

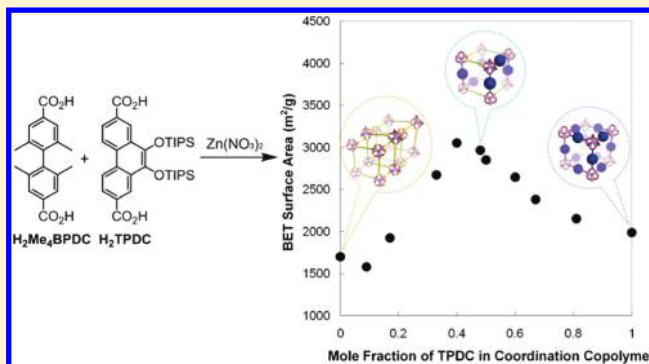
# Nonlinear Properties in Coordination Copolymers Derived from Randomly Mixed Ligands

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**S** Supporting Information

**ABSTRACT:** Random copolymerization is a core strategy of the polymer industry, enabling broad tuning of materials properties through mixing monomers with similar reactivities. In coordination polymers, analogous results have recently been achieved using combinations of isomorphous linkers copolymerized by appropriate metals; in general, the properties of the resultant coordination copolymers can be described as a linear combination of the properties of the constituent building blocks. Here we demonstrate that this need not be the case: coordination copolymerization is a powerful strategy for directing phase formation. For example, reaction of 1,4-benzenedicarboxylic acid with  $\text{Zn}^{2+}$  typically affords phase-impure material in *N,N*-dimethylformamide whereas using an amino functionalized linker leads to pure high surface area material with the structure of MOF-5. However, mixed-linker copolymers derived from a combination of both linkers display surface areas comparable to that of MOF-5 synthesized in *N,N*-diethylformamide, indicating that even a minor linker component can direct phase selection. In a second illustration, the pore blockage of the bulky group in 9,10-bis(triisopropylsilyloxy)phenanthrene-2,7-dicarboxylate (TPDC) not only suppresses the framework interpenetration of biphenyl-based IRMOF architectures but also blocks adsorption sites, yielding a low surface area material. However, the random coordination copolymerization of  $\text{Zn}^{2+}$  with a mixture of TPDC and 3,3',5,5'-tetramethyl-4,4'-biphenyldicarboxylate ( $\text{Me}_4\text{BPDC}$ ) controls the level of framework interpenetration and the degree of pore blockage, resulting in higher surface area (up to  $\sim 3000 \text{ m}^2/\text{g}$ ) copolymers than the noninterpenetrated  $\text{Zn}_4\text{O}(\text{TPDC})_3$  and interpenetrated  $\text{Zn}_4\text{O}(\text{Me}_4\text{BPDC})_3$  frameworks.



The possible modes of assembling metal clusters/ions with ligands are sufficiently diverse that structural prediction remains a major challenge for even simple coordination polymers; nonetheless, significant progress has been made in methods that construct porous architectures from organic and inorganic building blocks,<sup>1</sup> and such materials are referred to here as crystalline microporous coordination polymers (MCPs). Discovering new MCPs still relies predominantly on serendipity and, in most cases, requires extensive trial and error in optimizing crystalline material growth.

Using the principle of isostructurality, established MCP geometries can sometimes be reproduced in analogs with different metals or functionalized linkers.<sup>2</sup> Relaxing the requirements for similarity to encompass having the same net, (as in the case of isorecticular series) further expands the possibilities to include geometrically extended linkers.<sup>2a,c</sup> Although such approaches offer an element of synthetic predictability and facilitate characterization, subtle variation in reaction conditions and the building blocks often leads to geometrically different metal clusters or connectivities resulting in nonisorecticular networks.<sup>2d,3</sup> We have recently developed a coordination copolymerization approach using topologically distinct linkers<sup>4</sup> and employing two topologically identical

