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Building liquid crystals from the 5-fold symmetrical pillar[5]arene core†

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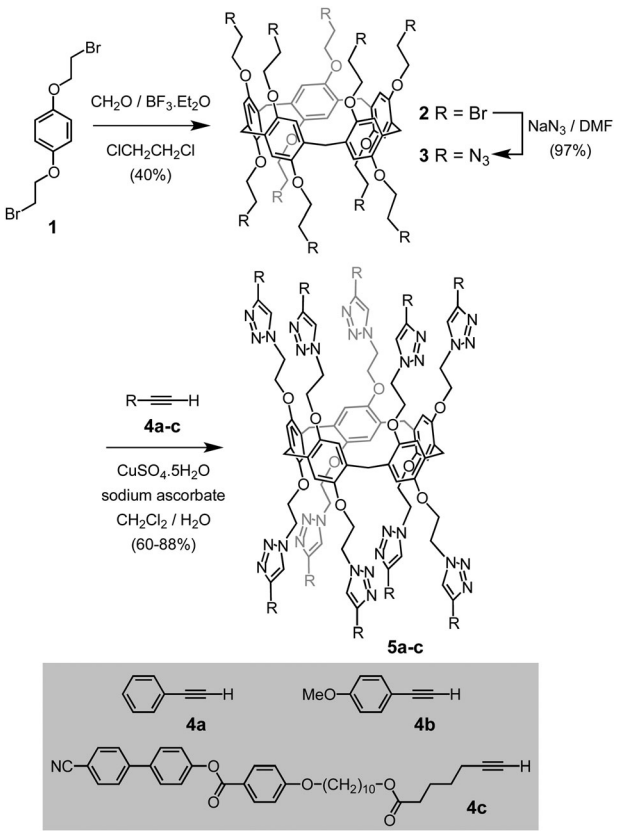
Comparison of the liquid-crystalline properties of a pillar[5]arene core functionalized with 10 mesogenic cyanobiphenyl units with those of a corresponding model compound revealed the strong influence of the macrocyclic pillar[5]arene core on the mesomorphic properties.

Pillar[*n*]arenes are unique tubular-shaped macrocyclic compounds made of 1,4-disubstituted hydroquinone subunits linked by methylene bridges in their 2,5-positions.[1] They are usually prepared from 1,4-dialkoxybenzene derivatives and paraformaldehyde in the presence of a Lewis acid catalyst.[2] Owing to the reversibility of the Friedel–Crafts reaction, the cyclooligomerization is thermodynamically driven thus allowing the preparation of pillar[*n*]arenes in high yields.[3] Depending on the solvent and/or the Lewis acid catalyst, the major cyclooligomerization product is either the cyclopentamer ($n = 5$) or the cyclohexamer ($n = 6$).[4] Whereas significant research efforts have been devoted to the study of inclusion complexes obtained from pillar[5]arenes,[1] their tubular shape has not been exploited so far. With its unique pentagonal rigid structure, the pillar[5]arene moiety appears to be an attractive core unit for the preparation of novel liquid-crystalline materials with unconventional shape. It is known that isolated molecules with point groups displaying 5-fold symmetry must reduce their symmetry when forming crystalline monolayers.[5] Thus, pentagon-shaped subunits within closely packed smectic layers may result in orientational and/or positional disorder. As a result, the crystalline phase may be destabilized but, at the same time, the intermolecular interactions between neighboring pentagon-shaped moieties should contribute to the stabilization of the liquid-crystalline phase. With this idea in mind, we have prepared a pillar[5]arene core decorated with cyanobiphenyl moieties. Comparison of its liquid-crystalline properties with those of a corresponding model compound revealed the dramatic influence of the macrocyclic pillar[5]arene core on the mesomorphic properties.

The synthetic approach to the pillar[5]arene derivative relies on the copper-catalyzed alkyne–azide cycloaddition (CuAAC) reaction used to introduce the mesomorphic subunits on both rims of the macrocyclic core. This methodology has proven to be a powerful procedure for the grafting of multiple mesogens onto a compact multifunctional core unit[6] and clickable pillar[5]arene building blocks are easily available.[7] As shown in Scheme 1, pillar[5]arene derivative **3** was obtained in two steps from compound **1**.

Treatment of **1** and paraformaldehyde with $BF_3{\cdot}Et_2O$ in 1,2-dichloroethane gave pillar[5]arene **2** in 40% yield.[8] Under these conditions, no traces of the corresponding pillar[6]arene derivative could be detected. Subsequent reaction with sodium azide in DMF at room temperature gave clickable building block **3** in 97% yield.[9] Owing to the high number of azide



Scheme 1 Synthesis of clicked pillar[5]arene derivatives **5a–c**.

