

Host–Guest Systems

A Perylene-Based Microporous Coordination Polymer Interacts Selectively with Electron-Poor Aromatics

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Abstract: The design, synthesis, and properties of the new microporous coordination polymer UMCM-310 are described. The unique electronic character of the pery-lene-based linker enables selective interaction with electron-poor aromatics leading to efficient separation of ni-troaromatics. UMCM-310 possesses high surface area and large pore size and thus permits the separation of large organic molecules based on adsorption rather than size exclusion.

Microporous coordination polymers (MCPs), a class of crystalline solids composed of metal clusters connected by organic linkers, excel in a variety of applications, including gas sorption, separations, and catalysis due to their porosity, high surface area, well-defined pore sizes/shapes, as well as tunable chemistries. In particular, using MCPs as separation media for liquid-phase separation has considerable potential for purification of petrochemicals, structural isomers, and stereoisomers, among other classes of adsorbates.^[1] Such separations can be strongly influenced by the presence and nature of coordinatively unsaturated metal sites,^[2] sorbent pore size,^[2a, 3] and linker electronic nature. For example, the separation of ethyl benzene and styrene by using HKUST-1 as stationary phase is remarkably efficient due to olefin-metal interaction causing selective retention of styrene.^[2a, c] An isomeric mixture of transand cis-piperylene is resolved with MIL-96 due to the cage structure and narrow cage windows, which selectively facilitate the efficient packing of the *trans* isomers inside the pore.^[3c] Yet, examples of MCPs for liquid-phase separation based on electronic interaction between the linkers and guest molecules are rare.^[4] Electronic interaction, particularly the π - π donor-acceptor, is one of the most predictable interactions between aromatics with opposing electronic character and thus could act as an orthogonal recognition element for electron-poor aromatics (e.g., nitroaromatics). Based on this hypothesis, a new separation material can be designed specifically to allow the

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selective separation of these compounds. As a secondary consideration, it is important to note that unlike typical silica-gelbased sorbents used in separations, the vast majority of MCPs employed as separation media contain relatively small pores (less than 12 Å), which limits separations to low-molecularweight molecules. Herein, the new MCP UMCM-310 was designed specifically to address these problems and to explore the potential of a ligand with unique electronic character to affect a difficult class of separations.

Perylene, a polycyclic aromatic compound commonly found in dye molecules and used as a donor in donor–acceptor complexes, was chosen to construct UMCM-310.^[5] Due to its large conjugated π system, perylene frequently serves as a π donor, and thus can have strong interactions with electron-deficient nitroaromatics.^[6] Keeping this in mind, the ligand 2,5,8,11-tetrakis(4-carboxyphenyl)perylene (H₄L; Scheme 1) was designed



 $\label{eq:scheme1.Synthesis of 2,5,8,11-tetrakis(4-carboxyphenyl)perylene H_4L (cod = 1,5-cyclooctadiene; dba = dibenzylideneacetone).$

and synthesized based on the fact that the appended benzoic acid moieties will significantly increase the size of the linker and thus result in the formation of a MCP with large pores and high surface area. It is important to note that the use of perylene as a building unit for coordination polymers has not yet succeeded, thus emphasizing the challenging of the linker synthesis. Unlike pyrene, 2,5,8,11-tetra-substituted perylene cannot be prepared simply by traditional halogenation reactions. Yet, these specific C—H bonds can be activated and borylated by



a one-step lr-catalyzed direct C–H borylation reaction to form tetra-borylated perylene (1; Scheme 1).^[7] This tetraborylated compound 1 was then subjected to Suzuki coupling with butyl-4-iodobenzoate to give a tetra-ester intermediate (2), which was hydrolyzed to form the desired linker H₄L (see the Supporting Information).

Solvothermal reaction of H_4L with $Cu(NO_3)_2$ in the presence of the co-linker 4,4'-bipyridine (bpy) gave the green crystalline UMCM-310. The structure of UMCM-310 was evaluated by single-crystal analysis. The selective interaction of UMCM-310 toward electron-poor aromatics was demonstrated through separation experiments with nitroaromatics due to the fact that these are an important class of industrial compounds and have been widely used as explosives, dyes, insecticides, as well as herbicides. Additionally, an example of employing UMCM-310 as stationary phase for the separation of large organic molecules is presented.

