

Supporting Information to:

Controlled Preparation of Amphiphilic Triblock-Copolyether in a Metal- and Solvent-Free Approach for Tailored Structure-Directing Agents

Alexander Balint^a, Marius Papendick^a, Manuel Clauss^b, Carsten Müller^c, Frank Giesselmann^c
and Stefan Naumann^{a,*}

^aUniversity of Stuttgart, Institute for Polymer Chemistry, 70569 Stuttgart, Germany

^bGerman Institutes of Textile and Fiber research, 73770 Denkendorf, Germany

^cUniversity of Stuttgart, Institute for Physical Chemistry, 70569 Stuttgart, Germany

E-Mail: stefan.naumann@ipoc.uni-stuttgart.de

Contents

Experimental.....	S1
Starting materials and catalyst synthesis.....	S1
General procedure for the preparation of PPO _n -PEO _m -PPO _n via NHO-catalysis.....	S2
General procedure for the preparation of PBO _n -PEO _m -PBO _n via NHO-catalysis	S3
General procedure for the preparation of mesoporous carbons	S3
Characterization and analysis	S4
Results.....	S6
References	S16

Experimental

Starting materials and catalyst synthesis

Propylene oxide (PO) and butylene oxide (BO) were dried over CaH₂, distilled under nitrogen atmosphere, degassed and then stored under protective conditions (glove box

freezer, -36°C , LabMaster, *MBraun*, Germany). α,ω -Dihydroxylated PEG 8000 and PEG 4000 are hygroscopic and therefore also require drying; this was achieved by dissolving portions of the polymer (10 g) in dry dichloromethane (glove box) and storing over molecular sieve for at least 72 h. Afterwards, the molecular sieve was filtered off and the solvent removed by evacuation (several hours, repeated checking by ^1H NMR). Phenol and solutions of formaldehyde were used as received.

All NHOs were prepared according to published procedures^[i,iii] and their identity confirmed by ^1H and ^{13}C NMR (Figure S1). Characterization of compounds **1**^[iii] and **2**^[iv] is available from the cited sources. The NHOs were stored under nitrogen at -36°C .

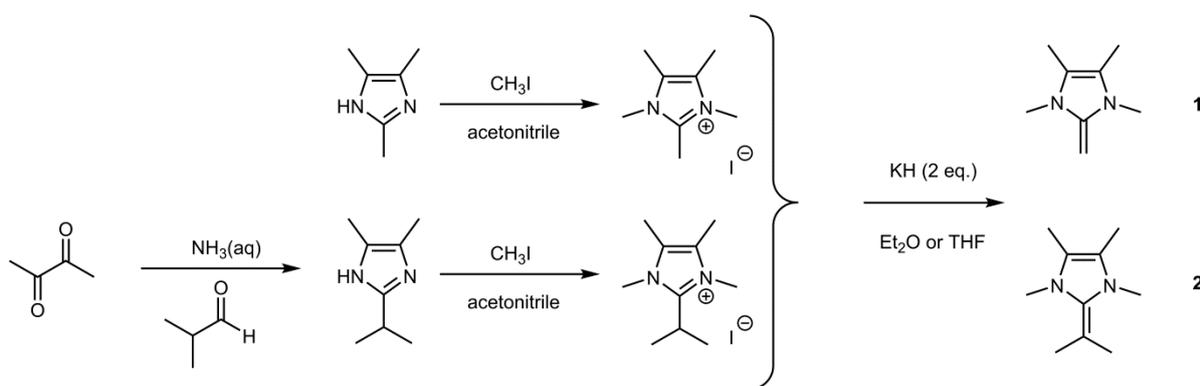


Figure S1. Synthesis of NHO **1** and **2**.

General procedure for the preparation of $\text{PPO}_n\text{-PEO}_m\text{-PPO}_n$ via NHO-catalysis

For a typical polymerization reaction, NHO **1** (3.5 mg, 0.025 mmol), macroinitiator (PEG 8000, 500 mg; 0.0625 mmol = 0.125 mmol OH-end groups = 5 eq.), and PO (1.45 g, 25 mmol, 1000 eq.) were combined in a glass pressure tube. The reaction vessel was removed from the glove box and placed in a pre-heated oil bath (80°C). If aliquots were removed during reaction, this was done under nitrogen gas-flow, using heat-dried pipettes. The reaction was stopped by evaporation of the PO (4h). The remaining solid was dissolved in THF and precipitated from diethyl ether to yield a white polymer, which was subsequently dried to a constant weight under reduced pressure (typical yields were 500-1250 mg (isolated)). The molar mass of the polyether was determined by GPC (CHCl_3). The number of PO-repeating units was calculated from ^1H NMR (CDCl_3). From the initial $[\text{PO}]/\text{-}[\text{OH}]$ ratio and the experimentally determined number of incorporated PO units, conversion is directly accessible. Typically, after a conversion of 50-60% regarding PO, the polymerization

mixtures became too viscous for efficient propagation of the reaction, since PO was employed both as solvent and monomer in this setup.

General procedure for the preparation of PBO_n -PEO_m-PBO_n via NHO-catalysis

These polymerizations were assembled as described above for PPO_n-PEO_m-PPO_n using BO instead of PO. Work-up was conducted in the same manner. A typical setup employed 7 mg of NHO **1** (0.05 mmol), macroinitiator (PEG 8000, 500 mg; 0.0625 mmol = 0.125 mmol OH-end groups = 2.5 eq.) and BO (1.8 g).