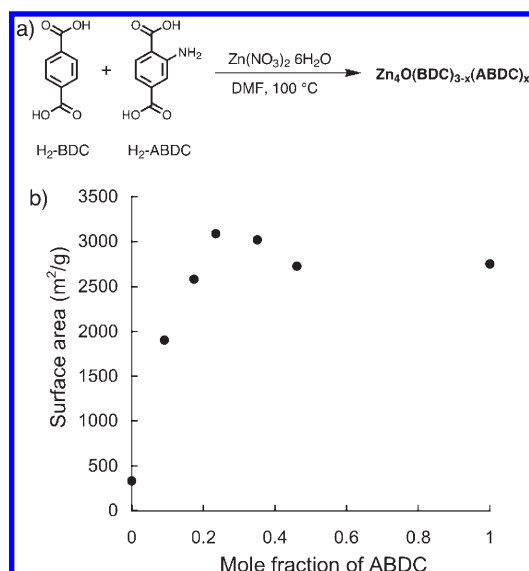
linkers within the same framework.<sup>5</sup> This latter approach allows simple variation of functionality level within a material by control of linker ratios and has shown the ability to optimize MCPs for a variety of applications;<sup>6</sup> notably, randomly incorporated second linkers within a crystalline structure have been utilized for postsynthetic functionalization of the framework,<sup>6c</sup> and the various functionalities of randomly distributed multiple linkers within pores have been shown to enhance the adsorption selectivity of a guest.<sup>6d</sup> Besides such examples, this mixed-linker coordination copolymerization can potentially provide a limitless number of tailor-made well-defined MCPs useful for several emergent applications.<sup>7</sup>

Against this background, it must be recognized that the properties of most mixed linker MCPs derived from isomorphous linkers can be understood as a linear combination of the parent structures. A question, therefore, is *can new properties arise?* Herein, we illustrate the unique utility of the coordination copolymerization approach for effecting phase selection and

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**Figure 1.** (a) Synthetic scheme for random mixed-linker coordination copolymers,  $\text{Zn}_4\text{O}(\text{BDC})_{3-x}(\text{ABDC})_x$ . (b) BET surface areas of  $\text{Zn}_4\text{O}(\text{BDC})_{3-x}(\text{ABDC})_x$  ( $0 \leq x \leq 3$ ) as a function of ABDC mole fraction in MCPs.

improving properties compared to MCPs derived from a single linker. This represents an imminently practical approach because, as in organic copolymer synthesis, these advantages are attained without incurring the expense of new linker/monomer synthesis.

**Phase Selection of Coordination Copolymers in DMF.** Its highly porous open framework and exceptional gas sorption ability have made MOF-5 one of the most studied MCPs to date. Despite a broad set of synthetic conditions and procedures developed, high surface area MOF-5 crystals (BET surface area  $\geq 3000$ ) have generally been obtained only from the reaction of 1,4-benzenedicarboxylic acid ( $\text{H}_2\text{BDC}$ ) and  $\text{Zn}(\text{NO}_3)_2$  salt in DEF as a solvent,<sup>8</sup> synthesis in DMF typically leads to phase impure material and surface areas of under  $1000 \text{ m}^2/\text{g}$ .<sup>8c</sup> In contrast, we have observed that the assembly of 2-amino-1,4-benzenedicarboxylic acid ( $\text{H}_2\text{ABDC}$ ) and  $\text{Zn}(\text{NO}_3)_2$  in DMF affords IRMOF-3, displaying porosity comparable to material synthesized in DEF.<sup>5</sup> Such phase selectivity has been utilized for the IRMOF-3 seeded growth of MOF-5 ( $\text{MOF-5}@\text{IRMOF-3}$ ) in DMF as well as DEF.

