

Metal–Organic Conjugated Microporous Polymers**

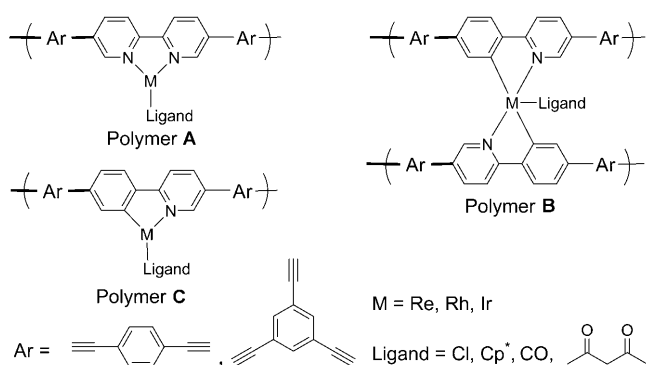
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Microporous materials have potential applications in areas including molecular separation, gas sorption and catalysis.^[1] Materials such as metal–organic frameworks (MOFs),^[2] covalent organic frameworks (COFs),^[3] microporous organic polymers,^[4] and porous organic molecular solids^[5] all contain organic functionalities which, in principle, can allow significant synthetic diversification. A particular advantage of microporous organic polymers^[4] is the potential to introduce a range of useful chemical functionalities into the pores.^[6] This stems from the chemical and thermal stability of these networks which facilitates a variety of chemical transformations.

Conjugated microporous polymers (CMPs)^[4a] can exhibit extended π -conjugation and have been the subject of much recent interest. A variety of CMPs (and closely related structures) have been developed.^[4a,7] The incorporation of metal sites into CMPs could open up second-generation porous materials with useful combined chemical and physical properties such as catalytic activity, electrical conductivity, or light-absorption/emission.^[8] For example, metalated CMP materials might be of interest in heterogeneous catalysis or photocatalysis, where high surface areas would be beneficial. There are, however, few demonstrations of the functionalization of CMP networks with metals at the molecular level. The incorporation of metal nanoparticles into microporous networks has been demonstrated.^[4c,7c,9a] Also, a lithiated CMP showing very high H₂ sorption was described recently but the precise nature of the metal incorporation at the molecular level was not clear.^[9b] Another recent report details a porphyrin-derived microporous organic polymer which shows high catalytic activity for the oxidation of thiols.^[10] Beyond this, there are no reports on the purposeful synthesis of metal-functionalized CMPs. Here, we report two versatile strategies for preparing metal–organic CMPs (MO-CMPs). Unlike MOFs,^[2] the resulting metal-containing conjugated polymers are amorphous. Another significant difference is that the metal sites need not be nodes in the network but can also be attached pendant to the polymer chains, thus allowing

the introduction of vacant metal sites and a range of chemically active functionalities. The introduction of pendant metal sites rather than metal nodes also allows the preparation of materials with unbroken extended conjugation.

The MO-CMP networks were prepared either by post-treating a bipyridine-functionalized CMP precursor with a metal complex or by the direct Sonogashira–Hagihara cross-coupling of 1,3,5-triethylbenzene or 1,4-dibromobenzene and a halogenated metal–organic co-monomer. These two strategies can be defined as post-synthetic metalation and direct metal incorporation by copolymerization. The representative structures of the target MO-CMP networks are shown in Scheme 1. These polymers combine conjugation along the main chain with functional units such as bipyridine or phenylpyridine in the backbone in order to provide sites for incorporating various metal complexes. We note that neither bipyridine nor phenylpyridine units have been incorporated previously within CMP networks.



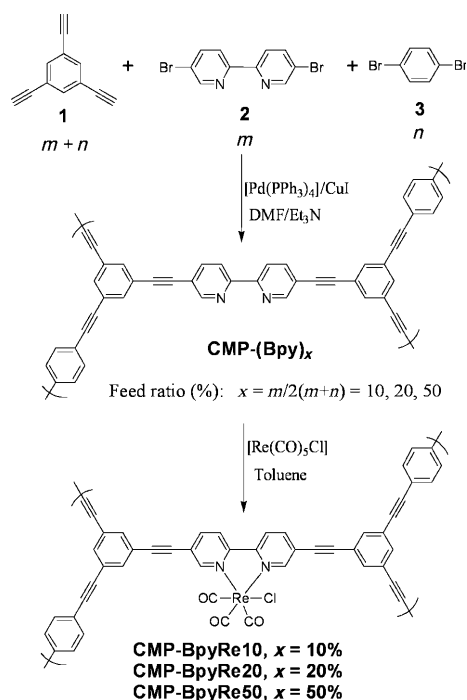
Scheme 1. Representative structures of the target metal–organic conjugated microporous polymers (MO-CMPs); Cp* is pentamethylcyclopentadiene.

