

# Supporting Information

for

## Host-guest tuning of the CO<sub>2</sub> reduction activity of an iron porphyrin cage

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# 1. General information

## 1.1 Materials

Chemicals obtained from commercial sources were used without further purification. Extra dry *N,N*-dimethylformamide (99.8%) , ferrocene (98%), anhydrous potassium carbonate, methanol and acetonitrile were obtained from Fischer scientific. Potassium carbonate, iron(III)chloride hexahydrate, tetrabutylammonium tetrafluoroborate, sodium tetrafluoroborate (98%), potassium tetrafluoroborate (99.99%), potassium bicarbonate (99.95%), sodium bicarbonate, tetraethylammonium bicarbonate (99%), sodium sulfate, boron trifluoride diethyl etherate, chloroform-*d*, *nafion* perfluorinated resin solution (5 wt% in a mixture of lower aliphatic alcohol and water) and 2 M lithium chloride in ethanol were obtained from Sigma Aldrich. 2,3-Dichloro-5-6-dicyano-1,4-benzoquinone (DDQ) was obtained from Fluorochem. Carbon dioxide (4.5 instrument grade) was obtained from Linde Gas. Carbon black (Vulcan XC-72R) was purchased from Fuel Cell Store. The aqueous Ag/AgCl reference electrode – 3 M KCl (product number: 6.0733.100), non-aqueous double junction Ag/AgCl reference electrode (inner filling electrolyte: 2 M lithium chloride in ethanol and outer filling electrolyte: electrolyte of the particular experiment) (Product number: 6.0726.100), and glassy carbon electrode (3.0 mm diameter) were purchased from Metrohm. *Nafion* N -117 membrane (0.180 mm thick,  $\geq 0.90$  meq/g exchange capacity), and Toray carbon paper (TGP-H-60), platinum gauze (99.9%) (52 mesh woven from 0.1 mm dia wire) were obtained from Alfa Aesar.

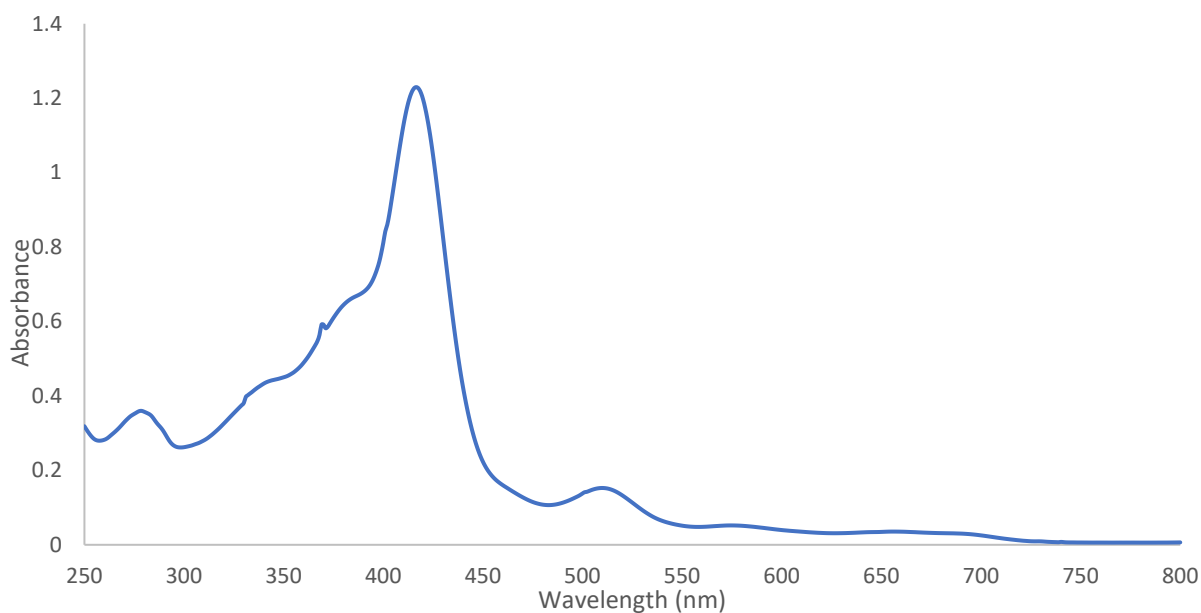
## 1.2 Instrumental details

ESI-mass spectra were recorded using a Thermo Finnigan LCQ Deca mass spectrometer. NMR spectra were measured using a Bruker Avance III 400 MHz spectrometer. All electrochemical measurements were done using a Metrohm PGSTAT204 potentiostat at 25 °C. Gas products were analysed using CompactGC<sup>4.0</sup> Global Analyser Solutions from Interscience. Ivium pocketSTAT2 was used for coupling electrochemistry with the mass spectrometer. A 5 KV USB isolator from Intona was used to isolate the potentiostat from the ground connection to operate under floating. UV-vis spectra were recorded on a JASCO V-630 UV-Vis spectrophotometer and emission spectra were recorded on a JASCO FP-8300ST spectrofluorometer. The baseline was always measured for the same solvent and in the same cuvette as the samples.

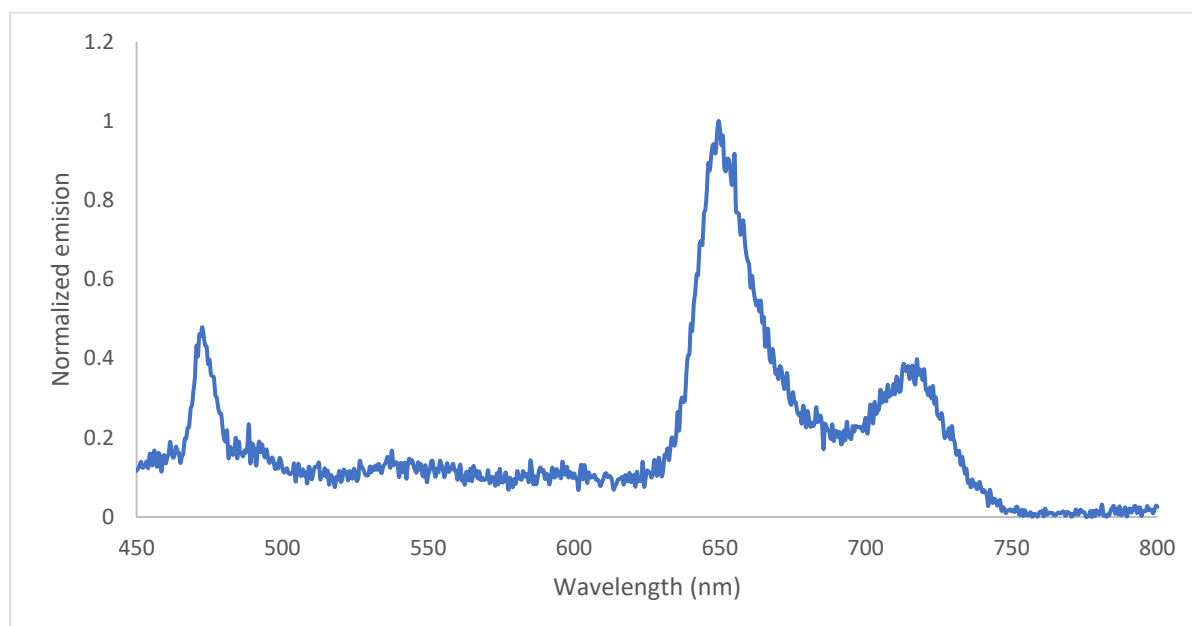
## 2. Catalyst synthesis

[(**1**)Fe<sup>III</sup>Cl]: **H<sub>2</sub>1** (0.11 g, 80  $\mu$ mol) (prepared according to Gilissen et al.)<sup>[1]</sup> and iron(II)chloride tetrahydrate (0.18 g, 0.92 mmol) were dissolved in DMF (10 mL) and the mixture was refluxed for 3 h. The reaction mixture was allowed to cool to 20°C, poured into water (100 mL) and extracted with DCM (3 x 100 mL). The combined organic layers were washed with water (2 x 100 mL) and subsequently vigorously stirred open to air with brine (100 mL) for 4 h. The organic layer was concentrated in vacuo. The residue was purified with silica gel column chromatography (0  $\rightarrow$  10% MeOH in DCM). The purified product was precipitated from DCM/*n*-heptane and washed with *n*-pentane (5 times) to yield [(**1**)Fe<sup>III</sup>Cl] (74 mg, 53  $\mu$ mol, 66%) as a brown powder. **MALDI-TOF**: calcd. for [C<sub>84</sub>H<sub>62</sub>N<sub>8</sub>O<sub>10</sub>Fe]<sup>+</sup> 1398.4, found 1398.0. **UV-vis** (CHCl<sub>3</sub>)  $\lambda_{\max}$ , nm ( $\epsilon$ ): 416 (3.07  $\times 10^5$  L·mol<sup>-1</sup>·cm<sup>-1</sup>), 510 (3.81  $\times 10^4$  L·mol<sup>-1</sup>·cm<sup>-1</sup>),

574 ( $1.30 \times 10^4 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1}$ ). **Emission** ( $\text{CHCl}_3$ ,  $\lambda_{\text{excitation}} = 416 \text{ nm}$ )  $\lambda_{\text{max}}$ , nm: 472, 650, 717. **HRMS**: calcd. for  $[\text{C}_{84}\text{H}_{62}\text{N}_8\text{O}_{10}\text{Fe}\cdot\text{CH}_3\text{OH}]^+$  1430.42037, found 1430.39428. UV-Vis spectra were in accordance with the formation of the  $\text{Fe}^{\text{III}}$ porphyrin chloride species.<sup>[2]</sup>



**Figure S1.** UV-vis spectrum of  $[(1)\text{Fe}^{\text{III}}]\text{Cl}$  ( $4.0\mu\text{M}$ ) in  $\text{CHCl}_3$



**Figure S2.** Emission spectrum of  $[(1)\text{Fe}^{\text{III}}]\text{Cl}$  ( $4.0\mu\text{M}$ ) in  $\text{CHCl}_3$  irradiated at  $\lambda = 416 \text{ nm}$

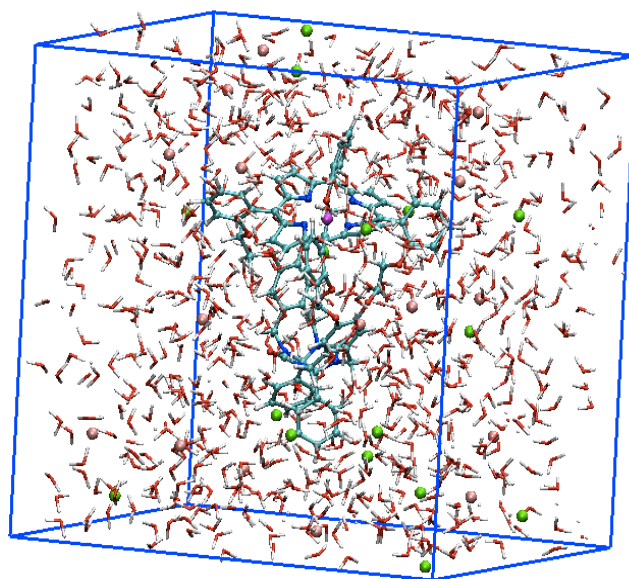
### 3. Force-field molecular dynamics simulations

We conducted classical molecular dynamics simulations of a system consisting of a metalloporphyrin cage catalyst in an aqueous solution of potassium chloride and sodium chloride. Although this model differs in the transition metal ion (Co vs. Fe) from that studied in the present paper, it yields a detailed picture of the association of alkali metal cations to a metalloporphyrin cage. Important to note is that the simulations provide a rather realistic picture of the system that is actually modelled, including effects of explicit solvation and finite temperature fluctuations.

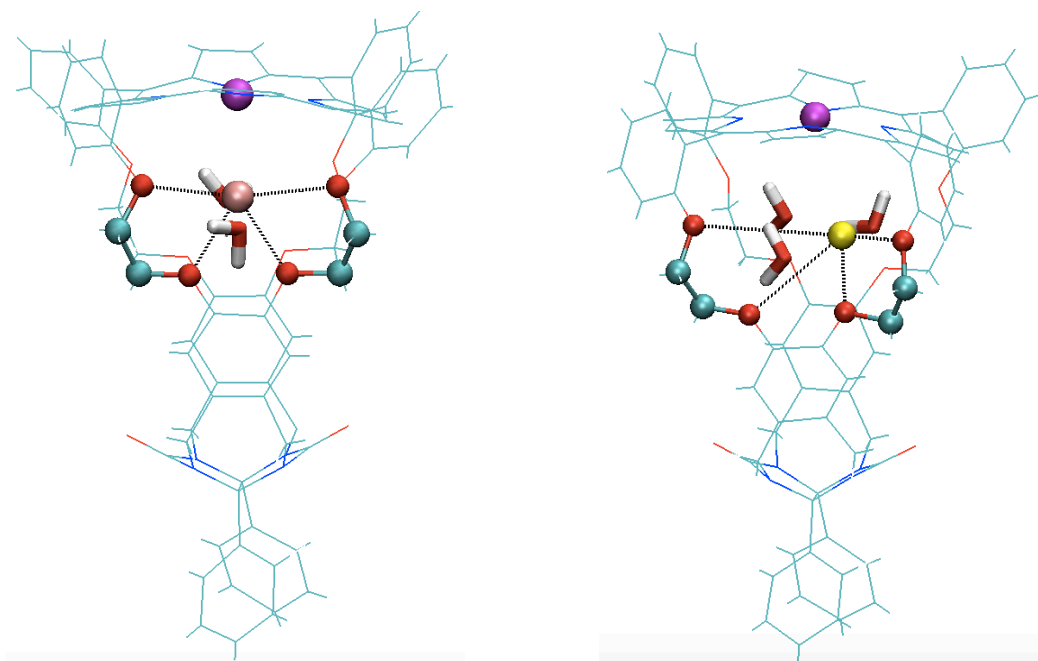
The setup of the model is as follows. The empirical force field for the Co-porphyrin cage is CHARMM36 FF<sup>[3][4]</sup> based on the non-standard Co-porphyrin parameters taken from (3). The Co Lennard-Jones parameters were adjusted to reproduce the experimental position of the Co – oxygen peak of Co(II) – water radial distribution function. The partial charges for the Co-porphyrin moiety for Co(II), Co(I), Co(0) were calculated according to ref (11)<sup>[5]</sup>. The cage was then solvated by 824 TIP3P water molecules<sup>[6]</sup>, in a cubic box of approximately 3 nm. For each of the charge states, 10 independent configurations with different cage conformations were prepared. Subsequently, 32 water molecules were randomly replaced by 16 K<sup>+</sup> or Na<sup>+</sup> ions, and 16 Cl<sup>-</sup> ions, see Figure S3. The systems were then simulated for 10 ns at 300 K and 1 bar with a 1 fs time step employing periodic boundary conditions in Gromacs 2018.6 package<sup>[7]</sup>. Overall, 2 x 30 independent trajectories were collected.

Preliminary results indicated that the potassium and sodium cations associate with the cage by preferentially coordinating with the crown-ether like moieties independently on the overall charge of the cage. There is a notable distinction between the complexes with the potassium and the sodium ions. The potassium ion typically positions near the center of a mostly undistorted crown-ether-like moiety, whereas the sodium ion is positioned off-center interacting mostly with only a part of a crown-ether-like moiety. This is demonstrated in Figure S4 with typical snapshots showing the relevant parts of the system, including the cations, the metallo-porphyrin cage and coordinating water molecules.

This can be understood as an effect of the effective size of the cations that are more (potassium) or less (sodium) commensurate with the crown-ether-like window size. As these observations are robust with respect to the overall charge of the cage, we believe that they might be generic for aqueous solvents, irrespective of the nature of the metal in the porphyrin moiety.



**Figure S3.** Solvated Co-porphyrin cage in the center of the box filled with aqueous 1 M KCl solution, with Co colored in magenta. The color coding of atoms is O (red), H (white), N (blue), C (green),  $\text{Cl}^-$  (light green) sphere,  $\text{K}^+$  (pink sphere).



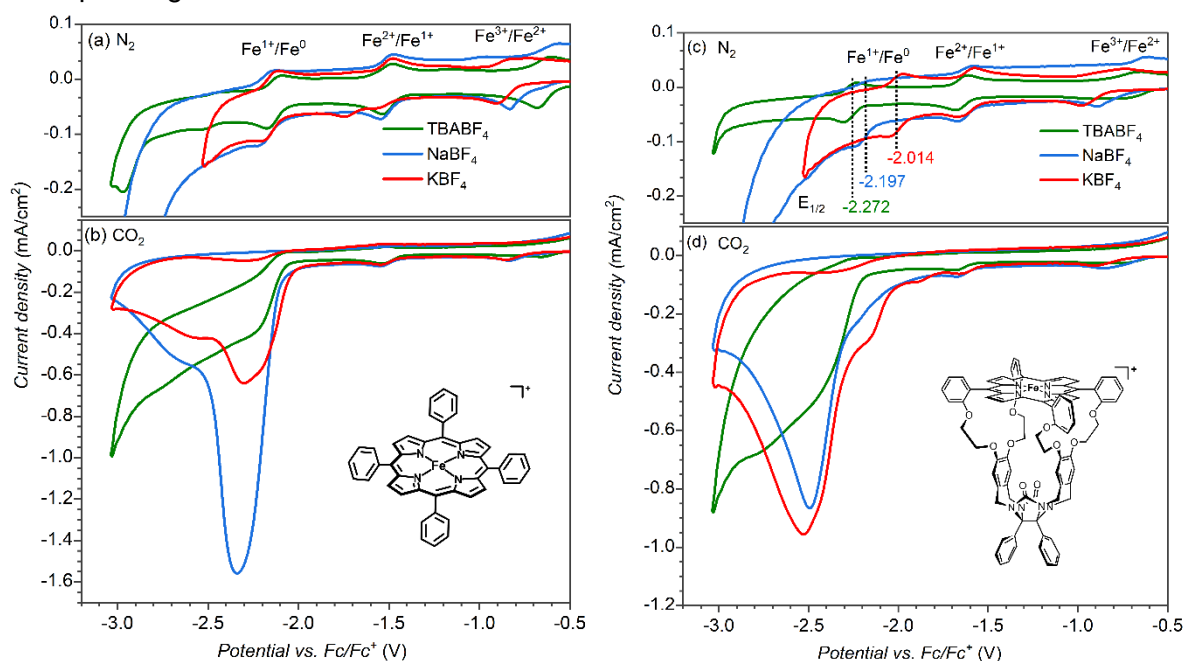
**Figure S4.** Snapshots of the Co-porphyrin cage (lines) with  $\text{K}^+$  (pink, left) and  $\text{Na}^+$  (yellow, right). Only the 1<sup>st</sup> shell water molecules of the alkali metal cation (sticks) is shown. The rest of the system is omitted in the visualization, for clarity.

## 4. Electrochemical measurements

### 4.1 Homogeneous CV experiments

Homogeneous cyclic voltammetry (CV) experiments were performed using a standard three electrode assembly in a solution of 0.25 mM catalyst  $[(1)Fe^{III}Cl]$ , 0.1 M of the corresponding supporting electrolyte (TBABF<sub>4</sub>, NaBF<sub>4</sub> and KBF<sub>4</sub>) and 0.5 M H<sub>2</sub>O in DMF (10 mL). A glassy carbon working electrode (WE) was used and polished between the measurements. A double junction non-aqueous Ag/AgCl reference electrode (RE) filled with 2 M LiCl in ethanol as the inner electrolyte and the corresponding electrolyte (TBABF<sub>4</sub>, NaBF<sub>4</sub> and KBF<sub>4</sub>) as the outer electrolyte were used. The counter electrode (CE) was a platinum mesh of 2 cm<sup>2</sup> area. The reference electrode was calibrated against the ferrocene/ferrocenium redox couple. Prior to the measurements the solution was bubbled with N<sub>2</sub> or CO<sub>2</sub> for 30 min and during the measurements the corresponding gas was kept flowing through the head space.

The TBA<sup>+</sup> ion is too bulky to enter in to the cage and the response in this electrolyte corresponds to the activity of the free cage catalyst.  $[Fe(TPP)]$  was used as a reference catalyst to understand the effect of the cage cavity in the presence of Na<sup>+</sup> and K<sup>+</sup> ions. The shift of the Fe<sup>1+</sup>/Fe<sup>0</sup> redox couple under different electrolytes was calculated from their corresponding E<sub>1/2</sub> values.