General procedure for the preparation of mesoporous carbons

The procedure reported by Zhao was applied.^[v]

a) Synthesis of the resole precursor

Phenol (0.61 g, 6.48 mmol) was molten at 40-42 °C and mixed with aqueous sodium hydroxide solution (20 wt.-%; 0.13 g; 0.65 mmol) under stirring (10 min). Afterwards, formalin (37 wt %; 1.05g; 12.94 mmol) was added dropwise. The reaction mixture was then heated to 70-75 °C and stirred for 1 h. The solution was allowed to cool down to room temperature and adjusted with HCl solution (0.6 M) to a pH value of ~7. Water was removed by vacuum evaporation below 50°C and the product was dissolved in 4 g EtOH. Insoluble parts were removed by filtration.

b) Synthesis of the mesoporous carbons

1.0 g of the tailor-made PPO_n-PEO₁₈₀-PPO_n ($n = 20, 25, 40, 50, 66, 90$) was dissolved in 20 g EtOH. Subsequently, 5 g of the resole precursor solution was added. After stirring for 10 min, the homogenous solution was poured into dishes to evaporate EtOH at room temperature overnight. The following day, the resulting polymer films were thermally cross-linked (100 °C for 24 h). Carbonization of the samples was conducted at 700°C (N₂, 2.5 h) to result in black films/flakes. The mesoporous carbons were characterized by SAXS, SEM and N₂ gas sorption.

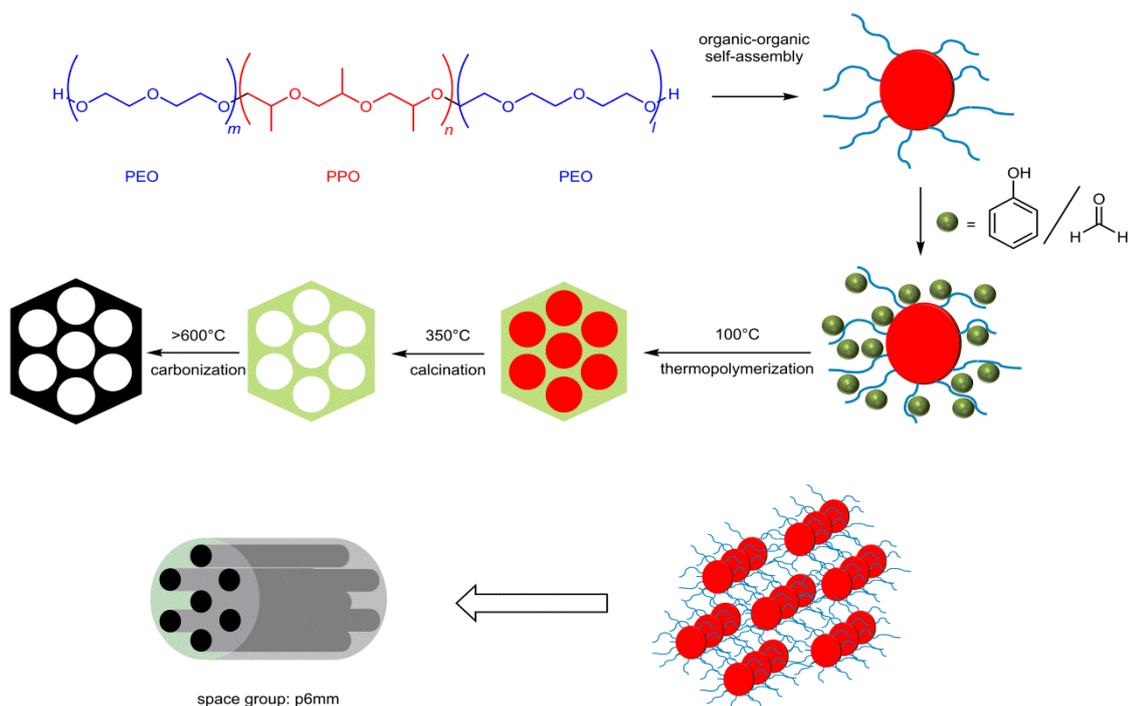


Figure S2. Simplified scheme of the organic self-assembly process as described by Zhao and Dai,^[v-vi] here shown for regular Pluronics. The self-organization takes place upon evaporation of the solvent (EtOH) and is supported and influenced by interaction with oligomerized phenolic resins (= carbon precursor). These can be thermally cross-linked, setting the mesoporous structure. Further thermal treatment will carbonize the sample, whereby the less dense lipophilic regions are burned off. The size of the lipophilic block is one major factor impacting pore sizes and morphologies. For reverse Pluronics, the formation of highly ordered mesophases is more difficult; micellar networks easily form with one polymer chain connecting two different micelles via its two PPO-termini.

Characterization and analysis

For NMR analysis a *Bruker* Avance III 400 spectrometer was used. All chemical shifts are listed in reference to peaks of deuterated chloroform ($\delta = 7.26$ ppm for ^1H / $\delta = 77.16$ ppm for ^{13}C). IR measurements were recorded on a *Bruker* Alpha FT-IR-spectrometer (4000 – 400 cm^{-1}).

GPC (chloroform, 35°C) was used to determine molar masses and polydispersity, employing a calibration versus polystyrene in the range of 800 g/mol – $2 \cdot 10^6$ g/mol). A chromatographic assembly consisting of a *PSS* SDV 5 μm 8*50mm precolumn, three *PSS* SDV 100 000 Å 5 μm 8*50mm columns in combination with an *Agilent* 1200 Series G1362A RI- detector, was employed. A flow rate of 1 ml/min and a sample concentration of 2 mg/mL were applied for GPC analysis (100 μL injection).

A *Bruker* Autoflex III was employed for MALDI-ToF MS analysis (337 nm, reflector mode). The samples were prepared by mixing matrix solution (2,5-dihydroxybenzoic acid, 5 mg/mL in THF), PBO solution (10 mg/ml in THF), and sodium trifluoromethanesulfonate solution (0.1 M in 90% acetone/water = 9:1) with a ratio of 2:1:2. For calibration, a polystyrene standard was used.

