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Facile Synthesis of a Conjugated Microporous Polymeric Monolith via Copper-Free Sonogashira-Hagihara Cross-Coupling in Water Under Aerobic Conditions

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A conjugated microporous polymer was synthesized via a modified Sonogashira-Hagihara cross-coupling reaction under aerobic conditions in water and in the absence of copper. These conditions allowed for the directing of the CMP format during synthesis into a monolithic structure. Post-modification of the polymer with thiol-yne chemistry followed by Ag[I] uptake led to a catalytically active material for a heterocyclization reaction.

Development of conjugated microporous polymers (CMPs), as first described by Andrew Cooper et al.,[1] has attracted interest in the search of materials for energy storage and conversion.[2] These extended π-π conjugated materials are known to demonstrate properties such as photoactivity, insolubility, high surface areas and microporosity. Given these properties, applications such as heterogeneous (photo)catalysis,[3,4] gas storage and separation,[5] and light harvesting[6] have been recently explored. Functionality within the monomers implemented in a CMP is a key component with regards to most of these specific applications since it allows for both electronic and morphological control of the CMP.[7]

Along with the chemical design of CMPs, there is scope for improvements with regards to the difficult post-reaction processability resulted from their generally poor solubilities. Several synthetic strategies have been explored to help forge the product format during synthesis of these CMPs. These include electropolymerization (thin films),[8] emulsion polymerization (monoliths),[9] aerogels[10] and even soluble materials.[11] However, these strategies are still under-explored with large scope for further developments.

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The ability to tailor CMPs into different physical forms, along with the functional flexibility of the monomers, underpins the rich potential that CMPs offer for catalysis and many other applications. Homogeneous catalysis is used widely in commercial and industrial applications, as well as smaller laboratory conditions.[12] However, implementation of heterogeneous catalysis in place of its homogeneous counterpart has added benefits, especially within industrial settings. These include easy recovery and reusability of the catalyst, and application in continuous flow processes, which minimizes time and cost of the overall catalytic reaction and potentially increases productivity. There is therefore a need to develop, in a sustainable fashion, catalytically active materials in different forms and formats.

CMPs are mainly synthesized using palladium-mediated Suzuki-Miayura and Sonogashira-Hagihara cross-coupling reactions.[2] Both of these methodologies provide different levels of control in designing a material. Suzuki-Miayura has proven to be a compatible with emulsion polymerization,[9] whereas Sonogashira-Hagihara allows for easy post-modification of CMPs at the alkyne moiety.[13]

While a major characteristic of CMPs is their metal-free composition, post-synthetic strategies allow for the addition of functional groups, including metals.[14] Judicious post-modification strategies also allow access to further applications such as sorption of specific metal ions, which in turn can potentially enhance the CMP materials performance in heterogeneous (photo)catalysis.

Herein is described a versatile synthetic strategy in the development CMPs via a copper-free Sonogashira-Hagihara cross-coupling reaction in water under aerobic conditions.[15] These conditions provide a more sustainable route for the facile synthesis of monolithic CMPs. Further post-modification of the monolith using thiol-yne chemistry gives rise to a material with selectivity to silver ions. Finally, the silver-rich CMP is shown to have enhanced catalytic activity and reusability.

Scheme 1. Synthetic scheme for the conjugated microporous polymer monolith (CMP_1).

Facile synthesis. Given the flexible reaction conditions we chose to carry out the polymerisation for 24h at 85 °C in a 7.5 mL vial without any form of stirring or agitation. The monomer building blocks chosen are commercially available: 1,3,5-tribromobenzene (TBB) and 1,4-diethynylbenzene (DEB). This methodology led to the formation of a brown material with a cylindrical monolithic structure shaped by the reaction vessel (Scheme 1, Figure 1). As expected, the monolithic CMP_1 is insoluble in all conventional solvents investigated (CHCl$_3$, CH$_2$Cl$_2$, THF, MeCN, EtOH, MeOH, H$_2$O and acetone).
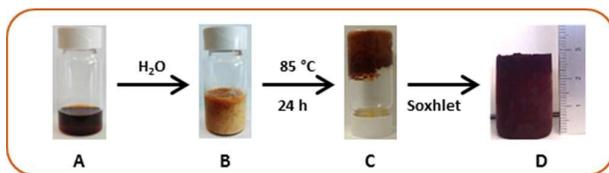
Figure 1. Synthetic evolution of CMP_1: a) TBB, DEB and PdCl$_2$ dissolved in pyrrolidine; b) Addition of water and subsequent precipitate formation; c) Solidification of monolith after heating; d) Purified and dried monolithic CMP_1.

