JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

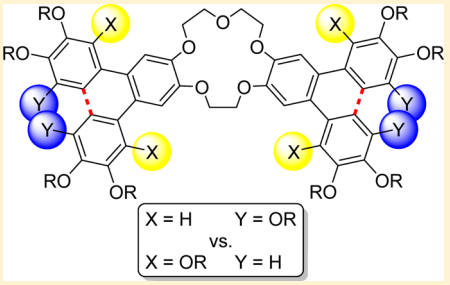
Pushing Steric Bias in the Scholl Reaction to Access Liquid Crystalline Crown Ethers

Tobias Wöhrle, Jochen Kirres, Martin Kaller, Markus Mansueto, Stefan Tussetschläger, and Sabine Laschat*

Institut für Organische Chemie, Universität Stuttgart, 70569 Stuttgart, Germany

Supporting Information

ABSTRACT: Sterically congested *o*-terphenyl crown ethers with alkoxy substituents at the 2,3,4-position or 3,4,5-position were synthesized from the corresponding tetrabromodibenzo[15]crown-5 and the corresponding boronic acids or borolanes via Suzuki cross-coupling and subsequently cyclized to the corresponding triphenylenes utilizing the Scholl reaction. Both series of compounds were investigated by differential scanning calorimetry, polarizing optical microscopy, and X-ray diffraction (SAXS, WAXS) regarding their mesomorphic properties. While all but one of the 3,4,5-substituted derivatives displayed liquid crystalline behavior (Col_h and Col_r), only the 2,3,4-substitituted triphenylene with the shortest alkoxy chains was liquid crystalline (Col_r).

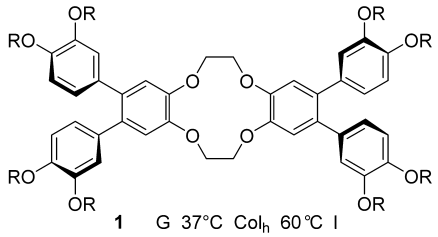


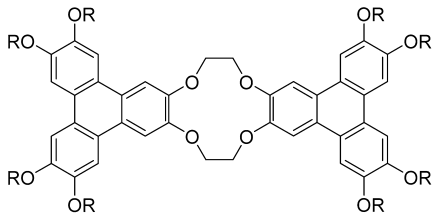
INTRODUCTION

The ability of shape anisotropic, e.g., disk-shaped, molecules with aliphatic side chains to self-assemble upon change of temperature into columnar supramolecular arrays with 2D orientational long-range order in the mesophase has led to the development of a variety of novel thermotropic liquid crystalline materials with important physical properties, such as 1D electric and photoconductivity and self-healing of defects. These features are highly desirable for applications in molecular electronics (e.g., OFETs) or energy conversion (OLEDs, organic photovoltaics).[1] Very shortly after their initial discovery, crown ethers and aza crowns have been utilized by Lehn,[2] Matsuda,[3] and co-workers and other pioneers as building blocks for thermotropic liquid crystals,[4] which provide the opportunity to control their mesophase behavior by metal salt complexation,[5] thus further extending their range of applications toward sensors[6] or ion-conductive membranes.[7] We have recently studied liquid crystalline crown ethers bearing *o*-terphenyls as mesogenic subunits regarding effects of chain length, side chain polarity, crown size, metal salt, and counterion on the mesomorphic properties.[8] It was furthermore found that the mesophase range of these columnar crown ethers could be significantly increased by flattening the mesogenic units, i.e., converting the twisted *o*-terphenyl units into triphenylenes via the Scholl reaction (e.g., **1**, **2**, Scheme 1).[9−12] In addition, mesophases were extended by reduction of the overall symmetry of the crown.[13] Both parameters were beneficial for the photoconductivity of the crown ethers.[14]

The self-assembly of disk-shaped molecules to columns resulting in columnar mesophases with different symmetry can be strongly influenced by the shape of the disks. Previous work by Müllen, Pisula, and Feng on hexaperihexabenzo coronenes[15] and by Würthner and co-workers on perylenebisimides[16] revealed that either twisting of the peripheral groups or core twisting had a strong effect on both columnar packing and physical properties (e.g., absorption, fluorescence, charge carrier mobility, molecular dynamics) as compared to the corresponding planar systems. Thus, synthetic methods that introduce core twisting into planar discotics are highly interesting. Dehydrogenative aromatic couplings such as the Scholl reaction have been extensively used for the preparation of polycyclic aromatic hydrocarbons,[11] which are useful as graphene derivatives in material science. Previous exciting results by Bock, Durola,[17] Chen,[18] and King[12d,e,19] groups and others[12a,b,20] showed that the Scholl reaction is particularly

Scheme 1. Known Liquid Crystalline Crown Ethers

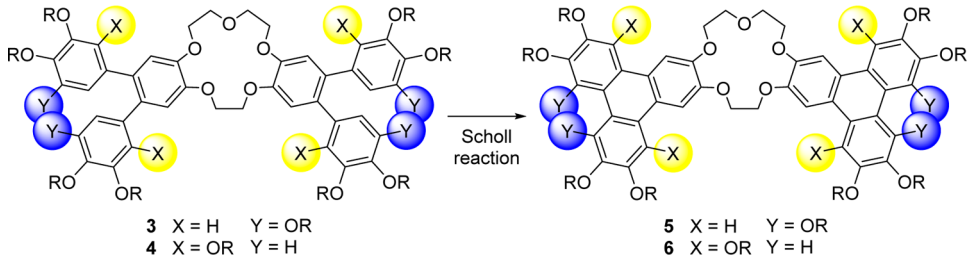




Received: August 4, 2014
Published: October 15, 2014

dx.doi.org/10.1021/jo501790d | J. Org. Chem. 2014, 79, 10143−10152

Scheme 2



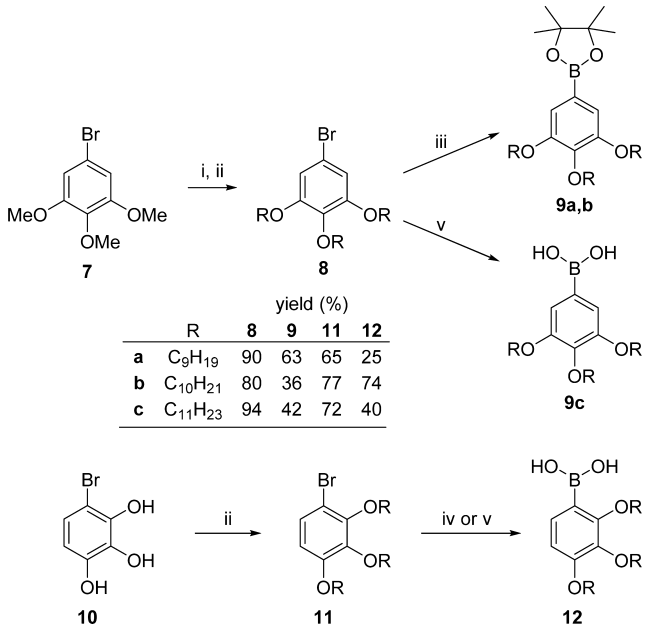
well-suited for sterically congested substrates. However, as Bock pointed out, the outcome of the intramolecular Scholl reaction remains only partially predictable.[17] Thus, motivated by these literature precedences, we were curious whether even sterically highly congested *o*-terphenyl crown ethers bearing alkoxy substituents at the 3,4,5-position (**3**) and 2,3,4-position (**4**), respectively, would undergo the dehydrogenative aromatic coupling (Scheme 2). Furthermore, we anticipated that the beneficial effect of the triphenylene unit on the mesomorphic properties of the resulting compounds **5**, **6** might overcome unfavorable steric hindrance decreasing mesophase stabilities. The outcome of such study would extend the scope of crown ethers in liquid crystals. The results toward Scholl reaction of crown ethers **3**, **4** to **5**, **6** and the resulting mesomorphic properties are discussed below.

RESULTS AND DISCUSSION

Following our previously established procedure for *o*-terphenyl crown ethers,[8f,13] a 4-fold Suzuki cross-coupling was anticipated as a key step. In order to obtain the required boronic acid derivatives, the 5-bromo-2,3,4-trialkoxybenzenes **8**[21,22] were prepared from commercially available 5-bromo-2,3,4-trimethoxybenzene **7** by demethylation with boron tribromide, followed by alkylation of the intermediate with various alkyl bromides in analogy to a procedure from Maeda et al. in 80–94% yield (Scheme 3).[23] The 5-bromo-2,3,4-trisalkoxybenzenes **8a,b** were treated with *n*-BuLi in THF at −78 °C, followed by addition of $B(OMe)_3$ at −78 °C and finally transesterification with pinacol in the presence of HOAc at room temperature, to yield the pinacol borolanes **9a,b** in 63% and 36%, respectively. In the case of 5-bromo-2,3,4-trisundecylbenzene **8c**, 1.07 equiv of TMEDA was added during the halogen–lithium exchange and, after treatment with $B(OMe)_3$, the boronate was hydrolyzed with aqueous HCl at room temperature to provide the boronic acid **9c** in 42% yield. Williamson etherification of 4-bromopyrogallol **10** with different alkyl bromides under the conditions described above yielded 6-bromo-1,2,3-trisalkoxybenzenes **11** in 65–77%. Compounds **11** were either converted to the corresponding boronic acids **12** by deprotonation with *n*BuLi in THF at −78 °C, followed by treatment with $B(OMe)_3$ and subsequent acidic hydrolysis with aqueous HCl, to give **12a** in 25% yield, or converted via method (v) to **12b,c** in 74% and 40% yields, respectively.

Suzuki cross-coupling of known tetrabromodibenzo[15]-crown-5 **13**[13] with the borolane **9a**, **9b** or boronic acids **9c**, **12a–c** with 15 mol % of $Pd(PPh_3)_4$ in the presence of K_2CO_3 in DME/H_2O under reflux,[13] followed by extractive removal of the potassium salt with ethylene diamine/hexane, gave the desired *o*-terphenyl crowns **3**, **4** (Scheme 4). While the use of borolanes **9a,b** resulted in moderate yields of 45% and 54% for **3a,b**, respectively, the corresponding boronic acids **9c**, **12a–c** provided the *o*-terphenyl crowns **3c**, **4a–c** in good yields (74–84%).

Scheme 3. Synthesis of the Borolanes and Boronic Acids[a]



yield (%)

	R	8	9	11	12
a	C_9H_{19}	90	63	65	25
b	$C_{10}H_{21}$	80	36	77	74
c	$C_{11}H_{23}$	94	42	72	40

[a]Reagents and conditions: (i) BBr_3, CH_2Cl_2, −78 °C. (ii) K_2CO_3, RBr, DMF, 60 °C. (iii) *n*-BuLi, THF, −78 °C; $B(OMe)_3$, −78 °C; pinacol, rt; HOAc, rt. (iv) *n*-BuLi, THF, −78 °C; $B(OMe)_3$, −78 °C; 2N HCl, rt. (v) *n*-BuLi, TMEDA, THF, −78 °C; $B(OMe)_3$, −78 °C; 2N HCl, rt.

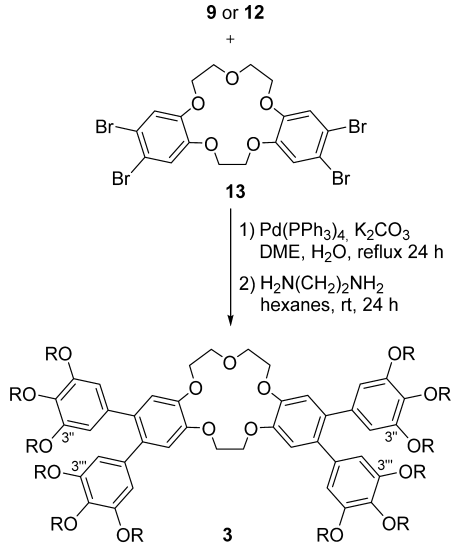
Scholl reaction was performed by treatment of *o*-terphenyl crowns **3**, **4** with 15 equiv of $FeCl_3$ in CH_2Cl_2/CH_3NO_2 at 0 °C, followed by rapid quenching with $MeOH/H_2O$ after 5 min (Scheme 5). After column chromatography, the desired triphenylene crowns **5**, **6** were isolated as colorless solids. Surprisingly, the sterically more hindered *o*-terphenyls **3** with 3″/3‴ OR interaction gave the corresponding triphenylenes **5** in similar yields (69–77%) as compared to the less bulky *o*-terphenyls **4** with 6-H/2″ OR (3-H/2‴ OR) interaction (61–81%).

Mesomorphic properties were analyzed via differential scanning calorimetry (DSC), polarizing optical microscopy (POM), and X-ray diffraction (SAXS, WAXS). DSC curves are shown in Figure S1 (Supporting Information). The results of the DSC experiments are summarized in Table 1.

