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New lead(II) nano-porous three-dimensional coordination polymer; pore size effect on iodine adsorption affinity

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Abstract: A three-dimensional (3D) nano-porous coordination polymer, $[Pb(4\text{-bpdb})(\mu\text{-}NO_3)(\mu\text{-}SCN)]_n.1.5\ CH_3OH$ (**TMU-15**), has been synthesized from reaction of Pb(II) salt and 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (4-bpdb) in branched tube. Compound **TMU-15** is stable for loading of guests. In this compound, we successfully loaded the porous crystals with I_2 by suspending them in a solution of I_2 in cyclohexane. The delivery of I_2 from **TMU-15** performed in ethanol, a nonaromatic solvent, at room temperature was determined by UV/vis spectroscopy. The delivery and desorbed rate of iodine in **TMU-15** has been compared with analog compounds such as $[Pb(4\text{-bpdh})(NO_3)_2(H_2O)]_n$ (**TMU-1**) and $[Pb(4\text{-bpdh})(NO_3)_2]_n$ (**TMU-2**) too.

Metal–organic frameworks (MOFs) are among the most exciting, high-profile developments in nanotechnology in the last decade.[1,2] MOFs have been composed of metals (or metal clusters, chains, or layers) connected by organic linkers, they show some of the highest porosities known, with pore sizes between 0.4 and 6 nm, which is suitable for capture, storage, and delivery applications.[3] MOFs have been particularly highlighted for their excellent storage, separation and adsorption properties. Up to now many coordination polymers of lead(II) had been reported[4,5] but a few of them have a porous structure.[6,7] Metal–organic frameworks are predominantly synthesized in molecular solvents under hydro(solvo)thermal conditions or by slow solution diffusion methods, which take several days or a longer time for a reaction cycle. Here, we report on the assembly of a 3D porous coordination polymer, $[Pb(4\text{-bpdb})(\mu\text{-}NO_3)(\mu\text{-}SCN)]_n.1.5\ CH_3OH$ (**TMU-15**), through a thermal gradient method. Driven by the recent successful encapsulation of functional species such as drugs,[8,9] dyes,[10,11] light emitters,[12,13] magnetic molecules,[14] explosives,[15] etc. into the pores, we further explore its kinetics of iodine loading, release in ethanol and pore size effect of MOFs on rate and amount of adsorption. **TMU-15** was obtained by branched tube method and with a thermal gradient method. Reaction between 1,4-bis(4-pyridyl)-2,3-diaza-1,3-butadiene (4-bpdb), lead(II) nitrate and ammonium thiocyanate in MeOH leads to the formation of the new lead(II) porous 3D coordination polymer, $[Pb(4\text{-bpdb})(\mu\text{-}NO_3)(\mu\text{-}SCN)]_n.1.5\ CH_3OH$ (**TMU-15**). On the other hand, the ligand and ammonium thiocyanate solution have been added to lead(II) nitrate solution slowly under ultrasonic irradiation for synthesized nano-**TMU-15**. Determination of the structure of compound **TMU-15** by X–ray crystallography (Figure1, Table S1-S2 and Figure S1-S4 (Supporting Information)) showed that the lead(II) ions are coordinated by $\mu\text{-}NO_3^-$, 4-bpdb ligands and one $\mu\text{-}SCN^-$ ion (Figure S1), resulting in a nine-coordinate 3D coordination polymer (Figure S2). The lead(II) atoms are connected into infinite chains through the ligands and the chains are further linked into porous 3D coordination polymer by $\mu\text{-}NO_3^-$ and $\mu\text{-}SCN^-$ anions (Figure S3). Fragment of π-stacking ligands (the stacks are parallel with the crystallographic axis *a*) have been shown in Figure S4. The angle between the mean planes of pyridine moieties and the distance between their centers for the pairs of cycles denoted A and B', B and D', A' and C are equal to, respectively, 8.3º and 3.58Å; that for the A' and B, B' and D, A and C' cycles - to 7.0º and 3.78Å

Acceptable matches in powder XRD and IR spectroscopy between **TMU-15** and nano-**TMU-15** synthesized by sonochemical method indicates that the compound is single crystalline phase and that these phases are identical to those obtained by single crystal diffraction (Figure S5,S6 (Supporting Information)).

