# Syntheses of two Imidazolate-4-amide-5-imidate Linker Based Hexagonal Metal-Organic Frameworks with Flexible Ethoxy Substituent

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# 1 Experimental Details

The linker precursors 2-ethoxy-4,5-dicyanoimidazole (L1)[1] was synthesized following published procedure. Elemental analysis (C, H, N) was performed on Elementar Vario EL elemental analyzer.

## Materials

All chemicals were purchased from commercial suppliers (Sigma-Aldrich, Fluka, Alfa Aesar and others) and used without further purification.

## Synthetic procedure

### IFP-9:

In a sealed tube (Typ A, company: Ace) 0.20 g of (1.35 mmol) 4,5-dicyano-2-ethoxy-imidazole (L1), $Zn(NO_3)_2 \cdot 4H_2O$ (0.39 g, 1.35 mmol) were dissolved in $DMF/EtOH/H_2O$ (v:v =. 2:1:0.5 mL). The sealed tube was closed and the mixture was heated at 120 °C for 48 h and then allowed to cool down to room temperature with 5 °C per hour. The obtained fine crystalline material was named IFP-9. Yield for IFP-9: ~ 65 % based on $Zn(NO_3)_2 \cdot 4H_2O$; elemental analysis of activated IFP-9; $C_7H_8N_4O_3Zn$; calcd., C 32.15, H 3.08, N 21.42; found, C 31.91, H 3.44, N 21.08; IR (KBr pellet): $\tilde{v}$ = 3341 (br), 3280 (vs), 3116 (s), 1657 (s), 1552 (m), 1466 (m), 1104 (m), 802 $cm^{-1}$ (m).

### IFP-10:

In a sealed tube (Typ A, company: Ace) 0.20 g of (1.35 mmol) 4,5-dicyano-2-ethoxy-imidazole (L1), $Co(NO_3)_2 \cdot 6H_2O$ (0.39 g, 1.35 mmol) were dissolved in DMF (5 mL). The sealed tube was closed and the mixture was heated at 125 °C for 48 h and then allowed to cool down to room temperature with 5 °C per hour. The obtained material was named IFP-10. Yield for IFP-10: ~ 58 % based on $Co(NO_3)_2 \cdot 6H_2O$; elemental analysis of activated IFP-10; $C_7H_8N_4O_3Co$; calcd., C 32.96, H 3.16, N 21.96; found, C 32.81, H 3.44, N 21.66; IR (KBr pellet): $\tilde{v}$ = 3335 (br), 3116 (vs), 1660 (s), 1547 (s), 1473 (m), 1282 (m), 1104 (m), 802 $cm^{-1}$ (m),684 $cm^{-1}$ (m).

