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Size-Selective Binding of Sodium and Potassium Ions in Nanoporous Thin Films of Polymerized Liquid Crystals

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The development of a nanoporous material from a columnar liquid crystalline complex between a polymerizable benzoic acid derivative and a 1,3,5-tris(1Hbenzo[d]imidazol-2-yl)benzene template molecule is described. The morphology of the liquid crystalline complex is retained upon polymerization and quantitative removal of the template molecule affords a nanoporous material with the same lattice parameters. The nanoporous material selectively binds cations from aqueous solution, with selectivity for sodium and potassium ions over lithium and barium ions, as shown with FT-IR. Binding is also quantified gravimetrically with a quartz crystal microbalance with dissipation monitoring, a technique that is used for this purpose for the first time here.

1. Introduction

The use of self-assembling organic building blocks is a promising but challenging approach to develop nanostructured porous materials.^[1-4] A promising approach to nanoporous materials is based on the self-assembly of block copolymers.^[5-9] Utilizing the nanosegregation of two covalently-connected, incompatible polymer blocks, nanoporous materials can be obtained with pore diameters down to 10 nm after selective phase removal. Inorganic nanoporous materials, like aluminosilicate structures known as zeolites, have pore sizes below 1 nm and are robust materials. However, processing of these inorganic materials is difficult and costly.^[10,11] Over the last couple of years, much progress has also been made on the development of synthetic organic nanostructured materials with smaller features by using the self-assembly properties of

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liquid crystals.^[12–14] Within this field, the development of organic materials with molecular sieving properties is an area with very high relevance for applications. Tschierske and co-workers have demonstrated the first examples of liquid crystalline superstructures that resemble the structure of some zeolites.^[15,16] The first development of an organic nanoporous material with 1D-aligned nanochannels was reported by Gin and co-workers.^[17–20] They demonstrated that lyotropic liquid crystals (LCs) could be aligned on a macroscopic scale to form a well-defined nanoporous material for water filtration

applications. Feringan et al.,^[21,22] Kraft et al.,^[23] Kishikawa et al.,^[24] and Lee et al.^[25] have shown examples of columnar LC complexes between benzoic acid derivatives and different kinds of template molecules that form multiple mesophases depending on the length of the alkyl tails applied to the benzoic acid derivatives. The latter two papers (Kishikawa et al. and Lee et al.) used acrylate-functionalized benzoic acids to obtain a cross-linked matrix from which the template molecule could be removed. Both demonstrated >90% template removal, but the polymer nanostructure was not fully retained.

Here, we use the self-assembly of a hydrogen-bonded columnar LC complex to develop a nanoporous thin film with high retention of the nanostructure after cross-linking and quantitative removal of the template. The nanopores thus obtained bind metal cations in a size-selective manner. (Figure 1). The nanoporous material was obtained using complex of 1,3,5-tris(1H-benzo[d]imidazol-2-yl)benzene а (BTB)^[26] with a polymerizable benzoic acid derivative to form a columnar hexagonal (Col_{hex}) mesophase, polymerizing via acyclic diene metathesis (ADMET)^[27,28] followed by quantitative template removal. Finally, size-selective binding studies were performed and quantified with Fourier-transform infrared spectroscopy (FT-IR), X-ray photoelectron spectroscopy (XPS), and a quartz crystal microbalance with dissipation monitoring (QCM-D), with QCM-D as a new characterization tool.

2. Thermotropic Liquid Crystalline Properties of the 3:1 Complex between Polymerizable Benzoic Acid and 1,3,5-*tris*(1H-benzo[d]imidazol-2-yl)benzene

Mixing the polymerizable benzoic acid 1 and BTB in a 3:1 ratio afforded a complex that demonstrated thermotropic

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Figure 1. Self-assembly approach for the template-assisted development of a nanoporous material and size-selective ion binding. The 3:1 complex between benzoic acid 1 and BTB assembles in a Col_{hex} mesophase cross-linked by ADMET polymerization and the BTB template is quantitatively removed, after which metal ion studies were conducted.

