Synthesis and Characterization of Tris-Methacrylated 3,4,5-Tris[(alkoxy)benzyloxy]benzoate Derivatives

Uwe Beginn,* Gabriela Zipp, and Martin Möller[a]

Abstract: The synthesis of liquid crystalline 3,4,5-tris(11-methacryloylundecyl-1-oxybenzyloxy)benzoic acid, 2-methyl-(1,4,7,10,13-pentaoxacyclopentadecane)-3,4,5-tris[4-(11-methacryloylundecyl-1-oxy)benzyloxy] benzoate and its 1:1 complex with sodium triflate is described. The observed mesophases were identified, by polarized optical microscopy and contact preparation techniques, to be of hexagonal columnar disordered structure. The amphiphiles form lyotropic columnar phases in concentrated methacrylate solvents, while at low solute contents supramolecular organogels emerge.

Keywords: amphiphiles · benzoates · crown compounds · mesophases · organogelators

Introduction

Although the present-day technical polymeric materials have rather complicated microscopic superstructures, the molecular-level structures remain much less complex than those of biological functional units. Here specific transport units, such as carrier molecules and ion pores or channels, are able to recognize and selectively transport ions or molecules.[1] A major reason for this gap in development is that the structures of synthetic macromolecules are polydisperse and their intermolecular interactions are also for the most part not directed or localized.[2] Yet, supramolecular chemistry that is directed towards the formation of exactly defined assemblies mostly works with rather small molecules. In addition, well-defined supramolecular complexes are typically rather rigid and have only limited abilities to undergo complex changes depending on slight variations of the environment; this limits their function as molecular devices, in contrast to the flexible biomolecular assemblies. Hybrid materials composed of supramolecular aggregates that are connected to macromolecules may raise new opportunities to combine the specificity of supramolecular recognition with the flexibility and long-range effects of macromolecular systems.[3]

We are interested in the preparation of functional membranes containing self-organized transport channels based on such supramolecular/macromolecular hybrids. Our synthetic approach exploits the self-organization ability of wedge-shaped molecules, which stack to form well-defined supramolecular columns.[4, 5] Each column represents a solid aggregate consisting of regularly arranged, densely packed molecular units (Figure 1). The molecules bear a receptor function at the tip of the wedge and have polymerizable groups at the rim.[6] As they assemble to a solid supramolecular column, the receptor groups stack along the cylinder axis, thus forming a potential transport channel. Since the polymerizable groups are located at the outer rim of the aggregates, each cylinder is surrounded by a coat of monomer units. If the cylinders assemble in solution, a gel is

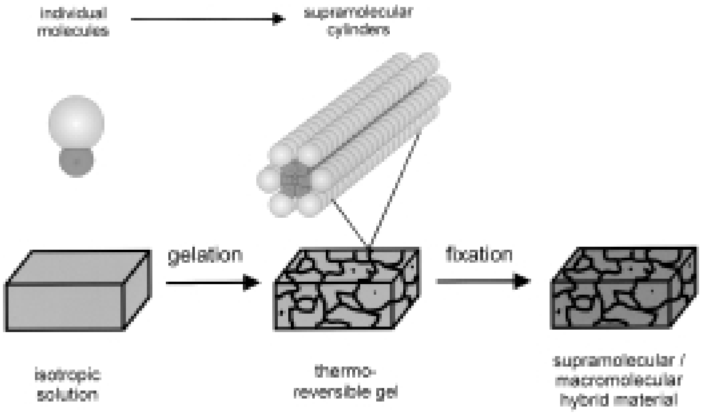

Figure 1. Schematic representation of the self-assembly of wedge-shaped amphiphiles in monomeric solvents. The self-organization into networks of solid supramolecular cylindrical aggregates causes the gelation of the liquid. Subsequent polymerization yields a hybrid material containing supramolecular channels, covalently anchored to the polymeric matrix phase ("matrix-fixed supramolecular channel") process.

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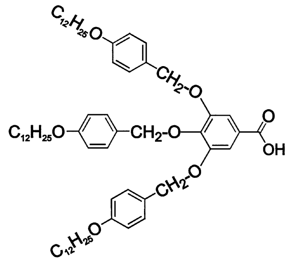
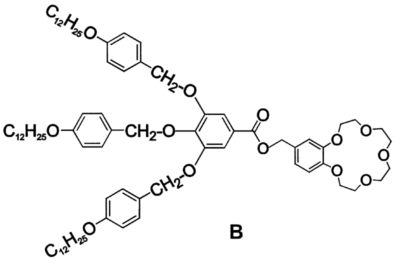
formed, at rather low concentrations.[7] When the solvent is a monomer, possibly mixed with a cross-linker, which can be photopolymerized, the cylinders can be embedded and covalently linked in a polymer matrix. Corresponding thin films may serve as a new type of membrane containing "matrix-fixed supramolecular channels" (Figure 1).

In a first approach, we focussed on alkali-ion-selective membranes. Crown ether compounds such as 1,4,7,10,13-pentaoxacyclopentadecane ("15-c-5") selectively form complexes with alkali metal cations, the stability of the complex being ruled by the radius of the cation.[8] In earlier reports, crown-ether-containing compounds such as 2-hydroxymethyl-[1,4,7,10,13-pentaoxabenzocyclopentadecane]-3,4,5-tris[4-(*n*-dodecyl-1-oxy)benzyloxy]benzoate (**B**) were shown to form a hexagonal columnar mesophase,[9] in which the stacked crown ether moieties form potential ion channels parallel to the column axis. In fact, it was reported that **B** exhibits ionic conductivity in the mesophase.[9]



A

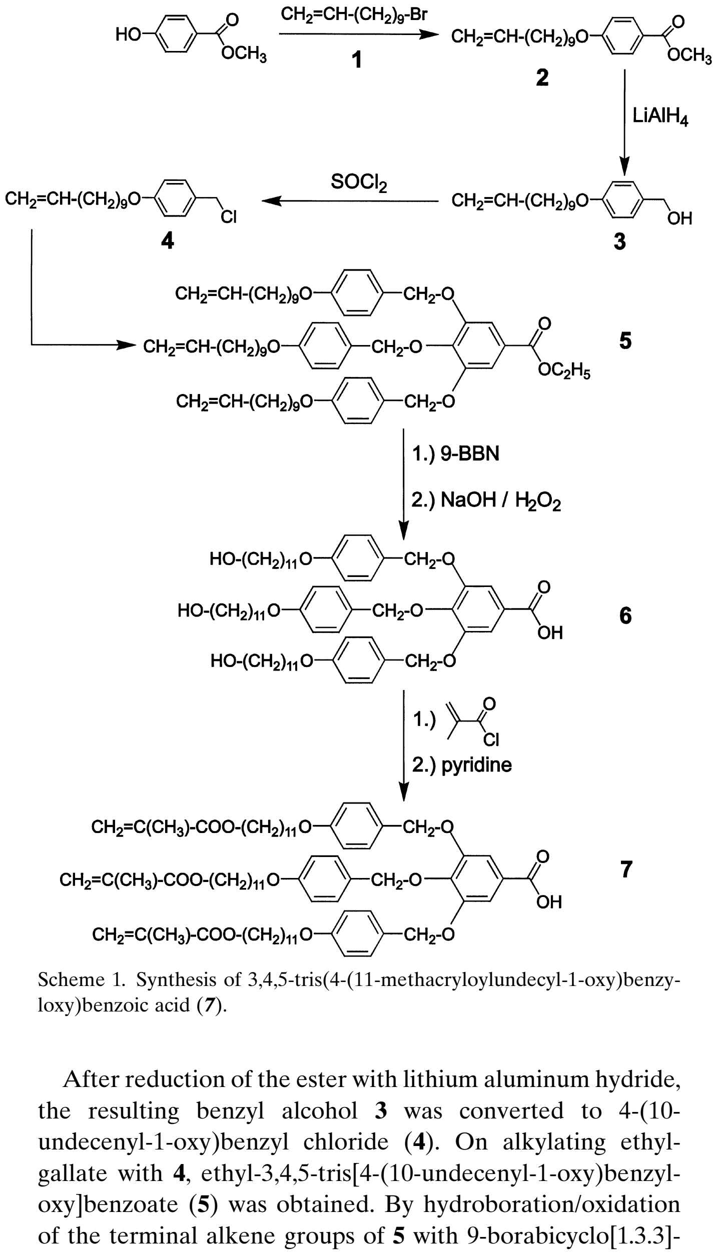


In an earlier report, we described derivatives of **B** with one alkyloxybenzyloxy group replaced by an 11-methacryloylundecyl-1-oxy unit.[4] Here we describe the synthesis of tris-methacrylate-functionalized **B** analogues. Because of the symmetrical substitution pattern, the stability of self-assembled structures should be enhanced relative to the mono-methacrylated **B** compound.[4, 5] In addition, the increased number of polymerizable groups should improve the connectivity between the supramolecular aggregates and the surrounding cross-linked matrix.

