Supporting Information

Trojan horse thiocyanate: induction and control of high proton conductivity in CPO-27/MOF-74 metal-organic frameworks by metal selection and solvent-free mechanochemical dosing

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Synthetic procedures and control experiments

All chemicals and solvents (of analytical grade) were purchased from commercial sources (Merck, TCI, Avantor, Polmos) and were used without further purification. Ethanol (Polmos) contained water (8% by volume).

Synthesis of CPO-27(Zn)
CPO-27(Zn) was synthesized according to a method described in literature.\(^1\) H\(_4\)DOBDC (0.25 g, 1.3 mmol) and Zn(NO\(_3\))\(_2\)·4H\(_2\)O (1.0 g, 3.8 mmol) were dissolved in 50 mL of DMF with stirring, followed by the addition of 2.5 mL of deionized water. The mixture was heated in an oven at 100°C for 20 hours yielding the yellow microcrystalline, porous material, CPO-27(Zn).

Synthesis of CPO-27(Mg)
CPO-27(Mg) was synthesized according to a method described in literature.\(^2\) To a solid mixture of H\(_4\)DOBDC (0.111 g, 0.559 mmol) and Mg(NO\(_3\))\(_2\)·6H\(_2\)O (0.475 g, 1.85 mmol) was added a 15:1:1 (v/v/v) mixture of DMF–ethanol–water (50 mL) in a 100 mL screw cap jar. The suspension was mixed and ultrasonicated until homogeneous and placed in an oven at 100°C. After 20 hours, the samples were removed from the oven and allowed to cool to RT. The mother liquor was decanted from the yellow microcrystalline material and replaced with methanol. The methanol was decanted and replenished four times over two days, yielding the dark yellow microcrystalline, porous material.

Synthesis of CPO-27(Ni)
CPO-27(Ni) was synthesized according to a method described in literature.\(^2\) To a solid mixture of H\(_4\)DOBDC (0.0956 g, 0.48 mmol) and Ni(NO\(_3\))\(_2\)·6H\(_2\)O (0.4756 g, 1.64 mmol) was added a 1:1:1 (v/v/v) mixture of DMF–ethanol–water (40 mL) in a 100 mL screw cap jar. The suspension was mixed and ultrasonicated until homogeneous and placed in an oven at 100°C. After 20 hours, the samples were removed from the oven and allowed to cool to RT. The mother liquor was decanted from the yellow microcrystalline material and replaced with methanol. The methanol was decanted and replenished four times over two days, yielding the yellow-brown microcrystalline, porous material.

Synthesis of CPO-27(Co)
CPO-27(Co) was synthesized according to a method described in literature.\(^2\) To a solid mixture of H\(_4\)DOBDC (0.0964 g, 0.47 mmol) and Co(NO\(_3\))\(_2\)·6H\(_2\)O (0.4754 g, 1.73 mmol) was added a 1:1:1 (v/v/v) mixture of DMF–ethanol–water (40 mL) in a 100 mL screw cap jar. The suspension was mixed and ultrasonicated until homogeneous and placed in an oven at 100°C. After 20 hours, the samples were removed from the oven and allowed to cool to RT. The mother liquor was decanted from the dark red-purple microcrystalline material and replaced with methanol. The methanol was decanted and replenished four times over two days, yielding the dark red-purple microcrystalline, porous material.

Synthesis of CPO-27(Zn)-NCS - \{(NH\(_4\))\(_3\)\_3[Zn\(_6\)(dobdc)\(_3\)(NCS)\(_3\)(dmf)(H\(_2\)O)\(_2\)]\_xH\(_2\)O\}
CPO-27(Zn) (100.0 mg, 0.197 mmol) and NH\(_4\)SCN (15.0 mg, 0.197 mmol) were ground in an agate mortar in air at room temperature for approx. 10 min. with addition of 57.5 μL 92%
EtOH (LAG, liquid-assisted grinding; 6:3 metal/thiocyanate ratio). Elem. anal.: Calc. for C_{30}H_{43}Zn_6N_7O_{28}S_6 \{([NH_4]_3[Zn_6(dobdc)_3(NCS)_3(H_2O)]_2 \cdot 7H_2O)\}: C 24.75, H 3.46, N 6.87, S 6.29%. Found: C 24.20, H 3.08, N 6.23, S 6.06%. IR (ATR, cm\(^{-1}\)): v(COO\(_2\)) 1548vs, v(CN) 1575vs, v(CO) 1521m. To synthesize CPO-27(Zn)-NCS at lower stoichiometric ratios (6:1 and 6:2), the amounts of NH\(_4\)SCN were reduced to 5 mg and 10 mg, and the amount of EtOH used was 53.2 \(\mu\)L and 55 \(\mu\)L, respectively.

