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Polynuclear Complexes as Precursor Templates for Hierarchical Microporous Graphitic Carbon: An Unusual Approach

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Porous carbon, template precursor, coordination complex, hydrogen storage

ABSTRACT: A highly porous carbon was synthesised using a coordination complex as an unusual precursor. During controlled pyrolysis a trinuclear copper complex, $[\text{Cu}^{\text{II}}_3\text{Cl}_4(\text{H}_2\text{L})_2]\cdot\text{CH}_3\text{OH}$, undergoes phase changes with melt and expulsion of different gases to produce a unique morphology of copper-doped carbon which, upon acid treatment, produces highly porous graphitic carbon with a surface area of $857\text{ m}^2\text{g}^{-1}$ and a gravimetric hydrogen uptake of 1.1 wt% at 0.5 bar pressure at 77 K.

Ordered mesoporous carbons have attracted much attention recently due to their potential applications in a versatile range of areas,¹ such as gas separation,² water purification,³ carbon dioxide capture,⁴ hydrogen storage,⁵ supercapacitance,⁶⁻⁸ catalyst supports,⁹ electromagnetic wave absorption,¹⁰ etc. The versatile range of applications require a great diversity in the structure of the carbon-based materials, and takes advantage of a large range of pore dimensions; namely, microporosity (pore diameter of $< 2\text{ nm}$), mesoporosity (pore diameter of $2\text{-}50\text{ nm}$), and macroporosity (pore diameter of $> 50\text{ nm}$), depending on the desired applications.¹¹⁻¹²

A number of different kinds of templates have been employed to prepare and control the structure of the porous carbon materials.¹³ Primarily, the templates can be divided in two types: hard templates and soft templates. In hard templating, the empty ordered space of the template is used to accommodate the carbon precursor, and after formation of the carbon (by thermal treatment) the solid template is etched away, often by acid/base treatment. A number of different kinds of hard templates have been used, including microporous zeolites, silica, and microporous metal oxides.¹⁴⁻¹⁵ In the soft templating methods, the carbon precursor itself can act as a preorganised template with ordered structures. For example, a self-assembled structure comprising of block copolymers and surfactants, phenolic resin, and cationic electrolyte has been used as a

soft template to prepare ordered microporous carbon by controlled thermal treatment.¹⁶⁻¹⁷ Apart from traditional hard and soft templates, unusual templates such as tealeaves, fabric, biomass, lignin, and cigarette butts have recently been used as templates for preparing porous carbon.¹⁸⁻²⁰ Herein, we report the use of a rather unusual precursor, a polynuclear copper complex of a quinoline-based ligand, for synthesising a microporous graphitic carbon (ComDC-1; ComDC stands for complex derived carbon) with a surface area of 857 m²g⁻¹ and a gravimetric hydrogen uptake of 1.1 wt% at 0.5 bar and 77 K.

Polynuclear transition metal complexes have been of high interest recently because of their potential applications in single-molecule magnets (SMMs) and high-density data storage devices.²¹ Many of the active sites of different enzymes are also made of polynuclear transition metal complexes, and a large number of polynuclear complexes have been developed to study biomimetic catalysis in the past few decades.²² In recent years, metal-organic frameworks (MOFs) have been used as precursors for synthesising various ordered porous carbon materials, taking advantage of the rich carbon content in the linkers.²³⁻²⁴ It is now well established that the highly pre-organised linkers in the regular three-dimensional crystalline structures of the MOFs play a key role in template synthesis of highly ordered microporous carbon materials.²⁵ Despite the presence of a large numbers of reported polynuclear cluster complexes, they have not been studied so far as possible precursors for synthesising porous carbon materials. The presence of supramolecular interactions, such as hydrogen bonds and π - π interactions often lead to self-assembly of the cluster complexes in regular three-dimensional networks similar to MOFs, with the only exception of the covalent bonds present between the building units.²⁶⁻²⁷ However, the preorganised ligands present in the cluster complexes can act as precursor for synthesising porous carbon in a way similar to the MOFs. Use of such complex based precursors can be energy efficient