LC behavior. Comparison of the FT-IR spectra of the individual components with the complex showed that a hydrogenbonded complex was formed (**Figure 2A**). The carbonyl stretching vibration of the benzoic acid shifts from 1686 to 1676 cm⁻¹ in the complex, which demonstrated the formation of a carboxylate salt. Furthermore, an N–H stretching vibration around 3200 cm⁻¹ was absent in the complex, while a pronounced band arose in the complex at 3264 cm⁻¹, typical for the formation of an imidazolium salt. These changes confirmed that an acid–base reaction had taken place between the template (p K_a of the protonated 2-phenylbenzimidazolium is 5.23) and the benzoic acid (p K_a of gallic acid is 4.41).^[29]

The thermotropic LC properties of the complex were further assessed by differential scanning calorimetry (DSC), X-ray diffraction (XRD), and polarized optical microscopy (POM). The DSC showed two phase transitions: a crystalline-to-LC phase transition at 45 °C and isotropization at 230 °C (Figure 2B). Upon annealing of the 3:1 complex in the isotropic state at 240 °C, phase separation of needle-shaped crystals was observed by POM (Figure S1, Supporting Information). Most likely these crystals consist of solid template or a 1:2 or 1:1 complex with benzoic acid 1. Utilizing 3.3 equivalents of benzoic acid 1 made it possible to prevent phase separation at 100 °C with a focal conical texture typical for a discotic columnar mesophase (Figure 2C). With variable-temperature X-ray diffraction (VT-XRD), the mesosphere was characterized in detail (Figure S2, Supporting Information). Diffraction peaks with q-ratios of $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$, characteristic for a Col_{hex} phase, were observed. An intercolumnar distance of 3.25 nm and an interdisc distance of 0.37 nm at 150 °C were calculated (Figure 2D). The

lattice parameters correspond to a density of 1.13 g cm⁻³ at 150 °C. The BTB molecule has a diameter of 1.6 nm (Figure S3, Supporting Information), and when this template molecule is removed from a polymerized benzoic acid matrix, formation of pores similar in size to the diameter of BTB can be expected.

3. Polymerization of the 3:1 Complex between Benzoic Acid and BTB

ADMET was used to cross-link the alkene functionalities of benzoic acid 1.^[27,28] ADMET is a polycondensation reaction and therefore only leads to cross-linking when more than two of the three double bonds on each molecule react with neighboring molecules. An LC mixture of BTB with 3 equivalents of benzoic acid 1 was heated under vacuum at 100 °C with 2 mol% of Grubbs' 2nd generation metathesis catalyst (3) to achieve high conversion of the terminal double bonds via ADMET. Network formation was finished after 3 h according to FT-IR analysis. From the decrease of the end-terminal =C–H bending vibration at 908 cm⁻¹, depicted in **Figure 3**A, a conversion of 82% was determined. The product was an insoluble polymer film, indicating enough cross-linking to fixate the morphology.

Comparison of the XRD diffraction patterns of the complex before and after polymerization of a bulk sample showed no change in the lattice parameters of the Col_{hex} phase (Figure 3B). Slight broadening of the peaks was observed, which is common for polymerized materials.^[30–33] Shear-induced alignment was also retained after polymerization, as can be seen in the 2D XRD image of Figure 3C. In this diffractogram, the interdisc reflection



Figure 2. A) FT-IR of complex formation at a 3:1 ratio of carboxylic acid and template. B) DSC of the first cooling and second heating run from the 3:1 complex. C) XRD of the 3:1 complex at 150 °C, Col_{ho} phase with unit cell parameters: a = 3.25 nm and c = 0.37 nm. D) POM image of the template and 3.3 equivalents of carboxylic acid at 100 °C.



