Supporting Information for the manuscript entitled

“Atmospheric-Pressure Conversion of CO₂ to Cyclic Carbonates over Constrained Dinuclear Iron Catalyst”

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1. Experimental

1.1 Materials and Methods

The pro-ligand (H$_2$L) and di-iron complex were prepared according to literature procedures.$^{1,2}$ The chemicals required for all these syntheses were purchased from Aldrich and used as received unless
otherwise noted. The deuterated solvent for NMR studies, i.e. CDCl$_3$ was acquired from Aldrich and used as received. The common reagents and common solvents were acquired locally and used as received. All $^1$H and $^{13}$C NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer at 25 °C with chemical shifts given in parts per million (ppm) using the residual solvent peak as reference, located at 7.26 ppm in the case of CDCl$_3$ and at 2.5 ppm in the case of $d_6$-DMSO. Fourier transform infrared spectra (FTIR) were recorded on a Nicolet 8700 FTIR spectrometer equipped with an attenuated total reflection (ATR) stage. ICP-OES analyses were done on a Thermo Scientific ICP Spectrometer ICAP 6300 DUO. Samples were digested in 1 ml conc. HCl by stirring at 65 °C for 12 h, and the resulting solution was diluted with deionized water prior to ICP-OES analysis. TGA-MS measurements were performed on a SETARAM Labsys-Evo coupled to a Hiden QGA-pro using synthetic air as the carrier gas (20% O$_2$ in Ar, 30 ml/min, 5 °C/min). High resolution X-ray photoelectron spectroscopy (HR-XPS) measurements were performed in an analysis chamber (UV – 2×10$^{-10}$ Torr during analysis) using a Versaprobe III – PHI instrument (PHI, USA). The sample was irradiated with a Focused X-Ray AlK$_\alpha$ monochromated X-ray source (1486.6eV) using an X-ray beam (size 200 micron, 50W, 15 kV). The outcoming photoelectrons were directed to a Spherical Capacitor Analyzer (SCA). The sample charging was compensated by a Dual Beam charge neutralization based on a combination of a traditional electron flood gun and a low energy argon ion beam. Diffuse reflectance UV-vis spectra were recorded on an Agilent Cary 5000 UV-vis spectrophotometer with a DRA-2500 integrating sphere. Electron paramagnetic resonance (EPR) spectra were obtained on a Bruker EMX EPR spectrometer controlled with a Bruker ER 041 XG microwave bridge at 15 or 77 K. The EPR spectrometer was equipped with a continuous-flow liquid He cryostat and an ITC503 temperature controller made by Oxford Instruments, Inc.

1.2 Synthesis Procedures:

Synthesis of LFe$_2$Cl$_4$:

Reduced Robson macrocycle ligand (LH)$_2$ and the corresponding di iron (II) complex (LFe$_2$Cl$_4$)$_2$ were synthesized by slight modification of reported procedure. The clear dry THF solution of ligand LH$_2$ (933 mg, 1.69 mmol) in dry flask was kept in a glove box freezer for 0.5 h. KH (147 mg, 3.4 mmol) was slowly added by small portions to this cold THF solution. After 12 h of stirring, the reaction mixture was centrifuged, then [FeCl$_3$(DME)] (860 mg, 3.4 mmol) was added to this colorless solution, and immediately the reaction mixture changed to dark blue. The resulting mixture was left to stir at RT for 24 h. The white KCl precipitates were eliminated by centrifugation, and the dark blue THF supernatant was removed in vacuum. The dark blue solid residue was finally washed with hexane (3 × 15 mL), then dried under vacuum for 24 h. (yield: 1.3 g, 96 %). Elemental Anal. for C$_{42}$H$_{70}$Cl$_4$Fe$_2$N$_4$O$_4$: Calculated; C, 53.18; H, 7.44; N, 5.91; O, 6.75 Found; C, 52.55; H, 7.11; N, 6.23; O, 5.91.

