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Tröger's-Base-Derived Infinite Co-ordination Polymer Microparticles**

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Particles that derive from infinite co-ordination polymers (ICPs) are an interesting new class of material.^[1–10] These structures, similar to their crystalline macroscopic metal–organic–framework (MOF) counterparts,^[11–30] have many unusual and potentially useful properties. They often have very high surface areas, exhibit tailorable chemical and physical properties through particle-core or -surface chemical functionalization and, because of their size, are highly dispersible materials.^[1–10] Consequently, ICP particles are attractive for many applications in asymmetric catalysis, mixture separations, gas storage, and biosensing.^[1,2,9]

ICP particles are typically synthesized from transition metal ions and multifunctional organic or organometallic ligand building blocks. The reactions are arrested at the nano-or microparticle stage through solvent-induced precipitation and the resulting ICP particles are typically amorphous, not crystalline, structures. These structures exhibit fast ion-exchange properties and it has been shown that one particle type can be rapidly interconverted into several others through such exchange reactions.^[3]

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Herein, we report a new type of ligand based upon Tröger's base^[31] that can be used to generate ICPs with Zn^{2+} ions as ligand interconnecting nodes. These ICPs exhibit selective H_2 adsorption properties in the presence of N_2 , and a scanning electron microscopy (SEM) study of the structures that lead to their formation provides significant insight into how this novel class of ICP forms.

Tröger's base was chosen as a structure-building motif since with the appropriate coordinating functionalities (CO_2H), its rigid shape should lead to a zigzag-type co-ordination polymer with transition metal ion nodes. We hypothesized that this would lead to the formation of ICPs with small channels or pores that could exhibit gas-uptake properties and may have the ability to differentiate gases with small kinetic diameters from ones with larger kinetic diameters. The Tröger's-base-derived ligands **4a** and **4b** were synthesized in two steps. An initial Suzuki coupling of 2,8-dibromo-4,10-dimethyl-6*H*,12*H*-5,11-methanodibenzo [*b,f*]-diazocine **1** and (methoxycarbonyl)phenylboronic acid **2** led to the formation of **3a** and **3b** in 80 and 76% yield, respectively. Subsequent hydrolysis of the methyl esters in **3a** and **3b** led to the formation of target compounds **4a** and **4b**, respectively (Scheme 1).

Fluorescent amorphous ICP particles **5a** and **5b** were prepared by slow diffusion of diethyl ether into a dimethylformamide (DMF) solution of precursors consisting of a 1:1 mixture of $\text{Zn}(\text{OAc})_2$ and ligands, **4a** and **4b**, respectively (Scheme 1). The micrometer-sized particles were collected from the reaction mixture by centrifugation and washed with methanol via three successive centrifugation and redispersion cycles.

The ICP particles were characterized by field-emission scanning electron microscopy (FE-SEM), optical microscopy (OM), and fluorescence microscopy (FM) as well as a variety of other analytical techniques (Figure 1). These images show spherical structures with an average diameter of $2.18 \pm 0.44 \mu\text{m}$ and $2.84 \pm 0.62 \mu\text{m}$ for **5a** and **5b**, respectively. The particles remain spherical with similar morphologies in most organic solvents, water, and even in the dried state but in pyridine they are depolymerized into derivatives of their molecular and metal ion precursors.^[1,2,4] The chemical compositions of **5a** and **5b**, determined by energy-dispersive X-ray (EDX) spectroscopy and elemental analysis (EA), are consistent with the formation of a 1:1 structure derived from the deprotonated ligands (**4a** – H_2 or **4b** – H_2) and $\text{Zn}(\text{II})$ ions with one acetate anion per repeat unit (the chloride contents of **5a** and **5b**, determined by elemental analysis, were 0.71% and 0.66%, respectively, and are consistent with the conclusion that acetate predominantly replaces the Cl^- ion during the polymerization process; Scheme 1).

To better understand how these structures form, we followed their transformation from precursors to particles using time-dependent SEM. In a typical experiment, ligand **4a** and $\text{Zn}(\text{OAc})_2$ were dissolved in DMF, and diethyl ether was allowed to slowly diffuse into the solution. Mild stirring (50 rpm) was used to mix the solvents during diethyl ether diffusion. 200 μL aliquots were taken from the reaction mixture after 5, 10, 20, 30, 40, 50, 60, and 120 min. Each sample was centrifuged to isolate the precipitate, which was washed with methanol twice and then analyzed by FE-SEM (Figure 2). At early stages of the particle formation process (5 min, Figure 2a), nanometer-sized globular seeds are observed. These seeds then agglomerate and begin to form spherical particles with rough surfaces (10 min, Figure 2b). Magnified images of the globular seeds (Figure 2a, right) and particle surfaces (Figure 2b, right) show that they are composed of aggregates of linked nanoparticles (mean diameter is $\approx 27 \text{ nm}$). As the reaction continues, the surfaces of the particles become smoother (Figure 2c) and, eventually, almost perfect spheres with smooth surfaces form (1 h, Figure 2d). The ICP particle **5b** and the $\text{Zn}(\text{II})$ -salen-based ICP particles^[2] exhibit similar growth behavior and stages (Figure S2–4 of the Supporting Information).

