

Supporting Information

Efficient Catalytic Electrode for CO₂ Reduction Realized by Physisorbing Ni(cyclam) Molecules with Hydrophobicity based on Hansen's Theory

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Materials

1,4,8,11-Tetraazacyclotetradecane (i.e., cyclam; Tokyo Chemical Industry Co. Ltd.), nickel(II) chloride hexahydrate (Wako Pure Chemical Industries Ltd.), sodium tetraphenylborate (BPh₄) (Dojindo Laboratories), and other solvents were used as purchased.

Synthesis

Elemental compositions of [Ni(cyclam)(MeCN)₂](BPh₄)₂ (**1**) and [Ni(cyclam)]Cl₂ were obtained using elemental analysis (Vario EL cube; Elementar). The crystal structure of **1** was analysed using X-ray single crystal diffraction (VariMax with RAPID; Rigaku/MSK) at -100°C with Mo-K α radiation.

[Ni(cyclam)]Cl₂ was synthesized using a previously reported method.^{1,2} Anal. Calcd for C₁₀H₂₄Cl₂N₄Ni: C, 36.40; H, 7.33; N, 16.98. Found: C, 36.34; H, 7.35; N, 16.92.

1 was synthesized as follows. Cyclam (50 mg, 0.25 mmol) dissolved in MeOH (1.5 mL) was mixed with NiCl₂·(H₂O)₆ (61.8 mg, 0.26 mmol) dissolved in MeOH (1.5 mL); then the mixture solution was stirred for 1 h. Subsequently, NaBPh₄ (427.8 mg, 1.25 mmol) dissolved in MeOH (2.0 mL) was added to the solution to produce yellow precipitate; then the solution stirred for 1 h to replace the counter anions completely from Cl⁻ to BPh₄⁻. After stirring, the precipitate was filtrated and washed with water and MeOH, followed by drying in vacuum to give yellow powder products (192 mg, 78.5%). The powder products were then recrystallized by cooling crystallization from a saturated solution dissolving the powder products in 1:1 acetonitrile (MeCN)/ tetrahydrofuran (THF), to produce light-green block crystals (4.1 mg, 1.7%). The structure of the block crystal is illustrated in Figure S1. Anal. Calcd for C₆₂H₇₀B₂N₆Ni·0.75(H₂O)·1.0(C₂H₃N): C, 74.33; H, 7.26; N, 9.48. Found: C, 74.43; H, 7.21; N, 9.32.

Coating procedure of complex molecules on Sn disks

Sn disks (99.9% Sn; Nilaco Corp.) with ϕ 3.0 mm diameter were polished to a mirror finish with 0.05 μ m Al₂O₃ slurry before use. A droplet of 10 mM **1** dissolved in 6:4 MeCN/THF was dispensed on the Sn disk surface. Then the droplet was absorbed by Kimwipes® tissue to leave a thin liquid film, followed by solvent evaporation at r.t. under an atmospheric environment. Although we were unable to quantify the thin liquid film, the amount of **1** molecules remaining on the surface of Sn disks after solvent evaporation was estimated as approximately 8×10^{-8} mol cm⁻² from the quantity of Ni evaluated using inductively coupled plasma optical emission spectrometry (ICP-OES, CIROS 120EOP; Rigaku Corp.). The **1**-coated glassy carbon disk electrode, whose CV is shown in Figure S5 for comparison, was prepared by a similar procedure. **1** molecules adsorbed on either the Sn or glassy carbon surface could be washed off by rinsing the electrodes in MeCN/THF, indicating that **1** molecules are not chemi-

cally bonded to either surface. [Ni(cyclam)]Cl₂ was coated onto Sn disks with a similar procedure using MeOH instead of MeCN/THF as a solvent.

