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Coordination Copolymerization Mediated by $Zn_4O(CO_2R)_6$ Metal Clusters: a Balancing Act between Statistics and Geometry

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Abstract: Isolated successes of coordination copolymerization for the production of microporous coordination polymers (MCPs) have been reported recently; the logic for this synthetic approach has not been established nor have the key features of the synthetic conditions needed to generalize the method. Here, we establish guidelines for application of the copolymerization technique by exploring coordination modes and report, in addition to details on two previous coordination copolymers with exceptional properties, three new MCPs: UMCM-3 (Zn_4O(2,5-thiophenedicaboxylate)$_{1.2}$(1,3,5-tris(4-carboxyphenyl)benzene)$_{1.2}$), UMCM-4 (Zn_4O(1,4-benzenedicarboxylate)$_{3/2}$(4,4′,4′′-tricarboxytriphenylamine)), and UMCM-5 (Zn_4O(1,4-naphthalenedicarboxylate)(1,3,5-tris(4-carboxyphenyl)benzene)$_{4/3}$). The MCPs prepared by the copolymerization technique demonstrate Brunauer−Emmett−Teller (BET) surface areas between 3500−5200 m^2/g and high pore volumes (1.64−2.37 cm^3/g). In addition, the alignment of poly(3-hexylthiophene) within mesoporous channels of UMCM-1 is reported as a demonstration of the unique properties of these hosts.

Introduction

The field of crystalline microporous coordination polymers (MCPs) continues to grow at an explosive pace driven primarily by potential applications such as fuel gas storage,[1−3] separations,[4] and size selective catalysis.[5,6] The dominant synthetic paradigm exercised is rather simple, involving self-assembly of metals with symmetric ligands under suitable solvothermal conditions. At the same time, this strategy is starting to show its limitations for the generation of new materials; extending existing linkers to make analogues by insertion of spacer groups is synthetically cumbersome and can meet with failure modes including structural collapse and formation of alternative assembly modes. Interpenetration, for example, plagues cubic and tetrahedral networks leading to blockage of much of the internal surface area[7] albeit accompanied by the potential for stabilizing structure and constricting pores. More complex linker design can sometimes avoid such problems with the considerable disadvantage of multistep organic synthesis. Recently, an alternative has emerged: coordination copolymerization of topologically distinct linkers with identical coordinating functionality[8,9] can drive new modes of assembly.[10−12] For example, the first such MCP, UMCM-1 (UMCM = University of Michigan Crystalline Material), has structural features and physical properties that are not observed in materials derived from the pure linkers.[10] This discovery suggests that coordination copolymerization is a method to develop novel porous solids with exceptional levels of functionality while simultaneously avoiding the expense and time associated with exploring new

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(9) In a broad terms, all coordination polymers built with mixed ligands are copolymers. In this context, there the mixed linker systems employing both carboxylate-based ligands and pyridyl-based ligands must be mentioned. The carboxylate ligands coordinate with metal atoms to generate metal clusters. The pyridyl-based ligands coordinate to coordinatively unsaturated metal sites on the metal clusters. Because of their somewhat orthogonal reactivity, the mole fraction of the two linkers is not a significant factor for determining geometry of the structures. On the other hand, in identical functionality mixed linker system, two carboxylate-based linkers compete for coordinating metal atoms to build metal clusters (in this contribution, $Zn_4O(CO_2)_6$ clusters). Some of the MCPs assembled with both carboxylate-based linkers and pyridyl-based linkers are reported in the following:(a) Kitaura, R.; Iwahori, F.; Matsuda, R.; Kitagawa, S.; Kubota, Y.; Takata, M.; Kobayashi, T. C. *Inorg. Chem.* **2004**, *43*, 6522–6524. (b) Ma, B.-Q.; Mulfort, K. L.; Hupp, J. T. *Inorg. Chem.* **2005**, *44*, 4912–4914. (c) Chun, H.; Dybtsev, D. N.; Kim, H.; Kim, K. *Chem.*−*Eur. J.* **2005**, *11*, 3521–3529.