Due to the nature of H_4L , a flat conjugated tetracarboxylic acid, its reaction with Cu^{II} salts was predicted to form a 2D coordination polymer. As a consequence, a 4,4'-bipyridine (bpy) pillar linker is necessary to organize 2D sheets into a 3D structure. With that in mind, bpy was added as co-linker for the MCP-formation reaction. UMCM-310 crystals were formed after approximately 4.5 h incubation of the solution containing H_4L , bpy, and Cu(NO₃)₂ in NMP/DMF/ethanol/H₂O/CF₃COOH mixture. Conducting the reaction with additional glass surfaces (see the Supporting Information) for crystals to grow also induces the formation of small particle size MCPs (10–90 µm; Figure S3 in the Supporting Information), which are desirable to increase the column-packing efficiency and thus separation performance of the MCPs.^[8] The isostructural MCP can be obtained with zinc (Figure S4 in the Supporting Information).

Single-crystal X-ray diffraction of the green cuboctahedronshaped UMCM-310 revealed that the framework consists of Cu paddlewheels linked together by perylene-based H₄L linkers and bpy. Each Cu paddlewheel is coordinated to four H₄L linkers. The co-linker bpy coordinates to the axial position of two Cu paddlewheels, making every Cu paddlewheel a five-connected node in the framework-such coordination has been rarely observed in Cu paddlewheel-based MCPs (Figure 1a). In the ligand, the four carboxylate groups and phenyl rings are twisted; the dihedral angle between the carboxylates and the perylene plane is 38.5°. The structure contains both mesopores and micropores. The mesopores are constructed with 16 paddlewheels and eight perylene linkers into a cuboctahedron shape (Figure 1b). The internal diameter is 26 Å and the largest pore window is 16.6 Å (Figure 1 c). A smaller micropore (internal diameter 13 Å) was formed with four Cu paddlewheels in a tetrahedral shape (Figure 1a). Topology analysis of UMCM-310 revealed a new net. Most of the previously reported MCPs, composed of Cu paddlewheels and tetracarboxylate linkers, crystallize in the nbo net.^[9] When bpy was used as co-linker, bimetallic paddlewheels and tetracarboxylate linkers coordinate and form 2D sheets. These sheets are connected by bpy and the obtained MCPs are fsc net.^[10] On the other hand, UMCM-310 crystalizes in a 2,4,5-c net, which has not been reported to date. We designate the net LYT.



Figure 1. a) Structure of UMCM-310 with large pore (blue) and small pore (green) indicated. b) Structure of mesoporous cage (large pore). c) Largepore window with Cu–Cu distance measured to be 16.6 Å.

UMCM-310 was activated by flowing supercritical CO₂ from methanol or acetone-soaked crystals.^[11] The Brunauer-Emmett-Teller (BET) surface area was measured from the N₂-sorption isotherm and calculated to be in the range of 4511–5110 m^2g^{-1} depending on the sample (Figure 2); this value is



Figure 2. N₂-sorption isotherm of UMCM-310 (\bullet adsorption, \odot desorption). Insert: Pore-size distribution from NLDFT fitting of the Ar-sorption isotherm.

relatively high compared with other reported MCPs. Pore-size distribution was evaluated though Ar-sorption experiment and revealed that UMCM-310 has two types of pores corresponding to the dimensions of 17 and 25 Å (Figure 2). Due to the presence of the mesopores and large pore windows (Figure 1c), UMCM-310 can potentially be used for the separation of large molecules. Despite the fact that UMCM-310 can be fully activated to have high surface area, the framework gradually collapses after guest removal as the BET surface area drops to approximately 2700 m²g⁻¹ after nine days. However, the UMCM-310 is stable in acetone or methanol, suggesting that application in liquid-phase separations is feasible.

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The separation performance of UMCM-310 toward nitroaromatic compounds was initially studied with the nitrobenzene series. A suspension of UMCM-310 (ca. 24 mg) in hexanes/dichloromethane (DCM) was packed into an HPLC column (50 \times 2.1 mm), and hexanes was chosen as the mobile phase. A mixture of nitrobenzene (NB), o-dinitrobenzene (o-DNB), and 1,3,5trinitrobenzene (TNB) were fully separated with UMCM-310 as stationary phase (Figure 3a). Similar baseline separation was obtained with the series of NB, p-dinitrobenzene (p-DNB), and TNB. The order of retention time is NB (1.2 min) < o-DNB $(4.5 \text{ min}) \approx p$ -DNB (5.6 min) < TNB (12 min). Calculation of resolution (R) between these compounds gave the value of 1.32-2.49 (see Table 3 in the Supporting Information). These high R values demonstrate the ability of UMCM-310 to fully resolve the mixture of nitrobenzenes. Overall, UMCM-310 showed strong preference for compounds containing a higher number of nitro groups consistent with a model, in which the more electron-deficient aromatic systems interacts more strongly with the perylene-based framework.

