
Flux-mediated ligand exchange restructures metal–organic framework glasses

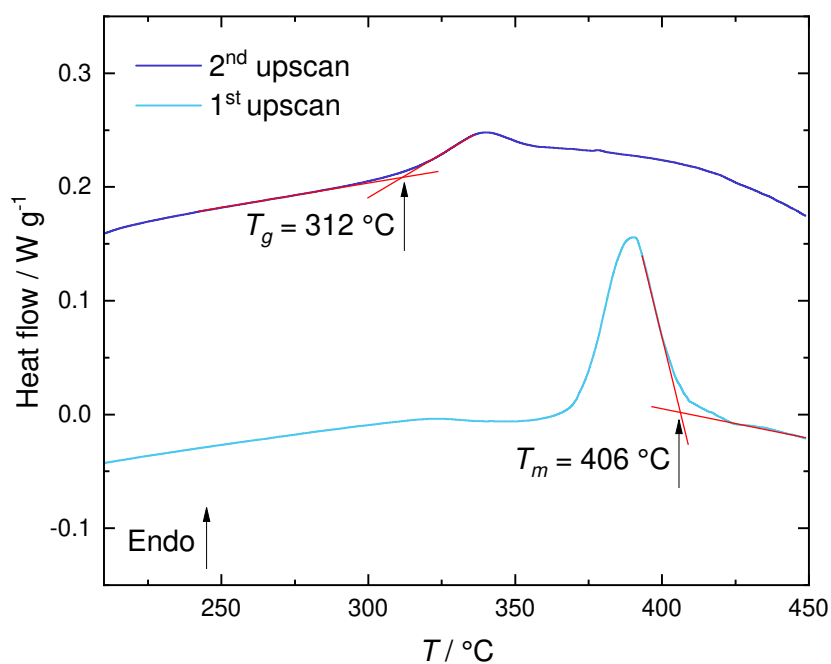
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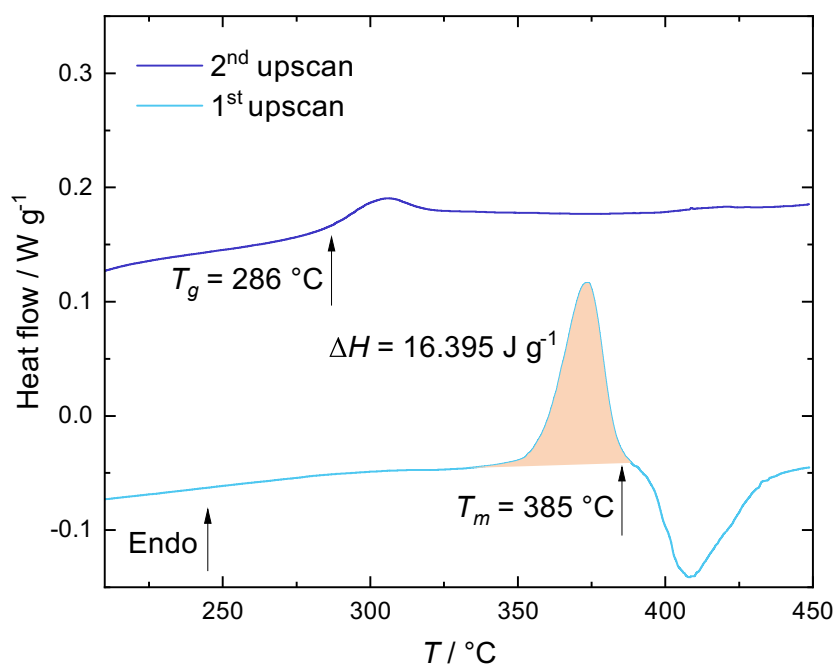
Supplementary Notes 1 – Determination of glass transition and melting temperatures

Glass transition temperatures (T_g) were determined as the intersection point of two tangents fitted to the DSC endotherm before and during the heat capacity increase associated with the transition. Melting points (T_m) were determined as the intersection of two tangents fitted to the peak offset of the corresponding melting endotherm (Supplementary Fig. 1).

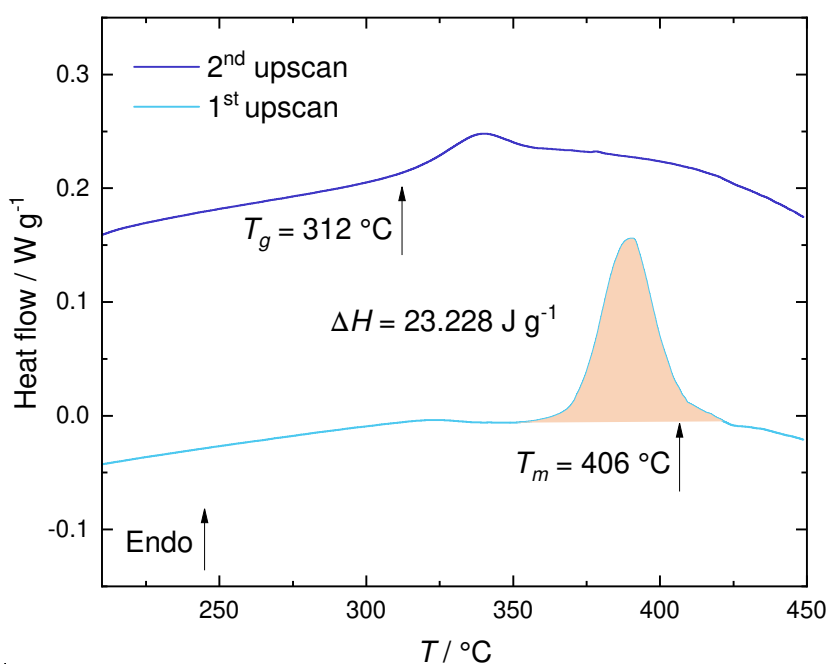


Supplementary Figure 1. Determination of T_g and T_m using the DSC thermogram of ZIF-62(Co) as an example.

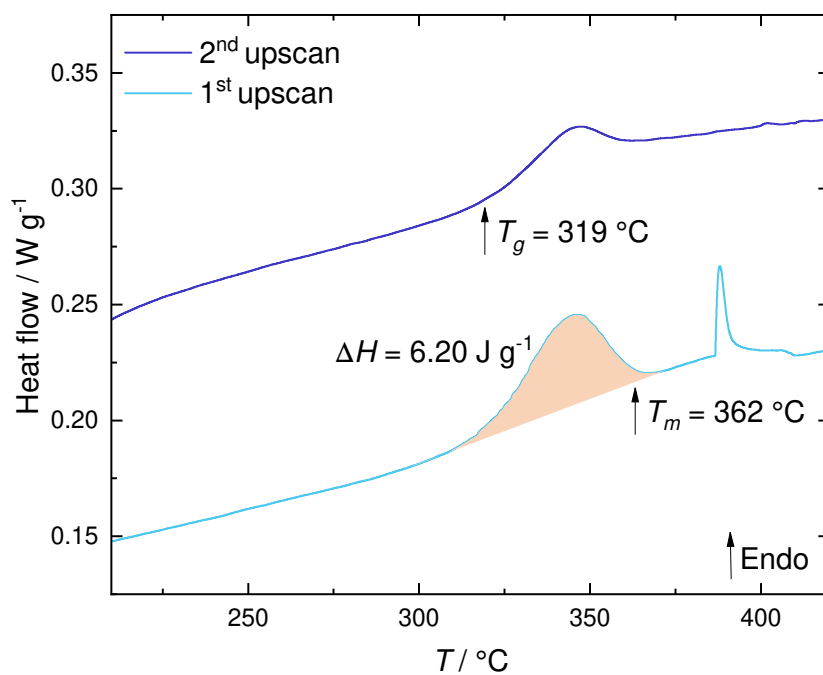
Supplementary Methods 1 – Differential scanning calorimetry



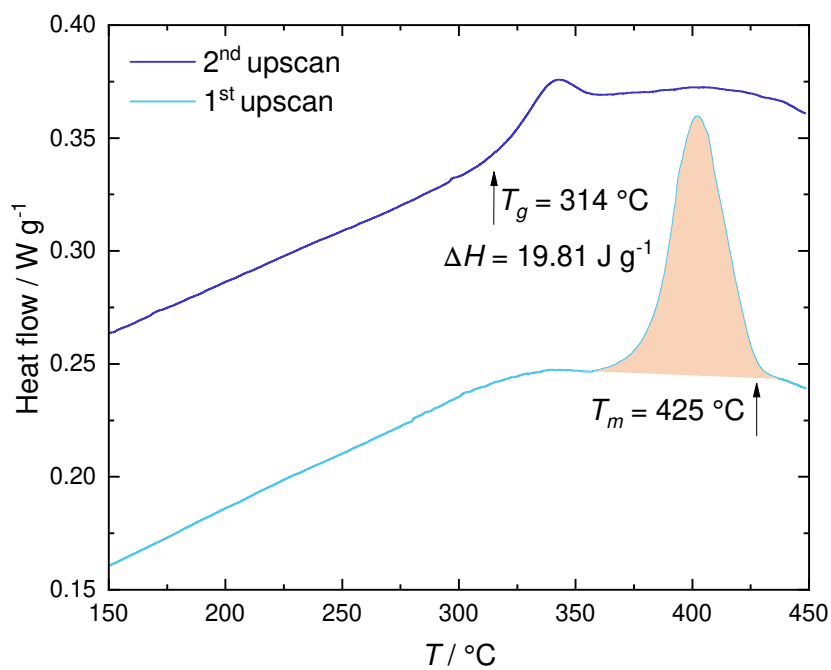
Supplementary Figure 2. DSC traces of ZIF-62(Co) in a sealed crucible.



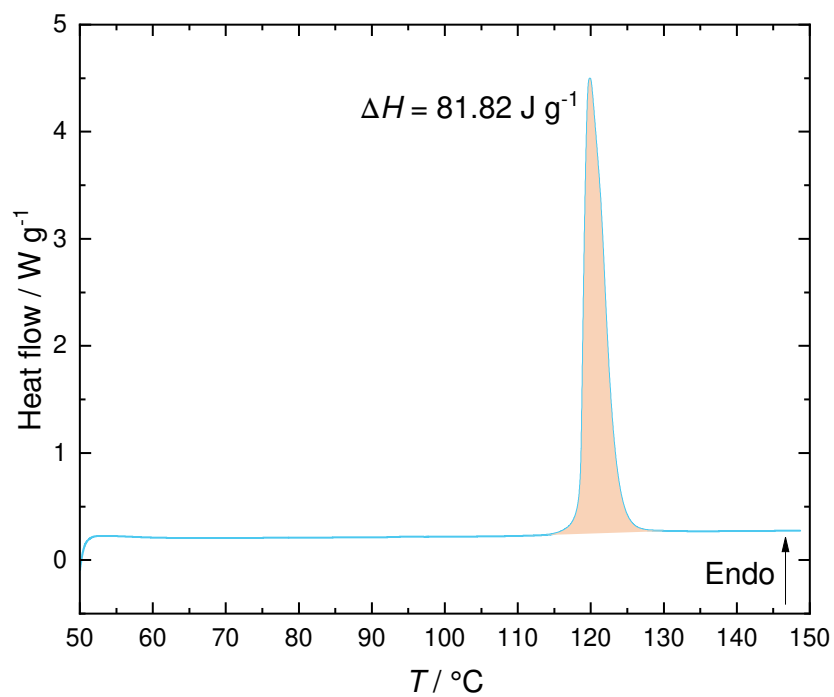
Supplementary Figure 3. DSC traces of ZIF-62(Co) in an open crucible.



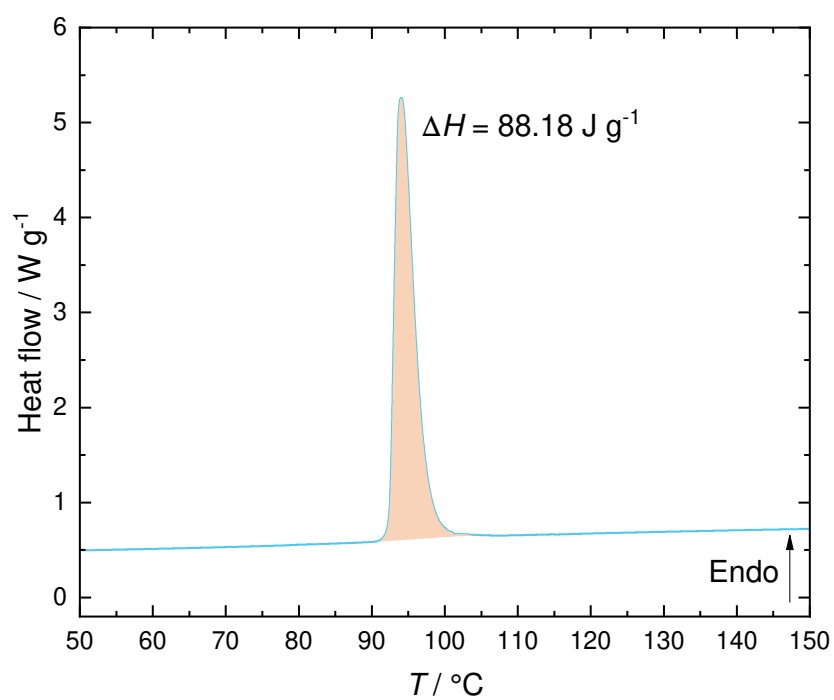
Supplementary Figure 4. DSC traces of ZIF-62(Zn) in a sealed crucible.



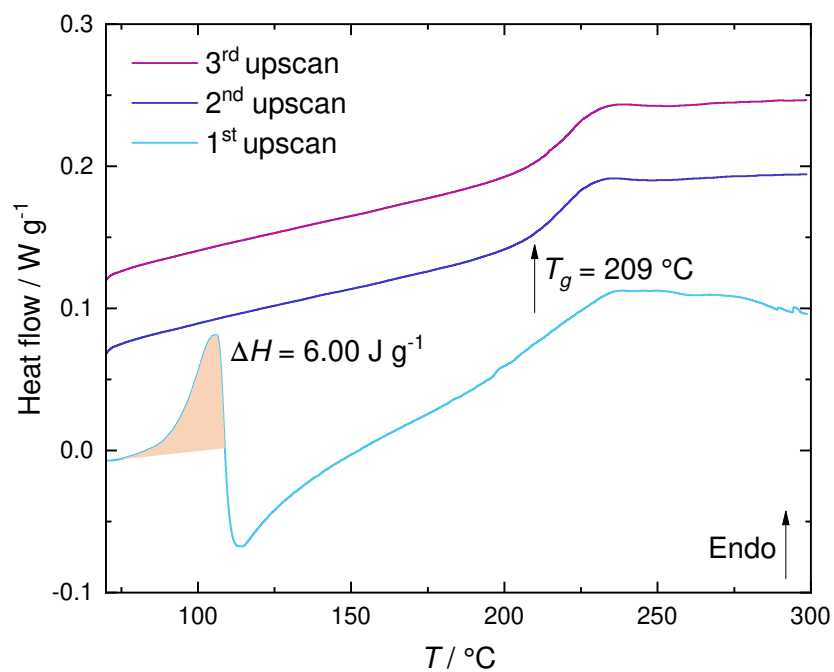
Supplementary Figure 5. DSC traces of ZIF-62(Zn) in an open crucible.



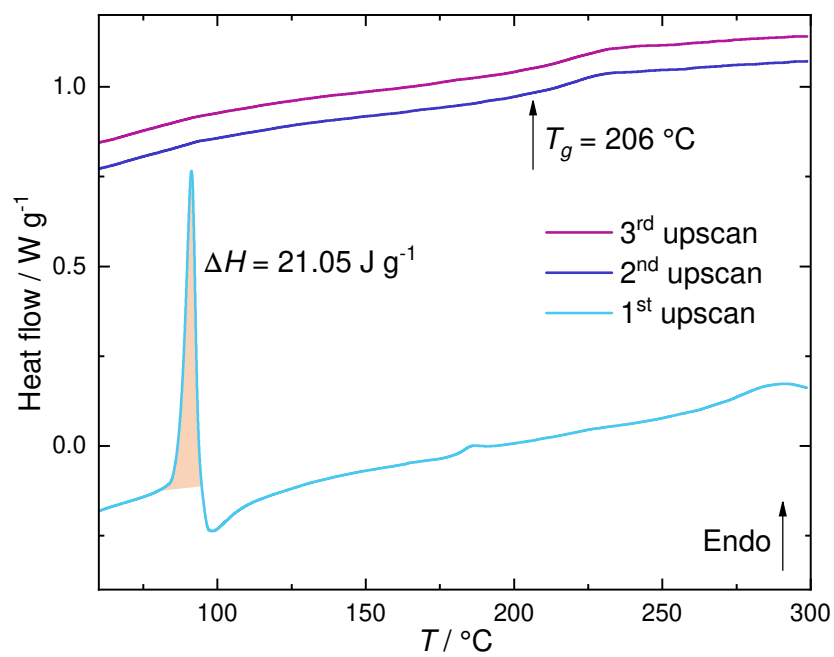
Supplementary Figure 6. DSC traces of 1,10-phenanthroline anhydrate.



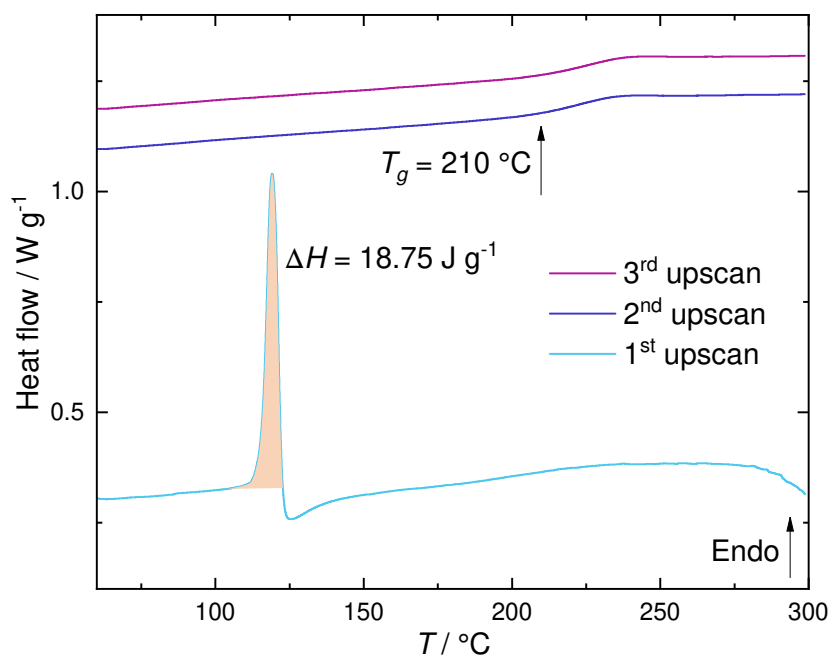
Supplementary Figure 7. DSC traces of 1,10-phenanthroline monohydrate.



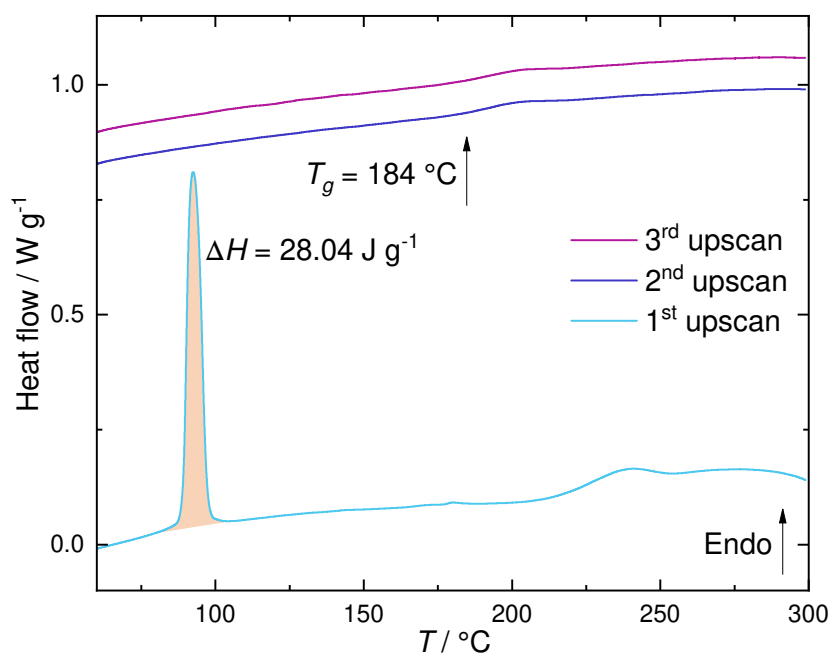
Supplementary Figure 8. DSC traces of phen_{0.49}ZIF-62(Co) prepared by ball-milling.



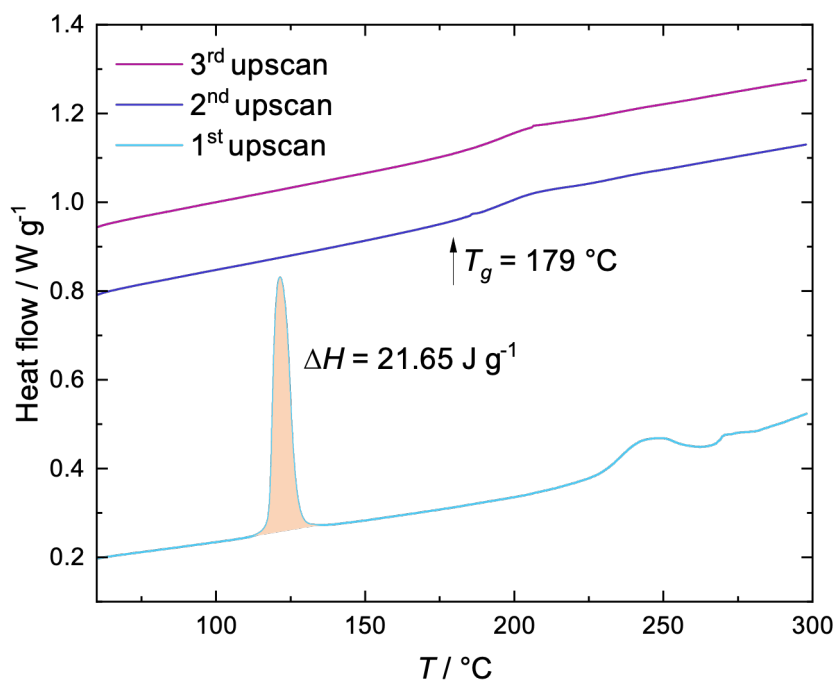
Supplementary Figure 9. DSC traces of phen_{0.49}ZIF-62(Co) prepared under ambient conditions.



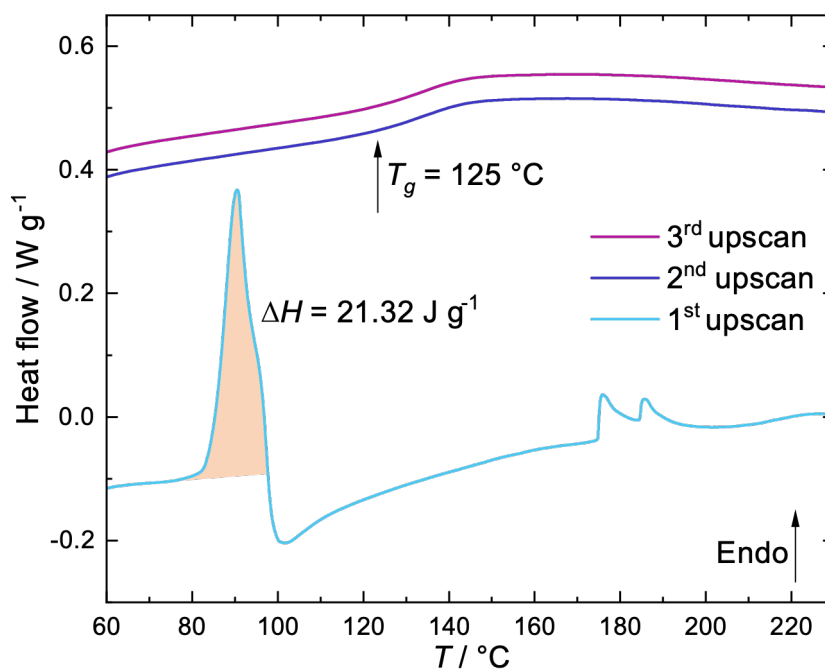
Supplementary Figure 10. DSC traces of phen_{0.49}|ZIF-62(Co) prepared under moisture-free conditions.



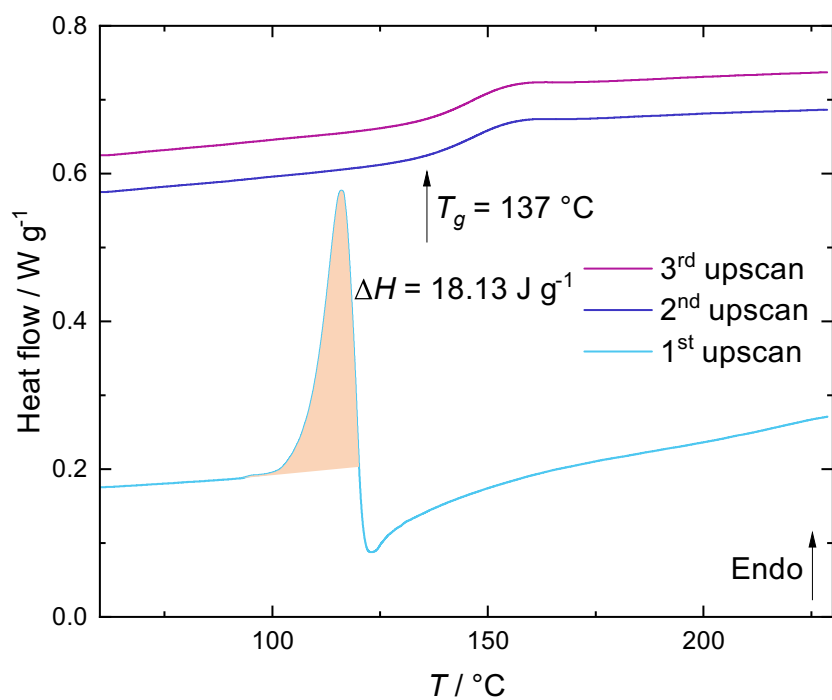
Supplementary Figure 11. DSC traces of phen_{0.51}|ZIF-62(Zn).



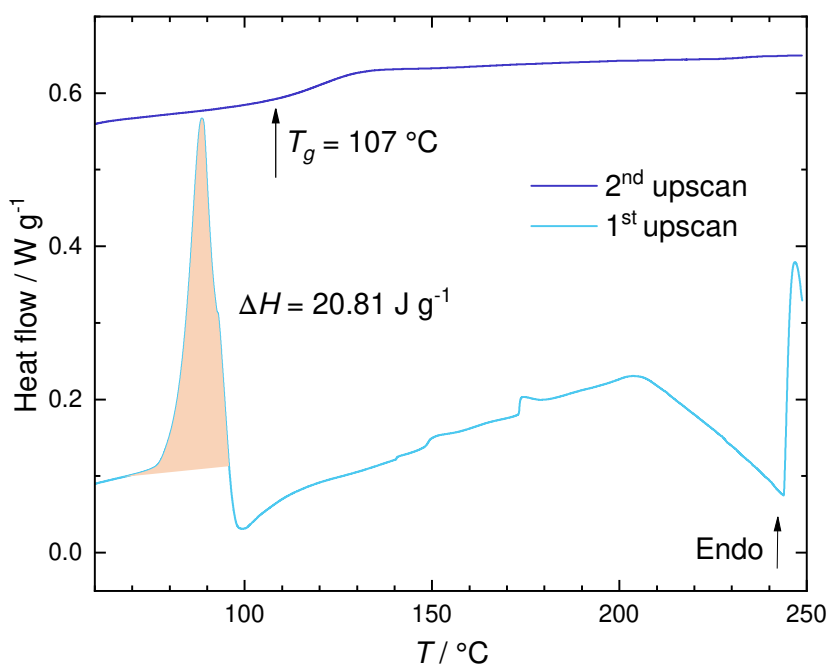
Supplementary Figure 12. DSC traces of phen_{0.51}|ZIF-62(Zn) prepared under moisture-free conditions.



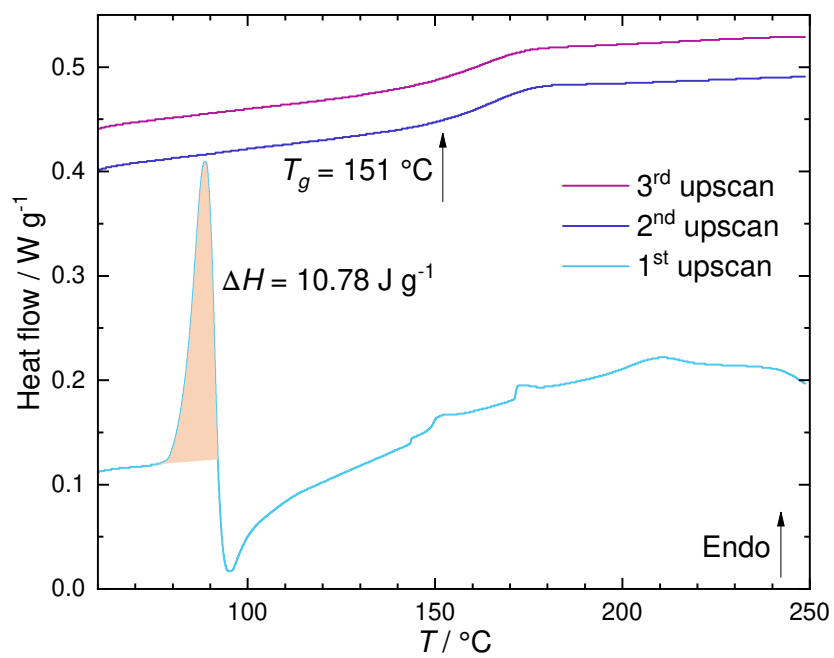
Supplementary Figure 13. DSC traces of phen_{1.33}|ZIF-12 prepared under ambient conditions.



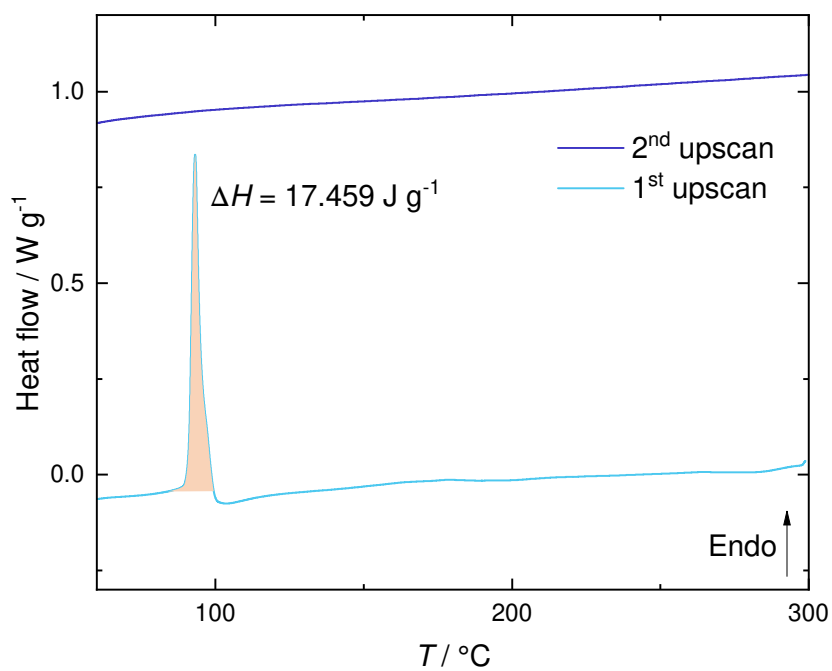
Supplementary Figure 14. DSC traces of phen_{1.33}[ZIF-12 prepared under moisture-free conditions.



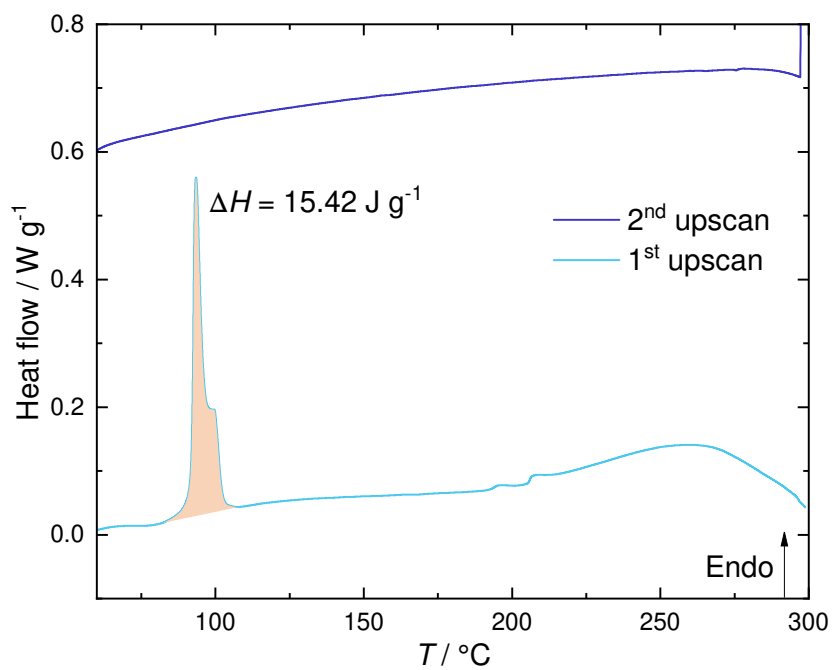
Supplementary Figure 15. DSC traces of phen_{0.31}[ZIF-12.



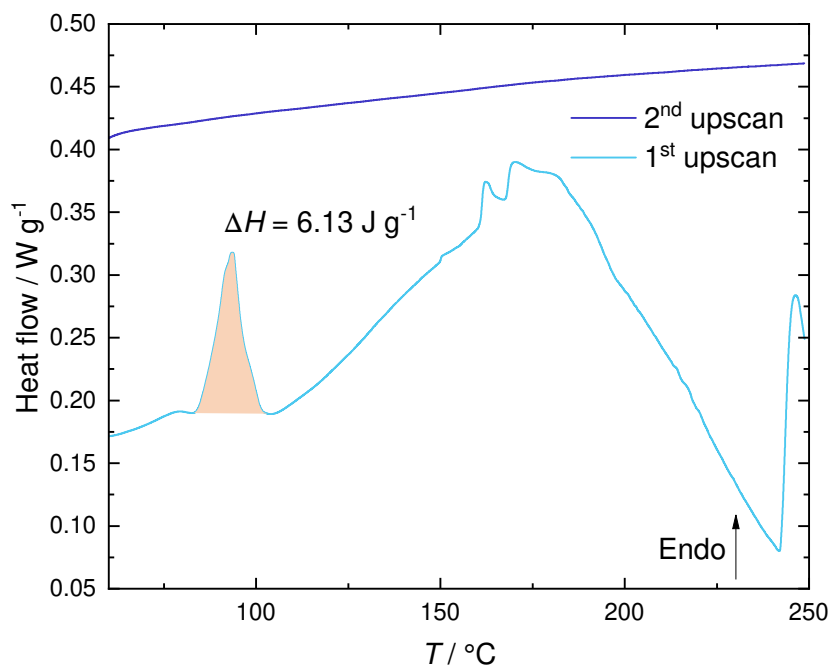
Supplementary Figure 16. DSC traces of phen_{1.00}|ZIF-12.



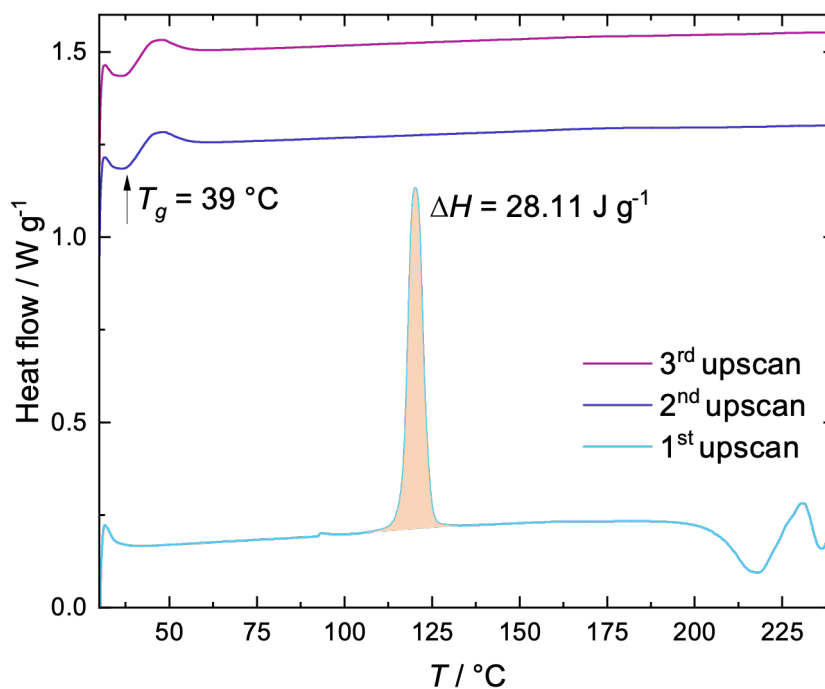
Supplementary Figure 17. DSC traces of phen_{0.29}|ZIF-11.



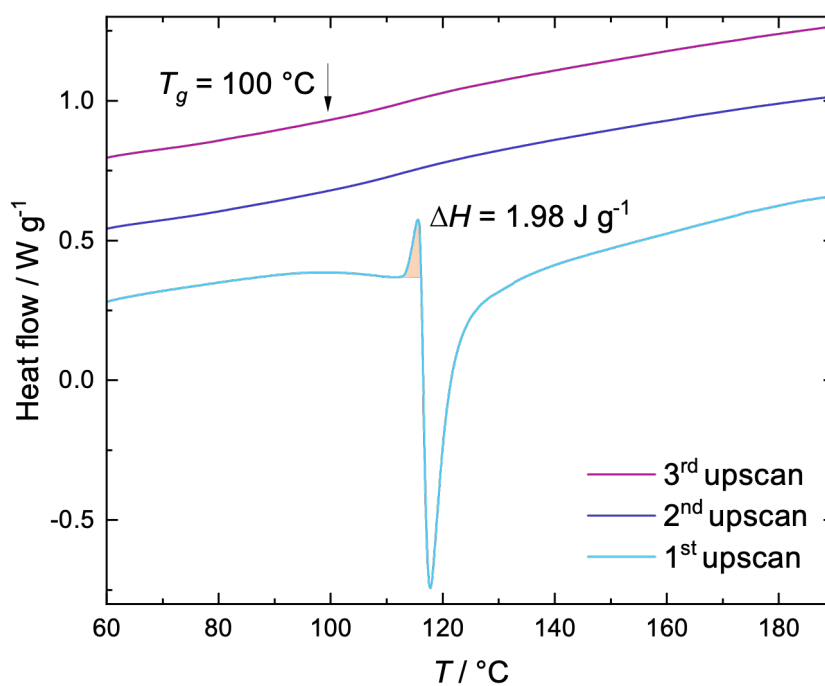
Supplementary Figure 18. DSC traces of phen_{0.49}|ZIF-8.



Supplementary Figure 19. DSC traces of phen_{0.47}|ZIF-67.



Supplementary Figure 20. DSC traces of phen_{0.5}[Cu(im)₂] prepared under moisture-free conditions.