Synthesis of LFe$_2$Cl$_3$ClO$_4$:

Calculated amount of LFe$_2$Cl$_4$ (2.26 g, 28 mmol) was dissolved in dry THF (30 mL) and transferred into a Schlenk tube containing silver perchlorate (0.6 g, 28.6 mmol) in dry acetonitrile (70 mL) and stirred at 65 °C for 24 h. After the reaction, the obtained dark blue solution was filtered through Celite and washed with acetonitrile. The filtrate was concentrated and dried under vacuum (yield: 2.3 g, 94 %). Molecular cation (MALDI-TOF): ~849 gmol$^{-1}$ [LFe$_2$Cl$_3$ClO$_4$–1CH$_3$–4H]$^+$. The sample was dissolved in TA30 (30:70 acetonitrile:TFA of 0.1% in water), drop casted on a HCCA (alpha cyano 4-hydroxy cinnamic acid) matrix and analyzed on a Bruker MALDI autoflex speed.
Elemental Anal. for C$_{34}$H$_{54}$Cl$_4$Fe$_2$N$_4$O$_6$: Calculated; C, 47.03; H, 6.27; N, 6.45; O, 11.06 measured: C, 47.18; H, 6.55; N, 6.27; O, 11.42.

**Synthesis of LFe$_2$-NH/SiO$_2$:**

A clear solution of LFe$_2$Cl$_3$ClO$_4$ (755 mg, 0.87 mmol) in 20 mL of dry acetonitrile was transferred into a Schlenk tube and to this a suspension of 3-aminopropyl silica (0.7 g) in 15 mL acetonitrile was added. The reaction mixture was vigorously stirred at 85 °C for 48 h under argon. The resulting solid product was separated by centrifugation and washed seven times with fresh acetonitrile, three times THF, two times diethyl ether and the obtained solid product was dried under vacuum (yield: 0.589 g).

**Synthesis of LFe$_2$-O/SiO$_2$:**

A solution of N, N-diisopropylethylamine (112 mg, 0.87 mmol) in 5 mL of dry acetonitrile was transferred into a Schlenk tube containing a suspension of silica support (SiO$_2$-200, 0.7 g) in 10 mL acetonitrile, and the resulting mixture was stirred for two hours at room temperature. To this, the clear solution of LFe$_2$Cl$_3$ClO$_4$ (755 mg, 0.87 mmol) in 20 mL of acetonitrile was added. The reaction mixture was vigorously stirred at 85 °C for 48 h under argon. The resulting solid product was purified in the same manner as above (yield: 0.625 g).

**Synthesis of LFe$_2$-O-NH$_2$/SiO$_2$:**

A solution of N, N-diisopropylethylamine (224 mg, 1.74 mmol) in 5 mL of dry acetonitrile was transferred into a Schlenk tube containing a suspension of 3-aminopropyl silica (0.7 g) in 10 mL acetonitrile, and the resulting mixture was stirred for two hours at room temperature. To this, the clear solution of LFe$_2$Cl$_3$ClO$_4$ (755 mg, 0.87 mmol) in 20 mL of acetonitrile was added. The reaction mixture was vigorously stirred at 85 °C for 48 h under argon. The resulting solid product was purified in the same manner as above (yield: 0.611 g).

1.3 Typical procedure for the synthesis of cyclic carbonate from an epoxide and 1 atm CO$_2$

The catalytic conversion of CO$_2$ to cyclic carbonate was carried out in a 25 mL glass flask refluxing with a CO$_2$ balloon. In a typical catalytic cycloaddition, dry cyclohexene oxide (CHO, 9.2 mmol) and the dry di iron (III) catalyst LFe$_2$-O-NH$_2$/SiO$_2$ (0.036 g, 9.2×10$^{-3}$ mmol, according to the amount of LFe$_2$Cl$_3$ClO$_4$) followed by bis(triphenylphosphino)iminium chloride (PPNCl) (10.6 mg, 18.4×10$^{-3}$ mmol) were placed in a 25 mL glass flask equipped with a magnetic stirrer. After being sealed, three times the flask was carefully evacuated and refilled with CO$_2$. After that, the reaction was carried out at 80 °C temperature by refluxing with a CO$_2$ balloon for the desired period of time. After the reaction, the pressure was released and the resulting mixture was diluted with CH$_2$Cl$_2$. After which, the reaction mixture was centrifuged to remove the solid catalyst and evaporated and dried in vacuo overnight. The product was analyzed by $^1$H NMR spectroscopy without further purification as the vacuum was sufficient to remove unreacted cyclohexene oxide. Turn-over-number (TON) was calculated as [number of moles of epoxide consumed based on epoxide conversion/moles of solid catalyst]. These number were obtained by: [(isolated cyclic carbonate yield – weight of PPNCl)/142.1]/moles of solid catalyst. The calculated error is based on three separate reaction runs.

