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### COMMUNICATION

#### Enantioselective catalysis with a chiral, phosphane-containing PMO material<sup>†</sup>

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A novel bistriethoxysilyl-BINAP monomer was prepared and co-condensed with a biphenylene-bridged siloxane precursor in the presence of surfactant templates to give periodic mesoporous organosilicas (PMOs) functionalized with BINAP. Complexation of ruthenium followed by asymmetric catalytic hydrogenation and asymmetric transfer hydrogenation were carried out, and demonstrated that high levels of activity and selectivity are achievable with the chiral material.

Organic-inorganic hybrid materials have attracted attention from a variety of disciplines since they combine the functionality of the organic spacer with the mechanical strength of an inorganic network.<sup>1</sup> In particular, polysilsesquioxanes can be prepared using templated approaches that give fine control over micro, meso and macroscopic ordering, providing a wide array of structured organic-inorganic hybrid materials (Fig. 1).<sup>2-4</sup> Although amorphous materials can be prepared without the benefit of a sacrificial template and still have high surface areas, pore structures can be expected to be significantly disordered, burying active sites inside the wall and decreasing permeation of substrates.<sup>5</sup> On the other hand, surfactant-templated synthetic methods permit greater control over morphology and porosity, with the ultimate example being the 2002 report by Inagaki and co-workers who showed that a biphenylene-bridged (2) periodic mesoporous organosilica (PMO) materials could be prepared that displayed molecular scale order in the walls.<sup>2</sup> Sayari and co-workers succeeded in preparing PMOs employing the same biphenylene-bridged precursor under acidic conditions in 2007.<sup>6</sup>

Previous work from our group showed that a mixed PMO could be synthesized in which a functional chiral organic monomer can be introduced directly into the backbone by the co-condensation of **2** and **3**.<sup>7</sup> It was the first example of a chiral PMO which employed an axially chiral molecule, and in which a chiral dopant was employed to induce chirality in the material *via*  $\pi$ - $\pi$  stacking interactions between aromatic systems in the solid state.

One of the main goals for the development of these materials in our lab and others is for their use as heterogeneous catalysts if appropriate ligands can be introduced.<sup>8</sup> In this case, it is especially



Fig. 1 Organic-bridged siloxane precursors with biphenyl and binaphthyl structure.

important that the placement of the ligand within the wall can be controlled and that the porosity of the material is not disrupted to permit appropriate access to the eventual catalyst. As compared to typical grafting methods, the ability to incorporate ligands directly in the walls of porous materials is expected to provide considerable advantages in this regard, and also with respect decreased cleavage of the ligand from the support.

BINAP is one of the most practical and widely used chiral bidentate phosphane ligands.<sup>8</sup> Its use in the enantioselective hydrogenation of alkenes and carbonyl compounds with Rh or Ru catalysts was the subject of the 2001 Nobel Prize in Chemistry.<sup>9</sup> Considering its importance in organic synthesis, then, it is not surprising that there have been various supported versions reported.<sup>10</sup> For example, van Koten and co-workers reported the immobilization of BINAP on amorphous silica using di-ureyl functionalized BINAPO monomer  $(4)^2$ , and Yang and co-workers co-condensed 4 with tetramethylorthosilicate (TMOS, Si(OMe)<sub>4</sub>) under acidic conditions employing the tri-block copolymer P123 as a surfactant template to obtain BINAP-supported in all silica porous materials.11 However, mesoporous materials prepared from monomers that have the siloxane groups directly attached to the backbone of BINAP have not been prepared, and the synthesis of the dual hybrid PMO materials employing such a functionalized chiral ligand has also not yet been realized.

Herein, we describe the synthesis of the title material in which an immobilization of BINAP was successfully achieved *via* the co-condensation of 1 along with 2 under acidic conditions employing Brij76 surfactant permitting us to adjust the pore diameter to about 26 Å. In addition, we present the application of the resulting functional material to heterogeneous asymmetric hydrogenation both under high-pressure hydrogenation conditions and atmospheric hydrogen transfer.

Functionalized BINAPO monomer 1 was prepared from commercially available BINAP 5 in three steps (Scheme 1). Protecting the phosphanes of BINAP as a bisphosphane oxide

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 $<sup>\</sup>dagger$  Electronic supplementary information (ESI) available: Material preparations and characterizations including N<sub>2</sub> isotherms, CP MAS NMR spectra and powder XRD spectra are available. See DOI: 10.1039/c2cc31247f



Scheme 1 Synthesis of the 5,5'-bistriethoxysilyl-BINAPO (1).

(BINAPO, 6) was accomplished by oxidation with hydrogen peroxide. Following this, bisiodination at the 5- and 5'-positions gives bisiodoBINAPO 7. Direct installation of the triethoxysilyl moieties on the binaphthyl structure was performed *via* a Rh-catalyzed Masuda reaction. This last step proved to be a significant challenge since the Masuda reaction resulted in bissilylation along with monosilylation/monoreduction. The desired bissilylated ligand precursor 1 could only be obtained cleanly after chromatographic separation of the monosilylated byproduct. Thus the low yield of this product resulted from a combination of the poor selectivity in the Masuda coupling and losses during the chromatography of the sensitive bis siloxane. Regardless, since all other steps are high yielding (>90%), and the lowest yielding step was the final step, this route provided sufficient material to prepare and test PMO materials containing 1 as an additive.

