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Electronic Supporting Information for:

An Expanded MIL-53-Type Coordination Polymer With a Reactive Pendant Ligand

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S1: Synthesis of 4S-PNO Ligand

4-Styrylpyridine[1]

A mixture of 4-methylpyridine (18.6 g, 19.5 cm^3, 0.2 mol), benzaldehyde (21.2 g, 20.3cm^3, 0.2 mol) and acetic anhydride (20.4 g, 18.9 cm^3, 0.2 mol) was stirred and heated to reflux overnight. The mixture was cooled and poured slowly with stirring into water (200 cm^3) and allowed to stand with occasional stirring for 15 min by which time a brown solid had formed. This was collected by filtration, washed with a little water, dried with suction and then recrystallised from the minimum volume of hot ethanol. The crystals were filtered and dried under vacuum. The ^{1}H NMR spectrum of the material matched that previously reported.[1,2] Yield 60%, mp 126-127 °C (Lit. [2] 128 °C). ^{1}H NMR (300 MHz, CDCl$_3$) 8.59 (2H, br d), 7.36(5H, m), 7.31 (1H, d, *J* = 16 Hz) and 7.03 (1H, d, *J* = 16 Hz).

4-Styrylpyridine-*N*-oxide[3]

A mixture of 4-styrylpyridine (2 g, 11 mmol) in acetic acid (6 cm^3) and hydrogen peroxide (1.5 cm^3 30% (w/w) solution, ~13.2 mmol)) was stirred at 70 °C overnight. The mixture was diluted with water (20 cm^3) and extracted with ethyl acetate (3 × 15 cm^3). The combined organic extracts were washed once with water (20 cm^3), dried with magnesium sulphate, filtered and the solvent removed by rotary evaporation. The compound was purified by column chromatography on silica. The column was started using dichloromethane with increasing amounts of ethyl acetate to pure ethyl acetate and finally 10% methanol in ethyl acetate. The material was recrystalised from dichloromethane/ petrol as a white powder with a ^{1}H NMR spectrum matching that previously reported.[2] Yield 32%, mp 166-168 °C (Lit. [2] 170 °C). ^{1}H NMR (300 MHz, CDCl$_3$) 8.17(2H, d, *J* = 7.4 Hz), 7.51 (2H, dd, *J* = 8+1.5 Hz), 7.37(3H, m), 7.15 (1H, d, *J* = 16 Hz) and 6.96 (1H, d, *J* = 16 Hz).

S2: Experimental Details

Room temperature powder XRD patterns were measured using a Siemens D5000 diffractometer operating with Cu K$\alpha_{1/2}$ radiation. Thermodiffraction experiments were carried out using a Bruker D8 powder diffractometer operating with Cu K$\alpha_{1/2}$ radiation and fitted with an HTK900 gas chamber and VÅNTEC-1 detector. Patterns were recorded in flowing air on heating from room temperature to 600 °C in intervals of 20 °C with a 10 min equilibration time before scans lasting 10 min were made. Thermogravimetric analysis and differential scanning calorimetry were performed using a Mettler Toledo TGA/DSC 1-600 instrument under static air with a heating rate of 10 °C min^{-1} from room temperature to 1000 °C.

Scanning electron microscopy (SEM) analysis was carried out on a Zeiss Gemini 500 microscope. EDS elemental maps were produced using a 150 mm^2 Oxford Instrument SDD detector with SEM operating voltage of 7 kV.

^{1}H and ^{13}C solid-state NMR spectra were recorded using a Bruker Avance III spectrometer equipped with a wide-bore 14.1 T superconducting magnet. Samples were packed into 3.2 mm or 1.9 mm rotors and rotated at the magic angle at 12.5 kHz (3.2 mm rotors) or 40 kHz (1.9 mm rotors). ^{13}C CP spectra were acquired at 12.5 kHz MAS in a 3.2 mm rotor, with a CP contact time of 2.5 ms, a recycle interval of 3 s and 1200 (as-made) or 4096 (brominated) transients. ^{1}H and ^{1}H-^{13}C HETCOR spectra were acquired at 40 kHz MAS in a 1.9 mm rotor. ^{1}H spectra were acquired using a spin echo with an echo delay of 30 μs, a recycle interval of 30 s and 16 transients. The ^{1}H-^{13}C HETCOR spectrum was acquired with a CP contact time of 2.5 ms, a relaxation delay of 3 seconds and 568 transients for each of 38 t_1 increments of 50 μs. ^{1}H and ^{13}C chemical shift scales are reported in ppm relative to TMS.

The ^{81}Br NMR spectrum was recorded at the UK 850 MHz solid-state NMR facility using a Bruker Avance Neo spectrometer equipped with a wide-bore 20.0 T superconducting magnet. The small amount of sample was packed into a 2.5 mm rotor. The spectrum was recorded on the static sample using the WURST-QCPMG experiment[4] with a WURST excitation bandwidth of 1 MHz (pulse length 50 μs) and 100 echoes of 167 μs recorded in the echo train. 94208 transients were recorded with a recycle interval of 0.25 s. The chemical shift scale is reported in ppm relative to solid KBr.

S3: Crystal structure of 4S-PNO – H_2BDC co-crystal

A suitable crystal was selected and mounted on a glass fibre with Fomblin oil and placed on an Xcalibur Gemini diffractometer with a Ruby CCD area detector. The crystal was kept at 150(2) K during data collection. Using Olex2,[5] the structure was solved with the XS[6] structure solution program using Direct Methods and refined with the ShelXL[7] refinement package using least squares minimisation.