Supplementary Figure 21. DSC traces of phen₆[Cu₃(btc)₂] prepared under moisture-free conditions.

Supplementary Methods 2 – Modulated differential scanning calorimetry

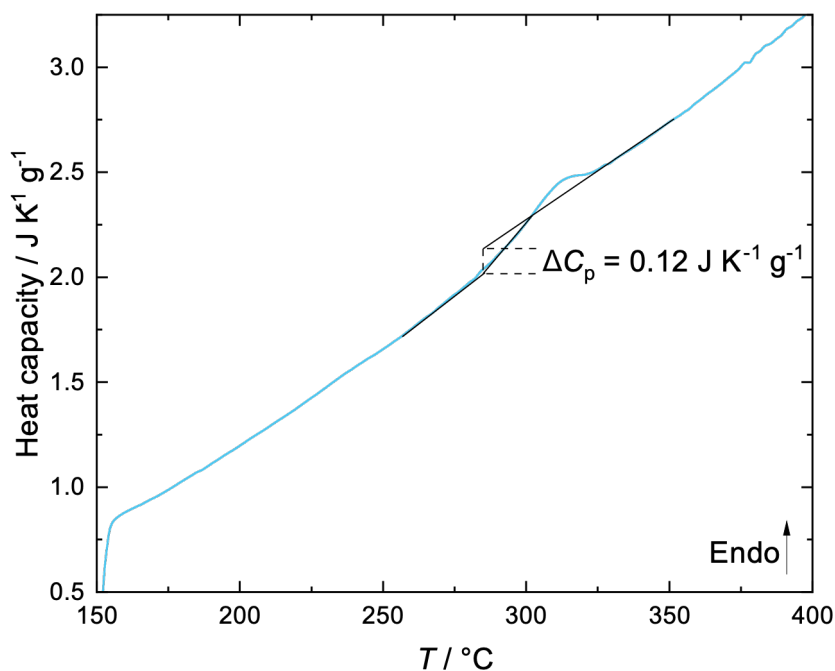
To determine heat capacity changes at the glass transition (ΔC_p), modulated DSC measurements were performed. The absolute C_p values of these measurements are not reliable due to small variations in the masses of the aluminium pans, but this does not affect the relative ΔC_p values.

The ΔC_p values were determined with the following procedure: Two tangents along the baseline (before and after the glass transition) were chosen. At the intersection of the baseline tangent after the glass transition and the heat capacity curve, a third tangent was set. At the intersection of this third and the baseline tangent before the glass transition, ΔC_p was determined as the difference in C_p between the two baseline tangents.

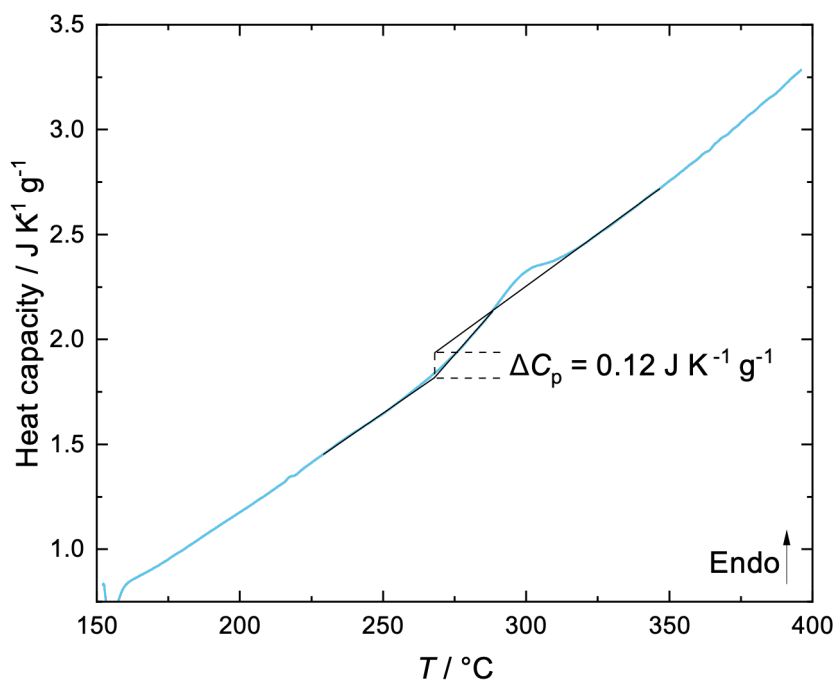
In the case of $gphen_{0.51}ZIF-62(Zn)$, melting of phen is observed in the mDSC measurement. This is suspected to be a consequence of the low heating rate (2 K min^{-1}) compared to the normal DSC measurement in which no melting of phen is observed. The low heating rate likely allows for the cold crystallization of phen upon reheating, so that melting of phen is observed around $110\text{ }^{\circ}\text{C}$.

Supplementary Table 1. Heat capacity changes ΔC_p at the glass transition determined by mDSC. The molar heat capacities are referenced per mole of metal ions.

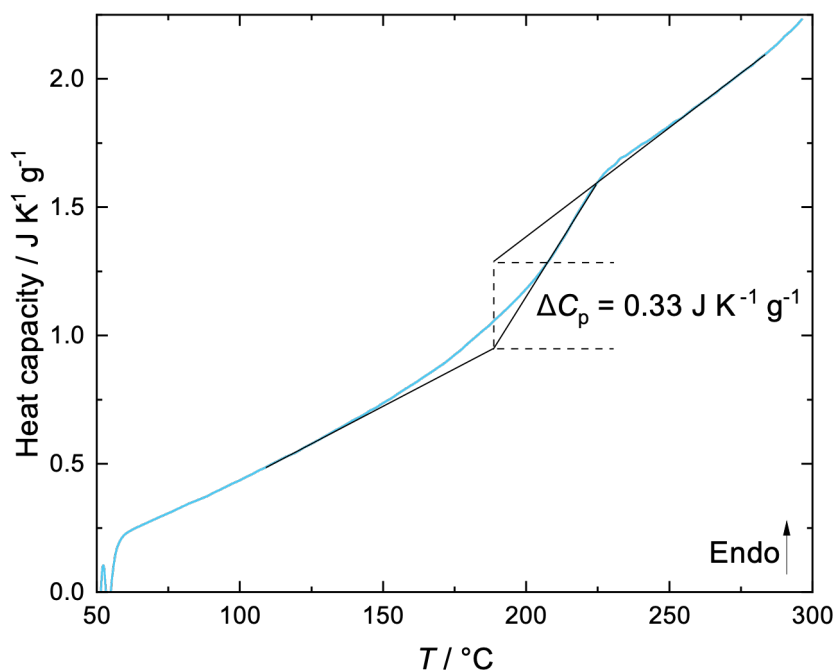
Sample	$\Delta C_p / \text{J g}^{-1} \text{K}^{-1}$	$\Delta C_p / \text{J mol}^{-1} \text{K}^{-1}$
<i>g</i> ZIF-62(Co)	0.12	25
<i>g</i> ZIF-62(Zn)	0.12	26
<i>gphen</i> _{0.49} ZIF-62(Co)	0.33	98
<i>gphen</i> _{0.51} ZIF-62(Zn)	0.13	40
<i>gphen</i> _{1.33} ZIF-12	0.28	149



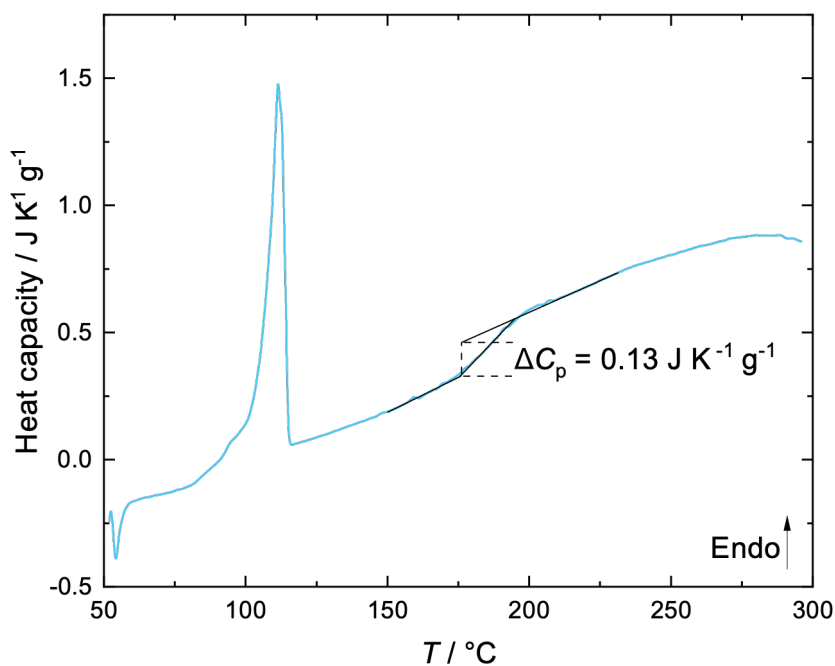
Supplementary Figure 22. Total heat capacity curve of ZIF-62(Co) measured with mDSC. Notice that the absolute C_p values of these measurements are not reliable due to small variations in the masses of the aluminium pans, but this does not affect the relative ΔC_p values.



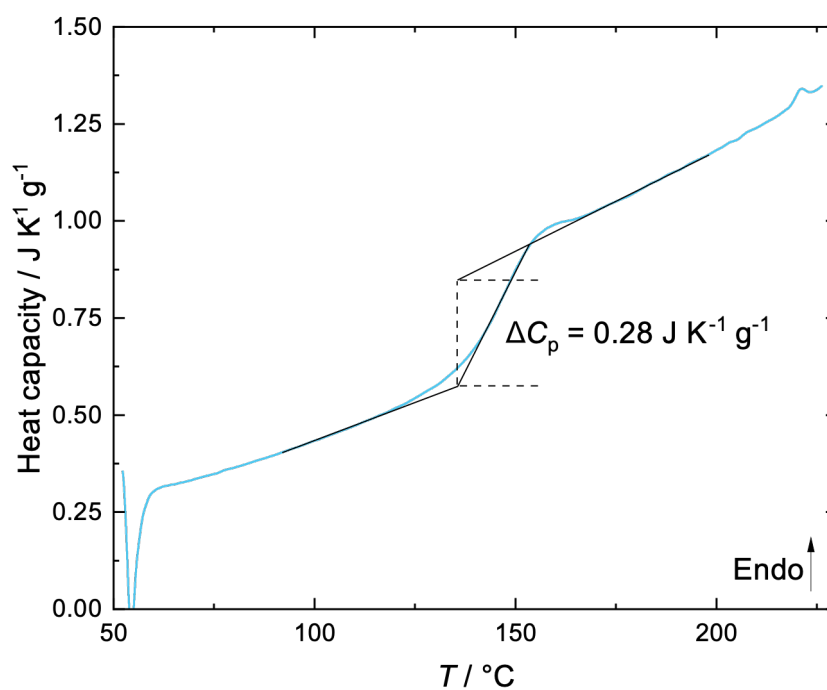
Supplementary Figure 23. Total heat capacity curve of ZIF-62(Zn) measured with mDSC. Notice that the absolute C_p values of these measurements are not reliable due to small variations in the masses of the aluminium pans, but this does not affect the relative ΔC_p values.



Supplementary Figure 24. Total heat capacity curve of gphen_{0.49}ZIF-62(Co) measured with mDSC. Notice that the absolute C_p values of these measurements are not reliable due to small variations in the masses of the aluminium pans, but this does not affect the relative ΔC_p values.



Supplementary Figure 25. Total heat capacity curve of gphen_{0.51}ZIF-62(Zn) measured with mDSC. Notice that the absolute C_p values of these measurements are not reliable due to small variations in the masses of the aluminium pans, but this does not affect the relative ΔC_p values.



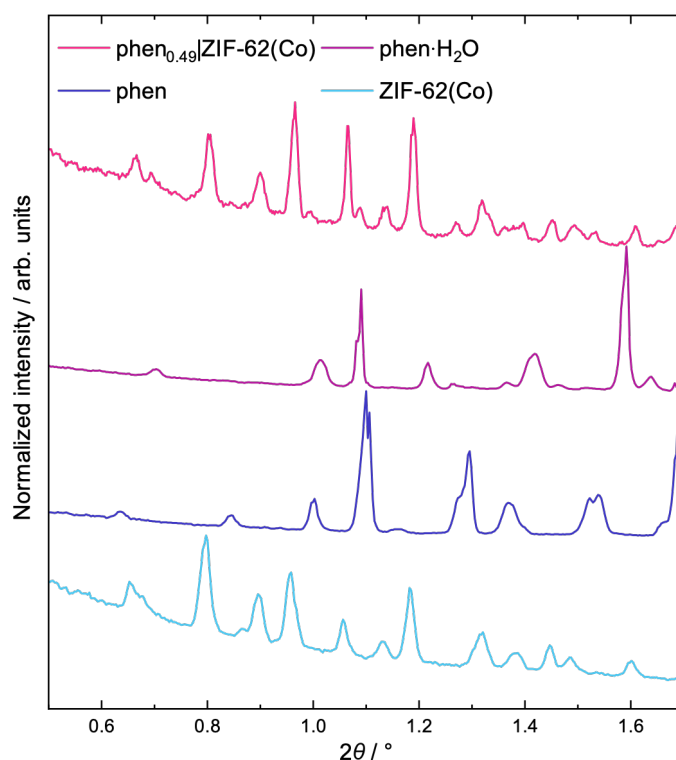
Supplementary Figure 26. Total heat capacity curve of *gphen*_{1.33}ZIF-12 measured with mDSC. Notice that the absolute C_p values of these measurements are not reliable due to small variations in the masses of the aluminium pans, but this does not affect the relative ΔC_p values.

Supplementary Notes 2 – Hygroscopicity of physical mixtures

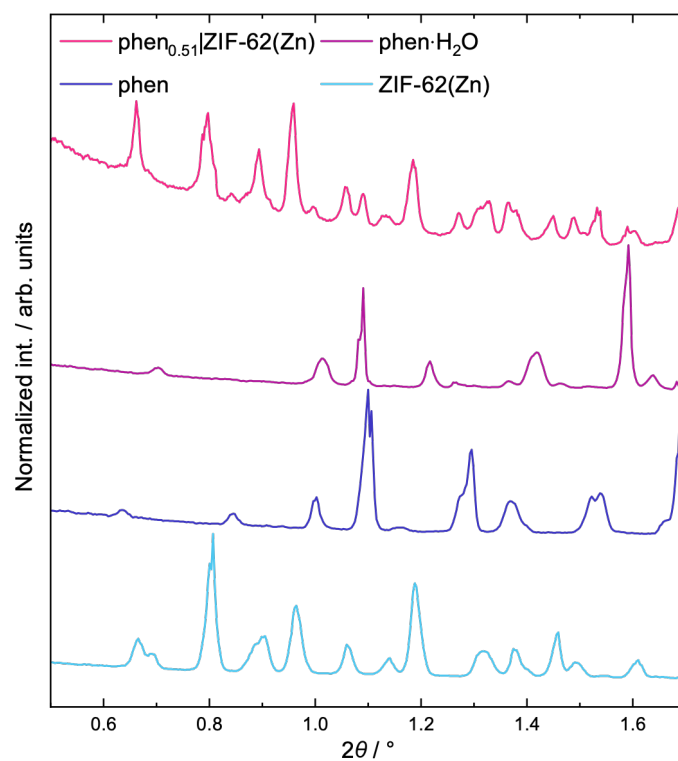
All physical mixtures were prepared with dried 1,10-phenanthroline. During the grinding process, the sample absorbed moisture, and the DSC scans of all physical mixtures prepared under ambient conditions show a melting event that matches 1,10-phenanthroline monohydrate (see **Supplementary Figure 7**). The transformation from 1,10-phenanthroline to 1,10-phenanthroline monohydrate has previously been shown to happen on a time scale of ~10 min under ambient conditions.¹ In the case of phen_{0.49}ZIF-62(Co), the material prepared under ambient conditions shows a glass transition at $T_g = 206$ °C, while the material prepared under inert conditions shows a glass transition at $T_g = 210$ °C. This observation is in line with the observation that the addition of water to a coordination polymer reduces its T_g value.² The mid-IR spectrum of gphen_{0.49}ZIF-62(Co) shows broad bands in the region 3160-3560 cm⁻¹. These bands belong to the symmetric and asymmetric stretching vibrations of H₂O. A coordination of H₂O or OH⁻ to the Co²⁺ nodes can be ruled out because the spectra do not show any vibrations above 3600 cm⁻¹.³ In the case of phen_{1.33}ZIF-12, the exclusion of water in the preparation process leads to an increase in the glass transition temperature from $T_g = 125$ °C to $T_g = 137$ °C (see **Supplementary Figs 13 and 14**). Interestingly, the mid-IR spectra of the gphen_{1.33}ZIF-12 prepared under ambient and moisture-free conditions look nearly identical (see **Supplementary Figure 116**). This is likely due to the hydrophobic nature of ZIF-12, leading to the exclusion of water from the pores. The substantial reduction in T_g in the presence of H₂O is hypothesised to result from the increased H₂O content in gphen_{1.33}ZIF-12 (attributed to the higher phen concentration), which, in turn, elevates the H₂O pressure in the gas phase of the DSC crucible, thereby lowering T_g . Since for both materials H₂O does not interact with the metal nodes, any effect of water introduced during grinding of the materials in ambient air on the structural and property analyses presented herein is expected to be negligible.

Supplementary Methods 3 – Variable temperature powder X-ray diffraction

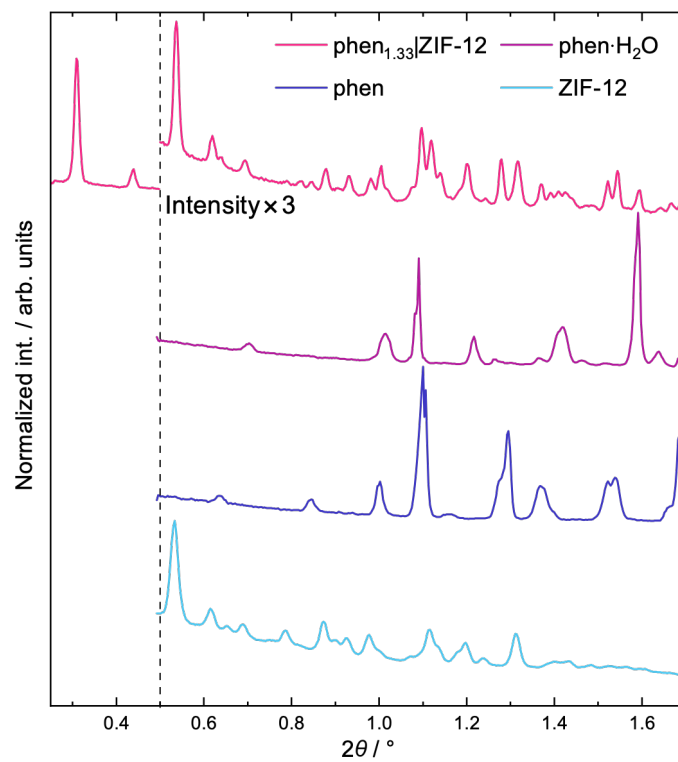
It was found that the VT PXRD patterns of $\text{phen}_{0.49}\text{ZIF-62}(\text{Co})$ and $\text{phen}_{0.51}\text{ZIF-62}(\text{Zn})$ show reflections of phenanthroline anhydrate and the VT PXRD patterns of $\text{phen}_{1.33}\text{ZIF-12}$ show reflections of phenanthroline anhydrate and phenanthroline monohydrate, despite all materials showing melting of only phenanthroline monohydrate in the DSC. This can be explained by the transformation of phenanthroline monohydrate to phenanthroline during the preparation of the capillaries for the VT PXRD measurements in the glovebox. It was shown that this transformation takes place at relative humidities below 10%.¹



Supplementary Figure 27. PXRD patterns of $\text{ZIF-62}(\text{Co})$, phen , $\text{phen}\cdot\text{H}_2\text{O}$, and $\text{phen}_{0.49}\text{ZIF-62}(\text{Co})$ at 50 °C. $\lambda = 0.6199 \text{ \AA}$.

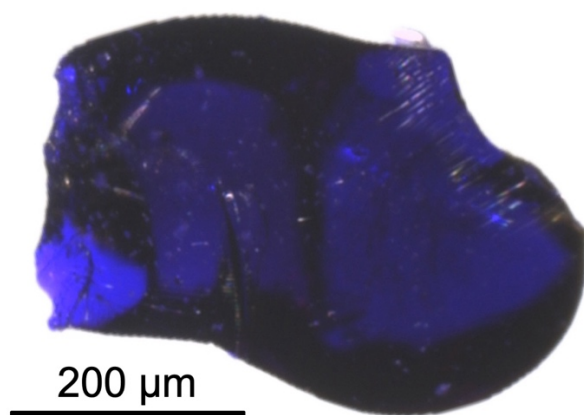


Supplementary Figure 28. PXRD patterns of ZIF-62(Zn), phen, phen·H₂O, and phen_{0.51}|ZIF-62(Zn) at 50 °C. $\lambda = 0.6199 \text{ \AA}$.

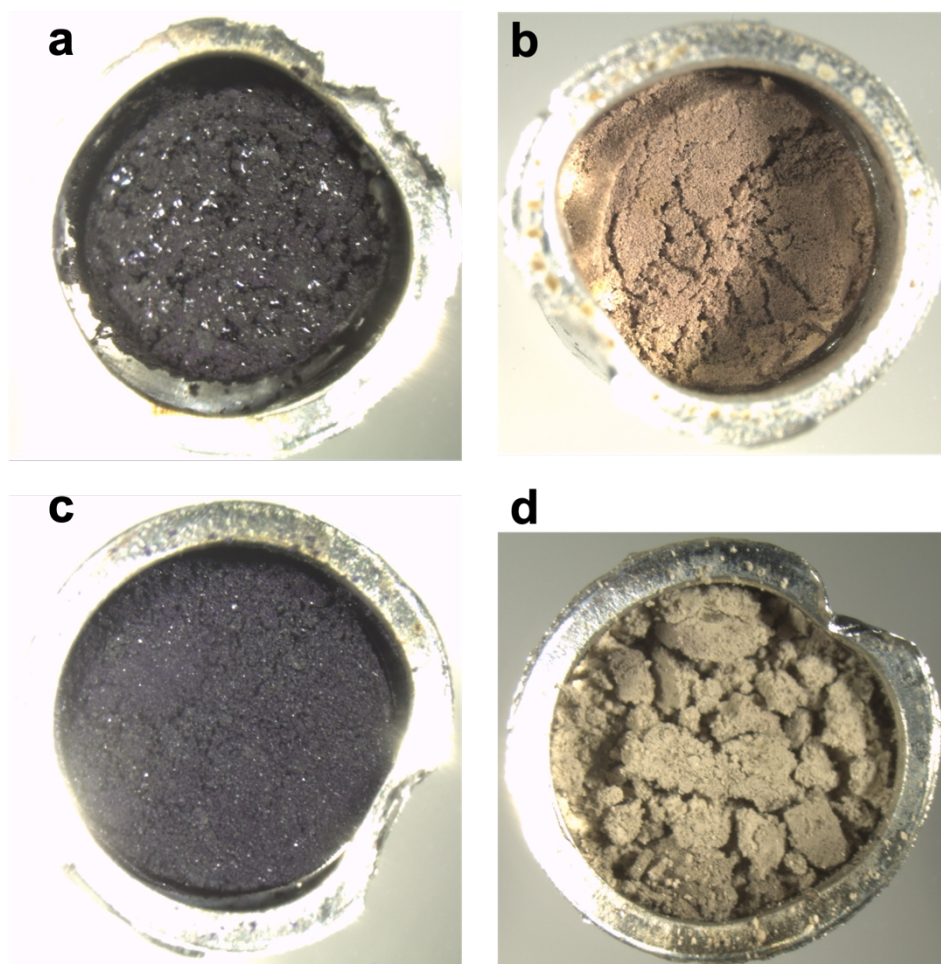


Supplementary Figure 29. PXRD patterns of ZIF-12, phen, phen·H₂O, and phen_{1.33}|ZIF-12 at 50 °C. $\lambda = 0.6199 \text{ \AA}$.

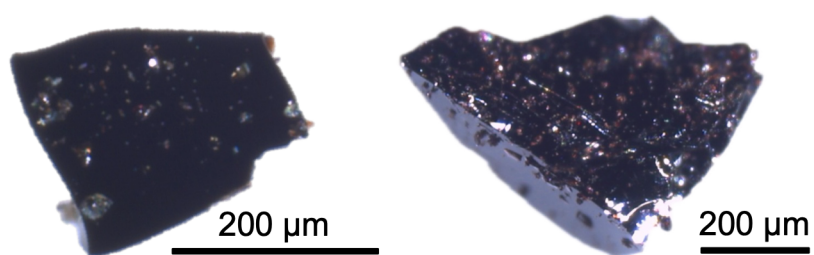
Supplementary Methods 4 – Microscopy



Supplementary Figure 30. Microscopy image of *g*ZIF-62(Co).

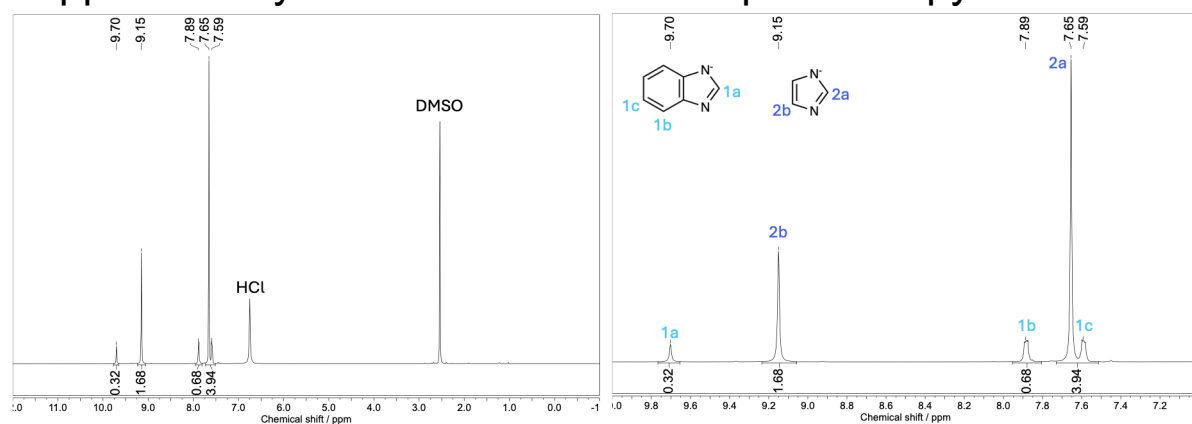


Supplementary Figure 31. Microscopy images of *gphen*_{0.31}ZIF-12 (a), *gphen*_{0.29}ZIF-11 (b), *gphen*_{0.47}ZIF-67 (c), and *gphen*_{0.49}ZIF-8 (d).

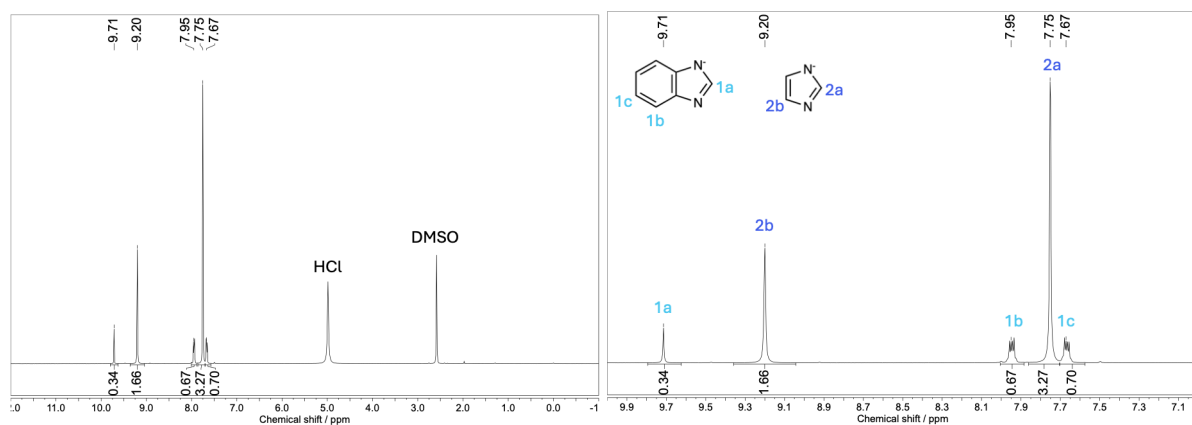


Supplementary Figure 32. Microscopy images of $\text{gphen}_{0.5}\text{Cu}(\text{im})_2$ (left) and $\text{gphen}_6\text{Cu}_3(\text{btc})_2$ (right).

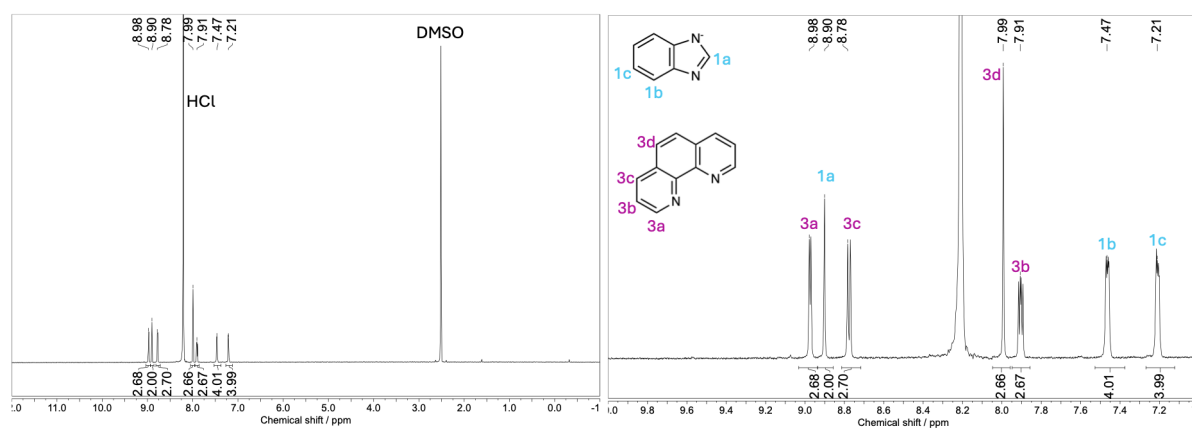
Supplementary Methods 5 – ^1H NMR spectroscopy

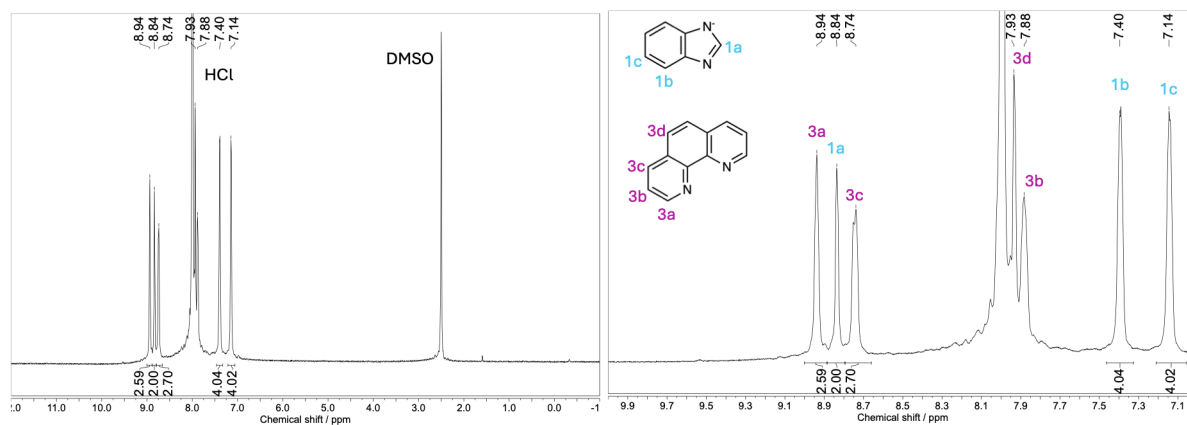


Supplementary Figure 33. ^1H NMR spectrum (full and zoom) of ZIF-62(Co) digested in DMSO and DCl/D₂O.

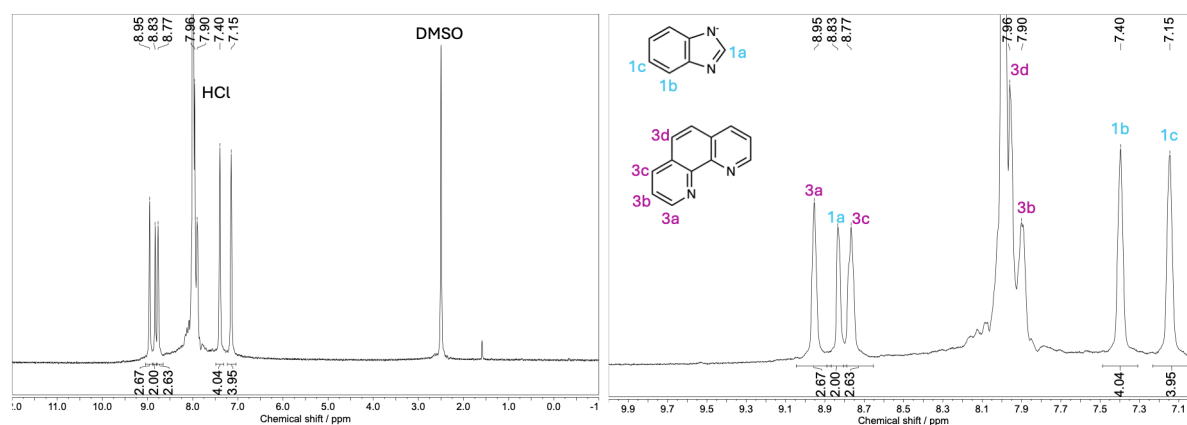


Supplementary Figure 34. ^1H NMR spectrum (full and zoom) of ZIF-62(Zn) digested in DMSO and DCl/D₂O.

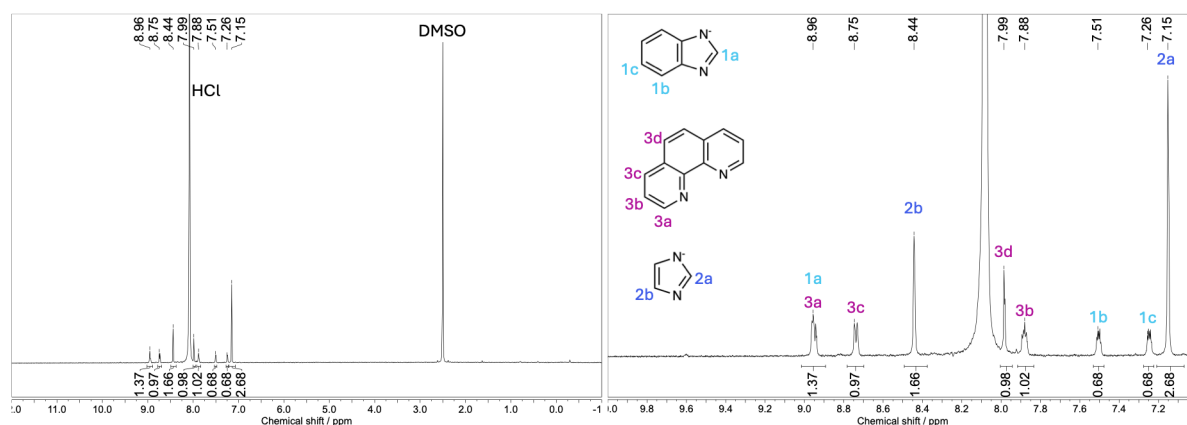




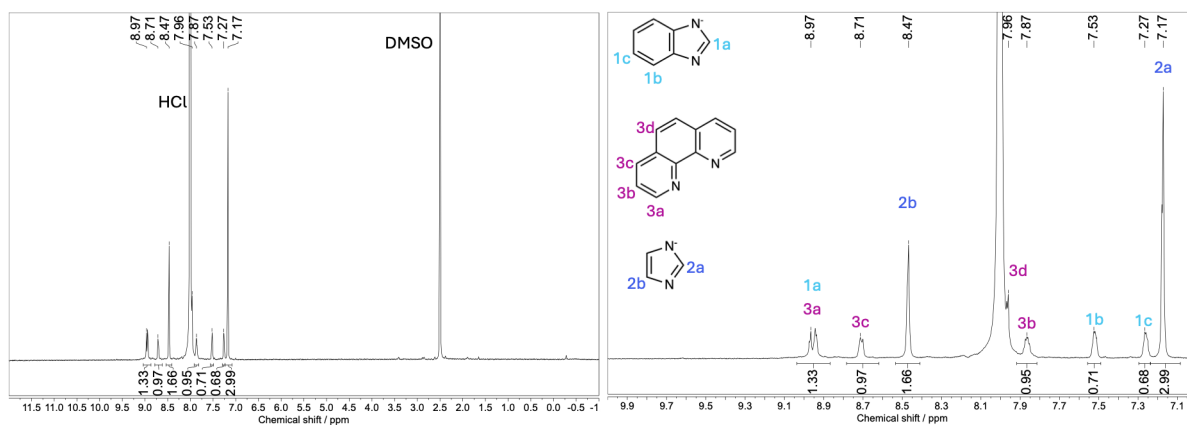
Supplementary Figure 36. ^1H NMR spectrum (full and zoom) of $\text{gphen}_{1.33}\text{ZIF-12}$ prepared in a DSC pan digested in DMSO and $\text{DCI/D}_2\text{O}$.



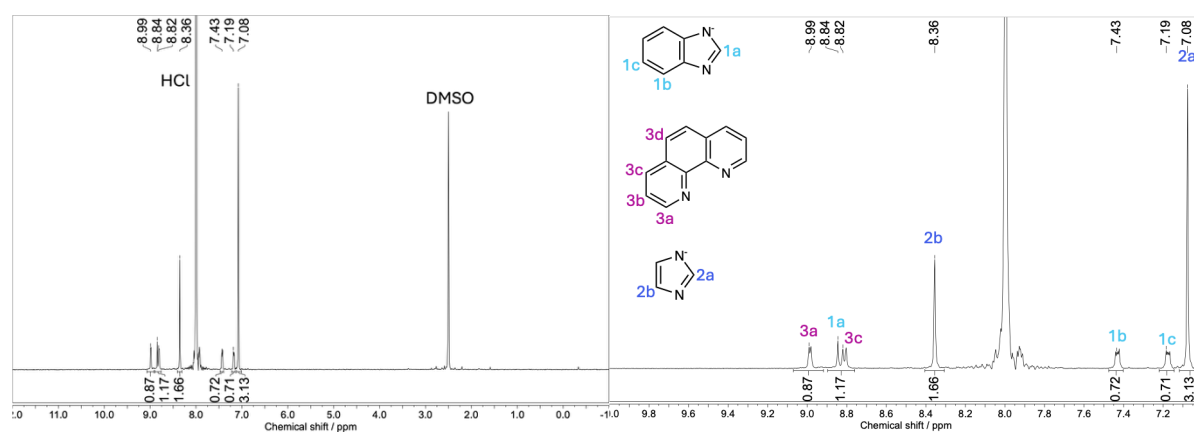
Supplementary Figure 37. ^1H NMR spectrum (full and zoom) of $\text{gphen}_{1.33}\text{ZIF-12}$ prepared in a tube furnace digested in DMSO and $\text{DCI/D}_2\text{O}$.