compared to using the MOFs, which often require solvothermal treatment over long time for synthesis. Herein, we are reporting this novel approach of use of such polynuclear cluster complexes as precursors for synthesising porous carbon materials using the example of a trinuclear copper complex. The trinuclear copper(II) complex, $[\text{Cu}^{\text{II}}_3\text{Cl}_4(\text{H}_2\text{L})_2]\cdot\text{CH}_3\text{OH}$ (where $\text{H}_3\text{L} = (2-(8\text{-hydroxyquinolin-2-yl)oxazolidine-4,4-diyl)dimethanol}$) (Figure 1) was synthesised in a one-pot reaction between 8-hydroxyquinoline-2-carboxaldehyde (0.25 mmol, 42 mg), tris(hydroxymethyl)aminomethane or TRIS (0.25 mmol, 30.5 mg), and copper(II) chloride dihydrate (1 mmol, 170 mg) in methanol. The oxazolidine ligand H_3L formed *in situ* during the reaction, as has been reported elsewhere recently.²⁸

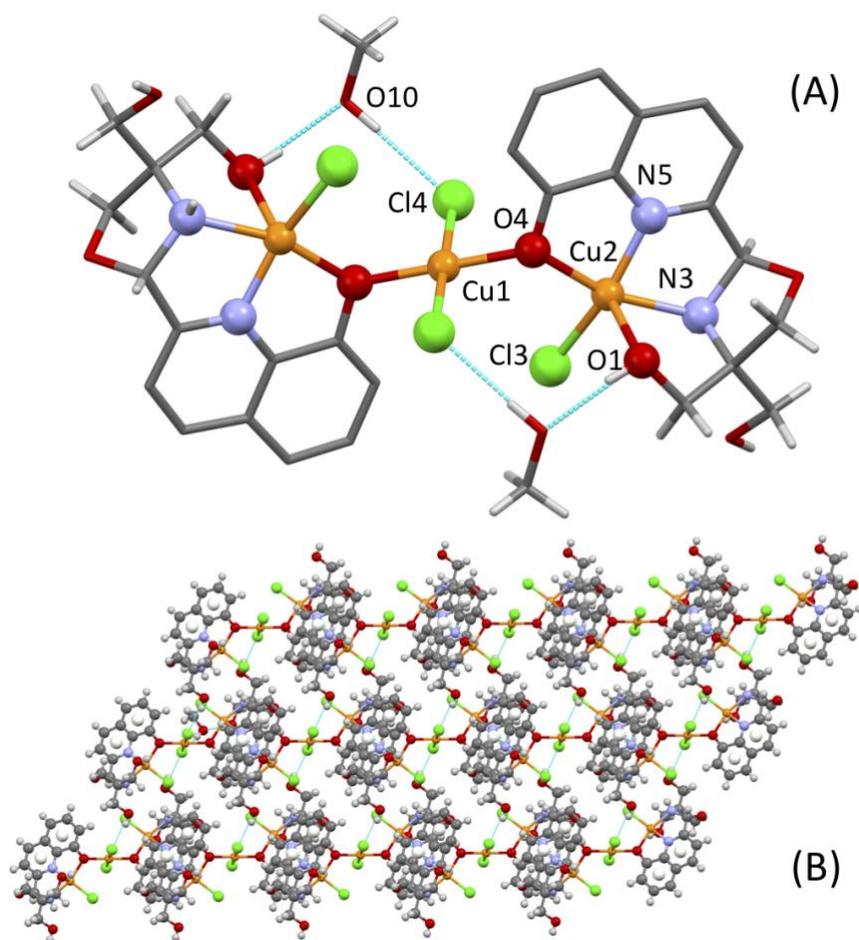


Figure 1. (A) The molecular structure of Compound **1** is shown with the hydrogen bond interactions with the neighbouring methanol. (B) Two-dimensional network formed by the intermolecular hydrogen bond interactions between the hydroxyl hydrogen and the chlorine atom, and the π - π stacking. Colour code for the atoms: grey (carbon), blue (nitrogen), white (hydrogen), green (Cl), orange (copper), red (oxygen).