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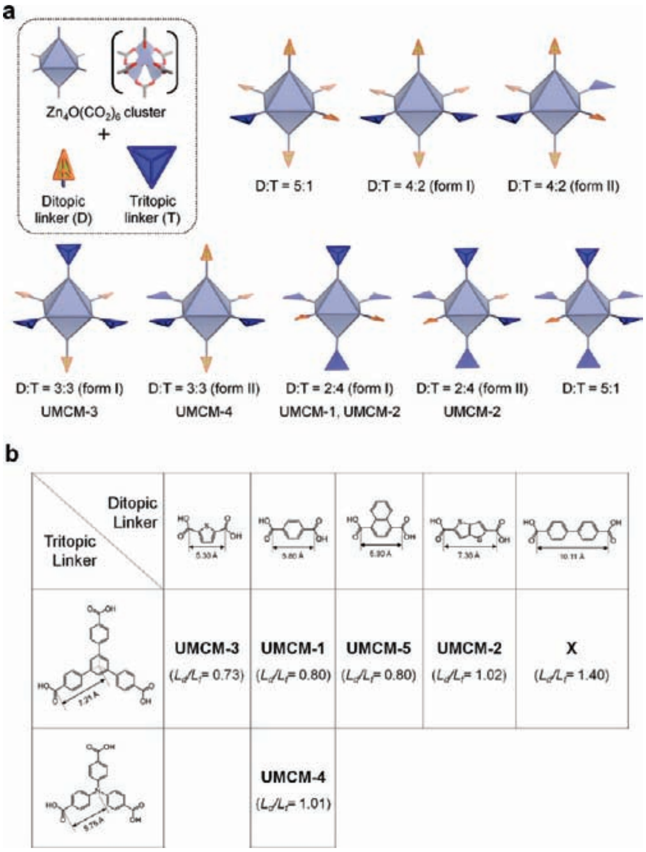

Figure 1. Coordination modes of $Zn_4O(CO_2R)_6$ clusters with two different linkers. (a) Illustration of possible modes. Blue triangles represent tritopic linkers and orange arrows correspond to ditopic linkers. (b) The combinations of tritopic and ditopic linkers tested for the preparation of MCPs.

organic linkers by leveraging existing ones. Here, we describe in detail the factors to consider in conducting discovery of materials through coordination copolymerization, present five materials, including three new structures with exceptional porosity (UMCM-3, UMCM-4, and UMCM-5), and illustrate how the unique structural properties of UMCM-1 can lead to unprecedented guest inclusion behavior.

Distinct from linear copolymerizations commonly encountered in organic polymer synthesis through covalent means, copolymerization for MCP production is an assembly technique that includes two- or three-dimensional connectivity. Therefore, the connection modes of linking units are controlled by both a geometric factor (length ratio between two linkers and connectivity to the cluster) and a statistical factor (mole fraction of two linkers and their relative reactivities). These factors are discussed below in the context of synthetic inputs to the coordination copolymerization process.

Results and Discussion

Coordination Modes of Two Different Linkers to a $Zn_4O(CO_2R)_6$ Cluster. The $Zn_4O(CO_2R)_6$ metal cluster is one of most explored building units of MCPs due to its relatively reliable formation under a variety of synthetic conditions. It has an octahedral geometry that makes six connections to organic linkers enforcing the construction of three-dimensional networks. When symmetrical ditopic and tritopic linkers with the same functionality, such as carboxylate, coordinate to an octahedral metal cluster, eight different coordination modes can arise (Figure 1a). The ratio and position of ditopic and tritopic linkers coordinated to a metal cluster serve as a means of definition. For example, when four ditopic linkers and two tritopic linker are coordinated to a metal cluster, the coordination mode is termed 4:2 (D:T) and two different modes exist differing by positioning of the linkers. Having two tritopic linkers adjacent is termed Form I and the nonadjacent arrangement is Form II. The selection of coordination modes is the result of a complex interplay of geometric and statistical factors as illustrated for the six different combinations of ditopic and tritopic linkers that we have explored (Figure 1b). The lengths of ditopic linkers are defined by the distances (L_d) between two carboxyl carbons at both ends of the ditopic linkers whereas the lengths of tritopic linkers are defined by the distance (L_t) between centroids of the tritopic linkers and carboxyl carbons. Two different behaviors resulting from a change of the L_d/L_t ratio can be envisaged, namely, building an isostructural material with perturbed pore dimensions and constructing a new structure type. In some cases, a small change of L_d/L_t causes significant connectivity alterations; as shown in Figure 1b and Figure 2, the variation of L_d/L_t yields structural diversity. In the case of the highest L_d/L_t ratio explored (1.4), a mixture of two MCPs derived from each pure linker was observed instead of the copolymer (Figure 1b); this behavior may illustrate a thermodynamic limitation arising from two geometrically mismatched linkers or may merely be a kinetic result.