The four series of crown ethers differed significantly regarding their mesomorphism. The 3,4,5-trialkoxy-substituted *o*-terphenyls **3a,c** with C9 and C11 side chains, respectively, displayed enantiotropic mesophases between 30 and 38 °C for **3a** and −6 and 39 °C for **3c**. Compound **3b** with a C10 side

dx.doi.org/10.1021/jo501790d | J. Org. Chem. 2014, 79, 10143–10152

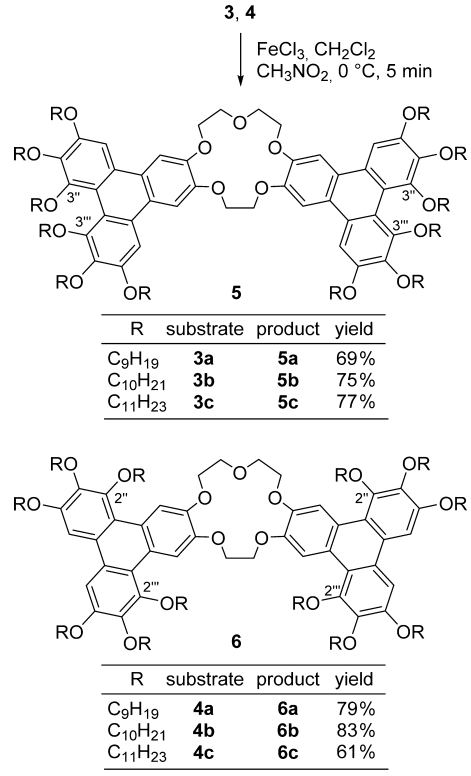
Scheme 4. Suzuki Coupling



R	substrate	product	yield
C_9H_{19}	**9a**	**3a**	45%
$C_{10}H_{21}$	**9b**	**3b**	54%
$C_{11}H_{23}$	**9c**	**3c**	83%

R	substrate	product	yield
C_9H_{19}	**12a**	**4a**	80%
$C_{10}H_{21}$	**12b**	**4b**	84%
$C_{11}H_{23}$	**12c**	**4c**	74%

Scheme 5. Scholl Reaction of 3,4 to 5,6



R	substrate	product	yield
C_9H_{19}	**3a**	**5a**	69%
$C_{10}H_{21}$	**3b**	**5b**	75%
$C_{11}H_{23}$	**3c**	**5c**	77%

R	substrate	product	yield
C_9H_{19}	**4a**	**6a**	79%
$C_{10}H_{21}$	**4b**	**6b**	83%
$C_{11}H_{23}$	**4c**	**6c**	61%

chain and all 2,3,4-trialkoxy-substituted *o*-terphenyls **4a–c** were low melting solids that did not show any liquid crystalline phases. As can be seen in Table 1, the conversion of *o*-terphenyls to triphenylenes via the Scholl reaction has a major impact on the mesomorphism. Triphenylenes **5a–c** were already liquid crystalline at room temperature with a clearing transition at 78, 74, and 76 °C, respectively, into the isotropic phase. Triphenylene **6a** was also liquid crystalline at room temperature, albeit with a lower clearing temperature at 48 °C.

POM investigations of compounds **3a,c** showed only unspecific textures (Figure 1). In contrast, compounds **5a–c** showed fan-shaped textures typical for columnar mesophases. For triphenylene **6a**, again, an unspecific texture was found.

SAXS/WAXS experiments clearly revealed the presence of a Col_h phase for **3a** (Figure 2a). The typical SAXS pattern for Col_h in a ratio of $1:1/\sqrt{3}:1/2$ is fulfilled and were indexed as (10), (11), and (20). A broad diffuse halo was observed at 4.4 Å, which is caused through the interactions of the alkyl chains in their liquid-like order. In contrast to this result, **3c** (Figure 2b) showed in the small-angle region eight characteristic reflections, which have been indexed as (02), (03), (10), (12), (13), (05), (14), and (06), respectively, the high number of observed reflections pointing at Col_r mesophase geometry for a centered lattice. However, for all three symmetric triphenylenes **5a–c**, a single reflection indexed as (10) was observed in the small-angle region (see Figure S2, Table S1, Supporting Information). The higher order reflections are missing maybe caused by the molecular form factor. Nevertheless, a Col_h phase is assumed for all three compounds due to POM imaging.[24] Assignment of the mesophase of **6a** via WAXS/SAXS revealed a rectangular columnar mesophase (see Figure S2, Table S1, Supporting Information) with three reflexes indexed as (11), (20), and (02), respectively). While triphenylene **6b** was not liquid crystalline, the corresponding homologue **6c** showed several glass and glass-to-crystal transitions.

The different mesomorphic behavior of the two *o*-terphenyl series **3,4** and the triphenylenes **5,6** might be rationalized as follows. The out-of-plane tilting of the *o*-terphenyl units in **3** should lead to a considerable decrease of steric hindrance between the alkoxy side chains, allowing intracolumnar antiparallel packing of two neighboring molecules. The observation that the shorter chain derivative **3a** favors the Col_h packing while the derivative **3c** with the longer chain is organized in a Col_r lattice is in good agreement with previous results of dibenzo[24] crown-8 derivatives.[8a] Thus, with increasing chain lengths, the disk shape of the dimer unit turns into an ellipsoid shape, which is better accommodated in a rectangular columnar mesophase Col_r. In contrast, for compounds **4**, the twisting of the *o*-terphenyl unit does not overcome the steric hindrance of the backfolded alkoxy chains at the 2‴-position. The steric bias seems to disfavor both parallel and antiparallel packing of direct neighbors within a column, and therefore, no liquid crystalline behavior was observed.

For the triphenylene series **5**, **6**, the situation is slightly different (Figure 3). Two different effects have to be considered, the sterical strain induced by the alkoxy chains in the 3″- and 3‴-position for compounds **5** and the steric restrictions because of the backfolding of the alkoxy chains in the 2″- and 2‴-position for compounds **6** (Figure 3).

dx.doi.org/10.1021/jo501790d | J. Org. Chem. 2014, 79, 10143–10152

Table 1. Phase Transitions of the Mesogenic *o*-Terphenyl Crown Ethers 3 and 4 and the Corresponding Triphenylene Crown Ethers 5 and 6[a,b]

compd	phase	T_m [°C] (ΔH [kJ·mol^{-1}])	phase	T_c [°C] (ΔH [kJ·mol^{-1}])	phase	cycles
3a	Cr	30 (17.5)	Col_h	38 (1.6)	I	2nd heating
3b	Cr	30 (27.2)			I	2nd heating
3c	Cr	−6[c] (24.8)	Col_r	39 (39.4)	I	2nd heating
4a	highly viscous oil					2nd heating
4b	Cr	22[c] (5.5)			I	2nd heating
4c	Cr	−10 (129.3)			I	2nd heating
5a			Col_h	78 (5.4)	I	2nd heating
5b			Col_h	74 (9.1)	I	2nd heating
5c			Col_h	76 (7.5)	I	2nd heating
6a			Col_r	48 (6.1)	I	2nd heating
6b	Cr	61[c] (76.3)			I	1st heating
6c	G_1 −5 G_2 16[c] (−71.8) Cr 33 Cr 59[c] (103.7) I					2nd heating

[a]The following phases were observed: crystalline (Cr), glass (G), columnar hexagonal (Col_h), columnar rectangular (Col_r), isotropic liquid (I). [b]Transition temperatures were determined by DSC (heating/cooling rate: 10 K/min). [c]Peak temperature.

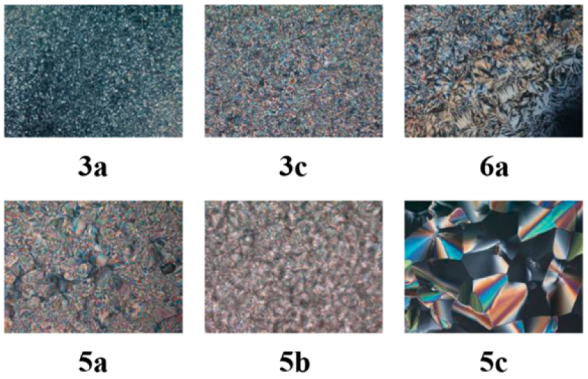


Figure 1. Textures of **3a**, **3c**, **5a**–**c**, and **6a** as seen between crossed polarizers upon cooling from isotropic liquid (cooling rate: 5 K/min, magnification: ×100).

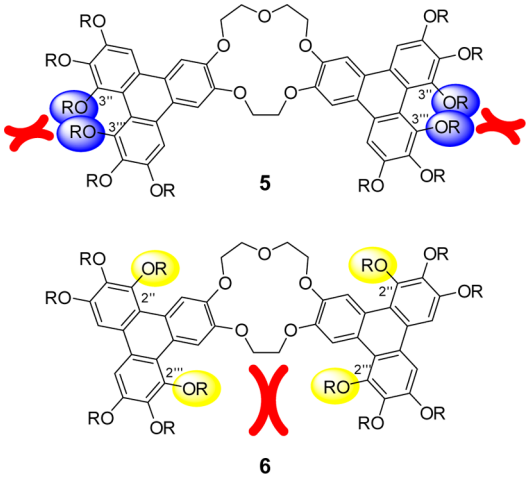


Figure 3. Visualization of the two main sterical influences on the molecular structure of **5** and **6**.

For compounds **5a**–**c**, the sterical hindrance in the 2″- and 2‴-position can be neglected, yet the sterical bias between the 3″- and 3‴-position is severe and should lead to a twisting of the triphenylene unit.[25] However, simple molecular modeling shows that the tiphenylene units are no longer in-plane but have a slight twist. As a result of core bending the whole disk, containing the central crown and the two triphenylene units, is no longer planar. (Figure 4).[26]

For the accumulation of the molecules of **5** to supramolecular columns that form the columnar hexagonal mesophase, two different variants are conceivable, parallel and antiparallel. In the parallel stacking, each molecule assembles in the same orientation relative to the neighboring ones. In the antiparallel stacking, however, the molecules align 180° rotated around their long axis, leading to columns in which every second molecule has the same orientation. The antiparallel packing is suggested for **5** since it exhibits a better space filling than the parallel one. As shown in Figure 5, the single molecules stack antiparallely and form single columns that then arrange in a hexagonal lattice giving the Col_h mesophase geometry.

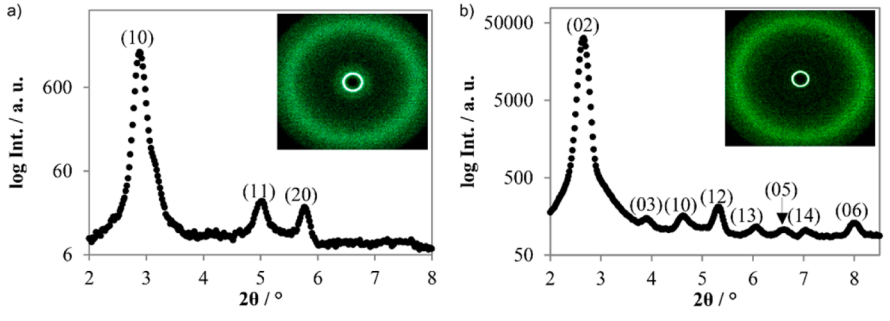


Figure 2. Small-angle X-ray scattering (SAXS) profile of the liquid crystalline phase of (a) **3a** at 30 °C and (b) **3c** at 25 °C (Inset: wide-angle X-ray scattering, WAXS).

dx.doi.org/10.1021/jo501790d | J. Org. Chem. 2014, 79, 10143–10152

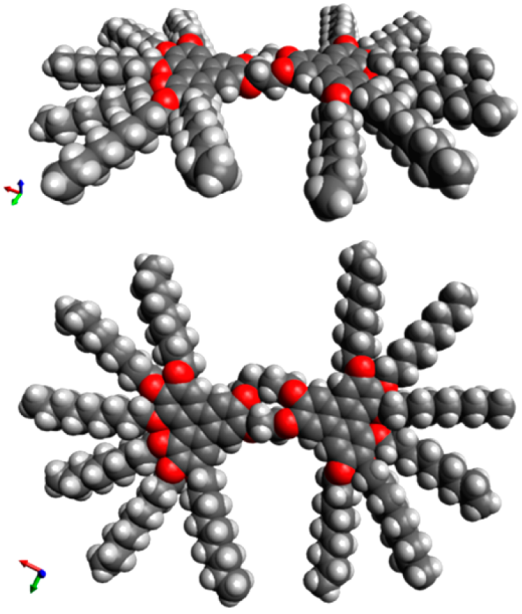


Figure 4. Molecular models of **5a** (top: side view, bottom: top view).

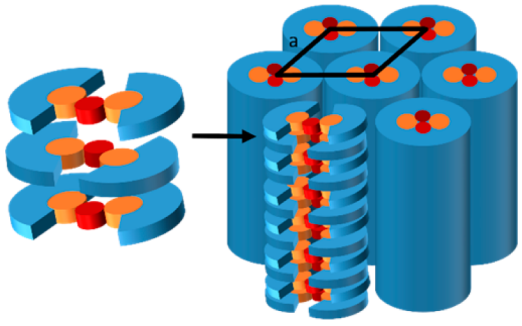


Figure 5. Proposed packing scheme of **5** in the hexagonal columnar mesophase (Col_h) with lattice constant *a*.

