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# Columnar and Smectic Liquid Crystals Based on Crown Ethers

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*Dedicated to Professor Günther Helmchen on the occasion of his 65th birthday*

**Abstract:** Unsymmetrical benzo[15]-crown-5 ethers **5** with one lateral *ortho*-terphenyl unit bearing alkoxy side chains of varying chain lengths (C5–C14) were prepared from 3,4-dialkoxyphenylbromides **2**. Complexation with metal salts MX (M = Na, Cs) afforded the corresponding derivatives MX·**5**. The uncomplexed crown ethers **5h** and **5i**, with dodecyloxy and tetradecyloxy side chains, respectively, exhibit liquid crystalline properties. In the series of complexed crown ethers, liquid crystal properties appeared as early as NaI·**5f** with $C_9H_{19}$ side chains. Whereas the uncomplexed **5h**,**i** form smectic mesophases, the complexed NaI·**5g** and NaI·**5h** exhibit textures typical of columnar mesophases. These results were supported by X-ray diffraction measurements (WAXS, SAXS), which revealed smectic (**5h**,**i**), rectangular columnar (NaI·**5g**), and hexagonal columnar (NaI·**5h**) mesophases. As the liquid crystalline phase might retain packing features of the solid-state structure, single-crystal X-ray analyses were also performed for some of the uncomplexed and complexed crown ether derivatives. The complex $NaI_3$·**5a** displays a sandwich-type structure, with the crown ether cores mutually antiperiplanar and maintaining an almost perfect crown conformation. In contrast, non-mesogenic uncomplexed crown ether **5b** displays a layer-type ordering in the solid phase.

**Keywords:** columnar liquid crystals · crown compounds · mesophases · smectic liquid crystals · structure elucidation

## Introduction

The ability of crown ethers to selectively coordinate metal salts has made them attractive building blocks in supramolecular chemistry and material science.[1] Particularly in the field of liquid crystal chemistry, crown ethers and their metal complexes have been used as terminal or lateral groups to modify mesomorphic properties.[2] In addition, molecular-recognition-directed self-assembly of supramolecular liquid crystalline polymers and dendrimers containing crown ethers has been reported.[3,4] Recently, we showed that compounds with a central crown ether and two terminal *ortho*-terphenyl units form thermotropic hexagonal columnar mesophases, the mesophase stability of which could be increased by complexation with KI.[5] Based on these results, the question arose as to whether benzo[15]crown-5 derivatives with only one lateral *ortho*-terphenyl unit might form columnar mesophases even in the absence of metal salts. In this context, it should be mentioned that Möller and Beginn[4] and Percec[3a,6] have described the self-organization of taper-shaped methacrylates and perfluoroalkyl-substituted monodendrons with crown ether head groups to form columnar mesophases.

X-ray diffraction methods such as wide angle X-ray scattering (WAXS) and small angle X-ray scattering (SAXS) provide information pertaining to the lattice constants and symmetries of liquid crystals.[7] However, to obtain a detailed molecular picture of the mesophase, molecular modeling studies are most useful. In contrast, data from single-crystal X-ray structure analyses have only been used very rarely to elucidate the packing behavior of liquid crystalline compounds.[8–15] Among the few examples reported to date

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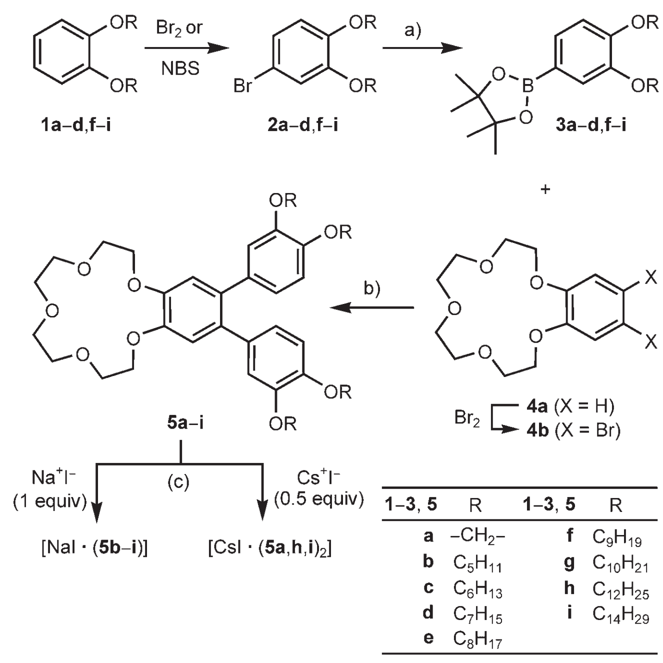
have been dimesogens,[8] metallomesogens,[10] donor–acceptor complexes,[11,12] and hydrogen-bonded systems.[14,15] It has recently been shown that the solid-state structure of tetraethyl perylene 3,4,9,10-tetracarboxylate displays similar packing behavior to the hexagonal columnar mesophase of this compound.[16] Thus, we decided to prepare functionalized benzo[15]crown-5 derivatives with potential mesomorphic properties. We further investigated the possibility of finding some useful similarities between the lattice parameters of the mesophases and the corresponding crystal structures. Results relevant to this goal are reported herein.

## Results and Discussion

**Synthesis of crown ether derivatives 5 and their complexes with metal salts**: As shown in Scheme 1, the known 3,4-dialkoxyphenyl bromides **2** were accessible in 68–93 % yield by bromination of the respective dialkoxybenzenes **1** with $Br_2$[17] or N-bromosuccinimide (NBS)[18] (Table 1).



| 1–3, 5 | R | 1–3, 5 | R |
|---|---|---|---|
| a | $-CH_2-$ | f | $C_9H_{19}$ |
| b | $C_5H_{11}$ | g | $C_{10}H_{21}$ |
| c | $C_6H_{13}$ | h | $C_{12}H_{25}$ |
| d | $C_7H_{15}$ | i | $C_{14}H_{29}$ |
| e | $C_8H_{17}$ | | |

Scheme 1. Preparation of crown ether derivatives **5**: a) BuLi (1.25 equiv), −78 °C, $B(OMe)_3$ (1.25 equiv), −78 °C→RT, pinacol (1.25 equiv), AcOH (1.25 equiv), 18 h; b) DME/$H_2O$, + **3** (2.2 equiv), $K_2CO_3$, KF (10 equiv each), $[Pd(PPh_3)_4]$, 95 °C, two days; c) + MX, 1–2 h, RT.

Bromides **2** were converted to the corresponding boronates **3** in 29–71 % yield following a modification of a procedure by Müller et al.[19] Dibromination of benzo[15]crown-5 (**4a**) gave **4b**,[20] twofold Suzuki coupling of which with boronates **3**[19] afforded the *ortho*-terphenyl crown ethers **5** in 52–88 % yield (Scheme 1, Table 1). Malthête and co-workers have demonstrated that even non-mesogenic analogues can serve as useful models for establishing structural correlations between the crystalline and liquid crystalline state.[14]

Table 1. Yields of compounds **2**, **3**, and **5**.

| | R | Yield [%] 2 | 3 | 5 |
|---|---|---|---|---|
| **a** | $-CH_2-$ | 93[a] | 54 | 61 |
| **b** | $C_5H_{11}$ | 68[b] | 33 | 52 |
| **c** | $C_6H_{13}$ | 72[b] | 71 | 88 |
| **d** | $C_7H_{15}$ | 75[b] | 38 | 77 |
| **e** | $C_8H_{17}$ | – | – | 65 |
| **f** | $C_9H_{19}$ | 88[a] | 29 | 67 |
| **g** | $C_{10}H_{21}$ | 90[a] | 45 | 80 |
| **h** | $C_{12}H_{25}$ | 90[a] | 37 | 82 |
| **i** | $C_{14}H_{29}$ | 91[a] | 40 | 86 |

[a] Prepared according to reference [18]. [b] Prepared according to reference [17].

In analogy to previous observations with symmetrical dibenzo[18]crown-6-derived columnar liquid crystals,[5] we had difficulty in growing single crystals of suitable quality from derivatives **5** with long alkoxy chains. Thus, the non-mesogenic analogues **5a**, bearing dioxolane moieties, and **5b**, with C5 side chains, were chosen.

Complexation of compounds **5** with two metal salts $M^+X^-$ (M = Na, Cs) was achieved according to the method developed by Pedersen.[21] Metal salts were chosen according to the cation sizes that form the most stable 1:1 or 2:1 complexes with benzo[15]crown-5.[18]

Initial screening experiments resulted in the formation of suitable single crystals. Complexes [CsI·(**5a**)$_2$], [CsI·(**5h**)$_2$], and [CsI·(**5i**)$_2$] were selectively obtained by reacting **5a**,**h**,**i** with CsI in a molar ratio **5**:CsI of 2:1.

**Mesomorphic properties and X-ray crystal structure analyses of uncomplexed crown ethers 5**: All derivatives **5** were investigated by differential scanning calorimetry (DSC) and polarizing optical microscopy (POM). The DSC results presented in Table 2 reveal only isotropic melting for derivatives **5b**–**g** with short alkyl chain lengths (C5 to C10). However, crown ether derivatives **5h** and **5i**, with dodecyloxy and tetradecyloxy side chains, respectively, were found to exhibit liquid crystalline properties. Compound **5h** showed a melting transition at 40 °C and a clearing transition at 71 °C during the second heating cycle. The first heating cycle deviates from subsequent cycles due to different crystal packings resulting from recrystallization. The phase transitions were

Table 2. Phase transition temperatures [°C] and enthalpies [$kJ\,mol^{-1}$] (in parentheses) of crown ether derivatives **5**.

| Compd. | Cr | | Sm | | I | Heating cycle[a] |
|---|---|---|---|---|---|---|
| **5b** | ● | 64 (82) | – | | ● | 1st heating |
| **5c** | ● | 60 (92) | – | | ● | 1st heating |
| **5d** | ● | 59 (76) | – | | ● | 1st heating |
| **5e** | ● | 55 (63) | – | | ● | 1st heating |
| **5f** | ● | 62 (79) | – | | ● | 1st heating |
| **5g** | ● | 65 (87) | – | | ● | 1st heating |
| **5h** | ● | 40 (48) | ● | 71 (24) | ● | 2nd heating[b] |
| **5i** | ● | 55 (69) | ● | 77 (1) | ● | 2nd heating[b] |

[a] The heating rate in the case of **5b** to **5g** was 5 $K\,min^{-1}$, in the case of **5h** and **5i** 1 $K\,min^{-1}$. [b] Scans after the first heating gave reproducible results.

enantiotropic. For derivative **5i**, transitions from the crystalline to the liquid crystalline phase at 55 °C and from the liquid crystalline to the isotropic phase at 77 °C were observed. In both cases, the formation of the mesophase was strongly dependent on the heating rate: an increase from 1 $\mathrm{K\,min^{-1}}$ to 5 $\mathrm{K\,min^{-1}}$ led to the disappearance of the mesophase. This behavior can be attributed to kinetically hindered reorientation of the large molecules of **5h** and **5i**. A similar phenomenon has been reported previously for saddle-shaped octaalkoxytetraphenylenes,[22] for which a slow heating/cooling rate was necessary in order to observe the phase transition. As can be seen from Table 2, extension of the side chains from $C_{12}H_{25}$ (**5h**) to $C_{14}H_{29}$ (**5i**) leads to a significant decrease in the clearing transition enthalpies, while the enthalpies for the melting transition are comparable.

Under the microscope, a fan-shaped texture with rather small domains was observed for derivative **5i** at room temperature upon slow cooling (0.1 $\mathrm{K\,min^{-1}}$) from the isotropic phase. In analogy to known examples, the texture was assigned to a smectic phase (Figure 1).

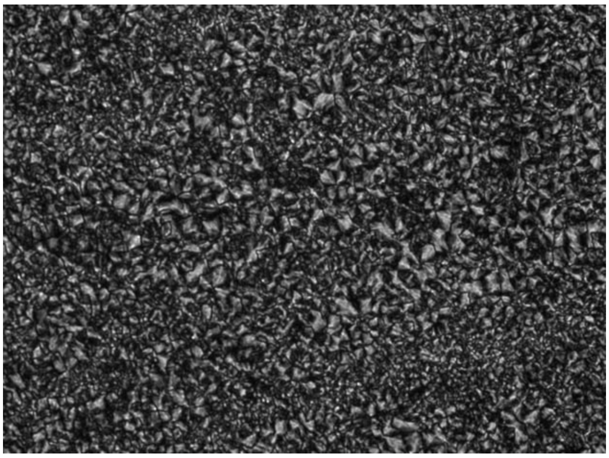


Figure 1. Fan-shaped texture of derivative **5i** as seen between crossed polarizers at room temperature upon cooling (cooling rate 0.1 $\mathrm{K\,min^{-1}}$) from the isotropic phase (magnification ×200).

