

Supporting information for
Ugi's amine based coordination polymers as a synergistic catalysts for
electrocatalytic reduction of carbon dioxide

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General All reactions and manipulations were carried out under dry pure N₂ in standard Schlenk apparatus. All solvents were distilled from sodium/benzophenone or phosphorus pentoxide and stored under nitrogen before use. The NMR spectra were recorded on a Bruker MSL-400 (¹H 400 MHz, ³¹P 161.7 MHz, ¹³C 100.6 MHz). SiMe₄ was used as internal reference for ¹H and ¹³C NMR chemical shifts, and 85% H₃PO₄ as external reference for ³¹P. All experiments were carried out using standard Bruker pulse programs. Infrared (IR) spectra were recorded on a Bruker Vector-22 spectrometer. The elemental analyses were carried out on a EuroEA elemental Analyser at the microanalysis laboratory of the Arbuzov Institute of Organic and Physical Chemistry, Russian Academy of Sciences.

Reagent *R,Sp/S,Rp*-2-(*N,N*-dimethyl- α -aminoethyl)ferrocenylphosphinic acid (1**) and Ni(bpy)₂L₂ (**2**)** was prepared according to the literature procedure.^[1]

Synthesis of Co(bpy)₂L₂ (3**):** Co(NO₃)₂·6H₂O (68 mg, 0.23 mmol), acid **1** (150 mg, 0.47 mmol), and 4,4'-bipyridine (73 mg, 0.47 mmol) were dissolved in water (10 ml). The mixture was heated to 90 °C for 24 h in a Pyrex tube. After cooling to room temperature, brown single crystals formed were isolated by decanting the mother liquid and washed with water, MeOH and dried in air. Yield: 49%. EA for [Co(bpy)₂L₂·7H₂O]_n: calcd.: C 50.68 %, H 6.02 %, N 7.39 %, P 5.45 %, found: C 51.03 %, H 5.87 %, N 7.48 %, P 5.11 %

Electrochemical parts Electrochemical measurements were taken on a BASiEpsilonE2P electrochemical analyzer (USA). The program concerned Epsilon-EC-USB-V200 waves. A

conventional three-electrode system was used with glassy carbon for carbon paste electrode (CPE) solutions for powder samples as the working electrode, the An Fc⁺/Fc system served as the reference electrode, and a Pt wire as the counter electrode. 0.1 M Et₄NBF₄ was used as the supporting electrolyte to determine the current–voltage characteristics. To study the powder samples, a modified CPE working electrode was used, which was prepared as follows: the carbon particles/phosphonium salt (dodecyl(tri-tert-butyl)phosphonium tetrafluoroborate) composite electrode was prepared by grinding a mixture of graphite powder and phosphonium salt with a 90/10 (w/w) ratio in a mortar giving it a homogeneous mass. A modified electrode was also devised in a similar manner except that a portion (ca. 5%) of the graphite powder was replaced by the CPs under study. As a result, a portion of the resulting paste was packed firmly into (3 mm in diameter) a Teflon holder cavity.

Electrochemical preparative experiments utilized Elins P-40X (Russia) and PARSTAT 4000A (USA) as power sources. The reaction potential was set relative to values obtained from cyclic voltammetry analysis. The electrode for preparative catalysis was fabricated similarly to the CV methodology.

Absorption parts

The porous structure was analyzed based on the adsorption/desorption isotherms of N₂ at 77 K and the adsorption isotherms of CO₂ at 273 K. The isotherms were measured using the ASAP 2460 instrument (Micromeritics). Prior to adsorption measurements, the samples were out gassed by heating up to 363 K, at a heating rate of 5 K/min under vacuum (5*10⁻³ mmHg) for 6 h using a degassing system. The specific surface area (SBET) was calculated according to the Brunauer-Emmett-Teller (BET) method within relative pressure range of 0.05–0.3 while the Pore Size Distribution (PSD) and the total pore volume (VT) were evaluated by Barrett-Joyner-Halenda (BJH) analysis. Adsorption–desorption isotherms of CO₂ were measured within relative pressure range of 0.0–0.03. Experimental data was assessed with adsorption isotherm model of Langmuir.

X-ray Structure Determination (XRD) The X-ray diffraction data for the single crystal of **3** was collected on a Bruker AXS Smart Apex diffractometer at 100(2) K using Mo K α radiation ($\lambda = 0.71073 \text{ \AA}$). The structure was solved by direct methods using APEX3^[2] for data collection, SAINT for data reduction, SADABS^[3] for multi-scan absorption correction, SHELXT^[4] for structure solution, SHELXL^[5] for structure refinement by full-matrix least-squares against F. ^[6] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms

at carbon atoms were placed into calculated positions and refined as “riding” atoms. The other hydrogen atoms were revealed from difference Fourier series and refined isotropically. CCDC 2345249 contains the supplementary crystallographic data for this paper. Compared to the Ni-complex [https://pubs.rsc.org/en/content/articlelanding/2021/nj/d0nj04783j/unauth], one of the HL acid is determined in this structure, but all attempts to localize other HL ligand on the second Co atoms failed because of the HL fragment disorder.

