polyMOF Formation from Kinked Polymer Ligands via *ortho*-Substitution

Joseph M. Palomba, Sergio Ayala Jr., and Seth M. Cohen*

Abstract: Reticular chemistry is an important tool in the crystal engineering of metal-organic frameworks (MOFs). Isoreticular chemistry allows for the preparation of MOFs of the same topology from ligands with related geometries. In this work, reticular chemistry is used to explore the scope of polyMOFs, which are frameworks synthesized from polymer ligands. “linked” *ortho*-substituted benzene dicarboxylate polymer ligands with varying length alkyl spacers were used to synthesize polyMOFs and elucidate the effects of polymer architecture on resulting crystal formation. It was found that these “kinked” polymer ligands were able to form polyIRMOF architectures, but not polyUiO-66 topologies.

Metal-organic frameworks (MOFs) are a class of porous, hybrid materials that are constructed of inorganic secondary building units (SBUs) and rigid, multitopic ligands.[1] Due to their regular coordination patterns, metal-ligand bonding creates 2- and 3-dimensional crystalline structures, in many cases with large unit cells and high porosity.[2] These structures are often categorized as reticular, or net-like, given their diverse, open networks and are often related to isoreticular, or same net, structures. Using reticular chemistry, the SBUs and ligands of MOFs are easily modified, opening up numerous possibilities for interesting, crystallographically ordered chemical environments with isostructural topologies.[3] Yaghi and co-workers reported the first preparation of isoreticular metal-organic frameworks (IRMOFs),[4] synthesized from octahedral Zn_4O SBUs and linear, ditopic benzene carboxylate (H_2bdc) linkers that differed in size (lateral extension), and/or functional group substituents. Since then, isoreticular chemistry has been applied to other series of MOFs.[5] With careful choice of organic linker and SBU, the concept of reticular chemistry can be used to fine-tune the properties of MOF materials.

Recently, polymer ligands have been used as building blocks for MOF materials producing a hybrid material termed polyMOFs. In contrast with other polymer-MOF hybrid systems, polyMOFs use pre-synthesized organic polymers containing H_2bdc units that act as ligands for MOF preparation. In a series of reports, a variety of polyMOF structures, including IRMOFs, UiO-66, pillared-MOFs, and isoreticular structures with laterally extended linkers have been described.[3b, 6] All polyMOFs to date are synthesized from ligands connected through *para*-substituted terephthalic acid (H_2bdc) with alkoxy linkages of various lengths (Figure 1). No previous reports have investigated the effects of linkage position in these polymers, and the subsequent effects on polyMOF formation. In this work we explore the tolerance of polyMOFs to *ortho*-substituted polymer ligands. This change in architecture reveals how a small modification in polymer connectivity can affect polymer properties and polyMOF formation.

The synthesis of *ortho*-substituted benzene dicarboxylate polymers (*o*-pbdc, pbdc = ‘poly’ benzene dicarboxylate) was achieved using acyclic diene metathesis (ADMET) polymerization (Scheme 1). These polymers are direct analogs to the *para*-substituted polymer ligands reported previously (Figure 1).[6a] From these *ortho*-substituted polymers, we formed polyIRMOF, the polyMOF derived from the prototypical IRMOF series synthesized by Yaghi and coworkers.[4]

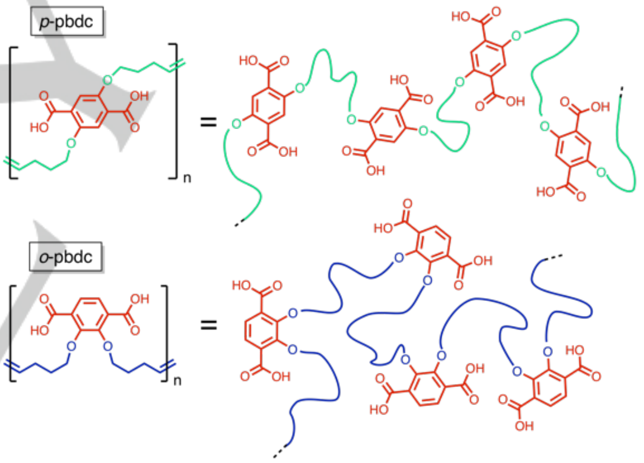

Figure 1. Comparison of *para*-substituted (*top*) and *ortho*-substituted (*bottom*, this work) polymer ligands.