Synthesis of CPO-27(Mg)-NCS - \{([NH_4]_3[Mg_6(dobdc)_3(NCS)_3(H_2O)]_2 \cdot xH_2O\}

CPO-27(Mg) (100.0 mg, 0.292 mmol) and NH\(_4\)SCN (22.2 mg, 0.292 mmol) were ground in an agate mortar in air at room temperature for approx. 10 min. with addition 61.1 \(\mu\)L 92% EtOH (LAG, liquid-assisted grinding; 6:3 metal/thiocyanate ratio). Elem. anal.: Calc. for C_{27}H_{34}Mg_6N_6O_{26}S_3 \{([NH_4]_3[Mg_6(dobdc)_3(NCS)_3(H_2O)]_2 \cdot 5H_2O)\}: C 29.46, H 3.11, N 7.64, S 8.74%. Found: C 28.52, H 3.84, N 8.68, S 8.60%. IR (ATR, cm\(^{-1}\)): v(COO\(_2\)) 1575vs, v(CO\(_2\)) 1417s, v(CN) 2078vs, v(NH\(_{ammonium}\)) 3221m. To synthesize CPO-27(Mg)-NCS at lower stoichiometric ratios (6:1 and 6:2), the amounts of NH\(_4\)SCN were reduced to 7.4 mg and 14.8 mg, and the amount of EtOH used was 53.7 \(\mu\)L and 57.4 \(\mu\)L, respectively.

Synthesis of CPO-27(Ni)-NCS - \{([NH_4]_3[Ni_6(dobdc)_3(NCS)_3(H_2O)]_2 \cdot xH_2O\}

CPO-27(Ni) (100.0 mg, 0.254 mmol) and NH\(_4\)SCN (19.2 mg, 0.254 mmol) were ground in an agate mortar in air at room temperature for approx. 10 min. with addition 59.6 \(\mu\)L 92% EtOH (LAG, liquid-assisted grinding; 6:3 metal/thiocyanate ratio). Elem. anal.: Calc. for C_{27}H_{42}Ni_6N_6O_{30}S_3 \{([NH_4]_3[Ni_6(dobdc)_3(NCS)_3(H_2O)]_2 \cdot 9H_2O)\}: C 23.52, H 3.07, N 6.09, S 6.98%. Found: C 23.21, H 3.18, N 7.09, S 6.98%. IR (ATR, cm\(^{-1}\)): v(COO\(_2\)) 1548vs, v(CO\(_2\)) 1404s, v(CN) 2101vs, v(NH\(_{ammonium}\)) 3206m. To synthesize CPO-27(Ni)-NCS at lower stoichiometric ratios (6:1 and 6:2), the amounts of NH\(_4\)SCN were reduced to 6.4 mg and 12.8 mg, and the amount of EtOH used was 53.2 \(\mu\)L and 56.4 \(\mu\)L 92%, respectively.

Control experiments to test the possibility of formation of CPO-27-NCS in solution

Several trials described below have been carried out with various solvents. In all experiments CPO-27 (100 mg) and NH\(_4\)SCN (at 1:10 CPO-27 to NH\(_4\)SCN ratio) were mixed in a solvent (10.0 mL) and left for approx. 72h at room temperature.

1) CPO-27(Mg); NH\(_4\)SCN (74 mg); ethanol or methanol
2) CPO-27(Ni); NH\(_4\)SCN (64 mg); ethanol or methanol
3) CPO-27(Zn); NH\(_4\)SCN (50 mg); ethanol or dimethylformamide

Analogous trials were also performed for saturated alcohol solutions of NH\(_4\)SCN. All solid samples have been screened with IR (Figures S6 and S7 below). Quantitative formation of CPO-27(Mg, Zn, Ni)-NCS was not formed.