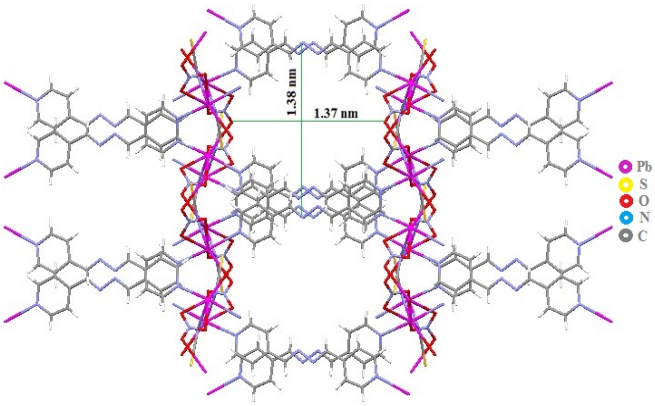

Figure 1. A fragment of nano-porous 3D coordination polymer in $[Pb(4\text{-bpdb})(\mu\text{-}NO_3)(\mu\text{-}SCN)]_n.1.5\ CH_3OH$ (**TMU-15**), showing guest free channals of 1.38× 1.37 nm (Pb = purple, O = red, C = gray, N = blue S= yellow and H = white).

The structure of **TMU-15** consists of Pb(II) atoms bridged by NO_3^- and produce novel lead(II) nitrate chains. Compound **TMU-15** crystallizes in the monoclinic and space group *C2/c*. The environment of lead(II) atoms in compound **TMU-15** is PbN_4O_4S. For the structure described here, coordination around the lead(II) atoms is holodirected and the arrangement of the 4-bpdb ligand, thiocyanate and nitrate anions do not suggest any

gap or hole in coordination geometry around the metal, indicating that the lone pair of electrons on lead(II) is sterically inactive.[16] Compound **TMU-15** is a porous 3D coordination polymer with nano-size pores (1.38 × 1.37 nm). These observations imply that the porous structure in **TMU-15**, combining firmness and flexibility, is architecturally suitable for adsorption of some molecules with special directional physical properties.[17,18] Appropriate nano-sized particles of compound **TMU-15** were obtained by ultrasonic irradiation. According to Figure 2, the nano-**TMU-15** with average diameter of about 100 nm obtained at a concentration of 0.1M in MeOH and their morphology is mixture of particles and rods.

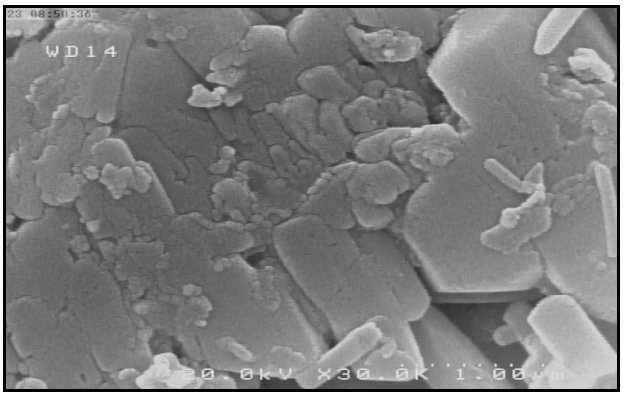

Figure 2. SEM image of compound **TMU-15** nano-size structure prepared by 0.1 M concentration of initial reagents by ultrasonic irradiation.

These particular properties thus prompted us to search for absorption properties for other molecules. We successfully loaded the porous crystals with I_2 by suspending there in a solution of I_2 in cyclohexane.[18] We try to get the single crystal of the **TMU-15** filled by the iodine guest through physical adsorption method, but after iodine adsorption structure of the framework containing iodine molecules wasn't single crystal. To study the uptake and release of iodine in **TMU-15**, different tests were performed. First we tested for the amount of iodine that can be inserted in the pores. We immersed a few samples (100 mg of activated **TMU-15** in 140◦C) in a sufficient amount of a cyclohexane solution of I_2 (about 0.07 gram I_2 in 3 ml cyclohexane) in a small sealed flask at room temperature, and observed that the dark brown solutions of I_2 fade slowly to very pale red (Figure 3), while the crystals of **TMU-15** get darker.

