 reporting the catalytic activity of this complex for CO<sub>2</sub> reduction.<sup>[8]</sup> In both cases, the catalyst  
61 was immobilized *via* electropolymerization of [Re(vbpy)(CO)<sub>3</sub>Cl] (vbpy = 4-vinyl-4'-methyl-  
62 2,2'-bipyridine) on an electrode to afford catalytic poly-[Re(vpby)(CO)Cl] films, allowing  
63 electroreduction of CO<sub>2</sub> to CO with very high faradaic yields in CH<sub>3</sub>CN. However, these films  
64 were shown to exhibit limited stability. A similar polymerization approach was recently  
65 developed by Kubiak and co-workers using 5-ethynyl-bipyridine derivatives, instead of vinyl-  
66 bipyridine, however, in that case very fast deactivation of the catalytic films was observed.<sup>[9]</sup> A  
67 different strategy for electropolymerization of a variant of Re(bpy)(CO)<sub>3</sub>Cl was reported by  
68 Deronzier and co-workers.<sup>[10]</sup> Upon electrochemical oxidation of a solution of  
69 Re(pyrbpy)(CO)<sub>3</sub>Cl (pyrbpy = 4-(4-Pyrrol-1-ylbutyl)4'-methyl-2,2'-bipyridine) using a Pt  
70 electrode, a polypyrrole-based film was deposited and found to catalyze the electroreduction in  
71 CH<sub>3</sub>CN of CO<sub>2</sub> leading to CO as the only reduction product. However, the polymer was highly  
72 unstable and substantial loss of current was observed during electrolysis. In 1993, Kaneko and  
73 co-workers reported the immobilization, *via* simple adsorption, of Re(bpy)(CO)<sub>3</sub>Br within a

74 Nafion<sup>®</sup> membrane, which is conductive and stable in various solvents and easily interfaces  
75 with electrode surfaces.<sup>[11]</sup> The polymer-confined catalyst was active for CO<sub>2</sub> electroreduction  
76 in neutral aqueous electrolyte, leading to mixtures of CO, H<sub>2</sub> and formic acid, with a selectivity  
77 depending on the applied potential.

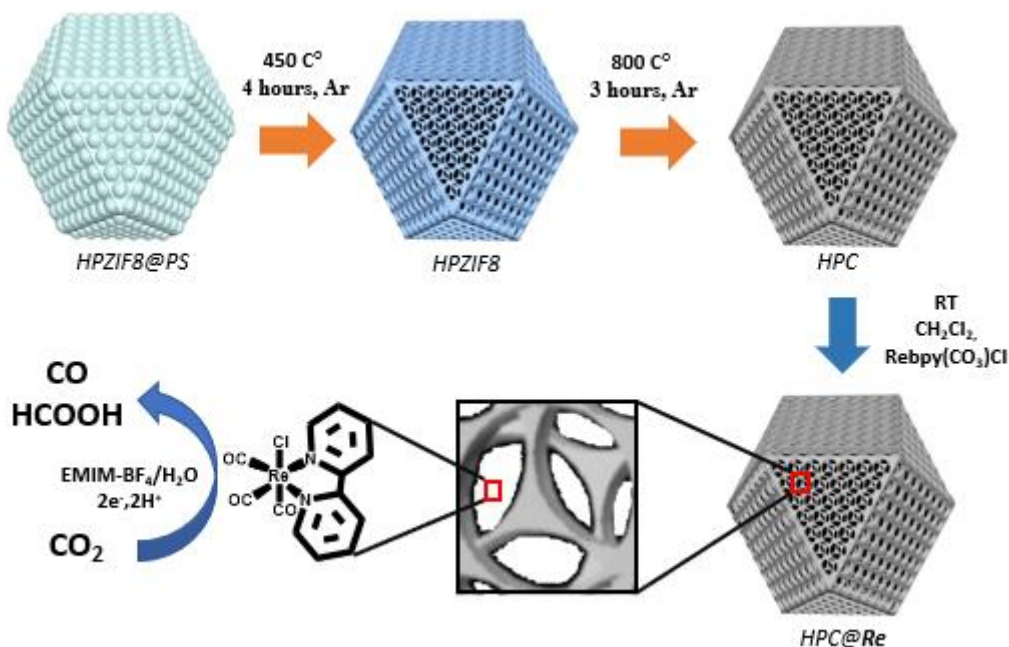
78 Besides this immobilization involving polymers and membranes, covalent grafting to the  
79 electrode has also been explored. As *o*-quinone moieties found on the edge planes of graphite  
80 can condense with substituted *o*-phenylenediamines, Re(5,6-diamino-phenanthroline)(CO)<sub>3</sub>Cl  
81 was used to modify graphite electrodes.<sup>[12]</sup> The increased conjugation between the catalyst and  
82 the electrode was proposed to overcome poor conductivity issues in other polymeric films  
83 deposited onto electrodes. This system was very selective for CO formation (faradaic yield of  
84 96%) in CH<sub>3</sub>CN with high TONs. A conjugated polymer material incorporating  
85 Re(bpy)(CO)<sub>3</sub>Cl motifs and covalently attached to a glassy carbon electrode was obtained by  
86 electropolymerization of a Re complex containing 2,2'-bipyridine-5,5'-bis-(diazonium)  
87 ligands.<sup>[13]</sup> These molecular films proved highly stable, allowing thousands of turnovers for  
88 selective production of CO in CH<sub>3</sub>CN.