As in the case of copolymerization of olefins, when considering the composition of a coordination copolymer, the ratio of ditopic and tritopic linkers in the synthetic feed is a critical factor as are their relative reactivities. For chemically similar aryl carboxylates, it might be expected that, in a kinetically controlled assembly, the reactivity of a given aryl carboxylate would be equivalent. However, statistically the consumption rate of tritopic linkers is 1.5 times faster than that of ditopic linkers at identical concentration due to the greater number of functional groups in the former. The probability of each coordination mode forming as a function of the mole ratio of ditopic and tritopic linkers provides a useful guideline for exploring the optimum synthetic condition of pure copolymers.[10] Significantly, it predicts that an excess of ditopic linker in the feed, compared with its composition in the product, is needed to produce pure copolymer. Moreover, even though certain coordination modes cannot yield energetically stable connectivity among metal clusters, the coordination reaction is reversible; therefore, defects can be repaired to build geometrically reasonable structures.

We previously reported the synthesis and structure of UMCM-1 and UMCM-2. However, these MCPs are briefly discussed here in order to highlight their relevance to the principles of 2:4 (D:T) coordination modes.

UMCM-1. This is the first MCP prepared by the copolymerization technique, and it adopts Form I of a 2:4 (D:T) coordination mode (Figure 2a). In a mole ratio range of 6:4−5:5 (1,4-benzenedicarboxylic acid (H_2BDC)/1,3,5-tris(4-carboxyphenyl)-benzene(H_3BTB)), pure UMCM-1 can be prepared (Figure 2e).

UMCM-2. The second example of an MCP prepared via coordination copolymerization, UMCM-2, has two different coordination modes of both Forms I and II of a 2:4 (D:T) mode (Figure 2b). Similar to UMCM-1, a pure product can be obtained at a mole ratio range of 6:4−5:5 (thieno[3,2-b]thiophene-2,5-dicarboxylic acid (H_2T^2DC)/H_3BTB).

UMCM-3. When Zn^{2+} reacts with 2,5-thiophenedicarboxylic acid (H_2TDC), paddlewheel clusters form rather than $Zn_4O(CO_2R)_6$ clusters, resulting in the assembly of a two-dimensional

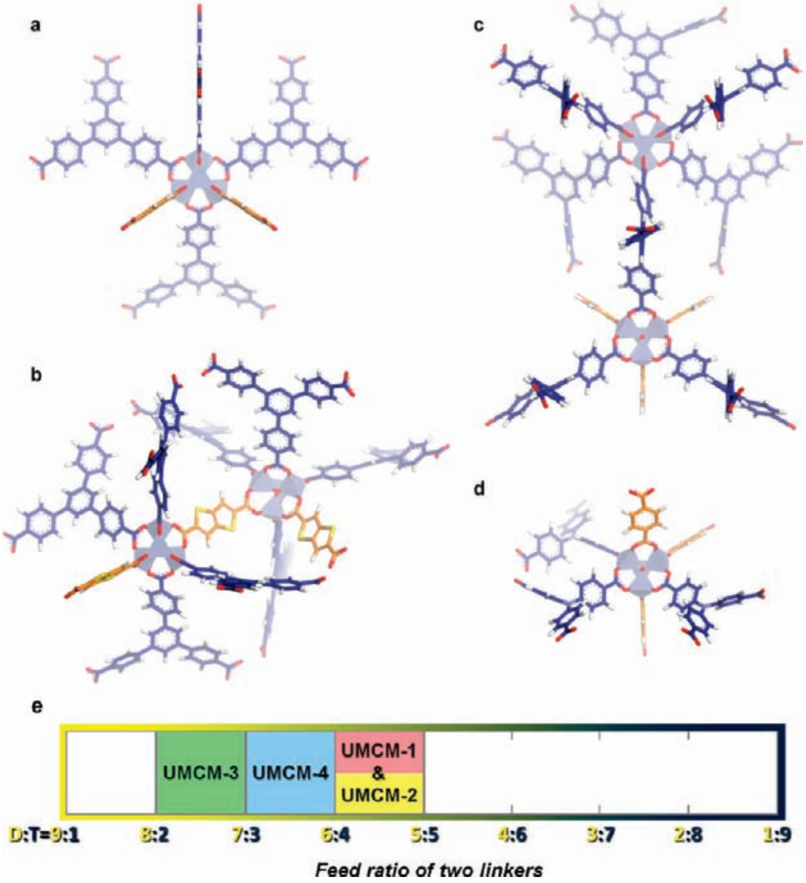

Figure 2. Zn_4O clusters coordinated to ditopic linkers and tritopic linkers. (a) UMCM-1 (UMCM-5), (b) UMCM-2, (c) UMCM-3, (d) UMCM-4, (e) the synthetic feed ratios over which they form.