In contrast, compounds **6** display minor sterical hindrance in the 3″- and 3‴-position, comparable to known triphenylenes.[27] The strong sterical strain in the 2″-position and especially in the 2‴-position due to the backfolding of the alkoxy chains results in a bending of the central crown unit (Figure 6). Simple molecular modeling shows that the triphenylene units are no longer in-plane but have a slight twist as a result of core bending the whole disk, containing the central crown and the two triphenylene units, is no longer planar.[26]

Because of the twist in the molecular geometry of **6**, a parallel stacking of neighboring molecules seems favorable, leading to tilted disks assembled into columns (Figure 7). For **6a**, these columns are arranged in a rectangular lattice, giving the Col_r mesophase geometry. However, for longer alkoxy chains (**6b**,**c**), the twisting of the molecules due to the backfolding of the alkoxy side chains at the 2‴-position is too strong, thus preventing the columnar self-assembly and loss of mesomorphism.

CONCLUSION

In conclusion, the results show that the Scholl reaction is indeed suitable to provide rapid access to sterically biased triphenylene crown ethers. The mesomorphism of these compounds and their *o*-terphenyl precursors was found to be strongly dependent on the substitution pattern. Triphenylenes

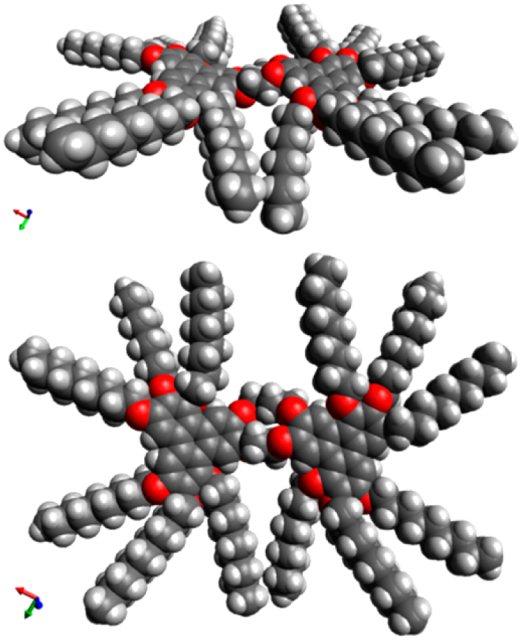


Figure 6. Molecular models of **6a** (top: side view, bottom: top view).

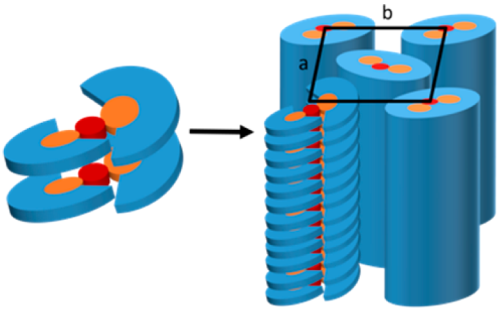


Figure 7. Proposed packing scheme of **6a** in the rectangular columnar mesophase (Col_r) with lattice constants *a* and *b*.

5 can accommodate stable hexagonal columnar phases despite the close neighborhood of the alkoxy chains in the 3″- and 3‴-position, while their *o*-terphenyl precursors **3** display Col_h (for C9) and Col_r (for C11) phases. In contrast, for triphenylenes **6** with alkoxy substituents in the 2″- and 2‴-position, the "backfolding" of a C9 chain seems to be tolerated in a columnar rectangular mesophase (for **6a**). However, for large alkyl chains, this kind of nanosegregation is disfavored and either mesomorphism is lost (for **6b**) or glass phases are observed (for **6c**), while neither of the corresponding *o*-terphenyls **4** revealed any mesomorphism. The results suggest that such balancing of steric contribution may be used as a design principle for other organic materials as well.

EXPERIMENTAL SECTION

General Information, Experimental Procedures, and Analytical Data. ^1H and ^{13}C NMR spectra were referenced to TMS (Me_4Si δ_H = 0.0 ppm, δ_C = 0.0 ppm) as an internal standard. Unless otherwise stated, spectra were recorded at room temperature. Assignment of the resonances was supported by chemical shift calculations and 2D experiments (COSY and HMBC). Infrared spectra (IR) were obtained by using an ATR system and are reported in wavenumbers. High-resolution mass spectra (HRMS) were measured using electrospray ionization time of flight (ESI-TOF). X-ray diffraction patterns (WAXS, SAXS regions) were recorded using a

dx.doi.org/10.1021/jo501790d | J. Org. Chem. 2014, 79, 10143−10152

Ni-filtered Cu Kα radiation (λ = 1.5418 Å) source. Melting points and phase transitions were determined via differential scanning calorimetry (DSC). Flash chromatography was performed on silica gel, grain size 40−63 μm, and aluminum sheets precoated with silica gel 60 μm were used for thin-layer chromatography (TLC). All commercial reagents were used without further purification. Solvents were dried and distilled under nitrogen prior to use, and unless otherwise stated, all reactions were carried out under a nitrogen atmosphere with Schlenk-type glassware. 5-Bromo-1,2,3-trimethoxybenzene **7** and 4-bromopyrogallol **10** are commercially available, and 4,4′,5,5′-tetrabromodibenzo[15]crown-5 **13** was prepared according to a literature procedure.[13]

General Procedure for the Preparation of 5-Bromo-1,2,3-trisalkoxybenzenes (8a−c). Following a procedure from Wu et al.,[28] a solution of 5-bromo-1,2,3-trimethoxybenzene **7** (5.00 g, 20.3 mmol) in dry CH_2Cl_2 (40 mL) was slowly treated at −78 °C with boron tribromide (67.0 mL, 67.0 mmol, 1 M solution in dichloromethane). After warming to room temperature and stirring for 17 h, the mixture was cooled in an ice bath and quenched by addition of ice-cooled water. The aqueous layer was extracted with dichloromethane (3 × 50 mL), and the combined organic layers were washed with brine (3 × 50 mL) and dried over magnesium sulfate. Evaporation of the solvent yielded crude 5-bromobenzene-1,2,3-triol (3.00 g, 14.6 mmol), which was dissolved in dry DMF (60 mL). Dissolved oxygen was removed by passing nitrogen through the solution; then, potassium carbonate (10.8 g, 78.0 mmol) was added and the mixture was stirred for 30 min at room temperature. After addition of the corresponding 1-bromoalkane (65.7 mmol), the mixture was heated to 60 °C for 4 h and cooled to room temperature and the solvent was evaporated. The residue was taken up in dichloromethane and vacuum-filtered through a glass frit. The filtrate was washed with water (3 × 50 mL) and dried over $MgSO_4$, and the solvent was removed in vacuo. The crude products were purified as described below.

*5-Bromo-1,2,3-tris(nonyloxy)benzene (**8a**).* Recrystallized from ethanol, colorless solid, (5.97 g, 10.2 mmol, 70%); mp 40 °C; ^{1}H NMR (250 MHz, $CDCl_3$, δ) 0.82−0.95 (m, 9H, CH_3), 1.19−1.54 (m, 36H, CH_2), 1.65−1.86 (m, 6H, CH_2CH_2), 3.86−3.97 (m, 6H, OCH_2), 6.67 (s, 2H, H-2); ^{13}C NMR (63 MHz, $CDCl_3$, δ) 14.1 (CH_3), 22.7 (CH_2CH_3), 26, 26.1, 29.3, 29.4, 29.6, 29.7, 30.3, 31.9, 31.91 (CH_2), 69.3 (OCH_2-3), 73.5 (OCH_2-4), 110.1 (C-2), 115.6 (C-1), 137.4 (C-4), 153.82 (C-3). Spectroscopic data are in good agreement with those reported in ref 21.

*5-Bromo-1,2,3-tris(decyloxy)benzene (**8b**).* Recrystallized from ethanol, colorless solid, (7.92 g, 12.7 mmol, 80%); mp 38 °C; ^{1}H NMR (300 MHz, $CDCl_3$, δ) 0.81−0.99 (m, 9H, CH_3), 1.19−1.52 (m, 42H, CH_2), 1.66−1.85 (m, 6H, CH_2CH_2), 3.87−3.96 (m, 6H, OCH_2), 6.67 (s, 2H, H-2); ^{13}C NMR (63 MHz, $CDCl_3$, δ) 14.1 (CH_3), 22.7 (CH_2CH_3), 26, 26.1, 29.3, 29.4, 29.6, 29.7, 30.3, 31.9, 31.91 (CH_2), 69.3 (OCH_2-3), 73.5 (OCH_2-4), 110.1 (C-2), 115.6 (C-1), 137.4 (C-4), 153.82 (C-3). Spectroscopic data are in good agreement with those reported in ref 21.

*5-Bromo-1,2,3-tris(undecyloxy)benzene (**8c**).* Recrystallized from ethanol, colorless solid, (9.16 g, 13.7 mmol, 94%); mp 52 °C; ^{1}H NMR (250 MHz, $CDCl_3$, δ) 0.84−0.92 (m, 9H, CH_3), 1.19−1.52 (m, 48H, CH_2), 1.65−1.85 (m, 6H, OCH_2CH_2), 3.86−3.98 (m, 6H, OCH_2), 6.67 (s, 2H, H-2); ^{13}C NMR ($CDCl_3$, 63 MHz) δ = 14.1 (CH_3), 22.7 (CH_2CH_3), 26.0, 26.2, 29.30, 29.37, 29.4, 29.6, 29.63, 29.70, 29.73, 30.3, 31.9 (CH_2), 69.3 (OCH_2-3), 73.5 (OCH_2-4), 110.1 (C-2), 115.6 (C-1), 137.4 (C-4), 153.8 (C-3). Spectroscopic data are in good agreement with those reported in ref 22.

General Procedure for the Preparation of 5-Bromo-1,2,3-trisalkoxybenzenes (11a−c). A solution of 4-bromobenzene-1,2,3-triol **10** (3.00 g, 14.6 mmol) in dry DMF (60 mL) was degassed by passing nitrogen through the solution. Then, potassium carbonate (10.8 g, 78.0 mmol) was added and the mixture was stirred for 30 min at room temperature. After addition of the corresponding 1-bromoalkane (65.7 mmol), the mixture was heated to 60 °C for 4 h and cooled to room temperature and the solvent was evaporated. The residue was taken up in dichloromethane, and the slurry was vacuum-filtered through a fritted funnel. The filtrate was washed with water (3 × 50 mL) and dried over $MgSO_4$, and the solvent was removed in vacuo. The residue was purified by flash chromatography on silica gel using mixtures of petroleum ether and ethyl acetate as eluents.

*4-Bromo-1,2,3-tris(nonyloxy)benzene (**11a**).* Brown, viscous oil, 5.54 g (9.49 mmol, 65%); R_f = 0.18 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (500 MHz, $CDCl_3$, δ) 0.88 (t, 9H, CH_3), 1.20−1.41 (m, 30H, CH_2), 1.41−1.54 (m, 6H, $OCH_2CH_2CH_2$), 1.71−1.85 (m, 6H, OCH_2CH_2), 3.91−4.06 (m, 6H, OCH_2), 6.54 (d, $J_{5,6}$ = 9.0 Hz, 1H, H-5), 7.15 (d, $J_{6,5}$ = 8.9 Hz, 1H, H-6) ppm.; ^{13}C NMR (126 MHz, $CDCl_3$, δ) 14.1 (CH_3), 22.7 (CH_2CH_3), 26.08, 26.10, 26.12, 29.30, 29.32, 29.33, 29.36, 29.42, 29.51, 29.57, 29.59, 29.63, 29.68, 30.27, 30.30, 31.92, 31.95 (CH_2), 68.9 (OCH_2-2), 73.9 (OCH_2-4), 74.0 (OCH_2-3), 108.6 (C-1), 109.4 (C-5), 126.5 (C-6), 143.2 (C-3), 150.6 (C-2), 153.1 (C-4); FTIR (ATR, cm^{-1}): $\tilde{\nu}$ = 2956 (m), 2921 (vs), 2872 (m), 2852 (s), 1711 (w), 1573 (w), 1464 (s), 1442 (s), 1378 (m), 1296 (m) 1265 (w), 1229 (m), 1209 (s), 1141 (w), 1124 (w), 1089 (s), 1002 (m), 972 (w), 923 (w), 873 (w), 788 (m), 721 (w), 652 (w), 636 (w), 591 (w); MS (ESI): *m*/*z*: 584 (100) $[M + H]^+$, 504 $[M + H - Br]^+$ (4), 458 (5), 330 (7), 203 (61); HRMS-ESI: (*m*/*z*) $[M + Na]^+$ calcd for $C_{33}H_{59}BrO_3Na^+$, 607.3519; found, 607.3509; Anal. Calcd for $C_{33}H_{59}BrO_3$: C, 67.90; H, 10.16; Br, 13.69; found: C, 67.85; H, 10.12; Br, 13.40.

