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Synthesis and disassembly of an organometallic polymer comprising redox-active Co₄S₄ clusters and Janus biscarbene linkers†

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Here, we show for the first time that main-chain organometallic polymers (MCOPs) can be prepared from Janus N-heterocyclic carbene (NHC) linkers and polynuclear cluster nodes. The cross-linked framework Co₄S₄-MCOP is synthesized via ligand displacement reactions and undergoes reversible electron transfer in the solid state. Discrete molecular cluster species can be excised from the framework by digesting the solid in solutions of excess monocarbene. Finally, we demonstrate a synthetic route to monodisperse framework particles via coordination modulation.

Rigid, non-chelating, poly-N-heterocyclic carbene (NHC) ligands are emerging building blocks in the assembly of functional main-chain organometallic polymers (MCOPs).^{1,2} Structurally, such materials consist of bridging, poly-NHC organic linkers and single transition metal ions that serve as branching points of extension. So far, the dimensionality of this class of polymer has been dictated by the topology and geometry of the poly-NHC linker. Specifically, one,^{3,4} two,^{5–8} and three-dimensional (3D)^{9,10} MCOPs have all been reported using various poly-NHC ligands and single-metal atoms including palladium,^{3,6,9,11} platinum,¹¹ nickel,¹¹ iridium,^{4,10} and gold.^{5,7,8} Utilizing polynuclear complexes or ensembles of multiple metal atoms could afford further control over dimensionality and polymer structure. However, the investigation of NHC-based MCOPs comprising molecular clusters remains an open issue. This is surprising for several reasons. For instance, there are numerous known NHC-stabilized metal cluster compounds, including those containing metal-carbonyl,¹² noble metal,^{13–15} metal-chalcogenide,^{16,17} and metal-halide¹⁸ cluster-cores. Thus, similar synthetic protocols used to

prepare these discrete clusters can be applied to incorporate them into poly-NHC MCOPs. Additionally, molecular clusters are attractive from a structural standpoint. They are well-defined and can be prepared in a variety of sizes and geometries.^{19–22} In fact, the abstraction of clusters as polyhedral nodes is central to the field of reticular chemistry and gave rise to the first crystalline metal organic frameworks (MOFs).²³ Substituting single metal atoms for clusters could, therefore, lead to crystalline NHC-MCOPs. This is significant, as all known NHC-MCOPs have all been isolated as amorphous solids. Finally, molecular cluster compounds have rich catalytic,^{24,25} photophysical,^{26,27} magnetic,^{28,29} and redox^{30–32} properties beyond what single transition metals can offer. Consequently, a diverse new class of functional MCOPs can be envisioned from the coupling of clusters with poly-NHC linkers.

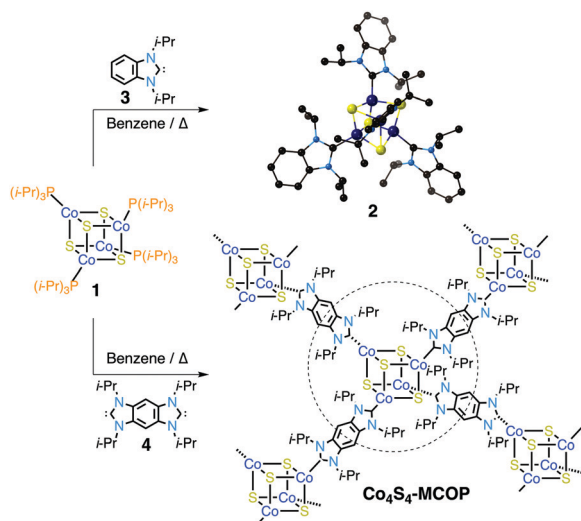
Our group is using metal chalcogenide clusters as building blocks for redox active MOF-hybrids.^{33,34} This is accomplished using pre-assembled clusters stabilized with bifunctional phosphine ligands. Ancillary sites on the phosphines, and periphery of the cluster, then undergo further assembly in the presence of metal cations. However, bifunctional phosphine ligands are nonlinear linkers and produce distorted frameworks with bent connections between building units. The use of phosphine linkers thus makes the prediction of the final structure challenging, preventing the reticular design principles of MOF synthesis from being applied. Other organic ligands have been used to crosslink metal-chalcogenide clusters but suffer from similar issues. For example, coordination polymers assembled from benzenedithiolate ligands and both [Fe₄S₄]²⁺ and [Mo₃S₇]⁴⁺ clusters, respectively, have recently been reported.^{35,36} However, these polymers are 1D chains, presumably due to the flexibility and bent nature of the metal-sulfur bond between the bridging ligands and the cluster cores. Rigid, linear linkers are therefore essential in order to develop metal-chalcogenide clusters as building blocks in reticular chemistry. Here, we report that aromatic-fused, Janus di-NHC ligands are efficient bridging units for the assembly of Co₄S₄ clusters into redox active MCOPs.