Slow evaporation of the resulting solution produced dark-green crystals, which were collected and analysed by single-crystal X-ray diffraction.[‡] The trinuclear copper complex crystallised in triclinic

space group *P-1*, with three copper(II) ions in two different coordination geometries (Figure 1A). The central copper(II) is four coordinate with a square planar geometry, while the two symmetrically equivalent terminal copper(II) ions are five coordinate with square pyramidal geometry. The ligand H₃L coordinates to the terminal copper ions with four donor atoms (ONOO). The fifth position is occupied by a chloride ion. The central copper ion is coordinated by two chloride ions, and two hydroxide groups that bridge between the central and the terminal copper ions. The trinuclear cluster complexes are highly ordered and self-assembled in a two-dimensional network assisted by strong inter-molecular hydrogen bonding and π - π stacking as shown in Figure 1B. The porous carbon material was synthesised serendipitously while studying the thermal stability of Compound **1**. The crystalline material was heated up to 600 °C under nitrogen atmosphere at a rate of 5 °C min⁻¹ and a porous hierarchical structure was obtained (Figure 2D). The material was analysed by Raman spectroscopy, and the peaks at 1349 cm⁻¹ and 1580 cm⁻¹ were observed (Figure 3), confirming the presence of both disordered (D) and graphitic sp² (G) carbon.²⁰ A high ratio of peak intensity ($I_D/I_G = 1.38$) indicates the presence of significant amount of disorder in the graphitic carbon.²⁹ The formation of the material was thoroughly studied in real time using DSC and TGA-MS. It was confirmed that methanol, water, carbon dioxide and hydrogen chloride evolved at different temperatures during the thermolysis process (Figure 3). A phase change was visually observed using a hot-stage microscope around 190 °C which corresponds to a transient melting phase followed by the loss of methanol which forms bubble-like morphology at this temperature (Figure 2C). This event was also identified in the DSC thermogram where the endothermic dip was observed at 190 °C followed by an exothermic peak at 230 °C (Figure 3). The exothermic DSC peak at 230 °C indicates possible re-orientation of the structure followed by immediate melting. The pyrolysed material was collected after treating at

600 °C and examined using scanning electron microscopy. The hierarchical porous structure was observed with very small pores on the surface as well as the larger pores as shown in Figure S7.

