Pergamon

Tetrahedron 57 (2001) 3769–3783

TETRAHEDRON

Discotic liquid crystalline hexabenzocoronenes carrying chiral and racemic branched alkyl chains: supramolecular engineering and improved synthetic methods

Andreas Fechtenkötter, Natalia Tchebotareva, Mark Watson and Klaus Müllen*

Max-Planck-Institut für Polymerforschung, Ackermannweg 10, D-55128 Mainz, Germany

Received 3 November 2000; accepted 22 January 2001

Abstract—In this paper we present the synthesis and characterization of three different thermotropic liquid crystalline derivatives of hexabenzocoronene (HBC), substituted at the periphery by six chiral or racemic branched (3,7-dimethyloctanyl) chains, namely the chiral **5a**, racemic **5b**, and *mono*-bromo functionalized **18** carrying five alkyl chains. Improved methods for synthesis of HBC precursors, largely relying on transition-metal catalyzed coupling reactions, are also described. Solubility and processability are increased while the thermal $K \rightarrow D_H$ transitions are shifted to lower temperatures, relative to analogous HBCs carrying *n*-alkyl chains. In case of substitution with a chiral branched alkyl chain, **5a**, strong signals have been recorded by means of circular dichroism spectroscopy. All new compounds were characterized by ^1H, ^{13}C NMR, and UV–Vis spectroscopy, and FD-MS. Preliminary mesophase characterization is carried out by differential scanning calorimetry (DSC) and polarized light microscopy. In the course of the DSC experiments, optically pure and racemic HBC derivatives were compared.

1. Introduction

Once a chemical substance crosses the border from being simply a new compound to the stage were its materials properties become most dominant and relevant for its application in devices, one has to think of designing the synthesis to be as easy, inexpensive and efficient as possible. For one class of compound this border has been crossed some time ago. Discotic liquid crystals[1–3] are being recognized for their potential applications in photovoltaic devices,[4,5] field effect transistors (FETs)[6] and molecular electronics.[7] Since Chandrasekhar in 1977 discovered the first discotic liquid crystalline material,[8] immense research efforts have lead to a variety of novel discotic mesogens such as phthalocyanines,[9,10] porphyrines,[9] triphenylenes,[11–15] dibenzopyrenes,[13,16,17] perylenes[18,19] and hexabenzocoronenes (HBCs, Fig. 1).[20–29]

The latter four belong to the class of large polyaromatic hydrocarbons (PAHs).[30] Perylene is a well-known chromophore, which displays high extinction coefficients and nearly quantitative fluorescence quantum yields with outstanding photochemical and thermal stability.[18,19] However, it suffers from its low processability. This was overcome with the introduction of solubilizing side groups, also yielding perylene derivatives that exhibit discotic liquid crystallinity over temperature ranges of up to 200°C.[18] These materials combine several target properties: (a) stable mesophases over large temperature ranges, (b) high thermal and photochemical stability, and (c) intense absorption at long wavelengths.[18]

Among the above-mentioned liquid-crystalline PAHs, triphenylenes are the ones that have been studied most extensively in view of their mechanism of charge transport,[31–33] one-dimensional energy transport,[34,35] photoconductivity,[4,5,36–39] ordering of multilayers (investigated by using Langmuir–Blodgett techniques),[40] orientation of two-dimensional crystals[41,42] (investigated using scanning tunneling microscopy (STM)) and their alignment under the influence of a magnetic field.[43] Further, liquid crystalline polymers with triphenylenes both in the main and in the side chain have been prepared and analyzed.[13,44–47] Photophysical properties of several different alkoxy substituted dibenzopyrene derivatives have been determined to study the phase transitions with the help of absorption and fluorescence spectroscopy.[17] Two switchable ferroelectric phases of a columnar dibenzopyrene derivative have been reported by Bock et al.[16] Here, the co-existence of different columnar phases depends on the strength of an applied electric field, thus opening possible applications for electro-optical displays.

Alkyl-, or phenyl-alkyl substituted hexabenzocoronenes (Fig. 1) and their functionalized derivatives[20–29] are discotic liquid crystalline materials with one of the largest PAH cores (approximately three times the size of triphenylene).