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Scheme 1 Synthesis of $[\text{Co}_4\text{S}_4(\text{Pr}^i_2\text{NHCbz})_4]$ (**2**) and $\text{Co}_4\text{S}_4\text{-MCOP}$. Single crystal X-ray structure of **2**. Hydrogen atoms omitted.

The synthetic methodology to prepare $\text{Co}_4\text{S}_4\text{-MCOP}$ is based on a report by Holm and coworkers that the phosphine ligated cluster $[\text{Co}_4\text{S}_4(\text{P}^i\text{Pr}_3)_4]$ (**1**) undergoes high yielding, global ligand exchange in the presence of mono-NHC, 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene ($\text{Pr}^i_2\text{NHCMe}_2$).³⁷ This conversion can be completed in 12 hours with heating to yield the discrete cluster $\text{Co}_4\text{S}_4(\text{Pr}^i_2\text{NHCMe}_2)_4$. We prepared a benzo-bis-imidazolylidene (**4**) with isopropyl “wingtips” to match the steric profile of $\text{Pr}^i_2\text{NHCMe}_2$ using a modified prep reported by Bielawski.³⁸ The free biscarbene **4** is planar based on single-crystal X-ray diffraction (SCXRD) analysis (Fig. S1, ESI†). The flat, rigid nature of **4** coupled with the tetrahedral cluster core of **1** compelled us to combine the two building blocks and study their compatibility (Scheme 1). $\text{Co}_4\text{S}_4\text{-MCOP}$ is obtained as a purple solid when **1** and **4** are heated in solutions of benzene or toluene at 100 °C for 12 hours (Fig. S3, ESI†).

Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were used to analyze $\text{Co}_4\text{S}_4\text{-MCOP}$. SEM micrographs of the dried polymer show the material to be non-uniform in size with an irregular, foam-like morphology (Fig. S3, ESI†). The EDS spectra confirm the distribution of Co, S, N, and C throughout the solid (Fig. S3, ESI†). Trace amounts of phosphorous were also observed in some scans at the margin of the detection limit. We ascribe this intermittent phosphorous signal to residual phosphine, which could either be trapped inside the solid or still bound to a fraction of the Co_4S_4 clusters.

A zero-dimensional, molecular analog to $\text{Co}_4\text{S}_4\text{-MCOP}$ was also prepared from a comparable, benzoannulated mono-NHC ligand, $\text{Pr}^i_2\text{NHCbz}$ (**3**) (Scheme 1). SCXRD analysis of $[\text{Co}_4\text{S}_4(\text{Pr}^i_2\text{NHCbz})_4]$ (**2**) confirmed the tetrahedral nature of the Co_4 core and the coordination of four NHC ligands around the cubane unit. This nanocluster serves as a representative fragment of $\text{Co}_4\text{S}_4\text{-MCOP}$ and was used for spectroscopic comparison to further characterize the polymeric material.

Evidence for the polymerization was first obtained *via* ^1H -nuclear magnetic resonance (NMR) spectroscopic studies.

Specifically, when **1** and **4** were heated in C_6D_6 and monitored *via* NMR we observed a steady attenuation of the phosphine methine proton signal at 14.75 ppm. Concurrently, a new peak between 12 and 13.5 ppm emerged (Fig. S5, ESI†). This broad, new singlet matches closely to the position of the methyl protons on the discrete model cluster **2** and its appearance signifies that phosphine–NHC exchange is occurring. Full ligand substitution, however, cannot be monitored as the insoluble MCOP begins to form over time. ^{31}P -NMR spectroscopy confirmed the formation of free phosphine under the same conditions (Fig. S7, ESI†). This is in accord with the biscarbene **4** effectively displacing the phosphine ligands of **1**. Unfortunately, the paramagnetic nature of both **2** and $\text{Co}_4\text{S}_4\text{-MCOP}$ precluded their analysis *via* solid-state ^{13}C -spectroscopy (Fig. S8, ESI†). Infrared (IR) spectroscopy was also performed to analyze the polymer (Fig. S9, ESI†). The IR spectrum of $\text{Co}_4\text{S}_4\text{-MCOP}$ contains two signals of medium intensity at 1679 and 1704 cm^{-1} , respectively. We attribute the absorbances at these frequencies to C=N stretching, due to the presence of the biscarbene linkers.³⁹ The IR spectra of cluster **2** and free biscarbene **4** also contain distinct signals in this region at 1694 and 1668 cm^{-1} , respectively. The presence of two, different C=N stretches in the polymer may be due to a mixture of free and bound **4** or sites of monotopic coordination.

