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Columnar Propeller-like 1,3,5-Triphenylbenzenes: Probing the Effect of Chlorine on the Suzuki Cross Coupling and Liquid Crystalline Properties

Marco André Grunwald,[a] Tobias Wöhrle,[a] Robert Forschner,[a] Angelika Baro,[a] and Sabine Laschat*[a]

Abstract: Suzuki cross couplings either between chlorinated *N*-methyliminodiacetic acid (MIDA)-protected aryl boronates and 1,3,5-tribromobenzene or between chlorinated aryl bromides and phenyltrisboronic species to star-shaped 1,3,5-triphenylbenzenes with different substitution patterns and chloro substituents at the outer phenyl rings were studied. The chlorinated precursors required for the respective reaction were synthesized and characterized. Depending on the used coupling reaction target triphenylbenzenes were isolated in yields between 42% and 88%. Their mesomorphic properties were influenced by the substitution pattern and number of peripheral chlorine atoms. Triphenylbenzene with 3,5-alkoxy substitution and H in *para*-position self-assembled into either columnar hexagonal ($\mathrm{Col_h}$) mesophases or a soft crystal. While threefold chloro substitution in *meta*-position of the outer phenyl rings led to stable room temperature $\mathrm{Col_{ho}}$ phases, triphenylbenzenes with threefold *para*-chloro or 3,5-dichloro substitution were non-mesomorphic. Based on X-ray diffraction data a helical packing model for the observed phases similar to that of related alkoxy-substituted triphenylbenzenes was proposed.

Keywords: cross coupling • triphenylbenzenes • liquid crystals • MIDA-boronates • mesophases

Key Topic: Cross Coupling

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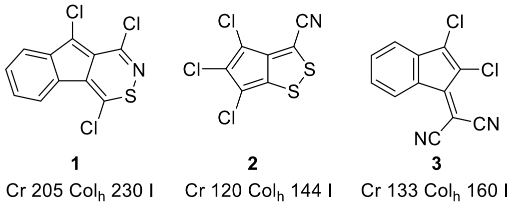
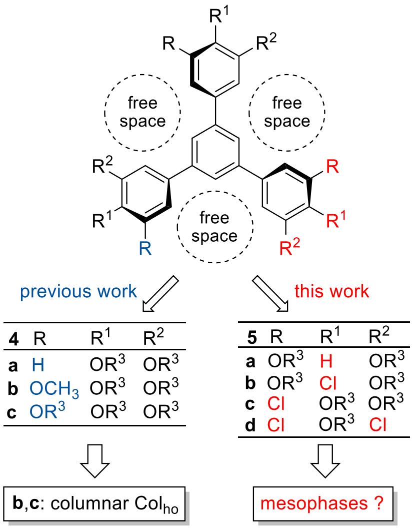
Introduction

The archetypal discotic liquid crystal contains a central rigid aromatic or heteroaromatic core surrounded by peripheral flexible chains, which self-assembles into columnar mesophases due to $\pi-\pi$ interactions of the core, while the chains stabilize the columnar phase through van der Waals interactions and suppress crystallization due to their flexibility.[1,2] These self-assembled structures are interesting because their 1D charge carrier mobility and self-healing of defects make them suitable for molecular electronics applications.[3,4] However, long alkoxy side chains can cause synthetic challenges (e.g., purification and solubility) and furthermore, limit applications by clearing points close to the thermal decomposition temperature.[5,6] Thus, discotic liquid crystals where peripheral alkoxy chains have been replaced by some surrogate would be highly attractive. In a groundbreaking work Ros and Torroba demonstrated that small aromatic and heterocyclic compounds **1**–**3** devoid of any alkoxy groups, but carrying polarizable chlorine atoms form stable columnar mesophases (Scheme 1).[7,8] In addition, a beneficial effect of chloro (or fluoro) substituents on the mesomorphic properties and a decrease of phase transition temperatures were independently reported for bent core liquid crystals by Twieg[9,10] and for ionic liquid crystals by Binnemans.[11]



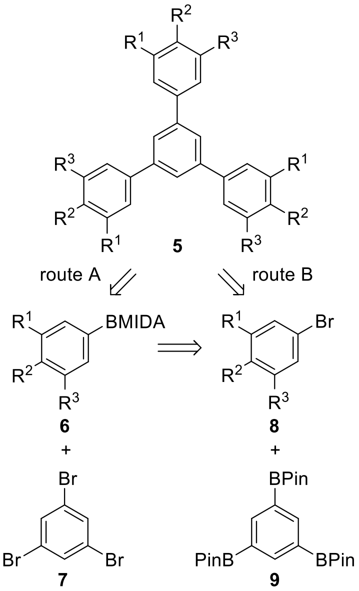
Scheme 1. Selected liquid crystalline pseudoazulenes (**1**, **2**) and indene derivative **3**.[7,8]

Star-shaped 1,3,5-triphenylbenzenes such as **4** (Scheme 2) belong to the class of shape-persistent hekates which are able to form columnar mesophases.[12–15] Space-filling between the three arms are achieved either by helical twisting along the columnar axis, or by incorporation of bulky guest molecules covalently or non-covalently bound to the star, giving rise to unique self-assembled structures.[5,16–20]



Scheme 2.

In previous work on tris(trialkoxyphenyl)benzenes **4** the methoxy group was reported to serve as a minimalistic alkoxy unit at the outer phenyl rings, resulting in decreased clearing temperature while keeping the stable columnar mesophase.[5] Motivated by this observation we surmised that omission or successive replacement of alkoxy side chains by chloro substituents might affect the phase behaviour in a similar fashion. Furthermore, the relevance of van der Waals interactions vs. halogen bonding and dipolar interactions on the self-assembly and the resulting phase transitions temperatures could be elucidated. To study the effects in more detail, convenient synthetic access to (poly)chlorinated triphenylbenzenes **5** is required. In contrast to the plethora of well-explored Suzuki-Miyaura cross coupling of aryl halides with aryl boron species,[21–25] the use of di- and poly-chlorinated reactants has been mostly devoted to access polychlorinated biphenyl (PCB) derivatives for ecotoxicity and analytical property studies.[26–33] In order to get access to triphenylbenzenes **5** we followed two synthetic strategies involving a cross coupling as key step (Scheme 3). Compound **5** is derived either from Suzuki-Miyaura cross coupling between aryl boronic species **6** (e.g., *N*-methyliminodiacetic acid (MIDA) boronates[34–39]) and 1,3,5-tribromobenzene **7** (route A) or alternatively, by the connection of aryl bromides **8** and 1,3,5-phenyltrisboronic species **9** (e.g., pinacole boronate) (route B). The results towards the synthesis of compounds **5** and study of their mesomorphic properties are reported below.

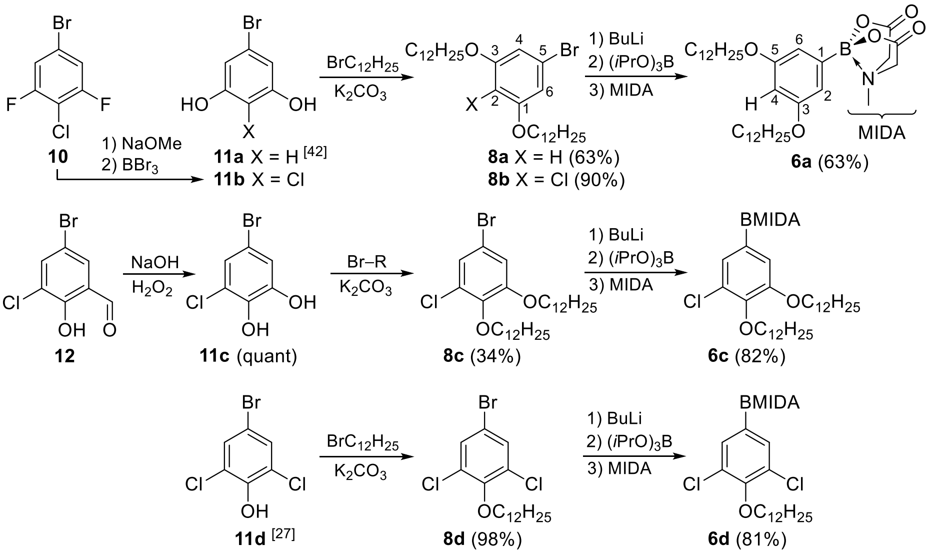


Scheme 3. Retrosynthetic pathways to star-shaped triphenylbenzenes **5**.