89 Finally, non-covalent immobilization was achieved, exploiting  $\pi$ - $\pi$  interactions between  
90 pyrolytic graphite and Re(pyrene-bpy)(CO)<sub>3</sub>Cl, containing a pyrene-substituted bpy.<sup>[14]</sup> This  
91 system was catalytically active for CO production but was rapidly deactivated, likely because  
92 of reduction of the pyrenyl moiety. The best result with such a non-covalent immobilization  
93 strategy was obtained by Kubiak and co-workers who developed a hybrid electrode resulting  
94 from the incorporation of Re(tBu-bpy)(CO)<sub>3</sub>Cl, with tBu-bpy = 4,4'-di-*tert*-butyl-2,2'-  
95 bipyridine, into multi-walled carbon nanotubes (MWCNTs). This material proved stable and  
96 active in an aqueous electrolyte for highly selective CO production, at relatively low  
97 overpotential and with a current density of 4 mA.cm<sup>-2</sup>.<sup>[15]</sup>

98 One of the drawbacks of all these immobilization strategies, with the exception of the MWCNT/  
99 Re(tBu-bpy)(CO)<sub>3</sub>Cl system, resides in the need to introduce functionalities to the bipyridine  
100 ligand. This not only generates synthetic issues but also results in significant modifications of  
101 the electronic properties of the catalyst as well as of its reactivity. We thus thought of  
102 developing methods that allow the immobilization of the [Re(bpy)(CO)<sub>3</sub>Cl] itself without  
103 synthetic modifications. Here we report the preparation and characterization of an original  
104 conductive carbon porous material and its utilization as a support for the [Re(bpy)(CO)<sub>3</sub>Cl]  
105 catalyst, which can be easily fixed within the pores of the solid material. The novel hybrid  
106 material proved stable and active as a catalyst for CO<sub>2</sub> electroreduction, with high current

107 densities and high turnover numbers. Interestingly, this catalyst converts CO<sub>2</sub> into a mixture of  
108 CO and HCOOH, whose ratio depends on the applied potential.

109



110

111 **Scheme 1:** Synthesis of HPC and HPC@Re.

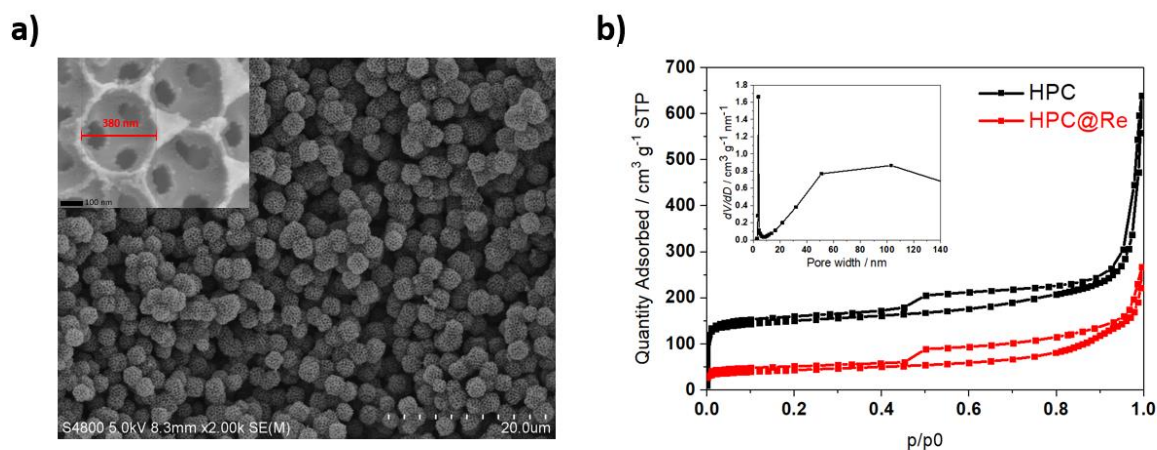
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## 113 RESULTS AND DISCUSSION

### 114 Synthesis and characterization of the hierarchical porous ZIF8-derived carbon-HPC

115 The synthesis of hierarchical porous carbon (named HPC in the following) derived from the  
116 Metal Organic Framework ZIF8 was synthesized following a previous report,<sup>[16]</sup> however with  
117 significant modifications (Scheme 1). First, the ZIF8 precursor was infiltrated into the  
118 polystyrene spheres (PS) template and crystallized using a solution of CH<sub>3</sub>OH/NH<sub>3</sub>·H<sub>2</sub>O.  
119 Second, a treatment at 450 °C under argon atmosphere, instead of washing with organic  
120 solvents used in the previous report,<sup>[16]</sup> was carried out in order to remove the PS template and  
121 thus obtain the hierarchical porous ZIF8 (HPZIF8). HPZIF8 shows slightly lower BET surface  
122 area (Figure S1 and Table S1) as compared to the previous report,<sup>[16]</sup> likely due to remaining  
123 PS beads in the sample. Scanning electronic microscope (SEM) and powder x-ray diffraction  
124 (XRD) characterizations of HPZIF8 show expected well-defined ZIF8 crystals (Figures S2-S3).  
125 HPZIF8 was finally pyrolyzed under inert atmosphere at 800 °C to obtain the final hierarchical  
126 porous carbon (HPC) material. HPC was characterized by various techniques. XRD pattern