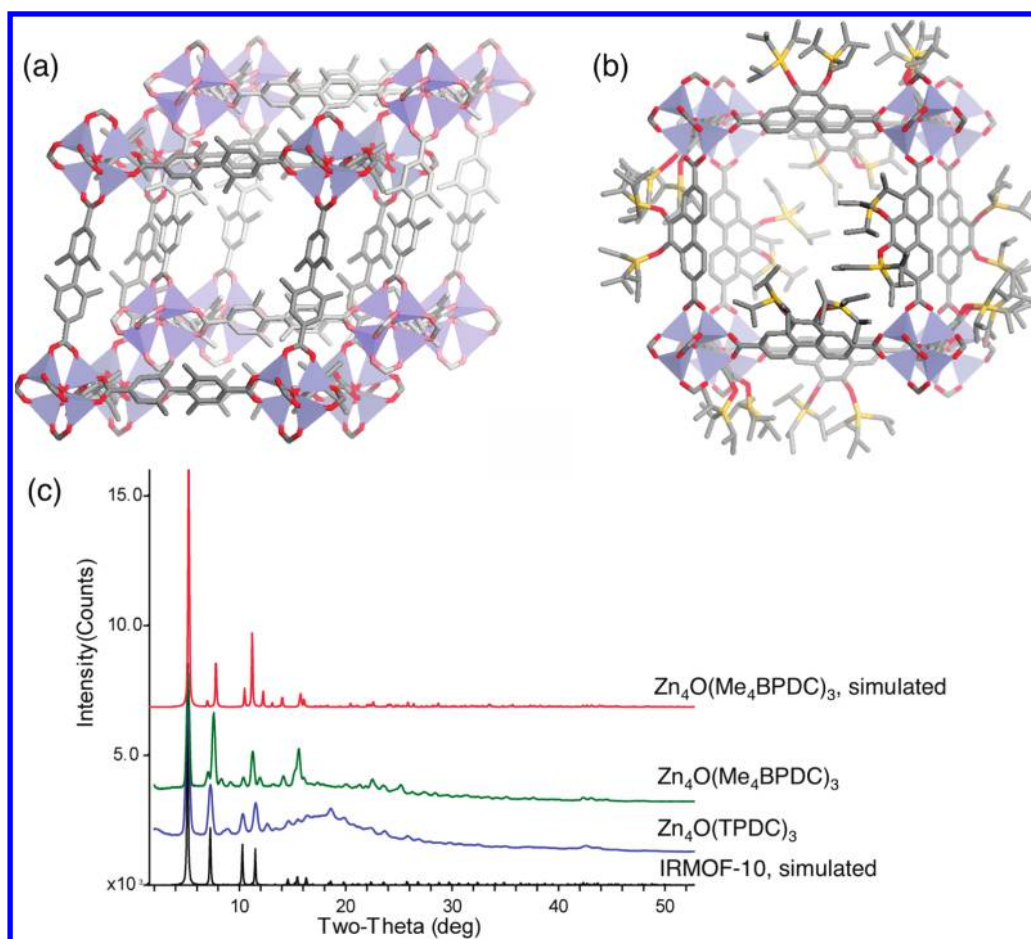
We have previously reported that the solvothermal reaction of a mixture of  $\text{H}_2\text{BDC}$  and  $\text{H}_2\text{ABDC}$  in the presence of  $\text{Zn}(\text{NO}_3)_2$  and DEF affords a coordination copolymer with the MOF-5 architecture, where the feed ratio of the two linkers controls the composition of the product, and as the ABDC content increases, the BET surface areas of the products decrease approximately linearly from that of MOF-5 to that of IRMOF-3.<sup>5</sup> On the other hand, the same coordination copolymerization reaction in DMF results in a very different relationship between surface area and copolymer composition (Figure 1). The addition of  $\text{H}_2\text{ABDC}$  to the reaction mixture of  $\text{H}_2\text{BDC}$  and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in DMF dramatically increases the BET surface areas of copolymers  $\text{Zn}_4\text{O}(\text{BDC})_{3-x}(\text{ABDC})_x$  ( $0 \leq x \leq 3$ ) from less than  $500 \text{ m}^2/\text{g}$  (pure BDC) to  $3090 \text{ m}^2/\text{g}$  for the randomly mixed coordination copolymer  $\text{Zn}_4\text{O}(\text{BDC})_{2.28}(\text{ABDC})_{0.72}$ ; this BET surface area compares favorably to MOF-5 produced in DEF.<sup>5</sup> This drastic difference, in contrast to the linear surface area change for

