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Porous Organic Polymers in Catalysis: Opportunities and Challenges

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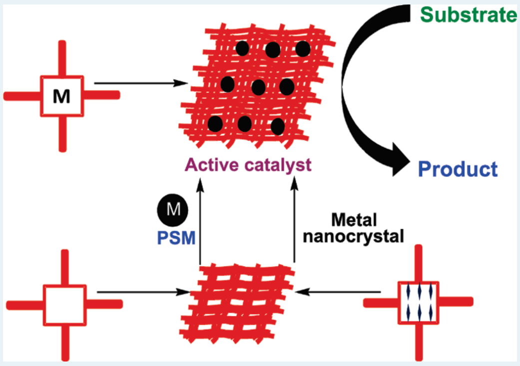
ABSTRACT: Porous organic polymers (POPs), a class of highly cross-linked, amorphous polymers possessing micropores, have recently emerged as a versatile platform for the deployment of catalysts. These materials can be divided into three major classes: POPs that incorporate rigid well-defined homogeneous catalysts as building blocks, POPs that can be modified post-synthesis, and POPs that encapsulate metal particles. This perspective article summarizes the recent developments in POP-based catalysis and outlines the potential of POPs as platforms of heterogeneous catalysts along with some of the challenges.

KEYWORDS: porous organic polymers, conjugated porous polymers, hyper-cross-linked polymers, heterogeneous catalysis



1. INTRODUCTION

Over the past two decades, microporous materials[1−7] have garnered considerable attention from both the academic and the industrial communities due to their wide range of potential applications in storage,[8] separation,[9−13] and catalysis.[14] Microporous (i.e., having pore sizes <2 nm) zeolites, silicas, and activated carbon have been extensively employed as catalysts and catalyst supports[15] given their high surface areas and pore sizes that are comparable to small molecules. Their heterogeneous structure and chemical nature, however, limits their potential for chemoselective processes. Primarily during the past decade, a variety of newer classes of micro- and meso-porous (2−50 nm) materials, such as metal−organic frameworks (MOFs),[1−8] crystalline covalent-organic frameworks (COFs),[16−22] and amorphous microporous/porous organic polymers (POPs)[3,23,24], have been constructed from catalytically active, molecular building blocks and then employed for chemical catalysis, often with high selectivity. While POPs arguably are the easiest to make among the three aforementioned classes of materials, they are noncrystalline and have nonuniform pores that are typically somewhat ill-defined. Thus, their behaviors in catalysis are often more difficult to understand, and their designs are more difficult to control. As development of the general field of molecule-derived porous materials is progressing at a rapid rate and studies reporting the catalytic behavior of POPs are beginning to appear, we would like to offer our perspectives on the opportunities and challenges that lie ahead for this intriguing class of materials.

Porous polymers have been intentionally synthesized since at least the early 1960s[25,26] by incorporating di/multitopic monomers into well-known step growth and chain-growth polymerization processes (radical, anionic, cationic, and condensation, for example) to provide cross-links between propagating polymer chains, yielding three-dimensional (3D)-network materials. It can be argued that the most successful class of these materials are those based on the polystyrene-divinylbenzene system, which have been extensively manufactured as resins and membranes for many uses, including water purification, water softening, and supports for synthesis. In the late 1980s, the copolymerization strategy was combined with the use of discrete molecular porogens to create molecularly imprinted polymers (MIPs). These latter materials have moderate (200−800 m^2/g) Brunauer−Emmett−Teller (BET) surface areas and have been extensively investigated in solid phase extraction and sensing applications.[27−30] While they have also been explored for catalysis, as well-documented in several reviews,[31−36] their chemo- and stereoselectivities are generally low because of their mainly macroporous (>50 nm) nature. In part, these limitations can be attributed to the inadequacy of the synthetic strategies available at the time: although the idea of using molecules to template pores that are capable of molecular recognition and selective catalysis within a network is a sensible one, the limited range of monomers and bond-forming reactions available from the traditional polymerization literature did not allow researchers to closely mimic the molecular features of the template. In addition, the polymerization/cross-linking kinetics is often too fast and difficult to control, yielding macro- instead of micropores.

Attempts were made in the late 1990s[37] to synthesize microporous organic polymer materials from monomers possessing

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Table 1. Representative List of Catalytic Porous Organic Polymers and the Reactions They Have Been Shown to Catalyze[a]

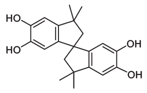
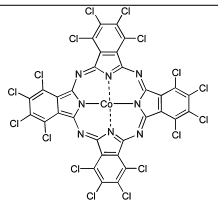
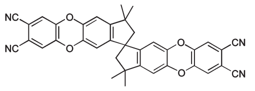
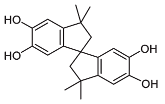
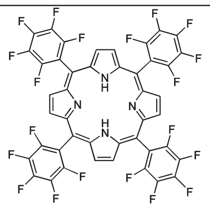
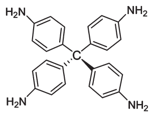
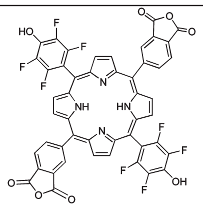
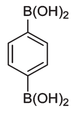
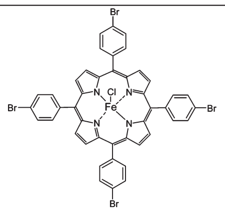
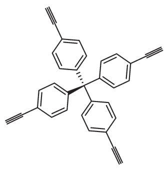
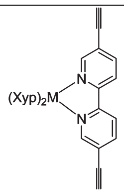
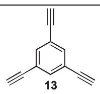
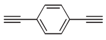
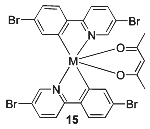
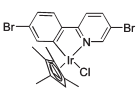
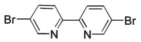
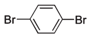
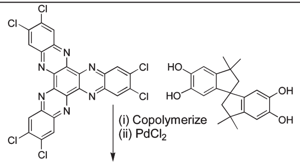
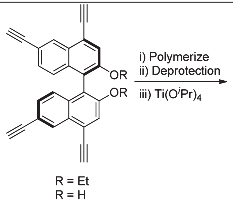
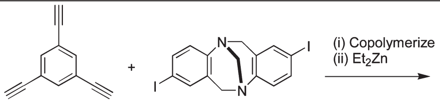
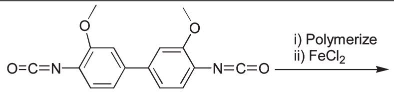
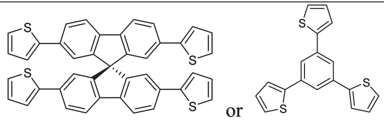
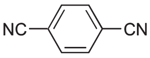
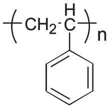
Porous Organic Polymers[a]	**Monomers**	**Substrates and Reagents**	**Catalyzed Reactions**	**Reference**
CoPc-PIM	 and  or in situ formation of metallophthalocyanine from 	Hydrogen peroxide Cyclohexene Hydroquinone Sulfide	Decomposition Oxidation Oxidation Oxidation	59 59 59 62
FeP-PIM	 and  i) Copolymerize, then ii) Post-synthesis metalation	Hydroquinone	Oxidation	59
Mn-PPOP and **Fe-PPOP**	 and  i) Copolymerize, then ii) Post-synthesis metalation	Styrene Cyclohexane	Epoxidation Oxidation	77 77
FeP-CMP	 and 	Sulfides	Oxidation	75
Ru- and **Ir-PCPs**	 and  M = Ru, Ir	**[M = Ir, Ru]**: Aromatic amines **[M = Ru]**: Bromomalonate **[M = Ru]**: 3-phenylpropanal	aza-Henry α-arylation oxyamination	79 79 79
MO-CMPs	 **13**  **14**  **15**  **16**  **17**  **18**	**[13 + 14 + 16]**: Ketones	Reductive amination	80

Table 1. Continued

Porous Organic Polymers[a]	Monomers	Substrates and Reagents	Catalyzed Reactions	Reference
Hatn-derived network polymers		N/A	N/A	81
CCPs		Aldehyde	Et_2Zn addition	82
Troger's base-derived polymer		Aldehyde	Et_2Zn addition	85
PICU		Alcohol	Oxidation	86
CMPTA-encapsulated Pd nanoclusters	 i) Polymerize, then ii) PSM incorporation of Pd nanoclusters	Diphenylacetylene	Reduction	93
CTF-encapsulated Pt nanoclusters	 i) Polymerize, then ii) PSM incorporation of Pt nanoclusters	Glycerol	Oxidation	98
HPS-encapsulated Pt nanoclusters	 i) React with ditopic cross-linkers, then ii) PSM incorporation of Pt nanoclusters	L-sorbose	Oxidation	103

[a] CCPs = chiral cross-linked polymers; **CoPc-PIM** = cobalt phthalocyanine polymer of intrinsic microporosity; CMPTA = conjugated microporous poly(thienylene arylene); CTFs = covalent triazine frameworks; **FeP-PIM** = iron porphyrin polymer of intrinsic microporosity; **Fe-PPOP** = iron porphyrin porous organic polymer; **FeP-CMP** = iron(III) porphyrin conjugated microporous polymers; Hatn = hexaazatrinaphthylene; **Mn-PPOP** = manganese porphyrin porous organic polymer; MO-CMPs = Metal-organic conjugated microporous polymers; PICU = polyisocyanurate; **Ru-** and **Ir-PCPs** = Ruthenium and Iridium porous cross-linked polymers.

higher valency/topicity and more complex shapes so that better molecular recognition features could be engendered in the pores. In addition, slower bond-forming reactions were employed to allow for the formation of pores that more closely match the dimensions of potential guest molecules.[7] In this perspective article, we will focus on the potential of this emerging class of microporous organic polymers to serve as selective heterogeneous catalysts. Although an appreciable amount of work has been carried out on the use of these materials in gas storage and chemical separations,[3,7,38−40] only a small number of reports have explored their use in chemical catalysis.

Microporous polymeric materials of different types have been denoted by many different names, including polymers of intrinsic microporosity (PIMs), porous organic frameworks (POFs), conjugated microporous polymers (CMPs), and porous aromatic frameworks (PAFs). These materials are amorphous but typically possess relatively high, internal surface areas, attributable to micro- and mesopores that are constructed from rigid, multitopic building blocks. Here, we will use the term porous organic polymers (POPs) to broadly label amorphous, microporous organic polymer materials. For convenience, we will separate the few POPs that are catalytically active into three classes: (a) those that employ homogeneous catalysts as polymer building blocks, (b) those that can be modified post-synthetically to create POP-based catalysts, and (c) those that encapsulate well-defined metal nanoclusters and nanoparticles in their pores. Representative examples of these materials are listed in Table 1, along with their compositions and the reactions that they are known to catalyze. In addition to summarizing the composition and catalytic activities of these POPs, we will discuss the potential advantages of an all-organic microporous framework design, the incorporation of active catalyst sites that enable pore-based instead of opportunistic catalysis, and the challenges inherent to developing POPs that can usefully function as catalyst platforms.