X-ray diffraction results (WAXS, SAXS) for the tetradecyloxy-substituted derivative **5i** confirm this observation. The presence of commensurate (001) layer reflections together with the absence of any (11) reflection in the small-angle regime (Figure 2) clearly indicates a purely one-dimensional smectic-like ordering. At 65 °C, first- and third- to sixth-order layer reflection peaks were observed, which result in a smectic layer spacing of $d = 50.5$ Å (Table 3). In the wide-angle regime, two broad maxima ($d \approx 3.8$ Å and $d \approx 4.2$ Å) were found, which can be assigned to the chain–chain and core–core distance correlations, respectively.

The dodecyloxy-substituted derivative **5h** also exhibits a smectic mesophase. At 55 °C, four distinct maxima were observed in the small-angle regime. The corresponding $d$ spacings show the characteristic ratio of 1:1/2:1/3:1/4. The related scattering angles $\theta = 1.03°$, 2.05°, 3.06°, and 4.09° consistently result in a smectic layer spacing of $d = 43.1$ Å (Table 3).

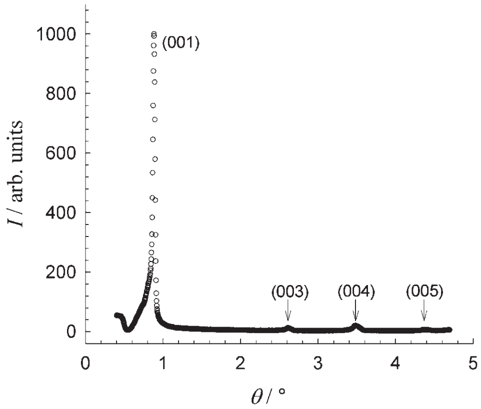


Figure 2. Small-angle X-ray scattering profile of derivative **5i** at 65 °C, which confirms a smectic mesophase.

Table 3. X-ray diffraction data for the uncomplexed derivatives **5h** and **5i** and the complexes NaI·**5g** and NaI·**5h**.

| Compound | Mesophase | Lattice spacing [Å] | $d$ spacing [Å] obsd (calcd) | Miller indices |
|---|---|---|---|---|
| **5h** | Sm at 55 °C | $d = 43.1$ | 42.7 (43.1) | (001) |
| | | | 21.5 (21.5) | (002) |
| | | | 14.4 (14.4) | (003) |
| | | | 10.8 (10.8) | (004) |
| | | | 4.5 diffuse | |
| | | | 4.2 diffuse | |
| **5i** | Sm at 65 °C | $d = 50.5$ | 50.0 (50.5) | (001) |
| | | | 16.9 (16.8) | (003) |
| | | | 12.7 (12.6) | (004) |
| | | | 10.1 (10.1) | (005) |
| | | | 8.4 (8.4) | (006) |
| | | | 4.2 diffuse | |
| | | | 3.8 diffuse | |
| NaI·**5g** | $\mathrm{Col_r}$ at 110 °C | $a = 61.2$ | 30.5 (30.6) | (20) |
| | | $b = 20.5$ | 19.4 (19.4) | (11) |
| | | | 15.4 (15.3) | (40) |
| NaI·**5h** | $\mathrm{Col_h}$ at 160 °C | $a = 40.0$ | 34.2 (34.6) | (10) |
| | | | 20.4 (20.0) | (11) |
| | | | 17.2 (17.3) | (20) |
| | | | 14.2 (13.1) | (21) |

We anticipated that the liquid crystalline phase might retain some structural features of the solid-state structure, such as type of stacking, and hence we performed single-crystal X-ray analyses of the non-mesogenic homologue **5b**.[23] As can be seen from Figure 3, the most important feature is the formation of a periodic ladder structure in which the crown ethers are stacked on top of one another along the $c$ axis, with two neighboring crown ethers being mutually oriented in an antiparallel manner with partial overlap of the crowns. The pentyloxy side chains form the rungs of the ladder along the $ab$ plane, thus favoring hydrophobic interactions (28.3 Å, $Z = 2$, space group $P\bar{1}$).

In both single-crystal X-ray analysis of the crystalline short-chain derivative (**5b**) and X-ray diffraction analysis of

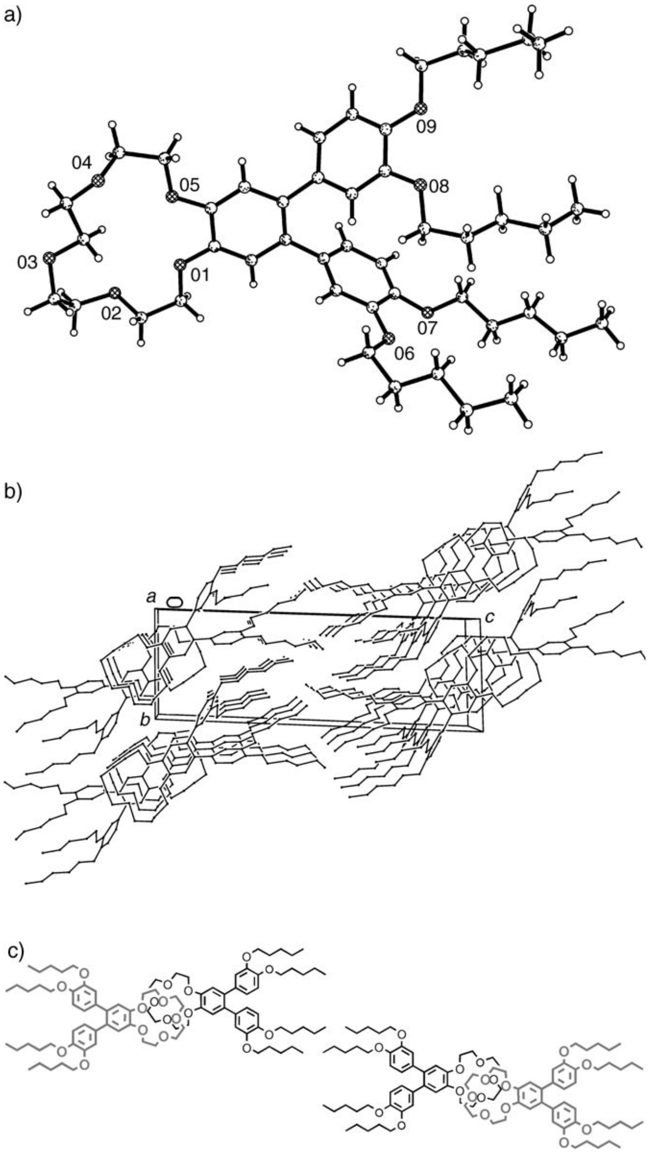


Figure 3. a) X-ray crystal structure of **5b**. b) The cell plot shows an antiparallel orientation of the molecules with a preferred stacking vector of the crowns along the *a* axis. In addition, a bilayer-type hydrophobic interaction in the *ab* plane was found. c) Schematic illustration of the layer.

the liquid-crystalline long-chain derivative (**5i**), a similar orientation of the molecules was observed. In molecular modeling studies, the interlayer distance of crystalline **5b** with five C atoms in the side chains was extended to 14 C atoms as in **5i**, resulting in a value of 51.6 Å, which is remarkably close to the value of 50.5 Å observed for **5i** by X-ray diffraction. Thus, we may draw conclusions from the single crystal about the mesophase behavior.

**Mesomorphic properties and X-ray crystal structure analyses of the complexed crown ethers**: As expected, complexation of the crown ether derivatives with NaI to give NaI·(**5b**–**i**) changed the mesomorphic behavior (Table 4).

Table 4. Phase transition temperatures [°C] and enthalpies [kJ mol$^{-1}$] (in parentheses) of sodium complexes NaI·(**5b**–**i**) in the second heating cycle.

| Compd | $Cr_1$ | | $Cr_2$ | | Col | | I |
|---|---|---|---|---|---|---|---|
| NaI·**5b** | ● | – | – | – | – | 192 (27) | ● |
| NaI·**5c**[a] | ● | 45 (1) | ● | – | – | 187 (19) | ● |
| NaI·**5d** | ● | – | – | – | – | 184 (16) | ● |
| NaI·**5e** | ● | – | – | – | – | 179 (18) | ● |
| NaI·**5f** | ● | −15 (3) | ● | 29 (3) | ● | 166 (9) | ● |
| NaI·**5g** | – | – | ● | 43 (3) | ● | 163 (6) | ● |
| NaI·**5h** | ● | 15 (7) | ● | 55 (19) | ● | 162 (4) | ● |
| NaI·**5i** | – | – | ● | 43 (42) | ● | 171 (8)[b] | ● |

[a] Only a crystal to crystal transition and an isotropic melting was observed. [b] Observed only in the first heating cycle.

Whereas complexes NaI·(**5b**–**e**) with short alkyl chains (C5 to C8) displayed only isotropic melting in the range 179–192 °C, derivatives with nine or more C atoms in the side chains showed a melting transition between 29 and 55 °C and a clearing transition at about 160 °C. As can be deduced from the DSC data and polarizing microscopy studies, liquid-crystalline behavior first appeared for the complex NaI·**5f** with nonyloxy side chains, and its mesophase width of up to 120 °C is significantly extended in comparison with that of the uncomplexed analogues (22–30 °C).

Under the microscope, fan-shaped textures typical of smectic or columnar mesophases were observed. Typical examples are shown for NaI·**5g** (Figure 4) and NaI·**5h** (Figure 5). As a result of incomplete complexation, the latter also showed residues of crystalline NaI.

Figure 4. Fan-shaped texture of the complex NaI·**5g** as seen between crossed polarizers at 148.5 °C upon slow cooling from the isotropic phase (magnification ×200).

X-ray diffraction measurements on complexes NaI·**5g** and NaI·**5h** confirmed the formation of columnar phases, these being rectangular in the case of the complexed decyloxy crown ether NaI·**5g** and hexagonal for the dodecyloxy crown ether NaI·**5h**. The diffuse scattering pattern observed for the isotropic melt of NaI·**5g** at 220 °C changes below 180 °C into a profile with pronounced reflections in the small-angle regime (Figure 6) originating from long-range intercolumnar ordering.

Figure 5. Fan-shaped texture of the complex NaI·**5h** as seen between crossed polarizers at 139 °C upon slow cooling from the isotropic phase (magnification ×200).

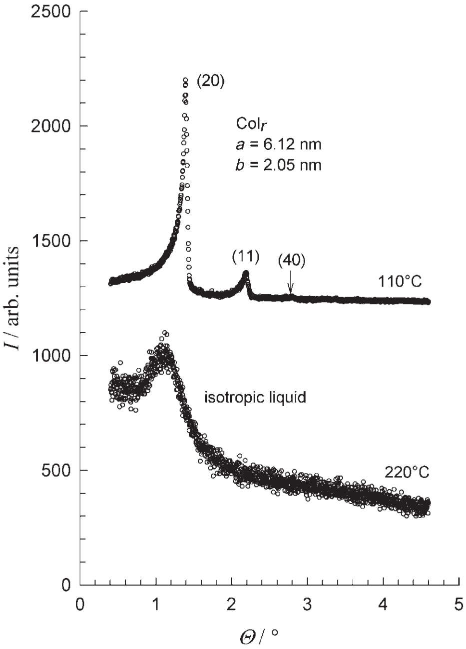


Figure 6. Small-angle X-ray scattering profiles of the isotropic (220 °C, lower curve) and the liquid crystalline (110 °C, upper curve) phases of compound NaI·**5g**. The latter confirms a rectangular-columnar mesophase Col$_r$.

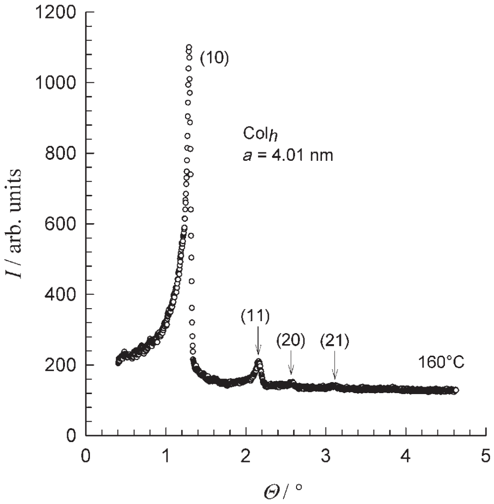


Figure 7. SAXS profile from the mesophase of derivative NaI·**5h** at 160 °C confirming a hexagonal columnar mesophase Col$_h$.