Keywords: polyaromatic hydrocarbons (PAH); hexabenzocoronenes; discotic liquid crystals; chiral mesophase.

* Corresponding author. Tel.: +49-6131-379151; fax: +49-6131-379100; e-mail: muellen@mpip-mainz.mpg.de

0040–4020/01/$ - see front matter
PII: S0040-4020(01)00252-6

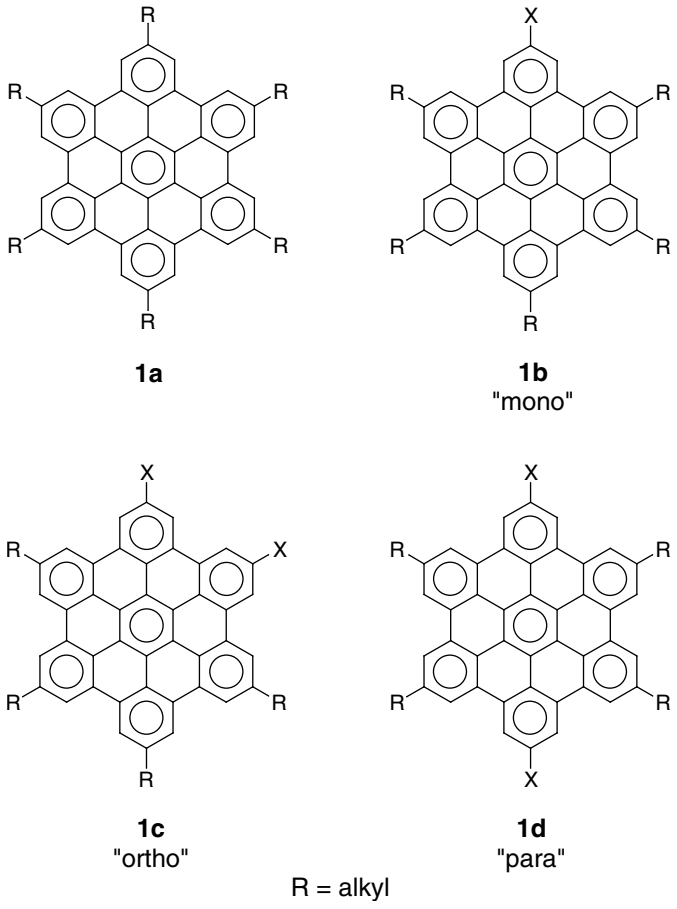


Figure 1. Hexabenzocoronene derivatives with differing substitution patterns.

This class of mesogen is being well recognized for its extremely large phase widths (up to 250°C)[21] and its record charge carrier mobilities along the columnar axis ($1.13\ cm^2\ V^{-1}\ s^{-1}$).[23,27]

From the examples given above, it can be seen that by varying the size and geometry of the aromatic core of discotic liquid crystals, the properties change dramatically. Increasing the size of the core results in enhanced $\pi-\pi$ overlap, thus giving rise to larger phase widths and more stable mesophases. Vast differences for the mesoscopic properties are also seen by changing the periphery, e.g. a hexahexylthiotriphenylene[5] exhibits a helical columnar phase and was the previous record holder for charge carrier mobilities of organic materials other than in single crystals.[5] Simmerer et al. showed that by changing the substituents on the perimeter of the triphenylene disc from pentyloxy to butyloxy, one does not only proceed from a columnar