Abstract in German: *Die Synthese der flüssigkristallinen Verbindungen 3,4,5-Tris(11-methacryloyl-undeceyl-1-oxybenzyloxy)benzoesäure, 2-Methyl-(1,4,7,10,13-pentaoxacyclopentadecan)-3,4,5-tris[4-(11-methacryloyl-undecyl-1-oxy)benzyloxy]benzoats und seines 1: 1 Komplexes mit Natriumtrifluorsulfonat wird beschrieben. Die beobachteten Mesophasen wurden mittels Polarisationsmikroskopie und Kontaktpräparaten charakterisiert. Die Amphiphile bilden sowohl in bulk, als auch aus konzentrierten Lösungen in Methacrylat-Solventien hexagonal columnare Phasen aus, während verdünnte Lösungen unter Ausbildung supramolekularer Organogele thermoreversibel gelieren.*

Results and Discussion

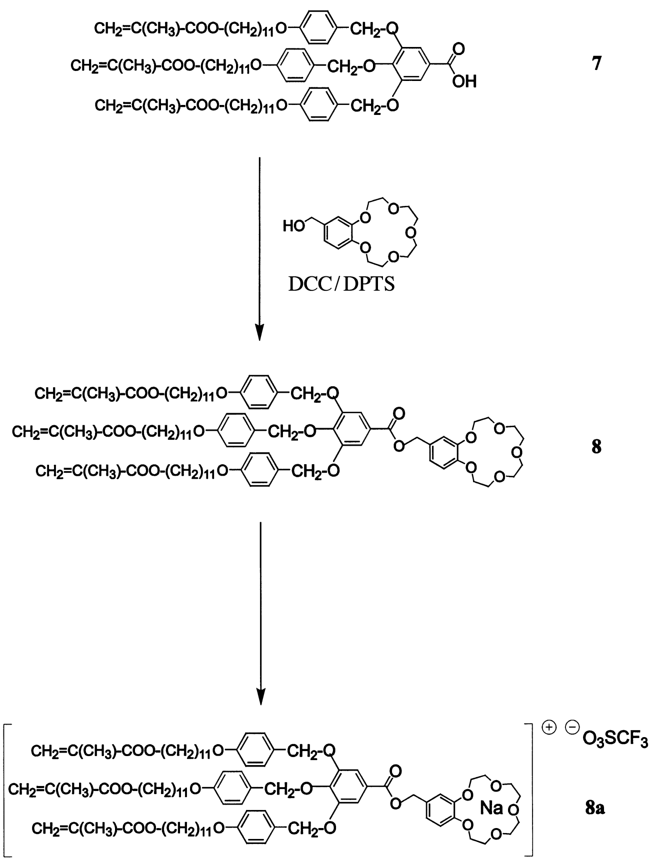
The synthesis of 3,4,5-tris[4′-(11-methacryloylundecyl-1-oxy)-benzyloxy]benzoic acid (**7**) was carried out as depicted in Scheme 1. Methyl-4-hydroxybenzoate (**1**) was alkylated with 11-bromo-1-undecene to yield methyl-4-(10-undecenyl-1-oxy)benzoate (**2**).



Scheme 1. Synthesis of 3,4,5-tris(4-(11-methacryloylundecyl-1-oxy)benzyloxy)benzoic acid (**7**).

After reduction of the ester with lithium aluminum hydride, the resulting benzyl alcohol **3** was converted to 4-(10-undecenyl-1-oxy)benzyl chloride (**4**). On alkylating ethylgallate with **4**, ethyl-3,4,5-tris[4-(10-undecenyl-1-oxy)benzyloxy]benzoate (**5**) was obtained. By hydroboration/oxidation of the terminal alkene groups of **5** with 9-borabicyclo[1.3.3]-nonane and an alkaline hydrogen peroxide solution, three hydroxy functions were introduced in the anti-Markovnikov position; the ester group was simultaneously saponified to yield **6**. Finally, the tris-methacrylated acid **7** was synthesized from **6** and methacryloyl chloride.

As shown in Scheme 2, 2-methyl-(1,4,7,10,13-pentaoxacyclopentadecane)-3,4,5-tris(4-(11-methacryloylundecyl-1-oxy)benzyloxy)benzoate (**8**) was obtained simply by DPTS-catalyzed, DCC-activated reaction of **7** with (2-hydroxymethyl)benzo-15-crown-5.



Scheme 2. Synthesis of 2-methyl-(1,4,7,10,13-pentaoxacyclopentadecane)-3,4,5-tris(4-(11-methacryloyl-undecyl-1-oxy)benzyloxy)benzoate (**8**) and its 1:1 $NaSO_3CF_3$ complex (**8a**).

Stoichiometric amounts of **8** and $NaSO_3CF_3$ were mixed in THF, to convert the crown ether derivative **8** into the 1:1 sodium complex **8a**. After slow evaporation of the solvent, the complex was dried in vacuum until the weight remained constant. Table 1 summarizes the phase behavior of **7** and **8** as obtained by DSC measurements.

The pure compound **7** was a waxy white material with a glass transition temperature at −33 °C and a softening/recrystallization transition at −6 °C. On further heating, the compound melted at 25 °C into a liquid crystalline phase which transformed into the isotropic melt at 62.5 °C (see DSC trace of **7** in Figure 2). The highly viscous, optically anisotropic phase observed by thermo-optical analysis between 23 and 62.5 °C confirmed the occurrence of a mesophase. From the broken fan-shaped texture (seen in the optical micrograph in Figure 3) and the large melt viscosity, the presence of a columnar mesophase was concluded.

Table 1. Transition temperatures of compounds **7**, **8** and **8a**.[b]

	$T_{C\rightarrow M}$ [°C]	$\Delta H_{C\rightarrow M}$ [kJ mol^{-1}]	$T_{M\rightarrow I}$ [°C]	$\Delta H_{M\rightarrow I}$ [kJ mol^{-1}]
7	25.0	29.0	62.7	0.5
8	17.0	42.7	28.0[b]	0.9[b]
8a	25.5	43.0	46.0	1.5

[a] C = crystalline phase, M = mesophase, I = isotropic phase; DSC measurements, heating rate = 10 °C min^{-1}—first heating only. [b] Heating rate = 5 °C min^{-1}.

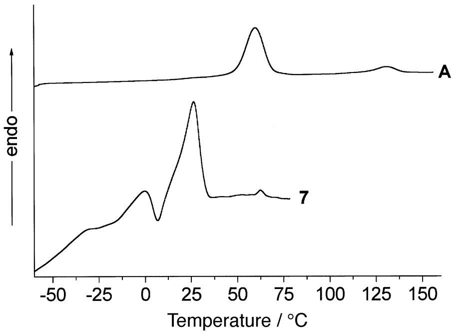


Figure 2. Representative DSC trace of the non-methacrylated acid **A** and **7**. Heating rate: 10 K min^{-1}, second heating run.