Results and Discussion

Synthesis of Star-Shaped Triphenylbenzene Derivatives

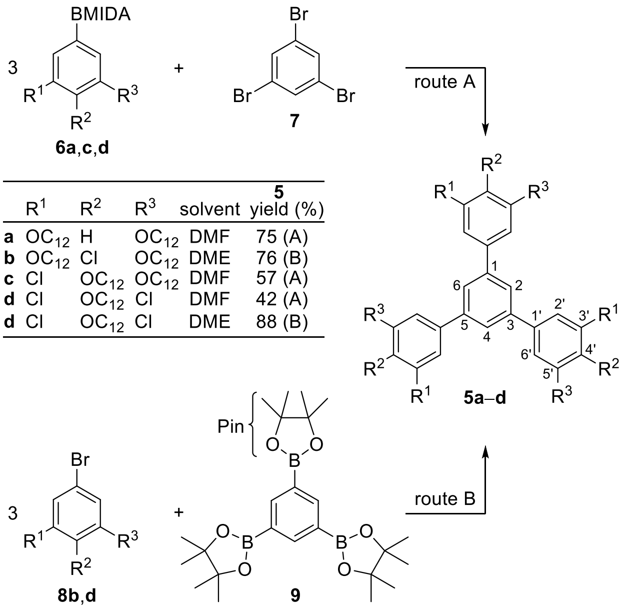
The synthesis of precursor MIDA-protected aryl boronates **6** for Suzuki-Miyaura cross coupling[40,41] according to route A and aryl bromides **8** is depicted in Scheme 4. Williamson etherification of 5-bromo-3-hydroxyphenol **11a**[42] with bromododecane in the presence of K_2CO_3 gave aryl bromide **8a** in 63% yield (Scheme 4).[43] Subsequent treatment with *n*-BuLi in THF at –78 °C, triisopropyl borate and finally *N*-methyliminodiacetic acid (MIDA) according to literature procedures[37,44] yielded boronate **6a** in 63%. Dakin oxidation of 5-bromo-3-chloro-2-hydroxybenzaldehyde **12**[36] gave bromide **11c** quantitatively, which was etherified with bromododecane to yield bromide **8c**. Conversion of **8c** under the conditions described above for **8a** afforded MIDA boronate **6c** in 28% overall yield. Williamson etherification of 4-bromo-2,6-dichlorophenol **11d**[27] with bromododecane yielded aryl bromide **8d** in 98%. Its conversion into MIDA boronate **6d** proceeded in 81% without any event.



Scheme 4. Synthesis of precursors **6** and **8** (numbering for NMR assignment; for details see also the Supporting Information).

The preparation of the *para*-chloro-substituted aryl bromide **8b** commenced with a nucleophilic displacement of 3-bromo-2-chloro-1,3-difluorobenzene **10** using NaOMe in dimethylacetamide. Demethylation of the resulting 5-bromo-2-chloro-1,3-dimethoxybenzene with BBr_3 and subsequent Williamson etherification afforded bromide **8b** in 90% over 2 steps.

We next studied the Suzuki-Miyaura coupling reaction following route A (Scheme 5).[37,45] Treatment of aryl MIDA boronate **6a** (3 equivalents) with 1 M NaOH in THF at room temperature for 15 min removed the MIDA group. To the resulting free boronic acid were immediately added 1,3,5-tribromobenzene **7** (1 equivalent) in the presence of $Pd(PPh_3)_4$ (6 mol%) and K_2CO_3 (4.5 equivalents) in DMF / H_2O, and the reaction mixture was stirred at 90 °C for 24 h. After workup and chromatographic purification, the desired star-shaped compound **5a** was isolated in 75% yield. Under these reaction conditions chlorinated MIDA boronates **6c**,**d** were coupled with **7** to the corresponding triarylbenzenes **5c**,**d** which were isolated in 57 and 42% yield, respectively (Scheme 5). Owing to decrease of yield we were worried that the chloro substituent might interfere with Pd-catalyzed cross coupling, because the Suzuki-Miyaura reaction was planned as a key step in both routes A and B. While the higher bonding dissociation enthalpy of the C–Cl bond as compared to the C–Br bond should favor participation of the latter in the oxidative addition step of the Suzuki-Miyaura reaction,[21–25,46–49] examples of competitive participation of C–Cl bonds are known.[46–49] In the presence of suitable catalysts the reactivity of aryl chlorides was not only increased,[50–52] but in some cases it even exceeded that of the corresponding aryl bromides.[46–49] Therefore, to improve the yield and prevent multiple borylation of star-shaped compound **5d**, the Suzuki-Miyaura coupling reaction via route B was studied (Scheme 5).



	R^1	R^2	R^3	solvent	**5** yield (%)
a	OC_{12}	H	OC_{12}	DMF	75 (A)
b	OC_{12}	Cl	OC_{12}	DME	76 (B)
c	Cl	OC_{12}	OC_{12}	DMF	57 (A)
d	Cl	OC_{12}	Cl	DMF	42 (A)
d	Cl	OC_{12}	Cl	DME	88 (B)

A: 1) 1M $NaOH_{aq}$, THF, rt, 15 min;
2) **6**, K_2CO_3, $[Pd(PPh_3)_4]$, H_2O, solvent, N_2, 90 °C, 24 h
B: K_2CO_3, $[Pd(PPh_3)_4]$, H_2O, solvent, N_2, 95 °C, 24 h

Scheme 5. Synthesis of the 1,3,5triphenylbenzenes **5** (numbering for NMR assignment).

Commercially available 1,3,5-tris(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)benzene **9** was reacted with 3,5-dichlorinated aryl bromide **8d** in the presence of 6.5 mol% of $Pd(PPh_3)_4$ under otherwise identical conditions to provide the desired triarylbenzene **5d** in 88% yield. Analogously, the Suzuki-Miyaura cross coupling between borolane **9** and aryl bromide **8b** yielded 76% of the star-shaped triphenylbenzene derivative **5b**, which is complementary to compound **5a**, i.e. carrying a chloro substituent rather than a H atom in the *para*-position (Scheme 5). When comparing both routes, route B apparently is favoured against route A. Obviously, when central borolane core **9** has fully reacted to the desired triphenylbenzene **5b** or **5d** additional coupling reactions are unlikely.

Mesomorphic properties of MIDA-boronates and triphenylbenzenes

Mesomorphic properties of triphenylbenzenes **5** as well as the MIDA-boronates **6** were investigated by differential scanning calorimetry (DSC), polarized optical microscopy (POM) and X-ray diffraction (WAXS, SAXS). The DSC results are summarized in Table 1 (for DSC traces see Figures S3 and S4) and visualised in Figure 1.

During examination of precursors **6** by DSC and POM we noticed liquid crystalline behaviour for MIDA boronate **6a**,**c**,**d** which is in line with previous studies.[44]

Table 1. Phase transition temperatures [°C] and enthalpies ΔH [kJ mol^{-1}] of MIDA-boronates **6** and triphenylbenzenes **5** upon second heating (H) and cooling (C) (rate 5 K min^{-1}).[a]

Compound	Phase	*T* (ΔH)	Phase	*T* (ΔH)	Phase	
6a	Cr[b]	75	Col$_h$	119 (0.86)	I	H
	Cr[b]	75	Col$_h$	118 (0.84)	I	C
6c	Cr	97 (39.1)	Col$_h$	141 (0.5)	I	H
	Cr	78 (2.1)	Col$_h$	140 (0.4)	I	C
6d	Cr	164 (10.9)	SmA	198 (2.1)	I	H[c]
	Cr	112 (6.2)	SmA	197 (2.0)	I	C[c]
5a	Cr	20 (59.7)	Col$_{ho}$	49 (33.2)	I	H
	Cr	16 (68.3)	Col$_{ho}$	40 (35.0)	I	C
5b	Cr	115 (50.0)	–	–	I	H
	Cr	110 (47.9)	–	–	I	C
5c	Cr	17 (16.8)	Col$_{ho}$	89 (14.3)[d]	I	H
	Cr	6 (25.9)	Col$_{ho}$	94 (16.8)[d]	I	C
5d	Cr	38 (18.6)	–	–	I	H[f]
	Cr[e]	–78	–	–	I	C[f]

[a] Without additional Cr–Cr transitions. The onset points of the heat flow peaks were used for the determination of the corresponding transition temperature. Phases observed: Cr crystalline; SmA smectic A; Col$_h$ columnar hexagonal; I isotropic; X unknown phase. [b] Determined by POM. [c] First cycle. [d] Peak temperatures: 95 °C (H) and 91 °C (C). [e] Glass transition (supercooled). [f] Heating/cooling rate 10 K min^{-1}.

