Integration of Fluorescent Functionality into Pressure Amplifying Metal-Organic Frameworks

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The flexibility of soft porous crystals, i.e., their ability to respond to external stimuli with structural changes, is one of the most fascinating features of metal-organic frameworks. In addition to breathing and swelling phenomena of flexible MOFs, negative gas adsorption and pressure amplification is one of the more recent discoveries in this field, initially observed in the cubic DUT-49 framework. In recent years the structural contraction was monitored by physisorption, X‑ray diffraction, NMR and EPR techniques, providing only limited information about the electronic structure of the ligand. In this work we designed a new ligand with a fluorescent core in the linker backbone and synthesized three new MOFs, isoreticular to DUT-49, denoted as DUT-140(M) (M - Cu, Co, Zn) crystalizing in space group. DUT-140(Cu) can be desolvated and is highly porous with an accessible apparent surface area of 4870 m²g⁻¹ and a pore volume of 2.59 cm³g⁻¹. Furthermore, it shows flexibility and NGA upon adsorption of subcritical gases. DUT-140(Zn), synthesized using post-synthetic metal exchange, could only be studied with guests in the pores. In addition to the investigation of the adsorption behavior of DUT-140(Cu) spectroscopic and computational methods were used to study the light absorption properties.

File list (2)

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Integration of Fluorescent Functionality into Pressure Amplifying Metal-Organic Frameworks

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ABSTRACT: The flexibility of soft porous crystals, i.e., their ability to respond to external stimuli with structural changes, is one of the most fascinating features of metal-organic frameworks (MOFs). In addition to breathing and swelling phenomena of flexible MOFs, negative gas adsorption (NGA) and pressure amplification (PA) is one of the more recent discoveries in this field, initially observed in the cubic DUT-49 framework. In recent years the structural contraction was monitored by physisorption, X-ray diffraction, NMR and EPR techniques, providing only limited information about the electronic structure of the ligand. In this work we designed a new ligand with a fluorescent core in the linker backbone and synthesized three new MOFs, isoreticular to DUT-49, denoted as DUT-140(M) (M - Cu, Co, Zn) crystalizing in space group $Fm\overline{3}m$. DUT-140(Cu) can be desolvated and is highly porous with an accessible apparent surface area of 4870 m$^2$g$^{-1}$ and a pore volume of 2.59 cm$^3$g$^{-1}$. Furthermore, it shows flexibility and NGA upon adsorption of subcritical gases. DUT-140(Zn), synthesized using post-synthetic metal exchange, could only be studied with guests in the pores. In addition to the investigation of the adsorption behavior of DUT-140(Cu) spectroscopic and computational methods were used to study the light absorption properties.

INTRODUCTION

Over the last two decades, metal-organic frameworks (MOFs) have been established as a new class of highly porous coordination networks consisting of inorganic nodes (metal ions or metal-oxo clusters) and linker molecules. In this context, linkers are defined as polydentate organic ligands which interconnect the inorganic nodes. MOFs contain voids accessible for various probe molecules that can be used for many applications. Due to this modular design, there are almost no limits regarding structural nodes combination, resulting in a wide variety of frameworks with different topologies. In addition to excellent tunability of the material properties, MOFs often show immense surface areas with permanent porosity. A limited number of MOFs show also structural flexibility, reflected in a distinct structural response to external stimuli which can be considered among the most unique and fascinating properties compared to traditional porous solids. The phenomenon was first predicted in 1998 as an attribute of the third generation of MOFs, which are also known as flexible MOFs or soft porous crystals. Dynamic behavior of soft porous crystals could be exploited in the last decades in a range of different applications like gas separation, molecular sensing, drug delivery and improved storage and release of gases outperforming the rigid analogues. Different types of flexibility phenomena such as breathing, swelling, and subnetwork displacement have been described, reflected in very specific adsorption characteristics and isotherm shapes.

In 2016 a previously unknown phenomenon, later denoted as Negative Gas Adsorption (NGA), was discovered in the metal organic framework DUT-49, reflected by a spontaneous gas desorption and pressure amplification upon breathing. DUT-49 is built from tetratopic 9,9'-([1,1'-biphenyl]-4,4'-diyl)-bis(9H-carbazole-3,6-dicarboxylate) ligand (BBCDC) and copper paddle wheel units. From a structural point of view, the material consists of cuboctahedral metal-organic polyhedra (MOP) formed by copper paddle wheels and 3,6-carbazole-dicarboxylates which are interconnected by 4,4'-biphenyl units forming close cubic packing. This linkage generates a hierarchical pore system of cuboctahedral (10 Å), tetrahedral (17 Å) and octahedral (24 Å) pores. During adsorption of subcritical gases at conditions close to the standard boiling point, the network shows a transition to a contracted pore phase (cp) while previously adsorbed gas is expelled, leading to a pressure amplification (PA) in the measurement cell. This transformation is, different to other materials, uniquely caused by a
switch-like, out of plane buckling of the sp²-hybridized biphenyl part of the BBCDC linker. Molecular simulations have highlighted the responsible for the contraction during methane adsorption and in later work also the effect of crystallite size and pore size in an isoreticular series on the mechanical properties and the transition were investigated. Recent research on this material enlightens the switching behavior and the effect of defects using NMR techniques. Furthermore the impact of temperature and choice of adsorbate on the NGA step was examined more in detail. Today pressure amplification by NGA can approach higher pressures beyond 400 kPa which may be valuable for pneumatic applications.

The guest dependent flexibility of DUT-49 was extensively investigated by in situ X-ray diffraction/adsorption experiments, computational methods and in situ NMR experiments. However, none of these techniques addresses the changes in electronic states of the ligand molecule in detail. This aspect can be tackled by optical spectroscopic techniques and would give a deeper insight into changes in the electronic and molecular structure of the linker in response to the contraction trajectory. Further investigation of the linker in the closed pore phase allows a consideration of the question if the contraction of the network can be used to arrest a fragment of the linker in unnatural conformational states. This can be interesting for uncommon fluorescence properties but also for activation of reactive centers by increasing the accessibility for example.

In 2002, fluorescence was mentioned for the first time in connection with MOFs. Since then, different strategies were used to integrate fluorescent moieties into MOFs especially for sensing applications. For instance, it was found that the stiffening of luminophores in networks increases their fluorescence intensity because of decreased vibrational decay. Furthermore, the precise spatial fixation of fluorophores within a lattice can significantly influence the fluorescence properties and lead to interesting effects like J dimer emission or multi emission. Also, phenomena like charge and energy transfer, known from classical coordination chemistry, were observed. In addition to pure ligand-based fluorescence, MOFs containing d10 ions often exhibit metal-to-ligand (MLCT) and ligand-to-metal charge transfer (LMCT). Alternatively, fluorophores can be introduced into the pore system, which can lead to interesting emission properties. Another possibility is offered by lanthanide based MOFs in which highly absorbing linker molecules are used to populate the emissive states of the lanthanide and to increase its luminescence.

In this work a fluorescent probe was introduced into DUT-49 framework. For this reason, the

**EXPERIMENTAL SECTION**

**Synthesis of microcrystalline MOF powders**

The microcrystalline powder of metal organic framework DUT-140(Cu) was synthesized by a solvothermal approach. In a 500 ml round bottom flask H$_2$FBCDC ligand (500 mg, 7.73 mmol, 1.00 eq.) was dissolved in 200 ml of N,N-Dimethylformamide (DMF) under inert atmosphere and 20 ml of acetic acid was added. Sometimes, a part of the ligand is precipitating again after addition of the acetic acid. Careful heating of the mixture up to 80 °C supports the solution procedure in this case. Subsequently, Cu(NO$_3$)$_2$(H$_2$O)$_{12}$(423 mg, 1.82 mmol, 2.50 eq.) was added and the reaction mixture stirred for 72 h at 80 °C while fine green powder precipitated. After the reaction is finished the obtained powder was washed five times with DMF. A small amount of the washed precipitate was used for PXRD measurements, referred to as “as made” MOF. Desolvation of DUT-140(Cu) was achieved using a supercritical point dryer and resulted in 212 mg (36%) of pure and highly crystalline MOF powder.