Monomer synthesis was achieved in one step by Williamson ether synthesis with two equivalents of bromo-alkene ($Br(CH_2)_yCHCH_2$, $y = 3–4$) and dimethyl 2,3-dihydroxyterephathalate (Scheme 1). ADMET polymerization was employed in a concentrated solution of monomer (>1.5 M) with Grubbs’ 2nd generation metathesis catalyst, resulting in ester-protected polymer ligands (*o*-pbdc-*x*e-u, where “*x*” denotes methylene spacers between bdc ethers, “e” denotes ester, and “u” denotes unsaturation). Polymer esters were hydrolyzed to produce polymer acid ligands (*o*-pbdc-*x*a-u, where “a” indicates acid) which were used for polyMOF synthesis.

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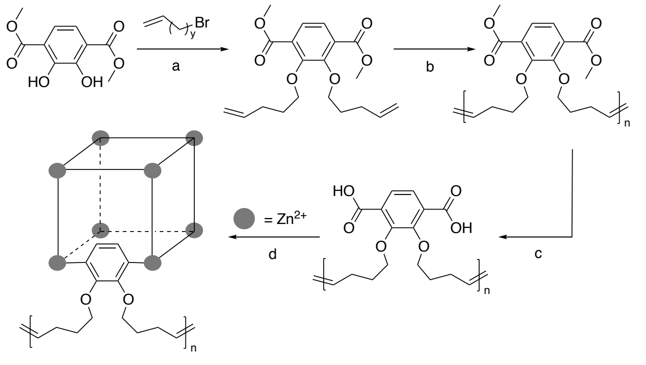

Scheme 1. Synthesis of *o*-pbdc-*x*a-u and subsequent formation of polyIRMOF-1. Shown for *o*-pbdc-8a-u, where *y* = 3. Reagents and conditions: a) K_2CO_3, DMF, 80 °C, 12 h; b) Grubbs G2 catalyst, CH_2Cl_2, 50 °C, 5 h.; c) H_2O: THF 1:1, 45 °C, 12 h; d) $Zn(NO_3)_2$, DMF, 100 °C, 24 h.

Analysis of polymer esters by ^1H NMR (Figure S1-S2) and gel permeation chromatography (GPC) (Table 1, Figure S3) reveals that polymerization yielded reasonably high molecular weight polymers. Polymer ester ligands were analyzed by GPC, as opposed to polymer acid ligands, due to the better solubility of the polyesters. Despite their high dispersity (Table 1) the polymers used throughout were free of any monomer and small-chain oligomers. While we were able to fractionate the *o*-pbdc-8e-u polymer products into narrower dispersity populations (Table S1, Figure S4, Figure S10), it was shown previously that polyMOF formation is possible using high dispersity polymers.[6a] Complete hydrolysis of polymer esters was confirmed by ^1H NMR (Figure S5) and subsequent polyMOF formation was performed using high dispersity polymers.

Table 1. Molecular weight determination of polymer esters

Polymer	M_n	M_w	Đ	DP
o-pbdc-8e-u	16100	80100	4.99	44
o-pbdc-10e-u	12200	30400	2.49	31

o-polyIRMOF-1 was synthesized from zinc nitrate and the corresponding polymer acids (*o*-pbdc-8e-u or *o*-pbdc-10e-u) under the same solvothermal conditions reported for *p*-polyIRMOF.[6b] polyMOF formation was confirmed using powder X-ray diffraction PXRD (Figure 2). The relative intensities of *o*-polyIRMOF reflections match closely to an IRMOF-1 calculated pattern, indicating that a highly crystalline material is synthesized from the amorphous *o*-pbdc polymer. Digestion of the *o*-polyIRMOF using acid dissolves the MOF structure, yielding intact polymer ligand as confirmed by ^1H NMR (Figure S5-S6). This confirms that *o*-pbdc polymer acts as the sole ligand source in polyMOF formation.

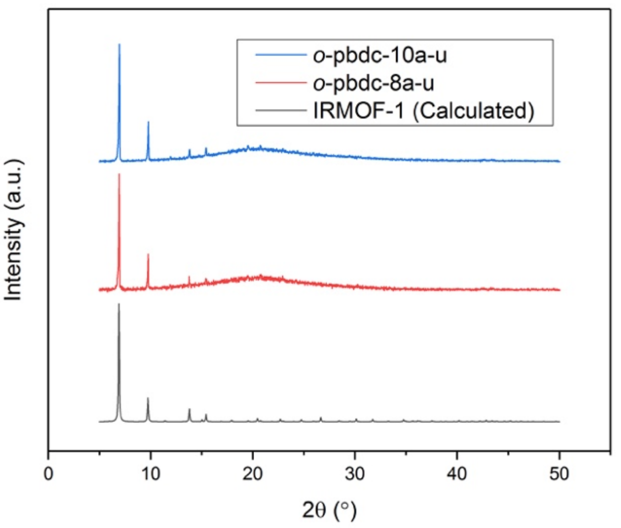

Figure 2. PXRD patterns for *o*-polyMOFs synthesized with two polymer ligands, *o*-pbdc-8a-u in red, *o*-pbdc-10a-u in blue, and calculated IRMOF-1 in black.