Reversibility of CPO-27-NCS formation

In all experiments CPO-27-NCS (50 mg) were immersed in methanol (5.0 mL) for approx. 5 days at 60°C. During this time methanol was changed 4 times a day.

All solid samples have been screened with IR and PXRD (Figure S8 below). In all the trials CPO-27(Mg, Zn, Ni) were recovered.

Analogous trials carried out in methanol at approx. 25°C did not lead to removal of coordinated thiocyanate after 7 days.
Samples preparation for EIS measurements

Prior to a series of EIS measurements at a given relative humidity (RH), approx. 30 mg of the material was equilibrated in a humidity chamber for 1 day at a specified RH (90 or 75 or 60 or 45 or 30%) at 25°C.

Details of physical measurements

Carbon, hydrogen and nitrogen were determined using an Elementar Vario MICRO Cube elemental analyzer.

Thermogravimetric analyses (TGA) were performed on a Mettler-Toledo TGA/SDTA 851° instrument with a heating rate of 10°C min⁻¹ in a temperature range of 25 – 600°C (approx. sample weight of 10 mg). The measurements were performed at atmospheric pressure under argon flow.

FTIR spectra were recorded on a Thermo Scientific Nicolet iS10 FT-IR spectrophotometer equipped with an iD7 diamond ATR attachment.

Powder X-ray diffraction (PXRD) patterns were recorded at room temperature (295 K) on a Rigaku Miniflex 600 diffractometer with Cu-Kα radiation (λ = 1.5418 Å) in a 2θ range from 3° to 45° with a 0.02° step and 3° min⁻¹ scan speed. Additional measurement was carried out for CPO-27(Mg)-NCS on a Panalytical X-Pert Pro equipped with a sealed LFF Cu X-ray source operating at 40kV and 30 mA, a focusing mirror, a capillary sample holder and a PIXCEL detector.

Electrochemical Impedance Spectroscopy (EIS) measurements were performed using Hioki IM3570 impedance analyzer on pre-conditioned samples (see Samples preparation above) pressed between two metallic electrodes (5.0 mm diameter) in a PTFE tube, and kept in KK 115 TOP+ or Memmert HCP 246 climatic chamber with ultrasonic humidifier and temperature control. The measurements were carried out in a quasi-four-probe setup in a frequency range from 4 Hz to 5MHz, alternating potential of 200 mV and temperature range from 25 to 60 °C (for 30-90% RH), and with pre-measurement sample conditioning for 1 h at each temperature. The proton conductivity (σ, S cm⁻¹) of the sample was estimated by using the equation:

\[ \sigma = \frac{L}{RA} \]

where L (cm) is the sample thickness and A (cm²) is the cross-sectional area of the measured pellet; R (Ω) is the resistance as the real part of the measured impedance.

Adsorption isotherms were measured using static volumetric Autosorb IQ apparatus (Quantachrome Instruments) at 77 K for nitrogen and 298 K for water. All samples were activated under vacuum for 8 h at 100°C (2°C/min).

Computational details

All the quantum-chemical calculations of energies, geometries, and vibrational analyses were performed by using of DMol3 code at the periodic DFT level of theory, the RPBE correlation-exchange functional. This functional was chosen since it provides a better description of the hydrogen bonds than PBE or revPBE. The orbitals were expanded in the
basis set of DND quality. The basis set spatial cutoff distance of 4.2 Å was set and, as a convergence accelerator, the Gaussian smearing with the window width of $5 \cdot 10^{-3} \text{ Ha}$ was used. The SCF convergence criterion was set to $1 \cdot 10^{-6} \text{ Ha}$, whereas for geometry optimisation – to the threshold value of $2 \cdot 10^{-5} \text{ Ha}$ change between two successive iterations, the gradient norm lower than $3 \cdot 10^{-3} \text{ Ha/Å}$, and the maximal atom displacement lower than $4 \cdot 10^{-3} \text{ Å}$.

