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M4FT-15OR03100415: Update on COF-based Adsorbent Survey

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OAK RIDGE NATIONAL LABORATORY
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Chemical Sciences Division

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ABSTRACT

This letter report provides an update on activities focused on generating nanoporous adsorbents involving covalent organic frameworks (COF) and zeolitic imidazolium frameworks (ZIF). The adsorbents have been generated and screened in a uranyl-spiked brine (6 ppm U) to understand uranyl-binding behavior. Porous organic polymers (POP) also qualify under this title and are similar to the COF PPN-6 that is discussed herein. Seven COF/POP and one 1 ZIF were synthesized and screened for uranyl adsorption. These materials are summarized in Table 1 below. Seawater screening is on-going via batch testing while flow screening systems are being developed at PNNL.

Name	Description	6ppmU Screening Capacity (g-U/kg-ads.)
ZIF-CN	Nitrile-containing zeolitic imidazolium framework	n/a
TATA	Non-nitrile containing COF from melamine and terephthaldehyde	0
PPN-CH_2Cl	Aminated chloromethyl-PPN-6 structure	0
PPN-CH_2CN	Cyanomethylated PPN-6 structure	n/a
SHA	Crosslinked salicylhydroxamic acid	0
Cationic Polymer	Cationic polymer based upon tris-(dimethylamino)ethyl)-amine and tris(bromomethyl)-trimethylbenzene	n/a
Cationic 2D COF	Triclorotriazine-phenylboronic acid based 2-dimensional COF generating a cationic superstructure	On-going
PPN-PAN	ATRP growth of poly(acrylonitrile) from PPN-CH_2Cl followed by conversion to poly(amidoxime)	59.5
PPN-PAN/MBA	ATRP growth of poly(acrylonitrile-co-N,N'-methylenebisacrylamide) from PPN-CH_2Cl followed by conversion to poly(amidoxime)	55.0
PPN-PAN/PAM	ATRP growth of poly(acrylonitrile-co-acrylamide) from PPN-CH_2Cl followed by conversion to poly(amidoxime)	25.5

Covalent organic frameworks are nanomaterials with typically high surface areas and ordered structure, often without crystallinity. The high surface areas have potential to translate into high capacities, provided the binding site is accessible and the density of binding sites are sufficiently high. This report relates efforts to translate COF materials into adsorbents to extract uranyl from seawater. One result for zeolitic imidazolium frameworks (ZIF) is reported as well.

1. COF BASED ADSORBENTS:

Initially, melamine and terephthaldehyde were used to generate an adsorbent that did not possess nitriles. The COF was synthesized with different solvents, DMSO, DMSO/water mixture. The resulting covalent organic framework with triazine building units was prepared, with a surface area of 160 m^2/g; however the capacity is very low in laboratory screening (6 ppm uranyl brine). This could be due to incomplete deprotonation of the framework, but is expected to be primarily due to the lack of nitriles present. The structure is proposed in Figure 1.

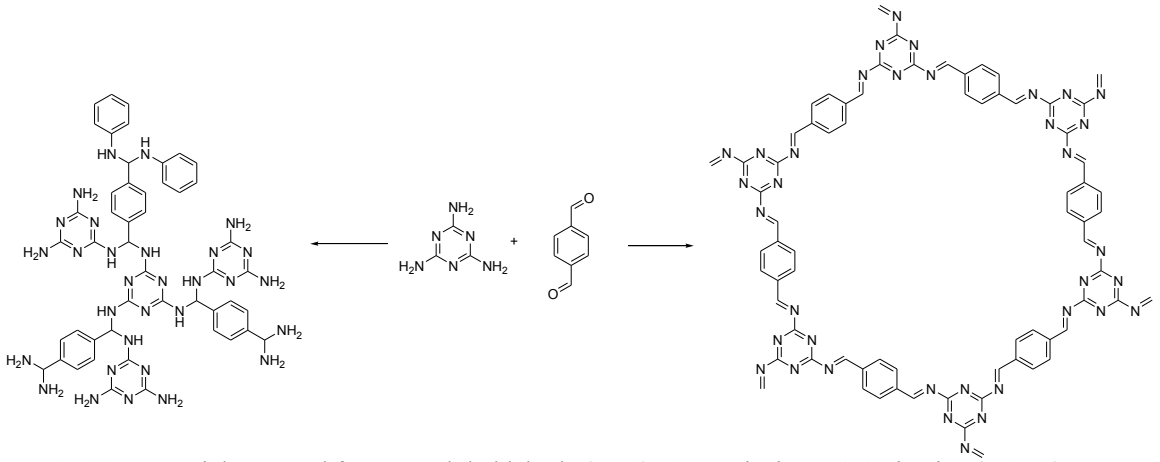

Figure 1. COF material prepared from terephthaldehyde (TPA); 1,3,5-triazine-2,4,6-triamine (TATA).

