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# A new class of hybrid materials for detection, capture, and “on-demand” release of carbon monoxide.

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**ABSTRACT:** Carbon monoxide (CO) is both a substance hazardous to health and a side-product of a number of industrial processes, such as methanol steam reforming, and large-scale oxidation reactions. The separation of CO from nitrogen (N<sub>2</sub>) in industrial processes is considered to be difficult because of the similarities of their electronic structures, sizes, and physicochemical properties (*e.g.* boiling points). Carbon monoxide is also a major poison in fuel cells because of its adsorption onto the active sites of the catalysts. It is therefore of the utmost economic importance to discover new materials that enable effective CO capture and release under mild conditions. However, methods to specifically absorb and easily release CO in the presence of contaminants, such as water, nitrogen, carbon dioxide, and oxygen at ambient temperature are not available. Here, we report the simple and versatile fabrication of a new class of hybrid materials that allows capture and release of carbon monoxide under mild conditions. We found that carborane-containing metal complexes encapsulated in networks made of polydimethylsiloxane (PDMS) react with CO, even when immersed in water, leading to dramatic color and infrared signature changes. Furthermore, we found that the CO can be easily released from the materials by simply dipping the networks into an organic solvent for less than one minute, at ambient temperature and pressure, which not only offers a straightforward recycling method, but also a new method for the “on-demand” release of carbon monoxide. We illustrated the utilization of the “on-demand” release of CO from the networks by carrying out a carbonylation reaction on an electron-deficient metal complex that led to the formation of the CO-adduct, with concomitant recycling of the gel. We anticipate that our sponge-like materials and scalable methodology will open-up new avenues for the storage, transport, and controlled-release of CO, the silent killer and a major industrial poison.

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## Introduction

Selective adsorption and facile release of carbon monoxide (CO) is a major challenge owing to the number of industrial processes in which CO acts as a poison.<sup>1</sup> The production of molecular hydrogen (H<sub>2</sub>) via steam reforming of hydrocarbon fuels requires a second purification step (*e.g.* water-gas shift reactions) to remove the CO contained in the H<sub>2</sub> produced.<sup>2</sup> CO is also one of the major poisons in low temperature fuel cells.<sup>3</sup> CO poisoning can occur by adsorption onto the active sites of the catalysts (*e.g.* platinum) leading to no or reduced sites available for reaction with H<sub>2</sub>. Platinum-ruthenium catalysts for fuel cells are promising because they can resist carbon monoxide contamination,<sup>4</sup> but a number of issues are associated to these systems, such as metal leaching from the alloy, which decreases the promotion efficiency of these catalysts.<sup>5</sup> Furthermore, the separation of CO from nitrogen (N<sub>2</sub>) in industrial processes is a technical challenge because of the similarities of their electronic structures, sizes, and physicochemical properties (*e.g.* boiling

points).<sup>6</sup> There has therefore been a long and significant academic and industrial interest in the development of materials capable of reversibly detecting and capturing CO,<sup>7–10</sup> but this is still an extremely challenging quest. Chemisorption of carbon monoxide is generally based on the formation of a strong bond between a transition metal and CO acting as a ligand (originating from CO’s combination of high-energy filled and low-energy vacant orbitals engaged in synergic  $\sigma$  bonding and  $\pi$  back-bonding with the d orbitals of transition metals).<sup>11</sup> The main limitation of this strategy is that high temperatures are required to release CO, and most of the materials are irreversibly damaged by the treatment.<sup>12</sup> The utilization of copper complexes to capture CO has also been extensively studied,<sup>13–14</sup> but the application of reduced pressure at room temperature leads to the dissociation of the ligand rendering the isolation of the adducts as solids difficult. Efficient and reversible capture of CO in carbanion-functionalized ionic liquids were also reported.<sup>15–16</sup> A recent breakthrough for CO separation was reported by Matsuda, Kitagawa, and co-workers, with the design of a

Cu(II)-containing soft nanoporous crystal which showed remarkable CO sorption and desorption properties, even in the presence of  $N_2$ , a gas most competitive to CO in industrial processes.<sup>6</sup> However, water molecules preferentially coordinate to the Cu(II) CO-trapping sites of the materials,<sup>6</sup> and pre-cleanup of the exhaust gases to remove contaminants may be necessary.