Calculation of HSPs of complex molecules

HSPs were calculated using commercial HSP calculation software.³ To obtain HSP of [Ni(cyclam)]Cl₂, the following substances were used as probe solvents to judge the solubility of [Ni(cyclam)]Cl₂: benzyl alcohol, formamide, EtOH, ethylene glycol, di-propylene glycol, MeOH, glycerol, chloroform, dimethyl sulfoxide (DMSO), propionaldehyde, acetone, dimethylformamide (DMF), THF, MeCN, hexane, propyl amine, diethyl ether, nitromethane, and acrylonitrile. The HSPs of the solvents above were referred from the database in the HSP software.³ Water was not used as a probe solvent because it is not recommended in the HSP user's handbook because of the lack of predictability of HSP of water.⁴ [Ni(cyclam)]Cl₂ (2.0–3.0 mg) was added to the individual probe solvents (1.0 mL) at r.t.; then the solution was stirred. The solubility was investigated by visual observation, in which the solvents that dissolved [Ni(cyclam)]Cl₂ within 1 min were categorized as good solvents and the others as poor solvents.

HSP of **1** was calculated using a method similar to that above using the following substances as probe solvents: acrylonitrile, cyclopentanone, propionitrile, cyclobutanone, propionaldehyde, acetone, DMF, methyl ethyl ketone (MEK), cyclohexanone, DMSO, MeCN, methylene dichloride, THF, propyl amine, chloroform, benzyl alcohol, chlorobenzene, 2-butanol, diethyl ether, EtOH, hexane, MeOH, and formamide.

Distance R_a between HSPs of two substances, a substance with HSP of (δ_{D1} , δ_{P1} , δ_{H1}) and another substance with HSP of (δ_{D2} , δ_{P2} , δ_{H2}), can be calculated using HSP software with the equation, $R_a = \{4(\delta_{D1}-\delta_{D2})^2 + (\delta_{P1}-\delta_{P2})^2 + (\delta_{H1}-\delta_{H2})^2\}^{1/2}$, according to the HSP user's handbook.⁴

Evaluation of catalytic activity for electrochemical CO₂ reduction

Cyclic voltammetry (CV) was performed using potentiostat (IviumStat) on 10 mL of pre-degassed aqueous electrolyte saturated with CO₂ by bubbling CO₂ gas for 10 min until immediately before the CV measurements under Ar atmosphere in glove box. The electrolyte contained 0.1 M KCl as a supporting electrolyte and NaOH as a pH-conditioning agent. Ag/AgCl was used as a reference electrode. Pt wire was used as a counter electrode. All potentials of CV shown in figures are converted from Ag/AgCl to SHE by adding +0.199 V.

Gas analysis

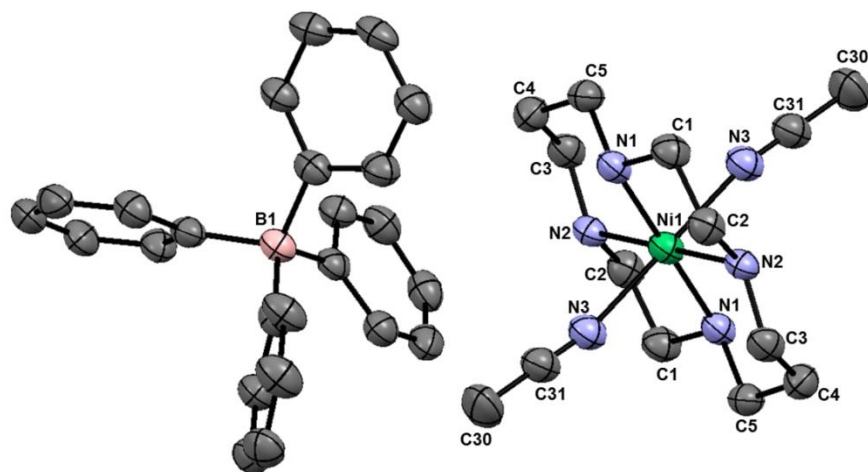
The amounts of CO and H₂ in gas samples of 0.5 mL after controlled potential electrolysis (CPE) were analyzed using gas chromatography (GC, GC-2014; Shimadzu Corp.). The 40 mL cell containing 10 mL of electrolyte was sealed during CPE. Gas

samples were collected using a syringe from the approximately 30 mL gaseous space in the sealed cell through a septum cap after CPE. The CPE was conducted at -1.40 V vs. SHE for 10–30 min. The same compositions of electrolyte and electrodes were used for CV experiments.

