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Synthesis and Characterization of Chiral Benzylic Ether-Bridged Periodic Mesoporous Organosilicas

Jürgen Morell,[b] Sangam Chatterjee,[c] Peter J. Klar,[d] Daniel Mauder,[e]
Ilja Shenderovich,[e] Frank Hoffmann,[a] and Michael Fröba*[a]

Abstract: The first synthesis of a chiral periodic mesoporous organosilica (PMO) carrying benzylic ether bridging groups is reported. By hydrolysis and condensation of the new designed chiral organosilica precursor 1,4-bis-(triethoxysilyl)-2-(1-methoxyethyl)benzene (BTEMEB) in the presence of the non-ionic oligomeric surfactant Brij 76 as supramolecular structure-directing agent under acidic conditions, an ordered mesoporous chiral benzylic ether-bridged hybrid material with a high specific surface area was obtained. The chiral PMO precursor was synthesized in a four-step reaction from 1,4-dibromobenzene as the starting compound. The evidence for the presence of the chiral units in the organosilica precursor as well as inside the PMO material is provided by optical activity measurements.

Keywords: chirality · mesoporous materials · optical activity · organosilicas · structure-directing agents

Introduction

In 1999, a new class of organic–inorganic hybrid materials called periodic mesoporous organosilicas (PMOs) was developed by three groups working independently.[1–3] The synthesis of this kind of materials can be carried out by hydrolysis and condensation of bridged organosilsesquioxane precursors [$(R'O)_3Si$-R-$Si(OR')_3$] in the presence of supramolecular structure-directing agents. There are enormous possibilities to deliberately tune the chemical and physical properties of the PMOs by varying the organic spacer groups of the organosilica precursors, which makes these materials interesting for applications such as catalysis, adsorption, chromatography, or host–guest chemistry.[4,5] The organic bridging groups of the organosilica precursors that have been successfully converted into PMO materials include, for instance, methylene,[6] ethylene,[1,3] ethenylene,[2,3] phenylene,[7] biphenylene,[8] thiophene,[7,9] and divinylphenylene[10,11] units. It was also possible to prepare PMOs possessing molecular-scale periodicity inside the channel walls instead of the common observed amorphous pore walls as a result of a highly cooperative process.[12,13] To obtain larger pore sizes in PMO materials, non-ionic triblock copolymers can be employed as structure-directing agents instead of the commonly used ionic alkylammonium halides.[9,14] Moreover, it was possible to prepare PMOs with defined morphologies such as spherical particles, which have proved to be suitable for chromatography applications.[15] Furthermore, the synthesis of bifunctional PMO materials has been reported.[16] However, so far only a few attempts have been undertaken to link molecular chirality and organic–inorganic hybrid materials, which would make these materials even more interesting for potential applications such as enantioselective catalysis or chromatography. Hitherto, either chiral mesoporous organosilicas with a limited loading of chiral organic groups (obtained via the co-condensation approach),[17–19] or chiral organosilicas lacking true periodicity were reported.[20] Polarz and Kuschel[21] reported on a PMO composed of a

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[a] Dr. F. Hoffmann, Prof. Dr. M. Fröba
Institute of Inorganic and Applied Chemistry
University of Hamburg
Martin-Luther-King-Platz 6, 20146 Hamburg (Germany)
Fax: (+49) 40-428-38-6348
E-mail: michael.froeba@chemie.uni-hamburg.de

[b] Dr. J. Morell
Institute of Inorganic and Analytical Chemistry
Justus Liebig University Giessen
Heinrich-Buff-Ring 58, 35392 Giessen (Germany)

[c] Dr. S. Chatterjee
Faculty of Physics and Material Sciences Center
Philipps University Marburg
Renthof 5, 35032 Marburg (Germany)

[d] Prof. Dr. P. J. Klar
Institute of Experimental Physics I
Justus Liebig University Giessen
Heinrich-Buff-Ring 16, 35392 Giessen (Germany)

[e] D. Mauder, Dr. I. Shenderovich
Institute of Chemistry, Free University of Berlin
Takustrasse 3, 14195 Berlin (Germany)

chiral silsesquioxane precursor; however, neither information on the enantiomeric excess of the precursor was given nor a proof of the chirality of the PMO. Very recently, Inagaki et al. reported the synthesis of a new PMO material carrying chiral phenylethylene bridging groups, for which the enantiomeric purity was determined by eluting the organic groups from the solids.[22] Here we present the synthesis of the completely novel chiral organosilica precursor 1,4-bis(triethoxysilyl)-2-(1-methoxyethyl)benzene (BTEMEB) carrying benzylic ether bridging groups, which was used as a single-source precursor to prepare a homochiral genuine PMO (see Scheme 1). Furthermore, we demonstrate that the chirality of the PMO can be directly and in a non-destructive way proven by measurements of the optical activity, which is a novelty for the solid-state.

