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Amorphous Infinite Coordination Polymer Microparticles: A New Class of Selective Hydrogen Storage Materials

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Hydrogen gas is considered an abundant, clean, environmentally friendly fuel and is therefore one of the most promising alternatives to hydrocarbon fuels.^[1,2] One of the keys to being able to use it effectively in transportation and portable applications is the development of materials that allow one to effectively and safely store it. Many candidate materials have been studied for their H₂ storage capabilities, including metal hydrides,^[3] light hydrides,^[4] carbon-based materials,^[5] organic microporous polymers,^[6] and crystalline metal–organic frameworks (MOFs).^[2,7-11] The crystalline MOFs are a particularly interesting class of materials as they have highly tailorable porosities and internal chemical functionalization, and significant advances have been realized through the generation of structures that can not only selectively uptake H₂ in the presence of N₂ but also differentiate other gases such as O₂ and CO₂.^[7,11,12] Our group recently introduced the concept of amorphous infinite coordination polymer (ICP) (nano- and micro)particles, which are prepared from organometallic ligands and metal ion connecting nodes (Scheme 1).^[13,14]

There are now a variety of ways of making ICP particles and related structures from a broad class of metal nodes and both organic and organometallic ligands.^[13-15] Like MOFs, these structures are assembled via coordination chemistry principles, however, the resulting

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materials are typically amorphous, not crystalline. The ICP particles are attractive for many applications because of their high degree of tailorability through choice of transition metal nodes and ligand precursors, high thermal stability in many cases, and the ability to readily access their interior sites, at least in solution. Indeed, we have shown that one type of ICP particle can be readily converted into three other classes of particles through metal ion exchange without significantly changing the physical structure of the particles.^[13] This observation made us curious about the accessibility of the interior of the ICP particle in the dried state. Therefore, we decided to investigate the gas sorption properties of these novel materials, especially for hydrogen. Interestingly, we have discovered a novel type of ICP particle based on metallo-salen connector groups and Zn^{2+} nodes that shows moderately high H_2 uptake properties and almost no N_2 adsorption properties. This small-molecule discrimination occurs in spite of the fact that these particles are amorphous and do not possess the well-defined channels typically used to explain such selectivity in MOFs.

The homochiral acid-functionalized salen ligand (AFSL) **1** was synthesized by the reaction of the corresponding acid-functionalized salicylaldehyde and (1*R*,2*R*)-(–)-1,2-diaminocyclohexane according to literature procedures.^[16] The salen pocket of AFSL **1** was metallated with $\text{Zn}(\text{OAc})_2$ (Ac: acetyl) to form metallo-salen $\text{Zn}(\text{AFSL})$ **2** in pyridine. Interestingly, compound **2** can be used to prepare either an amorphous ICP particle **3** or a discrete [2+2] metallomacrocyclic compound **4** based upon the addition of Zn^{2+} and the choice of solvent system (Scheme 2). For example, when diethyl ether is allowed to slowly diffuse into a 1:1 mixture of compound **2** and $\text{Zn}(\text{OAc})_2$ in *N,N*-dimethyl formamide (DMF), the amorphous coordination particles **3** form at the interface and settle to the bottom of the reaction vessel. On the other hand, when compound **2** and $\text{Zn}(\text{OAc})_2$ are dissolved in pyridine and diethyl ether is allowed to diffuse into the solution, yellow crystals of macrocyclic compound **4** form (Fig. 1). Both the particles and the macrocycles can be formed directly from the free base ligand **1** by using two equivalents of $\text{Zn}(\text{OAc})_2$, rather than one, and the appropriate solvent mixture (Scheme 2).

Crystals of **4** suitable for X-ray diffraction analysis were grown by the slow diffusion of diethyl ether into a pyridine solution of **1** and $\text{Zn}(\text{OAc})_2$ (Scheme 2 and Fig. 1c and d).^[17] Macrocyclic **4** consists of two $\text{Zn}(\text{AFSL})$ **2** ligands which are connected by two Zn^{2+} metal ions to form a [2+2] metallomacrocyclic (Fig. 2). Each connecting Zn^{2+} ion is in a distorted octahedral coordination geometry with three pyridine, one *k*¹-carboxylate, and one *k*²-carboxylate ligands with the following inter-atomic distances: $\text{Zn}(2)–\text{O}(3)$ 1.978 Å, $\text{Zn}(2) \cdots \text{O}(4)$ 3.105 Å, $\text{Zn}(2)–\text{O}(9)$ 2.040 Å, and $\text{Zn}(2)–\text{O}(10)$ 2.559 Å. The coordination geometry of these bridging Zn^{2+} metal ions is similar to that observed for the monomeric model complex, $(2,6\text{-dichlorobenzoate})_2\text{Zn}(\text{NC}_5\text{H}_5)_3$.^[18] The metal-to-metal distance of the two bridging Zn^{2+} ions, $\text{Zn}(2) \cdots \text{Zn}(3)$, is 20.83 Å. The two Zn^{2+} metals in each salen pocket, $\text{Zn}(1) \cdots \text{Zn}(4)$, are separated by 11.43 Å. The metallomacrocycles form stacks that are parallel to one another, which results in the formation of linear channels with one-dimensional accessibility (Fig. 2b). The average interplane distance for the two adjacent metallomacrocycles is 7.38 Å. There are seven free pyridine molecules in the unit cell, including two within the channels and five in-between them (Figs. S1 and S2).