2. DESIGN FEATURES AND ADVANTAGES OF POROUS ORGANIC POLYMERS

In contrast to traditional syntheses of macroporous polymers, where long chains of polymerized monomers are interconnected by ditopic cross-linkers,[41] POPs are generally constructed from monomer units that are multitopic (three or more connection points). While the degree of cross-linking in a macroporous polymeric material depends on the concentration of cross-linking molecules added, cross-linking in POPs is dictated by the valency/topicity of the monomer or co-monomer unit(s). Cross-links in POPs, formed between rigid building blocks, are also different from those in polymer gels, which are usually formed between flexible chains and side chains. Interested readers should consult the excellent reviews by McKeown and Budd[3] and Jiang and Cooper.[40]

As in many porous materials, POPs can only achieve permanent microporosity when they are constructed from comparatively rigid monomers that, when cross-linked, yield pores with similarly rigid walls. Biphenylene-containing POPs, made by linking tetrakis(phenyl) subunits using Yamamoto coupling, have been shown to have specific surface areas (SSAs) as high as 5640 m^2/g,[42−44] exceeding those of most MOFs and rivaling those for MOFs with the very highest surface areas (ca. 6200 m^2/g).[45−47] Key to the extraordinary surface area is the absence of network interpenetration (most POPs are at least partially interpenetrated) and the near completeness of the coupling chemistry (thereby eliminating mesoporosity). Additionally, the combination of these two characteristics appears to yield, for the POPs with ultrahigh SSAs, micropores of uniform size (albeit, still lacking crystallinity). As discussed further below, pore-size uniformity is rare for POP materials.

Among the POPs that have been applied to catalysis, covalent triazine frameworks (CTFs) have the highest reported SSA (>2,500 $m^2\ g^{-1}$).[48] Other catalytically active POPs such as PIMs, CMPs, and porphyrin-based POPs (PPOPs) have more modest SSAs, in the range of 300−1100 $m^2\ g^{-1}$, where in each case the area is derived from gas-sorption measurements. However, specific surface areas are not necessarily good indicators of how well these materials will perform in catalysis reactions involving substrates dissolved in a solvent (as opposed to volatilized into the gas phase). A more important parameter is the size of the POP aperture, as this dictates the upper size limit for substrates entering the pores. As implied above, POP pore (and aperture) sizes can be difficult to control synthetically, if cross-links form quickly and irreversibly and/or if framework interpenetration occurs. Finally, it is important to note that the degree of connectivity between the building blocks constituting POPs usually is high enough to yield mainly micropores as well as preclude swelling via sorbed vapor or solvent molecules. Indeed, only rarely has evidence for sorbate-induced plasticization been reported—and then only for POPs known to contain a significant fraction of mesopores.

Beyond traditional polymerization processes, the syntheses of POPs have drawn from an enormous number of modern bond-forming methodologies to yield a wide range of structural frameworks. Among the most popular reactions for the construction of POPs are the following: Pd-catalyzed coupling,[49] imidization,[50] amidation,[50] imine formation,[51] aminal formation,[52] dibenzodioxane formation,[38] Friedel−Crafts alkylation,[48,53] and nitrile polymerization.[48] This broad base of bond-formation chemistry contributes to the stability advantage that POPs typically have, compared with most MOFs and COFs. While the latter two classes of materials feature well-defined and uniformly sized pores, their reversible coordination-bond-based (or hydrolytically unstable B−O bond-based) construction often limits the conditions under which they can be used. In contrast, many POPs can be safely exposed to a wide range of aggressive media. The exceptional chemical stability of certain POPs can enable their use as catalysts in many wet chemical environments without framework degradation or loss of microporosity. For example, several POPs have been shown to be stable under commonly encountered catalytic reaction conditions such as high moisture,[24] high acidity, and/or high basicity[54] because of their irreversible bond formation chemistries.

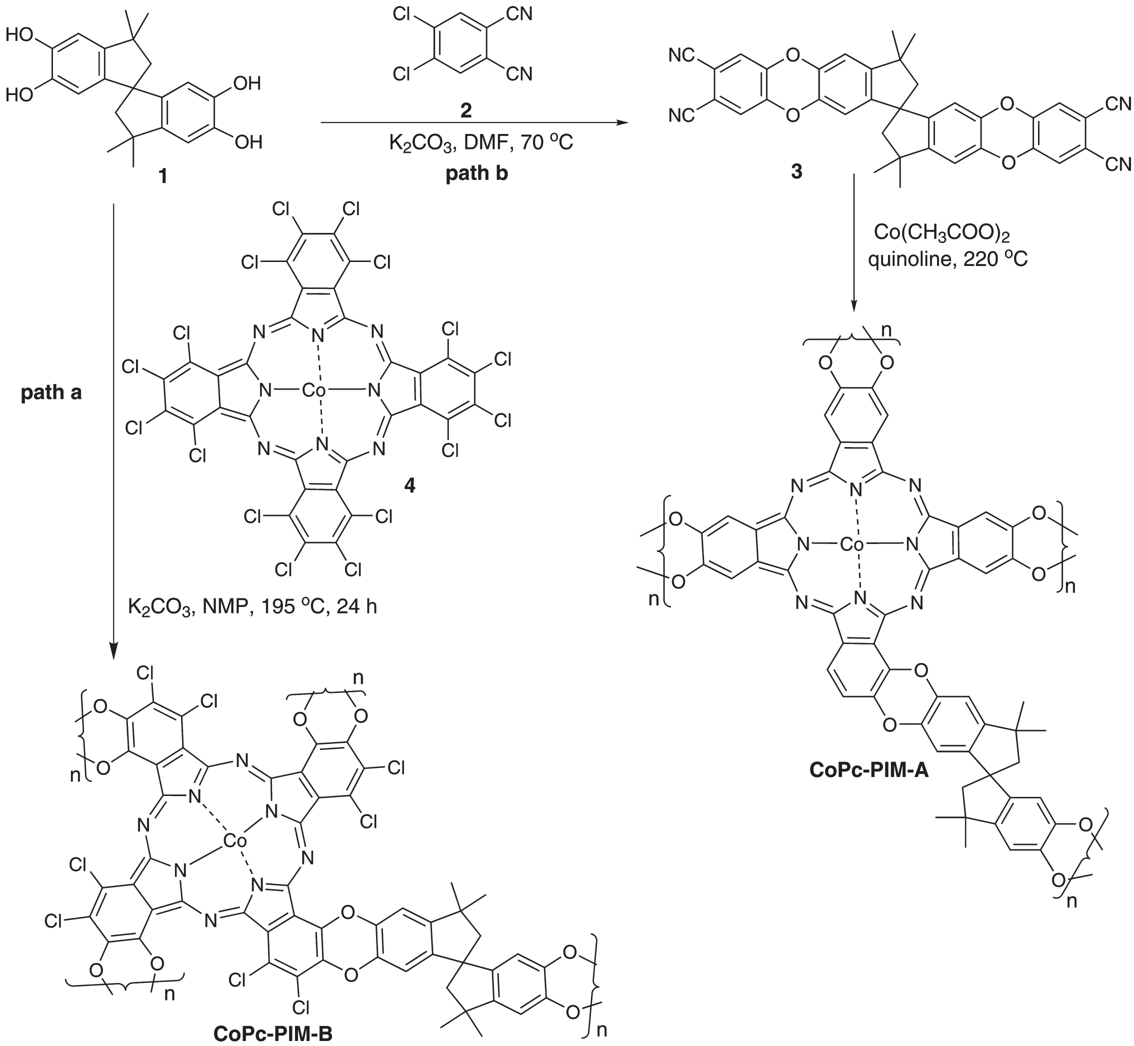
While the amorphous nature of POPs can be considered a disadvantage from the perspective of structural characterization, it is also advantageous in the sense that viable materials can be obtained rapidly from a reaction mixture without the need to wait for crystal formation. In addition, building blocks for POPs can be made with a wide range of handles that are either orthogonal POP synthetic chemistry or can be masked via common protection/deprotection strategies. Such handles can then be modified after POP synthesis (i.e., post-synthesis modification) to yield new POPs with similar architectures but different functionalities in their pores.

3. POROUS ORGANIC POLYMERS THAT EMPLOY WELL-DEFINED HOMOGENEOUS CATALYSTS AS BUILDING BLOCKS

3.1. Cobalt Phthalocyanine Polymers of Intrinsic Microporosity (PIMs). Metal complexes of phthalocyanines are well-known in homogeneous catalysis for a wide range of reactions. Although cross-linked polymers of metallophthalocyanine have been made and studied for over 40 years,[55] these materials are nonporous and have very low surface areas (<1 $m^2\ g^{-1}$),[56−58] presumably due to their two-dimensional (2D) nature, which arises from the tendency of the subunits to display strong noncovalent $\pi-\pi$ stacking interactions. Elimination or exclusion of these van der Waals interactions should lead to more porous materials.