Results and Discussion

The synthesis of the chiral PMO precursor 1,4-bis(triethoxysilyl)-2-(1-methoxyethyl)benzene (BTEMEB) (**4**) with a high enantiomeric excess of 88 % *ee* (determined by enantioselective chromatography) was achieved in a four-step reaction from 1,4-dibromobenzene by using synthesis procedures established in the literature (see Scheme 1). 2,5-Dibromoacetophenone (**1**) was synthesized from 1,4-dibromobenzene by Friedel–Crafts acylation[23] followed by an asymmetric hydrogenation of **1** in the presence of the chiral ruthenium catalyst **6** to obtain chiral 1-(2,5-dibromophenyl)ethanol (**2**).[24] The OH group of **2** was methylated by treatment with NaH and CH_3I, leading to 1,4-dibromo-2-(1-methoxyethyl)benzene (**3**).[25] The last synthesis step leading to the novel chiral organosilica precursor BTEMEB (**4**) was achieved by carrying out a Grignard reaction. The new chiral benzylic ether-bridged PMO material **5** was prepared by hydrolysis and condensation of BTEMEB in the presence of the non-ionic oligomeric surfactant Brij 76 as structure-directing agent under acidic conditions (see the details of the synthesis procedures in the Experimental Section).

The powder X-ray diffraction pattern of the solvent-extracted benzylic ether-bridged PMO material (Figure 1) exhibits one intense Bragg reflection at $2\theta = 1.52°$, which confirms the existence of an ordered mesostructure with an interplanar d spacing of 5.81 nm of the pore arrangement with approximately uniform pore sizes. The absence of any other reflections in the low-angle region indicates limited periodicity in the long-range order of the mesopore system. Thus, it can be assumed that the mesostructure of the material resembles that of the HMS silica phases.[26] The occurrence of only one intense reflection indicates the existence of smaller scattering domain sizes inside the product compared to those of typically highly ordered PMO materials. Furthermore, the pore wall structure is not crystal-like as no reflections in the higher angle region are observed.

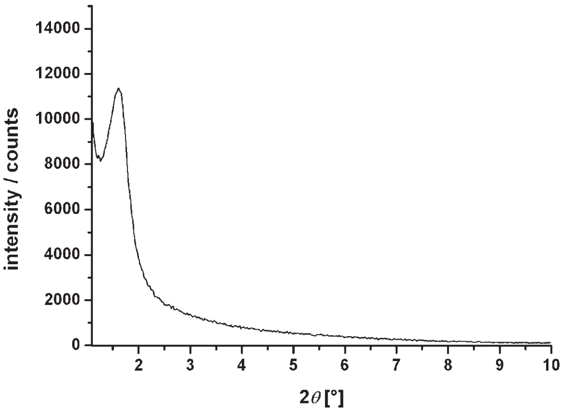
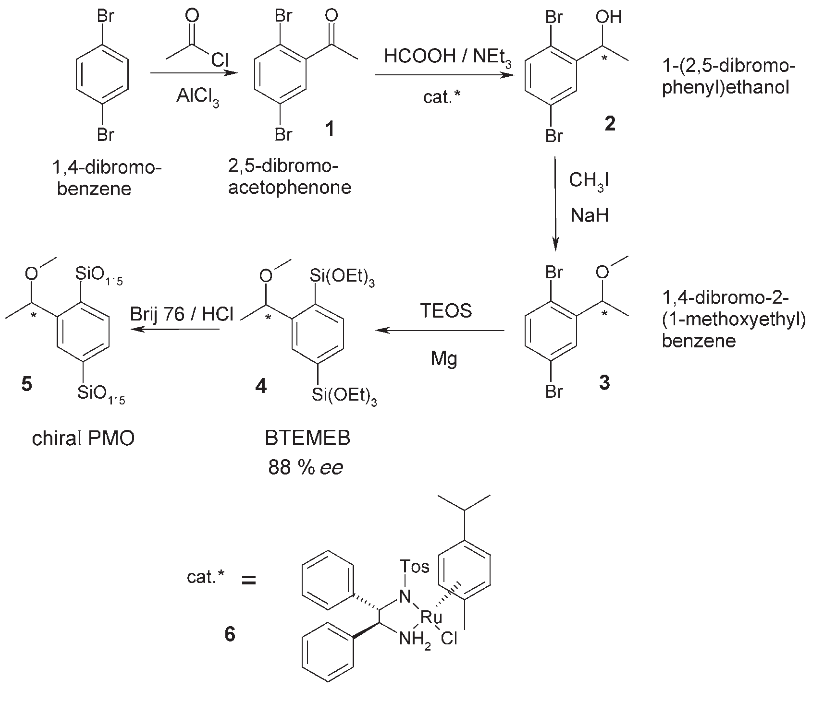