Crystal data:

The coordination polymer crystallizes in monoclinic space group P2/c. The asymmetric part of unit cell contains two Co atoms and each atom coordinated by half a bpy molecule by nitrogen atom, located at 2-fold axis, and 2-(N,N-dimethyl- α -aminoethyl)ferrocenylphosphinic acid by oxygen atom, also neighboring cobalt atoms are linked by bridging 4,4'-bpy molecule, thus the cobalt atom shows octahedral coordination geometry with Co-O and Co-N bonds of 2.049(9) Å and 2.13(2)-2.21(2) Å, respectively (Fig.1). Crystal packing is formed by 2D Co(bpy)₂ layers located orthogonal (101) diagonal of unit cell (Fig.1). The distance between layers is equal to 8.21(3) Å, which is similar to described Ni-complex. Compared to the Ni-complex, one of the HL acid is determined in this structure, but all attempts to localize other HL ligand on the second Co atoms failed because of the HL fragment disorder.

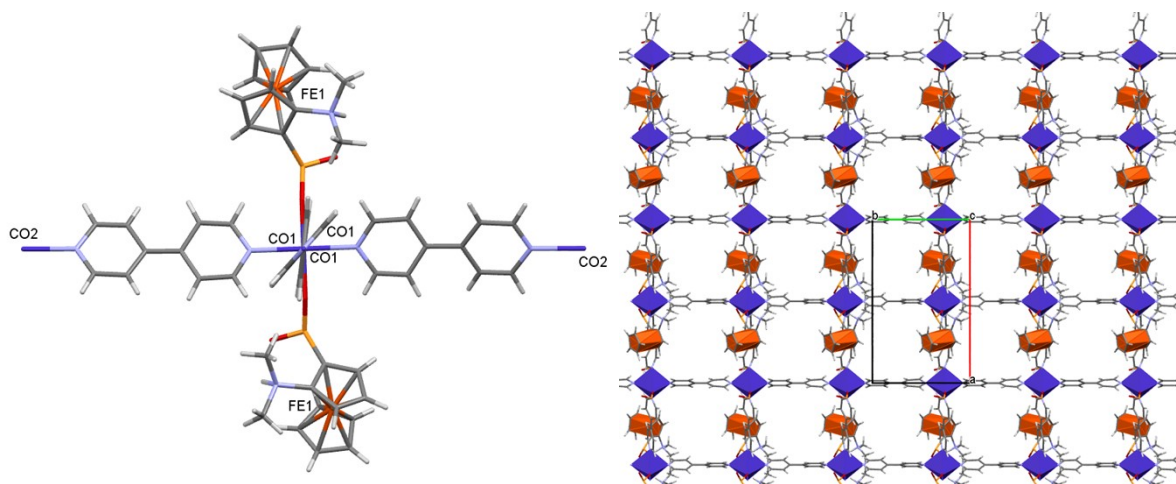


Fig. S1. Geometry of the molecule of the MOF 3 (left) and fragment of crystal packing demonstrating 2D layer (right).

$C_{32}H_{31}CoFeN_5O_4P_2$, $M = 726.347$ g/mol, monoclinic, space group P2/c (No. 13), $Z = 4$, $a = 20.9939(16)$ Å, $b = 11.4106(9)$ Å, $c = 21.1115(16)$ Å, $\beta = 114.368(2)^\circ$, $V = 4606.8(6)$ Å³, ρ_{calc}

= 1.047 g·cm⁻³, μ = 0.776 mm⁻¹, θ range = 2.64° to 28.57°, 303 refined parameters, R_1 = 0.1947, wR^2 = 0.2297, max. residual electron density 3.155 (−1.924) e Å⁻³.

Below are the powder X-ray diffraction patterns of **3**: calculated from the modelled structure (black), calculated from the crystal structure (red). (Fig.S1)