## 2 IR spectra

IR spectra were recorded on a FT-IR Nexus from Thermo Nicolet in the region of 4000- 400 cm-$^1$ as KBr pellets.
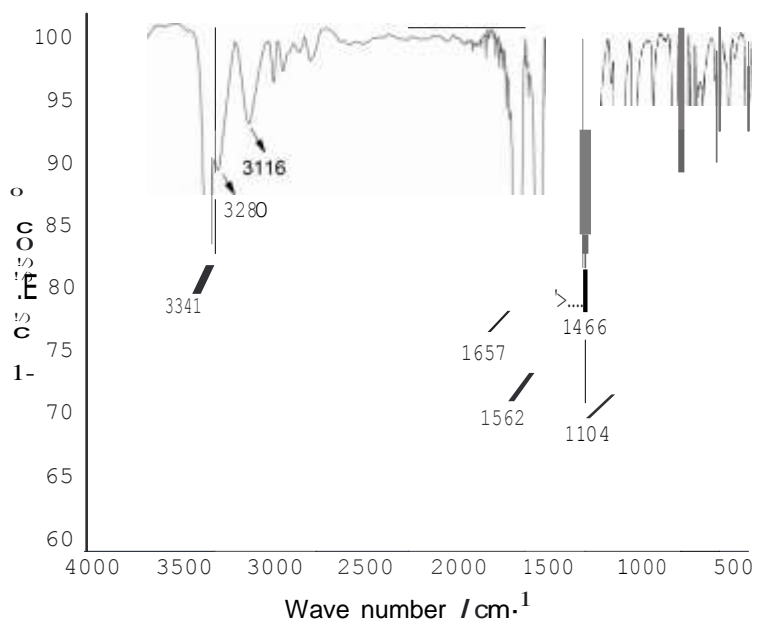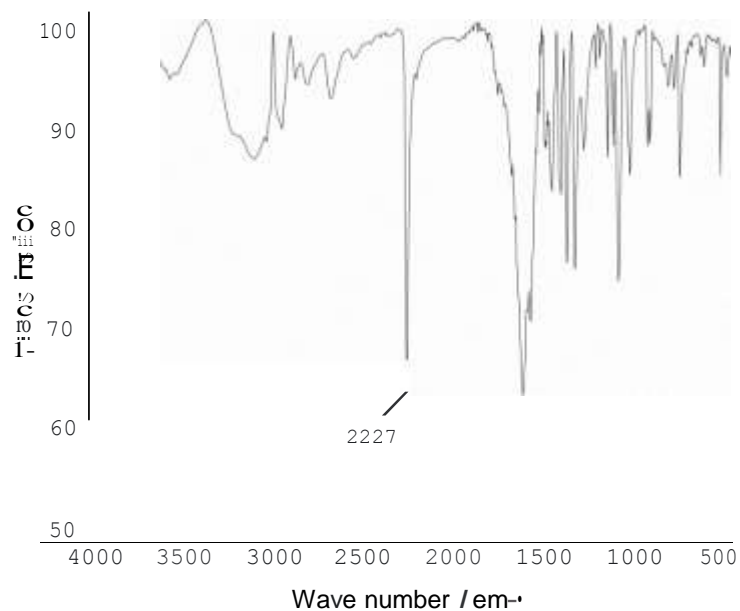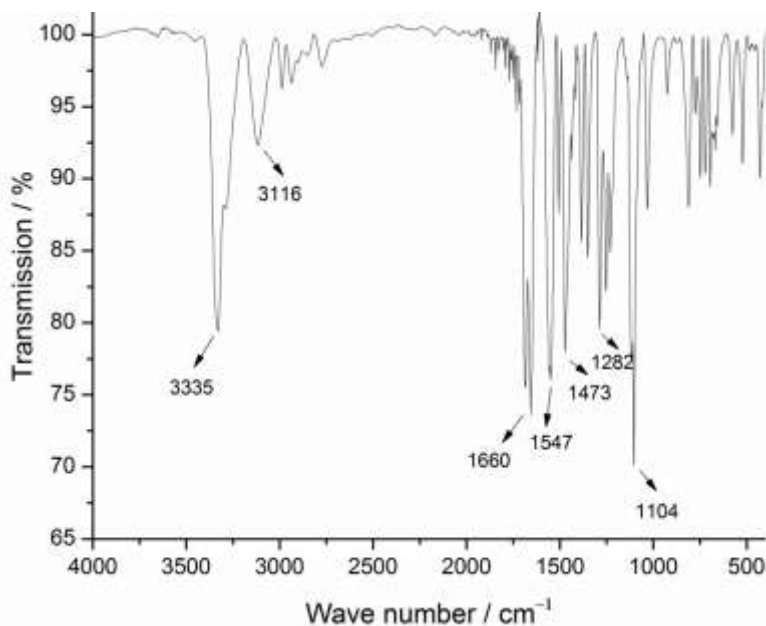
**Fig. S1**. IR-spectra of: **A**) 4,5-dicyano-2-ethoxy-imidazole (L1); **B**) as-synthesized IFP-9; **C**) as-synthesized IFP-10.