**Typical procedure for the synthesis of cyclic carbonate from an epoxide and 15 atm. CO$_2$**
For high-pressure cycloaddition reactions, the di-iron (III) catalyst $\text{LFe}_2\text{O-NH}_2\text{/SiO}_2$ (0.036 g, 9.2×10$^{-3}$ mmol), PPNCl (10.6 mg, 18.4×10$^{-3}$ mmol) and cyclohexene oxide (CHO, 0.092 mol) were placed in a 25 mL stainless-steel Parr reaction vessel (which was dried in an oven at 140 °C overnight) under argon. After being sealed, the reactor was carefully evacuated and refilled with CO$_2$. The reaction was carried out at the specified temperature and CO$_2$ pressure for the desired period of time. After the reaction, the reactor was cooled in an ice-water bath and slowly depressurized. The product purification was carried out in the same manner as above.

1.4 Characterization of cis-cyclic carbonate products:

**Cyclohexene carbonate (CHC)**

$^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta = 4.68$ (m, 2H, OCHCH$_2$CH$_2$), 1.89 (m, 4H, OCHCH$_2$CH$_2$), 1.61 (m, 2H, OCHCH$_2$CH$_2$), 1.42 (m, 2H, OCHCH$_2$CH$_2$).

**Propylene carbonate (PC)**

$^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta = 4.85$ (m, 2H, OCH$_2$C$_2$H$_3$), 4.55 (t, 1H, OCH$_2$C$_2$H$_3$), 4.02 (m, 1H, OCH$_2$CHCH$_3$), 1.48 (m, 3H, OCH$_2$CHC$_3$H$_3$).

**Styrene carbonate (SC)**

$^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta = 5.6$ (t, 1H, OCH$_2$CHC$_6$H$_5$), 4.72 (t, 1H, OCH$_2$CHC$_6$H$_5$), 4.27 (t, 1H, OCH$_2$CHC$_6$H$_5$), 7.21-7.36 (m, 5H, OCH$_2$CHC$_6$H$_5$).

**Phenyl glycidyl cyclic carbonate (PGCC)**

$^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta = 5.0$ (m, 1H, OCH$_2$CHC$_6$OC$_6$H$_5$), 4.6 (t, 1H, OCH$_2$CHC$_6$OC$_6$H$_5$), 4.5 (m, 1H, OCH$_2$CHCH$_2$OC$_6$H$_5$), 4.2 (m, 1H, OCH$_2$CHCH$_2$OC$_6$H$_5$), 4.1 (m, 1H, OCH$_2$CHCH$_2$OC$_6$H$_5$), 7.3 (m, 2H, OCH$_2$CHCH$_2$OC$_6$H$_5$), 7.0 (t, 1H, OCH$_2$CHCH$_2$OC$_6$H$_5$), 6.9 (t, 2H, OCH$_2$CHCH$_2$OC$_6$H$_5$).