127 confirmed that the material was not crystalline anymore (Figure S2). SEM images (Figure 1a)  
 128 showed well-defined and well-distributed carbon particles with a three-dimensional  
 129 tetrakaidecahedron morphology and with a uniform (monodisperse) diameter of 2  $\mu\text{m}$ . This  
 130 specific morphology is due to the use of PS latex as a template which controls the shape of the  
 131 material.<sup>[16]</sup> The highly ordered porous carbon material showed a hexagonal-close-packed  
 132 arrangement of PS nanospheres ??? (inset Figure 1a) with interconnected windows and porosity  
 133 uniformly distributed.<sup>[17,18]</sup>  $\text{N}_2$  physisorption analyses (Figure 1b and Figure S1) allowed to  
 134 establish a BET surface area of  $495 \text{ m}^2 \cdot \text{g}^{-1}$  and total pore volume of  $1 \text{ cm}^3 \cdot \text{g}^{-1}$  with around 25%  
 135 of the total pore volume assigned, by the Horwart-Kawazoe method, to the micropores. The  
 136 increase of the surface area due to the pyrolysis step leading to HPC ( $495 \text{ m}^2 \cdot \text{g}^{-1}$ ) from HPZIF8  
 137 ( $145 \text{ m}^2 \cdot \text{g}^{-1}$ ) is likely due to a complete removal of PS.  $\text{N}_2$  adsorption isotherms are of typical  
 138 type I, indicating the microporous character of the material with a pore size located at 0.5 nm.  
 139 The presence of mesopores and macropores has been revealed by two  $\text{N}_2$  adsorption uptakes at  
 140  $p/p_0$  of 0.5 and 0.95-1.0, respectively, as shown in Figure 1b. The BJH analysis method gives a  
 141 very sharp pic centered at 5 nm, corresponding to the hysteresis loop at  $p/p_0$  of 0.5 <sup>[19]</sup> while the  
 142 sharp  $\text{N}_2$  adsorption uptake at  $p/p_0$  of 0.95-1.0 is generated by the macropores of 380 nm  
 143 observed by SEM (Figure 1a). The above analysis suggests HPC material contains a  
 144 hierarchical macro-meso-microporous structure.  
 145



146  
 147 **Figure 1:** a) SEM image of HPC with enlargement (inset); b)  $\text{N}_2$  adsorption-desorption  
 148 isotherms of HPC and Re@HPC and pore size distribution (inset) made by BJH method of  
 149 HPC.

150

151 **Functionalization of HPC material with a molecular complex**

152 HPC was then used as a support for heterogeneizing the molecular  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$  complex,  
153 named Re in the following. Re was immobilized without any further functionalization taking  
154 advantage of the interconnected porosity of the support which improves the hosting properties.  
155 The heterogenization of Re on HPC has been carried out as follows. First, Re was dissolved in  
156  $\text{CH}_2\text{Cl}_2$  and the solution added dropwise to a sonicated dispersion of HPC in the same solvent  
157 (Scheme 1). The solution was stirred for 1 hour and after centrifugation the supernatant  
158 removed. Finally, the as-obtained hybrid system was dried overnight at room temperature. The  
159 relative amounts of starting precursors were chosen in order to obtain an initial weight Re:HPC  
160 ratio of 1:9. Then, the obtained HPC@Re material was characterized not only to check for the  
161 presence of the molecular complex within the solid but also to define morphology and structure  
162 of the final material.

163 SEM images of Re@HPC showed that the morphology of the carbon particles was retained  
164 (Figure S4). The presence of Re within the solid has been verified by Energy Dispersive X-Ray  
165 mapping (EDX) (Figure S4) showing a uniform dispersion of the complex, as well as the  
166 presence of residual Zn from ZIF8, even after pyrolysis.  $\text{N}_2$  physisorption analysis after Re  
167 loading showed a decrease of the BET surface area, indicating clearly the incorporation of the  
168 molecular complex within the pores of the support (Figure 1b). The integrity of Re within the  
169 solid material was proved by  $^1\text{H}$  NMR spectroscopy after releasing the complex from Re@  
170 HPC by washing with  $\text{CDCl}_3$ . The spectrum of the solution proved identical to that of the pure  
171 freshly prepared homogeneous complex (Figure S5). Finally, the amount of extractible complex  
172 from 30 mg of HPC@Re using an organic solvent ( $\text{CH}_2\text{Cl}_2$ ) was determined by UV-Visible  
173 spectroscopy from the intensity of the absorption band at 387 nm, characteristic of the complex  
174 (Figure S6). It was determined by ICP-MS that the sample contained  $4.8 \mu\text{mol}$  of complex  
175 leading to  $0,16 \mu\text{mol}/\text{mg}$  of complex within Re@HPC.

176

### 177 **Preparation and characterization of the working HPC@Re/GDL electrode**

178 An Re@HPC /GDL electrode ( $1\text{cm}^2$ ) was prepared by deposition of 5 mg HPC@Re on a  
179 commercial gas diffusion layer (GDL), as described in the experimental section. The total  
180 amount of Re in that electrode was determined by UV-Visible spectroscopy as described above  
181 for HPC@Re (Figure S6). The electrode was shown to contain  $0.6 \mu\text{mol}\cdot\text{cm}^{-2}$ . The CV of  
182 HPC@Re/GDL electrode in 0.1 M TBAPF<sub>6</sub> in  $\text{CH}_3\text{CN}$  at low scan rate of  $10 \text{mV}\cdot\text{s}^{-1}$  (Figure  
183 S7) served to calculate the density of electroactive species from the charge integration of the  
184 peak at about  $-1.6 \text{V}$  vs  $\text{Fc}/\text{Fc}^+$ , corresponding to the reoxidation of the complex.<sup>[20]</sup> The data



