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Supplementary Information for

Bifunctional single-molecular heterojunction enables completely selective CO₂-to-CO conversion integrated with oxidative 3D nano-polymerization

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1. Experimental details

1.1 Chemicals

Multi-walled carbon nanotubes (>98%, Length: 10–20 μ m, Timesnano, China), carbon fabric paper (CFP, Toray, TGP-H-060, 30% waterproof, Shanghai Hesen Electric Co., Ltd, China), SiO₂ (200–300 mesh, Huanghai, China), aluminium oxide (200–300 mesh, neutral, Greagent, China), 1,8-diazabicyclo-(5,4,0)-undec-7-ene (DBU) (99%, Aladdin, China), 4nitrophthalonitrile (98%, Aladdin, China), 3-bromo-2,2-bis(bromomethyl)propanol (>98%, Adamas, China), nickel (II) acetate tetrahydrate (98%, Sinopharm Chemical Reagent, China), Levodopa (99%, Adamas, China), dimethyl sulfoxide-D₆ (Adamas, (D, 99.9%), TMS (0.03%), China), chloroform-D (Adamas, (D, 99.8%), TMS (0.03%), China), Nafion D-520 dispersion (5% w/w in water and 1-propanol, \geq 1.00 meq/g exchange capacity, Alfa Aesar), potassium bicarbonate (99.5%, Sinopharm Chemical Reagent, China). Deionized water was generated by the HHitech purified water system (18.2 MΩ cm).

1.2 Instrumentation

¹H NMR spectra were recorded on an ECZ400S 400 MHz spectrometer. The elemental analytical (EA) data were performed on a vario MICRO elemental analyzer. UV/Vis spectra were recorded on a Lambda 365 spectrophotometer. High-resolution mass spectrometry (HR-MS) data were recorded on an Impact II UHR-TOF and FT-ICR-MS 7T from Bruker. The metal contents of the catalysts were analyzed using ICP-AES on Ultima 2. Powder X-ray diffraction (PXRD) patterns were collected on a desktop X-ray diffractometer (Rigaku-Miniflex 600) at 40 kV voltage and 15 mA current with Cu Ka radiation. Transmission electron microscope (TEM) and high-resolution transmission electron microscope (HRTEM) characterizations were carried out on TALOS F200X G2 field emission transmission electron microscope (ThermoFisher Scientific) at an acceleration voltage of 200 kV. Aberration-corrected high angle annular dark-field scanning transmission electron microscope (AC-HAADF-STEM) was performed with a Titan Cubed Themis G2 300 (FEI) high-resolution transmission electron microscope operated at 200 kV. The X-ray photoelectron spectroscopy (XPS) data were collected on a Thermo Fisher ESCALAB 250Xi spectrometer, using Si 2p (103.4 eV, SiO₂) as the reference line. Fourier-transform infrared (FT-IR) spectra were recorded with KBr pellets using VERTEX70 infrared spectrometer from Bruker. Raman spectra were recorded on a Labram HR800 Renishaw inVia system (Horiba) by using a 532 nm laser. XAFS spectra at the Ni K-edge were measured at the BL14W1 beam line station of the Shanghai Synchrotron Radiation Facility, China. The Ni K-edge XANES data were recorded in a fluorescence mode with Ni foil as a reference. The gas products were determined by the gas chromatograph (Agilent 7820A) equipped with a molecular sieve 5A and HayeSep Q 80/100 mesh with Ar (≥99.999%) flowing as a carrier gas.

1.3 Synthesis

Synthesis of Br_3 - CN_2 : The compound Br_3 - CN_2 was synthesized according to reported literature method with slight modification ^{S1}. 3-Bromo-2,2-bis(Bromomethyl)propanol (3.98 g, 12 mmol) and anhydrous K₂CO₃ (3.77 g, 27 mmol) were stirred in dry DMF (15 mL) at room temperature for 2 h, then 4-nitrophthalonitrile (1.59 g, 9 mmol) was rapidly added and unceasingly stirred for 72 h. Then, the reaction mixture was poured into 50 mL of NH₄Cl saturated deionization water. And the obtained precipitate was collected, dissolved in ethyl acetate and washed with NH₄Cl saturated deionization water for five times. Then the crude product was purified by SiO₂ (200–300 mesh) column chromatography using ethyl acetate/petroleum ether (1/10–1/6) as eluents to give white crystalline solid. Yield: 86.6 %. ¹H NMR (CDCl₃), δ /ppm: 7.78–7.76 (d, 1H, Ar-H), 7.35–7.34 (d, 1H, Ar-H), 7.28–7.25 (m, 1H, Ar-H), 4.17 (s, 2H, -CH₂-), 3.66 (s, 6H, -CH₂-).