Figure 1. Powder X-ray diffraction pattern of the chiral benzylic ether-bridged periodic mesoporous organosilica.



Scheme 1. Synthesis pathway of the PMO precursor BTEMEB as well as the chiral PMO product.

The transmission electron microscope (TEM) image of the PMO material (Figure 2) also shows the presence of a wormhole-like structure rather than a 2D hexagonal mesostructure as expected from the XRD pattern. Thus, the mesostructural order of the product occurs in

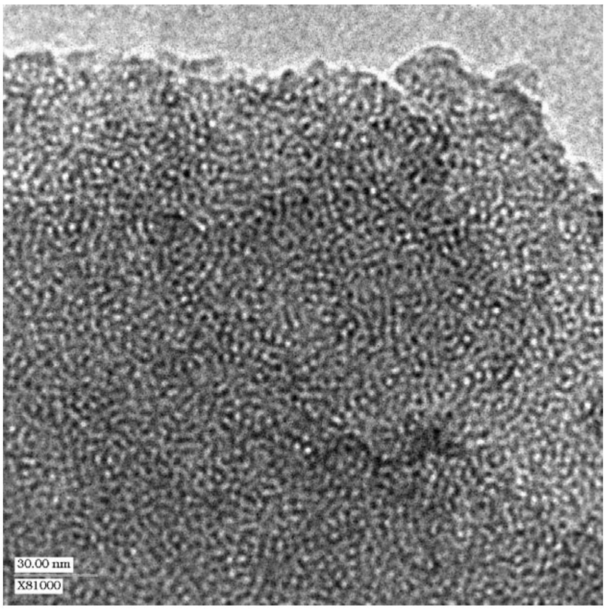


Figure 2. TEM image of the chiral benzylic ether-bridged periodic mesoporous organosilica.

the range between unordered compounds and highly ordered periodic mesoporous organosilicas.

The N_2 physisorption measurements on the PMO material reveal an isotherm, which can best be assigned to type IV, but which also exhibits features of type I, indicating the presence of both meso- and micropores inside the material (Figure 3). The isotherm shows a not very distinctive capillary condensation step at a p/p^0 of about 0.22, and furthermore no hysteresis loop is observed that is typical of mesoporous materials with small pore sizes.[27] The pore size distribution actually shows the existence of both mesopores with an average pore diameter of 2.3 nm and also micropores inside the product (Figure 4). The specific surface area of the PMO is 820 $m^2 g^{-1}$ (BET) with a total mesopore volume of 0.46 $cm^3 g^{-1}$.

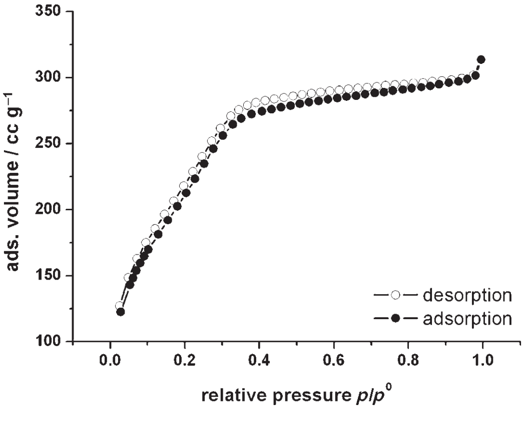


Figure 3. Nitrogen adsorption/desorption isotherm of the chiral benzylic ether-bridged periodic mesoporous organosilica.