Carborane-containing precious metal complexes, such as  $[Os(\eta^6\text{-}p\text{-cymene})(1,2\text{-dicarba-closo-dodecarborane-1,2-dithiolato})]$  and  $[Ir(\eta^5\text{-pentamethylcyclopentadienyl})(1,2\text{-dicarba-closo-dodecarborane-1,2-dithiolato})]$  (**1**, **2**, Fig. 1) exhibit unusual coordination chemistry in solution.<sup>17–22</sup> They are 16-electron (16-e) complexes and therefore electron-deficient at the metal centers. The steric hindrance due to the bulky carborane ligand prevents the dimerization of these 16-e complexes and the formation of more stable 18-e adducts.<sup>23</sup> Herein, inspired by the unusual properties of such stable electron-deficient carborane precious metal complexes in solution, we investigated the CO sorption process on the metal center of complexes **1** and **2** and the formation of the 18-e adducts  $[Os(\eta^6\text{-}p\text{-cymene})(1,2\text{-dicarba-closo-dodecarborane-1,2-dithiolato})CO]$  and  $[Ir(\eta^5\text{-pentamethylcyclopentadienyl})(1,2\text{-dicarba-closo-dodecarborane-1,2-dithiolato})CO]$  (**[1-CO]**, **[2-CO]**). We then encapsulated complexes **1** and **2** in networks made of polydimethylsiloxane (PDMS – a porous matrix; gels **G1**, and **G2**, respectively), in the absence and in the presence of usual contaminants in industrial processes (water, nitrogen, and carbon dioxide). The formation of networks **G1-CO**, **G2-CO** via coordination of CO to the metal centers is evidenced by a change of color of the networks not only upon addition of CO under 1 atmosphere of carbon monoxide, but also in water (by bubbling CO in the solution), and in air (with different concentrations of CO). The coordination of CO is demonstrated by UV-visible and infrared (IR) spectroscopies. Crucially, the straightforward release of CO from the networks and the recovery of the original materials are shown at ambient temperature and ambient pressure. We illustrate the potential utilization of such materials by carrying out the carbonylation reaction of iridium complex **2** by releasing CO from an osmium gel **G1-CO**, leading to the formation of the iridium complex **[2-CO]** with concomitant recycling of the osmium gel **G1**.

## Results and Discussion

### Reactivity of carborane-complexes **1** and **2** with $CO(g)$ in solution.

We first studied the reactivity of complexes **1** and **2** with CO in solution. Bubbling CO in a dichloromethane solution ( $10^{-4}$  M, 298 K) of the 16-e complexes **1** and **2** readily forms the 18-e adduct  $[Os(\eta^6\text{-}p\text{-cymene})(1,2\text{-dicarba-closo-dodecarborane-1,2-dithiolato})(CO)]$  and  $[Ir(\eta^5\text{-pentamethylcyclopentadienyl})(1,2\text{-dicarba-closo-dodecarborane-1,2-dithiolato})(CO)]$ , respectively (**[1-CO]**, **[2-CO]**, Figs. 1a and 1b). The addition of the CO ligand is

evidenced by the apparition of a characteristic infrared (IR) absorption CO signal at *ca.* 1970  $cm^{-1}$  (Figs. 1c and 1d), as well as by a dramatic change of the solution color from red (**Os**) or blue (**Ir**) to yellow. UV-visible absorption spectroscopy also suggests the formation of the CO 18-e adduct (Figs. 1d and 1e), with the dramatic decrease of the absorption bands observed between 480–530 nm (associated to ligand-to-metal charge-transfer transitions that are commonly observed in 16-electron complexes<sup>24</sup>) which is in accordance with the formation of an 18-e species<sup>22</sup>.

