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ARTICLE

An ionothermally synthesized Mg-based coordination polymer as a precursor for preparing porous carbons

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A new magnesium coordination polymer (Mg-CP), namely $[Bmim]_2[Mg_6(NDC)_5(HNDC)_2(HCOO)_2]$ (**1**, H_2NDC = 1, 4-naphthalenedicarboxylic acid, [Bmim] = 1-Butyl-3-methyl-imidazolium ion) has been ionothermally synthesized and structurally characterized. Single-crystal X-ray structural determination indicated that the title compound possessed an anionic three-dimensional (3D) framework constructed by the interconnections of unprecedented hexanuclear magnesium-carboxylate clusters as second building units (SBUs) via bridging NDC ligands. Compound **1** exhibited blue luminescent emission at 440 nm when excited at 360 nm. Significantly, the title non-porous Mg-CP could be utilized as a precursor for preparing porous carbons through thermal decomposition in optimized conditions. Different from the reported high decomposition temperature (> 1000 ▫) mostly based on the porous Zn-CP precursors, the optimum decomposition temperature for **1** was only 700 ▫, and the resulting porous carbons showed 465 $cm^3 \cdot g^{-1}$ adsorption volume for N_2. The as-prepared carbon exhibited finely selective N_2 adsorption ability over H_2 and CO_2. This work may provide a certain guiding significance for exploiting ionothermally synthesized Mg-CPs as a new type of precursor towards porous carbons.

Introduction

Metal coordination polymers (CPs) have been well studied in the past two decades motivated by their potential applications in diversified fields.[1] As a new application, the CPs have been exploited as starting materials or templates for synthesizing nano-oxides and porous carbons recently, which might be applicable for lithium ion batteries, gas storage and separation, and so on.[2] Typically, as a carbon precursor, the CPs usually have permanent porosity, which are suitable for the inclusion of furfuryl alcohol (FA) as the second carbon source.[2a, 2b] In addition, some nonporous Zn-based CPs such as Zn-NDC, Zn-PAA and MOF-2 have also been applied to prepare porous carbons.[3] Noticeably, the recent researches about CPs as templates for the preparation of porous carbons are mostly based on the Zn, Fe, Al metals.[2d, 2e, 4]

As a type of low-cost, non-toxic and abundant metal ion, the Mg^{2+} ion deserves more attention in constructing CPs. With the similar flexible coordination modes as that of d-block metal ions such as Zn^{2+}, the Mg^{2+} can be coordinated by carboxylate ligands to form different types of second building units (SBUs) and colorful structures.[5] More importantly, the Mg-CPs have also exhibited unique functional properties in gas adsorption, luminescent detection, white emitting and so on.[5e, 6] Nevertheless

the Mg-based CPs as precursors for preparing porous carbons by thermolysis have never been explored thus far.

The ionothermal synthesis, that is the use of ionic liquids as reaction media, has become a highly promising synthetic method for the preparation of novel MOFs in the past decades.[7] Compared to the molecular solvents in the hydro(solvo)thermal synthesis, the ion liquids (ILs) may not only serve as reaction media, but also function as structure directing agents during the synthetic process.[8] Furthermore, the cations of ILs usually serve as charge compensating agents occupying the cavities of the anionic frameworks of the CPs, which may be utilized as the second carbon source like the FA molecules included in the pores of the normal CPs.

Herein, we successfully adopted imidazolium-based IL [Bmim]Cl ([Bmim] = 1-Butyl-3-methyl-imidazolium ion) as reaction media and structure directing agent to synthesize a new three-dimensional (3D) Mg-CP, namely $[Bmim]_2[Mg_6(NDC)_5(HNDCH)_2(HCOO)_2]$ (**1**, H_2NDC = 1, 4-naphthalenedicarboxylic acid,). The crystal structure, luminescent and thermos-stability of the compound were investigated. Moreover, we firstly used the title non-porous Mg-CP as starting material to prepare porous carbons through thermolysis and the decomposition conditions were fully optimized. The optimum thermolysis temperature was

as low as 700 □, lower than that of the reported Zn or Al-CP precursors. The adsorption volume of N_2 for the as-prepared carbon was 465 $cm^3 \cdot g^{-1}$, and those of H_2 and CO_2 were 45 and 20 $cm^3 \cdot g^{-1}$, respectively.