Three distinct maxima associated with $d$ values of 30.5 Å, 19.4 Å, and 15.4 Å were detected (Table 3), which clearly do not appear in the ratio $1:1/\sqrt{3}:1/\sqrt{4}$ necessary for a hexagonal unit cell. Instead, as for other compounds reported in the literature,[24–26] the peaks can be indexed as (20), (11), and (40) reflections, assuming a 2D rectangular (Col$_r$) lattice with parameters $a$ = 61.2 Å and $b$ = 20.5 Å. In contrast, NaI·**5h** shows a hexagonal (Col$_h$) mesophase. Four sharp peaks were observed in the small-angle regime (Figure 7), the $d$ spacings of which are in the ratio $1:1/\sqrt{3}:1/\sqrt{4}:1/\sqrt{7}$ (Table 3).

Indexing the first peak as (10), the ratios are consistent with the expected values for a 2D hexagonal lattice with $a$ = 40.1 Å. X-ray patterns obtained with a Guinier film camera show additional fine peaks in the wide-angle region. These are believed to originate from residual NaI present as a result of incomplete complexation.

Similar crossovers from columnar rectangular to columnar hexagonal mesophases with increasing side chain lengths have been observed in several columnar systems.[25,26] This behavior has generally been attributed to the enhanced core–core interaction necessary for the formation of Col$_r$ phases.[27]

To gain further insight into the conformations of the complexed crown ether moieties, we attempted single-crystal formation from mesomorphic complexes NaI·**5f**–**i**. Unfortunately, no suitable single crystals could be grown from these waxy materials. Attempted crystallizations of the more rigid compounds **5a** and **5b** with NaI also failed. However, in the case of **5a**, replacing NaI by $NaI_3$ solved this problem and led to suitable crystals, the molecular structure of which was determined by single-crystal X-ray analysis (Figure 8).[23] The structure of $NaI_3$·**5a** was found to be of a sandwich

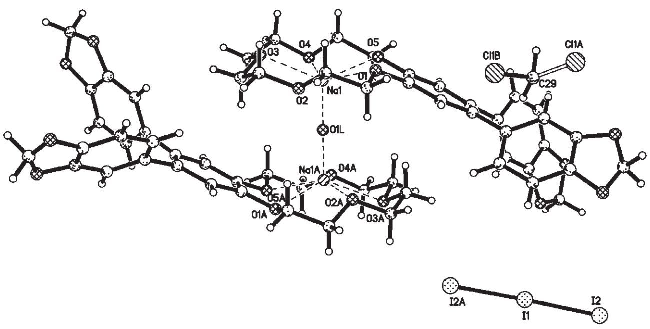


Figure 8. X-ray crystal structure of the complex $NaI_3$·**5a**. This figure shows the sandwich form of the system. One sodium cation is disordered above and below the sandwich with 50 % probability. The crystal structure contains one solvent water within the sandwich and one dichloromethane as a free solvent molecule.

type, with the two crown ether cores being oriented in a mutually antiperiplanar manner, allowing optimal space filling and avoiding steric interactions. The twist angle of the terphenyl unit was measured as 61.1°. An almost perfect crown conformation of the central macrocycle is maintained. The sodium cation is positioned slightly above the crown unit, thus allowing optimal coordination of the five crown ether oxygen atoms. An additional water molecule from the solvent could also be located.

Although any correlation between the solid-state structure of compound $NaI_3$·**5a** and the liquid crystalline packing of NaI·**5g** or NaI·**5h** should be viewed with caution, due to the different influences of the dioxolane and dialkoxybenzene moieties on the packing behavior, some similarities are evident. The symmetry of both the solid $NaI_3$·**5a** and the rectangular columnar mesophase of NaI·**5g** is monoclinic C-centered.

As crown ethers are known to form sandwich complexes with large alkali metal cations,[28] we intended to prepare sandwich-type complexes of crown ether derivatives, because extended core units should influence the mesomorphic properties. Complexation of dodecyloxy-substituted crown ether **5h** with 0.5 equivalents of CsI led to the corresponding 1:2 complex [CsI·(**5h**)$_2$]. While DSC revealed two endothermic peaks at 41 °C and 53 °C upon heating, by polarizing microscopy a colorless precipitate was seen to segregate from areas having the texture of the metal-free compound **5h**.

## Conclusion

Based on the single-crystal X-ray structures of [15]crown-5 derivatives and their metal complexes, we anticipated that some structural guidelines might emerge concerning the possible mesophase type of the corresponding [15]crown-5 ethers and metal complexes thereof with long alkoxy chains. Indeed, for both metal-free crown ethers and metal complexes, similarities between the crystal structure in the solid state of non-mesogenic derivatives and the mesophase structure of derivatives with long alkoxy chains were found. For example, pentyloxy-substituted [15]crown-5 **5b** has a layer-type packing in the solid state and the corresponding derivatives **5h** and **5i** with 12 and 14 carbon atoms, respectively, in the side chains give rise to smectic mesophases. In contrast, alkali metal ions form either 1:1 or 1:2 complexes with crown ethers, resulting in stacked arrangements in the solid state. Derivatives with nine or more carbon atoms in the side chains display columnar mesophases. X-ray diffraction patterns of metal complexes NaI·**5g** and NaI·**5h** are supportive of columnar mesophases, for which two orientations are conceivable. From a thermodynamic point of view, nematic and smectic mesophases are usually more closely related to the isotropic liquid as opposed to the crystalline solid. Thus, melting enthalpies are typically much larger than the clearing enthalpies. In contrast, for columnar systems melting and clearing enthalpies are of similar magnitude, indicating that columnar mesophases are energetically closer to the crystalline structure in the solid state.

One might have expected similar mesomorphic properties of the CsI sandwich-type complexes such as [CsI·(**5h**)$_2$] compared to the corresponding NaI complexes; however, the CsI complexes decompose on heating.

Although we have found some similarities between the mesophases and solid-state structures of related crown ethers, it should be emphasized that this is not a strong correlation. However, these relationships may be used as an additional tool in the design of novel thermotropic liquid crystals.

## Experimental Section

**General methods**: The following compounds were prepared following literature procedures: **2a–d,f–i**.[5] Column chromatography was carried out using Merck silica gel 60, with hexanes (PE, b.p. 40–60 °C) and ethyl acetate (EA) as eluents. $^{13}C$ NMR multiplicities were determined by means of DEPT experiments.

X-ray experiments were performed with Ni-filtered $Cu_{K\alpha}$ radiation ($\lambda$ = 1.5418 Å). Small-angle scattering data from unaligned samples (placed in Mark capillary tubes of diameter 0.7 mm) were obtained using a Kratky compact camera (A. Paar) equipped with a temperature controller (A. Paar) and a one-dimensional electronic detector (M. Braun).

**General procedure for the preparation of borolanes 3**: Under an inert gas atmosphere, *n*BuLi (1.25 equivalents of a 1.6 M solution in hexane) was added dropwise to a solution of the respective 4-bromo-1,2-dialkoxybenzene **2** (6 mmol) in absolute THF (100 mL) at −78 °C, and the reaction mixture was stirred for 10 min. $B(OMe)_3$ (1.25 equiv) was then added, and the reaction mixture was stirred for a further 30 min at −78 °C and was then allowed to warm to room temperature. After stirring for 2 h, a solution of pinacol in THF (1.25 equiv) was added and the reaction mixture was stirred for a further 2 h at room temperature. Glacial acetic acid (1.25 equiv) was added and after stirring for a further 18 h, the solvent was removed under vacuum. The residue was taken up in $CH_2Cl_2$, and this solution was washed with water, dried ($MgSO_4$), and concentrated. The crude product was purified by chromatography on $SiO_2$ with petroleum ether/ethyl acetate (PE/EA).

**5-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-1,3-benzodioxole (3a)**: Yield 54 %; m.p. 42 °C; $^1H$ NMR ($CDCl_3$, 500 MHz): $\delta$ = 1.33 (s, 12 H; $OC(CH_3)_2C(CH_3)_2O$), 5.95 (s, 2 H; $ArOCH_2OAr$), 6.83 (d, $J_{5,6}$ = 7.7 Hz, 1 H; 5-H), 7.23 (d, $J_{2,6}$ = 0.9 Hz, 1 H; 2-H), 7.36 ppm (dd, $J_{6,5}$ = 7.7 Hz, $J_{6,2}$ = 0.9 Hz, 1 H; 6-H); $^{13}C$ NMR ($CDCl_3$, 125 MHz): $\delta$ = 24.9 ($OC(CH_3)_2C(CH_3)_2O$), 83.7 ($OC(CH_3)_2C(CH_3)_2O$), 100.7 ($ArOCH_2OAr$), 108.3, 113.9 (5-C, 6-C), 129.7 (2-C), 147.2, 150.2 ppm (3-C, 4-C); FTIR (film): $\tilde{\nu}$ = 2982 (w), 1618 (w), 1433, 1352 (s), 1294, 1232, 1137, 1103, 1034 $cm^{-1}$ (ms); MS (EI): *m*/*z* (%): 250 (2), 249 (13), 248 (100) [$M^+$], 247 (24); elemental analysis calcd (%) for $C_{13}H_{17}BrO_4$ (248.1): C 62.94, H 6.91; found: C 63.15, H 6.97.

**2-[3,4-Bis(pentyloxy)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3b)**: Yield 33 %; $^1H$ NMR ($CDCl_3$, 500 MHz): $\delta$ = 0.91–0.94 (m, 6 H; $CH_3$), 1.33–1.48 (m, 20 H; $OCH_2CH_2(CH_2)_2CH_3$, $OC(CH_3)_2C(CH_3)_2O$), 1.81–1.84 (m, 4 H; $OCH_2CH_2CH_2$), 4.00–4.04 (m, 4 H; $OCH_2CH_2CH_2$), 6.87 (d, $J_{5,6}$ = 8.1 Hz, 1 H; 5-H), 7.29 (d, $J_{2,6}$ = 1.1 Hz, 1 H; 2-H), 7.34 ppm (dd, $J_{6,5}$ = 8.1 Hz, $J_{6,2}$ = 1.1 Hz, 1 H; 6-H); $^{13}C$ NMR ($CDCl_3$, 125 MHz): $\delta$ = 14.0 ($CH_3$), 22.4, 22.5, 24.9, 28.2, 28.3, 28.9, 29.1 ($OCH_2(CH_2)_3CH_3$, $OC(CH_3)_2C(CH_3)_2O$), 68.9, 69.3 ($OCH_2(CH_2)_3CH_3$), 83.6 ($OC(CH_3)_2C(CH_3)_2O$), 112.8, 119.5 (5-C, 6-C), 128.6 (2-C), 148.6, 151.9 ppm (3-C, 4-C); FTIR (film): $\tilde{\nu}$ = 2955, 2931, 2869 (s), 1599 (s), 1416, 1349 (s), 1255, 1216, 1135 $cm^{-1}$ (ms); MS (EI): *m*/*z* (%): 378 (3), 377 (22), 376 (100) [$M^+$], 375 (23), 306 (9) [$M^+-C_5H_{11}$], 236 (48) [$M^+-2C_5H_{11}$]; elemental analysis calcd (%) for $C_{22}H_{37}BO_4$ (376.3): C 70.21, H 9.91; found: C 70.26, H 9.95.