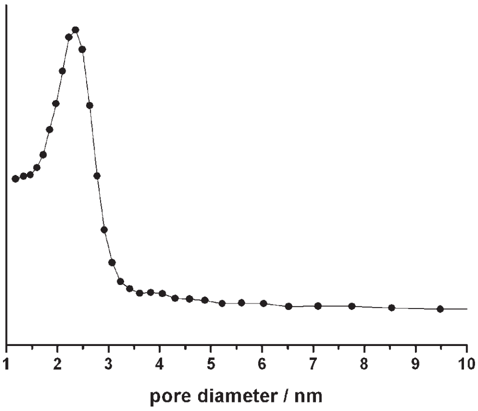


Figure 4. Pore size distribution of the chiral benzylic ether-bridged periodic mesoporous organosilica.

To confirm the presence of the organic moieties inside the PMO material, ^{29}Si and ^{13}C MAS NMR spectroscopic measurements were carried out. The ^{13}C CPMAS NMR spectrum (Figure 5) shows the characteristic signals of the benzylic ether bridging group, which can be attributed to the *C* species as follows: $\delta=23.8$ ($\mathrm{C_{aryl}\text{-}CH\text{-}\mathit{C}H_3}$); 55.9 ($\mathrm{O\text{-}\mathit{C}H_3}$); 78.5 ($\mathrm{C_{aryl}\text{-}\mathit{C}H\text{-}CH_3}$); 126.6, 130.0, 130.1, 137.1, 145.6, 154.0 ppm ($\mathit{C}_{\mathrm{aryl}}$). The ^{29}Si CPMAS NMR spectrum (Figure 6) exhibits three T^n signals, which can be assigned to the following *Si* species covalently bonded to the carbon atoms: T^1 [C-*Si*-(OSi)(OH)$_2$, $\delta=-58.4$ (2.6%)], T^2 [C-*Si*(OSi)$_2$(OH), $\delta=-72.0$ (38.8%)], and T^3 [C-*Si*(OSi)$_3$, $\delta=-79.3$ (43.9%)]. As Q^n signals ($n=2$–4, $\delta=-92$ to -113) only appear with a proportion of less than 15%, the MAS NMR spectroscopic measurements clearly indicate that almost all benzylic ether units are still intact inside the pore walls of the PMO material after the synthesis and extraction procedure.

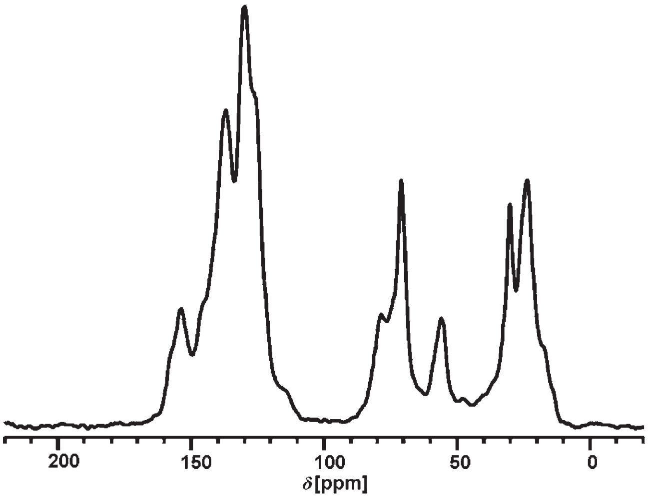


Figure 5. ^{13}C CPMAS spectrum of the chiral benzylic ether-bridged periodic mesoporous organosilica.

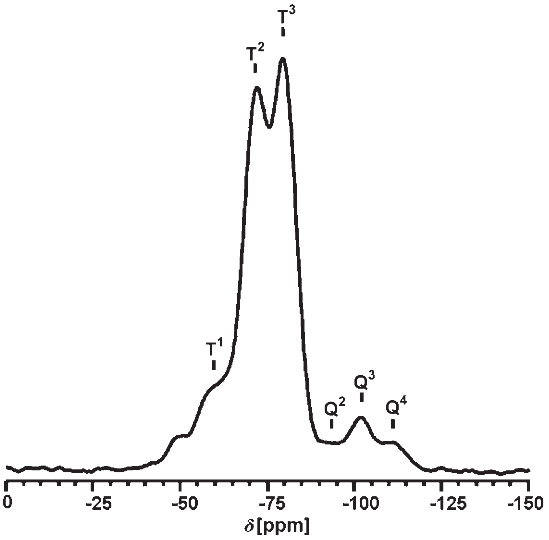


Figure 6. ^{29}Si CPMAS spectrum of the chiral benzylic ether-bridged periodic mesoporous organosilica.