*4-Bromo-1,2,3-tris(decyloxy)benzene (**11b**).* Yellow oil, 7.04 g (11.2 mmol, 77%); R_f = 0.22 (petroleum ether/ethyl acetate 100:1); ^{1}H NMR (500 MHz, $CDCl_3$, δ) 0.88 (t, 9H, CH_3), 1.21−1.40 (m, 36H, CH_2), 1.41−1.53 (m, 6H, $OCH_2CH_2CH_2$), 1.71−1.84 (m, 6H, $OCHCH_2$), 3.91−4.05 (m, 6H, OCH_2), 6.54 (d, $J_{5,6}$ = 8.9 Hz, 1H, H-5), 7.15 (d, $J_{6,5}$ = 8.9 Hz, 1H, H-6); ^{13}C NMR (126 MHz, $CDCl_3$, δ) 14.1 (CH_3), 22.7 (CH_2CH_3), 26.08, 26.10, 26.12, 29.31, 29.36, 29.37, 29.40, 29.42, 29.51, 29.57, 29.59, 29.63, 29.67, 29.73, 30.2, 30.3, 31.93, 31.94, 31.95 (CH_2), 68.9 (OCH_2-2), 73.9 (OCH_2-4), 74.0 (OCH_2-3), 108.6 (C-1), 109.4 (C-5), 126.5 (C-6), 143.2 (C-3), 150.7 (C-2), 153.1 (C-4); FTIR (ATR, cm^{-1}): $\tilde{\nu}$ = 2957 (m), 2921 (vs), 2851 (s), 1573 (w), 1464 (s), 1442 (s), 1378 (m), 1296 (m), 1265 (w), 1230 (m), 1209 (m), 1141 (w), 1125 (w), 1090 (s), 1008 (m), 983 (w), 938 (w), 896 (w), 870 (w), 851 (w), 789 (m), 721 (w), 654 (w), 638 (w), 606 (w); MS (ESI): *m*/*z*: 626 (100) $[M + H]^+$, 546 $[M + H - Br]^+$ (7), 486 (4), 344 $[M + H - 2 \times C_{10}H_{21}]$ (8), 203 (53); HRMS-ESI: (*m*/*z*) $[M + Na]^+$ calcd for $C_{36}H_{65}BrO_3Na^+$, 649.3989; found, 649.3976; Anal. Calcd for $C_{36}H_{65}BrO_3$: C, 69.09; H, 10.47; Br, 12.77; found: C, 69.42; H, 10.37; Br, 12.73.

*4-Bromo-1,2,3-tris(undecyloxy)benzene (**11c**).* Recrystallized from acetone, yellow solid, 6.98 g (10.5 mmol, 72%); ^{1}H NMR (500 MHz, $CDCl_3$, δ) 0.88 (t, 9H, CH_3), 1.21−1.39 (m, 42H, CH_2), 1.41−1.53 (m, 6H, $OCH_2CH_2CH_2$), 1.71−1.84 (m, 6H, OCH_2CH_2), 3.91−4.05 (m, 6H, OCH_2), 6.54 (d, $J_{5,6}$ = 8.9 Hz, 1H, H-5), 7.15 (d, $J_{6,5}$ = 8.9 Hz, 1H, H-6); ^{13}C NMR (126 MHz, $CDCl_3$, δ) 14.1 (CH_3), 22.7 (CH_2CH_3), 26.07, 26.10, 26.12, 29.12, 29.31, 29.37, 29.40, 29.41, 29.50, 29.57, 29.64, 29.67, 29.70, 29.71, 30.2, 30.3, 31.93, 31.94, 31.95 (CH_2), 68.9 (OCH_2-2), 73.9 (OCH_2-4), 74.0 (OCH_2-3), 108.6 (C-1), 109.4 (C-5), 126.5 (C-6), 143.2 (C-3), 150.7 (C-2), 153.1 (C-4); FTIR (ATR, cm^{-1}): $\tilde{\nu}$ = 2957 (m), 2920 (vs), 2851 (s), 1739 (w), 1573 (w), 1464 (s), 1442 (m), 1378 (m), 1296 (m), 1266 (w), 1230 (w), 1209 (m), 1141 (w), 1126 (w), 1090 (s), 996 (w), 947 (w), 910 (w), 870 (w), 788 (m), 721 (w), 654 (w), 638 (w), 608 (w); MS (ESI): *m*/*z*: 686 (100), 684 (95) $[M + NH_4]^+$, 669 (13) $[M^+]$, 606 (14) $[M + NH_4, - Br]^+$, 589 (7) $[M^+ - Br]$; HRMS-ESI (*m*/*z*): $[M + NH_4]^+$ calcd for $C_{39}H_{75}BrNO_3^+$, 684.4925; found, 684.4925.

Method A: Synthesis of 4,4,5,5-Tetramethyl-2-(3,4,5-tris(dodecyloxy)phenyl)-1,3,2-dioxaborolane (9a, 9b). A solution of 5-bromo-1,2,3-tris(dodecyloxy)-benzene **6c** (12.0 mmol) in dry THF (150 mL) was treated with *n*-Buli (12.0 mL, 19.2 mmol, 1.6 M solution in hexane) at −78 °C, and the resulting mixture was stirred for 30 min. Then, trimethyl borate (2.30 mL, 2.18 g, 21.0 mmol) was added and the mixture was stirred for a further 30 min. After warming to room temperature (∼2 h), pinacol (2.40 g, 20.4 mmol) was added, the mixture was stirred for 1.5 h, glacial acetic acid (1.2 mL, 1.26 g, 21.0 mmol) was added, and again the mixture was stirred for 16 h. The solvents were removed in vacuo, the residue was taken up in dichloromethane (30 mL), and the solution was washed with water (3

dx.doi.org/10.1021/jo501790d | J. Org. Chem. 2014, 79, 10143−10152

× 20 mL) and dried over $MgSO_4$. Evaporation of the solvent yielded the crude product, which was purified by flash chromatography.

General Procedure for the Synthesis of Boronic Acids (9c) and (12a−c). A mechanically stirred solution of the respective trialkoxybenzene **8** or **11** (4.50 mmol) in dry THF (150 mL) was treated with *n*-Buli and tetramethylethylenediamine (for quantities, see methods B and C) at −78 °C, and the resulting mixture was stirred for 30 min at this temperature. Then, trimethyl borate was added and the mixture was stirred for a further 30 min at −78 °C and finally warmed to room temperature. After evaporation of the solvent, the residue was taken up in dichloromethane (50 mL), hydrochloric acid (50 mL, 2 M aqueous solution) was added, and the mixture was stirred for 10 min. The organic layer was separated, washed with water (3 × 50 mL), dried over $MgSO_4$, and evaporated to dryness. The crude products were purified by flash chromatography and/or recrystallization.

Method B: *n*-BuLi (3.38 mL, 5.40 mmol, 1.6 M solution in hexane), trimethyl borate (1.53 mL, 13.5 mmol), without TMEDA.

Method C: *n*-BuLi (3.10 mL, 4.95 mmol, 1.6 M solution in hexane), TMEDA (0.72 mL, 4.77 mmol), trimethyl borate (0.77 mL, 6.75 mmol).

*4,4,5,5-Tetramethyl-2-(3,4,5-tris(nonyloxy)phenyl)-1,3,2-dioxaborolane (**9a**).* From **8a**, 2.63 g (4.50 mmol). Yield: 1.79 g (2.84 mmol, 63%), colorless oil; R_f = 0.28 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (250 MHz, $CDCl_3$, δ) 0.84−0.93 (m, 9 H, CH_3), 1.22−1.54 (m, 48 H, CH_2, 2 × C(CH_3)$_2$), 1.67−1.86 (m, 6 H, OCH_2CH_2), 3.94−4.04 (m, 6 H, OCH_2), 6.99 (s, 2 H, H-2); ^{13}C NMR (63 MHz, $CDCl_3$, δ) 14.1 (CH_3), 22.7 (CH_2CH_3), 24.9, 26.1, 29.3, 29.7, 30.4, 31.9 (CH_2, C(CH_3)$_2$), 69.1 (OCH_2-3), 73.4 (OCH_2-4), 83.8 (CCH_3), 112.8 (C-2), 141.2 (C-4), 152.9 (C-3); FTIR (ATR, cm^{-1}): $\tilde{\nu}$ = 2922 (s), 2854 (s), 1573 (w), 1466 (w), 1413 (s), 1361 (vs), 1316 (w), 1217 (w), 1144 (s), 1108 (s), 1004 (w), 989 (w), 910 (w), 854 (w), 713 (w), 694 (w), 633 (w); MS (EI): *m*/*z*: 632(37), 631 (100), 630 (20) [M$^+$], 504 (12) [M$^+$ − $C_6H_{12}BO_2$], 378 (3) [M$^+$ − 2 × C_9H_{19}], 251 (14) [M$^+$ − $C_6H_{12}BO_2$, − 2 × C_9H_{19}]; Anal. Calcd for $C_{39}H_{71}BO_5$: C, 74.26; H, 11.35; found: C, 74.37; H, 11.25.

*4,4,5,5-Tetramethyl-2-(3,4,5-tris(decyloxy)phenyl)-1,3,2-dioxaborolane (**9b**).* From **8b**, 4.01 g (6.43 mmol). Yield: 1.56 g (2.32 mmol, 36%), colorless solid; R_f = 0.29 (petroleum ether/diethyl ether 20:1); ^{1}H NMR (300 MHz, $CDCl_3$,δ) 0.88 (m, 9H, CH_3), 1.24−1.51 (m, 54H, CH_2, 2 × C(CH_3)$_2$), 1.69−1.86 (m, 6H, OCH_2CH_2), 3.94−4.05 (m, 6H, OCH_2), 6.99 (s, 2H, H-2); ^{13}C NMR (63 MHz, $CDCl_3$,δ) 14.1 (CH_3), 22.7 (CH_2CH_3), 24.8 [C(CH_3)$_2$], 26.1, 26.9, 29.37, 29.43, 29.49, 29.61, 29.66, 29.75, 30.4, 31.9 (CH_2), 69.1, 73.4 (OCH_2), 83.7[C(CH_3)$_2$], 112.7 (C-2), 141.2, 152.9 (C-3, C-4); FTIR (ATR, cm^{-1}): $\tilde{\nu}$ = 2921 (vs), 2852 (s), 1573 (w), 1467 (m), 1413 (s), 1360 (vs), 1316 (w), 1214 (m), 1145 (s), 119 (vs), 970 (m), 854 (m), 694 (m); HRMS-ESI: (*m*/*z*) Calcd for [$C_{42}H_{77}BO_5Na^+$ (M + Na)$^+$] 695.5764; found 695.5756 Anal. Calcd for $C_{42}H_{77}BO_5$: C, 74.97; H, 11.53; found: C, 75.17; H, 11.63.

*(3,4,5-Tris(undecyloxy)phenyl)boronic Acid (**9c**).* From **8c**, 3.00 g (4.50 mmol). Yield: 1.20 g (1.89 mmol, 42%), colorless solid; R_f = 0.3 (petroleum ether/ethyl acetate 20:1); ^{1}H NMR (500 MHz, $CDCl_3$, δ) 0.84−0.93 (m, 9H, CH_3), 1.19−1.40 (m, 42H, CH_2), 1.40−1.54 (m, 6H, $OCH_2CH_2CH_2$), 1.73−1.85 (m, 6H, OCH_2CH_2), 3.95−4.06 (m, 6H, OCH_2), 5.69 (s, 1H, BO*H*), 6.99 (s, 2H, H-2); ^{13}C NMR (126 MHz, $CDCl_3$, δ) 14.1 (CH_3), 22.7 (CH_2CH_3), 26.15, 26.17, 29.39, 29.42, 29.47, 29.50, 29.64, 29.68, 29.69, 29.73, 29.76, 29.78, 30.4, 31.9, 32.0 (CH_2), 69.2, 73.5 (OCH_2), 113.00 (C-2), 131.65 (C-1), 141.06 (C-4), 152.90 (C-3); FTIR (ATR, cm^{-1}): $\tilde{\nu}$ = 3437 (w), 2956 (w), 2917 (s), 2872 (w), 2849 (s), 1572 (w), 1502 (w), 1467 (w), 1407 (s), 1377 (w), 1337 (s), 1284 (w), 1240 (w), 1199 (w), 1115 (s), 1067 (w), 1002 (w), 972 (w), 943 (w), 888 (w), 845 (w), 831 (w), 703 (w), 640 (w), 607 (w), 586 (w); MS (ESI): *m*/*z*: 632 [M − H]$^-$, 604. 472; HRMS-ESI: (*m*/*z*) [M − H]$^-$ calcd for [$C_{39}H_{73}BO_5$] 631.5478, found 631.5453.