**2-[3,4-Bis(hexyloxy)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3c)**: Yield 71 %; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ = 0.85–0.93 (m, 6H; $CH_3$), 1.33–1.48 (m, 24H; $OCH_2CH_2(CH_2)_3CH_3$, $OC(CH_3)_2C(CH_3)_2O$), 1.76–1.84 (m, 4H; $OCH_2CH_2CH_2$), 3.99–4.04 (m, 4H; $OCH_2CH_2CH_2$), 6.87 (d, $J_{5,6}$ = 8.0 Hz, 1H; 5-H), 7.29 (d, $J_{2,6}$ = 1.4 Hz, 1H; 2-H), 7.38 ppm (dd, $J_{6,5}$ = 8.0 Hz, $J_{6,2}$ = 1.4 Hz, 1H; 6-H); $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ = 13.8, 13.9 ($CH_3$), 22.4, 22.5, 24.8, 25.5, 25.6, 26.8, 29.0, 29.3, 31.4, 31.5 ($OCH_2(CH_2)_4CH_3$, $OC(CH_3)_2C(CH_3)_2O$), 68.8, 69.2 ($OCH_2(CH_2)_4CH_3$), 83.4 ($OC(CH_3)_2C(CH_3)_2O$), 112.7, 119.4 (5-C, 6-C), 128.5 (2-C), 148.5, 151.9 ppm (3-C, 4-C); FTIR (film): $\tilde{\nu}$ = 2928, 2859 (s), 1599 (s), 1418, 1353 (s), 1256, 1217, 1137 cm$^{-1}$ (ms); MS (EI): $m/z$ (%): 407 (1), 406 (5), 405 (25), 404 (100) [$M^+$], 403 (23), 320 (10) [$M^+-C_6H_{13}$], 236 (52) [$M^+-2\,C_6H_{13}$]; elemental analysis calcd (%) for $C_{24}H_{41}BO_4$ (404.3): C 71.28, H 10.22; found: C 71.39, H 10.33.

**2-[3,4-Bis(heptyloxy)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3d)**: Yield 38 %; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ = 0.87–0.91 (m, 6H; $CH_3$), 1.30–1.49 (m, 28H; $OCH_2CH_2(CH_2)_4CH_3$, $OC(CH_3)_2C(CH_3)_2O$), 1.78–1.85 (m, 4H; $OCH_2CH_2CH_2$), 3.99–4.04 (m, 4H; $OCH_2CH_2CH_2$), 6.87 (d, $J_{5,6}$ = 8.0 Hz, 1H; 5-H), 7.29 (d, $J_{2,6}$ = 1.1 Hz, 1H; 2-H), 7.38 ppm (dd, $J_{6,5}$ = 8.0 Hz, $J_{6,2}$ = 1.1 Hz, 1H; 6-H); $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ = 14.0, 14.1 ($CH_3$), 22.5, 22.6, 24.8, 25.9, 26.0, 26.9, 29.0, 29.1, 29.4, 31.7, 31.8 ($OCH_2(CH_2)_5CH_3$, $OC(CH_3)_2C(CH_3)_2O$), 68.8, 69.2 ($OCH_2(CH_2)_5CH_3$), 83.5 ($OC(CH_3)_2C(CH_3)_2O$), 112.7, 119.5 (5-C, 6-C), 128.6 (2-C), 148.5, 151.9 ppm (3-C, 4-C); FTIR (film): $\tilde{\nu}$ = 2925, 2856 (s), 1599 (s), 1417, 1350 (s), 1256, 1216, 1136 cm$^{-1}$ (ms); MS (EI): $m/z$ (%): 435 (1), 434 (5), 433 (26), 432 (100) [$M^+$], 431 (22), 334 (8) [$M^+-C_7H_{15}$], 236 (45) [$M^+-2\,C_7H_{15}$]; elemental analysis calcd (%) for $C_{26}H_{45}BO_4$ (432.4): C 72.21, H 10.49; found: C 72.18, H 10.41.

**2-[3,4-Bis(nonyloxy)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3f)**: Yield 29 %; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ = 0.88–0.89 (m, 6H; $CH_3$), 1.24–1.47 (m, 36H; $OCH_2CH_2(CH_2)_6CH_3$, $OC(CH_3)_2C(CH_3)_2O$), 1.78–1.84 (m, 4H; $OCH_2CH_2CH_2$), 3.99–4.04 (m, 4H; $OCH_2CH_2CH_2$), 6.87 (d, $J_{5,6}$ = 8.0 Hz, 1H; 5-H), 7.27 (d, $J_{2,6}$ = 1.3 Hz, 1H; 2-H), 7.37 ppm (dd, $J_{6,5}$ = 8.0 Hz, $J_{6,2}$ = 1.3 Hz, 1H; 6-H); $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ = 13.9, 14.1 ($CH_3$), 22.7, 24.8, 24.9, 25.4, 26.0, 26.1, 26.2, 26.9, 29.2, 29.3, 29.4, 29.5, 29.6, 31.9 ($OCH_2(CH_2)_7CH_3$, $OC(CH_3)_2C(CH_3)_2O$), 68.9, 69.3 ($OCH_2(CH_2)_7CH_3$), 83.6 ($OC(CH_3)_2C(CH_3)_2O$), 112.8, 119.6 (5-C, 6-C), 128.7 (2-C), 148.6, 152.0 ppm (3-C, 4-C); FTIR (film): $\tilde{\nu}$ = 2922, 2854 (s), 1599 (s), 1417, 1352 (s), 1257, 1217, 1137 cm$^{-1}$ (ms); MS (EI): $m/z$ (%): 490 (6), 489 (9), 488 (26) [$M^+$], 487 (1), 362 (3) [$M^+-C_7H_{15}$], 236 (9) [$M^+-2\,C_7H_{15}$]; elemental analysis calcd (%) for $C_{30}H_{53}BO_4$ (488.6): C 73.75, H 10.93; found: C 73.71, H 11.05.

**2-[3,4-Bis(decyloxy)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3g)**: Yield 45 %; m.p. 37 °C; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ = 0.87–0.89 (m, 6H; $CH_3$), 1.27–1.47 (m, 40H; $OCH_2CH_2(CH_2)_7CH_3$, $OC(CH_3)_2C(CH_3)_2O$), 1.78–1.84 (m, 4H; $OCH_2CH_2CH_2$), 3.99–4.04 (m, 4H; $OCH_2CH_2CH_2$), 6.87 (d, $J_{5,6}$ = 8.1 Hz, 1H; 5-H), 7.27 (d, $J_{2,6}$ = 1.1 Hz, 1H; 2-H), 7.37 ppm (dd, $J_{6,5}$ = 8.1 Hz, $J_{6,2}$ = 1.1 Hz, 1H; 6-H); $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ = 14.1 ($CH_3$), 22.7, 24.9, 26.0, 26.1, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 ($OCH_2(CH_2)_8CH_3$, $OC(CH_3)_2C(CH_3)_2O$), 68.9, 69.3 ($OCH_2(CH_2)_8CH_3$), 83.5 ($OC(CH_3)_2C(CH_3)_2O$), 112.8, 119.6 (5-C, 6-C), 128.7 (2-C), 148.6, 152.0 ppm (3-C, 4-C); FTIR (film): $\tilde{\nu}$ = 2922, 2853 (s), 1599 (s), 1417, 1351 (s), 1255, 1216, 1136 cm$^{-1}$ (ms); MS (EI): $m/z$ (%): 519 (1), 518 (7), 517 (33), 516 (100) [$M^+$], 515 (22); elemental analysis calcd (%) for $C_{32}H_{57}BO_4$ (516.6): C 74.40, H 11.12; found: C 74.53, H 11.12.

**2-[3,4-Bis(dodecyloxy)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3h)**: Yield 37 %; m.p. 42 °C; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ = 0.87–0.89 (m, 6H; $CH_3$), 1.26–1.47 (m, 48H; $OCH_2CH_2(CH_2)_9CH_3$, $OC(CH_3)_2C(CH_3)_2O$), 1.78–1.84 (m, 4H; $OCH_2CH_2CH_2$), 3.99–4.04 (m, 4H; $OCH_2CH_2CH_2$), 6.87 (d, $J_{5,6}$ = 7.8 Hz, 1H; 5-H), 7.27 (d, $J_{2,6}$ = 1.1 Hz, 1H; 2-H), 7.37 ppm (dd, $J_{6,5}$ = 7.8 Hz, $J_{6,2}$ = 1.1 Hz, 1H; 6-H); $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ = 13.9, 14.1 ($CH_3$), 22.7, 24.8, 24.9, 25.4, 26.0, 26.1, 26.2, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 ($OCH_2(CH_2)_{10}CH_3$, $OC(CH_3)_2C(CH_3)_2O$), 68.9, 69.3 ($OCH_2(CH_2)_{10}CH_3$), 83.6 ($OC(CH_3)_2C(CH_3)_2O$), 112.8, 119.6 (5-C, 6-C), 128.7 (2-C), 148.6, 152.0 ppm (3-C, 4-C); FTIR (film): $\tilde{\nu}$ = 2915, 2849 (s), 1602 (s), 1420, 1352 (s), 1259, 1210, 1136 cm$^{-1}$ (ms); MS (EI): $m/z$ (%): 575 (1), 574 (7), 573 (35), 572 (100) [$M^+$], 571 (22); elemental analysis calcd (%) for $C_{36}H_{65}BO_4$ (572.7): C 75.50, H 11.44; found: C 75.49, H 11.39.

**2-[3,4-Bis(tetradecyloxy)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3i)**: Yield 40 %; m.p. 49 °C; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ = 0.87–0.89 (m, 6H; $CH_3$), 1.26–1.47 (m, 64H; $OCH_2CH_2(CH_2)_{11}CH_3$, $OC(CH_3)_2C(CH_3)_2O$), 1.78–1.84 (m, 4H; $OCH_2CH_2CH_2$), 3.99–4.04 (m, 4H; $OCH_2CH_2CH_2$), 6.87 (d, $J_{5,6}$ = 8.1 Hz, 1H; 5-H), 7.28 (d, $J_{2,6}$ = 0.8 Hz, 1H; 2-H), 7.34 ppm (dd, $J_{6,5}$ = 8.1 Hz, $J_{6,2}$ = 0.8 Hz, 1H; 6-H); $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ = 14.1 ($CH_3$), 22.7, 24.9, 26.0, 26.1, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9 ($OCH_2(CH_2)_{12}CH_3$, $OC(CH_3)_2C(CH_3)_2O$), 68.9, 69.2 ($OCH_2(CH_2)_{12}CH_3$), 83.6 ($OC(CH_3)_2C(CH_3)_2O$), 112.6, 119.4 (5-C, 6-C), 128.6 (2-C), 148.5, 151.9 ppm (3-C, 4-C); FTIR (film): $\tilde{\nu}$ = 2923, 2853 (s), 1599 (s), 1417, 1353 (s), 1257, 1210, 1137 cm$^{-1}$ (ms); MS (EI): $m/z$ (%): 630 (6), 629 (40), 628 (100) [$M^+$]; elemental analysis calcd (%) for $C_{40}H_{73}BO_4$ (628.8): C 76.40, H 11.70; found: C 76.34, H 11.82.

**General procedure for the preparation of [15]crown-5 derivatives 5**: The appropriate boronate **3** (2.2 equiv), $K_2CO_3$ (10 equiv), KF (10 equiv), and [$Pd(PPh_3)_4$] were successively added to a solution of **4b**[29] (2 mmol) in a degassed mixture of dimethoxyethane/$H_2O$ and the reaction mixture was stirred at 95 °C for two days. After concentration, the residue was taken up in $CH_2Cl_2$, and this solution was washed with $H_2O$, dried ($MgSO_4$), and concentrated. The crude products were purified by chromatography and recrystallized from EtOH to give compounds **5** as colorless solids.

**4,5-Bis(3′,4′-methylenedioxyphenyl)benzo[15]crown-5 (5a)**: Yield 61 %; m.p. 95 °C; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ = 3.35, 3.50 (2s, 6H; $OCH_2OCH_3$), 3.78 (s, 8H; $CH_2OCH_2CH_2OCH_2CH_2OCH_2$), 3.93 (s, 4H; $ArOCH_2CH_2O$), 4.19–4.20 (m, 4H; $ArOCH_2CH_2O$), 4.95, 5.20 (2s, 4H; $OCH_2OCH_3$), 6.83–6.86 (m, 4H; 2′-H, 5′-H), 6.91 (s, 2H; 3-H, 6-H), 7.05–7.06 ppm (m, 2H; 6′-H); $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ = 55.9, 56.2 ($OCH_2OCH_3$), 69.5, 69.7 ($CH_2O(CH_2CH_2O)_2CH_2$), 70.7, 71.2 ($ArOCH_2CH_2O$), 95.4, 95.5 ($OCH_2OCH_3$), 116.3, 116.4 (5′-C, 2′-C), 123.5 (6′-C), 133.1, 136.0 (5-C, 4-C, 1′-C), 145.8, 146.8, 148.3 ppm (1-C, 2-C, 3′-C, 4′-C); FTIR (film): $\tilde{\nu}$ = 2869 (ms), 1604 (w), 1495, 1453, 1354 (s), 1244, 1196, 1153, 1132, 1070 cm$^{-1}$ (ms); MS (EI): $m/z$ (%): 663 (1), 662 (6), 661 (23), 660 (65) [$M^+$], 45 (100) [$CH_2OCH_3$]; HR-MS: $m/z$: calcd for $C_{34}H_{44}O_{13}$: 660.2782; found: 660.2782.