Small-angle X-ray scattering (SAXS) analyses were performed on a SAXSess system from *Anton Paar GmbH*. Powdered samples (filled into Hilgenberg Mark capillary tubes of 0.7 mm diameter) were mounted in a temperature controlled sample holder unit (TSC 120). The X-ray beam was focused by a bent multilayer mirror and shaped by a line collimation block to receive CuK α (1.5418 Å) radiation. The X-ray scattering was recorded with a CMOS detector (Dectris, Mythen 1K) and processed and analysed using the SAXSquant 3.5 software.

Carbonization of the crosslinked polymeric material was performed using a *Gero* HTK 8GR/24-2G high temperature furnace under nitrogen atmosphere. The material was placed in graphite shuttles and carbonized for 2.5 hours at 700 °C, applying a heating/cooling rate of 10 K/min.

SEM (scanning electron microscopy) imaging of the carbonaceous material including sample preparation was conducted on a *Zeiss Auriga* scanning electron microscope (conductive tape sample carrier, Pt/Pd sputtering).

The specific surface area (BET-method, multipoint determination) and pore size distribution (BJH-method) were determined via nitrogen adsorption/desorption using an *Autosorb-1* gas sorption analyzer from *Quantachrome*. All samples were degassed for 16-20 hours at 80-120 °C in high vacuum before characterization.

Results

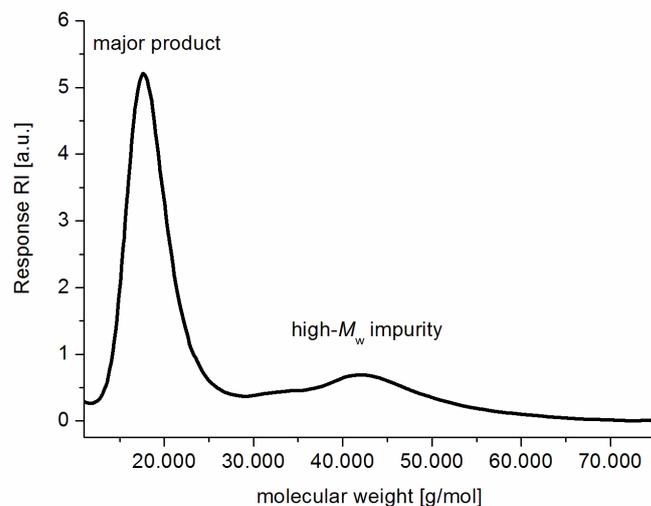


Figure S3. GPC trace of polymer received by the action of NHO **2**. NHO/-OH/PO = 1:5:1000, 17 h, 50°C.

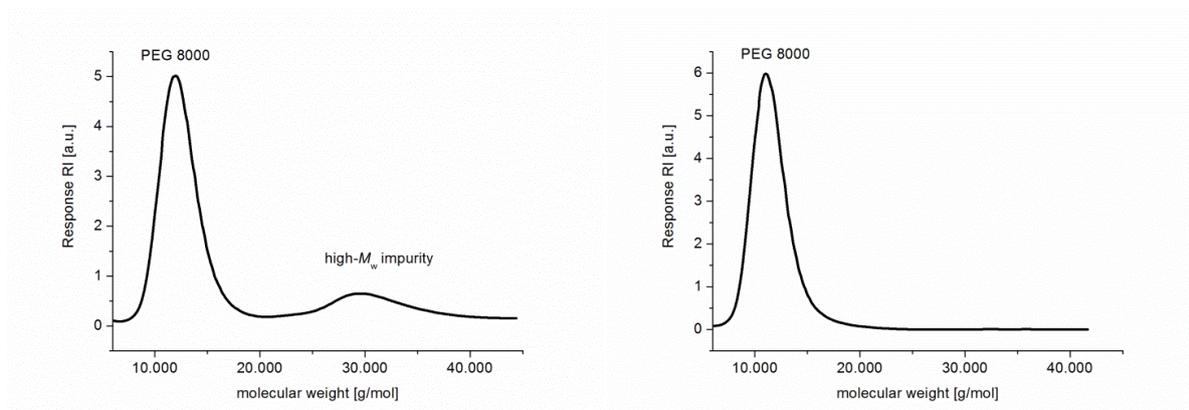


Figure S4. Chromatogram of macroinitiator HO-PEG-OH (PEG 8000) after being held for 18 h at 80°C with (left, 0.8 wt.-%) and without (right) NHO **2** (**no** PO present). The additional peak in the presence of the organocatalyst has about the double molar mass compared to PEG 8000, which fits to a condensation reaction between two polymer chains. The release of water most likely prohibits a more pronounced condensation peak by deactivating the NHO catalyst.

