

An *ad-hoc* Pyrolized *Phoenix*-like Covalent Triazine Framework for the Selective CO₂-to-Formate Electroreduction

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Experimental Section

CTF^{ph} was prepared under classical ionothermal conditions according to literature procedures.¹ In brief, 1,3-dicyanobenzene (*m*DCB) was mixed in a glove-box with an excess of anhydrous ZnCl₂ (5 eq.) and transferred in a quartz ampule. After drying under vacuum for 3 h, the ampule was flame-sealed and heated in a furnace (10 h at 400 °C + 10 h at 600 °C). After cooling down to rt, the ampule was carefully opened (caution: the ampule is under pressure) and the recovered black monolith crushed and submitted to sequential washing cycles (water, HCl 1M, NaOH 1M, water and THF) before being dried to constant weight (91 % yield).

Characterization. *Elemental analysis* was performed on a Thermo FlashEA 1112 series CHNS-O elemental analyzer and elemental average values for each sample were calculated over three independent measurements (accepted tolerance ± 2 %). *Acid-Base Titration.* In a typical procedure, 5 mg of the CTF^{ph} were suspended in 7 mL of a HCl solution (standardized with Na₂CO₃ chosen as a primary standard), sonicated for 15 minutes and maintained under stirring in the dark for 48 h. Afterwards, the suspension was centrifugated and three aliquots of the supernatant titrated with a standardized NaOH solution. The basic sites content (mmol/g) was calculated as average value over three independent measurements. *Porosimetry.* Brunauer-Emmett-Teller (BET) Specific Surface Area (SSA) values were calculated from N₂ physisorption isotherms recorded at 77 K on an ASAP 2020 Micromeritics® instrument while pore size distribution was determined by density functional theory (DFT) N₂-model for pores of slit geometry via Micro-Active (version 1.01). Micropore volume has been evaluated by *t*-Plot method. Before measurement, CTF^{ph} was degassed/activated at 250 °C under high vacuum for 12 h. *X-ray Powder Diffraction (PXRD)* measurements were performed at room temperature on a Panalytical X'PERT PRO powder diffractometer equipped with a mirror on the incident beam, a beam knife and a PIXcel[®] solid state detector in the 4-60° 2 θ region, operating with Cu K α radiation ($\lambda = 1.5418$ Å). *FT-IR spectroscopy* was performed on a PerkinElmer Spectrum BX FT-IR spectrophotometer in the 400-4000 cm⁻¹ wavenumber range and with a resolution of 1 cm⁻¹. Samples for analyses were prepared mixing 2-3 wt.% of either CTF^{ph} or 1,3-dicyanobenzene

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with spectroscopic grade KBr. *X-ray photoemission spectroscopy* (XPS) measurements were performed in an ultra-high vacuum system equipped with a non-monochromatized Mg-Ka X-ray source (1253.6 eV) and a VSW HAC 5000 hemispherical electron energy analyzer. The sample was fixed on a vacuum-compatible carbon adhesive tape and kept in the introduction chamber under vacuum overnight. The spectrum was calibrated on the C $1s$ sp^2 component at 285.0 eV² and the high-resolution signals fitted with mixed Gaussian-Lorentzian peaks. *SEM-EDX* analysis was carried out on a dual beam GAIA 3 Tescan FIB/SEM microscope equipped with an EDS-X-ray microanalysis system (EDAX, AMETEK, USA) TEAM EDS Basic Software Suite TEAMTH, operating a 10 keV electron beam. Samples for analyses were suspended in ethanol upon sonication before being drop casted on the surface of aluminum stubs. *Inductively Coupled Plasma* (ICP) analyses were performed on an ICP-OES Agilent 5800 instrument by dissolving 50 mg of CTF material in 9 mL of an acid solution (HCl/HNO₃ = 1:2) followed by dilution to of 50 mL.