The micrometer-sized particles **3** were collected from the reaction mixture by centrifugation and washed with toluene several times. The morphology of the particles was characterized by optical microscopy (OM), fluorescence microscopy (FM), and field-emission scanning electron microscopy (FE-SEM) (Fig. 1a and b). The spherical nature of ICP particles **3** does not change in most organic solvents (chloroform, methanol, acetone, DMF, dimethyl sulfoxide (DMSO), and non-polar hydrocarbons), water, and the dried state, as evidenced by OM, FM, and SEM analysis. The SEM images show that the particles have a spherical shape with an average diameter of $(0.997 \pm 0.182) \mu\text{m}$ (Fig. 1a). The dynamic light scattering (DLS)-determined mean particle diameter of $1.195 \mu\text{m}$ is in reasonable agreement with the SEM determined value ($0.997 \mu\text{m}$). The DLS experiment was carried out in solution while the SEM work was done under high vacuum, which could account for the 20% difference in the determined average size.^[13,14] Infrared spectra of the particles show that the carboxylate groups are coordinating to Zn metal ions, as evidenced by a shift of the carboxylate stretching frequency from 1658 cm^{-1} in Zn(AFSL) **2** to 1562 cm^{-1} (ν_{anti}) and 1451 cm^{-1} (ν_{sym}) for the ICP particles **3**. These values compare very well with the stretching frequencies for Zn(OAc)₂ at 1562 cm^{-1} and 1446 cm^{-1} , consistent with k^2 -coordination of the carboxylate groups to the Zn^{2+} centers through their anionic O atoms.^[19] The chemical compositions of **3** and **4** were determined by energy dispersive X-ray (EDX) spectroscopy and elemental analysis (Fig. S4). These data support the 1:1 composition of the deprotonated metallo-salen Zn(AFSL) **2** and Zn^{2+} metal ion in both complexes with different coordinating solvent molecules.

Thermogravimetric analysis (TGA) of **3** and **4** under a nitrogen atmosphere show that although they exhibit initial weight loss due to solvent liberation (11.2% and 21.6%, respectively), they do not exhibit significant subsequent weight change up to 400°C , Figure S5a. However, X-ray powder diffraction data show that the one-dimensional channel structures in the crystals of **4** are not stable, as evidenced by a decrease in crystallinity upon drying. To measure the H_2 uptake and release properties of the amorphous ICP particle **3**, a series of gas sorption experiments were carried out at 77 K after removal of solvent by thermal activation under a dynamic vacuum at 300°C (Fig. 3a). Surprisingly, Brunauer–Emmett–Teller (BET) surface area measurements of **3** show that the ICP particles do not exhibit significant nitrogen sorption (typically $19 \text{ m}^2 \text{ g}^{-1}$). Interestingly, however, slow but significant hydrogen uptake was observed under similar conditions. The H_2 uptake of **3** ($64 \text{ cm}^3 \text{ g}^{-1}$, $0.57 \text{ wt } \%$) is comparable to that of zeolites such as ZSM-5 ($0.71 \text{ wt } \%$) and the mesoporous material MCM-41 ($0.57 \text{ wt } \%$) at 77 K and 1 atm ,^[20] but lower than those values determined for the best MOFs.^[7,10,11,21,22] The isosteric heat of adsorption (Q_{st}) for H_2 in **3**, which was obtained by fitting 77 K and 87 K isotherms to appropriate virial equations,^[23] was determined to be ca. 8 kJ mol^{-1} at the limit of zero coverage (Figs. 3b and S7). The high Q_{st} is comparable with the values of other crystalline MOF materials.^[8,24] This relatively high value and the stability of Q_{st} below $10 \text{ cm}^3 \text{ g}^{-1}$ indicate the possibility of strong physisorption of H_2 onto the unsaturated Zn metal centers of **3**.^[8,24] Since the H_2 sorption isotherm of **3** is not fully saturated, a higher adsorption capacity may be expected under higher pressures. Such preferential adsorption for H_2 over N_2 in amorphous particles is unprecedented but has been observed in a few crystalline microporous MOFs: $\text{Ni}_3(5\text{-bbdc})_6(\mu_3\text{-OH})_4$ (5-bbdc =