The DSC results for MIDA boronate **6c** exhibit that one chloro substituent in the *meta*-position led to a higher melting temperature of 97 °C, but lowered the mesophase-to-isotropic liquid transition to 141 °C in the heating scan relative to the transition temperatures of [3,4-bis(dodecyloxy)phenyl]-MIDA boronate **13**[44] (Figure 1, Table 1). Upon cooling the clearing temperature is maintained while supercooling for the mesophase–Cr transition to 78 °C and two further Cr–Cr transitions at 66 °C and 60 °C were observed. The chloro substituent seems to decrease the crystallization temperature in a similar fashion as compared to flexible alkoxy chains. Boronate **6d** carrying lateral chlorine atoms in 3,5-position revealed increased melting and clearing transitions upon heating (Table 1). In the cooling cycle the melting transition is shifted to lower temperature and this supercooling is accompanied by glassy solidification of the sample, which could already be seen under the POM due to the absence of crystallization. These observations further strengthen the previous assumption that chlorine would counteract crystallization. For [3,5-bis(dodecyloxy)phenyl]-MIDA-boronate **6a**, a melting transition at 75 C° and a clearing temperature lower than that of the 3,4-disubstituted **13** were observed (119 °C vs 169 °C) (Figure 1).

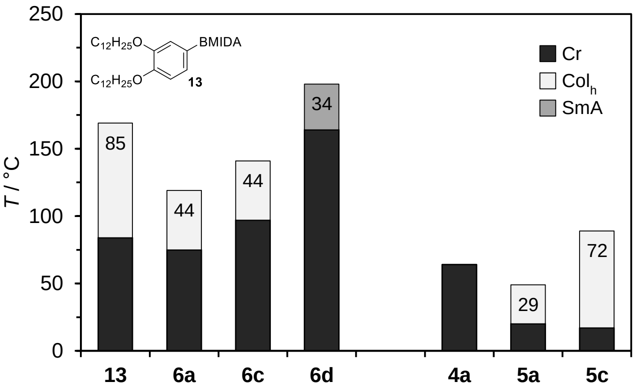


Figure 1. Mesophase widths of liquid crystalline MIDA-boronates **6** and star-shaped triphenylbenzenes **5** obtained by DSC upon second heating (heating rate 5 K min^{-1}). Data for [3,4-bis(dodecyloxy)phenyl]-MIDA boronate **13** and **4a** were taken from the literature.[5,44]

Under the POM, similar textures were found for mono-chlorinated **6c** and 3,5-dialkoxy-substituted boronate **6a** (Figure 2a), which most likely hinted to Col$_h$ phases.[53] In contrast, dichlorinated boronate **6d** formed maltese cross textures indicating a SmA phase (Figure 2b).[53]

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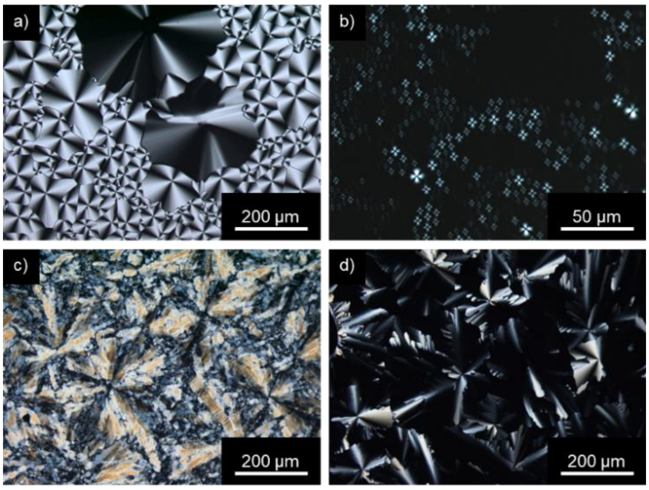

Figure 2. Textures as seen between crossed polarizers. a) Focal conic texture of boronate **6a** with homeotropic areas at 118 °C (heating rate 2 K min^{-1}), b) maltese crosses of boronate **6d** at 206 °C (heating rate 5 K min^{-1}), c) uncharacteristic texture of **5a** at 40 °C and d) pseudo-focal conic texture with large areas of homeotropic alignment of triphenylbenzene derivative **5c** at 80 °C (cooling rate 5 K min^{-1}).

To further determine the phase geometry of the liquid crystalline boronates **6a**,**c**,**d**, XRD experiments were conducted (for characteristic diffraction profile see Supporting Information). In the wide-angle X-ray scattering (WAXS) profile of **6a** a diffuse halo at 4.8 Å in the wide-angle region and a sharp (10) reflection in the small-angle regime are visible (Figure S5a). Boronate **6c** behaved similarly showing only the (10) reflection together with a broad halo at 4.8 Å. Due to the lack of higher order reflections the phase geometry could not be determined. Therefore, based on the characteristic textures and comparison with similar derivatives,[44] Col$_h$ phases were assumed as well. In the case of boronate **6d**, the WAXS profile displayed a sharp (10) reflection and a diffuse halo (Figure S6a). Decreasing layer distances with increasing temperatures (Figure S6b) as well as the texture confirmed the proposed SmA phase.[54–56] Because of a similar structure and layer thickness as compared to known MIDA-boronates,[44] a bilayer packing (SmA$_d$) was suggested. However, due to decreasing transition temperatures (and enthalpies) with increasing number of heating and cooling cycles (Figure S3c), it could be assumed that the sample starts to decompose nearly above its clearing point.

Next, the triphenylbenzenes **5** were investigated. As can be seen from Table 1, only derivatives **5a** and **5c** showed liquid crystallinity. Triphenylbenzenes **5b** and **5d** were devoid of mesomorphism. The DSC curve of 3,5-dialkoxy-substituted derivative **5a** showed melting and clearing transitions at 20 °C and 49 °C upon heating and slightly supercooled transitions at 16 °C and 40 °C upon cooling (Figure S4a). Under the POM, uncharacteristic focal conic-like textures were observed (Figure 2c). Despite the relatively narrow phase width, the phase behaviour of **5a** contradicts the assumption that six-fold alkoxy-substituted hekates (e.g. **4a**) could not form any mesophases.[5,57,58] However, it becomes evident that phase formation is associated with the (increasing) number of alkoxy substituents, but also with a suitable substitution pattern (symmetry) on the outer phenyl rings. The small-angle X-ray scattering profile of the mesophase of **5a** revealed a set of reflections in the ratio $1 : 1/\sqrt{3} : 1/\sqrt{7} : 1/\sqrt{9}$ indexed as (10), (11), (21), and (30) which are characteristic of a $\mathrm{Col_h}$ phase with *p6mm* symmetry (Figure 3b).[2,59]

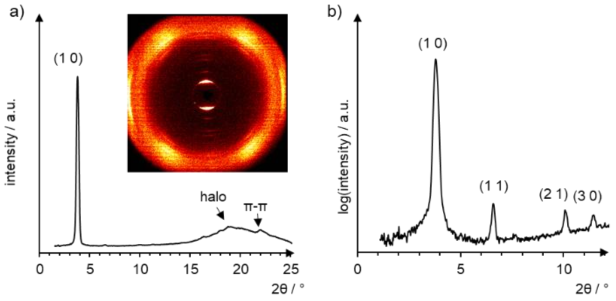

Figure 3. a) WAXS profile and diffraction pattern (inset) and b) SAXS diffraction profile of triphenylbenzene **5a** at 40 °C.