CO₂ Reduction (CO₂RR) measurements

A SP-150 potentiostat (*Biologic Instruments*) workstation and a custom-made electrochemical cell³ equipped with a three-electrode configuration were used to determine the properties of CTF^{ph} towards CO₂ reduction reaction (CO₂RR). The innovation of this custom-made cell is the WE placed face-up in the bottom of cell, and the CE (mesh Pt) separate from electrolyte by porous frit. With this configuration the gas products can go directly towards the Gas Chromatograph (GC) for detection while a separate compartment avoids that liquid products eventually react whit CE. An Ag/AgCl was used as a reference electrode (LowProfile 3.5mm OD of *PINE research*). The peculiarity of this electrode is the use of a gel instead of a KCl solution. The gel and the ceramic porous frit guarantee a low mobility of the chloride ions, preventing them from escaping from the electrode with consequent poisoning of the catalyst. To study the electrochemical proprieties of CTF^{ph}, a thin film was deposited on glassy carbon electrode through evaporative drop-casting of a constant loading of electrocatalyst equal to 207 $\mu\text{g cm}^{-2}$. To this end, a 0.5 v./v.% of Nafion in DMF was used for creating

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a catalyst ink (1.6 mg mL^{-1}) for deposition. Higher CTF^{ph} loading (such as 255 and $340 \text{ } \mu\text{g cm}^{-2}$) give rise too high resistance values due to the low conductivity of the deposited sample.

Electrolysis was performed in a near-neutral bicarbonate buffer, KHCO_3 0.5 M, pre-electrolysed before use to guarantee high purity. Pre-electrolysis was carried out under Ar in a cell with two-electrodes configuration, with Pt wire as a counter electrode and a Pt mesh as a working electrode for at least 16 h at a current of 0.1 mA while stirring the solution.⁴ A high electrode area was used (GCE geometric surface area = 1 cm^2) in order to have a higher concentration of reaction products and hence guaranteeing the reliability and reproducibility of their concentration measurements. Current values registered during analyses were normalized on the basis of the geometric electrode area and indicated as j_{geom} . The CO₂RR activity was evaluated by chronoamperometry (CA) of 1 hour and 51 minutes in CO₂-saturated electrolytes. The gaseous products were analyzed during measurements by on-line Gas Chromatography (GC) directly connecting the headspace of the electrochemical cell to the sample loop of a GC, while liquid solution was analyzed by Ionic Chromatography (IC) at the end of each electrolysis test. The gas phase quantification was carried out during the electrolysis with sampling every 20 minutes. It should be noticed that on-line FEs quantification for gaseous products might be affected by lack of accuracy ($\pm 4 \%$ maximum) whereas that of liquid products (measured in bulk on the accumulated products all over the electrolysis time) is affected to a lesser extent ($\leq \pm 3\%$). The Faradaic Efficiency (FE) for the gas products of CO₂RR was quantified following the procedure previously described by Baltrusaitis *et al.* (eq.1):⁵

$$FE (\%) = \frac{nF\varphi F_m}{I} \quad (\text{eq. 1})$$

where n is the number of electrons needed for CO₂RR; F is the Faraday constant; φ is the volume fraction of the gas; I is the current and F_m is the molar Ar gas flow rate.

Liquid products were measured by means of a Metrohm model 850 Professional IC Ion Chromatograph with suppression module equipped with a Metrosep a Supp 4-250/4.0 anion column

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and a conductivity detector. The eluent used was 1.7 mM NaHCO₃, 1.8mM Na₂CO₃. The Faradaic Efficiency (FE) for the formic acid products was quantified using eq. 2:

$$FE = \frac{Q(HCOO^-)}{Q_{TOT}} * 100 \quad (\text{eq. 2})$$

For all electrochemical measurements the potentials were reported versus RHE and corrected for ohmic drop. Potential values correction was accomplished according to Nernst equation: $E_{RHE} = E_{Ag/AgCl} + 0.0591 \times \text{pH} + 0.197 \text{ V}$, considering a pH value of 7.20. The potentials were corrected post measurement for the ohmic drop, considering the resistance of system (pH = 7.2).