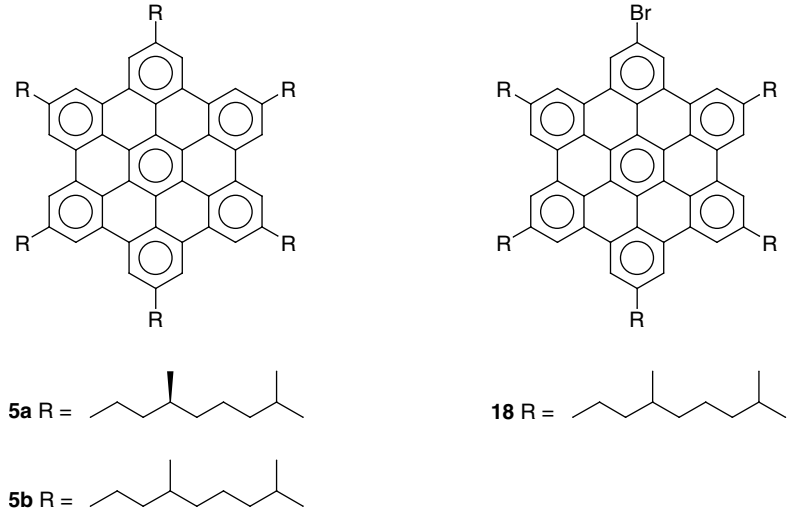
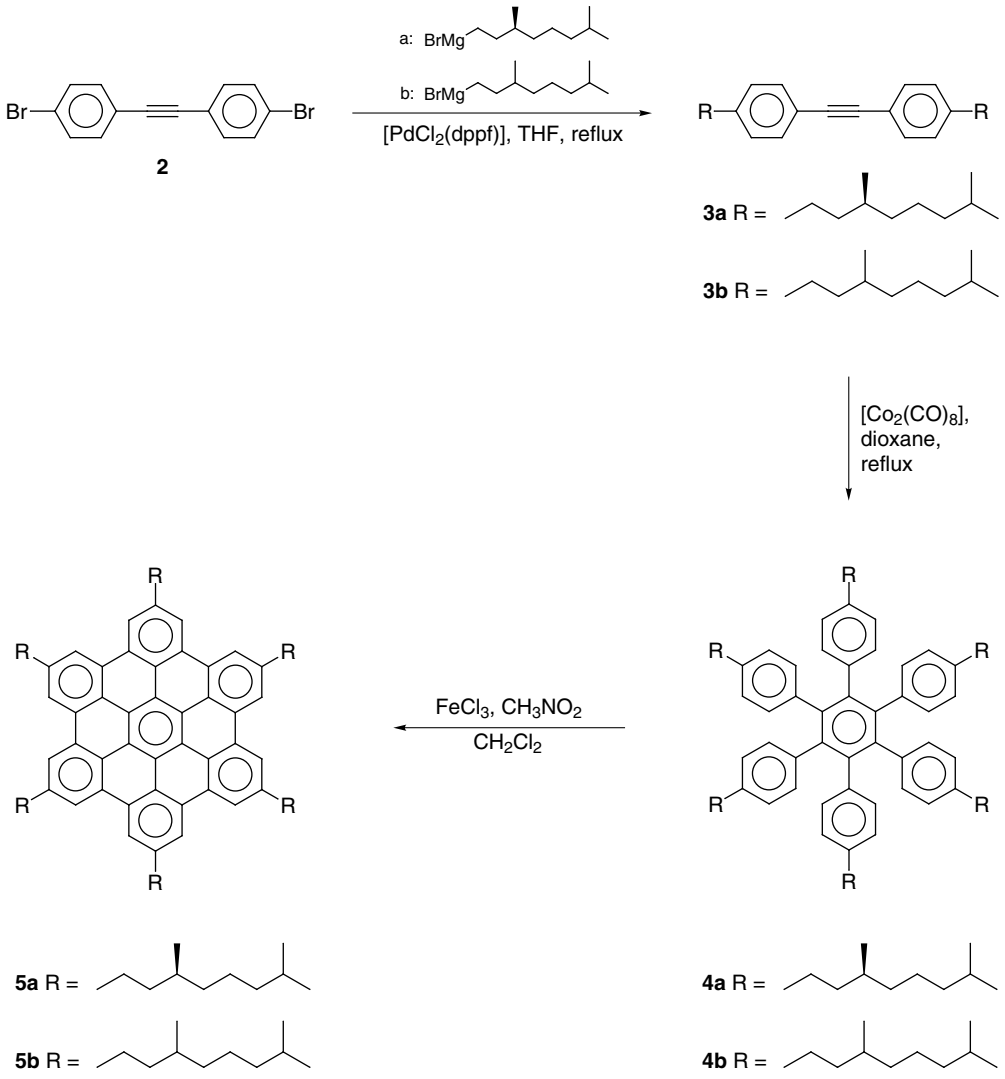


Figure 2. All-alkyl and *mono*-bromo-functionalized hexabenzocoronenes **5a**, **5b** and **18**.