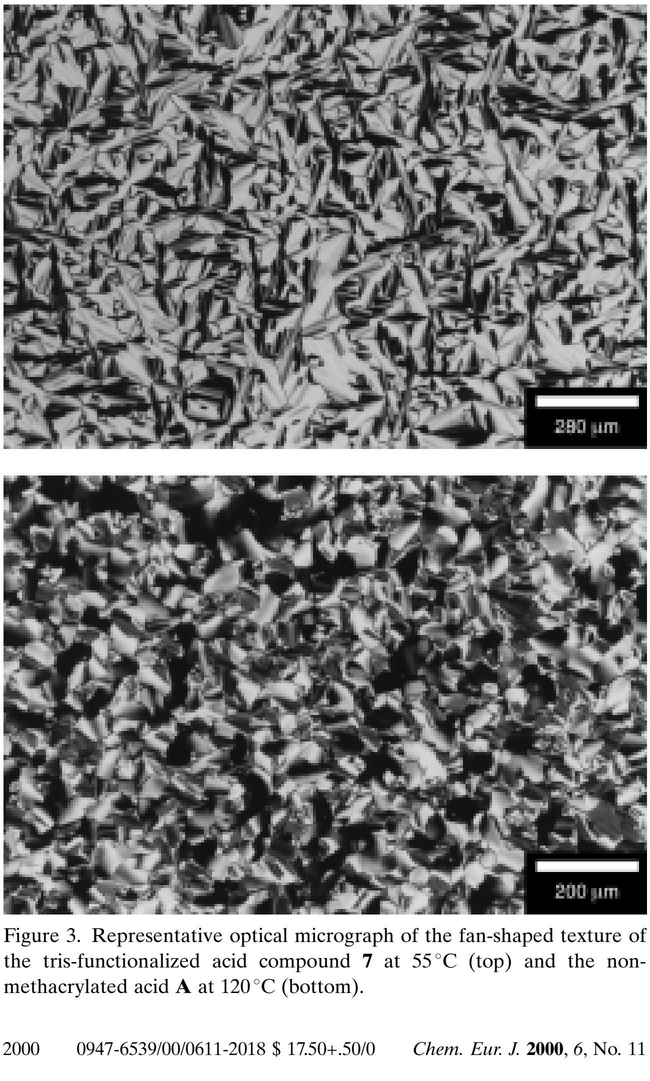


Figure 3. Representative optical micrograph of the fan-shaped texture of the tris-functionalized acid compound **7** at 55 °C (top) and the non-methacrylated acid **A** at 120 °C (bottom).

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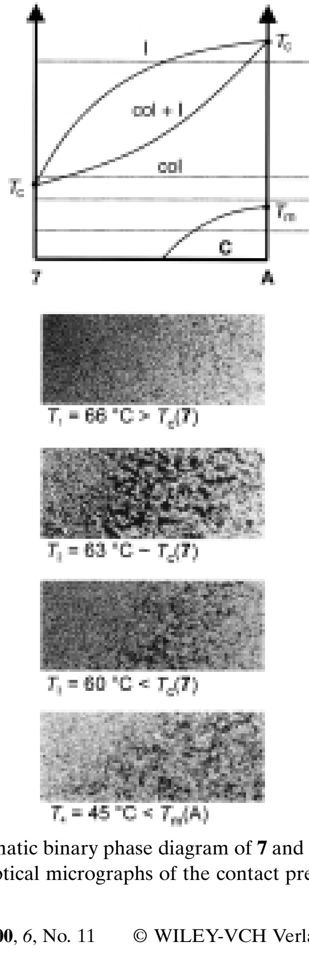
Figure 2 also shows a representative DSC trace of the non-methacrylated 3,4,5-tris(4-dodecyl-1-oxy-benzyloxy)benzoic acid (**A**). The attachment of the methacrylate groups to the acid resulted in a decrease in the melting temperature, from 60 °C to 25 °C, while the isotropization temperatures reduced from 132 °C to 63 °C.

According to the Arnold–Sackmann miscibility rule, two mesogens exhibit identical mesophases if the bordering regions of the two phases are connected by a continuous series of (liquid) mixed crystals.[10] The binary phase diagrams of **7** and **A** were investigated by means of Kofler's contact preparation technique.[11] Small drops of the molten compounds were brought in contact and were observed between crossed polarizers. In the contact zone, the two compounds diffused into one another, creating a region in which all possible compositions of binary mixtures were realized. At a given temperature, the interdiffusion area represents the complete isothermal section of the phase diagram.

Because of their chemical similarity to the substances under investigation, the non-methacrylated compounds **A** and **B** were chosen as standard mesogens for the miscibility experiments.

Figure 4 depicts the contact zone of **7** and **A** at different temperatures. A miscibility gap would create a black border separating the two mesogens; this phenomenon was not observed. Instead, when the temperature was decreased from 135 °C, a columnar texture formation was found that started from pure **A**, gradually moved into the diffusion zone, and finally into the pure amphiphile **7**. Even the thermodynamically required two-phase region, separating the isotropic melt from the mesophase, was distinguished (see Figure 4).



T_1 = 66 °C > T_c(7)

T_1 = 63 °C – T_c(7)

T_1 = 60 °C < T_c(7)

T_4 = 45 °C < T_m(A)

Figure 4. Schematic binary phase diagram of **7** and **A** and the corresponding polarized optical micrographs of the contact preparation.

When the crown ether compound **8** was heated, two broad, partially overlapping endothermic signals appeared in the DSC trace (Figure 5); the two signals could be separated by a reduction in the heating rate. Polarized optical investigations confirmed that **8** also has a crystalline phase (m.p. 17 °C) and a mesophase ($T_i = 28$ °C), see Table 1.

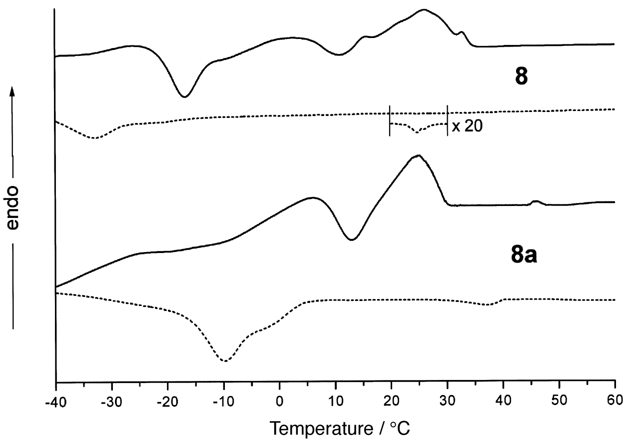


Figure 5. Representative DSC trace of **8** and **8a** (solid lines: first heating run, dashed lines: first cooling run, heating rate: 10 K min^{-1}).

Since it is known that the addition of alkali metal triflate to **B** destabilizes its crystalline phase and favors the hexagonal columnar mesophase,[9] the sodium triflate complex of compound **8** was prepared (**8a**).

From the DSC traces (Figure 5), compound **8a** was found to have a recrystallization transition at 13 °C. Further heating caused the compound to melt at 25.5 °C into a liquid-crystalline phase, which transformed into an isotropic melt at 46 °C. Thus, the addition of sodium triflate ($NaSO_3CF_3$) to **8** caused the clearing temperature to increase by 13 °C above that of uncomplexed **8**.

Miscibility experiments demonstrated that **8** and **8a** formed the same type of mesophase. Compounds **8** and **8a** can be mixed in all proportions without any miscibility gap forming in the mesophase region; the same was found to be true for **8a** and the **B**:$NaCF_3SO_3$ complex. Since this complex exhibits a hexagonal columnar disordered mesophase,[9] according to the Arnold–Sackmann rule, both the synthesized amphiphiles formed this mesophase (Scheme 3).