**Figure S5.** Homogeneous cyclic voltammograms of  $[Fe(TPP)]$  (left) and  $[(1)Fe]$  (right) (0.25 mM) measured in TBABF<sub>4</sub> (green), KBF<sub>4</sub> (red), NaBF<sub>4</sub> (blue) electrolytes (0.1 M in DMF + 0.5 M H<sub>2</sub>O; scan rate 100 mV/s) under N<sub>2</sub> (for (a) & (c)) and under CO<sub>2</sub> (for (b) & (d)).

#### 4.1.1 Calculation of the number of transferred electrons in a reduction process

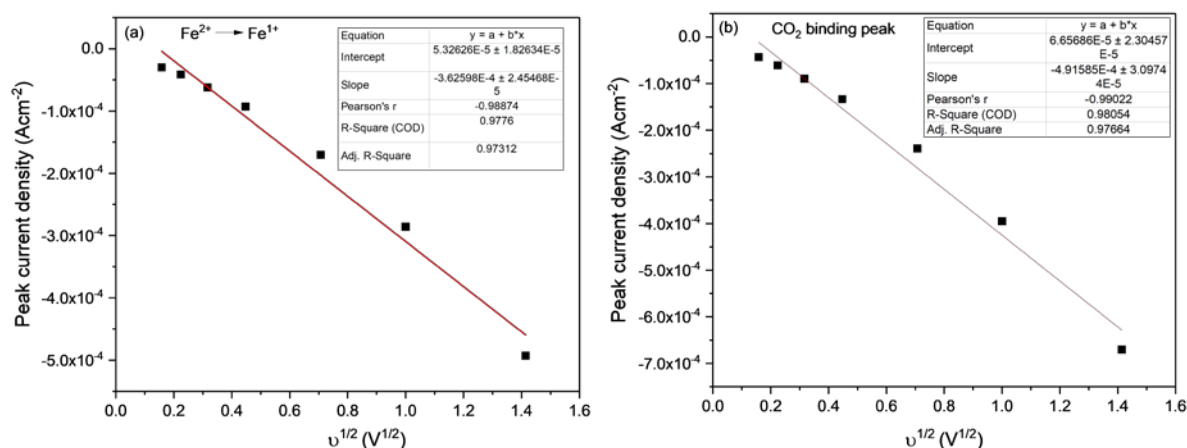
The number of the transferred electrons in the “CO<sub>2</sub> binding peak” (the peak at -1.8 V in Figure 2b, orange line) observed for [(1)Fe] in the KBF<sub>4</sub> electrolyte under CO<sub>2</sub> is calculated using the Randles - Ševčík equation (Equation-1). First, the diffusion coefficient (*D*) is obtained from the redox peak Fe<sup>2+</sup> → Fe<sup>1+</sup>, where we know that the number of the transferred electrons is one (*n*=1).

$$i_p = 0.4463 nFAC \left( \frac{nFvD}{RT} \right)^{\frac{1}{2}} \quad \text{Equation-1,}$$

where *i<sub>p</sub>* = peak current; *n* = number of electrons; *F* = faradaic constant (96485 C.mol<sup>-1</sup>); *D* = diffusion coefficient; *v* = scan rate (V/s); *A* = area of the electrode (0.07 cm<sup>2</sup>), *C* = concentration of the catalyst (0.25 mM), *R* = universal gas constant (8.314 J.mol<sup>-1</sup>.K<sup>-1</sup>); *T* = temperature (298 K).

The diffusion coefficient can be obtained from the dependence of the peak current on the scan rate (Figure S6). The fit provides *D* = 2.91 × 10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup>.

The obtained diffusion coefficient is used for the determination of ‘*n*’ for the “CO<sub>2</sub> binding peak” in the same way. Hence, plotting the dependence of the peak current on the scan rate assuming *D* = 2.91 × 10<sup>-5</sup> cm<sup>2</sup> s<sup>-1</sup> units provides the number of the transferred electrons, which is equal to 1.22 (Figure S6b). This value is close to one, confirming that the peak corresponds to a 1 electron process.



**Figure S6.** Plot of the peak current density vs  $v^{1/2}$  of [(1)Fe] (0.25 mM) in 0.1 M KBF<sub>4</sub> (DMF + 0.5 M H<sub>2</sub>O) for the reduction (a) Fe<sup>2+</sup> → Fe<sup>1+</sup> (b) the “CO<sub>2</sub> binding peak”.

#### 4.1.2 Calculation of the CO<sub>2</sub> binding rate constant

We have calculated the CO<sub>2</sub> binding rate constant of [(1)Fe] in the KBF<sub>4</sub> in DMF electrolyte employing Equation-2, which was previously reported in the literature.<sup>[8]</sup> The anodic shift of the Fe<sup>+</sup> → Fe<sup>0</sup> reduction wave in the presence of CO<sub>2</sub> is used for the estimation of the binding rate constant. The peak potential ( $E_p$ ) of the CO<sub>2</sub> binding peak is related to the scan rate ( $\nu$ ) of the measurement through the following equation:

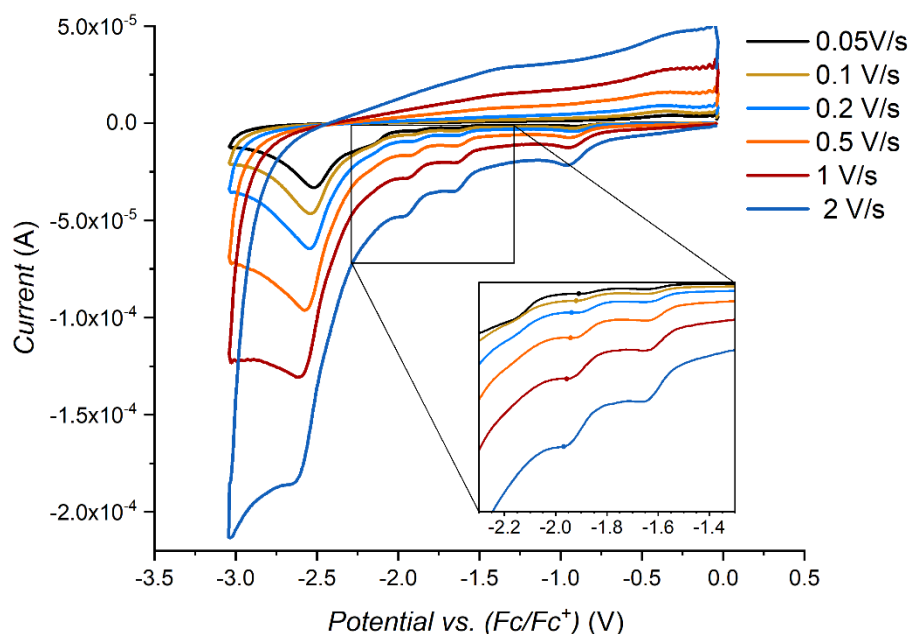
$$E_p = E_{1/2}^0(Fe^{I/0}) - 0.78 \frac{RT}{F} + \frac{RT}{2F} \ln \frac{RTkC}{F\nu} \quad \text{Equation -2}$$

Simplified to,

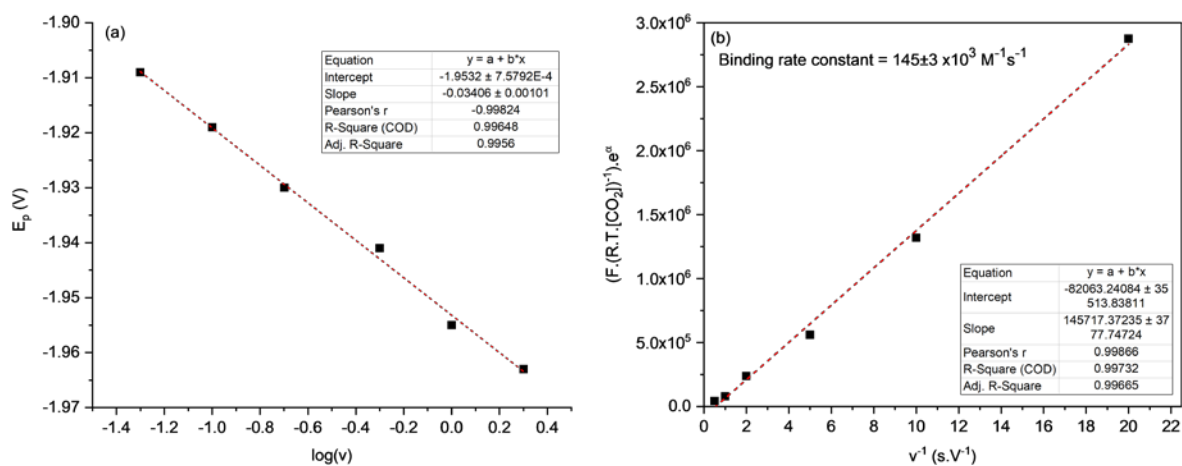
$$\frac{F}{RTC} e^{\alpha} = \frac{k}{\nu}; \quad \alpha = \frac{(E_p - E_{1/2}^0(Fe^{I/0}) + \frac{0.78RT}{F})2F}{RT} \quad \text{Equation-3}$$

$E_p$  = Peak potential;  $E_{1/2}^0(Fe^{I/0}) = -2.014$  V (Fe<sup>+</sup> → Fe<sup>0</sup> redox potential under N<sub>2</sub>);  $k$  = CO<sub>2</sub> binding rate constant;  $R = 8.314$  J.mol<sup>-1</sup>.K<sup>-1</sup> (universal gas constant);  $T = 298$  K (temperature);  $F = 96485$  C.mol<sup>-1</sup> (faradaic constant);  $C = 0.23$  M (concentration of CO<sub>2</sub> in the DMF electrolyte).<sup>[9]</sup>  $\nu$  = Scan rate in V/s.

We have performed the experiments under different scan rates of 0.05 V/s to 2 V/s (Figure S7). At scan rates above 2 V/s, we could not differentiate the small faradaic peak from the large capacitive charging current. The slope of 0.03 V for the plot of  $E_p$ (V) vs log( $\nu$ ) is diagnostic for the validity of the plot (Figure S8). The CO<sub>2</sub> binding rate constant is obtained from the slope of the linear regression of Equation-3. The obtained binding rate constant is  $145 \pm 3 \times 10^3$  M<sup>-1</sup>s<sup>-1</sup>.

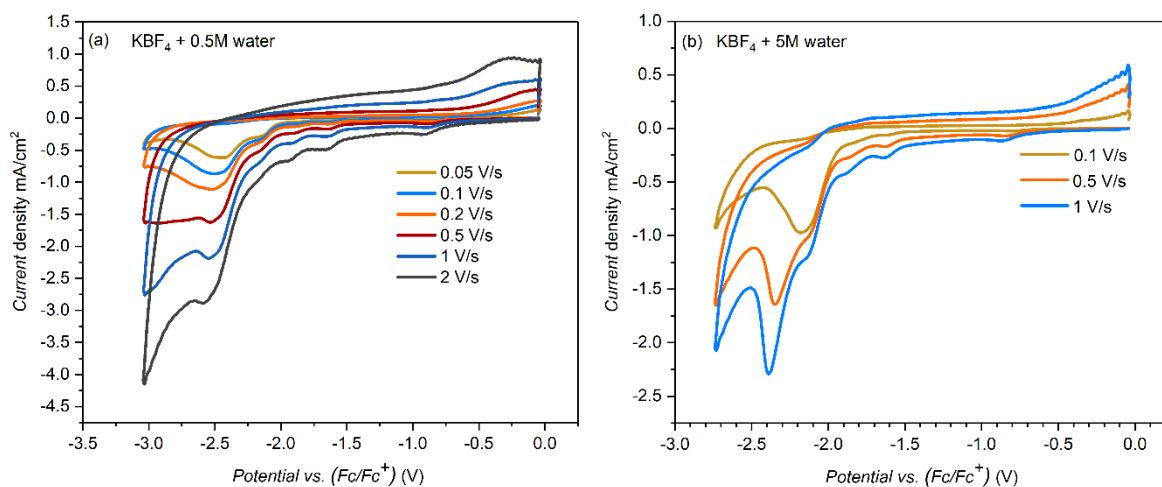


**Figure S7.** Cyclic voltammogram of [(1)Fe<sup>III</sup>]Cl (0.25 mM) measured in KBF<sub>4</sub> electrolyte (0.1 M in DMF, no water added), at various scan rates 0.05 V/s → 2 V under CO<sub>2</sub>; the inset displays the enlarged view of the region -1.4 to -2.2 V and the peak potentials used for the analysis are marked with a dot.



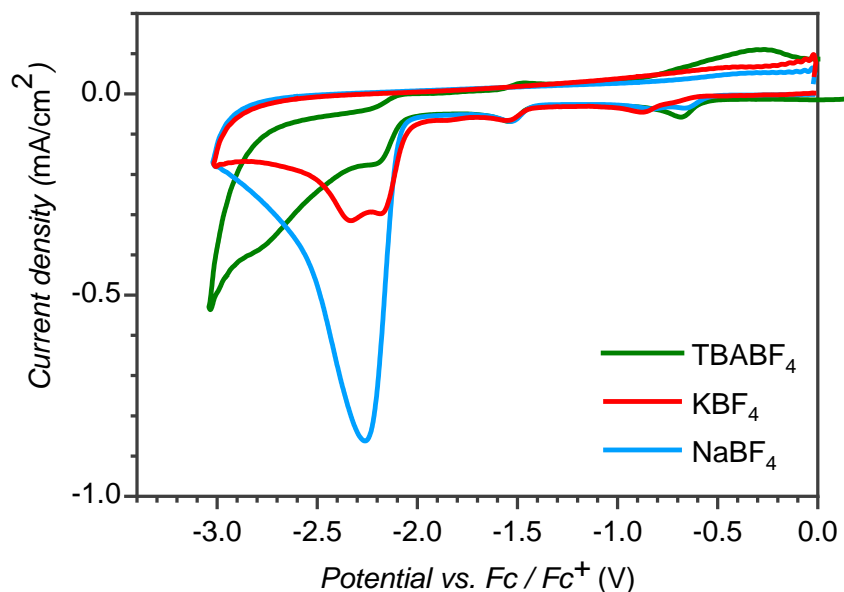
**Figure S8.** (a) Dependence of the peak potential ( $E_p$  (V)) on the logarithm of the scan rate ( $\log(v)$ ). (b) Determination of the binding rate constant for the "CO<sub>2</sub> binding peak" (shown in Figure 2 at -1.8 V) according to Equation-3.

### 4.1.3 Scan rate studies



**Figure S9.** Cyclic voltammogram of [(1)Fe] (0.25 mM) measured in 0.1 M KBF<sub>4</sub> (in DMF) electrolyte under CO<sub>2</sub> (a) with 0.5 M water at various scan rates 0.05 V/s → 2 V/s (b) with 5 M water at scan rates 0.1 V/s → 1 V/s.

### 4.1.4 CO<sub>2</sub>RR activity for the [Fe(TPP)] complex in the absence of water



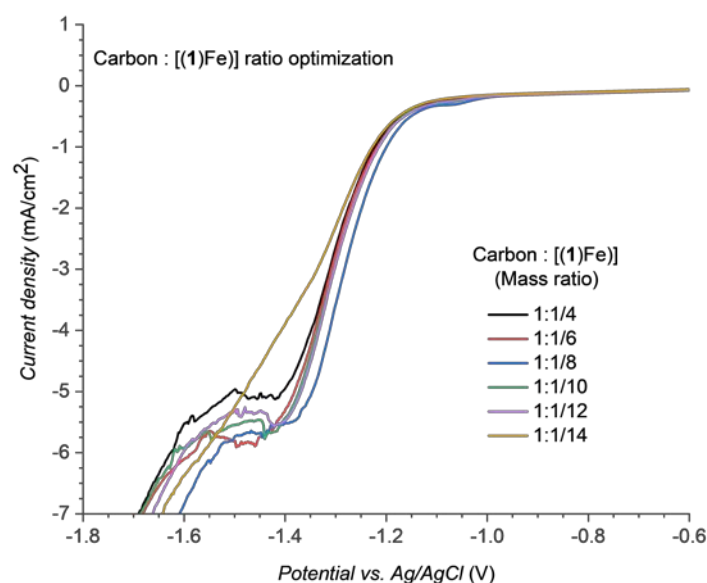
**Figure S10.** Cyclic voltammogram of [Fe(TPP)] (0.25 mM) measured in TBABF<sub>4</sub>, KBF<sub>4</sub>, NaBF<sub>4</sub> electrolytes (0.1 M in DMF) in the absence of water at a scan rate of 100 mV/s under CO<sub>2</sub>.

## 4.2 Heterogeneous experiments

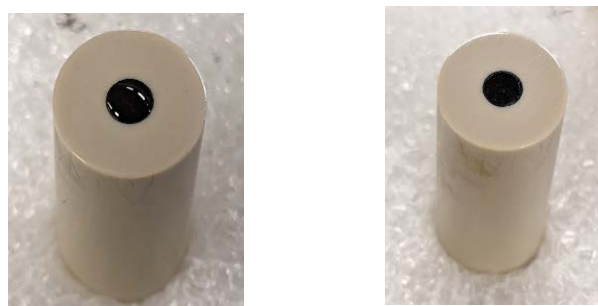
### 4.2.1 Preparation of the carbon-catalyst ink

Prior to the heterogeneous CV experiments, the mass ratio between carbon and the catalyst was optimized. The amount of carbon was kept constant (2.5 mg/mL) and the amount of cage catalyst ([**1**]Fe) was varied systematically (0.625, 0.416, 0.312, 0.250, 0.208, 0.178 mg/mL). Vulcanized carbon black (2.5 mg) was dispersed in 2 mL of DCM and the dispersion was sonicated for 45 min. The [**1**]Fe complex was dissolved in 0.5 mL of DCM and the solution was added to the carbon black dispersion, and the resulting mixture was sonicated for 30 min. The catalyst-carbon dispersion was evaporated to dryness. The obtained catalyst-carbon composite was re-dispersed in isopropanol (IPA) (970  $\mu$ L) along with 30  $\mu$ L of *Nafion* binder. This final dispersion (catalyst ink) was directly drop-casted on a clean glassy carbon electrode and allowed to dry in the air using IR lamp (Figure S12). Linear sweep voltammetry (LSV) analysis was performed for the different carbon-to-catalyst ratios in an aqueous solution of  $\text{KHCO}_3$  (0.5 M) saturated with  $\text{CO}_2$ . The maximum  $\text{CO}_2\text{RR}$  activity was observed at a carbon-to-catalyst ratio of 1:1/6 (2.5:0.416 mg). The optimized ratio was then used for all heterogeneous experiments.

For experiments with [Fe(TPP)], the same amount of moles as of [**1**]Fe was used.



**Figure S11.** Linear sweep voltammogram (LSV) of [**1**]Fe@carbon (at various mass ratios) measured in (0.5 M) aq.  $\text{KHCO}_3$  electrolyte (scan rate 10 mV/s) under  $\text{CO}_2$ .



**Figure S12.** Preparation of catalyst@carbon modified glassy carbon electrode: (left) catalyst ink drop casted on a clean glassy carbon electrode, (right) after drying under an IR lamp.