structure.[13] The combination of H_2TDC and H_3BTB at a ratio between 8:2 and 7:3 in the presence of zinc nitrate results in UMCM-3, which includes two different types of coordination modes (Figure 2c). A 3:3 (D:T) coordination mode (Form I), where three ditopic linkers are perpendicular to each other (facial), coexists with a cluster having exclusively tritopic linkers coordinated to the $Zn_4O(CO_2)_6$ cluster (0:6 (D:T) coordination mode). The presence of this latter coordination mode illustrates the key role of reaction reversibility (vide infra).

UMCM-4. Whereas 4,4′,4″-tricarboxytriphenylamine (H_3TPA), a tritopic linker, reacts with Zn^{2+} to construct an interpenetrated structure,[14,15] copolymerization of H_3TPA and H_2BDC in the presence of Zn^{2+} results in the noninterpenetrated framework of UMCM-4 and can yield a pure product between 7:3 and 6:4 mol ratio of ditopic and tritopic linker in the feed (Figure 2e). As shown in Figure 2d, the coordination mode of UMCM-4 is a 3:3 (D:T) (Form II) with three ditopic linkers located in the same plane (meridional).

UMCM-5. Construction of an isostructural MCP is an efficient approach for adding functionality or introducing subtle modulation of pore structure. For example, UMCM-1-NH_2 is assembled from 2-aminodibenzenedicarboxylate (ABDC) as ditopic linker (instead of BDC), BTB, and the Zn_4O metal clusters.[16] An isostructural analog of UMCM-1 using 1,4-naphthalenedicarboxylic acid (1,4-H_2NDC) ditopic linkers can also be obtained (UMCM-5). When 1,4-H_2NDC and H_3BTB are mixed at a mole ratio of 7:3 in the presence of zinc nitrate, the 2:4 (D:T) coordination mode (Form I) is obtained.

Characterization of Pore Structures and Porosities. As described above, both UMCM-1 and UMCM-2 contain a 2:4 (D:T) coordination mode of Form I, and this feature results in constructing polyhedral cages in both structures (red cages in Figure 3a and b). In the structure of UMCM-1, which consists of exclusively of 2:4 (D:T) mode Form I, six polyhedral cages assemble together to form a hexagonal mesoporous channel; by contrast, UMCM-2 contains the 2:4 (D:T) Form II coordination mode as well as Form I, and the presence of this latter arrangement induces structural alteration. As a result, the channel-like mesopores of UMCM-1 are replaced by microporous and mesoporous cages (Figure 3b).

UMCM-3 includes both 3:3 (D:T) coordination modes (Form I) and the 0:6 (D:T) coordination mode. Synthetic conditions for UMCM-3 statistically favor a 3:3 (D:T) coordination mode, but due to the low L_d/L_t value, the connection among the metal clusters cannot be completed by this coordination mode alone. However, the reaction is reversible, and replacement with a 0:6 (D:T) coordination mode takes place leading to complete connectivity of the framework. In the 3:3 (D:T) coordination