Recently, McKeown and co-workers reported the synthesis of microporous, amorphous phthalocyanine-based polymer networks by incorporating a contorted tetrahedral co-monomer (**1**). The role of the co-monomer was to separate phthalocyanine subunits and preclude them from orienting cofacially within the resulting polymer. Together, these effects were expected to greatly reduce $\pi-\pi$ stacking, thereby enabling formation of

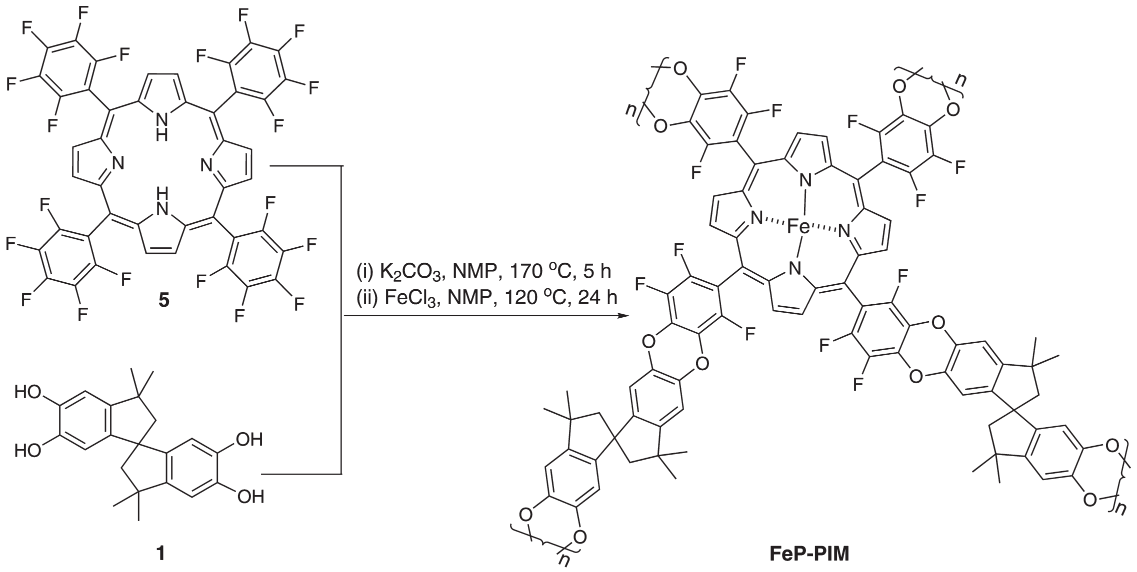
Scheme 1. Synthesis of Cobalt Phthalocyanine-Based Polymers of Intrinsic Microporosity from Preformed Chlorinated Phthalocyanine 4 (path a) and by in Situ Metal-Mediated Cyclization of Bis(phthalonitrile) Precursor 3 (path b)



interconnected cavities and engendering permanent microporosity. In the first phthalocyanine-based synthesis of a PIM, the McKeown group combined a preformed chlorinated phthalocyanine, **4** (Scheme 1, path a), with **1** in a dibenzodioxane-forming reaction to yield **CoPc-PIM-A**, a material indeed displaying permanent microporosity along with a moderate surface area (120 $m^2 g^{-1}$).[59] The comparatively low surface area was thought to reflect partial aggregation of the preformed macrocycle before and during polymer synthesis.

Subsequently, a related material (**CoPc-PIM-B**) having much higher surface area (450−600 $m^2 g^{-1}$ for Co)[59] was obtained via the in situ metal-mediated synthesis of the desired cross-linked metallophthalocyanine from the rigid bis(phthalonitrile) precursor, **3** (Scheme 1, path b).[57] The rigid spirocyclic unit in **3** was designed to orthogonally direct the phthalocyanine units as they form, thereby inhibiting aggregation and yielding, as indeed observed, a network of substantially higher surface area. Extension of this in situ approach to other metal-ion templates yielded materials with even higher surface area, for example, 895 $m^2 g^{-1}$ with Zn,[57] and 750 $m^2 g^{-1}$ with Cu.[57] That the SSA (and by inference porosity) depends on the identity of the templating metal-ion, is intriguing. One explanation centers on the rates at which different metals template the formation of phthalocyanine units. If macrocycle formation is fast relative to polymerization, opportunities for aggregation (prior to polymerization) will be greater than the case where macrocycle formation is slow. Consistent with this explanation, Co^{II} ions are faster phthalocyanine templaters than are Zn^{II} and Cu^{II},[60] and afford a higher yield of cross-linked polymers over the same reaction time.

CoPc-PIM-A and **CoPc-PIM-B** are both reported to exhibit highly hysteretic nitrogen adsorption isotherms, consistent with wide distributions of pore sizes, spanning the microporous (<2 nm) and mesoporous (2−50 nm) range.[57] Both materials have been used to catalyze the decomposition of hydrogen peroxide, and both show higher activity than powders of CoPc, the molecular cobalt phthalocyanine analogue.[59] Catalysis by these porous materials was well-behaved over a wide range of conditions, and the corresponding rate expressions were similar to that for the molecular analogue, suggesting that the catalytic species are the same in the three cases. The activity of **CoPc-PIM-A** (Scheme 1, path a) is 20 times that of insoluble molecular CoPc (powder), presumably because of the exclusive presence of pores in the former, and the consequent enhanced accessibility of reactants to catalytic metal sites. Consistent with this hypothesis



Scheme 2. Synthesis of Iron Porphyrin-Based Network from a Spiro-*bis*-Indane and a Preformed, Fluorinated Porphyrin

is the observation that the in situ-prepared cobalt phthalocyanine material (**CoPc-PIM-B**, Scheme 1, path b), with its even higher SSA is 2 orders of magnitude more active than molecular CoPc powder.

McKeown and co-workers also employed the aforementioned cobalt phthalocyanine network polymers as catalysts for the oxidation of cyclohexene by *tert*-butylhydroperoxide. Significantly enhanced catalytic activity was again observed with the polymers relative to molecular CoPc powder. Interestingly, catalytic oxidation of hydroquinone using the McKeown **CoPc-PIMs** is more rapid (v = 33 mol-cat^{-1} h^{-1}) than the oxidation carried out in the presence of CoPc encapsulated by zeolite Y (v = 10.4 mol-cat^{-1} h^{-1});[61] molecular CoPc exhibited no detectable catalytic activity. Presumably, both the polymeric network structure and the zeolite spatially constrain the cobalt phthalocyanine, preventing it from suffering inactivation via dimer formation or radical-type oxidative macrocycle degradation that occurs via cannibalistic catalyst-catalyst encounters.

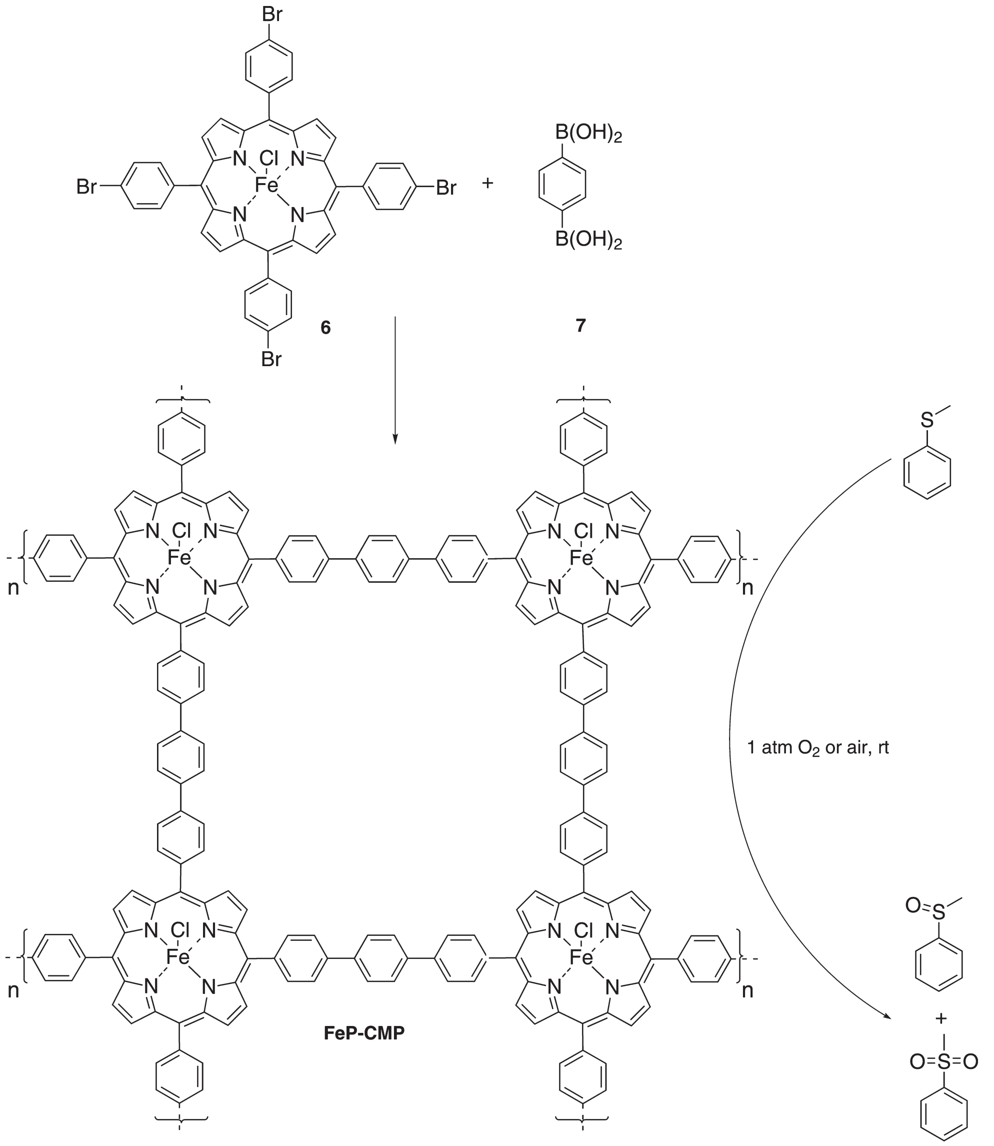
Recently, Maksheed et al. used **CoPc-PIM-A** to oxidize sulfide to elemental sulfur using O_2 (in air) as the oxidant.[62] While catalytic activity increased with temperature, it decreased over time because of the accumulation of the sulfur product in the pores, which blocks access by new sulfide ions. This interpretation was supported by nitrogen adsorption experiments that showed a large drop in the surface area of **CoPc-PIM-A** (from 650 to 3 m^2 g^{-1}) after ~13 turnovers.[62] The catalyst can be repeatedly reactivated by extracting the product using hot ethanol.

3.2. Iron Porphyrin-Based PIMs and CMPs. Metalloporphyrins, well-known analogues of the heme cofactor and many metalloenzymes, have been extensively used in both homo- and heterogeneous catalysis. Like phthalocyanines, metalloporphyrins have been copolymerized as thin films,[63,64] stacked coordination polymers,[65−67] and powders,[68] and subsequently used as oxidation catalysts.[69−73] These materials, however, are not known to be microporous.