The polymer was characterised by solid-state ^{13}C-NMR, thermogravimetric analysis (TGA), FTIR spectroscopy, SEM imaging, Raman spectroscopy, CO$_2$ gas sorption and energy-dispersive X-ray spectroscopy (EDX). TGA (Figure S2) on the monolithic polymer reveals no weight loss up to 250 °C, indicative of the non-volatile polymeric nature of the product. In the FTIR spectra (Figure S9), C-H stretching mode (terminal alkynes) from starting material (1,4-diethynylbenzene) at 3263 cm^{-1} is absent in the resulting CMP; the typical C≡C stretching mode at about 2200 cm^{-1} can be observed both in FTIR and Raman spectra (Figure S9).

The monolithic polymer sample exhibits no significant N$_2$ sorption at 77 K. Nevertheless, at 273 K, CO$_2$ sorption does take place (pressure range: from 8 x 10^{-3} to 780 mmHg) with reproducible isotherms indicating a BET surface area of 374 m^2/g^{-1}. Such different sorption behaviour towards N$_2$ and CO$_2$ is often seen in porous polymers, wherein the pores blocked at 77 K become more accessible (e.g., to CO$_2$ gas) at higher temperatures due to stronger thermal motions.[16] DFT analysis (fitting error, 0.055%) on pore size distribution and pore volume (Figure S5) of the CO$_2$ adsorption isotherms indicates an average pore width of 0.48 nm and a micropore volume of 0.113 cm^3/g. EDX (Figure S3) shows that there is still a small amount of bromine in CMP_1, indicating potential unreacted sites of the TBB monomer. Solid state ^{13}C- NMR (Figure S1) shows the aromatic nature of the material and the presence of the alkyne groups, which can be used for the post-modification of CMP_1, as we have previously demonstrated.

Electron microscopy (Figure S6) reveals in detail the microstructure of the polymer network. CMP_1 is primarily composed of hollow fibres with diameters in the range of a few hundred of nanometers. The formation of these tubular shapes is most likely induced via the cross-coupling reaction and directed by a self-assembly mechanism of the aromatic building-blocks during synthesis. Although this phenomenon is not new, there are only a few reports describing the formation of tubular-shape nanofibers of conjugated networks, with very little details on their mechanism of formation.[17]

Post-modification of the monolithic CMP_1. Thiol-yne chemistry was employed for the post-modification of CMP_1 as it generally results in a high yielding reaction in both homogeneous (Scheme S1) and heterogeneous conditions.[13] Furthermore, with the introduction of a sulfur moiety, when using this strategy, arises the possibility of metal chelation for different applications.

As shown in Scheme 2, the addition of sulfur methyl (-SCH$_3$) to alkyne groups was performed on monolithic polymer by simply treating the insoluble solid with sodium methanethiolate in DMF under N$_2$ atmosphere.

The typical C≡C stretching mode at about 2200 cm^{-1} of CMP_S is largely diminished in both the FTIR and Raman spectra (Figure S9) when compared to the original CMP_1. Solid state ^{13}C-NMR (Figure S7) also confirms the reduction of the alkyne signal, indicating that the thiol-yne reaction was successful. Furthermore, this post-modification strategy is confirmed by EDX (Figure S8) where sulfur can be readily seen.
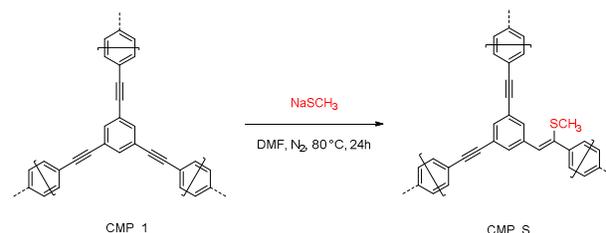
Scheme 2. Post-modification of CMP_1 monolith using a thiol-yne reaction to produce CMP_S.