To prepare MO-CMP **A**, we first synthesized the bipyridine-functionalized precursor network (CMP-Bpy) by Sonogashira–Hagihara cross-coupling of 1,3,5-triethylbenzene (**1**) with 5,5-dibromo-2,2'-bipyridine (**2**) and 1,4-dibromobenzene (**3**) to produce a series of porous networks with varying incorporations of the bipyridine monomer, **2**. Monomer **3** can therefore be considered as a co-monomer which contributes to porosity but does not incorporate metal binding sites. After purification, the resulting polymeric precursors were treated with [Re(CO)₅Cl] in toluene under reflux to produce networks containing the *fac*-[ReCl(CO)₃(bipy)] (CMP-BpyRe) moiety. As a control reaction, the bipyridine-free network, CMP-2, was prepared as described previously^[4a,7a] and was

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[**] We gratefully acknowledge the EPSRC for funding (EP/F057865/1 and EP/H000925).

Supporting information for this article (MO-CMP synthesis, gas sorption and SEM data) is available on the WWW under <http://dx.doi.org/10.1002/ange.201005864>.



Scheme 2. Synthetic routes for the bipyridine-containing polymer precursors and the Re-containing polymer networks.

also post-treated with $[\text{Re}(\text{CO})_5\text{Cl}]$ to afford CMP-Re-2 (Scheme 2).

Compared with the FT-IR spectra of the CMP-Bpy polymer precursors, the rhenium-containing polymers show three additional strong vibration peaks located at 2020, 1920 and 1885 cm^{-1} (Figure 1), characteristic features of carbonyl

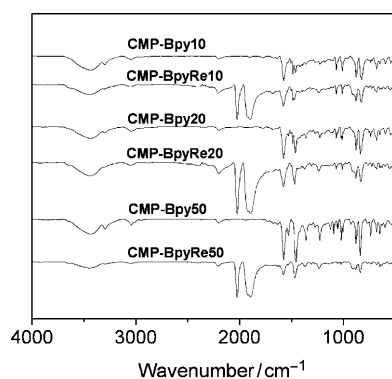


Figure 1. The FT-IR spectra of CMP-Bpy networks and the corresponding rhenium-containing MO-CMPs. The spectra are shown offset for clarity.

groups in the $\text{fac}-[\text{ReCl}(\text{CO})_3(\text{bipy})]$ moiety.^[11] As expected, these carbonyl vibrations did not appear in the FT-IR spectrum of CMP-Re-2, which does not contain the bipyridine unit (see Figure S1 in the Supporting Information). Rhenium was detected in all of the MO-CMP networks by inductively coupled plasma-optical emission spectroscopy (ICP-OES) analysis and the content of rhenium increased with the

Table 1: Physical properties for Re-containing MO-CMPs compared to those of the parent nonmetalated networks.

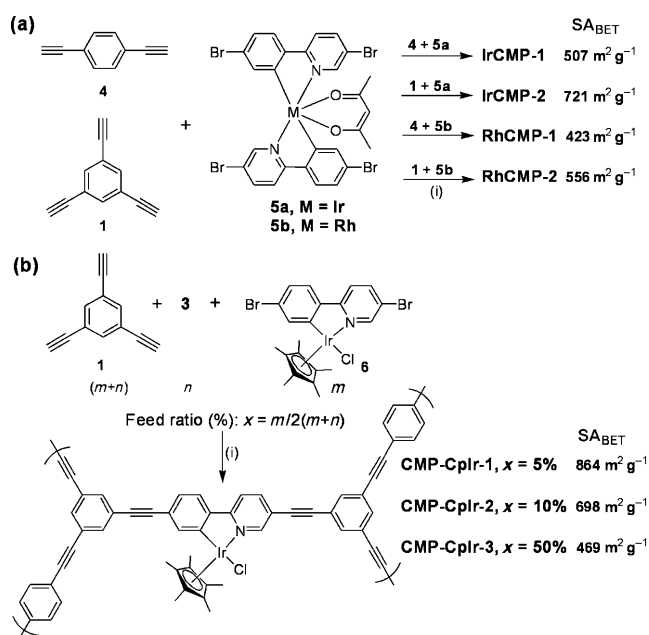
Polymer	SA_{BET} [m^2g^{-1}] ^[a]	SA_{micro} [m^2g^{-1}] ^[b]	V_{total} [cm^3g^{-1}] ^[c]	Re_{calcd} [wt. %] ^[d]	Re_{ICP} [wt. %] ^[e]
CMP-Bpy10	822	339	0.52	0	0
CMP-BpyRe10	744	335	0.47	13.03	12.19
CMP-Bpy20	859	374	0.69	0	0
CMP-BpyRe20	664	295	0.63	20.54	15.06
CMP-Bpy50	652	469	0.33	0	0
CMP-BpyRe50	328	239	0.29	33.36	15.34