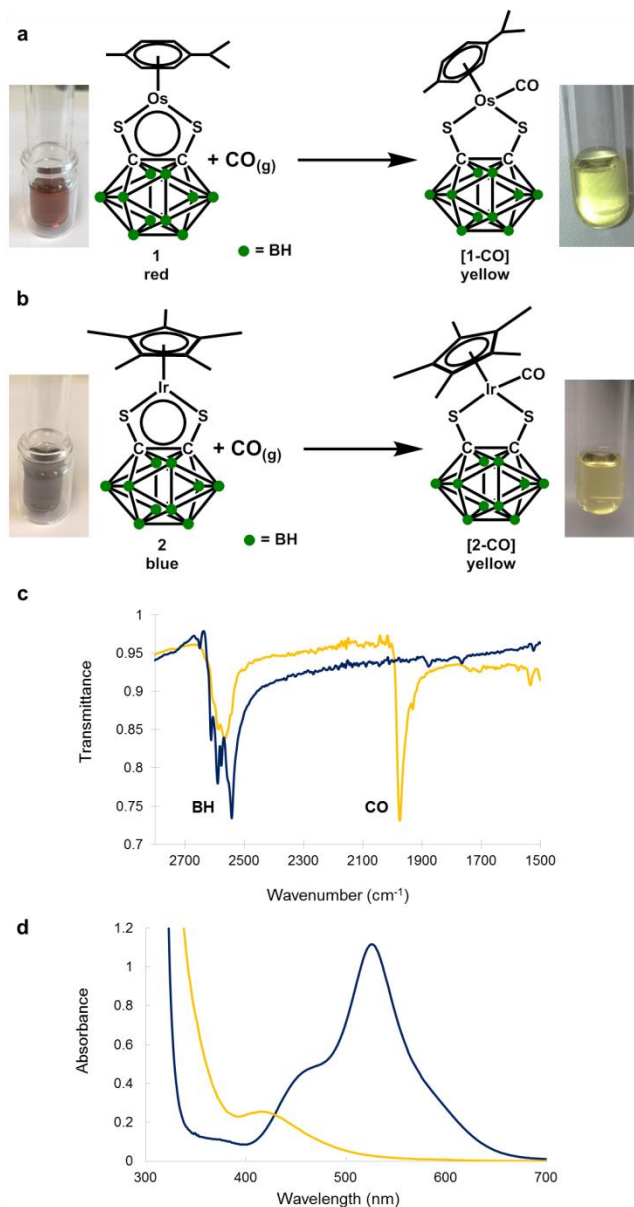


Figure 1. Synthesis of the CO 18-e adducts **[1-CO]** and **[2-CO]** by bubbling CO in a dichloromethane solution of 16-e precursors **1** and **2** ( $10^{-4}$  M, 298 K). **a** and **c**, Synthetic scheme and colors of the respective solutions in dichloromethane. **b**, Infrared absorption spectra of **1** and **[1-CO]** (recorded as solid; **1** blue line, **[1-CO]** yellow line). **d**, UV-visible absorp-

tion spectra of complexes **2** and [2-CO] ( $10^{-4}$  M, dichloromethane; **2** blue line, [2-CO] yellow line).

In tetrahydrofuran (THF) solution, complexes [1-CO] and [2-CO] slowly reverse to complexes **1** and **2** after one week in solution (de-coordination of the CO ligand), leading to color changes from yellow to red (**1**) or blue (**2**). Metal complexes **1** and **2** are stable in a 16-electron configuration owing to the non-innocent bulky carborane ligand. Such stability previously led to the observation that in dichloromethane solutions at ambient temperature, the 16-e complexes only partially form adducts with  $\sigma$ -donor and/or  $\sigma$ -donor +  $\pi$ -acceptor ligands to give the corresponding yellow 18-electron adducts, and that these 18-e complexes are in equilibrium with the stable 16-e parent compounds.<sup>16,22</sup> Furthermore, the thermal displacement of these equilibria results in marked thermochromic properties. This makes the 16-e complexes reactive with CO, but with a weak binding strength, as demonstrated by the DFT calculations study below. The weak binding of CO to the metal centers is therefore believed to lead to de-coordination of the ligand in non-polar solvents in-which CO is slightly soluble<sup>25</sup> (such as THF).

#### Geometry optimizations and calculated spectra.

Electronic spectroscopic data for DFT-optimized complexes **1**, **2**, [1-CO], and [2-CO] in a THF conductor-like CPCM solvation model field<sup>26</sup> were calculated by computing the lowest 80 singlet states via time-dependent DFT calculations using the M11-L DFT functional<sup>27</sup> coupled with the SDD basis set<sup>28</sup> for the metal ions and the def2-TZVP basis set<sup>29</sup> for the lighter elements. The singlet, triplet and quintet spin states were considered for all the models (Fig. 2a). The coordination of CO to both osmium and iridium systems was computed to be slightly exothermic by 14 and 17 kcal/mol, respectively. The calculation values for the thermochemistry of the CO addition, and electronic energies for all complexes can be found in Table S1-S17.

The DFT-optimized complexes [1-CO], and [2-CO] complexes have the typical piano-stool structure of carbonyl-containing half-sandwich metal complexes characterized by X-ray crystallography. Recent examples include [RuCp\*(CO)(HL)]BPh<sub>4</sub><sup>30</sup> as well as a Fe(II) piano-stool complex with NHC ligand and one CO ligand.<sup>31</sup>