Interpretation of the peaks observed above -0.95 V in CVs in Figure 2

(i) In CV obtained for the bare Sn disk electrode under Ar atmosphere, an upward peak appeared at approximately -0.75 V in the cathodic sweep and a downward peak appeared at approximately -0.65 V in the anodic sweep. The upward and downward peaks have been reported to be due to the reduction of Sn(II) to Sn(o) and the oxidation of Sn(o) to Sn(II), respectively.⁵ (ii) In CV obtained for the bare Sn disk electrode when CO₂ was present, an upward peak appeared at -0.6 V, which was more anodic than the peak at -0.75 V obtained for bare Sn disk electrode under Ar atmosphere. On the basis of the reported Nernst equation,⁶ the anodic shift may be induced by an increase in H⁺, i.e., a decrease in OH⁻, on dissolution of CO₂. No downward peak appeared in the anodic sweep because the peak shifted in the anodic direction for the same reason and shifted outside the measured potential range. (iii) In CV obtained for the **1**-coated Sn disk electrode under Ar atmosphere, an upward peak appeared at -0.8 V, which was more cathodic and whose width was broader than those of the peak at -0.75 V recorded with the bare Sn disk electrode under Ar atmosphere. We assume that the cathodic shift and broadening of the peak are attributable to the inhibition of H₂O diffusion to the Sn surface by a layer of **1** molecules. For the same reason, a downward peak at approximately -0.63 V in anodic sweep showed an anodic shift and broadening compared to that of bare Sn disk electrode obtained under Ar atmosphere. (iv) In CV obtained for the **1**-coated Sn disk electrode when CO₂ was present, an upward peak appeared at approximately -0.876 V, and this is the most cathodic peak compared to the other measured peaks. In addition, a downward peak became so anodic that it did not appear in the potential range that we swept. We have not elucidated the causes of these large shifts yet, but one possible speculation is that molecular CO₂ might be adsorbed on the layer of **1** molecules, enhancing the inhibition of H₂O diffusion to the Sn surface. Further interfacial analysis should be performed to clarify this.

a)



b)