A miscible with **7** $\Rightarrow$ mesophase(**A**) = col$_{hd}$ = mesophase(**7**)

8 miscible with **8a** $\Rightarrow$ mesophase(**8**) = mesophase(**8a**)

8a miscible with **B** $\Rightarrow$ mesophase(**8a**) = mesophase(**B**) = col$_{hd}$

Scheme 3. The contact preparation technique[11] proves that the structure of the thermotropic mesophase of **7**, **8** and **8a** is hexagonal columnar disordered (Col$_{hd}$).

As the most stable thermotropic mesophase was observed with complex **8a**, this substance was chosen for the first investigation of lyotropic mesomorphism. In previous studies,[5, 12] “Lowicryl HM20”—a methacrylate mixture that undergoes low volume shrinkage on polymerization—was found to be a good solvent for the presented class of compounds.

Figure 6 depicts the pseudo-binary phase diagram of the system **8a**/HM20. The solid–solid transition, the melting and the isotropisation transition of **8a** were detected for mixtures that contained as little as 10 wt % of the solute. Gelation of the **8a**/HM20 mixtures was observed when the samples, which contained at least 10 wt % **8a**, were cooled for several hours below 15 °C or annealed for 20 minutes at −18 °C. The gels were all clear and transparent. Details on the gel formation and the gel morphologies will be reported elsewhere.[13]

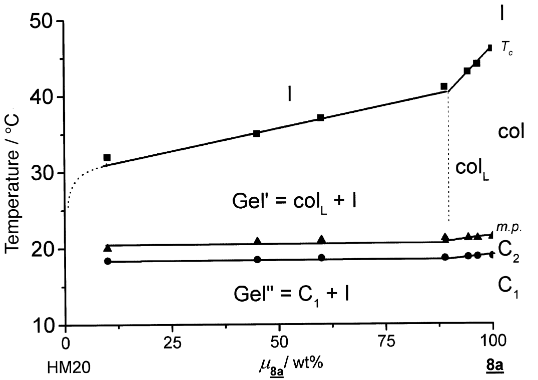


Figure 6. Pseudo-binary phase diagram of the system **8a**/HM20, obtained from DSC measurements. Heating rate: 10 K min^{-1}, isotropisation temperature (■), melting temperature (▲), low temperature peak (●). C = crystalline phase, Col = columnar mesophase, L = lyotropic phase, I = isotropic phase.

The presence of a mesophase was observed over the whole concentration range. From 0 wt % to 10 wt % solvent content, the isotropization temperatures of **8a**/HM20 decreased considerably (ca. 0.6 °C/wt %). In this region, polarized microscopy showed the whole sample to have a uniform texture (Figure 7). This was attributed to a lyotropic columnar mesophase. In mixtures with larger solvent concentrations, this texture was found in single islands, surrounded by an isotropic liquid (see Figure 7 bottom). The fraction of the isotropic phase increased with higher dilution of the mesogen. When a solvent content of about 10 wt % was exceeded, the melting temperatures became constant and the isotropization temperature varied more slowly (ca. 0.09 °C/wt %) with concentration.

It was deduced that the columnar mesophase of **8a** can include up to approximately 10 wt % of the solvent. At higher solvent content, phase separation into the lyotropic columnar phase and an isotropic methacrylate phase occurred. Below 17 °C, the mixtures are solid gels that consist of coexisting solids and a liquid phase. Between 20 and 32 °C, the crystalline phase melted into the mesophase and the gels decomposed due to macroscopic phase separation.

Conclusion

The tris-methacrylated wedge-like molecules **7** and **8** and complex **8a** exhibited columnar thermotropic and lyotropic mesomorphism. We thus demonstrated the formations of novel supramolecular tectons with a functional core enveloped by a coat of polymerizable groups. Methacrylation caused the transition temperatures to decrease relative to that of the nonfunctionalized substances. Miscibility experiments proved that all the functionalized amphiphiles formed a hexagonal columnar disordered (Col$_{hd}$) mesophase.

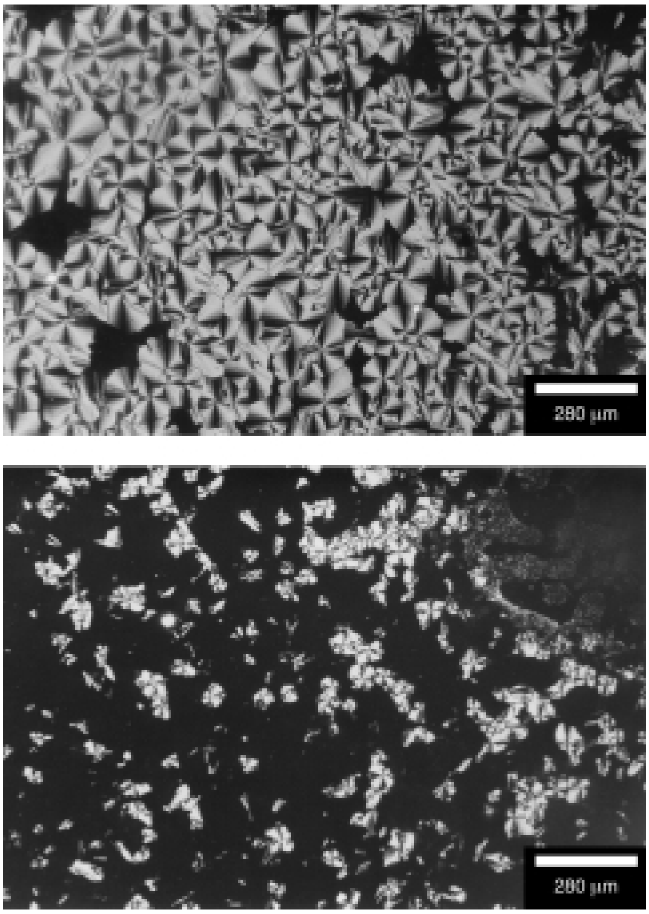


Figure 7. Optical micrographs of **8a**/HM20 mixtures between crossed polarizers. Top: **8a** at 28 °C. Bottom: **8a**/HM20 = 15 wt %/85 wt % at 21 °C.

In a parallel approach, Gin et al. recently reported the synthesis and self-assembly of 3,4,5-tris(acryloylalkyloxy)benzoates.[14, 15]

Unusual aspects of the compounds described here are the stacking of a receptor group in the center of the columns and the lyotropic-ordering reported above. This class of supramolecular assembly can provide new opportunities for the synthesis of supramolecular gels and the preparation of functional membranes that contain self-organized transport channels. The latter will be the subject of forthcoming reports.

Experimental Section

General: Infrared spectra were were run on a BRUKER IFS 113V spectrophotometer. The samples were placed in KBr pellets for the measurements which were performed in transmission mode. GC chromatograms were recorded with a Perkin–Elmer Autosystem gas chromatograph with a 25 m Optima 5 column (95 % PDMS, 4 % PDPhS, 1 % PDVS, film thickness 0.5 µm, ID 0.32 mm). Helium was used as carrier gas at a flow rate of about 2 mL min^{-1}. ^{1}H NMR (200 MHz) and ^{13}C NMR (50.4 MHz) spectra were recorded at 25 °C on a BRUKER AC200 spectrometer, with tetramethylsilane as internal standard. DSC measurements were obtained with samples of about 4–6 mg on a Perkin–Elmer DSC 7 equipped with a TAS 7 data processor. The samples were heated by 10 °C min^{-1}, after being cooled from room temperature by 10 °C min^{-1}. Transition temperatures were taken as the onset of the endotherm during the second heating scan. Water, gallium, indium, cyclopentane, and cyclohexane were used as calibration standards. A Zeiss Axioskop equipped with a Mettler Hotstage FP 82 and a Zeiss MC 80 photoautomat was used for the thermo-optical analyses. GC/MS analyses were performed with a Finnigan MAT SSQ 700 mass spectrometer coupled to a Varian 3400 gas chromatograph. The GC-column (DB 5 MS from J&W Scientific) had a length of 30 m, an internal diameter of 0.25 mm, and a film thickness of 0.25 μm. Helium was used as carrier gas at a flow rate of ca. 1 mL min^{-1}. Abbreviations: s = singlet, d = doublet, t = triplet, qui = quintet, m = multiplet, t_{Ret} = retention time, R_F = retention factor.