## 3 Powder X-ray-diffraction patterns

Powder X-ray diffraction (PXRD) patterns were measured on a Siemens Diffractometer D5005 in Bragg-Brentano reflection geometry. The diffractometer was equipped with a copper tube, a scintillation counter, automatical incident- and diffracted-beam soller slits and a graphite secondary monochromator. The generator was set to 40 kV and 40 mA. All measurements were performed with sample rotation. Data were collected digitally from 3° to 70° $2\theta$ using a step size of 0.02° $2\theta$ and a count time of 4 seconds per step. The simulated powder pattern for IFPs was calculated using single-crystal X-ray diffraction data and processed by the free Mercury v1.4.2 program provided by the Cambridge Crystallographic Data Centre.

## 4 Single crystal X-ray structure determination of IFP-9

The crystals were embedded in perfluoropolyalkylether oil and mounted on a glass fibre. Intensity data were collected at 210 K using a STOE Imaging Plate Diffraction System IPDS-2 with graphite monochromatized $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at 50 kV and 40 mA (360 frames, $\Delta\omega=1°$, exposure time per frame: 4 min. The data were corrected by a numerical absorption correction using the program X-Area (Stoe, 2004) as well as for Lorentz and polarisation effects. The structure was resolved with direct methods using SHELXS-97[2] and

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refined with full-matrix least-squares on $F^2$ using the program SHELXL-97[3] (Sheldrick, 1997). All non-hydrogen atoms were refined anisotropically.

The amide and imidate hydrogen atoms were located from the differences in Fourier map and refined with $U_{iso}(H) = 1.2\ U_{eq}(N)$. The other hydrogen atoms were calculated in their expected positions and refined with $U_{iso}(H) = 1.2\ U_{eq}(CH_2)$ or $U_{iso}(H) = 1.2\ U_{eq}(CH_3)$. The unit cell contains channels filled with disordered solvent molecules. In spite of several attempts, no chemically reasonable solution could be received for the solvent species in the channels of the crystal material. Very high displacement parameters, high estimates and partial occupancy due to the disorder make it impossible to determine accurate atomic positions for that molecules. PLATON/SQUEEZE[4] calculated a solvent-accessible void volume in the unit cell of 1196.2 Å$^3$ (22.9 % of the total cell volume), corresponding to 336 electrons (residual electron density after the last refinement cycle) per cell. This number agrees with about 0.5 molecules of DMF (0.5x40x18=360) per asymmetric unit. The contributions of the disordered solvent species was subtracted from the structure factor calculations, but included in D(calc), $F_{000}$ and the Molecular weight. The deposited atom data (cif) reflect only the known cell content.

CCDC 956082 for IFP-9 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Table S1** Crystal Data, Details of Intensity Measurements, and Structure Refinement for IFP-9.

| | |
|---|---|
| Chemical formula | $C_{8.5} H_{11.5} N_{4.5} O_{3.5}$ Zn |
| Formula Mass | 298.09 |
| Crystal system | trigonal |
| Space group | $R\bar{3}$ |
| $a$/Å | 18.0166(5) |
| $b$/Å | 18.0166(5) |
| $c$/Å | 18.6077(5) |
| $\alpha$/° | 90.00 |
| $\beta$/° | 90.00 |
| $\gamma$/° | 120.00 |
| Unit cell volume/Å$^3$ | 5230.8(2) |
| Temperature/K | 210 |
| No. of formula units per unit cell, $Z$ | 18 |
| Radiation type | MoK$\alpha$ |
| Absorption coefficient, $\mu$/mm$^{-1}$ | 1.873 |
| Reflections collected | 29403 |
| No. of independent reflections | 2681 |
| $R_{int}$ | 0.0211 |
| $R_1$ / $wR_2$  [$I > 2\sigma(I)$] | 0.0212/0.0559 |
| $R_1$ / $wR_2$  (all data) | 0.0236/0.0569 |
| Goodness of fit on $F^2$ | 1.049 |

**Table S2** Selected bond lengths [Å] for [Zn(L2)] 0.5 DMF (IFP-9).

| | |
|---|---|
| N1–Zn1 | 2.075(1) |
| N2–Zn1$^V$ | 2.131(1) |
| N3–Zn1$^V$ | 1.997(1) |
| O2–Zn1 | 2.004(1) |
| O3–Zn1 | 2.166(1) |

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**Table S3** Selected bond angles [°] for Zn(L2)] 0.5 DMF (IFP-9).