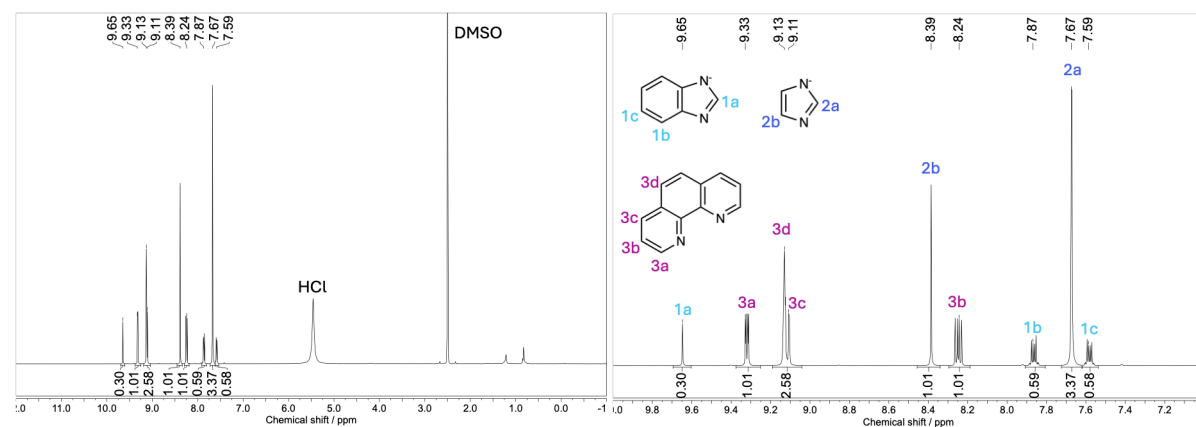
Supplementary Figure 38. ^1H NMR spectrum (full and zoom) of $\text{phen}_{0.49}\text{ZIF-62(Co)}$ digested in DMSO and $\text{DCI/D}_2\text{O}$.



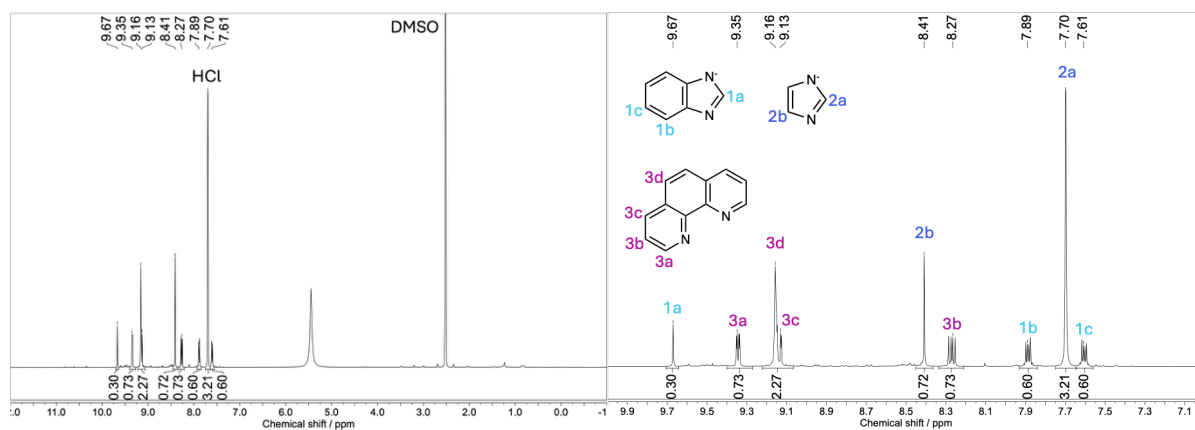
Supplementary Figure 39. ^1H NMR spectrum (full and zoom) of $\text{gphen}_{0.49}\text{ZIF-62}(\text{Co})$ digested in DMSO and $\text{DCl}/\text{D}_2\text{O}$.



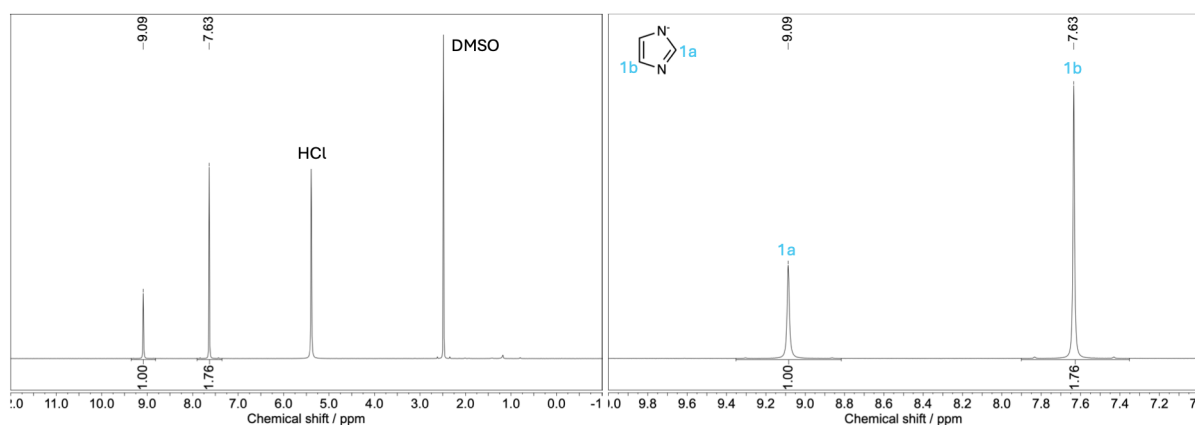
Supplementary Figure 40. ^1H NMR spectrum (full and zoom) of $\text{gphen}_{0.49}\text{ZIF-62}(\text{Co})$ prepared in a tube furnace digested in DMSO and $\text{DCl}/\text{D}_2\text{O}$.



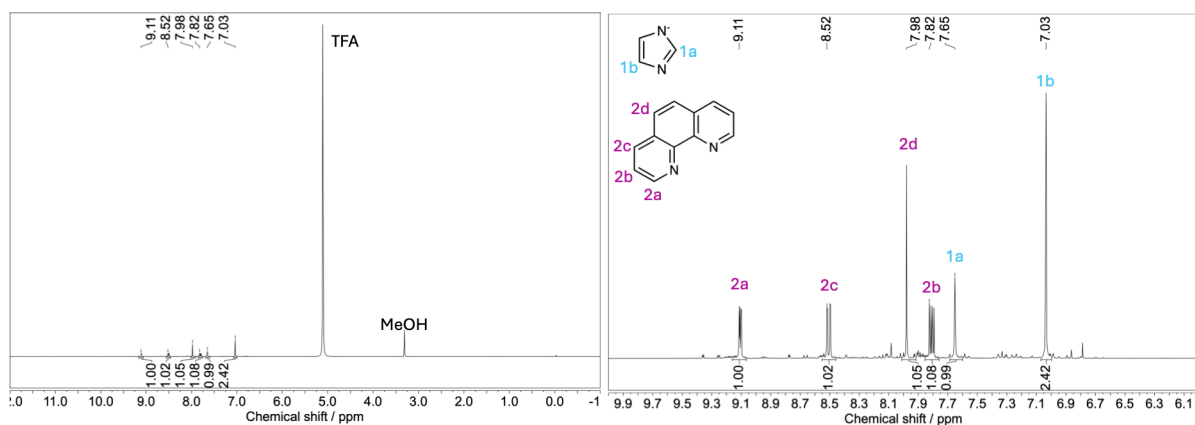
Supplementary Figure 41. ^1H NMR spectrum (full and zoom) of $\text{phen}_{0.51}\text{ZIF-62}(\text{Zn})$ digested in DMSO and $\text{DCl}/\text{D}_2\text{O}$.



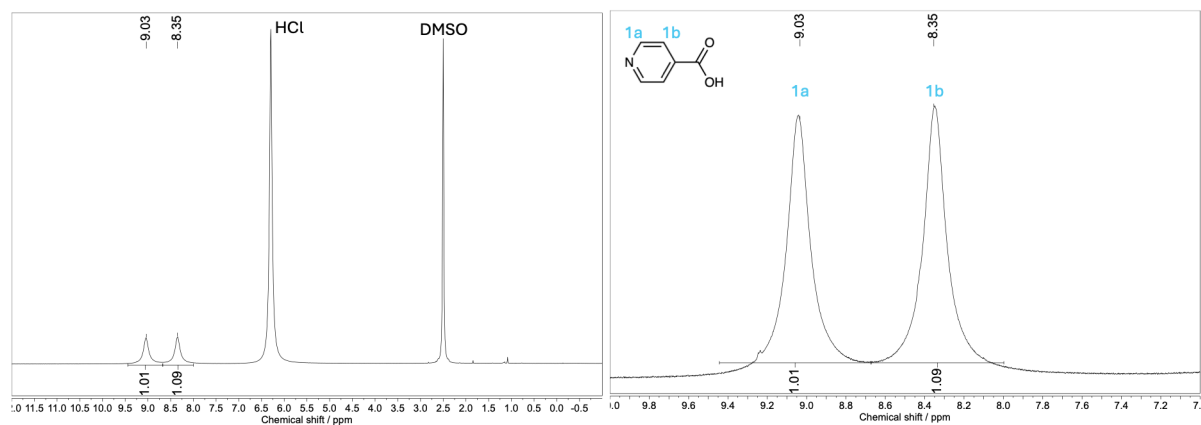
Supplementary Figure 42. ^1H NMR spectrum (full and zoom) of $\text{gphen}_{0.51}\text{ZIF-62}(\text{Zn})$ digested in DMSO and $\text{DCl}/\text{D}_2\text{O}$.



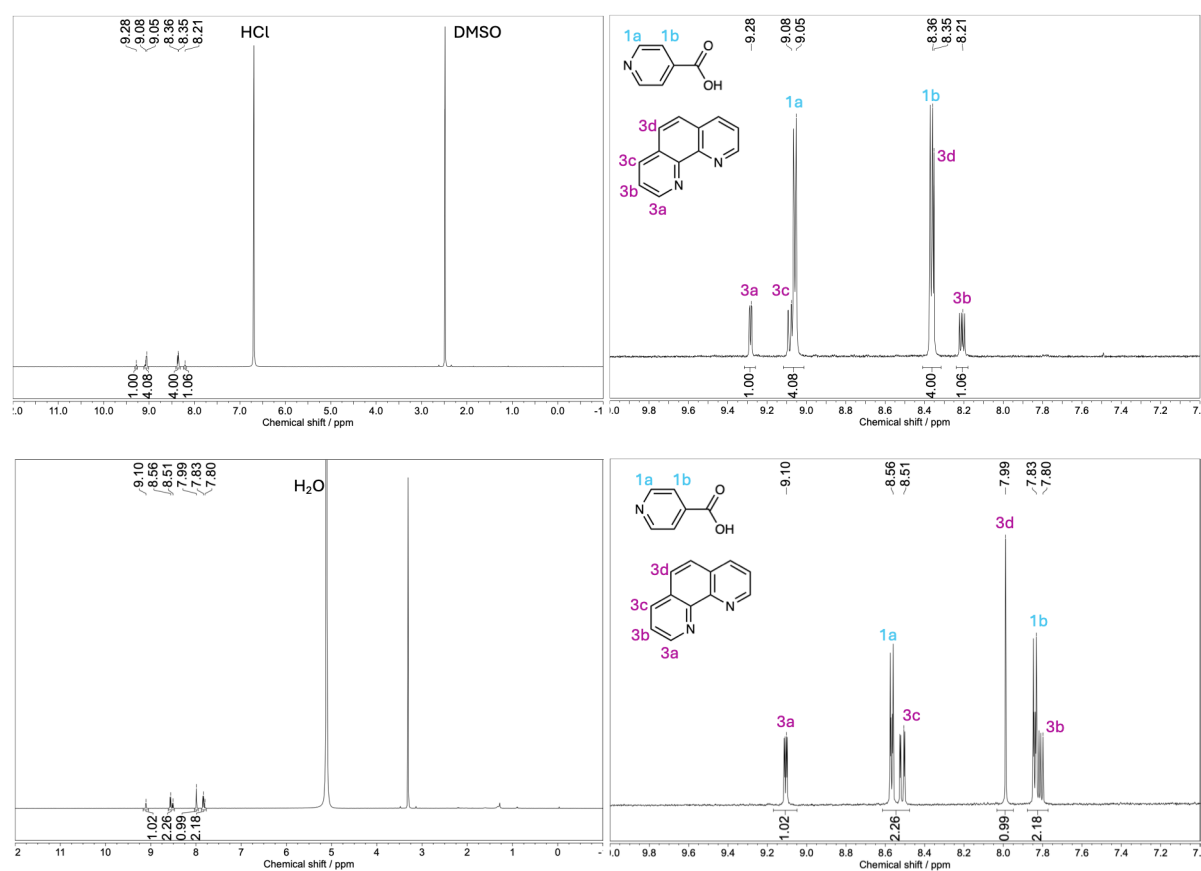
Supplementary Figure 43. ^1H NMR spectrum (full and zoom) of $\text{Cu}(\text{im})_2$ digested in DMSO and $\text{DCl}/\text{D}_2\text{O}$.



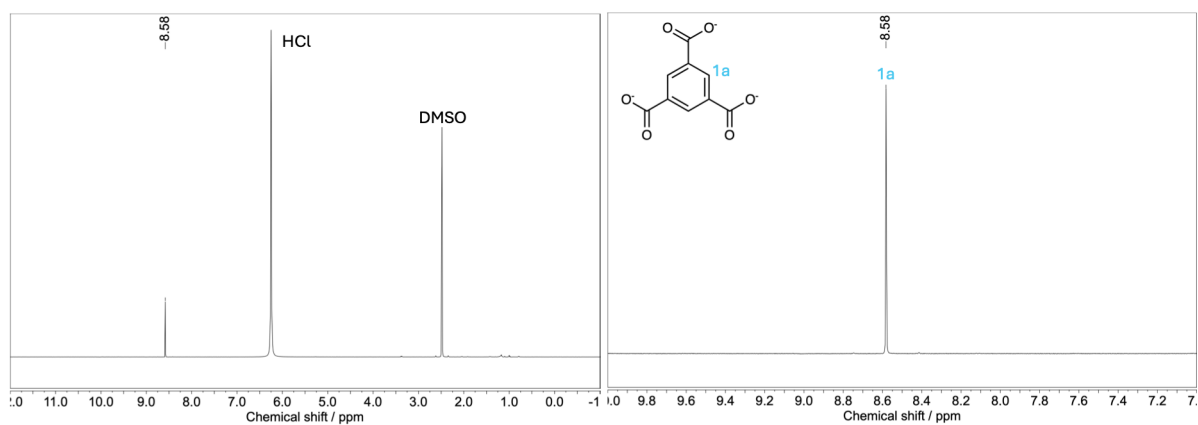
Supplementary Figure 44. ^1H NMR spectrum (full and zoom) of $\text{gphen}_{0.5}\text{Cu}(\text{im})_2$ digested in MeOD and TFA and subsequently treated with Na_2S to precipitate CuS .



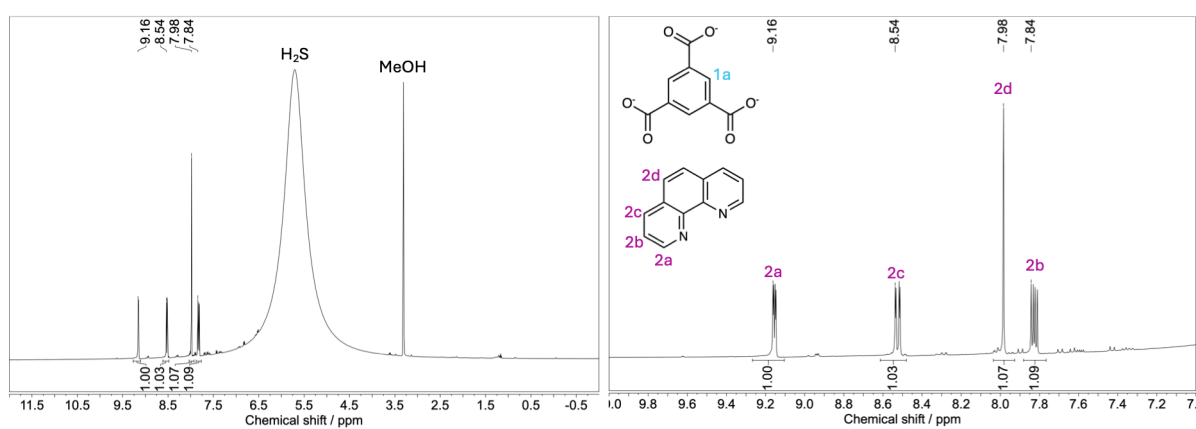
Supplementary Figure 45. ^1H NMR spectrum (full and zoom) of $\text{Ni}(\text{inic})_2$ digested in DMSO and DCI/ D_2O .



Supplementary Figure 46. ^1H NMR spectrum (full and zoom) of $\text{gphen}_2\text{Ni}(\text{inic})_2$ digested in DMSO and DCI/ D_2O (top) and digested in MeOD and subsequently treated with Na_2S to precipitate NiS (bottom). The measurement of the sample digested in DMSO and DCI/ D_2O shows the absence of impurities, but a misleading ratio between isonicotinate and phen due to the partial coordination of phen to paramagnetic Ni^{2+} . The measurement of the sample treated with Na_2S shows the expected ligand ratios, but shows impurities of the solvent due to the low concentration of the sample and potentially impurities of Na_2S .

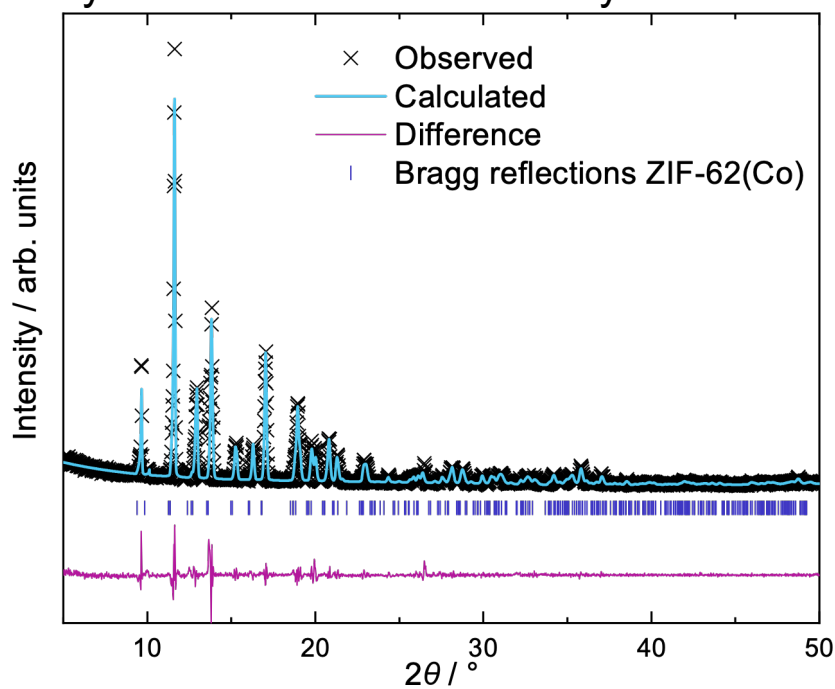


Supplementary Figure 47. ^1H NMR spectrum (full and zoom) of $\text{Cu}_3(\text{btc})_2$ digested in DMSO and $\text{DCl}/\text{D}_2\text{O}$.

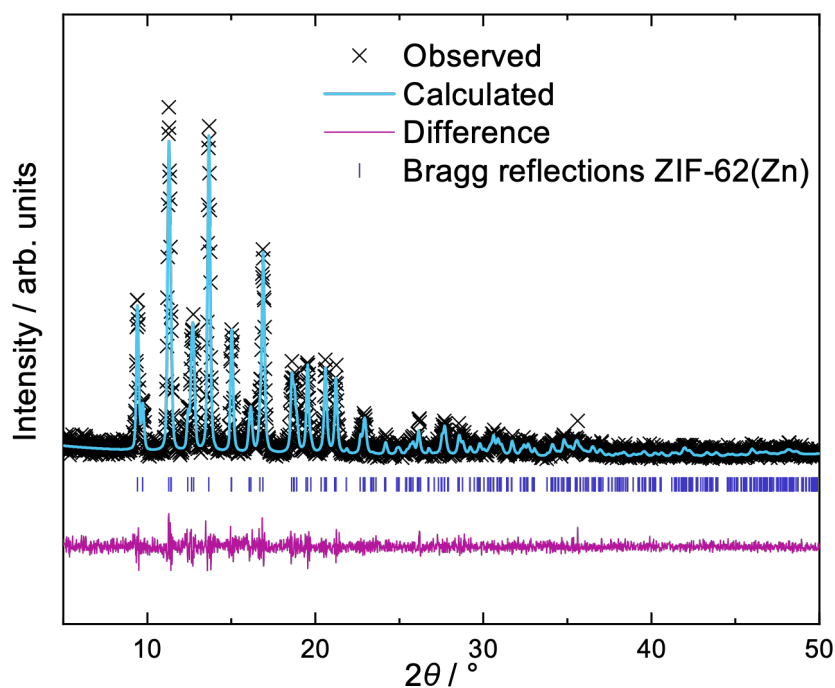


Supplementary Figure 48. ^1H NMR spectrum (full and zoom) of $\text{gphen}_6\text{Cu}_3(\text{btc})_2$ digested in MeOD and subsequently treated with Na_2S to precipitate CuS .

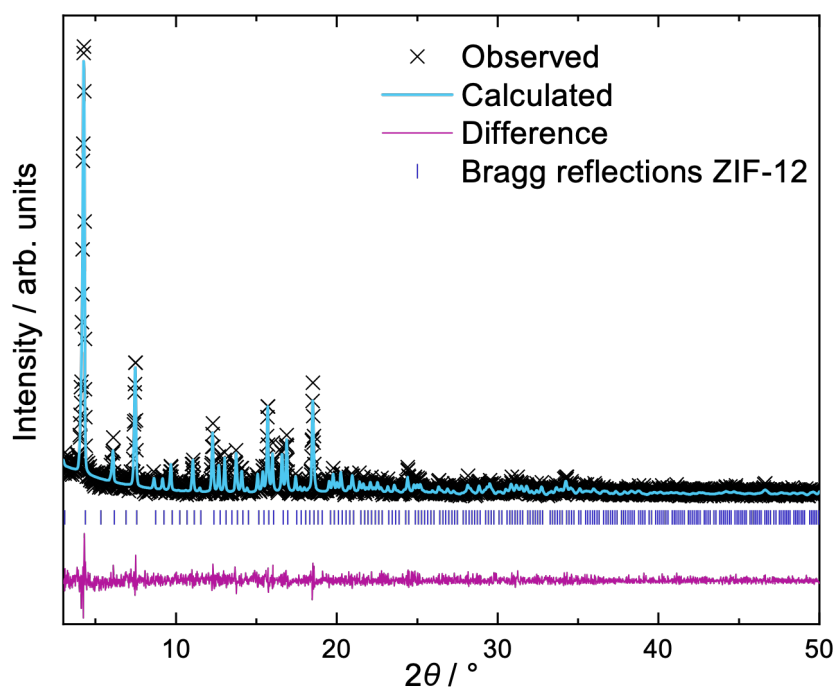
Supplementary Methods 6 – Powder X-ray diffraction



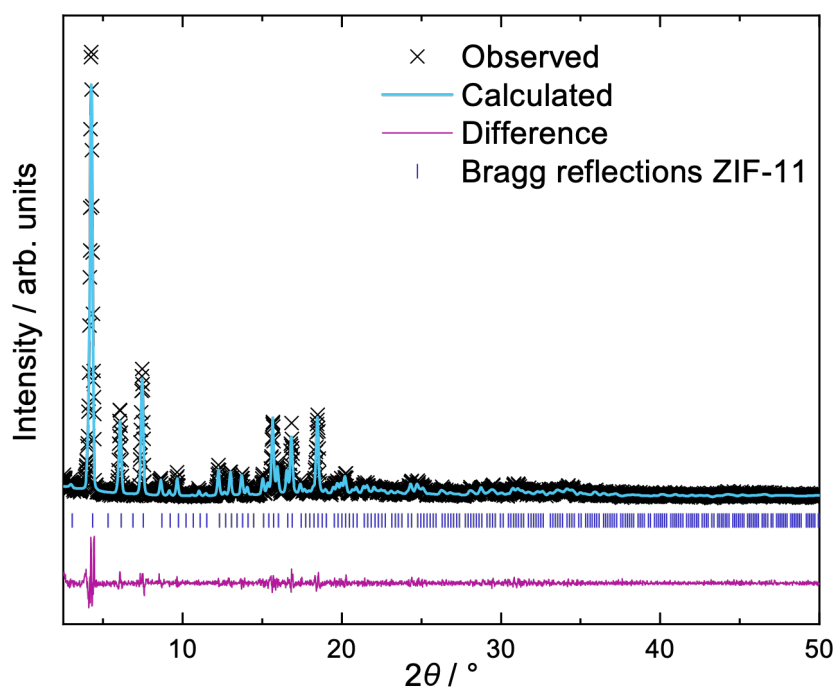
Supplementary Figure 49. Profile fit (Pawley method) to the PXRD pattern of ZIF-62(Co).



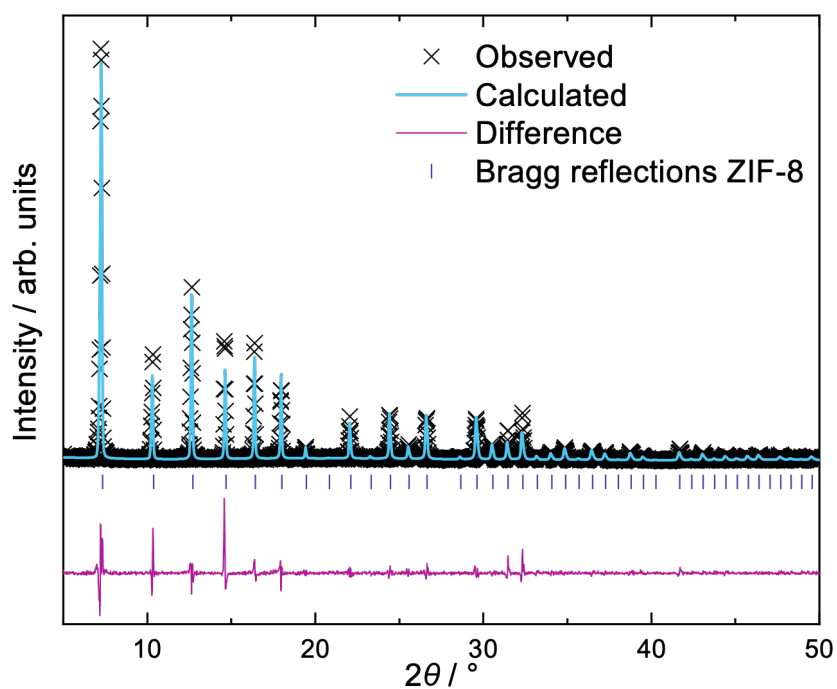
Supplementary Figure 50. Profile fit (Pawley method) to the PXRD pattern of ZIF-62(Zn).



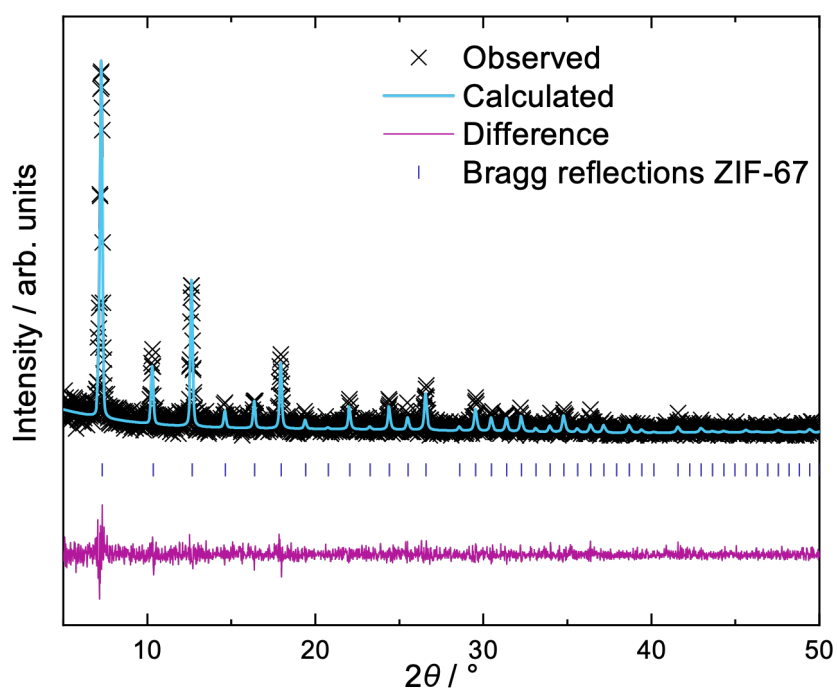
Supplementary Figure 51. Profile fit (Pawley method) to the PXRD pattern of ZIF-12.



Supplementary Figure 52. Profile fit (Pawley method) to the PXRD pattern of ZIF-11.



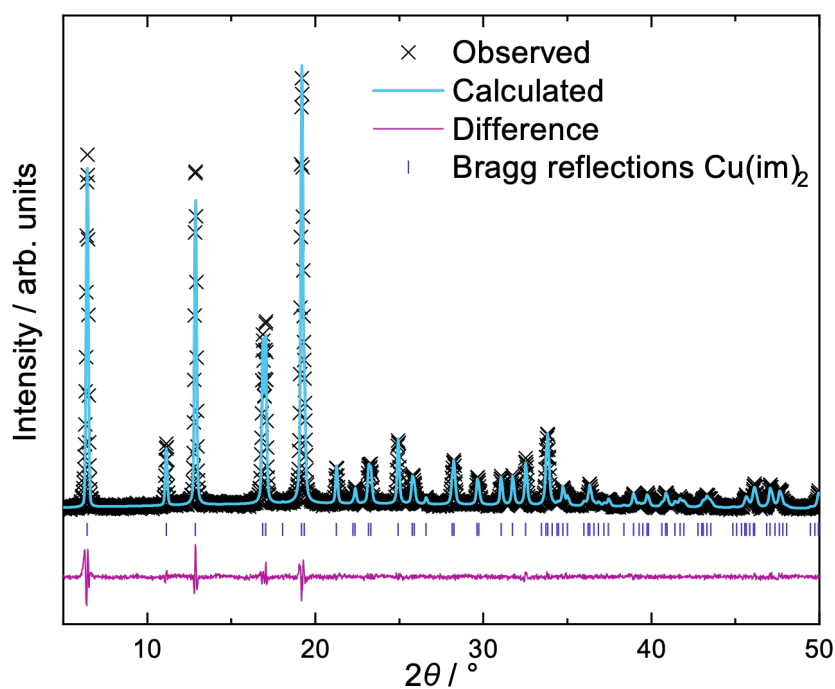
Supplementary Figure 53. Profile fit (Pawley method) to the PXRD pattern of ZIF-8.



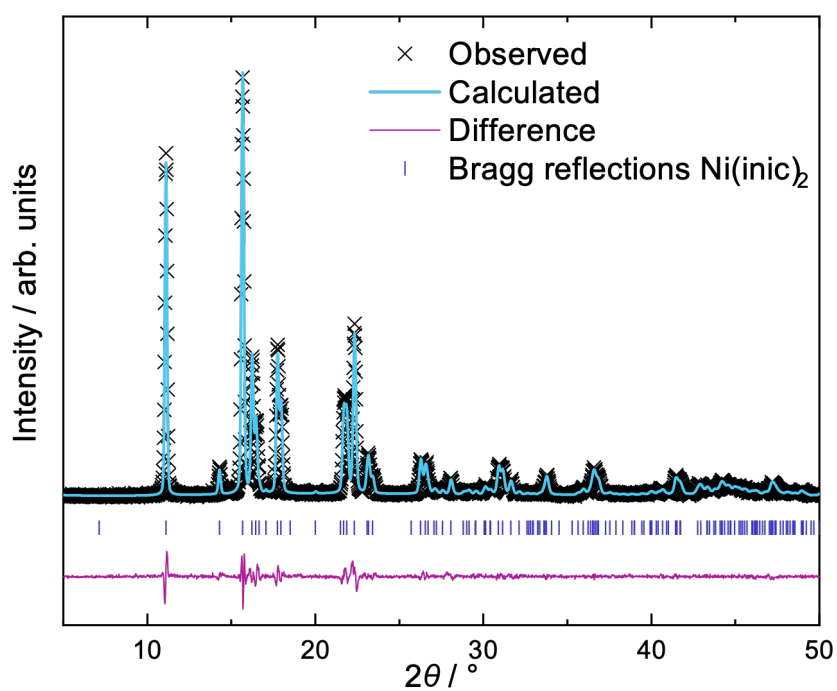
Supplementary Figure 54. Profile fit (Pawley method) to the PXRD pattern of ZIF-67.

Supplementary Table 2. Unit cell parameters and corresponding R_{wp} , R_{exp} , and χ values determined by the above displayed structureless profile fits (Pawley method).

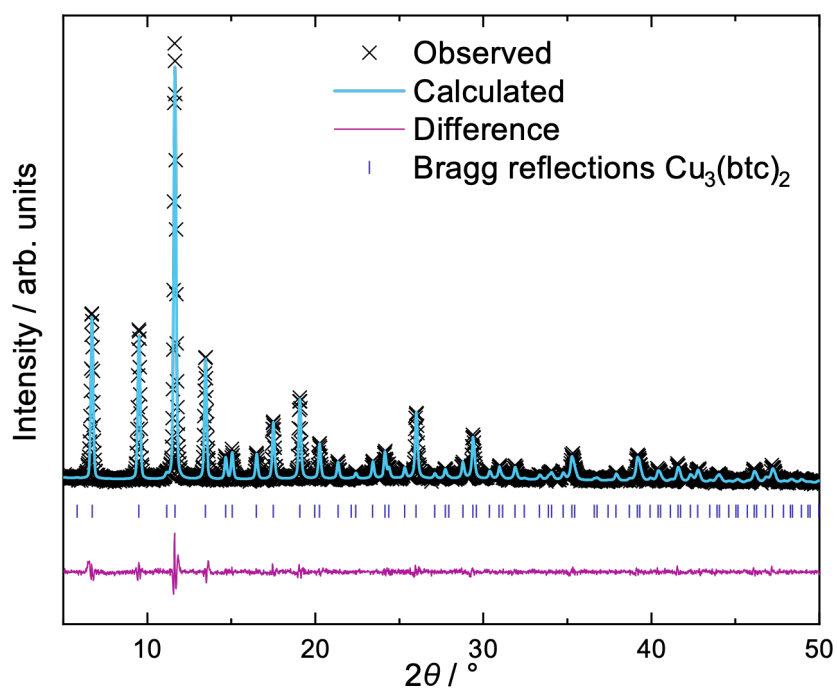
Compound	ZIF-67	ZIF-11	ZIF-62(Co)	ZIF-8	ZIF-62(Zn)	ZIF-12
CCDC number	671073	602545	2130184	864309	2130251	602546
crystal system	cubic	cubic	orthorhombic	cubic	orthorhombic	cubic
space group	<i>I</i> -43 <i>m</i>	<i>Pm</i> -3 <i>m</i>	<i>Pbca</i>	<i>I</i> -43 <i>m</i>	<i>Pbca</i>	<i>Pm</i> -3 <i>m</i>
<i>a</i> / Å	17.087(3)	28.736(4)	15.713(5)	17.0417(10)	15.521(14)	28.616(4)
<i>b</i> / Å	17.087(3)	28.736(4)	15.550(5)	17.0417(10)	15.484(13)	28.616(4)
<i>c</i> / Å	17.087(3)	28.736(4)	17.962(5)	17.0417(10)	18.175(15)	28.616(4)
α / °	90	90	90	90	90	90
β / °	90	90	90	90	90	90
γ / °	90	90	90	90	90	90
<i>V</i> / Å ³	4988(3)	23729(10)	4389(2)	4949.2(9)	4368(7)	23433(9)
R_{wp} / %	38.45	20.77	14.02	25.88	26.78	33.35
R_{exp} / %	36.19	15.63	7.81	17.00	23.61	26.99
χ	1.06	1.33	1.80	1.52	1.13	1.24



Supplementary Figure 55. Profile fit (Pawley method) to the PXRD pattern of Cu(im)₂.



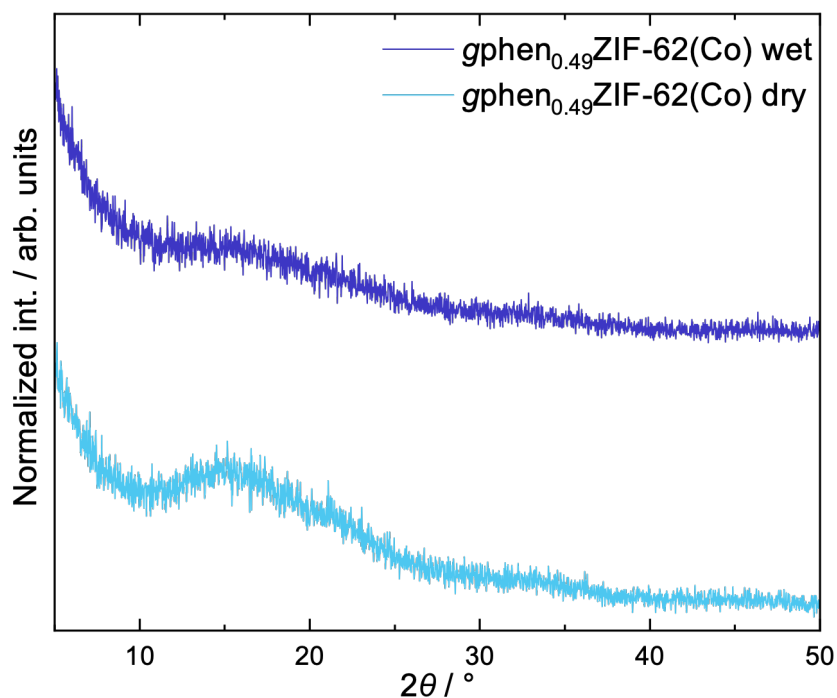
Supplementary Figure 56. Profile fit (Pawley method) to the PXRD pattern of Ni(inic)₂.



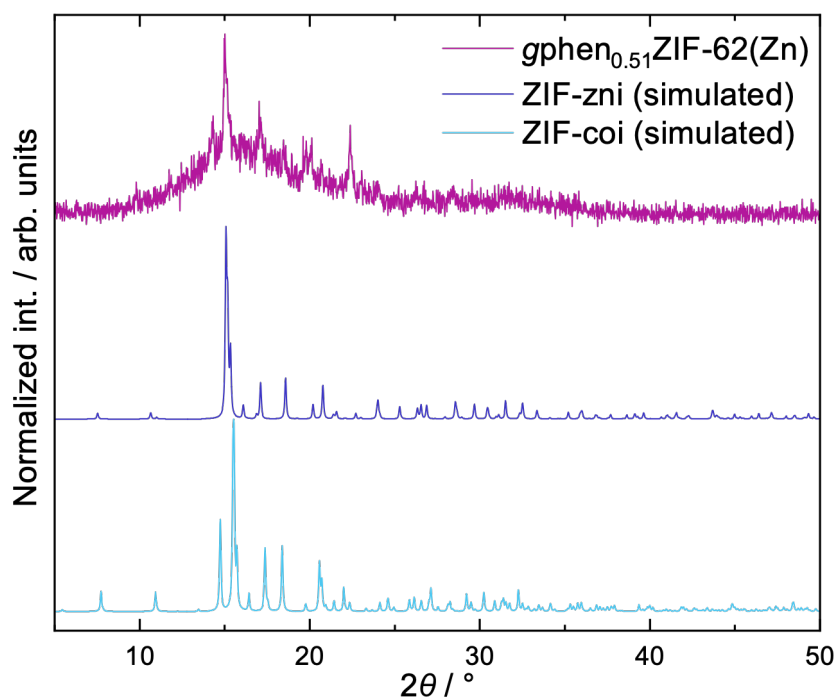
Supplementary Figure 57. Profile fit (Pawley method) to the PXRD pattern of Cu₃(btc)₂.