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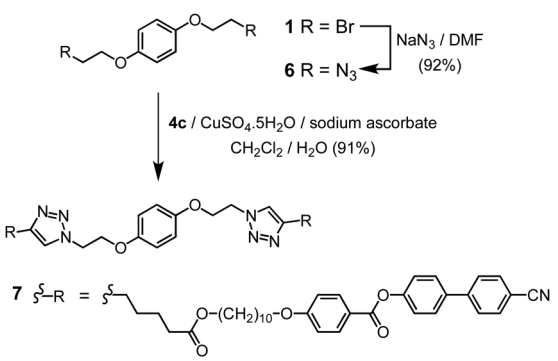
residues, compound **3** was handled with special care: upon evaporation, compound **3** was not dried under high vacuum and the use of metallic spatula avoided. Furthermore, this compound was always prepared on small scales (< 500 mg). The functionalization of **3** with terminal alkynes under the typical CuAAC conditions used for the functionalization of multi-azide cores[10] ($CuSO_4{\cdot}5H_2O$, sodium ascorbate, CH_2Cl_2–H_2O) was first attempted from commercially available alkynes **4a–b**. The clicked derivatives **5a** and **5b** were thus obtained in 60 and 86% yield, respectively. The structures of compounds **5a–b** were confirmed by their ^1H and ^{13}C NMR spectra as well as by mass spectrometry. Inspection of the ^1H NMR spectra clearly indicates the disappearance of the CH_2-azide signal at δ 3.67 ppm. IR data also confirmed that no azide residues (2089 cm^{-1}) remain in the final products (Fig. S1, ESI†). Importantly, the ^1H NMR spectra of **5a–b** show the typical singlet of the 1,2,3-triazole unit at δ 7.92 and 7.83 ppm, respectively (Fig. S2, ESI†). The reaction conditions used for the preparation of **5a–b** from **4a–b** were then applied to the mesomorphic subunit **4c** (Cr → SmA: 114 °C; SmA → N: 156 °C; N → I: 158 °C) (Fig. S4, ESI†). A mixture of **3** (1 equiv.), **4c** (11 equiv.), CuSO4·$5H_2O$ (0.1 equiv.) and sodium ascorbate (0.3 equiv.) in CH_2Cl_2–H_2O (1 : 1) was vigorously stirred at room temperature for 12 h. After work-up and purification by column chromatography on SiO_2 followed by gel permeation chromatography (Biobeads SX-1, CH_2Cl_2), compound **5c** was obtained in 81% yield. The structure of compound **5c** was confirmed by ^1H and ^{13}C NMR spectroscopy. In particular, the ^1H NMR spectrum of **5c** (Fig. S5, ESI†) is in full agreement with its D_{5h}-symmetrical structure and shows the expected signals for the 10 equivalent mesogenic subunits. Finally, the model compound **7** bearing two mesomorphic groups was prepared by following a similar synthetic route (Scheme 2). Treatment of **1** with sodium azide in DMF gave **6** (92%). Reaction of the latter with **4c** under CuAAC conditions afforded compound **7** in 91% yield.

The liquid-crystalline and thermal properties of compounds **5c** and **7** were investigated by polarized optical microscopy (POM) and differential scanning calorimetry (DSC). On heating, model compound **7** melted at 145 °C (ΔH = 127 kJ mol^{-1}) from the crystalline state into the isotropic liquid (Fig. 1). The formation of a monotropic smectic A phase (focal-conic fan texture) was observed during the cooling run followed by the crystallization of the sample (I → SmA: 149 °C, ΔH = 5.8 kJ mol^{-1}; SmA → Cr: 125 °C, ΔH = 119 kJ mol^{-1}). On the other hand, pillar[5]arene **5c** gave rise to an enantiotropic smectic A phase (focal-conic



Scheme 2 Synthesis of model compound **7**.

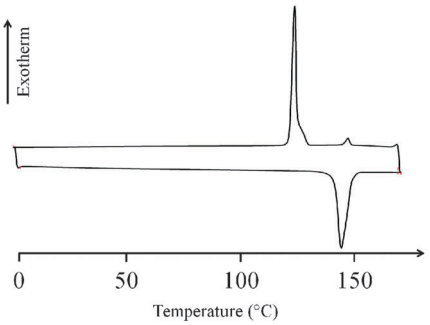


Fig. 1 Differential scanning thermogram of compound **7** registered during the second heating–cooling cycle.