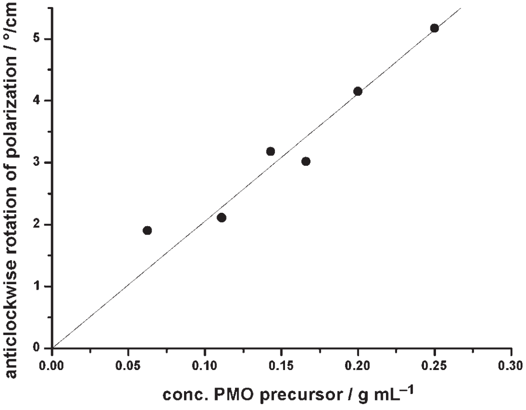


Figure 7. Results of the optical activity measurements on the chiral PMO precursor. Anticlockwise rotation of the polarization plotted against the PMO precursor concentration as well as the resulting linear fit.

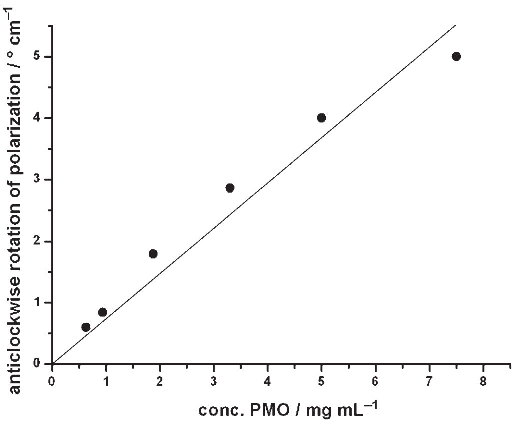


Figure 8. Results of the optical activity measurements of the chiral PMO material. Anticlockwise rotation of the polarization plotted against the PMO concentration as well as the resulting linear fit.

Figure 7 and Figure 8 depict the results of the optical activity measurements of solutions of the precursor BTEMEB in chloroform and suspensions of the PMO product in ethanol/chloroform, respectively. In both cases the rotation angle $\Delta\theta$ depends linearly on the concentration of the chiral compound, as expected by theory. The specific optical activity of BTEMEB determined at 633 nm is about $-200°(\mathrm{dm\,mL\,g^{-1}})^{-1}$. A value for the specific optical activity in ° per dm ($°\,\mathrm{dm}^{-1}$) of the solid PMO powder can be roughly estimated from the measurements of the corresponding suspension as follows. We obtain a rotation of the polarization by 6° for a PMO concentration of 8 mg mL^{-1} of 1:1 ethanol/chloroform from the linear fit to the experimental data in Figure 8. As the PMO material is floating in the ethanol–chloroform solution, we assume that its density is the same as the average density of the ethanol–chloroform mixture, that is, $\rho = 1.135\,\mathrm{g\,mL^{-1}}$. Therefore, the concentration of 8 mg mL^{-1} corresponds to a volume ratio V_{PMO}:V_{tot} of about 1:110. Furthermore, assuming that the suspension is isotropic, the effective length of the light path through the PMO, L_{PMO}, is related to the length of the light path through the cuvette, $L_{tot} = 0.1$ dm, by $L_{PMO} = (V_{PMO}/V_{tot})^{1/3}\cdot L_{tot} \approx 0.021$ dm. Finally, we obtain the value of $-275°\,\mathrm{dm}^{-1}$ for the specific optical activity at 633 nm for the synthesized solid PMO product. Our results provide unambiguous proof that both the precursor BTEMEB and the corresponding PMO material carrying benzylic ether bridging groups, are chiral compounds.

Conclusion

In summary, we have synthesized the first chiral PMO material bearing benzylic ether bridging groups. The PMO material was prepared from the novel chiral organosilica precursor 1,4-bis(triethoxysilyl)-2-(1-methoxyethyl)benzene (BTEMEB) in the presence of the surfactant Brij 76 as structure-directing agent. The PMO precursor can be synthesized with an enantiomeric excess of 88 % *ee*. We have clearly proved the chirality of the organic moieties inside the organosilica precursor as well as in the PMO material by measuring the optical activity of the samples. With regard to potential applications such as enantioselective chromatography, the chiral PMO product represents a very promising new kind of periodic mesoporous hybrid material with interesting adsorption properties, which are still under further investigation.