Synthesis of $(N_3)_3$ - CN_2 : Br_3 - CN_2 (1.35 g, 3 mmol) and NaN₃ (1.17 g, 18 mmol) were stirred in dry DMF (15 mL) at 80 °C for 24 h ⁵². Then, the reaction mixture was poured into 50 mL of NH₄Cl saturated deionization water. After extracting with ethyl acetate, the obtained organic phase was washed with NH₄Cl saturated deionization water (100 mL) for five times. Then the crude product was purified by SiO₂ (200–300 mesh) column chromatography using ethyl acetate/petroleum ether (1/3) as eluents to give white crystalline solid. Yield: 74.7 %. ¹H NMR (CDCl₃), δ /ppm: 7.77–7.75 (d, 1H, Ar-H), 7.32-

7.31 (d, 1H, Ar-H), 7.25–7.22 (m, 1H, Ar-H), 3.93 (s, 2H, -CH₂-), 3.51 (s, 6H, -CH₂-). HR-MS (ESI): Calcd for C₁₃H₁₁N₁₁NaO ([M + Na]⁺): 360.1040; Found: 360.1042.

Synthesis of N₃NiPc: (N₃)₃-CN₂ (675 mg, 2.0 mmol), nickel (II) acetate tetrahydrate (149 mg, 0.6 mmol) and dried 1pentanol (5 mL) were added and stirred at 110 °C for 30 min under Ar atmosphere. Then 0.9 mL of 1,8-diazabicyclo [4.5.0] undec-7-ene (DBU) was added and stirred at 135 °C for 24 h. After the mixture was cooled to room temperature, the black green product was precipitated and washed with n-hexane for several times. The dried crude product was dissolved in dichloromethane and purified by neutral aluminium oxide column chromatography using CH₂Cl₂/MeOH (v/v=100/1) as eluents to give a dark violet solid. Yield: 24.7 %. IR (KBr, u_{max} , cm⁻¹): 2928, 2870, 2102 (–N₃), 1610, 1532, 1484, 1462, 1417, 1386, 1350, 1280, 1238, 1123, 1093, 1066, 814, 749. Elem. Anal. Calcd for C₅₂H₄₄N₄₄O₄Ni: C, 44.36; H, 3.15; N, 43.77; Found: C, 44.77; H, 3.06; N, 43.45. HRMS (MALDI): Calcd for C₅₂H₄₄N₄₄NiO₄ ([M]⁺): 1406.3946; Found: 1406.3929. UV-Vis (THF, λ_{max} , nm): 328, 380, 604, 671.

Synthesis of **MeNiPc**: The synthesis was performed following the same procedures as Ref. S3. Yield: 30.1 %. IR (KBr, ν_{max} , cm⁻¹): 2997, 2930, 2831, 1610, 1527, 1485, 1412, 1332, 1278, 1242, 1125, 1093, 1066, 817, 751. UV-Vis (THF, λ_{max} , nm): 328, 605, 671.

1.4 Preparation

Pretreatment of **CNT**: 1.0 g of commercial CNT was stirred in 5 M HNO₃ solutions at 80 °C for overnight, and then the acid-treated CNT was collected and rinsed with deionized water for many times and dried in an oven at 100 °C for overnight. The acid-treated CNT (0.6 g) and ascorbic acid (6.0 g) were stirred in 50 mL deionization water at 60 °C for overnight. Then the CNT was collected and rinsed with deionized water for many times and dried in an oven at 100 °C for overnight.

Preparation of N_3NiPc -*CNT*: 50 mg of **CNT** was dispersed in 90 mL THF by ultrasound for 30 min, and then 10 mL THF solution of N_3NiPc (0.6 mg mL⁻¹) was gradually added. After stirring for 1 h, the mixture was heated to reflux for 24 h ^{S4}. Then the catalyst was collected by hydrophobic membrane, rinsed with THF several times and dried in an oven at 60 °C for overnight.