Figure 3. A) FT-IR of ADMET polymerization of the complex with 2 mol% catalyst at 100 °C with application of vacuum for 3 h. B) Comparison of XRD before and after ADMET polymerization of the complex and after template removal. C) 2D image of XRD after ADMET polymerization of shear-aligned 3:1 complex. D) UV–vis and fluorescence measurements on extraction of the template with DMSO.

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is perpendicular to the intercolumnar reflection, showing that the disc-shaped complexes stack with their plane perpendicular to the column axis, as well as the flexible alkyl tails.

The morphology of unpolymerized thin films was studied with grazing incidence wide-angle X-ray scattering. Thin films (≈50 nm) of the complex without catalyst were prepared by spin-coating from MeOH/CHCl₃ solution (1:9 v/v) on clean glass substrates. The diffraction pattern of the Colhex phase was observed when the spin-coated samples were heated above 50 °C (Figure S4, Supporting Information). Polymerized films were prepared by addition of 2 mol% catalyst and heating at 100 °C under vacuum. The hexagonal morphology of the unpolymerized complex was retained in the polymer matrix. In linecuts of the multidomain planar samples, reflections were at an angle of 60°, characteristic for a hexagonal lattice with planar orientation of columns.^[34,35] Varying the angle of the incidence beam probed the morphology of the surface and the bulk of the material (Figure S5, Supporting Information). At low angles of 0.14°, mainly the surface is probed, while at higher incident angles, more of the bulk material is probed. Both the lower and the higher angles showed the same diffraction pattern, therefore the structure was uniform throughout the entire material.

4. Preparation of Nanoporous Films by Removal of Template

Nanoporous films were prepared by extraction of BTB from cross-linked thin films on glass (thickness 50–200 nm) with DMSO (a good solvent for BTB). The samples were shaken three times for 1 h in 15 mL of solvent. The amount of remaining template in the film after each extraction was determined by fluorescence spectroscopy (Figure 3D). Fluorescence measurements on the thin films were performed by excitation at 330 nm and recording the emission spectra after every subsequent extraction (Figure S6, Supporting Information). The emission spectra were normalized and the emission band of BTB at 522 nm was set to 100% before the extractions. After three extractions, the template had been removed quantitatively from the thin film.

Another method to quantify the template removal is gravimetry using a QCM-D, which has been used frequently for biological binding studies^[36,37] and is rapidly finding applications in materials science.^[38–40] In QCM-D, the change in frequency of a quartz crystal resonator is monitored upon mass changes. The adsorbed mass, $M_{\rm fr}$ and the frequency-shift, $\Delta f_{\rm n}$, are related by the Sauerbrey Equation (1)

$$\Delta f_{\rm n} = -2n f_{\rm q}^2 \frac{M_{\rm f}}{\rho_{\rm q} \iota} \tag{1}$$

where *n* denotes the overtone order, f_q is the frequency of the quartz crystal ($f_q = 5$ MHz), ρ_q is the density of the quartz crystal ($\rho_q = 2.65$ g cm⁻³), and *v* is the speed of light ($v = 3.00 \times 10^8$ m s⁻¹). The Sauerbrey Equation (1) is only valid for sufficiently rigid thin films, i.e., with low dissipation changes during mass adsorption measurements.^[41]

For the QCM-D measurements, thin films of the BTB with benzoic acid 1 complex were spin-coated on an empty gold



Table 1. QCM-D results on template removal.