Table S1: Crystal structure data for 4S-PNO – H_2BDC

Empirical formula	$C_{17}H_{14}NO_3$
Formula weight	280.29
Temperature / K	150(2)
Crystal system	Monoclinic
Space group	$P2_1/n$
a / Å	7.43953(14)
b / Å	20.7625(4)
c / Å	8.87540(15)
α (°)	90
β (°)	102.7663(18)
γ (°)	90
V / Å^3	1337.03(4)
Z	4
ρ_{calc} / g cm^{-3}	1.392
μ / mm^{-1}	0.785
F(000)	588.0
Crystal size / mm^3	0.4 × 0.2 × 0.01
Radiation	CuK$_\alpha$ (λ = 1.54184 Å)
2θ range for data collection (°)	8.518 to 156.448
Index ranges	$-9 \leq h \leq 8$, $-20 \leq k \leq 25$, $-6 \leq l \leq 11$
Reflections collected	5234
Independent reflections	2775 [R_{int} = 0.0205, R_{sigma} = 0.0267]
Data / restraints / parameters	2775 / 0 / 191
Goodness-of-fit on F^2	1.072
Final R indexes [$I \geq 2\sigma(I)$]	R_1 = 0.0423, wR_2 = 0.1195
Final R indexes [all data]	R_1 = 0.0477, wR_2 = 0.1252
Largest diff. peak/hole / e Å^{-3}	0.25 / –0.19

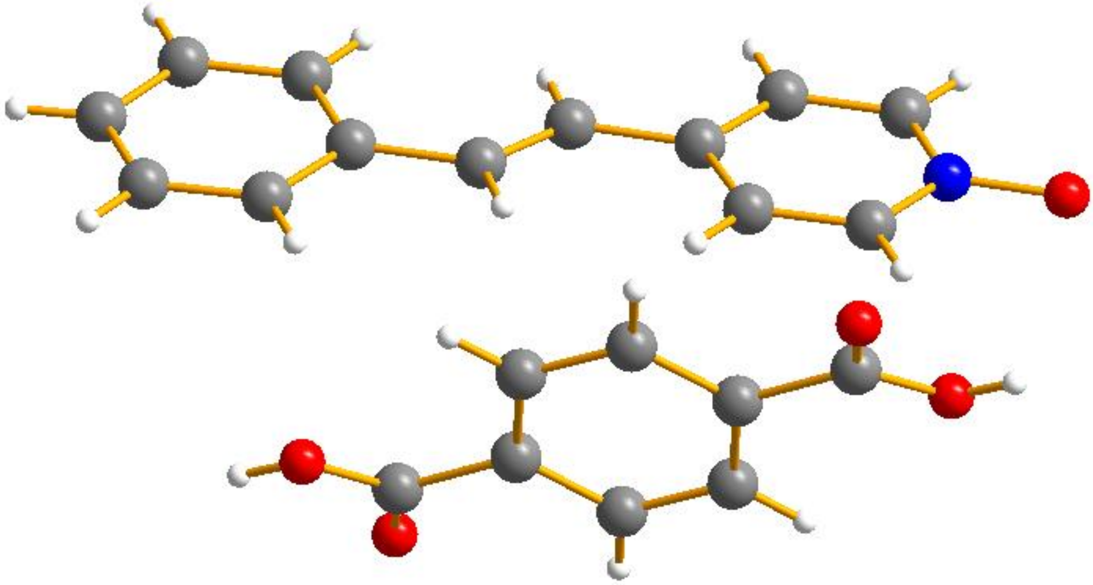


Figure S1: Relative orientation of non-interacting neighbouring 4S-PNO and H_2BDC molecules. Grey spheres are carbon, red oxygen, blue nitrogen and white hydrogen.

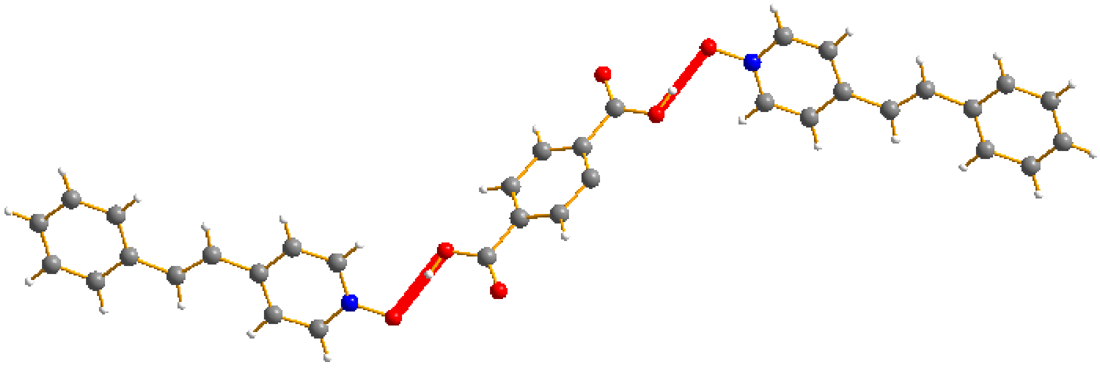


Figure S2: Hydrogen bond interactions (red line) at 2.48 Å between H_2BDC and neighbouring 4S-PNO molecules.