Experimental

Materials and physical measurements

$Mg(NO_3)_2 \cdot 6H_2O$ ($\geq$ 99%), ChengDu KeLong Chemical Co. Ltd.; 1,4-NDCH$_2$ ($\geq$ 99%), Beijing HWRK Chem Co. Ltd.; [Bmim]Cl (99%) was purchased from Lanzhou Institute of Chemical Physics. all reagents and chemicals were used without further purification. Powder X-ray diffraction (PXRD) patterns were recorded on a Rigaku Miniflex-II diffractometer using a Cu$K\alpha$ radiation. Microprobe elemental analyses were performed by using a field-emission scanning electron microscope (FESEM, JSM6700F) equipped with an energy-dispersive X-ray spectroscope (EDXS, Oxford INCA). Elemental analyses for C, H, N were performed on a German Elementary Vario EL III instrument. Thermogravimetric analyses were carried out with a NETZSCH STA 449F3 unit at a heating rate of 5 □/min under a nitrogen atmosphere. Emission and excitation spectra of the compounds were recorded on a PerkinElmer LS55 luminescence spectrometer. Gas adsorption measurement was performed in an ASAP (Accelerated Surface Area and Porosimetry) 2020 System.

Synthesis of compound 1

0.256 g (1 mmol) $Mg(NO_3)_2 \cdot 6H_2O$ and 0.161 g (1 mmol) H_2NDC were mixed with 1.0 g [Bmim]Cl; then the mixture was sealed in a 20 mL Teflon-line stainless-steel autoclave which was heated at 160 $^{\circ}$C for 6 days, followed by being cooled to room temperature to get colorless block crystals of **1**. The crystals were washed with absolute ethanol for several times and dried at ambient conditions with 35.8% (0.120 g) yield based on Mg. Anal. calc. for **1**: C 59.53%, H 4.71%, N 7.93%. Found: C 59.73%, H 4.56%, N 8.04%.

Preparation of the porous carbons

The as-prepared crystals of compound **1** were put into a ceramic boat, transferred to a tube furnace and carbonized under a nitrogen gas flow at 600℃, 700℃, 800℃, 900℃ and 1000℃, respectively, with a heating rate of 5℃/min. The crystals were maintained in the setting temperature for 5 h, after which it was cooled to room temperature with a cooling rate of 5℃/min. The prepared carbon materials were named as sample-600, 700, 800, 900 and 1000, respectively. The obtained MgO/C composites of C-700 was further washed with diluted HCl and ethanol, then dried at 100 ℃ in vacuum for 5h before the gas adsorption experiments.

Single–crystal structure determination

A suitable single crystal of compound **1** was carefully selected under an optical microscope and glued to a thin glass fiber. Intensity data were collected on a Xcalibur E Oxford diffractometer with graphite-monochromated Mo$K\alpha$ radiation (λ = 0.71073 Å) at 293(2) K. The structure was solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELX-97 program

package.[9] All non-hydrogen atoms were refined anisotropically, while the hydrogen atoms bound to carbon were located by geometrical calculations, and their positions and thermal parameters were constrained during structural refinements. Pertinent crystallographic data and structural refinement details for **1** are listed in Table 1. CCDC 1055558 (**1**) contains the supplementary crystallographic data for this paper.

Table 1 Crystallographic data and structural refinement details for **1**.