From the time-dependent SEM analysis, we have constructed a working mechanism for the particle formation process, which involves nucleation, followed by oligomerization, aggregation of the seeds, fusion, growth, and then annealing (Scheme 2). At high concentrations of ligand and metal ion, the first three steps are very fast. However, as the reaction proceeds, the concentration of precursor decreases and the growth and annealing processes become dominant and produce spherical ICP particles with smooth surfaces. The particle-growth step involves both the coalescence of the nanometer-sized seeds or aggregates into smooth larger particle structures along with the subsequent adsorption of additional nanoparticles onto the larger particle core. Note that the surfaces of the seeds and particles contain many active sites for further polymerization and nucleation via co-ordination chemistry.

Thermogravimetric analysis data reveal that the ICP particles **5a** and **5b** are stable up to 400 °C after an initial weight loss of 3.7 and 5.5%, respectively, due to solvent liberation in the 50–150 °C temperature range (Figure S5). To measure the gas uptake and release properties of the amorphous ICP particles, a series of gas-sorption experiments were carried out after their thermal activation under vacuum at 250 °C for 12 h (Figure 3). Interestingly, gas-sorption measurements show that the ICP particles **5a** and **5b** do not adsorb any noticeable amount of nitrogen at 77 K but adsorb a significant amount of CO₂ (**5a**: 35.0 cm³ g⁻¹, 6.87 wt%, **5b**: 37.6 cm³ g⁻¹, 7.39 wt%) even at 258 K. The apparent Brunauer–Emmett–Teller (BET) surface areas of **5a** and **5b** calculated from the CO₂ adsorption isotherms at 258 K are 244 m² g⁻¹ and 264 m² g⁻¹, respectively. However, significant and reversible hydrogen uptake was observed for both particle types at 77 K and 1 atm. The H₂ uptake capability of **5a** (77.0 cm³ g⁻¹, 0.69 wt%) is higher than that for **5b** (63.4 cm³ g⁻¹, 0.56 wt%), Zn(II)-salen ICP particle (0.57 wt%),^[2] and even the mesoporous material MCM-41 (0.57 wt %).^[32] This value is comparable to that of zeolite ZSM-5 (0.71 wt%)^[33] but lower than those for several well-defined crystalline MOFs.^[14,15,17,22,27–30]

The type-I behavior in the sorption isotherms for H₂ and CO₂ is typical of microporous materials^[26–28,30] and suggests the presence of channel structures in **5a** and **5b**. This allows these ICPs to discriminate these gases based upon their small differences in kinetic diameter (2.89 Å for H₂, 3.3 Å for CO₂, and 3.64 Å for N₂).^[34] Note that the CO₂ isotherms were taken at 258 K, where there is significantly more motion and presumably greater accessibility to the internal framework of the material as compared with H₂ and N₂. Moreover CO₂, unlike H₂ and N₂, has a significant quadrupole moment, which could lead to interactions with the metal co-ordination network. These additional factors may contribute to the enhanced CO₂-uptake properties of the ICP particles in comparison with N₂.

The preferential adsorption for H₂ also has been observed in amorphous Zn(II)-salen ICP particles^[2] and a few other crystalline MOF systems.^[12,14,17,22,28] The isosteric heat of adsorption (Q_{st}) for H₂ in **5a** and **5b** was obtained by fitting the isotherms recorded at 77 and 87 K to the appropriate virial equations (Figure 3b and Figure S6).^[35] The high Q_{st} value (≈ 8 kJ mol⁻¹) at the limit of zero coverage is consistent with strong physisorption of H₂ onto the metal centers of the particles.^[2,11,13,15,16,19,21,36] In addition, the high and constant Q_{st} value in **5a** at higher H₂ loadings as compared with the analogous value for **5b** suggests that the ICP particle **5a** may have a higher binding affinity for hydrogen than **5b**. Note that, although there is a substantial difference in H₂ uptake properties for **5a** and **5b**, there is only a small difference in CO₂ uptake. These data are consistent with the conclusion that the channel diameter distribution in **5a** is well matched with the kinetic diameter of H₂ and as a consequence can lead to increased van der Waals interactions between the channel side walls and H₂.