Preparation of **MeNiPc/CNT**: For comparison, **MeNiPc/CNT** sample with the same molar loading to that of **N**₃**NiPc-CNT** was prepared following the same procedures.

Preparation of working electrodes: To prepare catalyst ink, 5 mg of catalyst powder was dispersed in 0.5 mL of mixture solution with 350 μ L of deionized water, 100 μ L of DMF and 50 μ L of Nafion D-520 solution, and then the mixture was ultrasonicated for 60 min to generate a homogeneous ink. Then, this ink was drop-casted onto a CFP with a loading mass of 0.3 mg cm⁻² (Area: 1.0 × 1.0 cm²) and air-dried overnight.

In addition, 5 mg of N_3 NiPc was dissolved in 0.5 mL of mixture solution with 450 µL of DMF and 50 µL of Nafion D-520 solution, Then, this solution was drop-casted onto a CFP with a loading mass of 0.3 mg cm⁻² (Area: 1.0 × 1.0 cm²) and air-dried overnight.

1.5 Electrochemical measurements

All the electrochemical measurements were performed with a CHI760E electrochemical workstation (Shanghai Chen-Hua Instrument Corporation, China) at 25 °C in 0.5 M KHCO₃ (pH = 7.2) electrolyte with an airtight electrochemical H-type cell (Gaossunion), two compartments (50 mL) with 30 mL of electrolyte on each side were separated by an exchange membrane (Nafion^{*}117). Before testing, the Nafion membrane was treated in 5% H₂O₂ solution, pure water, 1 M H₂SO₄ solution and pure water for 1 h, respectively. A CFP supported catalyst, saturated Ag/AgCl electrode and Pt net were served as the working electrode, reference electrode and counter electrode, respectively.

Before the CO_2 reduction experiments, the electrolyte (0.5 M KHCO₃) was saturated by bubbling pure CO_2 (99.999%) at a flow rate of 20.0 mL min⁻¹ (using Mass flow controller D07-7B) for 30 min. The gas products was continuously conveyed into the gas-sampling loop (250 µL) of a gas chromatograph (GC, Agilent 7820A) for analyzing the gas products using thermal conductivity detector (TCD) and flame ionization detector (FID). The GC calibration curves for H₂ and CO were fitted by five times independent single point sampling (1.020% H₂, 0.982% CO, 0.982% CH₄, Ar balance, Linde Gases, China), respectively. Liquid products were analyzed by quantitative NMR using dimethyl sulphoxide (DMSO) as an internal standard after CO₂ reduction electrolysis for 2800 s (500 µL electrolyte was mixed with 100 µL D₂O containing 0.1 µL DMSO). Solvent presaturation technique was implemented to suppress the water peak. The working electrodes were cycled 40 times with a scan rate of 0.1 V s⁻¹ over the potential range (-0.18 V to -0.98 V vs. RHE) by cyclic voltammetry (CV) before other measurements. The electrolyte was stirred with magnetic stir bar (Length: 2.0 cm) at a speed of 1000 rpm. The linear sweep voltammetry (LSV) polarization curves were tested at a scan rate of 5.0 mV s⁻¹. Tafel plots were obtained from the extrapolation of the linear region of a plot of overpotential versus current density. Every CFP work electrode were performed I-t curve measurements from -0.53 to -0.93 V vs. RHE, intermittently running it for 2800 s each time. The electrochemical impedance spectroscopy (EIS) at potential -0.58 V vs. RHE from 100 KHz to 0.1 Hz with an amplitude of 5.0 mV. To estimate the ECSA, cyclic voltammograms (CV) were tested by measuring double-layer capacitance (C_{dl}) under the potential window of -0.50 to -0.60 V vs. Ag/AgCl at various scan rates from 20 to 100 mV s⁻¹. Potential was measured vs. Ag/AgCl electrode and the results were reported vs. reversible hydrogen electrode based on the Nernst equation: E (vs. RHE) = E (vs. Ag/AgCl) + 0.1989 V + 0.059 × pH. Each measurement was repeated three times in order to avoid any incidental error. All potentials were without *iR* corrected if without annotation.