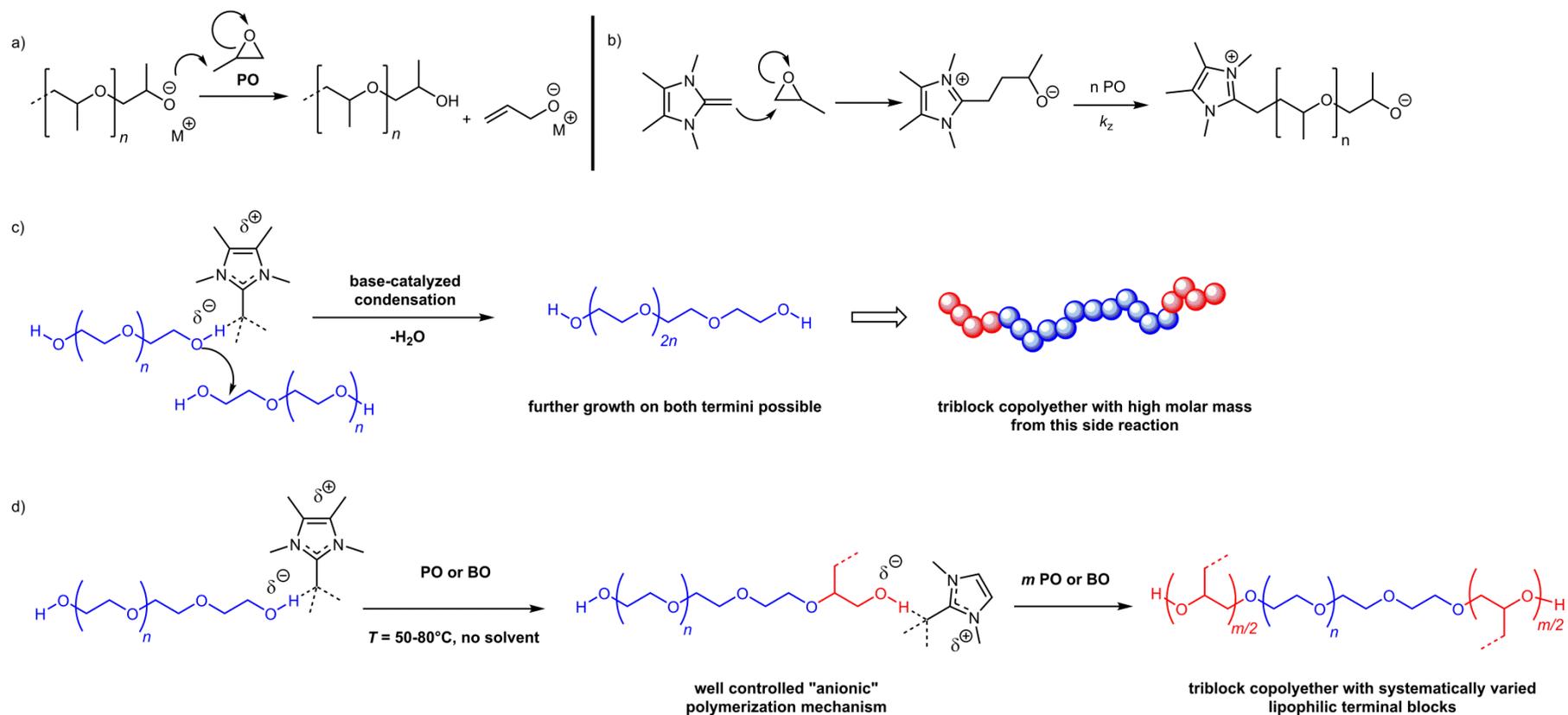


Figure S5. a) transfer-to-monomer as a general complication for polyether synthesis; b) zwitterionic ROP as side side reaction, initiated by an NHO organocatalyst; c) schematic representation of the proposed NHO-mediated condensation reaction in the system with HO-PEG-OH/PO. Only primary alcohol end groups (= macroinitiator where PO has not yet been added) engage in this side reaction. After condensation, the polymer can still grow by addition of PO; d) desired, anionic mechanism which enables a controlled polymerization to prepare triblock copolyether.

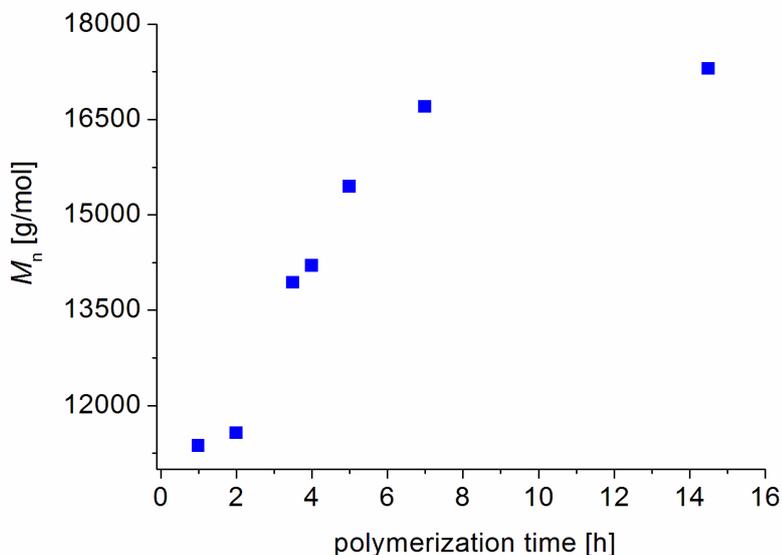


Figure S6. Polymerization time vs. M_n (GPC) reveals an induction period of slower conversion at the beginning (1/-OH(PEG 8000)/PO = 1:5:1000, 80°C). Potentially, this can be attributed to the transition of the primary oxyanionic chain end to a secondary one when the first PO units are added. With increasing conversion and viscosity the **molar mass** plateaus.

Table S1. Synthesis of PPO-*b*-PEO-*b*-PPO polyether using NHO 2 and the impact of reaction conditions on the occurrence of high-molar mass side product.

HO-PEG-OH	2/-OH/PO	T [°C]	t [h]	PO [repeating units]	M_n (PDI) ^{a)b)} [g/mol]	ratio ^{c)} [main/condensation product]
PEG 4000	1:5:1000	50	17	63	12 900 (1.02)	93/7
PEG 8000	1:5:1000	50	17	46	17 900 (1.02)	92/8
PEG 10000	1:5:1000	50	17	85	23 600 (1.02)	93/7
PEG 8000	1:5:1000	rt	65	65	18 800 (1.02)	98/2
PEG 8000	1:20:1000	rt	65	10	13 700 (1.02)	97/3