The EDX analyses on the pyrolysed sample are

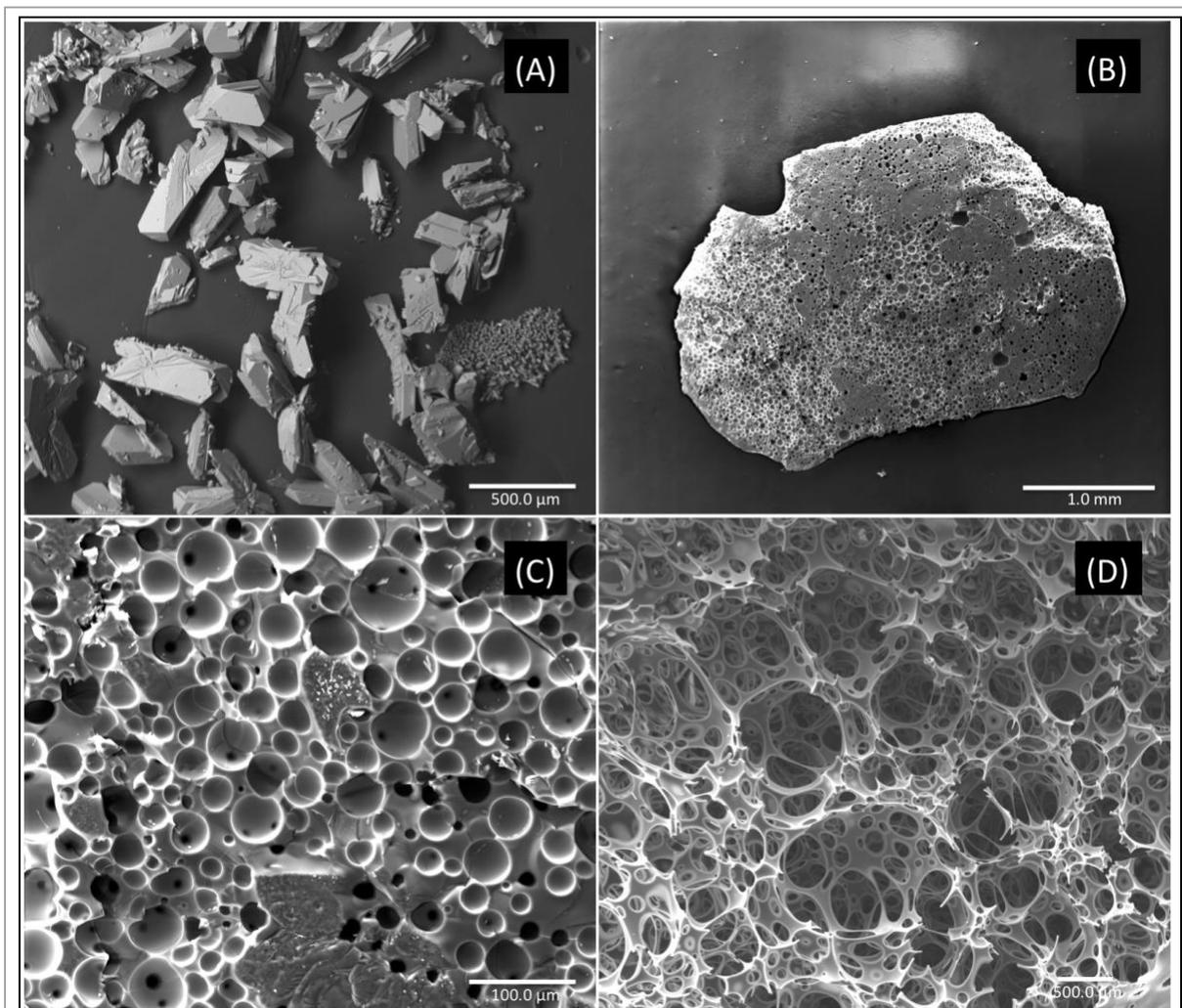


Figure 2. The scanning electron microscopy images of pristine crystals of Compound **1** (A), and the surface morphology after heat treatment at 190 °C (B, C), and 600 °C are shown. Scale bars: 500 μm, 1.0 mm, 100.0 μm, and 500.0 μm, for A, B, C, and D, respectively.

in agreement with the presence of copper chloride and oxide particles. The powder XRD analysis (Figure S11) showed a broad halo indicating the presence of ultra small particles in the bulk material. This observation is in good agreement with the high ratio of I_D/I_G in Raman spectra,

indicating the presence of disordered or amorphous carbon. The material was etched in concentrated hydrochloric acid for 24 hours to remove the copper salts. The EDX analysis of the post-acid-treated sample suggests nearly complete removal of copper salts from the bulk material (see Figure S12-S13 in the ESI). The BET surface area analyses suggest negligible surface area for the pre-acid-treated ComDC-1 and a surface area of $857 \text{ m}^2\text{g}^{-1}$ for the post-acid-treated