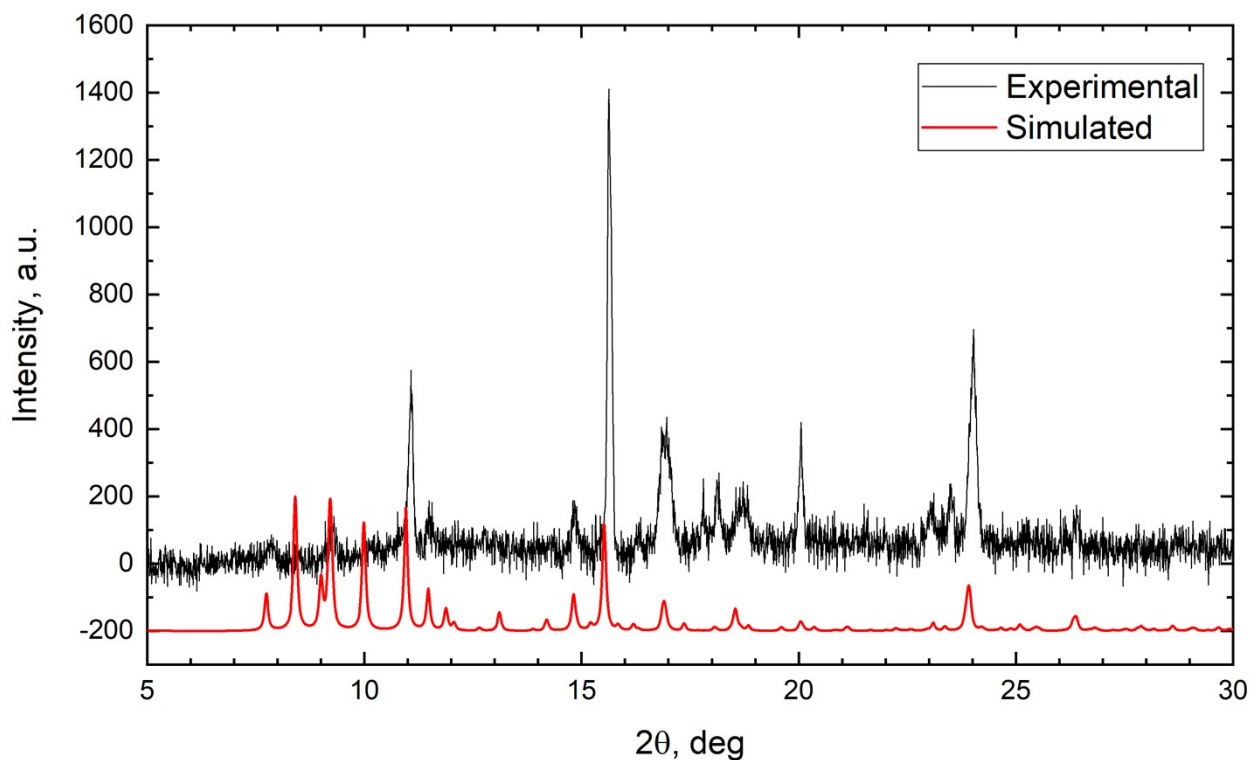


Fig. S2. Powder X-ray diffraction patterns of **3**: calculated from the crystal structure (red), as-made material (black)

Thermogravimetry (TGA)

The thermal stability of **2** and **3** was investigated by thermogravimetric (TG) analysis using NETZSCH (Selb, Germany) STA449 F3 instrument. Approximately 5–6 mg of sample was placed into an Al₂O₃ crucible with a pre-hole on the lid and heated from 30 to 1000 °C. The same empty crucible was used as the reference. High-purity argon was used with a gas flow rate of 50 mL min⁻¹. TG measurement was performed at the heating rates of 10 °C min⁻¹