UV-vis spectra were computed using the time dependent density functional theory (TD-DFT) method on the optimized structures using the same DFT functionals and basis sets in a THF model field (Fig. 2b). An excellent agreement between experimental and calculated spectra was observed, with strong absorption bands for complexes **1** and **2** at 512 and 588 nm, respectively, due to a mixture of ligand-to-metal charge-transfer (LMCT) from sulfur  $\sigma$  and  $\pi$  orbitals to the metal ion, plus d-d transitions, plus metal-to-ligand charge-transfer (MLCT) from M-S  $\pi$  orbitals to Os-*p*-cymene/Ir-Cp\*  $\delta^*$  molecular orbitals. As experimentally observed, these bands are absent in

the calculated spectra of complexes [1-CO] and [2-CO], leading to a dramatic change of color upon coordination of CO ligand to the metal center. Vibrational frequencies were calculated to ensure the absence of imaginary frequencies and to obtain calculated IR spectra (Figs. 2c) and 2d). An excellent agreement between experimental and calculated spectra was also observed, with the intense C=O stretching frequencies in the metal-carbonyl complexes [1-CO] and [2-CO] at 2016 and 2079 cm<sup>-1</sup>, respectively.

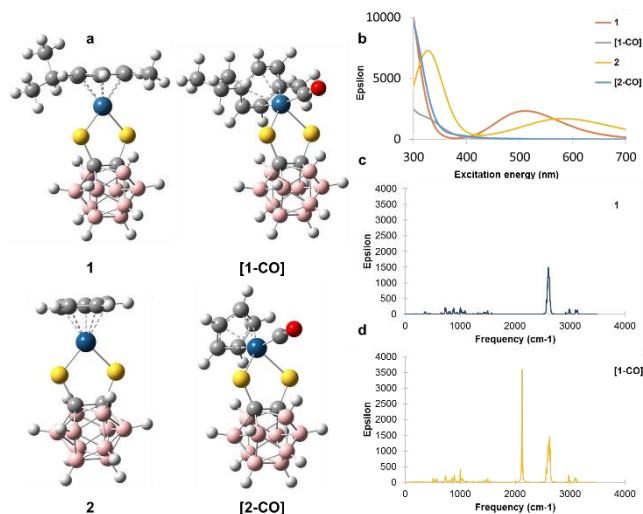


Figure 2. DFT-optimized structures of complexes **1**, **2**, [1-CO], and [2-CO] in a tetrahydrofuran CPCM solvation model field and calculated UV-vis and IR spectra. **a**, DFT-optimized complexes **1**, **2**, [1-CO], and [2-CO] in a tetrahydrofuran CPCM solvation model field (color code: boron: pink; sulfur: yellow; metal ion: blue; carbon: grey; hydrogen: white; oxygen: red). **b**, Calculated UV-vis spectra of complexes **1**, **2**, [1-CO], and [2-CO] in tetrahydrofuran model field. **c**, Infrared absorption spectrum of complex **1**. **d**, Infrared absorption spectrum of complex [1-CO].

#### Formation of networks by encapsulation of the carborane-complexes.

Complexes **1** and **2** were then encapsulated in networks made of PDMS to form metal complex-doped gels (**G1** and **G2**, respectively). The preparation of the networks is straightforward, and is achieved by mixing the complex with the silicone and the cross-linker, and then by heating the resulting mixture for 3 minutes at ca. 150 °C (Fig. S2). Several films were fabricated with different loading degrees in complexes **1** and **2**, ranging from 0.03 weight% (wt%) of complex in silicone-cross-linker (10:1 weight ratio) mixture to 0.27 wt% (Fig. 3(A)). The networks possess very different textures depending on the loading degree in metal complex. PDMS gel without any metal complex is quite flexible and solid, but upon loading the networks become increasingly liquid and deformable.