The McKeown group has extended their contorted tetrahedral co-monomer strategy to the synthesis of a microporous porphyrin network polymer from 5,5′,6,6′-tetrahydroxy-3,3,3′,3′-tetramethyl-1,1′-spirobisindane and a preformed, fluorinated porphyrin (Scheme 2).[74] In this iron-containing polymer (**FeP-PIM**), the metalloporphyrin moieties are connected to the spiro co-monomers through C−C-bonded dibenzodioxane units that, at first glance, appear to yield structures insufficiently rigid to sustain porosity. However, rotation of dibenzodioxanes around the C−C bonds is substantially restricted, because of substantial steric interactions between the perfluorinated benzene rings and the porphyrins. As a consequence, deleterious $\pi-\pi$ stacking of adjacent porphyrins is largely precluded, and the resulting polymer is characterized by a more open and porous structure than the corresponding network polymer made from preformed cobalt phthalocyanine. As one might anticipate, the surface area of **FeP-PIM** (900−1000 m^2 g^{-1}) is much larger than that of **CoPc-PIM-A**. Consistent with its enhanced porosity and substantial surface area, **FeP-PIM** catalyzes the oxidation of hydroquinone at a rate (v = 64 mol-cat^{-1} h^{-1}) that is competitive with (slightly faster, in fact) than the rate obtained with a soluble homogeneous analogue, [$(PhF_5)_4$porphyrin]FeCl (v = 43 mol-cat^{-1} h^{-1}).[59]

Jiang and co-workers recently reported the synthesis of a CMP-type iron porphyrin network via Suzuki−Miyaura cross-coupling of a [tetrakis(4′-bromophenyl)porphyrin]Fe^{III} derivative ([*p*-Br]$_4$PFe), **6**, and 1,4-phenyldiboronic acid (PDBA), **7** (Scheme 3).[75] This polymer, **FeP-CMP**, has a comparatively large surface area (1270 m^2 g^{-1}) and evidently contains only nanometer-scale pores (0.47 and 2.69 nm); that is, the large mesopores found in PIM-type porphyrin networks are absent. **FeP-CMP** was reported to have good catalytic activity and selectivity for the oxidation of sulfides to sulfones using O_2 as the oxidant, with the larger of its pores allowing for the oxidation of substrates as large as diphenylsulfide. In addition, the constrained spacing of iron porphyrins inside the network likely inhibits oxidative decomposition of these catalysts (via porphyrin attack by a neighboring catalyst) and precludes detrimental formation of μ-oxo dimers.[76] As a consequence, turnover numbers at least as high as 97,000 can be obtained and **FeP-CMP** can be recycled with no loss of surface area and good retention of catalytic activity.

Scheme 3. Synthesis of a CMP-Type Iron Porphyrin Network and Its Catalytic Oxidation of Sulfides

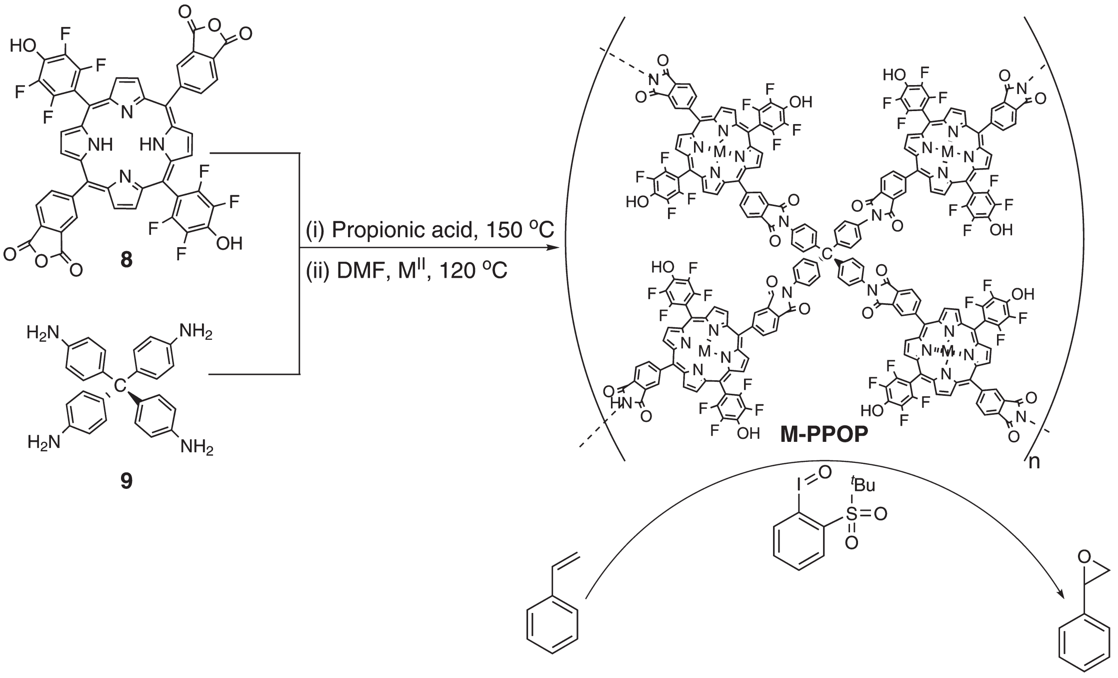


3.3. Other Metalloporphyrin-Containing POPs.

Very recently, our groups have synthesized several porphyrin-containing porous organic polymers using diimide chemistry (Scheme 4).[23,24,77] By condensing the tetrahedral amine monomer **9** with the free-base porphyrin monomer **8** in refluxing propionic acid, a microporous free-base porphyrin POP (**Fb-PPOP**) can be obtained in good yield (~70%). Notably, this material can be post-synthetically metalated with any of several elements, including Fe,[77] Mn,[77] Pd,[78] and Zn.[78] Both **Fb-PPOP** and its metalated derivatives (**M-PPOP**) are moderately porous (~20% weight loss (solvent) in TGA experiments) and feature moderate surface areas (370 to 450 m^2 g^{-1}). Interestingly, the metalation of **Fb-PPOP** only reaches about 60% of the level anticipated based on the amount of porphyrin used in the **Fb-PPOP** synthesis. At least two explanations seemed plausible: either a substantial number of polymerized porphyrin rings are inaccessible or otherwise unreactive toward metal ions, or diimide formation during polymerization is incomplete (i.e., not all of the amines have reacted and, therefore, not all of the available porphyrins have been incorporated into the network). Subsequent experiments using premetalated porphyins as co-monomers likewise yielded lower than anticipated amounts of porphyrin incorporation, strongly suggesting that the second scenario is the culprit. Presumably, the large size of the porphyrin building blocks makes it difficult to connect the unit to all the available amine sites of the tetramine building block **9**, a species that is more sterically congested than the tetrafunctional monomers used to form **FeP-PIM** and **FeP-CMP**.

In the epoxidation of styrene (Scheme 4) with a soluble form of iodosobenzene as oxidant, both **Fe-** and **Mn-PPOPs** had proved more persistent as catalysts (>2000 turnovers) than did the soluble molecular (i.e., homogeneous) analogues **(TPFPP)M** (TPFPP = *meso*-tetrakis(pentafluorophenyl)porphine, M = FeCl and MnCl), which degraded after 170 and 780 turnovers, respectively. Although both **M-PPOPs** can be recycled, catalytic activities were greatly reduced presumably because of the oxidation of the individual pyrrolic rings by the iodosobenzene compound (either directly, or catalytically via a neighboring metallo-porphyrin), with concomitant loss of

Scheme 4. Synthesis of a Porphyrinic Porous Organic Polymer and Its Use As Catalyst for Styrene Epoxidation



macrocycle aromaticity. Consistent with this picture, prolonged use of the **M-PPOPs** as catalysts resulted in polymer bleaching, but no loss of metal and no change in polymer particle morphology. In the presence of an iodosobenzene-type oxidant, the two **M-PPOPs** also showed moderate catalytic activities for the oxidation of cyclohexane, suggesting that the scope of **M-PPOP** catalytic activity will prove similar to that of homogeneous metalloporphyrins.

3.4. POPs That Contain Bipyridyl Metal Complexes. In 2011, Lin and co-workers described the synthesis of bpy-ligated, Ru- and Ir-incorporating porous cross-linked polymers (PCPs) by copolymerizing monomers [(ppy)$_2$Ir(debpy)]Cl and [(bpy)$_2$Ru(debpy)]Cl$_2$ (bpy = 2,2′-bipyridine, ppy = 2-phenylpyridine, debpy = 5,5′-diethynyl-2,2′-bipyridine) with tetrakis(4-ethynylphenyl)methane using Co$_2$(CO)$_8$-mediated trimerization (Scheme 5).[79] The remarkable stability of the resulting materials is illustrated by the resistance of the (bpy)Ir and (bpy)Ru species to the acidic work up that is necessary for the removal of the Co trimerization catalyst. Both materials possess high SSAs (1547 and 1348 m^2 g^{-1} for **Ir-PCP** and **Ru-PCP**, respectively) as well as a relatively broad range of micro- (pore widths = 7.5, 11.0, 13.5, to 16.5 Å) and mesopores.

Because the trimerization reaction used to form the aforementioned PCPs results in organic "nodes", the ligated (bpy)Ru and (bpy)Ir complexes are nonstructural, meaning that the polymer can survive their loss. The polymer-immobilized complexes are efficient catalysts for light-driven reactions, such as the aza-Henry reaction, the α-arylation of bromomalonate, and the oxyamination of aldehyde, where yields are comparable to those of the homogeneous analogues.[79] The catalytic activity of both PCPs remained robust after several cycles; analyses of reaction mixtures revealed no leaching of metal ions, underscoring the robust nature of this platform.