Materials: 9-Borabicyclo[3.3.1]nonane (0.5 M in THF, Aldrich), dicyclohexylcarbodiimide (99 + %, Aldrich), *N*,*N*-dimethylaminopyridine (99%, Aldrich), 2-methyl-1,2-diphenylethanone (photoinitiator, 99 + %, Aldrich), lithium aluminium hydride (99%, Fluka), methyl-4-hydroxybenzoate (99 + %, Aldrich), methyl-3,4,5-trihydroxybenzoate (98% Aldrich), methacryloyl chloride (98% Aldrich), potassium carbonate (Merck, 99%), phosphorus tribromide (95%, Aldrich), pyridine (p.a. grade, Merck), ruthenium trichloride dihydrate (90%, Aldrich), sodium hypochlorite (10 wt% solution, Janssen Chimica), thionyl chloride (99 + %, Aldrich), and 10-undecen-1-ol (95% Aldrich) were used as received. Acetone, cyclohexane, dichloromethane, *N*,*N*-dimethylformamide (DMF), ethyl acetate, hexane, hydrogen peroxide (30 wt% in water), sodium sulfate, sodium hydrogen carbonate, sodium hydroxide, tetrahydrofuran (THF), and 2-propanol were gifts from the "Fonds der Chemischen Industrie". The solvents were purified by standard procedures. 2-Methyl-[1,4,7,10,13-pentaoxabenzocyclopentadecane] was synthesized according to a literature method. The methacrylate resin was selected to exhibit low shrinkage upon polymerization and consisted of 80 mol% 2-ethylhexylmethacrylate, 13 mol% *n*-hexylmethacrylate and 7 mol% triethylene glycol dimethacrylate (HM20, Low GmbH).

11-Bromo-1-undecene (1): The reaction between 11-undecen-1-ol (130 mL, 0.645 mol) and phosphorus tribromide was performed in diethyl ether, according to a literature procedure,[16] to yield 117.62 g, 78.4%, of a clear yellowish liquid. B.p. 68–70 °C (0.07 torr); purity >99% according to GC (t_{Ret} = 5.91 min); GC-MS: *m*/*z*: 418 [M^+]; ^{1}H NMR (CDCl$_3$): δ = 1.31 (m, 12 H; $CH_2{=}CHCH_2(C\mathit{H}_2)_6-$), 1.78 (qui, ^3J(H,H) = 6.9 Hz, 2 H; $(CH_2)_6C\mathit{H}_2$-CH_2-), 2.03 (qui, ^3J(H,H) = 6.3 Hz, 2 H; $CH_2{=}CHC\mathit{H}_2-$), 3.44 (t, ^3J(H,H) = 6.7 Hz, 2 H; $C\mathit{H}_2Br$), 5.00 (m, 2 H; $C\mathit{H}_2{=}CH-$), 5.81 (m, ^3J(H^a,H^b) = 10.3 Hz, ^3J(H^a,H^c) = 35 Hz, ^3J(H^b,H^c) = 16.9 Hz, 1 H; $CH^bH^c{=}C\mathit{H}^a$); ^{13}C NMR (CDCl$_3$): δ = 33.72 (C(*C*-Br)), 28.11–33.65 (C2–C9), 111.05 (C($\mathit{C}H_2{=}CH-$)), 138.9 (C($CH_2{=}\mathit{C}H$)); elemental analysis calcd (%) for $C_{11}H_{21}Br$: C 77.14, H 10.0; found C 77.98, H 10.16.

Methyl (10-undecenyl-1-oxy)benzoate (2): In analogy to a literature method,[17] 11-bromo-1-undecene (67.5 g, 0.289 mol), methyl 4-hydroxybenzoate (**1**) (41.9 g, 0.275 mol), potassium carbonate (114.0 g, 0.825 mol) and acetone (600 mL) were converted into **2**, which was recrystallized from hexane. Yield: 79.5 g (94.9%) white plate-like crystals; m.p. 57–59 °C (DSC measurement 10 °C min^{-1}); TLC (silica gel 60/CH$_2$Cl$_2$): R_f = 0.8; GC (t_{Ret} = 11.15 min): purity >99.5%; ^{1}H NMR (CDCl$_3$): δ = 1.31 (m, 12 H; $CH_2{=}CHCH_2(C\mathit{H}_2)_6-$), 1.78 (qui, ^3J(H,H) = 6.8 Hz, 2 H; $-(CH_2)_6$-$C\mathit{H}_2CH_2O-$), 2.04 (qui, ^3J(H,H) = 6.2 Hz, 2 H; $CH_2{=}CHC\mathit{H}_2-$), 3.88 (s, 3 H; $COOC\mathit{H}_3$), 3.96 (t, ^3J(H,H) = 6.5 Hz, 2 H; $-C\mathit{H}_2OPh-$), 4.96 (m, 2 H; $C\mathit{H}_2{=}CH-$), 5.82 (m, ^3J(H^b,H^a) = 10.3 Hz, ^3J(H^a,H^c) = 35 Hz, ^3J(H^b,H^c) = 16.9 Hz, 1 H; $CH^bH^c{=}C\mathit{H}^a$), 6.91 (d, ^3J(H,H) = 8.7 Hz, 2 H; H$_{\mathrm{aromatic}}$, *ortho* to O), 7.27 (d, ^3J(H,H) = 8.4 Hz, 2 H; H$_{\mathrm{aromatic}}$, *ortho* to CH$_2$ group); ^{13}C NMR (CDCl$_3$): δ = 25.87–33.695 (C$_{\mathrm{alkyl}}$), 51.66 ($-COO\mathit{C}H_3$), 68.04 ($-\mathit{C}H_2OPh-$), 113.92 ($\mathit{C}H_2{=}CH$), 114.037 (C$_{\mathrm{aromatic}}$, *ortho* to alkoxy chain), 122.8 (C$_{\mathrm{aromatic}}$, α to $-COOCH_3$ group), 130.7 (C$_{\mathrm{aromatic}}$, *ortho* to $-COOCH_3$ group), 139.009 ($CH_2{=}\mathit{C}H-$), 162.833 (C$_{\mathrm{aromatic}}$, α to alkyloxy chain), 166.72 ($-\mathit{C}OOCH_3$)); elemental analysis calcd (%) for $C_{19}H_{28}O_3$: C 74.96, H 9.27; found C 74.34, H 9.17.