185 led to a high surface density of  $20 \text{ nmol.cm}^{-2}$ , corresponding to approximately 3% of the total  
186 amount of complex present in the solid material. These numbers compare well with those  
187 determined for the best hybrid  $[\text{Re}(\text{tBu-bpy})(\text{CO})_3\text{Cl}]/\text{MWCNT}$  material ( $13 \text{ nmol.cm}^{-2}$ , 1-8%  
188 of the total catalyst loaded) reported by Kubiak *et al.*<sup>[15]</sup>

189

### 190 **Electrocatalytic CO<sub>2</sub>RR in water/1-Ethyl-3-methylimidazolium tetrafluoroborate** 191 **(EMIM) electrolyte**

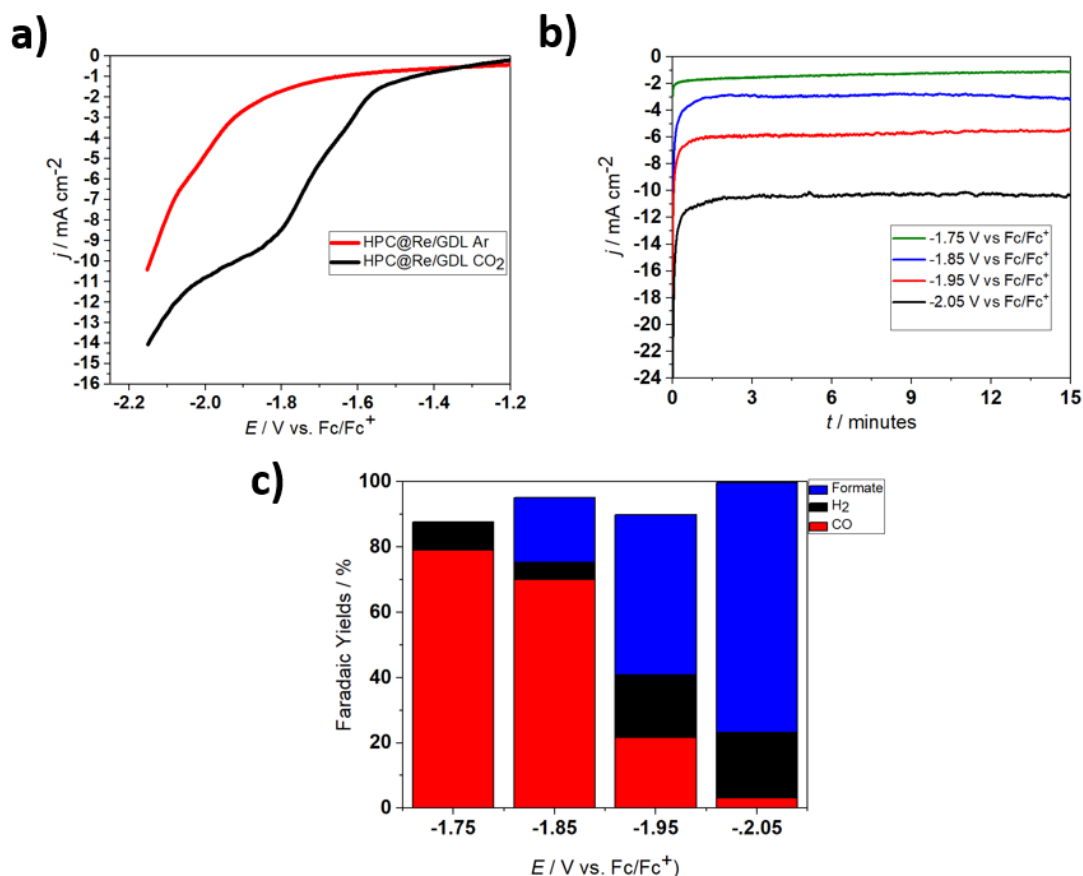
192 Since the electroreduction of CO<sub>2</sub> using the HPC@Re/GDL in water yielded mainly hydrogen  
193 (data not shown), the reaction was studied in a CO<sub>2</sub>-saturated solution of an ionic liquid in the  
194 presence of a small amount of water as a source of protons. Indeed, ionic liquids have been  
195 shown to facilitate CO<sub>2</sub> electroreduction catalyzed by solid catalysts due to their ability to  
196 increase CO<sub>2</sub> solubility and activate CO<sub>2</sub>.<sup>[21]</sup> A previous report showed that using an ionic liquid  
197 as both the solvent and electrolyte resulted in decreased overpotential and increased second-  
198 order rate constant for CO<sub>2</sub> electroreduction to CO catalyzed by  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$ .<sup>[22]</sup>  
199 However, with such homogeneous systems, the viscosity of the medium results in strong  
200 limitations in mass transport (small diffusion coefficients) of the molecular catalyst and low  
201 current densities. This issue does not apply to an immobilized molecular complex. Thus, a  
202 mixture of an ionic liquid (1-Ethyl-3-methylimidazolium tetrafluoroborate) and water (named  
203 H<sub>2</sub>O/EMIM in the following) has been chosen as the electrolyte for further CO<sub>2</sub>  
204 electroreduction studies using the HPC@Re/GDL electrode. The Linear Sweep  
205 Voltammograms (LSVs) of the HPC@Re/GDL electrode in 5% v/v H<sub>2</sub>O/EMIM saturated with  
206 either Ar or CO<sub>2</sub> are presented in Figure 2a. A catalytic wave at an onset potential of -1.55 V  
207 vs Fc/Fc<sup>+</sup> and developing further up to an applied potential of -2.05 V was observed only in the  
208 presence of CO<sub>2</sub> and was thus assigned to CO<sub>2</sub> reduction (Figure 2a). At potentials more  
209 negative than -2.1 V, a second wave was observed however also present for the HPC@Re/GDL  
210 electrode under argon, thus likely corresponding to proton reduction to H<sub>2</sub>. Unfortunately, the  
211 evaluation of overpotential values is not trivial here as the equilibrium potentials of the  
212 CO<sub>2</sub>/HCOOH and CO<sub>2</sub>/CO couples in H<sub>2</sub>O/EMIM are unknown.