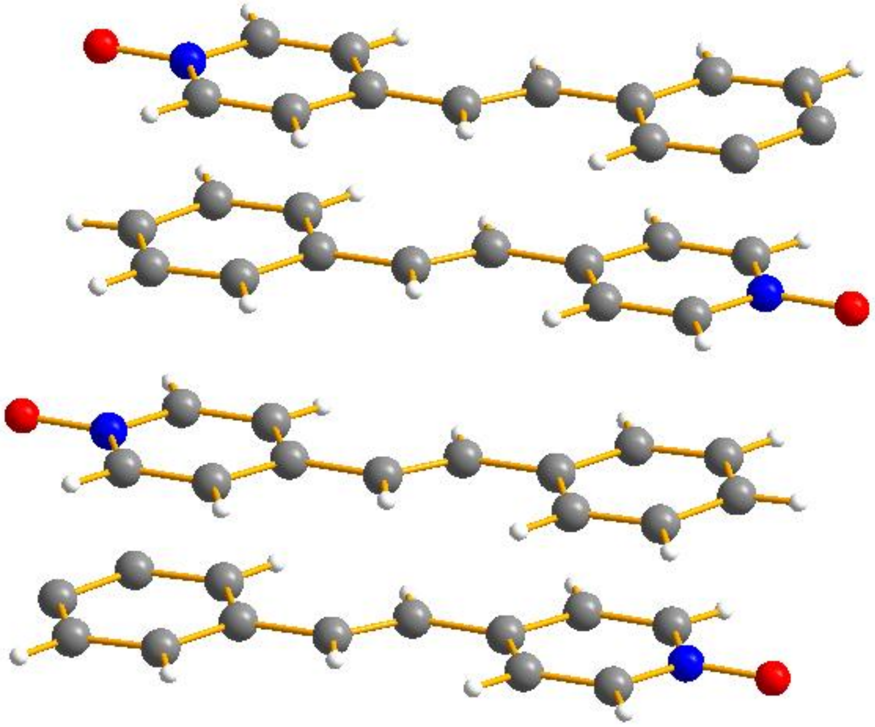


Figure S3: Relative orientation of neighbouring 4S-PNO molecules showing their head-to-tail orientation and co-planar arrangement.

<u>S4: Crystal structure of Co(4S-PNO)(BPBDC)·0.25H_2O</u>

A suitable crystal was selected and mounted on a glass fibre with silicon grease on a Xcalibur Gemini diffractometer with a Ruby CCD area detector. The crystal was kept at 296(1) K during data collection. Using Olex2,[5] the structure was solved with the XS[6] structure solution program using Direct Methods and refined with the ShelXL[7] refinement package using least squares minimisation.

The long axis of the diphenyl dicarboxylate sits on special position 4e with symmetry *mm*2 (two mirror planes and a 2-fold axis). The carboxyl carbon (C17), the first carbon of the phenyl group (C18) and the carbon (C21) that links it to the symmetry related phenyl of the biphenyl-4,4'-dicarboxylate still sit on the mirror plane but the other carbons that make up the ring (C19 and C20) lie just off the mirror plane so were modeled over two positions either side of the mirror plane. Their occupancies were originally linked to a free variable but fixed at 50:50 for the final stages of the refinement. The 4-styrylpyridine *N*-oxide also sits on special position 4e with symmetry *mm*2 (two mirror planes and a 2-fold axis). Only the *N*-oxide oxygen (O1) still sits on the special position, the rest of the ligand lies just off the 2-fold axis and mirror planes.

The disorder was modeled by building the complete *N*-oxide ligand and refining behind a PART-1 instruction. DFIX and SIMU restraints and AFIX 66 constraints were used to give these disordered components reasonable bonds lengths, angles and thermal parameters. Additionally a small amount of electron density was modeled as a partially occupied water sitting on special position 8i on a mirror plane. It was refined at 0.125 occupancy to reflect the observed electron density. No hydrogens were located for this solvent but were included in the formula to calculate the correct density.

Table S2: Crystal structure data for Co(4S-PNO)(BPBDC)·0.25H_2O

Empirical formula	$C_{27}H_{19.5}CoNO_{5.25}$
Formula weight	504.36
Temperature / K	296(1)
Crystal system	Orthorhombic
Space group	*Imma*
a / Å	25.1697(4)
b / Å	7.16550(10)
c / Å	16.6823(2)
α (°)	90
β (°)	90
γ (°)	90
V / Å^3	3008.71(7)
Z	4
ρ_{calc} / g cm^{-3}	1.113
μ / mm^{-1}	4.744
F(000)	1036.0
Crystal size / mm^3	0.3 × 0.06 × 0.06
Radiation	CuK_α (λ = 1.54184 Å)
2θ range for data collection (°)	10.606 to 156.084
Index ranges	$-21 \le h \le 31$, $-8 \le k \le 8$, $-21 \le l \le 20$
Reflections collected	8486
Independent reflections	1751 [R_{int} = 0.0353, R_{sigma} = 0.0251]
Data / restraints / parameters	1751 / 159 / 177
Goodness-of-fit on F^2	1.070
Final R indexes [$I \ge 2\sigma(I)$]	R_1 = 0.0535, wR_2 = 0.1631
Final R indexes [all data]	R_1 = 0.0591, wR_2 = 0.1712
Largest diff. peak/hole / e Å^{-3}	0.54 / –0.51

