

This item is the archived peer-reviewed author-version of:

Post-synthesis bromination of benzene bridged PMO as a way to create a high potential hybrid material

Reference:

Huybrechts Ward, Mali G., Kuśtrowski P., Willhammar Tom, Mertens M., Bals Sara, Van der Voort Pascal, Cool Pegie.- Post-synthesis bromination of benzene bridged PMO as a way to create a high potential hybrid material
Microporous and mesoporous materials: zeolites, clays, carbons and related materials - ISSN 1387-1811 - 236(2016), p. 244-249

Full text (Publishers DOI): <http://dx.doi.org/doi:10.1016/j.micromeso.2016.09.003>

Post-synthesis bromination of benzene bridged PMO as a way to create a high potential hybrid material.

W. Huybrechts,^{*,a} G. Mali,^b P. Kuśtrowski,^c T. Willhammar,^d M. Mertens,^e S. Bals,^d P. Van Der Voort^f and P. Cool^a

^a *Laboratory of Adsorption and Catalysis, University of Antwerp, Universiteitsplein 1, 2610 Wilrijk, Belgium*

^b *Laboratory of Inorganic Chemistry and Technology, National Institute of Chemistry, Hajdrihova 19, SI-1001, Ljubljana, Slovenia*

^c *Department of Chemical Technology, Jagiellonian University, Ingardena 3, 30-060 Krakow, Poland*

^d *EMAT, University of Antwerp, Groenenborgerlaan 171, 2020 Wilrijk, Belgium*

^e *Flemish Institute for Technological Research (VITO N.V.), Boeretang 200, 2400 Mol, Belgium*

^f *Centre for Ordered Materials, Organometallics & Catalysis, Ghent University, Krijgslaan 281 (S3), 9000 Ghent, Belgium*

KEYWORDS: Periodic mesoporous organosilica; PMOs; structural stability; bromination; post-modification

Abstract

Periodic mesoporous organosilicas provide the best of two worlds: the strength and porosity of an inorganic framework combined with the infinite possibilities created by the organic bridging unit. In this work we focus on post-synthetical modification of benzene bridged PMO, in order to create bromobenzene PMO. In the past, this proved to be very challenging due to unwanted structural deterioration. However, now we have found a way to brominate this material whilst keeping the structure intact. In-depth structural analysis by solid state NMR and XPS shows both vast progress over previous attempts as well as potential for improvement.

* Corresponding author. Tel.: +3232652380; E-mail address: ward.huybrechts@uantwerpen.be

1 Introduction

In 1999, three research groups working independently from one another synthesized the first periodic mesoporous organosilica (PMO) [1–3]. PMOs are organosilicon materials based on silsesquioxane precursors which act as bridges and can therefore be built into the nanoporous framework with a uniform distribution. Some interesting reviews on PMOs can be found in literature [4–6]. This class of hybrid inorganic-organic materials possesses interesting properties brought forward by the symbiosis between the strength and high porosity of the inorganic framework, combined with the chemical functionality of the organic component. Contrary to pure silica materials, PMOs do not suffer the drawbacks of instability in harsh conditions [7–9] and the lack of true active sites. These two properties in particular can be of paramount importance for applications in catalysis [10–14], coatings [15], biomedical applications [16–18], low- κ films [19–21], light-harvesting [22,23], adsorption [24,25], etc. Further activation of PMO materials can occur via post-synthetical modification of the organic bridge, leading to stable carbon-carbon bonds. This post-synthetical modification approach provides a vast array of possible pathways.

A great deal of PMO research has focused on aromatic ring bridged type PMOs because of their π - π stacking which leads to a certain degree of order [26–29] and due to their hydrophobic properties, leading to a high hydrothermal, chemical and mechanical stability [8,30]. Moreover, it is well known that aromatic compounds are, for example, prone to electrophilic aromatic substitution reactions [26,31,32].