*(2,3,4-Tris(nonyloxy)phenyl)boronic Acid (**12a**).* From **11a**, 3.00 g (4.50 mmol). Yield: 0.62 g (1.13 mmol, 25%), colorless oil; R_f = 0.2 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (250 MHz, $CDCl_3$, δ) 0.84−0.92 (m, 9H, CH_3), 1.19−1.57 (m, 36H, CH_2), 1.68−1.87 (m, 6H, OCH_2CH_2), 3.89−4.06 (m, 6H, OCH_2-3, −4), 4.11−4.21 (m, 2H, OCH_2-2), 6.69 (d, $J_{5,6}$ = 8.8 Hz, 1H, H-5), 7.47 (d, $J_{6,5}$ = 8.8 Hz, 1H, H-6); ^{13}C NMR (63 MHz, $CDCl_3$, δ) 14.1 (CH_3), 22.7 (CH_2CH_3), 25.9, 26.1, 26.2, 29.30, 29.35, 29.37, 29.4, 29.5, 29.61, 29.65, 29.68, 29.74, 30.3, 30.4, 31.9 (CH_2), 68.6 (OCH_2-4), 73.7 (OCH_2-2), 74.7 (OCH_2-3), 108.5 (C-5), 130.9 (C-6), 140.3 (C-3), 156.4 (C-2), 158.4 (C-4); FTIR (ATR, cm^{-1}): $\tilde{\nu}$ = 2957 (m), 2924 (vs), 2851 (vs), 2362 (w), 1738 (w), 1596 (s), 1488 (s), 1451 (m), 1379 (m), 1260 (w), 1228 (w) 1198 (m), 1146 (w), 1070 (m), 1044 (m), 970 (m), 926 (w), 905 (w), 866 (w), 822 (m), 801 (w), 756 (s), 693 (m), 639 (w); MS (ESI): *m*/*z*: 565 (100), 550 (25) [M$^+$ + H], 505 (60) [M$^+$ − BH_2O_2], 405 (10) [M$^+$ − C_9H_{19}]. HRMS-ESI: (*m*/*z*) [M + H]$^+$ calcd for $C_{33}H_{62}BO_5^+$, 549.4690; found, 549.4691.

*(2,3,4-Tris(decyloxy)phenyl)boronic Acid (**12b**).* From **11b**, 2.82 g (4.50 mmol). Yield: 1.97 g (3.33 mmol, 74%), yellow oil; R_f = 0.2 (petroleum ether/ethyl acetate 15:1); ^{1}H NMR (250 MHz, $CDCl_3$, δ) 0.83−0.93 (m, 9H, CH_3), 1.22−1.53 (m, 42H, CH_2), 1.70−−1.89 (m, 6H, OCH_2CH_2), 3.91−4.03 (m, 6H, 3-, 4-OCH_2), 4.15−4.20 (m, 2H, OCH_2-2), 6.70 (d, $J_{5,6}$ = 8.8 Hz, 1H, H-5), 7.48 (d, $J_{6,5}$ = 8.8 Hz, 1H, H-6); ^{13}C NMR (63 MHz, $CDCl_3$, δ) 14.1 (CH_3), 22.7 (CH_2CH_3), 25.9, 26.1, 26.2, 26.9, 29.28, 29.34, 29.37, 29.41, 29.46, 29.61, 29.64, 29.66, 29.7, 30.3, 30.4, 31.9 (CH_2), 68.6 (OCH_2-4), 73.7 (OCH_2-2), 74.8 (OCH_2-3), 108.5 (C-5), 130.9 (C-6), 140.4 (C-3), 156.5 (C-2), 158.5 (C-4); FTIR (ATR, cm^{-1}): $\tilde{\nu}$ = 3391 (br w), 2955 (w), 2918 (vs), 2850 (vs), 1597 (s), 1566 (w), 1496 (w), 1466 (s), 1453 (s), 1376 (s), 1354 (s), 1339 (s), 1215 (s) 1168 (w), 1129 (w), 1081 (s), 1051 (w), 1013 (s), 994 (w), 956 (w), 931 (w), 895 (w), 857 (w), 828 (w), 811 (w), 788 (w), 720 (w), 706 (w), 624 (w); MS (EI): *m*/*z*: 546 (100) [M$^+$ − B(OH)$_2$], 406 (24) [M$^+$ − B(OH)$_2$ − $C_{10}H_{21}$], 266 (23) [M$^+$ − B(OH)$_2$ − 2 × $C_{10}H_{21}$], 126 (31) [M$^+$ − B(OH)$_2$ − 3 × $C_{10}H_{21}$]; Anal. Calcd for $C_{36}H_{67}BO_5$: C, 73.20; H, 11.43; found: C, 73.45; H, 11.34.

*(2,3,4-Tris(undecyloxy)phenyl)boronic Acid (**12c**).* From **11c**, 3.00 g (4.50 mmol). Yield: 1.14 g (1.8 mmol, 40%), yellow oil; R_f = 0.23 (petroleum ether/ethyl acetate 30:1); ^{1}H NMR (250 MHz, $CDCl_3$, δ) 0.83−−0.93 (m, 9H, CH_3), 1.17−1.55 (m, 48H, CH_2), 1.69−1.88 (m, 6H, OCH_2CH_2), 3.91−4.04 (m, 6H, 3-, 4-OCH_2), 4.14−4.22 (m, 2H, OCH_2-2), 6.69 (d, $J_{5,6}$ = 8.8 Hz, 1H, H-5), 7.48 (d, $J_{6,5}$ = 8.8 Hz, 1H, H-6); ^{13}C NMR (63 MHz, $CDCl_3$, δ) 14.1 (CH_3), 22.7 (CH_2CH_3), 26.1, 26.2, 29.2, 29.3, 29.4, 29.5, 29.6, 29.7, 30.3, 30.4, 31.9 (CH_2), 68.6 (OCH_2-4), 73.6 (OCH_2-2), 74.7 (OCH_2-3), 108.5 (C-5), 130.9 (C-6), 140.4 (C-3), 156.4 (C-2), 158.5 (C-4); FTIR (ATR, cm^{-1}): $\tilde{\nu}$ = 3341 (br w), 2954 (w), 2916 (vs), 2849 (s), 1594 (w), 1567 (w), 1464 (s), 1376 (s), 1344 (w), 1290 (s), 1276 (w), 1225 (w), 1170 (w), 1120 (w), 1093 (s), 1084 (s), 1051 (w), 1011 (w), 963 (w), 898 (w), 826 (w), 778 (w), 720 (w), 705 (w); MS (EI): *m*/*z*: 589.5 (41) [M + H$^+$ − B(OH)$_2$], 588.5 (100) [M$^+$ − B(OH)$_2$], 434.3 (24) [M$^+$ − B(OH)$_2$ − $C_{11}H_{23}$], 280.2 (10) [M$^+$ − B(OH)$_2$ − 2 × $C_{11}H_{23}$], 126.0 (36) [M$^+$ − B(OH)$_2$ − 3 × $C_{11}H_{23}$]; HRMS-ESI: (*m*/*z*) [M]$^+$ calcd for $C_{39}H_{73}BO_5^+$, 632.5541; found, 632.5516.

General Procedure for the Preparation of *o*-Terphenyl Crown Ethers (3) and (4). To a solution of either a borolane (**9a**, **9b**) or a boronic acid (**9c** or **12a−c**) (0.95 mmol) and 4,4′,5,5′-tetrabromodibenzo[15]crown-5 **13** (100 mg, 0.16 mmol) in degassed dimethyl ether (20 mL) were subsequently added pottasium carbonate (1.85 g, 13.2 mmol), tetrakis(triphenylphosphine)palladium(0) (27.7 mg, 0.024 mmol), and degassed water (20 mL), and the resulting mixture was heated to reflux for 16 h. Then, the mixture was flushed with air and further refluxed for 3 h. After cooling to room temperature, the solvent was removed in vacuo and the residue was taken up in dichloromethane (90 mL). The solution was washed with water (3 × 50 mL), dried over magnesium sulfate, and evaporated to dryness. The crude product was dissolved in petroleum ether (30 mL), ethylenediamine (15 mL) was added, and the mixture was stirred for 16 h at room temperature. The resulting slurry was vacuum-filtered, and the mud cake was washed with dichloromethane. The filtrate was washed with water (3 × 50 mL), dried over magnesium sulfate, and evaporated to dryness. The obtained residues were purified by flash chromatography on silica gel and/or by recrystallization to yield products **12** and **13**.

dx.doi.org/10.1021/jo501790d | J. Org. Chem. 2014, 79, 10143−10152

*4,4′,5,5′-Tetrakis[3″,4″,5″-bis(nonyloxy)phenyl]dibenzo[15]-crown-5 (**3a**).* From **9a**, 0.60 g (0.95 mmol). Yield: 0.16 g (0.07 mmol, 45%), colorless, waxy solid; R_f = 0.5 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (500 MHz, $CDCl_3$, δ) 0.87−0.89 (m, 36H, CH_3), 1.28−1.49 (m, 144H, CH_2), 1.65−1.75 (m, 24H, OCH_2CH_2), 3.73 (t, J = 6.4 Hz, 16H, 3″-OCH_2, 5″-OCH_2, 3‴-OCH_2, 5‴-OCH_2), 3.88 (t, J = 6.4 Hz, 8H, 4″-OCH_2, 4‴-OCH_2), 3.99−4.01 (m, 4H, H-b), 4.28−4.30 (m, 4H, H-a), 4.47 (s, 4H, H-c), 6.305, 6.313 (2 × s, 2 × 4H, H-2″, H-6″, H-3‴, H-6‴), 7.00, 7.01 (2 × s, 2 × 2H, H-3, H-6, H-3′, H-6′); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 14.1 (CH_3), 22.7 (CH_2CH_3), 26.1, 26.2, 29.36, 29.39, 29.42, 29.5, 29.6, 29.7, 30.4, 31.95, 31.98 (CH_2), 68.4 (C-c), 69.2 (3″-OCH_2, 5′-OCH_2, 3‴-OCH_2, 5‴-OCH_2), 69.8 (C-b), 70.5 (C-a), 73.5 (4″-OCH_2, 4‴-OCH_2), 108.7 (C-2″, C-6″, C-2‴, C-6‴), 117.0, 117.9 (C-3, C-6, C-3′, C-6′), 134.2, 134.3, 136.2, 136.3, 137.08, 137.12 (C-4, C-5, C-4′, C-5′, C-1″, C-1‴), 148.3, 148.5 (C-1, C-2, C-1′, C-2′), 152.6 (C-3″, C-4″, C-5″, C-3‴, C-4‴, C-5‴); FTIR (ATR, cm^{-1}): $\tilde{\nu}$ = 2921 (vs), 2852 (vs), 2578 (w), 1490 (s), 1467 (s), 1430 (w), 1407 (w), 1378 (w), 1254 (s), 1198 (w), 1158 (w), 1110 (vs), 1005 (w), 893 (w), 837 (w), 776 (w), 721 (w), 698 (w), 656 (w), 623 (s), 565 (w), 553 (w); MS (MALDI-TOF): (m/z) [M]$^+$ calcd for $C_{150}H_{252}O_{17}^+$, 2326.89; found, 2325.97; Anal. Calcd for $C_{150}H_{252}O_{17}$: C, 77.40; H, 10.91; found: C, 77.57; H, 10.76.

*4,4′,5,5′-Tetrakis[3″,4″,5″-bis(decyloxy)phenyl]dibenzo[15]-crown-5 (**3b**).* From **9b**, 1.26 g (1.88 mmol). Yield: 0.65 g (0.26 mmol, 83%), colorless, waxy solid; R_f = 0.5 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (500 MHz, $CDCl_3$, δ) 0.85−0.90 (m, 36H, CH_3), 1.22−1.49 (m, 168H, CH_2), 1.65−1.75 (m, 24H, OCH_2CH_2), 3.73 (t, J = 6.4 Hz, 16H, 3″-OCH_2, 5″-OCH_2, 3‴-OCH_2, 5‴-OCH_2), 3.88 (t, J = 6.4 Hz, 8H, 4″-OCH_2, 4‴-OCH_2), 3.98−4.02 (m, 4H, H-b), 4.27−4.30 (m, 4H, H-a), 4.47 (s, 4H, H-c), 6.307, 6.314 (2 × s, 2 × 4H, H-2″, H-6″, H-3‴, H-6‴), 7.00, 7.01 (2 × s, 2 × 2H, H-3, H-6, H-3′, H-6′); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 14.1 (CH_3), 22.7 (CH_2CH_3), 26.1, 26.2, 29.38, 29.42, 29.44, 29.5, 29.66, 29.68, 29.73, 29.74, 29.8 30.4, 31.9, 32.0 (CH_2), 68.5 (C-c), 69.2 (3″-OCH_2, 5′-OCH_2, 3‴-OCH_2, 5‴-OCH_2), 69.8 (C-b), 70.5 (C-a), 73.5 (4″-OCH_2, 4‴-OCH_2), 108.7 (C-2″, C-6″, C-2‴, C-6‴), 116.9, 117.9 (C-3, C-6, C-3′, C-6′), 134.2, 134.3, 136.2, 136.3, 137.07, 137.11 (C-4, C-5, C-4′, C-5′, C-1″, C-1‴), 148.3, 148.5 (C-1, C-2, C-1′, C-2′), 152.57, 152.58 (C-3″, C-4″, C-5″, C-3‴, C-4‴, C-5‴); FTIR (ATR, cm^{-1}): $\tilde{\nu}$ = 2920 (vs), 2851 (vs), 1578 (w), 1491 (s), 1468 (s), 1430 (w), 1407 (w), 1378 (w), 1255 (s), 1196 (w), 1158 (w), 1112 (vs), 1010 (w), 896 (w), 843 (w), 782 (w), 721 (w), 698 (w), 656 (w); MS (MALDI-TOF): (m/z) [M]$^+$ calcd for $C_{162}H_{276}O_{17}^+$, 2494.07; found, 2495.72; Anal. Calcd for $C_{162}H_{276}O_{17}$: C, 77.96; H, 11.15; found: C, 77.84; H, 11.26.