copolymers  $\text{Zn}_4\text{O}(\text{BDC})_{3-x}(\text{ABDC})_x$  synthesized in DEF, demonstrates the ability of ABDC (the minor component) and  $\text{Zn}_4\text{O}$  clusters to selectively assemble into the copolymer phase isostructural to MOF-5, which directs the major component (BDC) into this phase even in DMF. The general utility of this phase-directing role of a second ligand is an example of a nonlinear composition/property relationship with great potential impact for cost-effective scalable synthesis.

#### Control of Interpenetration of Coordination Copolymers.

Ideally, the elongation of an organic linker within a known MCP type should lead to an increase in pore dimension and surface area.<sup>9</sup> However, empty space within the enlarged pore often promotes the formation of doubly, or higher, interpenetrated frameworks, greatly reducing the available pore space within the MCP and reducing surface area through introducing linker-linker contacts.<sup>2a</sup> For example, the replacement of BDC with 4,4'-biphenyldicarboxylate (BPDC) in the MOF-5 framework is proposed to yield IRMOF-10; in fact, the crystals obtained from the reaction of  $\text{H}_2\text{BPDC}$  and  $\text{Zn}(\text{NO}_3)_2$  are phase impure and significantly dominated by the interpenetrated form of  $\text{Zn}_4\text{O}(\text{BPDC})_3$ : IRMOF-9.<sup>10</sup> While Snurr and co-workers computed that noninterpenetrated IRMOF-10 can reach a BET surface area of  $\sim 5000 \text{ m}^2/\text{g}$  theoretically,<sup>11</sup> the BET surface area of IRMOF-9 is only  $1900 \text{ m}^2/\text{g}$  due to interpenetration.<sup>10</sup> Accordingly, the suppression of interpenetration remains a challenge, especially in very high symmetry (cubic, diamond) networks. Noninterpenetrated MCPs have been obtained using very dilute mixtures and controlling the reaction temperature<sup>12</sup> or by a surface-induced crystal growth technique,<sup>13</sup> but these methods are not suitable to the bulk synthesis of MCPs. For preparing noninterpenetrated MCPs on large-scale, templating agents<sup>14</sup> or bulky linkers have been used,<sup>15</sup> but structural instability of frameworks or blockage of pore apertures can result in poor accessible surface area for noninterpenetrated MCPs.<sup>9,15b</sup> Other approaches employing geometrically predisposed highly symmetric linkers<sup>16</sup> or reduced symmetry linkers have been recently used to avoid interpenetration<sup>3c</sup> but these methods are specific to certain ligand classes.

The high percentage of empty space within the noninterpenetrated biphenyl-based IRMOFs, such as IRMOF-10, IRMOF-12, and IRMOF-14, and the apparent impossibility of preparing these as pure materials has led us to test the approach that bulky functional groups on the linker should lead to pore blockage, suppressing the formation of the second framework within the pore.<sup>15</sup> For this purpose, two biphenyl-based dicarboxylic acid linkers, 2,2',6,6'-tetramethylbiphenyl-4,4'-dicarboxylic acid ( $\text{H}_2\text{Me}_4\text{BPDC}$ )<sup>17</sup> and 9,10-bis(triisopropylsilyloxy)phenanthrene-2,7-dicarboxylic acid ( $\text{H}_2\text{TPDC}$ ), were synthesized. A crystalline solid was obtained under conditions where a mixture of  $\text{H}_2\text{Me}_4\text{BPDC}$  and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in DEF was heated at  $100^\circ\text{C}$  for 12 h. The single crystal X-ray structure of  $\text{Zn}_4\text{O}(\text{Me}_4\text{BPDC})_3$  shows it to have a doubly interpenetrated framework (Figure 2a) where, apparently, the steric bulk of the four methyl groups and the orthogonal phenyl-phenyl conformation of the aromatic rings are not sufficient to suppress framework interpenetration. The BET surface area of  $1700 \text{ m}^2/\text{g}$  for  $\text{Zn}_4\text{O}(\text{Me}_4\text{BPDC})_3$  is slightly lower than that of IRMOF-9, in line with expectations.<sup>9</sup> On the other hand, the solvothermal reaction between  $\text{H}_2\text{TPDC}$  and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in DEF afforded yellow cubic crystals. Although extensive disorder of the TIPS group limits the quality of the refined structure, a single crystal X-ray diffraction study reveals that the crystal belongs to a cubic space group and the dimension of the