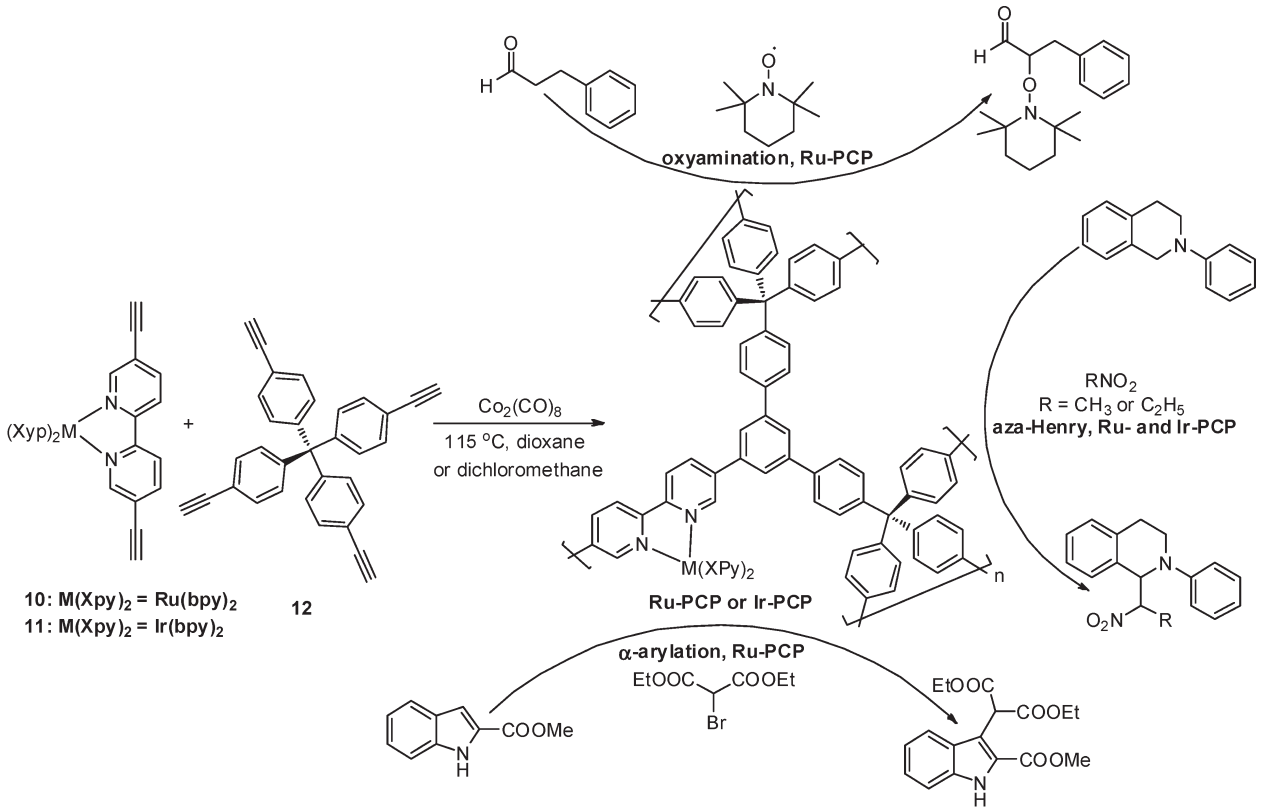
Recently, Cooper and co-workers extended their cross-coupling strategy to synthesize amorphous metal−organic CMPs (**MO-CMPs**) via the direct Sonogashira−Hagihara reaction of either 1,3,5-triethynylbenzene or 1,4-diethynylbenzene with several multiply brominated metal−organic monomers (Scheme 6, paths a and b) to yield microporous materials with a small percentage of mesopores.[80] SSAs in the 423−721 m^2 g^{-1} range were obtained for **CMPs** prepared from the tetrafunctional octahedral acac monomer **15** (Scheme 6, path a). However, **CMPs** prepared from the difunctional CpIr monomer **16** (Scheme 6, path b) require the inclusion of 1,4-dibromobenzene as a porosity-inducing co-monomer to reach SSA values in the 469−864 m^2 g^{-1} range. Interestingly, among the three types of **CMP-CpIr-3** materials tested as catalysts for the reductive amination of several ketones, the one having the lowest SSA was the most active, with comparable activities to that of the corresponding homogeneous Ir catalyst **16**. These observations are reminiscent of the discussion presented in section 2 on the relevancy (or not) of gas-determined surface areas in predicting the relative reactivities of related catalytic POPs in condensed-phase environments.

4. CATALYTICALLY ACTIVE POROUS ORGANIC POLYMERS MADE VIA THE POST-SYNTHESIS METALATION OF POROUS ORGANIC POLYMERS

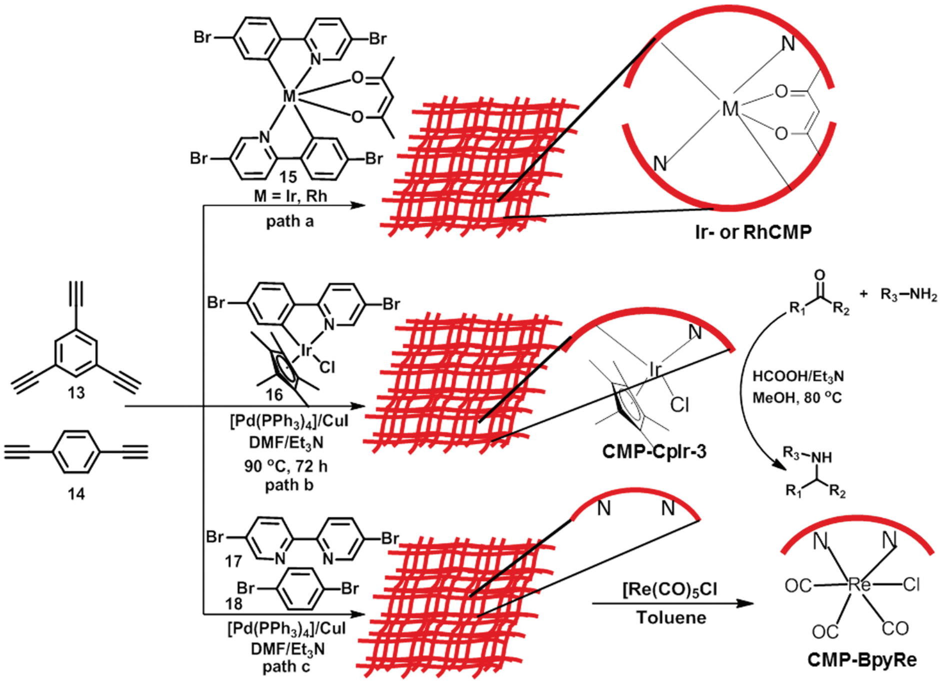
Similar to the post-synthesis modification (PSM) of highly cross-linked polystyrene, which has been a primary strategy for creating new resin-based materials, PSM has begun to emerge as an important strategy for developing new porous organic polymers. Most prominent, relative to catalysis in POPs, is the post-synthesis metalation of materials possessing Lewis-basic moieties that can also function as ligands.

4.1. Post-synthesis Metalation of POPs Containing Bipyridine Moieties. In addition to the aforementioned Rh-, and Ir-containing **MO-CMPs**, Cooper and co-workers also synthesized a bipyridine-functionalized CMP by coupling 1,3,5-triethynylbenzene with 4,4′-dibromo-2,2′-bipy **17** (Scheme 6, path c).[80] As

Scheme 5. Synthesis of PCPs Containing (bpy)M from $[(ppy)_2Ir(debpy)]Cl$ and $[(bpy)_2Ru(debpy)]Cl_2$ and Their Use As Photochemical Catalysts for the aza-Henry Reaction, the α-Arylation of Bromomalonate, and the Oxyamination of Aldehyde

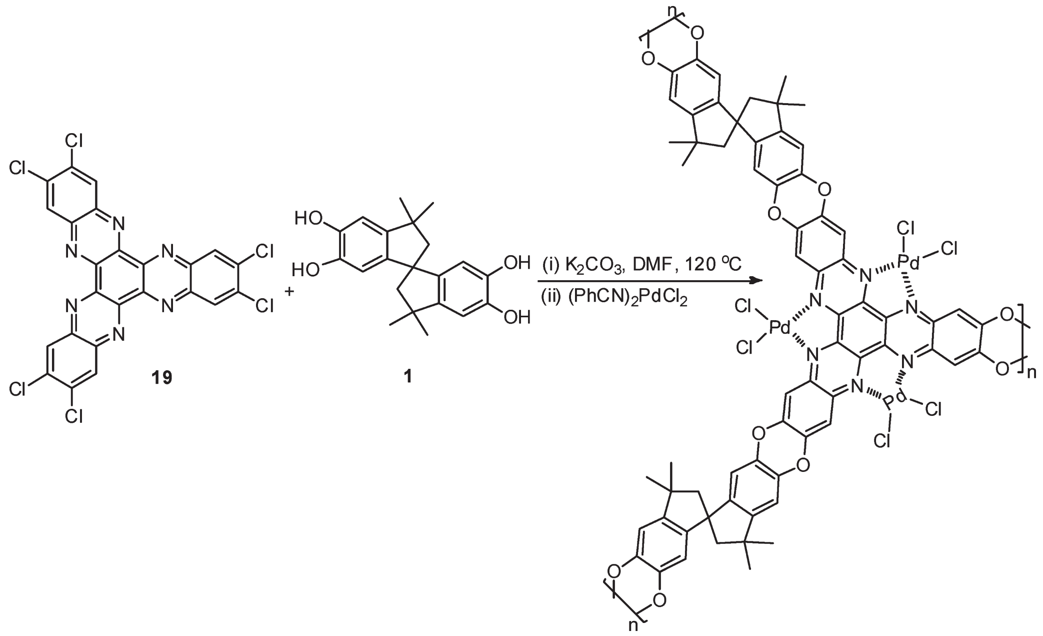


Scheme 6. Synthesis of Amorphous Metal-Organic CMPs via the Sonogashira−Hagihara Cross-Coupling Reaction between Several Multiply-Brominated Metal−Organic Monomers and Either 1,3,5-Triethynylbenzene or 1,4-Diethynylbenzene

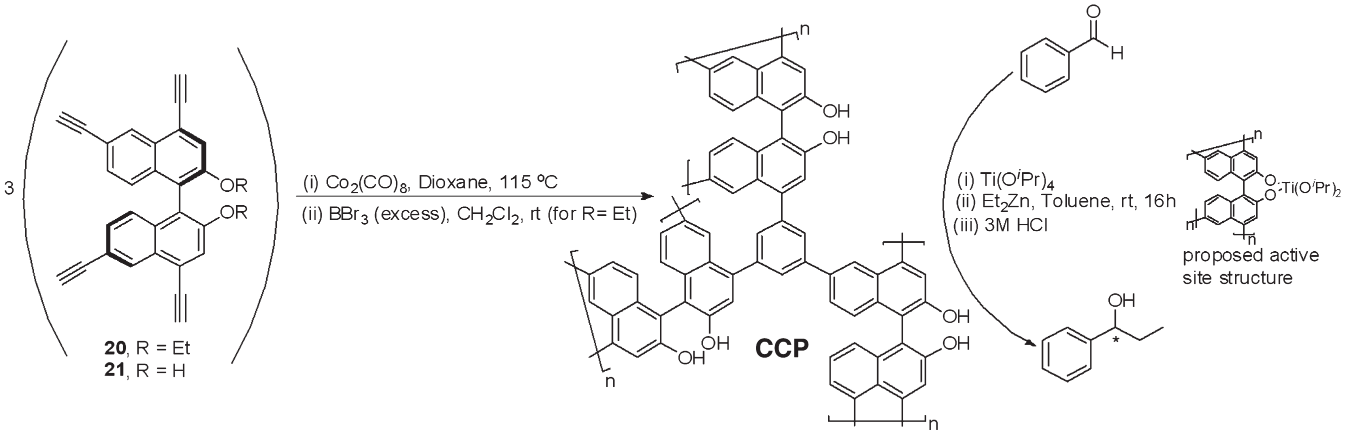


in the case of the difunctional CpIr monomer **16** (Scheme 6, path b), the inclusion of 1,4-dibromobenzene **18** as a porosity-inducing co-monomer leads to microporous bpy-containing CMPs with moderate SSA (652−859 $m^2\ g^{-1}$). Metalation with $Re(CO)_5Cl$ resulted in corresponding reductions in gravimetric surface areas (328−744 $m^2\ g^{-1}$) that are attributed to relative

Scheme 7. Synthesis of a Hatn-Derived Network Polymer Containing Bipyridine Moieties and Its Subsequent Post-synthesis Metalation with Bis(Benzonitrile) Dichloropalladium



Scheme 8. Synthesis of BINOL-Containing CCPs via the $Co_2(CO)_8$-Catalyzed Trimerization of Tetraalkynyl BINOL Monomers and the Subsequent Post-synthesis Metalation of These Materials with $Ti(O^iPr)_4$[a]



[a] The resulting materials can be used as catalysts for the enanatioselective addition of $ZnEt_2$ to aldehydes.

mass increases, as well partial pore blocking by the incorporated metal complex.