It must be noted here that prior to the synthesis of **1**, we attempted to prepare 4,4'-functionalized BINAP by several routes. Although both bromination and iodination at the 4,4'-position could be achieved, successive rhodium catalyzed silylation did not give any of the desired product, only reduction.

Thus with a viable route to compounds 1 and 2, these were mixed in a 15/85 and 5/95 molar ratio along with surfactant Brij-76 as the structure-directing agent under acidic conditions (Molar ratio: Si/water/HCl/NaCl/EtOH/Brij-76 = 1.00/600/8.40/19.0/ 18.4/0.533). After extraction of the surfactant, nitrogen adsorption analysis of this material showed that it was highly ordered with a pore diameter of ca. 26 Å (Table 1, entry 1-4. Fig. S-1, 2 (ESI<sup>+</sup>)). Similar materials were prepared employing TEOS (Si(OEt)<sub>4</sub>) as the bulk constituent (1/TEOS = 7.5/92.5 molar ratio) (entries 6 and 7). These primarily silica materials had less ordered and smaller pores making them micro- rather than mesoporous, but they were characterized by high surface areas and good pore volumes. These results clearly showed that installing the functionality in the wall structure gives functionalized PMOs with larger surface areas, compared with the PMO which was functionalized via monomers prepared with longer, more flexible tethers (entry 8).

To generate an effective heterogeneous catalyst from this material, three post-condensation steps were employed: TMS capping of free silanols, phosphane oxide reduction, and complexation of ruthenium. <sup>29</sup>Si CPMAS NMR of the silylated materials showed large T3-sites, appearing concomitantly with disappearance of T1-sites, implying successful capping of the silanols (Table S-1, entry 1. Fig. S-4, B, ESI†).

The reduction of phosphane oxides to phosphanes in solution is typically carried out with excess trichlorosilane at

Table 1 Physical characteristics of BINAPO-PMOs

Entry	Surfactant	Molar ratio of 1/2	Surface area/m <sup>2</sup> g <sup>-1</sup> $a$	Pore size/Å <sup>b</sup>	$\frac{\text{Pore volume}}{\text{cm}^3 \text{ g}^{-1}}$
1	Brij76	rac-15/85	785	25.1	0.549
2	•	(S)-15/85	626	26.4	0.461
3		(R)-15/85	703	24.2	0.626
4		(R)-5/95	708	26.9	0.574
5		0/100	668	27.0	0.540
6 <sup><i>c</i></sup>		(S)-7.5/92.5	701	18.1	0.345
$7^c$		(R)-7.5/92.5	786	16.5	0.347
$8^d$	P123	( <i>R</i> )-11/89	331	77	0.61
<sup>a</sup> Calc	ulated from	BET plot. <sup>l</sup>	BJH adsorpti	on avera	age pore size.

<sup>*c*</sup> TEOS (Si(OEt)<sub>4</sub>) was employed instead of **2**. <sup>*d*</sup> Compound **4** and TMOS (Si(OMe)<sub>4</sub>) were co-condensed, reported by Wang *et al.*<sup>11</sup>

elevated temperatures,<sup>12</sup> conditions that can result in dramatic losses of surface area and porosity in mesoporous materials, possibly by agglomeration of the silane on the surface of the materials. To address this, we have found that ultra high purity trichlorosilane is needed, along with the use of triethylphosphite as an oxygen scavenger.<sup>13</sup> The reaction was furthermore carried out at 80 °C on material that had previously been deactivated by silylation of the surface. <sup>31</sup>P CP MAS NMR was used to probe the success of the reduction as the signal at 30 ppm for BINAPO shifted to -15 ppm for the trivalent phosphane of BINAP (Fig. S-4A, ESI†). The reaction occurred without loss of mesoporosity or order (Table S-1, entry 2, ESI†). It is notable that clean and complete conversion of the phosphane oxide to the phosphane implies a *remarkable complete accessibility of all BINAP functionalities contained within the material.* 

With the reduction successfully completed, complexation of ruthenium on the BINAP unit was carried out following literature conditions<sup>14</sup> after drying the PMO under high vacuum at 80 °C in an oil bath overnight prior to use. Successive filtration and washing with copious amounts of methanol followed by dichloromethane gave a pale red powder. This powder was stored in a vial filled with argon, but still could be handled in open air when it was dry. <sup>31</sup>P CP MAS NMR analysis of this material (Ru/5%(R)-BINAP-PMO) showed successful complexation (Fig. S-4, ESI†).