Supplementary Table 3. Unit cell parameters and corresponding R_{wp} , R_{exp} , and χ values determined by the above displayed structureless profile fits (Pawley method).

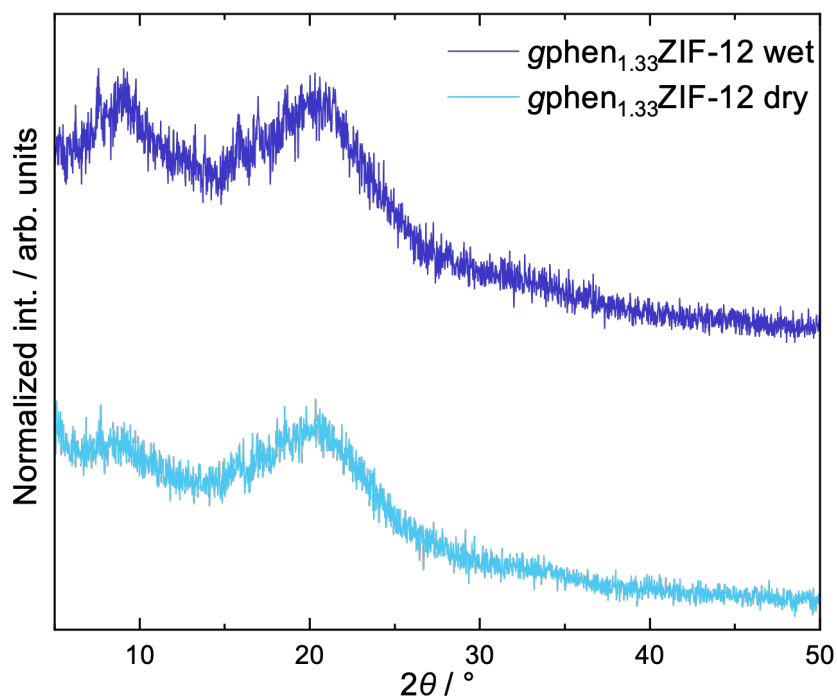
Compound	$\text{Cu}(\text{im})_2$	$\text{Cu}_3(\text{btc})_2$	$\text{Ni}(\text{inic})_2$
CCDC number	159161	1508166	112954
crystal system	hexagonal	cubic	monoclinic
space group	$R\bar{3}$	$Fm\bar{3}m$	Pn
$a / \text{\AA}$	27.5150(9)	26.3066(9)	6.3530(3)
$b / \text{\AA}$	27.5150(9)	26.3066(9)	12.3865(15)
$c / \text{\AA}$	5.38707(18)	26.3066(9)	10.3899(10)
$\alpha / ^\circ$	90	90	90
$\beta / ^\circ$	90	90	90.892(4)
$\gamma / ^\circ$	120	90	90
$V / \text{\AA}^3$	3532.0(2)	18205.1(19)	817.50(14)
$R_{wp} / \%$	6.90	7.98	8.41
$R_{exp} / \%$	4.84	6.17	5.49
χ	1.43	1.29	1.53



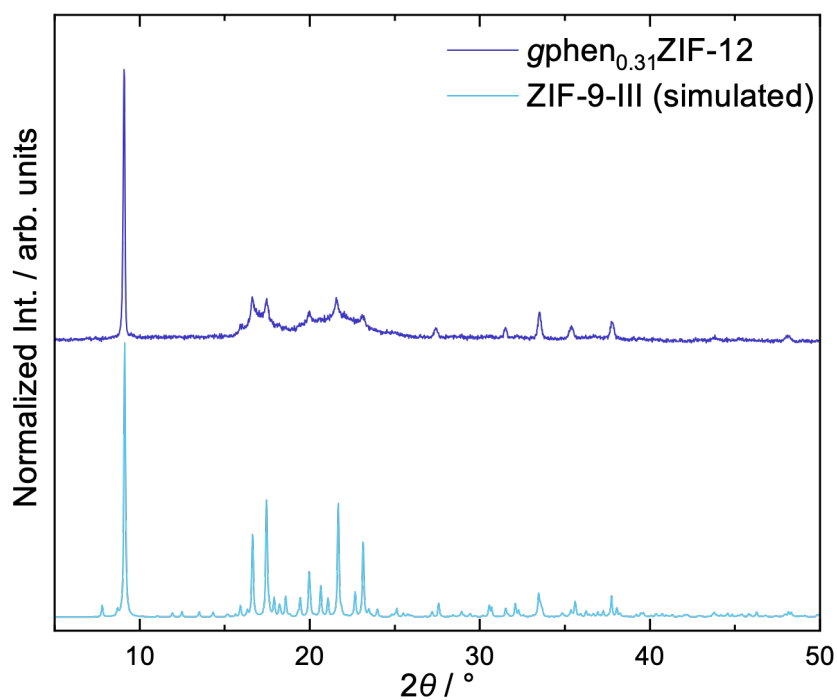
Supplementary Figure 58. PXRD patterns of $\text{gphen}_{0.49}\text{ZIF-62}(\text{Co})$ prepared under dry and ambient conditions.



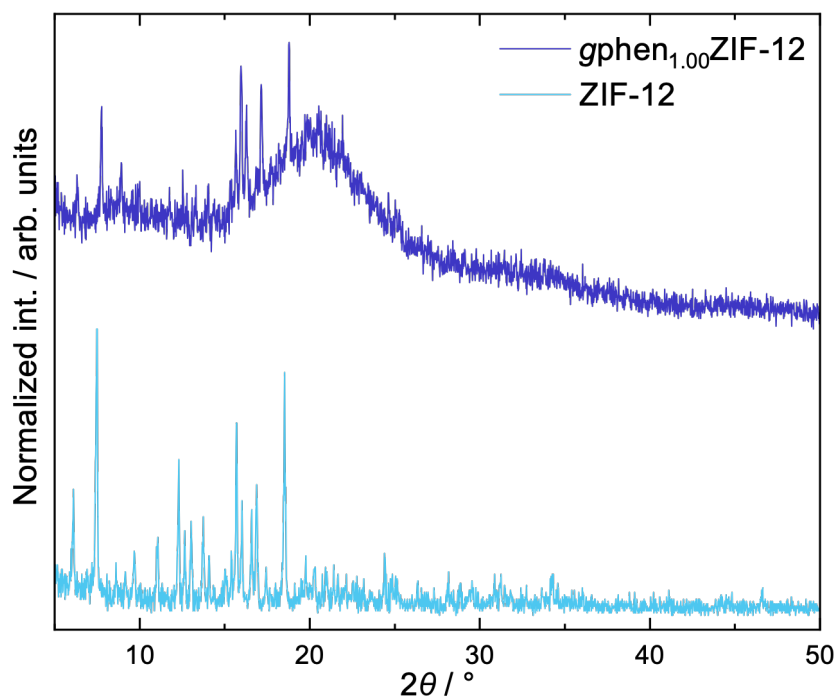
Supplementary Figure 59. PXRD pattern of $\text{gphen}_{0.51}\text{ZIF-62(Zn)}$ and simulated PXRD patterns of ZIF-coi (CCDC No 212357) and ZIF-zni (CCDC No 1180194).



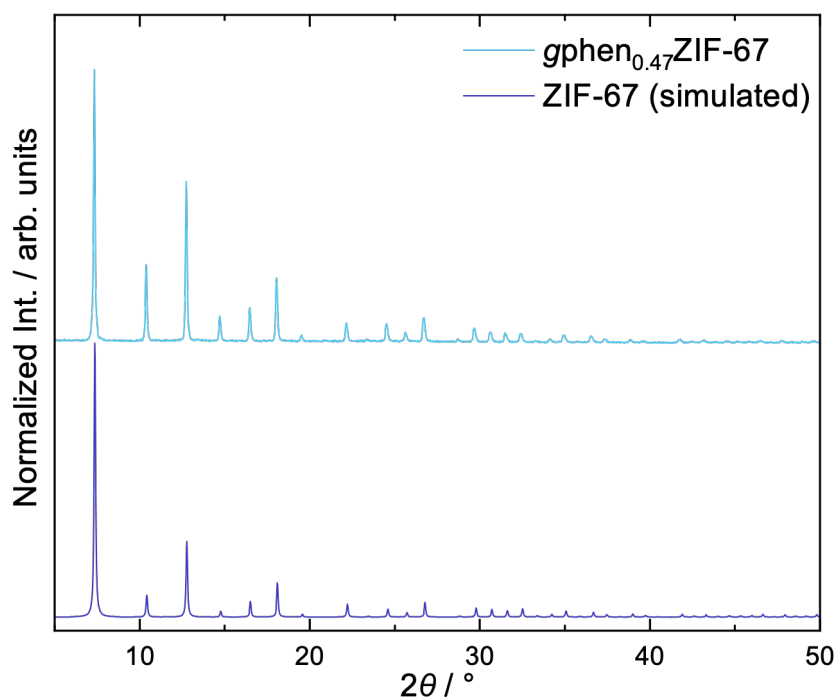
Supplementary Figure 60. PXRD patterns of $\text{gphen}_{1.33}\text{ZIF-12}$ prepared under dry and ambient conditions.



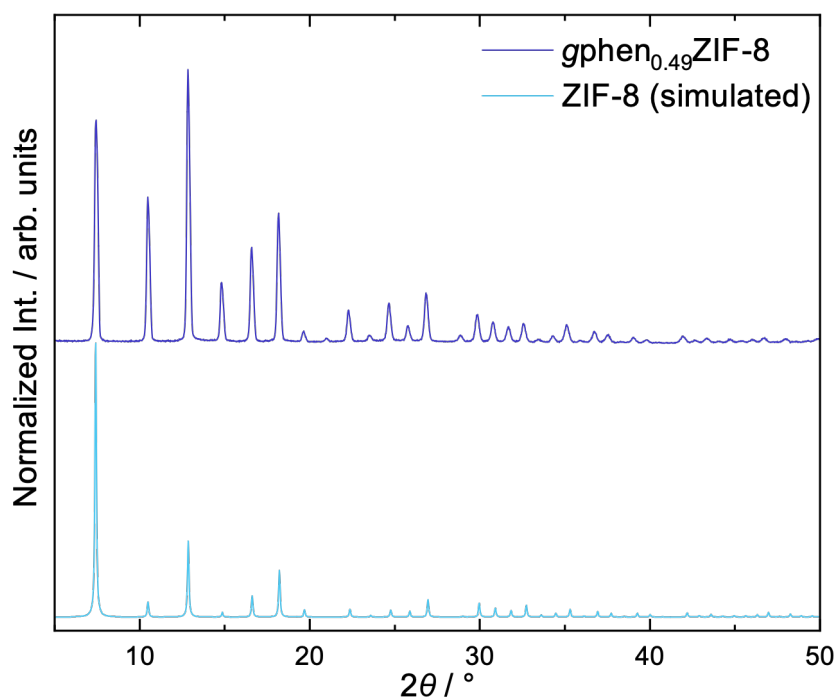
Supplementary Figure 61. PXRD pattern of $\text{gphen}_{0.31}\text{ZIF-12}$ and simulated PXRD patterns of ZIF-9-III (CCDC No 988184).



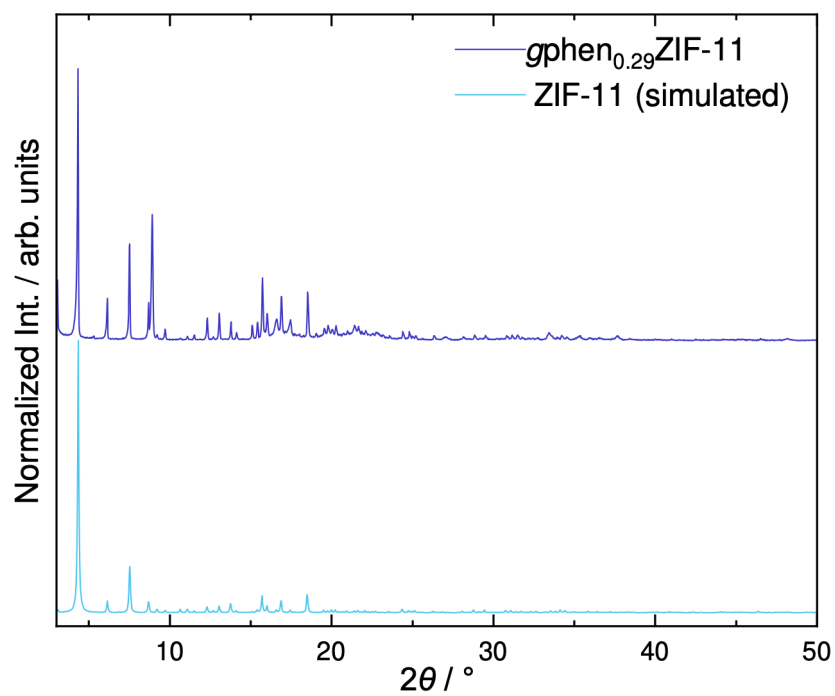
Supplementary Figure 62. PXRD pattern of $\text{gphen}_{1.00}\text{ZIF-12}$ and simulated PXRD pattern of ZIF-12 (CCDC No 602546).



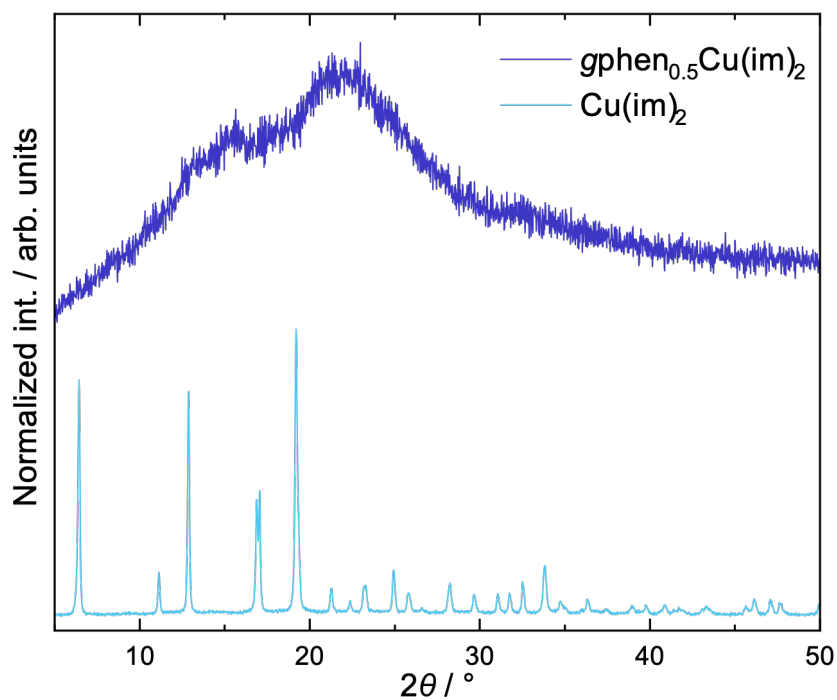
Supplementary Figure 63. PXRD pattern of $gphen_{0.47}ZIF-67$ and simulated PXRD pattern of ZIF-67 (CCDC No 671073).



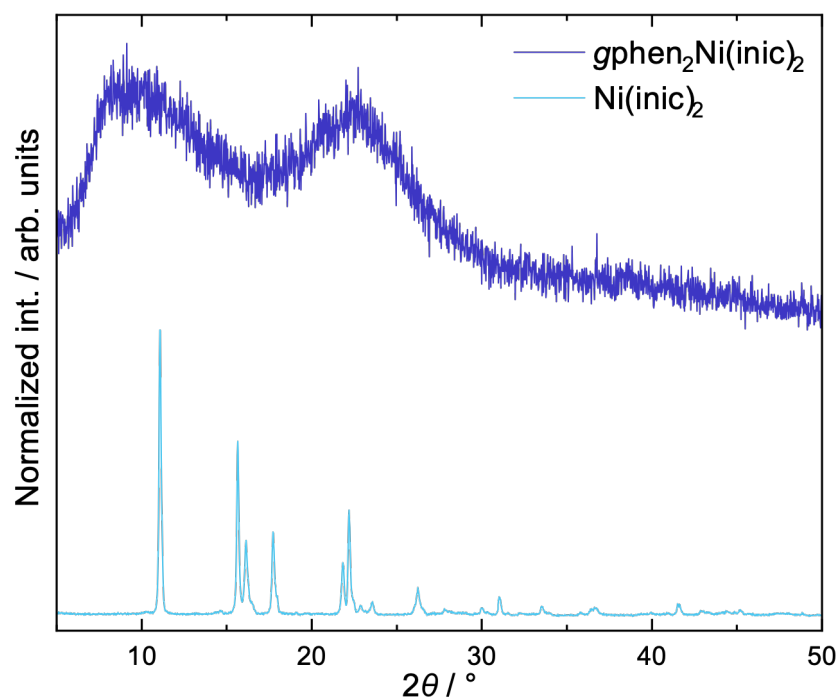
Supplementary Figure 64. PXRD pattern of $gphen_{0.49}ZIF-8$ and simulated PXRD pattern of ZIF-8 (CCDC No 864309).



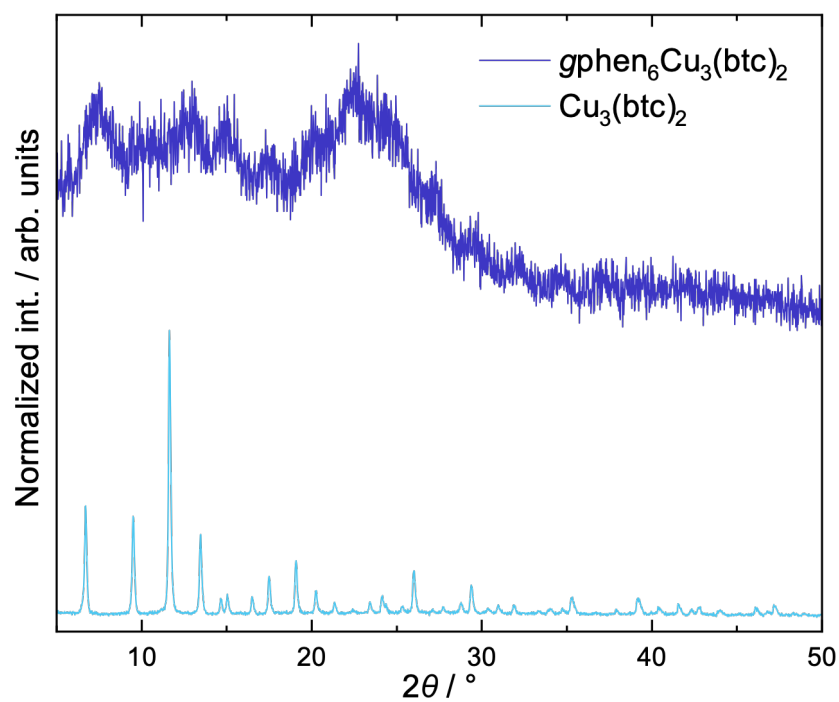
Supplementary Figure 65. PXRD pattern of $gphen_{0.29}ZIF-11$ and simulated PXRD pattern of ZIF-11 (CCDC No 602545).



Supplementary Figure 66. PXRD patterns of $Cu(im)_2$ and $gphen_{0.5}Cu(im)_2$.



Supplementary Figure 67. PXRD patterns of Ni(inic)₂ and gphen₂Ni(inic)₂.



Supplementary Figure 68. PXRD patterns of Cu₃(btc)₂ and gphen₆Cu₃(btc)₂.

Supplementary Methods 7 – Density functional theory calculations

Supplementary Table 4. Wavenumbers (in cm^{-1}) of the symmetrical and asymmetrical in-plane ring distortions of phenanthroline obtained from DFT calculations of imidazole-based model complexes (Method: PBE-D4 def2-TZVP).

	Symmetric in-plane ring distortion	Asymmetric in-plane ring distortion
phen	402	610
Co(phen)(imH) $_4^{2+}$	416	628
Co(phen)(imH) $_3^{2+}$	419	632
Co(phen)(bimH) $_4^{2+}$	414	625
Co(phen)(bimH) $_3^{2+}$	419	631
Zn(phen)(imH) $_4^{2+}$	415	631

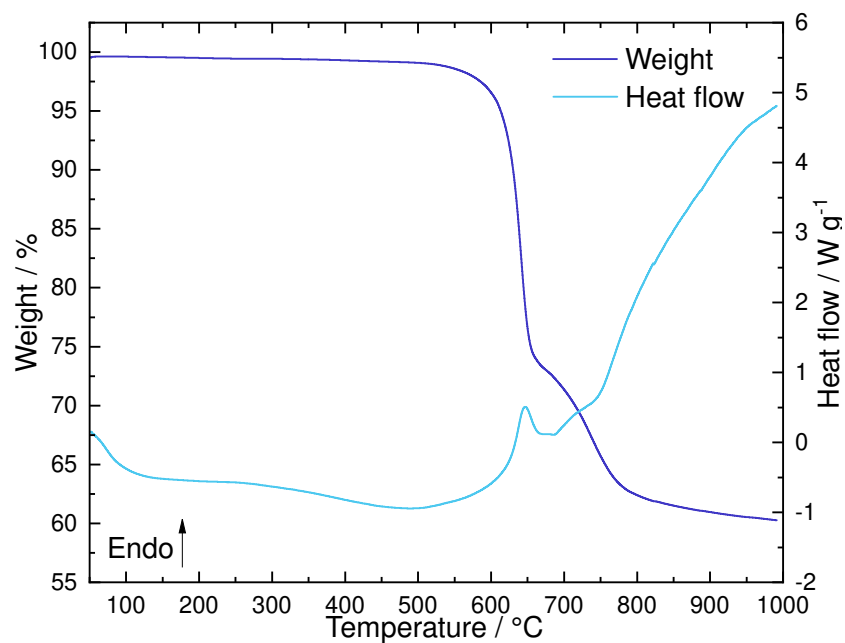
Supplementary Table 5. Wavenumbers (in cm^{-1}) M–N stretching vibrations obtained from DFT calculations.

	M–N stretching vibrations
Co(imH) $_4^{2+}$	309, 297, 296
Co(bimH) $_4^{2+}$	294, 293, 285, 272
Zn(imH) $_4^{2+}$	274, 264, 263
Co(phen)(imH) $_3^{2+}$	296, 264, 256
Co(phen)(imH) $_4^{2+}$	250, 246, 214
Co(phen)(bimH) $_3^{2+}$	294, 292, 267, 247, 234
Co(phen)(bimH) $_4^{2+}$	224, 222, 213
Zn(phen)(imH) $_4^{2+}$	210, 202, 195

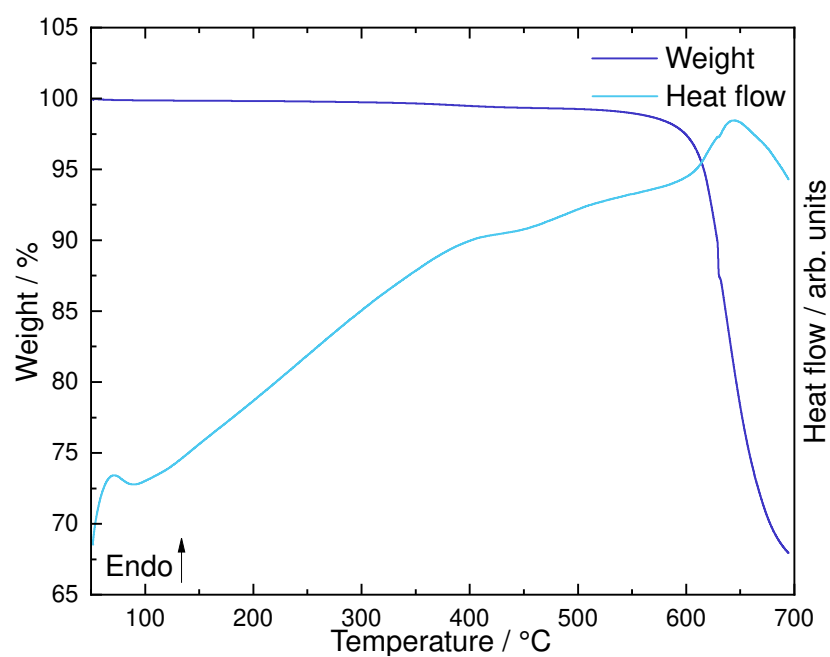
Supplementary Table 6. Wavenumbers (in cm^{-1}) of the symmetrical and asymmetrical in-plane ring distortions of phenanthroline obtained from DFT calculations of isonicotinate-based model complexes (Method: r^2 SCAN-3c).

	Symmetric in-plane ring distortion	Asymmetric in-plane ring distortion
phen	416	633
Ni(phen) $_2$ (inic) $_2$	433	655, 656
Ni(phen)(inic) $_2$ (inicH) $_2$	432	654

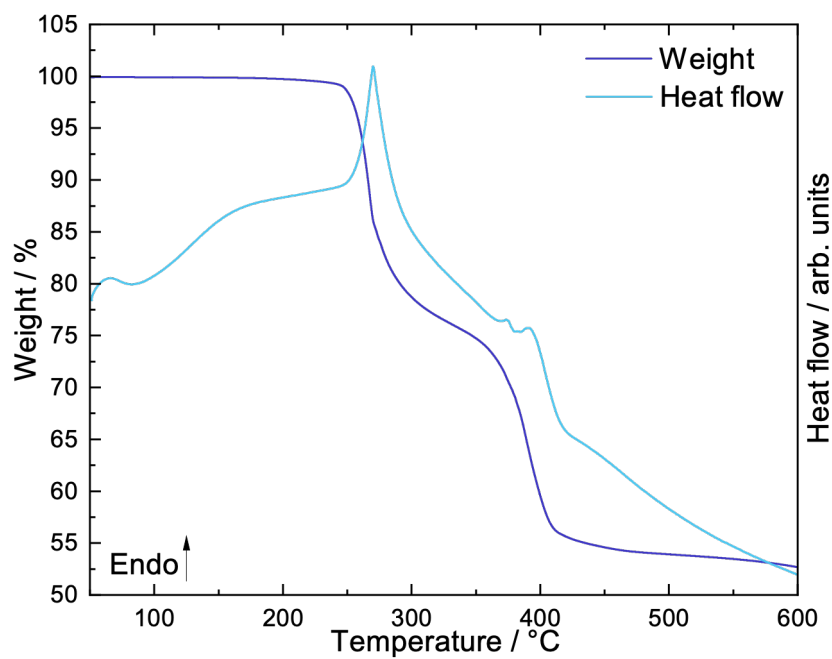
Supplementary Methods 8 – Simultaneous thermal analysis



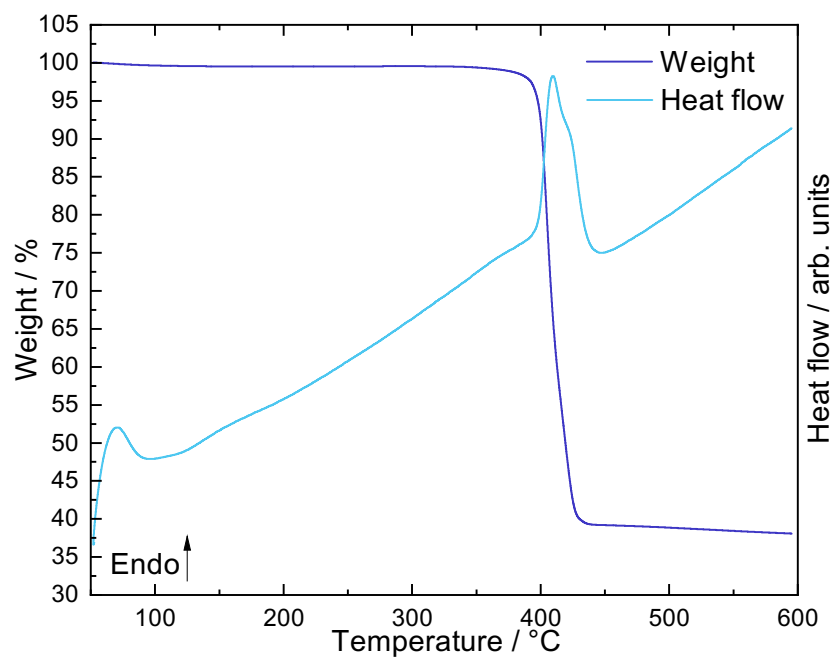
Supplementary Figure 69. DSC and TG traces of ZIF-12.



Supplementary Figure 70. DSC and TG traces of ZIF-11.



Supplementary Figure 71. DSC and TG traces of $\text{Cu}(\text{im})_2$.



Supplementary Figure 72. DSC and TG traces of $\text{Ni}(\text{inic})_2$.

Supplementary Methods 9 – Hard X-ray spectroscopy

The data preparation has been performed by “Athena” of the demeter program package (0.9.26). The background of the spectrum was removed by subtracting a Victoreen-type polynomial.⁴ E0 was defined as the first inflection point of the first derivative of the corresponding spectrum. Afterwards a piecewise polynomial was used to determine the smooth part of the spectrum and was adjusted in a way that the low-R components of the resulting Fourier transform were minimal. The background subtracted spectrum was divided by its smoothed part and the photon energy was converted to photoelectron wavenumber k . For evaluation of the EXAFS spectra the resulting functions were weighted with k^3 and calculated with EXCURVE98, working based on the EXAFS function and according to a formulation in terms of radial distribution functions:⁵

$$\chi(k) = \sum_j S_0^2(k) F_j(k) \int P_j(r_j) \frac{e^{-2r_j/\lambda}}{kr_j^2} \sin[2kr_j + \delta_j(k)] dr_j$$

The number of independent points N_{ind} was calculated according to information theory to determine the degree of overdeterminacy:⁵

$$N_{ind} = \frac{2\Delta k \Delta R}{\pi}$$

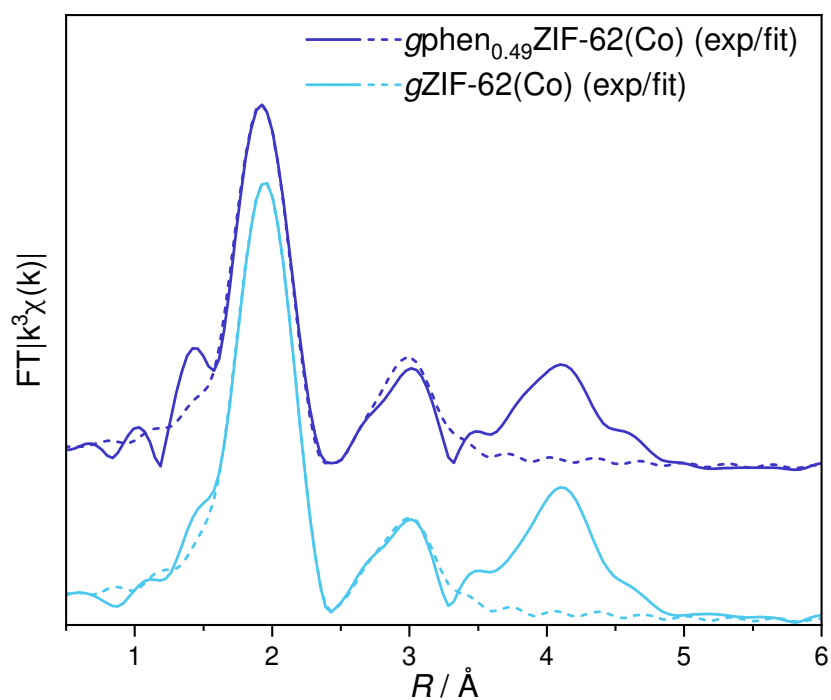
Here, Δk describes the range in k -space used for data analysis and ΔR corresponds to the distance range in the Fourier filtering (1.35-6 Å) process. Fourier filtering was applied due to non-physical artefacts in the region below 1.35 in the case of the ZIF-12 system. For the analysis a Δk -range of 9 Å⁻¹ and a ΔR -range of 3.4 Å was used, which yielded a number of independent points of 20. The quality of a fit was determined using two methods. The reduced χ_{red}^2 considers the degree of overdeterminacy of the system and the number of fitted parameters p . It therefore allows a direct comparison of different models:⁶

$$\chi_{red}^2 = \frac{(N_{ind}/N)}{N_{ind} - p} \sum_i \left(\frac{k_i^n}{\sum_j k_j^n |\chi_j^{exp}(k_j)|} \right)^2 (\chi^{exp}(k_i) - \chi^{theo}(k_i))^2$$

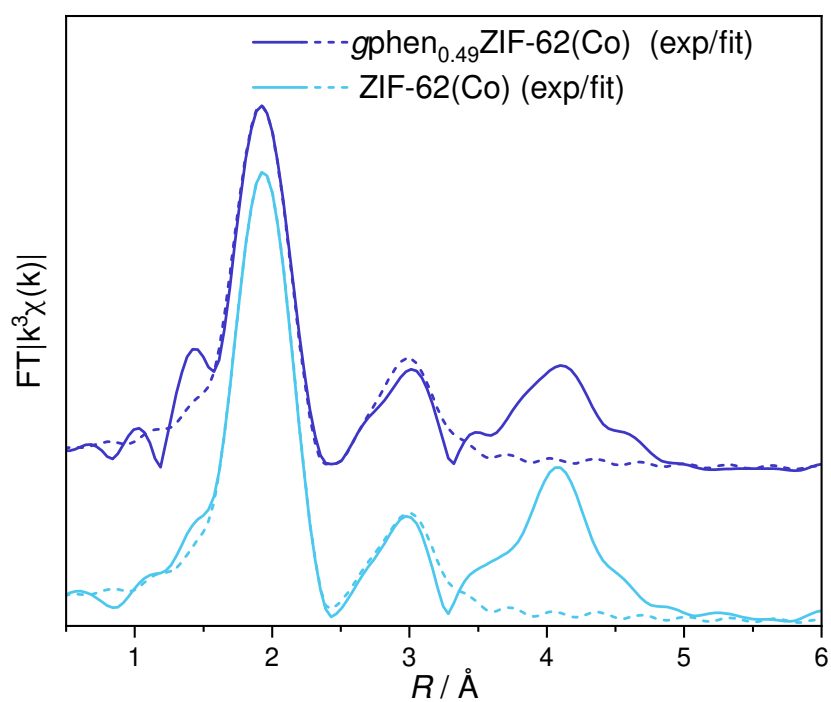
The R-factor, which represents the percentage disagreement between experiment and adjusted function and considers both systematic and random errors according to the equation:

$$R = \sum_i \frac{k_i^n}{\sum_j k_j^n |\chi_j^{exp}(k_j)|} |\chi^{exp}(k_i) - \chi^{theo}(k_i)| \cdot 100\%$$

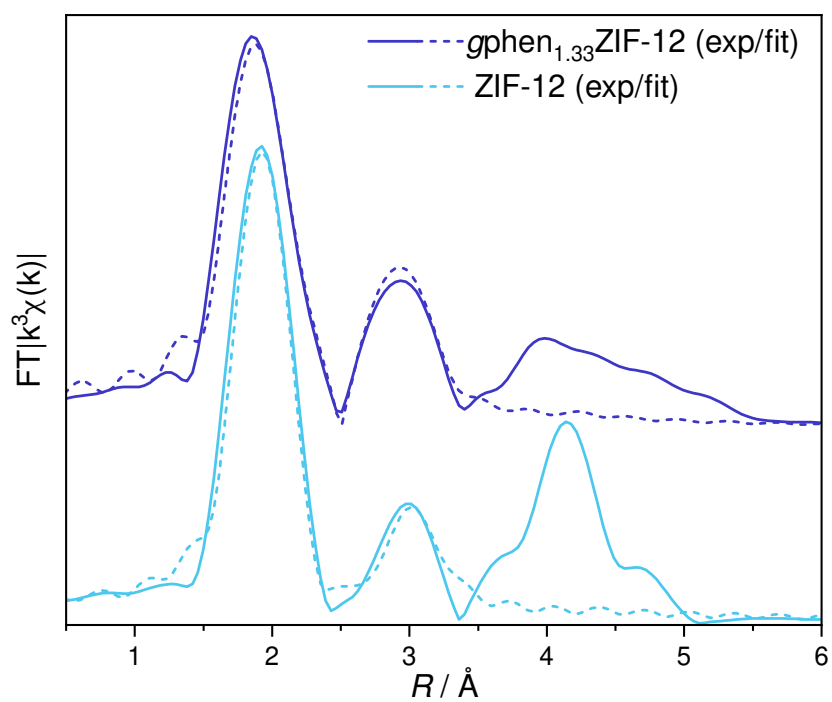
The accuracy of the determined distances is 1%, that of the Debye–Waller-like factors is 10%, and that of the coordination numbers is 5–15%, depending on the distance.⁷ Initial values for coordination numbers and distances were adopted from single-crystal structures and afterwards iterated free in every fit as well as the Debye–Waller-like factor.



Supplementary Figure 73. Fourier transformed function of the EXAFS spectra of *g*ZIF-62(Co) and *gphen*_{0.49}ZIF-62(Co).



Supplementary Figure 74. Fourier transformed function of the EXAFS spectra of ZIF-62(Co) and *gphen*_{0.49}ZIF-62(Co).



Supplementary Figure 75. Fourier transformed function of the EXAFS spectra of ZIF-12 and $gphen_{1.33}$ ZIF-12.

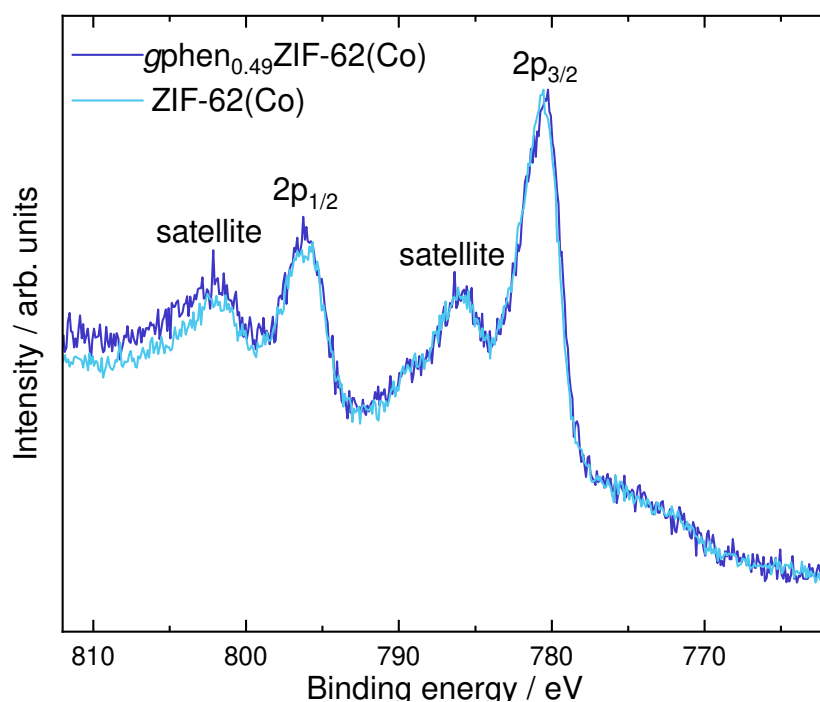
Supplementary Table 7. EXAFS analysis fitting parameters of the investigated ZIF-62 system. Fourier filtering was applied in the range of 1.3 to 4.7 Å.