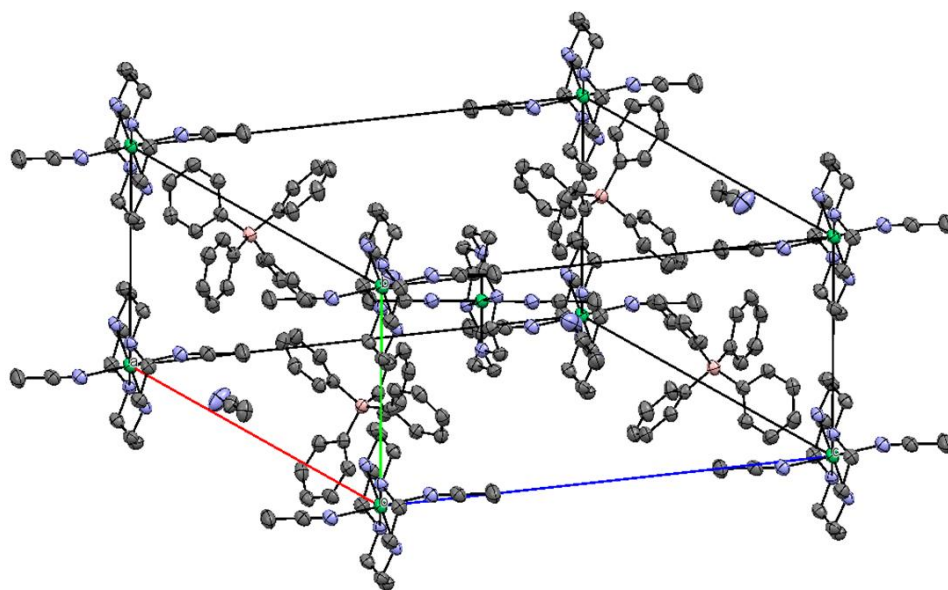


Figure S1. ORTEP drawing of crystal structure of **1** with ellipsoids at the 50% probability level: (a) molecular and (b) packing drawing. All hydrogen atoms were omitted for clarity. Bond lengths (Å) and angles (deg) of $[\text{Ni}(\text{cyclam})(\text{MeCN})_2]^{2+}$: Ni1–N1 2.062 (3); Ni1–N2 2.071 (3); Ni1–N3 2.166 (4); Ni1–C1 1.481 (6); N2–C2 1.493 (5); N2–C3 1.482 (5); Ni1–C5 1.481 (5); N3–C31 1.145 (7); C1–C2 1.507 (6); C3–C4 1.523 (5); C4–C5 1.519 (7); C30–C31 1.444 (9). CIF file can be obtained from The Cambridge Crystallographic Data Centre (CCDC 1483584).

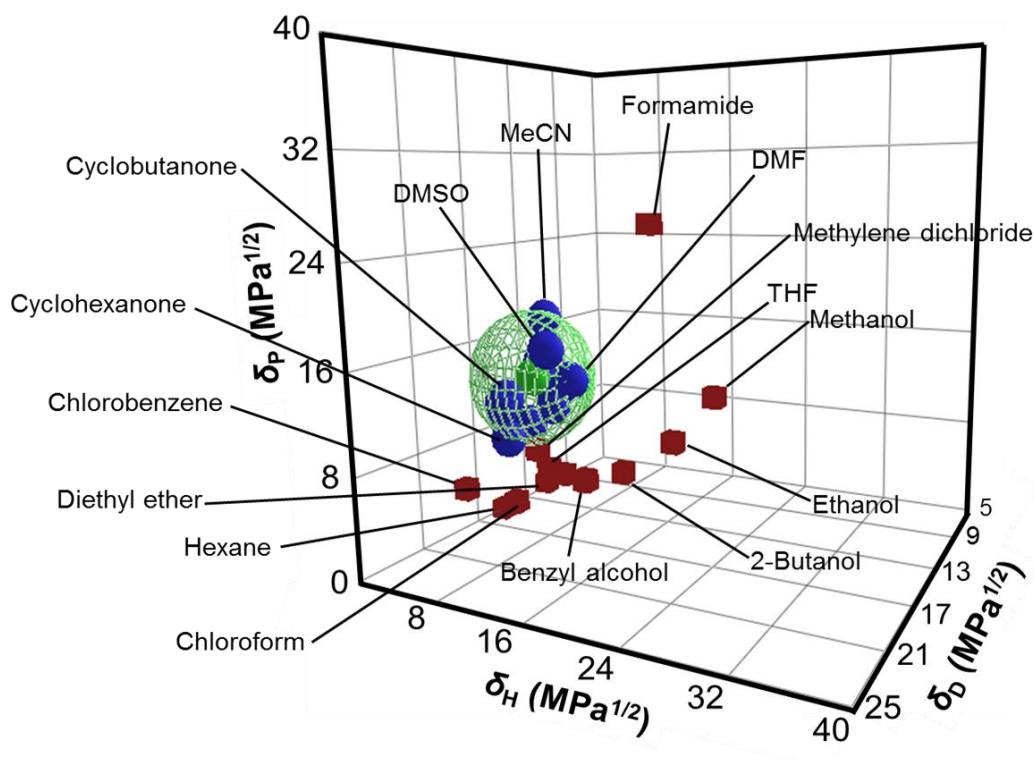


Figure S2. 3D vector space showing calculated HSP ($\delta_D = 16.9 \text{ MPa}^{1/2}$, $\delta_P = 13.4 \text{ MPa}^{1/2}$, $\delta_H = 6.7 \text{ MPa}^{1/2}$, $R_o = 5.6 \text{ MPa}^{1/2}$) of **1** with a green plot and sphere. Blue plots indicate HSPs of good solvents for **1**: acetone, MeCN, acrylonitrile, cyclobutanone, cyclohexanone, cyclopentanone, DMF, DMSO, MEK, propionaldehyde, and propionitrile. Red plots indicate HSPs of poor solvents for **1**: chlorobenzene, MeOH, hexane, THF, methylene dichloride, propyl amine, 2-butanol, EtOH, diethyl ether, chloroform, benzyl alcohol, and formamide. All HSPs of probe solvents were referred from the HSP software.³ The interaction sphere included all good solvents and excluded all poor solvents, giving the data fit⁴ as 1.000.