The next work utilized 2,5-dichlorobenzonitrile and 3,5-dihydroxylbenzonitrile to prepare a COF material via a solid-state reaction. The polymer was expected to be generated during grinding of the precursors, however, an incomplete reaction was observed. After this, a hydrothermal synthesis in an autoclave was attempted using basic conditions to crosslink the trihydroxybenzonitrile with dichlorobenzonitrile in an autoclave (Figure 2). The resulting polymer demonstrated low capacities though.

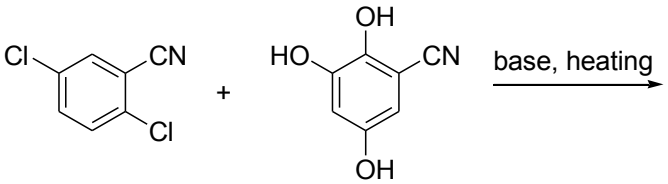

Figure 2. COF material prepared from 2,3,5-trihydroxybenzonitrile and 2,5-dichlorobenzonitrile.

The precursors for the COF PPN-6 were prepared by reacting tetrakis(4-bromophenyl)methane with iodine (I_2) at room temperature. Then a modified Yamamoto homocoupling polymerization was utilized to synthesize the COF PPN-6. The PPN-6-CH_2Cl was further prepared according to reported literature (Figure 3).[1] Briefly, the PPN-6 COF was reacted with paraformaldehyde and concentrated HCl, resulting in the

chloromethylated PPN-CH_2Cl. The initial PPN-6 exhibited a surface area of 3350 m^2/g prior to chloromethylation. Post-chloromethylation, the surface area dropped to 1252 m^2/g. Further amination decreased the surface area. Again, no nitriles were present. The capacity is low, due to the low selective adsorption ability of amine under the specified screening parameters. In addition to amination, the pendant chlorides were exposed to potassium cyanide (KCN) in an attempt to exchange the chlorides for nitriles. No nitriles were observed after the reaction. This route was abandoned due to the presence of an ATRP initiator on the PPN-6 structure (to be discussed later in this report).

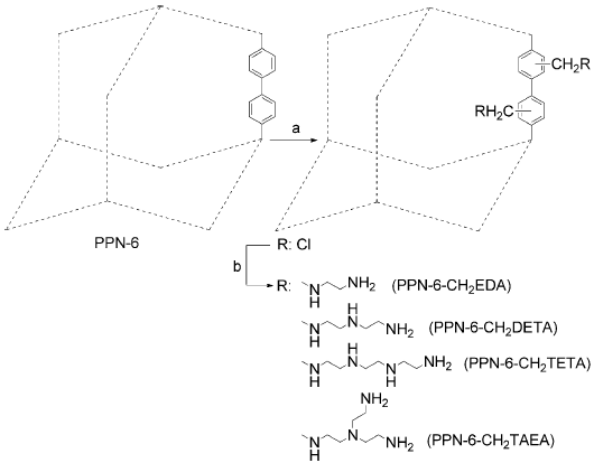

Figure 3. Synthetic route to polyamine-tethered PPNs. a) CH3COOH/HCl/H3PO4/HCHO, 90°C, 3 days; b) amine, 90°C, 3 days.

Given the understanding of seawater uranyl extraction, a porous polymer containing an oxime was attempted through the use of salicylhydroxamic acid. The salicylhdyroxamic acid was reacted with hexamethylene diamine and formaldehyde to generate the porous polymer (Figure 4). A light yellow solid was obtained and screened against the uranyl-spiked brine.

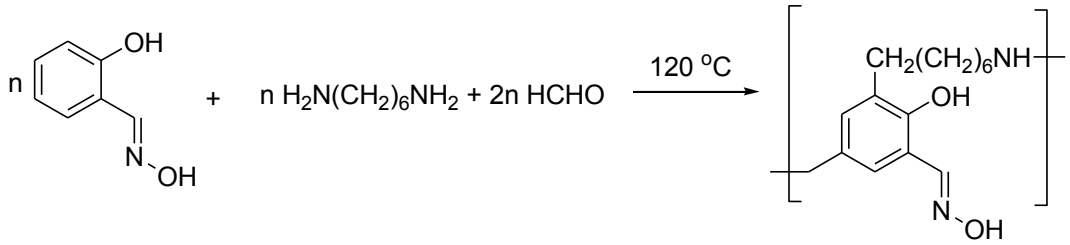

Figure 4. COF material tried from salicylhydroxamic acid, hexamethylene diamine and formaldehyde.