**tert-butyl glycidyl cyclic carbonate (TGCC)**

$^1$H NMR (400 MHz, CDCl$_3$, ppm): $\delta = 4.7$ (m, 1H, OCH$_2$CHCH$_2$OC(CH$_3$)$_3$), 4.4 (t, 1H, OCH$_2$CHCH$_2$OC(CH$_3$)$_3$), 4.3 (m, 1H, OCH$_2$CHCH$_2$OC(CH$_3$)$_3$), 3.6 (m, 1H, OCH$_2$CHCH$_2$OC(CH$_3$)$_3$), 3.5 (m, 1H, OCH$_2$CHCH$_2$OC(CH$_3$)$_3$), 1.2 (s, 9H, OCH$_2$CHCH$_2$OC(CH$_3$)$_3$).
2. Supplementary Figures and Tables

Figure S1. Mass spectrum (MALDI-TOF) of \( \text{LFe}_2\text{Cl}_3\text{ClO}_4 \).
Figure S2. TGA-MS analysis of flexible di-nuclear solid catalyst LFe$_2$-NH/SiO$_2$. Dashed line marks the 252 °C onset for complex decomposition.

Figure S3. TGA-MS analysis of semi-rigid di-nuclear solid catalyst LFe$_2$-O-NH$_2$/SiO$_2$. Dashed line marks the 243 °C onset for complex decomposition.
**Figure S4.** TGA-MS analysis of rigid di-nuclear solid catalyst \( \text{LFe}_2\text{O}/\text{SiO}_2 \). Dashed line marks the 224 °C onset for complex decomposition.
Figure S5. FT-IR spectra of (a) LFe$_2$Cl$_3$ClO$_4$ (b) APS (c) Aerosil-200 (d) LFe$_2$O/SiO$_2$ (e) LFe$_2$O-NH$_2$/SiO$_2$ (f) LFe$_2$-NH/SiO$_2$. 
Figure S6. UV-vis diffuse reflectance spectra of: (a) $\text{LFe}_2\text{Cl}_4$ (black line), (b) $\text{LFe}_2\text{Cl}_3\text{ClO}_4$ (blue line) and (c) $\text{LFe}_2\text{-O/SiO}_2$ (red line).

Figure S7. UV-vis spectra of: (a) $\text{LFe}_2\text{Cl}_3\text{ClO}_4$ (blue line), (b) $\text{LFe}_2\text{-O-NH}_2\text{/SiO}_2$ (purple line) and (c) $\text{LFe}_2\text{-NH}_2\text{/SiO}_2$ (green line).
Table S1. Interpretation of proposed models by comparing the experimental and theoretical peak areas from XPS.

| S.No | Sample name                  | Theoretical peak area ratio | Experimental peak area ratio |
|------|------------------------------|-----------------------------|------------------------------|
| 1    | LFe₂-NH/SiO₂                 | N’ = 5X0.25mmol = 1.25mmol  | N = 0.75mmol                 |
|      |                              | N’ (H.B) 401.42 eV 399.52 eV | N (L.B) 399.52 eV            |
|      |                              | 1.25mmol : 0.75mmol         | ratio = 1.66:1               |
| 2    | LFe₂-O/SiO₂                  | N’ = 2                      | N = 6                        |
|      |                              | N’ (H.B) 401.65 eV 399.55 eV | N (L.B) 399.55 eV            |
|      |                              | 1.65mmol : 1.56mmol         | ratio = 1.54:1               |
| 3    | LFe₂-OH₂/SiO₂                | N’ = 3X0.27mmol = 0.81mmol  | N = 2X0.27mmol = 0.54mmol + 0.73mmol = 1.27mmol |
|      |                              | N’ (H.B) 401.36 eV 399.87 eV | N (L.B) 399.87 eV            |
|      |                              | 0.81mmol: 1.27mmol          | ratio = 2.3:1                |
| 4    | LFe₂Cl₄ reference            | N’ = N’ (H.B) 401.10 eV 399.55 eV | N = 1                       |
|      |                              | N (L.B) 399.55 eV           | ratio = 1:2                  |

H.B = higher binding energy; L.B = lower binding energy; N’= electron deficient, N= electron rich.