DUT-140(Co) was synthesized using the same procedure as for the copper analogue. H$_2$FBCDC linker (200 mg, 0.29 mmol, 1.00 eq.) was dissolved in 75 ml N-Methyl-2-pyrolidone (NMP). To this a solution cobalt nitrate hexahydrate (212 mg (0.73 mmol, 2.50 eq.) was added and the resulting mixture was stirred for 72 h at 80 °C under inert atmosphere until a brownish precipitate was formed. After completion of the reaction the crystals were washed 3 times with pure NMP. A part of the product was separated for as made PXRD. No further investigation of DUT-140(Co) was conducted since it was solely prepared to obtain DUT-140(Zn).

DUT-140(Zn) was produced by post-synthetic metal exchange from DUT-140(Co). Therefore, the solvent above the washed DUT-140(Co) crystals...
was exchanged by a 0.1 M solution of Zn(NO$_3$)$_2$(H$_2$O)$_6$. This solution was exchanged six times over two days. During the first three exchange steps, the supernatant solution turned violet. After the color completely faded, the zinc nitrate solution was refreshed three more times and the product subsequently washed three times with NMP.

In situ fluorescence measurements upon desolvation

The in situ desolvation experiment was performed in a solid-state sample holder filled with solvated material in acetone. The sample holder was positioned in 45° between the incident beam and the detector. The solvent was evaporated over 25 h and fluorescence spectra were measured every 5 min.

In situ PXRD upon desolvation

The powder of DUT-140(Zn) in ethanol was prepared using a background-free holder for measurements under inert conditions and covered by 7.5 µm thick Kapton® foil to ensure a slow solvent evaporation. The measurements were performed on Empyrean 2 diffractometer (Panalytical), using Cu-Kα1 irradiation and Pixcel3D detector. 173 measurements were performed in the 2θ range of 7 - 10° with exposition time of 100 s for each measurement.

RESULTS AND DISCUSSION

In silico investigations of DUT-140

The contraction/reopening mechanism responsible for NGA in DUT-49 is related to a deformation of the BBCDC linker, further denoted as ligand buckling. In previous work, a method was developed to allow an investigation of the mechanical properties of ligands, which directly reflect the switchability and the probability of NGA in frameworks isoreticular to DUT-49. This was achieved by calculating stress-strain curves for the single ligand using density functional theory (DFT) methods. Therefore, simulations were performed also for H$_4$FBCDC ligand before synthetic efforts were made.

The mechanical properties of the H$_4$FBCDC were determined by simulated compression of the linker at the carbazole nitrogen’s (orange arrows, Figure 1a, b) using the accurate tight-binding quantum chemical method, GFN2_xtb. From these calculations stress applied to the linker can be determined and the mechanical stability in addition to the response of network induced pressure can be explored as shown for H$_4$BBCDC (blue) and H$_4$FBCDC (orange) in Figure 1c. Initially increasing the compressive strain to both linkers results in an elastic response up to a certain point, defining the maximal stress. After reaching this point, the linker itself starts to buckle (Figure 2). This step in the stress strain curve is a common feature of all ligands, used for the synthesis of NGA materials. As derived from the graph in Figure 1c the maximum stress for each linker is reached at approximately 0.014 compressive strain. The H$_4$FBCDC ligand reaches the maximum yield stress at 1.30 nN, which is higher compared to the H$_4$BBCDC that demonstrates an inelastic transition at 1.02 nN. Furthermore, the Young’s modulus, reflected by the linear slope of the stress-strain curve, is also larger for H$_4$FBCDC. The demonstrated strain resistance behavior shows that the intended linker is more rigid than the DUT-49 linker, which follows chemical intuition based on comparison of the chemical structures.
These simulations also demonstrate the overall deflection for the H₄BBCDC is larger than for H₄FBCDC. The pore sizes of the related op-phases of corresponding MOFs do not differ significantly, as shown in the supplementary information section 3.3.7. The performance of an NGA material cannot be directly derived from the stress strain curve, however, the increased rigidity of H₄FBCDC is expected to permit a overloading of the metastable state, increasing the NGA step. However, increased rigidity may also lead to a reduction of the ligand’s deflection which in turn could lead to a hindered contraction.

Figure 1. H₄BBCDC (a) and H₄FBCDC linker molecules (b). (c) Stress-strain curve of the ligands (dotted line). Direction of the applied pressure is indicated by the orange arrows. Evolution of N-centroid-N angle of the ligands (solid line) while strain is applied.

Figure 2. Deflection of H₄FBCDC ligand at 0.00 nN (a) and 0.03 nN (b) compressive strain. Colour code: grey: carbon, blue: nitrogen, red: oxygen. Hydrogen atoms are omitted for clarity.
Experimental investigation of desolvated DUT-140(Cu)

As the theoretical calculations of H$_4$FBCDC predict the potential for NGA, the ligand was synthesized in a similar six step approach used for the synthesis of recently reported elongated versions of H$_4$BBCDC.$^{24}$ The carbazole was converted to dibutyl-9H-carbazole-dicarboxylate over four steps and the obtained dicarboxylate was used as starting material in an Ullman-coupling reaction with 2,7-dibromofluorenone. After the following hydrolysis and purification, the H$_4$FBCDC ligand was obtained in 28% yield over six steps. All compounds have been analyzed by $^1$H- and $^{13}$C-NMR as well as by mass spectroscopy and IR-spectroscopy as shown in supplementary information chapter 2.

Combination of H$_4$FBCDC with copper(II)nitrate in N,N-Dimethylformamide (DMF) yields the framework with a composition [Cu$_2$(FBCDC)](H$_2$O)$_x$(DMF)$_y$, denoted as DUT-140(Cu). The MOF was synthesized using two different synthesis routes yielding crystalline powders with an average particle size of 14 µm and single crystal sample with crystals up to 100 µm (supporting information chapters 3.1 and 3.3.5). The crystal structure of the DUT-140(Cu) was determined by means of synchrotron single crystal X-ray diffraction at MX BL14.3 beamline of the Bessy II light source. DUT-140(Cu) crystallizes in cubic space group Fm$\overline{3}$m (No 225) with lattice parameter $a = 46.14$ Å and is isostructural to DUT-49. Detailed analysis of the ligand molecule in the crystal structure shows elongated thermal ellipsoids even for carbazole moiety, indicating disorder that can be caused by vibration of the molecule in the direction perpendicular to the carbazole plane. Since the symmetry of the fluorenone backbone is lower than the symmetry of the corresponding position in the space group, the fluorenone moiety is disordered over four positions.

The material has a hierarchical pore system with three different voids (11 Å, 16 Å, 24 Å). The phase purity of DUT-140(Cu) was confirmed by PXRD (supporting information, chapter 3.3). The activated powder sample of DUT 140(Cu), was
subjected to physisorption experiments using nitrogen at 77 K and methane at 111 K as probe molecules (Figure 3a, c). The low-pressure range of nitrogen isotherm, shown in Figure 3a, displays superimposing steps up to $p/p_0 = 0.1$ indicating the consecutive filling of the pores before reaching saturation. The desorption branch shows no hysteresis and therefore no indications of the structural flexibility. The isotherm reaches saturation at 73.5 mmol/g, which is slightly lower than theoretical uptake of 74.6 mmol/g. The shape of methane adsorption isotherm at 111 K (Figure 3c) is similar to the methane isotherm for DUT-49 at the same temperature. In the low-pressure range, the stepwise pore filling occurs up to $p/p_0 = 0.075$, at which NGA event is observed with $\Delta n_{NGA} = 5.45$ mmol/g. The second step is observed at relative pressures between 0.4 and 0.6 and is associated with structure reopening in the case of DUT-49. The isotherm reaches the second plateau at $p/p_0 = 0.8$ with a resulting adsorption capacity of 63.4 mmol/g. The desorption branch of the isotherm is characterized by a plateau at $p/p_0 = 0.9 - 0.1$, which is followed by the steep desorption step and the second plateau at $p/p_0 < 0.1$. The intersection range of adsorption and desorption branches indicates the metastability range for the structure (Figure 3c). To monitor the structural transitions upon adsorption of methane at 111 K, the same experiment was reproduced in the external adsorption cell, inserted in the synchrotron beam of KMC-2 beamline (BESSY II). The PXRD patterns collected are shown as profile contour plots in Figure 3b. PXRD patterns confirm structural contraction from op to cp phase upon NGA event, showing shift of 111 reflection towards higher 2θ angle, similar as it was observed for DUT-49. In the relative pressure range of 0.1 - 0.5, a mixture of op and cp phase is observed that can be explained by broad crystallite size distribution, a phenomenon known for DUT-49.23