a) Main product; b) determined by GPC (CHCl₃); c) integral of GPC peak area

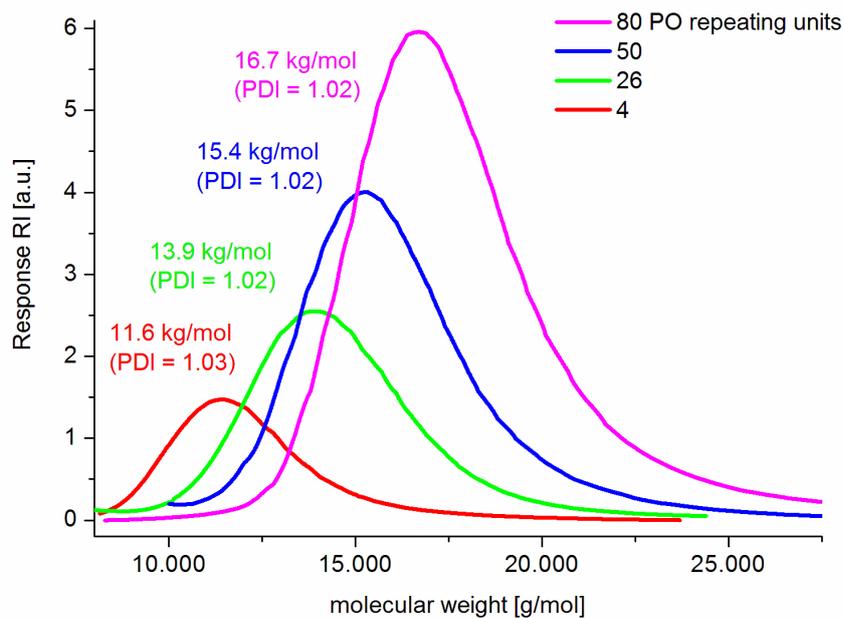


Figure S7. Representative chromatograms of reverse Pluronics based on PEG 8000 employing NHO 1 (1/-OH/PO = 1:5:1000, 80°C).

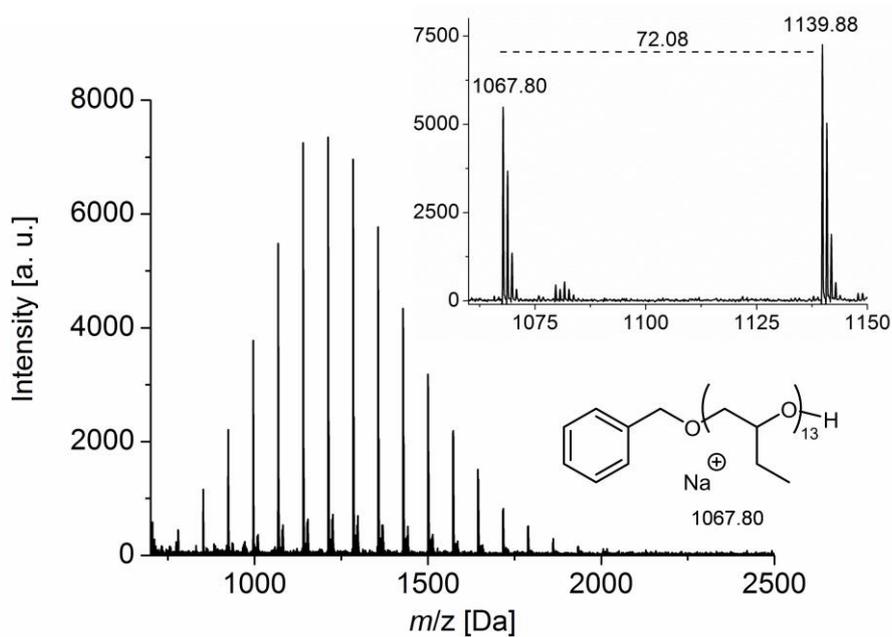


Figure S8. MALDI-ToF MS of PBO prepared by the action of NHO 1 (Table 1, entry 10), cationized by sodium.

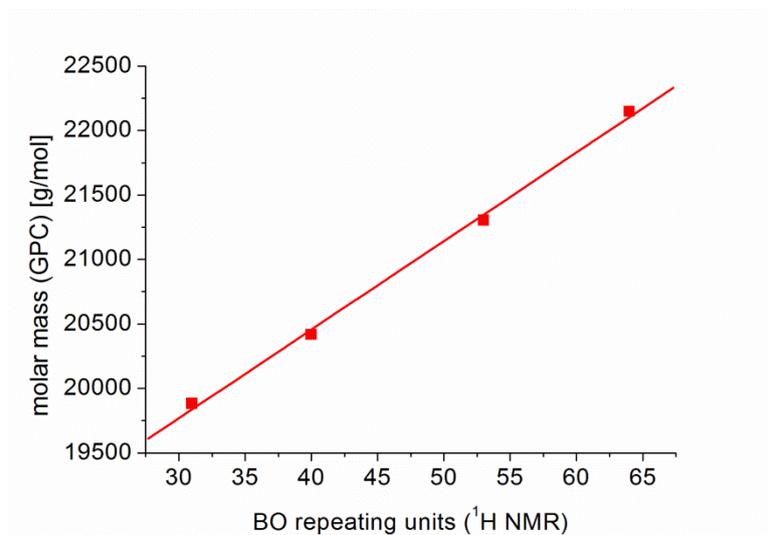


Figure S9. Correlation of M_n and BO repeating units ($1/-OH/BO = 2:5:1000$, 50°C), including linear fit.