Empirical formula	$C_{51}H_{37}Mg_3N_2O_{16}$
Formula Mass	1006.76
Crystal system	Monoclinic
Space group	$P2_1/n$
a/Å	14.7921(2)
b/Å	15.0566(2)
c/Å	21.4174(3)
β/°	99.8310(10)
V/Å^3	4700.01(11)
Z	4
T/K	293(2)
λ/Å	0.71073
$F(000)$	2084
ρ_{calcd}/g cm^{-3}	1.423
μ/mm^{-1}	0.142
Measured refls.	17447
Independent refls.	8231
No. of parameters	760
R_{int}	0.0349
R_1 ($I > 2\sigma(I)$)[a]	0.0860
$wR(F^2)$ ($I > 2\sigma(I)$)[b]	0.2218
GOF	1.039

[a] $R_1 = \sum \left\| F_o \right| - \left| F_c \right\| / \sum \left| F_o \right|$. [b] $wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}$.

Results and discussion

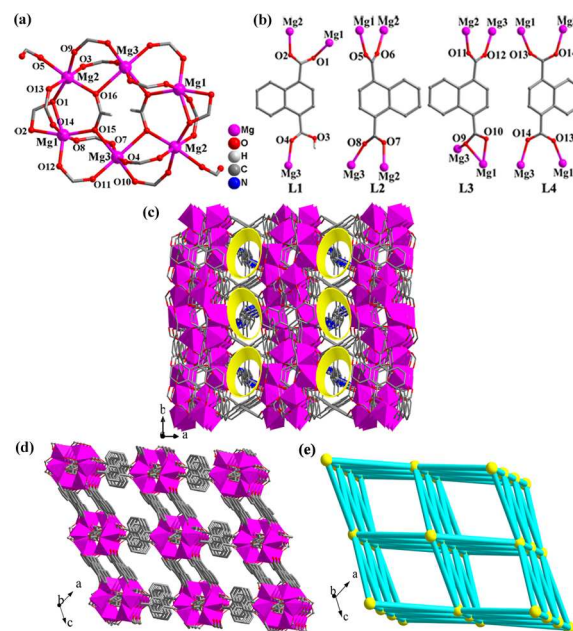### Crystal structure descriptions

Fig. 1 (a) The coordination environment of Mg^{2+} ions in the hexanuclear cluster SBU of **1**. (b) The four different coordination modes of the NDC ligands. (c) 3D framework of **1** viewed along the c axis. (d) The 3D framework of **1** viewed along the b axis; the imidazolium cations were excluded for clarity. (e) The 10-connected bct topology of **1**.

Single-crystal X-ray diffraction analysis reveals that compound **1** crystallizes in the space group of $P2_1/n$. Its asymmetric unit consists of half of the formula unit, i. e. one [Bmim]$^+$ cation, three Mg^{2+} ions, one HNDC, two and half of the NDCs, and one formate from the *in situ* decomposition of IL. All the Mg^{2+} ions are six coordinated with carboxylate oxygen atoms (Fig. 1a). The Mg1 ion is coordinated by six carboxylate oxygen atoms from one formate and four different NDC^{2-} ligands, one of which adopts bidentate chelating mode while the other three are monodentate; the Mg-O distances range from 1.993(4) to 2.288(4) Å. While both of the Mg2 and Mg3 ions are surrounded by six O atoms from five NDC ligands in monodentate mode and one formate with the Mg-O distances varying from 1.990(4) to 2.447(4) Å for Mg2 and 2.005(4) to 2.136(4) for Mg3, respectively. The NDC show four distinct linking fashions to the metal ions, Fig. 1b. Whereas the formate ligand acts as a tetradentate linker to bridge Mg1 and Mg3 with O15 and Mg2 and Mg3 with O16, respectively, Fig. 1a.