**4,5-Bis(3′,4′-dipentyloxyphenyl)benzo[15]crown-5 (5b)**: Yield 52 %; m.p. 64 °C; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ = 0.89–0.93 (m, 12H; $CH_3$), 1.32–1.47 (m, 16H; $OCH_2CH_2CH_2CH_2CH_3$), 1.64–1.66 (m, 4H; $OCH_2CH_2CH_2$), 1.78–1.82 (m, 4H; $OCH_2CH_2CH_2$), 3.66–3.69 (m, 4H; $OCH_2CH_2CH_2$), 3.78 (s, 8H; $CH_2OCH_2CH_2OCH_2CH_2OCH_2$), 3.92–3.95 (m, 8H; $ArOCH_2CH_2O$, $OCH_2CH_2CH_2$), 4.19–4.21 (m, 4H; $ArOCH_2CH_2O$), 6.56 (d, $J_{2',6'}$ = 1.9 Hz, 2H; 2′-H), 6.69 (dd, $J_{6',5'}$ = 8.2 Hz, $J_{6',2'}$ = 1.9 Hz, 2H; 6′-H), 6.74 (d, $J_{5',6'}$ = 8.2 Hz, 2H; 5′-H), 6.92 ppm (s, 2H; 3-H, 6-H); $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ = 14.0, 14.1 ($CH_3$), 22.4, 22.5, 28.2, 28.3, 28.8, 29.0 ($OCH_2(CH_2)_3CH_3$), 69.1, 69.3, 69.5, 69.8 ($OCH_2(CH_2)_3CH_3$, $CH_2OCH_2CH_2OCH_2$), 70.7, 71.2 ($ArOCH_2CH_2O$), 113.4 (5′-C), 116.2, 116.5 (6-C, 3-C, 2′-C), 121.9 (6′-C), 133.5, 134.4 (5-C, 4-C, 1′-C), 147.8, 148.2, 148.4 ppm (3′-C, 4′-C, 1-C, 2-C); FTIR (film): $\tilde{\nu}$ = 2931, 2857 (s), 1614 (w), 1501, 1450, 1383 (s), 1247, 1207, 1135, 1111, 1049 cm$^{-1}$ (ms); MS (EI): $m/z$ (%): 765 (4), 764 (15), 763 (30) [$M^+$]; elemental analysis calcd (%) for $C_{46}H_{68}O_9$ (765.0): C 72.22, H 8.96; found: C 72.41, H 8.87.

**4,5-Bis(3′,4′-dihexyloxyphenyl)benzo[15]crown-5 (5c)**: Yield 88 %; m.p. 62 °C; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ = 0.88–0.92 (m, 12H; $CH_3$), 1.23–1.46 (m, 24H; $OCH_2CH_2(CH_2)_3CH_3$), 1.63–1.66 (m, 4H; $OCH_2CH_2CH_2$), 1.77–1.80 (m, 4H; $OCH_2CH_2CH_2$), 3.67–3.69 (m, 4H; $OCH_2CH_2CH_2$), 3.78 (s, 8H; $CH_2OCH_2CH_2OCH_2CH_2OCH_2$), 3.92–3.95 (m, 8H; $ArOCH_2CH_2O$, $OCH_2CH_2CH_2$), 4.19–4.21 (m, 4H; $ArOCH_2CH_2O$), 6.56 (d, $J_{2',6'}$ = 1.9 Hz, 2H; 2′-H), 6.69 (dd, $J_{6',5'}$ = 8.3 Hz, $J_{6',2'}$ = 1.9 Hz, 2H; 6′-H), 6.74 (d, $J_{5',6'}$ = 8.3 Hz, 2H; 5′-H), 6.92 ppm (s, 2H; 3-H, 6-H); $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ = 14.0 ($CH_3$), 22.63, 22.65, 25.7, 25.8, 29.1, 29.4, 31.6, 31.7 ($OCH_2(CH_2)_4CH_3$), 69.2, 69.4, 69.5, 69.8 ($OCH_2(CH_2)_4CH_3$, $CH_2OCH_2CH_2OCH_2$), 70.7, 71.2 ($ArOCH_2CH_2O$), 113.5 (5′-C), 116.2, 116.5 (6-C, 3-C, 2′-C), 121.9 (6′-C), 133.5, 134.4 (5-C, 4-C, 1′-C), 147.8, 148.2, 148.5 ppm (3′-C, 4′-C, 1-C, 2-C); FTIR (film): $\tilde{\nu}$ = 2930, 2857 (s), 1615 (w), 1501, 1451, 1383 (s), 1246, 1207, 1135, 1112, 1056 cm$^{-1}$ (ms); MS (EI): $m/z$ (%): 824 (0.3), 823 (2), 822 (10), 821 (22), 820 (50)

[$M^+$], 736 (3) [$M^+-C_6H_{13}$], 650 (1) [$M^+-2\,C_6H_{13}$]; elemental analysis calcd (%) for $C_{50}H_{76}O_9$ (821.1): C 73.13, H 9.33; found: C 73.13, H 9.24.

**4,5-Bis(3′,4′-diheptyloxyphenyl)benzo[15]crown-5 (5d)**: Yield 77%; m.p. 62°C; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ = 0.87–0.90 (m, 12H; $CH_3$), 1.28–1.48 (m, 32H; $OCH_2CH_2(\mathit{CH}_2)_4CH_3$), 1.62–1.68 (m, 4H; $OCH_2\mathit{CH}_2CH_2$), 1.76–1.85 (m, 4H; $OCH_2\mathit{CH}_2CH_2$), 3.66–3.69 (m, 4H; $O\mathit{CH}_2CH_2CH_2$), 3.79 (s, 8H; $CH_2O\mathit{CH}_2\mathit{CH}_2O\mathit{CH}_2\mathit{CH}_2OCH_2$), 3.92–3.95 (m, 8H; Ar-$OCH_2\mathit{CH}_2O$, $O\mathit{CH}_2CH_2CH_2$), 4.19–4.21 (m, 4H; $ArO\mathit{CH}_2CH_2O$), 6.56 (d, $J_{2',6'}$ = 1.9 Hz, 2H; 2′-H), 6.69 (dd, $J_{6',5'}$ = 8.3 Hz, $J_{6',2'}$ = 1.9 Hz, 2H; 6′-H), 6.74 (d, $J_{5',6'}$ = 8.3 Hz, 2H; 5′-H), 6.92 ppm (s, 2H; 3-H, 6-H); $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ = 14.0, 14.1 ($\mathit{C}H_3$), 22.6, 25.9, 26.0, 29.0, 29.1, 29.2, 29.4, 31.8, 31.9 ($OCH_2(\mathit{C}H_2)_5CH_3$), 69.1, 69.3, 69.4, 69.7 ($O\mathit{C}H_2(CH_2)_5CH_3$, $CH_2O\mathit{C}H_2\mathit{C}H_2OCH_2$), 70.7, 71.2 ($ArO\mathit{C}H_2\mathit{C}H_2O$), 113.4 (5′-C), 116.2, 116.4 (6-C, 3-C, 2′-C), 121.9 (6′-C), 133.4, 134.4 (5-C, 4-C, 1′-C), 147.7, 148.1, 148.4 ppm (3′-C, 4′-C, 1-C, 2-C); FTIR (film): $\tilde{\nu}$ = 2917, 2856 (s), 1601 (w), 1501, 1451, 1383 (s), 1247, 1207, 1135, 1112, 1056 $\mathrm{cm^{-1}}$ (ms); MS (EI): $m/z$ (%): 878 (5), 877 (18), 876 (63), 875 (100) [$M^+$], 778 (2) [$M^+-C_6H_{13}$]; elemental analysis calcd (%) for $C_{54}H_{84}O_9$ (877.2): C 73.93, H 9.65; found: C 73.93, H 9.70.

**4,5-Bis(3′,4′-dioctyloxyphenyl)benzo[15]crown-5 (5e)**: Yield 65%; m.p. 46°C; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ = 0.87–0.90 (m, 12H; $CH_3$), 1.28–1.49 (m, 40H; $OCH_2CH_2(\mathit{CH}_2)_5CH_3$), 1.62–1.67 (m, 4H; $OCH_2\mathit{CH}_2CH_2$), 1.76–1.85 (m, 4H; $OCH_2\mathit{CH}_2CH_2$), 3.66–3.69 (m, 4H; $O\mathit{CH}_2CH_2CH_2$), 3.78 (s, 8H; $CH_2O\mathit{CH}_2\mathit{CH}_2O\mathit{CH}_2\mathit{CH}_2OCH_2$), 3.92–3.95 (m, 8H; Ar-$OCH_2\mathit{CH}_2O$, $O\mathit{CH}_2CH_2CH_2$), 4.19–4.21 (m, 4H; $ArO\mathit{CH}_2CH_2O$), 6.56 (d, $J_{2',6'}$ = 1.9 Hz, 2H; 2′-H), 6.69 (dd, $J_{6',5'}$ = 8.3 Hz, $J_{6',2'}$ = 1.9 Hz, 2H; 6′-H), 6.74 (d, $J_{5',6'}$ = 8.3 Hz, 2H; 5′-H), 6.92 ppm (s, 2H; 3-H, 6-H); $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ = 14.1 ($\mathit{C}H_3$), 22.6, 22.7, 26.0, 26.1, 29.2, 29.3, 29.4, 29.5, 31.9 ($OCH_2(\mathit{C}H_2)_6CH_3$), 69.2, 69.4, 69.5, 69.8 ($O\mathit{C}H_2$-$(CH_2)_6CH_3$, $CH_2O\mathit{C}H_2\mathit{C}H_2OCH_2$), 70.7, 71.2 ($ArO\mathit{C}H_2\mathit{C}H_2O$), 113.5 (5′-C), 116.2, 116.5 (6-C, 3-C, 2′-C), 121.9 (6′-C), 133.5, 134.4 (5-C, 4-C, 1′-C), 147.8, 148.2, 148.4 ppm (3′-C, 4′-C, 1-C, 2-C); FTIR (film): $\tilde{\nu}$ = 2920, 2852 (s), 1601 (w), 1495, 1467, 1451, 1386 (s), 1249, 1194, 1134, 1112, 1068 $\mathrm{cm^{-1}}$ (ms); MS (EI): $m/z$ (%): 934 (5), 933 (47), 932 (62), 931 (100) [$M^+$], 820 (3) [$M^+-C_6H_{13}$]; elemental analysis calcd (%) for $C_{58}H_{92}O_9$ (933.3): C 74.64, H 9.94; found: C 74.41, H 9.89.

**4,5-Bis(3′,4′-dinonyloxyphenyl)benzo[15]crown-5 (5f)**: Yield 67%; m.p. 62°C; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ = 0.87–0.90 (m, 12H; $CH_3$), 1.28–1.46 (m, 48H; $OCH_2CH_2(\mathit{CH}_2)_6CH_3$), 1.63–1.66 (m, 4H; $OCH_2\mathit{CH}_2CH_2$), 1.77–1.80 (m, 4H; $OCH_2\mathit{CH}_2CH_2$), 3.66–3.69 (m, 4H; $O\mathit{CH}_2CH_2CH_2$), 3.78 (s, 8H; $CH_2O\mathit{CH}_2\mathit{CH}_2O\mathit{CH}_2\mathit{CH}_2OCH_2$), 3.92–3.95 (m, 8H; Ar-$OCH_2\mathit{CH}_2O$, $O\mathit{CH}_2CH_2CH_2$), 4.19–4.21 (m, 4H; $ArO\mathit{CH}_2CH_2O$), 6.56 (d, $J_{2',6'}$ = 1.8 Hz, 2H; 2′-H), 6.69 (dd, $J_{6',5'}$ = 8.3 Hz, $J_{6',2'}$ = 1.8 Hz, 2H; 6′-H), 6.74 (d, $J_{5',6'}$ = 8.3 Hz, 2H; 5′-H), 6.92 ppm (s, 2H; 3-H, 6-H); $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ = 14.1 ($\mathit{C}H_3$), 22.7, 26.0, 26.1, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 31.9, 32.0 ($OCH_2(\mathit{C}H_2)_7CH_3$), 69.2, 69.4, 69.5, 69.8 ($O\mathit{C}H_2(CH_2)_7CH_3$, $CH_2O\mathit{C}H_2\mathit{C}H_2OCH_2$), 70.7, 71.2 ($ArO\mathit{C}H_2\mathit{C}H_2O$), 113.5 (5′-C), 116.2, 116.5 (6-C, 3-C, 2′-C), 121.9 (6′-C), 133.5, 134.4 (5-C, 4-C, 1′-C), 147.8, 148.2, 148.5 ppm (3′-C, 4′-C, 1-C, 2-C); FTIR (film): $\tilde{\nu}$ = 2918, 2850 (s), 1616 (w), 1504, 1466, 1451, 1386 (s), 1249, 1207, 1137, 1112, 1067 $\mathrm{cm^{-1}}$ (ms); MS (EI): $m/z$ (%): 992 (2), 991 (7), 990 (17), 989 (25) [$M^+$], 862 (2) [$M^+-C_6H_{13}$]; elemental analysis calcd (%) for $C_{62}H_{100}O_9$ (989.5): C 75.26, H 10.19; found: C 75.11, H 10.18.