Organic synthesis on PMOs is, however, not so straight-forward. As described in literature by Smeulders *et al.* [33], structural changes may occur due to unwanted side reactions. In this article, three different strategies for bromination of benzene bridged PMO are investigated: 1) Br_2 with AlCl_3 as catalyst, 2) *N*-bromosuccinimide (NBS) with azobisisobutyronitrile (AIBN) as radical initiator, and 3) NaBrO_3 in

combination with H_2SO_4 in order to create in situ generation of bromine. Although these reactions proved successful in liquid phase organic chemistry [34–40], they proved ineffective as a post-synthetic modification method on the PMO material. Moreover, it was difficult to prove the direct bonding site of the bromine on the PMO. Nonetheless, in said article, an important topic is touched upon which is summarized by its title *"Is there potential for post-synthetic brominating reactions on benzene bridged PMOs?"*. The authors conclude that, at that time, only pre-synthesized precursors can result in the desired brominated benzene bridged PMOs [33]. Bromobenzene bridged PMOs are susceptible for further chemical modification, because of the halogen-carbon bond. It is well-known that bromine is a very good leaving group in substitution reactions and plays a vital role in organometallic chemistry [31,41–44]. Consequently, further substitution of the bromine creates new synthetic opportunities towards functionalization of PMOs in a variety of different fields, for example: substitution with a thiol or amine containing group for adsorption [24,44,45]; tuning the hydrophobicity of the PMO using organometallic chemistry in order to perform coupling reactions on the brominated carbon for chromatographic applications [46–48]; heterogenization of catalytically active species on the PMO surface for catalytic purposes [49–52]. These are only a few examples of a plethora of new synthetic opportunities towards functionalization of benzene bridged PMOs via bromination. However, cleavage of the Si-C bond due to electrophilic desilylation has to be avoided in order to keep the framework of the PMO intact.

In this work, we have succeeded in finding a way to brominate a benzene bridged PMO whilst maintaining the structural integrity of the material. By first performing a nitration, followed by the reduction of the nitro group we obtained an aniline bridged PMO [32]. Secondly, we executed the bromination using a synthesis described by Baik *et al.* [53]. In this article, the authors were able to use a homogeneous one-step procedure for converting aminoarenes to haloarenes. At the same time they were able to avoid the environmental pollutants resulting from the traditional Sandmeyer reaction using

copper halides. Using this synthesis strategy, we were able to employ the amino function as a leaving group, thus creating a C-Br bond and avoiding the chance of Si-C cleavage. Thorough characterization of the brominated material with X-ray photoelectron spectroscopy (XPS) and solid state nuclear magnetic resonance (SS NMR) confirms this.

2 Experimental

2.1 Benzene bridged PMO

Benzene bridged PMO was synthesized using the following procedure. 10 g cetyltrimethylammonium bromide (CTAB, 99+%, Acros) was dissolved in 300 mL 0.35 M NaOH (NaOH pellets, 98.5%, Acros) solution and stirred for 1 h at 313 K. After cooling to room temperature, 10 mL 1,4-bis(triethoxysilyl)benzene (BTEB, 96%, Sigma-Aldrich) was added dropwise followed by ultrasonic treatment for 30 min. Subsequently, the solution was stirred for 20 h at room temperature. Following this step was the hydrothermal treatment in Teflon lined stainless steel autoclaves during 24 h at 373 K. The autoclaves were quenched and the solid was filtered and washed with water. Afterwards the organic template was removed by two consecutive extractions for 2 h in a 10 vol% HCl/EtOH mixture (HCl, 37%, Acros; ethanol, p.a., VWR).

2.2 Aniline bridged PMO

The recipe according to Inagaki *et al.* [32] was slightly adjusted. A mixture of 5 mL HNO₃ (65%, Acros) and 16 mL H₂SO₄ (96%, Acros) was added to 1 g of benzene bridged PMO and stirred at 300 K for 72 h. Afterwards, the solution was added to 600 mL cold water, followed by washing with a copious amount of water. After drying in open air at ambient temperature, the yellow solid was added to a solution

containing 31 mL HCl and 3.3 g SnCl_2 (98%, Sigma-Aldrich). This solution was stirred at 300 K for 72 h, followed by the addition of 600 mL water and filtration of the solid product. The obtained material was again washed with a copious amount of water, followed by washing with 25 mL *sec*-butylamine (>99%, Merck) and 200 mL EtOH. The resulting aniline bridged PMO was vacuum dried at 373 K for 24 h before further modifications were performed.