### Reactivity of the doped networks with CO<sub>(g)</sub>

The ability of the gels, **G1** and **G2** to capture CO was then investigated by placing the materials in a Schlenk tube under 1 atmosphere pressure of CO (pressure controlled at the outlet of the gas cylinder). The pink (Os) and blue (Ir) networks turned immediately yellow, which suggests the formation of the 18-e CO adduct complex (yellow)-containing gels **G1-CO**, **G2-CO** (Fig. 3b and Fig. S3 for networks loaded with more complexes and more intense color changes). To spectroscopically confirm that exposure of the electron deficient complexes-containing gels **G1** and **G2** to carbon monoxide leads to the formation of the 18-e CO-adducts-containing gels **G1-CO** and **G2-CO**, the materials exposed to CO were studied by infrared IR and UV-visible absorption spectroscopies. The characteristic intense C=O stretching signature at 2005 cm<sup>-1</sup> is clearly observable in the **G1-CO** spectrum and absent in the spectrum recorded for **G1** (Fig. 3c). Interestingly, there is a significant shift of energy (35 cm<sup>-1</sup>) for the C=O stretching frequency of [**1-CO**] upon encapsulation within the gel matrix (from 1970 to 2005 cm<sup>-1</sup>). The C=O stretching mode of free CO is at 2143 cm<sup>-1</sup>, which indicates that the coordinated CO ligand within the gel is less strongly coordinated than the CO ligand in [**1-CO**]. UV-visible absorption spectroscopy also indicates that reaction occurs between carbon monoxide and the metal centers encapsulated in the networks, since the decrease of the absorption bands at 480–530 nm is observed after CO exposure (Fig. 3d). Scanning electron microscopy experiments allowed us to gain an insight into the internal structure of the CO-sorption gel **G1**. The structure of **G1** is very similar from that of pure PDMS gel (Figs. 3e and 3f). Interestingly, the exposure of **G1** to CO leads to a dramatic transformation of the gel, and pores in the structure of **G1-CO** were clearly observed (Fig. 3g). The exposure to 1 atmosphere of CO disrupts the structure of the silicone-based materials, and increases its porosity, allowing facile capture of the gas by the encapsulated electron-deficient complexes.

To test the ability of the networks to selectively capture carbon monoxide in the presence of classic industrial contaminants such as carbon dioxide, nitrogen, and oxygen, the gels **G1** and **G2** were placed under pressure of such compounds but no reaction occurred. This control experiment demonstrates that the materials can be used in the presence of these contaminants without interference. This was expected since the metal complexes do not react with these molecules on their own.

Water being a usual contaminant for CO-absorbing materials, a further experiment was performed: gel **G1** was immersed in water and CO was bubbled in the solution (Fig. 3b inset with test tubes). The gel turned yellow within less than 30 seconds, which indicates that while the reaction between **1** and CO is slightly slower in water than under 1 atmosphere CO, water does not competitively bind to these complexes even in large excess, as demonstrated by IR and UV-vis spectroscopies. We ascertained

that the exposure of unloaded PDMS gel (without any metal complexes) to CO does not lead to any CO absorption (no spectroscopic signature for CO observed).

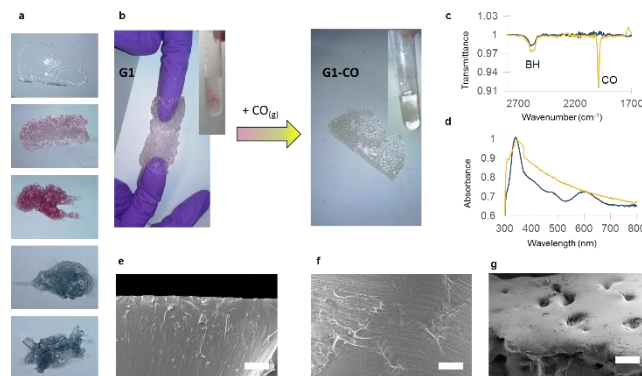


Figure 3. The hybrid materials **G1** and **G2** synthesized in this work and the formation and characterization of the CO-containing gels **G1-CO** and **G2-CO** after exposure to a pressure of CO, or by bubbling CO in water. **a**, The hybrid materials fabricated; from top to bottom: pure PDMS gel, gels **G1** with 0.03 and 0.08 wt% loading of Os complex **1**, gels **G2** with 0.05, and 0.11 wt% loading of Ir complex **2**, respectively. **b**, Formation of the Os gel **G1-CO** after exposure of **G1** to 1 atmosphere of CO (inset: after CO bubbling in water). **c**, Infrared spectra of Os gels **G1** (blue line) and **G1-CO** (yellow line). **d**, UV-visible absorption spectra of Ir gels **G2** (blue line) and **G2-CO** (yellow line). **e–g**, Scanning electron microscopy pictures of pure PDMS gel (**e**), gel **G1** loaded with 0.08 wt% Os complex **1** (**f**), gel **G1-CO** (after exposure of **G1** to CO) (**g**) – scale bars 400  $\mu$ m.

To gain an understanding on the properties of the networks, we investigated both the detection limits of the hybrid materials and their maximum loading capabilities. The threshold of detection of the networks was investigated by using a CO portable detector with a threshold detection of 1 ppm placed into a large desiccator. Using a balloon, we controlled the slow addition of CO<sub>(g)</sub> into the desiccator to achieve a CO-contaminated atmosphere with various CO concentrations (10, 100, and 500 ppm). The Os gel **G1** readily reacts with CO in a CO-rich environment (500 and 100 ppm concentrations), while a few minutes are needed to observe the color change at 10 ppm concentration. The Ir gel **G2** also absorbs CO in a CO-rich environment, but seems to be less reactive with CO than **G1**, since no visible reaction occurs at 10 and 100 ppm. These results demonstrate that the sensitivity of the materials towards carbon monoxide can be finely tuned depending on the metal used (Os *versus* Ir), which could be of interest for the design of products that detect gradients of carbon monoxide concentration (e.g. by juxtaposition of materials with various selectivity degrees on one strip).