Film thickness [nm]	Mass polymer with template [mg cm ⁻³]	Mass polymer without template [mg cm ⁻³]	Template removed [%]
181 ± 7	1131 ± 1	972 ± 3	98 ± 1

sensor and polymerized by heating to 100 °C for 3 h under vacuum. The results of the QCM-D measurements before and after template removal are summarized in Table 1. The amount of adsorbed mass of the film after spin-coating and polymerization on an empty gold sensor was $1131 \pm 1 \text{ mg cm}^{-3}$. This corresponds to a film thickness of 181 ± 7 nm. After three extractions with DMSO, the sensors were washed with MilliQ water and dried at 40 °C in a vacuum oven containing (P_2O_5) for 1 h. The sensor showed a decrease in mass equal to the removal of 98 \pm 1% of the BTB template. An example of the OCM-D measurements is depicted in Figure 4A. Ouantitative template removal was also confirmed by FT-IR analysis on the bulk of the film by the disappearance of the N-H stretching vibration at 3241 cm⁻¹ and the presence of free carboxylic acid groups with a carbonyl C=O stretching vibration at 1676 cm⁻¹ compared to 1685 cm⁻¹ in the complex (Figure 4B). After removal of the template, the structural properties were investigated with GISAXS (Figure 4C) and XRD (Figure 4D). The presence of peaks at 60° intervals at 30°, 90°, and 150°, and full retention of the diffraction signals with q-ratios of $1:\sqrt{3}:\sqrt{4}:\sqrt{7}$, demonstrated retention of the hexagonal structure after removal of the template.

5. Size-Selective Binding of Salt Ions from Aqueous Solutions

The FT-IR analysis after BTB template removal showed that the pore walls of the nanostructured materials were functionalized with free carboxylic acid groups due to the presence of the carbonyl stretching vibration at 1676 cm⁻¹ (vide supra, Figure 4B). Cross-linked films of the complex, from which the template had been removed, were soaked in aqueous solutions of hydroxide salts to deprotonate the carboxylic acid groups and form the corresponding metal carboxylate salts. After soaking for 3 h in 100×10^{-3} M solutions of the hydroxides of Li⁺, Na⁺, K⁺, Cs⁺, and NH₄⁺, the films were dried and analyzed with FT-IR spectroscopy (Figure 5A). Depending on the cation, the FT-IR spectrum showed a shift in the symmetric and asymmetric C=O stretching vibration from 1684 to 1558 cm⁻¹ (asymmetric stretching) and 1585 to 1376 cm⁻¹ (symmetric stretching), indicative of the formation of the metal carboxylate salt. None of the divalent cations were bound as carboxylate salts. Of the monovalent cations, only Na⁺ and K⁺ ions were capable of forming the corresponding carboxylate salt. Even the smaller Li⁺ ion was not bound, showing that selectivity was not determined by ionic radius alone. A potential explanation for the observed selectivity can be found in the size of the hydrated radii of the cations (Figure 5B). Divalent cations have larger hydrated radii than monovalent ions, and for monovalent cations the hydrated radius is smallest for Na⁺ and K⁺ ions, while the hydrated radii of Li⁺ and NH₄⁺ ions are

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Figure 4. A) Static QCM-D measurements of an empty gold sensor, after spin-coating and polymerization of the complex and after template removal. B) FT-IR before and after template removal. C) Linecuts of GISAXS measurements before and after template removal. D) XRD of the polymer material with and without the BTB template.

comparable in size to hydrated Cs⁺ ions. The exclusive binding of Na⁺ and K⁺ and rejection of the other tested monovalent and divalent inorganic ions and organic cations^[42] demonstrate the high size selectivity of this system.

QCM-D was used to quantify the amount of bound cations and to determine the specificity of the binding with static, ex situ measurements. The measurements were performed on spin-coated and polymerized films. QCM-D was performed before and after deposition of a thin film to the sensor, after template removal and after exposure to 10×10^{-3} $\scriptstyle\rm M$ NaOH/ LiOH/Ba(OH)_2 aqueous solution. Figure 6A shows an example of a set of ex situ static measurements for a single sample after drying of the sensor at every processing step (more examples in