10-Undecenyl-1-oxybenzyl alcohol (3): Under an argon atmosphere, LiAlH$_4$ (7.75 g, 0.204 mol) was suspended in absolute THF (50 mL), with vigorous stirring. A solution of methyl 10-undecenyl-1-oxybenzoate (35.5 g, 0.116 mol) in absolute THF (250 mL) was dropped slowly into the refluxing suspension, and the resulting reaction mixture was subsequently heated overnight. At ambient temperature, the excess hydride was destroyed by careful addition of moist THF, and the resulting slurry was acidified with 10 wt% dilute hydrochloric acid. After rotary evaporation of the THF/water mixture, the residue was taken up in diethyl ether and, after the solution was dried over sodium sulfate, the solvent was removed again. The raw product was purified by crystallization from hexane. Yield: 29.8 g (92.9%) white plate-like crystals; m.p. 49.5–50.5 °C; TLC (silica gel 60, CH$_2$Cl$_2$): R_f = 0.3, GC(t_{Ret} = 10.68 min): purity > 99.5%; GC-MS: *m*/*z*: 959 [M^+] (>99%); ^{1}H NMR (CDCl$_3$): δ = 1.31 (m, 12 H; $CH_2{=}CH$-$CH_2(C\mathit{H}_2)_6-$), 1.78 (qui, ^3J(H,H) = 6.9 Hz, 2 H; $-(CH_2)_6C\mathit{H}_2CH_2O-$), 2.06 (qui, ^3J(H,H) = 6.1 Hz, 2 H; $CH_2{=}CHC\mathit{H}_2-$), 3.96 (t, ^3J(H,H) = 5.8 Hz, 2 H; $-C\mathit{H}_2OPh-$), 4.63 (s, 2 H; $-C\mathit{H}_2OH$), 4.96 (m, 2 H; $C\mathit{H}_2{=}CH-$), 5.82 (m, 1 H; $CH_2{=}C\mathit{H}-$), 6.91 (d, ^3J(H,H) = 7.7 Hz, 2 H; H$_{\mathrm{aromatic}}$, *ortho* to O), 7.27 (d, ^3J(H,H) = 7.6 Hz, 2 H; H$_{\mathrm{aromatic}}$, *ortho* to CH$_2$ group); ^{13}C NMR (CDCl$_3$): δ = 26.07–33.84 (C$_{\mathrm{alkyl}}$), 65.07 ($-\mathit{C}H_2OH$), 68.08 ($-\mathit{C}H_2OPh-$), 114.09 ($\mathit{C}H_2{=}CH-$), 114.50 (C$_{\mathrm{aromatic}}$, *ortho* to alkyloxy chain), 128.65 (C$_{\mathrm{aromatic}}$, *ortho* to $-CH_2OH$ group), 132.953 (C$_{\mathrm{aromatic}}$, α to CH$_2$OH group), 139.254 ($CH_2{=}\mathit{C}H-$), 158.803 (C$_{\mathrm{aromatic}}$, α to alkoxy chain); IR (KBr): $\tilde{\nu}$ = 3324, 3220, 2936, 2920, 2850, 1643, 1613, 1583, 1512, 1475, 1470, 1424, 1395, 1367, 1337, 1319, 1256, 1208, 1198, 1169, 1112, 1049, 1038, 1016, 960, 911, 849, 837, 816, 773, 748, 719, 634, 590, 526, 510 cm^{-1}; elemental analysis calcd (%) for $C_{18}H_{28}O_2$: C 78.21, H 10.21; found C 78.06, H 10.16.

10-Undecenyl-1-oxybenzyl chloride (4): At room temperature, thionyl chloride (10.24 g, 0.86 mol) was dropped slowly into a solution of **3** (17 g, 0.615 mol) and dry DMF (5 mL) in absolute dichloromethane (200 mL). After the reaction mixture was stirred for two hours, the liquids were removed by vacuum distillation and the residue was dried at 20 °C/0.01 torr. Yield: 18.1 g (100%) pale yellow oil; TLC (silica gel 60, CH$_2$Cl$_2$): R_f = 0.9; GC (t_{Ret} = 10.5 min): purity >99.5%; ^{1}H NMR (CDCl$_3$): δ = 1.31 (m, 12 H; $CH_2{=}CHCH_2(C\mathit{H}_2)_6-$), 1.78 (qui, ^3J(H,H) = 6.8 Hz, 2 H; $-(CH_2)_6$-$C\mathit{H}_2CH_2O-$), 2.06 (qui, ^3J(H,H) = 6.1 Hz, 2 H; $CH_2{=}CHC\mathit{H}_2-$), 3.96 (t, ^3J(H,H) = 5.6 Hz, 2 H; $-C\mathit{H}_2OPh-$), 4.63 (s, 2 H; $-C\mathit{H}_2Cl$), 4.96 (m, 2 H; $C\mathit{H}_2{=}CH-$), 5.82 (m, 1 H; $CH_2{=}C\mathit{H}-$), 6.91 (d, ^3J(H,H) = 7.8 Hz, 2 H; H$_{\mathrm{aromatic}}$, *ortho* to O), 7.27 (d, ^3J(H,H) = 7.7 Hz, 2 H; H$_{\mathrm{aromatic}}$, *ortho* to CH$_2$ group); ^{13}C NMR (CDCl$_3$): δ = 26.07–33.49 (C$_{\mathrm{alkyl}}$), 46.011 ($-\mathit{C}H_2Cl$), 67.685 ($-\mathit{C}H_2OPh-$), 113.804 ($\mathit{C}H_2{=}CH-$), 114.320 (C$_{\mathrm{aromatic}}$, *ortho* to OCH$_2$ group), 129.731 (C$_{\mathrm{aromatic}}$, *ortho* to CH$_2$OH group), 130.029 (C$_{\mathrm{aromatic}}$, α to CH$_2$Cl group), 139.286 ($CH_2{=}\mathit{C}H-$), 159.358 (C$_{\mathrm{aromatic}}$, α to $-OCH_2$ group); IR (KBr): $\tilde{\nu}$ = 2926, 2854, 1640, 1612, 1584, 1514, 1467, 1391, 1302, 1247, 1175, 1110, 1028, 995, 910, 830, 733, 671, 665, 634 cm^{-1}.

3,4,5-Tris(10-undecenyl-1-oxybenzoyl)methylbenzoate (5): A well-stirred mixture of 3,4,5-tris-hydroxyethylbenzoate (3.96 g, 20 mmol), potassium carbonate (24 g, 180 mmol) and dry DMF (100 mL) was flushed with argon for 30 min. After the mixture was heated to 60 °C, benzyl chloride **4** (18.2 g, 61 mmol) was slowly added and left to react for 16 h. The reaction mixture was cooled to 20 °C and poured into well-stirred ice-water (1000 mL). The organic layer was separated and the aqueous phase was extracted with diethyl ether (3 × 200 mL). The combined organic phases were subsequently washed with diluted hydrochloric acid and water. The organic phase was dried over sodium sulfate, and after rotary distillation of the solvent, the resulting brown oil was recrystallized twice from 2-propanol. Yield: 9.73 g (50%) white powder; TLC: (silica gel 60, CH$_2$Cl$_2$: R_f = 0.6; GC (t_{Ret} = 9.7 min) purity >99.5%; ^{1}H NMR (CDCl$_3$): δ = 1.31 (m, 12 H; $CH_2{=}CHCH_2(C\mathit{H}_2)_6-$), 1.78 (qui, ^3J(H,H) = 6.6 Hz, 2 H; $-(CH_2)_6$-$C\mathit{H}_2CH_2O-$), 2.06 (qui, ^3J(H,H) = 6.3 Hz, 2 H; $CH_2{=}CHC\mathit{H}_2-$), 3.76 (t, ^3J(H,H) = 6.66 Hz, 3 H; $-OCH_2C\mathit{H}_3$), 3.95 (m, 6 H; $-C\mathit{H}_2OPh-$), 4.35 (quartet, 2 H; $-OCH_2CH_3$), 5.02 (m, 12 H; $C\mathit{H}_2{=}CH-$, $PhC\mathit{H}_2O-$), 5.83 (m, 1 H; $CH_2{=}C\mathit{H}-$), 6.76 (d, ^3J(H,H) = 8.65 Hz, 2 H; H$_{\mathrm{aromatic}}$, *ortho* to O$_{\mathrm{internal}}$), 6.91 (d, ^3J(H,H) = 8.6 Hz, 4 H; H$_{\mathrm{aromatic}}$, *ortho* to O$_{\mathrm{external}}$), 7.35 (m$_{\mathrm{broad}}$, 8 H; H$_{\mathrm{aromatic}}$, *ortho* to CH$_2$ group and *ortho* to $-CO$ group); ^{13}C NMR (CDCl$_3$): δ = 14.319 ($-COOCH_2\mathit{C}H_3$), 24.309–29.464 (C$_{\mathrm{alkyl}}$), 33.747 ($\mathit{C}H_2OPh$-CH_2O-), 60.957 ($-Ph\mathit{C}H_2OPh-$), 71.026 ($-COO\mathit{C}H_2CH_3$), 109.107 (C$_{\mathrm{aromatic}}$, *ortho* to $-COOCH_2CH_3$ group), 114.075 ($\mathit{C}H_2{=}CH-$), 114.375 (C$_{\mathrm{aromatic}}$, carbon in side unit, *ortho* to alkyloxy chain), 125.283 (C$_{\mathrm{aromatic}}$, α to $COOC_2H_5$ group), 128.5 (C$_{\mathrm{aromatic}}$, carbon in side unit, *ortho* to CH$_2$OPh group), 129.26 (C$_{\mathrm{aromatic}}$, carbon in side unit, α to CH$_2$OPh group), 139.254 ($CH_2{=}\mathit{C}H-$), 142.294 (C$_{\mathrm{aromatic}}$, 4′ and *para* to $COOC_2H_5$ group), 152.53 (C$_{\mathrm{aromatic}}$, 3′ and 5′ to $COOC_2H_5$), 166.171 ($\mathit{C}OOC_2H_5$); elemental analysis calcd (%) for $C_{62}H_{86}O_8$: C 77.62, H 9.04; found C 77.63, H 9.13.