Table S1. CTF samples as metal-free CO₂RR catalysts at comparison.^a

Entry	Sample name	Monomer/ synthesis conditions	CO ₂ RR product	FE (%) ^b @ (V)	Ref.
1	CTF ^{ph}	1,3-dicyanobenzene/ 10h@400°C+10h@600°C	HCOOH	66 @-0.4V	This work
2	TTF2	1,3-dicyanobenzene/ 40h@600°C	CO	21 @-0.4V	6
3	TTF-1	2,6-dicyanopyridine/ 40h@600°C	CO	47 @-0.4V	
4	Pyridine- linked CTF	2,6-dicyanopyridine/ 40h@400°C	<i>No catalytic activity</i>		
5	CTF	2,6-dicyanopyridine/ 40h@400°C	CO	< 5 @-0.6V	7
6	Por-CTF	4-cyanophenyl porphyrin/ 20h@400°C+20h@600°C	CO	54 @-0.4V	8
7	FN-CTF-400	Tetrafluoroterephthalonitrile/ 20h@400°C	CH₄	79 @-0.4V	9
8	FN-CTF-700	Tetrafluoroterephthalonitrile/ 20h@400°C+2h@700°C	CO	44 @-0.4V	
9	F-CTF-1-275	Tetrafluoroterephthalonitrile/ 24h@275°C	CO	< 5 @-0.4V	10
10	N-C	Terephthalamidine dihydrochloride/ 24h@300°C+48h@350°C	CO	15@-0.4V	11

^a Selection operated among the most representative examples of CTFs as metal-free catalysts reported in the literature so far. ^b FE values refer to those directly claimed in the original paper [at a given potential (V) value] or have been deduced from the respective graphs. For the sake of comparison, FE values have been expressed - whenever possible - at -0.4 V vs. RHE.