2.3 Brominated benzene bridged PMO

The procedure used to brominate aniline bridged PMO is based on the article of Baik *et al.* [53], in which they describe the bromination of *p*-nitroaniline, with the exception that we used NaNO_2 ($\geq 97.0\%$, Sigma-Aldrich) instead of KNO_2 . When performing a standard synthesis we added 180 μL HBr (p.a., Acros) to 10 mL dimethylsulfoxide (DMSO, 99.7%, Acros). This solution was added dropwise to a flask containing aniline bridged PMO (corresponding to 0.4 mmol N), 0.11 g NaNO_2 and 10 mL DMSO whilst stirring at 308 K. This results in an aniline-PMO:HBr: NO_2^- molar ratio of 1:4:4. The mixture was stirred at 308 K for 15 min to 1 h after which it was added to 2 g K_2CO_3 (p.a., Acros) in 40 mL ice water. The obtained solid was filtered, washed with a large amount of water and vacuum dried at 373 K for 24 h.

2.4 Characterization of materials

Porosity characterization was performed on a Quantachrome Quadrasorb SI automated gas adsorption system. The measurements were preceded by outgassing the samples on a Quantachrome Autosorb Degasser at 373 K for 16 h. Nitrogen sorption was carried out at liquid nitrogen temperature, 77 K. The specific surface area was calculated using the Brunauer-Emmet-Teller (BET) method, between a relative pressure of 0.05 and 0.35. Using the Barret-Joyner-Halenda (BJH) method, applied on the adsorption

isotherm, the pore size distribution was calculated. The total pore volume was obtained by determining the total amount of nitrogen adsorbed at $P/P_0 = 0.95$.

X-ray diffraction analysis was performed on a PANalytical X'Pert Pro with $\text{CuK}\alpha$ radiation and a proportional detector, using variable slits and a monochromator for the small angle measurements. Continuous scanning was used with a scanning speed of $0.04^\circ/4$ s. The generator voltage and tube current were 40 kV and 40 mA, respectively. The d spacing was calculated using Bragg's law: $n\lambda = 2d\sin(\theta)$.

Elemental analysis was performed on a Thermo Flash 2000 CHNS/O analyzer, using V_2O_5 as a catalyst.

In-situ DRIFT spectra were measured using a Nicolet 6700 Fourier Transform IR spectrometer and a DTGS detector. The samples were diluted to 2% with KBr and 200 scans were performed with a resolution of 4 cm^{-1} . All samples were measured under vacuum at the given temperature.

The X-ray photoelectron spectra (XPS) were acquired using a Prevac photoelectron spectrometer equipped with a hemispherical VG SCIENTA R3000 analyzer. The spectra were taken using a monochromatized aluminum source $\text{AlK}\alpha$ ($E = 1486.6\text{ eV}$) and a low-energy electron flood gun (FS40A-PS) to compensate for the charge accumulation on the surface of nonconductive samples. The spectra were processed and deconvoluted using the CasaXPS software. The binding energy values of measured regions were referenced to the C-C peak at 284.7 eV in the C 1s core level. The surface composition was studied based on the areas and binding energies of C 1s, N 1s, O 1s, Cl 2p, Br 3d, Sn 3d and Si 2p core levels.

Annular dark-field scanning transmission electron microscopy (ADF-STEM) images were acquired using a cubed FEI Titan operated at 300 kV. The sample was prepared for TEM analysis by crushing in an agate mortar, dispersing it in ethanol and attaching it to a copper grid covered with a holey carbon film.