Experimental Section

Powder X-ray diffraction measurements: The powder X-ray diffraction (P-XRD) pattern was recorded at room temperature with a PANalytical X'Pert PRO diffractometer using filtered $\mathrm{Cu_{K\alpha}}$ radiation.

TEM analysis: The transmission electron micrograph was obtained with a Philips C 30 microscope operating at 300 kV.

N$_2$-physisorption measurements: N$_2$-physisorption data were recorded with a Quantachrome Autosorb 6 at 77 K. The BET surface area was calculated from $p/p^0 = 0.03–0.3$ in the adsorption branch, and the BJH pore size distribution was calculated from the desorption branch.

MAS NMR measurements: The ^{13}C and ^{29}Si NMR measurements were performed on a Bruker MSL-300 instrument, operating at 7 T, equipped with a Chemagnetics-Varian 6 mm pencil CPMAS probe. The samples were spun at 6.0–8.0 kHz under magic angle spinning (MAS) conditions. The {^{1}H}–^{29}Si CPMAS spectrum was recorded by using a relatively long cross polarization (CP) contact time of 8 ms, which ensures sufficient polarization transfer to all different species of silica; further parameters were a recycle delay of 5 s and 2000 scans. The ^{13}C NMR measurement was performed by employing the {^{1}H}–^{13}C CPMAS technique with a CP contact time of 2 ms, a recycle delay of 15 s and 3000 scans. The typical π/2-pulse width in the CP experiments was 3.5 μs for ^{1}H. ^{29}Si and ^{13}C chemical shift values are referenced to solid TSP.

PMO precursor synthesis: 1,4-Bis(triethoxysilyl)-2-(1-methoxyethyl)benzene (BTEMEB) was synthesized in a four-step reaction starting from 1,4-dibromobenzene as follows:

Step 1: Synthesis of 2,5-dibromoacetophenone: The synthesis was carried out from 1,4-dibromobenzene in accordance with the synthesis protocol given in reference [23].

Step 2: Synthesis of chiral 1-(2,5-dibromophenyl)ethanol: The synthesis was carried out following a slightly modified version of the synthesis protocol given in reference [24]: In a three-necked flask with a condenser, [Ru^{II}Cl$_2$-(*p*-cymene)] (0.37 g, 0.624 mmol), 1*S*,2*S*-*N*-*p*-tosyl-1,2-diphenylethylenediamine (0.2 g, 1.24 mmol), and triethylamine (2.3 mL) were dissolved in 2-propanol (57.5 mL) under an argon atmosphere. After the solution had been heated for 1 h at 85 °C, 2-propanol and triethylamine were evaporated, whereon the preformed chiral catalyst remained. Then 2,5-dibromoacetophenone (34.6 g, 0.125 mol) and HCOOH/NEt$_3$ (62.1 mL) were added and the solution was stirred for 48 h under ambient conditions. After addition of saturated NaHCO$_3$ (100 mL), the crude product was extracted with ethyl acetate, and the organic layer was dried over MgSO$_4$. The ethyl acetate was evaporated, and the crude product was distilled in vacuo to obtain chiral 1-(2,5-dibromophenyl)ethanol (28.4 g, 0.102 mol, yield: 81 %). ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 1.43$ (d, $J = 6.4$ Hz, 3H, C$_{\text{aryl}}$-CH-CH_3), 2.47 (s, 1H, -OH), 5.13 (q, $J = 6.4$ Hz, 1H, C$_{\text{Aryl}}$-CH-CH$_3$), 7.44–7.64 ppm (m, 3H, C$_{\text{aryl}}$-H); ^{13}C NMR (100 MHz, CDCl$_3$): $\delta = 23.7$ (C$_{\text{aryl}}$-CH-CH$_3$), 68.7 (C$_{\text{ayl}}$-CH-CH$_3$), 121.4, 122.0, 128.0, 130.9, 134.9, 143.8 (C_{aryl}).