Table S2. Atomic composition for solid catalysts based on HR-XPS analysis

| S.No | Sample name | ICP analyzing the di-Fe (mmol/g) [%] | Cl (%) | Si (%) | N (%) | Fe (%) | C(%) | O(%)² |
|------|-------------|---------------------------------|--------|--------|-------|--------|------|-------|
| 1    | LFe₂-NH/SiO₂| 0.25 [0.5]                      | 1.5    | 23.3   | 3.0   | 0.5    | 21.3 | 50.5  |
| 2    | LFe₂-O/SiO₂ | 0.29 [0.58]                     | 0.7    | 20.1   | 1.5   | 1.0    | 25.8 | 50.9  |
| 3    | LFe₂-O-NH₂/SiO₂| 0.27 [0.54]              | 1.3    | 15.7   | 2.7   | 1.2    | 33.4 | 45.6  |

²Oxygen atomic composition reflects contributions of the grafted materials and of the (dominating) signal from the SiO₂ oxygen.
Table S3. LFe₂Cl₄ homogeneous complex molecular determination based on Fe, N, Cl and O atomic composition from HR-XPS analysis

| Peak    | Area  | Factor | N     | %AC  |
|---------|-------|--------|-------|------|
| Cl₂p    | 4348  | 1.0    | 4557.6| 6.4% |
| N1s     | 2534  | 0.5    | 5078.2| 7.1% |
| Fe₂p₃/₂ | 4942  | 2.0    | 2516.3| 3.5% |
| O1s     | 3985  | 0.7    | 5436.6| 7.6% |
| C1s     | 16884 | 0.3    | 53770.7| 75.4% |

By careful evaluation of atomic composition and XPS N 1s peak area, we are able to determine the molecular structure of the LFe₂Cl₄ homogeneous complex in solid state. N and O atomic concentrations were nearly double to Fe concentration. In addition, the presence of excess eight carbons per complex indicates the presence of two THF molecules per two iron (Note: In LFe₂Cl₄ synthesis THF was used as solvent). On the other hand, the N 1s signal of LFe₂Cl₄ showed two peaks at 399.5 eV and 401.1 eV with a ~2:1 area ratio, indicating the presence of two types of N species in a symmetrical macrocycle. Combining both atomic composition and XPS nitrogen peak area ratio, we speculate that the di-iron complex coexisted in three different forms in the solid state, where each had different portions of residual THF coordinated at the iron centers (see schematic in Table S1A), which leads to non-equivalent nitrogen atoms in a symmetrical macrocycle.

Figure S8. XPS analysis of Fe₂p binding energy regions in di-iron (III) solid catalysts. Spectra are offset for clarity.
Figure S9. XPS analysis of O1s binding energy regions in di-iron (III) solid catalysts.

Table S4. Conversion of CO$_2$ to cyclic carbonates using di-iron(III) catalysts at a CO$_2$ pressure of 15 atm and a temperature of 80 °C.$^a$

| Entry | Catalysts            | Time/h | Yield$^b$ | TON$^c$ | TOF/h$^{-1}$$^d$ | % CHC |
|-------|----------------------|--------|-----------|---------|------------------|-------|
| 1     | LFe$_2$Cl$_4$        | 10     | 0.41      | 233     | 23.3             | 99    |
| 2     | LFe$_2$Cl$_3$ClO$_4$ | 10     | 0.46      | 282     | 28.2             | 99    |
| 3     | LFe$_2$-NH/SiO$_2$   | 10     | 0.36      | 217     | 21.7             | 95    |
| 4     | LFe$_2$-O/SiO$_2$    | 10     | 0.42      | 259     | 25.9             | 98    |
| 5     | LFe$_2$-O-NH$_2$/SiO$_2$ | 10 | 0.62    | 377     | 37.7             | 98    |
| 6     | R-LFe$_2$-O/SiO$_2$  | 10     | 0.30      | 182     | 18.2             | 96    |

$^a$ Reactions carried out under neat epoxide at a loading of [di-iron(III) cat.]/PPNCl/cyclohexene oxide of 1:2:10000. $^b$ Determined by Measured weight of the isolated cyclic carbonate (yields were normalized per 10 mg of catalyst). $^c$ The turn over number (TON) = number of moles of cyclohexene oxide consumed / number of moles of [di-iron(III) cat.]. $^d$ The turn over frequency (TOF) = TON/reaction period.
Figure S10. Illustrates the proposed pathways for formation of active anionic species, iron-alkoxide species and iron-carbonate species via dual-activation mechanism by two iron metal centers.