^1H - ^{13}C and ^1H - ^{29}Si CPMAS (cross-polarization magic-angle spinning) NMR spectra were recorded on a 600 MHz Varian NMR system operating at ^1H , ^{13}C and ^{29}Si Larmor frequencies of 599.54, 150.76 and 119.11 MHz, respectively. The system is equipped with a 3.2 mm Varian HX MAS probe. Sample rotation frequency was 16 kHz for ^1H - ^{13}C CPMAS measurements and 10 kHz for ^1H - ^{29}Si CPMAS measurements. All measurements employed RAMP [54] on proton channel during CP block and high-power XiX [55] proton decoupling during acquisition. Contact time was 5 ms and repetition delay was 3 s. About 2000 scans were accumulated for ^1H - ^{13}C CPMAS measurements and 10 000 for ^1H - ^{29}Si CPMAS measurements. Chemical shifts of ^{13}C and ^{29}Si signals were referenced to the corresponding signals of tetramethylsilane, which was used as an external reference.

3 Results and discussion

Our approach comprises a multi-step post-synthetical modification of benzene bridged PMO (Fig. 1). By first introducing a nitro functionality, which can then be reduced to an amino functionality, we can create a reactive site on the benzene ring for further modification [32]. Moreover, by then performing a diazotation reaction followed by bromination [53], with the loss of N_2 gas, the bromobenzene bridged PMO product is obtained. The latter step involves the in situ generation of the bromodimethylsulfonium bromide nucleophile whilst forming the diazonium salt which acts as a leaving group, hence forming the bromobenzene bridged PMO. This PMO allows for further functionalization through simple nucleophilic aromatic substitution reactions.

Porosity information is obtained through nitrogen sorption and is summarized in Table 1. Converting the benzene bridged PMO into aniline bridged PMO, translates into a drop in specific surface area. This is to be expected as a combination of a mass increase of the sample originating from the additional amino group and a slight pore volume reduction. The average pore diameter decreases as well and can be

attributed to the presence of the amino groups which are faced towards the inside of the pores. The same observations can be made after bromination, thus confirming a successful substitution.

Nitrogen sorption isotherms of the three materials and their pore size distribution are displayed in Figure 2. The isotherms are all type IV(b), typical for adsorbents having mesopores < 4 nm [56].

Figure 3 shows the XRD spectra of both the benzene bridged PMO, as well as the brominated PMO. It is apparent that the molecular scale periodicity is retained after the modification steps. Three sharp diffractions can be observed and using Bragg's law one can calculate the d spacing at $d = 7.6$ Å ($2\theta = 11.66^\circ$), 3.8 Å ($2\theta = 23.46^\circ$) and 2.5 Å ($2\theta = 35.62^\circ$). This shows the preservation of the crystal-like periodicity at the molecular scale within the pore walls and is consistent with the literature [26]. This once more proves the chemical stability of the PMO structure in harsh conditions. The small angle spectra reveal the first order $[1\ 0\ 0]$ signal which shifts towards higher angles after the modifications, attributable to a smaller unit cell.

Figure 4 (left) shows the annular dark-field STEM image of the brominated PMO where one can see the mesoporous structure with straight channels at a distance of approximately 4 nm. An ADF-STEM image at a higher magnification is displayed in Figure 4 (right), showing the layered structure formed by alternating silicate and benzene layers running perpendicular to the mesoporous channels with a periodicity of approximately 7.8 Å. These results confirm the preservation of the mesostructure after the different modifications.

In order to assess the success of each reaction step, elemental analysis of the respective material was performed (Table 2). Only the results for N and C are shown here.

Considering the C signals can only originate from the benzene rings in the pore walls and the N signals solely from the NH_2 group, one can calculate the conversion of each step. The complete removal of CTAB

by our procedure is clear from the absence of the corresponding aliphatic peaks between 10 - 70 ppm in the ^1H - ^{13}C CPMAS NMR spectrum (Figure 3.A in the Supplementary Information). After the first reaction step, this results in 43% conversion of all benzene moieties to aniline. Taking into account that the benzene rings are also an inherent part of the PMO's structure, the actual conversion of accessible benzene rings is much higher. Remarkably, this is a much higher yield compared to that achieved by Inagaki *et al.* [32]. After the bromination step 63% of the converted benzene rings lose their NH_2 group, leaving only 16% of all benzene rings aminated.