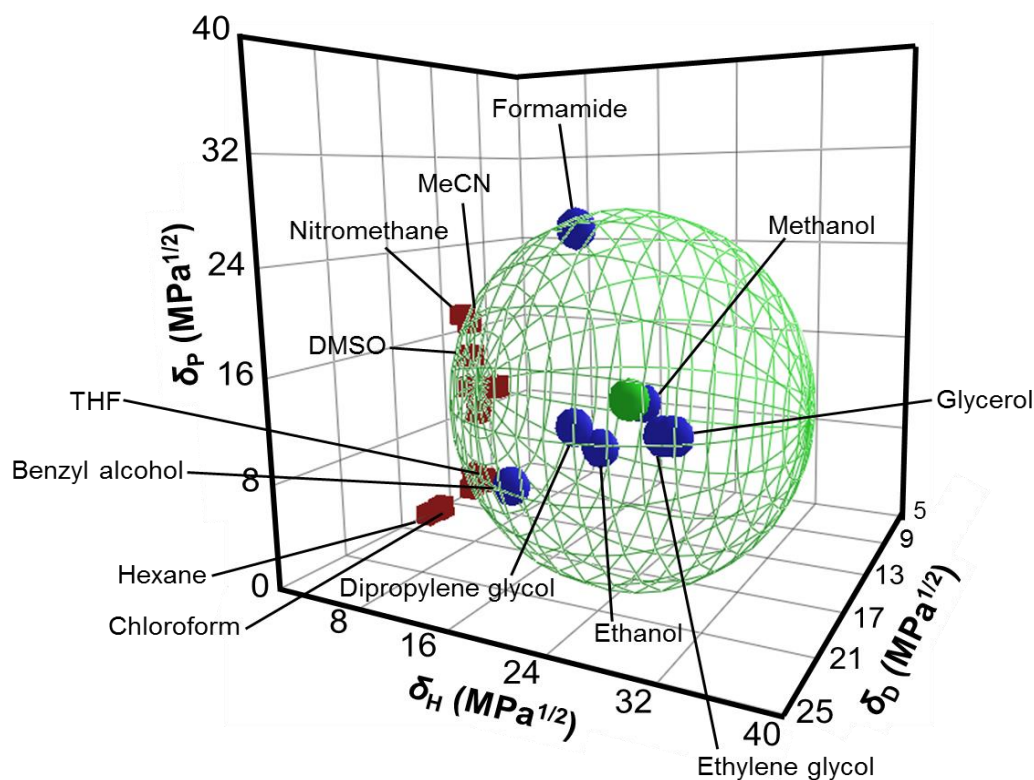


Figure S3. 3D vector space showing the calculated HSP ($\delta_D = 18.6 \text{ MPa}^{1/2}$, $\delta_P = 14.3 \text{ MPa}^{1/2}$, $\delta_H = 24.6 \text{ MPa}^{1/2}$, $R_o = 13.5 \text{ MPa}^{1/2}$) of $[\text{Ni}(\text{cyclam})]\text{Cl}_2$ with a green plot and sphere. Blue plots indicate HSPs of good solvents for $[\text{Ni}(\text{cyclam})]\text{Cl}_2$: benzyl alcohol, formamide, EtOH, ethylene glycol, dipropylene glycol, MeOH, and glycerol. Red plots indicate HSPs of poor solvents for $[\text{Ni}(\text{cyclam})]\text{Cl}_2$: chloroform, DMSO, propionaldehyde, acetone, DMF, THF, MeCN, hexane, propyl amine, diethyl ether, nitromethane, and acrylonitrile. All HSPs of probe solvents were referred from the HSP software.³ The interaction sphere included all good solvents and excluded all poor solvents, giving the data fit⁴ as 1.000.