IR and PXRD data showed the crystallinity of the host framework of the crystal and powder samples of **TMU-15**⊃xI_2 (Figures S7, S8 (Supporting Information)) are same. Most of the peaks in the XRPD remained at similar 2θ positions but were distinctly weakened and broadened. The change of intensity and width indicates that the resulting solid HMTI-1⊃xI_2 retains the host framework crystallinity as I_2 molecules diffused in.

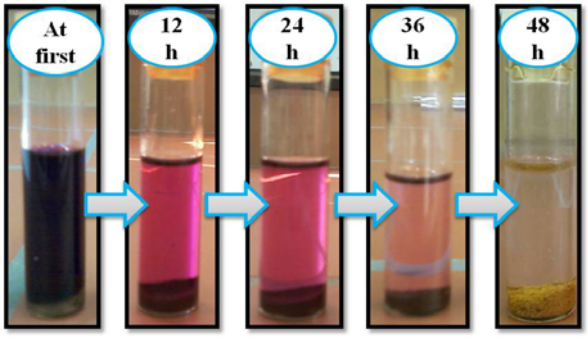

Figure 3. I_2 enrichment progress when 100 mg of crystals of **TMU-15** were soaked in 3 mL of a cyclohexane solution of I_2 (0.1 M/L).

Simple calculation on the experimental parameters presented that a cyclohexane solution of I_2 (about 0.07 gram I_2 in 3 ml cyclohexane) contains 0.55 mmol I_2 whereas 100 mg of TMU-15 (FW = 585.58) contains approximately 0.17 mmol Pb(II), so indicates the absorption of $3I_2$ for one lead(II) atom of **TMU-15**. Also thiosulfate determination of the I_2 content released from **TMU-15**⊃xI_2 indicates the absorption of $3I_2$ for one lead(II) atom of **TMU-15**. The exceptional affinity of **TMU-15** for I_2 may be attributed to the structural character of the regular π-electron walls made of 4-bpdb. That is, there is a striking difference compared to conventional adsorbent materials that are lacking an accessible interaction between I_2 and the host. A few examples of I_2 inclusion into organic/inorganic porous frameworks[17,18,19] and into MMOFs[20,21] are known, with the loading weight varying from 16.6% to 82.6%. Conversely, the regular confined nanospace combining abundant π-electron walls may cumulate the advantages to achieve a better controlled release of I_2, in contrast to conventional adsorbents. The delivery of I_2 from **TMU-15**⊃$3I_2$ performed in ethanol, a nonaromatic solvent, at room temperature under continuous stirring was determined by UV/vis spectroscopy (Figure 3). Figure S9 shows progress of the iodine release from **TMU-15**⊃$3I_2$ when the containing iodine crystals were immersed in ethanol. The iodine gradually released without disturbing the crystals induced the color of solution darker with increasing time. According to the elemental analysis, solid sample retain its structure after the first cycle of iodine release(Supporting Information).

The temporal evolution UV/vis spectrum for iodine in ethanol solution, which shows λ_{max} at 210, 280 and 360 nm, which become stronger with increasing I_2 content. The intensity of absorption band at 210 nm is proportional to concentration of I_2, and the absorption bands at 280 and 360 nm correspond to polyiodide I_3^-, which are generally stabilized by H^+ ions and obtained from the reaction I_2 with decomposed iodide.[18] Once these interactions fade out with increasing I_2 extrusion, the delivery in the second stage is mainly governed by a free diffusion process, and a complete I_2 release from **TMU-15**⊃$3I_2$ needs more than one week to attain the equilibrium state. The potential intermolecular interactions between I2 and π-electron walls are important, as they allow a single path for I_2 molecules to access and be restricted within well-regulated narrow limits within the nanochannels, inducing n $\nrightarrow$ σ^* charge transfer (CT).[22]