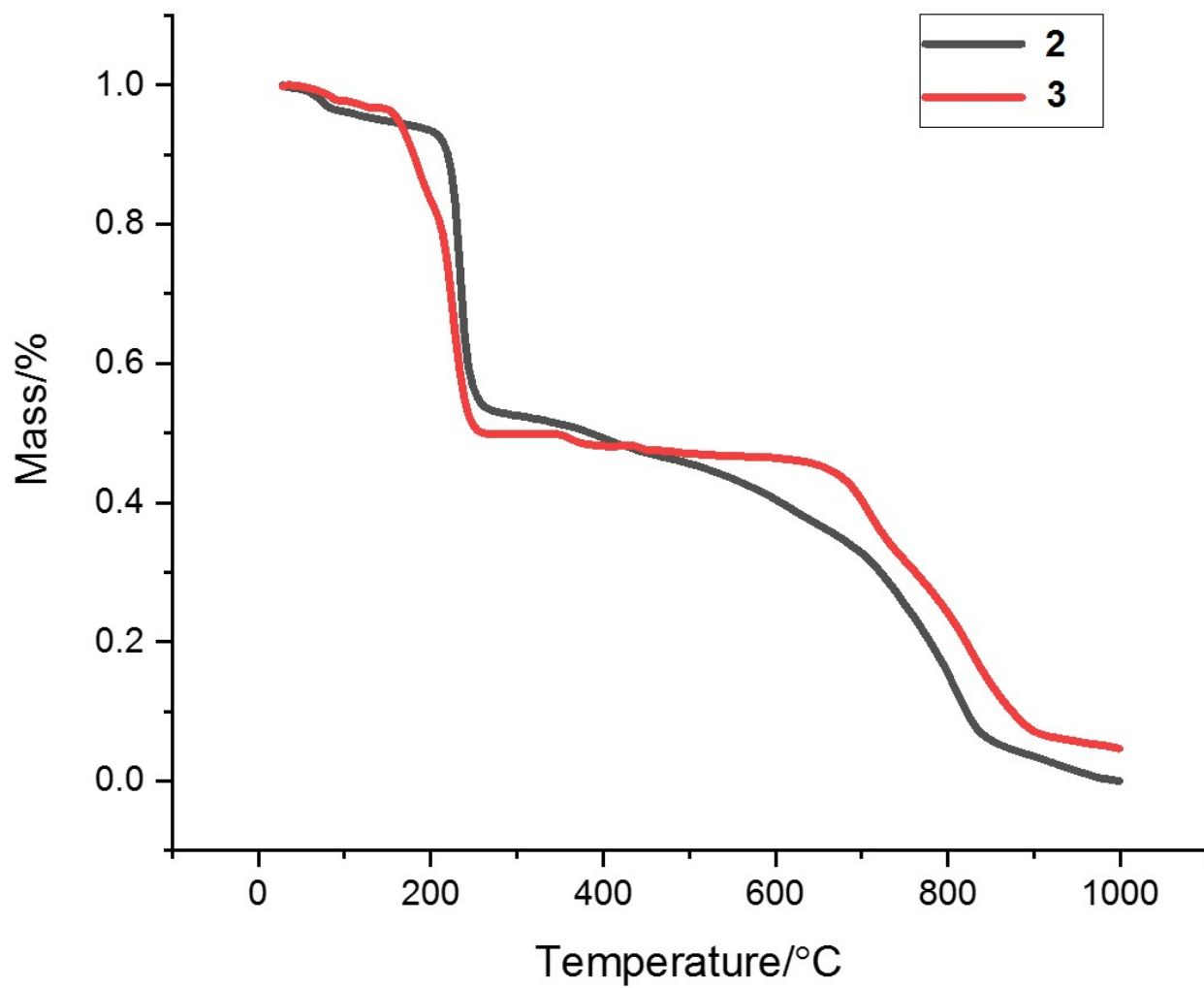


Fig. S3. Comparison powder TG of coordination polymers **2** and **3**

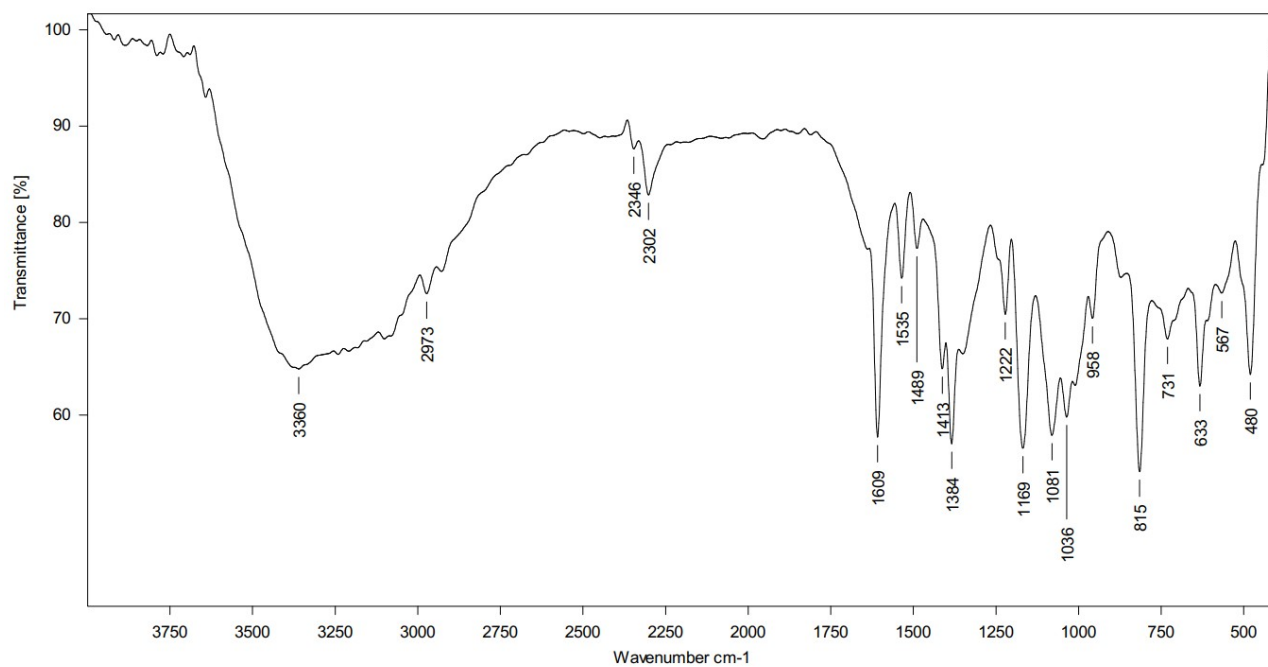


Figure S4. IR spectra for **2**

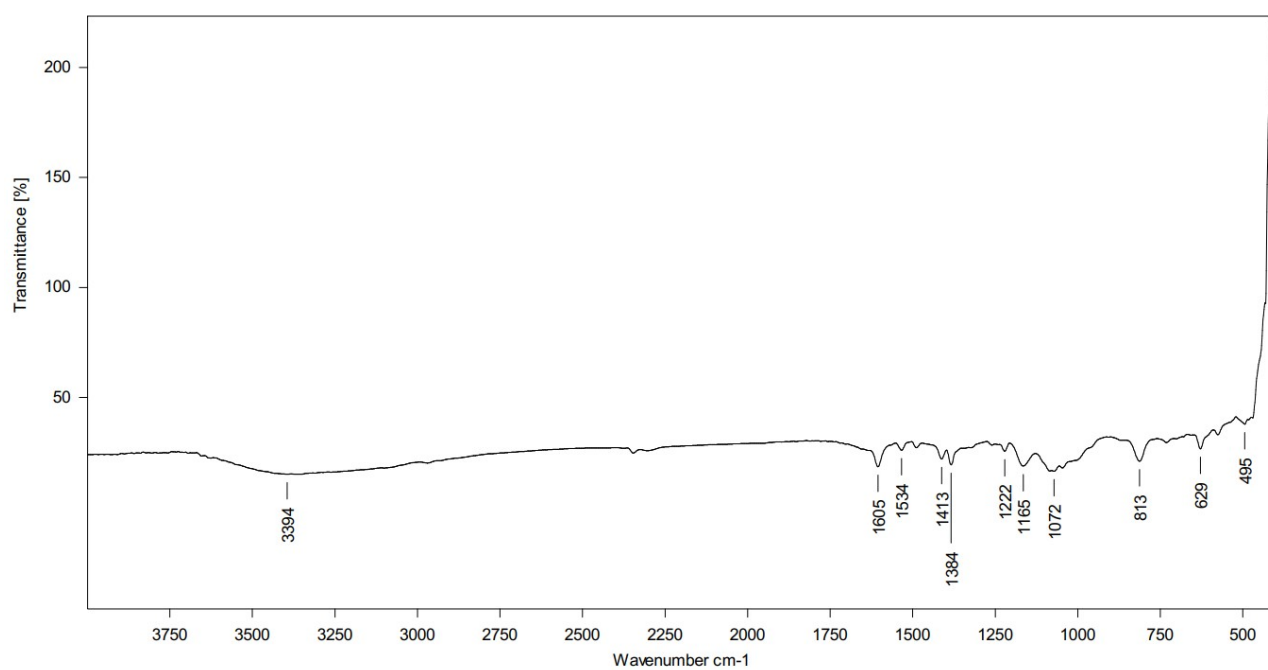


Figure S5. IR spectra for **3**

GC Analysis

Gas probe analysis was carried out on a GC-1000 gas chromatograph (Kristall, Moscow, Russia), equipped