In the WAXS a sharp (10) reflection as well as a broad halo at 4.5 Å and a π–π reflex at 4.0 Å are visible (Figure 3a). Moreover, triphenylbenzene **5a** showed a helical orientation in the WAXS diffraction pattern (Figure 4c), which resembled the helical stacking model proposed for derivatives **4b** and **4c**.[5] Data evaluation using the HELIX[60] program resulted in an azimuthal rotation angle $\varphi = 60°$, pitch $p = 8.1$ Å, repeat of three pitches $C = 24.2$ Å, π–π distance between two molecules $d = 4.0$ Å. The lattice parameter a of **5a** (26.6 Å) is smaller than the values of **4b** (28.4 Å) and **4c** (31.8 Å),[5] since the backfolding and interdigitation of the remaining alkoxy chains must be much stronger to fill the large void space due to the loss of a substituent. The hexagonal packing becomes denser and the lattice parameter decreases. Alternatively, a helical soft crystal or conformationally disordered (CONDIS) crystal phase[61] might be proposed based on the high clearing enthalpy, the rather high hysteresis, the number of very small reflections on the halo of the XRD pattern together with the uncharacteristic texture.[62–64] However, the fact that compound **5a** could be sheared under the POM agreed with the assignment of a hexagonal columnar phase $\mathrm{Col_{ho}}$ with helical order along the columnar axis. In addition, it should be noted that the high clearing enthalpies (in comparison with the corresponding melting enthalpies) have previously been observed for related triphenylbenzenes with $\mathrm{Col_{ho}}$ phases (see DSC curves in the Supporting Information of ref.[5] as well as chlorinated heterocycles[7]).

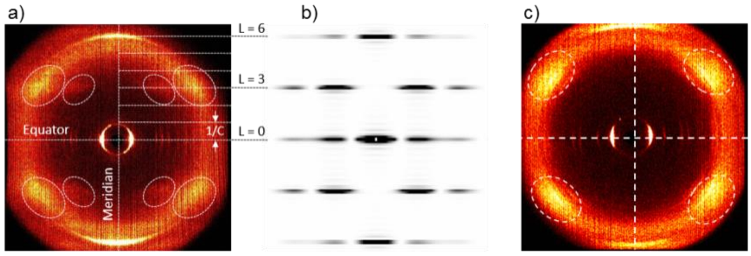

Figure 4. a) WAXS pattern of **4c** upon heating at 90 °C, b) a simulated WAXS pattern of **4c** (HELIX[60] program, $\varphi = 60°$, $d = 4.3$ Å) (both taken from the literature)[5] and c) WAXS pattern of **5a** upon heating at 40 °C.

In contrast to non-mesomorphic 3,4-disubstituted compound **4a** (Scheme 2) which melts at 64 °C,[5] the 5-chloro-3,4-dialkoxy-substituted analogue **5c** showed melting and clearing transitions at 17 °C and 89 °C, respectively, upon heating and a slightly supercooled melting transition at 6 °C upon cooling (Table 1). Homeotropic areas with pseudo-focal conic defects visible under the POM (Figure 2d) indicated a columnar phase.[65] Obviously, a chloro substituent in *meta*-position is sufficient for mesomorphism. However, the spherical chlorine atom fills less space than a flexible alkoxy chain and seems to inhibit crystallization and thus solid state packing. In the SAXS diffraction profile of **5c** three characteristic reflections in the ratio 1 : 1/√3 : 1/√7 indexed as (10), (11) and (21) were detected, which are in agreement with a Col_h phase (Figure S8b). In contrast to its methoxy-substituted analogue **4b**, triphenylbenzene **5c** did not show a helical orientation in the WAXS pattern. However, based on a related molecular structure to **4b**,**c** as well as phase behaviour a helical stacking model seems likely. The lattice parameter of **5c** (a = 29.3 Å) ranged between **4b** (28.4 Å) and **4c** (31.8 Å),[5] which suggests that the chloro substituent might take more space than the methoxy substituent. The necessary backfolding and interdigitation processes are correspondingly lower.

Triphenylbenzenes **5b** and **5d** showed only melting transitions at 115 °C and 38 °C, respectively, in the heating cycle (Table 1). Additionally, in the case of 3,5-dichloro-4-dodecyloxy-substituted triphenylbenzene **5d**, a cold crystallization was observed. In the cooling cycle, **5d** solidified like glass, however, upon reheating the sample crystallized. Upon further heating, the sample returned to the isotropic liquid when reaching the melting point. This phenomenon was already described by Illers for amorphous polymers.[66,67] The number of chloro substituents in **5d** seems to suppress completely the crystallization or self-assembly into a liquid crystalline phase in general. The three alkoxy chains in the molecule can hardly fill the empty space and thus, packing is no longer favoured. The increased inhibition of crystallization and the low melting point could also be explained by this effect.

The strikingly different behaviour of triphenylbenzenes **5** might be rationalized as follows. Introduction of one chloro substituent in the 3-position while maintaining an unsymmetric substitution pattern around the central aromatic core decreased the melting transition and stabilized the columnar phase in **5c** as compared to non-mesogenic **4a**. In contrast, introduction of a polarizable chlorine atom in the 4-position kept the overall C_3-symmetry but led to a much higher melting point as compared to **5c**, indicating strong intermolecular dipolar and halogen interactions and this preventing mesophase formation for **5b** in contrast to non-chlorinated counterpart **5a**. In the case of **5d**, the presence of an additional chloro substituent decreased the melting transition. However, the 3,5-dichloro substitution maintains C_3-symmetry and the presence of two polar substituents leads to strong intermolecular interactions suppressing mesophase formation. Furthermore, only three alkoxy chains seem to be insufficient to fill the space and thus disfavouring both crystalline and mesophase packing. These results show that mesomorphism in such star-shaped molecules is based on a delicate balance of intermolecular interactions involving the aromatic core and its π–π stacking and helical twisting of the propeller-shaped core in order to fill the void space as well as symmetry and number of polar or polarizable groups in the periphery. Our observations are in good agreement with detailed structure-property relationships disclosed by Ros on halogenated indenes and pseudoazulenes.[7]

Conclusion

A convenient access to chloro-substituted triphenylbenzene hekates was established using Suzuki-Miyaura cross coupling as the key step. If tris(tridodecyloxyphenyl)benzene **4c**[5] is considered as a benchmark columnar mesogen, removal of one dodecyloxy chain from each phenyl unit resulted in loss of mesomorphism for **4a**.[5] If the missing third dodecyloxy chain was replaced by a methoxy group as in **4b**, both melting and clearing points decreased, while the $\mathrm{Col_{ho}}$ mesophase was maintained.[5] This effect was even more pronounced, if the missing dodecyloxy chain was replaced by chloro, resulting in star-shaped compound **5c** with a room temperature $\mathrm{Col_{ho}}$ phase. When only two dodecyloxy chains in the 3,5-position were left as in **5a**, again both melting and clearing points decreased considerably and **5a** arranged in a $\mathrm{Col_{ho}}$ phase or soft crystal albeit with small phase width. Accordingly, the *meta*-position seems to play a greater role in mesophase stabilization than the *para*-position. Furthermore, if at least one chloro substituent was involved, tendency to crystallization was, depending on the substitution pattern, significantly reduced. The mesophase was also completely destabilized by onefold *para*- or twofold *meta*-chloro-substituted phenyl rings. In agreement with previous work by Twieg and Binnemans our results reveal that chloro substituents indeed lower phase transitions, however, with regard to the replacement of alkoxy side chains there is no easy rule of thumb available and thus, further work on other discotics is required.

Experimental Section

General. All chemicals were used as purchased. Anhydrous solvents were distilled and dried under nitrogen atmosphere, solvents for chromatography were distilled prior to use. 5-Bromobenzene-1,2-diol (**11a**),[42] 4-bromo-2,6-dichlorophenol (**11d**),[27] and 5-bromo-3-chloro-2-hydroxybenzaldehyde (**12**)[36] were synthesized following the literature. NMR spectra were recorded on Bruker Avance 400, 500 or 700 MHz instruments. All chemical shifts (δ) are given in ppm and are referenced to $CDCl_3$ with tetramethylsilane as an internal standard unless otherwise stated. IR spectra were recorded on a Bruker Vektor 22 or ALPHA instrument equipped with a MKII Golden Gate Single Reflection Diamond ATR. MS and HRMS were measured on a Bruker micro-TOF-Q spectrometer with electrospray ionisation (ESI) or atmospheric pressure chemical ionization (APCI), or on a Finnigan Varian MAT95 spectrometer with electron ionisation (EI). GC-MS was performed on an Agilent Technologies 6890N Network GC system equipped with an Agilent 5973 Network Mass Selective Detector. An Olympus BX50 combined with a Linkam TP93 central controller was used for polarizing optical microscopy (POM). Differential scanning calorimetry (DSC) was carried out on a Mettler Toledo DSC822^{e} and X-ray diffraction (XRD) measurements on a Bruker AXS Nanostar C with ceramic tube generator (1500 W) and cross-coupled Goebel mirrors (monochromatic $Cu_{K,\alpha 1}$ radiation, 1.5405 Å). Diffraction patterns were measured with a Bruker HI-STAR detector and were calibrated using a diffraction pattern of silver behenate at room temperature. The diffraction patterns were analyzed with Datasqueeze and Origin.