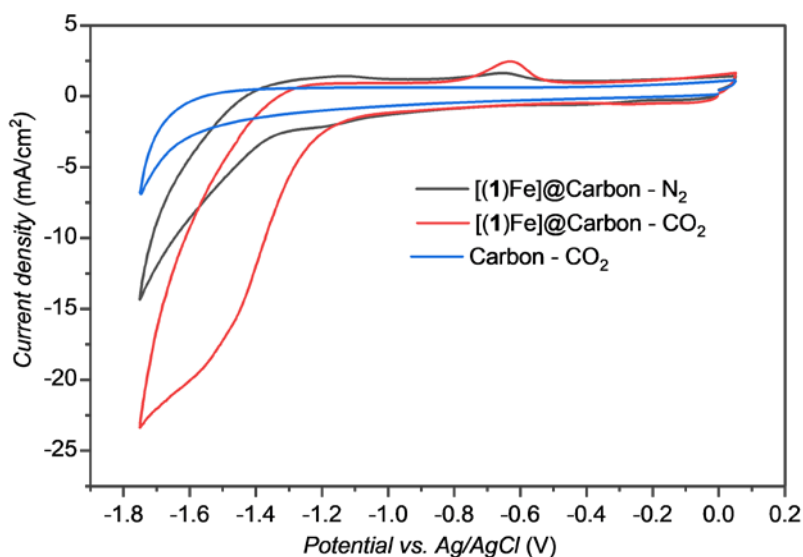
## 4.2.2 Heterogeneous CV experiments

Heterogeneous CV measurements were done using an aqueous Ag/AgCl reference electrode filled with 3 M aqueous KCl solution. The catalyst ink (10  $\mu$ L) was drop casted on a clean glassy carbon electrode and air-dried (using an IR lamp). The CVs of the modified electrode were recorded in aqueous bicarbonate solutions (0.5 M) of different electrolytes (TEAHCO<sub>3</sub>, NaHCO<sub>3</sub>, KHCO<sub>3</sub>) purged either with N<sub>2</sub> or with CO<sub>2</sub> for 30 min. A blank experiment, which was performed only with carbon black in aqueous KHCO<sub>3</sub> solution, did not show any CO<sub>2</sub>RR activity (Figure S13).

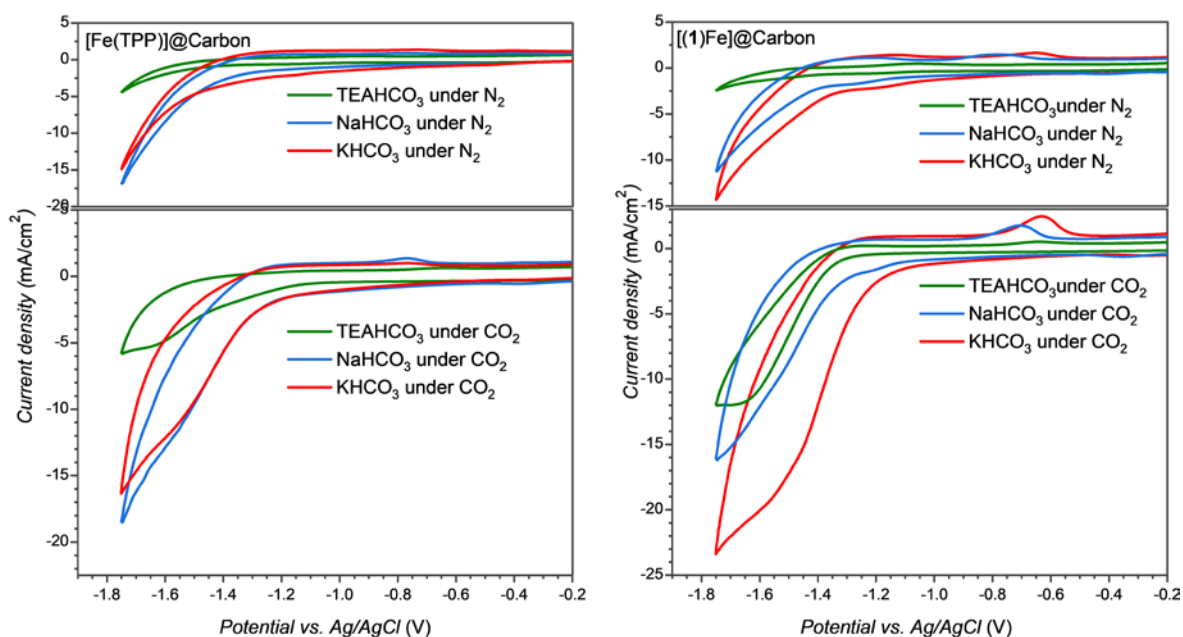
To investigate the activity of the [(1)Fe] catalyst without any alkali metal guest, we used the TEA<sup>+</sup> electrolyte (TEA<sup>+</sup> is too bulky to enter the cavity). First, we performed CV experiments with [Fe(TPP)] immobilized in the same manner as [(1)Fe] (Figure S14 left). The CO<sub>2</sub>RR activities of [Fe(TPP)]@carbon under different electrolytes (aqueous TEAHCO<sub>3</sub>, NaHCO<sub>3</sub>, KHCO<sub>3</sub>) were used as a reference. In general, a low current flow was observed in the TEA<sup>+</sup>-based electrolyte both in the presence of CO<sub>2</sub> and N<sub>2</sub> in comparison to the Na<sup>+</sup> and K<sup>+</sup>-based electrolytes. The electrolyte effects of Na<sup>+</sup> and K<sup>+</sup> ions were very similar for [Fe(TPP)]@carbon, both of them showed nearly the same CO<sub>2</sub>RR activity. The CO<sub>2</sub>RR onset potential of [Fe(TPP)] remains the same in all the electrolytes and it is therefore independent of the nature of the cation (Figure S15). The response from [Fe(TPP)]@carbon showed the effects of the electrolyte properties on the observed catalytic activity. Using this information we then evaluated the CO<sub>2</sub>RR activity of the [(1)Fe]@carbon under different electrolytes (Figure S14 right). The findings are as follows:

1. The CO<sub>2</sub>RR onset potential was found to be shifted to a lower overpotential by 110 mV in the presence K<sup>+</sup> ions while it shifted only 22 mV in the case of Na<sup>+</sup> ions (Figure S15). This is in agreement to the trend of E<sub>1/2</sub> potential for the generation of Fe<sup>(0)</sup> complexes in the homogeneous CV experiments (Figure S5). The potential shift confirms the binding interaction of Na<sup>+</sup> and K<sup>+</sup> ions to the cage after its immobilization.

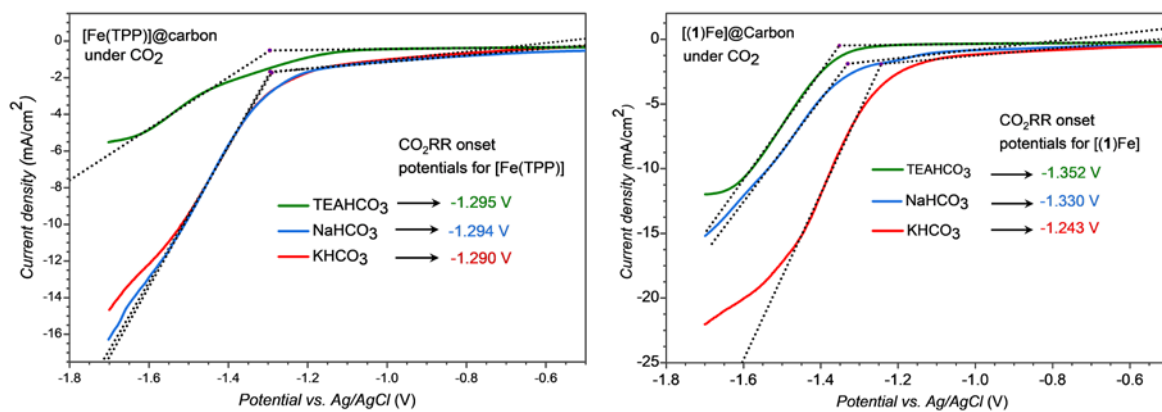
2. Due to the electrolyte effect, the catalytic current in the TEA<sup>+</sup>-based electrolyte is smaller than that in the Na<sup>+</sup> and K<sup>+</sup>-based electrolytes as a result of the electrolyte properties. Therefore, the effect of the host-guest chemistry cannot be easily obtained by using the TEA<sup>+</sup>-based electrolyte as a reference. However, the response for [Fe(TPP)] showed the same catalytic current in the Na<sup>+</sup> and K<sup>+</sup>-based electrolytes. Although both ions can interact with the cage catalyst, potassium ions showed much superior catalytic activities in the homogeneous phase. Hence, comparison of the activities in the Na<sup>+</sup> and K<sup>+</sup>-based electrolytes will provide an insight into the added value of favorable coordination of K<sup>+</sup> to the cage catalyst. Accordingly, a large increase (i.e.  $\sim 8$  mA/cm<sup>2</sup> at  $-1.55$  V) of the catalytic current in the K<sup>+</sup>-based electrolyte in comparison with the Na<sup>+</sup>-based electrolyte was observed. This is due to the specific binding interaction of the K<sup>+</sup> ions to the [(1)Fe].



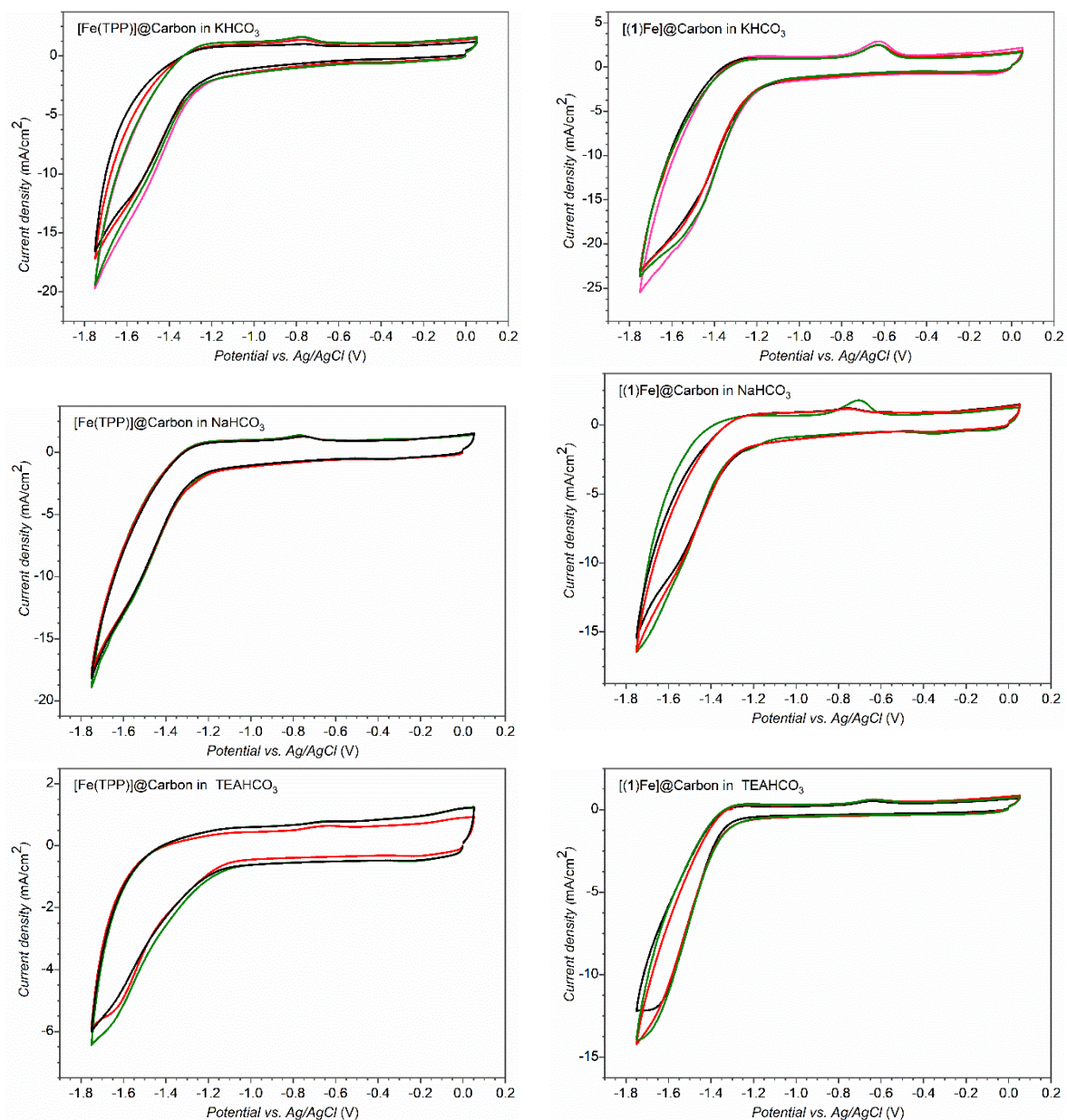
**Figure S13.** Heterogeneous CVs of [(1)Fe]@carbon (mass ratio 1:1/6) under  $N_2$  and  $CO_2$  and the blank experiment with carbon measured in aq.  $KHCO_3$  electrolyte (scan rate 100 mV/s) under  $CO_2$ .



**Figure S14.** Heterogeneous CVs of [Fe(TPP)]@carbon (left) and [(1)Fe]@carbon (right) measured in 0.5 M aqueous solutions of  $TEAHCO_3$  (green),  $KHCO_3$  (red),  $NaHCO_3$  (blue); the scan rate was 100 mV/s. The upper graphs show experiments under  $N_2$  and the lower graphs under  $CO_2$ .



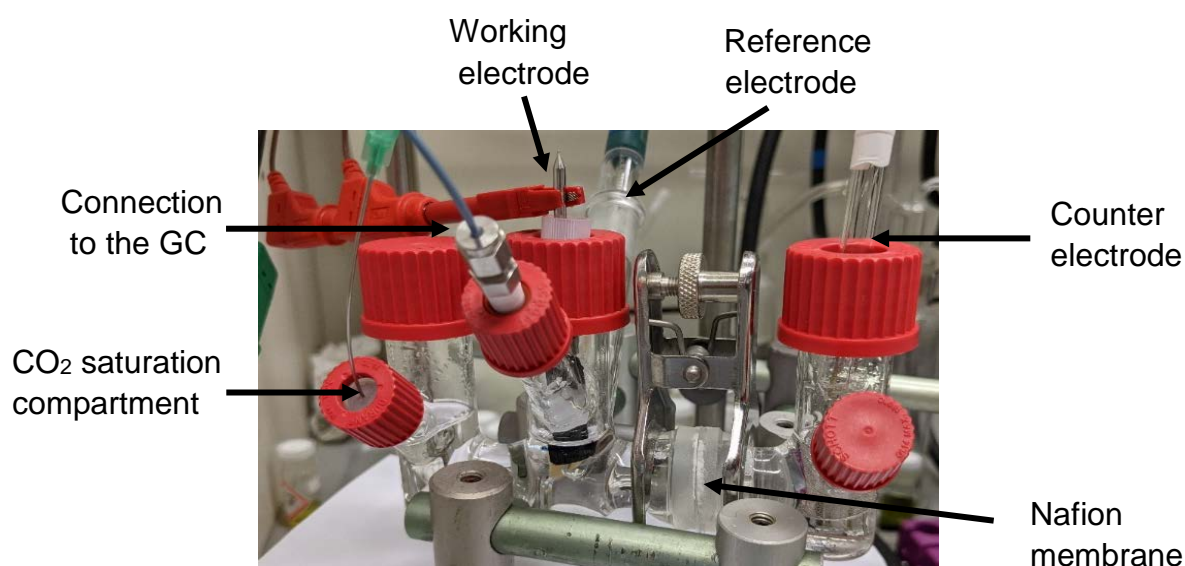
**Figure S15.** CO<sub>2</sub>RR onset potentials of the CVs shown in Figure S14. Left: [Fe(TPP)]@carbon; right: [(1)Fe]@carbon. The experiments were performed in 0.5 M aqueous solutions of TEAHCO<sub>3</sub> (green), KHCO<sub>3</sub> (red), NaHCO<sub>3</sub> (blue) with scan rate 100 mV/s under CO<sub>2</sub>.



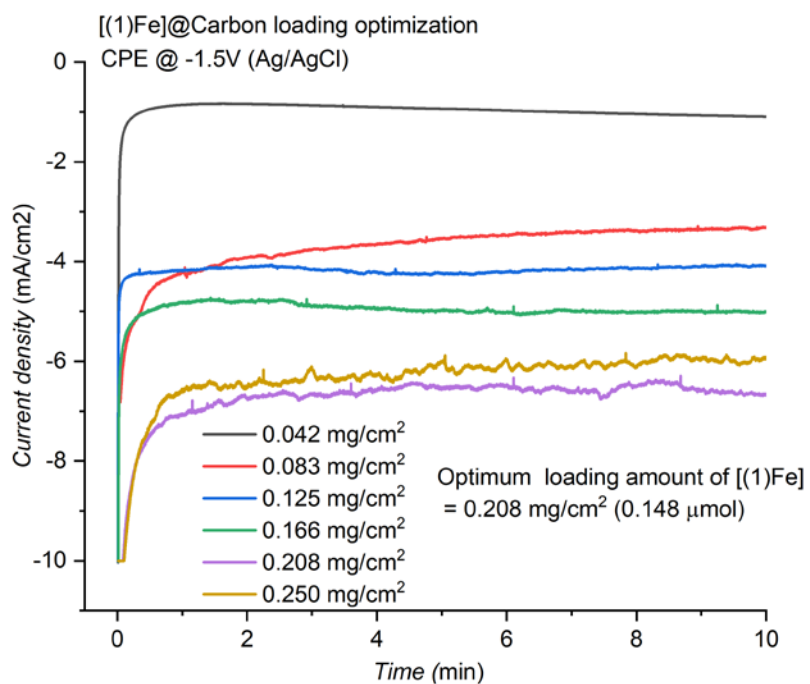
**Figure S16.** Multiplicate measurements of the CO<sub>2</sub>RR activity of [Fe(TPP)]@carbon and [(1)Fe]@carbon reproduced each time independently from new ink solutions. The measurements were performed in 0.5 M aqueous electrolytes (indicated in the figure) saturated with CO<sub>2</sub> at scan rates of 100mv/s.

### 4.2.3 Controlled potential electrolysis (CPE)

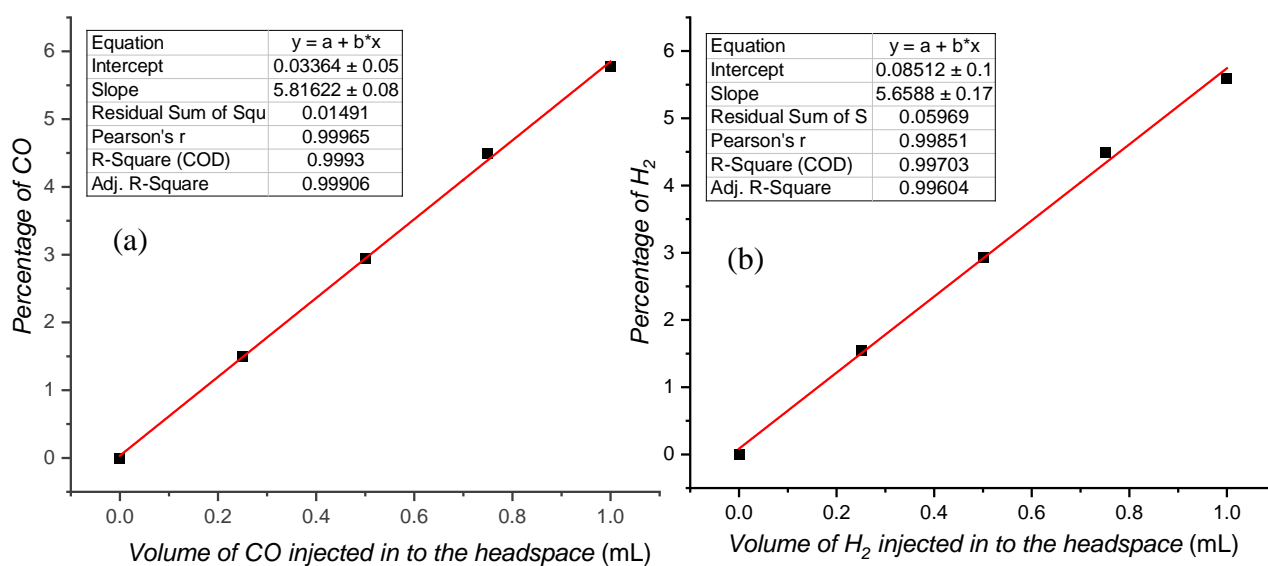
The product analysis was done by performing preparative scale electrolysis at different polarization voltages. A modified H-cell was designed and home-built for the bulk electrolysis experiments (Figure S17). The cell consists of three compartments: working electrode, counter electrode and an additional CO<sub>2</sub> saturation compartment. Working and counter electrode compartments were separated with a *Nafion* proton exchange membrane. The saturation compartment was attached to the working electrode through an opening, allowing the free mixing of electrolytes between the compartments. The head space of the working electrode was connected to an in-line gas chromatograph. The catalyst loading on the carbon paper (per cm<sup>2</sup>) was first optimized (Figure S18). Catalyst ink (500 μL) was drop casted (10 μL x 50) on a Toray carbon paper electrode (area = 1 cm<sup>2</sup>) and dried in the air (using IR lamp). The reference electrode (aq. Ag/AgCl-3M KCl) was placed close to the working electrode. A platinum wire gauze (geometrical area approx. 11 cm<sup>2</sup>) was used as the counter electrode. Prior to the assembly, the *Nafion* membrane was first activated using standard procedure. The head space of the cathode compartment was calibrated by injection of known volumes of CO and of H<sub>2</sub> (Figure S19). Before the measurements, the electrolyte was deoxygenated with N<sub>2</sub> purging and then saturated with CO<sub>2</sub>. The CO<sub>2</sub> bubbling was continued in the saturation compartment during the measurements and the stirring ensured the mixing of electrolyte with the working electrode compartment. CPE was performed at different polarization voltages (-1.2, -1.3, -1.4, -1.5, -1.55 and -1.6 V) for 10 min (Figure S20). The gaseous products were collected from the cathode head space and analyzed by the in-line GC. Extended electrolysis for 2 hrs at -1.4 V (Vs. Ag/AgCl) was carried out and NMR analysis was conducted to check for any liquid products.