**4,5-Bis(3′,4′-didecyloxyphenyl)benzo[15]crown-5 (5g)**: Yield 80%; m.p. 64°C; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ = 0.87–0.89 (m, 12H; $CH_3$), 1.27–1.46 (m, 56H; $OCH_2CH_2(\mathit{CH}_2)_7CH_3$), 1.63–1.67 (m, 4H; $OCH_2\mathit{CH}_2CH_2$), 1.77–1.80 (m, 4H; $OCH_2\mathit{CH}_2CH_2$), 3.66–3.69 (m, 4H; $O\mathit{CH}_2CH_2CH_2$), 3.78 (s, 8H; $CH_2O\mathit{CH}_2\mathit{CH}_2O\mathit{CH}_2\mathit{CH}_2OCH_2$), 3.92–3.95 (m, 8H; Ar-$OCH_2\mathit{CH}_2O$, $O\mathit{CH}_2CH_2CH_2$), 4.19–4.21 (m, 4H; $ArO\mathit{CH}_2CH_2O$), 6.56 (d, $J_{2',6'}$ = 1.8 Hz, 2H; 2′-H), 6.69 (dd, $J_{6',5'}$ = 8.3 Hz, $J_{6',2'}$ = 1.8 Hz, 2H; 6′-H), 6.74 (d, $J_{5',6'}$ = 8.3 Hz, 2H; 5′-H), 6.92 ppm (s, 2H; 3-H, 6-H); $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ = 14.1 ($\mathit{C}H_3$), 22.7, 26.0, 26.1, 29.2, 29.4, 29.5, 29.6, 29.7, 31.93, 31.96, 32.0 ($OCH_2(\mathit{C}H_2)_8CH_3$), 69.1, 69.3, 69.4, 69.7 ($O\mathit{C}H_2(CH_2)_8CH_3$, $CH_2O\mathit{C}H_2\mathit{C}H_2OCH_2$), 70.7, 71.2 ($ArO\mathit{C}H_2\mathit{C}H_2O$), 113.4 (5′-C), 116.2, 116.4 (6-C, 3-C, 2′-C), 121.9 (6′-C), 133.4, 134.4 (5-C, 4-C, 1′-C), 147.7, 148.1, 148.4 ppm (3′-C, 4′-C, 1-C, 2-C); FTIR (film): $\tilde{\nu}$ = 2918, 2849 (s), 1601 (w), 1503, 1467, 1451, 1385 (s), 1249, 1208, 1136, 1112, 1068 $\mathrm{cm^{-1}}$ (ms); MS (EI): $m/z$ (%): 1048 (8), 1047 (30), 1046 (76), 1045 (100) [$M^+$]; elemental analysis calcd (%) for $C_{66}H_{108}O_9$ (1045.6): C 75.82, H 10.41; found: C 76.07, H 10.49.

**4,5-Bis(3′,4′-didodecyloxyphenyl)benzo[15]crown-5 (5h)**: Yield 82%; m.p. 74°C; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ = 0.87–0.89 (m, 12H; $CH_3$), 1.26–1.46 (m, 72H; $OCH_2CH_2(\mathit{CH}_2)_9CH_3$), 1.63–1.65 (m, 4H; $OCH_2\mathit{CH}_2CH_2$), 1.77–1.80 (m, 4H; $OCH_2\mathit{CH}_2CH_2$), 3.66–3.68 (m, 4H; $O\mathit{CH}_2CH_2CH_2$), 3.78 (s, 8H; $CH_2O\mathit{CH}_2\mathit{CH}_2O\mathit{CH}_2\mathit{CH}_2OCH_2$), 3.92–3.95 (m, 8H; $ArOCH_2\mathit{CH}_2O$, $O\mathit{CH}_2CH_2CH_2$), 4.19–4.21 (m, 4H; $ArO\mathit{CH}_2$-$CH_2O$), 6.56 (d, $J_{2',6'}$ = 1.8 Hz, 2H; 2′-H), 6.69 (dd, $J_{6',5'}$ = 8.2 Hz, $J_{6',2'}$ = 1.8 Hz, 2H; 6′-H), 6.74 (d, $J_{5',6'}$ = 8.2 Hz, 2H; 5′-H), 6.92 ppm (s, 2H; 3-H, 6-H); $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ = 14.1 ($\mathit{C}H_3$), 22.7, 26.09, 26.12, 29.2, 29.41, 29.43, 29.44, 29.49, 29.53, 29.70, 29.73, 29.75, 29.77, 29.80, 31.96, 31.98, 32.0 ($OCH_2(\mathit{C}H_2)_{10}CH_3$), 69.2, 69.4, 69.5, 69.8 ($O\mathit{C}H_2$-$(CH_2)_{10}CH_3$, $CH_2O\mathit{C}H_2\mathit{C}H_2OCH_2$), 70.7, 71.2 ($ArO\mathit{C}H_2\mathit{C}H_2O$), 113.5 (5′-C), 116.3, 116.5 (6-C, 3-C, 2′-C), 121.9 (6′-C), 133.5, 134.5 (5-C, 4-C, 1′-C), 147.8, 148.2, 148.5 ppm (3′-C, 4′-C, 1-C, 2-C); FTIR (film): $\tilde{\nu}$ = 2916, 2848 (s), 1615 (w), 1504, 1467, 1452 (s), 1252, 1209, 1139, 1113 $\mathrm{cm^{-1}}$ (ms); MS (FAB): $m/z$ (%): 1184 (2), 1183 (8), 1182 (31), 1181 (75), 1180 (100) [$M$+$Na^+$], 1161 (2), 1160 (5), 1159 (17), 1158 (41), 1157 (60) [$M$]; elemental analysis calcd (%) for $C_{74}H_{124}O_9$ (1156.9): C 76.77, H 10.80; found: C 76.55, H 10.51.

**4,5-Bis(3′,4′-ditetradecyloxyphenyl)benzo[15]crown-5 (5i)**: Yield 86%; m.p. 77°C; $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ = 0.87–0.89 (m, 12H; $\mathit{CH}_3$), 1.26–1.47 (m, 88H; $OCH_2CH_2(\mathit{CH}_2)_{11}CH_3$), 1.63–1.65 (m, 4H; $OCH_2\mathit{CH}_2CH_2$), 1.76–1.82 (m, 4H; $OCH_2\mathit{CH}_2CH_2$), 3.66–3.68 (m, 4H; $O\mathit{CH}_2CH_2CH_2$), 3.78 (s, 8H; $CH_2O\mathit{CH}_2\mathit{CH}_2O\mathit{CH}_2\mathit{CH}_2OCH_2$), 3.92–3.95 (m, 8H; $ArOCH_2\mathit{CH}_2O$, $O\mathit{CH}_2CH_2CH_2$), 4.19–4.21 (m, 4H; $ArO\mathit{CH}_2$-$CH_2O$), 6.56 (d, $J_{2',6'}$ = 1.6 Hz, 2H; 2′-H), 6.69 (dd, $J_{6',5'}$ = 8.3 Hz, $J_{6',2'}$ = 1.6 Hz, 2H; 6′-H), 6.74 (d, $J_{5',6'}$ = 8.3 Hz, 2H; 5′-H), 6.92 ppm (s, 2H; 3-H, 6-H); $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ = 14.1 ($\mathit{C}H_3$), 22.7, 26.0, 26.1, 29.1, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 31.9 ($OCH_2(\mathit{C}H_2)_{12}CH_3$), 69.1, 69.2, 69.4, 69.7 ($O\mathit{C}H_2(CH_2)_{12}CH_3$, $CH_2O\mathit{C}H_2\mathit{C}H_2OCH_2$), 70.6, 71.2 ($ArO\mathit{C}H_2$-$\mathit{C}H_2O$), 113.3 (5′-C), 116.1, 116.4 (6-C, 3-C, 2′-C), 121.8 (6′-C), 133.4, 134.4 (5-C, 4-C, 1′-C), 147.7, 148.1, 148.4 ppm (3′-C, 4′-C, 1-C, 2-C); FTIR (film): $\tilde{\nu}$ = 2915, 2848 (s), 1602 (w), 1499, 1467 (s), 1251, 1196, 1135 $\mathrm{cm^{-1}}$ (ms); MS (DEI): $m/z$ (%): 1273 (4), 1272 (16), 1271 (42), 1270 (88), 1269 (100) [$M$]; elemental analysis calcd (%) for $C_{82}H_{138}O_9$ (1267.9): C 77.55, H 11.11; found: C 77.80, H 11.11.

**General procedure for complexation**: A solution of the alkali metal salt (1.0 equiv, or 0.5 equiv in the case of CsI) in acetone or MeOH was added to a solution of the respective crown ether **5** in acetone or $CH_2Cl_2$. After 1–2 h, the solvent was removed under a gentle stream of $N_2$ and the remaining product was dried under high vacuum.

**NaI·5b**: $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ = 0.87–0.94 (m, 12H; $CH_3$), 1.26–1.47 (m, 16H; $OCH_2CH_2(\mathit{CH}_2)_2CH_3$), 1.63–1.69 (m, 4H; $OCH_2\mathit{CH}_2CH_2$), 1.77–1.83 (m, 4H; $OCH_2\mathit{CH}_2CH_2$), 3.67–3.69 (m, 4H; $O\mathit{CH}_2CH_2CH_2$), 3.79–3.80, 3.91–3.92 (2m, 8H; $CH_2O\mathit{CH}_2\mathit{CH}_2O\mathit{CH}_2$-$\mathit{CH}_2OCH_2$), 3.93–3.96 (m, 4H; $O\mathit{CH}_2CH_2CH_2$), 4.09–4.10 (m, 4H; Ar-$OCH_2\mathit{CH}_2O$), 4.29–4.32 (m, 4H; $ArO\mathit{CH}_2CH_2O$), 6.53 (d, $J_{2',6'}$ = 1.9 Hz, 2H; 2′-H), 6.68 (dd, $J_{6',5'}$ = 8.4 Hz, $J_{6',2'}$ = 1.9 Hz, 2H; 6′-H), 6.75 (d, $J_{5',6'}$ = 8.4 Hz, 2H; 5′-H), 6.92 ppm (s, 2H; 3-H, 6-H); $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ = 14.04, 14.06 ($\mathit{C}H_3$), 22.4, 22.5, 28.2, 28.3, 28.8, 29.0 ($OCH_2(\mathit{C}H_2)_3CH_3$), 67.1, 67.9, 69.1, 69.2, 69.3 ($O\mathit{C}H_2(CH_2)_3CH_3$, $CH_2O$-$(\mathit{C}H_2\mathit{C}H_2O)_2CH_2$, $ArO\mathit{C}H_2\mathit{C}H_2O$), 113.5 (5′-C), 114.4, 116.1 (6-C, 3-C, 2′-C), 121.9 (6′-C), 133.7, 134.3 (5-C, 1′-C), 145.4, 148.1, 148.6 ppm (3′-C, 4′-C, 1-C, 2-C); FTIR (film): $\tilde{\nu}$ = 2926, 2868 (ms), 1602, 1559 (w), 1494, 1468 (s), 1244, 1192, 1137, 1100, 1041 $\mathrm{cm^{-1}}$ (ms); MS (ESI): $m/z$: 787.4 [$M^+-I$].