with a flame ionization detector and a thermal conductivity detector, to identify CO₂ reduction products.

CO₂ reduction selectivity was determined in a gas stream in the presence and absence of electrolysis.

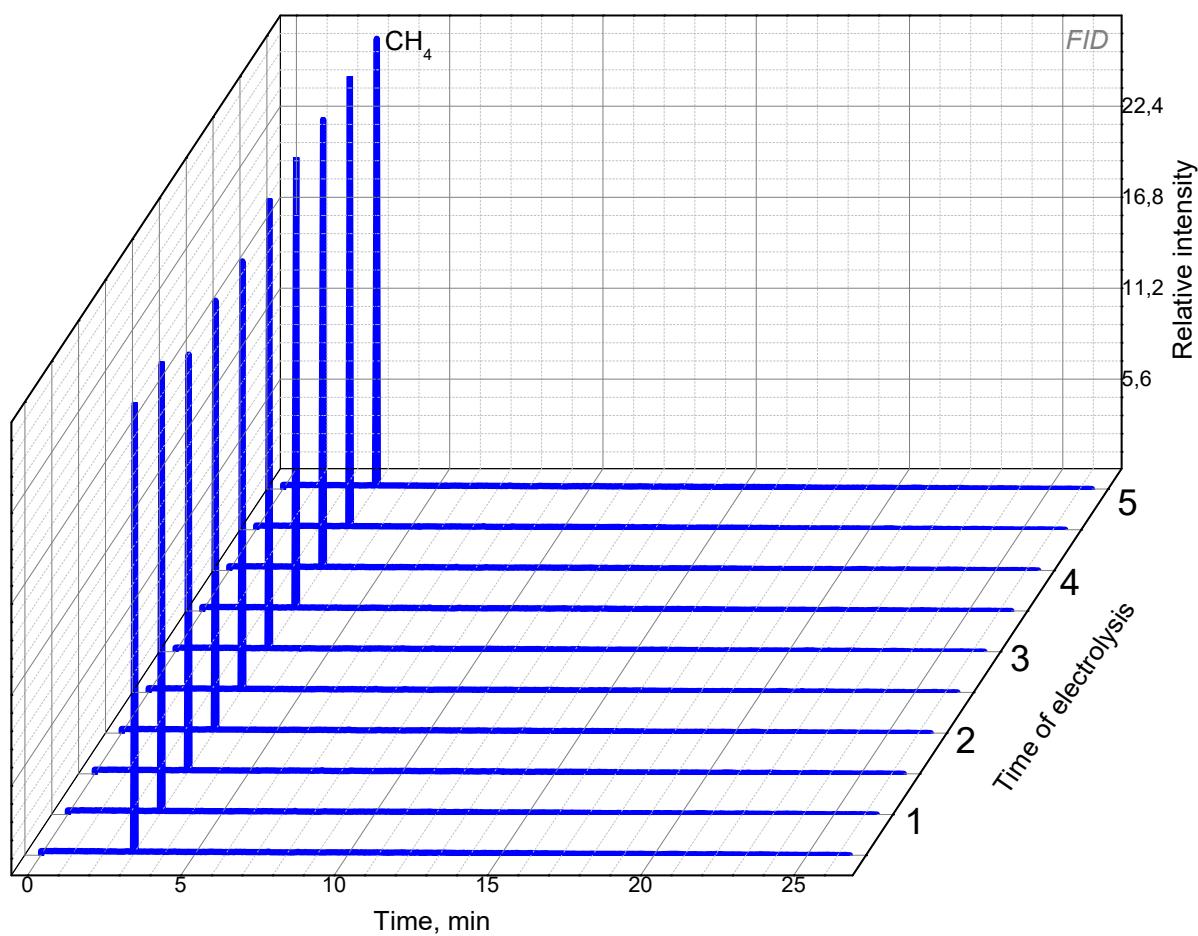


Fig. S6. Representative of GC trace of gas mixture after controlled-potential electrolysis by **3** polymer on CPE.