Figure 5 displays the DRIFT spectra of the benzene bridged and aniline bridged PMO materials, measured under vacuum at 393 K in order to remove any physisorbed water. The spectra are in compliance with the expectations, showing the typical absorption bands of isolated OH (3725 cm^{-1}) and aromatic C-H stretching ($3000\text{-}3100\text{ cm}^{-1}$) at higher wavelength. The 1,4-disubstituted benzene fingerprint, originating from the C-H deformation overtones between 1650 cm^{-1} and 2000 cm^{-1} , is clearly visible in the benzene PMO sample.

After modification the distinctive signals which can be attributed to aromatic C-NH₂ formation, are apparent. The absorbance at 1300 cm^{-1} can be assigned to the stretching mode of C-N, proving the covalent linkage. New bands also appear at 1595 cm^{-1} , 1624 cm^{-1} and $3390\text{-}3473\text{ cm}^{-1}$ attributable to N-H deformation, bending and stretching, respectively. The N-O stretching modes at 1350 cm^{-1} and 1550 cm^{-1} disappeared completely.

Since the C-Br bond is not IR active, the DRIFT spectrum of the bromobenzene bridged PMO is not displayed. In order to prove the existence of the latter bond, X-ray photoelectron spectroscopy (XPS) was performed (Figure 6).

Figure 6 shows the XPS spectrum with the Br $3d_{3/2}$ and Br $3d_{5/2}$ spin double recorded for the brominated PMO. The chemical state of Br $3d_{5/2}$ positioned at 70.0 eV is attributed to a C-Br bond, proving the

modification is successful [57]. To our knowledge this is the first time a post-synthetic bromination has successfully taken place on a PMO.

In order to exclude the possibility of structural decay during the modification reactions, our synthesis strategy comprises a multi-step approach with the formation of a good leaving group. As could be seen in Figure 2, the porosity of the material was maintained which suggests that no deterioration of the pore structure occurred. Moreover, by performing NMR analysis of the final product one can provide an in-depth view of the chemical stability before and after modification. As described by Smeulders *et al.* [33], assessment of the chemical linkages between the organic bridging units is of pivotal importance. **Figure 7** shows the ^1H - ^{29}Si CPMAS NMR spectra of benzene bridged and bromobenzene bridged PMO.

As can be seen in the ^1H - ^{29}Si CPMAS NMR spectra, only small differences exist between the starting material and the end product. The T signals vary slightly, evolving to a more condensed structure with the modification (Figure 1.A in the Supplementary Information). The Q signals are of greater importance, as these are correlated to Si-C breakage and are therefore a measure of structural deterioration. An important observation is that the Q signals in the bromobenzene bridged spectrum each represent less than 1% of the total intensity, confirmed by the analysis of the ^{29}Si MAS NMR spectrum (Figure 2.A in the Supplementary Information), meaning that our synthesis strategy is the right approach to create a halogenated PMO material whilst maintaining its structural integrity.

We also recorded the ^1H - ^{13}C CPMAS NMR spectrum, it shows that several new signals arise after modification. It is clear that the shoulder of the intense peak at 133 ppm, represented by point B, can be attributed to the carbon atoms of the modified benzene rings. The signals represented by point C and D can originate from the carbon atoms of bromobenzene, or alternatively from the carbon atoms of a phenol ring. A small contribution of phenol rings is confirmed by the signal at 160 ppm (point A in the spectrum), which can be assigned to the *ipso* carbon of phenol. This contribution suggests that water,

present in the reaction mixture, is also able to act as a nucleophile, creating a minor fraction of phenol bridges.