213 Controlled Potential Electrolysis (CPE) at different potentials between -1.75 V and -2.05 V  
214 *versus* Fc/Fc<sup>+</sup> coupled with quantification of CO<sub>2</sub> reduction products has been carried out for  
215 15 minutes in order to characterize the CO<sub>2</sub> reduction reaction. As expected the total current  
216 density increased with increased driving force up to  $11 \text{ mA.cm}^{-2}$  at -2.05 V and was found to  
217 be stable during electrolysis at all potentials (Figure 2b). The high current densities translate

218 into remarkably high turnover numbers (TONs) and high Turnover Frequencies (TOFs). For  
219 example, at -2.05 V, 2026 TONs are reached after 15 min, which corresponds to a TOF value  
220 of  $2.3 \text{ s}^{-1}$ . As shown below, under these conditions, formate was the major product.

221 The only detected products in all experiments were  $\text{H}_2$  and CO in the gaseous phase and formic  
222 acid in the liquid phase. Surprisingly, the selectivity of the reaction was found to be greatly  
223 dependent on the applied potential, with CO being the major product at the most anodic  
224 potentials and formic acid becoming the major product at potentials more cathodic than -1.9 V,  
225 while  $\text{H}_2$  was a minor product at all potentials. This is clearly shown in Figure 2c which displays  
226 the Faradaic yields (FY) of the various products at different potentials. At -1.75 V vs  $\text{Fc}/\text{Fc}^+$ ,  
227  $\text{FY}(\text{CO})$  and  $\text{FY}(\text{H}_2)$  were 79% ( $\text{TON}_{\text{CO}}$  258 and  $\text{TOF}_{\text{CO}}$   $0.3 \text{ s}^{-1}$ ) and 9% respectively, and no  
228 formate could be found in the liquid phase. Screening the reaction at more negative potentials,  
229 CO formation decreased dramatically while  $\text{FY}(\text{HCOOH})$  and  $\text{FY}(\text{H}_2)$ , the latter to a smaller  
230 extent, increased. At -2.05 V,  $\text{FY}(\text{CO})$ ,  $\text{FY}(\text{H}_2)$  and  $\text{FY}(\text{HCOOH})$  were 3%, 20% and 76%  
231 ( $\text{TON}_{\text{HCOOH}}$  1950 and  $\text{TOF}_{\text{HCOOH}}$   $2.2 \text{ s}^{-1}$ ) respectively (Figure 2c). Thus, the selectivity between  
232 CO vs HCOOH formation during electroreduction of  $\text{CO}_2$  catalyzed by HPC@Re can be finely  
233 tuned by varying the applied potential.

234



235

236 **Figure 2:** Controlled potential electrolysis of CO<sub>2</sub> using the HPC@Re/GDL electrode: **a)** LSV  
237 in 5% v/v H<sub>2</sub>O/EMIM saturated with CO<sub>2</sub> (black) or with Ar (red), scan rate 20 mV.s<sup>-1</sup>; **b)** total  
238 current density at various applied potentials as a function of time; **c)** Faradaic Yields for CO,  
239 H<sub>2</sub> and formate after 15 min electrolysis at different potentials in 5% v/v H<sub>2</sub>O/EMIM saturated  
240 with CO<sub>2</sub>.