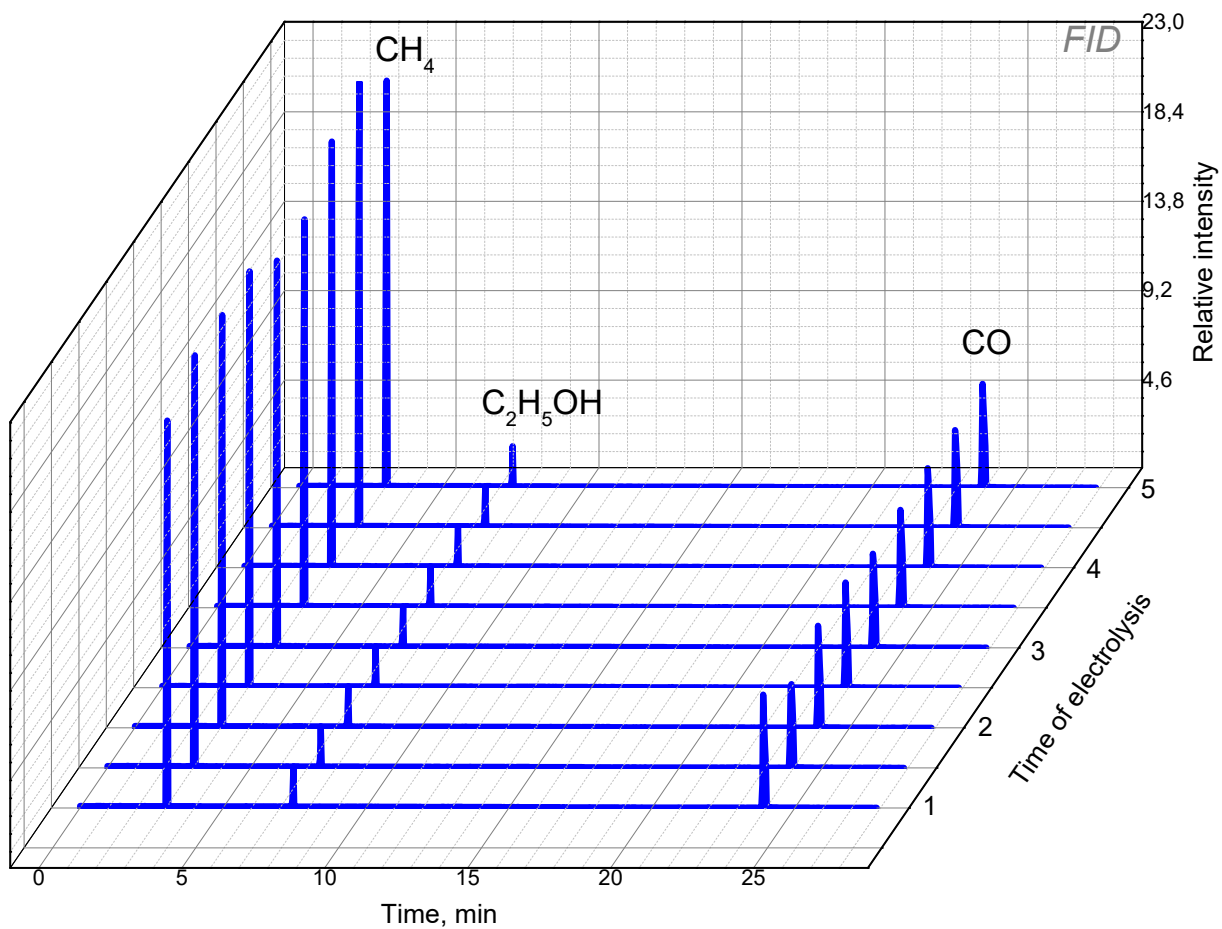


Fig. S7. Representative of GC trace of gas mixture after controlled-potential electrolysis by 2 polymer on CPE.

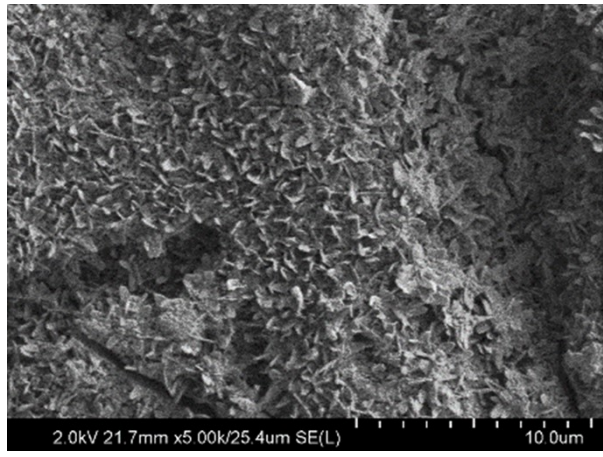
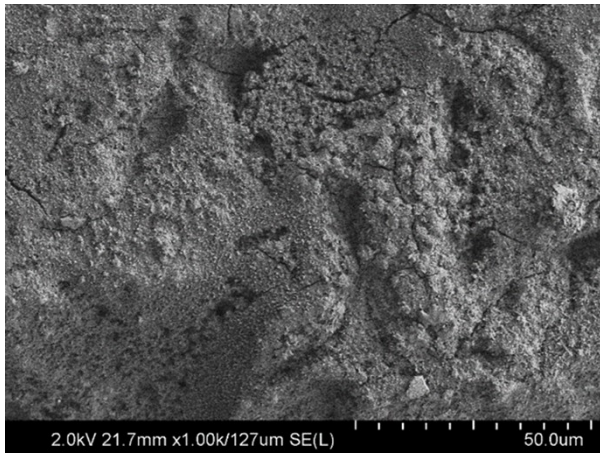


Fig. S8.SEM image of 2.