| | |
|---|---|
| N3–Zn1–O2$^{VIII}$ | 120.68(6) |
| N3–Zn1–N1$^{VIII}$ | 103.96(5) |
| O2–Zn1–N1$^{III}$ | 89.46(5) |
| N3–Zn1–N2$^{VIII}$ | 79.61(5) |
| O2–Zn1–N2$^{III}$ | 105.52(5) |
| N1–Zn1–N2$^{III}$ | 160.32(5) |
| N3–Zn1–O3$^{VIII}$ | 120.32(6) |
| O2–Zn1–O3$^{III}$ | 118.99(5) |
| N1–Zn1–O3 | 77.30(4) |
| N2–Zn1–O3$^{VIII}$ | 84.19(4) |

**Table S4** Hydrogen-bonding parameters [Å, °] for [Zn(L2)] 0.5 DMF (IFP-9).

| | D-H | H ... A | D ... A | D-H ... A |
|---|---|---|---|---|
| N3 - H30 … N2$^{I}$ | 0.76(2) | 2.50(2) | 3.211(2) | 156(2) |
| N4 - H40 … O3$^{II}$ | 0.86(2) | 2.17(2) | 3.030(2) | 175(2) |
| N4 - H41 … O2 | 0.91(2) | 1.93(3) | 2.788(2) | 156(2) |

Symmetry Operators: $^{I}$ x-y+1/3, x-1/3, 2/3-z; $^{II}$ 1-x, 1-y, -z; $^{III}$ 2/3+x-y, 1/3+x, 1/3-z
$^{IV}$ y, 1-x+y, -z; $^{V}$ 2/3-x+y, 4/3-x, 1/3+z; $^{VI}$ y-1/3, 1/3-x+y, 1/3-z
$^{VII}$ 1+x-y, x, -z; $^{VIII}$ 4/3-y, 2/3+x-y, z-1/3



**Fig. S2.** Asymmetric unit with coordination site of IFP-9.

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## 5 Theoretical calculations of crystal structure of IFP-10

DFT calculations (PBE functional[5]) were performed by using the SIESTA program package.[6] The DZP basis set used in the calculations was first tested on the structure of IMOF-3 (later, we named IMOF-3 as IFP-1) solved from single-crystal X-ray data,[7] and showed very good agreement with respect to unit cell parameters (compare; $a_{calcd} = 17.9119$ Å and $c_{calcd} = 18.2982$ Å vs. $a_{exptl} = 17.9244$ Å and $c_{exptl} = 18.4454$ Å), bond lengths and angles. Due to the large unit cell sizes, it was sufficient to include only the $\Gamma$-point of the Brillouin zone for the evaluation of integrals in the reciprocal space.

## 6 Thermogravimetric (TG) analysis

The TG measurements were performed in a stationary air atmosphere (no purge) from room temperature up to 850 °C using a Linseis thermal analyzer (Linseis, Germany) working in the vertical mode. The heating rate was 10 °C/min. The samples were placed in cups of aluminium oxide.
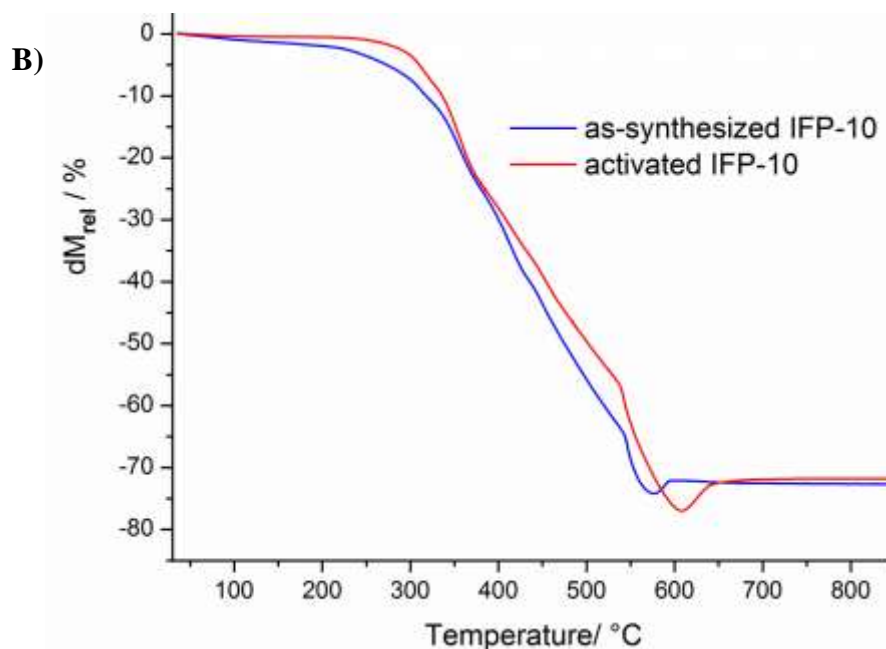
**A)**