To investigate the CO loading capability of the materials, we weighted the networks before and after exposure to 1 atmosphere of CO to determine the amount of CO the networks can absorb. A gel **G1** was prepared with 50

mg of complex **1** in silicone (0.9g) and cross-linker (0.1g) mixtures, to fabricate networks loaded at 0.5 wt% (and therefore containing 0.09 mmol of metal complex). The weight of the gel was measured at 1.0525 g after exposure with 1 bar of CO, which indicates that *ca.* 2.5 mg of CO were absorbed by the gel (*ca.* 0.09 mmol of CO for 0.09 mmol of complex), which gives a sorption capacity of 0.09 mol/kg with networks loaded at 0.5 wt% of complex **1**. These results demonstrate that the number of CO molecules absorbed by the hybrid materials is directly dependent on the number of metal complexes introduced into the materials, and as such has the potential to be highly controllable.

### Release of entrapped CO and recycling of the doped-networks.

The dissociation of CO from the Os and Ir metal complexes in the gels **G1-CO**, and **G2-CO** was then investigated. To test the release of CO from the networks, and their recyclability, an attempt to de-coordinate the CO by placing the networks under high-vacuum, at ambient temperature, and by heating up to 100 °C, was carried out, but without success, even after 48 hours. We also tried to release the CO by exposing the gels **G1-CO** and **G2-CO** to blue light in order to trigger the photo-dissociation of the ligand,<sup>32</sup> but without success.

Remarkably, by taking advantage of the unusual chemistry of carborane-containing metal complexes (CO-decoordination in THF solution, leading to recovery of the parent complexes), we successfully de-coordinated the CO molecules by simply dipping the gels **G1-CO** and **G2-CO** in a THF solution (Fig. 4a). The de-coordination of CO and the release of CO by the networks in the THF solution are characterized by a dramatic color change from yellow to pink (**G1-CO** to **G1**) and from yellow to blue (**G2-CO** to **G2**) and by some bubbles escaping from the gel (Video S2). IR absorption spectroscopy confirms that the recycled materials are free from CO (Fig. 4b), with the disappearance of the characteristic CO signature in the spectrum of the recycled gel. UV-visible spectroscopy also confirms the release of CO and the recycling of the gel, with the characteristic absorption bands observed between 480–530 nm for the 16-e species (Fig. 4c). SEM analysis confirmed that the internal, porous, structure of the materials remain unchanged after the recycling step, suggesting that the materials could be used a number of times for the absorption and controlled release of CO (Fig. 4d). We confirmed the re-usability of the recycled gel by carrying out a subsequent reaction between the pink recovered gels **G1** with CO and observed the formation of the yellow gels **G1-CO**, whilst the second recycling cycle led again to the recovery of **G1**. The capacity of absorption of the recycled materials was found to be the same after the first cycle than before recycling. However, it should be noted that after some minutes in THF (and thus after several recycling steps) the structures of the silicon networks tend to loss their integrity, which limits the re-

usability of these materials and some of their potential applications.

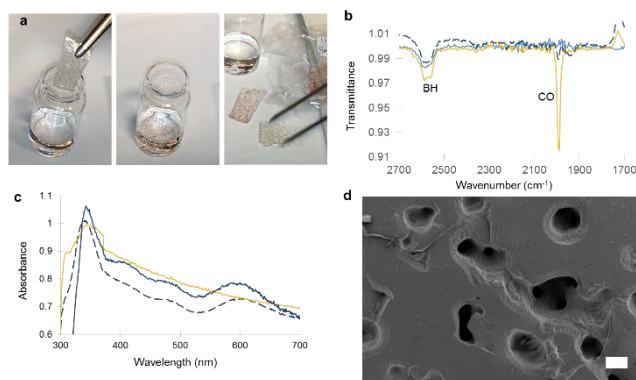


Figure 4. CO-release and recycling of the hybrid materials. **a**, Step-by-step release of carbon monoxide from the yellow CO-trapped Os gel **G1-CO** dipped in THF solution for 1 minute, and recovery of the pink CO-free gel **G1**. **b**, Infrared spectra of Os **G1** before (pale blue, plain line), after (yellow, plain line) CO exposure, and after CO-release and recycling (blue, dashed line). **c**, UV-visible absorption spectra of Ir **G2** before (pale blue, plain line), after (yellow, plain line) CO exposure, and after CO-release and recycling (blue, dashed line). **d**, SEM micrograph of **G1** after CO release and recycling step (scale bar: 200  $\mu\text{m}$ ).