X-Ray photoelectron spectroscopy (XPS) measurements were collected on $\text{Co}_4\text{S}_4\text{-MCOP}$, as well as clusters **1** and **2**, to compare their elemental composition and surface valence states (Fig. S11, ESI†). All three samples are air sensitive and display similar oxidized cobalt and sulfur profiles upon exposure to atmosphere with characteristic peaks for the Co^{2+} oxidation state, 802.5 and 786.1 eV, and an Sp^2 peak at 161.9 eV that is indicative of a metal sulfide bond. A second sulfur peak is also observed at 166 eV, which we assign to an oxidized sulfur species (SO_x^{n-}), based on the XPS of related Co–S based solids.⁴⁰ The high-resolution XPS spectra of both $\text{Co}_4\text{S}_4\text{-MCOP}$ and **2** show the nitrogen 1s peak at approximately 400 eV. The atomic proportion of Co:S:N in cluster **2** is 5.7:4.0:9.7, while $\text{Co}_4\text{S}_4\text{-MCOP}$ has an atomic ratio of 4.6:3.8:10.7 for Co:S:N. Finally, we observed a minor quantity of phosphorous in the XPS spectrum of $\text{Co}_4\text{S}_4\text{-MCOP}$ with a low signal to noise ratio. This residual phosphorous is consonant with the trace phosphorous periodically observed during EDS measurements.

The powder X-ray diffraction (PXRD) pattern of the polymer exhibits features centered around 2.25°, 5.7°, and 13.8° 2 θ (Fig. 1a). The broad diffraction peaks are in agreement with the morphology observed *via* SEM and are characteristic of a disordered solid with structural defects. Observation of diffraction peaks is particularly noteworthy, as all reported NHC-MCOPs are amorphous with no measurable PXRD patterns. The small number of peaks in the experimental PXRD, however, prevent assignment of an exact structure with high certainty. Nevertheless, a theoretical unit cell of $\text{Co}_4\text{S}_4\text{-MCOP}$ assuming complete crosslinking was modeled and its PXRD pattern was simulated for comparison. The calculated pattern exhibits a number of sharp peaks clustered around 2.5° 2-theta. The

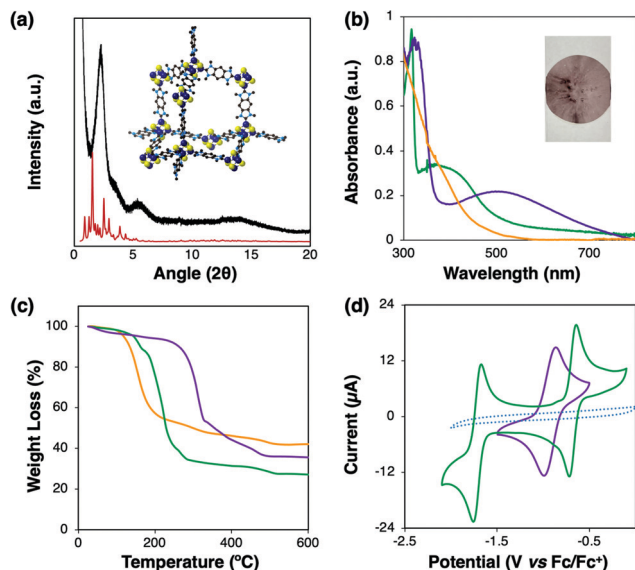


Fig. 1 (a) Synchrotron powder X-ray diffraction pattern of $\text{Co}_4\text{S}_4\text{-MCOP}$ (black) and simulated pattern (red) of model (inset), (b) normalized UV-vis absorption spectra (inset image of $\text{Co}_4\text{S}_4\text{-MCOP}$ in epoxy) and (c) TGA traces of $\text{Co}_4\text{S}_4\text{-MCOP}$ (purple), **2** (green), and **1** (orange), and (d) cyclic voltammograms of $\text{Co}_4\text{S}_4\text{-MCOP}$ (purple); solid-state modified glassy carbon working electrode, **2** (green), and background (blue dashed). Recorded at 100 mV s^{-1} in MeCN with TBAPF_6 .

center of this grouping aligns with the largest broad feature of the polymer pattern and suggests that portions of $\text{Co}_4\text{S}_4\text{-MCOP}$ may have a 3D, diamond structure.