The particle morphology of *o*-polyIRMOF was compared to that reported for *p*-polyIRMOF using scanning electron microscopy (SEM). The crystal morphology of *o*-polyIRMOF synthesized with *o*-pbdc-8a-u shows mixtures of cubes and intergrown crystallites (Figure 3) consistent with *p*-polyIRMOF.[6b] The morphology for the *o*-pbdc-10a-u polyMOF is similar to *o*-pbdc-8a-u, but with fewer intergrown crystallites, and rather a greater number of solitary cubic crystals that possessed softened, curved edges (Figure 3). This new morphology is distinct from any seen in *p*-polyIRMOFs. These results suggest that the increase in methylene spacer length affects the *o*-polyIRMOF-1 growth without affecting the crystallinity. Formation of *o*-polyIRMOF-1 with fractionated *o*-pbdc-8a-u gave materials that were essentially the same as those obtained with unfractionated *o*-pbdc-8a-u (Figure S10). Because no notable differences were observed, no attempts to investigate fractionated *o*-pbdc-10a-u were attempted.

Nitrogen gas adsorption measurements were used to investigate the sorption properties of *o*-polyIRMOF. These materials produce a type I isotherm,[7] revealing the microporous nature of these materials (Figure 4). The calculated Brunauer-Emmett-Teller (BET) surface areas[8] are 1090 m^2/g and 960 m^2/g for the *o*-pbdc-8a-u and *o*-pbdc-10a-u generated polyIRMOFs, respectively. The surface areas of both *o*-polyIRMOFs are nearly two-thirds lower than the BET surface area of the parent IRMOF-1 (2960±30 m^2/g),[6b] but still demonstrate that these materials have a high degree of microporosity. The lower surface area of the *o*-pbdc-10a-u derived *o*-polyIRMOF when compared to the *o*-pbdc-8e-u derived *o*-polyIRMOF logically follows due to increased pore blockage by the larger alkyl spacers in pbdc-10a-u.

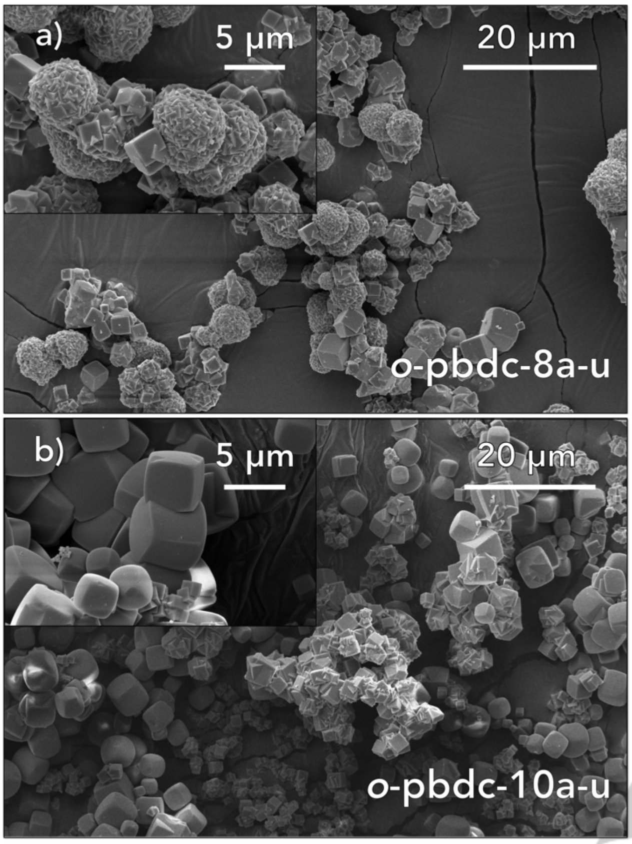

Figure 3. SEM images of *o*-polyMOFs synthesized with: a) *o*-pbdc-8a-u, and b) *o*-pbdc-10a-u.