Importantly, the recovery of the electron deficient-gels **G1** and **G2** take place within about 1 minute (Video S1), which suggests that the release of CO is much faster when the metal complexes **1** and **2** are encapsulated into the networks than when they are not formulated in the matrix (the de-coordination of CO from [**1-CO**] and [**2-CO**] takes about one week in a THF solution). This is consistent with the shift in the C=O frequency between the coordinated CO ligand within **G1** and the CO ligand in [**1-CO**]. Indeed, higher  $\nu(\text{CO})$  frequencies encountered in carbonyl species reflect a greater instability of the metal-CO bond.<sup>33</sup>

We then investigated the CO release from the networks in various solvents and a number of solvents were found to trigger the release of CO from the Os or Ir metal complexes encapsulated into the networks (Table 1).

Table 1. Solvents used to test the recyclability of the gels by dipping them into a solution for 1 minute. Values for relative polarity are normalized from measurements of solvent shifts of absorption spectra.<sup>8</sup>

Solvent	CO-release (Y/N)	Relative polarity	Polarity index	Dielectric constant
Benzene	Y	0.111	2.7 non polar	2.30
Toluene	Y	0.099	2.4 non polar	2.38
Diethyl ether	Y	0.117	2.8 non polar	4.30
Chloroform	Y	0.272	4.1 non	4.81

			polar	
Ethyl acetate	Y	0.228	4.4 non polar	6.02
THF	Y	0.207	4 non polar	7.50
Dichloromethane	Y	0.309	3.1 non polar	9.10
Propan-2-ol	N	0.546	3.9 polar protic	18
Acetone	N	0.355	5.1 polar aprotic	21
Ethanol	N	0.654	5.2 polar protic	24.55
Methanol	N	0.762	5.1 polar protic	33
Acetonitrile	N	0.460	5.8 polar aprotic	37.5
Water	N	1.000	polar protic	80

The role of the solvent in the de-coordination of ligand CO in coordination compounds has been extensively studied.<sup>34</sup> For example, rhenium complexes bearing substituted pyrrolyl ligands were found to lose one carbonyl ligand when refluxed in THF for two hours.<sup>35</sup> CO release was also found to occur by associatively supported substitution mechanism, which can take place in coordinating solvents such as water.<sup>36</sup> We found a direct correlation between the dielectric constant of the solvents and the propension of the networks to release CO when immersed in them (Table 1). All solvents with a dielectric constant lower than 10 allow the release of the CO ligand, whilst solvents with a dielectric constant greater than 15 do not allow the CO release, which indicates that nonpolar solvents should be used to perform the CO release. This is consistent with the findings by Bent and co-workers who observed that the polarity of the solvent plays a crucial role in reactions involving carbon monoxide insertion into metal-carbon bonds.<sup>37</sup> We also hypothesize that the complexes **1** and **2** encapsulated in PDMS have a more effective effect in releasing CO compared with non-encapsulated complexes **1** and **2** because of the ability of the silicone matrix to partially solubilises carbon monoxide.<sup>38</sup> Such ability might offer suitable conditions to trigger the ligand decoordination and subsequent CO release by using a solvent that also slightly solubilises CO.

#### Application of the release of CO molecules: carbonylation of complex **2** by using **G1-CO**.

The possibility of using the “on-demand release of CO” by the CO-loaded networks as a source of carbon monoxide to perform a chemical reaction was then investigated. On one hand, a 10 mL solution of the 16-e Ir complex **2** at  $10^{-5}$  M in THF was prepared in a vial (the colour of the solution being grey blue – Fig. 5a; and the number of moles for complex **2** is  $10^{-4}$  mmol). On the other hand, an Os gel **G1** loaded with 1.1 mg of complex **1** ( $20 \times 10^{-4}$  mmol;

20 times more complex **1** in the gel than complex **2** in the solution) was prepared, and then put under a CO atmosphere using a gas cylinder. The pink gel **G1** turned into the yellow gel **G1-CO** (Figs. 5(a-left) and 5(a-middle)).