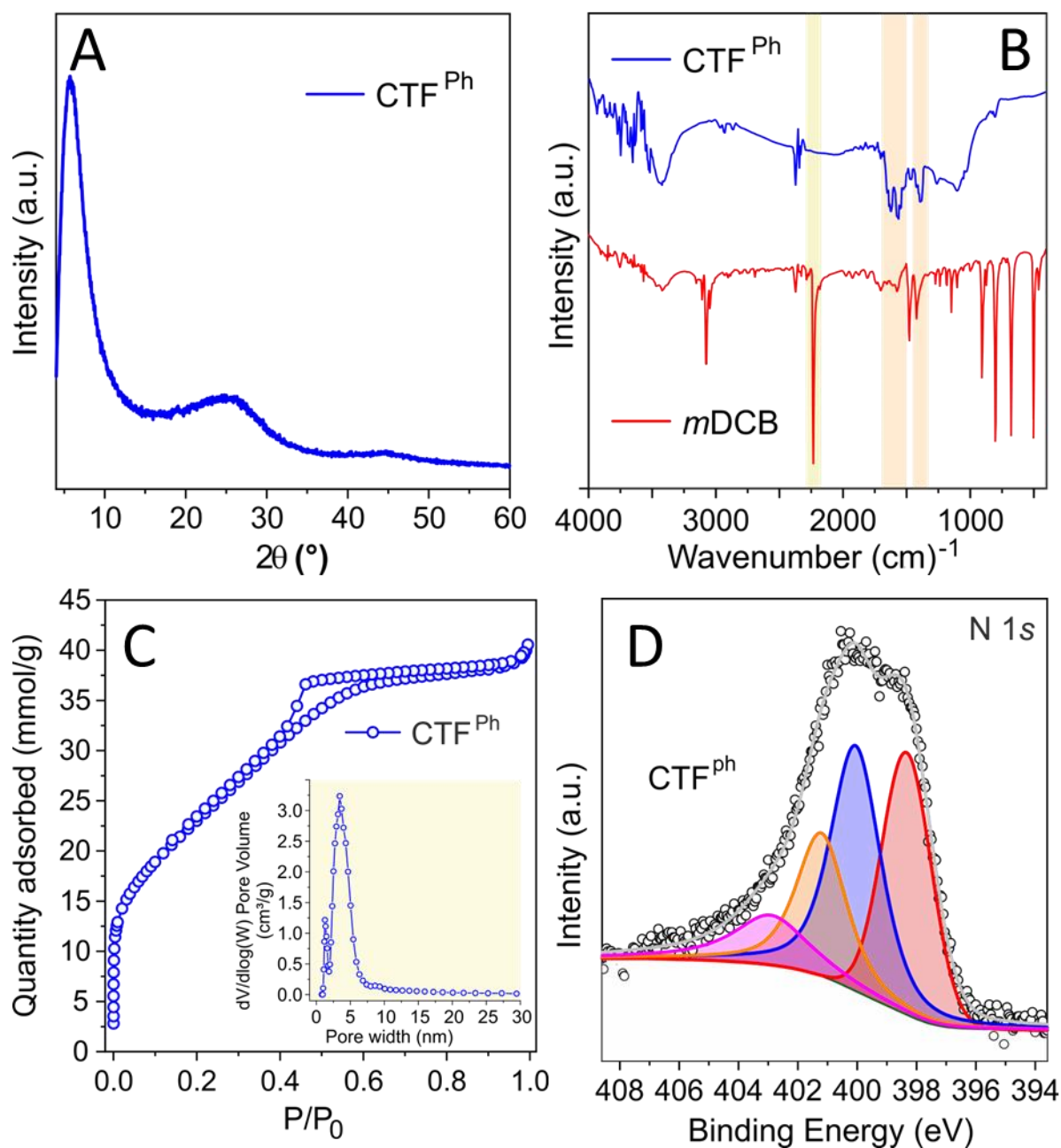


Figure S1. A) PXRD pattern of CTF^{Ph}. B) IR spectra of CTF^{Ph} and 1,3-dicyanobenzene (*m*DCB) at comparison. Light yellow and orange bands highlight the C≡N stretching mode [$\nu(\text{CN}) = 2235 \text{ cm}^{-1}$] and the triazine stretching/bending modes [$\nu(\text{C}=\text{N}) = 1620$ and $\delta(\text{C}=\text{N}) = 1380 \text{ cm}^{-1}$] in *m*DCB and