5-Bromo-2-chlorobenzene-1,3-diol (11b): To a solution of 5-bromo-2-chloro-1,3-dimethoxybenzene (503 mg, 2.00 mmol) in dry CH_2Cl_2 (30 mL) under nitrogen atmosphere at –78 °C a 1 M solution of boron tribromide in CH_2Cl_2 (4.6 mL, 4.60 mmol) was added slowly.

After warming to room temperature, the reaction mixture was stirred for 17 h. Additional BBr_3 (in total 15.4 mL, 15.4 mmol) was added over 14 d because of incomplete conversion (TLC control). The reaction was terminated by addition of ice-cold H_2O (25 mL). After phase separation, the aqueous phase was extracted with Et_2O (5 × 25 mL). The combined organic layers were dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was dried under reduced pressure for 2 d to give **11b** (463 mg, 2.07 mmol, quant., purity >95%) as white needles, which were used without further purification. ^1H NMR (400 MHz, [D$_6$]DMSO): δ=6.59 (s, 2H; 2×2-H), 10.42 ppm (s, 2H; 2×OH); ^{13}C NMR (101 MHz, [D$_6$]DMSO): δ=107.4 (C-4), 110.2 (C-2), 119.3 (C-1), 155.7 ppm (C-3); MS (GC-MS): *m/z* = 224 [*M*].

5-Bromo-3-chlorobenzene-1,2-diol (11c): To a suspension of 5-bromo-3-chloro-2-hydroxybenzaldehyde **12**[36] (2.50 g, 10.6 mmol) in aqueous NaOH (0.45 g, 11.2 mmol, 1.3 M) H_2O_2 (1.2 mL, 11.2 mmol, 9.8 M in H_2O) was added, and the suspension was stirred for 1 h at room temperature. The mixture was then poured into H_2O (30 mL), acidified with conc. H_2SO_4 and extracted with CH_2Cl_2 (600 mL). The organic layer was washed with brine (250 mL), and the solvent was removed under reduced pressure. The brown and oily residue was used without further purification and characterization.

1-Bromo-3,5-bis(dodecyloxy)benzene (8a): In analogy to ref.,[43] a solution of 5-bromo-3-hydroxyphenol **11a** (1.20 g, 6.35 mmol) in DMF (50 mL) was degassed for 20 min by a constant nitrogen flow. K_2CO_3 (5.30 g, 38.1 mmol) and bromododecane (3.4 mL, 14.0 mmol) were added, and the suspension was stirred at 80 °C overnight under a nitrogen atmosphere. The mixture was then poured into an aqueous solution of NaOH (150 mL, 1 M), and the aqueous layer was extracted with Et_2O (200 mL). The organic layer was washed with water (100 mL), dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was purified by chromatography on SiO_2 with hexanes to give **8a** (2.10 g, 3.99 mmol, 63%,

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purity >95%) as a white solid. M.p. 32.2 °C; R_f=0.6 (hexanes/EtOAc 50:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.83–0.93 (m, 6H; 3×CH_3), 1.18–1.51 (m, 36H; 18×CH_2), 1.68–1.82 (m, 4H; 2×OCH_2CH_2), 3.83–3.93 (m, 4H; 2×OCH_2), 6.36 (t, J = 2.2 Hz, 1H; 2-H), 6.63 ppm (d, J = 2.2 Hz, 2H; 4-H, 6-H); ^{13}C NMR (101 MHz, $CDCl_3$): δ=14.1 (CH_3), 22.7, 26.9, 29.1, 29.4, 29.58, 29.61, 29.66, 29.68, 31.9 (CH_2), 68.3 (OCH_2), 100.5 (C-2), 110.2 (C-4, C-6), 122.8 (C-5), 160.7 ppm (C-1, C-3). The spectroscopic data are in accordance with the literature.[43]

5-Bromo-2-chloro-1,3-bis(dodecyloxy)benzene (8b): According to ref.,[68,69] a suspension of **11b** (450 mg, 2.01 mmol) and K_2CO_3 (2.02 g, 14.6 mmol) in dry DMF (20 mL) was degassed for 20 min by a constant nitrogen flow prior to addition of bromododecane (1.2 mL, 5.00 mmol). The reaction mixture was stirred for 3 d at 80 °C. After cooling to room temperature, the mixture was poured into H_2O (30 mL), and the aqueous layer was extracted with Et_2O (3 × 75 mL), hexanes (75 mL) and CH_2Cl_2 (100 mL). The combined organic layers were dried ($MgSO_4$), the solvent was removed under reduced pressure and the crude product was purified by chromatography on SiO_2 with hexanes/CH_2Cl_2 (20:1) to give **8b** (1.01 g, 1.81 mmol, 90%, purity >95%) as a white solid. M.p. 65.8 °C; R_f=0.55 (hexanes/CH_2Cl_2 10:1); ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.88 (t, J = 6.9 Hz, 6H; 2×CH_3), 1.21–1.40 (m, 32H; 2×CH_2), 1.42–1.51 (m, 4H; 2×$OCH_2CH_2CH_2$), 1.82 (quin., J = 14.8 Hz, 6.7 Hz, 4H; 2×OCH_2CH_2), 3.98 (t, J = 6.6 Hz, 4H; 2×OCH_2), 6.70 ppm (s, 2H; 2×2-H); ^{13}C NMR (101 MHz, $CDCl_3$): δ=14.1 (CH_3), 22.7, 25.9, 29.0, 29.3, 29.4, 29.55, 29.59, 29.65, 29.67, 31.9 (CH_2), 69.6 (OCH_2), 109.3 (C-2), 111.0 (C-4), 120.1 (C-1), 156.2 ppm (C-3); FT-IR (ATR): $\tilde{\nu}$=2958 (m), 2943 (m), 2917 (vs), 2870 (m), 2846 (s), 1583 (s), 1557 (m), 1462 (s), 1419 (s), 1390 (s), 1308 (w), 1230 (s), 1199 (w), 1110 (vs), 1062 (s), 1030 (w), 936 (w), 908 (w), 853 (m), 811 (m), 798 (m), 767 (w), 725 (m), 694 (m), 634 (m), 571 (m), 543 (w) cm^{-1}; MS (EI): m/z = 560.3 $[M]^+$; HRMS (EI): m/z calcd for $C_{30}H_{52}BrClO_2$: 560.2820 $[M]^+$; found: 560.2825; elemental analysis calcd (%) for $C_{30}H_{52}BrClO_2$: C 64.33, H 9.36; found: C 64.63, H 9.26.

5-Bromo-1-chloro-2,3-bis(dodecyloxy)benzene (8c): A suspension of **11c** (2.37 g, 10.6 mmol), K_2CO_3 (8.80 g, 64.0 mmol) and 1-bromododecane (6.40 mL, 26.5 mmol) in MeCN (40 mL) was stirred for 17 h at 90 °C . The reaction mixture was poured into H_2O (200 mL) and extracted with Et_2O (2 × 150 mL). The combined organic layers were washed with aqueous NaOH (100 mL, 1 M), dried ($MgSO_4$), and the solvent was removed under reduced pressure. The crude product was purified by chromatography on SiO_2 with hexanes and subsequent crystallization from pentane at –30 °C to give **8c** (2.02 g, 3.60 mmol, 34%, purity >95%) as a white solid. M.p. 39.9 °C; ^{1}H NMR (400 MHz, $CDCl_3$): δ=0.84–0.93 (m, 6H; 2×CH_3), 1.20–1.54 (m, 36H; 18×CH_2), 1.71–1.86 (m, 4H; 2×OCH_2CH_2), 3.89–4.02 (m, 4H; 2×OCH_2), 6.90 (d, J = 2.2 Hz, 1H; 6-H), 7.10 ppm (d, J = 2.2 Hz, 1H; 4-H); ^{13}C NMR (101 MHz, $CDCl_3$): δ=14.1 (CH_3), 22.7, 25.97, 26.04, 29.1, 29.33, 29.38, 29.5, 29.61, 29.62, 29.67, 29.69, 29.71, 30.2, 31.9 (CH_2), 69.2 (*m*-OCH_2), 73.6 (*p*-OCH_2), 115.3, 115.6 (C-4, C-6), 124.1 (C-5), 129.3 (C-3), 144.4 (C-2), 153.9 ppm (C-1); FT-IR (ATR): $\tilde{\nu}$=2921 (vs), 2852 (s), 1575 (s), 1463 (s), 1405 (s), 1384 (s), 1289 (w), 1259 (s), 1222 (s), 1187 (w), 1099 (w), 1034 (s), 907 (w), 829 (s), 761 (w), 721 (w), 579 (w) cm^{-1}; MS (ESI): *m*/z = 999, 685, 625, 583 $[M+Na]^+$; HRMS (ESI): *m/z* calcd for $C_{30}H_{52}BrClO_2Na$: 583.2712 $[M(^{81}Br)+Na]^+$, 581.2731 $[M(^{79}Br)+Na]^+$; found: 583.2681 $[M(^{81}Br)+Na]^+$, 581.2684 $[M(^{79}Br)+Na]^+$.