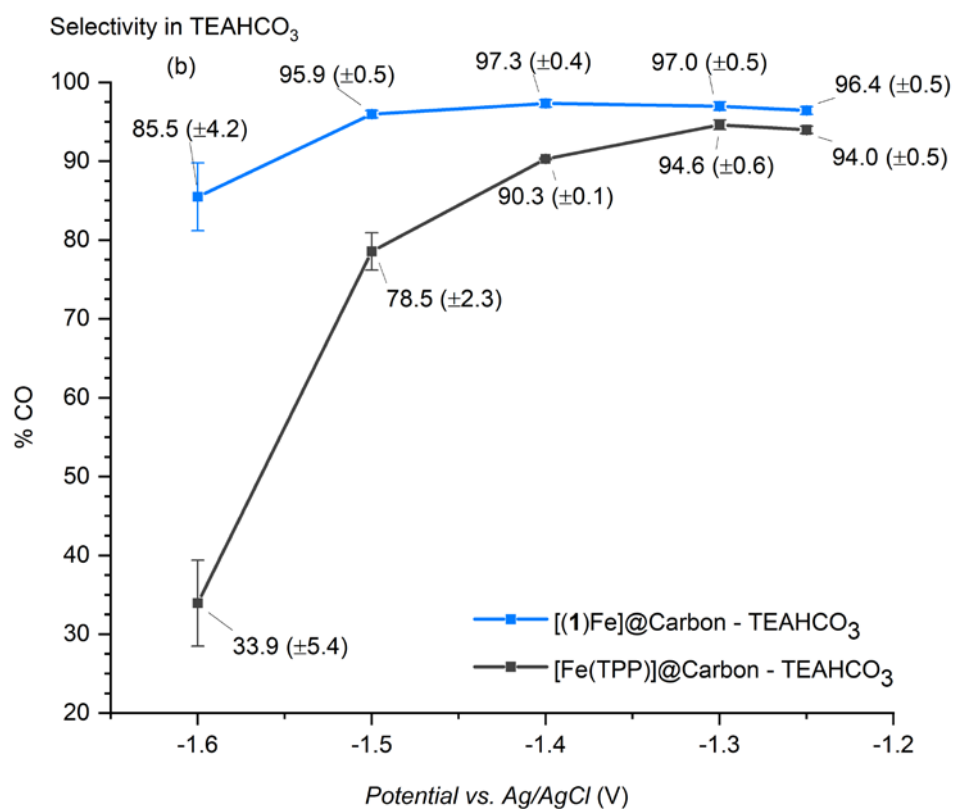
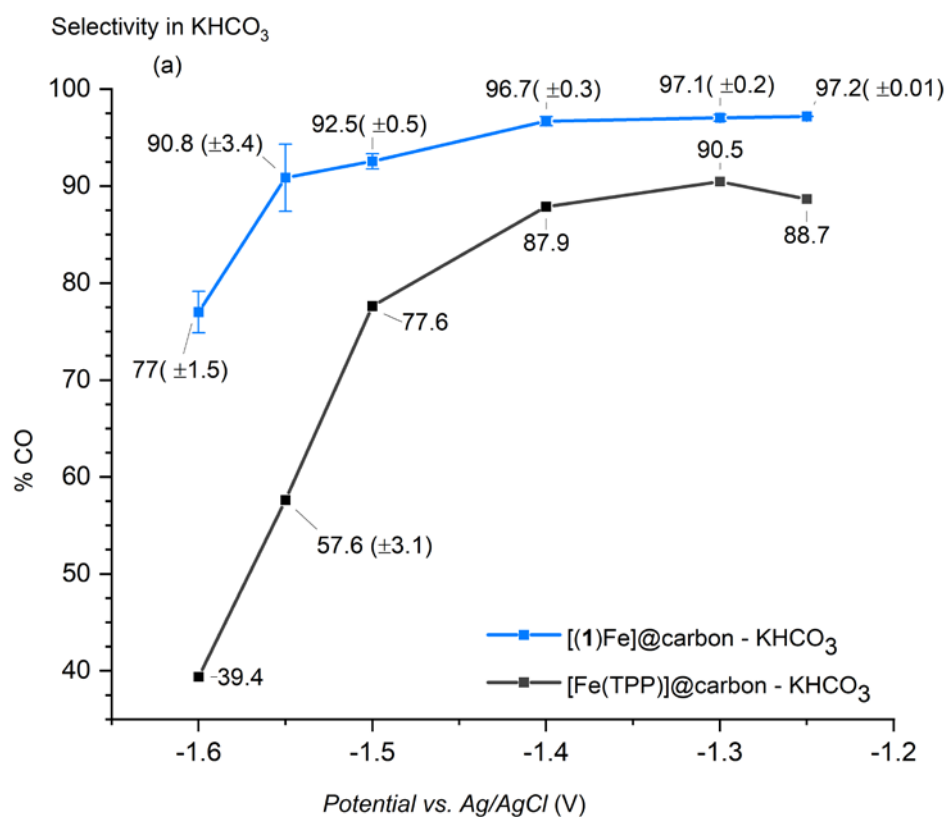
**Figure S17.** Heterogeneous bulk electrolysis cell used for the product analysis.



**Figure S18.** Optimization of the catalyst loading per cm<sup>2</sup> area of the carbon paper.



**Figure S19.** Head space calibration of the cathode compartment (a) CO and (b) H<sub>2</sub>.



**Figure S20.** CO selectivity at various over potentials for [(1)Fe]@carbon and [Fe(TPP)]@carbon in aqueous (a)  $\text{KHCO}_3$  and (b)  $\text{TEAHCO}_3$ . The experiments are described above.

#### 4.2.4 Gas Chromatography (GC) measurements

A multi-channel, multi detector gas chromatograph (CompactGC<sup>4.0</sup>) with a high detection sensitivity (CO and H<sub>2</sub> - 50 ppm) was used for the gas product analysis. Channel 1 is equipped with a flame ionization (FID) detector while channel 2 features a thermal conductivity detector (TCD) used for the detection of H<sub>2</sub>. Channels 3 and 4 both share another TCD detector. CO<sub>2</sub> and CO are detected at channels 3 and 4 respectively. Additionally, each channel is equipped with an appropriate pre-column. The sample is split-injected and independently analyzed at each channel. A vacuum generated by the instrument draws the sample from the head space of the catholyte, which is then equilibrated to the ambient pressure before injection into the columns. The peak area was converted to the volume of the gaseous product using the head space calibration curves (Figure S19).

#### 4.2.5 Faradaic efficiency in aqueous KHCO<sub>3</sub>-based electrolyte

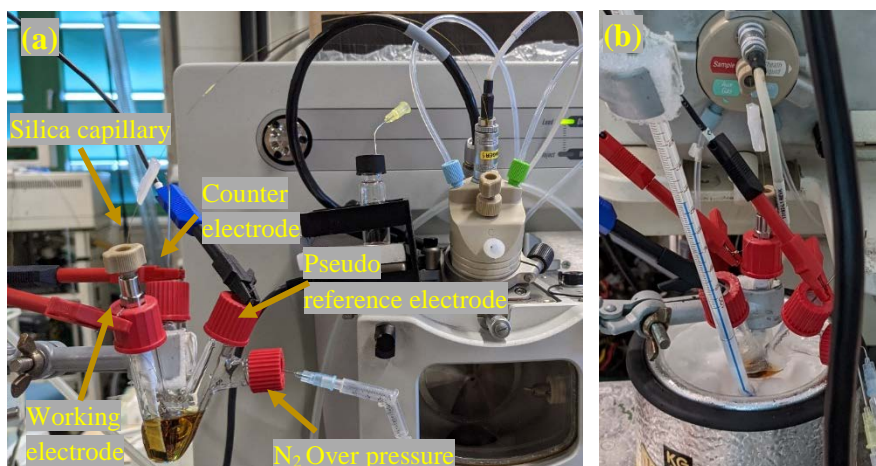
$$\text{Faradaic efficiency of CO} = \frac{\text{Experimental amount of CO (moles)}}{\text{Theoretical amount of CO (moles)}} \times 100$$

The bulk electrolysis was performed using a carbon paper electrode (1 cm<sup>2</sup>) which was coated with catalyst@carbon for 10 min in 0.5 M KHCO<sub>3</sub> in H<sub>2</sub>O at -1.55 V (vs. Ag/AgCl) for both [(1)Fe]@carbon and [Fe(TPP)]@carbon. The number of moles of the gas (CO and H<sub>2</sub>) was calculated using the head space calibration curves (Figure S19). The faradaic efficiency of CO obtained for [(1)Fe] was 91 % while for [Fe(TPP)] only 48 % was obtained.

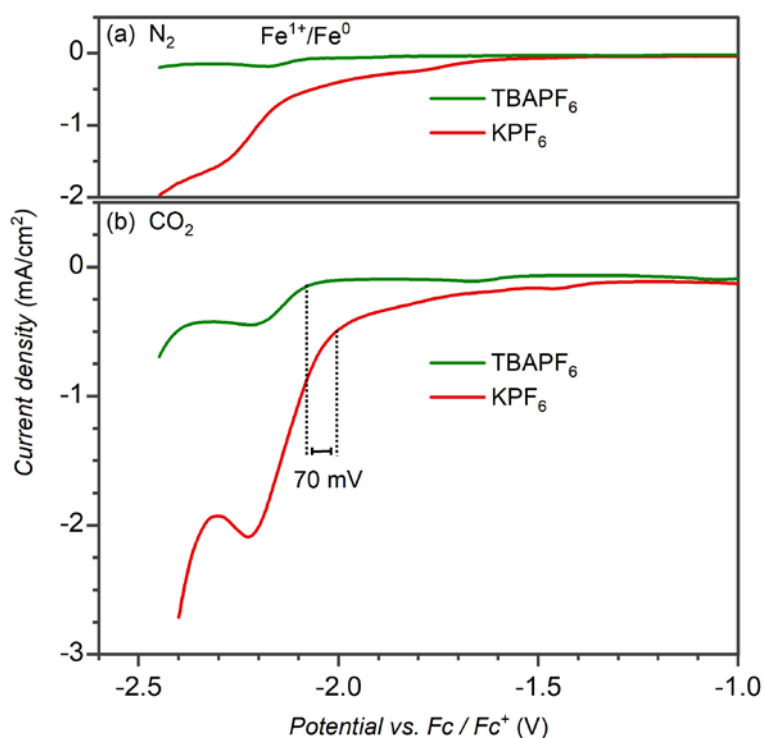
## 5. EC-ESI-MS experiments

### 5.1 EC-ESI-MS setup

The set-up follows a basic three electrode assembly (Figure S21): a stainless-steel counter electrode, a Pt wire reference electrode (pseudo-reference electrode) and a Toray carbon working electrode. Electrodes were mounted on a gas-tight single compartment electrochemical cell (home-built). The working electrode was made by sandwiching a silica capillary between 2 Toray carbon sheets. The electrochemically generated species on the surface of the working electrode flow through the capillary (with  $N_2/CO_2$  overpressure) to the mass spectrometer. The polarization of the electrode was controlled by a USB powered potentiostat (Ivium pocketSTAT2). The interference from the high voltage of ESI source was eliminated by operating the potentiostat without a ground connection. A 5 kV USB isolator was used to decouple the potentiostat from the ground contact. Higher concentrations of the analyte and of the supporting electrolyte were not suitable for the mass spectrometric analysis, hence a minimum concentration of the [(1)Fe] and  $KBF_4$  sufficient for the electrochemical reactions was used (indicated below).



**Figure S21.** EC-ESI-MS experimental setup under (a)  $N_2$  at room temperature (b)  $CO_2$  at  $-40\text{ }^\circ\text{C}$  used for the trapping of the  $CO_2RR$  intermediates.

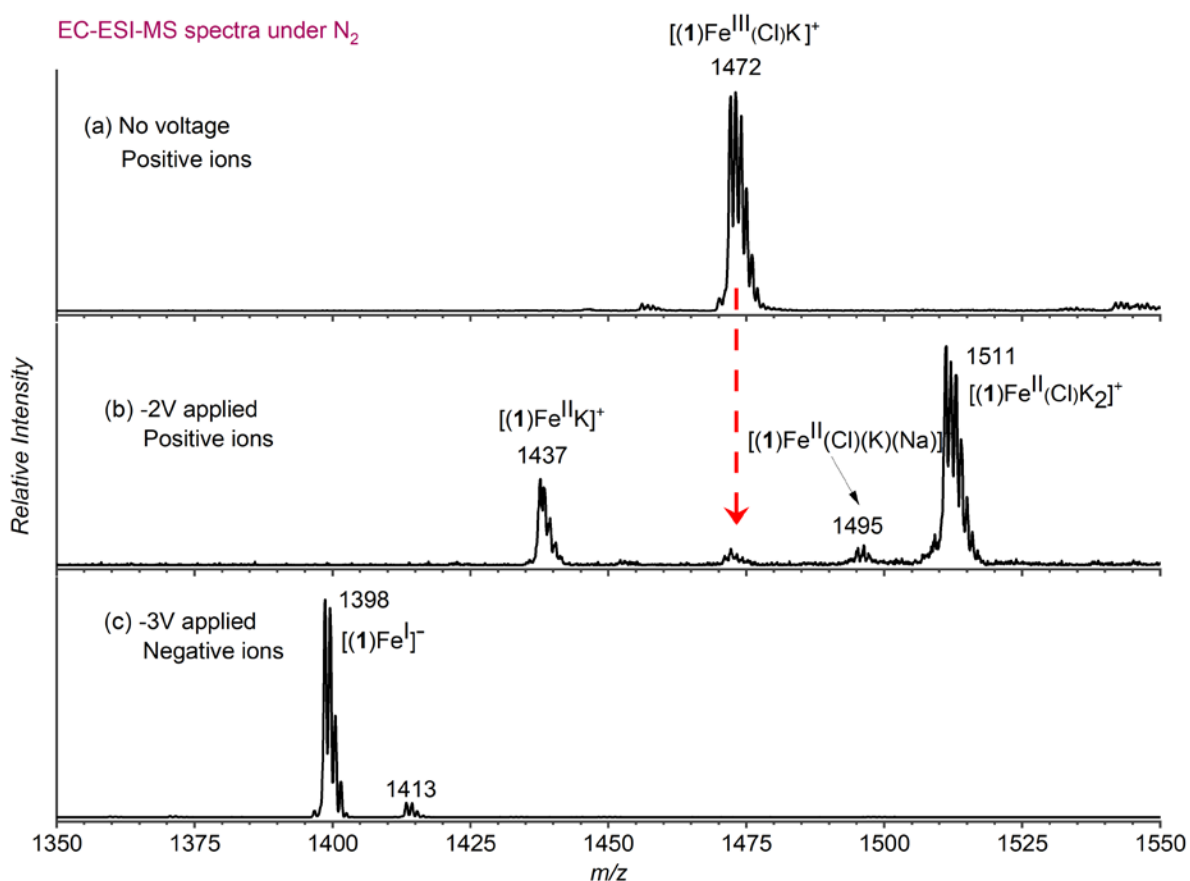


**Figure S22.** Homogeneous cyclic voltammograms of [(1)Fe] (0.25 mM) measured in TBAPF<sub>6</sub> (green), KPF<sub>6</sub> (red) electrolytes (0.1 M in ACN:DCM = 9:1) + 0.5 M H<sub>2</sub>O; scan rate 100 mV/s) under N<sub>2</sub> (for (a)) and under CO<sub>2</sub> (for (b)). (The [(1)Fe] complex is less soluble in acetonitrile(ACN), to increase the solubility [(1)Fe] was first dissolved in 1 mL of dichloromethane (DCM) and diluted with 9 mL of ACN. Hexafluorophosphate salts were used as supporting electrolytes due to the low solubility fluoroborate salts in ACN).

## 5.2 EC-ESI-MS experiment under N<sub>2</sub>

[(1)Fe<sup>III</sup>Cl] (0.8 mg) was dissolved in 0.5 mL of DCM (dichloromethane) and diluted to 4 mL with ACN (acetonitrile) to obtain the final concentration of 143  $\mu$ M. The KBF<sub>4</sub> salt (150  $\mu$ M) was used as both the supporting electrolyte and the K<sup>+</sup> ion source. The solution was purged with nitrogen for 10 minutes prior to the experiment. A nitrogen overpressure was applied to the sealed gas tight cell, allowing the sample to flow through the silica capillary to the mass spectrometer. A constant negative potential was applied to the working electrode and the evolution of the electrochemically generated ions was monitored by ESI-MS.

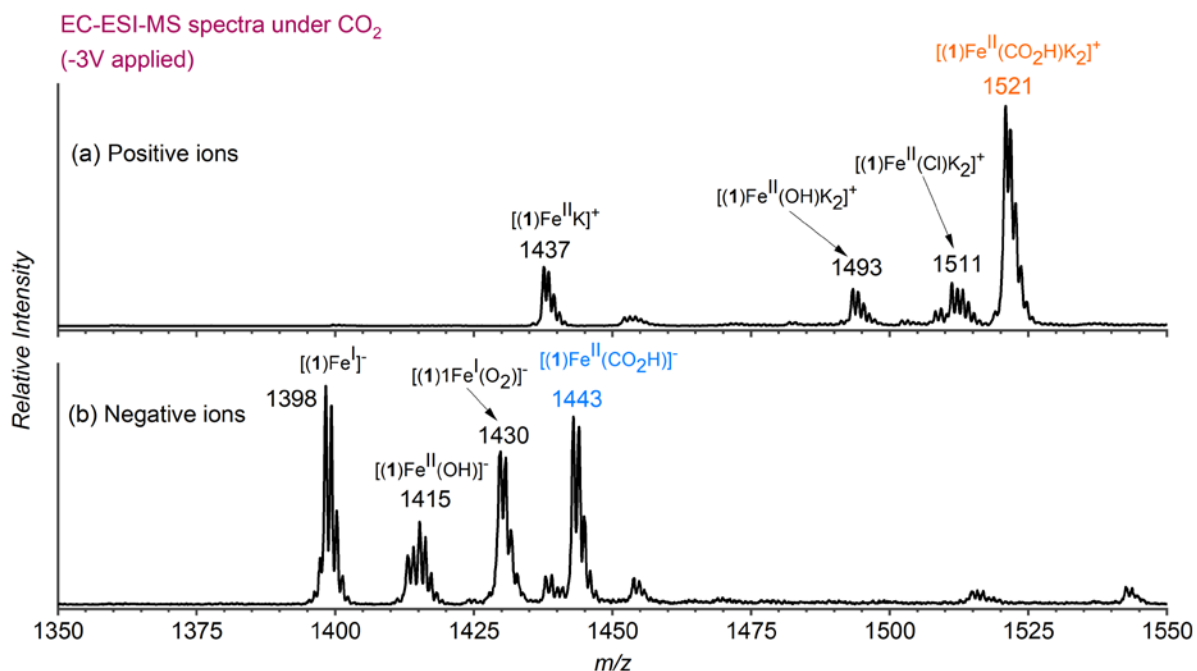
We observed the depletion of the [(1)Fe<sup>III</sup>(Cl)K]<sup>+</sup> complex with the applied voltage of -1.5 V to -2 V (vs. Pt) and we detected the reduced [(1)Fe<sup>I</sup>(Cl)K<sub>2</sub>]<sup>+</sup> and [(1)Fe<sup>II</sup>K]<sup>+</sup> ions (Figure S23). Applying a higher negative voltage (-2.5 V to -3 V) resulted in the generation of further reduced [(1)Fe<sup>I</sup>]<sup>-</sup> complex in the negative mode. We did not detect [(1)Fe<sup>0</sup>]<sup>2-</sup> and [(1)Fe<sup>0</sup>K]<sup>-</sup> complexes. The Fe<sup>(0)</sup> complexes are very reactive, they get probably easily oxidized to Fe<sup>(I)</sup> complexes during the electrospray ionization process.