TNT is the most prevalent explosive and is widely used for both military and industrial purposes. In the manufacture of TNT, after several nitration steps, crude TNT is produced contaminated with the *meta* (unsymmetrical isomers) TNT and dinitrotoluenes (mostly 2,4-dinitrotoluene). Meta TNT can be removed through the conventional sulphitation method.^[12] However, this method is not capable of eliminating other contaminants. To minimize the amount of dinitrotoluenes (DNT), a relatively harsh nitration condition is needed, which also facilitates the formation of oxidation products. Recrystallization of crude TNT in alcohol or nitric acid is effective, yet this method causes loss of TNT.^[12,13] These obstacles emphasize the need to search for a new separation method to purify TNT from DNT. Because UMCM-310 has demonstrated its ability to differentiate nitrobenzenes based on the number of nitro groups, it can potentially be used to purify TNT. A mixture of 2,4-dinitrotoluene (2,4-DNT) and TNT was passed through a column packed with UMCM-310 with hexanes as the eluent. A complete baseline separation was obtained (Figure 4a). As expected, TNT ($t_{\rm R}$ = 10.4 min) is more retained than 2,4-DNT ($t_{\rm R}$ = 3.5 min) due to its higher level of nitration. Moreover, UMCM-310 successfully separated the mixture of 2,4-DNT and 2,6-dinitrotoluene (2,6-DNT; Figure 4b). As demonstrated in the chromatogram, 2,4-DNT elutes first followed by 2,6-DNT ($t_{\rm R}$ = 9.5 min). In a higherperformance column configuration, TNT would be easily separable from the DNT isomers. Nonetheless, the difference in retention times between the isomeric dinitroluenes indicates that, in addition to purely electronic nature of the adsorbate, other factors, such as the substitution pattern of nitration and its influence on charge distribution and substituent conformation, influence the separation.

As mentioned previously, most of the examples using MCPs as stationary phases explore small-molecule separations. For example, for MIL-47 or MIL-53, 1,3,5-triisopropylbenzene is unretained and therefore was used to determine the bed void time.^[14,2b] The separation performance of UMCM-310 towards large-molecule mixtures was evaluated through analyzing a mixture of 1,3,5-triphenyl benzene and 1,3,5-tris(4-bromophenyl)benzene, which have kinetic diameters of 11.8 and 13.6 Å, respectively.^[2a] 1,3,5-Triphenyl benzene was unretained in the columns packed with HKUST-1, and the 1,3,5-tris(4-bromophenyl)benzene was unretained in MOF-5.^[2a] A binary mixture of these compounds was completely separated by UMCM-310 (Figure 5). 1,3,5-Tris(4-bromophenyl)benzene has the longer retention time, most likely because it is somewhat more electron deficient and has stronger van der Waals interaction with the framework. This example demonstrates the ability of UMCM-310 to be used for the separation of mixtures of large organic molecules.



Figure 3. Liquid-phase separation of nitrobenzenes on a UMCM-310 packed column at a flow rate 1 mL min⁻¹: a) mixture of nitrobenzene, *o*-dinitrobenzene, and 1,3,5-trinitrobenzene ($\lambda = 219$ nm); and b) mixture of nitrobenzene, *p*-dinitrobenzene, and 1,3,5-trinitrobenzene ($\lambda = 240$ nm).

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Figure 4. Liquid-phase separation of nitrotoluenes on a UMCM-310 packed column at a flow rate 1.5 mL min⁻¹: a) mixture of 2,4-dinitrotoluene and 2,4,6-trinitrotoluene ($\lambda = 224$ nm); and b) mixture of 2,4-dinitrotoluene, 2,6-dinitrotoluene ($\lambda = 227$ nm).



Figure 5. Liquid-phase separation of a mixture of 1,3,5-triphenyl benzene and 1,3,5-tris(4-bromobenzyl)benzene on a UMCM-310 packed column (flow rate 1.5 mL min⁻¹; λ = 260 nm).

In conclusion, a new MCP, designed to interact selectively with electron-deficient aromatic compounds, is reported. UMCM-310 composed of 2,5,8,11-tetrakis(4-carboxyphenyl)perylene linker, Cu₂ paddlewheels cluster, and 4,4'-bipyridine was successfully synthesized and characterized to have high surface area ($\approx 5000 \text{ m}^2\text{g}^{-1}$) and large pore sizes. UMCM-310 is very efficient for the purification and separation of large molecules and nitroaromatic compounds.

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