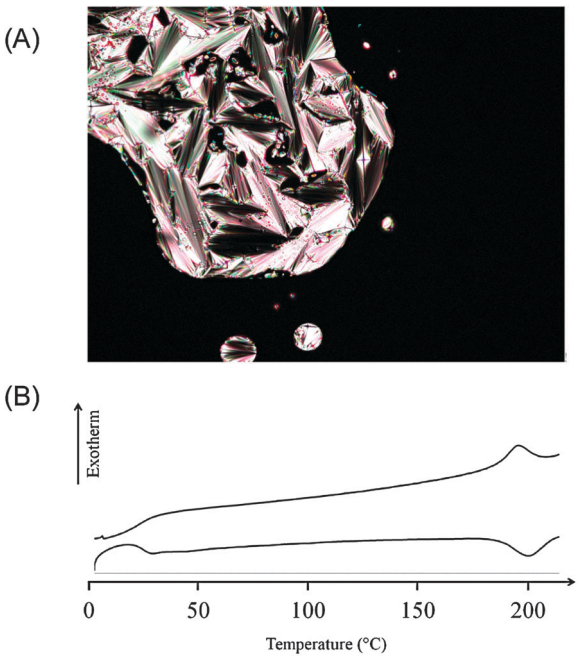


Fig. 2 (A) Thermal polarized optical micrograph of the texture displayed by compound **5c** in the smectic A phase at 183 °C. (B) Differential scanning thermogram of compound **5c** registered during the second heating–cooling cycle.

fan texture and homeotropic areas) (Fig. 2A) over a broad temperature range (T_g: 32 °C; SmA → I: 201 °C, ΔH = 53 kJ mol^{-1}) (Fig. 2B). The formation of a smectic A phase for both compounds is in agreement with the nature and structure of the cyanobiphenyl mesogenic units.[11]

Based on previous studies of liquid-crystalline compounds prepared with similar cyanobiphenyl mesogenic moieties[11] and on the calculated structure of compound **5c** (Fig. S11, ESI†), a possible model for the supramolecular organization of **5c** within the smectic A phase can be proposed. As shown in Fig. 3, the pillar[5]arene units form the central sublayer of the lamellar phase and the cyanobiphenyl mesomorphic units are oriented upward and downward with respect to the plane containing the pillar[5]arene units.

Comparison of the thermal behavior of **5c** and **7** reveals interesting features. Model compound **7** was isolated in a crystalline form suggesting favorable intermolecular π–π interactions between the central aromatic parts of neighboring molecules. By DSC, both the melting point and crystallization

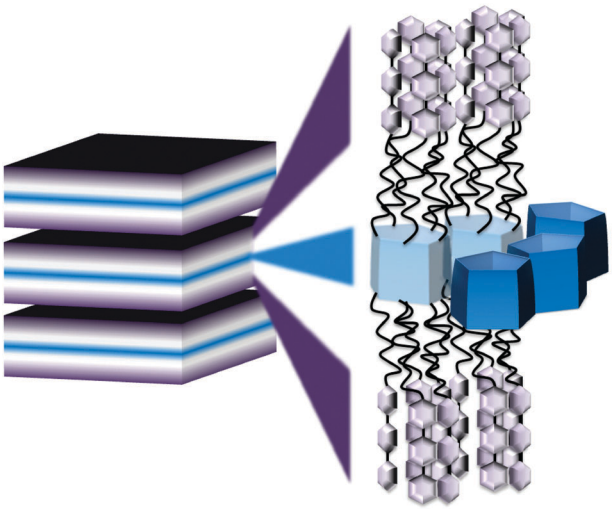


Fig. 3 Postulated supramolecular organization of **5c** within the smectic A phase.

temperature were detected during the heating–cooling cycles. As a consequence of the strong intermolecular π–π interactions, the crystalline phase is stabilized and only a monotropic mesophase could form. In contrast, by linking together five model subunits through the central macrocyclic pillar[5]arene core, the crystallization is prevented. Indeed, compound **5c** was isolated as a glass. At the same time, the broad enantiotropic mesophase observed for **5c** suggests also that intermolecular π–π interactions between neighboring pillar[5]arene cores play an important role in the stabilization of the smectic A phase, this is in perfect agreement with the proposed model depicted in Fig. 3.

In conclusion, we have reported the first example of a liquid-crystalline pillar[5]arene derivative. Interestingly, the macrocyclic core unit is capable of providing at the same time orientational and/or positional disorder within smectic layers to prevent crystallization and intermolecular π–π interactions between neighboring cores to stabilize the liquid-crystalline smectic A phase.

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