5-Bromo-1,3-dichloro-2-(dodecyloxy)benzene (8d): To a suspension of **11d**[27] (5.82 g, 24.1 mmol) and K_2CO_3 (17.3 g, 125 mmol) in MeCN (160 mL), degassed for 15 min by a constant nitrogen flow, was added bromododecane (5.8 mL, 24.1 mmol), and the reaction mixture was heated at reflux for 16 h. After cooling to room temperature, the solvent was removed under reduced pressure. The residue was taken up in CH_2Cl_2 (100 mL) and filtered through Celite®. The filtrate was concentrated under reduced pressure to give **8d** (9.64 g, 23.5 mmol, 98%, purity >95%) as white needles. M.p. 29.4 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=0.88 (t, J = 6.9 Hz, 3H; CH$_2$CH_3), 1.21–1.42 (m, 16H; 8×CH_2), 1.43–1.58 (m, 2H; OCH$_2$CH$_2$CH_2), 1.74–1.88 (m, 2H; OCH$_2$CH_2), 3.99 (t, J = 6.6 Hz, 2H; OCH_2), 7.43 ppm (s, 2H; 4-H); ^{13}C NMR

(126 MHz, $CDCl_3$): δ=14.1 (CH_2CH_3), 22.7 (CH_3), 25.8, 29.36, 29.39, 29.57, 29.61, 29.64, 29.66, 30.0, 31.9 (CH_2), 74.0 (OCH_2), 116.0 (C-5), 130.5 (C-3), 131.5 (C-4), 151.3 ppm (C-2); FT-IR (ATR): ṽ=2922 (vs), 2853 (s), 1567 (w), 1550 (m), 1451 (vs), 1379 (s), 1255 (s), 1192 (w), 1124 (w), 985 (w), 855 (m), 805 (s), 750 (m), 684 (w), 569 (w), 424 (w) cm^{-1}; MS (EI): m/z = 242 [M–$C_{12}H_{25}$], 410 [M]; elemental analysis calcd (%) for $C_{18}H_{27}BrCl_2O$: C 52.70, H 6.63; found: C 53.41 H 6.64.

General Procedure for the Preparation of MIDA-Boronates 6: Analogous to ref.,[37,70] to a solution of the appropriate bromobenzene **8a**,**c**,**d** (1.0 equiv.) in dry THF under nitrogen atmosphere at –78 °C a 1.6 M solution of *n*-BuLi in hexane (1.7 equiv.) was slowly added, and the mixture was stirred for a further 30 min at –78 °C. Triisopropylborate (1.7 equiv.) was added, and the reaction mixture was warmed to room temperature over 30 min. A hot 0.5 M solution of MIDA in DMSO (3.0 equiv.) was added, and the reaction mixture was stirred for 2 h at 125 °C. After cooling to room temperature, the mixture was poured into H_2O (200 mL) and Et_2O (50 mL) was added. The aqueous layer was extracted with CH_2Cl_2 (100 mL). The combined organic layers were washed with brine (100 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure, and the residue was purified by chromatography on SiO_2 with hexanes/EtOAc (1:1) and EtOAc.

[3,5-Bis(dodecyloxy)phenyl]-MIDA-boronate (6a): From **8a** (1.20 g, 2.28 mmol), *n*-BuLi (2.3 mL, 3.65 mmol), triisopropylborate (0.9 mL, 3.88 mmol), and MIDA (15.0 mL, 7.50 mmol) in dry THF (20 mL), white solid (860 mg, 1.43 mmol, 63%, purity >95%); R_f=0.1 (hexanes/EtOAc 1:1). M.p. 75.0 °C; ^1H NMR (500 MHz, $CDCl_3$): δ=0.83–0.92 (m, 6H; 2×CH_3), 1.17–1.47 (m, 36H; 18×CH_2), 1.70–1.80 (m, 4H; 2×OCH_2CH_2), 2.58 (s, 3H; NCH_3), 3.78 (d, J = 16.5 Hz, 2H; 2×a-H), 3.89–3.95 (m, 4H; 2×OCH_2), 4.00 (d, J = 16.5 Hz, 2H; 2×a-H), 6.48 (t, J = 2.2 Hz, 1H; 4-H), 6.60 ppm (d, J = 2.2 Hz, 2H; 2×2-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ=14.1 (CH_3), 22.7, 26.1, 29.36, 29.45, 29.60, 29.63, 29.65, 29.69, 31.9 (CH_2), 47.5

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(NCH$_3$), 61.8 (C-a), 68.1 (OCH$_2$), 102.6 (C-4), 110.2 (C-2), 160.6 (C-3), 167.7 ppm (O=C); FT-IR (ATR): ṽ=2999 (w), 2920 (s), 2851 (s), 1765 (s), 1584 (w), 1466 (w), 1455 (w), 1423 (w), 1384 (w), 1337 (s), 1287 (s), 1250 (w), 1161 (vs), 1126 (s), 1009 (s), 953 (w), 908 (w), 890 (w), 870 (w), 836 (s), 773 (w), 730 (w), 702 (w), 666 (w), 647 (w), 625 (w), 595 (w), 555 (w), 504 (w) cm^{-1}; MS (ESI): *m*/z = 624 [*M*+Na]$^+$, 602 [*M*+H]$^+$; HRMS (ESI): *m*/*z* calcd for $C_{35}H_{60}BNO_6Na$: 624.4412 [*M*+Na]$^+$; found: 624.4432 [*M*+Na]$^+$; elemental analysis calcd (%) for $C_{35}H_{60}BNO_6$: C 69.87, H 10.05, N 2.33; found: C 69.94, H 9.79, N 2.23.

[3-Chloro-4,5-bis(dodecyloxy)phenyl]-MIDA-boronate (6c): From **8c** (1.00 g, 1.79 mmol), *n*-BuLi (1.8 mL, 2.86 mmol), triisopropylborate (0.7 mL, 3.03 mmol), and MIDA (10.0 mL, 5.00 mmol) in dry THF (15 mL), white solid (930 mg, 1.46 mmol, 82%, purity >95%); R_f=0.1 (hexanes/EtOAc 1:1). M.p. 97.2 °C; ^{1}H NMR (500 MHz, CDCl$_3$): δ=0.84–0.92 (m, 6H; 2×CH_3), 1.20–1.39 (m, 32H; 16×CH_2), 1.42–1.54 (m, 4H; 2×OCH$_2$CH$_2$CH_2), 1.73–1.84 (m, 4H; 2×OCH$_2$CH_2), 2.60 (s, 3H; NCH_3), 3.76–3.82 (m, 2H; 2×a-H), 3.92–3.99 (m, 4H; 2×a-H, 3-OCH_2), 3.99–4.04 (m, 2H; 4-OCH_2), 6.92 (d, *J* = 1.6 Hz, 1H; 2-H), 7.05 ppm (d, *J* = 1.6 Hz, 1H; 6-H); ^{13}C NMR (126 MHz, CDCl$_3$): δ=14.1 (CH$_3$), 22.7, 26.0, 26.2, 29.38, 29.40, 29.44, 29.5, 29.64, 29.68, 29.72, 30.2, 31.9 (CH$_2$), 47.5 (NCH$_3$), 61.8 (C-a), 69.3 (C-3-OCH$_2$), 73.5 (C-4-OCH$_3$), 115.3 (C-2), 125.5 (C-6), 129.0 (C-5), 146.4 (C-4), 153.7 (C-3), 167.1 ppm (O=C); FT-IR (ATR): ṽ=3013 (w), 2953 (w), 2914 (s), 2847 (s), 1780 (s), 1747 (s), 1620 (w), 1587 (s), 1553 (w), 1490 (w), 1467 (w), 1390 (w), 1381 (w), 1344 (w), 1290 (s), 1245 (w), 1218 (w), 1164 (w), 1152 (w), 1095 (w), 1055 (s), 1031 (vs), 1003 (s), 950 (s), 911 (w), 881 (w), 857 (s), 752 (w), 718 (w), 677 (w), 608 (w), 506 (w) cm^{-1}; MS (ESI) *m*/z = 658 [*M*+Na]$^+$, 636 [*M*+H]$^+$, 561; HRMS (ESI): *m*/*z* calcd for $C_{35}H_{59}BClNO_6$: 658.4022 [*M*+Na]$^+$; found: 685.4020 [*M*+Na]$^+$; elemental analysis calcd (%) for $C_{35}H_{59}BClNO_6$: C 66.09, H 9.35, N 2.20; found: C 65.92, H 9.45, N 1.99.