Abs-Bs ^{a)}	N(Bs) ^{b)}	R(Abs-Bs)/Å ^{c)}	$\sigma/\text{\AA}$ ^{d)}	R/% ^{e)} χ^2_{red} ^{f)} E _f /eV ^{g)} A _{fac} ^{h)}
ZIF-62				
Co-N	1.6±0.1	1.912±0.019	0.039±0.003	33.77
Co-N	2.5±0.2	2.017±0.020	0.039±0.003	10.2 ×10 ⁻⁶
Co-C	7.1±0.4	2.972±0.029	0.112±0.011	2.923
				0.9105
gZIF-62				
Co-N	2.0±0.1	1.921±0.019	0.050±0.005	32.08
Co-N	2.2±0.1	2.024±0.020	0.032±0.011	9.0 ×10 ⁻⁶
Co-C	6.7±0.3	2.969±0.029	0.112±0.011	3.310
				0.9105
gphen _{0.49} ZIF-62(Co)				
Co-N	3.9±0.2	1.991±0.019	0.074±0.007	35.14
Co-N	0.8±0.1	2.199±0.022	0.112±0.011	9.9 ×10 ⁻⁶
Co-C	6.9±0.4	2.980±0.029	0.112±0.011	3.369
				0.9105
a) Abs=X-ray absorbing atom, BS=backscattering atom, b) number of backscattering atoms, c) distance between absorbing and backscattering atom, d) Debye-Waller-like factor, e) fit index, f) reduced χ^2 error (considers beside error to experiment the number of independent points and number of varied parameters), g) Fermi energy, that account for the shift between theory and experiment, h) amplitude reducing factor, i) Atom distances obtained from single crystal structure				

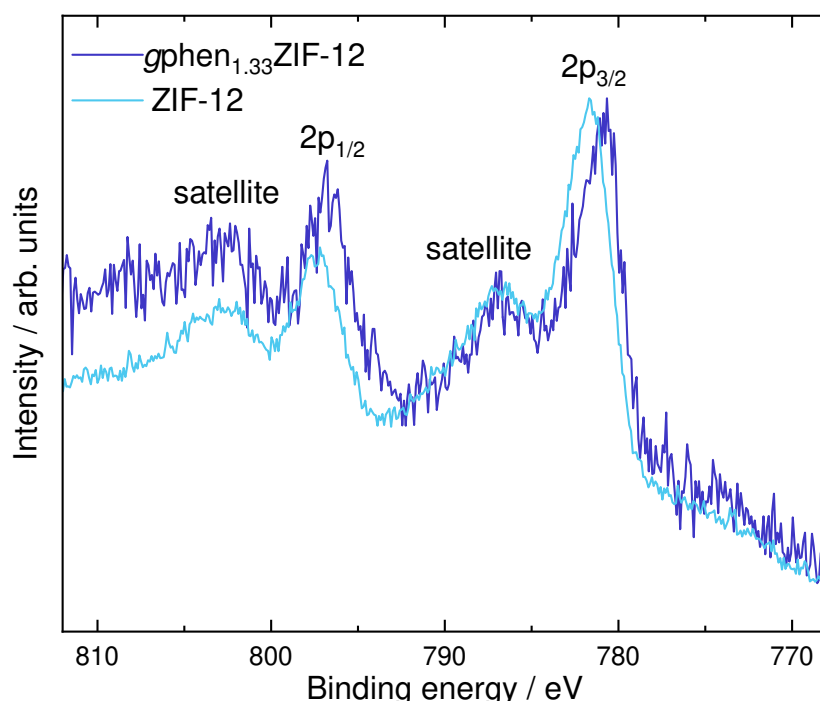
Supplementary Table 8. EXAFS analysis fitting parameters of the investigated ZIF-12 system. Fourier filtering was applied in the range of 1.35 to 6.0 Å.

Abs-Bs ^{a)}	N(Bs) ^{b)}	R(Abs-Bs)/Å ^{c)}	$\sigma/\text{\AA}$ ^{d)}	R/% ^{e)} χ^2_{red} ^{f)} E_f/eV ^{g)} Afac ^{h)}
ZIF-12				
Co-N	3.8±0.2	1.979±0.019	0.071±0.007	43.12
Co-C	6.2±0.3	3.006±0.030	0.112±0.011	22.7 ×10 ⁻⁶ 1.684 0.800
gphen _{1.33} ZIF-12				
Co-N	1.3±0.1	1.949±0.019	0.032±0.003	29.90
Co-N	3.7±0.2	2.025±0.020	0.087±0.008	14.6 ×10 ⁻⁶
Co-C	7.7±0.4	2.956±0.029	0.112±0.011	-4.776 0.800
a) Abs=X-ray absorbing atom, BS=backscattering atom, b) number of backscattering atoms, c) distance between absorbing and backscattering atom, d) Debye-Waller-like factor, e) fit index, f) reduced χ^2 error (considers beside error to experiment the number of independent points and number of varied parameters), g) Fermi energy, that account for the shift between theory and experiment, h) amplitude reducing factor, i) Atom distances obtained from single crystal structure				

Supplementary Methods 10 – X-ray photoelectron spectroscopy

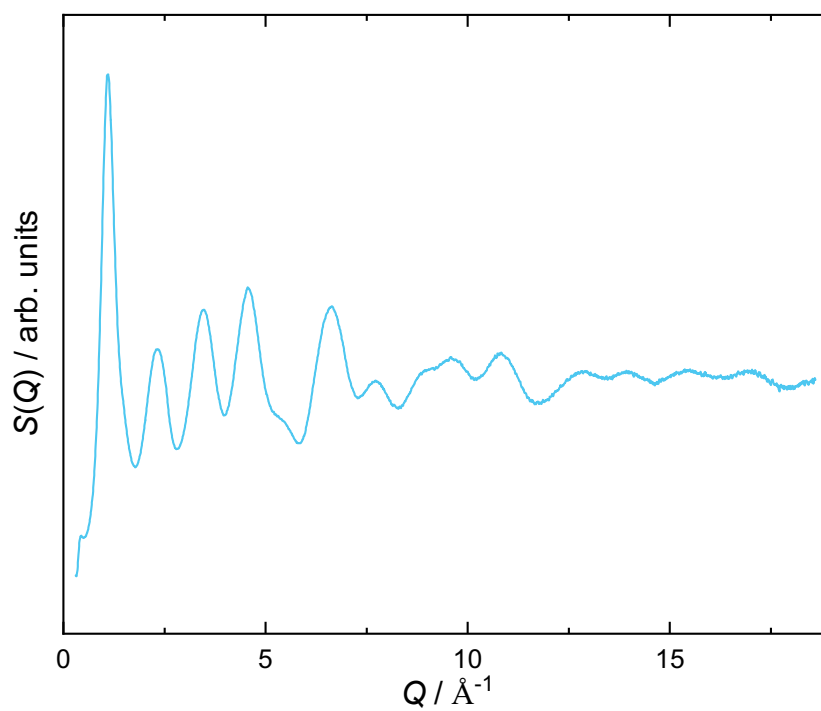


Supplementary Figure 76. Cobalt 2p_{3/2} and 2p_{1/2} peaks of the XPS spectra of ZIF-62(Co) and gphen_{0.49}ZIF-62(Co).

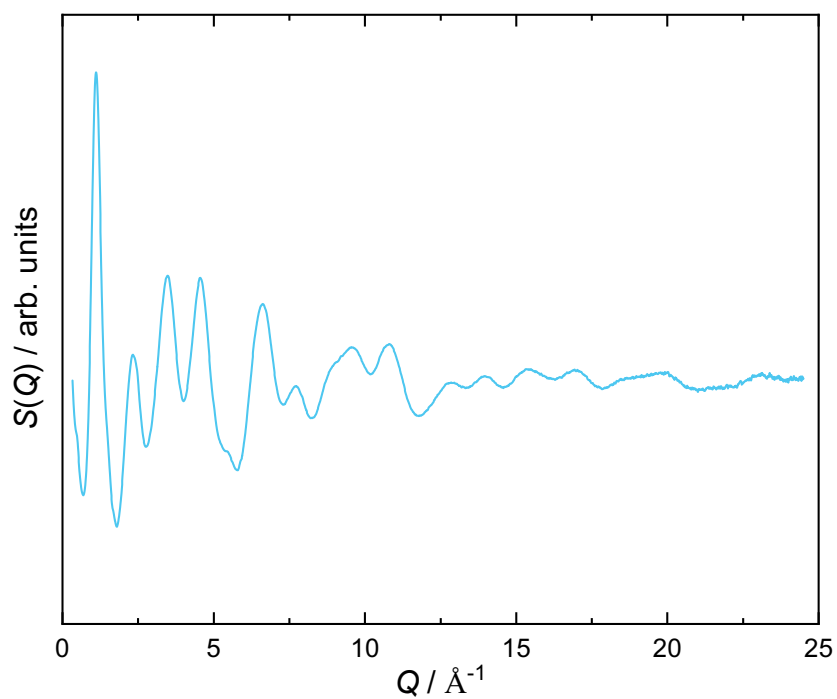


Supplementary Figure 77. Cobalt 2p_{3/2} and 2p_{1/2} peaks of the XPS spectra of ZIF-12 and gphen_{1.33}ZIF-12.

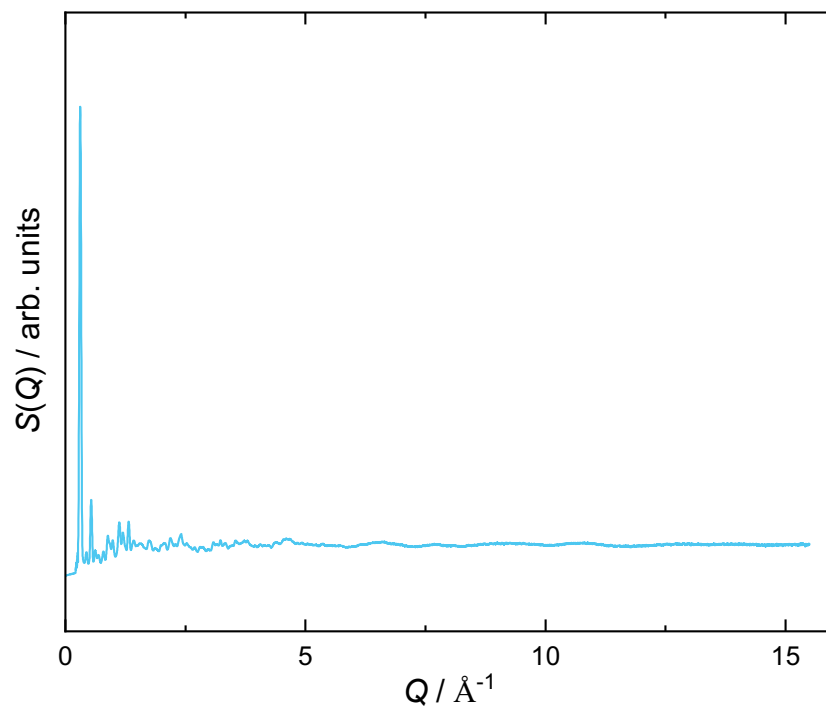
Supplementary Methods 11 – X-ray total scattering



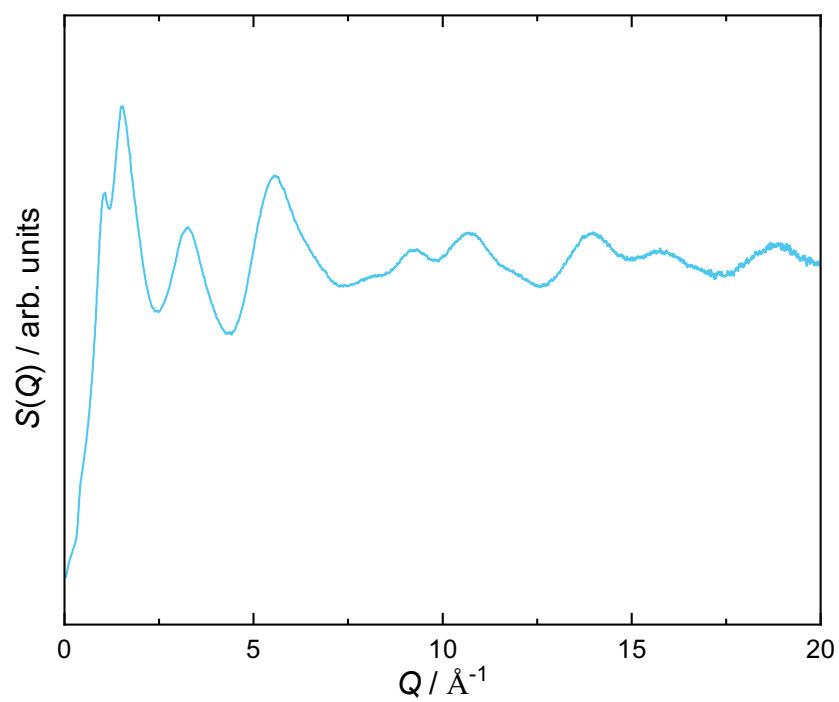
Supplementary Figure 78. X-ray total scattering data in the form of $S(Q)$ of *g*ZIF-62(Zn).



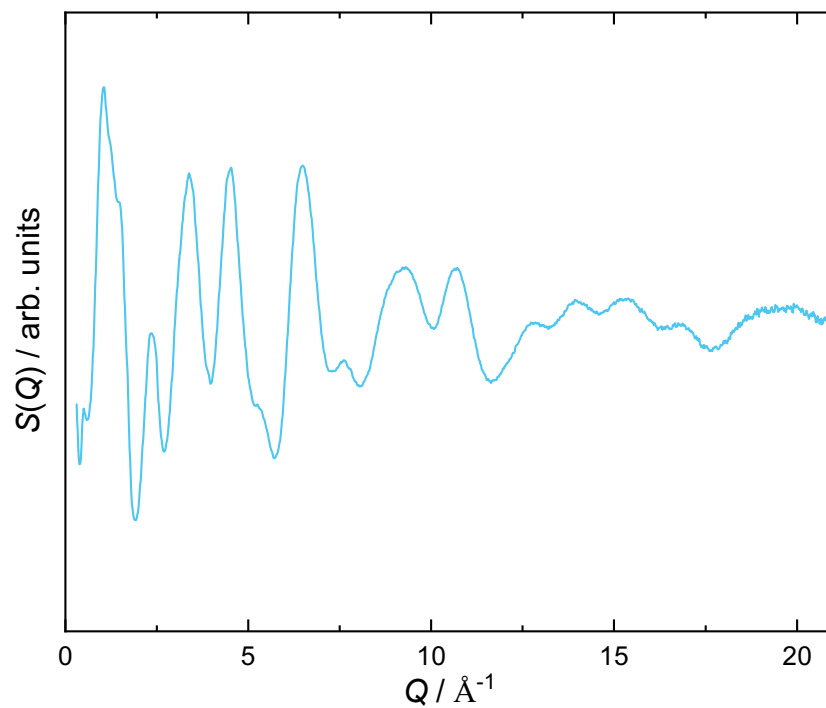
Supplementary Figure 79. X-ray total scattering data in the form of $S(Q)$ of *g*ZIF-62(Co).



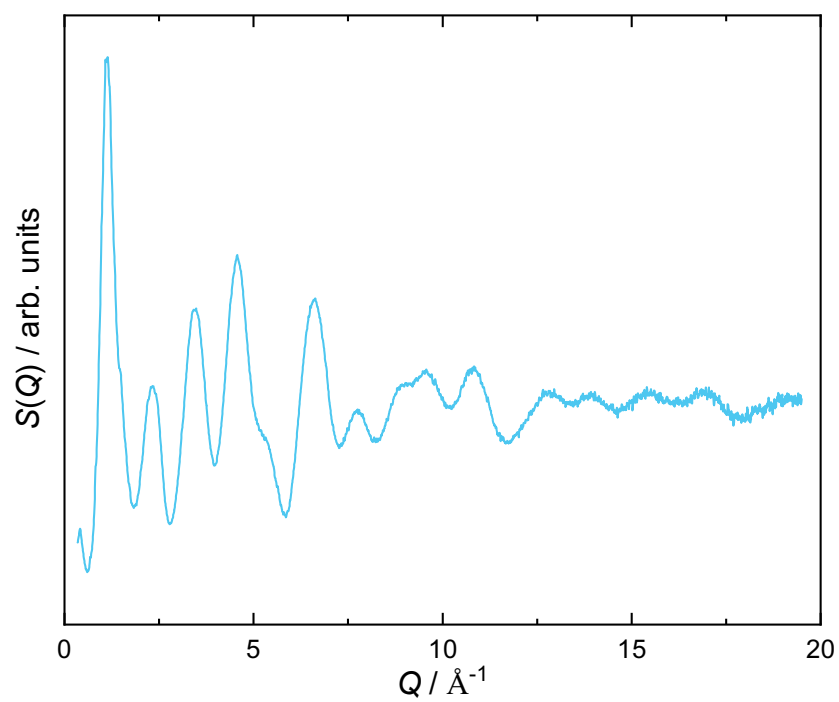
Supplementary Figure 80. X-ray total scattering data in the form of $S(Q)$ of ZIF-12.



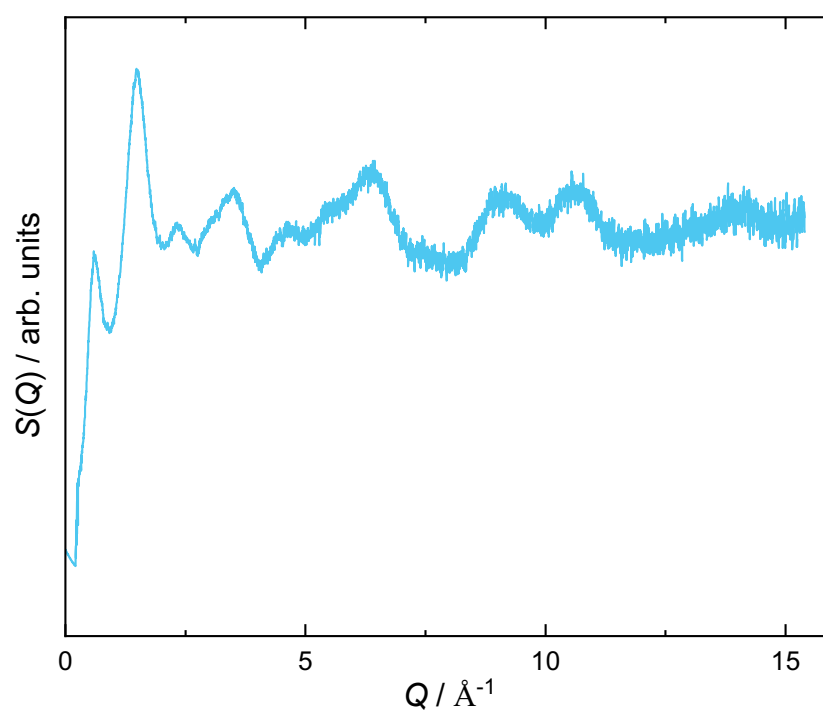
Supplementary Figure 81. X-ray total scattering data in the form of $S(Q)$ of phen at 150 °C.



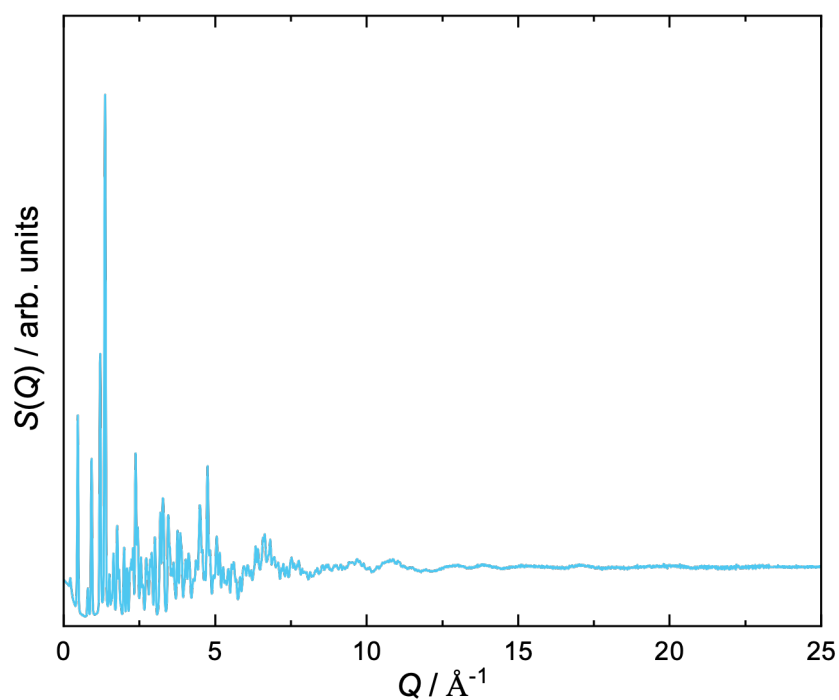
Supplementary Figure 82. X-ray total scattering data in the form of $S(Q)$ of gphen_{0.49}ZIF-62(Co).



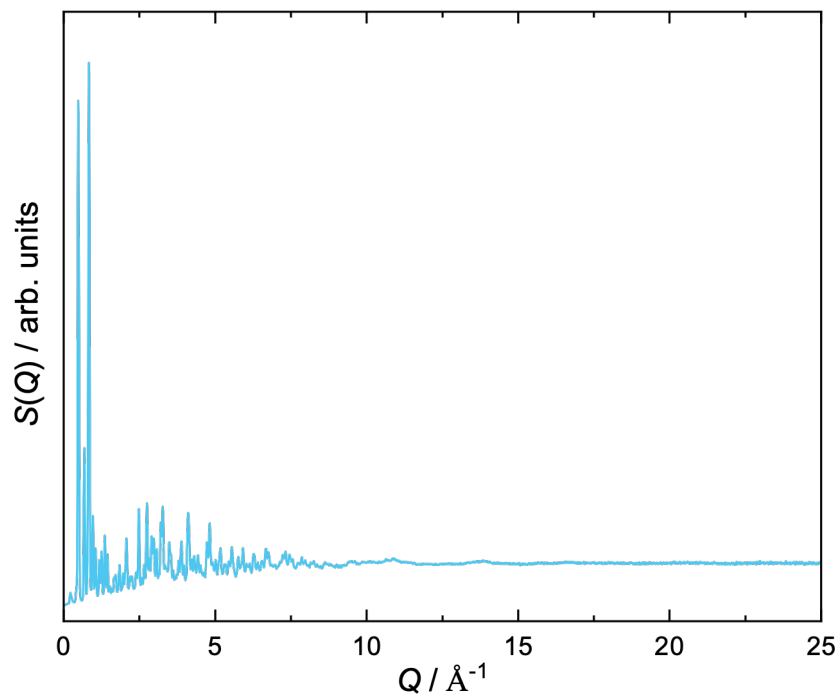
Supplementary Figure 83. X-ray total scattering data in the form of $S(Q)$ of gphen_{0.51}ZIF-62(Zn).



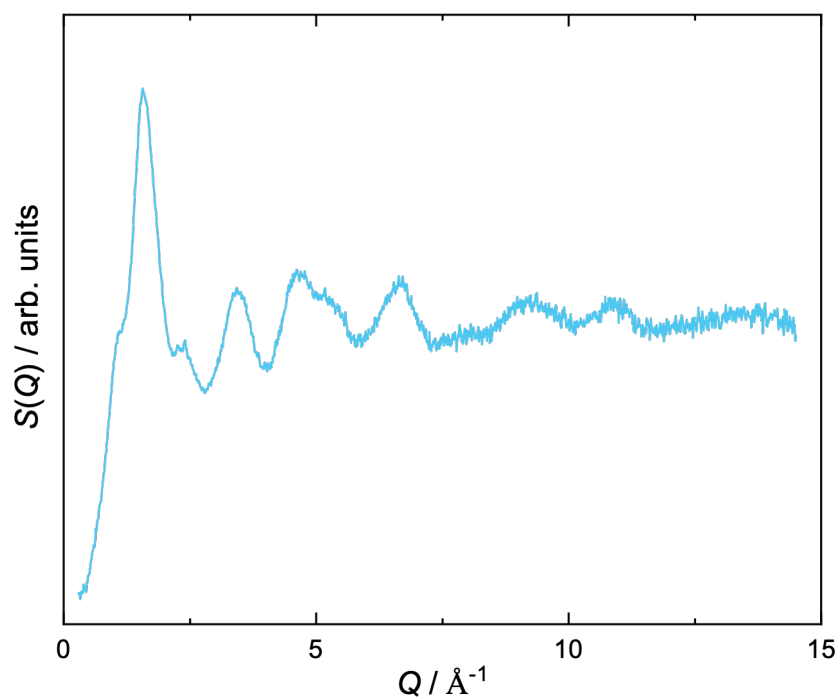
Supplementary Figure 84. X-ray total scattering data in the form of $S(Q)$ of $\text{gphen}_{1.33}\text{ZIF-12}$.



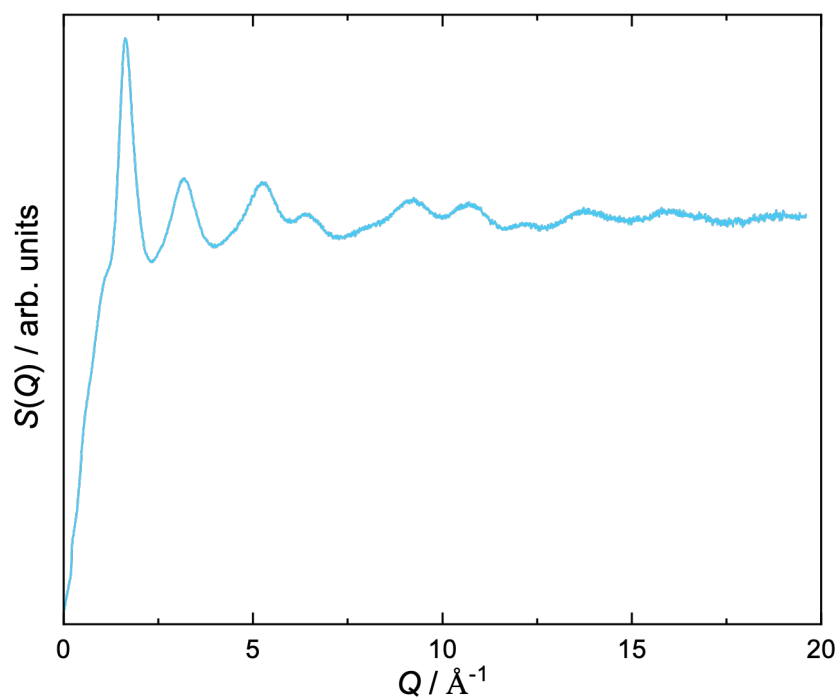
Supplementary Figure 85. X-ray total scattering data in the form of $S(Q)$ of Cu(im)_2 .



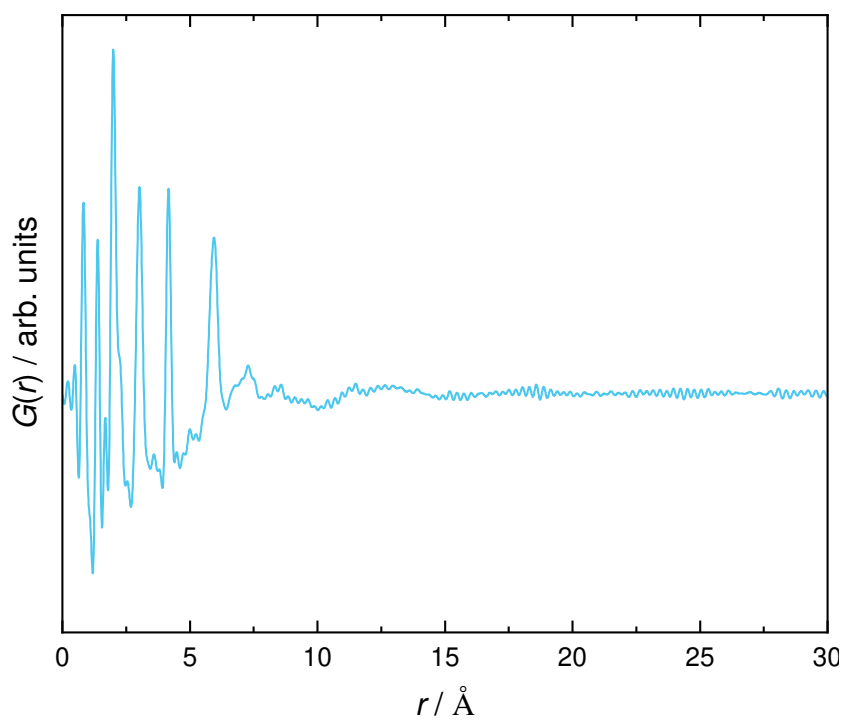
Supplementary Figure 86. X-ray total scattering data in the form of $S(Q)$ of $\text{Cu}_3(\text{btc})_2$.



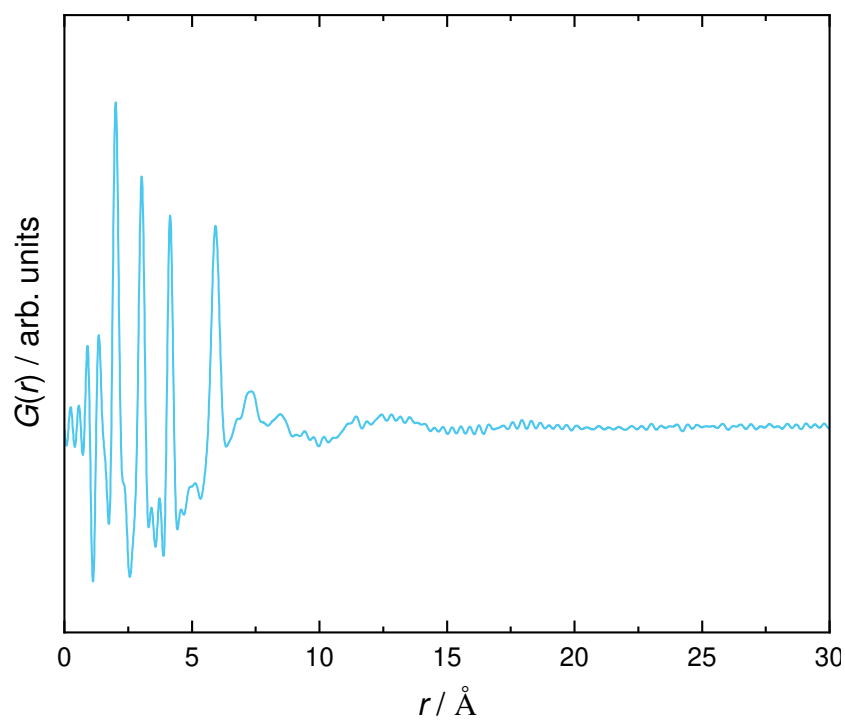
Supplementary Figure 87. X-ray total scattering data in the form of $S(Q)$ of $\text{gphen}_{0.5}\text{Cu}(\text{im})_2$.



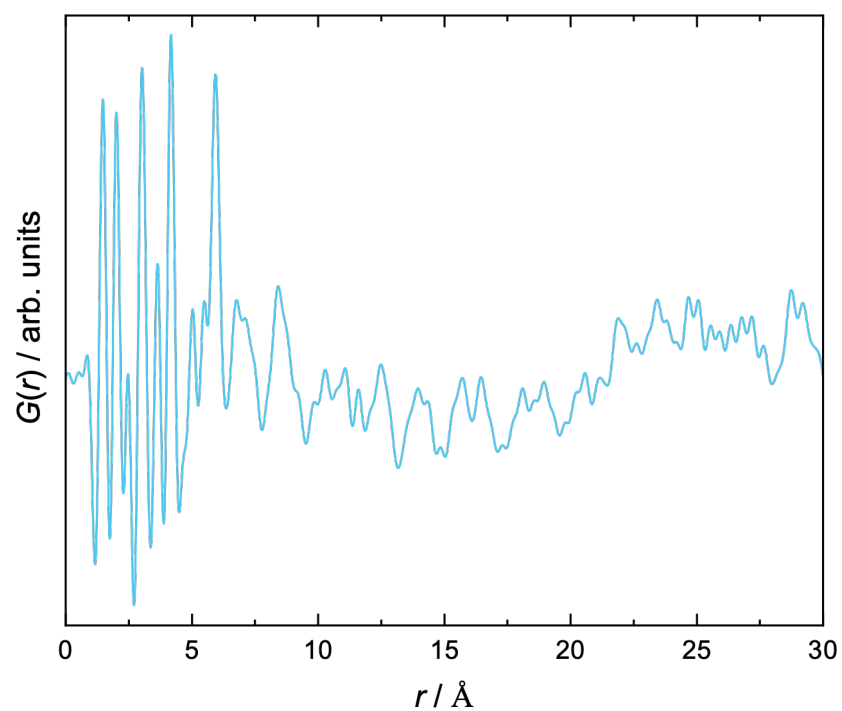
Supplementary Figure 88. X-ray total scattering data in the form of $S(Q)$ of $g\text{phen}_6\text{Cu}_3(\text{btc})_2$.



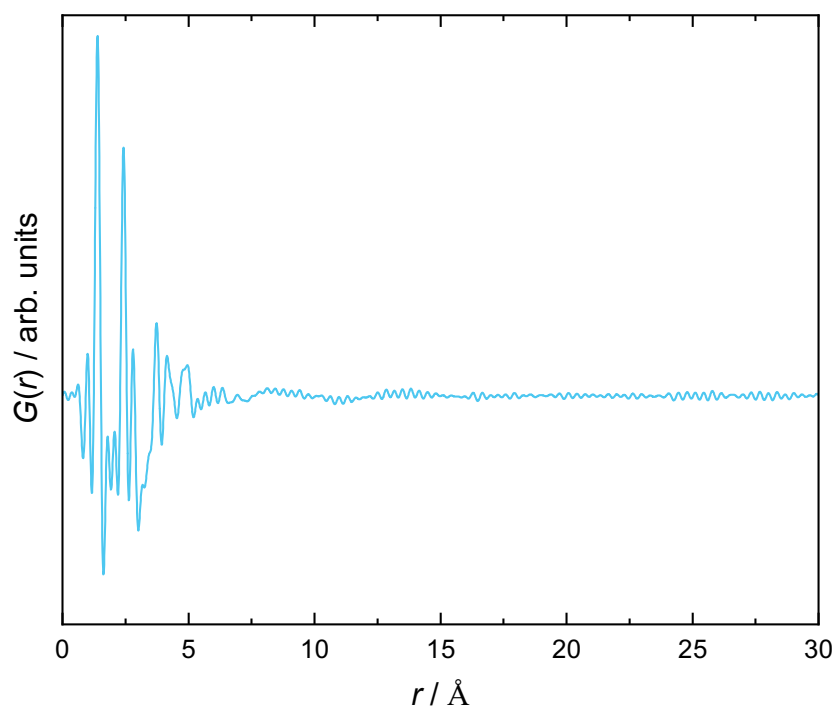
Supplementary Figure 89. Pair distribution function $G(r)$ of $g\text{ZIF-62}(\text{Co})$.



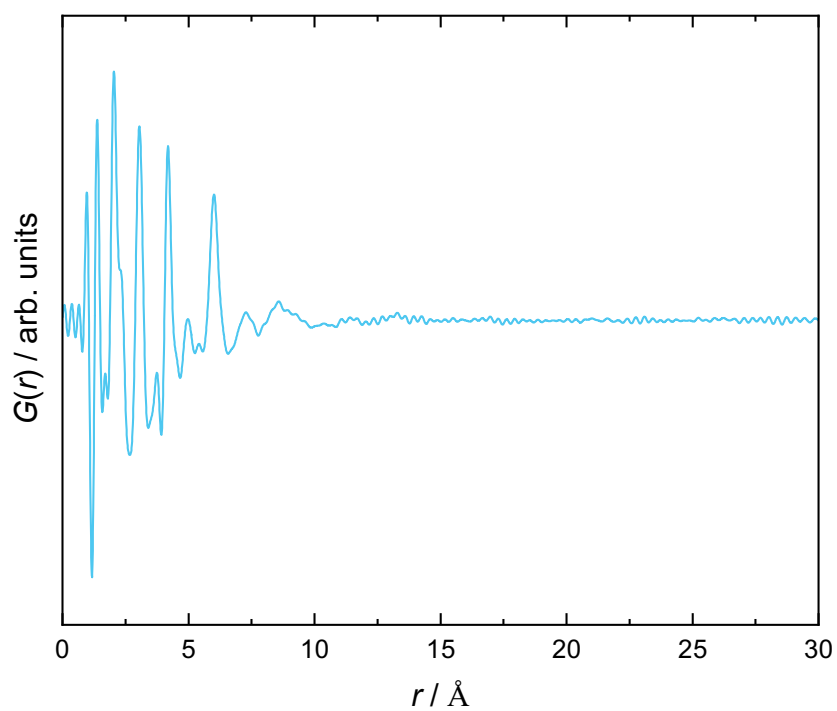
Supplementary Figure 90. Pair distribution function $G(r)$ of gZIF-62(Zn).



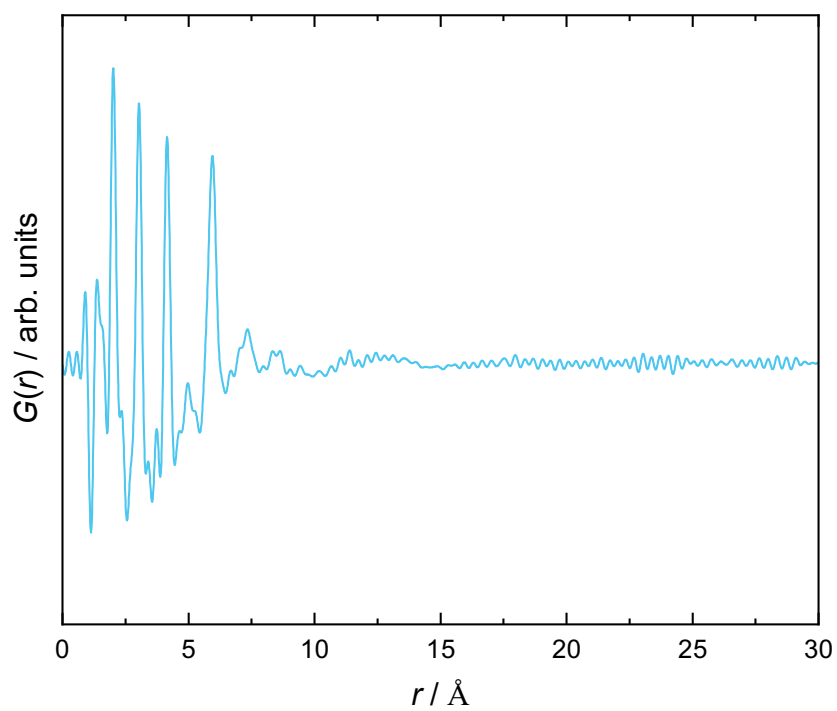
Supplementary Figure 91. Pair distribution function $G(r)$ of ZIF-12.