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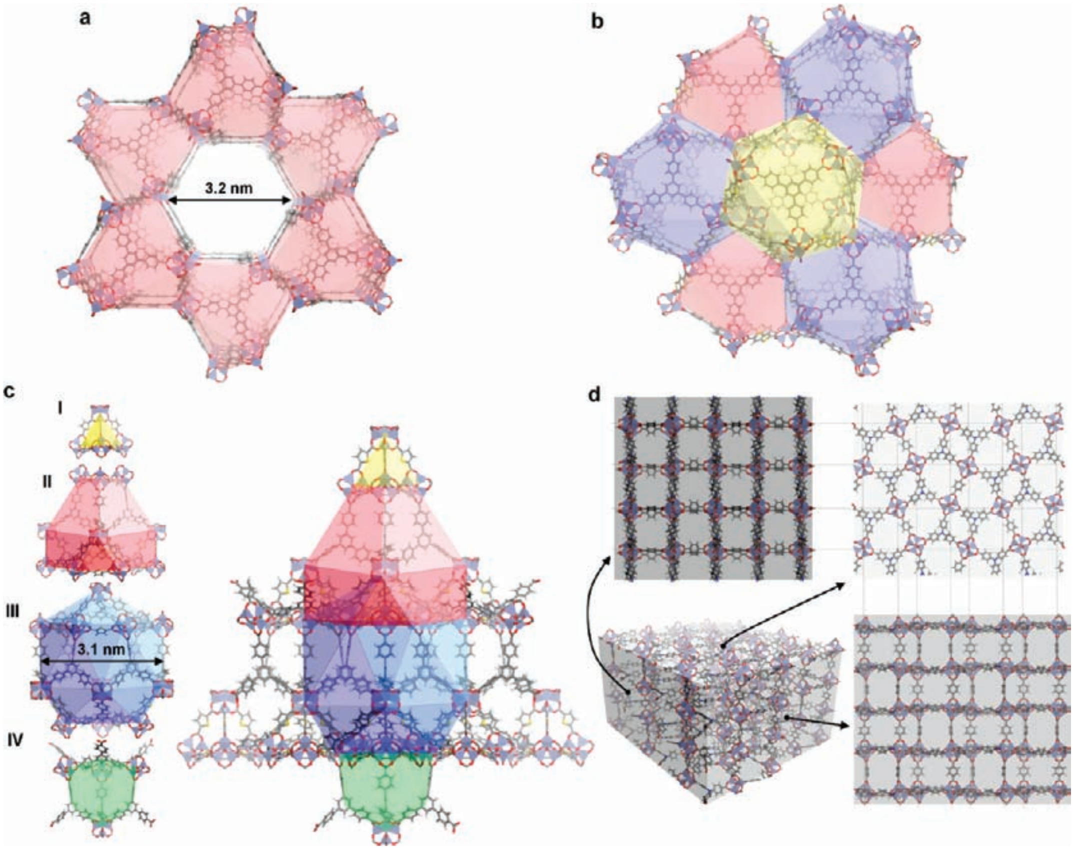

Figure 3. Structures of MCPs prepared by copolymerization. (a) UMCM-1, (b) UMCM-2, (c) UMCM-3, (d) UMCM-4.

mode, three ditopic linkers are adjacent to each other, and this orientation facilitates connection to other Zn_4O clusters, resulting in the construction of a pyramidal cage with the smallest dimension in the structure (Cage I in Figure 3c). Six tritopic linkers and four Zn_4O clusters assemble to build a cage structure (Cage IV in Figure 3c); one carboxylate of the tritopic linker does not participate in this cage structure and makes a connection in the 0:6 coordination mode to build new cages (Cage II in Figure 3c). A mesoporous cage can be observed in the framework (Cage III in Figure 3c), and its longest diameter is 3.1 nm.

Whereas UMCM-1, -2, and -3 have cagelike structures, UMCM-4 has a layered structure. UMCM-4 is assembled by a 3:3 (D:T) coordination mode (Form II), and three tritopic linkers and one ditopic linker are placed in the same plane to build layered structures. Two ditopic linkers, which are arranged opposite to each other, act as pillars rigidly spacing the layered structure.

On the basis of structural analysis, the MCPs synthesized by copolymerization are found to have highly porous structures. It should be noted that, if we consider metal clusters framework nodes, coordination of two different linkers to metal clusters results in symmetry breaking at nodes and this facilitates formation of porous frameworks without interpenetration. In many cases, such open structures do not have permanent porosity because collapse occurs upon removal of solvent guest molecules. Gratifyingly, the MCPs prepared by the copolymerization technique have high stability before and after evacuation. For example, upon discovery, UMCM-2 was the highest surface area MCP, with a Brunauer−Emmett−Teller (BET) and Langmuir surface area of 5200 and 6060 m^2/g, respectively. Recently, this record was exceeded by a material prepared through the same strategy with a different linker length ratio ($L_d/L_t = 1.03$).[17] In addition, UMCM-1 and UMCM-2 have very high N_2 saturation uptake (UMCM-1: 1500 cm^3/g; UMCM-2: 1490 cm^3/g). These values correspond to calculated pore volumes for UMCM-1 and UMCM-2 of 2.32 and 2.31 cm^3/g respectively.