Flow cell: Flow cell measurements for ECR were worked on a flow cell reactor with a bipolar membrane in 1.0 M KOH. N₃NiPc-CNT with a loading mass of 0.4 mg cm⁻² (Area: 1.0×1.0 cm²) and commercial RuO₂ with a loading mass of 1.0 mg cm⁻² (Area: 2.0×2.0 cm²) loaded gas diffusion electrodes and saturated Ag/AgCl electrode were used as cathode, anode and reference electrodes, respectively. During the measurements, the electrolyte was circulated through peristaltic pump with a rate of 7.0 mL min⁻¹, and CO₂ gas with a flow rate of 40.0 mL min⁻¹ was directly fed to the cathode.

1.6 Calculation of Faradaic efficiency and TOF

Faradaic efficiency was calculated as following ^{S5}:

$$FE_{x}(\%) = \frac{J_{x}}{J_{total}} = \frac{V_{x} \times N \times F}{J_{total}}$$

 FE_x : Faradaic efficiency for *x* production, *F*: Faradaic constant 96485 C mol⁻¹, V_x : The production rate of *x*, *N*: The number of electrons transferred for production formation, J_{total} : The recorded total current density, J_x : Partial current density for *x* production, *x*: CO or H₂.

The TOF for CO generation was calculated as following (Elapsed time for 1 h) ⁵⁵:

$$TOF = \frac{\frac{I_{CO} \times 3600}{N \times F}}{\frac{m_{cat} \times w\%}{M_{Ni}}}$$

 m_{cot} : Catalyst mass in the carbon paper (g), w%: Ni weight ratio loading in the catalyst (ICP results), M_{Ni} : Atomic mass of Ni (58.69 g mol⁻¹), I_{co} : Partial CO current, N: The number of electrons transferred for CO formation, F: Faradaic constant 96485 C mol⁻¹.

1.7 In situ ATR-IR

The *in situ* attenuated total reflection-infrared (*in situ* ATR-IR) measurements were performed on a Nicolet 6700 spectrometers (Thermo Fisher) with a reflection window integrated three-electrode cells at 25 °C in 0.5 M KHCO₃. A home-made carbon cloth electrode (8.00 mm in diameter), saturated Ag/AgCl electrode and Pt wires were served as the working electrode, reference electrode and counter electrode, respectively. The N₃NiPc-CNT ink were drop-casted onto a home-made carbon cloth electrode with a loading mass of 0.5 mg cm⁻² and air-dried overnight.

1.8 ECR integrated with oxidative nano-polymerization

The three working electrodes for anode were prepared as following:

 $N_3NiPc-CNT$ electrode: a CFP with a loading mass of 1.0 mg cm⁻² (1×1 cm²) $N_3NiPc-CNT$.

 RuO_2 electrode: a CFP with a loading mass of 1.0 mg cm^-2 (1×1 cm²) $RuO_2.$

Pt electrode: Pt net (1×1 cm²).

The 30 mL of electrolyte (0.5 M KHCO₃) with 1 mmol L-DOPA in anodic compartment and 30 mL of electrolyte (0.5 M KHCO₃) in cathodic compartment was used to the two-electrode system under a certain atmosphere. After electrolysis for 60 min with a speed of 1000 rpm, the polymer nanomaterials in anodic compartment were collected by centrifugation, wash and re-dispersion for further measurement. The scan rate of LSV curves was 10 mV s⁻¹, the potentials were not corrected by the *iR* compensation.

2. Supplementary figures



Fig. S1 1 H NMR spectrum of Br₃-CN₂ (400 MHz, CDCl₃).



Fig. S2 ¹H NMR spectrum of (N₃)₃-CN₂ (400 MHz, CDCl₃).



Fig. S3 HR-MS of $(N_3)_3$ -CN₂.



Fig. S4 HR-MS of N₃NiPc.



Fig. S5 UV/Vis absorption spectra of N_3NiPc and MeNiPc in THF ($C=1\times10^{-5}$ mol L⁻¹). N_3NiPc shows a strong Q-band absorption at 671 nm, which corresponds to the non-aggregated status of the N_3NiPc molecules. On the contrary, MeNiPc not only exhibits the very weak Q-band absorption, but also presents the obvious absorption of molecular aggregation at 605 nm. This result suggests that the introduction of functional azido groups onto phthalocyanine ring exerts a significant impact to regulate the existence form of Pc molecules in solution.