In conclusion, we have developed a new class of fluorescent spherical ICP microparticles **5a** and **5b** from the co-ordination chemistry of acid-functionalized modified Tröger's-base ligands and Zn(II) metal ions. By studying the process by time-dependent SEM we have identified a series of steps that account for particle formation. These include initial nucleation through oligomerization, aggregation of the nanoparticle seeds, fusion of the seeds, and addition growth through new layers of seeds, followed by annealing through co-ordination chemistry exchange processes. The resulting amorphous ICP particles exhibit highly selective H₂ uptake properties in the presence of N₂. Although the amount of H₂ uptake reported here is not exceptionally high compared to previously studied MOFs, we have shown that small structural differences in organic building blocks can yield ICP particles with significantly different uptake properties and the ability to differentiate gases.

Experimental Section

Microparticle 5a

A precursor solution was prepared by mixing ligand **4a** (25 mg, 47 μ mol) and Zn(OAc)₂ (9 mg, 49 μ mol) in DMF (2.5 mL). Diethyl ether was allowed to diffuse into the precursor solution over 2 h with stirring (50 rpm). White precipitates were isolated and washed with methanol via centrifugation and redispersion cycles. Each successive supernatant was decanted and replaced with fresh solvent (15 mg, 52%). IR (KBr pellet, cm⁻¹): 711 (w), 786 (s), 856 (m), 941 (w), 1131 (w), 1198 (w), 1327 (w), 1402 (vs), 1457 (m), 1474 (m), 1537 (s), 1606 (vs), 2950 (w). Elemental analysis for **5a** [C₃₃H₂₈N₂O₆Zn] Calcd.: C, 64.56; H, 4.60; N, 4.56. Found: C, 64.00; H, 4.25; N, 4.90. FTIR spectroscopy of **5a** shows the disappearance of the broad multiplet signature at 2500 cm⁻¹, diagnostic of the replacement of chloride with acetate ion. These data are consistent with EA results. The mean particle diameter determined by SEM analysis (161 particles) is 2.18 $\pm$ 0.44 μ m. Zeta potential: -32.34 $\pm$ 6.30 mV. Microparticle **5a** also can be synthesized without stirring; the diethyl ether was allowed to diffuse into DMF solution of precursors (**4a** (25 mg, 47 μ mol) and Zn(OAc)₂ (9 mg, 49 μ mol)) overnight without stirring. The resulting white precipitates were isolated and washed with methanol via centrifugation and redispersion cycles (12.5 g, 45%). The mean particle diameter determined by SEM analysis (161 particles) is 3.31 $\pm$ 1.44 μ m.

Microparticle 5b

Microparticle **5b** was synthesized according to the method of **5a** using **4b** (25 mg, 47 μ mol) and Zn(OAc)₂ (9 mg, 49 μ mol) in DMF (14 mg, 48%). IR (KBr pellet, cm⁻¹): 684 (w), 771 (m), 947 (w), 1219 (w), 1326 (w), 1385 (vs), 1411 (vs), 1474 (s), 1507 (m), 1562 (vs), 1594 (s), 2950 (m). Elemental analysis for **5b** [C₃₃H₂₈N₂O₆Zn] Calcd.: C, 64.56; H, 4.60; N, 4.56. Found: C, 63.96; H, 4.08; N, 4.88. Mean particle diameter determined by SEM analysis (169 particles): 2.84 $\pm$ 0.62 μ m. Zeta potential: -33.64 $\pm$ 5.42 mV.

Time-dependent SEM analysis of ICP particle formation

Diethyl ether was allowed to diffuse into the mixture of **4a** (25 mg, 47 μ mol) and Zn(OAc)₂ (9 mg, 49 μ mol) in DMF (2.5 mL) with stirring (50 rpm) over 2 h at room temperature. Aliquot amount of solution (0.2 mL) was taken from the reaction mixture periodically and washed with methanol twice by centrifugation and redispersion cycles. Each sample was analyzed by FE-SEM after a 4-nm coating with gold for higher image resolution.

Supplementary Material

Refer to Web version on PubMed Central for supplementary material.

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Figure 1.
SEM and dark-field OM images (inset: FM images): a, b) for **5a**, c, d) for **5b**.

Figure 2. Representative SEM images monitoring the formation of ICP particles **5a**: a) 5 min, b) 10 min, c) 30 min, and d) 60 min.

Figure 3.

a) Adsorption isotherms of H_2 , CO_2 and N_2 for **5a** (H_2 $\blacklozenge$, CO_2 $\bullet$, N_2 $\blacktriangle$) and **5b** (H_2 $\diamond$, CO_2 $\circ$, N_2 $\triangle$), measured at 77 K (for H_2 and N_2) and 258 K (for CO_2); solid lines in isotherms are visual aids. b) Isosteric heat of adsorption Q_{st} for H_2 in **5a** ($\blacklozenge$) and **5b** ($\diamond$).

Scheme 1.

Synthesis of the modified Tröger's base ligands and their ICP particles with Zn(II) metal ions. Although a racemic mixture is used, only one enantiomer is depicted.

Scheme 2.

Proposed mechanism for the ICP particle formation: a) oligomerization, b) nucleation, c) aggregation, d) fusion, e) growth, and f) annealing.