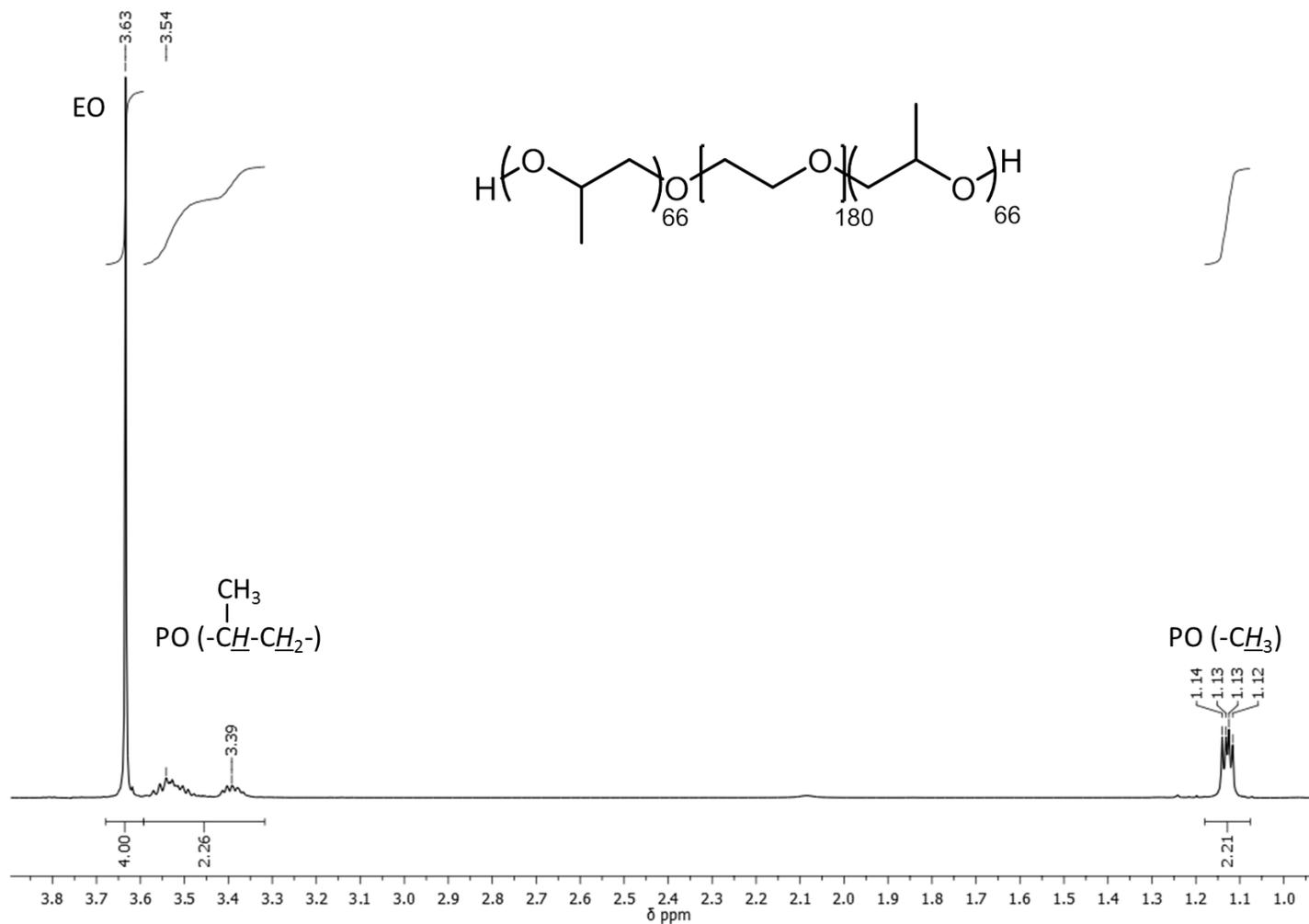


Figure S10. ^1H NMR analysis (CDCl₃, 400 MHz, 300 K) of a “reverse Pluronic” prepared by the action of NHO **1**.