Selective Ag^I uptake. Silver as a precious metal often occurs naturally in mineral forms together with ores of copper, nickel, zinc and lead. Separation of Ag^I from these base metal species is of great industrial importance.[18] In a view to assess the chelating ability of the sulfur rich CMP_S, we applied this material in the separation of different metal ions in solution. The concentration of each of the metal ions was set at 10 ppm (Table S1 and S2) by dissolving AgNO$_3$ and the following: Cu(NO$_3$)$_2$·3H$_2$O, Zn(NO$_3$)$_2$·6H$_2$O, Co(NO$_3$)$_2$·2H$_2$O, Cd(NO$_3$)$_2$·4H$_2$O, Ni(NO$_3$)$_2$·6H$_2$O, Pb(NO$_3$)$_2$ in water. CMP_S (10 mg, 0.04 mmol of the desired repeat unit) was placed into 10 mL of the above solution, which contains about 0.1 mg (9.2×10^{-4} mmol) Ag$^+$ and a total of 8.4×10^{-3} mmol of metal ions. The mixture was then stirred in the absence of light and sampled at different times (0 h, 2 h and 20 h) in order to monitor the concentrations of the metal species present in the solution. As a control experiment, the original monolithic CMP_1 was also tested under similar conditions (see SI for details).

Figure 2 shows for both CMPs that within the first 2 hours, Ag^I ions rapidly decrease in concentration, whereas concentrations of the other ions present remained the same, with the exception of Cu^{II} and Pb^{II}. By the 20th hour, 95% of Ag^I ions in solution were

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removed by the CMP_S monolith (Figure 2b), whilst more than 50% of the Ag^I ions were still present in solution when using the control CMP_1 (Figure 2a). These results show that selectivity towards Ag^I is largely enhanced by the sulfur present in CMP_S. Generally speaking, the strong selective binding of Ag^I is possibly driven by the higher (less negative) Gibbs free energy of hydration for silver ions than other metal ions, as well as by the kinetics/liability of the coordination properties of Ag^I.

Effective Ag^I uptake. To quantify the effective Ag^I uptake of CMP_S (40 mg, 0.16 mmol of the desired repeat unit) was placed in an aqueous solution containing excess AgNO$_3$ (156 mg, 0.92 mmol) in 3 mL of water. After the mixture was stirred for 1 day at 80 °C in the absence of light, the resulting solid was separated by filtration and washed repeatedly with water (5x10 mL) to remove residual unbound Ag$^+$ salts. EDX (Figure S10) showed the appearance of silver in CMP_S_Ag sample, ICP indicated Ag content to be 8.75%. This Ag^I uptake demonstrated by this sulfur rich porous polymer is found to be substantial compared to CMP_1 (Ag content is about 5.8%), under the given conditions.
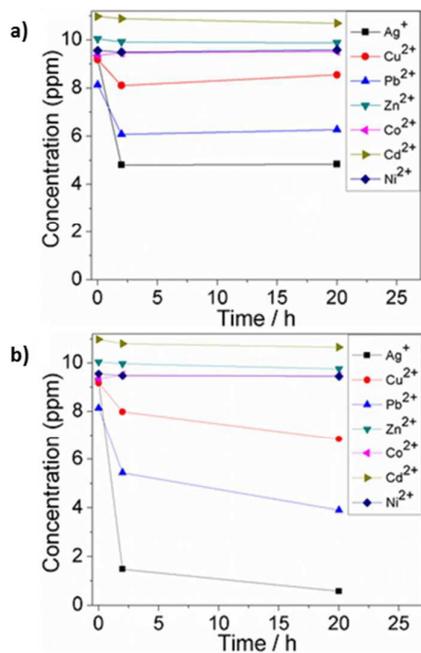
Figure 2. Uptake of individual metal ions from a solution over a 20h period using (a) CMP_1 and (b) CMP_S.