In an attempt to adsorb uranyl in a manner other than chelation, such as with the amidoxime, a charged adsorbent was generated. This ionic porous polymer was expected to complex the uranyl tricarbonate anion. This should result in enhanced kinetics since carbonate displacement is not required for chelation. Utilizing tris[2-(dimethylamino)ethyl]amine (Me_6tren) and 1,3,5-tris(bromomethyl)-2,4,6-

trimethylbenzene (TAMTMB) as precursors, the porous polymer was synthesized (Figure 5). However, the product was a gel that never solidified precluding screening.

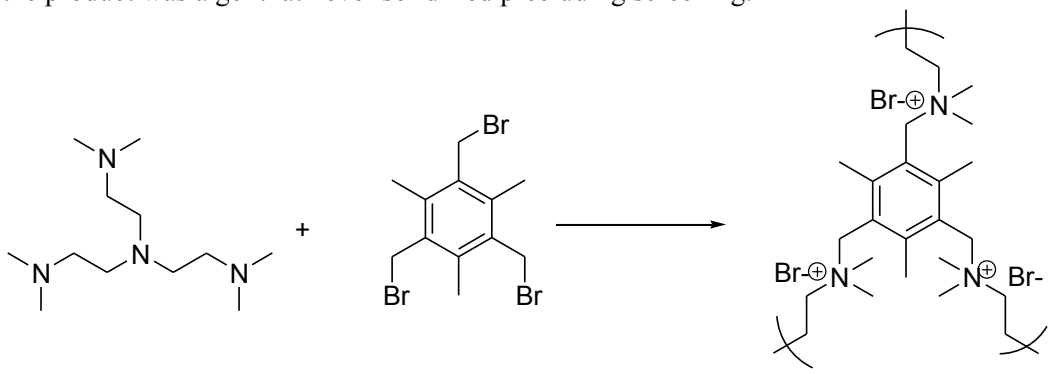

Figure 5. COF material tried from Me6tren and TAMTMB.

Due to the lack of a solid product, another avenue was attempted with this concept. Here, a more rigid structure is attempted using 2,4,6-trichloro-1,3,5-triazine (TCT) and pyridinylboronic acid as precursors to prepare a 2D layered COF material (Figure 6). This will have halide counter ions that can be exchanged by the uranyl tricarbonate anion. Work on this material is on-going.

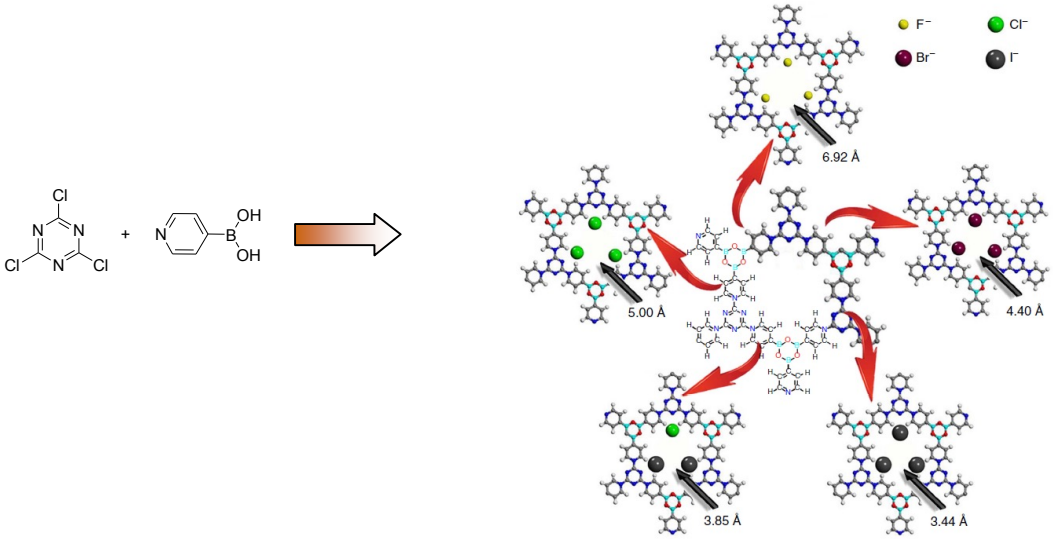

Figure 6. 2D layered COF adsorbent from TCT and 4-pyridinylboronic acid.