The potential free pore space in the structure was calculated using the SQUEEZE routine within PLATON, neglecting the presence of the occluded water.[8] This gave the following results per unit cell:

```
_platon_squeeze_void_nr
  _platon_squeeze_void_average_x
  _platon_squeeze_void_average_y
  _platon_squeeze_void_average_z
  _platon_squeeze_void_volume
  _platon_squeeze_void_count_electrons
```

```
  _platon_squeeze_void_content
  1  0.207 -0.032  0.000       188        33 ' '
  2  0.793 -0.033  0.000       189        33 ' '
  3  0.293 -0.033  0.500       189        33 ' '
  4  0.707 -0.026  0.500       188        33 ' '
_platon_squeeze_void_probe_radius                 1.20
```

This is equivalent to 754 Å^3 per unit cell, which has volume 3008.71 Å^3, *i.e.* 25.1 %.

S5: Crystal structure of Mg(4S-PNO)(BPBDC)

A suitable crystal was selected and mounted on a Mitegen head and placed on a Rigaku AFC11 diffractometer with a Rigaku HG Saturn944+ CCD area detector at the EPSRC's UK National Crystallography Service at the University of Southampton.[9] The crystal was kept at 100(2) K during data collection.

The asymmetric unit contains two magnesiums bridged by a 4,4'-biphenyldicarboxylate and both with a 4-styrylpyridine *N*-oxide ligand. This unit forms an infinite array of Mg chains, each Mg bridged by two carboxylates and a *N*-oxide. The magnesiums sit on special positions as does the oxygen of each *N*-oxide: Mg1 and O1A sit on special position d (mirror plane) Mg2 sit on special position b (inversion centre) O1B (coordinated to Mg2) sits on special position c (2 fold axis). Both *N*-oxide ligands are disordered about these special positions so a model was devised where a complete *N*-oxide ligand was modelled with sensible bond lengths and angles and refined behind a PART -1 instruction. Additionally, both the phenyl groups of the 4,4'-biphenyldicarboxylate were disordered about the long axis of the ligand. The occupancy of these disordered components were originally linked to separate free variables but at later stages of the refinement were described by the one free variable as their disorder appears linked and refined to an occupancy major to minor of 0.83:0.17. Voids in the structure did not have discreet electron density that could be modelled as a solvent molecule. Their contribution to the refinement was masked by the SQUEEZE procedure in PLATON.[8] This was also used to calculate the potential free void space in the structure, giving the following result per unit cell:

```
platon_squeeze_void_nr
  _platon_squeeze_void_average_x
  _platon_squeeze_void_average_y
  _platon_squeeze_void_average_z
  _platon_squeeze_void_volume
  _platon_squeeze_void_count_electrons
  _platon_squeeze_void_content
  1  1.000 -0.052  0.102       191        28 ' '
  2  0.500 -0.041  0.147       192        28 ' '
  3  0.500 -0.040  0.353       192        28 ' '
  4  0.000 -0.030  0.398       192        28 ' '
  5  0.000 -0.032  0.602       192        28 ' '
  6  0.500 -0.025  0.647       192        28 ' '
  7  0.500 -0.011  0.853       192        28 ' '
  8  0.000 -0.038  0.897       192        28 ' '
_platon_squeeze_void_probe_radius                 1.20
```

This is equivalent to 1535 Å^3 per unit cell, which has volume 5957.6 4 Å^3, *i.e.* 25.8 %.

Table S3: Crystal structure data for Co(4S-PNO)(BPBDC)·0.25H_2O

Empirical formula	$C_{54}H_{38}Mg_2N_2O_{10}$
Formula weight	923.48
Temperature / K	100(2)
Crystal system	Orthorhombic
Space group	*Pbcm*
a / Å	16.59874(19)
b / Å	7.14697(12)
c / Å	50.2201(8)
α (°)	90
β (°)	90
γ (°)	90
V / Å^3	5957.64(15)
Z	4
ρ_{calc} / g cm^{-3}	1.030
μ / mm^{-1}	0.771
F(000)	1920.0
Crystal size / mm^3	0.25 × 0.08 × 0.06 colourless block
Radiation	CuKα (λ = 1.54184)
2θ range for data collection (°)	5.324 to 134.804
Index ranges	$-19 \leq h \leq 19$, $-8 \leq k \leq 8$, $-60 \leq l \leq 59$
Reflections collected	44127
Independent reflections	5431 [R_{int} = 0.0270, R_{sigma} = 0.0120]
Data / restraints / parameters	5431/248/463
Goodness-of-fit on F^2	1.064
Final R indexes [$I \geq 2\sigma (I)$]	R_1 = 0.0772, wR_2 = 0.2424
Final R indexes [all data]	R_1 = 0.0819, wR_2 = 0.2474
Largest diff. peak/hole / e Å^{-3}	1.13/-0.45