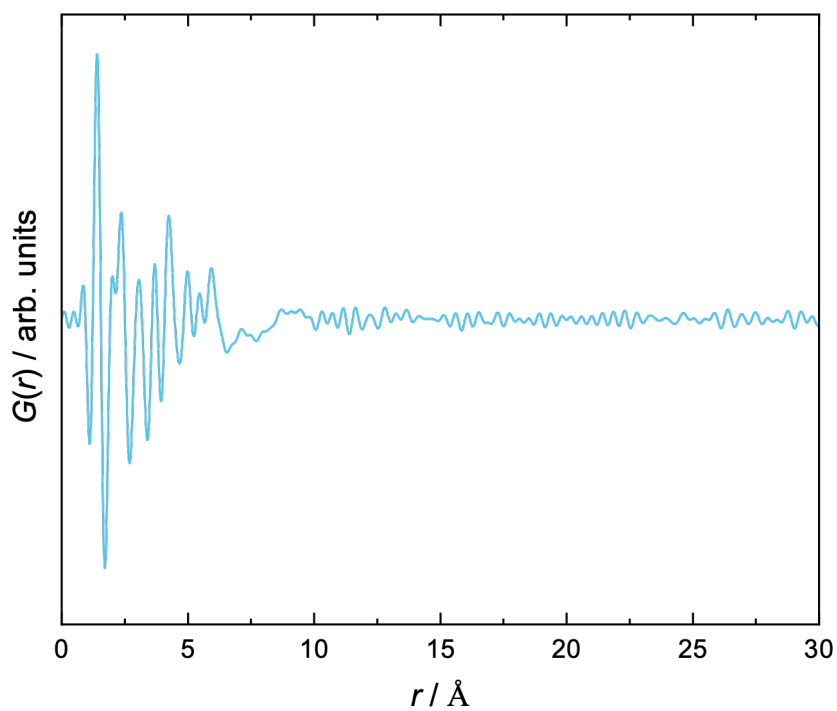
Supplementary Figure 92. Pair distribution function $G(r)$ of liquid phen at 150 °C.



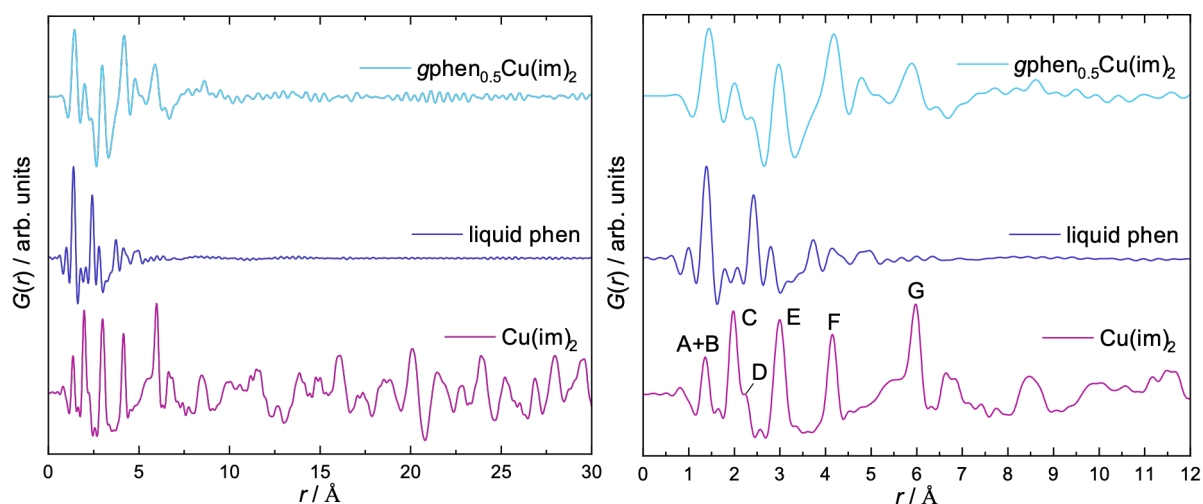
Supplementary Figure 93. Pair distribution function $G(r)$ of $\text{gphen}_{0.49}\text{ZIF-62}(\text{Co})$.



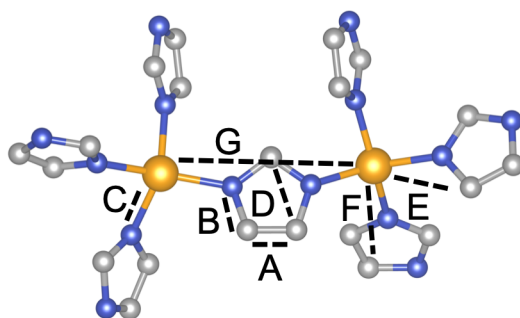
Supplementary Figure 94. Pair distribution function $G(r)$ of $\text{gphen}_{0.51}\text{ZIF-62}(\text{Zn})$.



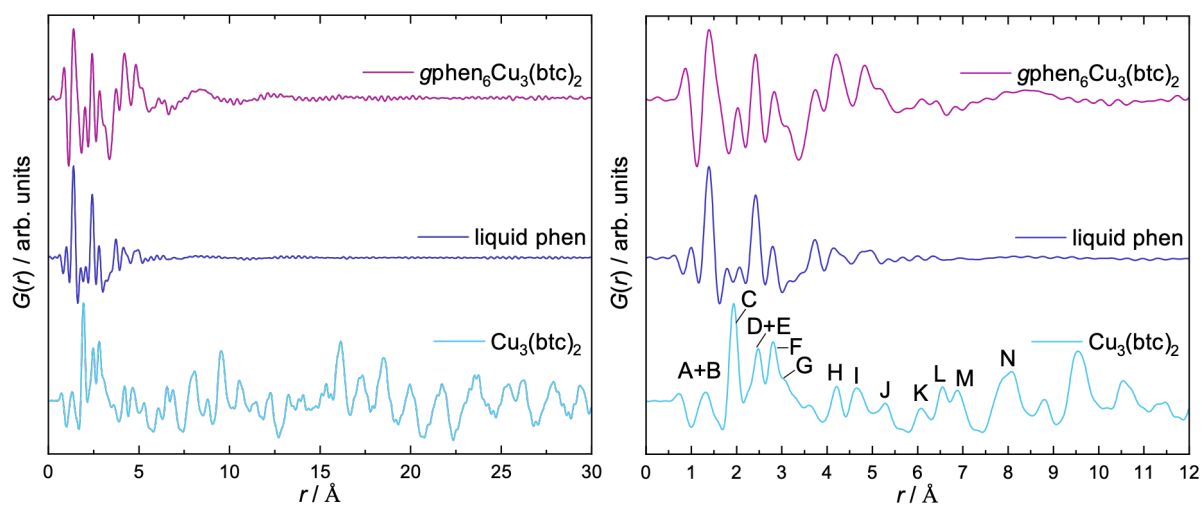
Supplementary Figure 95. Pair distribution function $G(r)$ of $\text{gphen}_{1.33}\text{ZIF-12}$.



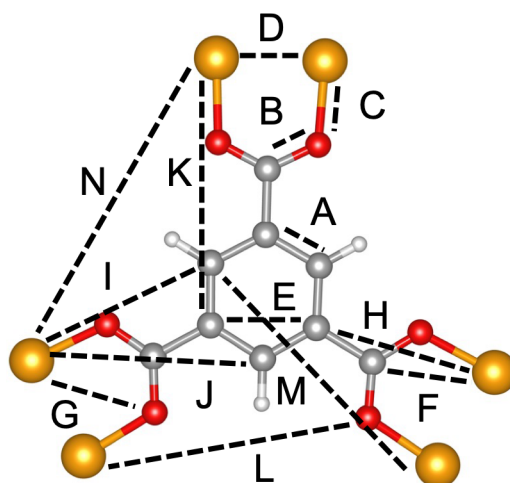
Supplementary Figure 96. Pair distribution functions $G(r)$ of $\text{Cu}(\text{im})_2$, liquid phen, and $\text{gphen}_{0.5}\text{Cu}(\text{im})_2$.



Supplementary Figure 97. Interatomic distances in $\text{Cu}(\text{im})_2$ up to 6 Å.

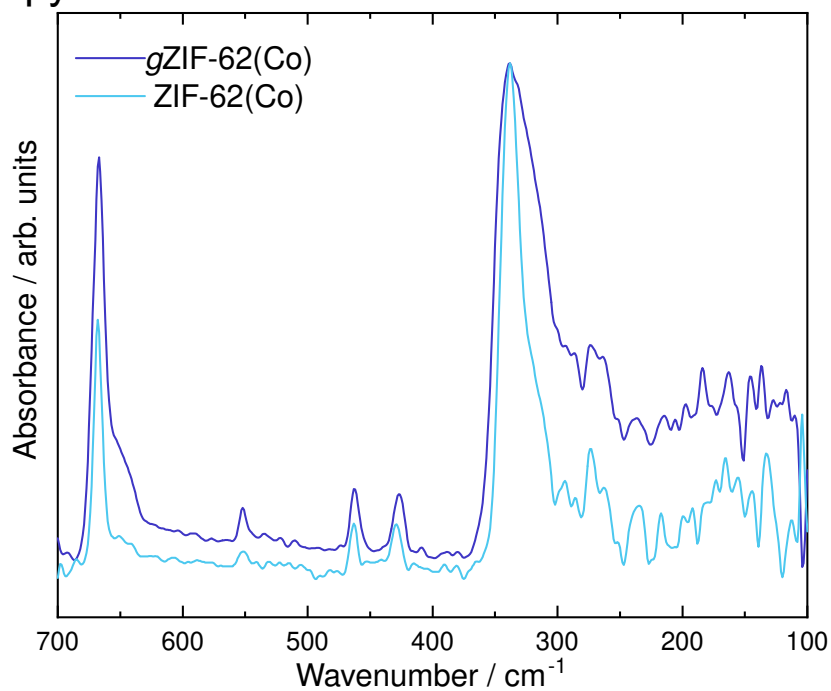


Supplementary Figure 98. Pair distribution functions $G(r)$ of $\text{Cu}_3(\text{btc})_2$, liquid phen, and $\text{gphen}_6\text{Cu}_3(\text{btc})_2$.

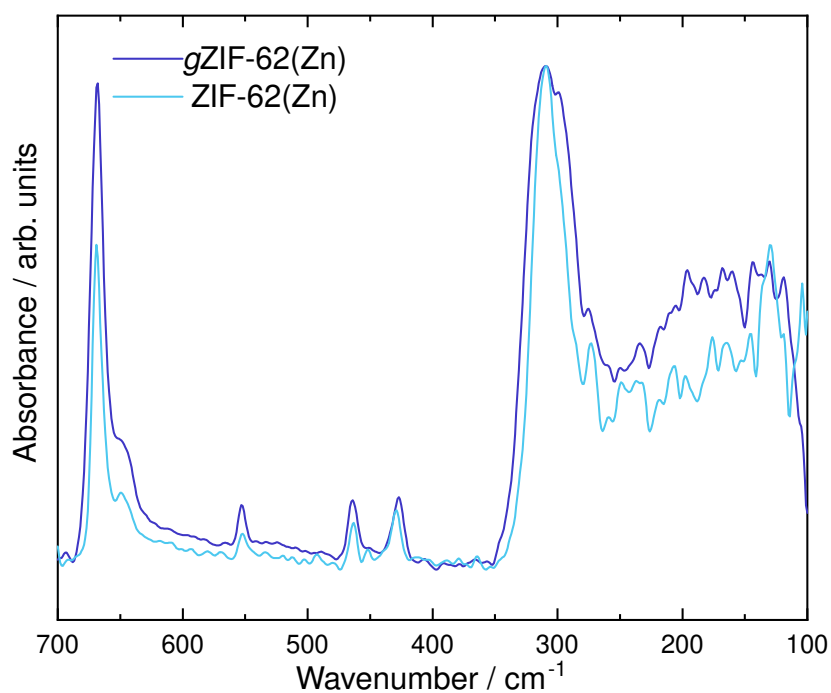


Supplementary Figure 99. Interatomic distances in $\text{Cu}_3(\text{btc})_2$ up to 8 Å.

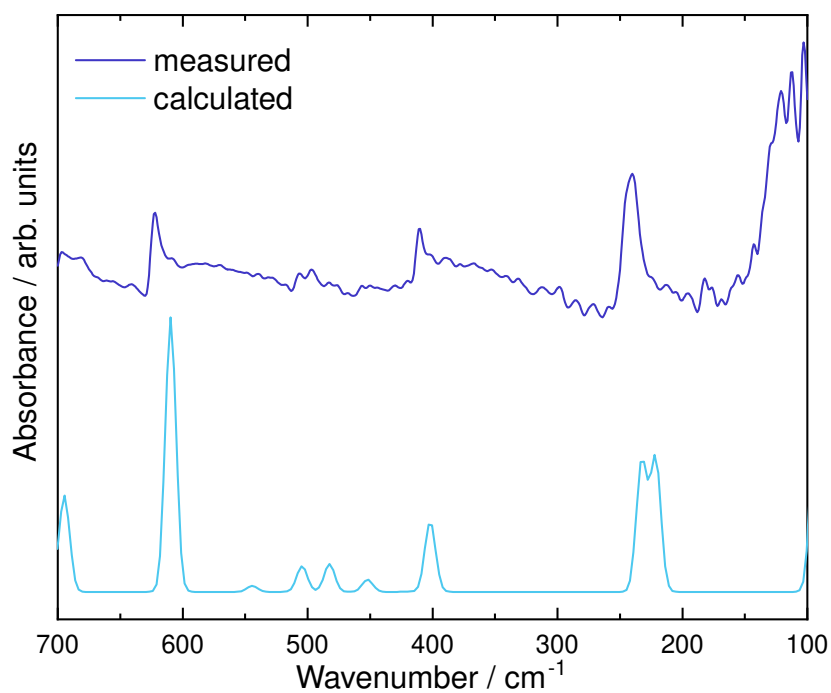
Supplementary Methods 12 – Fourier-transform far-infrared spectroscopy



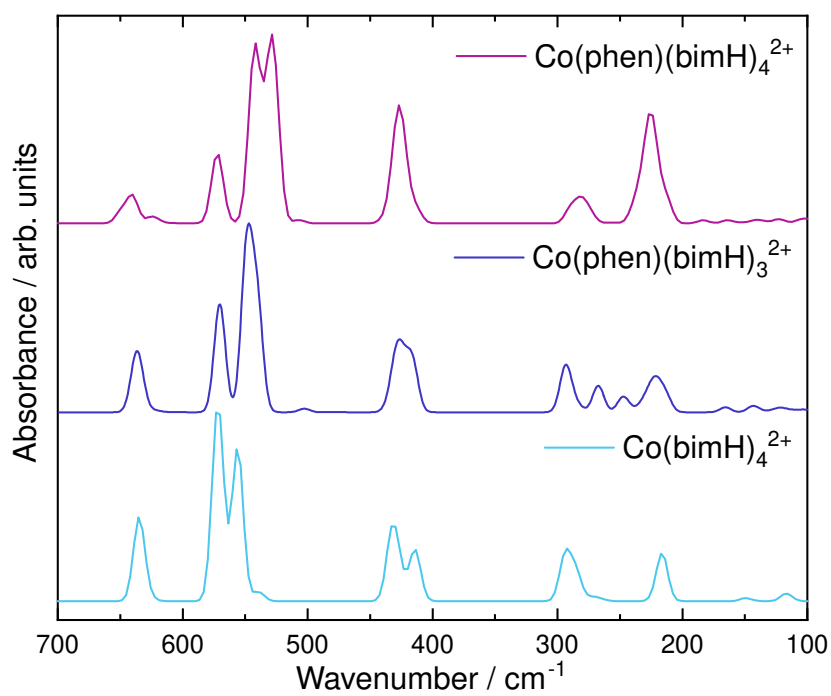
Supplementary Figure 100. Far-IR spectra of ZIF-62(Co) and the corresponding glass.



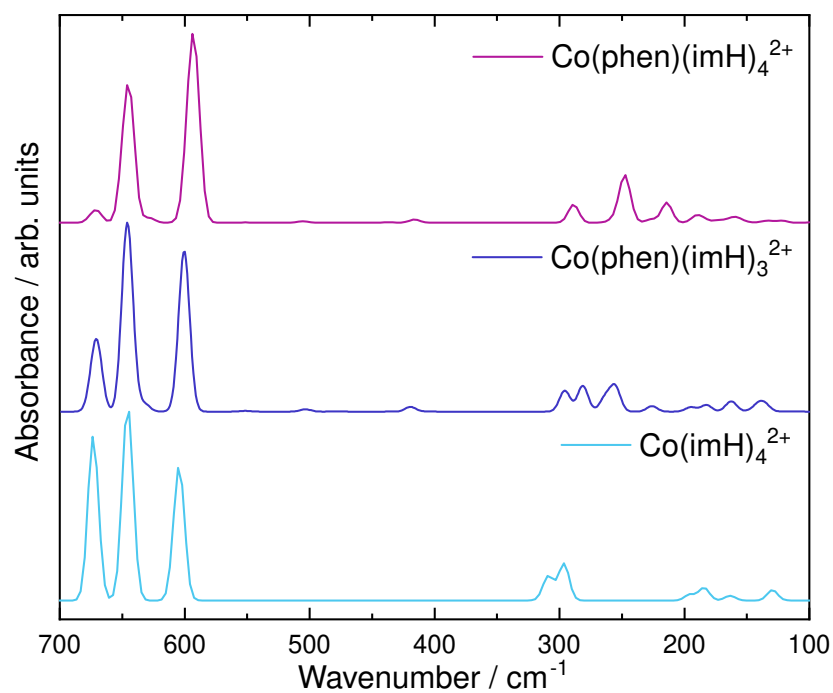
Supplementary Figure 101. Far-IR spectra of ZIF-62(Zn) and the corresponding glass.



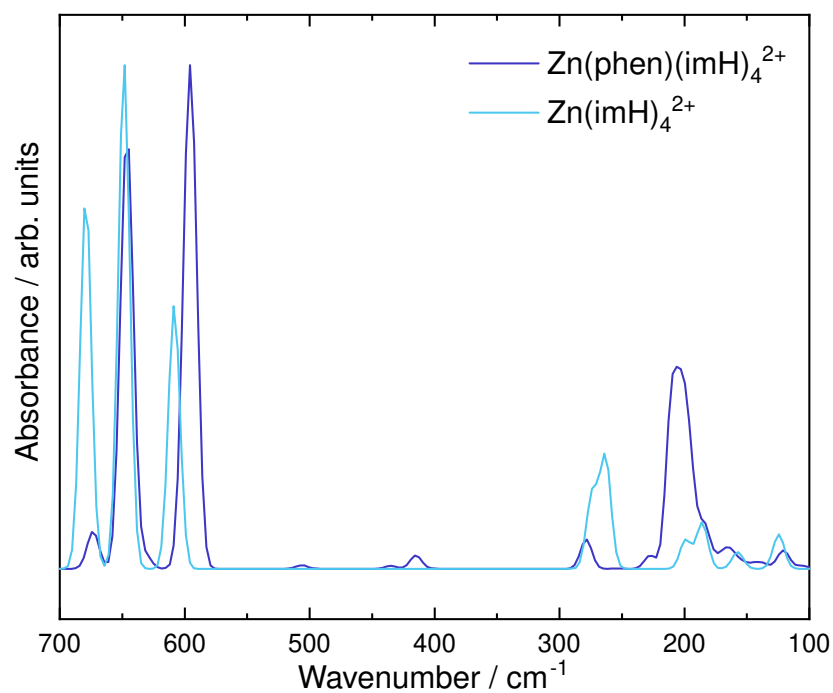
Supplementary Figure 102. Experimental and calculated far-IR spectrum of phen.



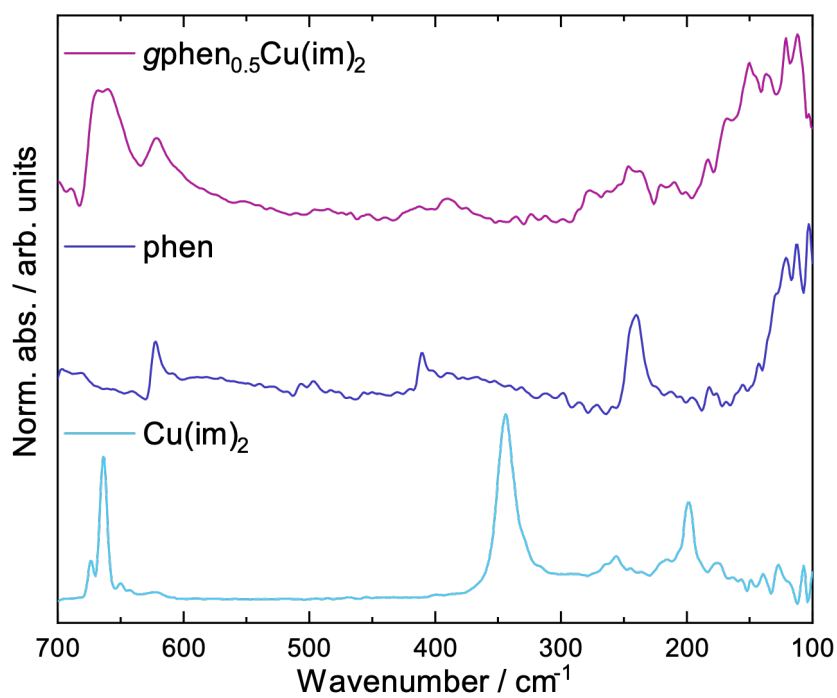
Supplementary Figure 103. Calculated far-IR spectra of the complexes $\text{Co}(\text{bimH})_4^{2+}$, $\text{Co}(\text{phen})(\text{bimH})_3^{2+}$, and $\text{Co}(\text{phen})(\text{bimH})_4^{2+}$.



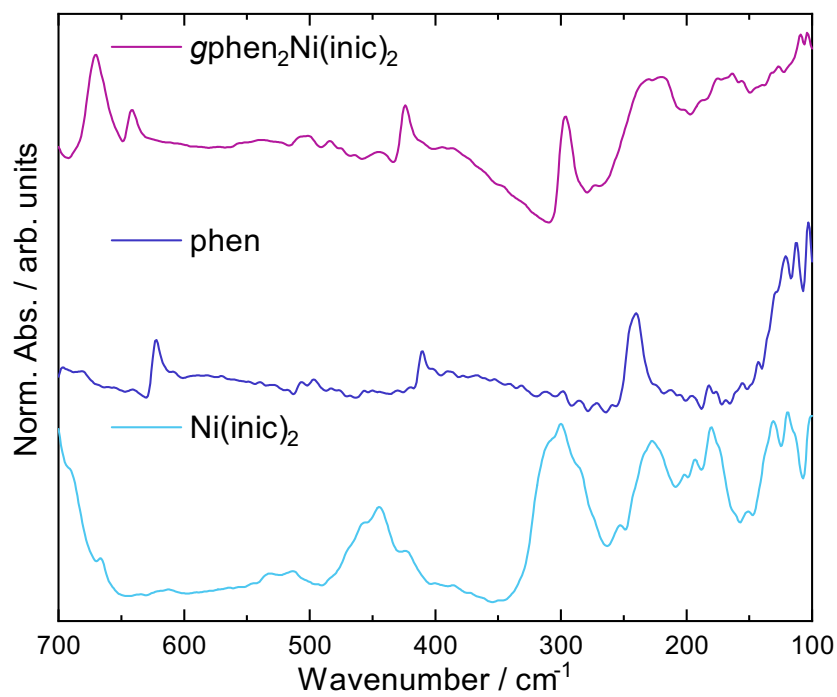
Supplementary Figure 104. Calculated far-IR spectra of the complexes $\text{Co}(\text{imH})_4^{2+}$, $\text{Co}(\text{phen})(\text{imH})_3^{2+}$, and $\text{Co}(\text{phen})(\text{imH})_4^{2+}$.



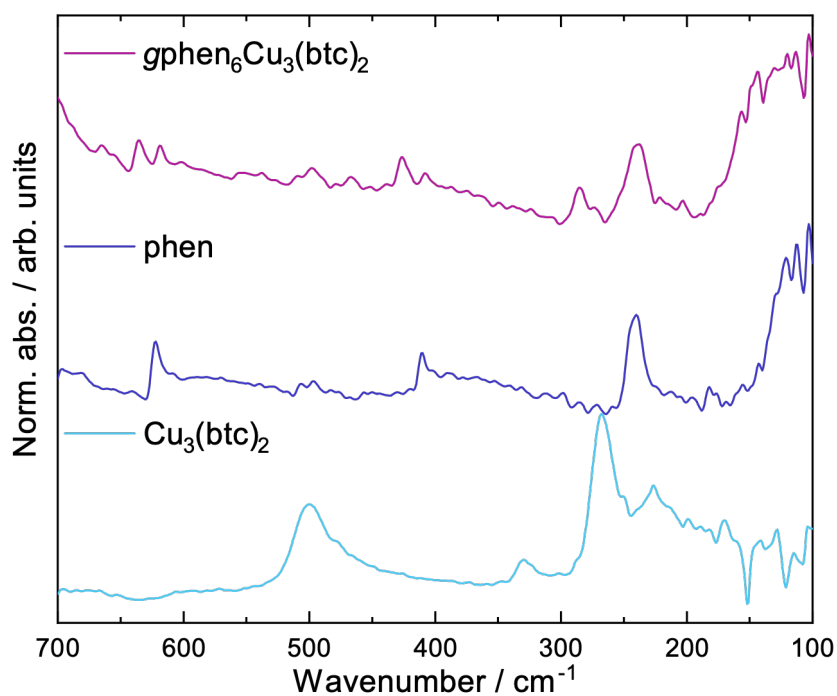
Supplementary Figure 105. Calculated far-IR spectra of the complexes $\text{Zn}(\text{imH})_4^{2+}$ and $\text{Zn}(\text{phen})(\text{imH})_4^{2+}$.



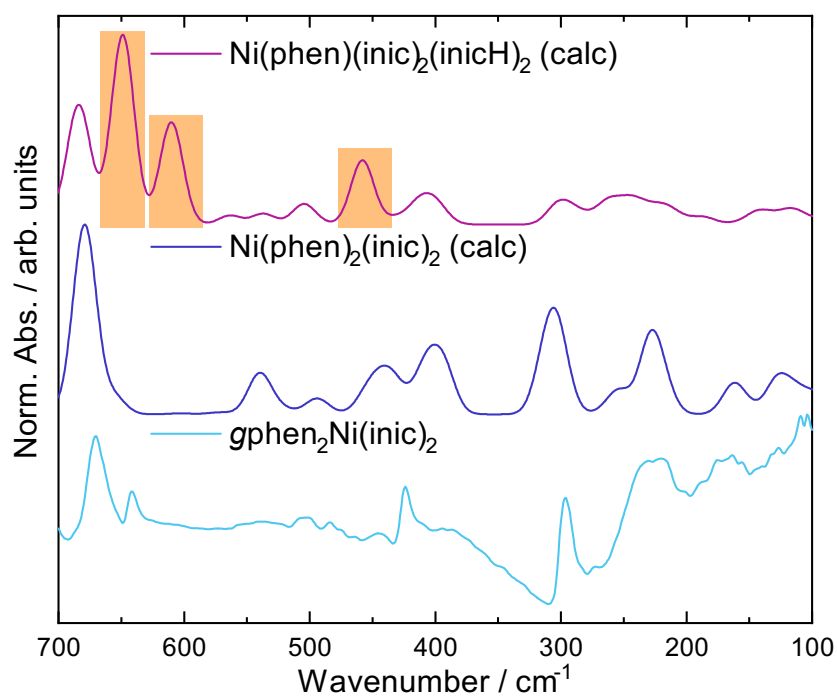
Supplementary Figure 106. Far-IR spectra of $Cu(im)_2$, phen, and $gphen_{0.5}Cu(im)_2$.



Supplementary Figure 107. Far-IR spectra of $Ni(inic)_2$, phen, and $gphen_2Ni(inic)_2$.

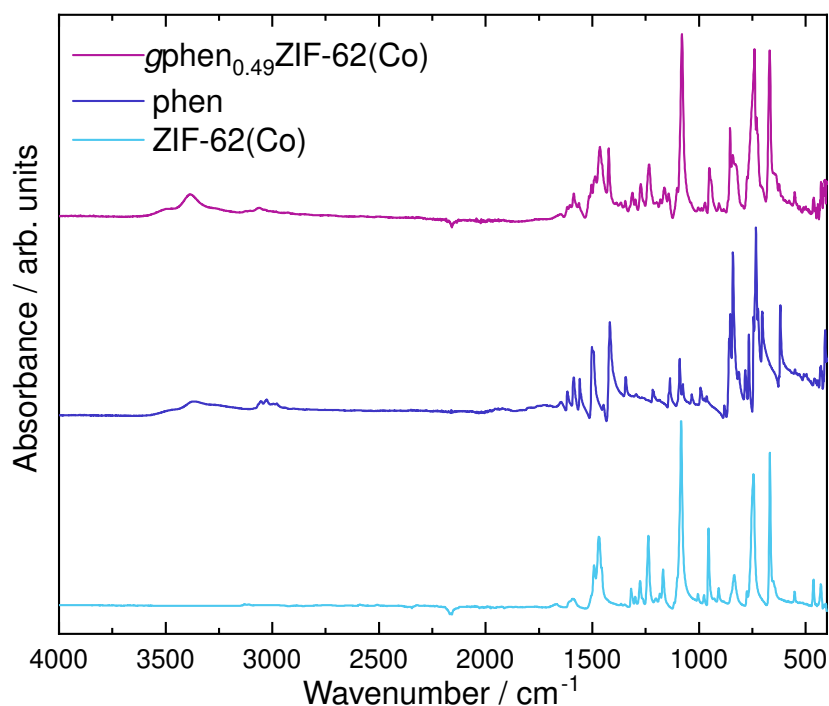


Supplementary Figure 108. Far-IR spectra of $Cu_3(btc)_2$, $phen$, and $gphen_6Cu_3(btc)_2$.

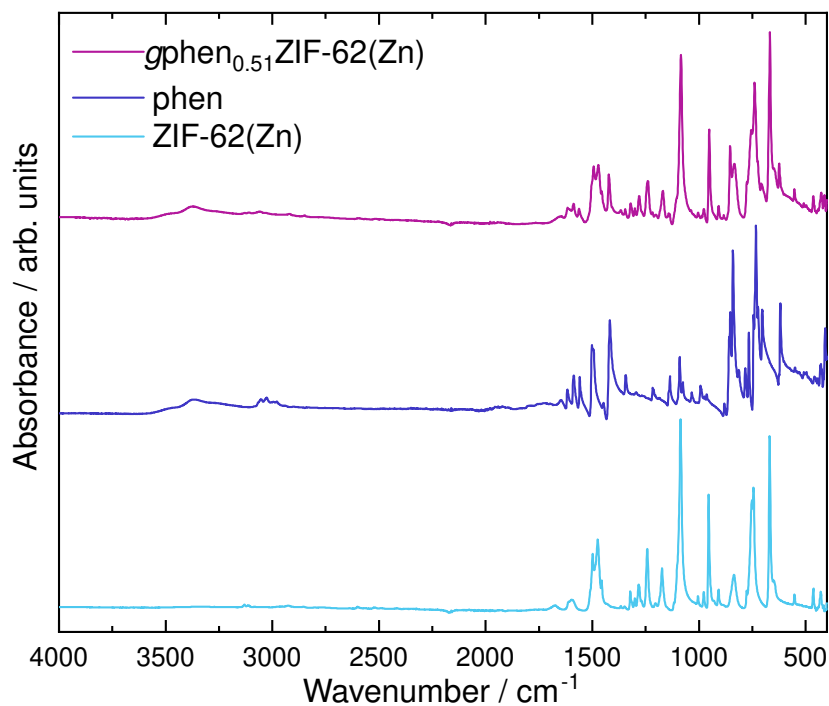


Supplementary Figure 109. Comparison of the experimental far-IR spectrum of $gphen_2Ni(inic)_2$ with the calculated far-IR spectra of the model complexes $Ni(phen)_2(inic)_2$ and $Ni(phen)(inic)_2(inicH)_2$. Orange areas mark vibrations of O-H bonds.

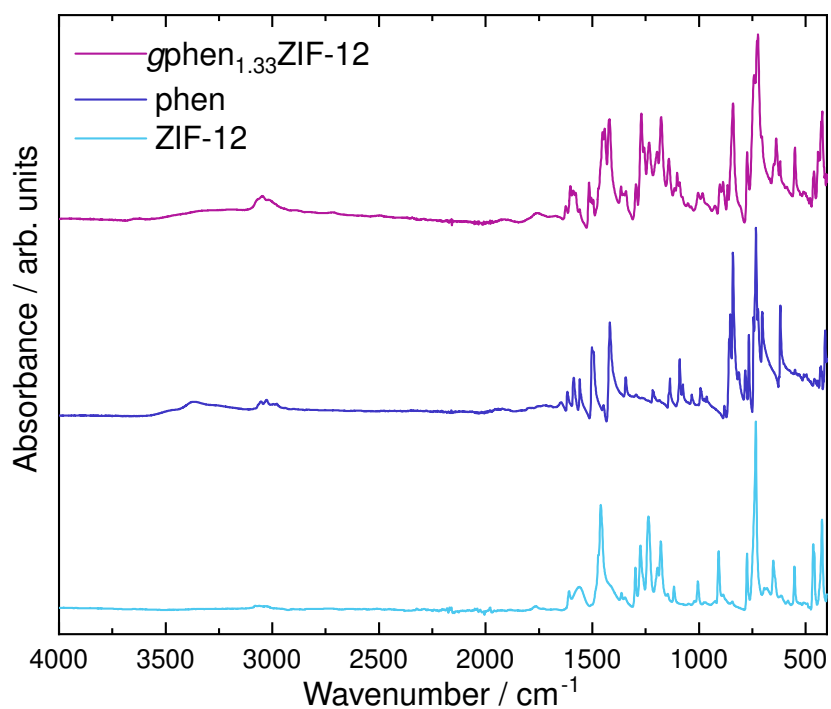
Supplementary Methods 13 – Fourier-transform mid-infrared spectroscopy



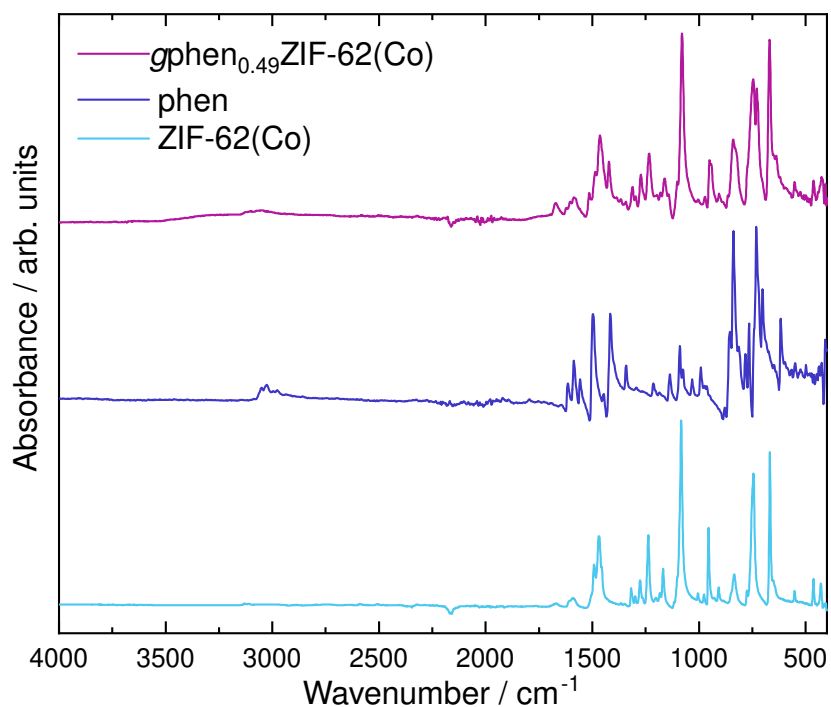
Supplementary Figure 110. Mid-IR spectra of ZIF-62(Co), phen·H₂O, and gphen_{0.49}ZIF-62(Co) prepared under ambient conditions.



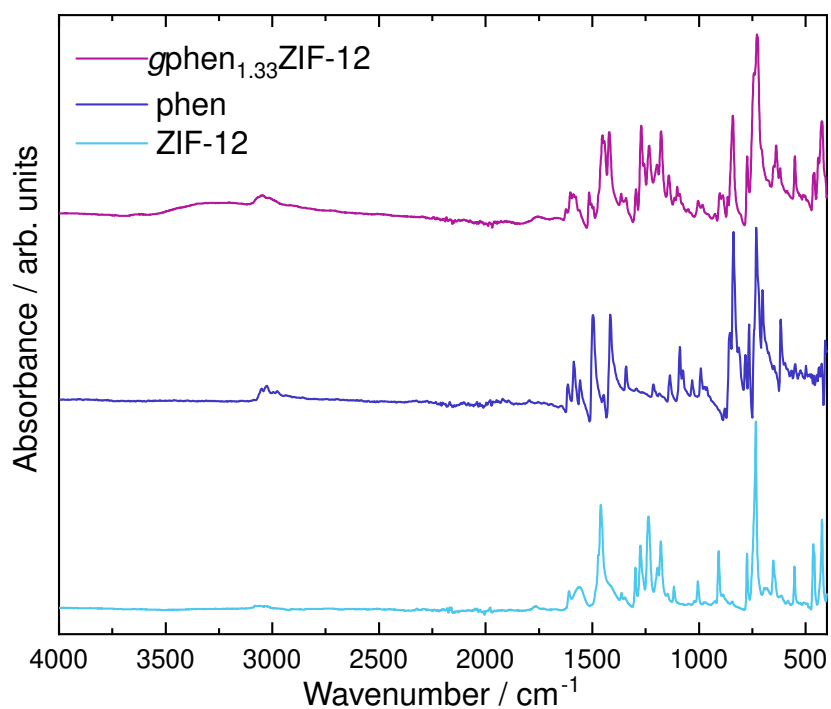
Supplementary Figure 111. Mid-IR spectra of ZIF-62(Zn), phen·H₂O, and gphen_{0.51}ZIF-62(Zn) prepared under ambient conditions.



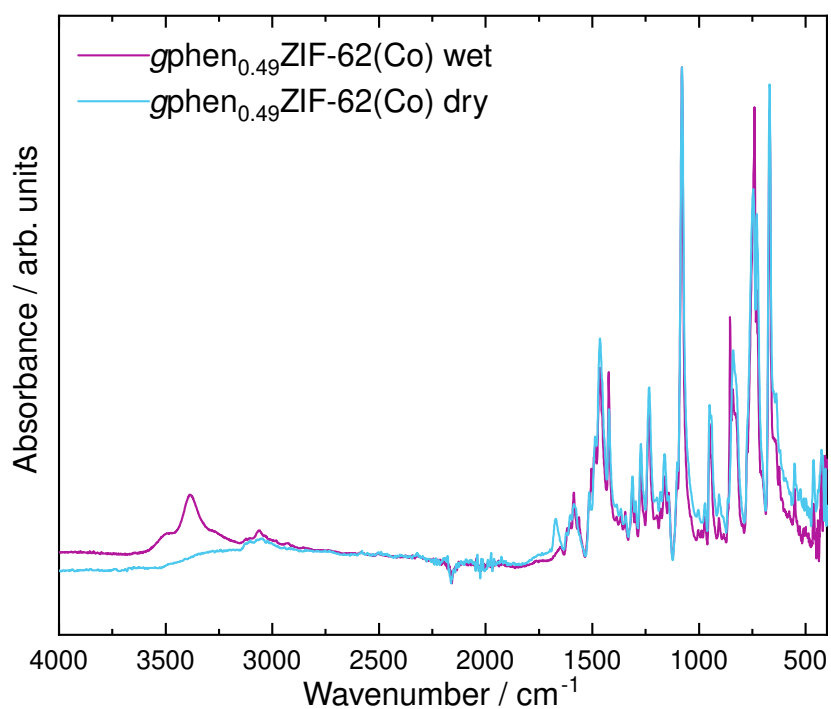
Supplementary Figure 112. Mid-IR spectra of ZIF-12, phen·H₂O, and gphen_{1.33}ZIF-12 prepared under ambient conditions.