Newly developed UMCM-3 and UMCM-4 also demonstrate high surface area and pore volumes. From the secondary uptake in the region $P/P_o \sim 0.13$, the N_2 sorption isotherm of UMCM-3 is classified as type IV (Figure 4a).[18] The BET surface area of UMCM-3 is calculated to be 4430 m^2/g up to the first plateau ($P/P_o \sim 0.1$). UMCM-3 also exhibits an exceptionally high N_2 saturation uptake (ca. 1530 cm^3/g) and pore volume of 2.37 cm^3/g. These values are among the highest values reported for MCPs.[19,20] The N_2 sorption isotherm of UMCM-4 follows the typical type I trend characteristic of microporous materials. UMCM-4 has a BET surface area of 3500 m^2/g and a pore volume of 1.64 cm^3/g. The stability of these highly porous materials to evacuation is hypothesized to arise from the fact that they form through an equilibrium process where, by optimizing linker identity, ratio, and disposition, optimal ar-

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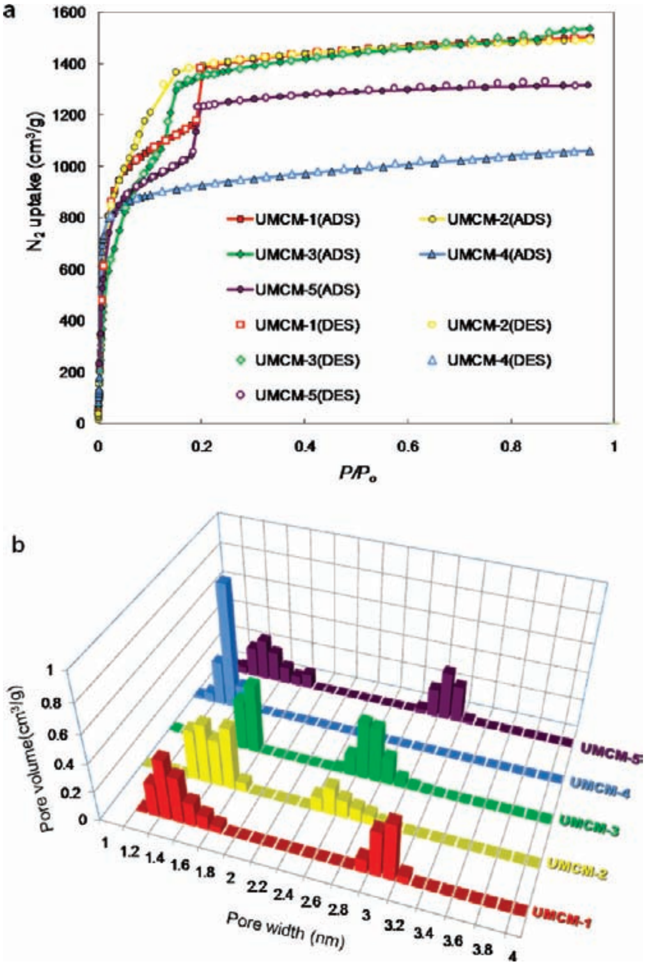

Figure 4. Pore structures and porosities of MCPs prepared by copolymerization. (a) N_2 sorption isotherms of MCPs prepared by copolymerization. (b) Comparison of pore size distribution data of MCPs. The data are calculated after fitting NLDFT models to argon gas adsorption data at 87 K.

rangements are attained that are energetically stable thus thwarting collapse.

Pore size distribution data (Figure 4b) reveal that only UMCM-4 demonstrates pure microporosity, whereas the other MCPs have both microporosity and mesoporosity. The porous structures built from the coordination copolymerization technique have not demonstrated any interpenetrated networks so far. As a result, these porous materials have large pore volumes, and they have propensity toward achieving mesoporosity. UMCM-5 has a similar pore size distribution as UMCM-1 due to the structural similarity. These results agree well with pore sizes derived from crystallography.

Conjugated Polymer Incorporation into UMCM-1. Because UMCM-1 has wide, accessible 1D channels, the potential for the material to serve as a host for large molecules was explored. Polycyclic dyes such as Nile red can readily diffuse into the framework, and Reichardt's dye, a solvatochromic zwitterion that is unable to enter MOF-177 to an appreciable extent, rapidly dyes UMCM-1 a light brown color.[21] A more dramatic example of this behavior is demonstrated by the incorporation of regioregular poly(3-hexylthiophene) (PHT, $M_n = 21\,700$, polydispersity index = 2.18) into the mesopores of UMCM-1 from solution. The highly oriented pores host and align PHT (Figure 5a). The chain diameter of PHT (ca. 1.6 nm) leads to chains intercalating exclusively in the mesopores.[22] The absorption spectrum of PHT in UMCM-1 shows marked linear dichroism; that is, a change in the absorbance is observed with respect to a change in the axis of polarized light (Figure 5b, c). This phenomenon is caused by the preferential alignment of anisotropic molecules.[23] The results here provide strong evidence that PHT molecules are aligned along the main needle axis coincident with the mesopores of UMCM-1. To assess the possibility that only oligomers are incorporated into UMCM-1, gel permeation chromatography of the PHT in UMCM-1 was performed after decomposition of the framework in aqueous base. Long polymer chains ($M_n = 17\,500$, polydispersity = 1.75) of PHT were incorporated into UMCM-1 (Table 1S in the Supporting Information), demonstrating by far the largest molecule absorbed into a coordination polymer to date and by association the absence of significant defects along the length of the mesoporous channels.