Heterogeneous silver-catalysed heterocyclization of 4-pentynoic acid. Silver-catalysed heterocyclization reactions have been widely investigated.[19] The cyclization of alkynols and acetylenic acids can be readily catalysed by silver salts as reported by Pale *et al.*[20] The catalytic activity of the AgNO$_3$ treated CMP_S (CMP_S_Ag) was tested under normal conditions for the cyclization of 4-pentynoic acid by simply heating the reactants and CMP_S_Ag (Ag/substrate molar ratio: 5%) in CDCl$_3$ (Scheme 3).
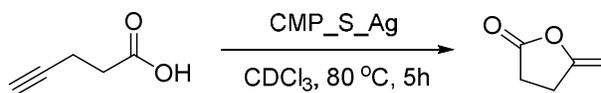
Scheme 3. CMP_S_Ag mediated cyclisation of 4-pentynoic acid.

It was found that 4-pentynoic acid can be readily converted to 5-methylenedihydrofuran-2(3H)-one in quantitative yield within 5 hours. The recyclability of this CMP_S_Ag heterogeneous catalyst was tested over 5 cycles showing no loss in efficiency (Figure 3) and the Ag content in the solids after the 5 catalytic cycles remained unchanged. The isolated supernatant exhibits no catalytic activity under similar reaction conditions (as verified by the NMR data in Figure S11).

As a comparative study to highlight the effective catalytic activity of CMP_S_Ag, AgNO$_3$ salt was employed in similar conditions (Ag/substrate molar ratio: 5%) for the cyclization of 4-Pentynoic acid. Very low conversions were measured via ^{1}H-NMR, even after 24 hours. (Figure S12).
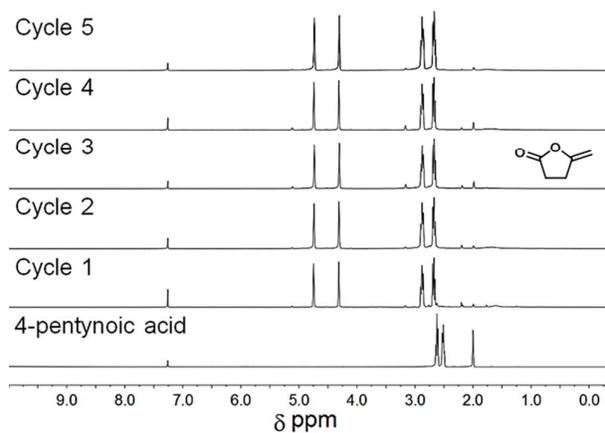
Figure 3. ^{1}H NMR of 4-pentynoic acid and the converted 5-methylenedihydrofuran-2(3H)-one after 5 cycles using CMP_S_Ag as the catalyst.

Conclusions

Taken together, these exercises have opened new grounds in the research of CMPs—by means of a unique and broad combination that include the convenient synthesis of the monolithic polymer solid, and the efficient post-synthetic reaction between the thiolate guest and the phenylalkyne backbone in the polymer host. The substantial post-synthetic modification serves to highlight the structural robustness of the polymer backbone as well as its functional flexibility. Such flexibility is further exploited in the selective Ag^I uptake that is enabled by the thioether donors thus installed, and in the effective, recyclable catalysis of the heterocyclization tests. The rich potential for further exploration is underpinned by the large array of phenylacetylene-based polymer frameworks and by the wide variety of the incoming thiolate molecules (e.g., cysteine and cysteamine).

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Notes and references

General experimental details are given in the supporting information section.

Synthesis of the monolithic CMP_1 via copper-free Sonogashira-Hagihara Cross-Coupling. 1,3,5-Tribromobenzene (157.5 mg, 0.50 mmol), 1,4-diethynylbenzene (95.0 mg, 0.75 mmol) and $PdCl_2$ (1.25 mg, 0.007 mmol) were dissolved in pyrrolidine (2.0 mL) with the aid of a sonication bath in a 7.5 mL sintering vial to get a clear dark brown solution. DI water (3.0 mL) was then added resulting in a milky suspension. The mixture was then sonicated for a further 2 minutes. The reaction mixture was heated at 85 °C in a heating block for 24 hours, after which a deep brown monolithic solid was formed. The monolith was washed with DI water and methanol for several times. The recovered material was calculated at 73.5%.

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