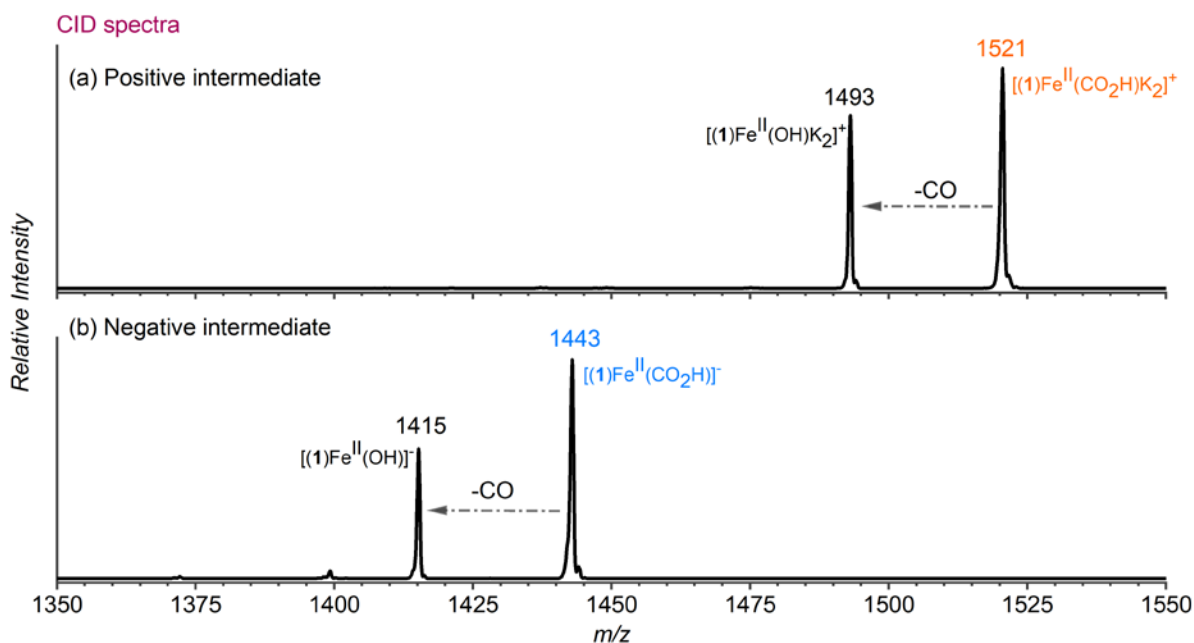
**Figure S23.** EC-ESI-MS mass spectra of  $[(1)\text{Fe}^{\text{III}}\text{Cl}]$  in  $\text{CH}_3\text{CN}$  (143  $\mu\text{M}$ ) in the presence of the  $\text{K}^+$  ions (150  $\mu\text{M}$   $\text{KBF}_4$ ) under  $\text{N}_2$  measured (a) before applying the voltage (original spectrum) in the positive ion mode; (b) with an applied voltage of  $-2$  V (vs. Pt) in the positive ion mode; and (c) with an applied voltage of  $-3$  V (vs. Pt) in the negative ion mode.

### 5.3 EC-ESI-MS experiment under $\text{CO}_2$

The experiments with  $\text{CO}_2\text{RR}$  were done under the same experimental conditions as those described in section 5.2. The only difference was that after the  $\text{N}_2$  bubbling, the solution was saturated with  $\text{CO}_2$ . No  $\text{CO}_2\text{RR}$  intermediates were detected during the experiments performed at room temperature. Therefore, after the saturation of the solution with  $\text{CO}_2$  at RT, we cooled the solution to  $-40$  °C and applied a nitrogen overpressure. At a constant negative potential within the range  $-3$  V to  $-3.5$  V (vs. Pt), we detected the  $\text{CO}_2\text{RR}$  intermediates  $[(1)\text{Fe}^{\text{II}}(\text{CO}_2\text{H})\text{K}_2]^+$  in the positive ion mode and  $[(1)\text{Fe}^{\text{II}}(\text{CO}_2\text{H})]^-$  in the negative ion mode (Figure S24). The ions were isolated in the gas phase and we studied their collision-induced dissociation (CID) properties using an ion trap mass spectrometer (Finnigan LCQ deca). The CID experiments showed the fragmentation of the intermediates leading to almost exclusive losses of CO molecules (a mass loss of 28 Da) resulting in the detection of the respective hydroxide fragment (Figure S25).

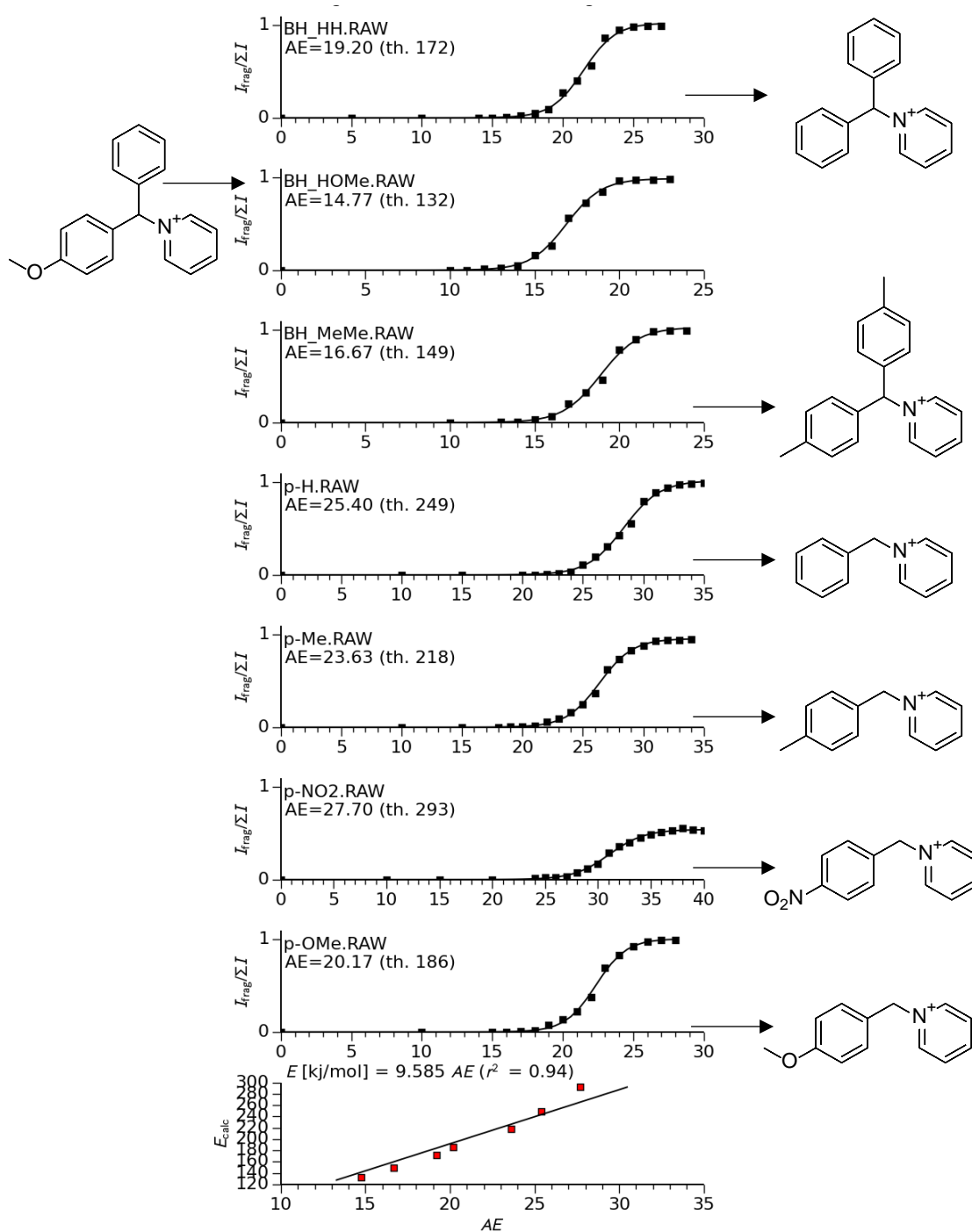


**Figure S24.** EC-ESI-MS mass spectra of  $[(1)FeCl]$  in  $CH_3CN$  (143  $\mu M$ ) in the presence of  $K^+$  (150  $\mu M$   $KBF_4$ ) and saturated  $CO_2$  at  $-40^\circ C$  measured with applied voltage  $-3$  V (vs. Pt) (a) in the positive ion mode (b) in the negative ion mode.

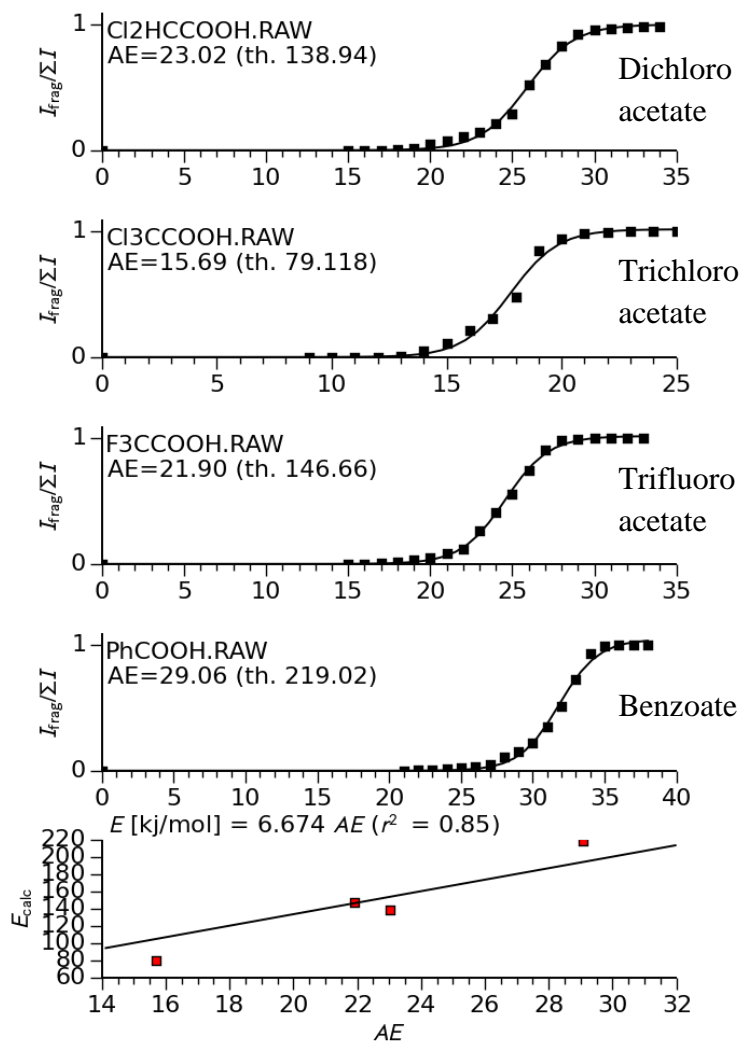


**Figure S25.** Collision-induced dissociation spectra of the isolated intermediates in the gas phase, (a) positive intermediate ( $m/z = 1521$ ) (b) negative intermediate ( $m/z = 1443$ ).

## 5.4 EC-ESI-MS energy resolved CID experiments



**Figure S26.** Calibration of the ion trap of the LCQ Deca - ESI-MS mass spectrometer in the positive ion mode using the thermometer ions with known bond dissociation energies (*BDEs*). The appearance energies (*AE*) were obtained from the sigmoidal fitting of the intensities of the fragment vs the applied collision energy. *AEs* of each thermometer ion were plotted against their known *BDEs*.

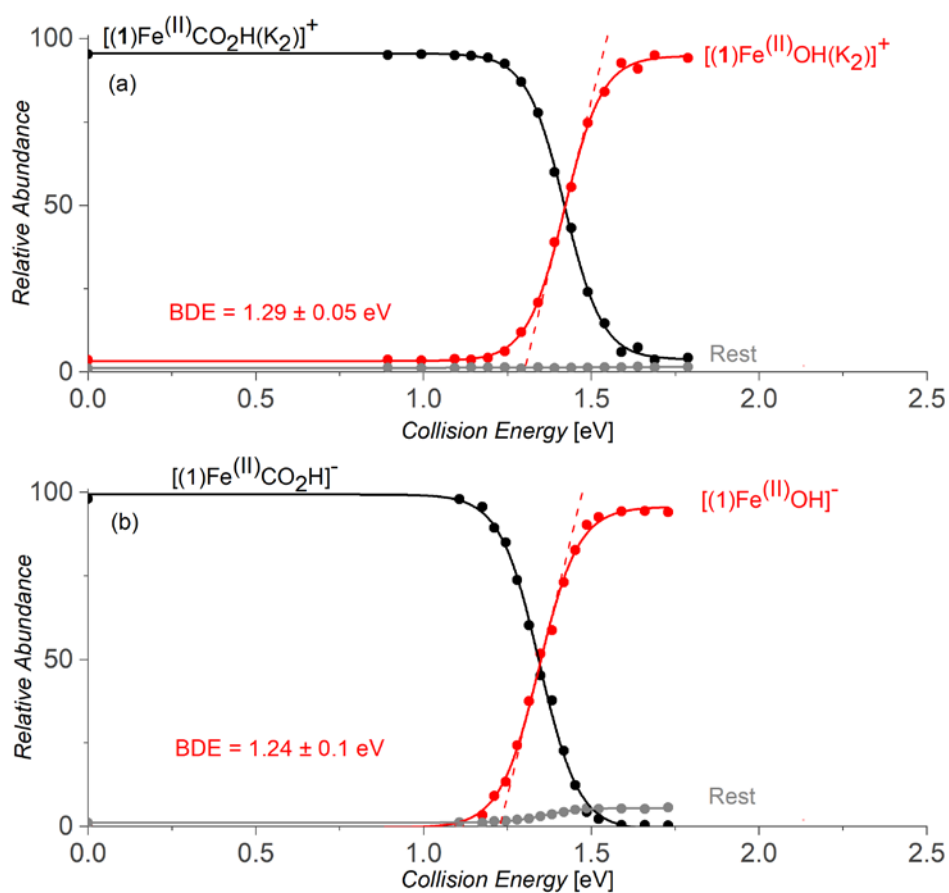


**Figure S27.** Calibration of the ion trap of the LCQ Deca - ESI-MS mass spectrometer in the negative ion mode using the thermometer ions of known bond dissociation energies (BDEs). The appearance energies (AEs) were obtained from the sigmoidal fitting of the intensities of the fragment vs the applied collision energy. AEs of each thermometer ion were plotted against their known BDEs.

Energy-resolved collision-induced dissociation experiments were performed using an ESI-LCQ Deca mass spectrometer to determine the bond dissociation energies. The molecular ions were mass selected and collided with the He buffer gas with an activation time of 30 ms and the parameter  $q = 0.25$ . The collision energies in the ion trap were calibrated separately in the positive and negative ion mode.

The positive ion mode was calibrated with known bond dissociation energies of benzylpyridinium and benzhydrylpyridinium thermometer ions from the Armentrout group using the Schröder's method (Figure S26).<sup>[10][11]</sup> The negative ion mode was calibrated with the reported *BDEs* of the carboxylate anions (benzoate, dichloroacetate, trichloroacetate and trifluoroacetate, Figure S27).<sup>[12]</sup> The energy-resolved CIDs of the intermediates were performed on the same day as the ion trap calibration. The experiments were repeated 2-3 times on different days to obtain the standard deviation of the determined *BDEs*.

Knowing the calibration of the collision energies, we could determine *BDEs* for CO eliminations from  $[(1)\text{Fe}^{\text{II}}(\text{CO}_2\text{H})\text{K}_2]^+$  and from  $[(1)\text{Fe}^{\text{II}}(\text{CO}_2\text{H})]^-$  (Figure S28). The results show that the C-O bond cleavage that leads to the CO elimination requires about the same energy in both intermediates. Hence, potassium ions do not significantly facilitate this step (at least in the gas phase).



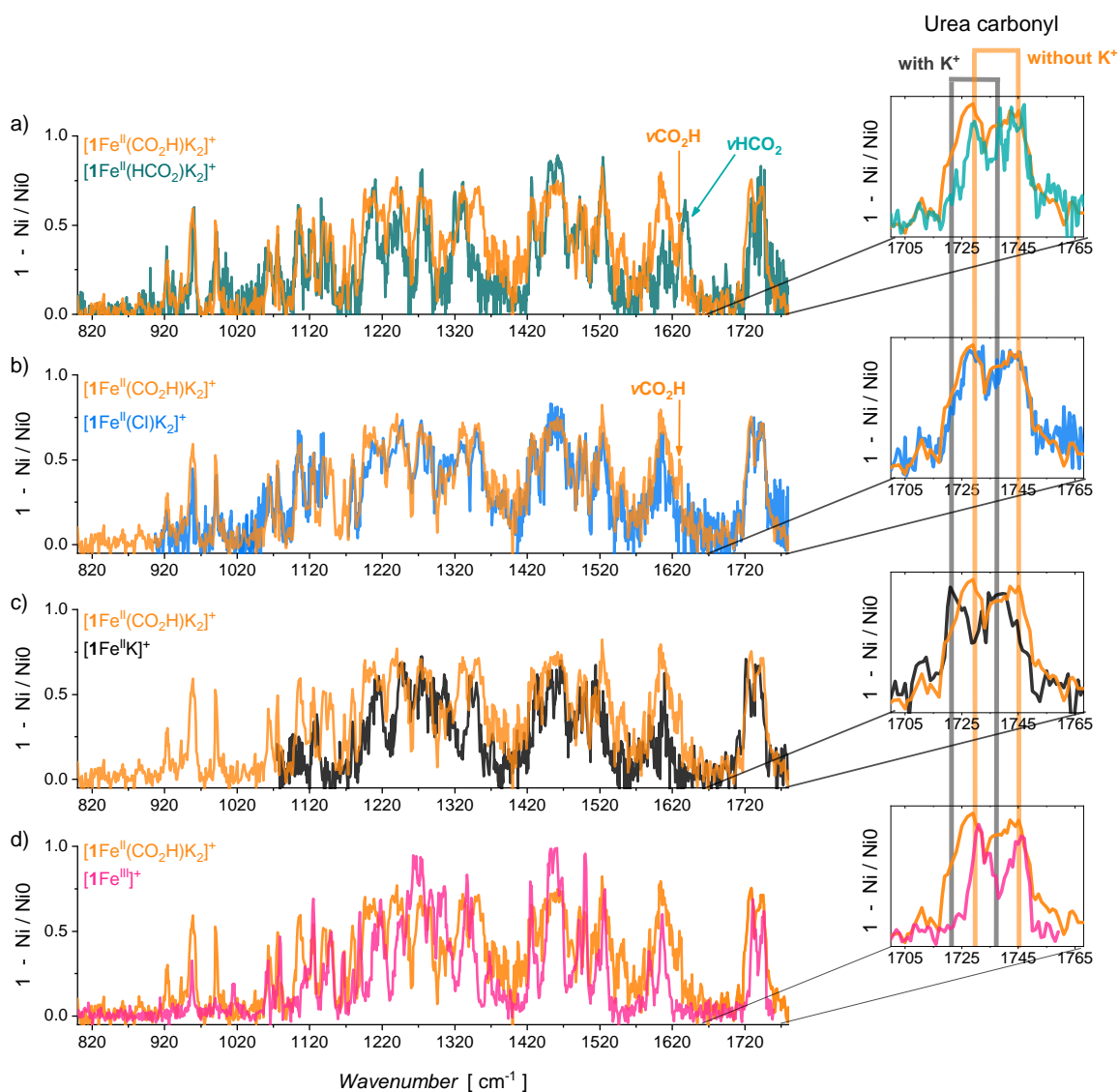
**Figure S28.** Energy-resolved CIDs and extrapolation of the fragmentation onset to determine the *BDEs* of CO in the intermediates: (a)  $[(1)\text{Fe}^{\text{II}}(\text{CO}_2\text{H})\text{K}_2]^+$  ( $m/z = 1521$ ) and (b)  $[(1)\text{Fe}^{\text{II}}(\text{CO}_2\text{H})]^-$  ( $m/z = 1443$ ).