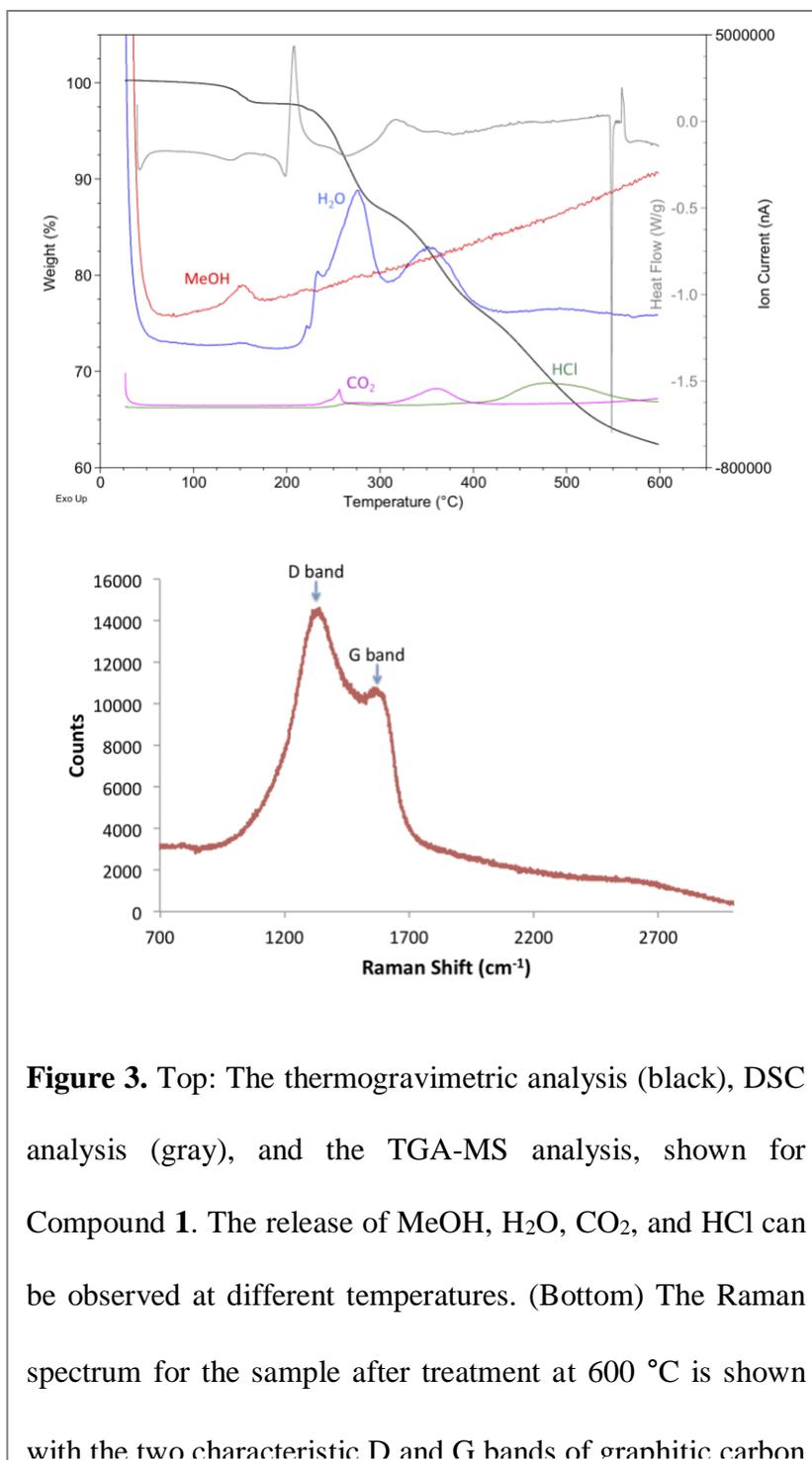


Figure 3. Top: The thermogravimetric analysis (black), DSC analysis (gray), and the TGA-MS analysis, shown for Compound **1**. The release of MeOH, H₂O, CO₂, and HCl can be observed at different temperatures. (Bottom) The Raman spectrum for the sample after treatment at 600 °C is shown with the two characteristic D and G bands of graphitic carbon

ComDC-1. Pore-size distribution of the post-acid-treated ComDC-1 indicates the presence of micropores with primary diameters of 5 Å and 8 Å (Figure 4). The hierarchical porous structure

with micropores on the surface was further observed in TEM images (Figure 5). TEM analysis of ComDC-1 also indicates the presence of the nanoparticles in the pre-acid-treated sample (see