Conclusions

To summarize, two major factors should be considered when building new MCPs by coordination copolymerization. The geometric factor (length ratio between two linkers) and statistical factor (mole fraction of two linkers) both play key, and

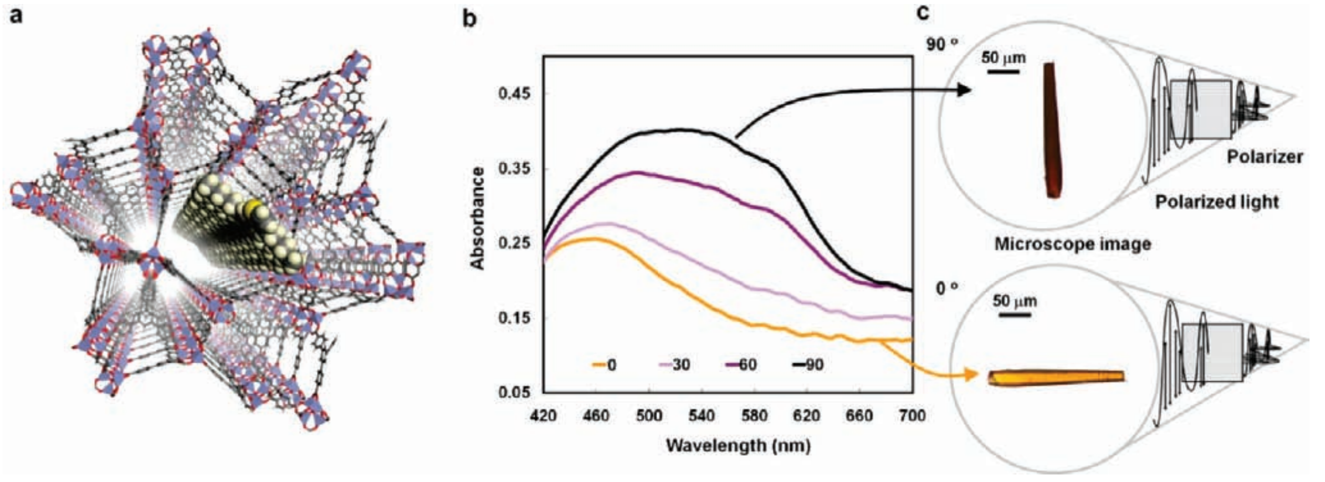

Figure 5. Incorporation of polymer chains into the mesoporous channel of UMCM-1. (a) Schematic representation of the inclusion of regioregular polyhexylthiophene (PHT, $M_n = 21700$, polydispersity index = 2.18) in UMCM-1. (b, c) UV−vis absorption spectra, and microscope images of regioregular PHT incorporated into a UMCM-1 crystal measured at several angles with respect to the plane polarized light.

interactive, roles. Subtle changes of L_d/L_t yield four different structure types (UMCM-1, 2, 3, and 4) or thwart copolymerization. In order to produce a pure copolymer, an excess concentration of ditopic linker, compared to its composition in the product, should be employed, and this consideration will be even more critical when highly functionalized linkers are employed as partners in the future. This copolymerization technique is useful for yielding highly porous materials. All five MCPs prepared by the copolymerization technique demonstrate BET surface areas between 3500 and 5200 m^2/g and high pore volumes (1.64−2.37 cm^3/g). The alignment of polymer chains within the mesoporous channels of UMCM-1 offers a glimpse at some of the unprecedented guest inclusion behavior that can be obtained in these unique materials.