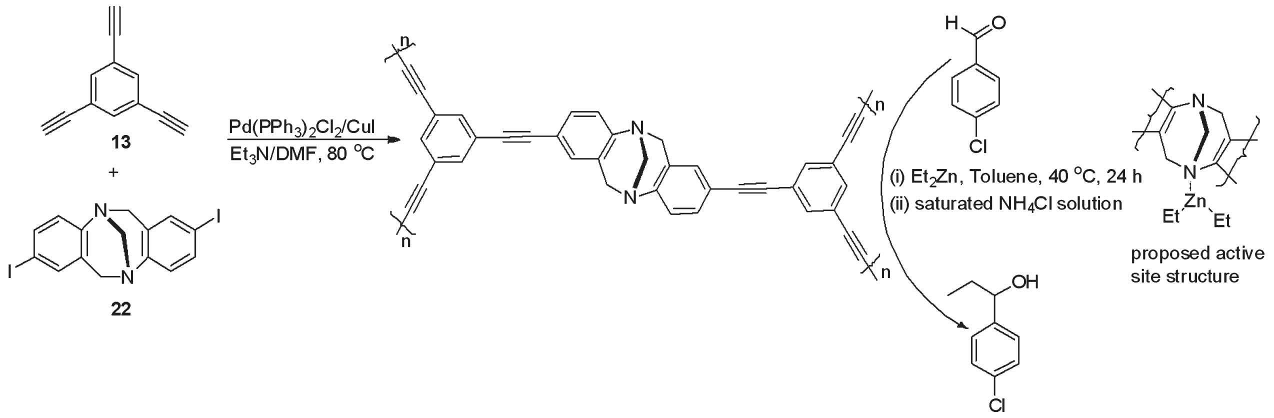
McKeown and co-workers also synthesized a bipyridine-containing porous network by condensing their spirobisindane monomer **1** with 5,6,11,12,17,18-hexaazatrinaphthylene (Hatn) **19** planar building block (Scheme 7).[81] As for the **CoPc-PIMs** discussed in section 3.1, the inclusion of **1** leads to Hatn-derived network polymers with SSAs in the 750−850 $m^2\ g^{-1}$ range and with a wide distribution of micro- and meso-pores (<2−50 nm). As expected, following exposure to excess bis(benzonitrile)-dichloropalladium at room temperature, these porous polymers can bind up to 3 palladium(II) dichloride moieties per Hatn unit, consistent with each presenting three potential chelation sites.

4.2. Post-synthesis Metalation of BINOLate-POPs.

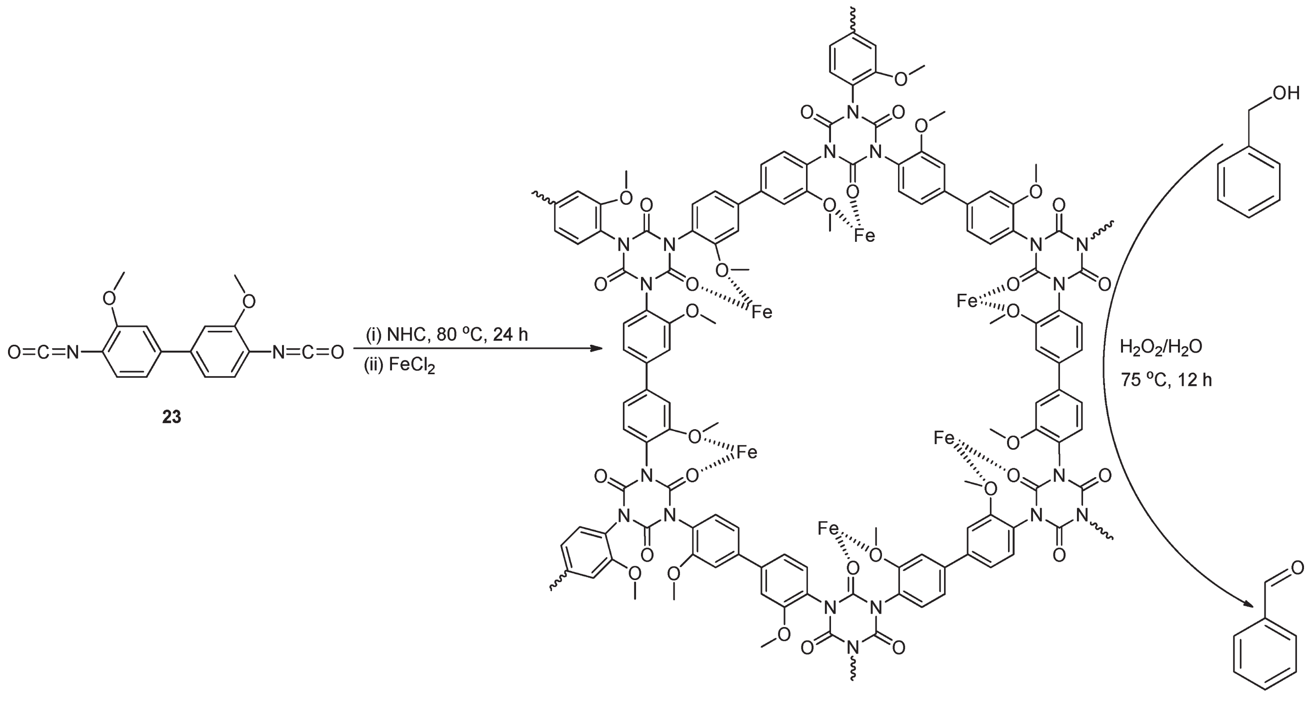
In this same issue, Lin and co-workers report the synthesis of three chiral cross-linked polymers (CCPs) via the $Co_2(CO)_8$ catalyzed trimerizations of various tetraalkynyl-1,1′-binaphthyls (Scheme 8).[82] While these materials possess some mesopores (pores <40 Å), they also are permanently microporous (pore volumes = 0.87−1.23 $cm^3\ g^{-1}$)). Post-synthesis, in situ metalation with $Ti(O^iPr)_4$ results in chiral catalysts that are active for the asymmetric addition of diethylzinc to aldehydes. The enantioselectivity of this reaction is modest to good (55 to 81 e.e.%) but is much lower than reported for either the homogeneous (molecular) catalyst[83] or the corresponding MOF.[84] These observations suggest that more than one type of active site is present in the CCPs, a property that could lead to erosion of ee. Nevertheless, all three CCPs could be readily recycled and reused up to 10 times without loss of conversion or enantioselectivity.

4.3. POPs That Contain Lewis Basic Nitrogens.

Recently, Wang and co-workers reported the synthesis of a porous organic polymer by combining the spirolinked Troger's base derivative, Scheme 9. Synthesis of a Porous Organic Polymer Possessing a Troger's Base Derivative on Its Strut and the in Situ Metalation of the Resulting Material to Be Used As a Catalyst for the Addition of $ZnEt_2$ to Aldehydes



Scheme 10. Synthesis of Porous Polyisocyanurate (PICU) via the *N*-Heterocyclic Carbene-Catalyzed Cyclotrimerization of Diisocyanate and Its Subsequent Metalation by $FeCl_2$[a]

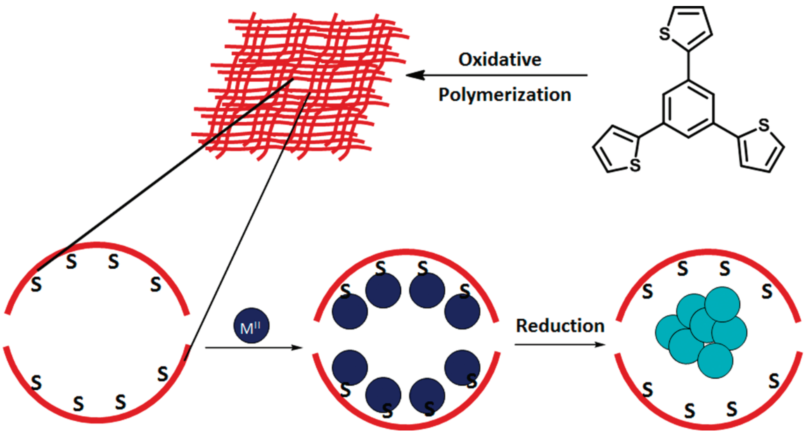


[a] Our proposal for the specific coordination of Fe is speculative.[88] The resulting material can be used as a catalyst for alcohol oxidation.

22, with 1,3,5-triethylbenzene, **13** (Scheme 9).[85] Similar to the McKeown strategy, the relatively high surface area (750 m^2 g^{-1}) of this amorphous material was attributed, in part, to the rigidity of **22**. Both micro- (0.6 and 1.3 nm in width) and mesopores exist, and these materials are stable up to 350 °C. Given that the Troger's base moiety is a part of this POP, the material was tested for the catalytic alkylation of an aldehyde using diethylzinc, and found to have activity that is slightly less than the homogeneous analogue.