Rietveld refinement procedure

The X-ray diffraction of the CPO-27(Mg)-NCS sample has been performed in a long collection time capillary experiment and a trial has been undertaken to determine the crystal structure of CPO-27(Mg)-NCS through the application of Rietveld refinement using the published structure as the starting model (CSD code: MOHGOI). Given the space group (R-3) of the initial CPO-27(Mg) structure, the insertion of NCS$^-$ and NH$_4^+$ ions results in their six-fold replication. We have tried to refine this model with 50% site occupancies which led us to problematic electron density from NH$_4^+$ ions which caused them to drift towards the centre of the main [001] channel (resulting distances between nitrogen atoms were not physical). At the same time, the NCS$^-$ ions were clearly visible in the Fourier maps in the proper locations consistent with the theoretical calculations. We have also tried lowering the symmetry of the loaded structure to R3 to overcome the problem introduced by the six-fold replication inside the channel (the XRD patterns are undistinguishable for R-3 and R3 apart from the intensity statistics that cannot be reliably performed for powder data) but it did not lead to a significant improvement. Most likely our data (laboratory X-ray source) are of insufficient quality to unambiguously locate the positions of NH$_4^+$ and SCN$^-$ ions. Also, there is a significant possibility of disorder in terms of their positions since there is no difference between the Mg sites that would make some of them preferential over the others. It is noteworthy that in the original work reporting MOHGOI structure$^6$ the authors used synchrotron radiation which provided powder X-ray diffraction data with excellent signal-to-noise ratios and allowed crystallographic studies with high level of detail, even including the localization of the adsorbed CO$_2$ molecules.
Figures and Tables

Figure S1. IR spectra (left): CPO-27 as-synthesized (black) and CPO-27(M)-NCS (CPO-27 after LAG with NH₄SCN at 6:3 molar ratio (red). PXRD patterns (right): CPO-27 calculated from SC-XRD data (green), the as-synthesized bulk material (black), and CPO-27(M)-NCS (red).
Figure S2. IR spectra (left) and PXRD patterns (right) of mixtures after grinding CPO-27 with various amounts of NH$_4$SCN; 6:1, 6:2, 6:3, 6:4, 6:6 (given as CPO-27 to NH$_4$SCN ratio). Characteristic reflections of NH$_4$SCN are labeled with ‘*’.
Figure S3. IR spectra of mixtures after grinding CPO-27 with various amounts of NH$_4$SCN; 6:1, 6:2, 6:3, 6:4, 6:6 (given as the CPO-27 to NH$_4$SCN ratio) showing $\nu$(CN) range.

Figure S4. N$_2$ adsorption measurement at 77 K for CPO-27-NCS, closed symbols: adsorption, open symbols: desorption.
Figure S5. Ar adsorption measurement at 87 K for CPO-27(Mg)-NCS. closed symbols: adsorption, open symbols: desorption.

Figure S6. IR spectra of the as-synthesized CPO-27 immersed in solvents (ethanol, methanol and dimethylformamide) containing dissolved NH$_4$SCN. The IR spectra of CPO-27-NCS are given for comparison.
Figure S7. IR spectra (left) and PXRD patterns (right) of the as-synthesized CPO-27 immersed in saturated solutions of NH₄SCN in ethanol. The IR spectra and PXRD patterns of CPO-27-NCS are given for comparison. PXRD patterns: CPO-27 calculated from SC-XRD data (green), CPO-27-NCS calculated from DFT+D optimized structures (black).
Figure S8. Reversibility of CPO-27-NCS formation: IR spectra (left) and PXRD patterns (right): CPO-27 as-synthesized (black), CPO-27-NCS (red) and CPO-27-NCS immersed in methanol at 60°C for 5 days - CPO-27-NCS MeOH (green).
Figure S9. TG (black) and dTG (red) curves for CPO-27-NCS showing stepwise weight loss upon heating.