**NaI·5c**: $^1$H NMR ($CDCl_3$, 500 MHz): $\delta$ = 0.88–0.93 (m, 12H; $CH_3$), 1.26–1.48 (m, 24H; $OCH_2CH_2(\mathit{CH}_2)_3CH_3$), 1.62–1.68 (m, 4H; $OCH_2\mathit{CH}_2CH_2$), 1.76–1.82 (m, 4H; $OCH_2\mathit{CH}_2CH_2$), 3.67–3.69 (m, 4H; $O\mathit{CH}_2CH_2CH_2$), 3.79–3.80, 3.90–3.92 (2m, 8H; $CH_2O\mathit{CH}_2\mathit{CH}_2O\mathit{CH}_2$-$\mathit{CH}_2OCH_2$), 3.93–3.95 (m, 4H; $O\mathit{CH}_2CH_2CH_2$), 4.08–4.09 (m, 4H; Ar-$OCH_2\mathit{CH}_2O$), 4.29–4.31 (m, 4H; $ArO\mathit{CH}_2CH_2O$), 6.53 (d, $J_{2',6'}$ = 1.9 Hz, 2H; 2′-H), 6.67 (dd, $J_{6',5'}$ = 8.3 Hz, $J_{6',2'}$ = 1.9 Hz, 2H; 6′-H), 6.75 (d, $J_{5',6'}$ = 8.3 Hz, 2H; 5′-H), 6.92 ppm (s, 2H; 3-H, 6-H); $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ = 14.0 ($\mathit{C}H_3$), 22.62, 22.63, 25.69, 25.7, 29.1, 29.3, 31.5, 31.6 ($OCH_2(\mathit{C}H_2)_4CH_3$), 67.2, 67.9, 69.1, 69.2, 69.3 ($O\mathit{C}H_2(CH_2)_4CH_3$, $CH_2O$-

(*CH*$_2$*CH*$_2$O)$_2$CH$_2$, ArO*CH*$_2$*CH*$_2$O), 113.5 (5′-C), 114.6, 116.1 (6-C, 3-C, 2′-C), 121.9 (6′-C), 133.8, 134.3 (5-C, 1′-C), 145.5, 148.1, 148.5 ppm (3′-C, 4′-C, 1-C, 2-C); FTIR (film): $\tilde{\nu}$ = 2926, 2868 (s), 1603 (w), 1495, 1467 (s), 1245, 1192, 1137, 1101, 1042 cm$^{-1}$ (ms); MS (ESI): *m*/*z*: 843.5 [$M^+-$I].

**NaI·5d**: $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ = 0.85–0.93 (m, 12H; CH$_3$), 1.24–1.48 (m, 32H; OCH$_2$CH$_2$(*CH*$_2$)$_4$CH$_3$), 1.62–1.67 (m, 4H; OCH$_2$*CH*$_2$CH$_2$), 1.76–1.82 (m, 4H; OCH$_2$*CH*$_2$CH$_2$), 3.67–3.69 (m, 4H; O*CH*$_2$CH$_2$CH$_2$), 3.79–3.80, 3.90–3.92 (2m, 8H; CH$_2$O*CH*$_2$*CH*$_2$O*CH*$_2$*CH*$_2$OCH$_2$), 3.93–3.95 (m, 4H; O*CH*$_2$CH$_2$CH$_2$), 4.08–4.10 (m, 4H; ArOCH$_2$*CH*$_2$O), 4.29–4.31 (m, 4H; ArO*CH*$_2$CH$_2$O), 6.53 (d, $J_{2',6'}$ = 1.9 Hz, 2H; 2′-H), 6.67 (dd, $J_{6',5'}$ = 8.3 Hz, $J_{6',2'}$ = 1.9 Hz, 2H; 6′-H), 6.75 (d, $J_{5',6'}$ = 8.3 Hz, 2H; 5′-H), 6.92 ppm (s, 2H; 3-H, 6-H); $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ = 14.08, 14.09 (*C*H$_3$), 22.6, 25.9, 26.0, 29.1, 29.13, 29.2, 29.4, 31.8, 31.9 (OCH$_2$(*C*H$_2$)$_5$CH$_3$), 67.1, 67.9, 69.1, 69.2, 69.3, 69.4 (O*C*H$_2$(CH$_2$)$_5$CH$_3$, CH$_2$O(*C*H$_2$*C*H$_2$O)$_2$CH$_2$, ArO*C*H$_2$*C*H$_2$O), 113.5 (5′-C), 114.5, 116.2 (6-C, 3-C, 2′-C), 121.9 (6′-C), 133.8, 134.3 (5-C, 1′-C), 145.4, 148.1, 148.6 ppm (3′-C, 4′-C, 1-C, 2-C); FTIR (film): $\tilde{\nu}$ = 2923, 2856 (s), 1601 (w), 1495, 1465 (s), 1243, 1191, 1125, 1101 cm$^{-1}$ (ms); MS (ESI): *m*/*z*: 899.6 [$M^+-$I].

**NaI·5e**: $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ = 0.87–0.93 (m, 12H; CH$_3$), 1.28–1.48 (m, 40H; OCH$_2$CH$_2$(*CH*$_2$)$_5$CH$_3$), 1.62–1.68 (m, 4H; OCH$_2$*CH*$_2$CH$_2$), 1.76–1.82 (m, 4H; OCH$_2$*CH*$_2$CH$_2$), 3.66–3.69 (m, 4H; O*CH*$_2$CH$_2$CH$_2$), 3.79–3.80, 3.90–3.91 (2m, 8H; CH$_2$O*CH*$_2$*CH*$_2$O*CH*$_2$*CH*$_2$OCH$_2$), 3.92–3.95 (m, 4H; O*CH*$_2$CH$_2$CH$_2$), 4.08–4.09 (m, 4H; ArOCH$_2$*CH*$_2$O), 4.29–4.31 (m, 4H; ArO*CH*$_2$CH$_2$O), 6.53 (d, $J_{2',6'}$ = 1.9 Hz, 2H; 2′-H), 6.67 (dd, $J_{6',5'}$ = 8.3 Hz, $J_{6',2'}$ = 1.9 Hz, 2H; 6′-H), 6.75 (d, $J_{5',6'}$ = 8.3 Hz, 2H; 5′-H), 6.92 ppm (s, 2H; 3-H, 6-H); $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ = 14.1 (*C*H$_3$), 22.6, 22.7, 26.05, 26.08, 29.2, 29.3, 29.4, 29.44, 31.9 (OCH$_2$(*C*H$_2$)$_6$CH$_3$), 67.2, 67.9, 69.2, 69.3, 69.4 (O*C*H$_2$(CH$_2$)$_6$CH$_3$, CH$_2$O(*C*H$_2$*C*H$_2$O)$_2$CH$_2$, ArO*C*H$_2$*C*H$_2$O), 113.5 (5′-C), 114.5, 116.2 (6-C, 3-C, 2′-C), 121.9 (6′-C), 133.8, 134.3 (5-C, 1′-C), 145.4, 148.1, 148.6 ppm (3′-C, 4′-C, 1-C, 2-C); FTIR (film): $\tilde{\nu}$ = 2924, 2857 (s), 1603, 1562 (w), 1497, 1464 (s), 1244, 1192, 1130, 1102 cm$^{-1}$ (ms); MS (ESI): *m*/*z*: 955.5 [$M^+-$I].

**NaI·5f**: $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ = 0.87–0.90 (m, 12H; CH$_3$), 1.28–1.47 (m, 48H; OCH$_2$CH$_2$(*CH*$_2$)$_6$CH$_3$), 1.62–1.67 (m, 4H; OCH$_2$*CH*$_2$CH$_2$), 1.76–1.82 (m, 4H; OCH$_2$*CH*$_2$CH$_2$), 3.66–3.69 (m, 4H; O*CH*$_2$CH$_2$CH$_2$), 3.78–3.80, 3.90–3.91 (2m, 8H; CH$_2$O*CH*$_2$*CH*$_2$O*CH*$_2$*CH*$_2$OCH$_2$), 3.92–3.95 (m, 4H; O*CH*$_2$CH$_2$CH$_2$), 4.07–4.08 (m, 4H; ArOCH$_2$*CH*$_2$O), 4.28–4.30 (m, 4H; ArO*CH*$_2$CH$_2$O), 6.53 (d, $J_{2',6'}$ = 1.9 Hz, 2H; 2′-H), 6.67 (dd, $J_{6',5'}$ = 8.3 Hz, $J_{6',2'}$ = 1.9 Hz, 2H; 6′-H), 6.75 (d, $J_{5',6'}$ = 8.3 Hz, 2H; 5′-H), 6.92 ppm (s, 2H; 3-H, 6-H); $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ = 14.1 (*C*H$_3$), 22.7, 26.06, 26.09, 29.2, 29.3, 29.34, 29.4, 29.46, 29.5, 29.6, 29.7, 31.9, 32.0 (OCH$_2$(*C*H$_2$)$_7$CH$_3$), 67.4, 68.1, 69.3, 69.4 (O*C*H$_2$(CH$_2$)$_7$CH$_3$, CH$_2$O(*C*H$_2$*C*H$_2$O)$_2$CH$_2$, ArO*C*H$_2$*C*H$_2$O), 113.5 (5′-C), 114.7, 116.2 (6-C, 3-C, 2′-C), 121.9 (6′-C), 133.8, 134.2 (5-C, 1′-C), 145.7, 148.1, 148.5 ppm (3′-C, 4′-C, 1-C, 2-C); FTIR (film): $\tilde{\nu}$ = 2920, 2851 (s), 1602 (w), 1495, 1465 (s), 1244, 1191, 1126, 1100 cm$^{-1}$ (ms); MS (ESI): *m*/*z*: 1011.6 [$M^+-$I].

**NaI·5g**: $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ = 0.87–0.89 (m, 12H; CH$_3$), 1.21–1.46 (m, 56H; OCH$_2$CH$_2$(*CH*$_2$)$_7$CH$_3$), 1.62–1.67 (m, 4H; OCH$_2$*CH*$_2$CH$_2$), 1.76–1.82 (m, 4H; OCH$_2$*CH*$_2$CH$_2$), 3.66–3.69 (m, 4H; O*CH*$_2$CH$_2$CH$_2$), 3.79–3.80, 3.83–3.84 (2m, 8H; CH$_2$O*CH*$_2$*CH*$_2$O*CH*$_2$*CH*$_2$OCH$_2$), 3.93–3.94 (m, 4H; O*CH*$_2$CH$_2$CH$_2$), 4.09–4.10 (m, 4H; ArOCH$_2$*CH*$_2$O), 4.30–4.31 (m, 4H; ArO*CH*$_2$CH$_2$O), 6.52 (d, $J_{2',6'}$ = 1.9 Hz, 2H; 2′-H), 6.67 (dd, $J_{6',5'}$ = 8.3 Hz, $J_{6',2'}$ = 1.9 Hz, 2H; 6′-H), 6.75 (d, $J_{5',6'}$ = 8.3 Hz, 2H; 5′-H), 6.93 ppm (s, 2H; 3-H, 6-H); $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ = 14.1 (*C*H$_3$), 22.7, 26.06, 26.09, 29.2, 29.39, 29.41, 29.48, 29.5, 29.68, 29.71, 29.73, 29.75, 29.79, 31.9 (OCH$_2$(*C*H$_2$)$_{10}$CH$_3$), 67.1, 67.9, 69.1, 69.3, 69.4 (O*C*H$_2$(CH$_2$)$_{10}$CH$_3$, CH$_2$O(*C*H$_2$*C*H$_2$O)$_2$CH$_2$, ArO*C*H$_2$*C*H$_2$O), 113.5 (5′-C), 114.5, 116.1 (6-C, 3-C, 2′-C), 121.9 (6′-C), 133.8, 134.3 (5-C, 1′-C), 145.4, 148.1, 148.5 ppm (3′-C, 4′-C, 1-C, 2-C); FTIR (film): $\tilde{\nu}$ = 2920, 2852 (s), 1603, 1560 (w), 1496, 1466 (s), 1244, 1193, 1121, 1102 cm$^{-1}$ (ms); MS (ESI): *m*/*z*: 1067.7 [$M^+-$I].