Detailed analysis of the crystal size distribution (supplementary information, chapter 3.3.5) shows a distinct number of crystallites smaller than 1 µm, which was defined as a critical particle size for structural transition in DUT-49 during adsorption of nitrogen at 77 K. However, since DUT-140(Cu) shows higher resistance to the adsorption stress, the particle size dependency could be transferred to the adsorption of methane at 111 K. The second step in the adsorption branch is characterized by the structural reopening. Interestingly, during the desorption no intermediated phases (ip) were observed, as it is known for DUT-49.20 After complete desorption of methane at 111 K, DUT-140 stays in the cp phase. The monitoring of the cell volume also points out that even the rigid part of the sample, namely the smaller crystals, shows a slight response to the stress associated with the adsorption of methane (Figure 3f).

**Fluorescence in DUT-140(Cu)**

Photoluminescent properties of the H$_4$FBCDC-linker in solution and within the suspended metal-organic framework in the solid state were investigated at room temperature. According to the fluorescence spectra (Figure 4b), a 3 mM solution of H$_4$FBCDC linker in NMP shows a yellow emission with maximum at 17,750 cm$^{-1}$ ($\lambda_{ext.} = 27,397$ cm$^{-1}$). However, no fluorescence of the solid linker powder can be observed. This fluorescence quenching in the solid state is most likely due to the efficient π-π-stacking of the linkers. In contrast, in the crystal of DUT-140 the MOPs are interconnected by the fluorenone containing backbones into a three-dimensional structure. As a result, the fluorenone moieties are isolated from other groups and therefore not involved in any weak interactions, which prevents

![Figure 4](image.png)
DUT-140(Co) and DUT-140(Zn) are isostructural to crystal X-ray diffraction experiments reveals that be clearly seen that the cubic morphology of the metal exchange procedure. Furthermore, it can the color evolution of the crystals during the metal exchange. T o confirm the complete metal supernatant solution indicates the metal orange with simultaneous violet coloration of the crystal color from initial brown to a distinct 0.1 M zinc nitrate solution in NMP. The change of brownish DUT-140(Co) crystals were washed with fresh NMP and afterwards the obtained single crystals were repeatedly exposed to 0.1 M zinc nitrate solution in NMP. The change of the crystal color from initial brown to a distinct orange with simultaneous violet coloration of the supernatant solution indicates the metal exchange. To confirm the complete metal exchange EDX measurements were conducted as shown in supplementary figure 7. Figure 4a shows the color evolution of the crystals during the metal exchange procedure. Furthermore, it can be clearly seen that the cubic morphology of the crystals remains after the metal exchange. Single crystal X-ray diffraction experiments reveals that DUT-140(Co) and DUT-140(Zn) are isostructural to DUT 140(Cu). The crystal structure of both materials was solved in space group \( Fm\tilde{3}m \) (No225) with lattice parameters \( a = 46.47 \) Å for DUT-140(Co) and \( a = 46.52 \) Å for DUT 140(Zn). The crystal structures confirm the trend for the M-M distance within the paddle wheel, previously observed in the DUT-49(M) frameworks and dictated by Irving-Williams series showing increasing M-M distance in the series DUT-140(Cu) < DUT-140(Co) < DUT-140(Zn).

In addition to the synthesis of a new responsive MOF and the successful metal replacement, the initial goal was finally achieved by this procedure as shown in Figure 4b. In addition to DUT-140(Cu) (blue line) and DUT-140(Co) (green line), which are both non-luminescent, the fluorescent properties of the linker in the DUT-140(Zn) (orange line) were observed.

**Fluorescence in DUT-140(Zn)**

In comparison to the ligand, the spectrum of DUT-140(Zn) shows a red shifted emission maximum at 17,000 cm\(^{-1}\). This behavior is attributed to coordination to the metal center. Since suspended crystals were used to record fluorescence spectra a comparison of luminescence intensity with that of the dissolved linker is not feasible.

Unfortunately, the desolvation of the DUT-140(Zn) framework even using supercritical CO\(_2\) drying leads to amorphization of the material. Therefore, studies on the guest-free DUT-140(Zn) are not possible at this stage and the following experiments were performed on solvated crystals.

**Time resolved desolvation experiment**

Garai et al. demonstrated a structural transition from op to intermediate (ip) phase taking place upon solvent desorption in case of DUT-49(Zn), identified by time resolved in situ PXRD. Therefore we conducted two experiments to investigate the effect of desolvation on the

![Figure 5](image)

**Figure 5.** Time dependent desolvation experiments on DUT-140(Zn). (a) fluorescence decay over desolvation from Acetone. Spectra recorded every 5 min for 25 h. (b) in situ PXRD over desolvation from EtOH. PXRD was recorded every 115 s over 5.5 h.
fluorescence properties of DUT-140(Zn). At first, the solvent in the pores of as made DUT-140(Zn) was replaced by acetone. In an in situ experiment, the evaporation of acetone was followed by fluorescence spectroscopy.

Figure 5a shows the fluorescence decay during desolvation from acetone. The spectra show two main features: a decrease in fluorescence intensity during desolvation and second, a slight red shift of the fluorescence maximum from about 17,000 cm\(^{-1}\) to about 16,500 cm\(^{-1}\). Accordingly, there is a change in the fluorescence properties during the desolvation of the material. To examine whether this change is related to a structural change of the material, an in situ PXRD experiment was performed. The contour plot in Figure 5b does not show a shift of the individual reflections with time. Therefore, no structural contraction to another crystalline phase can be assumed for DUT-140(Zn) compared to DUT-49(Zn), showing transition from op to ip phase upon solvent desorption before amorphization.\(^{42}\)

Although all previous experiments clearly indicate that there might be a change in fluorescence due to the structural change of the material, no evidence for this hypothesis can be found from these experiments and the red shift can be attributed to the amorphization and the rupture of some coordination bonds.

This behavior is most likely caused by the fine interplay of the lower stability of the zinc paddle wheel unit compared to the copper paddle wheel unit and the higher rigidity of the \(\text{H}_2\text{FBCDC}\) linker (DUT-140) compared to the \(\text{H}_2\text{BBCDC}\) linker (DUT-49). The more rigid \(\text{H}_2\text{FBCDC}\) linker does not even allow a small contraction of the network due to desorption stress and capillary forces before the coordination bond within the zinc paddlewheel breaks. For DUT-49(Zn) in comparison, the difference between the paddlewheel stability and the linker rigidity is exactly this much smaller a contraction can happen before the coordination bond breaks.

This finding leads to the assumption that a linker with smaller rigidity than that of DUT-49 linker could lead to a network that shows a full contraction before amorphization while solvent evaporation.

CONCLUSION

In brief, three new MOF materials DUT-140(M) (\(M = \text{Cu}, \text{Co}, \text{Zn}\)) were successfully synthesized. As predicted by mechanical considerations of the \(\text{H}_2\text{FBCDC}\) ligand, the metal-organic framework DUT-140(Cu) shows intrinsic flexibility as well as negative gas adsorption property with \(\Delta n_{\text{NGA}} = 5.45\) mmol/g. The contraction of the op-phase can be induced by adsorption of hydrocarbons like methane or butane as well as carbon dioxide. Adsorption experiments also confirm the assumption that the use of the \(\text{H}_2\text{FBCDC}\) linker leads to a more rigid network since the adsorption of nitrogen does not trigger the phase transformation.