Scheme 1. Synthesis of chiral and racemic hexaalkyl substituted hexabenzocoronenes **5a** and **5b**.

hexagonal packing to the formation of a so-called plastic discotic phase, but one also increases the mobilities by an order of magnitude.[36] Two different alignments in a magnetic field were observed when the triphenylene core is substituted with six 4-*n*-octyloxybenzoate groups.[43] And finally Langmuir–Blodgett films were obtained and investigated for an asymmetrically substituted triphenylene derivative carrying hydrophobic and hydrophilic side chains.[40]

This ample variety of functions, properties and applications also provided impetus for the development of new and improved syntheses of triphenylenes. Since Bachmann synthesized the first triphenylene[48] and Destrade et al. the first liquid crystalline derivative[49] in 1979, numerous improvements in the synthesis and processing of triphenylenes have been reported.

Initially, hexaalkyloxy triphenylenes with groups larger than methyl had to be prepared by a three-step route comprised of oxidative trimerization of veratrole with chloranil, demethylation of the hexamethoxy triphenylene, and then alkylation of the resulting hexahydroxy compound. It was later shown that various hexaalkoxy derivatives could be prepared directly from dialkoxy benzenes using suspended $FeCl_3$ as an oxidizing agent, followed by reductive workup with methanol.[50] Recently, Kumar and coworkers reported that $VOCl_3$ performs the same oxidation in high yield in very short reaction times (10 min), which was attributed to the high solubility of the oxidizing agent.[51] Further, unsymmetrically substituted triphenylenes were desired and a number of routes have been developed for the synthesis of such.[9]

Likewise, the very promising properties of alkyl-substituted HBCs prompted us to begin systematic investigations of various functionalized derivatives. The geometry of HBC suggests the name ‘superbenzene’ and we therefore use similar nomenclature for HBCs and for compounds built-up from HBC, such as the ‘supernaphthalene’ and the ‘supertriphenylene’, consisting of two and three ‘superbenzenes’, respectively.[52] Benzene-analogous nomenclature is also used to denote substitution patterns, e.g. HBC’s functionalized in the positions ‘*ortho*’ and ‘*para*’ as depicted in Fig. 1.[22] We have yet to implement alternative procedures to synthesize any ‘*meta*’ derivatives.

By benzene-analogous transition-metal catalyzed chemistry, HBC derivatives with cyano, ether, ester, amino, etc. functionality were prepared[22] from the bromo-functionalized HBCs (Fig. 1, X=Br). Their mesoscopic behavior as well as their packing in two and three dimensions was studied. The direct visualization of two-dimensional crystals and liquid crystals of hexabenzocoronene derivatives on surfaces such as HOPG (highly oriented pyrolytic graphite) and molybdenum disulfide was achieved by STM techniques.[20,22,53,54] From a *mono* bromo-substituted HBC (**1b**, R=*n*-$C_{12}H_{25}$, X=Br), a particularly interesting lattice structure was observed[22] with two types of arrangements: molecules associated in trimers (bromine atoms located in the center) and single molecules. The supramolecular arrangement reveals a hexagonal lattice in which single molecules fill positions in the center of an ensemble of six trimers.[22] Further, scanning tunneling *spectroscopy* revealed diode-like current–voltage curves for the cores of single molecules of a hexaalkyl HBC.[20]