4.4. POPs That Contain Lewis Basic Oxygens. The Ying group has employed the N-heterocyclic carbene-catalyzed cyclotrimerization of diisocyanate **23** to prepare samples of a microporous polyisocyanurate (PICU) with SSAs ranging from 320 to 569 m^2 g^{-1}. These low SSA values were attributed to the π stacking of flat organic-sheet substructures that formed during the synthesis.[86] The PICU materials are mainly microporous, with oxygen-rich pore environments that can act as multisite acceptors for hydrogen-bonds as well as for metal coordination (Scheme 10). Exposing these materials to $FeCl_2$ afforded an **Fe/PICU** complex (0.25 mmol Fe/g) that can catalyze the oxidation of benzyl alcohol to benzaldehyde by hydrogen peroxide. Notably, the **Fe/PICU**-catalyzed oxidation proceeded with much higher turnover number (100) and selectivity (98% for benzaldehyde) than those catalyzed by dissolved $FeCl_2$ (TON = 29 with only 51% selectivity)[86] or by nanoparticulate Fe_2O_3 (TON = 12−32 and selectivity = 35−97%).[87] **Fe/PICU** can be recovered and reused for at least 8 cycles without appreciable loss of activity and selectivity, a behavior that can presumably be attributed the presence of pore-based functional

Scheme 11. Synthesis of a 1,3,5-Tris(2-thienyl)benzene-Derived CMP (CMPTA) That Can Be Used to Encapsulate Monodisperse Metal Clusters Post-Synthesis



groups that stabilize the active Fe species and prevent formation of iron oxide nanoparticles.

5. CATALYTICALLY ACTIVE POROUS ORGANIC POLYMERS THAT ENCAPSULATE METAL NANOCLUSTERS

Among the various POPs, CMPs are the most extensively developed, with high flexibility in their structural design and relatively well-understood structure−property relationships regarding the synthetic control of pore sizes.[44,89−92] As such, significant attention has been focused on the post-synthesis construction of metal nanoclusters within CMPs. Importantly, the pores of CMPs can be fabricated from components that subsequently can stabilize enshrouded metal clusters against aggregation, and thus deactivation. Interestingly, though, metal nanoparticles incorporated into nanoporous hyper-cross-linked polystyrene materials lacking cluster-stabilizing functionalities (admittedly, much different materials than CMPs) also exhibit good, stable catalytic behavior.

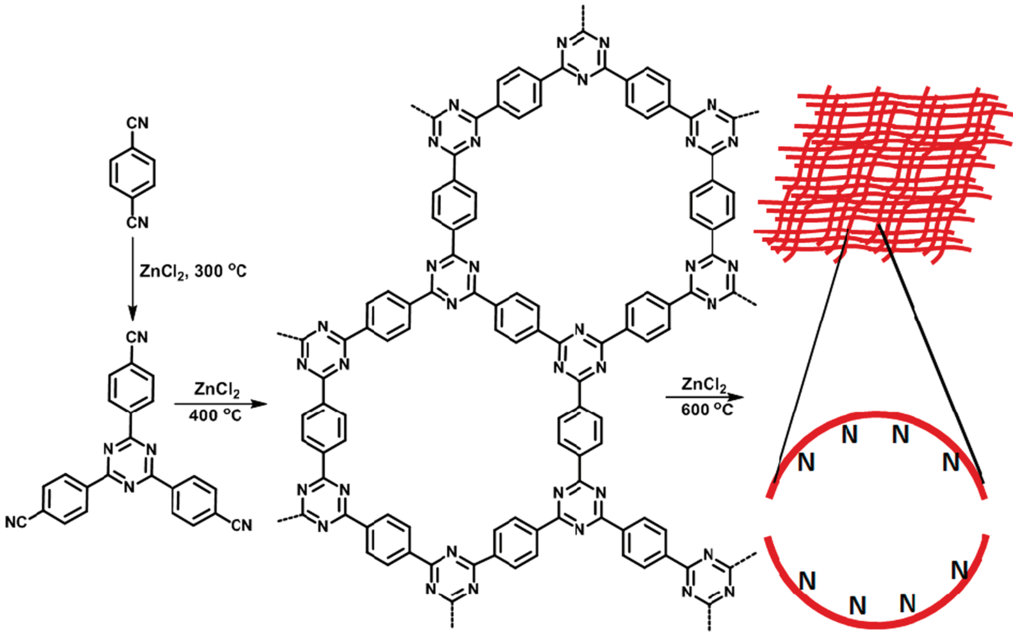
5.1. Metal Nanoclusters Encapsulated in Conjugated Poly(Thienylene Arylene) Networks. Thomas, Antionetti, and coworkers have synthesized CMPs based on the poly(arylene thienylene) motif via the oxidative polymerization of either 2,2′,7,7′-tetrakis(2-thienyl)-9,9′-spirobifluorene or 1,3,5-tris(2-thienyl)benzene (Scheme 11).[93] As expected for these rigid building blocks, the resulting CMPs have comparatively high surface areas (577 and 1060 m^2 g^{-1}, respectively) and porosities (0.61 cm^3 g^{-1} and 0.71 cm^3 g^{-1}, respectively). The pores of these materials are relatively large (average diameter = 1.6 nm) and are lined with thiophene functionalities, making them good candidates for the encapsulation of metal clusters. Exposing a 1,3,5-tris(2-thienyl)benzene-derived CMP (CMPTAs) to a solution of $PdCl_2$, followed by reduction, affords a material that is infused with monodisperse palladium clusters (1.5 nm). (This post-synthesis encapsulation approach mirrors an encapsulation strategy that has been developed for dendrimers[94] where the number of functional groups present inside the pores limits the number of Pd atoms constituting the final clusters.) The resulting CMPTA-encapsulated Pd particles are effective as catalysts for the complete hydrogenation of the relatively large substrate, diphenylacetylene, implying that the clusters either under-fill each pore or fill only a modest fraction of the available pores, such that substrate access to the encapsulated catalysts is retained.

5.2. Metal Nanoclusters Encapsulated in Covalent Triazine Frameworks. The Thomas group has also synthesized a triazine-linked POP from 1,4-dicyanobenzene using molten $ZnCl_2$ as the reaction medium (Scheme 12). While the thermal trimerization of 1,4-dicyanobenzene started at 300 °C, larger oligomeric structures only begins to form at 400 °C. When heated to 600 °C, cross-linking and cyano elimination lead to the formation of an insoluble network polymer possessing high surface area (>2400 m^2 g^{-1}) and both meso- and micropores.[95,96] Denoted covalent triazine frameworks (CTFs), these highly porous materials display admirable thermal and chemical stability, and contain a large number of nitrogen atoms (up to ∼10% by weight).[97] As such, they can be infused with Pd in the same manner as described above for the poly(arylene thienylene)-based CMP. Because of the presence of a mixtures of pores, the Pd clusters are both anticipated and observed to be larger and more disperse than those formed in CMPTA (cluster diameter in CTF = 3.08 ± 0.73 nm); however, the CTF-enshrouded palladium clusters are still considerably less polydisperse, for example, than are palladium clusters supported on activated charcoal (Pd/AC).

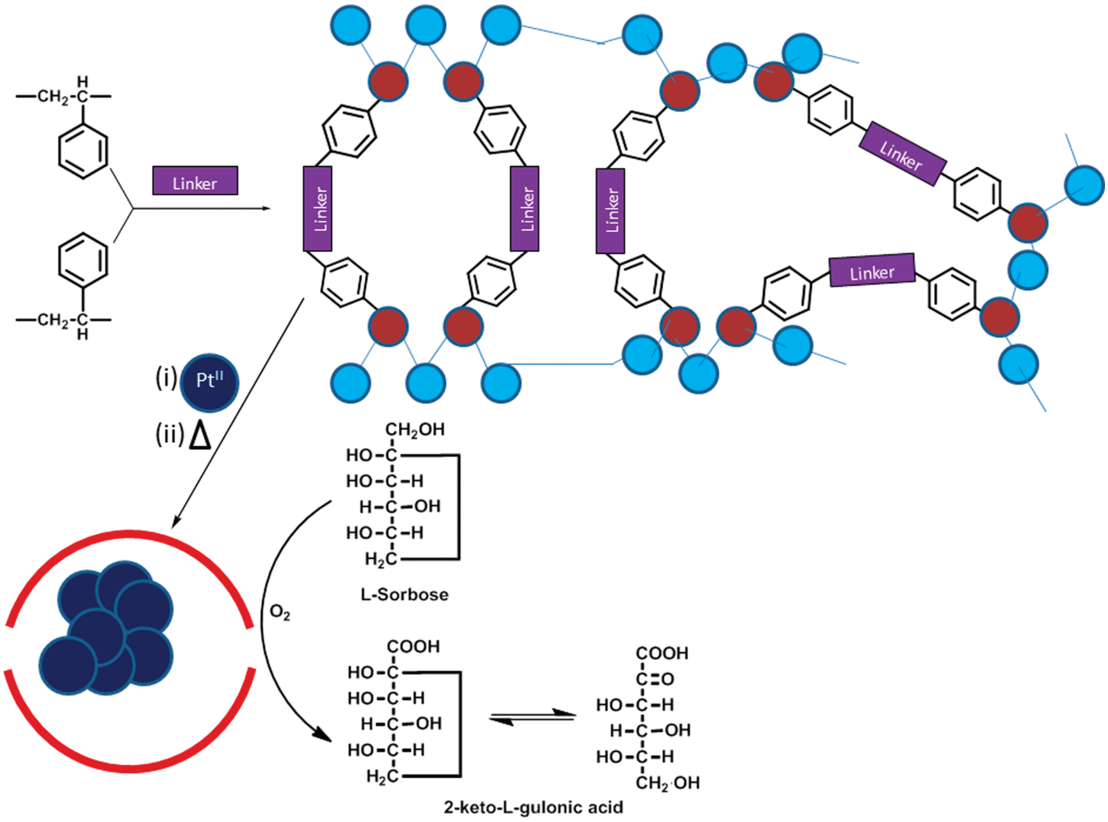
The Thomas group has employed CTF-encapsulated metal clusters as catalysts for the oxidation of glycerol by dioxygen.[98] Although this reaction has been carried out with a number of metals on activated carbon (AC) supports,[99−101] these catalysts are easily deactivated because of irreversible adsorption and overoxidation.[100] While CTF-encapsulated Pd clusters exhibited only slightly better selectivity for glyreric acid and slightly higher initial rate than did Pd/AC, they proved much more stable, completely converting glycerol to the desired product after 3 h, while Pd/AC was deactivated within 1 h with only 30% conversion. As in the case of CMPTAs, stabilization can be attributed to the presence of stabilizing ligands (nitrogen functionalities in this case) within the framework. Nevertheless, because of the comparatively weak interactions between ligands and nanoparticles, deactivation could not be completely eliminated, and Pd/CTF began to lose activity after three cycles of catalysis, concurrently with an increase in the average size of the Pd clusters (from 3.08 to 4.88 nm after three cycles).