UV/Vis investigations of DUT-140(Cu) showed a distinct change in the absorption spectrum which could be attributed to an excitation from the carbazole moiety to the fluorenone part by DFT calculations. Since this excitation is highly affected by the deformation of the linker, it can be concluded that the fluorescence spectrum also should change under the given conditions due to the structural transformation.

The fluorescence properties of the fluorescent linker could be unveiled by an exchange of the metal node to a zinc paddlewheel. However, the stiffening of the metal-organic framework did not lead to the desired increased resistance to desolvation stress for DUT-140(Zn), indicating the metal node to be the main limiting factor, leading to amorphization during desolvation in such highly porous framework materials, even under mild supercritical conditions.

In situ fluorescence studies provide clear evidence that a fluorescence change is caused by structural decomposition of the metal-organic framework and revealed the importance of the fine interplay of linker rigidity and metal node stability for the investigation of structural contraction by solvent desorption.

Overall, fluorenone moieties are valuable functional building blocks for the detection of structural dynamics in the organic sublattice of porous framework compounds.

ASSOCIATED CONTENT

Supporting Information. Supporting information can be accessed free of charge on the ACS Publication website at DOI:

Synthesis and characterization of organic compounds, PXRD, SEM, EDX, TGA.

Crystallographic data for DUT-140(Cu), DUT-140(Zn) and DUT-140(Co) (CCDC-2080449-208045) can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Adsorption information files (.aii) for nitrogen (77K) and methane (111K) are enclosed as supporting data.

ABBREVIATIONS

DUT, Dresden University of Technology; MOF, metal-organic framework; MOP, metal-organic polyhedra; NGA, Negative Gas Adsorption; op, open pore; cp, contracted pore, ip, intermediate pore; \(\text{H}_2\text{BBMDC}, 9,9'-(1,1'-biphenyl)-4,4'-diyl)-bis(9H-carbazole 3,6-dicarboxylic acid; \text{H}_2\text{FBCDC}, 9,9'-(9-oxo-9H-fluorene 2,7-diyl)-bis(9H-carbazole-3,6-dicarboxylic acid; MLCT, metal-to-ligand charge transfer; LMCT, ligand-to-metal charge transfer; DMF, N,N-Dimethylformamide; NMP, 1-Methylpyrrolidin-2-one; GCMC, Grand Canonical Monte Carlo;

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Author Contributions
F. Walenszus synthesized, activated, and performed characterization of organic ligands and MOF samples. F. Walenszus, V. Bon, D. Wallacher, and D. M. Többens contributed to in situ PXRD measurements. V. Bon performed refinement of PXRD data. F. Walenszus, V. Bon, J. Evans, I. Senkovska and S. Kaskel contributed to analysis, interpretation and discussion of adsorption and single crystal X-ray diffraction data. J. D. Evans performed computational analysis of mechanical and adsorption properties. F. Schwotzer performed SEM analysis. F. Walenszus, V. Bon, J. D. Evans, I. Senkovska and S. Kaskel organized the project. All authors contributed to writing and improving the manuscript.

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Supplementary Information for

Integration of Fluorescent Fuctionality into Pressure Amplifying Metal-Organic Frameworks

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1 Chemicals and Methods

1.1 Chemicals

All materials and gases used in the synthesis and analysis in this study were of high purity and summarized in Table S1.

Table S1. List of chemicals used for the synthesis of ligands and MOFs.

| Name                                                                 | CAS            | purity | Manufacturer       |
|----------------------------------------------------------------------|----------------|--------|--------------------|
| 1,1'-Ferrocenediyl-bis(diphenylphosphine), dppf                     | 12150-46-8     | 97%    | Sigma Aldrich      |
| 1,4,7,10,13,16-Hexaoxacyclooctadecane, 18-Crown-6                    | 17455-13-9     | 99%    | Sigma Aldrich      |
| 9H-Carbazole                                                         | 86-74-8        | >95%   | Sigma Aldrich      |
| Acetic acid                                                          | 64-19-7        | 99.9%  | Roth               |
| Tris(dibenzylideneacetone)dipalladium(0)                             | 32005-36-0     | 99%    | Sigma Aldrich      |
| Copper (powder)                                                      | 7681-65-4      | ≥99.5% | Sigma Aldrich      |
| Copper(II) nitrate hemi(pentahydrate)                               | 19004-19-4     | 99.9%  | Sigma Aldrich      |
| Ethanol                                                             | 64-17-5        | 80%    | Berkel AHK         |
| Hydrochloric acid                                                    | 7647-01-0      | 37%    | Sigma Aldrich      |
| Methanol                                                            | 67-56-1        | >95%   | Fisher Chemical    |
| N,N'-Ethylene diamine                                                | 107-15-3       | 99%    | Alfa Aesar         |
| N,N'-Dimethylethylene diamine                                        | 110-70-3       | 99%    | Alfa Aesar         |
| N,N-Dimethylformamide (DMF)                                          | 68-12-2        | 99%    | Fischer Scientific |
| N-Bromosuccinimide                                                  | 128-08-5       | 99%    | Sigma Aldrich      |
| Potassium hydroxyde                                                 | 1310-58-3      | 95%    | Fischer Scientific |
| Potassium carbonate                                                 | 584-08-7       | 99%    | Grüssing           |
| Sulfuric acid                                                       | 7664-93-9      | 99%    | Alfa Aesar         |
| Tetrakis(triphenylphosphine)palladium(0)                             | 14221-01-3     | 99%    | Sigma Aldrich      |
| Zinc (powder)                                                       | 7440-66-6      | >99%   | Riedel de Haen AG  |
| Zinc acetate dihydrate                                              | 5970-45-6      | 98%    | Alfa Aesar         |
| Zinc cyanide                                                        | 557-21-1       | 98%    | Sigma Aldrich      |

1.2 Instruments and Methods

1.2.1 Solution/liquid-state NMR

Nuclear magnetic resonance (NMR) spectra were measured on a BRUKER DRX-500 P spectrometer (500.13/600.16 MHz and 125.77/150.91 MHz for \(^1\)H and \(^{13}\)C respectively) and/or on a BRUKER AC 300 P (300 MHz, 282 MHz and 75.5 MHz for \(^1\)H and \(^{13}\)C, respectively). All \(^1\)H and \(^{13}\)C NMR spectra are reported in
parts per million (ppm) downfield of TMS and were measured relative to the residual signals of the solvents at 5.32 ppm (CH₂Cl₂), 1.79 ppm and 3.62 ppm (THF) or 2.54 ppm (DMSO). Data for ¹H NMR spectra are described as following: chemical shift (δ (ppm)), multiplicity (s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet; br, broad signal), coupling constant (J (Hz)), integration corresponding to amount of H, C or CH. Data for ¹³C NMR spectra are described in terms of chemical shift (δ (ppm)) and functionality were derived from DEPT spectra.

1.2.2 Mass spectrometry

High resolution-time of flight mass spectroscopy (HR-TOF-MS) was carried out on a maXis TOF by Bruker. The Samples were dissolved in dimethyl sulfoxide or ethyl acetate and diluted with a solution of 1 % ammonium formate in methanol. The solution was ionized by electron spray ionisation.

1.2.3 Elemental analysis

Elemental analysis was carried out on a VARIO MICRO-cube Elemental Analyzer by Elementar Analysator Systeme GmbH in CHNS modus. The composition was determined as the average of three individual measurements on three individually prepared samples.

1.2.4 DRIFT IR Spectroscopy

Diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy was performed on a BRUKER VERTEX 70 with a SPECAC Golden Gate DRIFT setup. Prior to the measurement 2 mg of sample were mixed with 10-15 mg dry KBr in a mortar and pressed in the DRIFT-cell. Assignments of peaks in wavenumber ν (cm⁻¹).

1.2.5 UV/Vis spectroscopy

Solid state UV/Vis spectra were recorded using a VARIAN CARY 5000 equipped with an integrating sphere. Analysis of solvated sample was carried out using a VARIAN CARY 4000. The Sample was filled in a HARRICK Praying Mantis reaction chamber and sealed with a dome equipped with UV/Vis transparent windows.