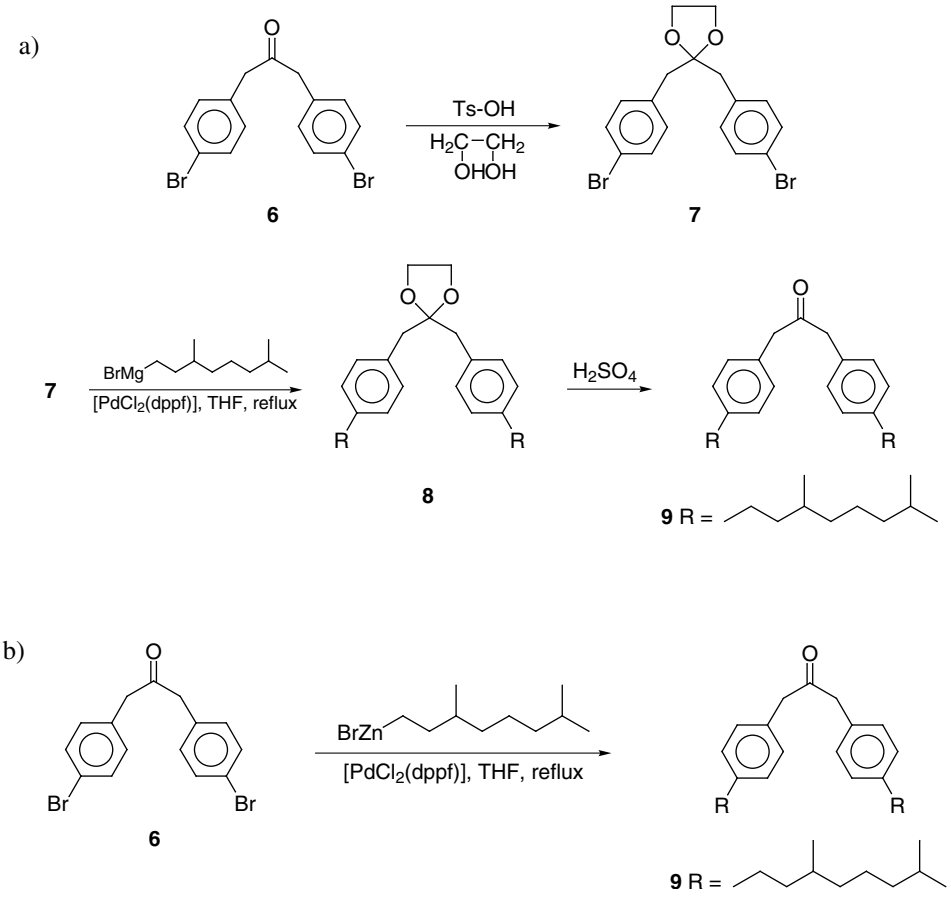
The *mono* bromo-substituted HBC was also used as a starting material for a surface active HBC with a tethered carboxylic acid group (**1b**, R=*n*-$C_{12}H_{25}$, X=$(CH_2)_{11}CO_2H$).[55] This derivative was then complexed with amino functionalized polysiloxane and polyethyleneimine resulting in remarkably long columns essentially free of defects.[25,56] The surface activity of this HBC was exploited to prepare LB films at the air–water interface.[57] These few examples taken together with the already existing vast number of triphenylene derivatives emphasize the wide horizon facing the field of discotic liquid crystalline PAHs.

More thorough understanding of the potential of HBCs as materials will require a library of derivatives, and improved synthetic routes to facilitate their preparation is desired. Recently published routes to prepare substituted hexabenzocoronenes relied on multistep syntheses and long term planning of the substitution pattern in cases with reduced symmetry and/or functionalized derivatives. Here, we discuss improved procedures for preparing the building blocks needed for HBC synthesis with symmetric six-fold alkyl substitution, namely the hexa-chiral HBC **5a** (HBC-C_8^*) and the racemic HBC **5b** (HBC-C_8) as well as bromo-functionalized compound **17** (Fig. 2). Dramatic increases in solubility and processability are noted compared to previous HBCs substituted with *n*-alkyl chains, and the effect of chirality in the side chains was preliminarily investigated.