[3,5-Dichloro-4-(dodecyloxy)phenyl]-MIDA-boronate (6d): From **8d** (555 mg, 1.35 mmol), *n*-BuLi (0.87 mL, 2.16 mmol, 2.5 M in hexane), triisopropylborate (0.6 mL, 2.60 mmol), and MIDA (10.0 mL, 2.80 mmol, 0.28 M in DMSO) in dry THF (30 mL), white solid (531 mg, 1.09 mmol, 81%, purity >99%); R_f=0.2 (hexanes/EtOAc 2:1). M.p. 164.1 °C; ^{1}H NMR (700 MHz, $CDCl_3$): δ=0.88 (t, J = 7.0 Hz, 3H; CH_2CH_3), 1.22–1.41 (m, 16H; 8 × CH_2), 1.47–1.52 (m, 2H; $OCH_2CH_2CH_2$), 1.75–1.88 (m, 2H; OCH_2CH_2), 2.59–2.68 (m, 3H; NCH_3), 3.80–3.87 (m, 2H; 2×a-H), 3.98–4.04 (m, 2H; OCH_2), 4.04–4.22 (m, 2H; 2×a-H), 7.43 ppm (s, 2H; 2×2-H); ^{13}C NMR (176 MHz, $CDCl_3$): δ=14.1 (CH_3), 22.7 (CH_2CH_3), 25.8, 29.36, 29.42, 29.60, 29.63, 29.64, 29.67, 30.1, 31.9 (CH_2), 48.0 (NCH_3), 62.1 (C-a), 73.9 (OCH_2), 130.0 (C-3), 132.7 (C-2), 152.9 (C-4), 167.9 ppm (*C*=O); FT-IR (ATR): $\tilde{\nu}$=3514 (w), 3012 (w), 2922 (s), 2853 (m), 2159 (w), 2047 (w), 2015 (w), 1982 (w), 1765 (vs), 1584 (w), 1537 (w), 1461 (m), 1369 (m), 1337 (m), 1261 (vs), 1217 (vs), 1151 (w), 1087 (m), 1050 (vs), 1022 (vs), 1008 (s), 965 (m), 946 (m), 907 (m), 894 (m), 858 (s), 827 (w), 796 (s), 735 (m), 668 (w), 624 (w), 584 (w), 543 (w), 502 (w), 459 (w) cm^{-1}; MS (APCI): m/z = 486.20 $[M+H]^+$; HRMS (APCI): m/z calcd for $C_{23}H_{34}BCl_2NO_5$: 486.1980 $[M+H]^+$; found: 486.1984 $[M+H]^+$; elemental analysis calcd (%) for $C_{23}H_{34}BCl_2NO_5$: C 56.81, H 7.05, N 2.88; found: C 57.03, H 6.97, N 2.83.

General Procedure for the Suzuki Coupling (*Route A*): Analogous to ref.,[37,68,69] to a solution of the appropriate MIDA-boronate **6** (3.8 equiv.) in THF (10 mL) a 1 M aqueous NaOH solution (11.8 equiv.) was added, and the mixture was stirred for 15 min at room temperature. The mixture was neutralized with a saturated NH_4Cl solution, extracted with CH_2Cl_2 (100 mL), and the solvent was removed under reduced pressure to give a crude mixture of the respective boronic acid and boroxine, which was dissolved in DMF or DME and degassed for 45 min by a constant nitrogen flow. Subsequently, K_2CO_3 (4.5 equiv.), **7** (1.0 equiv.), $Pd(PPh_3)_4$ and degassed H_2O (5.0 mL) were added, and the reaction mixture was stirred for 24 h at 90 °C under a nitrogen atmosphere. After cooling to room temperature, the mixture was poured into H_2O (200 mL), extracted with CH_2Cl_2 (200 mL). The organic layer was concentrated under reduced pressure and the residue was purified by chromatography on SiO_2.

General procedure for the Suzuki coupling (*Route B*): Analogous to ref.,[68,69] a suspension of **9** (1.0 equiv.), bromobenzene **8b** or **8d** (4.1 equiv.), K_2CO_3 (3.8 equiv.) and $Pd(PPh_3)_4$ in degassed DME (16 mL) / H_2O (4.0 mL) was stirred for 24 h at 95 °C under a nitrogen atmosphere. After cooling to room temperature, the mixture was poured into H_2O (120 mL) and extracted with CH_2Cl_2 (4 × 60 mL). The combined organic layers were washed with brine (80 mL), dried ($MgSO_4$), and the solvent was removed under reduced pressure. The residue was purified by chromatography on SiO_2.

1,3,5-Tris[3',5'-di(dodecyloxy)phenyl]benzene (5a): *According to Route A*: from **6a** (780 mg, 1.30 mmol), NaOH (4.0 mL, 4.00 mmol) in dry THF (10 mL); K_2CO_3 (212 mg, 1.53 mmol), **7** (107 mg, 340 µmol), $Pd(PPh_3)_4$ (5.00 mg, 4.33 µmol) in DMF (20 mL), H_2O (5.0 mL); purification by chromatography on SiO_2 with hexanes/EtOAc (80:1), followed by crystallization from pentane at –30 °C, white solid (360 mg, 255 µmol, 75%, purity >95%); R_f=0.5 (hexanes/EtOAc 20:1). M.p. 20.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=0.84–0.91 (m, 18H; 6×CH_3), 1.20–1.42 (m, 96H; 48×CH_2), 1.42–1.52 (m, 12H; 6×$OCH_2CH_2CH_2$), 1.80 (p, J = 6.7 Hz, 12H; 6×OCH_2CH_2), 4.00 (t, J = 6.7 Hz, 12H; 6×OCH_2), 6.49 (t, J = 2.2 Hz, 3H; 3×4'-H), 6.78 (d, J = 2.2 Hz, 6H; 6×2'-H), 7.72 ppm (s, 3H; 3×2-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ=14.1 (CH_3), 22.7, 26.1, 29.34, 29.36, 29.43, 29.60, 29.62, 29.64, 29.68, 31.9 (CH_2), 68.2 (OCH_2), 100.4 (C-2′), 106.1 (C-2'), 125.4 (C-2), 142.3 (C-1), 143.2 (C-1'), 160.6 ppm (C-3'); FT-IR (ATR): ṽ=2921 (vs), 2853 (s), 1585 (s), 1466 (w), 1433 (w), 1408 (w), 1384 (w), 1339 (w), 1324 (w), 1259 (w), 1159 (s), 1055 (w), 993 (w), 892 (w), 848 (w), 832 (w), 704 (w), 620 (w), 591 (w) cm^{-1}; MS (MALDI-TOF): *m/z* calcd for $C_{96}H_{162}O_6$: 1411.24

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$[M]^+$; found: 1408.4 $[M]^+$; elemental analysis calcd (%) for $C_{96}H_{162}O_6$: C 81.64, H 11.56; found: C 81.57, H 11.77.