Figure S7, Supporting Information). The figure shows a series of steps, corresponding to mass changes when the polymer film with the template was deposited, followed by mass loss when the BTB template was removed and a mass increase when Na⁺ ions were bound. The first mass change allowed for the determination of the number of carboxylic acid binding sites, which was 25.72 nmol. The next step in the graph corresponded to removal of 8.48 nmol of template (99%). Finally, the mass change after exposure to NaOH corresponded to 24.88 nmol of Na⁺ ions, occupying 98% of the available carboxylic acid binding sites. The same experiment was also performed without template removal, from which the nonspecific interaction of Na⁺ ions with the surface was calculated



Figure 5. A) Comparison of FT-IR spectra after exposure to different hydroxide salts (0.1 M (aq.). B) The hydrated radius of several cations, taken from the literature.^[42]





Figure 6. A) Static QCM-D measurements after template removal and exposure to 10×10^{-3} M NaOH (aq). Time-dependent measurements where each measurement takes approximately $\approx 1-2$ min after stabilization of the signal for 20 min. B) Bar diagram of QCM-D results on binding or removal: a) template removal as percentage of amount of polymer complex applied per area; b) percentage of total amount of carboxylic acid groups occupied; c) percentage of total amount of carboxylic acids occupied, with template still present.

to be 7 \pm 2% (Figure 6B). It was found that Li⁺ and Ba²⁺ ions occupy 3 \pm 7% and 5 \pm 2% of the carboxylic acid sites, respectively, less than the nonspecific binding of the Na⁺ ions. Finally, exposing a sodium-saturated film to deionized water partially removed the bound Na⁺ ions by 45 \pm 7% of the binding sites.

Angle-resolved XPS (AR-XPS) was performed to establish whether binding of the Na⁺ ions takes place throughout the bulk of the material or only at the surface of the thin films (Figure 7). At 0° is the highest penetration depth but lowest surface exposure; by increasing the angle to 60°, less of the bulk material is probed but more of the surface is exposed. The nitrogen-tocarbon ratio (N/C) before template removal demonstrated that the density of nitrogen is constant throughout the thickness of a 175-nm film (Figure 7A). After template removal, nitrogen was no longer detectable (Figure S8, Supporting Information). Finally, the ratio of alkali metal (i.e., Na, Li or Ba) to carbon (M/C) was determined from these measurements, before and after exposure to the corresponding hydroxide solutions (Figure 7B). The samples with BTB, without BTB, and the sample exposed to LiOH did not contain a measurable amount of metal. The absence of Li⁺ confirms that this ion is not absorbed by the nanoporous material. The amount of sodium was constant over all the angles, which shows a homogeneous distribution of sodium throughout the material. Moreover, in nanoporous films treated with $Ba(OH)_2$, the barium signal increased with increasing tilt angle, indicating nonspecific binding at the surface. This is due to an inhomogeneous distribution of the barium at the surface.

6. Conclusion

A successful strategy was developed to obtain a nanoporous material using self-assembly of a hydrogen-bonded complex, combined with a cross-linking reaction based on alkene metathesis. The approach provided films with a high density of nanopores, selective for the binding of Na⁺ and K⁺ ions over a number of other metal cations. The first example of quantitative gravimetric analysis on ion binding in organic nanoporous materials was demonstrated by QCM-D. Moreover, since all divalent cations and large (hydrated) monovalent salt ions tested were rejected by the film, the selectivity of binding of Na⁺ and K⁺ ions raises the question of whether these films are candidates for selective ion transport in nanofiltration applications. Future work will be focused on obtaining homeotropically aligned films and on integrating thin films with aligned pores on support materials for flow-trough experiments.



Figure 7. AR-XPS plot of nanoporous materials with or without BTB template or exposed to different hydroxide salts: A) the nitrogen-to-carbon ratio and B) the salt-to-carbon ratio.