2. Results

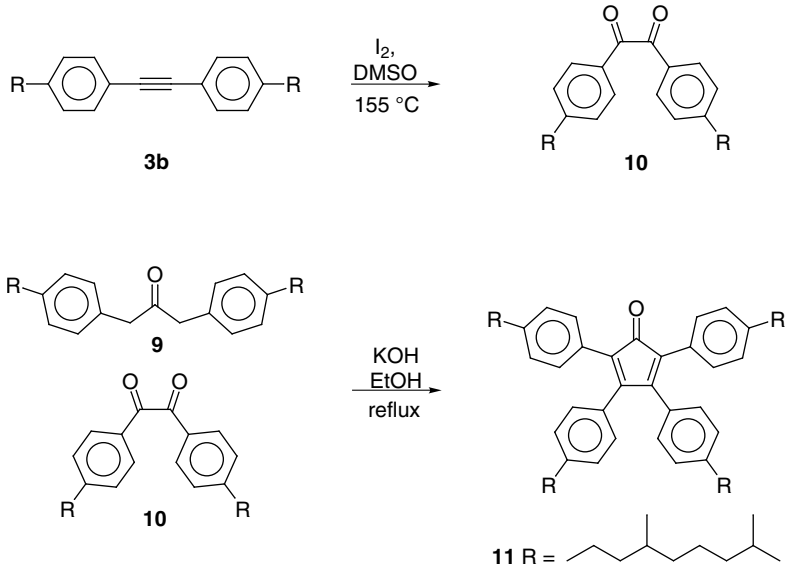
2.1. Syntheses

2.1.1. HBCs with C_6 symmetry. As reported by Herwig and co-workers in 1996, a four-step synthetic sequence was utilized to prepare alkyl substituted 4,4′-diphenylacetylenes,[21] the crucial building block for the hexafold-substituted HBC derivatives. Two disadvantages of this synthesis come

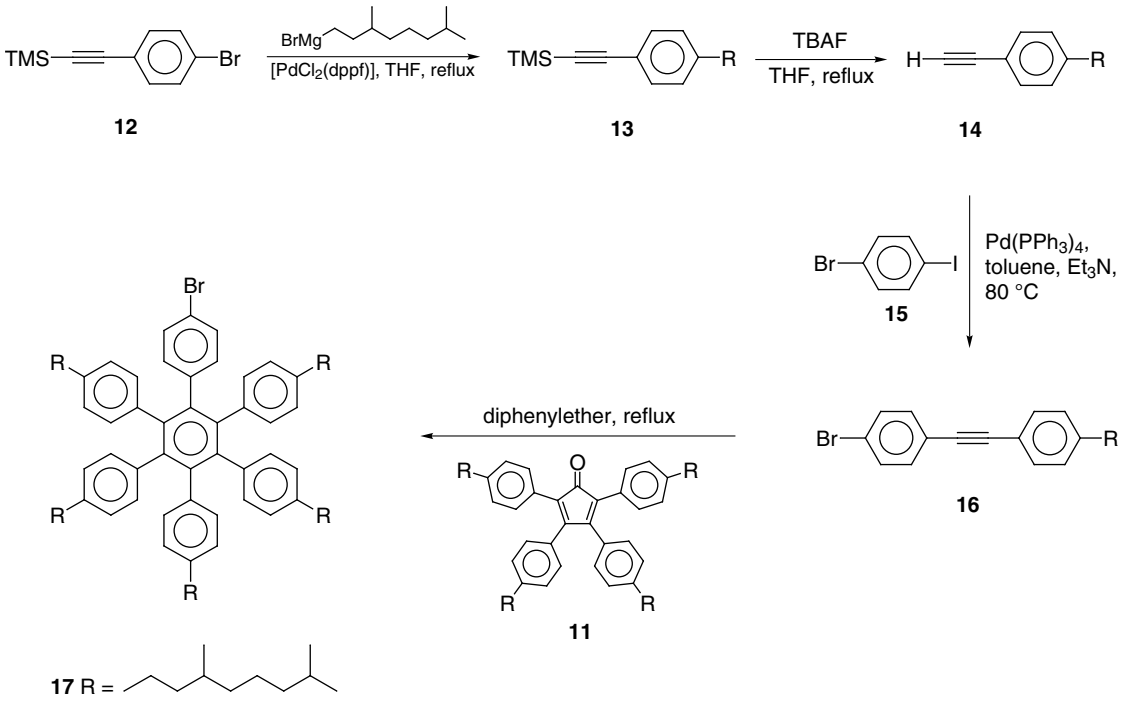


Scheme 2. (a) Protection, reaction, and deprotection sequence of compound **9**; (b) improved synthesis of **9** using a zinc metalated alkyl chain.