In compound **1**, the three independent Mg^{2+} ions are connected by formate and NDC ligands to generate a trinuclear magnesium unit with the Mg2-Mg1-Mg3 angle of 107.96(5) º, in which the Mg1 and Mg3 are bridged via an oxygen of formate ligand and two carboxylate groups of two NDC ligands, and the Mg1 and Mg2 are linked by an oxygen of NDC and two carboxylate groups respectively from one NDC and one formate. Then the two trinuclear magnesium units are jointed by bridging the Mg2 and Mg3 with an oxygen of formate ligand and two carboxylate groups of two NDC ligands to form an unusual centrosymmetric hexanuclear magnesium cluster as second building unit (SBU) (Fig. 1a).[5c] Subsequently, each SBU is connected to ten neighbour SBUs through NDC ligands to form a 3D framework with channels along the *c*-axis. The [Bmim]$^+$ cations as templates are located in the channels, Fig. 1c. The solvent accessible volume calculated by excluding [Bmim]$^+$ cations by *PLATON* is 26% of the unit cell volume (Fig. 1d). Topology analysis with *TOPOS* software[10] suggests that the 3D framework displays a 10-connected *bct* topology (Fig. 1e), in which the hexanuclear magnesium clusters act as 10-connect nodes and the NDC ligands are regarded as the linkers, respectively.
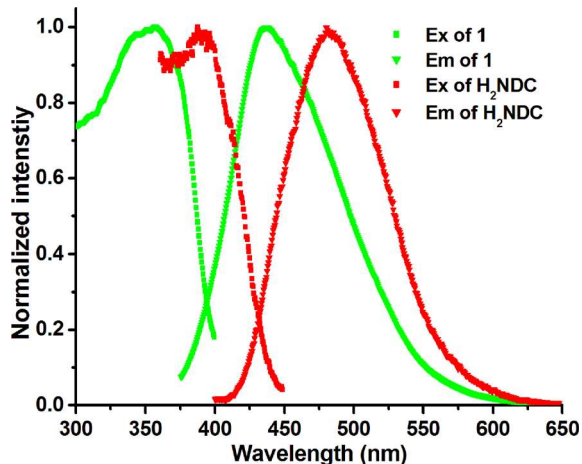
Luminescent property

Fig. 2 Emission and excitation spectra of compound **1** and the H$_2$NDC ligand in the solid state.

The luminescent spectra of compound **1** in the solid state exhibited blue-purple light emission (λ_{ex} = 360 nm) at room temperature showing emission bands at 440 nm (Fig. 2). The free H$_2$NDC ligand showed a 485 nm emission when excited by 400 nm light. The emission of **1** must originate from the organic ligand due to the electronic configuration of Mg^{2+} ion.[6d, 11] There is a blue-shift of emission of **1** compared to that of the free ligand, which is consistent with the former CPs constructed from the NDC ligand and can be attributed to the effectively increased rigidity of NDC after the incorporation of Mg^{2+} ion, which reduces the loss of energy via intramolercular vibrational and rotational motions.[11a]

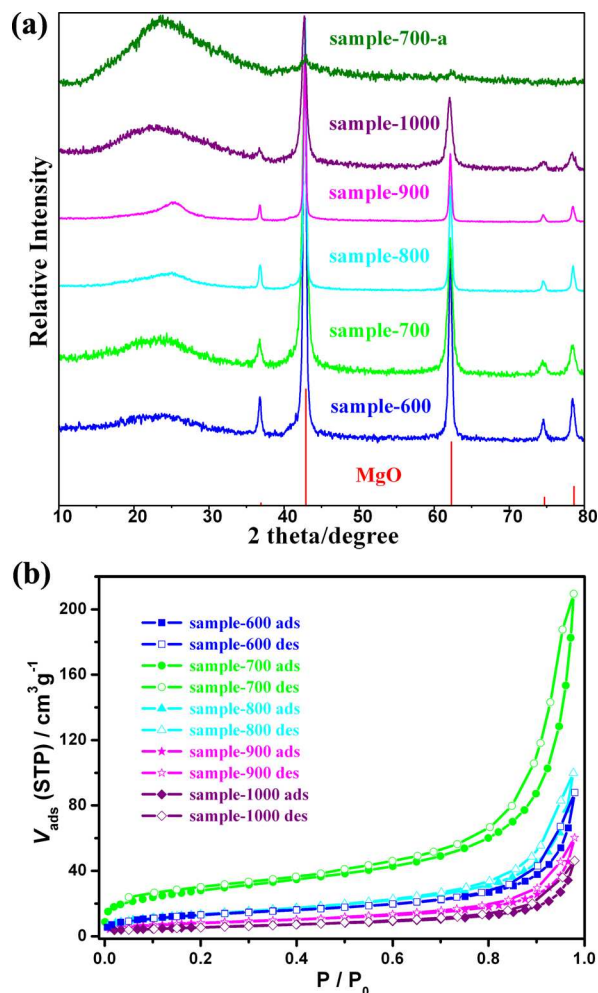**Preparation of the porous carbons and its adsorption ability**