S6: ^{13}C Solid-State NMR

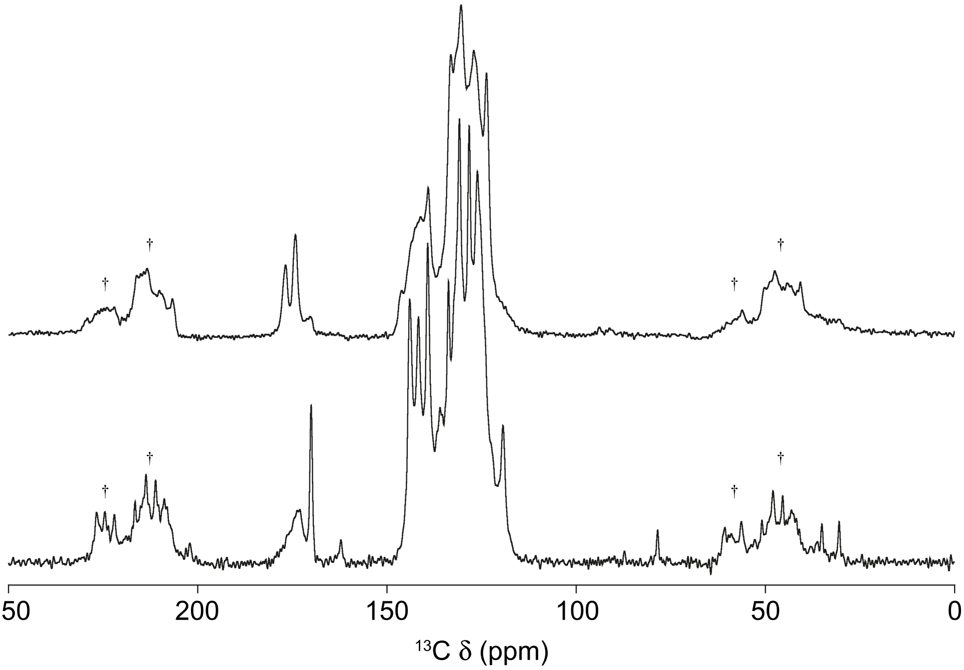


Figure S4: ^{13}C (14.1 T, 12.5 kHz CP MAS) NMR spectra of as made (bottom) (scaled × 4) and brominated (top) Mg(4S-PNO)(BPBDC).

The solid-state ^{13}C CP MAS NMR spectrum of Mg(4S-PNO)(BPBDC) (Figure S4) shows considerable changes in local structure upon bromination. However, the resonances remain sharp, indicating that the framework has not collapsed. The most notable change is a decrease in local order, indicated by a reduction in resolution for the ternary aromatic carbon resonances. This disorder is attributed to incomplete bromination of the alkene resulting in either non-brominated or mono-brominated 4S-PNO ligands. The ^{13}C NMR spectra do not directly provide evidence for C-Br bonds, however, owing to the typically very large $^{79/81}$Br quadrupolar coupling constant and the resultant broadening for the ^{13}C spectrum arising from the quadrupolar-dipolar cross-term, it is likely that any C-Br resonance would be broadened beyond the limit of detection.[10]

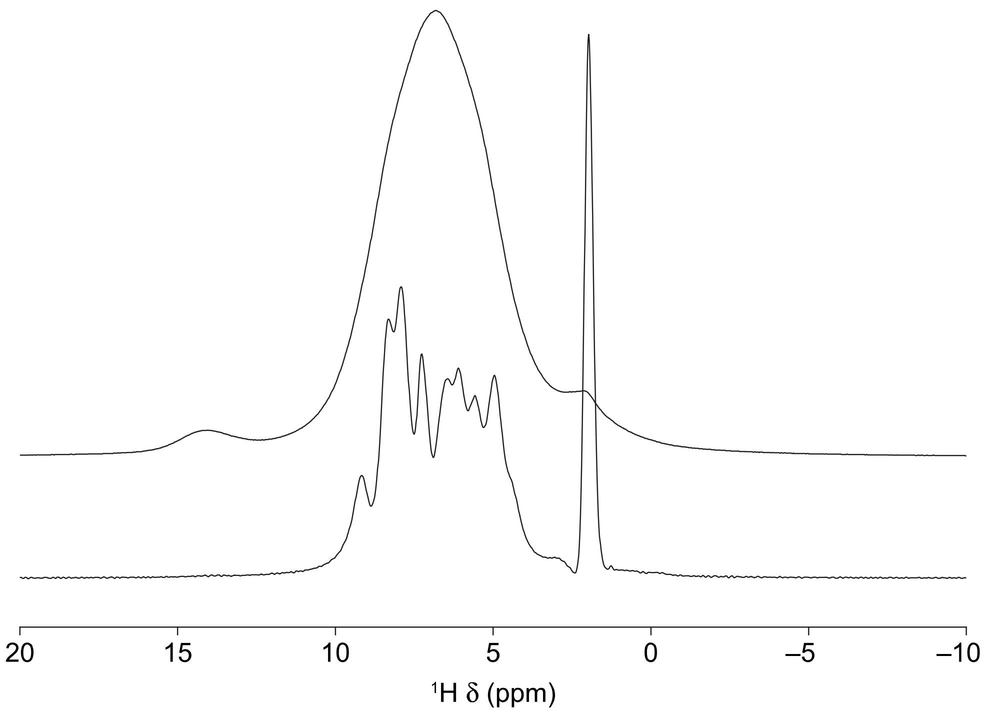


Figure S5: ^{1}H (14.1 T, 40 kHz MAS) NMR spectra of as made (bottom) and brominated (top) Mg(4S-PNO)(BPBDC). 40 kHz MAS, 14.1 T.