*4,4′,5,5′-Tetrakis[3″,4″,5″-bis(undecyloxy)phenyl]dibenzo[15]-crown-5 (**3c**).* From **9c**, 0.60 g (0.95 mmol). Yield: 0.24 g (0.09 mmol, 54%), colorless, waxy solid; recrystallized from isopropyl alcohol; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 0.85−0.90 (m, 36H, CH_3), 1.20−1.49 (m, 192H, CH_2), 1.64−1.75 (m, 24H, OCH_2CH_2), 3.73 (t, J = 6.4 Hz, 16H, 3″-OCH_2, 5″-OCH_2, 3‴-OCH_2, 5‴-OCH_2), 3.87 (t, J = 6.4 Hz, 8H, 4″-OCH_2, 4‴-OCH_2), 3.98−4.01 (m, 4H, H-b), 4.27−4.30 (m, 4H, H-a), 4.47 (s, 4H, H-c), 6.307, 6.314 (2 × s, 2 × 4H, H-2″, H-6″, H-3‴, H-6‴), 7.00, 7.01 (2 × s, 2 × 2H, H-3, H-6, H-3′, H-6′); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 14.1 (CH_3), 22.7 (CH_2CH_3), 26.16, 26.24, 29.40, 29.41, 29.5, 29.69, 29.73, 29.76, 29.76, 29.79, 29.8, 30.4, 31.97 (CH_2), 68.5 (C-c), 69.2 (3″-OCH_2, 5″-OCH_2, 3‴-OCH_2, 5‴-OCH_2), 69.8 (C-b), 70.5 (C-a), 73.6 (4″-OCH_2, 4‴-OCH_2), 108.7 (C-2″, C-6″, C-2‴, C-6‴), 117.0, 117.9 (C-3, C-6, C-3′, C-6′), 134.2, 134.3, 136.2, 136.3, 137.08, 137.13 (C-4, C-5, C-4′, C-5′, C-1″, C-1‴), 148.3, 148.5 (C-1, C-2, C-1′, C-2′), 152.6 (C-3″, C-4″, C-5″, C-3‴, C-4‴, C-5‴); FTIR (ATR, cm^{-1}): $\tilde{\nu}$ = 2920 (vs), 2851 (vs), 1578 (s), 1491 (s), 1467 (s), 1429 (w), 1406 (w), 1379 (w), 1254 (s), 1197 (w), 1158 (w), 1111 (vs), 1008 (w), 946 (w), 840 (w), 775 (w), 720 (w), 698 (w); MS (MALDI-TOF): (m/z) [M]$^+$ calcd for $C_{174}H_{300}O_{17}^+$, 2663.26; found, 2662.98; Anal. Calcd for $C_{174}H_{300}O_{17}$: C, 78.44; H, 11.35; found: C, 78.80; H, 11.29.

*4,4′,5,5′-Tetrakis[2″,3″,4″-bis(nonyloxy)phenyl]dibenzo[15]-crown-5 (**4a**).* From **12a**, 0.52 g (0.95 mmol). Yield: 0.30 g (0.13 mmol, 80%), yellow oil; R_f = 0.1 (petroleum ether/ethyl acetate 10:1); ^{1}H NMR (500 MHz, $CDCl_3$, δ) 0.82−0.91 (m, 36H, CH_3), 1.16−1.52 (m, 144H, CH_2), 1.63−1.81 (m, 24H, OCH_2CH_2), 3.71−3.89 (m, 24H, 2″-OCH_2, 3″-OCH_2, 4″-OCH_2, 2‴-OCH_2, 3‴-OCH_2, 4‴-OCH_2), 3.99−4.03 (m, 4H, H-b), 4.23−4.28 (m, 4H, H-a), 4.41 (s, 4H, H-c), 6.39 (t, J = 8.55 Hz, 4H, 5″-H, 5″-H) 6.59 (t, J = 8.55 Hz, 4H, 6″-H, 6‴-H), 7.02 (s, 4H, H-3, H-6, H-3′, H-6′); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 14.1 (CH_3), 22.7 (CH_2CH_3), 26.01, 26.2, 26.3, 26.9, 29.33, 29.37, 29.44, 29.50, 29.55, 29.62, 29.65, 29.7, 29.8, 30.30, 30.34, 31.92, 31.99 (CH_2), 68.3 (C-c), 68.6 (OCH_2), 69.9 (C-b), 70.4 (C-a), 73.22, 73.27, 73.5 (OCH_2), 107.23, 107.27, 125.8 (C-5″, C-6″, C-5‴, C-6‴), 117.3, 118.6 (C-3, C-6, C-3′, C-6′), 128.4, 128.5, 131.5, 131.8 (C-4, C-5, C-4′, C-5′, C-1″, C-1‴), 141.5, 151.2, 152.07, 152.12 (C-2″, C-3″, C-4″, C-2‴, C-3‴, C-4‴), 147.4, 147.9 (C-1, C-2, C-1′, C-2′); FTIR (ATR, cm^{-1}): $\tilde{\nu}$ = 2921 (vs), 2853 (s), 1597 (w), 1485 (s), 1467 (s), 1376 (w), 1289 (s), 1265 (w), 1190 (w), 1088 (vs), 919 (w), 794 (w), 721 (w), 597 (w); MS (MALDI-TOF): (m/z) [M]$^+$ calcd for $C_{150}H_{252}O_{17}^+$, 2326.89; found, 2325.45; Anal. Calcd for $C_{150}H_{252}O_{17}$: C, 77.40; H, 10.91; found: C, 77.27; H, 10.81.

*4,4′,5,5′-Tetrakis[2″,3″,4″-bis(decyloxy)phenyl]dibenzo[15]-crown-5 (**4b**).* From **12b**, 0.56 g (0.95 mmol). Yield: 0.33 g (0.13 mmol, 84%), yellow oil; R_f = 0.27 (petroleum ether/ethyl acetate 30:1); ^{1}H NMR (500 MHz, $CDCl_3$, δ) 0.83−0.91 (m, 36H, CH_3), 1.18−1.52 (m, 168H, CH_2), 1.61−1.81 (m, 24H, OCH_2CH_2), 3.71−3.89 (m, 24H, 2″-OCH_2, 3″-OCH_2, 4″-OCH_2, 2‴-OCH_2, 3‴-OCH_2, 4‴-OCH_2), 4.01 (m$_c$, 4H, H-b), 4.26 (m$_c$, 4H, H-a), 4.41 (s, 4H, H-c), 6.39 (m$_c$, 4H, 5″-H, 5″-H) 6.60 (m$_c$, 4H, 6″-H, 6‴-H), 7.01 (s, 4H, H-3, H-6, H-3′, H-6′); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 14.1 (CH_3), 22.7 (CH_2CH_3), 26.00, 22.06, 26.2, 26.3, 26.9, 29.40, 29.45, 29.52, 29.56, 29.64, 29.68, 29.71, 29.75, 29.8, 30.29, 30.32, 30.34, 31.93, 31.96, 31.98 (CH_2), 68.3 (C-c), 68.6 (OCH_2), 69.9 (C-b), 70.4 (C-a), 73.22, 73.24, 73.5 (OCH_2), 107.21, 107.26, 125.8 (C-5″, C-6″, C-5‴, C-6‴), 117.3, 118.6 (C-3, C-6, C-3′, C-6′), 128.4, 128.5, 131.6, 131.8 (C-4, C-5, C-4′, C-5′, C-1″, C-1‴), 141.6, 151.2, 152.08, 152.12 (C-2″, C-3″, C-4″, C-2‴, C-3‴, C-4‴), 147.4, 147.8 (C-1, C-2, C-1′, C-2′); FTIR (ATR, cm^{-1}): $\tilde{\nu}$ = 2921 (vs), 2852 (s), 1597 (w), 1556 (w), 1517 (w), 1485 (s), 1467 (s), 1376 (w), 1289 (s), 1265 (s), 1240 (s), 1189 (s), 1112 (w), 1088 (vs), 1009 (w), 934 (w), 891 (w), 794 (w), 721 (w), 601 (w), 562 (w); MS (MALDI-TOF): (m/z) [M]$^+$ calcd for $C_{162}H_{276}O_{17}^+$, 2495.08; found, 2492.60; Anal. Calcd for $C_{162}H_{276}O_{17}$: C, 77.96; H, 11.15; found: C, 78.05; H, 10.83.

*4,4′,5,5′-Tetrakis[2″,3″,4″-bis(undecyloxy)phenyl]dibenzo[15]-crown-5 (**4c**).* From **12c**, 0.61 g (0.95 mmol). Yield: 0.31 g (0.12 mmol, 74%), yellow oil; R_f = 0.19 (petroleum ether/ethyl acetate 30:1); ^{1}H NMR (500 MHz, $CDCl_3$, δ) 0.84−0.90 (m, 36H, CH_3), 1.18−1.56 (m, 192H, CH_2), 1.63−1.81 (m, 24H, OCH_2CH_2), 3.70−3.88 (m, 24H, 2″-OCH_2, 3″-OCH_2, 4″-OCH_2, 2‴-OCH_2, 3‴-OCH_2, 4‴-OCH_2), 4.01 (m$_c$, 4H, H-b), 4.26 (m$_c$, 4H, H-a), 4.40 (s, 4H, H-c), 6.36−6.41 (m, 4H, 5″-H, 5″-H) 6.57−6.62 (m, 4H, 6″-H, 6‴-H), 7.01 (s, 4H, H-3, H-6, H-3′, H-6′); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 14.1 (CH_3), 22.7 (CH_2CH_3), 25.99, 26.01, 26.18, 26.26, 29.39, 29.43, 29.45, 29.52, 29.56, 29.68, 29.72, 29.78, 29.82, 29.85, 30.29, 30.31, 30.34, 31.95, 31.99 (CH_2), 68.3 (C-c), 68.6 (OCH_2), 69.9 (C-b), 70.4 (C-a), 73.20, 73.24, 73.5 (OCH_2), 107.17, 107.22, 125.8 (C-5″, C-6″, C-5‴, C-6‴), 117.3, 118.6 (C-3, C-6, C-3′, C-6′), 128.4, 128.5, 131.5, 131.8 (C-4, C-5, C-4′, C-5′, C-1″, C-1‴), 141.5, 151.2, 152.08, 152.14 (C-2″, C-3″, C-4″, C-2‴, C-3‴, C-4‴), 147.4, 147.8 (C-1, C-2, C-1′, C-2′); FTIR (ATR, cm^{-1}): $\tilde{\nu}$ = 2921 (vs), 2852 (s), 1597 (w), 1485 (w), 1467 (s), 1376 (w), 1290 (s), 1240 (w), 1190 (w), 1087 (vs), 943 (w), 795 (w), 721 (w); MS (MALDI-TOF): (m/z) [M]$^+$ calcd for $C_{174}H_{300}O_{17}^+$, 2663.26; found, 2662.23; Anal. Calcd for $C_{174}H_{300}O_{17}$: C, 78.44; H, 11.35; found: C, 78.64; H, 11.31.

General Procedure for the Preparation of Triphenylene Crown Ethers (5) and (6). An ice-cooled solution of the corresponding *o*-terphenyl crown ether **3** or **4** (43.0 μmol) in dry CH_2Cl_2 (30 mL) was treated with a solution of iron(III) chloride (105 mg, 0.645 mmol) in nitromethane (3.5 mL), the mixture was stirred, and nitrogen was passed through the reaction mixture during stirring in order to remove the evolving hydrogen chloride. After 5 min at 0 °C, the reaction was quenched by addition of methanol (50 mL). Then, water (50 mL) was added to the reaction mixture, and the

dx.doi.org/10.1021/jo501790d | J. Org. Chem. 2014, 79, 10143−10152

organic layer was separated, washed with water (3 × 50 mL), and dried over $MgSO_4$. After evaporation of the solvent, the products **5** and **6** were purified by flash chromatography on silica gel and/or by recrystallization.