Step 3: Synthesis of chiral 1,4-dibromo-2-(1-methoxyethyl)benzene: The synthesis was carried out following a slightly modified version of the synthesis protocol given in reference [25]: In a three-necked flask with a condenser, chiral 1-(2,5-dibromophenyl)ethanol (28.4 g, 0.102 mol) was dissolved in THF (305 mL) under an argon atmosphere, and then NaH (6.1 g, 0.15 mol, 55–65 %) was added. After addition of methyl iodide (25.4 mL, 0.406 mol), the resulting suspension was stirred for 20 h under ambient conditions. Then the THF was evaporated and the crude product was extracted with dichloromethane. After the organic layer had been dried over MgSO$_4$, the dichloromethane was evaporated, and the remaining crude product was distilled in vacuo to obtain chiral 1,4-dibromo-2-(1-methoxyethyl)benzene (24.5 g, 0.083 mol, yield: 82 %). ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 1.37$ (d, $J = 6.4$ Hz, 3H, C$_{\text{aryl}}$-CH-CH_3), 3.25 (s, 3H, -O-CH_3), 4.65 (q, $J = 6.4$ Hz, 1H, C$_{\text{Aryl}}$-CH-CH$_3$), 7.34 (d, $J = 8.3$ Hz, 1H, C$_{\text{aryl}}$-H), 7.47 (d, $J = 8.3$ Hz, 1H, C$_{\text{aryl}}$-H), 7.68 ppm (s, 1H, C$_{\text{aryl}}$-H); ^{13}C NMR (100 MHz; CDCl$_3$): $\delta = 23.7$ (C$_{\text{aryl}}$-CH-CH$_3$), 56.8 (-O-CH$_3$), 77.9 (C$_{\text{ayl}}$-CH-CH$_3$), 121.1, 122.9, 128.2, 131.2, 134.7, 142.1 ppm (C_{aryl}).

Step 4: Synthesis of the PMO precursor 1,4-bis(triethoxysilyl)-2-(1-methoxyethyl)benzene (BTEMEB): In a three-necked flask with a condenser and dropping funnel under an argon atmosphere, a mixture of TEOS (88.6 g, 0.426 mol), THF (65 mL), magnesium turnings (3.1 g 0.129 mol), and a small crystal of iodine was heated to 95 °C, and then a solution of chiral 1,4-dibromo-2-(1-methoxyethyl)benzene (12.5 g, 0.0425 mol) in THF (22 mL) was added dropwise over 2 h. After the mixture had been refluxed for an additional 3.5 h, THF was evaporated in vacuo, and hexane (150 mL) was added. The precipitated magnesium salts were removed by filtration under an argon atmosphere, and then hexane and residual TEOS were evaporated. The remaining brown crude product was distilled in vacuo to obtain BTEMEB (6.7 g, 0.0146 mol, yield: 34 %) as a colorless oil. The *ee* value of BTEMEB was determined to 88 % by enatioselective gas chromatography. ^{1}H NMR (400 MHz, CDCl$_3$): $\delta = 1.26$ (t, $J = 7.11$ Hz, 18H, O-CH$_2$-CH_3), 1.41 (d, $J = 6.23$ Hz, 3H, C$_{\text{aryl}}$-CH-CH_3), 3.22 (s, 3H, O-CH_3), 3.89 (q, $J = 7.11$ Hz, 12H, O-CH_2-CH$_3$), 4.79 (q, $J =$ 6,23 Hz, 1H, Ar-CH-CH$_3$), 7.56 (d, $J = 7.68$ Hz, 1H, C$_{\text{aryl}}$-H), 7.77 (d, 1H, $J = 7.68$ Hz, C$_{\text{aryl}}$-H) 8.04 ppm (s, 1H, C$_{\text{aryl}}$-H); ^{13}C NMR (100 MHz; CDCl$_3$): $\delta = 16.9$ (O-CH$_2$-CH$_3$), 22.9 (C$_{\text{aryl}}$-CH-CH$_3$), 54,9 (O-CH$_2$-CH$_3$), 57.4 (O-CH$_3$), 77.2 (C$_{\text{ayl}}$-CH-CH$_3$), 123.2, 127.0, 127.2, 136.2, 141.2, 151.9 ppm (C_{aryl}).