The UV-visible absorption spectrum of $\text{Co}_4\text{S}_4\text{-MCOP}$ has a broad peak centered at 503 nm (Fig. 1b) and a strong absorbance below 350 nm. The optical band gap of $\text{Co}_4\text{S}_4\text{-MCOP}$ was calculated from the low energy transition to be 1.68 eV. In comparison, the spectrum of cluster **1** is less well-defined and has only one peak below 300 nm (Fig. 1b). The absorbance profile of the polymer more resembles that of **2** dissolved in THF, with two distinct absorbance peaks (Fig. 1b).

The porosity of the polymer was analyzed using N_2 adsorption data at 77 K. Desolvated samples of $\text{Co}_4\text{S}_4\text{-MCOP}$ exhibit a type II isotherm, with a rise in sorption at higher dinitrogen pressures (Fig. S13, ESI†). The Brunauer–Emmett–Teller (BET) surface area of $\text{Co}_4\text{S}_4\text{-MCOP}$ was determined to be $22.2 \text{ m}^2 \text{ g}^{-1}$. The low porosity may arise from framework collapse during solvent removal or a highly interpenetrated structure.⁴¹ Pore collapse is a common phenomenon observed when activating related MOF materials.⁴² $\text{Co}_4\text{S}_4\text{-MCOP}$ undergoes a significant volume change upon drying. Thus, we hypothesize that a structural change followed by pore occlusion occurs under vacuum.

Thermogravimetric analysis (TGA) was performed on samples of $\text{Co}_4\text{S}_4\text{-MCOP}$, discrete cluster **2**, and the precursor cluster **1** to compare their thermal stabilities (Fig. 1c). All three samples undergo a similar, major weight loss below 300°C that is likely a result of the dissociation of their organic ligands. The TGA traces reveal an increase in thermal stability as the phosphine ligands of **1** ($\approx 110^\circ\text{C}$) are substituted for NHC

ligands in **2** ($\approx 140^\circ\text{C}$). $\text{Co}_4\text{S}_4\text{-MCOP}$ is more stable than both molecular clusters **1** and **2**, exhibiting a degradation point at $\approx 240^\circ\text{C}$. We posit that the crosslinked structure is responsible for the augmented thermal stability observed in the polymer.

Cobalt sulfide clusters are well known for their rich electrochemistry.³² The cubane-type Co_4S_4 clusters are no exception and $\text{Co}_4\text{S}_4(\text{Pr}^i_2\text{NHCMe}_2)_4$ can be oxidized twice ($E_{1/2}^1 = -1.4$ and $E_{1/2}^2 = -0.2 \text{ V vs. Fc/Fc}^+$) to form $[\text{Co}_4\text{S}_4]^{1+}$ and $[\text{Co}_4\text{S}_4]^{2+}$, respectively.³⁷ Accordingly, cluster **2** also undergoes two oxidations at similar potentials ($E_{1/2}^1 = -1.7$ and $E_{1/2}^2 = -0.67 \text{ V}$) (Fig. 1d). This prompted us to investigate the redox properties of the polymer. We prepared electrodes modified with the insoluble $\text{Co}_4\text{S}_4\text{-MCOP}$ to study its electrochemistry the solid state (Fig. 1d). These electrodes were submerged in solutions of MeCN with tetrabutylammonium hexafluorophosphate (TBAPF_6) supporting electrolyte and subject to cyclic voltammetry (CV) scans. The $\text{Co}_4\text{S}_4\text{-MCOP}$ solid exhibits a single reversible redox event at $-0.9 \text{ V vs. Fc/Fc}^+$. This potential is in a similar voltage range to the corresponding, discrete cluster **2**. Therefore, we attribute this process to the reversible oxidation of the Co_4S_4 units in the solid. The lack of other features in the CV and relative uniformity of the redox wave indicates that all cluster entities in the framework are in the equivalent oxidation state with the same supporting ligands.