3,4,5-Tris(11-hydroxyundecyl-1-oxybenzyloxy)benzoic acid (6): Under an argon atmosphere, **5** (1 g, 1 mmol) dissolved in absolute THF (5 mL), was slowly added to a solution of 9-BBN in absolute THF (9 mL, 0.5 M, 4.5 mmol); the mixture was kept at 66 °C for one hour. After the complete conversion of **5** was shown by TLC, the mixture was cooled to 20 °C, and ethanol (5 mL) was added carefully to it. Subsequently, sodium hydroxide (10 mL, 6 N) and hydrogen peroxide (20 mL, 30 %) were slowly added, and the solution was refluxed for another hour. During the whole operation, the reaction apparatus was flushed with argon. The solvent was removed by rotary evaporation, the residue was dissolved in water, and this solution was acidified with diluted hydrochloric acid and extracted four times with dichloromethane. After the organic phases were dried over sodium sulfate, the solvent was evaporated, and the waxy raw material was taken up in a small amount of THF. It was purified by precipitation from 50 mL hexane. Yield: 0.8 g (78.4 %) white powder; m.p. 70–71 °C; TLC (silica gel 60, CH_2Cl_2): $R_f = 0$; GC ($t_{Ret} = 8.5$ min) purity >99.5 %; ^1H NMR ($CDCl_3$): $\delta =$ 1.31 (m, 52 H; $CH_2{=}CH{-}CH_2{-}(C\mathit{H}_2)_6{-}$), 1.57 (m, 6 H; $(CH_2)_6C\mathit{H}_2CH_2O{-}$), 1.77 (m, 6 H; $HOCH_2C\mathit{H}_2{-}$), 3.64 (t, $3J(H,H) = 6.6$ Hz, 6 H; $HOC\mathit{H}_2{-}$), 3.97 (m, 6 H; $-C\mathit{H}_2OPh{-}$), 4.58 (s, 1 H; $-O\mathit{H}$), 4.95 (s, 1 H; $-O\mathit{H}$), 5.02 (s, 2 H; $ArCH_2O$ internal), 5.05 (s, 4 H; $ArC\mathit{H}_2O$ external), 6.78 (d, $^3J(H,H) =$ 8.6 Hz, 2 H; $H_{aromatic}$, *ortho* to $O_{internal}$), 6.93 (d, $^3J(H,H) = 8.5$ Hz, 4 H; $H_{aromatic}$, *ortho* to $O_{external}$), 7.23–7.37 (m, 8 H; $H_{aromatic}$, *ortho* to CH_2 group and *ortho* to CO group); ^{13}C NMR ($CDCl_3$): $\delta = 25.601{-}32.637$ (C_{alkyl}), 36.183 ($-\mathit{C}H_2OPhCH_2O{-}$), 52.06 ($Ph\mathit{C}H_2OPh{-}$), 62.875 ($HO\mathit{C}H_2{-}$), 67.897 ($HO\mathit{C}H_2{-}$), 109.014 ($C_{aromatic}$, *ortho* to COOH group), 113.941 ($C(\mathit{C}H_2{=}CH\text{-})$), 114.317 ($C_{aromatic}$, in side unit, *ortho* to alkyloxy chain), 124.846 ($C_{aromatic}$, α to COOH group), 128.984 ($C_{aromatic}$, in side unit, *ortho* to CH_2OPh group), 130.121 ($C_{aromatic}$, in side unit, α to CH_2OPh group), 142.284 ($C_{aromatic}$, 4′ and *para* to COOH group), 152.48 ($C_{aromatic}$, 3′ and 5′ to $COOC_2H_5$), 166.625 ($\mathit{C}OOH$); elemental analysis calcd (%) for $C_{61}H_{90}O_{11}$: C 73.31, H 9.04; found C 76.44, H 9.41.

3,4,5-Tris(11-methacryloylundecyl-1-oxybenzyloxy)benzoic acid (7): Under a nitrogen atmosphere, a solution of **6** (0.78 g, 0.78 mmol), triethylamine (0.47 g, 3.4 mL), DMAP (95.34 mg, 0.78 mmol) and 2,6-di-*tert*-butyl-4-methylphenol (0.86 mg, 0.007 mmol) in dichloromethane (5 mL) was cooled to 0 °C. After slow addition of methacryloyl chloride (0.49 g, 4 mmol), the solution was allowed to warm to room temperature and was stirred for 48 h. On complete conversion of the acid chloride (TLC control), the mixture was filtered and the solvent was removed by rotary evaporation. The reaction product was refluxed with a solution of water (10 mL) in pyridine (30 mL) for 10 min; the resultant mixture was then cooled to 20 °C and acidified with diluted hydrochloric acid. Subsequently, the aqueous phase was extracted four times with diethyl ether, and the combined organic layers were washed with aqueous $NaHCO_3$ solutions (10 %) and were then dried over anhydrous sodium sulfate. The diethyl ether was removed and the remaining raw product was purified by column chromatography (silica gel 60, cyclohexane/ethylacetate 1:1). Yield: 0.8 g (81 %) oily to waxy material; TLC (silica gel 60, cyclohexane/ethylacetate 1:1): one spot, $R_f = 0.63$; ^1H NMR ($CDCl_3$): $\delta = 1.31$ (m, 52 H; $CH_2{=}C(CH_3)COOCH_2(C\mathit{H}_2)_6{-}$), 1.56 (m, 6 H; $-(CH_2)_6C\mathit{H}_2CH_2O{-}$), 1.78 (m, 6 H; $CH_2{=}C(CH_3)COOCH_2C\mathit{H}_2{-}$), 1.96 (s, 9 H; $CH_2{=}C(C\mathit{H}_3)COO{-}$), 3.94 (m, 2 H; $C\mathit{H}_2OPh$ internal), 3.97 (t, $^3J(H,H) = 7.0$ Hz, 4 H; $\text{-}C\mathit{H}_2OPh$ external), 5.02 (s, 2 H; $-ArC\mathit{H}_2O$ internal), 5.05 (s, 4 H; $-ArC\mathit{H}_2O$ external), 5.5 (s, $C\mathit{H}_2{=}C(CH_3)COO$ internal), 6.13 (s, $C\mathit{H}_2{=}C(CH_3)COO$ external), 6.78 (d, $^3J(H,H) = 8.6$ Hz, 2 H; $H_{aromatic}$, *ortho* to $O_{internal}$), 6.93 (d, $^3J(H,H) = 8.5$ Hz, 4 H; $H_{aromatic}$, *ortho* to $O_{external}$), 7.23–7.37 (m, 8 H; $H_{aromatic}$, *ortho* to CH_2 and *ortho* to CO); ^{13}C NMR ($CDCl_3$): $\delta = 18.31$ ($CH_2{=}C\mathit{C}H_3$), 25.95–30.287 (C_{alkyl}), 52.06 ($\mathit{C}H_2OPhCH_2O_{external}$), 64.80 ($\mathit{C}H_2OPhCH_2O_{internal}$), 67.997 ($\mathit{C}H_2OPh_{external}$), 74.64 ($\mathit{C}H_2OPh_{internal}$), 109.153 ($C_{aromatic}$, *ortho* to COOH group), 114.317 ($C_{aromatic}$, in side unit, *ortho* to alkyloxy chain), 124.846 ($C_{aromatic}$, α to COOH group), 125.489 ($\mathit{C}H_2{=}C(CH_3)$ of 3′,5′ position), 128.984 ($C_{aromatic}$, in side unit, *ortho* to CH_2OPh), 129.42 ($\mathit{C}H_2{=}C(CH_3)$, the 4′ position), 130.224 ($C_{aromatic}$, in side unit, α to CH_2OPh), 136.514 ($CCH_2{=}\mathit{C}(CH_3)$), 142.284 ($C_{aromatic}$, in 4′ and *para* position to COOH group), 152.60 ($C_{aromatic}$, in 3′ and 5′ position to COOH group), 166.625 ($C\mathit{C}OOCH_2$), 166.71 ($C\mathit{C}OOH$); IR (KBr): $\tilde{\nu} = 2926$, 2854, 1719, 1638, 1614, 1594, 1515, 1466, 1435, 1419, 1384, 1338, 1298, 1247, 1173, 1131, 1072, 1072, 939, 913, 862, 817, 764, 722, 657, 593, 514 cm^{-1}; elemental analysis calcd (%) for $C_{73}H_{102}O_{14}$: C 72.85, H 8.54; found C 72.40, H 8.21.