Experimental Section

Synthesis of $Zn_4O(TDC)_{1.2}(BTB)_{1.2}$: UMCM-3. H_2TDC (52.5 mg, 0.305 mmol) and H_3BTB (33.0 mg, 0.0753 mmol) were dissolved in 15 mL of *N*,*N*-diethylformamide, and the solution was clarified by filtration. $Zn(NO_3)_2 \cdot 6H_2O$ (0.320 g, 1.07 mmol) was added to the solution. The mixture was sonicated for 15 min and heated to 85 °C. After 3 days, crystals of a single phase were obtained. After cooling to room temperature, the product was isolated by decanting the mother liquor and washing with DMF (3 × 15 mL). The resulting solid was then immersed in 15 mL of CH_2Cl_2 for 2 days, during which time the CH_2Cl_2 was replaced three times. The yield of the reaction, determined from the weight of the solvent-free material (48.5 mg), is 32.1% based on H_3BTB. Anal. Calcd for $C_{39.6}H_{20.4}O_{13}S_{1.2}Zn_4$: C, 47.4; H, 2.05; S, 3.83. Found: C, 47.6; H, 2.06; S, 3.64.

Synthesis of $Zn_4O(BDC)_{3/2}(TPA)$: UMCM-4. H_2BDC (19.1 mg, 0.115 mmol) and H_3TPA (28.8 g, 0.0763 mmol) were dissolved in 30 mL of *N*,*N*-diethylformamide, and the solution was clarified by filtration. $Zn(NO_3)_2 \cdot 6H_2O$ (0.150 g, 0.504 mmol) was added to the solution. The mixture was sonicated for 15 min and heated to 85 °C. After 3 days, crystals of a single phase were obtained. After cooling to room temperature, the product was isolated by decanting the mother liquor and washing with DMF (3 × 15 mL). The resulting solid was then immersed in 15 mL of CH_2Cl_2 for 2 days, during which time the CH_2Cl_2 was replaced three times. The yield of the reaction, determined from the weight of the solvent-free material (22.8 mg), is 33.2% based on H_3TPA. Anal. Calcd for $C_{33}H_{21}O_{13}N_1Zn_4$: C, 44.0; H, 2.35; N, 1.55; Found: C, 42.6; H, 2.07; N, 1.57.

Synthesis of $Zn_4O(1,4\text{-NDC})(BTB)_{4/3}$: UMCM-5. H_2NDC (57.3 g, 0.265 mmol) and H_3BTB (29.0 g, 0.0661 mmol) were dissolved in 30 mL of *N*,*N*-diethylformamide, and the solution was clarified by filtration. $Zn(NO_3)_2 \cdot 6H_2O$ (0.250 g, 0.841 mmol) was added to the solution. The mixture was sonicated for 15 min and heated to 85 °C. After 3 days, crystals of a single phase were obtained. After cooling to room temperature, the product was isolated by decanting the mother liquor and washing with DMF (3 × 15 mL). The resulting solid was then immersed in 15 mL of CH_2Cl_2 for 2 days, during which time the CH_2Cl_2 was replaced three times. The yield of the reaction, determined from the weight of the solvent-free material (22.2 mg), is 31.3% based on H_3BTB. Anal. Calcd for $C_{48}H_{26}O_{13}Zn_4$: C, 53.8; H, 2.44. Found: C, 52.6; H, 2.73.

PHT Incorporation into UMCM-1. A 2 mL solution of 1 wt % regioregular PHT in chlorobenzene was added to 5 mg of UMCM-1 immersed in chlorobenzene. The mixture was heated to 100 °C, and the solvent was slowly evaporated under an N_2 purge. After 5 h, about a quarter of solvent in the mixture had evaporated; therefore, 0.5 mL of chlorobenzene was added to the mixture to keep the solvent volume constant. The solution was cooled to room temperature, and the solid was washed with chlorobenzene (5 × 10 mL) to remove unincorporated PHT.

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Supporting Information Available: Thermal gravimetric analysis of UMCM-3,-4,-5, X-ray crystallography of UMCM-3,-4, powder X-ray diffraction data of UMCM-3, -4, -5, gas sorption measurments of UMCM-3, -4, -5, quantification and chracterization of PHT in UMCM-1, microscope images of Nile red and Reichardt's dye incorporated in UMCM-1, and X-ray crystallographic files in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(21) UMCM-1 crystals (1−2 mg) were incubated in 0.5 mL of a 2.5 wt % solution of dye (Nile red or Reichardt's dye) in CH_2Cl_2 at room temperature. After 1 day, the crystals were rinsed with fresh CH_2Cl_2 and by optical microscopy the crystals were observed to be dyed throughout.

(22) Chain diameter refers to the distance spanned by alkyl side chains that are located 180° apart from each other perpendicular to the polymer backbone. This distance is calculated to be approximately 1.6 nm assuming an eclipsed conformation of all the methylene units in the side chain.

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