5-*tert*-butyl-1,3-benzenedicarboxylate), Cu(FMA) (4,4'-Bpe)_{0.5} · 0.5H₂O (FMA = fumarate, 4,4'-Bpe = *trans*-bis(4-pyridyl)ethylene), [Co₃(2,4-pdc)₂(μ₃-OH)₂]·9H₂O (2,4-pdc = 2,4-pyridinedicarboxylate), Mg₃(NCD) (NCD=2,6-naphthalenedicarboxylate), and Mn(HCO₂)₂.^[7,11,12] Interestingly, the ICP particle **3** shows a significant amount of CO₂ adsorption even at 258 K and the apparent BET surface area calculated from CO₂ sorption isotherm is 225 m² g⁻¹. The sorption isotherms of H₂ and CO₂ in **3** reveal a type I behavior typical for microporous materials,^[10,11,21] indicating that although **3** is an amorphous material, there must be some disordered pore structure. The selectivity of **3** for H₂ and CO₂ over N₂ follows the trend of their kinetic diameters (2.8 Å for H₂, 3.3 Å for CO₂, and 3.64 Å for N₂).^[25] The crystalline macrocycle **4** shows selectivity for H₂ similar to the ICP particles but with a lower H₂ uptake capacity (32 cm³ g⁻¹, 0.29 wt %) under the same conditions (Fig. S8).

In conclusion, we have developed a new class of micrometer-sized amorphous ICP particles **3** from the coordination chemistry of a metallo-salen building block **2** and Zn²⁺ ions. The reaction used to prepare them is highly solvent dependent. A DMF/ether mixture leads to amorphous particle formation while a pyridine/ether solvent mixture leads to the formation of a related crystalline macrocycle **4**, which has been crystal-lographically characterized. The spherical ICP particles **3** are stable up to more than 300 °C under high vacuum and show moderately high H₂ uptake and almost no N₂ adsorption even though they are amorphous materials and do not exhibit the well-defined channels typically used to explain such selectivity in MOF systems. These initial observations point towards a potential application for ICP particles as selective hydrogen storage and separation materials. Note that one can introduce many different transition metal ion nodes and poly-dentate organic or organometallic building blocks instead of the metallo-salen ligands used in this study to systematically tune the properties and evaluate the factors that control such selectivity and uptake capacity. Efforts in this direction are underway.

Experimental

Synthesis of Metallo-Salen Ligand Zn(AFSL) **2**:

AFSL **1** (100 mg, 148.1 μmol) and Zn(OAc)₂ (30 mg, 163.5 μmol) were combined in pyridine (10 mL) and refluxed over night. Solvent was removed under reduced pressure to yield a yellow precipitate. The product was resuspended in methanol and collected by filtration. This washing step was repeated three times. The product was then washed similarly with water and collected by filtration and dried under vacuum (106 mg, yield = 97%). ¹H NMR (DMSO-*d*₆, δ): 1.46 (br s, 11H, -C(CH₃)₃, -CH₂-), 1.85 (br s, 2H, -CH₂-), 3.21 (br s, 1H, -CH-), 7.38–7.44 (m, 3H, Ar-*H*), 7.68–7.78 (m, 2H, Ar-*H*), 8.12 (s, 1H, Ar-*H*), 8.46 (s, 1H, -CH=N-), 12.89 (br s, 1H, -CO₂H). IR (KBr pellet, cm⁻¹): 563 (w), 629 (w), 684 (w), 772 (m), 1089 (w), 1167 (w), 1270 (w), 1385 (s), 1410 (s), 1572 (s), 1626 (vs), 1658 (s), 2859 (w), 2931 (m). MS (MALDI-TOF, *m/z*): 736.37 (calcd for C₄₂H₄₄N₂O₆Zn, 736.25). MS (ESI in pyridine, *m/z*): 815.84 (calcd for [**2**] · (pyridine), C₄₇H₄₉N₃O₆Zn: 815.295) and 894.36 (calcd for [**2**] · 2(pyridine), C₅₂H₅₄N₄O₆Zn: 894.33). Anal. calcd for C₄₂H₄₄N₂O₆Zn · 2H₂O: C 65.16, H 6.25, N 3.62; found: C 64.94, H 5.84, N 3.77.