*Bis(5,6,7,8,9,10-hexakis(nonyloxy)triphenylene)[15]crown-5 (**5a**).* From **3a**, 0.10 g (43.0 μmol). Yield: 25.0 mg (11.0 μmol, 25%), yellow, waxy solid; R_f = 0.27 (petroleum ether/ethyl acetate 5:1); recrystallized from isopropyl alcohol; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 0.83−0.92 (m, 36 H, CH_3), 1.11−1.63 (m, 144 H, CH_2), 1.82−1.98 (m, 24 H, OCH_2CH_2), 3.58, 3.76 (2 × br s, OCH_2), 4.1 (m_c, 4 H, H-a), 4.18, 4.29 (2 × br s, OCH_2), 4.43 (m_c, 4 H, H-b), 4.67 (s, 4 H, H-c), 7.46, 7.48, 7.85, 7.89 (4 × s, 4 × 2 H, H-3, H-12, H-4, H-11); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 14.1 (CH_3), 22.7 (CH_2CH_3), 26.1, 26.30, 26.34, 26.36, 29.36, 29.38, 29.44, 29.58, 29.66, 29.68, 29.77, 30.47, 30.59, 31.95, 31.99 (CH_2), 69.0 (OCH_2), 69.5 (C-c), 70.0 (C-b), 71.0 (C-a), 73.57, 74.01 (OCH_2),109.8, 110.2 (C-3, C-4, C-11, C-12), 117.06, 117.12, 125.4, 125.5, 126.1 (C-3a, C-3b, C-7a, C-7b, C-11a, C-11b), 149.4, 152.13, 152.14, 152.22, 152.23 (C-5, C-6, C-7,C-8, C-9, C-10); FTIR (ATR, cm^{-1}): $\tilde{\nu}$ = 2921 (vs), 2852 (s), 1595 (w), 1564 (w), 1532 (w), 1495 (w), 1456 (w), 1426 (s), 1415 (s), 1375 (s), 1256 (s), 1228 (w), 1164 (s), 1097 (vs), 869 (w), 809 (w); MS (MALDI-TOF): (*m*/*z*) $[M]^+$ calcd for $C_{150}H_{248}O_{17}^+$, 2322.86; found, 2321.11; Anal. Calcd for $C_{150}H_{248}O_{17}$: C, 77.54; H, 10.76; found: C, 77.25; H, 10.64.

*Bis(5,6,7,8,9,10-hexakis(decyloxy)triphenylene)[15]crown-5 (**5b**).* From **3b**, 0.10 g (40.0 μmol). Yield: 75.0 mg (30.1 μmol, 75%), white, waxy solid; R_f = 0.27 (petroleum ether/ethyl acetate 5:1); ^{1}H NMR (500 MHz, $CDCl_3$, δ) 0.83−0.92 (m, 36 H, CH_3), 1.11−1.64 (m, 168 H, CH_2), 1.82−1.98 (m, 24 H, OCH_2CH_2), 3.59, 3.76 (2 × br s, OCH_2), 4.1 (m_c, 4 H, H-a), 4.19, 4.30 (2 × br s, OCH_2), 4.43 (m_c, 4 H, H-b), 4.67 (s, 4 H, H-c), 7.46, 7.48, 7.85, 7.89 (4 × s, 4 × 2 H, H-3, H-12, H-4, H-11); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 14.1 (CH_3), 22.7 (CH_2CH_3), 26.1, 26.29, 26.31, 26.34, 29.41, 29.45, 29.59, 29.66, 29.69, 29.72, 29.75, 30.77, 30.48,, 30.59, 31.95, 31.98 (CH_2), 69.0 (OCH_2), 69.5 (C-c), 70.0 (C-b), 71.0 (C-a), 73.54, 74.00 (OCH_2),109.8, 110.2 (C-3, C-4, C-11, C-12), 117.05, 117.11, 125.4, 125.5, 126.1 (C-3a, C-3b, C-7a, C-7b, C-11a, C-11b), 149.4, 152.13, 152.15, 152.22, 152.23 (C-5, C-6, C-7,C-8, C-9, C-10); FTIR (ATR, cm^{-1}): $\tilde{\nu}$ = 2920 (vs), 2851 (s), 1596 (w), 1563 (w), 1534 (w), 1495 (w), 1455 (w), 1430 (s), 1414 (s), 1377 (s), 1257 (s), 1227 (w), 1164 (s), 1101 (vs), 870 (w), 810 (w); MS (MALDI-TOF): (*m*/*z*) $[M]^+$ calcd for $C_{162}H_{272}O_{17}^+$, 2490.04; found, 2489.06; Anal. Calcd for $C_{162}H_{272}O_{17}$: C, 78.08; H, 11.00; found: C, 78.10; H, 10.90.

*Bis(5,6,7,8,9,10-hexakis(undecyloxy)triphenylene)[15]crown-5 (**5c**).* From **3c**, 114.4 mg (43.0 μmol). Yield: 39.9 mg (15.0 μmol, 33%), colorless, waxy solid; recrystallized from isopropyl alcohol; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 0.82−0.92 (m, 36H, CH_3), 1.10−1.64 (m, 192H, CH_2), 1.81−2.00 (m, 24H, OCH_2CH_2), 3.58, 3.77 (2 × br s, OCH_2), 4.1 (m_c, 4H, H-a), 4.19, 4.31 (2 × br s, OCH_2), 4.43 (m_c, 4H, H-b), 4.67 (s, 4H, H-c), 7.46, 7.48, 7.85, 7.89 (4 × s, 4 × 2H, H-3, H-12,H-4, H-11); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 14.1 (CH_3), 22.7 (CH_2CH_3), 26.1, 26.3, 29.40, 29.43, 29.6, 29.72, 29.76, 29.81, 29.85, 30.47, 30.58, 31.95, 31.97 (CH_2), 69.0 (OCH_2), 69.5 (C-c), 69.9 (C-b), 71.0 (C-a), 73.5, 74.0 (OCH_2),109.8, 110.2 (C-3, C-4, C-11, C-12), 117.0, 117.1, 125.4, 125.5, 126.0 (C-3a, C-3b, C-7a, C-7b, C-11a, C-11b), 149.4, 152.1, 152.2, (C-5, C-6, C-7,C-8, C-9, C-10); FTIR (ATR, cm^{-1}): $\tilde{\nu}$ = 2920 (vs), 2851 (s), 1595 (w), 1563 (w), 1533 (w), 1495 (w), 1456 (s), 1427 (s), 1416 (s), 1375 (s), 1258 (s), 1228 (w), 1165 (s), 1099 (vs), 941 (w), 893 (w), 832 (w), 809 (w), 721 (w), 625 (s), 556 (w), 545 (w); MS (MALDI-TOF): (*m*/*z*) $[M]^+$ calcd for $C_{174}H_{296}O_{17}^+$, 2659.23; found, 2657.96; Anal. Calcd for $C_{174}H_{296}O_{17}$: C, 78.56; H, 11.22; found: C, 78.59; H, 11.01.

*Bis(4,5,6,9,10,11-hexakis(nonyloxy)triphenylene)[15]crown-5 (**6a**).* From **4a**, 100 mg (43.0 μmol). Yield: 34.9 mg (15.0 μmol, 36%), colorless, waxy solid; recrystallized from isopropyl alcohol; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 0.80−0.92 (m, 36H, CH_3), 1.19−1.61 (m, 144H, CH_2), 1.83−1.96 (m, 24H, OCH_2CH_2), 3.94−4.00 (m, 8H, 4-, 11-, 4′-, 11′-OCH_2), 4.06−4.09 (m, 4H, H-b), 4.13−4.21 (m, 16H, 5-, 6-, 9-, 10-OCH_2) 4.42−4.46 (m, 4H, H-a), 4.64 (s, 4H, H-c), 7.61 (s, 4-H, H-7, H-8), 9.18, 9.21 (2 × s, 2 × 2H, H-3, H-12); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 14.1 (CH_3), 22.7 (CH_2CH_3), 26.17, 26.21, 26.3, 29.31, 29.34, 29.42, 29.49, 29.56, 29.63, 29.66, 29.71, 29.74, 30.57, 30.61, 30.64, 31.91, 31.94, 31.97 (CH_2), 67.9 (C-c), 68.9 (OCH_2), 69.9, 70.1 (C-a, C-b), 74.14 (OCH_2), 102.3 (C-7, C-8), 111.6, 113.1 (C-3, C-12), 118.97, 119.01, 124.2, 124.4, 126.5, 126.6 (C-3a, C-3b, C-7a, C-7b, C-11a, C-11b), 142.47, 142.49, 147.5, 147.9, 151.2, 151.75, 151.77 (C-4, C-5, C-6, C-9, C-10, C-11); FTIR (ATR, cm^{-1}): $\tilde{\nu}$ = 2954 (w), 2920 (vs), 2851 (vs), 1601 (w), 1571 (w), 1507 (w), 1489 (w), 1466 (s), 1436 (w), 1415 (s), 1378 (s), 1276 (s), 1257 (s), 1217 (w), 1167 (w), 1115 (w), 1091 (s), 908 (w), 819 (w), 721 (w), 631 (s); MS (MALDI-TOF): (*m*/*z*) $[M]^+$ calcd for $C_{150}H_{248}O_{17}^+$, 2322.86; found, 2321.74; Anal. Calcd for $C_{150}H_{248}O_{17}$: C, 77.54; H, 10.76; found: C, 77.35; H, 10.70.

*Bis(4,5,6,9,10,11-hexakis(decyloxy)triphenylene)[15]crown-5 (**6b**).* From **4b**, 107.3 mg (43.0 μmol). Yield: 89.7 mg (36.0 μmol, 83%), colorless, waxy solid; recrystallized from isopropyl alcohol; ^{1}H NMR (500 MHz, $CDCl_3$, δ) 0.79−0.92 (m, 36H, CH_3), 1.19−1.62 (m, 168H, CH_2), 1.84−1.96 (m, 24H, OCH_2CH_2), 3.94−4.00 (m, 8H, 4-, 11-, 4′-, 11′-OCH_2), 4.08 (t, $J_{b\text{-}a}$ = 4.95 Hz, 4H, H-b), 4.13−4.21 (m, 16H, 5-, 6-, 9-, 10-OCH_2), 4.44 (t, $J_{a\text{-}b}$ = 4.95 Hz, 4H, H-a), 4.65 (s, 4H, H-c), 7.62 (s, 4-H, H-7, H-8), 9.18, 9.21 (2 × s, 2 × 2H, H-3, H-12); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 14.1 (CH_3), 22.7 (CH_2CH_3), 26.1, 26.2, 26.31, 29.37, 29.39, 29.4, 29.50, 29.55, 29.6, 29.71, 29.76, 29.79, 30.58, 30.61, 30.65, 31.93, 31.97 (CH_2), 67.9 (C-c), 68.9 (OCH_2), 69.9, 70.0 (C-a, C-b), 74.14 (OCH_2), 102.33 (C-7, C-8), 111.7, 113.1 (C-3, C-12), 118.97, 119.01, 124.2, 124.4, 126.5, 126.6 (C-3a, C-3b, C-7a, C-7b, C-11a, C-11b), 142.46, 142.49, 147.5, 147.9, 151.2, 151.75, 151.77 (C-4, C-5, C-6, C-9, C-10, C-11); FTIR (ATR, cm^{-1}): $\tilde{\nu}$ = 2954 (w), 2919 (vs), 2850 (vs), 1601 (w), 1571 (w), 1507 (w), 1489 (w), 1466.73 (s), 1435 (w), 1414 (s), 1377 (s), 1275 (s), 1256 (s), 1216 (w), 1169 (w), 1139 (w), 1090 (s), 1051 (s), 974 (w), 920 (w), 819 (s), 789 (w), 720 (w), 640 (w), 611 (w), 563 (w), 547 (w); MS (MALDI-TOF): (*m*/*z*) $[M]^+$ calcd for $C_{162}H_{272}O_{17}^+$, 2491.05; found, 2489.58; Anal. Calcd for $C_{174}H_{296}O_{17}$: C, 78.56; H, 11.22; found: C, 78.50; H, 11.13.