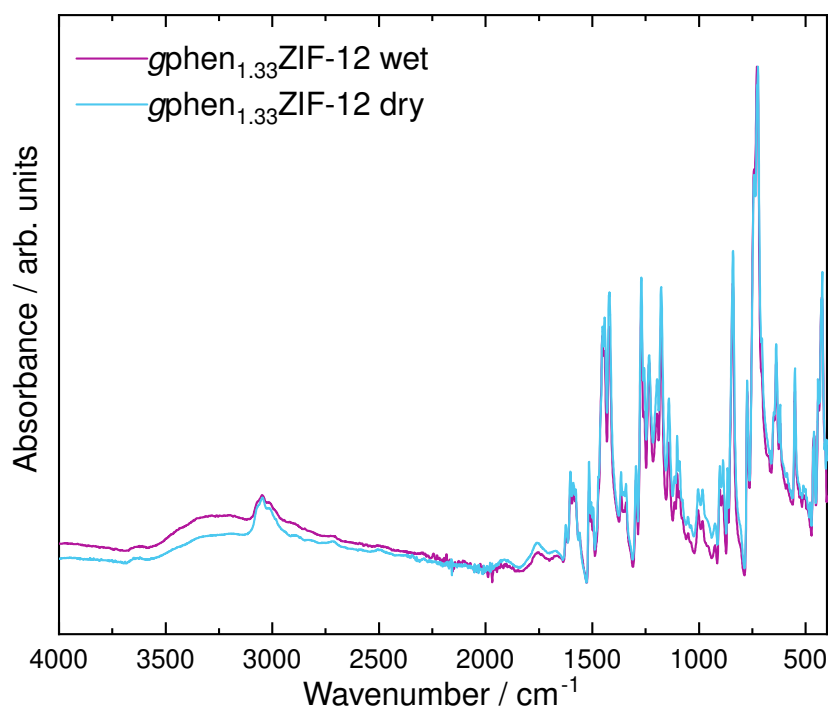
Supplementary Figure 113. Mid-IR spectra of ZIF-62(Co), phen, and gphen_{0.49}ZIF-62(Co) prepared under dry conditions.



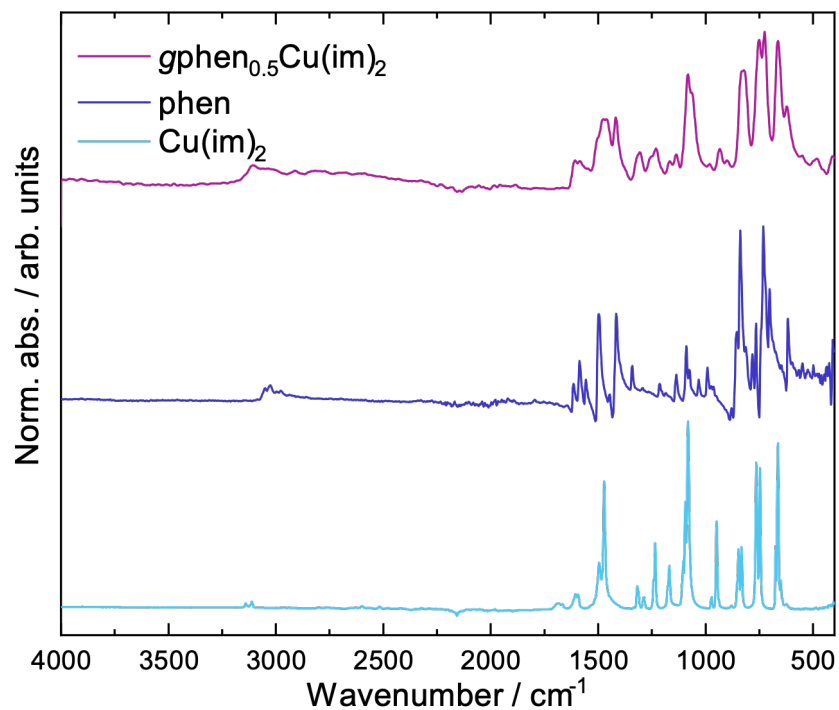
Supplementary Figure 114. Mid-IR spectra of ZIF-12, phen, and gphen_{1.33}ZIF-12 prepared under dry conditions.



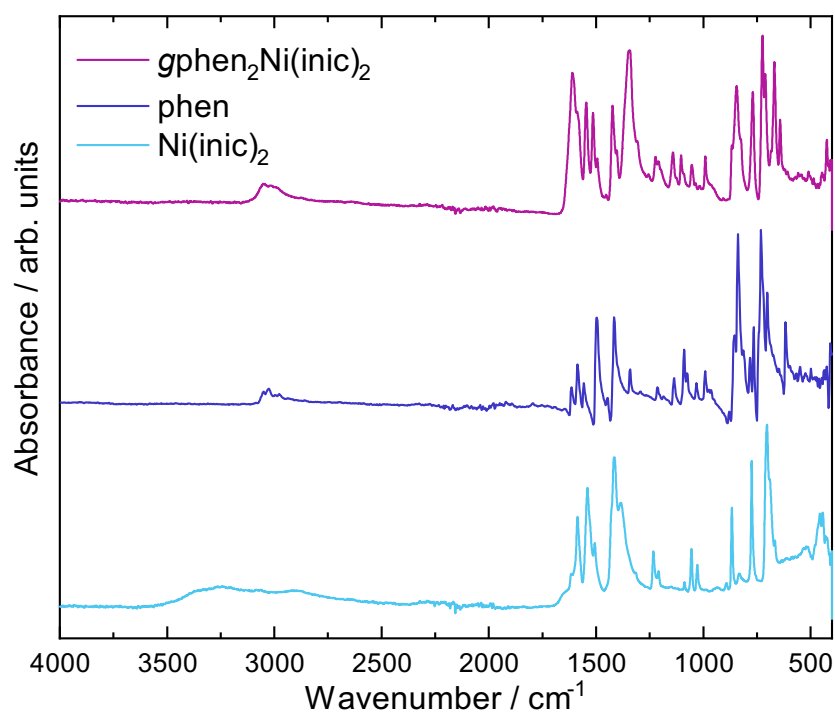
Supplementary Figure 115. Mid-IR spectra of gphen_{0.49}ZIF-62(Co) prepared under dry and ambient conditions.



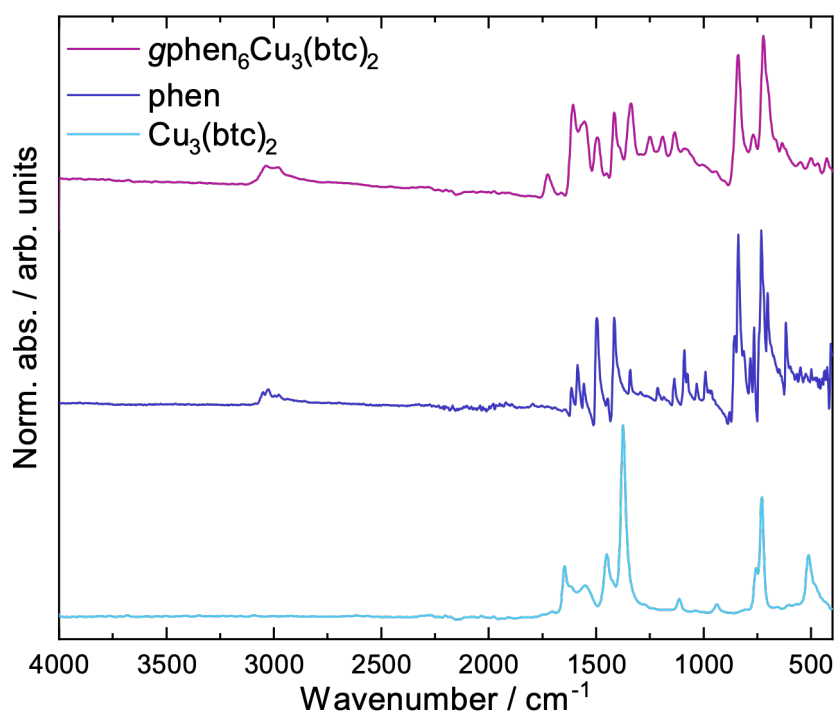
Supplementary Figure 116. Mid-IR spectra of gphen_{1.33}ZIF-12 prepared under dry and ambient conditions.



Supplementary Figure 117. Mid-IR spectra of Cu(im)₂, phen, and gphen_{0.5}Cu(im)₂.



Supplementary Figure 118. Mid-IR spectra of Ni(inic)_2 , phen, and $\text{gphen}_2\text{Ni(inic)}_2$.

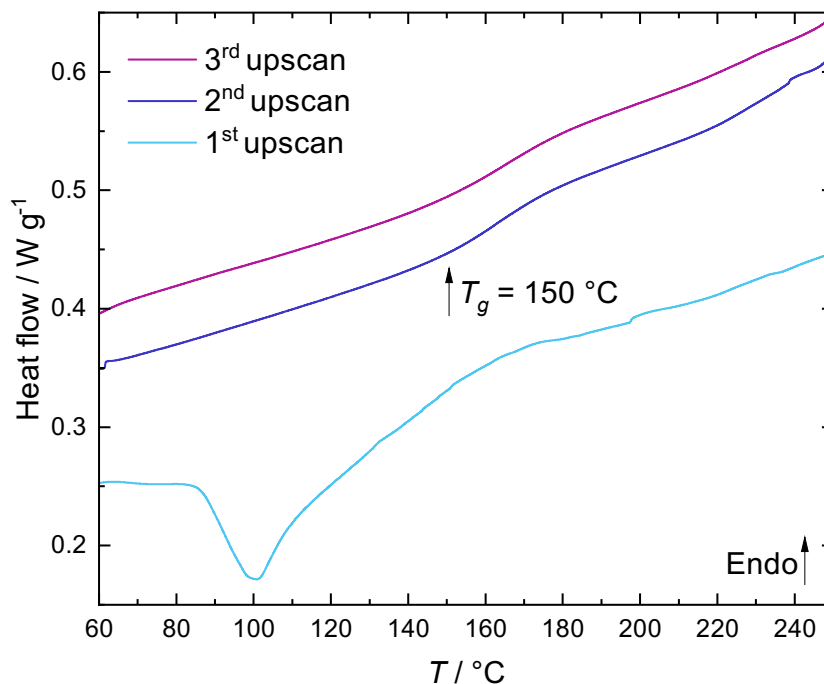


Supplementary Figure 119. Mid-IR spectra of $\text{Cu}_3(\text{btc})_2$, phen, and $\text{gphen}_6\text{Cu}_3(\text{btc})_2$.

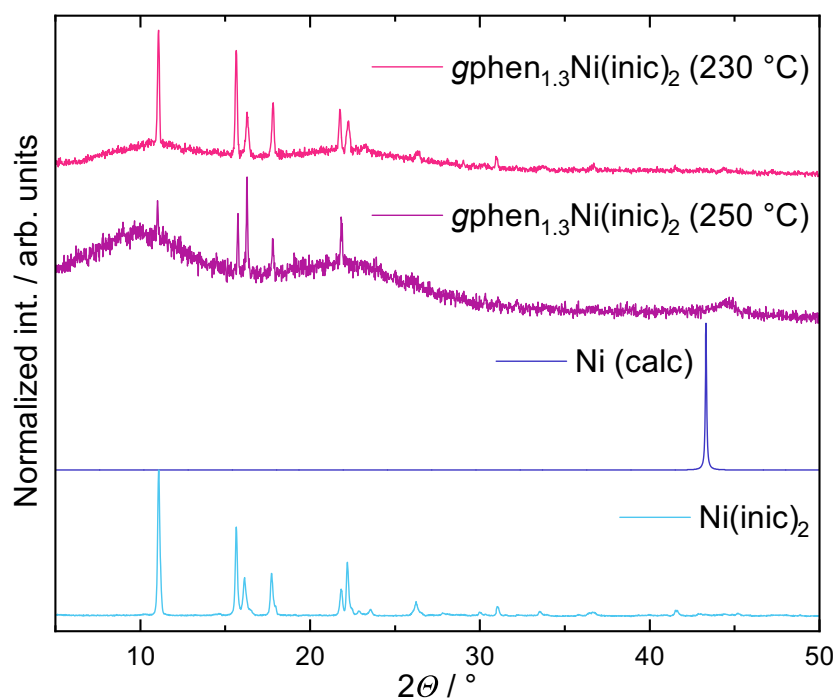
Supplementary Notes 3 – Choice of phen:MOF ratios for glasses based on Ni(inic)₂ and Cu₃(btc)₂

The physical mixtures phen_{1.3}[Ni(inic)₂] and phen₃[Cu₃(btc)₂] were chosen as a starting point. For phen_{1.3}[Ni(inic)₂], melt-quenching from 250 °C yielded a material with remaining crystalline reflections of Ni(inic)₂ and a broad reflection of elemental Ni, indicating decomposition (see **Supplementary Figure 121**). Therefore, the phen content was increased to phen₂[Ni(inic)₂] and melt-quenching from 230 °C yielded a fully amorphous material without detectable decomposition.

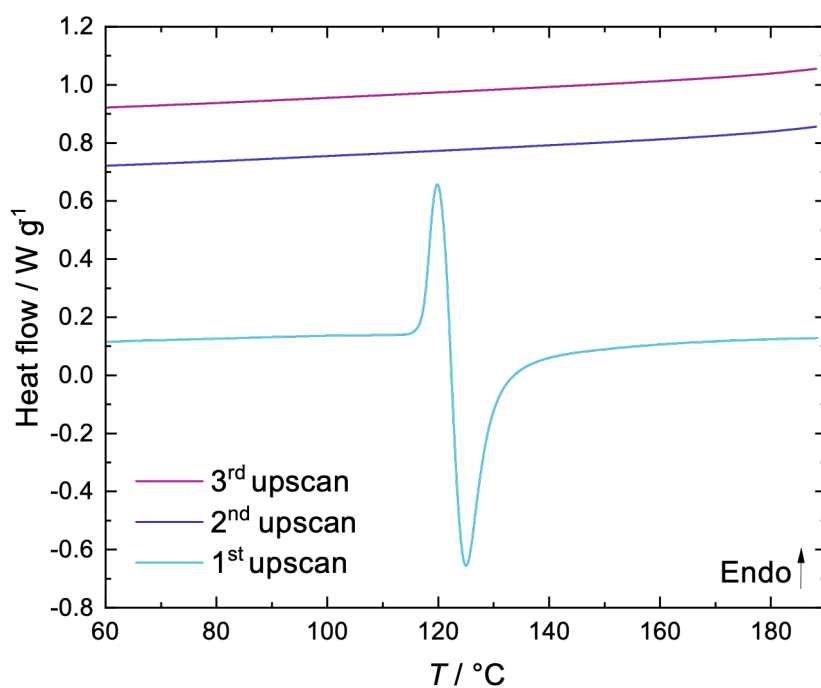
For phen₃[Cu₃(btc)₂], heating above 210 °C results in the decarboxylation of the btc³⁻ linker, which is evident by the bursting of the aluminium pans used for DSC measurements. Heating of phen₃[Cu₃(btc)₂] to 190 °C followed by cooling to room temperature resulted in the formation of a partially amorphous powder which still shows sharp Bragg reflections of Cu₃(btc)₂. Therefore, the phen content was increased to phen₆[Cu₃(btc)₂] and melt-quenching from 190 °C yielded a fully amorphous material featuring a glass transition in DSC.



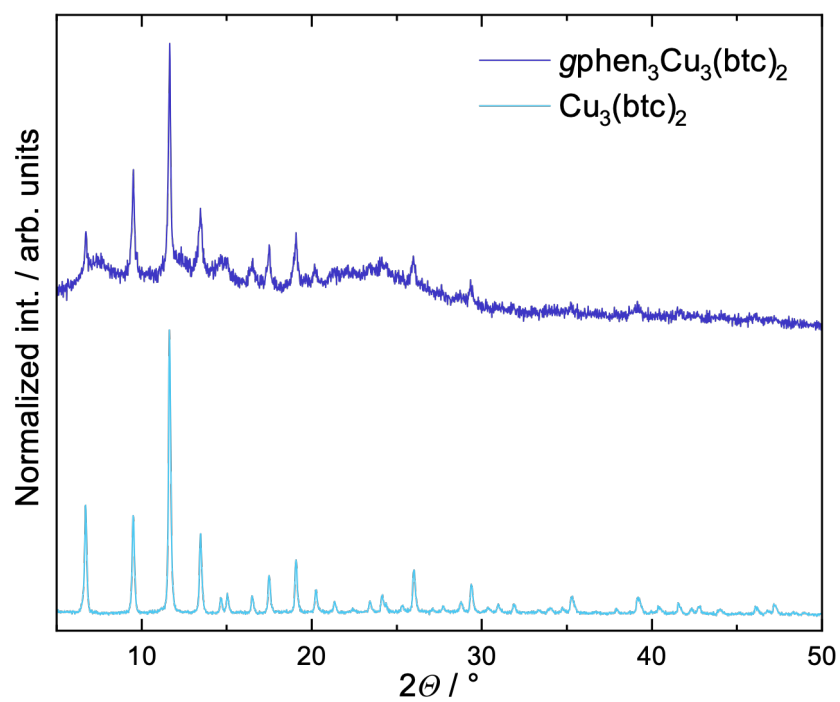
Supplementary Figure 120. DSC traces of phen_{1.3}[Ni(inic)₂] up to 250 °C.



Supplementary Figure 121. PXRD patterns of Ni(inic)₂, Ni (calculated), gphen_{1.3}Ni(inic)₂ (prepared by melt-quenching from 250 °C), and gphen_{1.3}Ni(inic)₂ (prepared by melt-quenching from 230 °C).

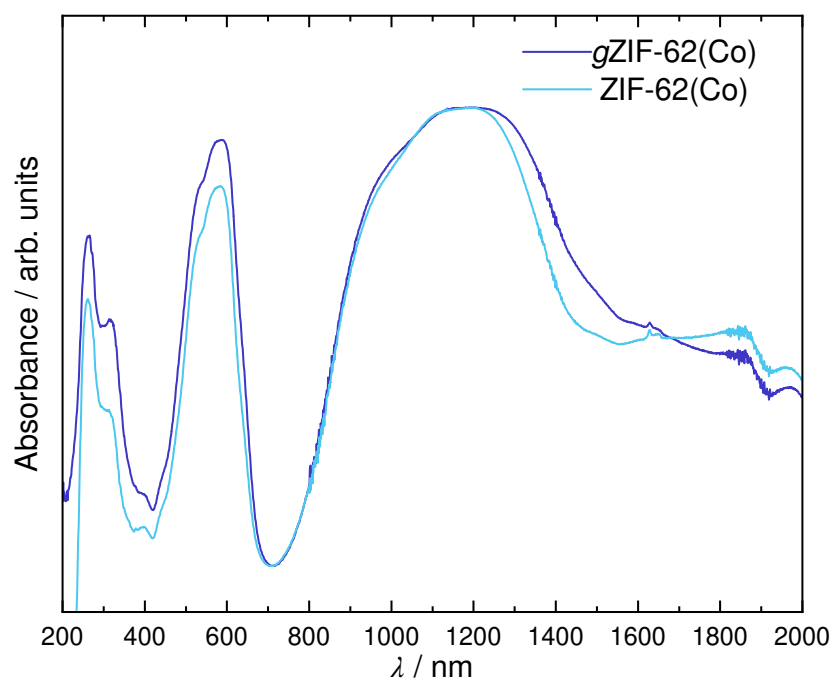


Supplementary Figure 122. DSC traces of phen₃[Cu₃(btc)₂].

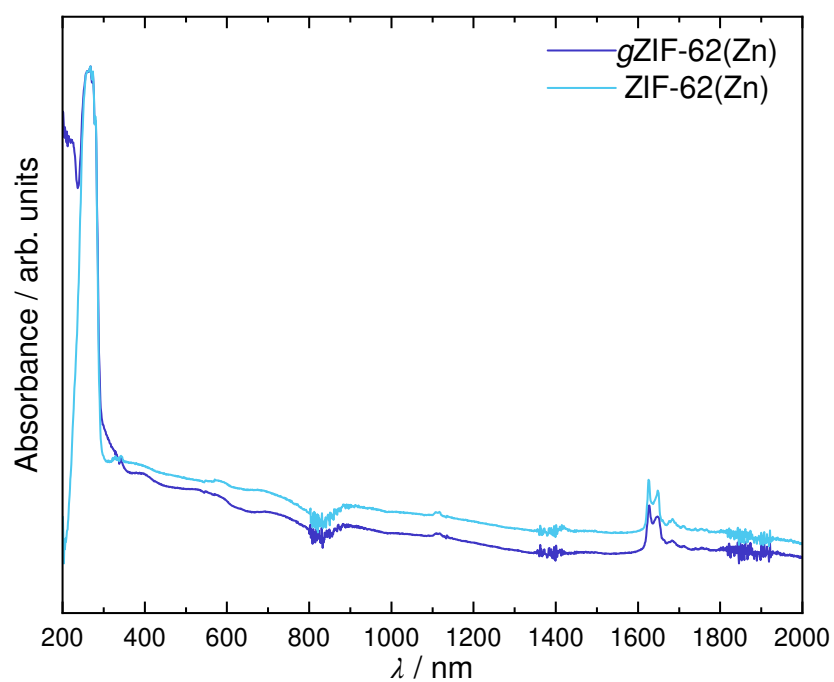


Supplementary Figure 123. PXRD patterns of $\text{Cu}_3(\text{btc})_2$ and $\text{gphen}_3\text{Cu}_3(\text{btc})_2$.

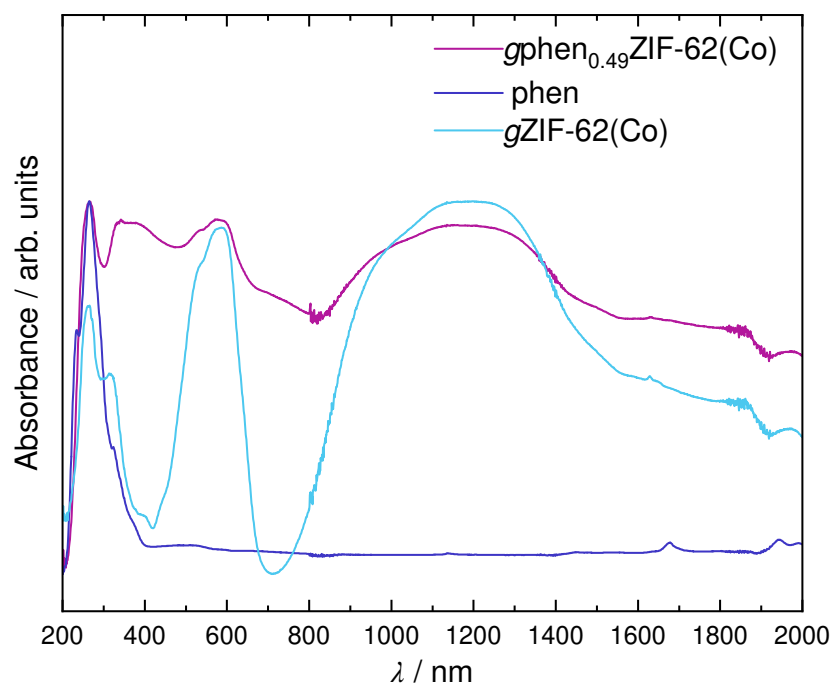
Supplementary Methods 14 – UV-vis-NIR spectroscopy



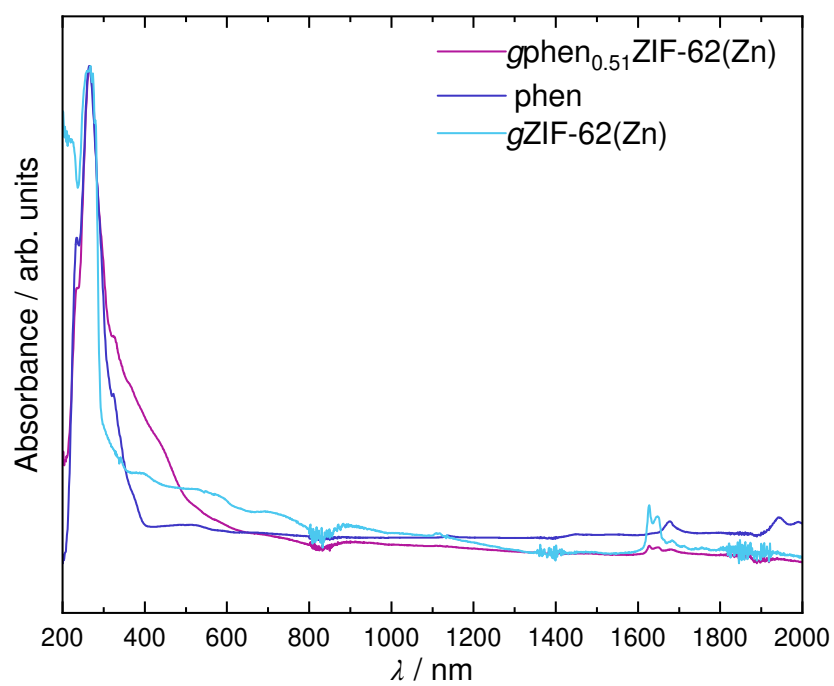
Supplementary Figure 124. UV-vis-NIR spectrum of ZIF-62(Co) and gZIF-62(Co).



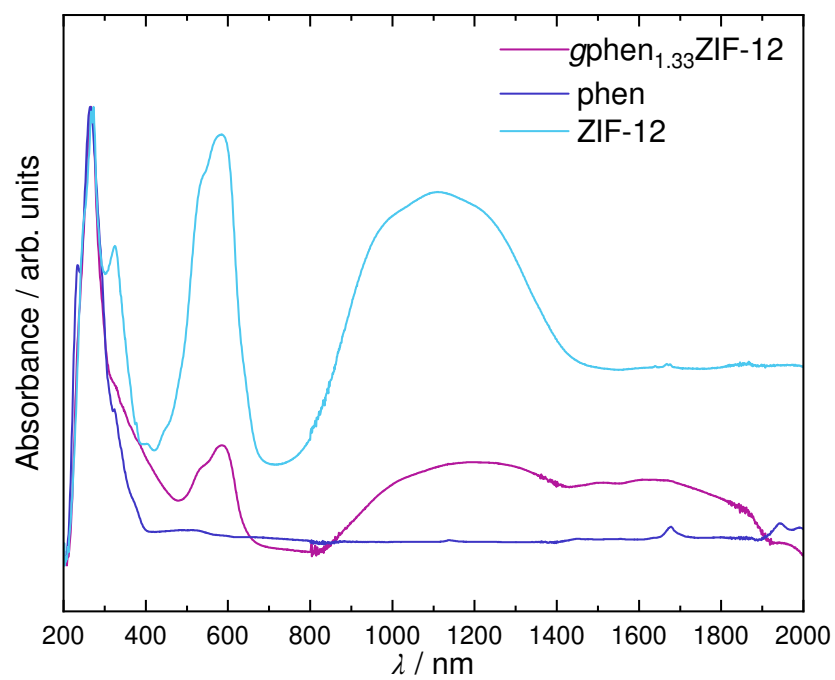
Supplementary Figure 125. UV-vis-NIR spectrum of ZIF-62(Zn) and gZIF-62(Zn).



Supplementary Figure 126. UV-vis-NIR spectrum of $gZIF-62(Co)$, $phen$, and $gphen_{0.49}ZIF-62(Co)$.

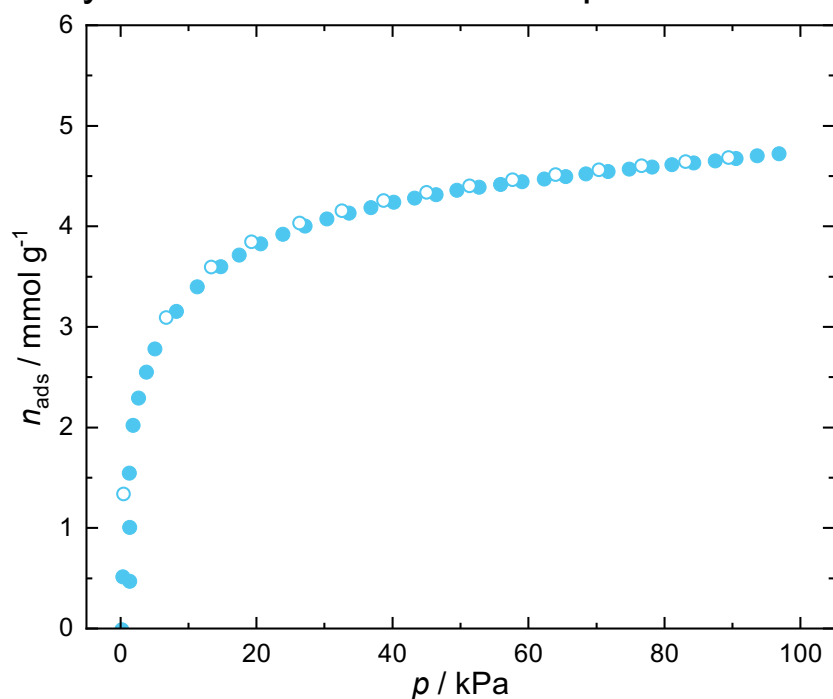


Supplementary Figure 127. UV-vis-NIR spectrum of $gZIF-62(Zn)$, $phen$, and $gphen_{0.51}ZIF-62(Zn)$.

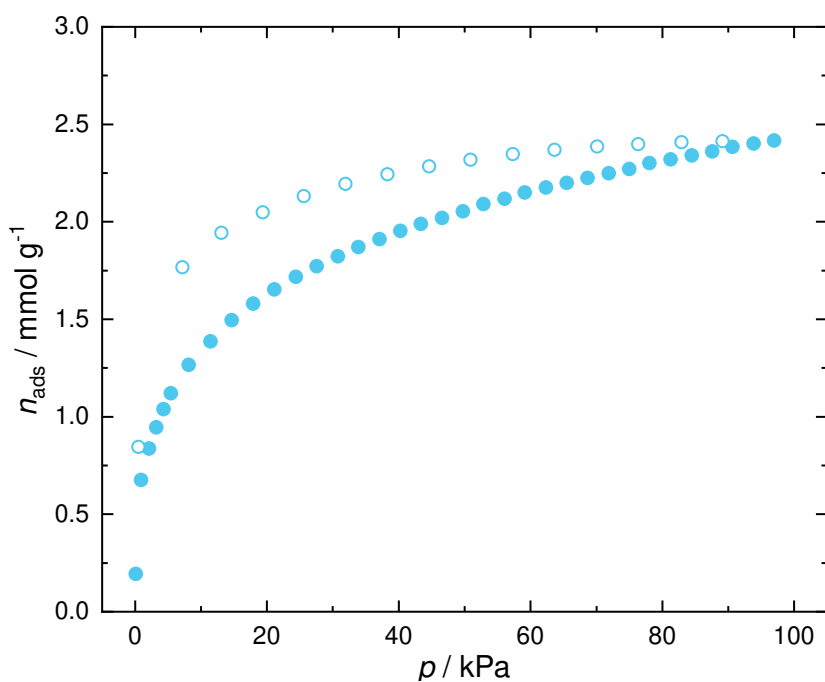


Supplementary Figure 128. UV-vis-NIR spectrum of ZIF-12, phen, and *gphen*_{1.33}ZIF-12.

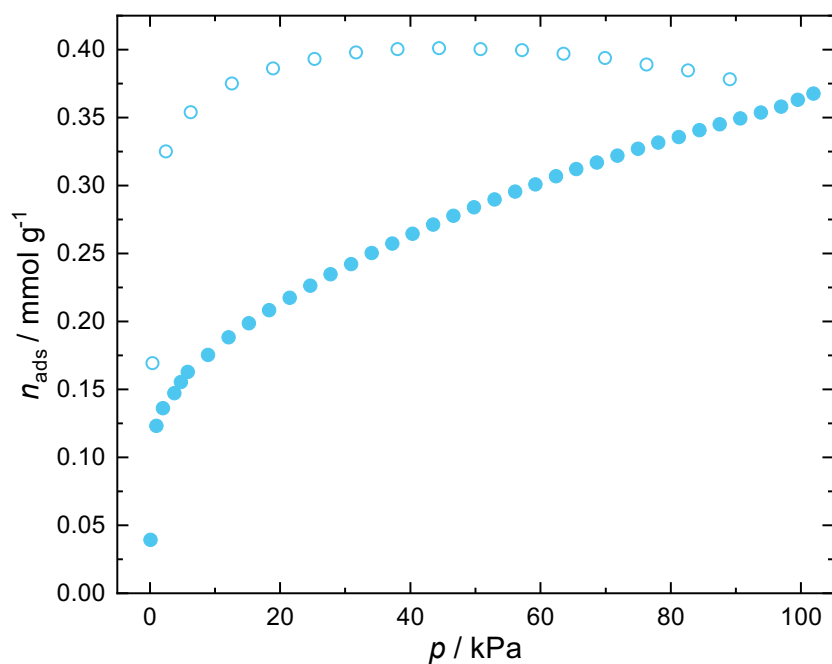
Supplementary Methods 15 – Gas adsorption



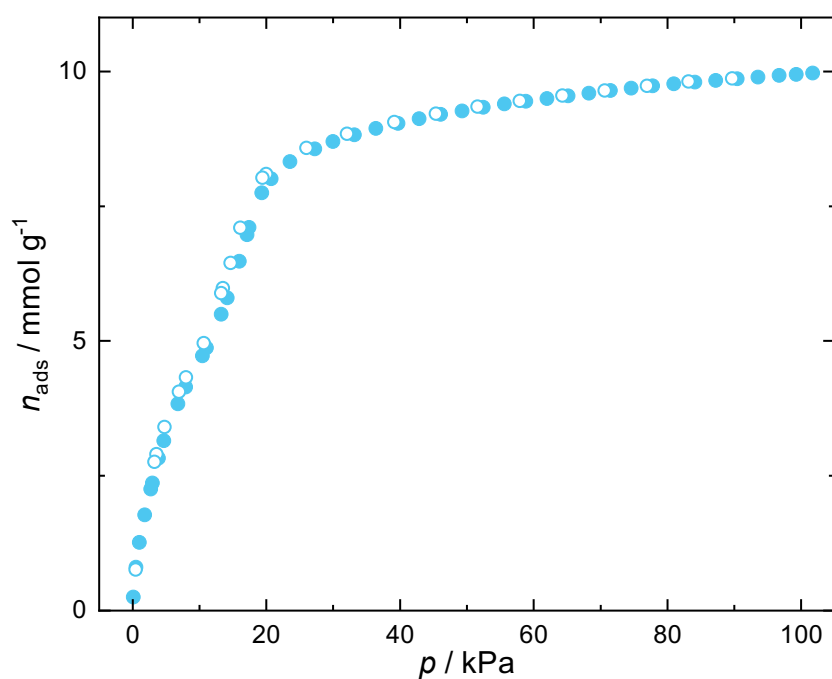
Supplementary Figure 129. CO₂ sorption isotherm of ZIF-62(Co) collected at 195 K. The adsorption branch is shown with filled symbols and the desorption branch is shown with open symbols.



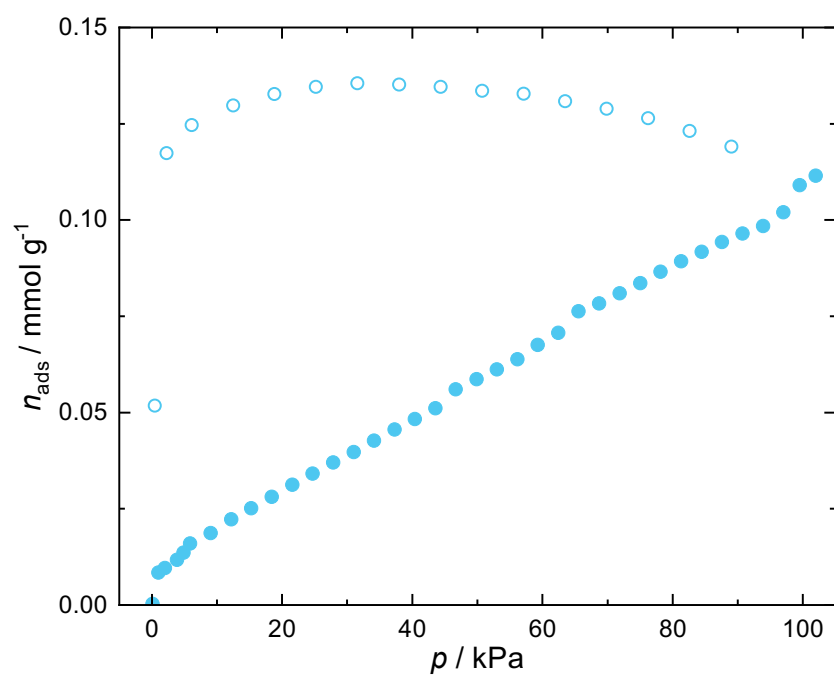
Supplementary Figure 130. CO₂ sorption isotherm of gZIF-62(Co) collected at 195 K. The adsorption branch is shown with filled symbols and the desorption branch is shown with open symbols.



Supplementary Figure 131. CO₂ sorption isotherm of gphen_{0.49}ZIF-62(Co) collected at 195 K. The adsorption branch is shown with filled symbols and the desorption branch is shown with open symbols.



Supplementary Figure 132. CO₂ sorption isotherm of ZIF-12 collected at 195 K. The adsorption branch is shown with filled symbols and the desorption branch is shown with open symbols.



Supplementary Figure 133. CO₂ sorption isotherm of *gphen*_{1.33}ZIF-12 collected at 195 K. The adsorption branch is shown with filled symbols and the desorption branch is shown with open symbols.

Supplementary Methods 16 – Nanoindentation

Supplementary Table 9. Indentation modulus (E^*), hardness (H), and corresponding test parameters.

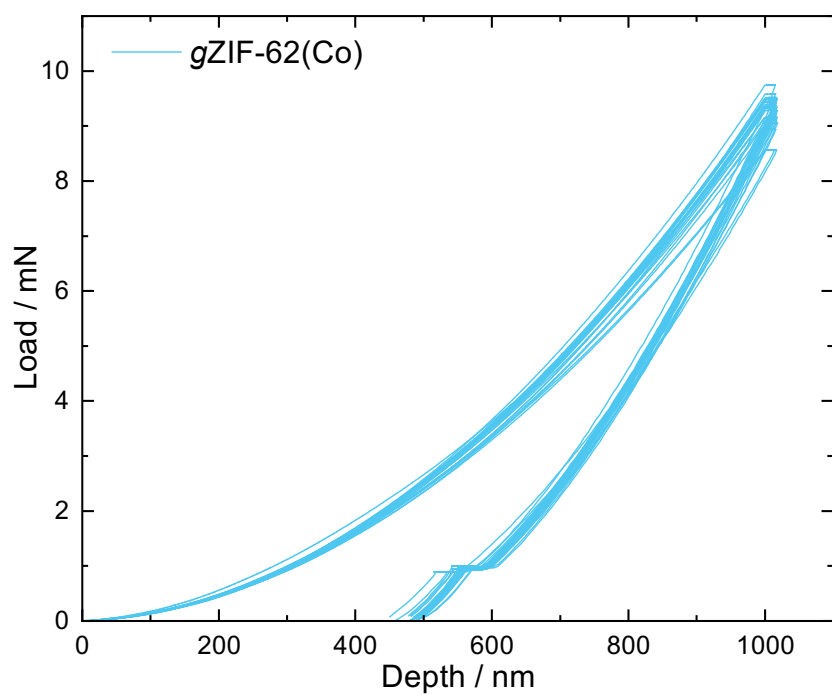
Sample	Max depth (nm)	Total number of tests	E^* (GPa)	H (MPa)
$g\text{ZIF-62}(\text{Co})$	1000	23	7.18 ± 0.24	886 ± 23
$g\text{phen}_{0.49}\text{ZIF-62}(\text{Co})$	1000	21	8.57 ± 0.23	934 ± 28

Supplementary Table 10. Fracture toughness (K_{Ic}) and corresponding test parameters.