1.2.6 Fluorescence spectroscopy

Fluorescence spectroscopy was conducted on a VARIAN CARY Eclipse Fluorescence Spectrometer. The pure linker was measured in a 10 mm quartz cuvette in NMP. The MOF-powders were measured in a 10 mm quartz cuvette suspended in NMP.

1.2.7 Thermogravimetric analysis

Thermal analysis (TGA) was carried out in Argon using a NETZSCH STA 409 thermal analyser at a heating rate of 5 K min⁻¹. The air sensitive MOF sample was prepared in an Ar-filled glovebox and inserted in the instrument with little exposure to ambient conditions.

1.2.8 X-Ray diffraction

The samples for X-ray diffraction analysis were placed between non-diffracting sheets of a MPET-foil (space blanket). “As made” samples were analysed while suspended in DMF (DUT-140(Cu)) or NMP (DUT-140(Co, Zn)). Activated samples were prepared under inert atmosphere. Theoretical PXRD patterns were calculated based on crystal structures using Mercury 3.9 software package. Powder X-ray diffraction
(PXRD) patterns were collected in transmission geometry on a STOE STADI P diffractometer, equipped with line focus Cu X-ray tube, operated at 40 kV / 30 mA, and focusing Ge (111) monochromator ($\lambda = 0.15405$ nm) and MYTHEN (DECTRIS) detector. A scan speed of 120 s/step and a detector step size of $2\Theta = 4$ was used in the measurements.

1.2.9 **SEM analysis of crystal size and morphology**

Scanning electron microscopy (SEM) images of DUT-49 were taken with secondary electrons in a HITACHI SU8020 microscope using 1.0 kV acceleration voltage and 15.2 - 16.4 mm working distance. The powdered samples were prepared on a sticky carbon sample holder. To avoid degradation upon exposure to air, an inert gas sample holder was used and the powder under argon atmosphere prepared. For crystal size determination a series of 15 images was recorded. The images were analysed with the ImageJ Software package.¹

A series of images was recorded at different magnifications and three different spots on the sample holder were investigated. The crystal size refers to the edge length of the cubic crystals as they are the easiest to measure. The analysis of the SEM images was performed with ImageJ Software package. Values for mean crystal size, as well as relative standard deviation (RSD) were obtained by using the ImageJ analyse-distribution function.
2 Synthesis of Organic Ligands

2.1 Synthetic approach for $H_4$FBCDC-linker

For the synthesis of highly pure FBCDC linker a previous described approach was used.\textsuperscript{2-4} The synthesis procedures were mainly adapted except the Ullmann coupling reaction which was not successful in the reaction with 2,7-dibromo fluorenone. Figure S1 shows the retrosynthesis of $H_4$FBCDC linker.

![Chemical structure and synthetic steps](image)
2.2 Synthesis of 9H-Carbazole Building Block and H$_2$FBCDC linker

2.2.1 3,6-Dibromo-9H-carbazole (a)

In a 2 L round bottom flask 150 g (0.90 mol, 1.00 eq.) 9H-carbazole was dissolved in 1.5 L dry THF while stirring. Afterwards, 351 g (1.97 mol, 2.20 eq.) of N-bromo succinimide was added stepwise over 60 min at room temperature and the solution was stirred at 40 °C over 67 h. The reaction solution was evaporated to around 300 ml and saturated sodium sulphite solution (300 ml) was added. Subsequently the remaining THF was also evaporated. Precipitating raw product was filtered off and dried in oven at 80 °C. The aqueous phase was extracted 3 times with ca. 200 ml of chloroform. The organic phases were collected, dried over MgSO$_4$, and remaining solvent was evaporated in vacuum. The raw product was collected, stirred for 30 min in 600 ml of boiling dichloromethane and filtered off. The filtered solid was dried in vacuum to yield 192 g (66%) of white powder.

$^1$H NMR (500 MHz, THF-$d_8$) δ (ppm): 7.36 (d, $J$=8.75 Hz, 2 H) 7.49 (dd, $J$=8.75, 1.97 Hz, 2 H) 8.26 (d, $J$=1.97 Hz, 2 H); 10.65 (br. s., 1 H).

$^{13}$C NMR (151 MHz, THF-$d_8$) δ ppm 112.61 (s, 1 C) 113.37 (s, 1 CH) 124.11 (s, 1 CH) 125.04 (s, 1 C) 129.72 (s, 1 CH) 140.23 (s, 1 CH).

ESI-TOF-HRMS (m/z): Calculated for [M-H]$: 323.885; found: 323.886 [M-H].

DRIFT, KBr, 298 K (cm$^{-1}$): 3426, 3079, 3065, 1872, 1740, 1601, 1564, 1476, 1466, 1433, 1370, 1322, 1297, 1288, 1245, 1210, 1190, 1128, 1055, 1018, 900, 868, 804, 790, 726, 722, 688, 641, 585, 564

2.2.2 9H-Carbazole-3,6-dicarbonitrile (b)

A 500 ml flame dried round bottom flask was charged with 80 g (246 mmol, 1.00 eq.) of dibromo carbazole and 635 mg (1.18 mmol, 0.0024 eq.) of 1,1’-bis-(diphenylphosphino)ferrocene (DPPF) and closed with a septum. The flask was evacuated and flushed with argon three times and the solids dissolved in 250 ml degassed DMF and 2.4 ml distilled water. In a 500 ml flame dried Schlenk flask 2.16 g (9.85 mmol, 0.04 eq.) zinc acetate dihydrate, 643 mg (9.85 mmol, 0.04 eq.) zinc powder, 460 mg (0.502 mmol, 0.002 eq.) tris(dibenzylideneacetone)dipalladium(0) and at last 40 g (344 mmol, 1.4 eq.) zinc cyanide were weighted in and the flask immediately sealed with a septum. The Schlenk flask was also evacuated and flushed with argon three times and 50 ml of degassed DMF was added. In the following, the previously prepared solution is transferred into the Schlenk flask using a cannula. The resulting mixture was stirred at 100 °C for 72 h. Afterwards the cooled, brown suspension was poured into a buffer solution consistent of 400 ml concentrated ammonia solution and 400 ml of saturated ammonium chloride solution. The brownish precipitate was filtered off and washed successively with the same amount of buffer and water. The remaining solid was then initially washed with 50 ml ethanol followed by three washing steps with 50 ml of toluene and twice with 30 ml with ethanol before being dried in vacuum at 50°C to yield 49 g (92%) of 9H-carbazole-3,6-dicarbonitrile.

Due to the high toxicity of zinc cyanide all surfaces and used glassware, equipment as well as remaining solutions were deactivated with an aqueous solution of 5% H$_2$O$_2$ containing ammonia. The solution had a pH-Value higher than 11. Solids were weighted-in a closed fume hood.

$^1$H NMR (500 MHz, DMSO-$d_6$) δ (ppm): 7.73 (d, $J$=8.51 Hz, 2 H) 7.86 (dd, $J$=8.51, 1.58 Hz, 2 H) 8.81 (d, $J$=1.58 Hz, 2 H) 12.39 (s, 1 H).

$^{13}$C NMR (151 MHz, DMSO-$d_6$) δ ppm 101.72 (s, 1 CH) 112.85 (s, 1 CH) 120.10 (s, 1 C) 121.84 (s, 1 C) 126.40 (s, 1 CH) 129.93 (s, 1 CH) 142.32 (s, 1 C).
ESI-TOF-HRMS (m/z): Calculated for [M+H]⁺: 218.071; found: 218.071 [M+H]⁺.