Realizing the PPN-CH_2Cl precursor that was previously aminated is an excellent ATRP initiator, polyacrylonitrile was grown via ATRP on the COF support. This is the first attempt to grow a polymer from a COF. Under inert conditions, acrylonitrile (AN) monomers were grafted on the COF substrate by ATRP, with copper(I) bromide/copper(II) bromide and tris[2-(dimethylamino)ethyl]amine (Me_6Tren) as the catalyst/ligand combination. The resulting AN grafted COF material was named as PPN-6-PAN

(Figure 7). This was amidoximated to generate the final adsorbent. In order to increase the hydrophilicity or induce conformational changes in the final polymer, co-monomers such as N,N'-methylenebisacrylamide (MBA) and acrylamide (Am) were grafted with AN via ATRP, with the products named as PPN-6-PAN/PMBA and PPN-6-PAN/PAM, respectively. The unreacted monomers and homopolymers after grafting were removed with N,N'-dimethylformamide (DMF) and then ethanol, subsequently the products were dried at 50 °C under vacuum. The degree of grafting (DOG) of PPN-6-PAN, PPN-6-PAN/PMBA and PPN-6-PAN/PAM is 150, 150 and 120 %, respectively, where the degree of grafting (%) = $[(W_g - W_o)/W_o] \times 100$. where, W_g and W_o denote the weights of the grafted products and ungrafted COF precursors.

The FTIR and nitrogen sorption surface areas of the products were conducted (Figure 8). The isotherms show the resulting loss in surface area as expected with some porosity maintained after chloromethylation. The FTIR spectrum shows the presence of nitriles in the polymers before amidoximation, and in the case of the MBA and Am samples, the presence of an amide carbonyl at approximately 1600 cm^{-1}. Batch screening tests were conducted with two different base (potassium hydroxide) pre-treatment temperatures (Figure 9). The screening tests for this series of material gave a capacity 59.5, 55.0, and 25.5 g-U/kg-ads. for PPN-6-PAN/PMBA, PPN-6-PAN and PPN-6-PAN/PAM, respectively, when base-treated at room temperature. When the base treatment was performed at 80^{o}C, as traditionally done with the polymeric adsorbents, only the PPN-PAN/PMBA exhibited a capacity for uranyl (30 g-U/kg-ads.), while the other two adsorbents exhibited no capacity. The reason behind this drop in capacity is still being investigated. A manuscript about the COF related sorbents is under preparation.

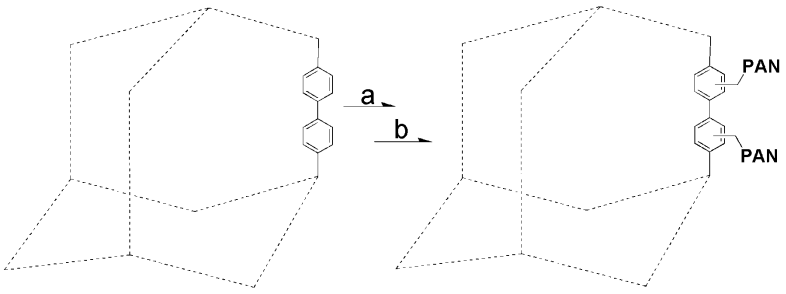

Figure 7. Generation of the PPN-CH_2Cl and PPN-PAN where a) $CH_3COOH/HCl/H_3PO_4/HCHO$, 90^{o}C, 72 hours; b) $Me_6Tren/CuBr_2/CuBr/DMSO/AN$, 60^{o}C, 24 hours ($Me_6Tren$ = tris[2-(dimethylamino)-ethyl]amine, DMSO = dimethyl sulfoxide).