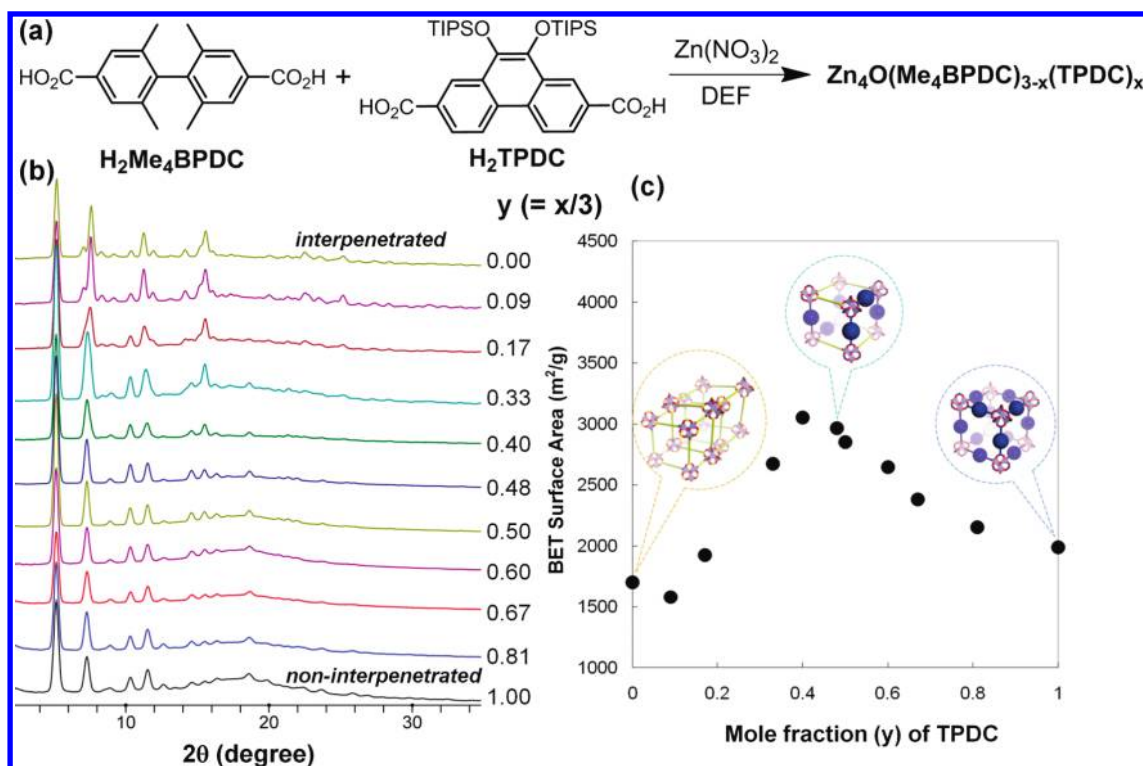
**Figure 2.** (a) Crystal structure of interpenetrated  $\text{Zn}_4\text{O}(\text{Me}_4\text{BPDC})_3$ . (b) Schematic representation of framework structure of noninterpenetrated  $\text{Zn}_4\text{O}(\text{TPDC})_3$  with disordered substituents placed at fixed positions. (c) From the top, PXRD patterns of  $\text{Zn}_4\text{O}(\text{Me}_4\text{BPDC})_3$  (red; simulated from the crystal structure),  $\text{Zn}_4\text{O}(\text{Me}_4\text{BPDC})_3$  (green),  $\text{Zn}_4\text{O}(\text{TPDC})_3$  (blue), and IRMOF-10 (black; simulated).<sup>2a,10</sup>