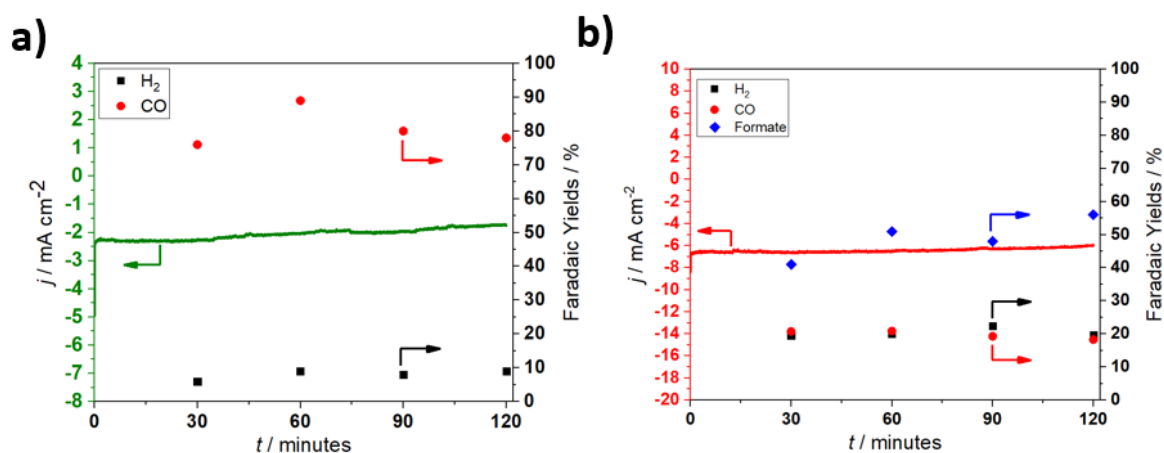
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242 The observation of formate formation is unexpected since the Re complex is known to be a very  
243 selective catalyst for CO<sub>2</sub> electroreduction to CO in organic solvents. Interestingly, when, as a  
244 control experiment, CPE was carried out using the soluble Re complex in the same CO<sub>2</sub>-  
245 saturated 5% v/v H<sub>2</sub>O/EMIM electrolyte, the reaction was shown to yield mainly H<sub>2</sub> with minor  
246 amounts of CO and almost no HCOOH, at all visited potentials (Figure S8). Furthermore, the  
247 current densities were much lower since at -1.85 V the current density reached a value of 0.3  
248 mA.cm<sup>-2</sup> (Figure S8) for 12 μmol of Re catalyst (1 mM in 12 ml) as compared to 3 mA.cm<sup>-2</sup>  
249 for 0.6 μmol Re catalyst present in HPC@Re/GDL (Figure 2). This thus demonstrates the great  
250 impact of the solid support on the reaction outcome, both in terms of the activity and the  
251 selectivity. The effect on the activity is likely to be partly due to the hydrophobic nature of the  
252 environment provided by the pores in which the catalyst is bound, favouring CO<sub>2</sub> uptake and  
253 increasing CO<sub>2</sub> local concentration and to the absence of mass transport limitations which  
254 challenge the homogeneous catalyst.

255 In contrast, the effect of the solid support on the selectivity is difficult to explain. Formation of  
256 formate cannot be explained by the catalytic properties of the support itself since, as a control  
257 experiment, CPE of CO<sub>2</sub> using an HPC/GDL electrode, not loaded with the Re complex, under  
258 identical conditions, gave very different results (Figure S9). For example, at -1.85 V, with a  
259 current density of 1 mA.cm<sup>-2</sup>, no formate could be detected, as compared to 3 mA.cm<sup>-2</sup> and a  
260 FY(HCOOH) of 20% for the HPC@Re/GDL electrode, and at -1.95 V, with a current density  
261 of 2 mA.cm<sup>-2</sup>, a FY(HCOOH) of 15% was obtained, as compared to 6 mA.cm<sup>-2</sup> and a  
262 FY(HCOOH) of 50% for the HPC@Re/GDL electrode. There is, to our knowledge, one study  
263 reporting formate production during electroreduction of CO<sub>2</sub> catalyzed by the Re complex, with  
264 a HCOOH/CO selectivity depending on the applied potential as well.<sup>[11]</sup> Interestingly, in that  
265 case, the catalyst was incorporated into a Nafion membrane and electrolysis was carried out in  
266 a phosphate aqueous electrolyte, explaining why the major product at almost all potentials  
267 applied was H<sub>2</sub>. The activity, in terms of current density, of that system was furthermore much  
268 lower than that reported here. While formate production using the HPC@Re catalyst is likely  
269 to proceed *via* a Re-H hydride species reacting with CO<sub>2</sub>,<sup>[23,24]</sup> in contrast to CO production  
270 which derives from a Re-CO<sub>2</sub> intermediate, it is so far unclear why the HPC support favours

271 such a mechanism at very cathodic potentials and how the support tunes the HCOOH/CO  
272 selectivity. These mechanistic aspects deserve further investigation.

273 Finally, long-term CPE was carried out for 2 hours at -1.75 V (formation of CO and H<sub>2</sub>) and -  
274 1.95 V (formation of CO, HCOOH, H<sub>2</sub>) vs Fc/Fc<sup>+</sup> (Figure 3). The system proved very stable  
275 during electrolysis in terms of both current density and selectivity. After 2 hours at -1.75 V,  
276 3155 TON<sub>CO</sub> were achieved corresponding to a TOF<sub>CO</sub> of 0.4 s<sup>-1</sup>. Furthermore, post-electrolysis  
277 characterization of the electrode by SEM showed that the porosity of the system was retained  
278 even if slight agglomeration of the particles was observed (Figure S10). Finally, the amount of  
279 Re released in solution after 2 hours electrolysis was measured by ICP-MS and found to be  
280 within 5 to 10%, from one experiment to another, with respect to the initial amount of Re  
281 initially present on the electrode. Based on the results given above (Figure S8), this amount is  
282 far too small to account for the CO<sub>2</sub> reduction activity of the electrode.



283

284 **Figure 3:** Long-term electrolysis: current density and FY as a function of time during CPE at -  
285 1.75 V vs Fc/Fc<sup>+</sup> (a) and at -1.95 V vs Fc/Fc<sup>+</sup> (b) under CO<sub>2</sub> in 5% v/v H<sub>2</sub>O/EMIM using the  
286 HPC@Re/GDL. Faradaic yields for CO (red dots), H<sub>2</sub> (black squares) and formate (blue  
287 diamonds).