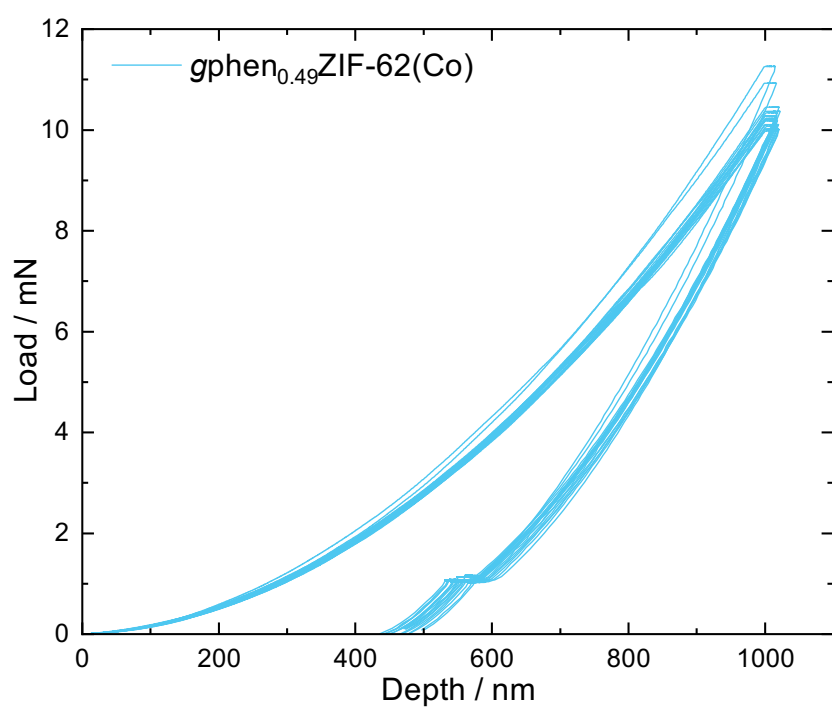
Sample	Max Load (mN)	Total number of tests	K_{Ic} (MPa $\sqrt{\text{m}}$)
$g\text{ZIF-62}(\text{Co})$	30	10	0.084 ± 0.031
$g\text{phen}_{0.49}\text{ZIF-62}(\text{Co})$	30	9	0.103 ± 0.041

Supplementary Table 11. Comparison of E^* , H , and K_{Ic} with corresponding values for $g\text{ZIF-62}(\text{Zn})$ from the literature.

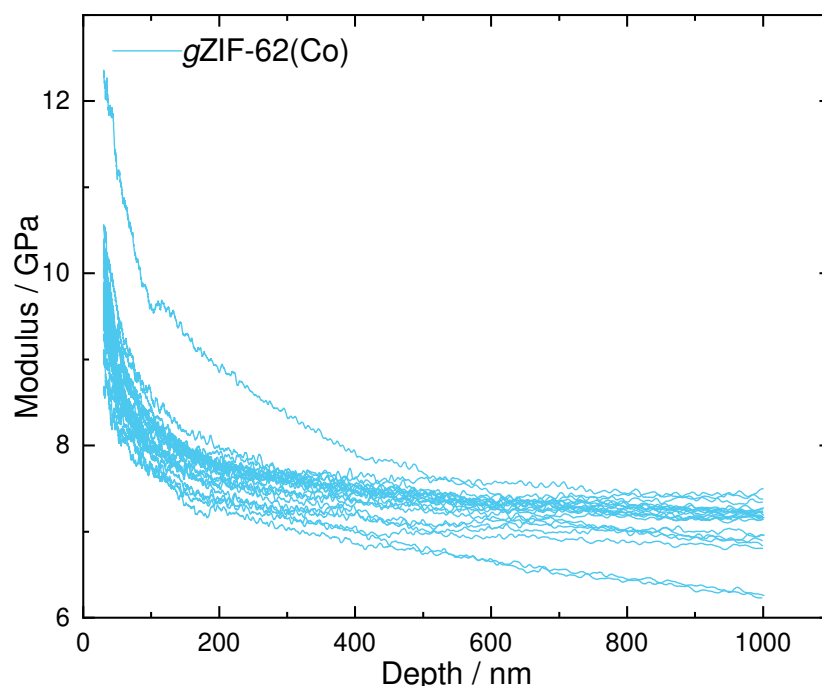
Sample	E^* (GPa)	H (MPa)	K_{Ic} (MPa $\sqrt{\text{m}}$)
$g\text{ZIF-62}(\text{Co})$	7.18	886	0.084
$g\text{phen}_{0.49}\text{ZIF-62}(\text{Co})$	8.57	934	0.103
$g\text{ZIF-62}(\text{Zn})$	6.58^8	656^8	0.104^9



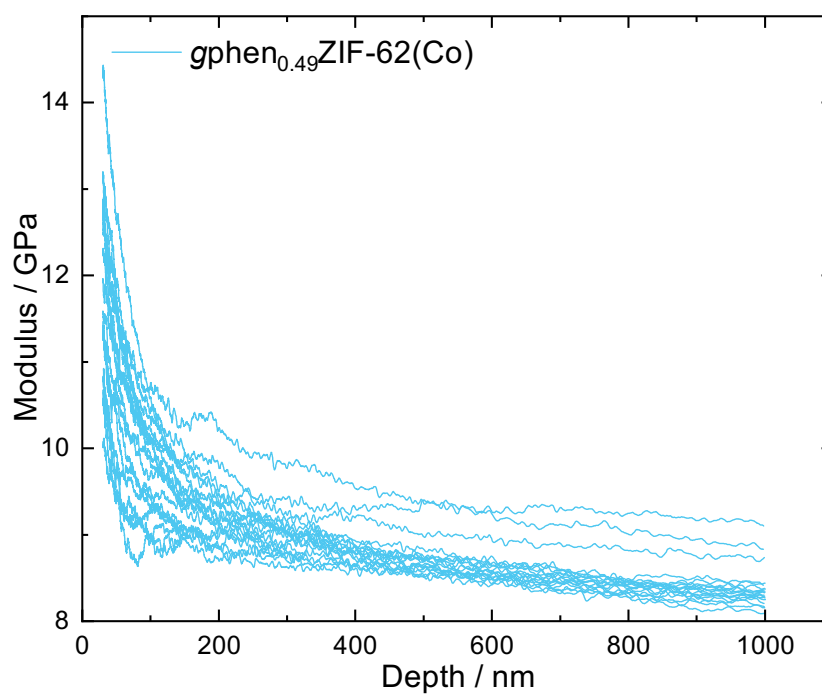
Supplementary Figure 134. Load-depth curves of the nanoindentation measurement of gZIF-62(Co).



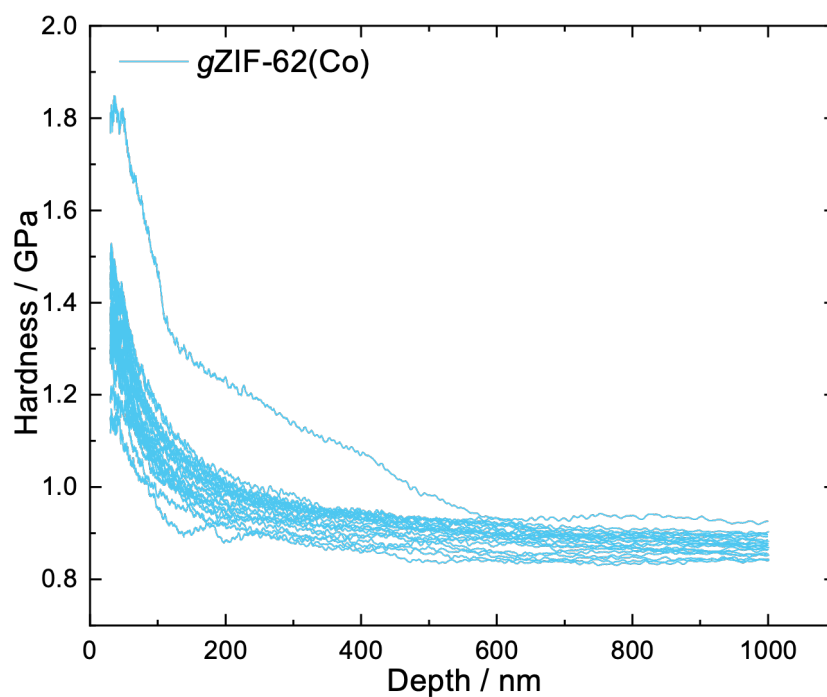
Supplementary Figure 135. Load-depth curves of the nanoindentation measurement of gphen_{0.49}ZIF-62(Co).



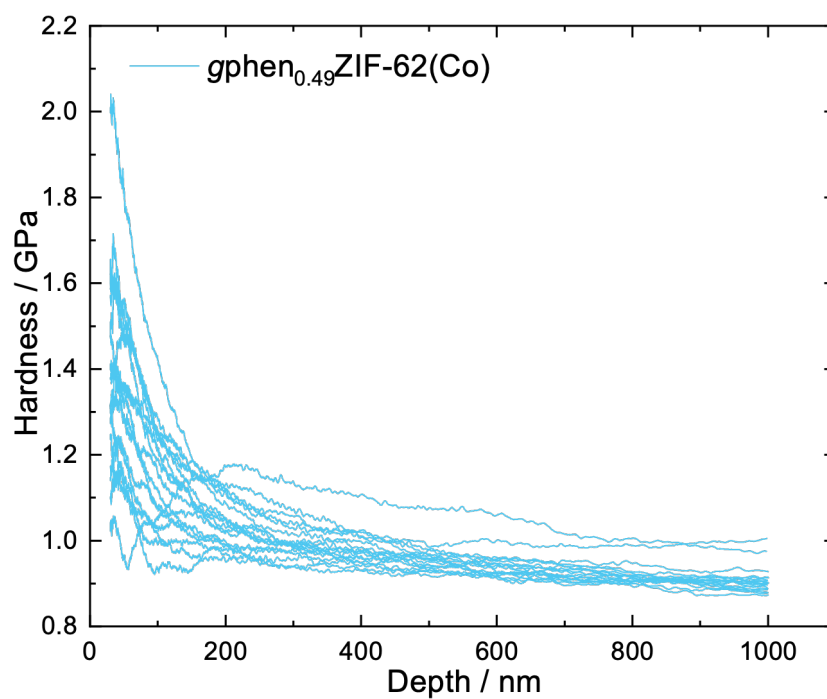
Supplementary Figure 136. Indentation modulus-depth curves of the nanoindentation measurement of *gZIF-62(Co)*.



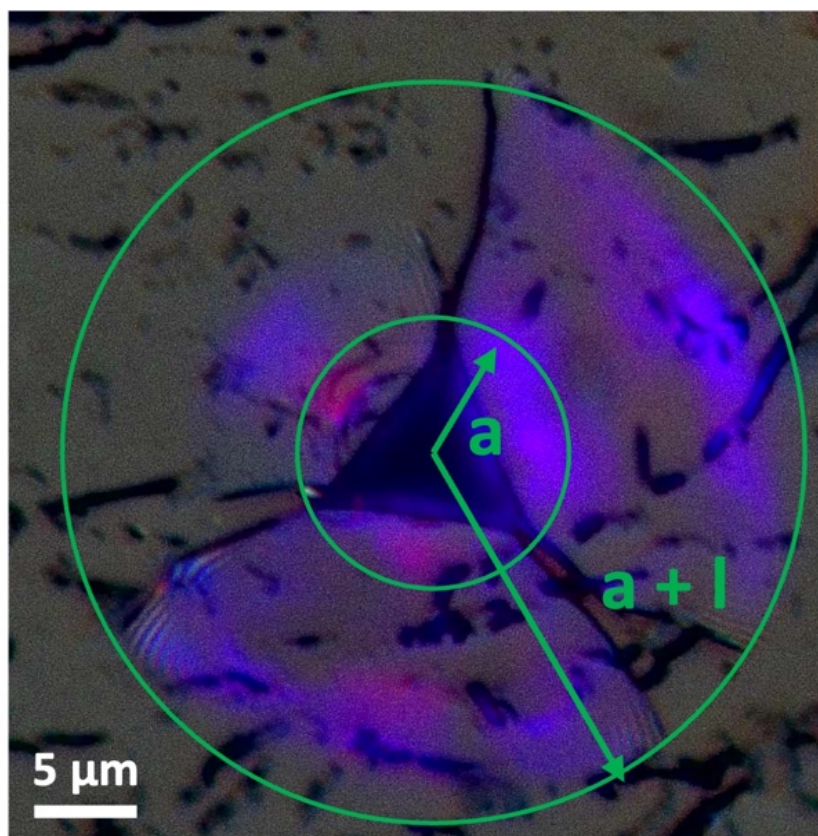
Supplementary Figure 137. Indentation modulus-depth curves of the nanoindentation measurement of *gphen_{0.49}ZIF-62(Co)*.



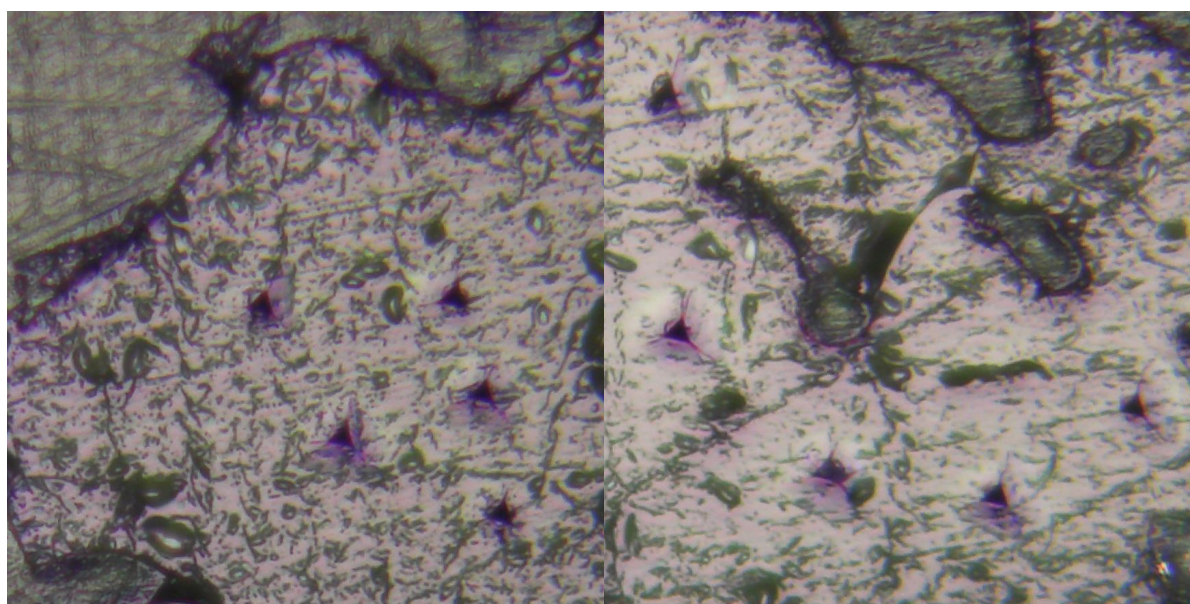
Supplementary Figure 138. Hardness-depth curves of the nanoindentation measurement of gZIF-62(Co).



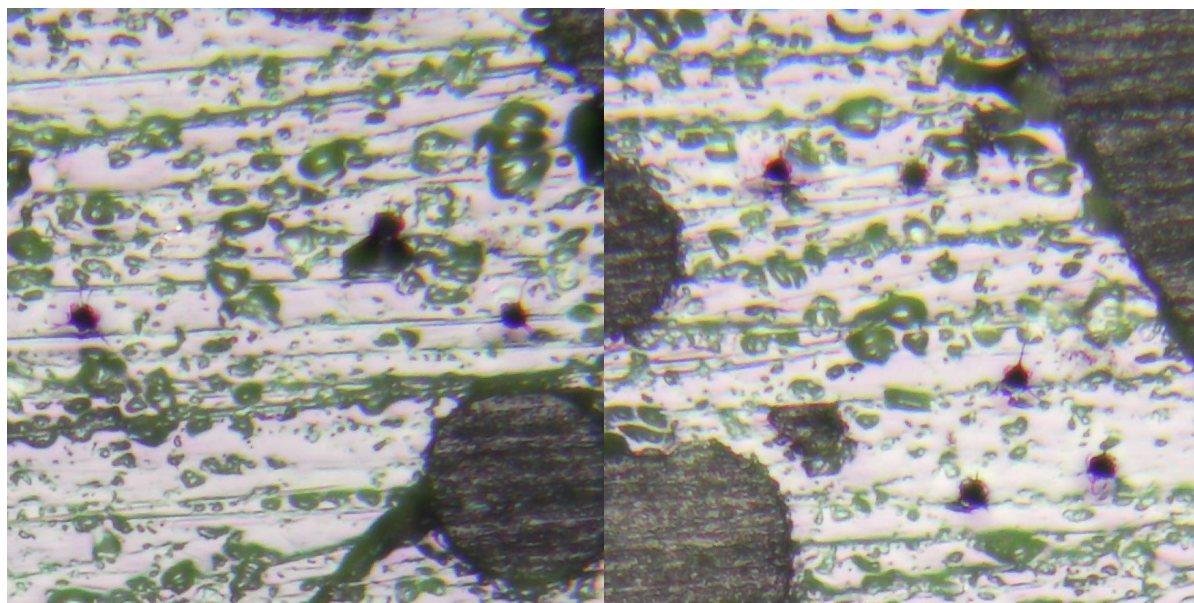
Supplementary Figure 139. Hardness-depth curves of the nanoindentation measurement of gphen_{0.49}ZIF-62(Co).



Supplementary Figure 140. Illustration of the parameters a and l used in the determination of the fracture toughness K_{Ic} using Laugier's formula.



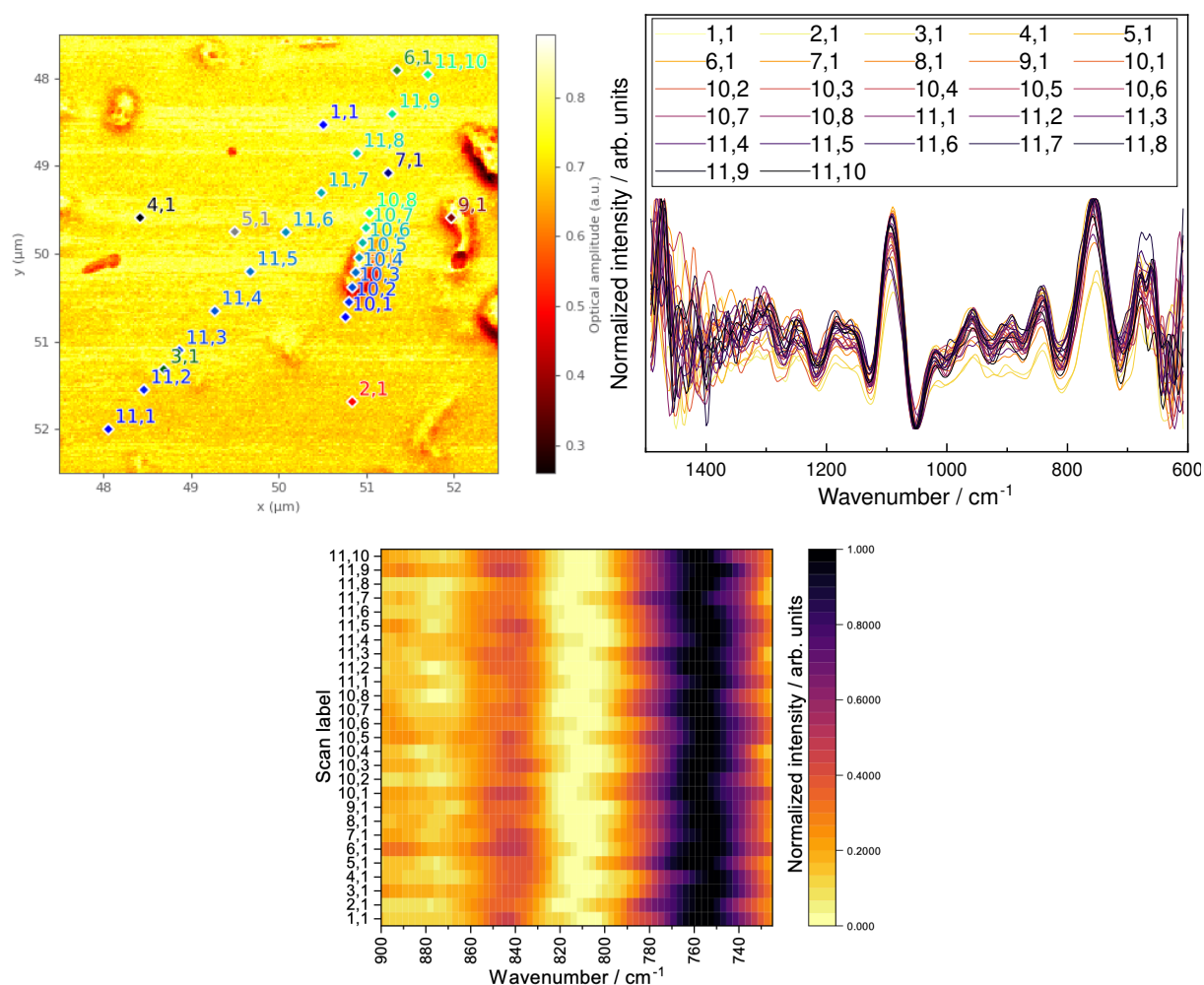
Supplementary Figure 141. Micrographs of the surface of gZIF-62(Co) after indentation tests for determination of fracture toughness.



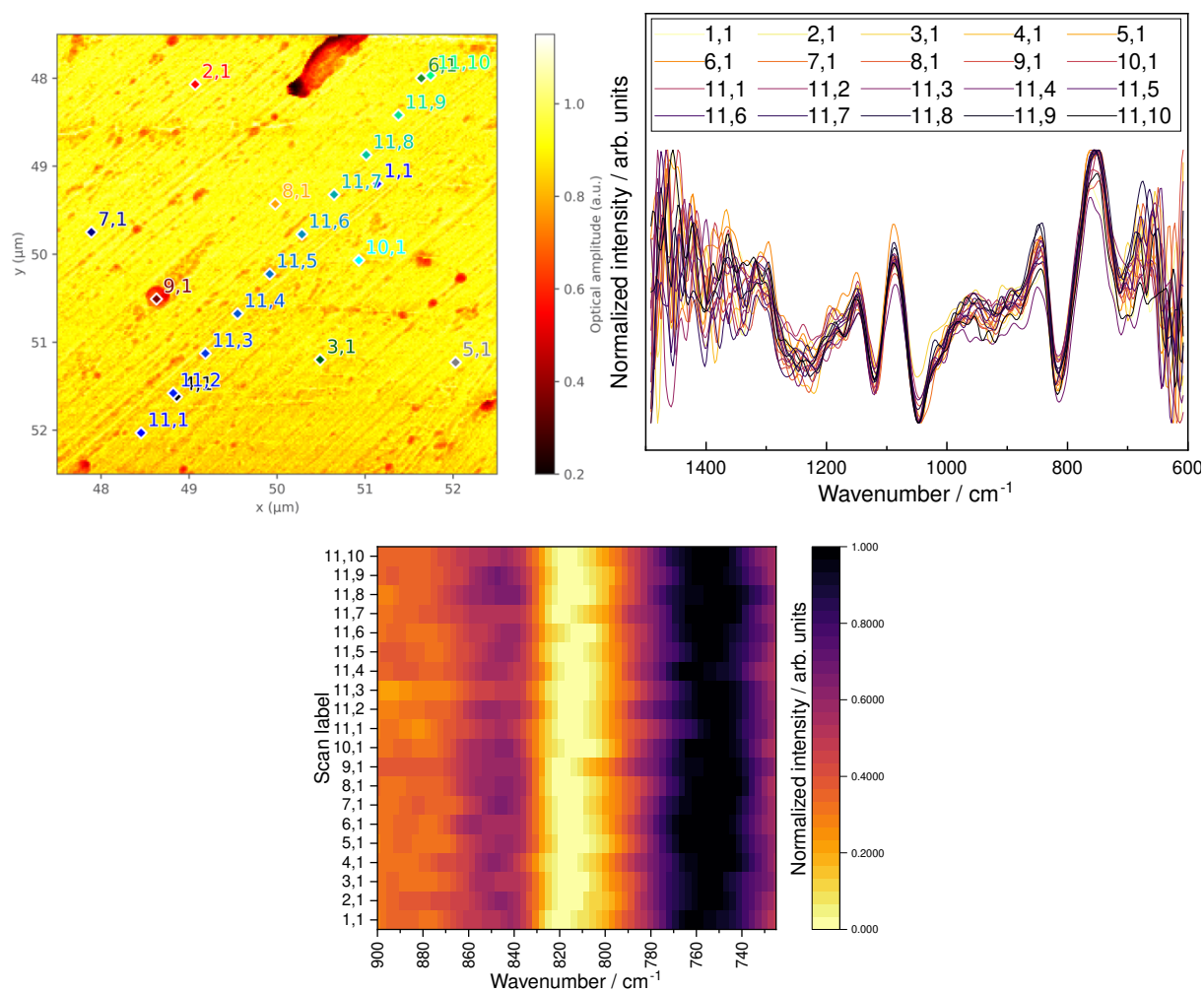
Supplementary Figure 142. Micrographs of the surface of gphen_{0.49}ZIF-62(Co) after indentation tests for determination of fracture toughness.

Supplementary Methods 17 – nano-FTIR

Among the spectra shown in the following figures, the spectra showing the greatest variation for each sample were chosen for Figures 4d and e in the main text. The spectra were normalized in the shown region ($900\text{--}725\text{ cm}^{-1}$).

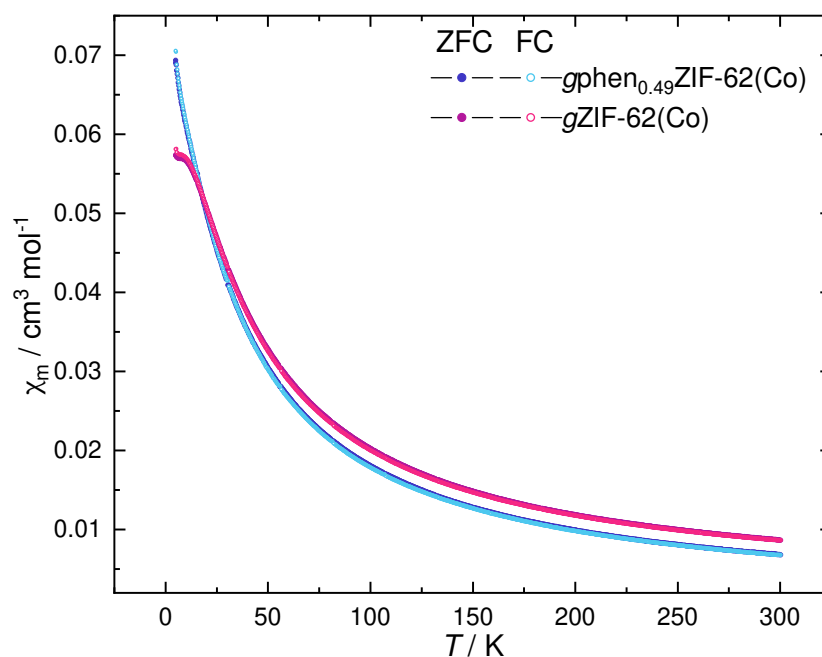


Supplementary Figure 143. Selected local nano-FTIR spectra of gZIF-62(Co) and their corresponding locations on the surface of the material (top). Normalized spectra in the region $900\text{--}725\text{ cm}^{-1}$ (bottom).

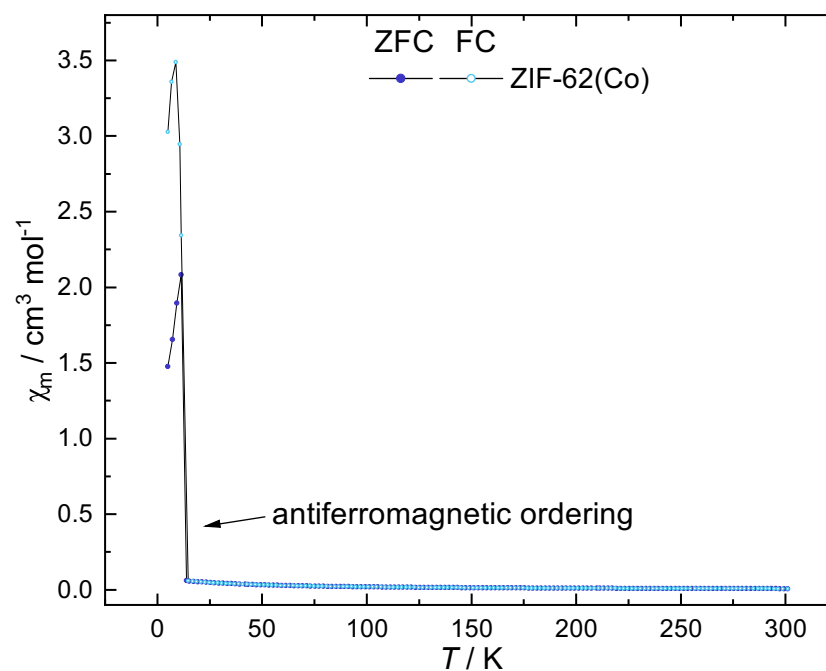


Supplementary Figure 144. Selected local nano-FTIR spectra of $gphen_{0.49}ZIF-62(Co)$ and their corresponding locations on the surface of the material (top). Normalized spectra in the region $900-725\text{ cm}^{-1}$ (bottom).

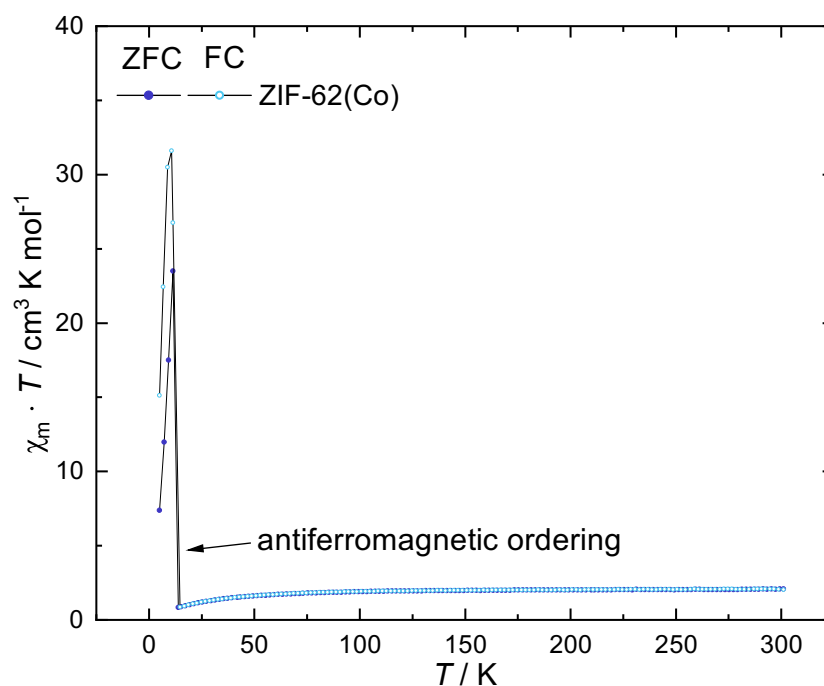
Supplementary Methods 18 – Magnetic properties



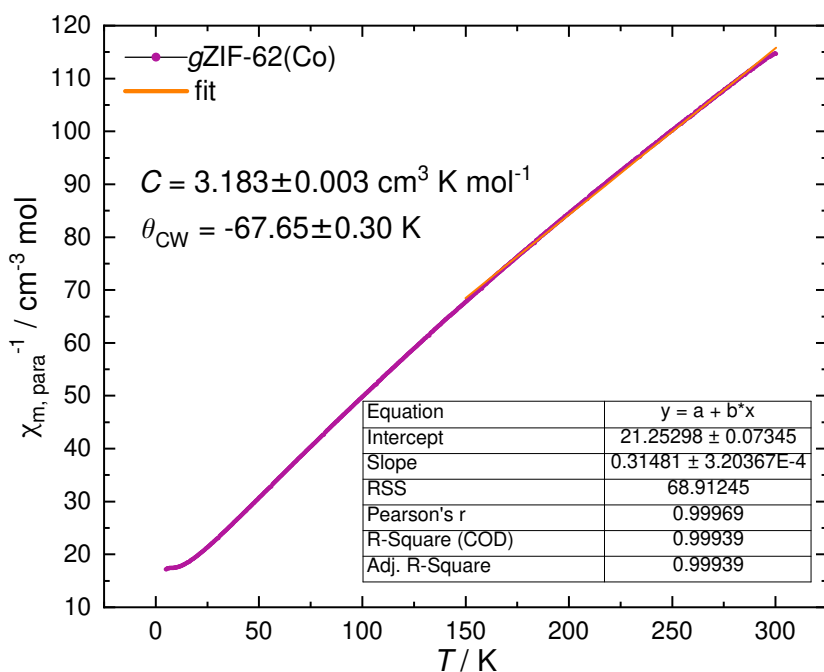
Supplementary Figure 145. Temperature dependence of the molar magnetic susceptibility χ_m obtained from zero field-cooled (ZFC) and field-cooled (FC) measurements of $g\text{ZIF-62}(\text{Co})$ and $g\text{phen}_{0.49}\text{ZIF-62}(\text{Co})$ in the range of 5–300 K under a magnetic field of 0.1 T.



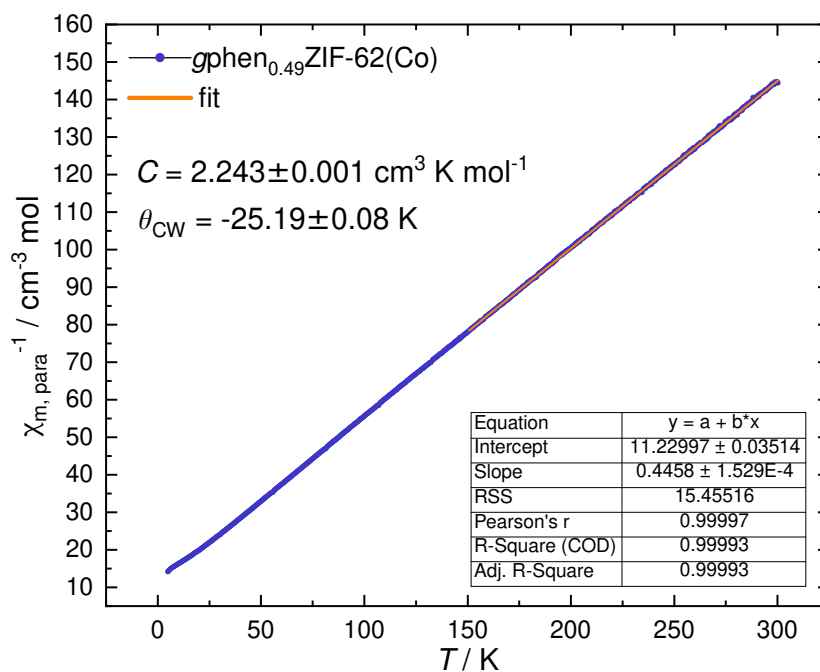
Supplementary Figure 146. Temperature dependence of the molar magnetic susceptibility χ_m obtained from zero field-cooled (ZFC) and field-cooled (FC) measurements of $\text{ZIF-62}(\text{Co})$ in the range of 5–300 K under a magnetic field of 10 mT.



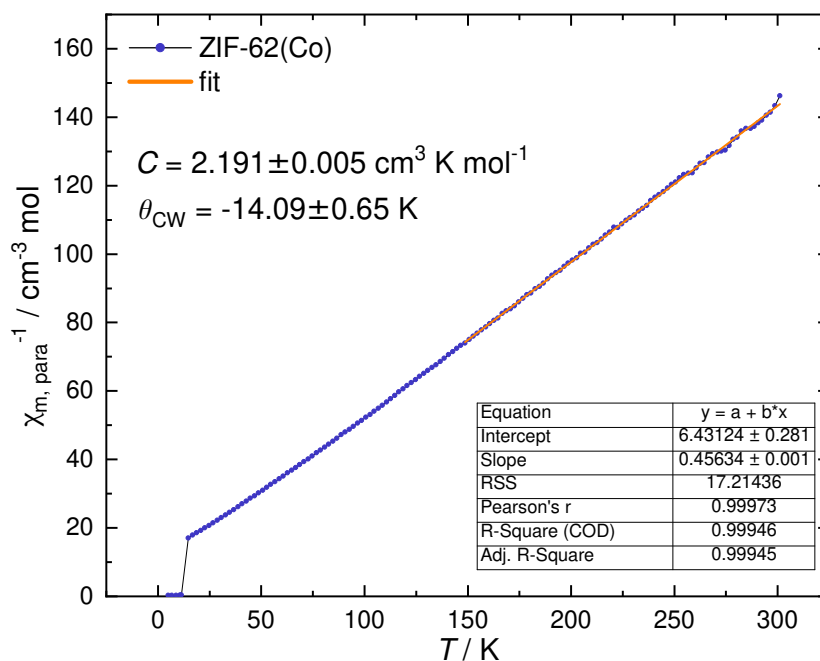
Supplementary Figure 147. Temperature dependence of the molar magnetic susceptibility multiplied with the temperature $\chi_m \cdot T$ obtained from zero field-cooled (ZFC) and field-cooled (FC) measurements of ZIF-62(Co) in the range of 5-300 K under a magnetic field of 10 mT.



Supplementary Figure 148. Temperature dependence of the inverse paramagnetic molar susceptibility $\chi_{m, \text{para}}^{-1}$ in the temperature range of 5-300 K for gZIF-62(Co). Although it is evident that the inverse susceptibility of gZIF-62(Co) does not follow Curie-Weiss behaviour (presumably due to trace magnetic impurities of metallic cobalt nanoparticles), the data have been fitted in the temperature range of 150-300 K using the Curie-Weiss law.



Supplementary Figure 149. Temperature dependence of the inverse paramagnetic molar susceptibility $\chi_{m, para}^{-1}$ in the temperature range of 5-300 K for $gphen_{0.49}ZIF-62(Co)$. The data have been fitted following the Curie-Weiss law in the temperature range of 150-300 K.



Supplementary Figure 150. Temperature dependence of the inverse paramagnetic molar susceptibility $\chi_{m, para}^{-1}$ in the temperature range of 5-300 K for ZIF-62(Co). The data have been fitted following the Curie-Weiss law in the temperature range of 150-300 K.

Supplementary Methods 19 – Autoclave for upscaled melt-quenching



Supplementary Figure 151. Photograph of the disassembled autoclave including quartz glass lining.

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