Some NHC-transition metal complexes and clusters have been shown to undergo exchange with different ligand types as well as other monomeric NHCs.^{3,43,44} These reports encouraged us to mix the polymer with a monocarbene in an effort to extract a molecular species. Thus, suspensions of $\text{Co}_4\text{S}_4\text{-MCOP}$ in C_6D_6 were heated with excess $\text{Pr}^i_2\text{NHCMe}_2$ (20 equivalents). After 24 hours, a trace amount of solid remained and the solution had changed from transparent to red-brown (Fig. S16, ESI†). A filtered aliquot of this solution was collected and studied *via* ^1H NMR spectroscopy (Fig. 2). The spectrum of the digested sample contains diagnostic signals at 5.3 and 7.3 ppm, which correspond to the NMR spectrum of the discrete cluster $\text{Co}_4\text{S}_4(\text{Pr}^i_2\text{NHCMe}_2)_4$.³⁷ Specifically, these

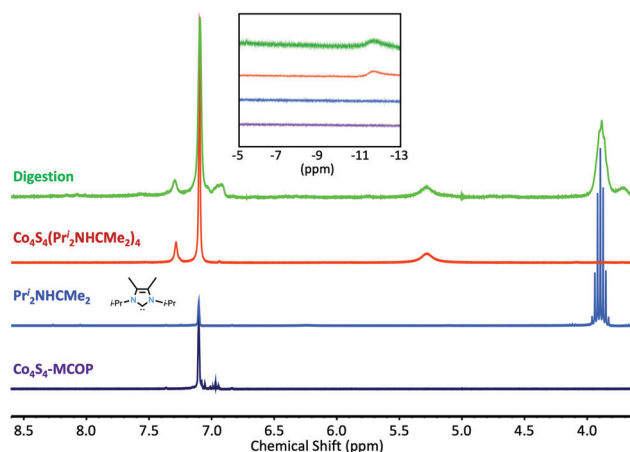


Fig. 2 NMR spectra overlay of $\text{Co}_4\text{S}_4\text{-MCOP}$ (purple); $\text{Pr}^i_2\text{NHCMe}_2$ (blue); discrete $\text{Co}_4\text{S}_4(\text{Pr}^i_2\text{NHCMe}_2)_4$ (red); and mixture of $\text{Co}_4\text{S}_4\text{-MCOP}$ and $\text{Pr}^i_2\text{NHCMe}_2$ after digestion (green) in C_6D_6 .

resonances are assigned to methyl protons on the isopropyl groups and methyl protons attached to the imidazolyldiene ring, respectively. Additionally, a broad singlet was observed at -11.8 ppm. This unique resonance from the isopropyl methine protons is also consistent with the spectrum of the 0D cluster and confirms that the Co_4S_4 unit can be excised from the polymer. The NMR experiment further indicates that the Co_4S_4 entity remains intact during polymerization and provides direct evidence for the dynamicity of the $\text{Co}-\text{C}_{\text{NHC}}$ bond in the polymer.

Finally, we sought to exploit the reversible nature of the $\text{Co}-\text{C}_{\text{NHC}}$ bonding to regulate the nucleation rate during polymerization. We hypothesized that a mono-NHC could act as a competitive capping agent (modulator) and decrease the rate of nucleation prior to solid formation. To this end, a series of solvothermal polymerizations were run in the presence of increasing equivalents of **3**. We found that larger amounts (5–15 equivalents) of modulator led to a decrease in the rate of solid formation. Polymerization does not occur at an appreciable rate under conditions of high modulator concentration (≥ 20 equivalents), further corroborating our observations in the digestion experiments. Precipitate isolated from reactions run in the presence of 10 equivalents of **3** also appeared markedly different *via* SEM (Fig. S17, ESI[†]). These modulated syntheses yielded product that was uniform in size (645 ± 166 nm), less stringy, and more particle-like than material isolated from reactions run in the absence of capping agents.

In summary, we have designed and synthesized the first example of a MCOP consisting of poly-NHC linkers and molecular cluster nodes. The material is redox active and can be depolymerized to obtain discrete, soluble Co_4S_4 entities. The rate of polymerization was found to be tunable, which may provide a means to single-crystalline NHC-MCOPs in the future. Finally, this study paves the way for a new class of functional MCOPs comprising poly(NHC) ligands and clusters of different sizes, geometries, and compositions.

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Conflicts of interest

There are no conflicts to declare.

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