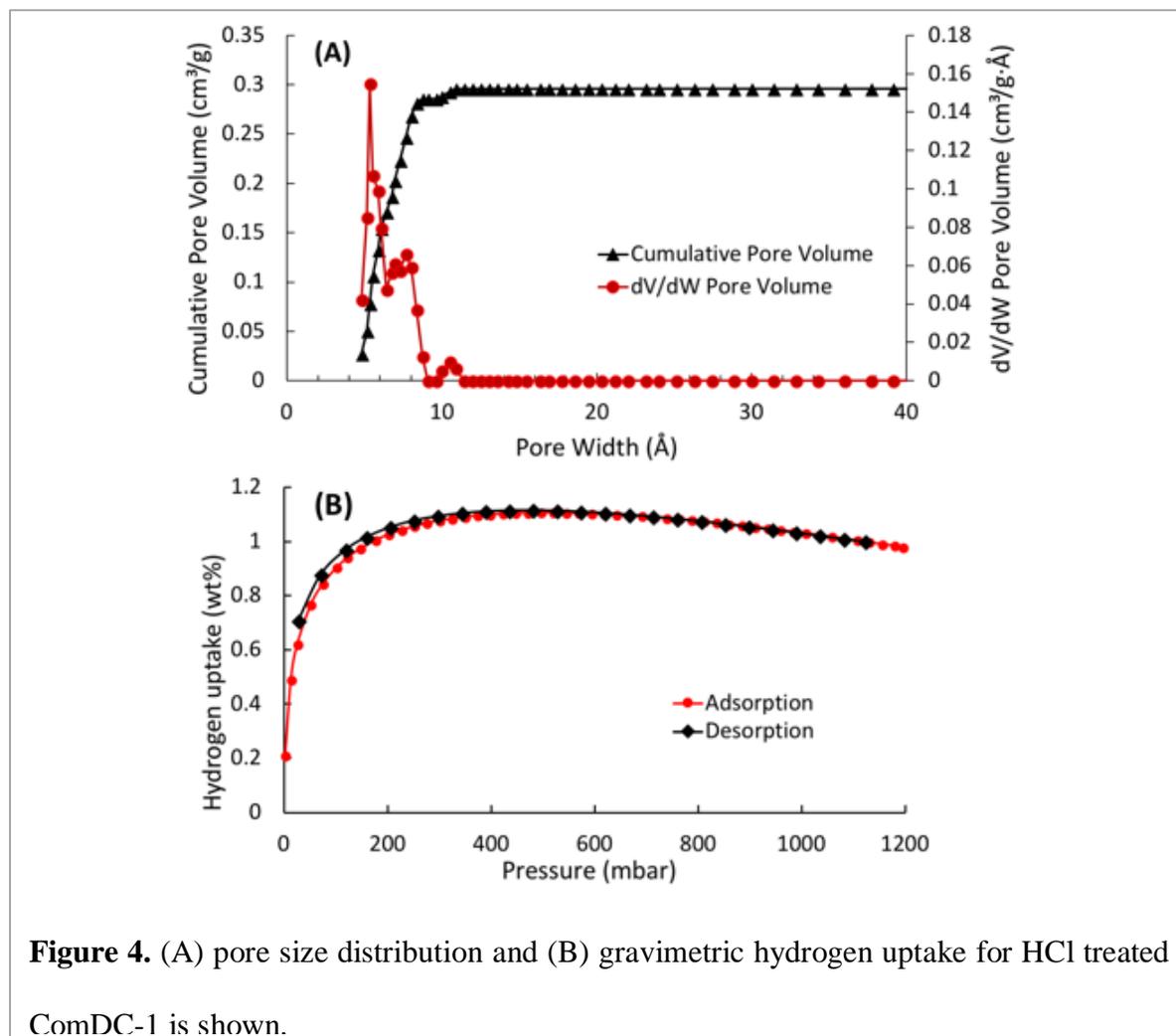
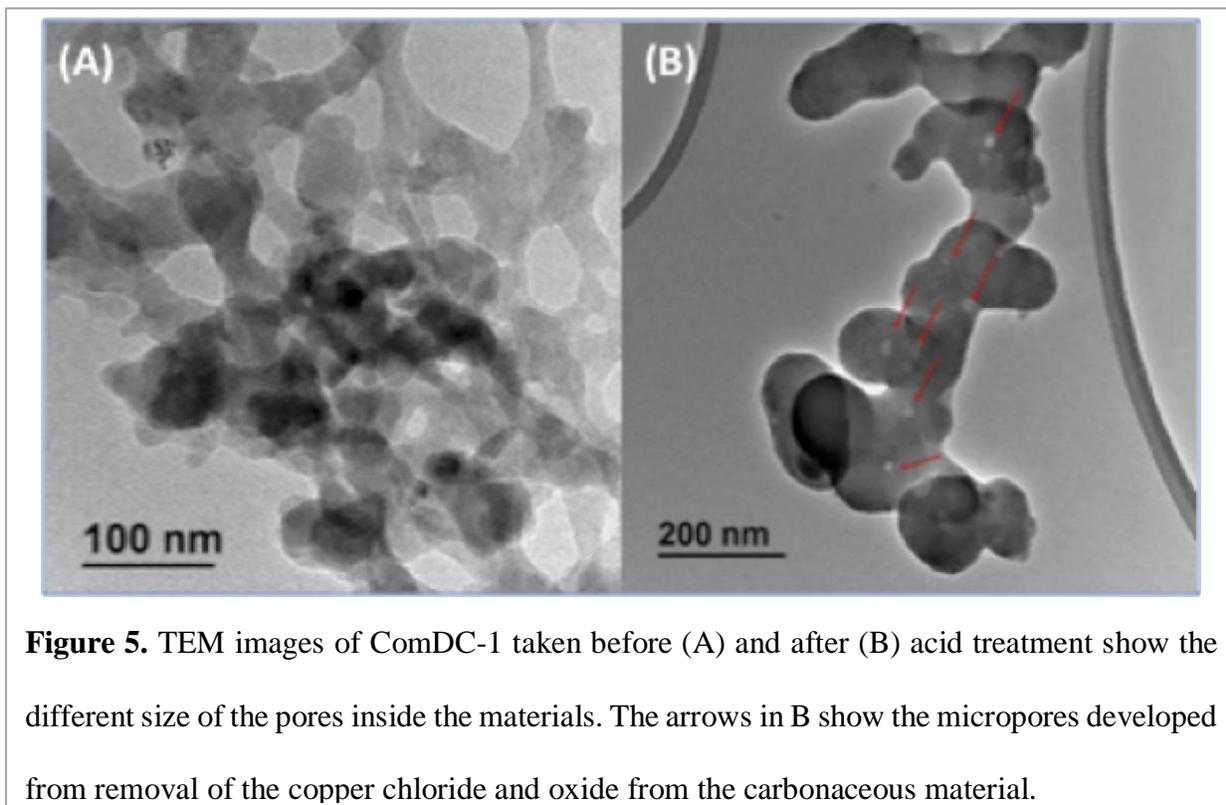