*Bis(4,5,6,9,10,11-hexakis(undecyloxy)triphenylene)[15]crown-5 (**6c**).* From **4c**, 114.4 mg (43.0 μmol). Yield: 66.5 mg (25.0 μmol, 57%), colorless, waxy solid; R_f = 0.08 (petroleum ether/ethyl acetate 40:1); ^{1}H NMR (500 MHz, $CDCl_3$, δ) 0.85−0.91 (m, 36 H, CH_3), 1.18−1.64 (m, 192 H, CH_2), 1.84−1.97 (m, 24 H, OCH_2CH_2), 3.94−4.00 (m, 8 H, 4-, 11-, 4′-, 11′-OCH_2), 4.06−4.09 (m, 4 H, H-b), 4.13−4.21 (m, 16 H, 5-, 6-, 9-, 10-OCH_2) 4.42−4.45 (m, 4 H, H-a), 4.64 (s, 4 H, H-c), 7.61 (s, 4-H, H-7, H-8, H-7′, H-8′), 9.18, 9.21 (2 × s, 2 × 2 H, H-3, H-12); ^{13}C NMR (125 MHz, $CDCl_3$, δ) 14.1 (CH_3), 22.7 (CH_2CH_3), 26.20, 26.24, 26.31, 29.39, 29.42, 29.50, 29.56, 29.69, 29.77, 30.57, 30.62, 30.64, 31.94, 31.96 (CH_2), 65.8 (C-c), 67.9 (OCH_2), 68.9, 70.0 (C-a, C-b), 74.1 (OCH_2), 102.3 (C-7, C-8), 111.8, 113.4 (C-3, C-12), 119.0, 126.5, 126.6, 128.5, 128.6 (C-3a, C-3b, C-7a, C-7b, C-11a, C-11b), 142.47, 142.50, 147.5, 147.9, 151.2, 151.74, 151.76 (C-4, C-5, C-6, C-9, C-10, C-11); FTIR (ATR, cm^{-1}): $\tilde{\nu}$ = 2954 (w), 2918 (vs), 2850 (vs), 1601 (w), 1572 (w), 1507 (w), 1489 (w), 1466 (s), 1436 (w), 1415 (s), 1377 (s), 1276 (s), 1258 (s), 1218 (w), 1171 (w), 1115 (w), 1090 (s), 937 (w), 891 (w), 820 (w), 806 (w), 788 (w), 721 (w), 630 (s), 540 (s), 519 (w); MS (MALDI-TOF): (*m*/*z*) $[M]^+$ calcd for $C_{174}H_{296}O_{17}^+$, 2659.23; found, 2657.61.

■ ASSOCIATED CONTENT

Supporting Information

^{1}H and ^{13}C NMR spectra for compounds **3**, **4**, **5**, **6**, **9**, and **12**; DSC traces; and further XRD data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: Sabine.Laschat@oc.uni-stuttgart.de (S.L.).

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Generous financial support by the International Max Planck Research School for Advanced Materials (fellowships for M.K.), the Bundesministerium für Bildung und Forschung, the Fonds der Chemischen Industrie, and the Ministerium für Wissenschaft, Forschung und Kunst des Landes Baden-Württemberg is gratefully acknowledged. We would like to thank Katharina Kress for performing molecular modeling studies.

■ REFERENCES

(1) Reviews: (a) Sergeyev, S.; Pisula, W.; Geerts, Y. H. *Chem. Soc. Rev.* **2007**, *36*, 1902−1929. (b) Laschat, S.; Baro, A.; Steinke, N.; Giesselmann, F.; Hägele, C.; Scalia, G.; Judele, R.; Kapatsina, E.; Sauer, S.; Schreivogel, A.; Tosoni, M. *Angew. Chem.* **2007**, *119*, 4916−4973; *Angew. Chem., Int. Ed.* **2007**, *46*, 4832−4887. (c) Grimsdale, A. C.; Müllen, K. *Angew. Chem.* **2005**, *117*, 5732−5772; *Angew. Chem., Int. Ed.* **2005**, *44*, 5592−5629.

(2) Lehn, J.-M.; Malthête, J.; Levelut, A.-M. *J. Chem. Soc., Chem. Commun.* **1985**, 1794−1796.

(3) He, G.-X.; Wada, F.; Kikukawa, K.; Matsuda, T. *J. Chem. Soc., Chem. Commun.* **1987**, 1294−1296.

(4) Reviews: (a) Kaller, M.; Baro, A.; Laschat, S. Liquid Crystal Crown Ethers and Related Compounds. In *Handbook of Liquid Crystals*; Tschierske, C., Ed.; Wiley: New York, 2013; Vol. *6*, pp 335−376. (b) Kaller, M.; Laschat, S. *Top. Curr. Chem.* **2012**, *318*, 109−192. (c) Akopova, O. B. *J. Struct. Chem.* **2006**, *47*, 120−129. (d) Blake, A. J.; Bruce, D. W.; Fallis, I. A.; Parsons, S.; Richtzenhain, H.; Ross, S. A.; Schroder, M. *Philos. Trans. R. Soc., A* **1996**, *354*, 395−414.

(5) (a) Percec, V.; Johansson, G.; Heck, J.; Ungar, G.; Batty, S. V. *J. Chem. Soc., Perkin Trans. 1* **1993**, 1411−1420. (b) Johansson, G.; Percec, V.; Ungar, G.; Abramic, D. *J. Chem. Soc., Perkin Trans. 1* **1994**, 447−459. (c) Percec, V.; Johansson, G.; Ungar, G.; Zhou, J. *J. Am. Chem. Soc.* **1996**, *118*, 9855−9866. (d) Percec, V.; Cho, W.-D.; Ungar, G.; Yeardley, D. J. P. *Chem.—Eur. J.* **2002**, *8*, 2011−2025.

(6) (a) Shinkai, S.; Nishi, T.; Ikeda, A.; Matsuda, T.; Shimamoto, K.; Manabe, O. J. *Chem. Soc., Chem. Commun.* **1990**, 303−304. (b) Kimura, K.; Kawai, Y.; Oosaki, S.; Yajima, S.; Yoshioka, Y.; Sakurai, Y. *Anal. Chem.* **2002**, *74*, 5544−5549. (c) Oosaki, S.; Yajima, S.; Kimura, K. *Anal. Sci.* **2007**, *23*, 963−967. (d) Wang, R.; Liu, W.; Chen, Y.; Zuo, J.-L.; You, X.-Z. *Dyes Pigm.* **2009**, *81*, 40−44. (e) Nishi, T.; Ikeda, A.; Matsuda, T.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1991**, 339−341. (f) Shinkai, S.; Nishi, T.; Matsuda, T. *Chem. Lett.* **1991**, 437−440. (g) Vögtle, F.; Knops, P. *Angew. Chem.* **1991**, *103*, 972−974; *Angew. Chem., Int. Ed.* **1991**, *30*, 958−960. (h) Wright, J. D.; Roisin, P.; Rigby, G. P.; Nolte, R. J. M.; Cook, M. J.; Thorpe, S. C. *Sens. Actuators, B* **1993**, *13*, 276−280.

(7) (a) Beginn, U.; Zipp, G.; Möller, M. *J. Polym. Sci., Part A* **2000**, *38*, 631−640. (b) Beginn, U.; Zipp, G.; Möller, M. *Chem.—Eur. J.* **2000**, *6*, 2016−2023. (c) Beginn, U.; Zipp, G.; Möller, M. *Adv. Mater.* **2000**, *12*, 510−513. (d) Beginn, U.; Zipp, G.; Mourran, A.; Walther, P.; Möller, M. *Adv. Mater.* **2000**, *12*, 513−516. (e) Beginn, U.; Zipp, G.; Möller, M.; Johansson, G.; Percec, V. *Macromol. Chem. Phys.* **1997**, *198*, 2839−2852. (f) Percec, V.; Zipp, G.; Johansson, G.; Beginn, U.; Moeller, M. *Macromol. Chem. Phys.* **1997**, *198*, 265−277.

(8) (a) Kaller, M.; Staffeld, P.; Haug, R.; Frey, W.; Giesselmann, F.; Laschat, S. *Liq. Cryst.* **2011**, *38*, 531−553. (b) Steinke, N.; Kaller, M.; Nimtz, M.; Baro, A.; Laschat, S. *Liq. Cryst.* **2010**, *37*, 1139−1149. (c) Steinke, N.; Frey, W.; Baro, A.; Laschat, S.; Drees, C.; Nimtz, M.; Hägele, C.; Giesselmann, F. *Chem.—Eur. J.* **2006**, *12*, 1026−1035. (d) Steinke, N.; Jahr, M.; Lehmann, M.; Baro, A.; Frey, W.; Tussetschläger, S.; Sauer, S.; Laschat, S. *J. Mater. Chem.* **2009**, *19*, 645−654. (e) Kaller, M.; Tussetschläger, S.; Fischer, P.; Deck, C.; Baro, A.; Giesselmann, F.; Laschat, S. *Chem.—Eur. J.* **2009**, *15*, 9530−9542. (f) Schultz, A.; Laschat, S.; Saipa, A.; Gießelmann, F.; Nimtz, M.; Schulte, J. L.; Baro, A.; Miehlich, B. *Adv. Funct. Mater.* **2004**, *14*, 163−168.

(9) Kaller, M.; Deck, C.; Meister, A.; Hause, G.; Baro, A.; Laschat, S. *Chem.—Eur. J.* **2010**, *16*, 6326−6337.

(10) Scholl, R.; Seer, C. *Justus Liebigs Ann. Chem.* **1912**, *394*, 111−177.

(11) Reviews: (a) Grzybowski, M.; Skonieczny, K.; Butenschön, H.; Gryko, D. T. *Angew. Chem.* **2013**, *125*, 10084−10115; *Angew. Chem., Int. Ed.* **2013**, *52*, 9900−9930. (b) Mullin, R. J.; Corbett, M. T. Scholl Reaction. In *Name Reactions for Carbocyclic Ring Formations*; Li, J. J., Ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2010; pp 409−422. (c) Musgrave, O. C. *Chem. Rev.* **1969**, *69*, 499−531.

(12) Mechanistic work on the Scholl reaction: (a) Danz, M.; Tonner, R.; Hilt, G. *Chem. Commun.* **2012**, *48*, 377−379. (b) Zhai, L.; Shukla, R.; Wadumethrige, S. H.; Rathore, R. *J. Org. Chem.* **2010**, *75*, 4748−4760. (c) Zhai, L.; Shukla, R.; Rathore, R. *Org. Lett.* **2009**, *11*, 3474−3477. (d) Rempala, P.; Kroulík, J.; King, B. T. *J. Org. Chem.* **2006**, *71*, 5067−5081. (e) Rempala, P.; Kroulík, J.; King, B. T. *J. Am. Chem. Soc.* **2004**, *126*, 15002−15003.

(13) Kaller, M.; Beardsworth, S. J.; Staffeld, P.; Tussetschläger, S.; Gießelmann, F.; Laschat, S. *Liq. Cryst.* **2012**, *39*, 607−618.

(14) Staffeld, P.; Kaller, M.; Beardsworth, S. J.; Tremel, K.; Ludwigs, S.; Laschat, S.; Giesselmann, F. *J. Mater. Chem. C* **2013**, *1*, 892−901.

(15) Pisula, W.; Feng, X.; Müllen, K. *Adv. Mater.* **2010**, *22*, 3634−3649.

(16) Chen, Z.; Baumeister, U.; Tschierske, C.; Würthner, F. *Chem.—Eur. J.* **2007**, *13*, 450−465.

(17) (a) Pradhan, A.; Dechambenoit, P.; Bock, H.; Durola, F. *J. Org. Chem.* **2013**, *78*, 2266−2274. (b) Pradhan, A.; Dechambenoit, P.; Bock, H.; Durola, F. *Angew. Chem.* **2011**, *123*, 12790−12793; *Angew. Chem., Int. Ed.* **2011**, *50*, 12582−12585.

(18) Chen, J.-D.; Lu, H.-Y.; Chen, C.-F. *Chem.—Eur. J.* **2010**, *16*, 11843−11846.

(19) King, B. T.; Kroulík, J.; Robertson, C. R.; Rempala, P.; Hilton, C. L.; Korinek, J. D.; Gortari, L. M. *J. Org. Chem.* **2007**, *72*, 2279−2288.

(20) (a) Wang, Z.; Dötz, F.; Enkelmann, V.; Müllen, K. *Angew. Chem.* **2005**, *117*, 1273−1276; *Angew. Chem., Int. Ed.* **2005**, *44*, 1247−1250. (b) Cameron, D. W.; Riches, A. G. *Tetrahedron Lett.* **1995**, *36*, 2331−2334.

(21) Martinez-Palau, M.; Perea, E.; Lopez-Calahorra, F.; Velasco, D. *Lett. Org. Chem.* **2004**, *1*, 231−237.

(22) Lee, H.; Kim, D.; Lee, H.-K.; Qiu, W.; Oh, N.-K.; Zin, W.-C.; Kim, K. *Tetrahedron Lett.* **2004**, *45*, 1019−1022.

(23) Maeda, H.; Haketa, Y.; Nakanishi, T. *J. Am. Chem. Soc.* **2007**, *129*, 13661−13674.

(24) Similar procedure as seen in: Attias, A.-J.; Cavalli, C.; Donnio, B.; Guillon, D.; Hapiot, P.; Malthête, J. *Chem. Mater.* **2002**, *14*, 375−384.

(25) Wang, Y.; Stretton, A. D.; McConnell, M. C.; Wood, P. A.; Parsons, S.; Henry, J. B.; Mount, A. R.; Galow, T. H. *J. Am. Chem. Soc.* **2007**, *129*, 13193−13200.

(26) Avogadro: an open-source molecular builder and visualization tool, Version 1.1.1. http://avogadro.openmolecules.net/.

(27) Ahmed, F. R.; Trotter, J. *Acta Crystallogr.* **1963**, *16*, 503−508.

(28) Wu, J.; Watson, M. D.; Zhang, L.; Wang, Z.; Müllen, K. *J. Am. Chem. Soc.* **2004**, *126*, 177−186.