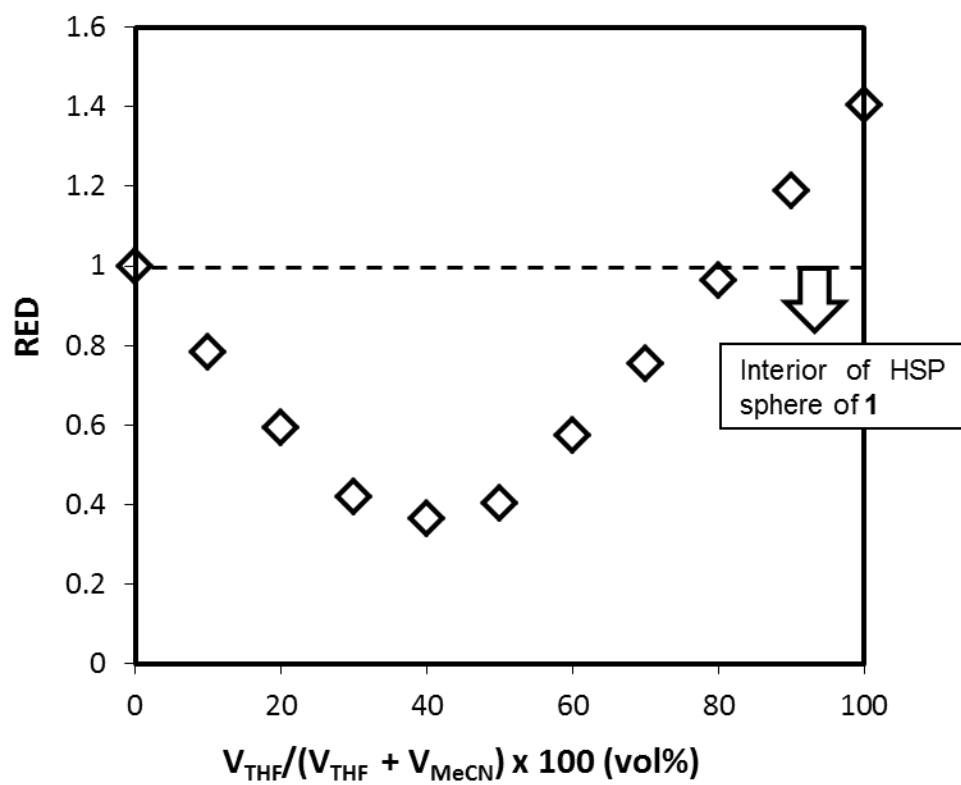


Figure S4. Relative energy difference (RED) between HSPs of **1** and MeCN/THF mixture solvents with different mixing ratios.