This means that, although we have obtained bromobenzene bridged PMO material, this is not the only product formed. Considering the synthetic approach used here (Figure 1), the last reaction step where de-diazotation takes place allows for side reactions to arise. When the diazonium salt is formed, any molecule or atom with sufficient nucleophilic character can substitute this leaving group. Except for the bromodimethylsulfonium bromide, molecular water can also be present in the reaction mixture as a potential nucleophile forming agent thus creating phenol bridged PMO.

4 Summary and outlook

In this work, we report a post-synthetic approach to successfully brominate benzene bridged PMOs, and simultaneously maintain its structural integrity. The reaction pathway involves nitration and successive reduction to aniline bridged PMO. This modification takes place with a high yield and provides a reactive site for the bromination reaction. By diazotation of the amino function, an excellent leaving group can be created. Using XPS analysis, we have proven the formation of bromobenzene. In order to assess structural deterioration NMR characterization was indispensable. This technique showed an intact structure after modification, although also showing the existence of side reactions in the reaction mixture.

Acknowledgements

The authors would like to thank financial support from the FWO-Flanders (project n° G.0068.13). The authors further acknowledge financial support of the University of Antwerp through BOF GOA funding.

S.B. acknowledges financial support from European Research Council (ERC Starting Grant #335078-COLOURATOM).

References

- [1] T. Asefa, M.J. MacLachlan, N. Coombs, G.A. Ozin, *Nature* 402 (1999).
- [2] S. Inagaki, S. Guan, Y. Fukushima, T. Ohsuna, *J. Am. Chem. Soc.* (1999) 9611–9614.
- [3] B.J. Melde, B.T. Holland, C.F. Blanford, a Stein, *Chem. Mater.* 11 (1999) 3302–3308.
- [4] W.J. Hunks, G.A. Ozin, *J. Mater. Chem.* 15 (2005) 3716.
- [5] F. Hoffmann, M. Cornelius, J. Morell, M. Fröba, *Angew. Chem. Int. Ed. Engl.* 45 (2006) 3216–3251.
- [6] P. Van der Voort, D. Esquivel, E. De Canck, F. Goethals, I. Van Driessche, F.J. Romero-Salguero, *Chem. Soc. Rev.* 42 (2013) 3913–3955.
- [7] K. Cassiers, T. Linssen, M. Mathieu, M. Benjelloun, P. Van Der Voort, P. Cool, E.F. Vansant, K. Schrijnemakers, *Chem. Mater.* (2002) 2317–2324.
- [8] G. Smeulders, V. Meynen, A. Silvestre-Albero, K. Houthoofd, M. Mertens, J. Silvestre-Albero, J.A. Martens, P. Cool, *Mater. Chem. Phys.* 132 (2012) 1077–1088.
- [9] F. Goethals, B. Meeus, A. Verberckmoes, P. Van der Voort, I. Van Driessche, *J. Mater. Chem.* 20 (2010) 1709.
- [10] B. Rác, P. Hegyes, P. Forgo, Á. Molnár, *Appl. Catal. A Gen.* 299 (2006) 193–201.
- [11] A. Kuschel, M. Drescher, T. Kuschel, S. Polarz, *Chem. Mater.* 22 (2010) 1472–1482.
- [12] D. Esquivel, C. Jiménez-Sanchidrián, F.J. Romero-Salguero, *J. Mater. Chem.* 21 (2011) 724.