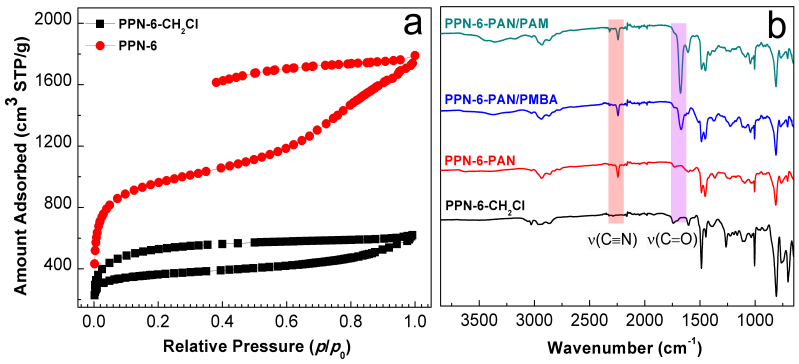

Figure 8. Nitrogen sorption isotherms of PPN-6 and PPN-6-CH2Cl (a) and Fourier transform infrared (FTIR) spectra of PPN-6-CH2Cl, PPN-6-PAN, PPN-6-PAN/PMBA and PPN-6-PAN/PAM.

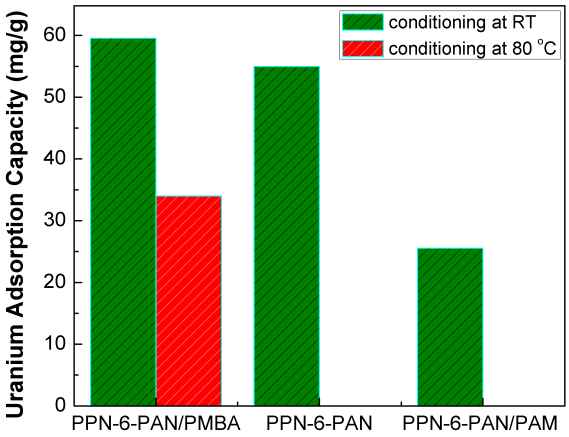

Figure 9. Laboratory screening capacities of the COF-based adsorbents conditioned under different temperatures. Conditioning was performed using a 0.44 M KOH solution.

2. ZIF BASED ADSORBENTS:

Zeolitic imidazolium frameworks (ZIF) are porous crystalline materials similar to metal organic frameworks. These materials exhibit high surface areas and periodic structures. The ability to coordinate uranyl from seawater within a crystalline matrix would simplify the spectroscopy to study uranyl binding. With this aim, a porous ZIF based adsorbent was prepared via ligand exchange followed by post-synthetic modification. ZIF-8 nanoparticles were synthesized using 2-methylimidaze (MIM) and nanosized ZnO precursors followed by ligand exchange to replace the MIM ligands with 4,5-Dicyanoimidazole (Figure 10). Although some crystalline ZIF material was obtained, the material was not stable toward hydroxylamine during the amidoximation step.

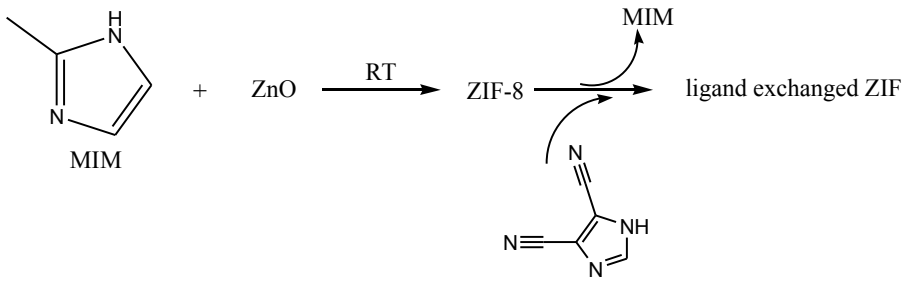

Figure 10. Schematic illustration for the preparation of the ZIF adsorbents based on ligand exchange and post synthetic modification.

3. SUMMARY:

A series of COF and porous polymers have been attempted. Of these, only those with PAN or PAN-copolymers grown from a COF have demonstrated potential for uranium extraction from seawater. The COF with grafted polymers attached via ATRP exhibited the highest capacity within the laboratory screening. The crosslinked polymer containing N,N'-methylenebisacrylamide exhibited the highest capacity at 60 g-U/kg-ads. with a room temperature conditioning. The seawater extraction analysis is currently on-going using batch testing methods, while an effective way to screen the small particle size adsorbents is developed at PNNL's Marine Sciences Laboratory.

References:

1. Lu, W.; Sculley, J.P.; Yuan, D.; Krishna, R.; Wei, Z.; Zhou., H.-C. *Angew. Chem. Int. Ed.* 2012, **124**(30), 7598-7602.