## 6. IRPD measurements and DFT calculations

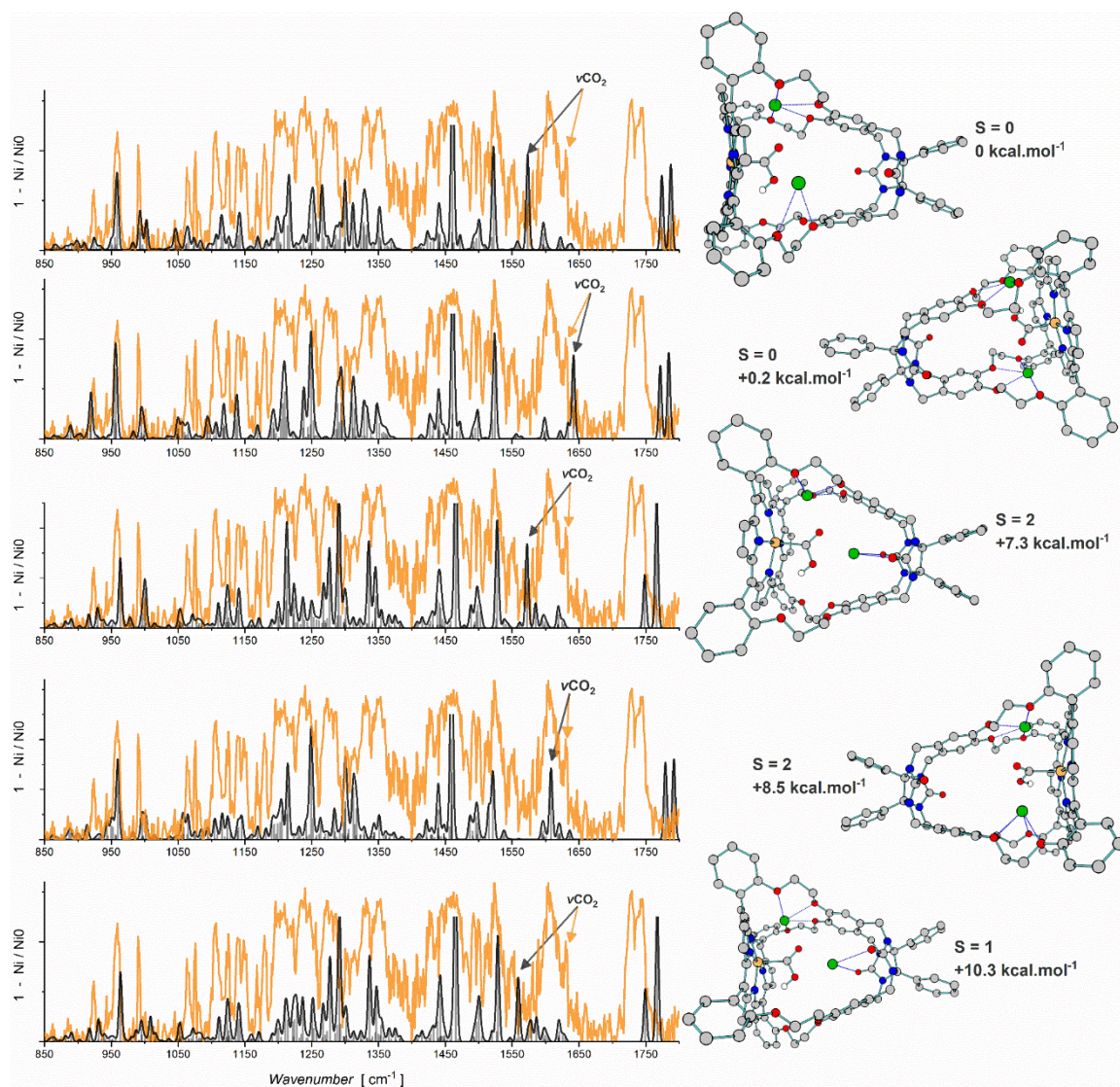
Ion spectroscopic measurements were performed in our homebuilt spectrometer ISORI (Ion Spectroscopy of Organic Reaction Intermediates) using helium tagging.<sup>[13–15]</sup> The ions were generated in the same way as for the electrochemistry mass spectrometry studies. The iron-formate complex  $[(1)\text{Fe}^{\text{II}}(\text{O}-\text{C}(\text{H})\text{O})\text{K}_2]^+$  was generated using an electrochemistry setup to reduce the iron(III) complexes to iron(II) (at  $-2$  V under  $\text{N}_2$  atmosphere) and with the addition of  $80 \mu\text{L}$  of a  $20$  mM aqueous solution of potassium formate to the solution.

The ions of interest were mass-selected by a quadrupole mass filter and guided into a cold ion trap ( $\sim 10$  K) by an octopole ion guide. The ions were trapped and thermalized in collisions with helium buffer gas. The cold ions formed complexes with helium  $[\text{M}(\text{He})_n]^+$ . The complexes  $[\text{M}(\text{He})_2]^+$  were used for monitoring IR photon absorption. The trapped ions were irradiated by a NdYAG laser pumped tunable OPO/OPA system (Laser Vision) operating at  $10$  Hz repetition rate. After the irradiation, the ions were extracted from the trap, mass-analyzed by a quadrupole and detected with a Daly-type detector working in the counting mode. The photon absorption ( $\nu_i$ ) was monitored as a depletion of the number of the  $[\text{M}(\text{He})_2]^+$  complexes ( $N_0$ ). The spectra are plotted as  $1 - N(\nu_i)/N_0$ , where  $N(\nu_i)$  and  $N_0$  were measured in alternating cycles ( $1$  Hz) with or without the laser beam admitted to the trap.

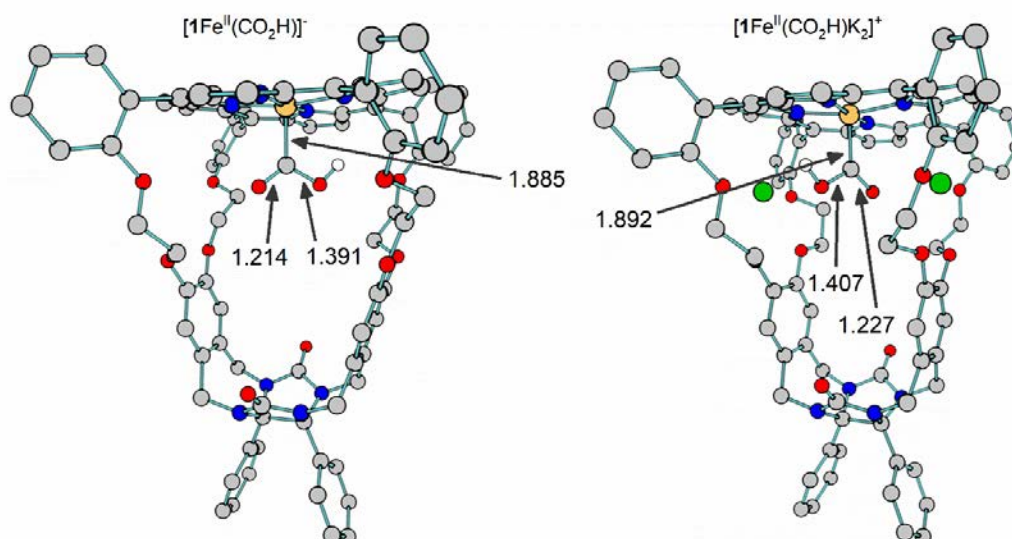
The experiment works at  $1$  Hz. Each cycle begins with the trapping of the ions using the helium buffer gas ( $200$  ms). Helium is injected by a piezo valve in several pulses of  $0.2$  ms separated by  $20$  ms delay. The thermalized ions attached helium atoms. About  $60\%$  of the trapped  $[(1)\text{Fe}(\text{X})\text{K}_n]^+$  ions were transformed to the helium-tagged  $[(1)\text{Fe}(\text{X})\text{K}_n\text{He}_n]^+$  complexes. The ions were irradiated by  $10$  laser pulses. In the range below  $900 \text{ cm}^{-1}$ , the experiment was performed with  $0.5$  Hz frequency in order to prolong the irradiation time, because the laser power was lower in this region.



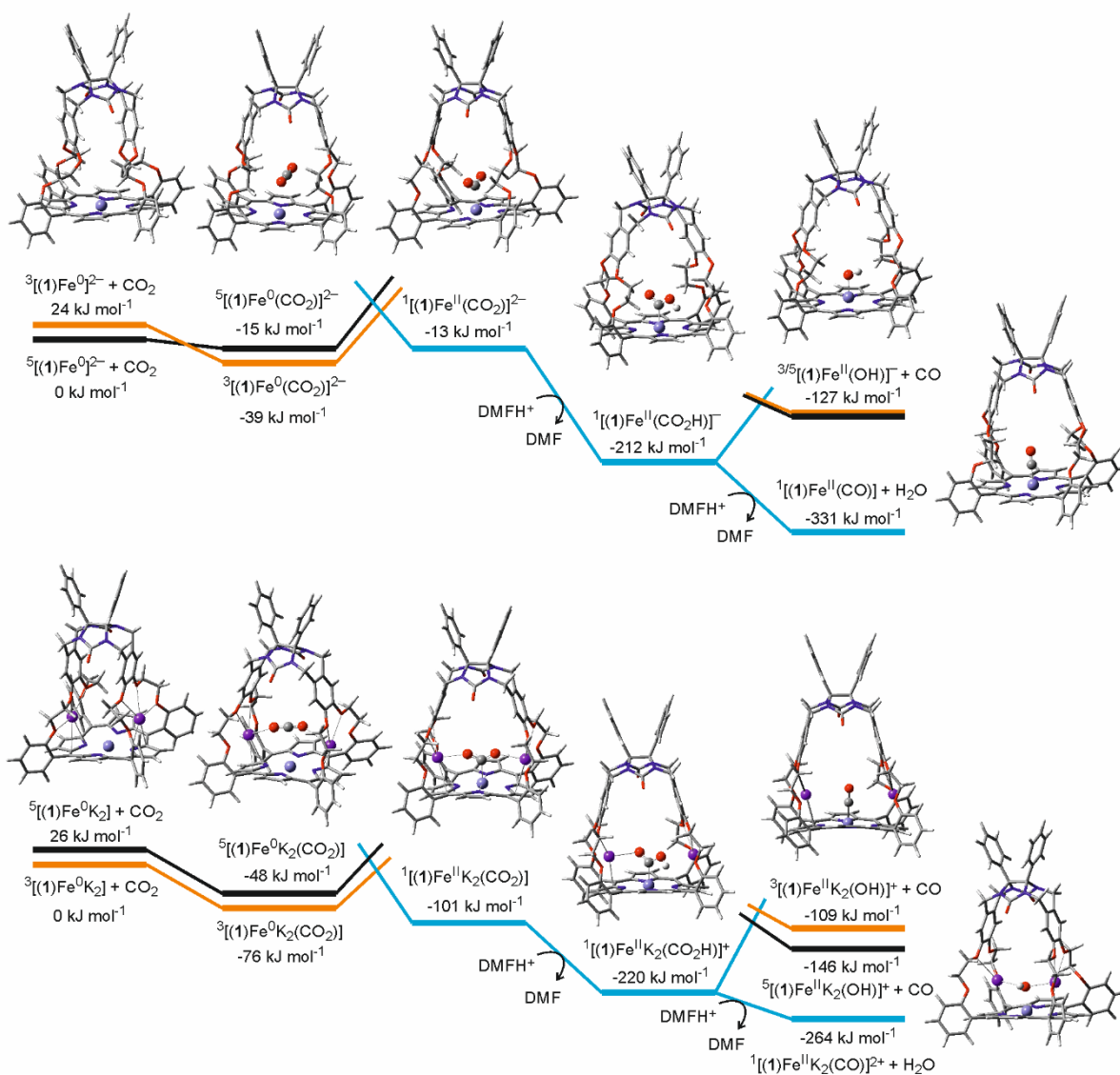
**Figure S29.** Helium tagging IRPD spectra of the individually mass selected ions a)  $[(1)\text{Fe}^{\text{II}}(\text{O}-\text{C}(\text{H})\text{O})\text{K}_2]^+$  (green), b)  $[(1)\text{Fe}^{\text{II}}(\text{Cl})\text{K}_2]^+$  (blue), c)  $[(1)\text{Fe}^{\text{II}}\text{K}]^+$  (black) and d)  $[(1)\text{Fe}^{\text{III}}]^+$  (pink). For comparison, the IR spectra of the  $[(1)\text{Fe}^{\text{II}}(\text{CO}_2\text{H})\text{K}_2]^+$  intermediate are presented together with every spectrum (orange lines). The bands at  $\sim 1340\text{ cm}^{-1}$  are composed by  $\text{CH}_2$  wagging modes (of the methylene groups from the oxyethyleneoxy units and of those at the alpha position to the urea moiety) and therefore they are also sensitive to the location of the potassium ion and/or the axial ligand of the iron center.



**Figure S30.** Orange: Helium tagging IRPD spectra of mass selected  $[(1)\text{Fe}^{\text{II}}(\text{CO}_2\text{H})\text{K}_2]^+$  (generated using the EC-MS set up). Black: B3LYP-D3/def2SVP theoretical spectra for different isomeric structures of gaseous  $[(1)\text{Fe}^{\text{II}}(\text{CO}_2\text{H})\text{K}_2]^+$  ( $S = 0, 1$  or  $2$ , where  $S$  is the total spin quantum number). The scaling factor is 0.978. Structures and relative energies are depicted next to the spectra. The energies include zero-point corrections. The atom's color code is grey for carbon, red for oxygen, blue for nitrogen, yellow for iron, green for potassium and white for hydrogen. Most of the hydrogen atoms were omitted for clarity.



**Figure S31.** DFT-optimized structures of  $[(1)\text{Fe}^{\text{II}}(\text{CO}_2\text{H})]^-$  (left) and  $[(1)\text{Fe}^{\text{II}}(\text{CO}_2\text{H})\text{K}_2]^+$  at the B3LYP-D3/def2SVP level of theory in the gas phase. The numbers represent the selected bond lengths given in ångstroms.



**Figure S32.** Minima on the potential energy surfaces (M06L-D3/def2SVP, SMD solvation model for DMF) for the reactions of  $[(1)Fe^0]^{2-}$  (top) and of  $[(1)Fe^0K_2]$  (bottom) with  $CO_2$ , respectively. The relative energies are energies at 0 K. The locations of Fe, K, and  $CO_2$  are highlighted by using ball and stick presentation. The depicted structures correspond to the given ground states. The energy levels are spin-state color-coded: blue = singlet, orange = triplet, black = quintet.

## XYZ coordinates

**[(1)Fe<sup>II</sup>(CO<sub>2</sub>H)K<sub>2</sub>]<sup>+</sup> S=0 E=0.0 kcal.mol<sup>-1</sup>**

C	-2.709762000	-3.989923000	-5.268010000
C	-2.973014000	-3.180646000	-4.157584000
C	-4.262562000	-2.650739000	-3.942819000
C	-5.274431000	-2.961788000	-4.860748000
C	-5.018304000	-3.770696000	-5.971892000
C	-3.733656000	-4.281334000	-6.174079000
O	-1.998012000	-2.893504000	-3.219737000
C	-0.729943000	-2.446086000	-3.696147000
C	0.103428000	-1.949890000	-2.535726000
O	0.435753000	-3.057924000	-1.675947000
C	1.615201000	-2.990283000	-0.973330000
C	1.604219000	-3.189175000	0.426194000
C	2.802850000	-3.032305000	1.134731000
C	4.014358000	-2.789074000	0.479333000
C	4.038417000	-2.695833000	-0.922917000
C	2.832868000	-2.776175000	-1.622913000
C	5.341261000	-2.452582000	-1.661555000
N	5.945085000	-1.169173000	-1.344413000
C	6.672060000	-0.943962000	-0.102616000
C	6.740510000	0.668558000	-0.034881000
N	6.014984000	1.056079000	-1.238384000
C	5.423223000	-0.009706000	-1.884630000
N	5.874761000	-1.265567000	1.074534000
C	5.353782000	-0.151044000	1.700881000
N	5.995328000	0.957470000	1.183917000
C	5.511731000	2.296186000	1.489729000
C	4.245600000	2.643704000	0.731625000
C	3.044184000	2.844239000	1.414639000
C	1.853850000	3.074660000	0.728052000
C	1.834198000	3.096992000	-0.681319000
C	3.041235000	2.898925000	-1.364974000
C	4.238976000	2.681434000	-0.675553000
O	0.628426000	3.341841000	-1.256292000
C	0.345087000	2.958607000	-2.596722000
C	-0.586889000	3.979851000	-3.207774000
O	-1.860434000	3.860962000	-2.607916000
C	-2.886939000	4.637768000	-3.068832000
C	-4.181380000	4.235960000	-2.675151000
C	-5.281756000	4.988264000	-3.093216000
C	-5.116529000	6.122923000	-3.896404000
C	-3.833158000	6.502104000	-4.289676000
C	-2.714421000	5.764447000	-3.883010000
C	-4.318410000	3.003257000	-1.843150000
C	-4.302783000	3.147053000	-0.450835000
N	-4.196764000	2.116342000	0.460190000
C	-4.066503000	2.717619000	1.693584000
C	-4.146599000	4.157986000	1.558611000
C	-4.283066000	4.424805000	0.230475000
C	-3.817194000	2.056157000	2.904534000
C	-3.525628000	2.888925000	4.110215000
C	-2.335043000	3.642084000	4.178437000

C	-2.068945000	4.468882000	5.275553000
C	-2.987686000	4.540351000	6.327530000
C	-4.163961000	3.788507000	6.287422000
C	-4.424198000	2.971545000	5.183511000
Fe	-4.183592000	0.151184000	0.052671000
O	0.693469000	3.163561000	1.461752000
C	-0.137579000	4.327659000	1.339420000
C	-0.699169000	4.626279000	2.710671000
O	-1.454354000	3.495684000	3.132205000
C	5.517329000	2.406351000	-1.446460000
C	5.285564000	-2.577638000	1.281266000
O	4.503335000	-0.149540000	2.572777000
O	4.608524000	0.057613000	-2.786409000
O	0.411388000	-3.552290000	1.002375000
C	0.301107000	-3.634270000	2.416885000
C	-0.800851000	-4.590413000	2.821928000
O	-2.069253000	-4.102033000	2.423633000
C	-3.199356000	-4.648755000	2.995609000
C	-4.408000000	-3.943618000	2.803616000
C	-5.579071000	-4.463233000	3.367423000
C	-5.571181000	-5.654845000	4.099858000
C	-4.371222000	-6.343923000	4.271009000
C	-3.183886000	-5.847318000	3.720690000
C	-4.434719000	-2.683118000	1.998084000
C	-4.076413000	-1.482186000	2.618788000
N	-4.099736000	-0.237215000	2.031724000
C	-3.805171000	0.657986000	3.035667000
C	-3.520599000	-0.047755000	4.272216000
C	-3.694661000	-1.375560000	4.010442000
C	-4.489448000	-1.769210000	-2.758058000
C	-4.738865000	-2.387699000	-1.522759000
N	-4.604980000	-1.783915000	-0.293932000
C	-4.761793000	-2.789580000	0.637159000
C	-5.092417000	-4.035335000	-0.022239000
C	-5.061209000	-3.787610000	-1.367010000
C	-4.356574000	-0.388884000	-2.917408000
C	-4.219873000	0.277926000	-4.197687000
C	-4.225631000	1.616004000	-3.944202000
C	-4.333088000	1.768320000	-2.506585000
N	-4.407901000	0.538919000	-1.898896000
K	-1.977757000	-3.435087000	-0.407836000
H	-4.174837000	2.437229000	-4.655120000
H	-4.378332000	5.391343000	-0.258228000
H	-4.115974000	4.864555000	2.384602000
H	-3.264895000	0.421706000	5.219180000
H	-3.610178000	-2.212634000	4.699972000
H	-5.314195000	-4.972130000	0.483796000
H	-5.254635000	-4.478370000	-2.184825000
H	-6.280724000	4.668526000	-2.787276000
H	-5.986526000	6.699768000	-4.217018000
H	-3.689941000	7.381706000	-4.922088000
H	-1.720856000	6.080977000	-4.200085000
H	-5.349669000	2.393460000	5.132268000
H	-4.883151000	3.845354000	7.107279000
H	-2.776098000	5.187122000	7.182367000