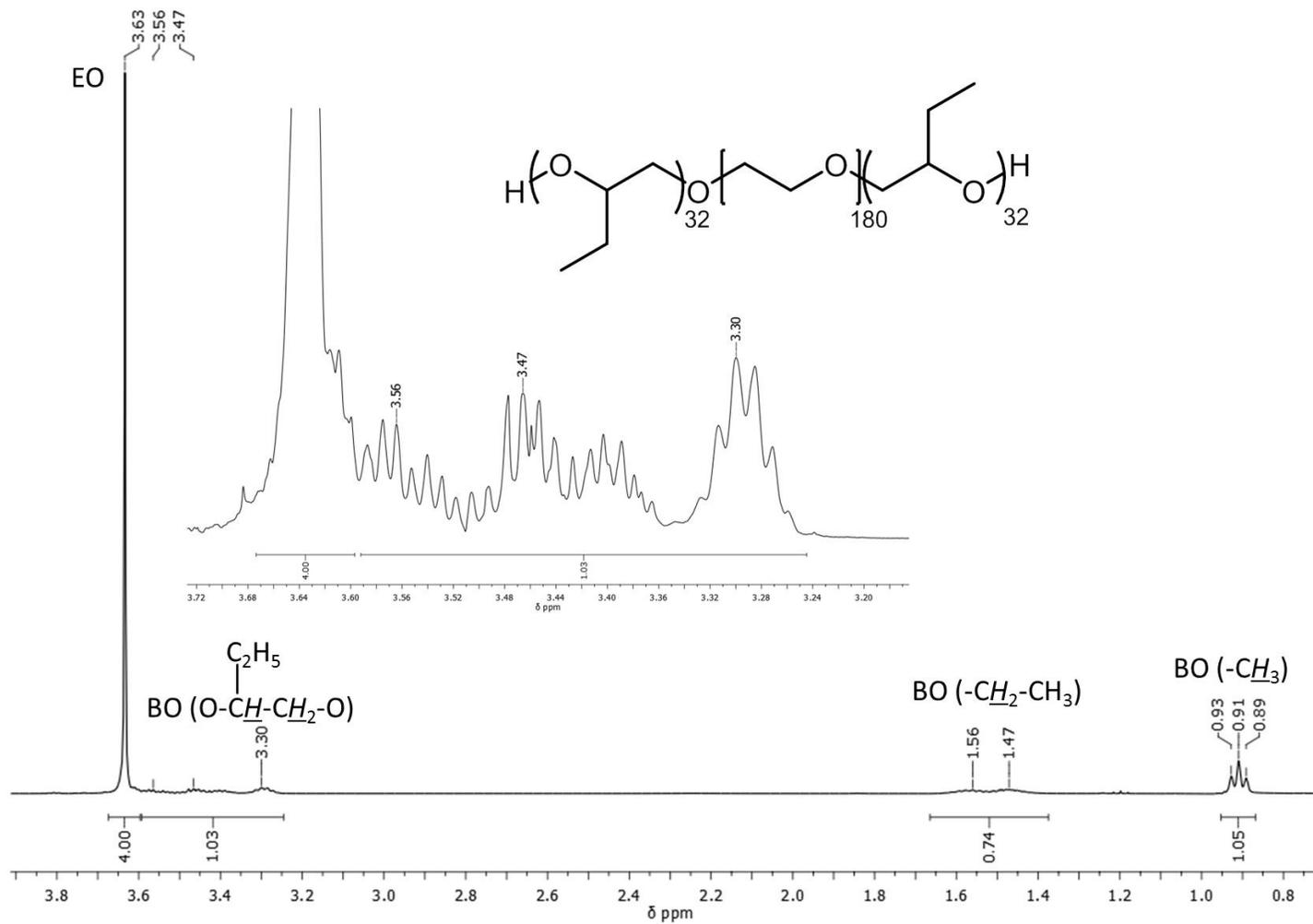


Figure S11. ^1H NMR analysis (CDCl_3 , 400 MHz, 300 K) of a PBO-PEO-PBO triblock copolymer prepared by the action of NHO **1**.

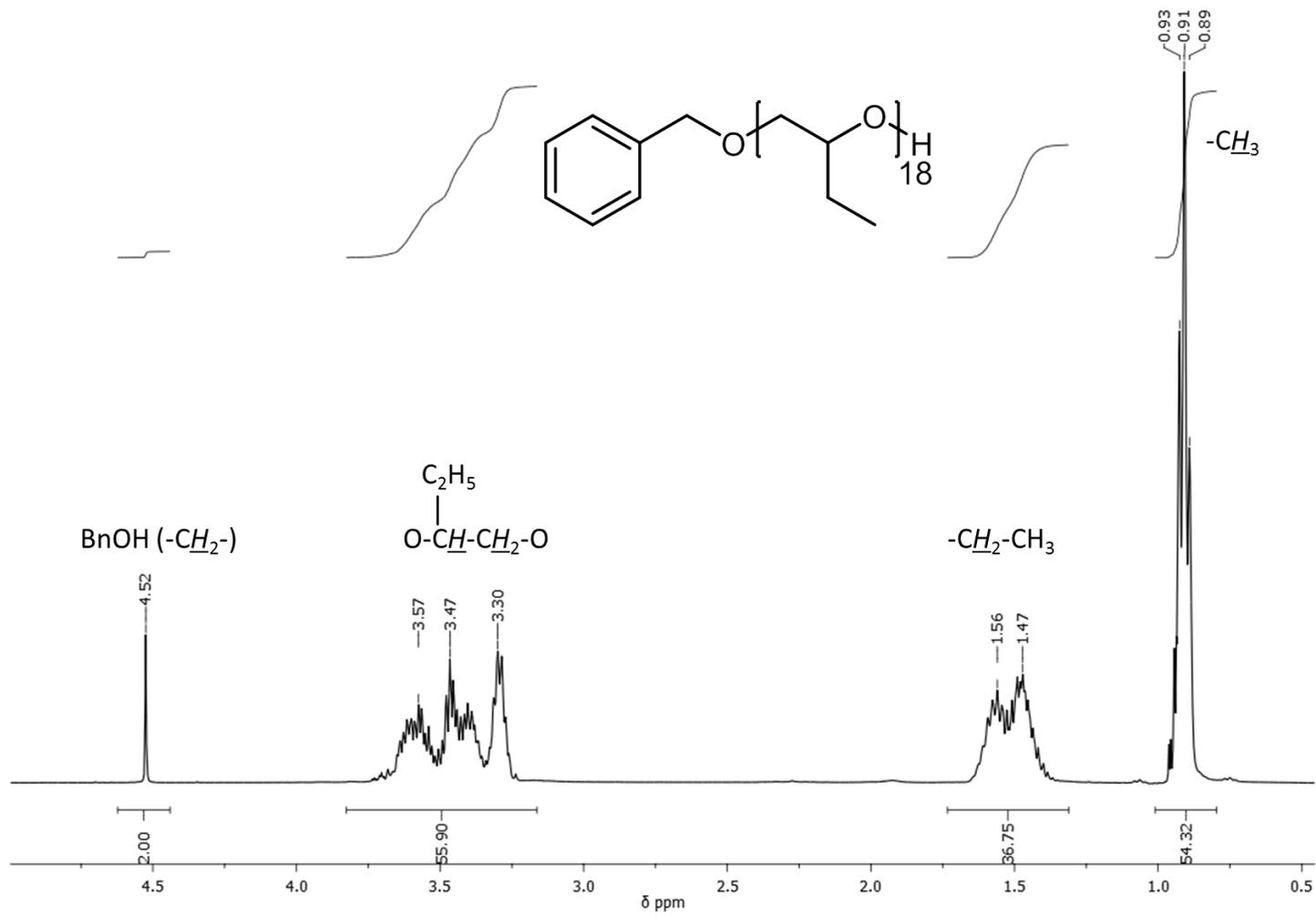


Figure S12. ^1H NMR analysis (CDCl₃, 400 MHz, 300 K) of a PBO homopolymer prepared by the action of NHO 1.