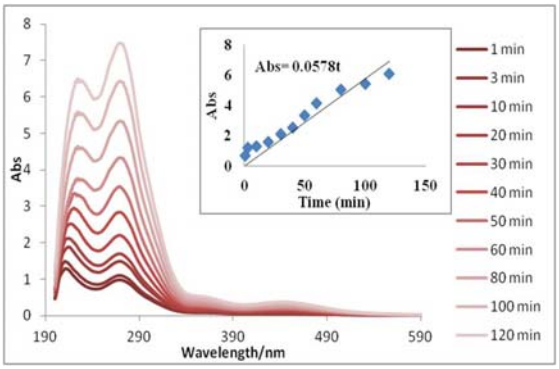

Figure 4. desorption process and desorbed rate of I_2 from**TMU-15.**

The delivery of I_2 in $[Pb(4\text{-bpdh})(NO_3)_2(H_2O)]_n$ (**TMU-1**) and $[Pb(4\text{-bpdh})(NO_3)_2]_n$ (**TMU-2**) performed in ethanol, at room temperature under continuous stirring was determined by UV/vis spectroscopy previously[23,24]. It seems that in **TMU-15** (1.38 × 1.37 nm) the pores are smaller than **TMU-1** (1.8 × 2.1 nm) and bigger than **TMU-2** (1.8 × 0.4 nm), so the delivery of iodine from the **TMU-15** can be faster from **TMU-1** and slower than **TMU-2** (Figure 5).

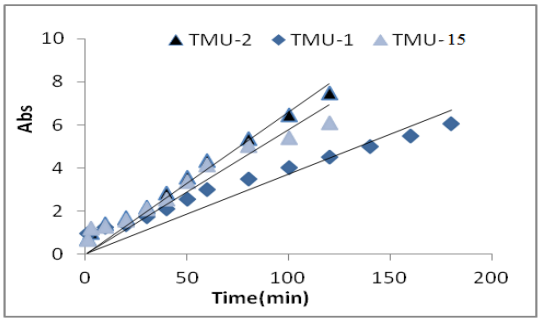

Figure 5. Comparison of desorbed rate of **TMU-15** with **TMU-1** and **TMU-2.**

In summary, we have constructed an unprecedented, stable MOF with rigid empty pores and rather high thermal stability. It may indeed be suitable for applications requiring frequent loading of guests. The empty phase has excellent and promising I_2 affinity, and it can be slowly delivered to ethanol controllably. Desorption rate of iodine compared between **TMU-1**, **TMU-2** and **TMU-15** too. Our results further support the idea that assembling MOFs with regular and suitable pores can find more applications in the encapsulation of functional substances to achieve novel oriented properties and delivery of iodine from the **TMU-15** can be faster from **TMU-1** and slower than **TMU-2**.

Supplementary material: Crystallographic data for the structure reported in the paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no, CCDC- 983874 for compound **TMU-15**.

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Notes

Single crystals of **TMU-15** suitable for X-ray diffraction were prepared by a thermal gradient methoud in branched tube. The ligand 4-bpdb (1 mmol, 0.210g), lead(II) nitrate (0.331g, 1mmol) and ammonium thiocyanate (1 mmol) were placed in the main arm of a branched tube. MeOH was carefully added to fill both arms. The tube was sealed and the ligand-containing arm immersed in an oil bath at 60°C while the other arm was kept at ambient temperature. After four days, orange crystals deposited in the cooler arm that were isolated, filtered off and dried. M.P.>300°C. Found; C, 29.65; H, 2.70; N, 14.35%, calculated for $C_{14.50}H_{16}N_6\ O_{4.50}PbS$; C, 29.71; H, 2.73; N, 14.34%. IR (cm^{-1}) selected bonds: ν = 515(w), 816(w), 993(w), 1255(w), 1367(s), 1600(m) and 2063(m).

Graphical Abstract:

New lead(II) nano-porous three-dimensional coordination polymer; pore size effect on iodine adsorption affinity ***Lida Hashemi, Ali Morsali****	A three-dimensional (3D) nano-porous coordination polymer, $[Pb(4\text{-bpdb})(\mu\text{-}NO_3)(\mu\text{-}SCN)]_n.1.5\ CH_3OH$ (**TMU-15**), has been synthesized. In this compound, we successfully loaded the porous crystals with I_2 by suspending them in a solution of I_2 in cyclohexane. The delivery of I_2 from **TMU-15** performed in ethanol, a nonaromatic solvent, at room temperature was determined by UV/vis spectroscopy. The delivery and desorbed rate of iodine in **TMU-15** has been compared with analog compounds such as $[Pb(4\text{-bpdh})(NO_3)_2(H_2O)]_n$ (**TMU-1**) and $[Pb(4\text{-bpdh})(NO_3)_2]_n$ (**TMU-2**) too.