Table S1. Calculated scaled wavenumbers, $v$ (in cm$^{-1}$) with CN bond lengths (in Å) for the modified CPO-27 materials compared with experimental wavenumbers (exp).

| Sample       | Mg$^{2+}$ | Zn$^{2+}$ | Ni$^{2+}$ (*) |
|--------------|-----------|-----------|---------------|
| Calc. M-SCN  | $v$, cm$^{-1}$ | 1983 | 2064 | (1996) |
|              | $d$(CN)   | 1,202 | 1,186 | 1,200 |
| Calc. M-NCS  | $v$, cm$^{-1}$ | 2078 | 2096 | (2079) |
|              | $d$(CN)   | 1,184 | 1,184 | 1,185 |
| Exp.         | $v$, cm$^{-1}$ | 2076 | 2089 | 2101 |

* values given in parentheses are estimated on the basis of CN bond length

Figure S10. PXRD patterns: CPO-27 calculated from SC-XRD data (green), CPO-27-NCS calculated from DFT+D optimized structures (black), and CPO-27-NCS recorded for the as-synthesized bulk material (red).
Figure S11. IR spectra (top), optical images (center) and PXRD patterns (bottom) of mixtures after grinding CPO-27(Co) with NH₄SCN at the 6:3 CPO-27 to NH₄SCN ratio. For comparison, IR spectra, optical image and PXRD pattern of the [Co(SCN)₄]²⁻ ions, are given.

Figure S12. Variable temperature EIS conductivity measurements at 30% RH for CPO-27(Mg)-NCS, CPO-27(Zn)-NCS and CPO-27(Ni)-NCS.
Figure S13. Variable temperature EIS conductivity measurements at 45% RH for CPO-27(Mg)-NCS, CPO-27(Zn)-NCS and CPO-27(Ni)-NCS.

Figure S14. Variable temperature EIS conductivity measurements at 60% RH for CPO-27(Mg)-NCS, CPO-27(Zn)-NCS and CPO-27(Ni)-NCS.

Figure S15. Variable temperature EIS conductivity measurements at 75% RH for CPO-27(Mg)-NCS, CPO-27(Zn)-NCS and CPO-27(Ni)-NCS.

Figure S16. Variable temperature EIS conductivity measurements at 90% RH for CPO-27(Mg)-NCS, CPO-27(Zn)-NCS and CPO-27(Ni)-NCS.
Figure S17. Arrhenius plots with activation energies indicated as numbers (in eV) for various RH values (top legend) for CPO-27-NCS.

Figure S18. Proton conductivity at different RH and temperatures for CPO-27(Mg)-NCS, CPO-27(Zn)-NCS and CPO-27(Ni)-NCS.

Figure S19. Variable temperature EIS conductivity measurements at 90% RH for CPO-27(Mg)-NCS with various stoichiometric ratios: 6:1, 6:2, 6:3 (CPO-27 to NH₄SCN).

Figure S20. Variable temperature EIS conductivity measurements at 90% RH for CPO-27(Ni)-NCS with various stoichiometric ratios: 6:1, 6:2, 6:3 (CPO-27 to NH₄SCN).
Figure S21. Variable temperature EIS conductivity measurements at 90% RH for CPO-27(Zn)-NCS with various stoichiometric ratios: 6:1, 6:2, 6:3 (CPO-27 to NH₄SCN).

Figure S22. Arrhenius plots with activation energies indicated as numbers (in eV) at 90% RH for CPO-27-NCS with various stoichiometric amounts of NH₄SCN added; given as 6:1, 6:2, 6:3 CPO-27 to NH₄SCN ratios.

Figure S23. Proton conductivity change with temperature at 90% RH for CPO-27-NCS with various stoichiometric amounts of NH₄SCN added; given as 6:1, 6:2, 6:3 CPO-27 to NH₄SCN ratios.
Table S2. Comparison of proton conductivities for CPO-27-NCS.