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291 **Conclusion**

292 We have developed a novel hybrid solid catalyst, HPC@Re, for CO<sub>2</sub> electroreduction to CO  
293 and HCOOH. Thanks to the hierarchical porosity of the porous and conductive carbon material  
294 HPC, large amounts of the molecular catalyst [Re(bpy)(CO)<sub>3</sub>Cl] can be easily immobilized  
295 without any functionalization. We anticipate that HPC can be further used for heterogeneization  
296 of other complexes. In order to optimize catalysis, CO<sub>2</sub> electroreduction has been studied in an  
297 ionic liquid electrolyte in the presence of water, known to favour CO<sub>2</sub> solubility and activation.  
298 To the best of our knowledge, this is the first example of a heterogenized molecular complex  
299 characterized for CO<sub>2</sub> reduction catalysis in an ionic liquid. HPC@Re/GDL electrodes thus  
300 provide high current densities (up to 11 mA.cm<sup>-2</sup>), high TOF<sub>CO+HCOOH</sub> (2.3 s<sup>-1</sup>) and display good  
301 stability. When compared to other hybrid solid electrodes in which [Re(bpy)(CO)<sub>3</sub>Cl] has been  
302 immobilized,<sup>[6-15]</sup> the HPC@Re/GDL electrode is among the most efficient and stable ones. In  
303 addition, this novel electrode is unique in providing not only CO but also HCOOH as CO<sub>2</sub>  
304 reduction products, with FY(H<sub>2</sub>) not exceeding 20%, in marked contrast with the other  
305 comparable systems which are selective for CO production and in contrast with the  
306 homogeneous catalyst which favours proton reduction over CO<sub>2</sub> reduction and is quite  
307 inefficient in the same water/ionic liquid system. The CO/HCOOH ratio can be tuned with the  
308 applied potential since it decreased as the potential is shifted to more cathodic values. The  
309 combination of a water/ionic liquid electrolyte system, the hierarchical porosity of the support  
310 facilitating mass exchange and transfer,<sup>[25]</sup> and the hydrophobic environment provided by the  
311 pores in which the molecular complex is fixed is likely to explain the remarkable and unique  
312 performances of HPC@Re as a CO<sub>2</sub> reduction catalyst. However, further studies are required  
313 to understand how the support drives and controls the reactivity of the immobilized complex.

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316

## 317 **Experimental section**

### 318 **General methods**

319 All chemicals were received from commercial sources and used as received. Zinc nitrate  
320 hexahydrate ( $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ , 99%), 2-methylimidazole (98%), tetrabutylammonium  
321 hexafluorophosphate (TBAPF<sub>6</sub>, 98%), Nafion<sup>®</sup> perfluorinated resin (10  $\mu\text{L}$  of a 5 wt% solution  
322 in mixture of lower aliphatic alcohols containing 5% water), absolute ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ),  
323 methanol ( $\text{CH}_3\text{OH}$ , 99%), dichloromethane ( $\text{CH}_2\text{Cl}_2$ , 99 %), acetonitrile ( $\text{CH}_3\text{CN}$ , 99.8%),  
324 chloroform-d ( $\text{CDCl}_3$ , 99.8%) and ammonia solution ( $\text{NH}_3 \cdot \text{H}_2\text{O}$ , 32% ) were purchased from  
325 Sigma-Aldrich. 1-Ethyl-3-methylimidazolium tetrafluoroborate (>98%) was purchased from  
326 IOLITEC Ionic liquid technologies GmbH.  $[\text{Re}(\text{bpy})(\text{CO})_3\text{Cl}]$  was synthesized as previously  
327 reported by Kubiak *et al.*<sup>[26]</sup>

328 UV–vis spectra were recorded using a Cary 100 UV–vis spectrophotometer (Agilent). <sup>1</sup>H  
329 spectra were recorded on a Bruker Avance-III 300 NMR spectrometer (300 MHz) at room  
330 temperature. The Rhenium concentrations in the electrolyte were assessed using an Agilent  
331 7900 quadrupole ICP-MS. Liquid samples were sprayed through a micro-nebulizer in a Scott  
332 spray chamber prior to ionization. An indium internal standard was injected after inline mixing  
333 with the samples to correct for signal drift. Calibration solutions with Re concentrations  
334 encompassing the full range of sample concentrations were used to convert measured counts to  
335 concentrations. Reported uncertainties were calculated using algebraic propagation of blank  
336 subtraction and sample count standard deviations (n=3).

### 337 **Material characterization**

338 Scanning electron microscope (SEM) images were performed by using a JEOL 7500F  
339 microscope operating at 15kV with EDX detector incorporated and a Hitachi S-4800 operating  
340 at 5kV. X-ray diffraction (XRD) characterization was carried out by Panalytical X'Pert PRO  
341 diffractometer (Cu K $\alpha$  radiation, Bragg-Brentano geometry, sealed tube operated at 45 mA 30  
342 kV X'Celerator linear detector). Nitrogen physisorption analyses were performed with ASAP  
343 2420 using a platinum resistance device and liquid nitrogen as adsorbed molecule.

### 344 **Synthesis of HPZIF8**

345 Polystyrene spheres (PS) (the size of 400 nm) were synthesized as previously reported<sup>[16]</sup> and  
346 used as a template for the preparation of a hierarchical porous ZIF8 (HPZIF8). HPZIF8 with  
347 polystyrene (HPZIF8@PS) was also prepared using a protocol from Chen *et al.*<sup>[16]</sup>, via  
348 infiltration of the ZIF8 precursor into the PS spheres template. The following steps were  
349 modified from the previous protocol to obtain the HPZIF8. This, was prepared from

350 HPZIF8@PS treating it at 450 °C during 4 hours under Argon atmosphere for removing the PS  
351 beads.

### 352 **Synthesis of HPC**

353 The hierarchical porous carbon (HPC) derived from ZIF8 was obtained by heating the HPZIF8  
354 at 800 °C during 3 hours under Argon atmosphere. The HPC was used without further  
355 treatment.