[a] BET surface area (SA) calculated over the pressure range (P/P_0) 0.025–0.1. [b] Micropore surface area calculated from the N_2 adsorption isotherm using the t-plot method based on the Harkins Jura Equation. [c] Total pore volume at $P/P_0 = 0.99$. [d] Data was calculated based on 100% reaction of bipyridine unit. [e] Data was obtained by inductively coupled plasma-optical emission spectroscopy (ICP-OES).

increasing bipyridine content in the polymers (Table 1) and the metal incorporation appeared to saturate in CMP-BpyRe20 at around 15 wt. %. No rhenium was detected in the control network, CMP-Re-2. The IR data show that the rhenium complex is incorporated into the main chain of the polymers as $\text{fac}-[\text{ReCl}(\text{CO})_3(\text{bipy})]$.

The porous properties of the networks were investigated by nitrogen adsorption analyses at 77.3 K. All of the rhenium-containing MO-CMPs gave rise to type I nitrogen gas sorption isotherm with H3 hysteresis loops which were similar to the isotherms exhibited by the parent CMP-Bpy polymers (see Figure S2 in the Supporting Information), indicating that these metalated polymers consist of both micropores and some mesopores. No significant change in pore size distribution was observed between the bipyridine-containing CMP precursors and the Re-containing MO-CMPs (see Figure S3 in the Supporting Information). The apparent Brunauer–Emmett–Teller (BET) surface areas, SA_{BET} , of CMP-BpyRe10 and CMP-BpyRe20 were somewhat lower than that of the non-metalated parent networks (Table 1) but the materials were still significantly microporous. The decrease in specific surface area with increased metal loading can be ascribed both to partial pore filling and to simple increase in mass.

We employed an alternative direct synthesis strategy to prepare MO-CMPs **B** and **C** (Scheme 1) from preformed metal–organic monomers. Iridium- and rhodium-containing polymers were prepared by Sonogashira–Hagihara coupling of 1,3,5-triethynylbenzene or 1,4-diethynylbenzene with the metalated monomers shown in Scheme 3. We synthesized two different types of metalated monomer. The first monomer, a cyclometalated Ir or Rh complex, was tetrafunctional with respect to the Sonogashira–Hagihara network formation reaction (Scheme 3a). A second, bifunctional monomer (Scheme 3b) comprised an Ir–Cp* complex. The resulting MO-CMPs prepared from the tetrafunctional cyclometalated complexes exhibited specific surface areas, SA_{BET} , of 507, 721, 423 and $556\text{ m}^2\text{g}^{-1}$ for networks IrCMP-1, IrCMP-2, RhCMP-1 and RhCMP-2, respectively. For the MO-CMPs formed from the bifunctional monomer (Scheme 3b), specific surface areas of 864, 698 and $469\text{ m}^2\text{g}^{-1}$ were obtained for CMP-CpIr-1, CMP-CpIr-2 and CMP-CpIr-3, respectively.



Scheme 3. a) Direct synthetic routes for Ir- and Rh-containing MO-CMPs produced from cyclometalated Ir and Rh complexes, respectively; see also Scheme 1. b) MO-CMPs produced from Cp*-containing Ir monomer. i) [Pd(PPh₃)₄], CuI, DMF and Et₃N, 90 °C, 72 h.

The MO-CMPs prepared from the tetrafunctional cyclometalated monomers have structures which differ from previous CMPs.^[4a,6,7,10,12] In particular, the metal atoms (i.e., Ir, Rh) act as linkers or spiro-centers to produce the cross-linked microporous networks (Scheme 3a). This may be compared with bonding patterns in MOFs^[13] where the metal atoms are integral nodes in the network structure. By contrast, the metal node in these MO-CMPs does not break the extended conjugation pathway in the network as it does in MOFs: to give just one example, the recently reported arylethynylene-connected material MOF-210^[14] exhibits such “broken” conjugation. Another key distinction is that most MOFs are crystalline^[15] whereas these MO-CMP networks are amorphous.