CTF^{Ph}, respectively. C) N₂ adsorption-desorption isotherm of CTF^{Ph} recorded at 77 K along with the sample pore-size distribution (light yellow inset) evaluated through Density Functional Theory (N₂ - DFT Model for slit-like pores). D) high resolution XPS N 1s core level region of CTF^{Ph} along with its relative curve fitting.

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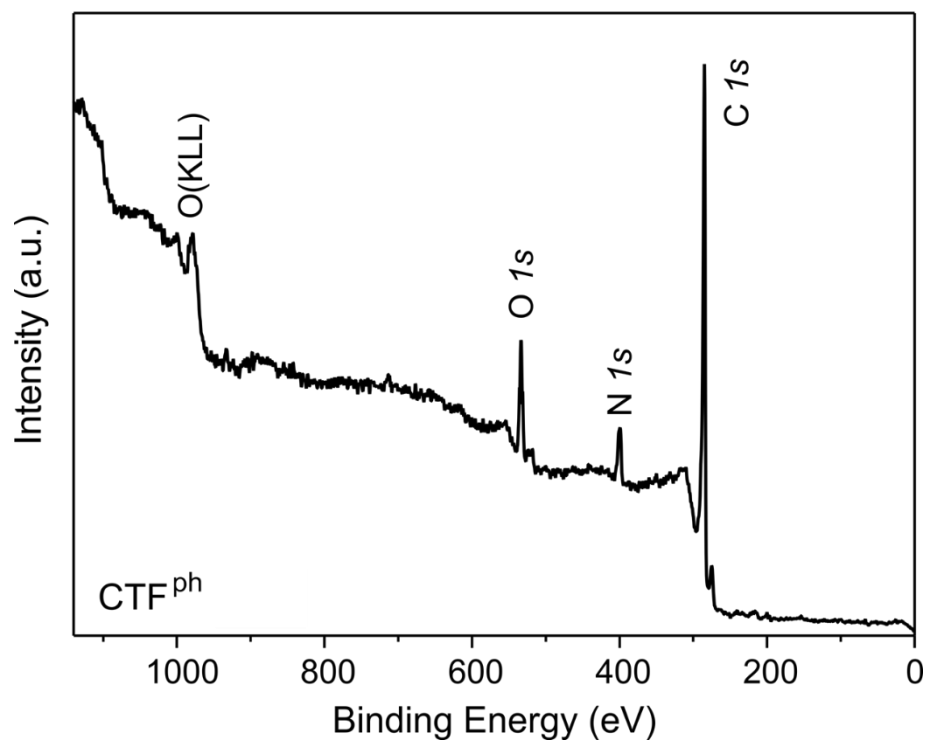