### 356 **Preparation of HPC@Re**

357 The preparation of Re complex loading on HPC material was carried out as follows: the solution  
358 of [Re(bpy)(CO)<sub>3</sub>Cl] (6 mg) in CH<sub>2</sub>Cl<sub>2</sub> (10 mL) was added dropwise to a sonicated dispersion  
359 of HPC (50 mg) in CH<sub>2</sub>Cl<sub>2</sub> (20 mL). The suspension was then centrifuged for removing the  
360 supernatant. The obtained material was then dried overnight under vacuum condition at room  
361 temperature and used without further treatments.

362 These materials were characterized by: N<sub>2</sub> physisorption analyses, SEM images, EDX mapping  
363 and XRD (Supporting Information).

364 The amount of Re complex loaded was quantified by UV-Visible spectroscopy (Figure S6):  
365 after extraction of 30 mg of HPC@Re with 20 mL of CH<sub>2</sub>Cl<sub>2</sub> the solution was analysed for its  
366 absorption at 387 nm, characteristic of [Re(bpy)(CO)<sub>3</sub>Cl] and the latter was compared to  
367 calibration curve prepared with pure [Re(bpy)(CO)<sub>3</sub>Cl]. HPC@Re was also treated with CDCl<sub>3</sub>  
368 for extraction of the complex and characterization by <sup>1</sup>H NMR (Figure S5), in order to confirm  
369 the integrity of the complex.

### 370 **Electrode preparation**

371 HPC@Re (5 mg) was sonicated 1 hour in absolute ethanol (200 μL) and a solution of Nafion  
372 perfluorinated resin (10 μL of a 5 wt% solution in mixture of lower aliphatic alcohols containing  
373 5% water). The suspension was then, carefully, deposited by drop casting on a gas-diffusion  
374 Layer, GDL (AVCarb GDS 3250; 1 cm<sup>2</sup>) in order to have a uniform deposition. The electrode  
375 was then dried in air overnight at room temperature. For all the experiments the working  
376 electrodes were prepared in the same way.

### 377 **Electrode characterization**

378 SEM images of the HPC@Re/GDL electrode were obtained before and after 2 hours  
379 electrolysis. The amount of Re complex present on the GDL was quantified by UV-Visible  
380 spectroscopy as described above via extraction of the complex from the HPC@Re/GDL  
381 electrode immersed in 20 mL of CH<sub>2</sub>Cl<sub>2</sub> (Figure S6) and quantification by comparison with the  
382 calibration curve.

### 383 **Electrochemical characterization**

384 All electrochemical characterization and electrolysis experiments were carried out using a Bio-  
385 logic SP300 potentiostat with two-compartment cell with an Ag/AgCl/3M KCl reference  
386 electrode, placed in the same compartment as the working HPC@Re/GDL electrode. A  
387 platinum counter electrode was placed in a separate compartment. The two compartments were  
388 separated by a membrane (Fumasep FBM-Bipolar Membrane). The electrolyte was CO<sub>2</sub>-  
389 saturated 5% v/v H<sub>2</sub>O/EMIM (12.5 mL). The electrochemical cell was first purged with CO<sub>2</sub> at  
390 a flow rate of 20 mL.min<sup>-1</sup> for 1 h prior to catalytic tests using a mass flow controller  
391 (Bronkhorst EL-FLOW model F-201CV). All potential values are given versus the potential of  
392 the Fc/Fc<sup>+</sup> couple added as an internal standard to the solution after measurement. In 5% v/v  
393 H<sub>2</sub>O/EMIM: E<sub>1/2</sub>(Fc/Fc<sup>+</sup>) = 0.35V vs Ag/AgCl (Figure S11)

394 CVs for the determination of surface density of electrochemically active sites were recorded in  
395 CH<sub>3</sub>CN, 0.1 M TBAPF<sub>6</sub> with a scan rate of 10 mV.s<sup>-1</sup>.

396 The surface loading ( $\Gamma[\text{Re}]$  as mol.cm<sup>-2</sup>) of the catalyst was calculated through the integration  
397 of the reoxidation wave in the CV scan (Figure S7) using the equation:

$$398 \quad \Gamma[\text{Re}] = \frac{q}{nFA}$$

399 where q is the charge (C) obtained from integration of the oxidation wave, n the number of  
400 electrons in the redox process per Re center (n = 1), F is the Faraday constant (96485 C.mol<sup>-1</sup>),  
401 and A is the geometrical electrode area (1 cm<sup>2</sup>).<sup>[27]</sup>

402 The homogeneous electrochemical experiments were carried out under the same conditions  
403 described above using the same electrochemical cell. A glassy carbon electrode (1 cm<sup>2</sup>) was  
404 used as working electrode in a solution 1 mM of [Re(bpy)(CO)<sub>3</sub>Cl] in 5% v/v H<sub>2</sub>O/EMIM.

405 H<sub>2</sub> and CO were identified and quantified using a gas chromatograph (SRI 8610C) equipped  
406 with a packed Molecular Sieve 5 Å column for permanent gases separation and a packed  
407 Haysep-D column for light hydrocarbons separation. Argon (Linde 5.0) was used as carrier gas.  
408 A flame ionization detector (FID) coupled to a methanizer was used to quantify CO while a  
409 thermal conductivity detector (TCD) was used to quantify H<sub>2</sub>. The liquid-phase products were  
410 quantified using an ionic exchange chromatography system (883 Basic IC plus; Metrohm).

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