**NaI·5h**: $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ = 0.87–0.89 (m, 12H; CH$_3$), 1.26–1.47 (m, 72H; OCH$_2$CH$_2$(*CH*$_2$)$_9$CH$_3$), 1.62–1.67 (m, 4H; OCH$_2$*CH*$_2$CH$_2$), 1.76–1.82 (m, 4H; OCH$_2$*CH*$_2$CH$_2$), 3.66–3.69 (m, 4H; O*CH*$_2$CH$_2$CH$_2$), 3.79–3.80, 3.90–3.91 (2m, 8H; CH$_2$O*CH*$_2$*CH*$_2$O*CH*$_2$*CH*$_2$OCH$_2$), 3.93–3.94 (m, 4H; O*CH*$_2$CH$_2$CH$_2$), 3.99–4.02 (m, 4H; ArOCH$_2$*CH*$_2$O), 4.22–4.28 (m, 4H; ArO*CH*$_2$CH$_2$O), 6.55 (d, $J_{2',6'}$ = 1.7 Hz, 2H; 2′-H), 6.68 (dd, $J_{6',5'}$ = 8.3 Hz, $J_{6',2'}$ = 1.7 Hz, 2H; 6′-H), 6.74 (d, $J_{5',6'}$ = 8.3 Hz, 2H; 5′-H), 6.93 ppm (s, 2H; 3-H, 6-H); $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ = 14.1 (*C*H$_3$), 22.7, 26.04, 26.07, 29.2, 29.3, 29.4, 29.44, 29.5, 29.59, 29.63, 29.64, 29.7, 31.91, 31.93 (OCH$_2$(*C*H$_2$)$_8$CH$_3$), 67.2, 68.0, 69.2, 69.3, 69.4 (O*C*H$_2$(CH$_2$)$_8$CH$_3$, CH$_2$O(*C*H$_2$*C*H$_2$O)$_2$CH$_2$, ArO*C*H$_2$*C*H$_2$O), 113.6 (5′-C), 114.6, 116.2 (6-C, 3-C, 2′-C), 121.9 (6′-C), 133.8, 134.3 (5-C, 1′-C), 145.5, 148.1, 148.6 ppm (3′-C, 4′-C, 1-C, 2-C); FTIR (film): $\tilde{\nu}$ = 2918, 2850 (s), 1605 (w), 1496, 1466 (s), 1245, 1193, 1121, 1100 cm$^{-1}$ (ms); MS (ESI): *m*/*z*: 1179.8 [$M^+-$I].

**NaI·5i**: $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ = 0.87–0.89 (m, 12H; C*H*$_3$), 1.26–1.47 (m, 88H; OCH$_2$CH$_2$(C*H*$_2$)$_{11}$CH$_3$), 1.60–1.67 (m, 4H; OCH$_2$C*H*$_2$CH$_2$), 1.76–1.82 (m, 4H; OCH$_2$C*H*$_2$CH$_2$), 3.66–3.68 (m, 4H; OC*H*$_2$CH$_2$CH$_2$), 3.79–3.80, 3.90–3.91 (2m, 8H; CH$_2$OC*H*$_2$C*H*$_2$OC*H*$_2$C*H*$_2$OCH$_2$), 3.93–3.95 (m, 4H; OC*H*$_2$CH$_2$CH$_2$), 4.04–4.06 (m, 4H; ArOCH$_2$C*H*$_2$O), 4.28–4.30 (m, 4H; ArOC*H*$_2$CH$_2$O), 6.54 (d, $J_{2',6'}$ = 1.9 Hz, 2H; 2′-H), 6.67 (dd, $J_{6',5'}$ = 8.2 Hz, $J_{6',2'}$ = 1.9 Hz, 2H; 6′-H), 6.75 (d, $J_{5',6'}$ = 8.2 Hz, 2H; 5′-H), 6.93 ppm (s, 2H; 3-H, 6-H); $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ = 14.1 (*C*H$_3$), 22.7, 26.0, 26.1, 29.1, 29.3, 29.4, 29.5, 29.6, 29.7, 29.8, 31.9 (OCH$_2$(*C*H$_2$)$_{12}$CH$_3$), 67.7, 68.4, 69.1, 69.2, 69.5, 69.6 (O*C*H$_2$(CH$_2$)$_{12}$CH$_3$, CH$_2$O(*C*H$_2$*C*H$_2$O)$_2$CH$_2$, ArO*C*H$_2$*C*H$_2$O), 113.3 (5′-C), 114.9, 116.0 (6-C, 3-C, 2′-C), 121.8 (6′-C), 133.8, 134.1 (5-C, 1′-C), 147.9, 148.4 ppm (3′-C, 4′-C, 1-C, 2-C); FTIR (film): $\tilde{\nu}$ = 2918, 2850 (s), 1604 (w), 1496, 1467 (s), 1245, 1194, 1121, 1100 cm$^{-1}$ (ms); MS (ESI): *m*/*z*: 1292.9 [$M^+-$I].

**NaI$_3$·5a**: M.p. 120 °C; $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ = 3.82–3.87, 3.89–3.91 (2m, 8H; CH$_2$OC*H*$_2$C*H*$_2$OC*H*$_2$C*H*$_2$OCH$_2$), 4.05–4.06 (m, 4H; ArOCH$_2$C*H*$_2$O), 4.31–4.33 (m, 4H; ArOC*H*$_2$CH$_2$O), 5.93 (s, 4H; OC*H*$_2$O), 6.58–6.61 (m, 4H; 2′-H, 5′-H), 6.69–6.70 (m, 2H; 6′-H), 6.91 ppm (s, 2H; 3-H, 6-H); $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ = 67.4, 68.4, 69.2, 69.4 (CH$_2$O(*C*H$_2$*C*H$_2$O)$_2$CH$_2$, ArO*C*H$_2$*C*H$_2$O), 101.0 (O*C*H$_2$O), 108.1 (5′-C), 110.3 (2′-C), 115.3 (6-C, 3-C), 123.3 (6′-C), 134.5, 134.6 (5-C, 4-C, 1′-C), 145.5, 146.5, 147.3 ppm (1-C, 2-C, 3′-C, 4′-C); FTIR (CDCl$_3$): $\tilde{\nu}$ = 2877 (ms), 1604 (w), 1499, 1482 (s), 1238, 1172, 1123, 1039 cm$^{-1}$ (ms); MS (ESI): *m*/*z*: 531.1 [$M^+-$I$_3$].

**[CsI·(5a)$_2$]**: M.p. 144 °C; $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ = 3.76–3.79 (m, 8H; CH$_2$OC*H*$_2$C*H*$_2$OC*H*$_2$C*H*$_2$OCH$_2$), 3.91–3.93 (m, 4H; ArOCH$_2$C*H*$_2$O), 4.17–4.19 (m, 4H; ArOC*H*$_2$CH$_2$O), 5.93 (s, 4H; OC*H*$_2$O), 6.58–6.60 (m, 4H; 2′-H, 5′-H), 6.68–6.69 (m, 2H; 6′-H), 6.85 ppm (s, 2H; 3-H, 6-H); $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ = 69.3, 69.7, 70.6, 71.2 (CH$_2$O(*C*H$_2$*C*H$_2$O)$_2$CH$_2$, ArO*C*H$_2$*C*H$_2$O), 100.9 (O*C*H$_2$O), 108.0 (5′-C), 110.4 (2′-C), 116.5 (6-C, 3-C), 123.3 (6′-C), 133.3, 135.4 (5-C, 4-C, 1′-C), 146.1, 147.2, 148.2 ppm (1-C, 2-C, 3′-C, 4′-C); FTIR (CDCl$_3$): $\tilde{\nu}$ = 2873 (w), 1601 (w), 1501, 1482, 1455 (s), 1239, 1129, 1039 cm$^{-1}$ (ms); MS (ESI): *m*/*z*: 1149.2 [$M^+-$I].

**[CsI·(5h)$_2$]**: $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ = 0.87–0.89 (m, 12H; C*H*$_3$), 1.26–1.47 (m, 72H; OCH$_2$CH$_2$(C*H*$_2$)$_9$CH$_3$), 1.62–1.67 (m, 4H; OCH$_2$C*H*$_2$CH$_2$), 1.76–1.82 (m, 4H; OCH$_2$C*H*$_2$CH$_2$), 3.65–3.68 (m, 4H; OC*H*$_2$CH$_2$CH$_2$), 3.75–3.78 (m, 8H; CH$_2$OC*H*$_2$C*H*$_2$OC*H*$_2$C*H*$_2$OCH$_2$), 3.90–3.94 (m, 8H; ArOCH$_2$C*H*$_2$O, OC*H*$_2$CH$_2$CH$_2$), 4.19–4.20 (m, 4H; ArOC*H*$_2$CH$_2$O), 4.22–4.28 (m, 4H; ArOC*H*$_2$CH$_2$O), 6.54 (d, $J_{2',6'}$ = 2.0 Hz, 2H; 2′-H), 6.68 (dd, $J_{6',5'}$ = 8.3 Hz, $J_{6',2'}$ = 2.0 Hz, 2H; 6′-H), 6.74 (d, $J_{5',6'}$ = 8.3 Hz, 2H; 5′-H), 6.92 ppm (s, 2H; 3-H, 6-H); $^{13}$C NMR (CDCl$_3$, 125 MHz): $\delta$ = 14.1 (*C*H$_3$), 22.7, 26.0, 26.1, 29.2, 29.3, 29.4, 29.47, 29.5, 29.68, 29.72, 29.73, 29.75, 29.8, 30.9, 31.9 (OCH$_2$(*C*H$_2$)$_{10}$CH$_3$), 69.1, 69.2, 69.3, 69.5, 70.3, 70.8 (O*C*H$_2$(CH$_2$)$_{10}$CH$_3$, CH$_2$O(*C*H$_2$*C*H$_2$O)$_2$CH$_2$, ArO*C*H$_2$*C*H$_2$O), 113.3 (5′-C), 116.1, 116.3 (6-C, 3-C, 2′-C), 121.8 (6′-C), 133.6, 134.2 (5-C, 1′-C), 147.7, 147.8, 148.4 ppm (3′-C, 4′-C, 1-C, 2-C); FTIR (neat): $\tilde{\nu}$ = 2955, 2918, 2872, 2850 (s), 1603 (w), 1496, 1467 (s), 1250, 1192, 1135 cm$^{-1}$ (ms); TOF-MS (ES): *m*/*z*: 1289.2 [$M^+-$I].

**[CsI·(5i)$_2$]**: $^1$H NMR (CDCl$_3$, 500 MHz): $\delta$ = 0.87–0.89 (m, 12H; C*H*$_3$), 1.26–1.47 (m, 88H; OCH$_2$CH$_2$(C*H*$_2$)$_{11}$CH$_3$), 1.57–1.66 (m, 4H; OCH$_2$C*H*$_2$CH$_2$), 1.76–1.82 (m, 4H; OCH$_2$C*H*$_2$CH$_2$), 3.64–3.67 (m, 4H; OC*H*$_2$CH$_2$CH$_2$), 3.76–3.78 (m, 8H; CH$_2$OC*H*$_2$C*H*$_2$OC*H*$_2$C*H*$_2$OCH$_2$), 3.90–3.94 (m, 8H; ArOCH$_2$C*H*$_2$O, OC*H*$_2$CH$_2$CH$_2$), 4.19–4.20 (m, 4H; ArOC*H*$_2$CH$_2$O), 6.54 (d, $J_{2',6'}$ = 2.1 Hz, 2H; 2′-H), 6.68 (dd, $J_{6',5'}$ = 8.3 Hz, $J_{6',2'}$ = 2.1 Hz, 2H; 6′-H), 6.74 (d, $J_{5',6'}$ = 8.3 Hz, 2H; 5′-H), 6.92 ppm (s, 2H; 3-H, 6-H); $^{13}$C NMR ($CDCl_3$, 125 MHz): $\delta$ = 14.1 ($CH_3$), 22.7, 26.0, 26.1, 29.1, 29.2, 29.3, 29.4, 29.48, 29.5, 29.6, 29.7, 29.8, 31.9 ($OCH_2(CH_2)_{12}CH_3$), 69.1, 69.3, 69.4 ($OCH_2(CH_2)_{12}CH_3$, $CH_2OCH_2CH_2OCH_2$), 70.1, 70.7 ($ArOCH_2CH_2O$), 113.3 (5′-C), 116.1, 116.3 (6-C, 3-C, 2′-C), 121.8 (6′-C), 133.6, 134.2 (5-C, 4-C, 1′-C), 147.8, 148.4 ppm (3′-C, 4′-C, 1-C, 2-C); FTIR (neat): $\tilde{\nu}$ = 2955, 2918, 2850 (s), 1498, 1467 (s), 1249, 1191, 1135 cm$^{-1}$ (ms); TOF-MS (ES): $m/z$: 1401.9 [$M^{+}$−I].

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