Further analysis of the material by pXRD indicated that the materials exhibit some degree of crystallinity within the walls due to local alignment of the organic groups (Fig. S-3, ESI†). This increased order will likely add to the stability of the material. It is notable that preparing a locally aligned PMO in acidic condensation condition with Brij76 template is quite rare, thus the use of a rigid binapthyl precursor **1**, which matches perfectly in size with the bulk biphenylene monomer **2**, is likely responsible for the highly ordered walls observed in these materials. The amount of ruthenium doped on the solid catalyst was determined to be 0.084 mmol g<sup>-1</sup> by ICP-MS elemental analysis. The TEM images of Ru/5%(R)-BINAP-PMO exhibited cleanly ordered long nano channels and hexagonal structure (Fig. 2).

Having prepared a well ordered, mesoporous organosilica material containing BINAP-modified Ru catalyst in the walls, we then set out to test its catalytic activity in the rutheniumcatalyzed asymmetric hydrogenation of  $\beta$ -ketoesters. Since the condensation points for the bis-trialkoxysilyl BINAP monomer are the 5,5'-positions which are not on the atropisomeric axis, and since there are no flexible spacer units between the BINAP and



Fig. 2 TEM images of Ru doped 5%(R)-BINAP-PMO.

 Table 2
 Asymmetric catalytic hydrogenation under high-pressure hydrogen gas

	$\begin{array}{c} O \\ R_2 \end{array} \xrightarrow{O \\ OR_1 \end{array} \begin{array}{c} [Ru] \text{ cat.} \\ MeOH, H \\ \hline 50^{\circ}C \end{array}$	$\begin{array}{c} 0.1 \text{mol\%} \\ \text{H}_2 600 \text{ psi} \\ \text{H}_2 600 \text{ psi} \\ \text{H}_2 600 \text{ psi} \\ \text{H}_2 \\ $	OR <sub>1</sub>
Entry	$R_1, R_2$	Yield [%] <sup><i>a</i></sup>	e.e. [%] <sup>b</sup>
1	Me, Me	99	99
2		99	99
3	Me. Et	99	99
4	Et, Me	99	99
5	Me, iPr	99	99
5	Me, 4-MeOPh	99	99
$7^c$	Me, Me	99	99

Ru/5%(R)-BINAP-PMO was employed.<sup>*a*</sup> Isolated yield. <sup>*b*</sup> Determined by supercritical fluid chromatography (SFC) using CHIRALPAK OD-H column with  $1 \sim 20\%$  MeOH additive at 50 °C, 2 mL min<sup>-1</sup>, 200 bar. <sup>*c*</sup> Homogeneous Ru/BINAP was employed under the same conditions.<sup>11</sup>

the polymerization points, we were concerned that the twist angle could be distorted upon inclusion of the ligand in the material. Since the twist angle controls the bite angle of the two phosphane units, and affects the transmission of chirality, it is possible that the BINAP-PMO will give different results compared to the solution catalyst, which is free to adopt the most favourable conformation around the central atropisomeric axis. Despite these concerns, our PMO catalyst was exceptionally reactive, giving the expected products in excellent yields and stereoselectivities, consistent with solution results for monomeric binap-based catalysts (Table 2). Since this is not often the case for supported catalysts, these results validate our approach to the design of novel catalytically active PMOs. Additionally, no differences in reactivity were observed relative to the size of the substrates employed, at least for typical substrates, indicating that the mesoporosity permits facile access to the active sites (entries 1-6). Furthermore, since the catalyst is completely heterogeneous, recycling of the catalyst was easily carried out by a quick centrifugation followed by taking the supernatant out then addition of a fresh substrate solution (entry 2). Another notable advantage from this heterogeneity is that a simple filtration is sufficient to purify the organic products. Importantly, analysis of the recovered PMOs indicated that the mesoporosity was maintained even after the treatment under highpressures of hydrogen (Table S-1, entry 4, ESI<sup>+</sup>).

Finally, we also employed the PMO catalyst in a rutheniumcatalyzed transfer hydrogenation (Scheme 2). Although it is still necessary to add a soluble chiral diamine to give the product stereoselectively, the hydrogenated product was obtained in excellent yield, and enantioselectivity. Compared to previous



Scheme 2 Asymmetric transfer hydrogenation of a simple ketone (4-methoxyacetophenone).

studies noting the base-sensitivity of mesoporous materials, the mesostructure of this material was highly maintained after being subjected to a solution of basic isopropyl alcohol at high temperature for an extended time (Table S-1, entry 5, ESI†).<sup>15</sup>

In conclusion, BINAP and biphenylene-bridged hybrid periodic mesoporous organosilicas (PMOs) were synthesized by co-condensation of a novel 5,5'-bistriethoxysilyl BINAP monomer with 4,4'-bistriethoxysilylbiphenyl, templated by Brij76 surfactant under acidic conditions. The resulting PMOs had well ordered mesopores and crystal-like local alignment of the organic groups within the walls. Since the chiral BINAP unit was polymerized *via* rigid linkers at the 5,5' positions, which is off the axis of chirality, the potential existed for detrimental effects on the bite angle of the ligand. However, no negative effects on asymmetric catalysis were observed for two different hydrogenation reactions. Further studies to apply this material to other catalytic reactions are in progress.

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