Fig. S6 UV-Vis spectra of (a) N_3NiPc in THF (0.05 mg mL⁻¹) and (b) filtrate after immobilizing N_3NiPc to CNT. This result suggests that N_3NiPc was completely immobilized onto CNT.

Nitrenes [2+1] cycloaddition reaction



Fig. S7 Schematic illustration for the possible covalent binding of $N_{\rm 3}NiPc$ onto CNT.



Fig. S8 LSVs in CO₂-saturated 0.5 M KHCO₃ solution at a scan rate of 5 mV s⁻¹ over N₃NiPc, CNT and N₃NiPc-CNT.



Fig. S9 LSVs in Ar or CO_2 -saturated 0.5 M KHCO₃ solution at a scan rate of 5 mV s⁻¹ over N₃NiPc-CNT.



Fig. S10 ¹H NMR of the possible liquid products over N_3NiPc -CNT at different potentials for CO_2 reduction. The signals in Fig. S10 elucidate the absence of liquid products during ECR.



Fig. S11 (a) FE and H₂/CO volume ratios, and (b) total current densities at different potentials in 2800-s electrolysis over CNT.



Fig. S12 (a) FE and H_2/CO volume ratios, and (b) total current densities at different potentials in 2800-s electrolysis over N_3 NiPc.



Fig. S13 Total current densities at different potentials over $N_3 NiPc\mbox{-}CNT$ in a flow cell.



Fig. S14 Raman spectra of MeNiPc/CNT, CNT and MeNiPc.



Fig. S15 (a) FE, CO/H₂ volume ratios and (b) total current densities at different potentials in 2800-s electrolysis over MeNiPc/CNT.



Fig. S16 Immobilization effect of N_3NiPc -CNT and MeNiPc/CNT for ECR: (a) LSVs in CO_2 -saturated 0.5 M KHCO₃ solution at a scan rate of 5 mV s⁻¹ over different catalysts, (b) Tafel plots, (c) Nyquist plots over the frequency ranging from 100 kHz to 0.1 Hz at -0.58 V vs. RHE.



Fig. S17 CVs of (a) N₃NiPc-CNT and (b) MeNiPc/CNT at different scan rates, (c) the corresponding capacitive current at 0.073 V vs. RHE as a function of scan rate.



Fig. S18 Durability test of MeNiPc/CNT at the potential of -0.68 V vs. RHE for 10 h.



Fig. S19 Schematic illustration of N $_3$ NiPc-CNT and MeNiPc/CNT.



Fig. S20 PXRD patterns of N_3NiPc -CNT before and after ECR test.



Fig. S21 Raman spectra of N₃NiPc-CNT before and after ECR test.



Fig. S22 TEM image of N₃NiPc-CNT after ECR test.



Fig. S23 Schematic illustration of in situ ATR-IR measurements.



Fig. S24 Proposed ECR pathway over N_3NiPc -CNT.



Fig. S25 SEM of poly-L-DOPA obtained from anode chamber.

3. Supplementary tables

Sample	Theoretical contents of metal	Experimental contents of metal (ICP) Ni: 0.43 wt% Ni: 0.44 wt%	
N ₃ NiPc-CNT	Ni: 0.45 wt%		
MeNiPc/CNT	Ni: 0.46 wt%		

Table S1 Contents of metal in the samples determined by ICP.

Table S2 Contents of nitrogen in N₃NiPc-CNT determined by EA.

Sample	Theoretical N content	Experimental N content (EA) ^b		
N ₃ NiPc-CNT	N: 4.26 wt% ^a	N: 4.26 ± 0.05 wt%		
CNT	N: 0.00 wt%	N: <0.3 wt%		

^a The value is based on the assumption that two tertiary amine groups are generated in each N₃NiPc molecule for linking to CNT, calculated as following:

$$N (\%) = \frac{\frac{m_{pc}}{M_{pc}} \times M_N \times N}{m_{cat.}}$$
$$= \frac{\frac{6 mg}{1407.9 \ g \ mol^{-1}} \times 14 \ g \ mol^{-1} \times (44 - 4)}{56 \ mg}$$

= 0.0426

^b Experimental contents of nitrogen were tested twice by EA.