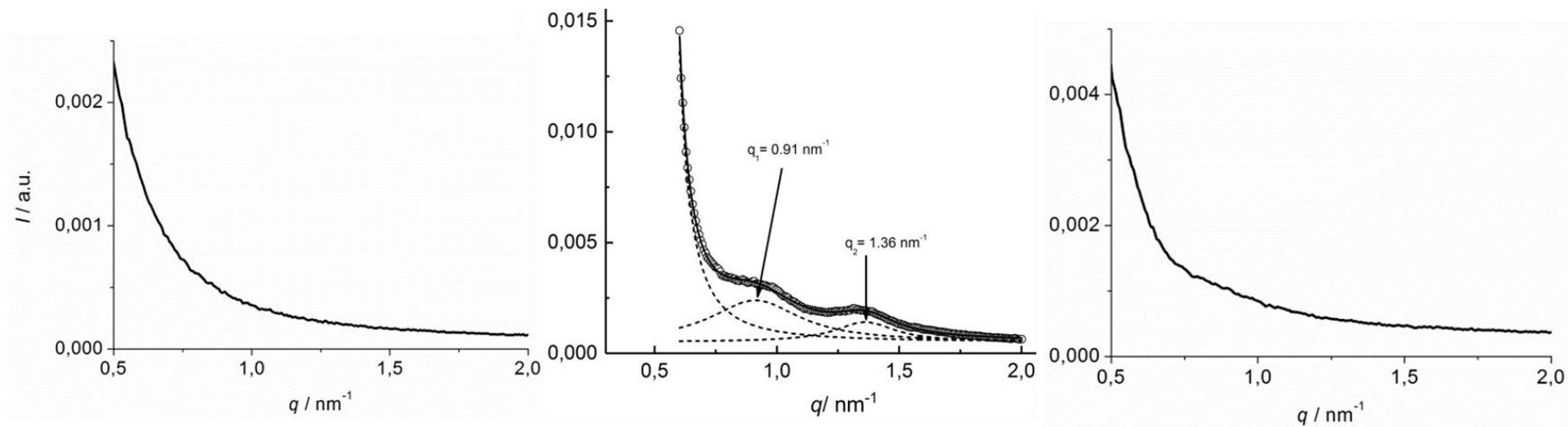


Figure S13. SAXS measurement of mesoporous carbons based on different $\text{PPO}_n\text{-PEO}_{180}\text{-PPO}_n$ polyethers as SDAs under otherwise identical conditions. Except for $\text{PPO}_{66}\text{-PEO}_{180}\text{-PPO}_{66}$, all other carbon materials remained virtually featureless, suggesting disordered pore arrangement. Examples shown from left to right: $n = 20, 66, 90$.



Figure S14. SEM recording of mesoporous carbon based on $\text{PPO}_{66}\text{-PEO}_{180}\text{-PPO}_{66}$ as structure-directing agent.

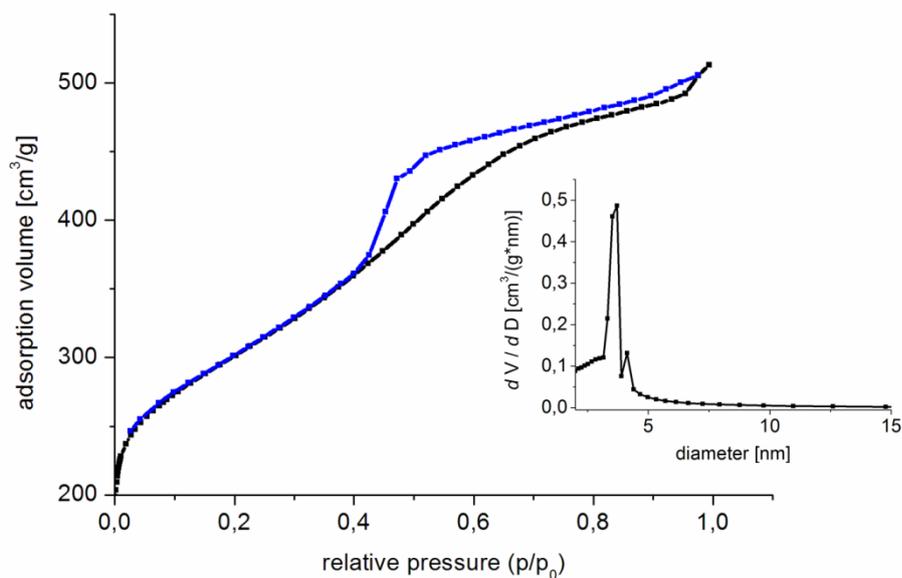


Figure S15. N₂ sorption-desorption isotherm (blue = desorption) of mesoporous carbon based on PPO₄₀-PEO₁₈₀-PPO₄₀ and corresponding pore-size distribution (BJH model). Specific surface = 990 m²/g, total pore volume = 0.8 cm³/g, average pore size (desorption) = 3.2 nm.

References

-
- [i] S. Naumann, A. W. Thomas and A. P. Dove, *Angew. Chem. Int. Ed.*, 2015, **54**, 9550.
 - [ii] S. Naumann, A. W. Thomas and A. P. Dove, *ACS Macro Lett.*, 2016, **5**, 134.
 - [iii] N. Kuhn, H. Bohnen, J. Kreutzberg, D. Bläser, R. Böse, *J. Chem. Soc., Chem. Commun.* 1993, 1136.
 - [iv] S. Kronig, P. G. Jones, M. Tamm, *Eur. J. Inorg. Chem.* 2013, **2013**, 2301.
 - [v] Y. Meng, D. Gu, F. Zhang, Y. Shi, L. Cheng, D. Feng, Z. Wu, Z. Chen, Y. Wan, A. Stein et al., *Chem. Mater.* 2006, **18**, 4447.
 - [vi] C. Liang, S. Dai, *J. Am. Chem. Soc.* **2006**, *128*, 5316.