- [13] J.Y. Shi, C.A. Wang, Z.J. Li, Q. Wang, Y. Zhang, W. Wang, *Chem. - A Eur. J.* 17 (2011) 6206–6213.
- [14] S.S. Park, M.S. Moorthy, C.-S. Ha, *Korean J. Chem. Eng.* 31 (2014) 1707–1719.
- [15] J. Gehring, D. Schleheck, B. Trepka, S. Polarz, *ACS Appl. Mater. Interfaces* 7 (2015) 1021–1029.
- [16] D. Esquivel, P. Van der Voort, F.J. Romero-salguero, *AIMS Mater. Sci.* 1 (2014) 70–86.
- [17] D.I. Fried, F.J. Brieler, M. Fröba, *ChemCatChem* 5 (2013) 862–884.
- [18] I. Munaweera, J. Hong, A. D'Souza, K.J. Balkus, J. Porous Mater. 22 (2014) 1–10.
- [19] F. Goethals, I. Ciofi, O. Madia, K. Vanstreels, M.R. Baklanov, C. Detavernier, P. Van der Voort, I. Van Driessche, *J. Mater. Chem.* 22 (2012) 8281.
- [20] M. Seino, W. Wang, J.E. Lofgreen, D.P. Puzzo, T. Manabe, G.A. Ozin, *J. Am. Chem. Soc.* 133 (2011) 18082–18085.
- [21] M.B. Krishtab, L. Zhang, Q.T. Le, K. Vanstreels, L. Souriau, M. Phillips, M.R. Baklanov, *MRS Proc.* 1428 (2012).
- [22] L. Grösch, Y.J. Lee, F. Hoffmann, M. Fröba, *Chem. - A Eur. J.* 21 (2015) 331–346.
- [23] Y. Ueda, H. Takeda, T. Yui, K. Koike, Y. Goto, S. Inagaki, O. Ishitani, *ChemSusChem* 8 (2015) 439–442.
- [24] Y. Gao, E. De Canck, M. Leermakers, W. Baeyens, P. Van Der Voort, *Talanta* 87 (2011) 262–267.
- [25] S. Martens, R. Ortmann, F.J. Brieler, C. Pasel, Y. Joo Lee, D. Bathen, M. Fröba, *Zeitschrift Für Anorg. Und Allg. Chemie* 640 (2014) 632–640.
- [26] S. Inagaki, S. Guan, T. Ohsuna, O. Terasaki, *Nature* 416 (2002) 304–307.
- [27] G. Temtsin, T. Asefa, S. Bittner, G.A. Ozin, *J. Mater. Chem.* 11 (2001) 3202–3206.

- [28] K. Okamoto, Y. Goto, S. Inagaki, *J. Mater. Chem.* 15 (2005) 4136.
- [29] M.P. Kapoor, S. Inagaki, *Bull. Chem. Soc. Jpn.* 79 (2006) 1463–1475.
- [30] A. Karam, J.C. Alonso, T.I. Gerganova, P. Ferreira, N. Bion, J. Barrault, F. Jérôme, *Chem. Commun.* (2009) 7000–7002.
- [31] P.Y. Bruice, *Organic Chemistry*, 5th Editio, Pearson Prentice Hall, Upper Saddle River, 2007.
- [32] M. Ohashi, M.P. Kapoor, S. Inagaki, *Chem. Commun.* (2008) 841–843.
- [33] G. Smeulders, V. Meynen, K. Houthoofd, S. Mullens, J.A. Martens, B.U.W. Maes, P. Cool, *Microporous Mesoporous Mater.* 164 (2012) 49–55.
- [34] G. Mehta, N.S. Likhite, C.S. Ananda Kumar, *Tetrahedron Lett.* 50 (2009) 5260–5262.
- [35] M.K. Ameriks, S.D. Bembenek, M.T. Burdett, I.C. Choong, J.P. Edwards, D. Gebauer, Y. Gu, L. Karlsson, H.E. Purkey, B.L. Staker, S. Sun, R.L. Thurmond, J. Zhu, *Bioorganic Med. Chem. Lett.* 20 (2010) 4060–4064.
- [36] K. Gedrich, M. Heitbaum, A. Notzon, I. Senkovska, R. Fröhlich, J. Getzschmann, U. Mueller, F. Glorius, S. Kaskel, *Chem. - A Eur. J.* 17 (2011) 2099–2106.
- [37] A. Senthilmnrujan, I.S. Aidhen, *European J. Org. Chem.* (2010) 555–564.
- [38] Q. Zhou, B.B. Snider, *J. Org. Chem.* 75 (2010) 8224–8233.
- [39] A. Bodzioch, K. Owsianik, J. Skalik, E. Kowalska, A. Stasiak, E. Różycka-Sokołowska, B. Marciniak, P. Bałczewski, *Synthesis (Stuttg.)* 48 (2016) A-F.
- [40] A. Groweiss, *Org. Process Res. Dev.* 4 (2000) 30–33.
- [41] A. Kuschel, S. Polarz, *Adv. Funct. Mater.* 18 (2008) 1272–1280.
- [42] J. Corral, M. López, D. Esquivel, M. Mora, C. Jiménez-Sanchidrián, F.J. Romero-Salguero, *Materials*

(Basel). 6 (2013) 1554–1565.