| RH (%) | Sample          | Conductivity (S·cm⁻¹) | Activation energy (eV) |
|--------|-----------------|------------------------|------------------------|
|        |                 | 25°C | 30°C | 40°C | 50°C | 60°C |
| 30     | CPO-27(Zn)-NCS  | 3.3·10⁻⁶ | 8.0·10⁻⁶ | 2.9·10⁻⁵ | 8.2·10⁻⁵ | 9.0·10⁻⁵ | 0.86 |
|        | CPO-27(Ni)-NCS  | 2.2·10⁻⁶ | 2.4·10⁻⁶ | 2.6·10⁻⁶ | 2.7·10⁻⁶ | -         | 0.08 |
|        | CPO-27(Mg)-NCS  | 7.0·10⁻⁵ | 8.7·10⁻⁵ | 1.4·10⁻⁴ | 1.6·10⁻⁴ | -         | 0.30 |
| 45     | CPO-27(Zn)-NCS  | 7.3·10⁻⁶ | 1.2·10⁻⁵ | 3.3·10⁻⁵ | 1.2·10⁻⁴ | 1.4·10⁻⁴ | 0.81 |
|        | CPO-27(Ni)-NCS  | 3.3·10⁻⁶ | 4.1·10⁻⁶ | 5.2·10⁻⁶ | 5.6·10⁻⁶ | 6.7·10⁻⁶ | 0.19 |
|        | CPO-27(Mg)-NCS  | 2.6·10⁻⁴ | 3.3·10⁻⁴ | 4.5·10⁻⁴ | 5.3·10⁻⁴ | 6.2·10⁻⁴ | 0.23 |
| 60     | CPO-27(Zn)-NCS  | 4.2·10⁻⁵ | 7.1·10⁻⁵ | 1.7·10⁻⁴ | 3.7·10⁻⁴ | 5.3·10⁻⁴ | 0.66 |
|        | CPO-27(Ni)-NCS  | 1.0·10⁻⁵ | 1.2·10⁻⁵ | 2.0·10⁻⁵ | 2.4·10⁻⁵ | 2.5·10⁻⁵ | 0.27 |
|        | CPO-27(Mg)-NCS  | 6.8·10⁻⁴ | 7.4·10⁻⁴ | 8.7·10⁻⁴ | 1.1·10⁻³ | 1.2·10⁻³ | 0.17 |
| 75     | CPO-27(Zn)-NCS  | 1.9·10⁻⁴ | 2.8·10⁻⁴ | 4.9·10⁻⁴ | 8.1·10⁻⁴ | 1.1·10⁻³ | 0.46 |
|        | CPO-27(Ni)-NCS  | 8.5·10⁻⁵ | 1.1·10⁻⁴ | 2.1·10⁻⁴ | 3.1·10⁻⁴ | 3.7·10⁻⁴ | 0.40 |
|        | CPO-27(Mg)-NCS  | 3.1·10⁻³ | 3.3·10⁻³ | 3.8·10⁻³ | 4.5·10⁻³ | 5.1·10⁻³ | 0.15 |
| 90     | CPO-27(Zn)-NCS  | 3.3·10⁻⁴ | 4.9·10⁻⁴ | 9.2·10⁻⁴ | 1.9·10⁻³ | 2.8·10⁻³ | 0.56 |
|        | CPO-27(Ni)-NCS  | 8.3·10⁻⁴ | 8.5·10⁻⁴ | 1.0·10⁻³ | 1.2·10⁻³ | 1.4·10⁻³ | 0.17 |
|        | CPO-27(Mg)-NCS  | 3.9·10⁻³ | 4.6·10⁻³ | 4.8·10⁻³ | 8.2·10⁻³ | 1.0·10⁻² | 0.26 |

Table S3. Comparison of proton conductivities for CPO-27(Mg)-NCS with various stoichiometric amounts of NH3SCN added; given as 6:1, 6:2, 6:3 CPO-27 to NH3SCN ratios.

| RH (%) | Sample        | Conductivity (S·cm⁻¹) | Activation energy (eV) |
|--------|---------------|------------------------|------------------------|
|        |               | 25°C | 30°C | 40°C | 50°C | 60°C |
| 90     | CPO-27(Mg)-NCS₆₁ | 6.4·10⁻⁴ | 6.8·10⁻⁴ | 8.0·10⁻⁴ | 9.5·10⁻⁴ | 1.1·10⁻³ | 0.16 |
|        | CPO-27(Mg)-NCS₆₂ | 9.9·10⁻⁴ | 1.0·10⁻³ | 1.1·10⁻³ | 1.2·10⁻³ | 1.5·10⁻³ | 0.13 |
|        | CPO-27(Mg)-NCS₆₃ | 3.9·10⁻³ | 4.6·10⁻³ | 4.8·10⁻³ | 8.2·10⁻³ | 1.0·10⁻² | 0.26 |