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7. Experimental Section

Materials and Instrumentation: Chemicals and solvents were purchased from Sigma-Aldrich or Biosolve, respectively, and used as received, unless stated otherwise. FT-IR spectra were recorded at room temperature on a Perkin Elmer Spectrum One spectrometer equipped with a universal attenuated total reflectance (ATR) sampling accessory. NMR spectra were recorded at room temperature on a Varian Mercury 400 (400 MHz) spectrometer. Chemical shifts are given in ppm with respect to tetramethylsilane (0 ppm) as internal standard. Coupling constants are reported as J values in Hz. Column or flash chromatography was carried out using silica gel (0.035-0.070 mm, ≈6 nm pore diameter). Matrix-assisted laser desportion ionization time-of-flight (MALDI-TOF) mass spectra were obtained on a PerSeptive Biosystems Voyager-DE PRO spectrometer with α -cyano-4-hydroxycinnamic acid as a matrix. POM images were recorded by a Jeneval microscope equipped with crossed polarizers and Polaroid DMC le CCD camera, equipped with a Linkam THMS 600 hot stage. DSC measurements were performed in hermetic T-zero aluminum sample pans using a TA Instruments Q2000 - 1037 DSC equipped with a RCS90 cooling accessory. All transition temperatures and enthalpies were determined from the first cooling and second heating run, with heating and cooling rates of 10 K min⁻¹. XRD images were recorded on a Ganesha lab instrument equipped with a Genix-Cu ultra-low divergence source producing X-ray photons with a wavelength of 1.54 Å and a flux of 1×10^8 photons per second. Diffraction patterns were collected on a Pilatus 300K detector with reversed-biased silicon diode array sensor. The detector contains 487 \times 619 pixels of 172 \times 172 μm^2 and consists out of three modules with an intermodule gap of 17 pixels in between, resulting in two dark bands on the image. Grazing incidence X-ray scattering measurements were performed on a sample-todetector distance of 1080 mm for wide-angle X-ray scattering (WAXS) or 1530 mm for small-angle X-ray scattering (SAXS). Temperaturedependent measurements were executed with a Linkam HFSX350 heating stage and cooling unit. Azimuthal integration of the obtained diffraction patterns was performed by utilizing the SAXSGUI software. Equation (2) was used to convert the scattering vector into d-spacing, where Bragg's law (Equation (3)) is fulfilled (λ is the wavelength, *n* is an integer, and θ is the angle of incidence). The beam center and the *q*-range were calibrated using silver behenate (0.107 Å⁻¹; 58.43 Å)

$$d = \frac{2\pi}{q} \tag{2}$$

$$q = \frac{4\pi}{n\lambda} \sin\theta \tag{3}$$

UV-vis experiments on solutions were performed on a Cary 300 UVvis spectrophotometer equipped with a Peltier temperature controller. All experiments were performed in 10×10 mm quartz cuvettes at 20 °C. Unknown concentrations were obtained from a calibration curve of known concentrations, according to Lambert-Beer's law. Fluorescence data were recorded on a Varian Eclipse fluorescence spectrometer equipped with a solid-state sample holder. QCM-D measurements were performed in a Q-Sense E4 4-channel quartz crystal microbalance with a peristaltic pump of Biolin Scientific. The AR-XPS measurements were carried out with a Thermo Scientific K-Alpha equipped with a monochromatic small-spot X-ray source and a 180° double-focusing hemispherical analyzer with a 128-channel detector. Spectra were obtained every 15° (starting close to 0°) using an aluminum anode (Al K α = 1486.6 eV) operating at 72 W and a spot size of 400 $\mu m.$ Survey scans were measured at a constant pass energy of 200 eV and region scans at 50 eV. The background pressure was $2\times 10^{-9}\,\text{mbar}$ and during measurement 3×10^{-7} mbar argon because of the charge compensation for the dual beam source.