**B)**
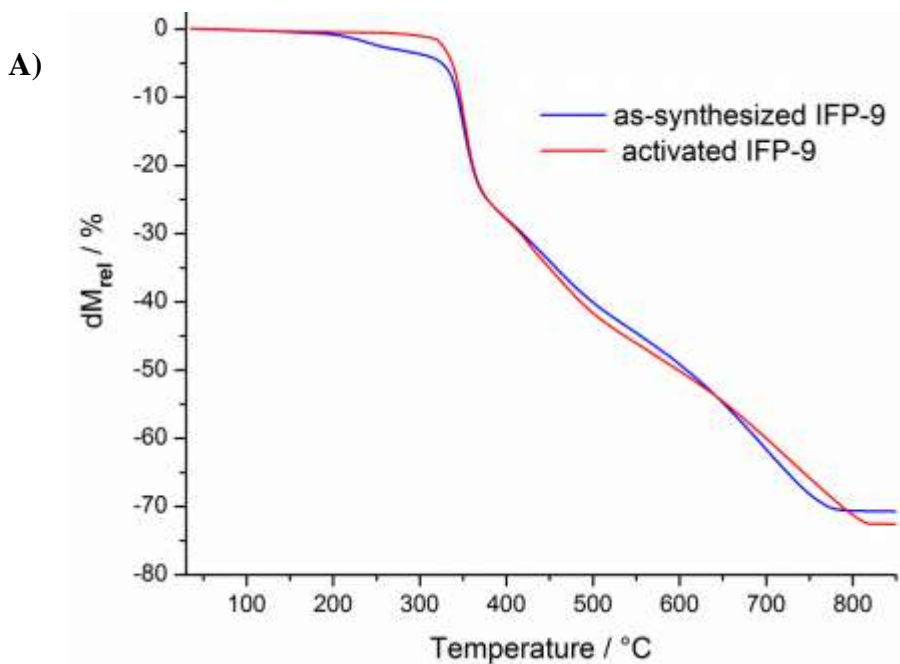


**Fig. S3.** TGA curves **A)** for IFP-9 and **B)** IFP-10.

## 7 Gas-sorption measurement

The sample was connected to the preparation port on a Micromeritics ASAP 2020 automatic gas sorption analyzer and degassed under vacuum until the out gassing rate, i.e., the rate of pressure rise in the temporarily closed manifold with the connected sample tube, was less than 2 µTorr/min at the specified temperature 200 °C for 24 h. After weighing, the sample tube was then transferred to the analysis port of the sorption analyzer. All used gases ($H_2$, He, $N_2$, $CO_2$, $CH_4$) were of ultra high purity (UHP, grade 5.0, 99.999%) and the STP volumes are given according to the NIST standards (293.15 K, 101.325 kPa). Helium gas was used for the determination of the cold and warm free space of the sample tubes. $H_2$ and $N_2$ sorption isotherms were measured at 77 K (liquid nitrogen bath), whereas $CO_2$ and $CH_4$ sorption isotherms were measured at 298±1 K (passive thermostating) and 273.15 K (ice/deionized water bath). The heat of adsorption value was calculated by using the ASAP 2020 v3.05 software.

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