Figure S14 in ESI). The origin of the micropores in the post-acid-treated ComDC-1 is possibly the direct result of etching and removal of the copper chloride and oxide nanoparticles from the bulk material by the acid treatment. This is important information and indicates that the cluster complexes can be successfully used as template precursors for preparing porous carbon materials, and can be considered along with the recently studied MOF-based precursors.^{7-8, 23-24} Motivated by the microporous morphology with a pore-size distribution close to the ideal recommended theoretical pore size for hydrogen storage, we studied the hydrogen uptake of the acid treated

material which shows an uptake of 1.1 wt% at 0.5 bar pressure at 77 K (Figure 4), in contrast to the untreated sample which showed negligible uptake. The result is promising and comparable with microporous carbon derived from some of the MOFs, specially at the low pressure region.³⁰



In summary, here we are reporting a novel class of precursors for preparing porous carbon materials. In this study a trinuclear copper complex was used as a precursor which on thermolysis produced a hierarchical morphology of carbon (ComDC-1). On acid treatment the copper salts inside ComDC-1 were etched away and resulted in a microporous graphitic carbon which was studied using Raman spectroscopy, SEM, TEM, EDX, and PXRD. The formation of the porous carbon was studied using DSC and TGA-MS. Analysis during the thermolysis revealed the intermediate melting phase and expulsion of different gases (MeOH, CO₂, and HCl) at different temperatures resulting in a porous hierarchical structure. The post-acid-treated ComDC-1 showed

a BET surface area of $857 \text{ m}^2\text{g}^{-1}$ and a gravimetric hydrogen uptake of 1.1 wt% at 0.5 bar pressure at 77 K. There is a large number of carbon-rich cluster complexes reported in literature, and this study shows that use of these clusters as precursors can lead to the development of highly porous carbon-based materials for applications, such as gas storage, separation, and many others where surface area plays a crucial role. There are several advantages to using discrete polynuclear complexes as precursors for porous carbon synthesis by thermolysis. The metal ions present in the precursor complexes form nano-sized metal components, which are removed by acid treatment to form the micropores. Therefore, the metal ions in the complexes play a crucial role to induce and control porosity in the resulting carbon and provide an advantage over simple organic precursors. The use of discrete polynuclear complex precursors will also allow the fabrication of thin films of porous carbon by drop casting or spin coating followed by thermolysis, which is technically challenging with other precursors, such as MOFs and COFs.

ASSOCIATED CONTENT

Supporting Information contain the additional details on synthesis, physical characterization, infrared spectra, powder XRD data, elemental analyses, SEM and TEM images, and crystal structure parameters for Compound 1.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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Notes

‡The crystal structure was deposited at the Cambridge Crystallographic Data Centre. The CCDC reference number for Compound **1** is 1842850.

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