DRIFT, KBr, 298 K (cm⁻¹): 3300, 3057, 2857, 2815, 2635, 2479, 2224, 1891, 1872, 1799, 1758, 1740, 1635, 1602, 1484, 1457, 1405, 1299, 1285, 1259, 1239, 1226, 1203, 1191, 1134, 1021, 932, 908, 901, 814, 802, 743, 636, 589, 536

### 2.2.3 9H-Carbazole-3,6-dicarboxylic acid (c)

[Chemical structure image]

In a 2 l round bottom flask 50 g (230 mmol, 1.00 eq.) of nitrile 9H-carbazole-3,6-dicarbonitrile was suspended along with 500 mg (115 mmol, 0.5 eq.) CuI in 1 l distilled water. To this suspension 147 g (3.68 mol, 16.00 eq.) NaOH was slowly added, and the reaction mixture was stirred under reflux about at least 24 h. Afterwards the reaction mixture was cooled down to room temperature and filtered through Celite®. While stirring, the clear solution was acidified with concentrated hydrochloric acid until white precipitate was formed. The solid was filtered off at ambient pressure, washed thoroughly with water. Finally, the product was dried at 80 °C to yield 52 g (88%) white powder.

\(^1\)H NMR (500 MHz, DMSO-\(d_6\)) δ ppm 7.59 (d, \(J=8.51\) Hz, 2 H) 8.05 (dd, \(J=8.51, 1.58\) Hz, 2 H) 8.84 (d, \(J=1.58\) Hz, 2 H) 12.05 (s, 1 H) 12.67 (br. s, 2 H)

\(^{13}\)C NMR (126 MHz, DMSO-\(d_6\)) δ ppm 111.12 (s, 1 CH), 121.94 (s, 1 C) 122.24 (s, 1 C) 122.79 (s, 1 CH) 127.62 (s, 1 CH) 143.09 (s, 1 C) 167.90 (s, 1 C).

ESI-TOF-HRMS (m/z): Calculated for [M+H]⁺: 256.060; found: 256.060 [M+H]⁺.

DRIFT, KBr, 298 K (cm⁻¹): 3852, 3474, 2828, 2638, 1914, 1792, 1678, 1633, 1606, 1584, 1492, 1471, 1453, 1421, 1354, 1322, 1303, 1285, 1256, 1241, 1216, 1133, 1099, 1023, 929, 899, 839, 771, 726, 683, 648, 561, 548

### 2.2.4 Dibutyl 9H-carbazole-3,6-dicarboxylate (d)

[Chemical structure image]

A 2 l round bottom flask was charged with 40 g (157 mmol, 1.00 eq.) of H₂CDC, 717 ml (7.84 mol, 50.00 eq.) butanol and 1.67 ml (31.3 mmol, 0.20 eq.) H₂SO₄. The suspension was refluxed for 3 d, with further addition of 1.5 ml H₂SO₄ after 2 d, before the excess butanol was removed in vacuum. Hereafter, the off-white powder was dissolved in chloroform and extracted with 0.5 M potassium carbonate solution. The combined organic phases were dried over MgSO₄ and the solvent removed in vacuum to obtain 53 g (92%) white powder.

\(^1\)H NMR (500 MHz, DCM-\(d_2\)) δ ppm: 1.02 (t, \(J=7.41\) Hz, 6 H) 1.50 – 1.58 (m, 4 H) 1.78 – 1.85 (m, 4 H) 4.37 (t, \(J=6.62\) Hz, 4 H) 7.52 (dd, \(J=8.51, 0.63\) Hz, 2 H) 8.16 (dd, \(J=8.51, 1.60\) Hz, 2 H) 8.82 (br. s., 1 H) 8.85 – 8.88 (m, 2 H).

\(^{13}\)C-NMR (126 MHz, DMSO-\(d_6\)): δ (ppm): 14.16 (1 CH₃), 19.94 (1 CH₃), 31.49 (1 CH₃), 65.29 (1 CH₃), 111.19 (1 CH), 123.29 (1 CH), 123.37 (1 C), 123.57 (1 CH), 128.49 (1 CH), 143.36 (1 C), 167.53 (1 C).

ESI-TOF-HRMS (m/z): Calculated for [M+H]⁺: 268.186; found: 268.186 [M+H]⁺.

DRIFT, KBr, 298 K (cm⁻¹): 3270, 3187, 3042, 2961, 2934, 2896, 2873, 1911, 1888, 1810, 1705, 1692, 1629, 1602, 1589, 1498, 1492, 1476, 1461, 1392, 1379, 1346, 1308, 1292, 1282, 1262, 1235, 1219, 1136, 1121, 1110, 1091, 1024, 978, 944, 906, 836, 818, 771, 729, 654, 636, 507
2.2.5  **Tetrabutyl 9,9'-(9-oxo-9H-fluorene-2,7-diyl)bis(9H-carbazole-3,6-dicarboxylate)** (e)

In a 250 ml flask 2 g (5.92 mmol, 1.00 eq.) 2,7-dibromo-9H-fluoren-9-one, 6.52 g (17.75 mmol, 3.00 eq.) H$_2$CDC, 1.5 g (23.67 mmol, 4.00 eq.) copper powder and 6.54 g (47.34 mmol, 8.00 eq.) K$_2$CO$_3$ was weighted in and the flask was evacuated and flushed with argon three times. Afterwards 100 ml degassed 1,2-dichlorobenzene along with 313 mg (1.18 mmol, 0.20 eq.) 18-crown-6 was added, and the reaction mixture stirred at 180 °C for 57 h. The reaction was cooled down to room temperature and, while stirring 50 ml, 0.5 M HCl solution added. Phases were separated and the aqueous phase was extracted three times with 100 ml chloroform. The combined organic phases were dried over MgSO$_4$ and the solvent removed in vacuum. The crude product was dissolved in a mixture of dichloromethane/isohexane (1:1) on a rotary evaporator at 50 °C and then cooled down while further rotation. The white precipitate (1.55 g, 4.22 mmol) was filtered off, dried, and found to be re-isolated CDBE. The remaining solution was evaporated and purified by column chromatography (dichloromethane/isohexane/EtOAc; 3:1:0.2) to obtain 3.17 g (59%) of pure yellow to orange powder.

$^1$H NMR (500 MHz, DCM-$d_2$) δ (ppm): 1.03 (t, $J$=7.41 Hz, 12 H) 1.50 - 1.61 (m, 8 H) 1.79 - 1.87 (m, 8 H) 4.39 (t, $J$=6.62 Hz, 8 H) 7.49 (d, $J$=8.61 Hz, 4 H) 7.82 (dd, $J$=7.88, 1.89 Hz, 2 H) 7.94 (d, $J$=1.89 Hz, 2 H) 7.98 (d, $J$=7.88 Hz, 2 H) 8.20 (dd, $J$=8.61, 1.73 Hz, 4 H) 8.96 (d, $J$=1.73 Hz, 4 H).

$^{13}$C-NMR (126 MHz, DMSO-$d_6$): δ (in ppm): 14.17 (1 CH$_3$), 19.95 (1 CH$_3$), 31.48 (1 CH$_3$), 65.40 (1 CH$_3$), 110.31 (1 CH), 123.08 (1 CH), 123.49 (1 CH), 123.66 (1 CH), 123.94 (1 C), 124.29 (1 C), 128.79 (1 CH), 134.00 (1 CH), 136.94 (1 C), 138.36 (1 C), 143.81 (1 C), 144.38 (1 C), 167.24 (1 C); 191.63 (1 C).

ESI-TOF-HRMS (m/z): Calculated for [M-H]-: 955.381; found: [M-H]-: 955.340.

DRIFT, KBr, 298 K (cm$^{-1}$): 3070, 2959, 2934, 2873, 1715, 1630, 1600, 1486, 1448, 1388, 1365, 1340, 1304, 1292, 1260, 1242, 1218, 1115, 1101, 1082, 1026, 974, 940, 902, 827, 790, 767, 737, 723, 706, 666, 641, 596, 534

2.2.6  **9,9'-(9-Oxo-9H-fluorene-2,7-diyl)bis(9H-carbazole-3,6-dicarboxylic acid)** (f)

In a 100 ml round bottom flask 1 g (1.09 mmol, 1.0 eq.) FBCDBE was suspended in a mixture of 45 ml THF, 2 ml H$_2$O and 4.5 ml MeOH. To this suspension 1 g (17.56 mmol, 16.0 eq.) KOH was added, and the reaction mixture refluxed for 48 h until the solid is completely dissolved and the solution becomes yellow. After completion of the reaction the THF and the MeOH was removed in vacuum and 25 ml of deionized water was added. The resulting solution was acidified with 6 M HCl to a pH of around 3. The precipitate was filtered and washed several times with deionized water. The wet product was washed two time with 5 ml EtOH and dried in an oven at 80 °C to yield 0.73 g (96%) of an intensive dark red powder.