The 18-e Os [**1-CO**]-containing gel **G1-CO** (yellow) was then added into the vial containing the  $10^{-5}$  M 16-e Ir **2** solution (Fig. 5a). After less than 1 minute, the gel became pink (with the recycling of the 16-e Os **1**-containing gel **G1** and release of the CO molecules in the THF solution), following the same process than the one shown in Figure 4. Concomitantly, the blue solution of the 16-e Ir complex **2** turned yellow (Fig. 5(a-right)), indicating the formation of the 18-e CO adduct [**2-CO**]. A record of the experiment can be found in Video S2. It is important to note that the CO ligand exchange does not occur when the 18-e Os complex [**1-CO**] and the 16-e Ir complex **2** are together in solution.

UV-visible spectroscopy (Fig. 5b) and infrared spectroscopy (Fig. 5d) confirmed the formation of the Ir complex [**2-CO**]. Interestingly, the pink gel can be reloaded with a gas cylinder, and be re-utilised to perform another carbonylation reaction (Fig. 5c for a schematic representation of the process). This proof-of-concept experiment demonstrates the transfer of CO from the Os gel to the Ir solution and highlights that the CO-containing networks can be used as a source of CO, therefore providing a safer solution than a compressed carbon monoxide gas cylinder for small-scale chemical reactions (the CO loaded networks being stable for weeks).

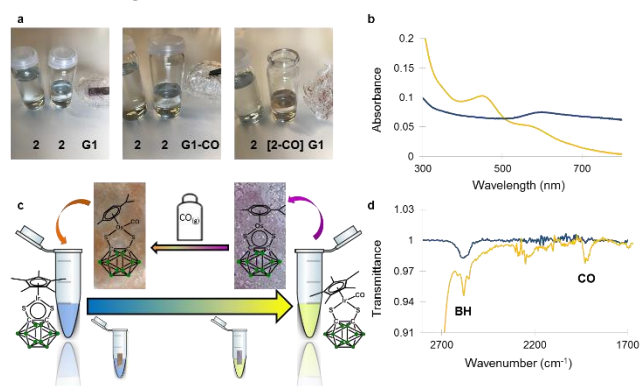


Figure 5. Utilization of the CO-release ability of the Os-CO gel [**G1-CO**] to perform a carbonylation reaction between the Ir complex **2** and CO, leading to the formation of the 18-e Ir complex [**2-CO**] with concomitant recycling of the Os gel **G1**. **a**, Reaction between [**G1-CO**] with a THF solution of complex **2** ( $10^{-5}$  M). **b**, UV-vis absorption spectra of the solution before (**2**;  $10^{-5}$  M in THF; blue line) and after ([**2-CO**];  $10^{-5}$  M in THF; yellow line) reaction with the CO released from the gel **G1**. **c**, General scheme of the utilization of the networks to trigger carbonylation reactions. **d**, IR spectra of the solution before (**2**;  $10^{-5}$  M in THF; blue line) and after ([**2-CO**];  $10^{-5}$  M in THF; yellow line) reaction with the CO released from the gel **G1**.



## Conclusions

Using a simple strategy for the fabrication of carborane-complexes-containing silicone networks, and by taking advantage of the unique reactivity of electron-deficient carborane-metal complexes, we have developed a novel system for the capture of carbon monoxide in the presence of N<sub>2</sub>, and in water, as indicated by the change of color of the networks, and the IR spectroscopic signature of CO. The release of the CO entrapped into the networks is easy and straightforward. We illustrated the potential of this “on demand” release of CO molecules from the networks by performing a chemical reaction between a 16-electron organometallic complex and CO, which led to the formation of the 18-electron CO-adduct.

The practical application of such hybrid materials to capture and release CO ‘on demand’ is highly promising for CO storage, release, transport, and also to scavenge CO, making it a potential safety device. The simplicity of the fabrication process may provide an inexpensive and scalable solution to a variety of large-scale industrial issues. Our material is potentially applicable to industrial processes in which CO acts as a poison, but also for the purification of CO-containing gas (e.g. by filtrating CO-containing H<sub>2</sub> through the networks). The versatility of the system seems to be significant, with possibilities of encapsulating other electron-deficient carborane-metal complexes (e.g. Ru and Co analogues of **1** and **2**), and possibilities to use other types of networks (e.g. silicone-based hydrogels, polymers). This proof-of-concept study demonstrates that the controlled release of CO from the networks has the potential to generate small quantities of CO for small-scale reactions. It is therefore anticipated that these novel hybrid materials might be of interest in academic and industrial laboratories, both in chemistry (e.g. for carbonylation reactions, as exemplified in this work) and in biology (e.g. for release of small amount of CO for characterization of cytochromes P450).

## ASSOCIATED CONTENT

**Supporting Information.** Materials and methods, calculations data, and supporting videos. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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