Polymers based on cyclometalated Ir complexes have been studied widely as components in light-emitting diodes,^[16] but no porous examples have been reported until now. The full N₂ isotherms for these polymers give rise to type I nitrogen gas sorption isotherms, indicating that these MO-CMPs are also microporous (see Figures S4–S7 in the Supporting Information).

These two strategies—post-synthetic metalation and direct metal incorporation by copolymerization—offer the possibility to design conjugated microporous materials with a range of functions. As a proof of concept, we have evaluated one of the networks as a heterogeneous catalyst. Recently, a few examples of CMPs showing catalytic activity have been reported.^[10,17] Polymer **C** contains a cyclometalated Ir^{III} complex which is closely related to a class of successful reductive amination catalysts.^[18] We therefore examined the heterogeneous catalytic activity of the CMP-CpIr networks. All of the networks were found to be catalytically active but

CMP-CpIr-3, which did not include 1,4-dibromobenzene (**3**), showed the highest activity. This network performed well with respect to homogeneous catalysis using the soluble compound **6** (see Table S1 in the Supporting Information). A range of substrates were subsequently surveyed using CMP-CpIr-3 as catalyst for reductive amination (Table 2). It was found that

Table 2: Reductive amination catalyzed by CMP-CpIr-3.^[a]

$R^1-C(=O)-R^2 + R^3-NH_2 \xrightarrow{\text{CMP-CpIr-3}} R^1-CH(R^2)-CH(R^3)-NH_2$			
Entry	Ketone	Amine	Yield [%] ^[b]
1			95
2			91
3			90
4			93
5			86

[a] Reaction conditions: ketone (0.5 mmol), amine (0.6 mmol), HCOOH/Et₃N (2.5:1 molar) = 0.5 mL, MeOH (3 mL), 1 mol% Ir based on ketone (the Ir content was determined from ICP analysis), 80 °C, 12 h. [b] Yield of isolated product.

CMP-CpIr-3 indeed displayed high catalytic activity across a range of substrates with yields of isolated product higher than 90 %, which are comparable with the results obtained for a related homogeneous Ir catalyst.^[18]

In summary, we have demonstrated two simple and versatile strategies for preparing metal–organic conjugated microporous polymers (MO-CMPs). Microporous networks containing rhenium, rhodium, and iridium have been prepared but the methodology should be readily extended to other metals. The metal loading is tunable and substantial metal incorporation can be achieved in microporous solids which retain high surface areas. We also give the first example of a microporous polymer network comprising a cyclometalated complex as a framework node. The resulting metal-containing networks are amorphous and thermally robust. A proof-of-concept study shows that this class of polymers is promising for heterogeneous catalysis, although it is likely in this case that simpler porous supports (e.g., silica, macroporous resins) would be much more cost effective. Uniquely, however, these MO-CMPs combine highly conjugated framework backbones with the incorporation of metal–organic moieties. We therefore foresee a modular synthetic platform for the preparation of porous materials with unique physicochemical properties. For example, other researchers have already demonstrated the potential for light harvesting and

energy transfer within nonmetalated CMP networks.^[8] We believe that MO-CMPs materials could be a platform for applications such as light harvesting, photocatalysis, and photocatalytic hydrogen evolution.^[19]

Experimental Section

Synthesis; typical procedure for IrCMP-1: 1,4-diethynylbenzene (190 mg, 1.5 mmol), monomer **5a** (460 mg, 0.5 mmol), tetrakis(triphenylphosphine)palladium (20 mg), and copper iodide (10 mg) were dissolved in the mixture of DMF (4 mL) and Et₃N (4 mL). The reaction mixture was heated to 90 °C, stirred for 72 h under a nitrogen atmosphere, and then cooled to room temperature. The precipitated network polymer was filtered and washed four times with chloroform, water, methanol, and acetone to remove any unreacted monomer or catalyst residues. Further purification of the polymer was carried out by Soxhlet extraction with dichloromethane for 24 h. The product was dried in vacuum for 24 h at 70 °C as red powder (yield: 422 mg, 65 %).

Received: September 18, 2010

Published online: December 22, 2010

Keywords: conjugated microporous polymers · coordination polymers · polymerization · porous materials

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