Table S4. Comparison of proton conductivities for CPO-27(Ni)-NCS with various stoichiometric amounts of NH3SCN added; given as 6:1, 6:2, 6:3 CPO-27 to NH3SCN ratios.

| RH (%) | Sample        | Conductivity (S·cm⁻¹) | Activation energy (eV) |
|--------|---------------|------------------------|------------------------|
|        |               | 25°C | 30°C | 40°C | 50°C | 60°C |
| 90     | CPO-27(Ni)-NCS₆₁ | 2.1·10⁻⁵ | 2.6·10⁻⁵ | 4.3·10⁻⁵ | 7.0·10⁻⁵ | 1.3·10⁻⁴ | 0.47 |
|        | CPO-27(Ni)-NCS₆₂ | 1.5·10⁻⁴ | 1.7·10⁻⁴ | 2.8·10⁻⁴ | 4.5·10⁻⁴ | 7.1·10⁻⁴ | 0.42 |
|        | CPO-27(Ni)-NCS₆₃ | 8.3·10⁻⁴ | 8.4·10⁻⁴ | 1.0·10⁻³ | 1.2·10⁻³ | 1.4·10⁻³ | 0.17 |

Table S5. Comparison of proton conductivities for CPO-27(Zn)-NCS with various stoichiometric amounts of NH3SCN added; given as 6:1, 6:2, 6:3 CPO-27 to NH3SCN ratios.

| RH (%) | Sample        | Conductivity (S·cm⁻¹) | Activation energy (eV) |
|--------|---------------|------------------------|------------------------|
|        |               | 25°C | 30°C | 40°C | 50°C | 60°C |
| 90     | CPO-27(Zn)-NCS₆₁ | 1.8·10⁻⁴ | 1.9·10⁻⁴ | 1.9·10⁻⁴ | 2.1·10⁻⁴ | 2.5·10⁻⁴ | 0.10 |
|        | CPO-27(Zn)-NCS₆₂ | 2.7·10⁻⁴ | 3.9·10⁻⁴ | 4.8·10⁻⁴ | 5.7·10⁻⁴ | 6.7·10⁻⁴ | 0.23 |
|        | CPO-27(Zn)-NCS₆₃ | 3.3·10⁻⁴ | 4.9·10⁻⁴ | 9.2·10⁻⁴ | 1.9·10⁻³ | 2.8·10⁻³ | 0.56 |
Table S6. Proton conductivities for selected MOFs including those with protonated amines/ammonia and those based on CPO-27(MOF-74) materials.