easily to mind: (a) two of the four steps are catalyzed by expensive palladium catalysts, and (b) the introduction of a different substituent cannot be accomplished on the level of the 4,4′-diphenylacetylene, but must be introduced right at the beginning of the reaction sequence. Here, we present a much faster, cheaper and higher yielding one-step synthesis for the desired diphenylacetylene starting from 4,4′-dibromodiphenylacetylene (**2**), which can be prepared according to a literature procedure[58] on several hundred gram scale. Previous attempts[22] to functionalize **2** under common Grignard coupling conditions using $NiCl_2$(dppe), $NiCl_2$(dppp), or $Pd(PPh_3)_4$ were unsatisfactory. It was just recently that we reported the aryl–aryl coupling of **2** with two equivalents 4-*n*-dodecylphenyl-magnesiumbromide using the [PdCl2(dppf)] catalyst.[29] The extension of this method to the coupling of alkylmagnesiumbromide species is outlined in Scheme 1. (*S*)-3,7-Dimethyloctylmagnesiumbromide is coupled with **2** under Kumada coupling conditions using [PdCl2(dppf)][59] as the catalyst in THF, to yield the enantiomerically pure alkyl substituted diphenylacetylene **3a** in 85% yield. In a similar fashion the racemic version of **3a**, i.e. **3b** was prepared in equally high yields. This procedure is highly attractive, especially when the group to be attached, 'R', is either expensive, or must be prepared by multistep synthesis. In a cyclotrimerization reaction under catalytic action of $Co_2(CO)_8$[60] **3a** and **3b** were both transferred to the hexaphenylbenzene derivatives **4a** and **4b**, respectively. These reactions have yields of



Scheme 3. Synthesis of substituted tetraarylcyclopentadienone **11**.



Scheme 4. [4+2] Diels–Alder reaction leading to the bromo-substituted hexaphenylbenzene **17**.

around 90% and the products are easily purified using standard column chromatography. The final step for this reaction sequence is the oxidative planarization of the six pending phenyl rings in **4a** and **4b**, with concurrent loss of twelve hydrogens. The cyclodehydrogenation[26] is achieved by adding a solution of $FeCl_3$ in nitromethane to the hexaphenylbenzene precursors **4a** and **4b** in dichloromethane to afford the alkyl substituted hexabenzocoronenes **5a** and **5b**, respectively. Isolated yields after purification using column chromatography and slow reprecipitation are of the order of 80%.

The HBCs **5a** and **5b**, substituted with branched alkyl chains show solubilities in common organic solvents more than ten times higher than HBC derivatives, substituted with *n*-alkyl chains, synthesized earlier by our group.[21,22,24] The above introduced compounds have been characterized by ^{1}H- and ^{13}C NMR, UV–Vis spectroscopy, and FD-MS. As a typical example for the hexaalkyl-substituted HBCs, the ^{1}H NMR spectrum of **5a** is depicted in Fig. 3.