PMO synthesis: The chiral PMO material was synthesized as follows: In a typical synthesis, Brij 76 (0.23 g, 0.32 mmol) was dissolved in a mixture of 2 M HCl (8.3 g, 0.014 mol) and distilled water (1.7 g, 0.094 mol). After addition of BTEMEB (0.77 g, 1.7 mmol), the reaction mixture was kept for 20 h at 50 °C under vigorous stirring. After additional hydrothermal treatment for 24 h at 90 °C in a teflon-lined stainless steel autoclave, the obtained white precipitate was filtered, washed with distilled water (3 × 50 mL), and dried in air overnight. Removal of the surfactant was accomplished by extraction with a mixture of ethanol/HCl (conc.) (100:3 v/v) using a Soxhlet apparatus for 48 h with subsequent drying of the product in air. The molar ratios of the components in the reaction mixture were: BTEMEB/Brij 76/HCl/H$_2$O = 1:0.19:8.24:55.

Optical activity measurements: The optical activity, that is, the rotation of the polarization of linearly polarized light passing through the sample, was measured by a difference method as depicted schematically in Figure 9. The light of a HeNe laser (633 nm) was linearly polarized to an angle θ of 45° with respect to the horizontal x-direction using the linear polarizer. The laser was modulated at 8 kHz using an optical chopper to enable the lock-in detection technique. The light then passed through the sample in a cuvette at normal incidence, and then through an iris diaphragm, which was used to suppress scattered light. Next, a Wollaston prism spatially separated the polarized light into a horizontally polarized component (x-component of the electric field vector E_x) and a vertically polarized component (y-component of the electrical field E_y). The difference in intensity of the two corresponding beams, $I_x = |E_x|^2$ and $I_y = |E_y|^2$, was measured by a pair of identical, balanced photodiodes by using the lock-in technique. A sample which is optically active changes the polarization angle by $\Delta\theta$. Thus Equation (1) holds:

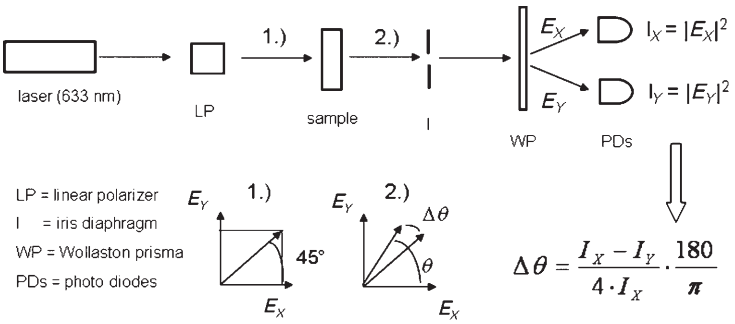


Figure 9. Experimental setup for the measurements of the optical activity.

$$\tan^2\theta = \frac{I_y}{I_x} \tag{1}$$

where θ is the angle between the x-direction and the polarization direction of the light after passing the sample. Expanding Equation (1) into a Taylor series about $\theta = 45°$ (= π/4) yields Equation (2):

$$\frac{I_y}{I_x} = \tan^2\left(\frac{\pi}{4} + \Delta\theta\right) \approx 1 + 4 \cdot \Delta\theta \tag{2}$$

and thus for $\Delta\theta$, in degrees, Equation (3) holds:

$$\Delta\theta = \frac{I_x - I_y}{4I_x} \cdot \frac{180^\circ}{\pi} \tag{3}$$

The chiral benzylic ether-bridged PMO product is of powder form. Thus its optical activity is difficult to measure because multiple scattering within the powder leads to a loss of polarization. This effect can be minimized by making a suspension of the powder with a non-chiral solvent of preferably the same refractive index. In this experiment a 1:1 mixture of ethanol/chloroform was used. The optical activity of the suspension was then measured with the latter inside a cuvette, where interfaces between air–cuvette–suspension are well defined, and, therefore, normal incidence of the light on the sample can be realized. Usually the refractive index matching between the constituents of a suspension is not perfect, that is, multiple scattering by the solid particles in the suspension still takes place. One preferentially detects photons which are still on axis, that is, mostly have gone through scattering events at normal incidence only by using a laser as the light source and the iris diaphragm after the sample as mentioned above. The high sensitivity of the differential measurement in combination with lock-in technique allows a very short optical path through the sample. Here, a 1 cm optical path is used to detect the optical activity, compared to the 10 cm used in standard set-ups. We measured a series of different concentrations of solutions of the precursor in chloroform and suspensions of the PMO product in ethanol/chloroform, respectively, to verify the linear dependence of the rotation of the polarization on the concentration of the chiral compounds. Prior, to each measurement the two photodiodes were balanced, that is, the difference signal was set to zero with an empty cuvette in the place of the sample.

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