H	-1.144879000	5.046839000	5.319070000
H	-6.511402000	-3.912497000	3.222562000
H	-6.497428000	-6.039647000	4.531546000
H	-4.347620000	-7.279647000	4.834576000
H	-2.260672000	-6.410356000	3.856510000
H	-1.710574000	-4.401529000	-5.419880000
H	-3.523093000	-4.915629000	-7.038456000
H	-5.819470000	-3.999215000	-6.678119000
H	-0.757782000	-4.693062000	3.921389000
H	-0.606263000	-5.584930000	2.378215000
H	1.226803000	-4.029540000	2.864167000
H	0.112517000	-2.629388000	2.836170000
H	2.837352000	-2.663790000	-2.708520000
H	2.813209000	-3.083716000	2.222539000
H	-0.440369000	-1.191583000	-1.946341000
H	1.015768000	-1.483089000	-2.938860000
H	-0.875039000	-1.617729000	-4.412622000
H	-0.188335000	-3.262026000	-4.205374000
H	-1.347738000	5.518524000	2.661506000
H	0.128663000	4.825885000	3.414130000
H	-0.940261000	4.138685000	0.609793000
H	0.459182000	5.186143000	0.990453000
H	3.061786000	2.881966000	-2.454256000
H	3.008113000	2.798703000	2.505079000
H	1.254238000	2.918735000	-3.214748000
H	-0.125350000	1.960917000	-2.586023000
H	-0.660674000	3.803897000	-4.297774000
H	-0.161375000	4.987325000	-3.047943000
H	6.325658000	3.001433000	1.260380000
H	5.329806000	2.343112000	2.571729000
H	5.348353000	2.531811000	-2.524177000
H	6.315433000	3.105731000	-1.152284000
H	6.079046000	-3.235207000	-1.424770000
H	5.170833000	-2.476745000	-2.746041000
H	-4.169775000	-0.224892000	-5.160693000
H	-6.272977000	-2.550231000	-4.696080000
H	5.079681000	-2.681059000	2.355224000
H	6.046540000	-3.329046000	1.016784000
C	-2.329420000	0.012909000	-0.136577000
O	-1.603440000	1.061604000	-0.676410000
O	-1.592367000	-0.908542000	0.254367000
C	8.144396000	1.257625000	-0.000280000
C	8.804524000	1.446861000	1.221446000
C	8.817907000	1.556118000	-1.192440000
H	8.286758000	1.209384000	2.152394000
H	8.310912000	1.404367000	-2.146972000
C	10.115028000	1.929301000	1.251113000
C	10.128572000	2.038647000	-1.163727000
H	10.618465000	2.071951000	2.210343000
H	10.642458000	2.267345000	-2.100494000
C	10.781007000	2.226436000	0.058300000
H	11.806088000	2.604104000	0.081132000
C	8.020458000	-1.651497000	-0.090839000
C	8.631189000	-1.993438000	1.123425000
C	8.697552000	-1.908516000	-1.290566000

H	8.111875000	-1.788367000	2.061291000
H	8.229548000	-1.636960000	-2.238381000
C	9.896237000	-2.585565000	1.138100000
C	9.962746000	-2.500540000	-1.276852000
H	10.361549000	-2.846577000	2.091664000
H	10.480257000	-2.694906000	-2.219348000
C	10.565802000	-2.840660000	-0.062358000
H	11.555463000	-3.303680000	-0.051414000
H	-2.199397000	1.774160000	-0.963541000
K	-0.554516000	0.854441000	2.067723000

**[(1)Fe<sup>II</sup>(CO<sub>2</sub>H)K<sub>2</sub>]<sup>+</sup> S=0 E=+0.2 kcal.mol<sup>-1</sup>**

C	2.611844000	5.045960000	-4.420513000
C	2.887644000	4.030882000	-3.495977000
C	4.224773000	3.663405000	-3.219428000
C	5.257040000	4.342273000	-3.876100000
C	4.987685000	5.362317000	-4.794593000
C	3.663542000	5.707329000	-5.064780000
O	1.899722000	3.354559000	-2.811605000
C	0.586749000	3.329405000	-3.361293000
C	-0.275652000	2.351066000	-2.590120000
O	-0.534208000	2.863690000	-1.279931000
C	-1.768090000	2.746771000	-0.685510000
C	-1.799108000	2.740123000	0.727243000
C	-3.030665000	2.703545000	1.385010000
C	-4.232970000	2.636907000	0.677700000
C	-4.202043000	2.612579000	-0.727659000
C	-2.973446000	2.680384000	-1.391055000
C	-5.485657000	2.394772000	-1.507102000
N	-6.065416000	1.087401000	-1.235668000
C	-6.838097000	0.806745000	-0.030590000
C	-6.833693000	-0.810991000	0.003975000
N	-6.107942000	-1.143812000	-1.216445000
C	-5.525416000	-0.042433000	-1.813752000
N	-6.119879000	1.143263000	1.192901000
C	-5.533605000	0.045120000	1.792436000
N	-6.065758000	-1.087206000	1.213156000
C	-5.471066000	-2.388283000	1.482377000
C	-4.184669000	-2.588095000	0.703222000
C	-2.953766000	-2.607943000	1.368444000
C	-1.747948000	-2.662989000	0.661258000
C	-1.782954000	-2.708036000	-0.752935000
C	-3.013859000	-2.697680000	-1.408011000
C	-4.217572000	-2.631103000	-0.699885000
O	-0.583033000	-2.805155000	-1.421825000
C	-0.367376000	-2.079542000	-2.639999000
C	0.473069000	-2.914802000	-3.584273000
O	1.806081000	-3.008150000	-3.089482000
C	2.765813000	-3.612477000	-3.874038000
C	4.116569000	-3.305639000	-3.585731000
C	5.120538000	-3.922815000	-4.340064000
C	4.811545000	-4.821108000	-5.366805000
C	3.475153000	-5.103079000	-5.649080000
C	2.450819000	-4.502439000	-4.908467000
C	4.431541000	-2.309234000	-2.515787000

C	4.630663000	-2.774831000	-1.208800000
N	4.601476000	-1.996512000	-0.067119000
C	4.625854000	-2.888644000	0.986067000
C	4.747316000	-4.244353000	0.499811000
C	4.743875000	-4.174696000	-0.864142000
C	4.394198000	-2.561546000	2.329757000
C	4.096195000	-3.677838000	3.280205000
C	2.779481000	-4.169844000	3.384977000
C	2.471180000	-5.211281000	4.264774000
C	3.473566000	-5.775698000	5.057766000
C	4.784419000	-5.298108000	4.967542000
C	5.088033000	-4.257935000	4.084391000
Fe	4.389234000	-0.009892000	0.045856000
O	-0.516375000	-2.662769000	1.255058000
C	-0.424827000	-2.646269000	2.676993000
C	1.027695000	-2.537497000	3.096614000
O	1.770693000	-3.656773000	2.584949000
C	-5.533408000	-2.465275000	-1.436127000
C	-5.548312000	2.464723000	1.413495000
O	-4.710115000	0.073902000	2.689273000
O	-4.699911000	-0.065513000	-2.708965000
O	-0.602487000	2.820750000	1.396310000
C	-0.374137000	2.036609000	2.580659000
C	0.419029000	2.860094000	3.573228000
O	1.737005000	3.061802000	3.071469000
C	2.683376000	3.627702000	3.896036000
C	4.032915000	3.288361000	3.648483000
C	5.027811000	3.873411000	4.440148000
C	4.706894000	4.768475000	5.465941000
C	3.368861000	5.080175000	5.709980000
C	2.355237000	4.513161000	4.929932000
C	4.354485000	2.288590000	2.583424000
C	4.281306000	0.933790000	2.913094000
N	4.443997000	-0.114306000	2.041074000
C	4.310253000	-1.250233000	2.801885000
C	4.053993000	-0.909392000	4.189429000
C	4.033507000	0.448175000	4.257644000
C	4.494752000	2.550085000	-2.258588000
C	4.669981000	2.872660000	-0.906055000
N	4.612054000	1.979026000	0.146251000
C	4.610951000	2.756057000	1.287604000
C	4.739689000	4.155560000	0.949213000
C	4.774995000	4.228579000	-0.414092000
C	4.442960000	1.241155000	-2.743555000
C	4.282846000	0.898542000	-4.139914000
C	4.258228000	-0.462907000	-4.211567000
C	4.407594000	-0.955353000	-2.859482000
N	4.506334000	0.097768000	-1.970169000
K	1.782954000	2.931736000	0.144954000
H	4.176578000	-1.089741000	-5.096362000
H	4.820889000	-4.988273000	-1.581572000
H	4.823920000	-5.127371000	1.129931000
H	3.933546000	-1.627819000	4.996779000
H	3.893786000	1.078519000	5.132553000
H	4.798646000	4.967472000	1.670266000

H	4.869780000	5.112780000	-1.039848000
H	6.161782000	-3.678225000	-4.117067000
H	5.610629000	-5.289342000	-5.945230000
H	3.216305000	-5.797899000	-6.451588000
H	1.413779000	-4.743545000	-5.140760000
H	6.110460000	-3.880259000	4.009040000
H	5.572766000	-5.736797000	5.583368000
H	3.230126000	-6.591666000	5.742317000
H	1.441593000	-5.573275000	4.307721000
H	6.069526000	3.604328000	4.249891000
H	5.497995000	5.210782000	6.075031000
H	3.102190000	5.772397000	6.512211000
H	1.315526000	4.774962000	5.127101000
H	1.584814000	5.337447000	-4.639686000
H	3.436065000	6.499423000	-5.782160000
H	5.808013000	5.877477000	-5.298613000
H	0.467405000	2.324798000	4.538734000
H	-0.095350000	3.824397000	3.730705000
H	-1.324168000	1.737797000	3.047843000
H	0.182776000	1.129283000	2.292468000
H	-2.971851000	2.651981000	-2.480442000
H	-3.059266000	2.700081000	2.475080000
H	0.238142000	1.381578000	-2.484947000
H	-1.204346000	2.196267000	-3.156570000
H	0.633188000	3.013232000	-4.419359000
H	0.120434000	4.329635000	-3.315941000
H	1.064941000	-2.531939000	4.198862000
H	1.470189000	-1.598676000	2.724576000
H	-0.878691000	-3.566384000	3.086633000
H	-0.964649000	-1.772936000	3.085411000
H	-3.046055000	-2.720518000	-2.497719000
H	-2.951136000	-2.533366000	2.454660000
H	-1.319502000	-1.844028000	-3.137644000
H	0.145141000	-1.133932000	-2.396553000
H	0.480577000	-2.440514000	-4.582567000
H	0.015418000	-3.915549000	-3.675515000
H	-6.218668000	-3.157411000	1.235203000
H	-5.280477000	-2.446078000	2.562204000
H	-5.386251000	-2.587290000	-2.517478000
H	-6.278653000	-3.209440000	-1.117120000
H	-6.243130000	3.155129000	-1.262323000
H	-5.294756000	2.452720000	-2.586964000
H	4.224827000	1.617210000	-4.953944000
H	6.288241000	4.050765000	-3.663134000
H	-5.400896000	2.585996000	2.494822000
H	-6.294053000	3.208674000	1.095039000
C	2.496864000	-0.003618000	0.079570000
O	1.822250000	0.083591000	-1.152013000
O	1.732474000	-0.052034000	1.037626000
C	-8.208483000	-1.464736000	0.044227000
C	-8.836117000	-1.722053000	1.270601000
C	-8.889207000	-1.759164000	-1.145008000
H	-8.312945000	-1.489611000	2.199795000
H	-8.406955000	-1.555180000	-2.102494000
C	-10.121894000	-2.267029000	1.307722000

C	-10.174960000	-2.303714000	-1.108738000
H	-10.599857000	-2.462899000	2.270596000
H	-10.694985000	-2.528039000	-2.043186000
C	-10.795217000	-2.559074000	0.117950000
H	-11.800878000	-2.985460000	0.146513000
C	-8.216248000	1.452874000	-0.077408000
C	-8.903073000	1.746112000	1.108572000
C	-8.840713000	1.703919000	-1.306734000
H	-8.423381000	1.546740000	2.068310000
H	-8.312910000	1.472046000	-2.233472000
C	-10.191718000	2.283419000	1.066184000
C	-10.129318000	2.241642000	-1.349975000
H	-10.716531000	2.506831000	1.998166000
H	-10.604826000	2.432527000	-2.315068000
C	-10.808733000	2.532610000	-0.163380000
H	-11.816664000	2.953251000	-0.196680000
H	2.517737000	0.109374000	-1.832029000
K	1.776906000	-2.960974000	-0.148936000

**[(1)Fe<sup>II</sup>(CO<sub>2</sub>H)K<sub>2</sub>]<sup>+</sup> S=2 E=+7.9 kcal.mol<sup>-1</sup>**

C	3.496641000	-5.069597000	4.683399000
C	3.361924000	-4.035074000	3.746521000
C	4.434682000	-3.144317000	3.512620000
C	5.605171000	-3.302149000	4.265855000
C	5.737411000	-4.317488000	5.217646000
C	4.681373000	-5.205321000	5.415433000
O	2.202058000	-3.839042000	3.019720000
C	1.030098000	-4.512977000	3.445230000
C	-0.216785000	-3.851194000	2.901167000
O	-0.325087000	-4.045180000	1.491664000
C	-1.479850000	-3.675909000	0.865159000
C	-1.503002000	-3.762761000	-0.553518000
C	-2.663012000	-3.385445000	-1.234882000
C	-3.821490000	-2.973998000	-0.555300000
C	-3.796304000	-2.881007000	0.844038000
C	-2.615786000	-3.209048000	1.532117000
C	-5.027292000	-2.458396000	1.625947000
N	-5.578473000	-1.167730000	1.251451000
C	-6.384120000	-0.976592000	0.050033000
C	-6.450904000	0.635381000	-0.052375000
N	-5.744676000	1.050885000	1.155701000
C	-5.038455000	0.009715000	1.720880000
N	-5.623489000	-1.328946000	-1.143572000
C	-4.999717000	-0.228354000	-1.699764000
N	-5.642692000	0.896666000	-1.239740000
C	-5.197227000	2.235704000	-1.602354000
C	-4.019449000	2.750080000	-0.796270000
C	-2.847516000	3.155206000	-1.448034000
C	-1.740601000	3.657795000	-0.753746000
C	-1.800840000	3.746888000	0.661291000
C	-2.967769000	3.321614000	1.314273000
C	-4.080066000	2.841385000	0.606966000
O	-0.701993000	4.223002000	1.296475000
C	-0.708243000	4.302314000	2.711827000

C	0.495728000	5.074734000	3.194069000
O	1.667609000	4.351755000	2.904385000
C	2.835203000	4.702096000	3.519513000
C	3.947353000	3.874445000	3.250928000
C	5.158815000	4.150804000	3.895600000
C	5.290499000	5.232081000	4.772979000
C	4.192097000	6.059320000	5.003491000
C	2.965294000	5.801272000	4.380899000
C	3.851736000	2.758501000	2.260946000
C	3.822556000	3.125952000	0.899309000
N	3.676745000	2.270207000	-0.164721000
C	3.769034000	3.016452000	-1.313611000
C	3.973304000	4.409445000	-0.958090000
C	3.998143000	4.478268000	0.404288000
C	3.701847000	2.527074000	-2.640195000
C	3.680431000	3.542126000	-3.737130000
C	2.630533000	4.488144000	-3.814247000
C	2.624304000	5.469999000	-4.812855000
C	3.661015000	5.513866000	-5.751597000
C	4.701779000	4.585827000	-5.696655000
C	4.703584000	3.612042000	-4.692724000
Fe	3.580027000	0.170220000	-0.080191000
O	-0.643998000	3.944367000	-1.485378000
C	0.150962000	5.106147000	-1.236997000
C	0.832462000	5.455864000	-2.541314000
O	1.657951000	4.364577000	-2.876167000
C	-5.328800000	2.431758000	1.365031000
C	-5.081881000	-2.663303000	-1.344369000
O	-4.038205000	-0.256937000	-2.454185000
O	-4.094534000	0.108725000	2.491403000
O	-0.367015000	-4.203083000	-1.168032000
C	-0.299317000	-4.160882000	-2.593093000
C	0.941502000	-4.863016000	-3.098620000
O	2.115678000	-4.137953000	-2.774042000
C	3.255223000	-4.381909000	-3.518133000
C	4.320076000	-3.459582000	-3.399115000
C	5.466756000	-3.665124000	-4.177188000
C	5.584627000	-4.757757000	-5.041183000
C	4.538733000	-5.675319000	-5.123043000
C	3.377061000	-5.493058000	-4.364692000
C	4.260412000	-2.320106000	-2.431954000
C	3.957560000	-1.033682000	-2.916789000
N	3.899814000	0.105018000	-2.157047000
C	3.710293000	1.160233000	-3.008356000
C	3.584387000	0.659941000	-4.369886000
C	3.733677000	-0.695626000	-4.311105000
C	4.351703000	-2.092009000	2.452744000
C	4.576199000	-2.533343000	1.128184000
N	4.334278000	-1.805533000	-0.011020000
C	4.544858000	-2.636792000	-1.082482000
C	4.981407000	-3.932262000	-0.607407000
C	4.998628000	-3.869856000	0.763082000
C	4.093619000	-0.761652000	2.837859000
C	3.991857000	-0.295860000	4.210406000
C	3.886337000	1.065219000	4.156831000

C	3.896687000	1.434664000	2.751708000
N	3.999186000	0.307658000	1.985508000
K	1.915377000	-3.308909000	0.079686000
H	3.814085000	1.762826000	4.988202000
H	4.159705000	5.356914000	1.024498000
H	4.116160000	5.222587000	-1.665484000
H	3.409011000	1.270460000	-5.251725000
H	3.714984000	-1.405739000	-5.135148000
H	5.254527000	-4.774812000	-1.239069000
H	5.292390000	-4.649890000	1.461867000
H	6.014433000	3.504401000	3.686592000
H	6.247340000	5.431071000	5.260153000
H	4.279762000	6.918635000	5.672917000
H	2.123148000	6.465007000	4.575162000
H	5.523646000	2.893316000	-4.628974000
H	5.515709000	4.623539000	-6.423813000
H	3.648595000	6.282280000	-6.528607000
H	1.808577000	6.191805000	-4.870542000
H	6.283863000	-2.945852000	-4.085503000
H	6.490945000	-4.893860000	-5.634898000
H	4.616630000	-6.546090000	-5.778434000
H	2.579922000	-6.231937000	-4.440458000
H	2.691966000	-5.784840000	4.850876000
H	4.769367000	-6.016648000	6.141978000
H	6.662206000	-4.417897000	5.789593000
H	0.830435000	-4.941113000	-4.194571000
H	0.986249000	-5.888262000	-2.686205000
H	-1.165042000	-4.690458000	-3.027096000
H	-0.314504000	-3.111149000	-2.936462000
H	-2.604652000	-3.097572000	2.615301000
H	-2.688113000	-3.409112000	-2.323098000
H	-0.210604000	-2.770491000	3.130103000
H	-1.075847000	-4.318900000	3.412578000
H	0.947558000	-4.478939000	4.546114000
H	1.052816000	-5.575087000	3.137543000
H	1.428402000	6.378704000	-2.407399000
H	0.075612000	5.639843000	-3.326641000
H	0.901850000	4.899005000	-0.460119000
H	-0.482883000	5.947133000	-0.906428000
H	-3.020170000	3.341362000	2.402013000
H	-2.758275000	3.085500000	-2.534309000
H	-1.610821000	4.832693000	3.066436000
H	-0.702170000	3.286284000	3.146584000
H	0.373194000	5.216451000	4.284240000
H	0.521104000	6.075149000	2.721757000
H	-6.064225000	2.905932000	-1.487191000
H	-4.937819000	2.215041000	-2.669050000
H	-5.173524000	2.567679000	2.443653000
H	-6.179721000	3.068450000	1.075595000
H	-5.828334000	-3.204299000	1.496732000
H	-4.792201000	-2.414445000	2.697835000
H	4.035667000	-0.928563000	5.094152000
H	6.429081000	-2.608232000	4.083927000
H	-4.885622000	-2.779778000	-2.418568000
H	-5.877605000	-3.377598000	-1.079114000