Figure S11. Backbiting reactions from carbonate and alkoxide to form cis-cyclohexene carbonate and trans-cyclohexene carbonate respectively.³
**Table S5:** Catalytic activity of different heterogeneous catalysts for cycloaddition of CO2 with terminal epoxides

| Entry | Sub. | Cat.            | Cocatalyst | $T^{\circ}$ C | $P$(bar) | $t$(h) | Yield (%) | TO N | TO F | Recycling (cycles reported) | Ref. |
|-------|------|-----------------|------------|---------------|----------|--------|-----------|------|-----|-----------------------------|------|
| 1     | SO   | COF-JLU-7       | TBAB       | 80            | 1        | 12     | 88        | 17   | 6   | 15                          | 5    |
| 2     | SO   | Eu(BTB)(p hen)  | TBAB       | 70            | 1        | 12     | 98        | 28   | 2.3 | 20                          | Inorg. Chem. 2016, 55, 9671–9676 |
| 3     | SO   | Hf-NU-1000      | TBAB       | r.t           | 1        | 26     | 10        | 52   | 2   | multiple<sup>a</sup>         | J. Am. Chem. Soc. 2014, 136, 15861 – 15864 |
| 4     | PO   | Co-CMP-100      | TBAB       | 25            | 1        | 48     | 81.5      | 16   | 7   | 3.5                         | Nature Communications, 2013, 4, 1960. |
| 5     | PO   | Co-CMP-100      | TBAB       | 10            | 30       | 1      | 98.1      | 20   | 1   | 20                          | Nature Communications, 2013, 4, 1960. |
| 6     | PO   | Co-MON          | TBAC       | 60            | 5        | 12     | 70        | 14   | 11  | NA<sup>b</sup>              | J. Mater. Chem. A, 2013, 1, 5517–5523 |
| 7     | SO   | gea-MOF-1       | TBAB       | 12            | 20       | 6      | 85        | 56   | 7   | 4                           | Nature Chemistry, 2014, 6, 673–680. |
| 8     | Bu GE| SBA-15-10-7     | -          | 50            | 1        | 24     | 80        | 32   | 13  | 5                           | Adv. Synth. Catal. 2019, |
| Entry | Cat. | Cocatalyst | $T$ (°C) | $P$ (bar) | t (h) | Yield (%) | TO N | TO F | Recycling (cycles reported) | Ref. |
|-------|------|------------|---------|----------|------|-----------|------|------|-----------------------------|------|
| 1     | SnCl$_4$ (0.66)-IL-Br@SiO$_2$ | -         | 100     | 15       | 48   | 83        | NA   | NA   | 5                           | Chemical Engineering Journal 422 (2021) 129930 |
| 2     | PS-Cat 5 | -         | 85      | 10       | 18   | 12        | NA   | NA   | 11                          | Green Chem., 2014, 16, 1552–1559 |
| 3     | YCl@SiO$_2$ | TBAC      | 80      | 10       | 48   | 79        | 24   | 0.5  | 5                           | Catal. Sci. Technol., 2019, 9, 6152–6165 |
| 4     | Amb-OH-I-910 | -         | 80      | 10       | 18   | 37        | 17   | 0.9  | 5                           | ACS Sustainable Chem. Eng. 2020, 8, 7993–8003 |
| 5     | FIP-Im | -         | 80      | 10       | 48   | 21        | 4.2  | 0.0  | 6                           | J. Mater. Chem. A, |