1,3,5-Tris[4'-chloro-3',5'-di(dodecyloxy)phenyl]benzene (5b): *According to Route B*: from **8b** (500 mg, 893 µmol), K_2CO_3 (252 mg, 1.83 µmol), **9** (101 mg, 221 µmol), $Pd(PPh_3)_4$ (18.8 mg, 15.4 µmol) in DME (20 mL), H_2O (3.5 mL); purification by chromatography on SiO_2 with hexanes/CH_2Cl_2 (gradient 15:1 to 8:1), white solid (255 mg, 168 µmol, 76%, purity >95%). M.p. 17.4 °C; R_f=0.19 (hexanes/CH_2Cl_2 10:1); ^1H NMR (700 MHz, $CDCl_3$): δ=0.87 (t, J = 7.1 Hz, 18H; 6×CH_2CH_3), 1.18–1.43 (m, 96H; 48×CH_2), 1.49 (p, J = 7.5 Hz, 12H; 6×$OCH_2CH_2CH_2$), 1.85 (quin., J = 6.8 Hz, 12H; 6×OCH_2CH_2), 4.08 (t, J = 6.6 Hz, 12H; 6×OCH_2), 6.80 (s, 6H; 6×2'-H), 7.63 ppm (s, 3H; 3×2-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ=14.1, 22.7, 26.0, 29.2, 29.4, 29.57, 29.60, 29.64, 29.7, 31.9 (CH_2), 69.6 (OCH_2), 105.2 (C-2'), 111.8 (C-4'), 125.6 (C-2), 140.2 (C-1), 142.6 (C-1'), 156.1 ppm (C-3'); FT-IR (ATR): $\tilde{\nu}$=2921 (vs), 2853 (s), 1572 (s), 1465 (m), 1415 (s), 1404 (m), 1379 (m), 1334 (m), 1246 (m), 1230 (m), 1196 (w), 1114 (vs), 1061 (m), 990 (w), 901 (w), 831 (m), 712 (w), 684 (w), 632 (w) cm^{-1}; MS (APCI): m/z = 1516.13 $[M+H]^+$; HRMS (APCI): m/z calcd for $C_{96}H_{159}Cl_3O_6$: 1516.1282 $[M+H]^+$; found: 1516.1269 $[M+H]^+$; elemental analysis calcd (%) for $C_{96}H_{159}Cl_3O_6$: C 76.08, H 10.57; found: C 75.87, H 10.30.

1,3,5-Tris[5'-chloro-3',4'-di(dodecyloxy)phenyl]benzene (5c): *According to Route A*: from **6c** (820 mg, 1.29 mmol), NaOH (4.0 mL, 4.00 mmol) in dry THF (10 mL); K_2CO_3 (220 mg, 1.58 mmol), **7** (110 mg, 350 µmol), $Pd(PPh_3)_4$ (4.00 mg, 3.46 µmol) in DMF (20 mL), H_2O (5.0 mL); purification by chromatography on SiO_2 with hexanes/EtOAc (80:1), white solid (302 mg, 200 µmol, 57%, purity >95%); R_f=0.5 (hexanes/EtOAc 50:1). M.p. 115.0 °C; ^1H NMR (500 MHz, $CDCl_3$): δ=0.83–0.92 (m, 18H; 6×CH_3), 1.19–1.43 (m, 96H; 48×CH_2), 1.43–1.58 (m, 12H; 6×$OCH_2CH_2CH_2$), 1.77–1.89 (m, 12H; 6×OCH_2CH_2), 4.02–4.09 (m, 12H; 6×OCH_2), 7.03 (d, J = 2.1 Hz, 3H; 3×2'-H), 7.24 (d, J = 2.1 Hz, 3H; 3×6'-H), 7.58 ppm

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(s, 3H; 3×2-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ=14.1 (CH_3), 22.7, 26.1, 26.2, 29.37, 29.39, 29.42, 29.5, 29.64, 29.67, 29.69, 29.73, 30.3, 31.93, 31.95 (CH_2), 69.3, 73.7 (OCH_2), 111.3 (C-2'), 120.7 (C-6'), 125.0 (C-2), 128.9 (C-5'), 137.0 (C-1'), 141.4 (C-1), 144.8 (C-4'), 153.7 ppm (C-3'); FT-IR (ATR): $\tilde{\nu}$=2921 (vs), 2852 (s), 1593 (w), 1562 (w), 1489 (s), 1467 (s), 1380 (w), 1303 (w), 1272 (w), 1239 (w), 1168 (w), 1127 (w), 1092 (w), 1039 (w), 958 (w), 916 (w), 862 (w), 830 (w), 721 (w), 677 (w), 593 (w) cm^{-1}; MS (MALDI-TOF): *m/z* calcd for $C_{96}H_{159}Cl_3O_6$: 1513.12 $[M]^+$; found: 1508.3 $[M]^+$; elemental analysis calcd (%) for $C_{96}H_{159}Cl_3O_6$: C 76.08, H 10.57; found: C 76.01, H 10.68.

1,3,5-Tris(3',5'-dichloro-4'-dodecyloxyphenyl)benzene (5d): *According to Route A*: from **6d** (405 mg, 833 µmol), NaOH (2.7 mL, 2.70 mmol) in dry THF (9 mL); K_2CO_3 (143 mg, 1.03 mmol), **7** (57.0 mg, 181 µmol), $Pd(PPh_3)_4$ (13.0 mg, 11.3 µmol) in DME (15 mL), H_2O (4.0 mL); purification by chromatography on SiO_2 with hexanes/CH_2Cl_2 (gradient 200:1 to 20:1), white solid (81.0 mg, 76.0 µmol, 42%, purity >82%). *According to Route B*: from **8d** (397 mg, 968 µmol), K_2CO_3 (122 mg, 883 µmol), **9** (107 mg, 235 µmol), $Pd(PPh_3)_4$ (18.0 mg, 15.6 µmol) in DME (16 mL), H_2O (4.0 mL); purification by chromatography on SiO_2 with hexanes/CH_2Cl_2 (gradient 200:1 to 20:1), white solid (220 mg, 206 µmol, 88%, purity >95%). R_f=0.24 (hexanes/CH_2Cl_2 100:1); M.p. 38.0 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ=0.88 (t, J = 6.9 Hz, 9H; 3×CH_2CH_3), 1.21–1.44 (m, 48H; 24×CH_2), 1.51–1.58 (m, 6H; 3×$OCH_2CH_2CH_2$), 1.82–1.95 (m, 6H; 3×OCH_2CH_2), 4.08 (t, J = 6.6 Hz, 6H; 3×OCH_2), 7.57 (s, 6H; 2'-H), 7.60 ppm (s, 3H; 2-H); ^{13}C NMR (126 MHz, $CDCl_3$): δ=14.1 (CH_3), 22.7 (3×CH_2CH_3), 25.9, 29.37, 29.44, 29.61, 29.64, 29.66, 29.68, 30.1, 31.9 (CH_2), 74.1 (OCH_2), 125.1 (C-2), 127.5 (C-2'), 130.1 (C-1'), 137.4 (C-1), 140.1 (C-3'), 151.5 ppm (C-4'); FT-IR (ATR): $\tilde{\nu}$=2921 (vs), 2852 (s), 2173 (w), 2074 (w), 1747 (w), 1597 (w), 1548 (m), 1479 (s), 1464 (vs), 1434 (s), 1380 (m), 1363 (s), 1270 (vs), 1235 (m), 1208 (w), 1077 (m), 1032 (w), 984 (m), 911 (w), 856 (s), 803 (vs), 722 (m), 665 (w), 626 (m), 580 (w), 514 (w), 459 (w) cm^{-1}; MS (APCI): *m/z* = 1065.46 $[M+H]^+$; HRMS (APCI): *m/z* calcd for $C_{60}H_{84}Cl_6O_3$: 1065.46 $[M+H]^+$; found:

1065.46 [*M*+H]$^+$; elemental analysis calcd (%) for $C_{60}H_{84}Cl_6O_3$: C 67.60, H 7.94; found: C 67.64, H 8.06.

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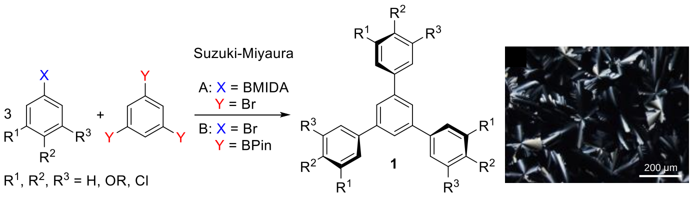
Graphical Abstract



Two variants A and B of the Suzuki-Miyaura cross coupling allow the synthesis of (poly)chlorinated shaped-persistent hekates **1**. Method B was found to be superior to A improving the yields up to 88%. Liquid crystalline properties of some hekates were observed.