^{1}H MAS NMR spectra (Figure S5) show a large increase in broadening upon bromination and a resonance at 14.1 ppm, which is likely to be from C**H**Br species. This ^{1}H resonance is correlated to several carbon resonances in the quaternary and ternary aromatic region in the ^{1}H-^{13}C CP-HETCOR spectrum (Figure S6), confirming that it is part of the MOF structure.

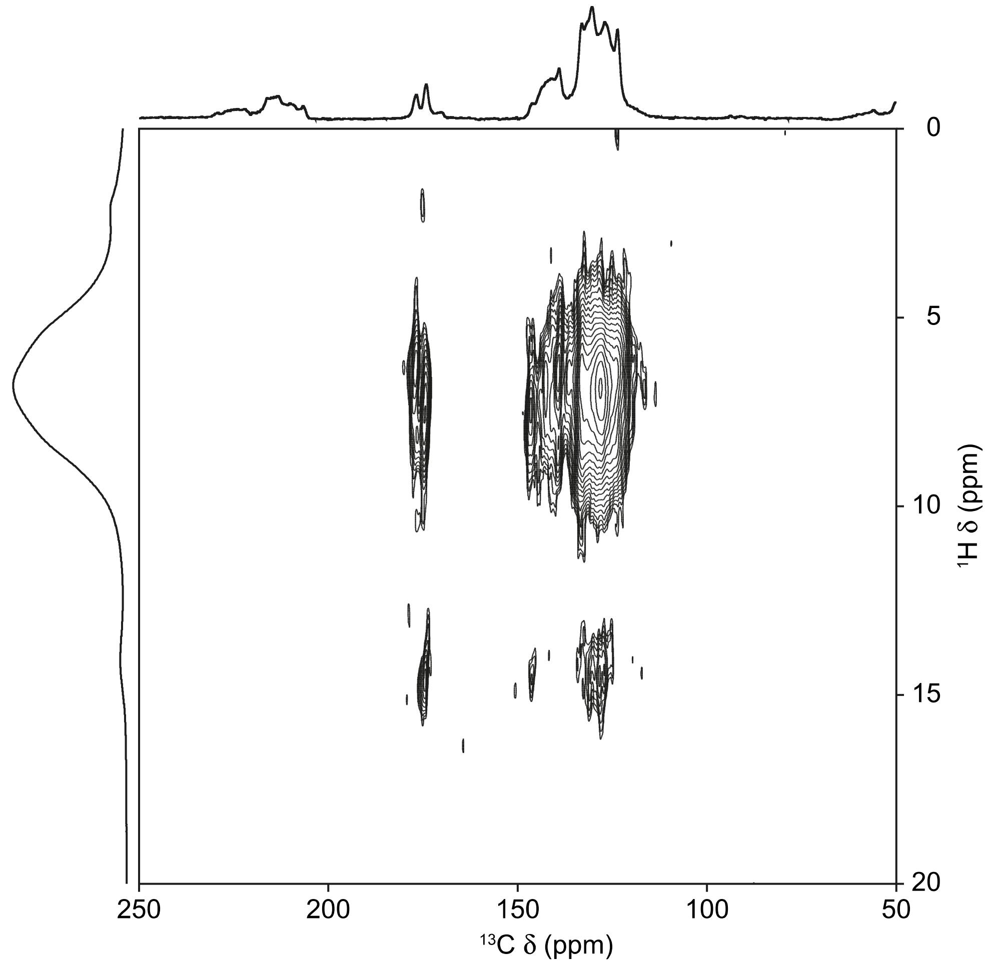
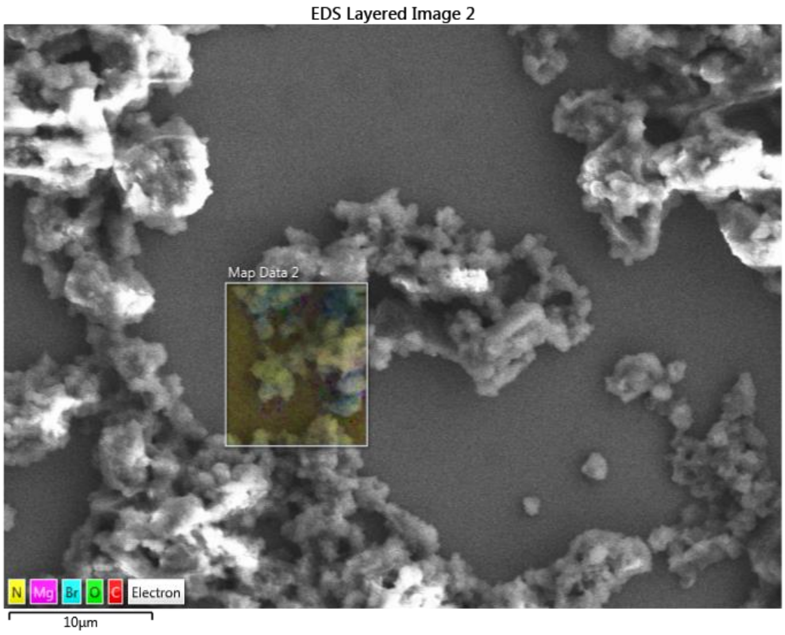
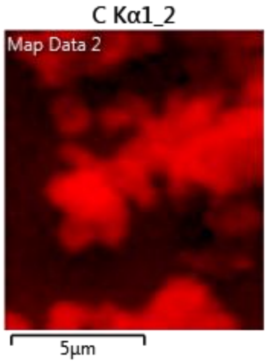
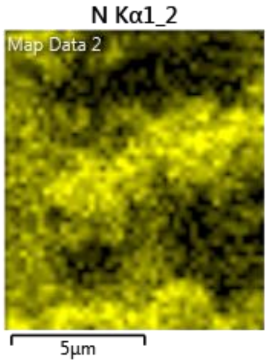