C	1.430928000	0.000648000	0.043880000
O	0.730916000	1.174436000	0.275595000
O	0.668722000	-0.983370000	-0.028489000
C	-7.849375000	1.218621000	-0.151841000
C	-8.459744000	1.381996000	-1.402788000
C	-8.573487000	1.526153000	1.007958000
H	-7.903987000	1.134275000	-2.309109000
H	-8.106122000	1.389655000	1.984847000
C	-9.771867000	1.852427000	-1.493238000
C	-9.885657000	1.996162000	0.917959000
H	-10.236675000	1.976897000	-2.474097000
H	-10.440300000	2.232789000	1.829015000
C	-10.488118000	2.160761000	-0.332932000
H	-11.514294000	2.529186000	-0.403321000
C	-7.728653000	-1.678400000	0.124636000
C	-8.401563000	-2.046945000	-1.048171000
C	-8.345994000	-1.895063000	1.364081000
H	-7.930399000	-1.868006000	-2.016326000
H	-7.831963000	-1.598293000	2.280279000
C	-9.669208000	-2.629662000	-0.982306000
C	-9.613624000	-2.478116000	1.430440000
H	-10.184387000	-2.912024000	-1.903440000
H	-10.084787000	-2.642031000	2.402446000
C	-10.278323000	-2.847177000	0.257242000
H	-11.269944000	-3.302984000	0.308719000
H	1.368454000	1.910241000	0.253634000
K	-1.783250000	0.080392000	-0.014391000

**[(1)Fe<sup>II</sup>(CO<sub>2</sub>H)K<sub>2</sub>]<sup>+</sup> S=2 E=+8.5 kcal.mol<sup>-1</sup>**

C	-2.995943000	4.823189000	4.658701000
C	-3.206888000	3.856325000	3.667145000
C	-4.507443000	3.351850000	3.432656000
C	-5.568537000	3.849282000	4.198547000
C	-5.363443000	4.821087000	5.182929000
C	-4.073793000	5.302034000	5.410790000
O	-2.182991000	3.365901000	2.882238000
C	-0.865898000	3.345543000	3.433667000
C	0.075314000	2.549390000	2.554375000
O	0.363935000	3.290994000	1.358632000
C	1.557523000	3.085569000	0.706564000
C	1.564767000	3.075779000	-0.705464000
C	2.781024000	2.918641000	-1.378968000
C	3.988727000	2.772119000	-0.695473000
C	3.986588000	2.802534000	0.711226000
C	2.774171000	2.956941000	1.387339000
C	5.280549000	2.628803000	1.485496000
N	5.913429000	1.338335000	1.260151000
C	6.677422000	1.050802000	0.052686000
C	6.796576000	-0.558999000	0.095046000
N	6.026922000	-0.886789000	1.286489000
C	5.399064000	0.203146000	1.855041000
N	5.902685000	1.265883000	-1.160609000
C	5.461339000	0.096647000	-1.747263000
N	6.119619000	-0.954300000	-1.132757000

C	5.712140000	-2.329083000	-1.385639000
C	4.428408000	-2.707117000	-0.668233000
C	3.287220000	-3.073671000	-1.386468000
C	2.079533000	-3.335533000	-0.741929000
C	1.966167000	-3.180058000	0.655785000
C	3.113559000	-2.818938000	1.374344000
C	4.339796000	-2.615422000	0.733186000
O	0.721469000	-3.375729000	1.193836000
C	0.504200000	-3.094365000	2.580205000
C	-0.506745000	-4.038244000	3.191000000
O	-1.828673000	-3.683168000	2.839029000
C	-2.858060000	-4.234216000	3.556771000
C	-4.136674000	-3.667524000	3.351966000
C	-5.220094000	-4.155400000	4.089668000
C	-5.062435000	-5.199695000	5.006959000
C	-3.800802000	-5.766614000	5.183313000
C	-2.697431000	-5.290339000	4.464820000
C	-4.300171000	-2.585076000	2.338163000
C	-4.206859000	-2.981046000	0.987943000
N	-4.089814000	-2.146358000	-0.092280000
C	-3.980589000	-2.937105000	-1.210012000
C	-4.048029000	-4.335817000	-0.820674000
C	-4.177150000	-4.361979000	0.536016000
C	-3.778791000	-2.470672000	-2.527171000
C	-3.594772000	-3.493095000	-3.604716000
C	-2.474485000	-4.357003000	-3.662450000
C	-2.363049000	-5.299612000	-4.694809000
C	-3.359756000	-5.399031000	-5.670638000
C	-4.473499000	-4.562120000	-5.626327000
C	-4.577854000	-3.622675000	-4.598397000
Fe	-4.057574000	-0.035910000	0.003562000
O	0.972754000	-3.625827000	-1.516601000
C	0.377514000	-4.921873000	-1.392065000
C	-0.464059000	-5.174696000	-2.622091000
O	-1.519312000	-4.222150000	-2.680164000
C	5.556769000	-2.231762000	1.556366000
C	5.277278000	2.542359000	-1.463914000
O	4.663390000	0.006431000	-2.660536000
O	4.564898000	0.169071000	2.740341000
O	0.381890000	3.288561000	-1.370242000
C	0.094671000	2.560803000	-2.568928000
C	-0.749674000	3.418084000	-3.485862000
O	-2.037705000	3.590567000	-2.902571000
C	-3.066730000	4.048570000	-3.695953000
C	-4.340072000	3.485038000	-3.470095000
C	-5.423314000	3.957614000	-4.220576000
C	-5.251919000	4.955266000	-5.186038000
C	-3.980970000	5.488957000	-5.409923000
C	-2.884737000	5.039768000	-4.666103000
C	-4.477231000	2.388368000	-2.460502000
C	-4.136404000	1.084606000	-2.883001000
N	-4.119921000	-0.044713000	-2.102924000
C	-3.815641000	-1.105364000	-2.919252000
C	-3.574163000	-0.619240000	-4.265690000
C	-3.778391000	0.732787000	-4.241902000

C	-4.708618000	2.288338000	2.399471000
C	-4.883413000	2.723570000	1.066609000
N	-4.719354000	1.946940000	-0.049573000
C	-4.814246000	2.765565000	-1.142823000
C	-5.119113000	4.117440000	-0.705930000
C	-5.147769000	4.094242000	0.663544000
C	-4.608056000	0.946906000	2.826246000
C	-4.458165000	0.521394000	4.205972000
C	-4.379353000	-0.843759000	4.195148000
C	-4.461297000	-1.259185000	2.805754000
N	-4.622910000	-0.156677000	2.012826000
K	-2.012340000	3.436801000	-0.029170000
H	-4.267119000	-1.513521000	5.044737000
H	-4.274833000	-5.232668000	1.180290000
H	-4.022949000	-5.180022000	-1.505178000
H	-3.307969000	-1.234324000	-5.121492000
H	-3.715732000	1.428897000	-5.075473000
H	-5.286437000	4.967854000	-1.363666000
H	-5.350588000	4.919575000	1.342773000
H	-6.203115000	-3.706998000	3.927399000
H	-5.920883000	-5.570343000	5.570849000
H	-3.661494000	-6.590626000	5.887339000
H	-1.724486000	-5.754982000	4.621515000
H	-5.448257000	-2.965010000	-4.546608000
H	-5.259201000	-4.640491000	-6.380470000
H	-3.255445000	-6.140594000	-6.466192000
H	-1.500258000	-5.960889000	-4.757840000
H	-6.409492000	3.519949000	-4.048628000
H	-6.107624000	5.307667000	-5.765893000
H	-3.835485000	6.265209000	-6.164945000
H	-1.896916000	5.471162000	-4.834281000
H	-1.996786000	5.216334000	4.846014000
H	-3.895396000	6.058466000	6.178806000
H	-6.205389000	5.193513000	5.770222000
H	-0.850170000	2.913910000	-4.463474000
H	-0.250320000	4.390996000	-3.639002000
H	1.014435000	2.285807000	-3.105281000
H	-0.446666000	1.639552000	-2.296582000
H	2.784116000	2.968766000	2.477643000
H	2.794361000	2.905645000	-2.469326000
H	-0.354300000	1.571496000	2.283123000
H	0.990832000	2.371456000	3.137752000
H	-0.898464000	2.879995000	4.434780000
H	-0.467734000	4.370252000	3.537526000
H	-0.873613000	-6.199319000	-2.565937000
H	0.171191000	-5.097171000	-3.522096000
H	-0.233811000	-4.978543000	-0.475008000
H	1.163913000	-5.694363000	-1.335879000
H	3.071190000	-2.646932000	2.448047000
H	3.307852000	-3.140520000	-2.475989000
H	1.432637000	-3.240824000	3.148566000
H	0.180610000	-2.045838000	2.686135000
H	-0.382444000	-3.976774000	4.288204000
H	-0.277217000	-5.075129000	2.881671000
H	6.545888000	-2.981673000	-1.081864000

H	5.582916000	-2.440886000	-2.470531000
H	5.324169000	-2.288953000	2.627992000
H	6.389851000	-2.925390000	1.360490000
H	6.010203000	3.407068000	1.211532000
H	5.091958000	2.718233000	2.563668000
H	-4.432661000	1.184158000	5.068019000
H	-6.570074000	3.452126000	4.016925000
H	5.082455000	2.562552000	-2.544585000
H	6.012730000	3.332962000	-1.244651000
C	-2.009015000	0.236113000	0.527098000
O	-1.465214000	-0.531062000	1.561851000
O	-1.143344000	0.861373000	-0.096325000
C	8.218030000	-1.102201000	0.166733000
C	8.946995000	-1.339604000	-1.006573000
C	8.837262000	-1.307765000	1.406935000
H	8.471829000	-1.173529000	-1.974971000
H	8.276885000	-1.117110000	2.323953000
C	10.271645000	-1.777714000	-0.941069000
C	10.161962000	-1.746465000	1.473512000
H	10.829102000	-1.957715000	-1.863444000
H	10.632924000	-1.902387000	2.447081000
C	10.883133000	-1.982400000	0.299488000
H	11.919385000	-2.325175000	0.350982000
C	8.005557000	1.796363000	0.024621000
C	8.630947000	2.085161000	-1.195851000
C	8.651101000	2.141630000	1.219605000
H	8.136125000	1.812215000	-2.129667000
H	8.171553000	1.912199000	2.172739000
C	9.879479000	2.711224000	-1.221600000
C	9.899786000	2.767199000	1.194941000
H	10.356134000	2.930537000	-2.180061000
H	10.392767000	3.030103000	2.133975000
C	10.517750000	3.053695000	-0.025960000
H	11.494439000	3.543246000	-0.045514000
H	-2.190782000	-0.993549000	2.016684000
K	-0.970783000	-1.851092000	-1.060252000

**[(1)Fe<sup>II</sup>(CO<sub>2</sub>H)K<sub>2</sub>]<sup>+</sup> S=1 E=+10.3 kcal.mol<sup>-1</sup>**

C	3.577408000	-5.037229000	4.676438000
C	3.415004000	-4.010772000	3.735518000
C	4.467434000	-3.102227000	3.484765000
C	5.651124000	-3.235466000	4.221034000
C	5.812654000	-4.243992000	5.175927000
C	4.773946000	-5.147787000	5.393543000
O	2.249288000	-3.838637000	3.015039000
C	1.086845000	-4.521345000	3.450715000
C	-0.163742000	-3.865170000	2.910154000
O	-0.265344000	-4.050931000	1.499599000
C	-1.419406000	-3.681290000	0.873401000
C	-1.443547000	-3.770686000	-0.544679000
C	-2.604911000	-3.398903000	-1.226340000
C	-3.764253000	-2.990860000	-0.546755000
C	-3.737733000	-2.893281000	0.851915000
C	-2.555472000	-3.214419000	1.539835000
C	-4.971051000	-2.481500000	1.635197000

N	-5.540396000	-1.200641000	1.256597000
C	-6.350368000	-1.024377000	0.055952000
C	-6.440818000	0.585859000	-0.049336000
N	-5.750840000	1.013636000	1.163627000
C	-5.020617000	-0.013758000	1.724935000
N	-5.585498000	-1.367797000	-1.137543000
C	-4.966504000	-0.259890000	-1.685469000
N	-5.626423000	0.857018000	-1.230441000
C	-5.198192000	2.201424000	-1.592333000
C	-4.036870000	2.736522000	-0.776618000
C	-2.867943000	3.163503000	-1.419080000
C	-1.777896000	3.689477000	-0.715916000
C	-1.851861000	3.778380000	0.698248000
C	-3.015640000	3.331763000	1.341770000
C	-4.111623000	2.829240000	0.625551000
O	-0.769575000	4.278576000	1.342364000
C	-0.780746000	4.339641000	2.757656000
C	0.434415000	5.087967000	3.248868000
O	1.592934000	4.351796000	2.938695000
C	2.771755000	4.680250000	3.542311000
C	3.871279000	3.847673000	3.243359000
C	5.095837000	4.103823000	3.871102000
C	5.251857000	5.169507000	4.763419000
C	4.164412000	6.001731000	5.025810000
C	2.925593000	5.764217000	4.419498000
C	3.760595000	2.748958000	2.235144000
C	3.817311000	3.114456000	0.879722000
N	3.695841000	2.250694000	-0.185133000
C	3.771759000	3.019958000	-1.322973000
C	3.984754000	4.400014000	-0.965378000
C	4.003491000	4.460924000	0.400866000
C	3.613416000	2.541640000	-2.639736000
C	3.572714000	3.544483000	-3.745454000
C	2.548434000	4.520191000	-3.783834000
C	2.528083000	5.496214000	-4.787979000
C	3.523383000	5.501330000	-5.771765000
C	4.536593000	4.541998000	-5.756359000
C	4.554057000	3.575608000	-4.745157000
Fe	3.690549000	0.203684000	-0.089806000
O	-0.682619000	3.998607000	-1.439973000
C	0.099090000	5.165958000	-1.179099000
C	0.789184000	5.518828000	-2.477877000
O	1.616933000	4.426934000	-2.802658000
C	-5.359826000	2.401359000	1.373250000
C	-5.027781000	-2.695470000	-1.335947000
O	-3.997580000	-0.277396000	-2.430705000
O	-4.076959000	0.103032000	2.492803000
O	-0.306741000	-4.209010000	-1.159243000
C	-0.258876000	-4.204063000	-2.584820000
C	0.992039000	-4.889614000	-3.085866000
O	2.147627000	-4.131051000	-2.774556000
C	3.288331000	-4.341160000	-3.524737000
C	4.325891000	-3.390578000	-3.400131000
C	5.479502000	-3.559898000	-4.175914000
C	5.627952000	-4.644413000	-5.045704000

C	4.607267000	-5.589501000	-5.134740000
C	3.440045000	-5.444143000	-4.376787000
C	4.233031000	-2.262740000	-2.422875000
C	3.808871000	-1.005861000	-2.854409000
N	3.750834000	0.134863000	-2.079203000
C	3.541038000	1.177545000	-2.955476000
C	3.345674000	0.661957000	-4.301665000
C	3.506704000	-0.686078000	-4.237794000
C	4.346763000	-2.057623000	2.422292000
C	4.655156000	-2.456488000	1.105583000
N	4.385953000	-1.715463000	-0.021750000
C	4.610454000	-2.547130000	-1.093837000
C	5.109987000	-3.816826000	-0.637654000
C	5.135860000	-3.760983000	0.735619000
C	3.963332000	-0.760980000	2.766343000
C	3.784839000	-0.306883000	4.134360000
C	3.652473000	1.045527000	4.082491000
C	3.721885000	1.423567000	2.681814000
N	3.854471000	0.302558000	1.893581000
K	1.991169000	-3.297709000	0.087353000
H	3.541491000	1.744638000	4.908016000
H	4.150058000	5.334421000	1.031754000
H	4.114775000	5.216499000	-1.671321000
H	3.131448000	1.270033000	-5.176463000
H	3.466453000	-1.409073000	-5.049354000
H	5.400512000	-4.644763000	-1.280284000
H	5.452062000	-4.534160000	1.432115000
H	5.942041000	3.453201000	3.637953000
H	6.218242000	5.352158000	5.237988000
H	4.270353000	6.849026000	5.707822000
H	2.092646000	6.432043000	4.637837000
H	5.353252000	2.831705000	-4.711765000
H	5.317473000	4.549638000	-6.519774000
H	3.500223000	6.265110000	-6.553099000
H	1.734811000	6.244181000	-4.815141000
H	6.276286000	-2.818728000	-4.079608000
H	6.538129000	-4.752475000	-5.639274000
H	4.710023000	-6.453835000	-5.795217000
H	2.663684000	-6.204642000	-4.455700000
H	2.786603000	-5.764952000	4.856737000
H	4.885417000	-5.952543000	6.124172000
H	6.746088000	-4.325561000	5.736722000
H	0.878263000	-4.986417000	-4.179978000
H	1.063222000	-5.907194000	-2.658422000
H	-1.119637000	-4.761936000	-2.992980000
H	-0.298690000	-3.164716000	-2.956789000
H	-2.544295000	-3.100876000	2.622768000
H	-2.631721000	-3.426545000	-2.314376000
H	-0.162644000	-2.785886000	3.145301000
H	-1.021992000	-4.340574000	3.416065000
H	1.011020000	-4.485989000	4.552031000
H	1.115739000	-5.583610000	3.144106000
H	1.383257000	6.442939000	-2.343039000
H	0.036897000	5.698899000	-3.268405000
H	0.843007000	4.962191000	-0.394521000

H	-0.544263000	6.001549000	-0.853486000
H	-3.079177000	3.355239000	2.428837000
H	-2.768111000	3.094664000	-2.504490000
H	-1.678289000	4.876050000	3.116958000
H	-0.787704000	3.318636000	3.180847000
H	0.319855000	5.212665000	4.342000000
H	0.472379000	6.095794000	2.793466000
H	-6.076484000	2.858616000	-1.487473000
H	-4.928215000	2.181938000	-2.656453000
H	-5.216513000	2.542871000	2.452854000
H	-6.218576000	3.023110000	1.074631000
H	-5.762483000	-3.238832000	1.512485000
H	-4.733023000	-2.428985000	2.706085000
H	3.813115000	-0.949275000	5.011553000
H	6.459862000	-2.527350000	4.026115000
H	-4.830048000	-2.811747000	-2.409947000
H	-5.815059000	-3.418727000	-1.069683000
C	1.532178000	0.011203000	-0.000054000
O	0.825360000	1.200568000	-0.014822000
O	0.772497000	-0.974956000	0.083241000
C	-7.846994000	1.147567000	-0.161911000
C	-8.448326000	1.300930000	-1.418481000
C	-8.586434000	1.444231000	0.991025000
H	-7.880417000	1.061509000	-2.319492000
H	-8.125814000	1.315278000	1.972119000
C	-9.766738000	1.750844000	-1.521248000
C	-9.904880000	1.893655000	0.888724000
H	-10.224388000	1.867709000	-2.506408000
H	-10.471535000	2.121867000	1.794527000
C	-10.498338000	2.048386000	-0.367738000
H	-11.529457000	2.400715000	-0.447724000
C	-7.684481000	-1.745275000	0.133710000
C	-8.354631000	-2.124086000	-1.037403000
C	-8.296276000	-1.969355000	1.374572000
H	-7.887906000	-1.939216000	-2.006584000
H	-7.784522000	-1.664533000	2.289410000
C	-9.613978000	-2.724148000	-0.968463000
C	-9.555599000	-2.569817000	1.444030000
H	-10.127158000	-3.014243000	-1.888318000
H	-10.022491000	-2.739351000	2.417140000
C	-10.217528000	-2.949017000	0.272514000
H	-11.202692000	-3.418361000	0.326381000
H	1.473490000	1.922996000	-0.102752000
K	-1.698972000	0.096536000	-0.018357000

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