Figure S2. XPS survey spectrum of CTF^{ph}

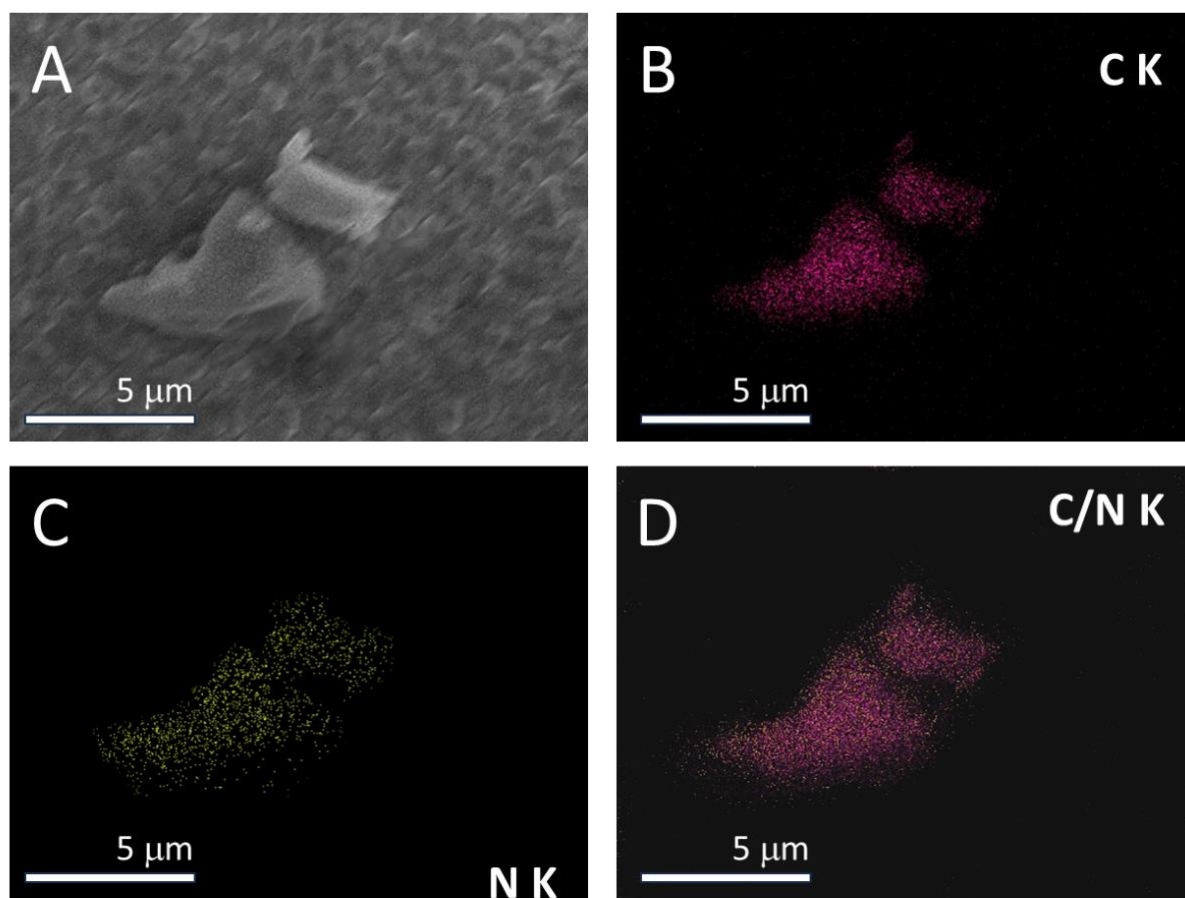


Figure S3. SEM image of CTF^{ph} (A) and EDX analyses (B-D) for the C and N distribution.

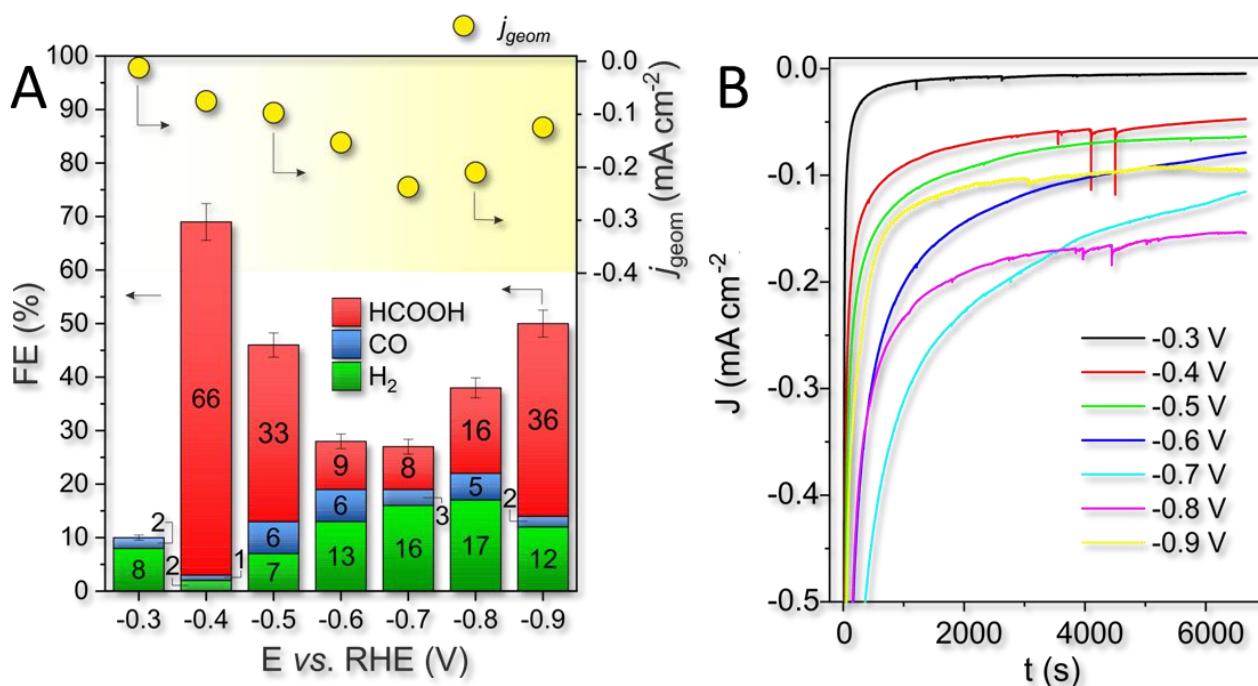


Figure S4. A) Faradaic Efficiency (FE) values registered with CTF^{ph} in the -0.3 ÷ -0.9 V vs. RHE potential range. B) Total current density values measured with CTF^{ph} during electrolysis tests in the -0.3 ÷ -0.9 V vs. RHE potential range.

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