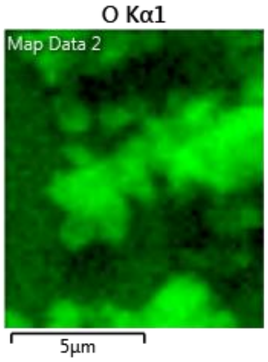
Figure S6: ^{1}H-^{13}C (14.1 T, 40 kHz MAS) CP-HETCOR spectrum of the brominated Mg(4S-PNO)(BPBDC).

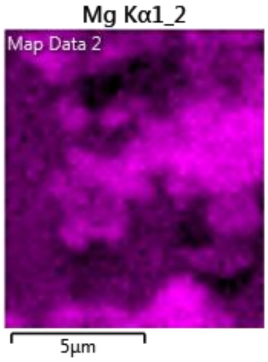
S7: Further element maps of brominated Mg(4S-PNO)(BPBDC)

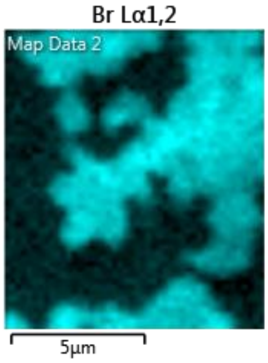




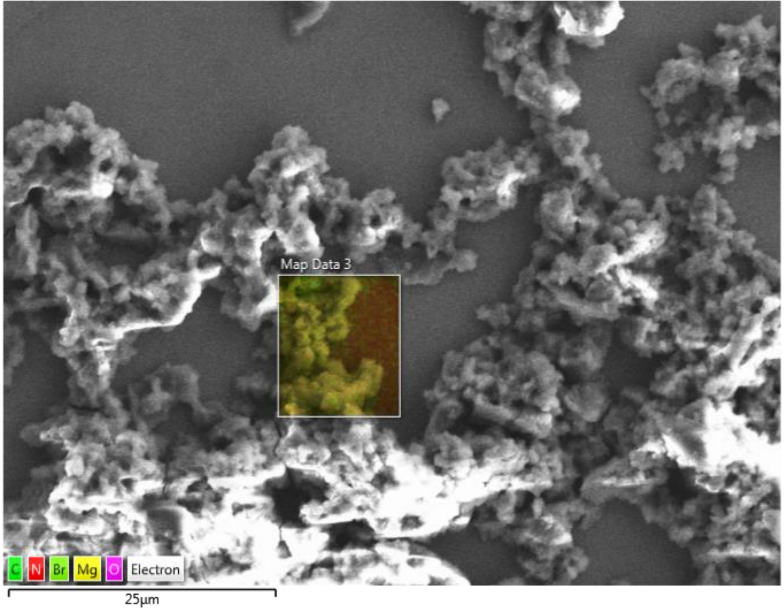




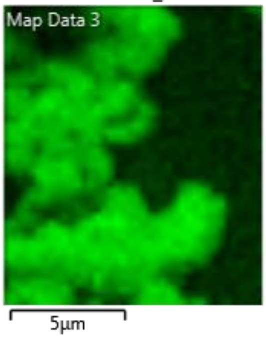




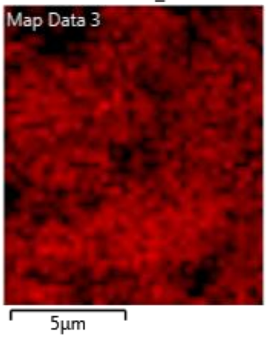
EDS Layered Image 3



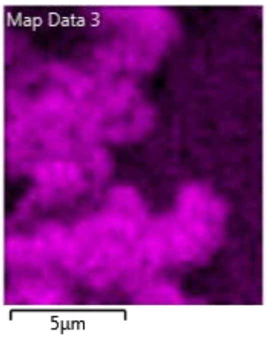
C Kα1_2



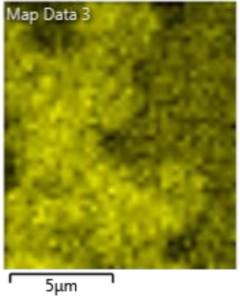
N Kα1_2



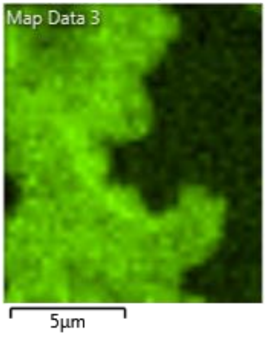
O Kα1



Mg Kα1_2