Fig. 3 (a) The PXRD patterns of the C-MgO composites obtained by the decompositions of **1** at different temperatures without treatment of HCl solution and the sample-700-a with treatment of HCl solution. (b) The N$_2$ adsorption isotherms of C-MgO samples obtained by the decomposition of **1** at varied temperatures from 600 to 1000 ºC

As seen from the TG curve in Fig. S2, the compound **1** exhibited thermal stability up to 350 ℃. The host framework began to decompose after 600 ℃ resulting in the MgO/C composites, which was verified by PXRDs (Fig. 3a) of the residues from the decompositions of **1** at varied temperatures from 600 to 1000 ▢. All the sharp peaks observed in the samples could be assigned to

the MgO species, while the two broad bands at around 24 and 44° were assigned to the carbon diffractions. In the previous reports, such as the carbonizations of MOF-5 and $[Zn_3(BTC)_2(H_2O)_3]_n$,[3b, 3c] the ZnO was reduced to metallic Zn species and vaporized away along with the Ar or N_2 flows when the temperature was higher than 800 □, and the carbon matrix materials were obtained. Different from the case of using Zn-CP precursors, the Mg metals in **1** have never disappeared until 1000 □, which may be due to the higher boiling point of Mg metal.

N$_2$ sorption porosimetry were utilised to analyse the porosity of the presented carbon materials from Mg-CP. As shown in Fig. 3b, the carbon material obtained at 700 ℃ appeared the highest N_2 uptakes in the entire operated pressure among the carbons from different carbonized temperature. The N_2 adsorption isotherms showed a less developed hysteresis profile. This indicates the apparent absence of ultramicropores, i.e. no swelling and rearrangement occurs which hinders desorption. Barret-Joyner-Halenda (BJH) analysis yields surface areas of 100 $m^2\ g^{-1}$ for such carbon. However, the BET surface area was reduced when the temperatures were beyond 700 ℃, which could be attributed to the higher temperature destroying the structure of the pores. The activation temperature of the title precursor is relatively lower than the reported ones which needed the decomposed condition as high as 1000 ℃.[2b]
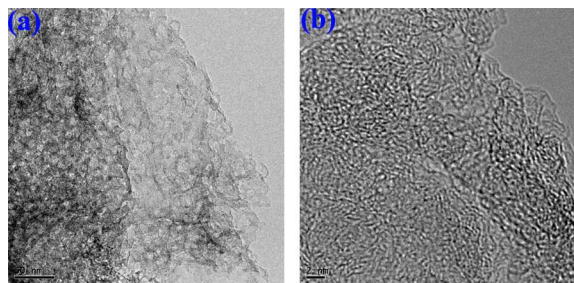

Fig. 4 The HRTEM of sample-700-a sample viewed at 50 nm (a) and 5 nm (b) scale.