unit cell is 34 Å, which closely resembles IRMOF-10 and its analogs.<sup>2a,15b</sup> Moreover, the nearly identical PXRD pattern for  $\text{Zn}_4\text{O}(\text{TPDC})_3$  to that simulated from the crystal structures of noninterpenetrated biphenyl-based  $\text{Zn}_4\text{O}(\text{linker})_3$  MCPs<sup>2a,15b</sup> in combination with the  $^1\text{H}$  NMR evidence for the existence of TIPS groups (Figure S1 of the Supporting Information) strongly support the formulation of a noninterpenetrated framework for  $\text{Zn}_4\text{O}(\text{TPDC})_3$ , where the TIPS groups of the linker barricade the pores, preventing the introduction of the second framework (Figure 2b). However, the bulky TIPS groups occupying the pores lead to a BET surface area of 1990  $\text{m}^2/\text{g}$  for  $\text{Zn}_4\text{O}(\text{TPDC})_3$ , very similar to interpenetrated IRMOF-9 but much smaller than the surface area theoretically predicted for IRMOF-10.<sup>11</sup>

The above results suggest that if a linker is sufficiently bulky to prevent interpenetration, then it may block adsorption sites, leading to little overall advantage.<sup>15b</sup> A solution for this dilemma is to mix both bulky and nonbulky linkers together. The solvothermal reaction between  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  and a mixture of  $\text{H}_2\text{Me}_4\text{BPDC}$  and  $\text{H}_2\text{TPDC}$  in DEF afforded yellow crystals. The composition of the product was determined by  $^1\text{H}$  NMR spectroscopy of a solution obtained from digesting the yellow crystals with HCl in  $\text{DMSO}-d_6$  (Supporting Information). PXRD measurements reveal the differences in structural features of a series of  $\text{Zn}_4\text{O}(\text{Me}_4\text{BPDC})_{3-x}(\text{TPDC})_x$  ( $0 \leq x \leq 3$ ) copolymers (Figure 3b). The  $\text{Zn}_4\text{O}(\text{Me}_4\text{BPDC})_3$  PXRD pattern is the

same as that simulated from its single crystal structure, exhibiting interpenetration (Figure 2c). As the concentration of the very bulky  $\text{H}_2\text{TPDC}$  is increased in the reaction mixture, the PXRD patterns of the resulting mixed-linker crystalline solid gradually change from the interpenetrated  $\text{Zn}_4\text{O}(\text{Me}_4\text{BPDC})_3$  phase to the noninterpenetrated  $\text{Zn}_4\text{O}(\text{TPDC})_3$  phase. At 9 mol % of TPDC incorporation ( $y = 0.09$ ), the pale yellow solid exhibits framework interpenetration. As the TPDC amounts increase to 40 mol % ( $0.1 \leq y \leq 0.4$ ), the noninterpenetrated framework appears and then gradually replaces the PXRD pattern of the interpenetrated copolymers. On the other hand, at over 40 mol % of TPDC ( $y > 0.4$ ), the PXRD patterns of the yellow cubic crystals obtained agree well with that of noninterpenetrated  $\text{Zn}_4\text{O}(\text{TPDC})_3$ , indicating that the bulky TIPS groups of TPDC drastically reduce the framework interpenetration within these random coordination copolymers. The dependence of surface area on composition reveals the advantage of this approach (Figure 3c). First, a slightly reduced surface area is observed for interpenetrated  $\text{Zn}_4\text{O}(\text{Me}_4\text{BPDC})_{2.33}(\text{TPDC})_{0.27}$  ( $y = 0.09$ ) compared to that of pure  $\text{Zn}_4\text{O}(\text{Me}_4\text{BPDC})_3$ ; the introduction of a small amount of the sterically demanding TPDC into the interpenetrated  $\text{Zn}_4\text{O}(\text{Me}_4\text{BPDC})_3$  framework results in a reduced surface area of the mixed-linker MCP. As the TPDC content within the mixed-linker coordination copolymers reaches the 40–50 mol % level of incorporation, the BET surface