Br Lα1,2



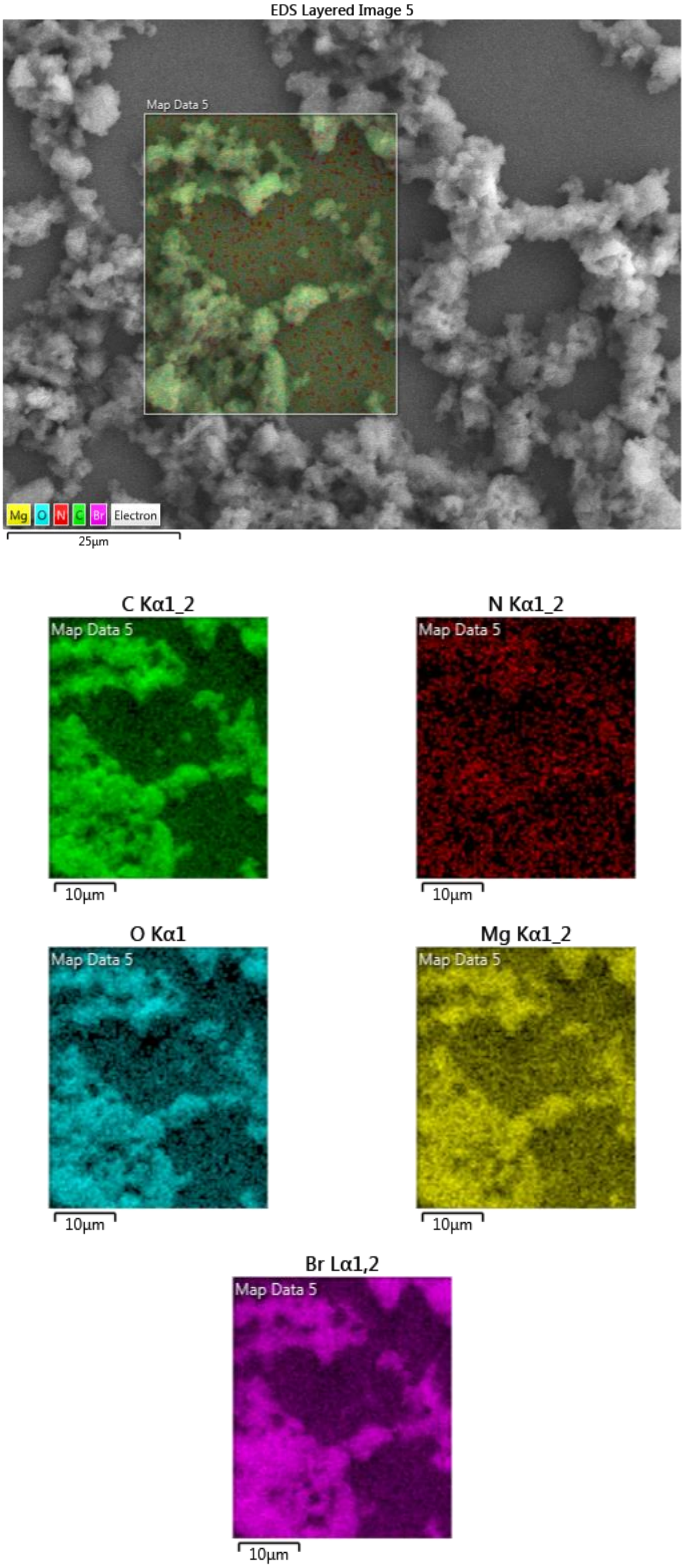


Figure S7: SEM EDXA maps from three further regions of the brominated Mg(4S-PNO)(BPBDC)

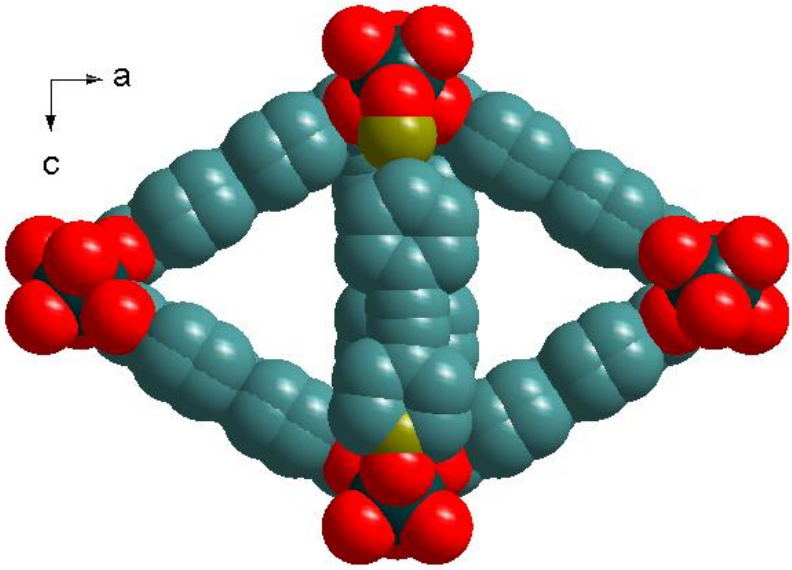


Figure S8: A space-filling representation of the structure of Mg(4S-PNO)(BPBDC) viewed along the* b*-axis showing the potential void space in the structure. The atoms are plotted with their van der Waals radii with cobalt dark grey, oxygen red, carbon grey and nitrogen olive. Only one orientation of the disordered 4-styrylpyridine-N-oxide ligand is shown.

References

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