Methods—*Sample Preparations*: The fabrication of porous materials was performed by making a stock solution of gallic acid alkene (3 equivalents) in MeOH/CHCl₃ (1:9 v/v) and adding this solution to the required amount of solid benzene-1,3,5-*tris*benzimidazole (BTB,

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1 equivalent) (35 mg mL⁻¹, final concentration). Prior to use, a solution of Grubbs catalyst (2nd generation, 2 mol%) in CHCl3 was added. Clean glass substrates (30×30 mm) were obtained by dipping the glass substrates in piranha solution (aqueous hydrogen peroxide 35% and concentrated sulfuric acid, 1:3 v/v) for 10 s, rinsing thoroughly with deionized water and drying. The liquid-crystal solution was spin-coated on the clean substrate, placed in a preheated oven at 100 °C, and vacuum was applied for 3 h. Subsequently, the sample was placed in 15 mL DMSO ($3\times$) and extracted by careful shaking for 1 h each.

Methods—Fluorescence Spectroscopy: Fluorescence measurements on the thin films were performed by excitation at 330 nm and recording the emission spectra after every subsequent extraction with DMSO (1 h each). The emission spectra were normalized, and the emission band of BTB at 522 nm before the extractions at 522 nm was set to 100%.

Methods—UV-Vis Spectroscopy: Concentrations were calculated using the extinction coefficient determined separately in DMSO at $\lambda_{max} = 316$ nm. The initial amount of template was calculated according to the thickness of the layer and the density of the polymerized complex of the XRD measurements. Layer thickness was determined by a Veeco Dektak 150 Surface Profiler.

Methods—Quartz Crystal Microbalance with Dissipation Experiments: Sensors were prepared by first cleaning them with piranha solution $(H_2SO_4/H_2O_2, 3:1, v/v)$ and extensive washing with MilliQ water, followed by acetone and drying by air flow. Subsequently, a \approx 50 mg mL⁻¹ of the complex (benzoic acid:template:catalyst, 3:1:0.06 mol/mol/mol) in CHCl₃/MeOH (9:1) was spin-coated on the sensors at 3000 rpm for 30 s to obtain layer thicknesses of 100-200 nm. The sensors were polymerized in a vacuum oven at 100 °C held under vacuum for 3 h. The sample was measured dry to determine the layer thickness and the amount of material on the sensor according to the Sauerbrey equation. The sensors were extracted three times with 15 mL DMSO for 1 h by careful shaking and finally rinsed with MilliQ water and dried in a vacuum oven at 40 °C containing P_2O_5 in vacuo for at least 1 h. Subsequently, the dry sensors were measured again to determine the amount of template that was removed. Subsequently, the sensors were equilibrated in MilliQ water for 3 h with a flow rate of 50 μ L min⁻¹ at 20 °C. The MilliQ water was exchanged for the NaOH (aq.) solution and measured for an additional 3 h with a flow rate of 50 μ L min⁻¹ at 20 °C. Finally, the sensors were quickly rinsed with MilliQ water and dried in a vacuum oven at 40 $^\circ$ C under vacuum and P₂O₅ before quantifying adsorbed sodium ions. All measurements were at least performed in triplicate. Errors are given as standard deviations.

Synthetic Procedures: The synthesis of BTB was performed according to literature.^[26]

Synthesis of Polymerizable Benzoic Acid 1:



To a stirred solution of methyl gallate (2.1 g; 11.5 mmol; 1.0 equiv.) in DMF (55 mL) was added K_2CO_3 (15.9 g; 115 mmol; 10.0 equiv.) and 11-bromo-1-undecene (8.85 g; 37.95 mmol;