**Figure 3.** (a) Synthetic scheme, (b) PXRD patterns, and (c) BET surface areas of coordination copolymer  $\text{Zn}_4\text{O}(\text{Me}_4\text{BPDC})_{3-x}(\text{TPDC})_x$  ( $0 \leq x \leq 3$ ) as a function of TPDC mole fraction ( $y = x/3$ ) in MCPs.

areas of the products dramatically increase to approximately  $3000 \text{ m}^2/\text{g}$ , which is the highest BET surface area experimentally obtained for biphenyl-based IRMOFs.<sup>2a,10,15b</sup> As the PXRD indicates, in the range of 40–50 mol % TPDC, the majority of crystals possess the noninterpenetrated frameworks, thus greatly increasing the surface area because the less bulky  $\text{Me}_4\text{BPDC}$  linkers within the noninterpenetrated framework reduce the proportion of inaccessible sorption sites and enlarge the pores with respect to those of  $\text{Zn}_4\text{O}(\text{TPDC})_3$ . As TPDC concentrations continue to increase, the surface areas, however, decrease because the TIPS group now fills the pores, thus blocking sorption sites. Importantly, we also note that in contrast to the nonlinear surface area change for the  $\text{Me}_4\text{BPDC}$ -TPDC coordination copolymers, the surface areas obtained from physical mixtures of pure  $\text{Zn}_4\text{O}(\text{Me}_4\text{BPDC})_3$  and  $\text{Zn}_4\text{O}(\text{TPDC})_3$  vary linearly based on that of pure  $\text{Zn}_4\text{O}(\text{Me}_4\text{BPDC})_3$  to that of  $\text{Zn}_4\text{O}(\text{TPDC})_3$  (Figure S2 of the Supporting Information). These results highlight the strategy of using mixed linkers in a coordination copolymerization fashion to control the level/extent of interpenetration of a framework by combining linkers that are metrically similar along one axis but quite dissimilar in the other two, thus ultimately influencing pore size and surface area.

Random mixed-linker coordination copolymers can achieve enhanced properties compared to either homopolymer. The presence of  $\text{H}_2\text{ABDC}$  in the reaction of  $\text{H}_2\text{BDC}$  and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  in DMF directs phase selective  $\text{Zn}_4\text{O}(\text{linker})_3$  formation, producing a copolymer comparing favorably with MOF-5 synthesized in DEF. This synthetic approach may significantly reduce the cost of bulk synthesis of a highly porous IRMOF by replacing DEF with DMF. The very bulky TIPS groups of TPDC prevent the interpenetration of the framework but result in a low surface area material due to pore blockage. Under conditions that

generate the  $\text{Zn}_4\text{O}$  cluster, TPDC and the nonbulky isomorphous linker  $\text{Me}_4\text{BPDC}$  can control the level of interpenetration depending upon the linker composition. The combined effect of the noninterpenetrated framework caused by TPDC and the reduced pore blockage due to the  $\text{Me}_4\text{BPDC}$  struts of the framework increases the surface areas of the copolymers to over  $3000 \text{ m}^2/\text{g}$ , the highest surface areas for biphenyl-based  $\text{Zn}_4\text{O}(\text{linker})_3$  coordination polymers. The limitless linker combination that can be employed in coordination copolymerization and unique properties obtainable will allow a variety of new applications not achievable economically from single linker systems.

## ■ ASSOCIATED CONTENT

**S Supporting Information.** Synthesis, characterization, X-ray crystallographic file (CIF), and disclaimer. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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