2-Methyl-(1,4,7,10,13-pentaoxacyclopentadecane)-3,4,5-tris[4-(11-methacryloyl-undecyl-1-oxy)benzyloxy]benzoate (8): Compound **8** was synthesized following the procedure described in ref. [9]. Compound **7** (1.178 g, 0.98 mmol) and 4-hydroxybenzo 15-crown-5 (0.292 g; 0.98 mmol) were dissolved in dry dichloromethane (5 mL) in a round-bottomed flask equipped with a magnetic stirrer. 4-Dimethylaminopyridinium toluene-*p*-sulfonate (DPTS) (57.7 mg, 2 mmol, 20 mol %) and 1,3-dicyclohexylcarbodiimide (DCC; 222 mg, 0.11 mmol) were added to this solution. The reaction mixture was stirred for 12 h at room temperature. Then the reaction was filtered and the filtrate was added to methanol to precipitate the product, which was collected by vacuum filtration and was purified by column chromatography (silical gel 60, cyclohexane/ethyl acetate 1:1). Yield: 1.1 g (90 %) yellowish oily-waxy material; TLC (silica gel 60, cyclohexane/ethyl acetate 1:1): one spot, $R_f = 0.87$; ^1H NMR ($CDCl_3$): $\delta = 1.31$ (m, 52 H; $CH_2{=}C(CH_3)COOCH_2(C\mathit{H}_2)_6{-}$), 1.56 (m, 6 H; $-(CH_2)_6\text{-}C\mathit{H}_2CH_2O{-}$), 1.78 (m, 6 H; $CH_2{=}C(CH_3)COOCH_2C\mathit{H}_2{-}$), 1.96 (s, 9 H; $CH_2{=}C(C\mathit{H}_3)COO{-}$), 3.76 (s, 8 H; $-OCH_2CH_2O{-}$), 3.94 (m, 2 H; $-C\mathit{H}_2OPh{-}$ internal), 3.97 (t, $^3J(H,H) = 7.0$ Hz, 4 H; $-C\mathit{H}_2OPh$ external), 4.11 (m, 4 H; $C_6H_4OCH_2C\mathit{H}_2O{-}$), 4.99 (s, 2 H; $-OC_6H_4C\mathit{H}_2OC_6H_2CO_2$ of 4′ position) 5.02 (s, 2 H; $-ArC\mathit{H}_2O{-}$ internal), 5.05 (s, 4 H; $-ArC\mathit{H}_2O{-}$ external), 5.24 (s, 2 H; $-C_6H_4CO_2C\mathit{H}_2C_6H_2{-}$), 5.5 (s, $C\mathit{H}_2{=}C(CH_3)COO{-}$ internal), 6.13 (s, $C\mathit{H}_2{=}C(CH_3)COO{-}$ external), 6.78 (d, $^3J(H,H) = 8.6$ Hz, 2 H; $H_{aromatic}$, *ortho* to $O_{internal}$), 6.93 (d, $^3J(H,H) = 8.5$ Hz, 4 H; $H_{aromatic}$, *ortho* to $O_{external}$), 6.90–6.93 (overlapping peaks, 3 H; aromatic crown protons), 7.26 (d, $3J(H,H) = 8.6$ Hz, 2 H; $H_{aromatic}$, *meta* to O of internal benzyl ring), 7.30 (d, $^3J(H,H) = 8.7$ Hz, 4 H; *meta* to O of external benzyl ring), 7.38 (s, 2 H; *ortho* to CO_2); ^{13}C NMR ($CDCl_3$): $\delta = 18.31$ ($CCH_2{=}C\mathit{C}H_3$), 25.95–30.287 (C_{alkyl}), 52.06 ($\mathit{C}H_2OPhCH_2O_{external}$), 64.80 ($\mathit{C}H_2OPhCH_2O_{internal}$), 67.997 ($\mathit{C}H_2OPh_{external}$), 74.64 ($\mathit{C}H_2OPh_{internal}$), 109.153 ($C_{aromatic}$, *ortho* to COOH group), 114.317 ($C_{aromatic}$, in side unit, *ortho* to alkyloxy chain), 124.846 ($C_{aromatic}$, α to COOH), 125.489 ($C\mathit{C}H_2{=}C(CH_3)$, 3′ ,5′), 128.984 ($C_{aromatic}$, in side unit, *ortho* to CH_2OPh), 129.42 ($C\mathit{C}H_2{=}C(CH_3)$, 4′ position), 130.224 ($C_{aromatic}$, in side unit, α to CH_2OPh), 136.514 ($CCH_2{=}\mathit{C}(CH_3)$), 142.284 ($C_{aromatic}$, in 4′ and *para* position to COOH), 152.60 ($C_{aromatic}$, in 3′ and 5′ position to COOH), 166.625 ($C\mathit{C}OOCH_2$), 166.71 ($C\mathit{C}OOH$); IR (KBr): $\tilde{\nu} = 3512$, 3405, 3074, 3075, 2976, 2926, 2854, 1716, 1640, 1613, 1586, 1514, 1467, 1446, 1431, 1392, 1368, 1331, 1302, 1248, 1102, 1057, 1030, 994, 963, 910, 864, 823, 768, 723, 637, 593, 518 cm^{-1}; elemental analysis calcd (%) for $C_{88}H_{122}O_{19}$: C 71.23, H 8.29; found C 70.80, H 8.01.

Preparation of the 1:1 sodium triflate complex 8a: Complex **8a** was prepared by mixing a solution of **8** (100 mg) in dry THF (5 mL) with an appropriate volume of dry THF that contained $NaSO_3CF_3$ (0.05 M). After slow evaporation of the solvent under reduced pressure at 20 °C, the solid was dried in vacuo at 40 °C until the weight remained constant.

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