The pure carbon materials, namely sample-700-a, was obtained by washing the sample-700-MgO with diluted HCl solution. The MgO residue was successfully removed, which was verified by absence of diffraction peaks of MgO in the PXRD pattern (Fig. 3). The HRTEM images showed a characteristic of turbostatic carbon materials with rough edges in prepared carbon materials. This can be associated with the formation of short and curved aromatic pre-graphitic domains leading to the pore formation within the carbon structure, Fig. 4. The N_2 adsorption measurement showed that the adsorption of sample-700-a sample exhibited the typical adsorption behavior of the mesoporous materials. The surface area of sample-700-a is greatly increased with respect to that of the parent sample-700 (an increase in BET surface areas up to 268 $m^2 \cdot g^{-1}$). The increase in surface area is predominantly related to the development of increased microporosity although some mesoporosity is also evolved. This mesoporosity was observed via the existence of cavitation-type sorption hysteresis such that mesopores empty at relative pressures of $p/p_0 \sim 0.45$. The development of microporosity also had a large impact on the H_2/CO_2 sorption ability.

The sample-700a exhibited 465 $cm^3 \cdot g^{-1}$ N_2 adsorption capacity at

77 K and 1 atm, Fig. 5a. Such surface areas are higher than that of the porous Al-PCP precursor, and are comparable to that of the porous Cu-BTC precursor.[12] While this value is lower than that of the reported porous Zn-CP precursors such as ZIF-8 and MOF-5,[2a, 2b] the inherent channel of which may have important affections on the resulting carbons. In the same measurement conditions, the H_2 had 46 $cm^3 \cdot g^{-1}$ uptake. While at 273 K, the adsorption capacity of the porous carbons for CO_2 is 20 $cm^3 \cdot g^{-1}$, Fig. 5b.
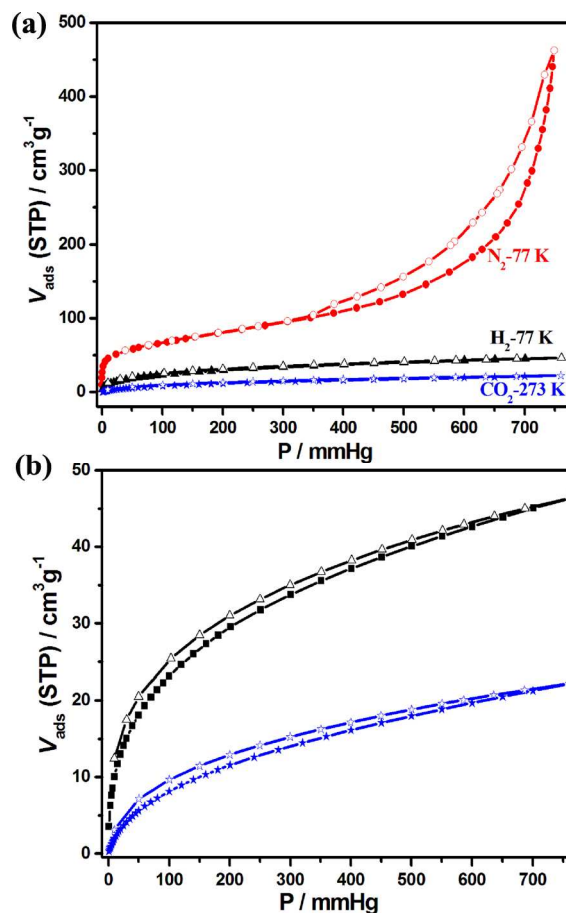

Fig. 5 (a) The N_2 adsorption isotherms of sample-700a. (b) The H_2 and CO_2 adsorption isotherms of sample-700a.

Conclusions

In summary, a new 3D Mg-CP, namely $[Bmim]_2[Mg_6(NDC)_5(HNDC)_2(HCOO)_2]$, has been ionothermal synthesized and structurally characterized. The title compound was utilized as a precursor for preparing porous carbons, which exhibited selective N_2 absorption ability over H_2 and CO_2. This work may have directive significance to the synthesis of porous carbons by utilizing Mg-CPs as starting material. Future work will be focused on constructing more Mg-CPs and exploring their applications as new type of precursors for porous carbons.

Acknowledgements

Notes and references

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† Electronic Supplementary Information (ESI) available: PXRD and TG figures. CCDC reference number 1055558. For ESI and crystallographic data in CIF or other electronic format, See DOI:10.1039/b000000x/

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Table of Contents

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