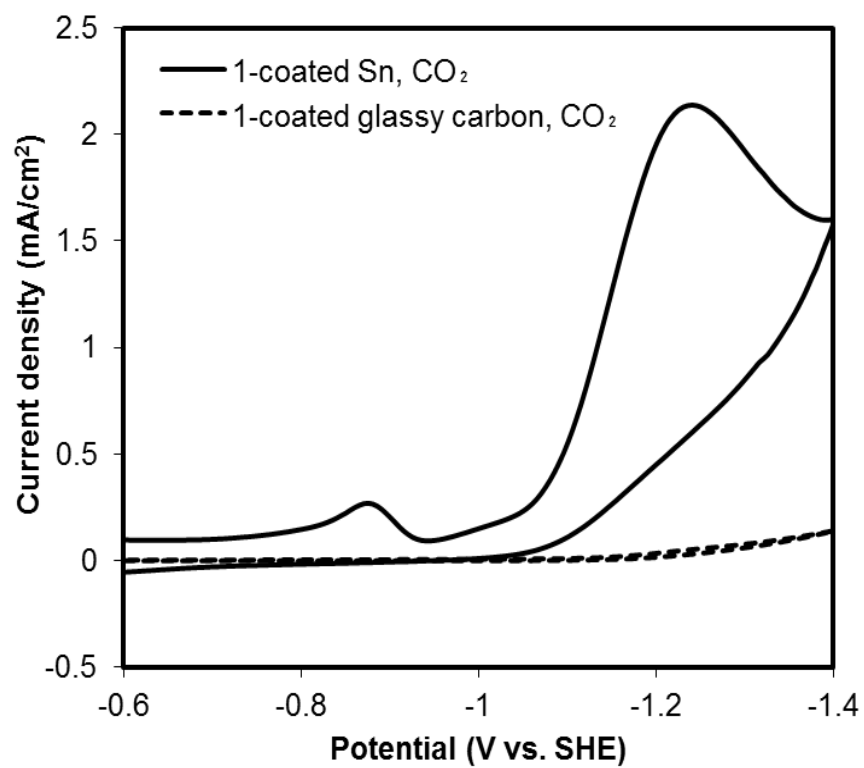


Figure S5. CVs of **1**-coated Sn disk electrode and **1**-coated glassy carbon disk electrode in 0.1 M KCl, pH 10 aqueous electrolyte; Scan rate = 0.1 V·s⁻¹.

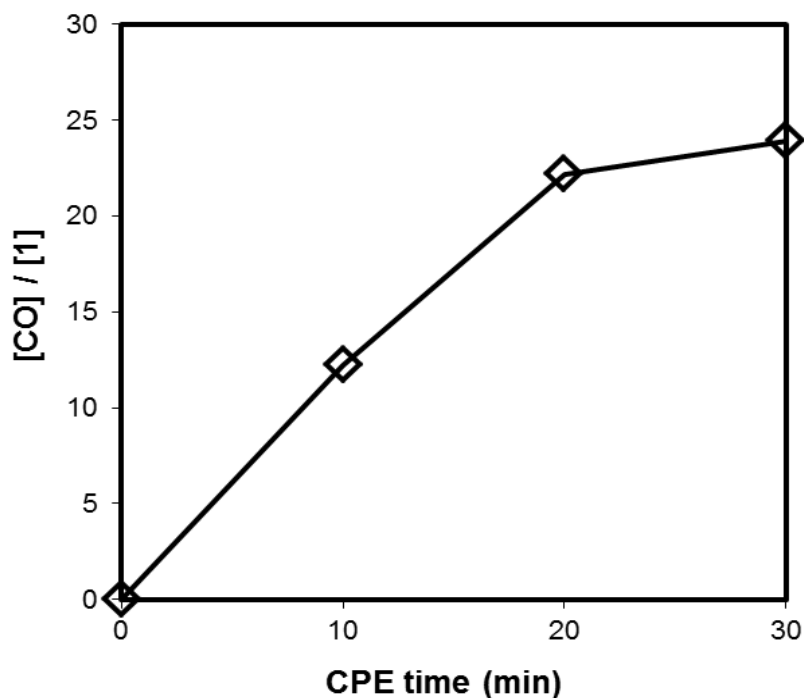


Figure S6. The amount of CO produced per mole of **1** evaluated at different CPE times. Monitored during CPE for 30 min, the amount of produced CO increased linearly until 20 min by retention of the CO production rate, and was inclined to stagnate at 30 min because of a decreased CO production rate. The decrease in the CO production rate at 30 min might result from desorption of **1** molecules from the Sn surface because of physical damage by bubbles of the produced CO and H₂ gas or because of degradation in hydrophobicity of **1** by dissociation of BPh₄[−]. Otherwise, the catalytic ability of **1** was deactivated.

Table S1. Calculated HSPs of **1** and [Ni(cyclam)]Cl₂, HSP of CO₂ referred from the HSP software,³ and the R_a and REDs from HSP of CO₂.

	HSPs (MPa ^{1/2})			REDs	R_a (MPa ^{1/2})
	δ_D	δ_P	δ_H		
1	16.9	13.4	6.7	1.3	7.5
[Ni(cyclam)]Cl ₂	18.6	14.3	24.6	1.6	21.3
CO ₂ ³	15.7	6.3	5.7	-	-

References

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