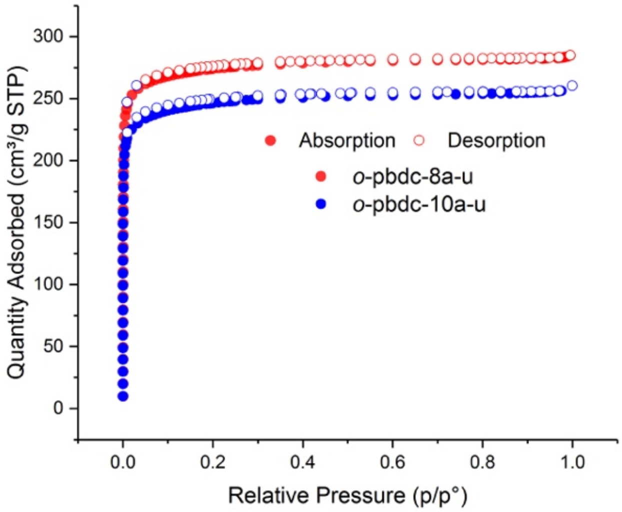

Figure 4. N_2 sorption isotherms for *o*-polyIRMOF synthesized with two polymer-ligands: *o*-pbdc-8a-u in red and *o*-pbdc-10a-u in blue.

The two *o*-pbdc ligands were also used to attempt the syntheses of *o*-polyUiO-66 materials using previously-reported polyMOF conditions that successfully formed *p*-polyUiO-66.[6a] Fractionated 8-spacer polymer ligands (*o*-pbdc-8a-u, fractions 1 and 2, Table S1, Figure S4) were also unsuccessful in producing polyUiO-66 under the same reaction conditions. In addition, *o*-pbdc-8a-u was utilized under two other reported UiO-66 synthesis conditions,[9] but were did not produce the desired polyMOF (see Supporting Information). Precipitates were obtained from these reaction solutions, indicating a Zr(IV)-coordination compound is formed, but no crystallinity was observed by PXRD analysis (Figure S7). The failure of *o*-pbdc polymer ligands to form the UiO-66 topology in these conditions may indicate the polymer is incapable of fitting into this structure type, but more exhaustive testing would be required to support this hypothesis.

There are many parallels of the *o*-pbdc polyMOFs reported here and to the isoreticular p-pbdc polyMOFs reported previously.[6a, 6b] Both systems are high molecular weight polymers with the ability to construct polyIRMOF without the aid of molecular (i.e., non-polymeric) ligands. These materials have similarly high BET surface areas (1090 and 860±16 m^2/g for *o*-pbdc-8a-u and *p*-pbdc-8a, respectively)[6b] despite the presence of polymer chains in pores of the materials. There are notable differences between the two polymer ligands and their ability to form polyMOFs, in that *o*-pbdc does not form polyUiO-66 under the same conditions used in the formation of polyUiO-66 with *p*-pbdc.

In this work, we expanded the understanding of polyMOFs by making changes to polymer ligand architecture and observing polyMOF formation ability. We are able to synthesize *ortho*-polymer ligands and synthesize some polyMOF topologies from these new polymer architectures. This work highlights the importance of the polymer ligand itself, proving that ligand architecture influences polyMOF formation. As the investigation of polyMOFs continues, designing and investigating polymer architecture will be critical to expanding the limits of these hybrid materials.

Acknowledgements

The authors would like to thank Kyle C. Bentz and Jessica C. Moreton for helpful discussions. SEM imaging was performed at the San Diego Nanotechnology Infrastructure (SDNI) of U.C. San Diego, a member of the National Nanotechnology Coordinated Infrastructure, which is supported by the National Science Foundation (Grant ECCS-1542148). This work was supported by a grant from the Department of Energy, Office of Basic Energy Sciences, Division of Materials Science and Engineering under Award No. DE-FG02-08ER46519 (S.M.C.). S.A. was supported, in part, by a fellowship from the Department of Education Graduate Assistance in Areas of National Need (GAANN) Training Grant and a fellowship funded by the Inamori Foundation.

Keywords: metal-organic frameworks • polymers • organic-inorganic hybrid materials • ligand design • reticular chemistry

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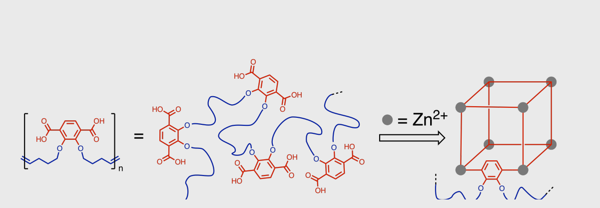

A new polymer architecture was used to generate polyMOF materials. The kinked architecture of the ligands allowed for the facile formation of Zn(II)-based IRMOFs, but not Zr(IV)-based UiO-66 materials.

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