**Table S6:** Catalytic activity of different heterogeneous catalysts for cycloaddition of CO$_2$ with cyclohexene oxide

a= reported as multiple (didn’t provide number); b= not available
|   |   | Al-iPOP-1 | COP-222 | LFe$_2$O-NH$_2$/SiO$_2$ | LFe$_2$O-NH$_2$/SiO$_2$ |   |   |   |
|---|---|-----------|---------|-------------------------|-------------------------|---|---|---|
| 6 |   | -         | -       | 80                      | 80                      | 100 | 100 | 40 |
| 7 |   | -         | -       | 80                      | 80                      | 100 | 40  | 10 |
| 8 |   | 15        | 12      | 15                      | 15                      | 24  | 24  | 8  |
| 9 |   | 23        | 23      | 23                      | 23                      | 23  | 23  | 23 |

2018, 6, 9172–9182
ChemSusChem 2017, 10, 2534–2541
Chem, 2019 5, 3232–3242
Chem, 2019 5, 3232–3242

This work
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This work

\(a=\text{Measured yield of cyclic carbonates in grams.}\)

**Figure S12.** $^1$H NMR spectrum (CDCl$_3$, 400 MHz, 298 K) of cis-cyclic cyclohexene carbonate (CHC) derived by using LFe$_2$O-NH$_2$/SiO$_2$ and [PPN]Cl at 1atm CO$_2$. LFe$_2$O-NH$_2$/SiO$_2$/PPNCl/epoxide = 1:2:1000, Table 1 entry 5.
Figure S13. $^1$H NMR spectrum (CDCl$_3$, 400 MHz, 298 K) of propylene carbonate (PC) derived by using LFe$_2$-O-NH$_2$/SiO$_2$ and [PPN]Cl at 1 atm CO$_2$. LFe$_2$-O-NH$_2$/SiO$_2$/PPNCl/epoxide = 1:2:1000, Table 2 entry 1.

Figure S14. $^1$H NMR spectrum (CDCl$_3$, 400 MHz, 298 K) of phenyl glycidyl cyclic carbonate (PGCC) derived by using LFe$_2$-O-NH$_2$/SiO$_2$ and [PPN]Cl at 1 atm CO$_2$. LFe$_2$-O-NH$_2$/SiO$_2$/PPNCl/epoxide = 1:2:1000, Table 2 entry 4.
Figure S15. $^1$H NMR spectrum (CDCl$_3$, 400 MHz, 298 K) of tert-butyl glycidyl cyclic carbonate (TGCC) derived by using LFe$_2$-O-NH$_2$/SiO$_2$ and [PPN]Cl at 1atm CO$_2$. LFe$_2$-O-NH$_2$/SiO$_2$/PPNCl/epoxide = 1:2:1000, Table 2 entry 3.

Figure S16. $^1$H NMR spectrum (CDCl$_3$, 400 MHz, 298 K) of styrene carbonate (SC) derived by using LFe$_2$-O-NH$_2$/SiO$_2$ and [PPN]Cl at 1atm CO$_2$. LFe$_2$-O-NH$_2$/SiO$_2$/PPNCl/epoxide = 1:2:1000, Table 2 entry 2.
Figure S17. The reaction setup used for the conversion of CO$_2$ to cyclic carbonate under 1 atm CO$_2$ pressure.
3. References:

(1) Dutta, B.; Bag, P.; Adhikary, B.; Flörke, U.; Nag, K. Efficient Proton-Templated Synthesis of 18- to 38-Membered Tetraimino(Amino)Diphenol Macrocyclic Ligands: Structural Features and Spectroscopic Properties. *The Journal of Organic Chemistry* **2004**, *69*(16), 5419–5427. https://doi.org/10.1021/jo049787s.

(2) Buchard, A.; Kember, M. R.; Sandeman, K. G.; Williams, C. K. A Bimetallic Iron (III) Catalyst for CO₂/Epoxide Coupling. *Chemical communications* **2011**, *47*(1), 212–214.

(3) Darensbourg, D. J.; Chung, W.-C. Availability of Other Aliphatic Polycarbonates Derived from Geometric Isomers of Butene Oxide and Carbon Dioxide Coupling Reactions. *Macromolecules* **2014**, *47*(15), 4943–4948. https://doi.org/10.1021/ma501004w.