Synthesis of ICP Particle 3:

A precursor solution was prepared by mixing **1** (20 mg, 29.6 μmol) and $\text{Zn}(\text{OAc})_2$ (11 mg, 59.9 μmol) in DMF (10 mL). Diethyl ether was allowed to diffuse into the precursor solution overnight. The resulting precipitate was isolated and subsequently washed with toluene via centrifugation and redispersion cycles. Each successive supernatant was decanted and replaced with fresh toluene. The product was then dried under vacuum (19 mg, yield = 80%). Microparticle **3** can be synthesized using metallo-salen precursor **2** (20 mg, 27.1 μmol) and one equivalent of $\text{Zn}(\text{OAc})_2$ (5 mg, 27.1 μmol) in DMF and ether (21 mg, yield = 88%). IR (KBr pellet, cm^{-1}): 685 (w), 771 (w), 1165 (w), 1340 (w), 1363 (w), 1386 (s), 1409 (s), 1451 (m), 1562 (m), 1612 (vs), 2946 (m). MS (ESI taken after dissolving in pyridine, m/z): 894.55 (calcd for $[\mathbf{2}] \cdot 2(\text{pyridine})$, $\text{C}_{52}\text{H}_{54}\text{N}_4\text{O}_6\text{Zn}$: 894.33) and 957.58 (calcd for $[\mathbf{2} - \text{H}] \cdot \text{Zn} \cdot 2(\text{pyridine})$, $\text{C}_{52}\text{H}_{55}\text{N}_4\text{O}_6\text{Zn}_2$: 957.25). Anal. calcd for $\text{Zn}(\mathbf{2} - 2\text{H}) \cdot \text{H}_2\text{O}$: C 61.55, H 5.41, N 3.42; found: C 61.65, H 5.25, N 3.51.

Synthesis of Metallomacrocycle 4:

Diethyl ether was diffused into a pyridine solution of AFSL **1** (20 mg, 29.6 μmol) and $\text{Zn}(\text{OAc})_2$ (11 mg, 59.9 μmol), which gave a yellow crystalline precipitate (17 mg, yield = 70%). IR (KBr pellet, cm^{-1}): 698 (w), 771 (w), 1160 (w), 1383 (s), 1449 (m), 1556 (m), 1612 (vs), 1620 (vs), 2942 (w). MS (ESI taken after dissolving in pyridine, m/z): 895.17 (calcd for $[\mathbf{2}] \cdot 2(\text{pyr-pyridine})$, $\text{C}_{52}\text{H}_{54}\text{N}_4\text{O}_6\text{Zn}$: 894.33) and 957.09 (calcd for $[\mathbf{2} - \text{H}] \cdot \text{Zn} \cdot 2(\text{pyridine})$, $\text{C}_{52}\text{H}_{55}\text{N}_4\text{O}_6\text{Zn}_2$: 957.25). Anal. calcd for $\text{Zn}(\mathbf{2} - 2\text{H}) \cdot 5(\text{pyridine})$: C 65.50, H 5.50, N 6.31; found: C 65.84, H 5.41, N 5.91.

Selected X-Ray Crystallographic Data for 4 (CCDC-638761):

$\text{C}_{159}\text{H}_{160}\text{N}_{19}\text{O}_{12.5}\text{Zn}_4$, Triclinic, space group $P1$, $a = 9.441(1) \text{ \AA}$, $b = 15.476(2) \text{ \AA}$, $c = 25.538(3) \text{ \AA}$, $\alpha = 92.895(2)^\circ$, $\beta = 95.013(2)^\circ$, $\gamma = 107.180(2)^\circ$, $V = 3539.8(7) \text{ \AA}^3$, $Z = 1$, $T = 293(2) \text{ K}$, $2\theta_{\text{max}} = 57.7^\circ$, $\text{MoK}\alpha$ ($\lambda = 0.71073 \text{ \AA}$), $R_1 = 0.0523$ ($I > 2\sigma(I)$), $wR_2 = 0.1282$ (all data), and GOF on $F^2 = 0.906$ for 1768 parameters and 28235 unique reflections.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1. Scanning electron microscopy and dark-field optical microscopy images (inset: fluorescence microscopy images): a,b) **3**, c,d) **4**.

Figure 2. The crystal structure of **4**: a) Ball-and-stick diagram of an asymmetric unit, b) 3D packing diagram. Hydrogen atoms and solvent molecules (7 pyridines and 1/2 water per asymmetric unit) have been omitted for clarity.

Figure 3.
 a) Adsorption isotherms of **3** for H_2 , CO_2 , and N_2 (H_2 ◆, CO_2 ●, N_2 ▲) (measured at 77 K for H_2 and N_2 and at 258 K for CO_2 , solid lines in isotherms are visual aids), b) isosteric heat of adsorption Q_{st} for H_2 in **3**. STP: standard temperature and pressure. 1 Torr = 1.333×10^2 Pa.

Scheme 1.

Schematic representation of ICP particle synthesis. Ac: acetyl.

Scheme 2.

Selective synthesis of the metallo-salen ligand $\text{Zn}(\text{AFSL})$ **2**, amorphous ICP particle **3**, and crystalline metallomacrocycle **4**. DMF: *N,N*-dimethyl formamide.