$^1$H NMR (500 MHz, DCM-$d_2$) δ (ppm): 1.03 (t, $J$=7.41 Hz, 12 H) 1.50 - 1.61 (m, 8 H) 1.79 - 1.87 (m, 8 H) 4.39 (t, $J$=6.62 Hz, 8 H) 7.49 (d, $J$=8.61 Hz, 4 H) 7.82 (dd, $J$=7.88, 1.89 Hz, 2 H) 7.94 (d, $J$=1.89 Hz, 2 H) 7.98 (d, $J$=7.88 Hz, 2 H) 8.20 (dd, $J$=8.61, 1.73 Hz, 4 H) 8.96 (d, $J$=1.73 Hz, 4 H).
$^{13}$C-NMR (126 MHz, DMSO-$d_6$): $\delta$ (in ppm): 14.17 (1 CH$_3$), 19.95 (1 CH$_2$), 31.48 (1 CH$_2$), 65.40 (1 CH$_3$), 110.31 (1 CH), 123.08 (1 CH), 123.49 (1 CH), 123.66 (1 CH), 123.94 (1 C), 124.29 (1 C), 128.79 (1 CH), 134.00 (1 CH), 136.94 (1 C), 138.36 (1 C), 143.81 (1 C), 144.38 (1 C), 167.24 (1 C); 191.63 (1 C).

ESI-TOF-HRMS (m/z): Calculated for [M+HCOO]-: 685.125; found: [M+HCOO]-: 685.104.

DRIFT, KBr, 298 K (cm$^{-1}$): 3073, 2641, 2552, 1906, 1695, 1630, 1602, 1482, 1447, 1421, 1359, 1340, 1291, 1259, 1238, 1200, 1139, 1114, 1027, 992, 925, 906, 826, 786, 767, 739, 724, 713, 643, 596.
3 Synthesis, and Characterisation of Metal-Organic Frameworks

3.1 Synthesis of MOF single crystals

The synthesis of single crystals for single crystal X-ray diffraction analysis of op-phases and metal exchange experiments was carried out in Pyrex tubes. Prior to heating in an oven for 5 - 7 days at 80 °C, the reaction mixture was prepared under inert atmosphere as for the powder in a round bottom flask. The previously prepared solution was then divided in several preheated tubes to prevent precipitation and all tubes were closed properly. DUT-140(Cu)

100 mg (0.15 mmol, 1.00 eq.) of FBCDC linker was dissolved in 40 ml of DMF and 4 ml acetic acid was added. This mixture was combined with a solution of 88 mg (0.36 mmol, 2.50 eq.) copper nitrate trihydrate dissolved in 2 ml DMF. The mixture was divided between five 10 ml tubes and stored in an oven at 80 °C for 7 days. After completion of the synthesis the obtained product was washed three times with 10 ml pure DMF.

3.1.1 DUT-140(Co)

100 mg (0.15 mmol, 1.00 eq.) of fluorenone linker was dissolved in 75 ml NMP. To this a solution of 106 mg (0.37 mmol, 2.50 eq.) Cobalt nitrate hexahydrate in 5 ml NMP was added. The reaction mixture was distributed over ten 10 ml Pyrex tubes and heated to 80 °C in an oven for 5 days. Subsequently, the obtained brownish crystals were washed three times with 10 ml of pure NMP.

3.2 Desolvation of microcrystalline MOF powder

After the synthesis and the washing procedure the metal-organic framework was desolvated for in-situ and ex-situ adsorption measurements. For the activation of DUT-140(Cu) the solvent was first replaced by dry acetone during several washing cycles and the material was dried by using supercritical drying technique using CO$_2$. Therefore, the suspended material was transferred to glass filters and placed in a Jumbo Critical Point Dryer 13200J AB (SPI Supplies). The autoclave was then filled with liquid CO$_2$ at 17 °C and around 60 bar. By opening the valve situated at the bottom of the autoclave the remaining acetone was removed while fresh liquid CO$_2$ was refilled from the top of the autoclave. This procedure was repeated two times per day over five days until no acetone traces were observed in the dry ice at the outlet. In the following step, all valves of the autoclave were closed, and the temperature increased to 37 °C in order to convert the CO$_2$ in supercritical state. The pressure in the autoclave was maintained at 110 bar during heat up. After equilibrating of the system 37 °C for one hour, the supercritical CO$_2$ was slowly released through the bottom valve. The autoclave was opened as far as the pressure was reduced to ambient pressure and the dried material directly brought into an argon filled glovebox. Each further handling was carried out exclusively under inert atmosphere. Subsequently for supercritical drying the material was additionally treated by heating up to 80 °C in dynamic vacuum in order to remove remaining guest molecules from the pores.
3.3 Characterisation of Metal-Organic Frameworks

3.3.1 Powder X-ray Diffraction

3.3.1.1 DUT-140(Cu)

Figure S2: X-ray powder diffraction patterns of DUT-140(Cu).

3.3.1.2 DUT-140(Co)

Figure S3: X-ray powder diffraction patterns of DUT-140( Co).

3.3.1.3 DUT-140(Zn)
Single crystals of DUT-140(Cu), DUT-140(Co), or DUT-140(Zn) were prepared in a borosilicate glass capillary (d = 0.3 mm) with small amount of the mother liqueur. The capillaries were sealed with wax from both sides in order to avoid evaporation. The datasets were collected at BESSY MX BL14.3 beamline of Helmholtz-Zentrum Berlin für Materialien und Energie at 298 K. After short test scans, the crystal symmetry and scan range were determined in each particular case using iMosflm program. The φ-scans with oscillation step of 0.5° were used for data collection. All datasets were processed automatically using XDSAPP 2.0 software. Crystal structures were solved by direct methods and refined by full matrix least-squares on $F^2$ using SHELX-2018/3 program package. All non-hydrogen atoms were refined in anisotropic approximation. Hydrogen atoms were refined in geometrically calculated positions using “riding model” with $U_{iso}(H)=1.2U_{iso}(C)$. In all structures, 2,7-fluorenone backbone is disordered over four positions, which were refined with corresponding reduced occupancies. Few restraints were used to fix the geometry and anisotropic parameters of the disordered fluorenone moiety. Disordered guest molecules could not be refined unambiguously from the difference Fourier map, hence, SQUEEZE routine in PLATON was used to generate the reflection intensities with subtracted solvent contribution.