| Sample                                                                 | Conductivity (S cm\(^{-1}\)) | Conditions         | Ref |
|------------------------------------------------------------------------|-------------------------------|--------------------|-----|
| (Me\(_2\)NH\(_2\))\(_2\)(SO\(_4\))\(_2\)[Zn\(_2\)(ox)]\(_3\)             | 4,2 \times 10\(^{-2}\)       | 98% RH (25°C)      | 7   |
| MOF-74(Mg)-Urea                                                        | 3,7 \times 10\(^{-2}\)       | 95% RH (55°C)      | 8   |
| VNU-15 Fe\(_3\)(BDC)\(_2\)(NDC)(SO\(_4\))\(_4\)(DMA)\(_4\)             | 2,9 \times 10\(^{-2}\)       | 60% RH (95°C)      | 9   |
| MROF-1 [Me\(_2\)NH\(_2\)][In(thb)(pbdc)]\(_2\).5DMF.3.5H\(_2\)O         | 1,7 \times 10\(^{-2}\)       | 97% RH (70°C)      |      |
| CPO-27(Mg)-NCS                                                        | 1,0 \times 10\(^{-2}\)       | 90% RH (60°C)      | 10  |
| PCMOF-20 (DMA)\(_3\)[Zr(HL)\(_2\)]\(_2\)H\(_2\)L = 2.4,6-tris(4-phosphonophenyl) pyridine | 1,0 \times 10\(^{-2}\)       | 95% RH (85°C)      | 11  |
| (Me\(_2\)NH\(_2\))[Eu(L)]\(_3\)                                       | 3,8 \times 10\(^{-3}\)       | 98% RH (100°C)     |      |
| CPO-27(Zn)-NCS                                                        | 2,8 \times 10\(^{-3}\)       | 90% RH (60°C)      |      |
| MOF-74(Ni)-Urea                                                       | 2,3 \times 10\(^{-3}\)       | 95% RH (55°C)      | 8   |
| CPO-27(Ni)-NCS                                                        | 1,4 \times 10\(^{-3}\)       | 90% RH (60°C)      |      |
| [{Co\(_2\)(BTC)\(_4\)/4\}] \cdot (Me\(_2\)NH\(_2\))\(_2\).4/3H\(_2\)O\(_n\) | 1,2 \times 10\(^{-3}\)       | 60% RH (50°C)      | 13  |
| NH\(_4\)Br@HKUST-1                                                   | 9,0 \times 10\(^{-4}\)       | 99% RH (25°C)      | 14  |
| Ti-CAT-5 Ti(THO)(DMA)\(_2\)                                          | 8,2 \times 10\(^{-4}\)       | 98% RH (25°C)      | 15  |
| NHMe\(_3\)(CH\(_2\)COOH)[FeCr(ox)\(_3\)]                             | 8,0 \times 10\(^{-4}\)       | 60% RH (25°C)      | 16  |
| CPM-102 [In(imdcH)-(ox)]\(_3\):NH\(_4\)\(_2\)(H\(_2\)O)\(_{1.5}\)      | 8,0 \times 10\(^{-4}\)       | 98.5% RH (22.5°C)  | 17  |
| {NH(prol)\(_3\)}[MCr(ox)\(_3\)]\(_n\)                               | 1,0 \times 10\(^{-4}\)       | 75% RH (25°C)      | 18  |
| (M=Mn\(_{II}\), Fe\(_{II}\), Co\(_{II}\); NH(prol)\(_3\)+ = tri(3-hydroxypropyl) ammonium) |               |                    |      |
| MOF-74(Ni)                                                           | 1,7 \times 10\(^{-5}\)       | 95% RH (55°C)      | 8   |
| MOF-74(Ni)-H\(_2\)O-Urea                                             | 1,1 \times 10\(^{-5}\)       | 95% RH (55°C)      | 8   |
| (NH\(_4\))\(_3\)[Co\(_2\)(bamdpH)\(_2\)](HCOO)(H\(_2\)O)\(_2\)       | 8,0 \times 10\(^{-6}\)       | 90% RH (25°C)      | 19  |
| MOF-74(Co)                                                           | 4,5 \times 10\(^{-3}\) *     | 95% RH (90°C)      | 20  |
| MOF-74(Co)                                                           | 1,4 \times 10\(^{-3}\) *     | 90% RH (60°C)      | 21  |

* proton conductivity along the [001] channels, measured on single crystals
Figure S24. H$_2$O adsorption cycling test for CPO-27-NCS.

Figure S25. H$_2$O vapor adsorption measurement at 298 K for CPO-27-NCS, closed symbols: adsorption, open symbols desorption.
Figure S26. IR spectra (left) and PXRD patterns (right) of the as-synthesized CPO-27-NCS compared with those of samples conditioned at 90% RH before EIS measurement (red) and after EIS measurement (green).
Figure S27. Representative temperature-dependent AC impedance plots at 45% RH for CPO-27(Zn)-NCS (numbers indicate temperatures in °C) with the equivalent circuit used for fitting the plots (ZSimpWin software).

The equivalent circuit proposal indicates the presence of components which may refer to bulk resistance, different orientation of crystal planes contribution, grain boundary resistance and electrode/electrolyte interface.

Figure S28. Time-dependent proton conductivity of CPO-27(Mg)-NCS at 60°C and 90% RH.

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