- [43] E. De Canck, I. Dosuna-Rodríguez, E. Gaigneaux, P. Van der Voort, *Materials (Basel)*. 6 (2013) 3556–3570.
- [44] K. Nakai, Y. Oumi, H. Horie, T. Sano, H. Yoshitake, *Microporous Mesoporous Mater.* 100 (2007) 328–339.
- [45] E. De Canck, I. Ascoop, A. Sayari, P. Van der Voort, *Phys. Chem. Chem. Phys.* 15 (2013) 9792–9799.
- [46] V. Rebbin, R. Schmidt, M. Fröba, *Angew. Chemie - Int. Ed.* 45 (2006) 5210–5214.
- [47] Y. Zhang, Y. Jin, P. Dai, H. Yu, D. Yu, Y. Ke, X. Liang, *Anal. Methods* 1 (2009) 123–127.
- [48] A. Carpio, D. Esquivel, L. Arce, F.J. Romero-Salguero, P. Van Der Voort, C. Jiménez-Sanchidrián, M. Válcárcel, *J. Chromatogr. A* 1370 (2014) 25–32.
- [49] A.P. Wight, M.E. Davis, *Chem. Rev.* 102 (2002) 3589–3614.
- [50] J. Lauwaert, E.G. Moschetta, P. Van Der Voort, J.W. Thybaut, C.W. Jones, G.B. Marin, *J. Catal.* 325 (2015) 19–25.
- [51] J. Lauwaert, E. De Canck, D. Esquivel, P. Van Der Voort, J.W. Thybaut, G.B. Marin, *Catal. Today* 246 (2015) 35–45.
- [52] S. Shylesh, Z. Zhou, Q. Meng, A. Wagener, A. Seifert, S. Ernst, W.R. Thiel, *J. Mol. Catal. A Chem.* 332 (2010) 65–69.
- [53] W. Baik, W. Luan, H.J. Lee, C.H. Yoon, S. Koo, B.H. Kim, *Can. J. Chem.* 83 (2005) 213–219.
- [54] G. Metz, X. Wu, S.O. Smith, *J. Magn. Reson. A* 110 (1994) 219–227.
- [55] A. Detken, E.H. Hardy, M. Ernst, B.H. Meier, *Chem. Phys. Lett.* 356 (2002) 298–304.
- [56] M. Thommes, K. Kaneko, A. V. Neimark, J.P. Olivier, F. Rodriguez-Reinoso, J. Rouquerol, K.S.W.

Sing, Pure Appl. Chem. 87 (2015) 1051–1069.

[57] Y.P. Zhang, J.H. He, G.Q. Xu, E.S. Tok, J. Phys. Chem. C 116 (2012) 8943–8949.

Table 1. Porosity data obtained through N₂ sorption at 77 K.

Table 2. Elemental analysis

Figure 1. Modification pathway

Figure 2. N₂ sorption isotherms at 77 K and the adsorption pore size distribution (BJH).

Figure 3. Wide angle and small angle (insets) powder X-ray diffraction patterns of the PMOs before and after the modifications.

Figure 4. Annular dark-field STEM images of brominated PMO showing (left) interchannel distance of approx. 4 nm and (right) periodicity of approx. 7.8 Å.

Figure 5. DRIFT spectra measured under vacuum at 393 K.

Figure 6. Br 3d XPS spectrum of brominated PMO.

Figure 7. ¹H-²⁹Si (left) and ¹H-¹³C (right) CPMAS NMR spectra of benzene bridged and bromobenzene bridged PMO.