Table S2. Experimental data on single crystal X-ray diffraction for as made phases of DUT-140(Cu), DUT-140(Co), and DUT-140(Zn).

|                         | DUT-140(Cu) | DUT-140(Co) | DUT-140(Zn) |
|-------------------------|-------------|-------------|-------------|
| Empirical formula       | $C_{41}H_{18}Cu_2N_2O_9$·2H$_2$O | $C_{41}H_{18}Co_2N_2O_9$·2H$_2$O | $C_{41}H_{18}Zn_2N_2O_9$·2H$_2$O |
| Formula weight, g mol$^{-1}$ | 841.65 | 832.43 | 845.31 |
| Crystal system, space group | cubic, $Fm\bar{3}m$ | cubic, $Fm\bar{3}m$ | cubic, $Fm\bar{3}m$ |
| Unit cell dimensions, Å  | $a = 46.140(5)$ | $a = 46.520(5)$ | $a = 46.470(5)$ |
| Unit cell volume, Å$^3$  | 98227(34) | 100674(35) | 100350(35) |
| $Z$                      | 24 | 24 | 24 |
| Calculated density, g cm$^{-3}$ | 0.341 | 0.330 | 0.336 |
| Temperature, K           | 293 | 293 | 293 |
| Wavelength, Å            | 0.895 | 0.895 | 0.895 |
| $\mu$, mm$^{-1}$         | 0.511 | 0.394 | 0.558 |
| $F(000)$                 | 10176 (after SQUEEZE) | 10224 (after SQUEEZE) | 10224 (after SQUEEZE) |
| $\Theta$ range, °        | 0.963 – 33.993 (SQUEEZE) | 0.955 – 32.173 | 0.956 – 32.188 |
| Limiting indices         | -57 ≤ h ≤ 56 | -44 ≤ h ≤ 45 | -42 ≤ h ≤ 46 |
|                         | -57 ≤ k ≤ 57 | -50 ≤ k ≤ 51 | -51 ≤ k ≤ 49 |
| Reflections collected / unique | 159256 / 4827 | 100674(35) | 45651 / 4050 |
| $R_{int}$                | 0.0891 | 0.0441 | 0.0319 |
| Data / parameters        | 4827 / 145 | 4080 / 142 | 4050 / 142 |
| GooF on $F^2$            | 1.147 | 1.932 | 1.138 |
| Final $R$ indices        | $R_1 = 0.0809/ wR_2 = 0.2426$ | $R_1 = 0.1445/ wR_2 = 0.3768$ | $R_1 = 0.0787/ wR_2 = 0.2415$ |
| [$l>2\sigma(l)$]         | $R_1 = 0.1070/ wR_2 = 0.2888$ | $R_1 = 0.1778/ wR_2 = 0.4208$ | $R_1 = 0.0922/ wR_2 = 0.2698$ |
| $wR$ indices (all data)  | $R_1 = 0.0809/ wR_2 = 0.2426$ | $R_1 = 0.1445/ wR_2 = 0.3768$ | $R_1 = 0.0787/ wR_2 = 0.2415$ |
Largest diff. peak / hole, eÅ³

1.603 / -0.443
2.296 / -1.755
1.217 / -0.286

3.3.3 Thermogravimetric analysis of desolvated DUT-140(Cu)

3.3.4 Elemental analysis of DUT-140(Cu)

C₄₁H₂₂N₂O₉Cu₂: Calculated: C: 60.52%, H: 2.73%, N: 3.44%
Found: C: 59.50%, H: 2.30%, N: 3.30%

3.3.5 Scanning electron microscopy and crystal size distribution of DUT-140(Cu)

Figure S5: TG/TDG curve of activated DUT-140(Cu) in argon atmosphere.

Figure S6: SEM images of DUT-140(Cu) and particle size distribution determined from the images.
3.3.6 Energy dispersive X-ray spectroscopy

3.3.7 Pore size distribution in DUT-140(Cu)$^{10,11}$
### 3.3.8 Adsorption isotherms of DUT-140(Cu)

#### Figure S9: Nitrogen physisorption isotherm of DUT-140(Cu) at 77 K. Inset: The same isotherm in semi-logarithmic scale.

#### Figure S10: Methane physisorption of DUT-140(Cu) at 111 K.
3.4 Representation of single pores with surrounding linker molecules

3.5 $\pi \rightarrow \pi^*$ Excitation

Figure S 1: Molecular orbitals involved in the $\pi \rightarrow \pi^*$ excitation.
3.6  
**In situ-PXRD investigations**

### 3.6.1 Experimental details

*In situ* PXRD and gas adsorption were measured at KMC-2 beamline of the BESSY II synchrotron, operated by Helmholtz-Zentrum Berlin für Materialien und Energie. Self-designed automated instrumentation, based on the volumetric adsorption instrument and closed-cycle Helium cryostat, equipped with adsorption chamber with beryllium domes was used in all experiments. PXRD patterns were measured at constant wavelength $\lambda = 0.15406$ nm ($E = 8048$ eV) in transmission geometry. The measurements were performed in the static mode using the sample with particle size ranging between 0.2 and 14.4 $\mu$m. The use of an area 2D detector (VANTEC 2000, Bruker) allowed to record diffraction images with reasonable particle statistics. Each 2D image was measured with 31 s exposure. For each experiment 10-12 mg of sample were used. In order to blend the reflections coming from the crystalline Be-dome, tungsten slits with 5 mm aperture were mounted on the detector cone. The obtained diffraction images were integrated using DATASQUEEZE 2.2.9 with further processing in FITYK 0.9 software. For all automated measurements the physisorption isotherms were measured using equilibrium settings for pressure change of 0.1% within 300 s.

### 3.6.2 Le Bail fit and Rietveld refinement of PXRD data

*In situ* PXRD patterns, measured during the adsorption of methane at 111 K on DUT-140(Cu) were indexed and PXRD profile was refined using Le Bail fit, implemented into the FullProf software. The evolution of the unit cell volume during adsorption of fluids on above mentioned MOFs is given in Fig. 3f.

PXRD patterns measured on DUT-140(Cu) upon adsorption of methane at 111 K at 22 kPa was used for the refinement of the crystal structure of the cp phase. Indexing of the PXRD patterns reveals the cubic cell $(Pa\overline{3})$ space group, however, the profile refinement shows the unsatisfying fit, which is the indication of the symmetry breaking. Therefore, the symmetry was reduced from cubic to orthorhombic symmetry and $Pbca$ space group was used for further refinements. The refinement was performed using Reflex tool of Materials Studio 5.0. Rietveld refinement with energy (contribution of UFF ~1%) was used rigid bodies were defined in order to increase the data / parameter ratio. Thus, copper paddlewheels, carbazole and fluorenone moieties were defined as rigid bodies. Since guest molecules significantly contribute to the intensities, 56 methane molecules were added in the pores and refined as rigid bodies. Since some minor impurity of op phase is still present in the PXRD, the 2θ range of 2 - 4° was omitted from the refinement.

Experimental data on DUT-140(Cu)$_{cp}$: $C_{41}H_{18}Cu_2N_2O_9\cdot19CH_4$, orthorhombic, $Pbca$ ($N 61$), $a = 35.8513(11)$ Å, $b = 36.1453(13)$ Å, $c = 35.9773(10)$ Å, $V = 46621.4$ Å$^3$, $Z = 24$, 2θ range 4 - 35°, zero point shift = 0, profile function Thompson-Cox-Hastings: $U = 0.02399$, $V = 0.00081$, $W = 0.00368$, $X = 0.07146$, $Y = 0.03110$, Asymmetry correction function Berar-Baldinozzi: $P_1 = 0.00855$, $P_2 = 0.00240$, $P_3 = 0.00654$, $P_4 = 0.00096$, $Rwp = 0.2455$, $Rp = 0.1869$.

The Rietveld plots are given in Fig. S14.
Figure S2: Rietveld plot for DUT-140(Cu)$_{cp}$. 
4 Computational methods

The mechanical response of the ligand comprising DUT-140 was investigated using a semiempirical quantum mechanical approach, namely GFN2-xtb.\textsuperscript{18} The structure for the corresponding acid of the ligand was optimised using ‘very tight’ optimisation thresholds. Subsequently, the response of this optimised structure was simulated by applying a series of constrained optimisation for decreasing length of N-N distance, from 10 Å to 9 Å in 100 steps. The stress was then calculated from this atom-atom distance scan as described previously.\textsuperscript{19}

UV/Vis absorption was simulated using density functional theory (DFT) and time-dependent DFT (TD-DFT) as employed in the ORCA quantum chemistry program package.\textsuperscript{20} The ligand was optimised at the RIJCOSX-B3LYP-D3(BJ)/cc-pVDZ level of theory\textsuperscript{20–25} with no constraints and an atom-atom distance constraint of 9.35712 Å to produce optimised structures of the ‘straight’ and ‘bent’ conformations. Excited states for these two conformers were examined at the same level of theory using the ‘%tddft’ block. A Davidson expansion space of 5 was used and 50 roots or transitions were calculated, in addition the Tamm-Dancoff approximation was applied.\textsuperscript{24} The resulting UV-VIS spectra were plotted using the ‘orca_mapspc’ program.
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