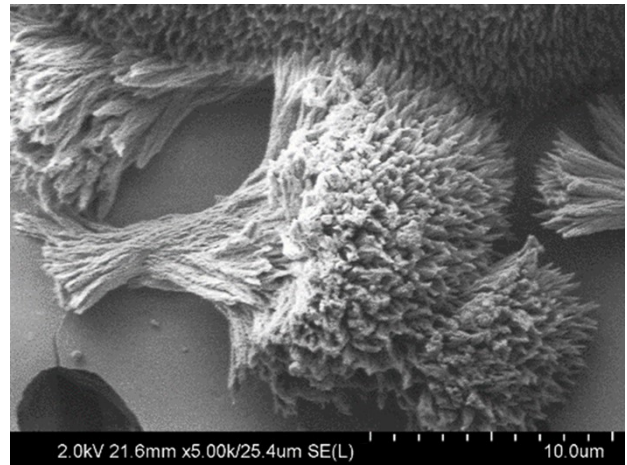
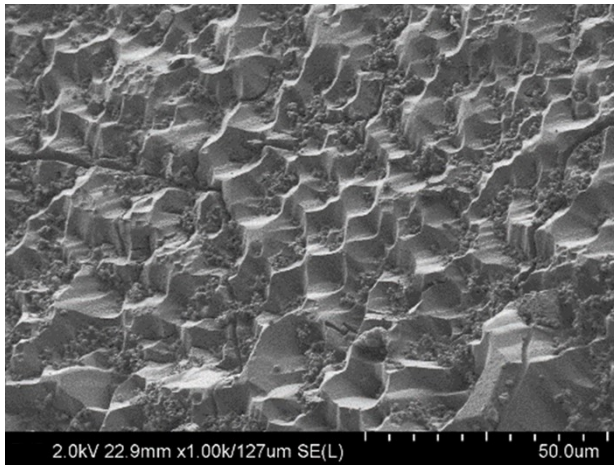


Fig. S9.SEM image of 3.

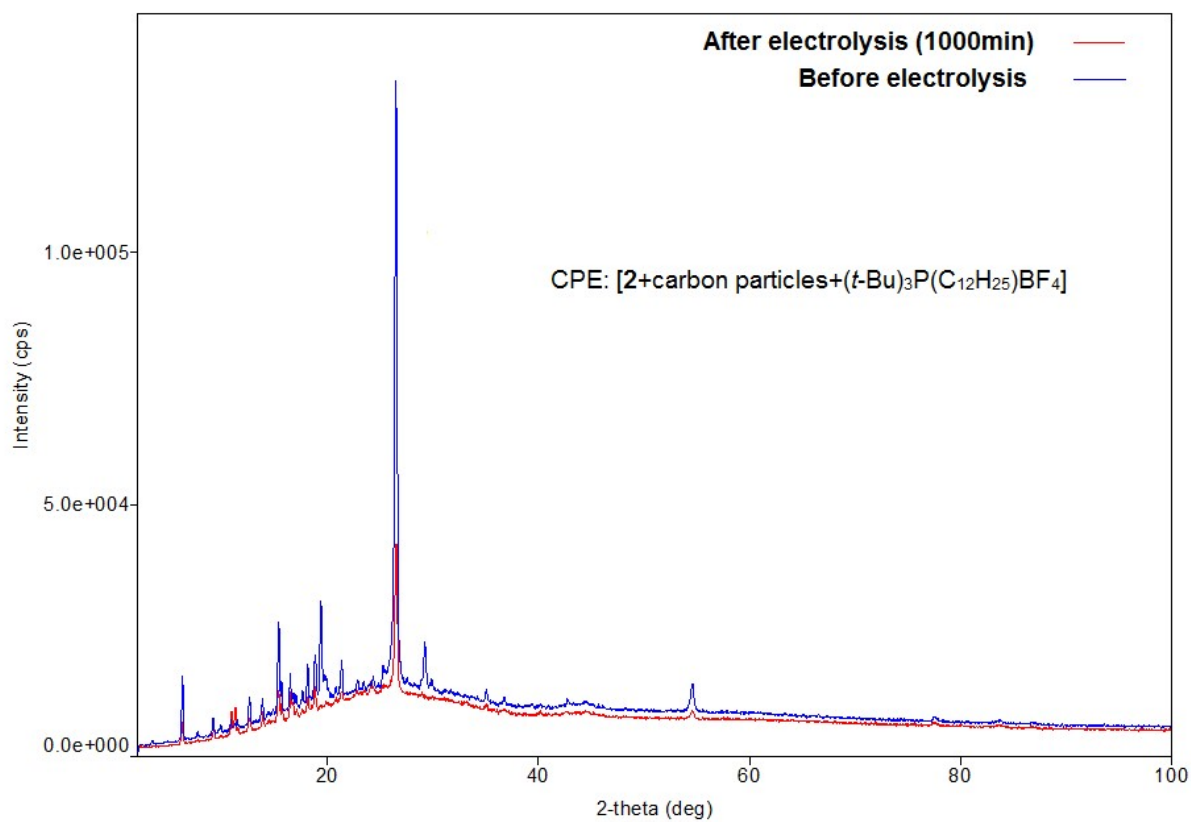


Fig. S10. Powder X-ray diffraction patterns of CPE with **2** before and after electrolysis.