5.3. Pt Nanoclusters Encapsulated in Hyper-Cross-Linked Polystyrene (HPS). Polystyrene networks with rigid nanoscale cavities measuring between 2 and 10 nm can be made by Friedel−Crafts cross-linking of the phenyl rings in dissolved linear polystyrene (or swelled polystyrene-divinylbenzene gels) with bifunctional organohalide linkers (Scheme 13).[53,102] When

Scheme 12. Synthesis of Covalent Triazine Frameworks (CTFs) Possessing *N*-Based Functionalities

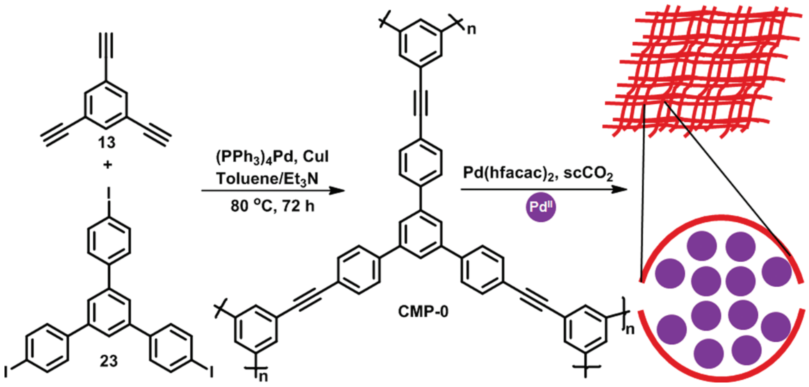


Scheme 13. Synthesis of Nanocluster-Encapsulated Hyper-Cross-Linked Polystyrenes (HPS) As Catalyst for Oxidation of L-Sorbose



the degree of cross-linking exceeds 40%, insoluble materials possessing surface areas as high as 1500 m^2/g can be obtained. Surface areas in the range of 600−1000 m^2/g are common in these so-called hyper-cross-linked polystyrene (HPS) networks, which tend to possess a mixture of micro-, meso-, and macropores. HPS materials can be swollen by many solvents, making them attractive matrices for the loading of various catalytic metal complexes or precursors, without the need for Lewis basic heteroatoms to be present inside the network. For example, Bronstein and co-workers loaded tetrachloroplatinic

Scheme 14. Synthesis of 1,3,5-Triethylnylbenzene Containing CMPs via Sonogashira−Hagihara Coupling and the Subsequent Impregnation with Palladium Nanoparticles Using Pd(hfacac)$_2$ and scCO$_2$ as Reaction Medium[a]



[a] Only the formation of nanoparticles inside the pores is predicted.

acid into a microporous HPS (surface area = 833 m^2/g, mean pore diameter = 2 nm)[53] to form HPS-encapsulated nanoclusters of platinum (diameter = 1.3 ± 0.3 nm).[103] These clusters were subsequently identified as consisting of a mixture of Pt^0/Pt^{II}/Pt^{IV} atoms/ions. The fraction present as Pt^0 was found to increase when the clusters were used as catalysts for the oxidation of L-sorbose to 2-keto-L-gulonic acid by O$_2$ (Scheme 13), suggesting that L-sorbose acts as a reducing agent at the beginning of the reaction.[102,103] While the rate of catalysis was comparatively good (0.54 mol/mol Pt-s),[103] subsequent use of a commercially available HPS that possesses both macro- and micropores (surface area = 738 m^2/g, total pore volume = 0.59 cm^3/g, 46% of the pore population in the 20−100 nm range, 13% with size <6 nm) yielded a 4.6-fold increase in activity.[103] The lower TON for the purely microporous HPS was attributed to the restricted transport of the substrate through the nanocluster-congested micropores. It was also proposed that the HPS material containing both micro- and macropores allows for better access of the reaction medium to the nanoparticles as well as better transport of the L-sorbose substrate to the encapsulated catalyst. These observations clearly point to the importance of transport dynamics in catalysis by porous materials, just as in the case of catalysts on traditional supports.

Recently, Cooper and co-workers have employed supercritical carbon dioxide (scCO$_2$) as a medium for loading Pd^0 nanoparticles into CMPs that contain only arene and acetylene moieties (Scheme 14). The Pd^{II} starting material, Pd(hfacac)$_2$ (hfacac = hexafluoro acetylaceonate), is soluble in scCO$_2$ and is carried into the pores of the CMPs by the negligible surface tension of scCO$_2$, which allows it to penetrate all the micropores. Subsequent removal of scCO$_2$ by depressurization leaves behind the Pd^{II} complex, presumably ligating to the acetylene and aromatic moieties if they are inside the pores or as free solid outside. Heating the CMP/Pd(hfacac)$_2$ mixture to high temperature results in decomposition of the Pd(hfacac)$_2$ complex and formation of uniformly sized Pd^0 nanoparticles inside the pores and less uniform particles outside. As expected, the particles inside the pores are much smaller (∼1−3 nm) than those grown on the surface of the polymer (∼5−10 nm). Increases in the wt % loading of Pd led to increases in the size of the surface-bound nanoparticles, but not in the size of the pore-bound ones. These observations support the hypothesis that scCO$_2$ impregnation, which delivers a fixed number of Pd^{II} complexes to each pore, is controlling both the size of the nanoparticles inside the pores as well as their dispersion, a feat that is not easily achieved by most conventional methods. The use of the low-surface-tension scCO$_2$ as a loading medium conceivably may also be advantageous for preventing pore collapse.

6. CHALLENGES AND OPPORTUNITIES

6.1. Challenges in Materials Characterization. To use POPs rationally in chemical catalysis, it is highly desirable to have a good understanding of both the chemical nature of the POP and the properties of its pores. To this end, comprehensive structural characterization of POP materials is desirable. Characterization by FT-IR and UV spectroscopies can shed light on the extent of polymerization (e.g., end-group detection and quantification) and on the composition of functional groups present. Gas adsorption and thermogravimetric analysis measurements are useful for quantifying pore-size distributions and overall polymer porosity. Solid-state NMR and Raman spectroscopies can serve as checks for carbon-based contaminants such as entrapped monomers or carbonized materials. In addition to traditional combustion analysis, results from other element-sensitive analytical techniques such as ICP-OES and ICP-MAS can be useful when the materials comprise non-CHNO elements.

Interestingly, many POPs that show reversible uptake of solvent molecules do not readily sorb N$_2$, even though N$_2$ is much smaller than all of the tested solvents. The absence of N$_2$ uptake presumably reflects kinetic accessibility issues. Unfortunately, when these experiments fail, evaluation of pore size distributions and pore volumes, via BET analyses that are routinely carried out for micro- and ultramicroporous materials,[104,105] is precluded.[77] Fortunately, CO$_2$-based adsorption measurements (which are carried out at much higher temperatures) often show substantial gas uptake, and indeed, the use of CO$_2$ as a probe molecule has become increasingly common.[90] Unfortunately, the BET method cannot be applied to CO$_2$ data. Furthermore, the degree of applicability and reliability of other isotherm analyses, such as NLDFT (nonlinear density functional theory), while clearly showing promise,[106,107] has yet to be fully established for these types of materials.[24,108] As mentioned in section 2, while gas-derived surface area measurements can provide guidance regarding the porosity of POP-based materials, these may not be directly relevant to the ability of POPs to facilitate catalysis of reactions involving species dissolved in solution (as opposed to volatilized into the gas phase).[109] To this end, vapor-phase uptake of volatile organic chemicals[110,111] might serve as a better measurement of porosity than sorption of permanent gases. From a chemical perspective, examining the degree of pore functionalization via chemical end-capping experiments[51] can yield information about pore accessibility by substrates, as well as the potential that uncross-linked sites can be exploited for PSM, because these sites can only be modified if they are accessible by the modifying compounds. Catalysis experiments with an appropriate range of differently sized substrates can sometimes allow pore-based reactivity to be distinguished from external-surface-based catalysis.

Wide-angle X-ray scattering (WAXS),[112] together with pair-wise distribution function (PDF) analysis, is emerging as a potentially important technique for resolving the structure of the active catalytic sites in POP, especially when these sites are populated with heavy-element scatterers. With proper modeling, PDF analyses could, in principle, reveal valuable information about defects and network interpenetration in a POP material. Density measurements using either pycnometry or classical solvent displacement can provide indirect information the degree of interpenetration of a microporous material.

6.2. Some Challenges and Opportunities in Making POPs into Unique Catalytic Platforms. Although POPs are generally more chemically stable than MOFs and COFs, their surface areas are (typically) still not very high and their pore distributions remain (in most cases) relatively polydisperse, consequences of their amorphous nature and their propensity for network interpenetration. The significant challenges of developing more ordered POPs with no catenation or interpenetration of the networks[44] are, for the most part, still to be addressed. As in MOFs, catenation decreases the pore sizes POPs, prevents substrates from accessing pores, and likely diminishes their efficacy as catalysts. The necessity of using rigid and 3D building blocks to ensure space-inefficient packing and porosity has also limited the range of structural diversity in POP synthesis. Thus, the ability to control pore sizes and surface areas via the choice of starting materials or mechanism and protocol for polymerization are problems that merit the attention and creative thinking of synthetic chemists and materials scientists who are interested in making new POPs. For example, the dependence of network "interpenetration" on building-block lengths and steric environments are, for the most part, not known. (Nor is the concept of interpenetration nearly as cleanly definable for POPs as it is for crystalline MOFs.) Tuning the steric environments of linkers to engender molecular-level size and shape selectivity is another challenge that has not been broadly examined.

The control of pore uniformity in POPs can be partially linked to the lack of sufficiently reversible reactions that can be used to form low-defect-density porous polymers under thermodynamic control.[44,113] POPs with uniform pores could likely be obtained if the cross-linking reactions were reversible under synthesis condition: bond-formation errors made at the beginning of POP synthesis could be corrected at the end to give the most thermodynamically stable structure.

As in the case of MOF-based catalysis, it is important to distinguish opportunistic catalysis from POP-based catalysis, where advantages of the pore environment and constrained catalyst structures should be apparent. Part of the challenge lies in doing the proper control experiments and another part lies in having a correct model of how molecules behave in a nanoscale environments. Many lessons can be applied to POPs from the supramolecular and biological worlds where cavity structure and environment play critical roles.

Ultimately, the end-impact of POP-based catalysis studies should increasingly be critically examined. With dozens of proof-of-concept experiments in hand, now may be the time to move beyond the important, but limited, notions of increased catalyst stability and recyclability upon heterogenization of homogeneous catalysts and metal clusters, as primary justifications for the creation and investigation of new POP-based catalysts. It seems likely that many of the most important new developments in POP-based catalysis will capitalize in some way on the unique aspects of polymer pore environments, such that access to chemical mechanisms and/or catalytic reactivity patterns that are simply not possible in homogeneous, supramolecular, or zeolitic environments, becomes the most significant feature.

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