3.3 equiv.). The resulting suspension was heated to reflux (110 °C) for overnight and after completion of the reaction, cooled to ambient temperature, filtered, and evaporated to dryness. The residue was redissolved in EtOAc (17 mL)/water (22 mL), extracted with EtOAc (2 \times 17 mL), dried with Na2SO4, and filtered. After removal of the solvent, the crude compound was purified by flash column chromatography (heptane/ethyl acetate, 7:3 to 1:1) to obtain a white solid (6.0 g, 82%). ¹H-NMR (CDCl₃, 400 MHz): δ = 7.25 (s, 2H, 2x CH arom.), 5.80 (ddt, 3 H, l = 7 Hz, 10 Hz and 17 Hz, 3x CH₂ = CH-CH₂), 4.97 (dd, 6H, J = 10 Hz and 17 Hz, 3x CH₂ = CH), 4.01 (t, 6H, 7 Hz, 3x CH_2 - CH_2 -O), 3.88 (s, 3H, CH_3O), 2.03 (dt, 6H, J = 8 Hz and 7 Hz, 3x CH₂ = CH-CH₂), 1.81 (m, 6H, 3x CH₂-CH₂-O), 1.36 (m, 36H, 18x CH₂- CH_2 -CH₂). ¹³C-NMR (CDCl₃, 100 MHz): δ = 167.0, 152.9, 142.4, 139.3, 124.8, 114.2, 108.0, 73.6, 69.2, 52.2, 34.0, 30.4, 29.8, 29.7, 29.7, 29.6, 29.5, 29.4, 29.3, 29.3, 29.1, 29.1, 26.2, 26.2. ATR FT-IR: 3076, 2924, 2853, 1721, 1641, 1587, 1500, 1465, 1430, 1386, 1334, 1216, 1115, 1014, 993, 908, 863, 812, 765, 722, 671, 636, 577, 554 cm⁻¹. MALDI-TOF MS: m/z





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calculated for $C_{41}H_{68}O_5~(M\!+\!H)^+$: 640.51, found: 640.50, $(M\!+\!Na)^+$: 663.50, found: 663.49.



A solution of methyl gallate alkene (3.0 g; 4.68 mmol; 1.0 equiv.) in MeOH/H₂O (3:1 v/v, 26 mL) was treated with KOH (2.13 g, 37.91 mmol; 8.1 equiv.) and heated at reflux overnight. The

reaction mixture was cooled to ambient temperature after completion of the reaction, neutralized to $pH \approx 3.0$ with 3.0 M HCl, and extracted with EtOAc (3 \times 20 mL). The organic phase was dried with Na₂SO₄, filtered, and evaporated to dryness to obtain the desired product as a white solid in quantitative yield (2.9 g). ¹H-NMR (CDCl₃, 100 MHz): δ = 11.37 (br. s, 1H, OH), 7.30 (s, 2H, 2 x CH arom.), 5.83 (ddt, 3H, J = 12 Hz, 21 Hz and 34 Hz, 3 x $CH_2 = CH-CH_2$), 4.95 (dd, 6H, J = 21 Hz and 34 Hz, $3 \times CH_2 = CH$, 4.02 (m, 6H, $3 \times CH_2 - CH_2 - O$), 2.05 (m, 6H, $3 \times CH_2 =$ CH-CH₂), 1.78 (m, 6H, 3 x CH₂-CH₂-O), 1.31 (m, 36H, 18 x CH₂- CH_2 -CH₂). ¹³C-NMR (CDCL₃, 100 MHz): $\delta = 177.9$, 172.2, 153.0, 143.2, 139.3, 123.8, 114.3, 108.6, 73.7, 69.3, 34.0, 30.5, 29.8, 29.7, 29.6, 29.6, 29.6, 29.6, 29.5, 29.4, 29.3, 29.3, 29.1, 29.1, 26.2, 26.2, 21.0. ATR FT-IR: 3078, 2976, 2922, 2851, 2636, 1686, 1641, 1586, 1504, 1464, 1431, 1390, 1328, 1275, 1228, 119, 1068, 991, 948, 908, 866, 767, 750, 724, 681, 626, 584, 543, 496, 479 cm⁻¹. Maldi-ToF MS: m/z calculated for $C_{40}H_{66}O_5$ (M+Na)⁺: 649.48, found: 649.48.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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