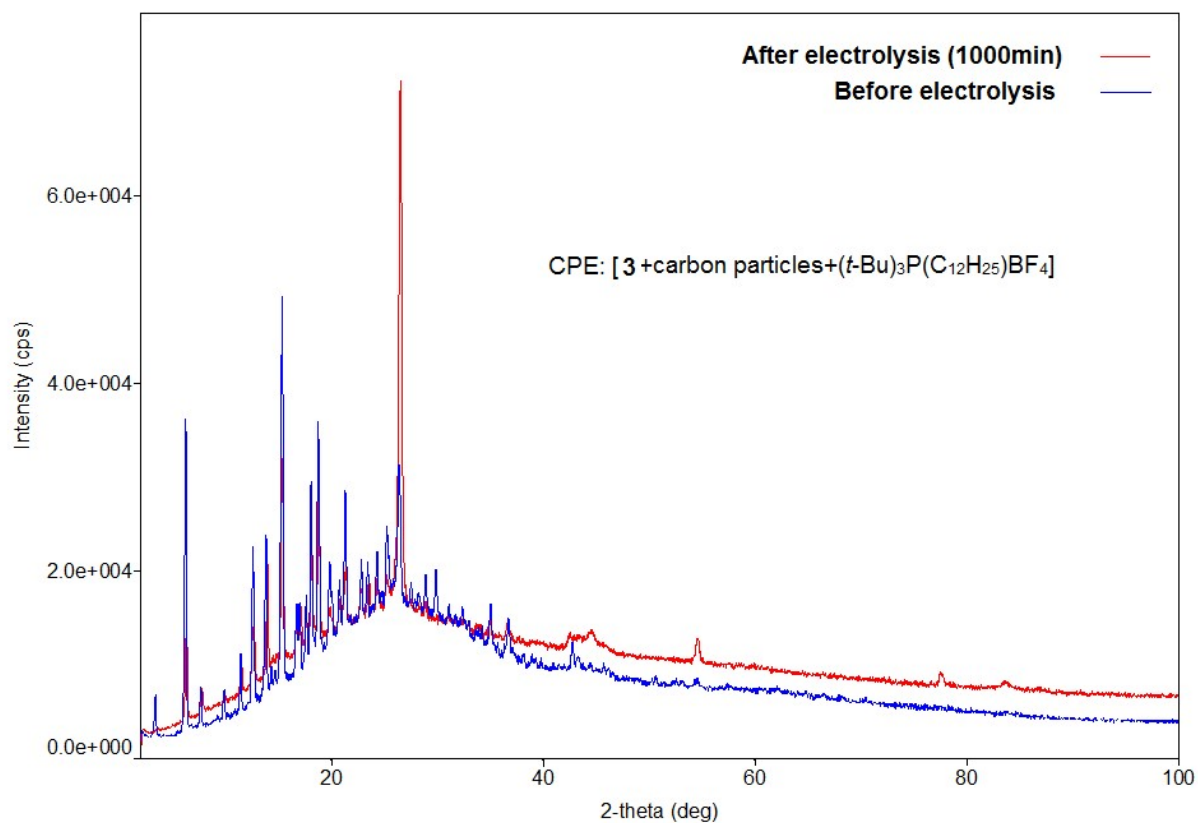


Fig. S11. Powder X-ray diffraction patterns of CPE with **3** before and after electrolysis.

Computational details

The quantum chemical calculations for all model structures were carried out at the PM6 level of theory with the help of the Gaussian-09 program package [7]. The Cartesian atomic coordinates for all optimized equilibrium model structures are presented in attached xyz-files.

Table S1. Calculated values of total electronic energy change for model processes (ΔE , in kcal/mol).

Model process	ΔE
MOF + CO ₂ → MOF⋯CO ₂ (via amine group)	-2.9
MOF + CO ₂ → MOF⋯CO ₂ (via Cp group)	39.3
MOF + CO → MOF⋯CO (via amine group)	-2.8
MOF + CO → MOF⋯CO (via Cp group)	40.1

Results of quantum chemical calculations (**Table S1**) confirm assumption about the selective (thermodynamically favorable) binding of both carbon dioxide and carbon monoxide molecules by *N*-containing fragments of MOF (viz. through its absorption on the weak basic amine groups).

Table S2. Calculated total electronic energies (*E*) for optimized equilibrium model structures.

Model structure	<i>E</i> , Hartree
CO	-0.021801
CO ₂	-0.135013
MOF	0.294767
MOF ⋯CO (via amine group)	0.268280
MOF ⋯CO (via Cp group)	0.336926
MOF ⋯CO ₂ (via amine)	0.155054
MOF ⋯CO ₂ (via Cp group)	0.222405

References

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