Catalysts	Cathode material	Electrolyte (pH)	FE (CO)	Potential (V vs. RHE)	TOF (h ⁻¹)	References
N₃NiPc-CNT	CFP ^a	0.5 M KHCO₃ (7.2)	100%	-0.58	2742	This work
N₃NiPc-CNT	CFP	0.5 M KHCO ₃ (7.2)	100%	-0.93	32338	This work
FeO _x /e-NiPc/G	Carbon paper	0.5 M KHCO ₃ (7.2)	86%	-0.40	~	S6
CoPc-CN/CNT (3.5%)	CFP	0.5 M KHCO₃ (7.2)	88%	-0.46 ^b	5040	S7
PyNiPc/CNT	CFP	0.5 M KHCO₃ (7.2)	100%	-0.93	12832	S8
CoPc©Fe-N-C	GDE °	0.5 M KOH (13.7)	>90%	–0.13 to –0.84 V	~	S9
CoFPc	Carbon cloth	0.5 M NaHCO ₃ (7.2)	93%	-0.80	5760	S10
CoPPc/CNT	Carbon paper	0.5 M NaHCO ₃ (7.4)	~90%	-0.61 ^b	4900	S11
CoTPP/CNT	Glassy carbon	0.5 M KHCO ₃ (7.2)	91%	-0.66	9900	S12
CoPP@CNT	Carbon paper	0.5 M NaHCO ₃ (7.2)	98%	-0.60	4932	S13
CCG/CoPc-A	CFP	0.1 M KHCO₃ (6.8)	77%	-0.59	~18000	S14
Ni-CNT-CC	Glassy carbon	0.5 M KHCO₃ (7.3)	99%	-0.71 ^b	100179	S15
Co(II)CPY/CNT	Carbon paper	0.1 M KHCO₃ (6.8)	96%	-0.70	34524	S16
CoPc-py-CNT	Carbon paper	0.2 M NaHCO ₃ (7.0)	98%	-0.63	124200	S17
Re(tBu-bpy)/MWCNT	Glassy carbon	0.5 M KHCO₃ (7.3)	99%	-0.56	5760	S18
Co-salophen	CFP	0.5 M KHCO ₃ (7.2)	75%	-0.70	~	S19
FePGH-H	Reticulated vitreous carbon	0.1 M KHCO ₃ (6.8)	96.2%	-0.39	2880	S20
NapCo@SNG	CFP	0.1 M KHCO₃ (6.8)	97%	-0.80	~	S21
CoPc2	Carbon paper	0.5 M NaHCO ₃ (7.3)	93%	-0.676	24516	S22
Co-PMOF	Carbon cloth	0.5 M KHCO₃ (7.2)	99%	-0.80	1656	S23
CoCp ₂ @MOF-545-Co	Carbon paper	0.5 M KHCO ₃ (7.2)	97%	-0.70	777 ^d	S24
MOF-1992/CB	Glassy carbon	0.1 M KHCO ₃ (6.8)	80%	-0.63	720	S25
CoPc-PDQ-COF	CFP	0.5 M KHCO ₃ (7.2)	96%	-0.66	11412	S26
PcCu-O ₈ -Zn	Carbon paper	0.1 M KHCO ₃ (6.8)	88%	-0.70	1404	S27
Co-TTCOF	Carbon cloth	0.5 M KHCO ₃ (7.2)	91.3%	-0.70	4608	S28
Co-TTCOF NSs	Carbon cloth	0.5 M KHCO ₃ (7.2)	99.7%	-0.80	~	S28
TTF-Por(Co)-COF	CFP	0.5 M KHCO₃(7.6)	95%	-0.70	676 ^d	S29
HNTM-Au-SA	GDE	0.1 M KHCO₃ (6.8)	95.2%	-0.80	~36000 ^d	\$30
STPyP-Co	Carbon paper	0.5 M KHCO₃ (7.2)	96%	-0.61	15156	S31
NNU-15	Carbon paper	0.5 M KHCO₃ (7.2)	99.2%	-0.60	~	\$32

Table S3 The ECR performances of the molecule-based catalysts from recent literatures.

^a Carbon fabric paper, ^b the potential was iR corrected, ^cgas diffusion electrode, ^d at -0.9 V vs. RHE.

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