2.1.2. HBC with reduced symmetry. After showing that the introduction of branched alkyl chains greatly increases

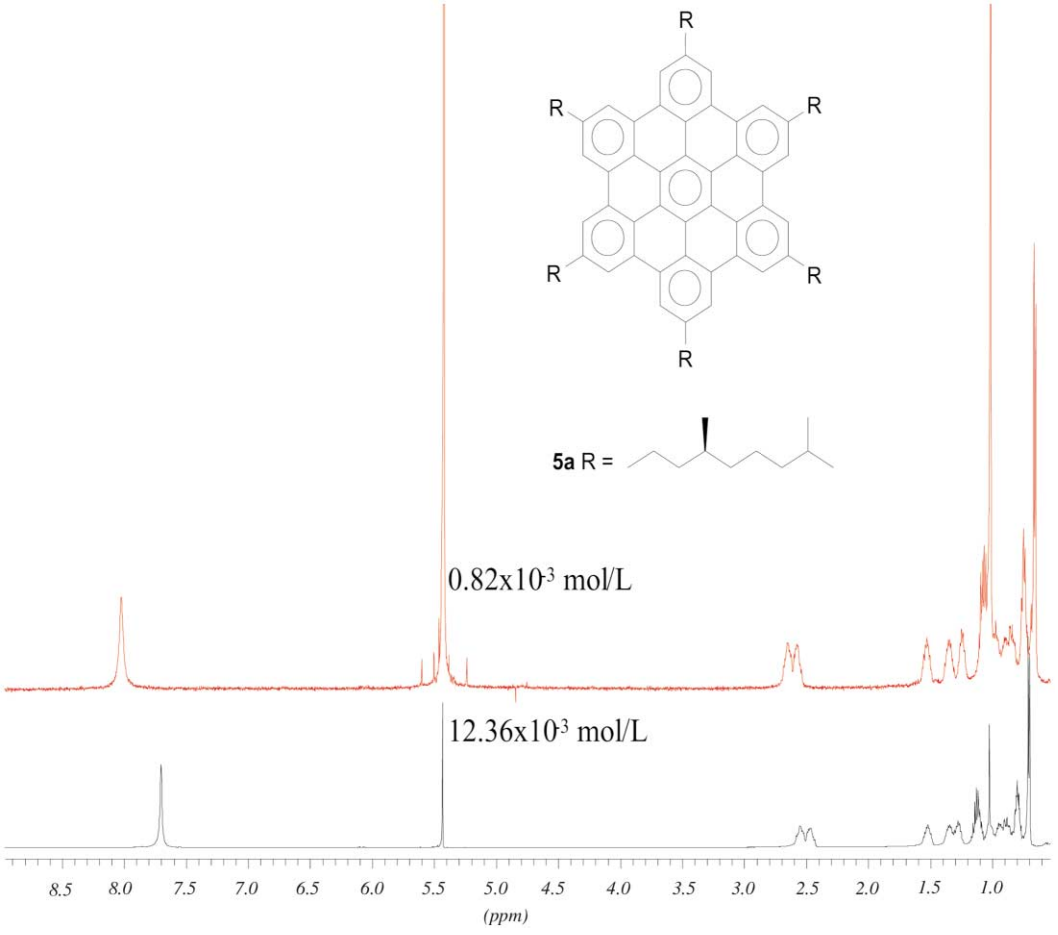
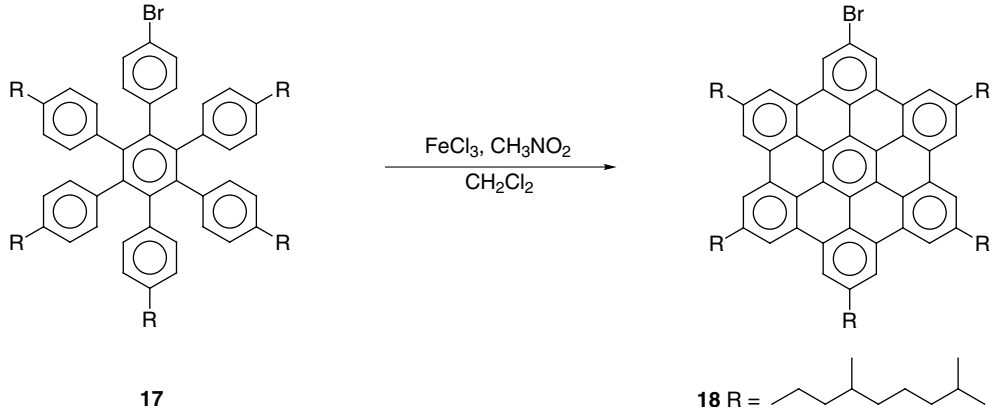


Figure 3. ^{1}H NMR spectra of **5a** at different concentrations ($C_2D_2Cl_4$, rt).



Scheme 5. Cyclodehydrogenation reaction of **17** yielding hexabenzocoronene **18**.

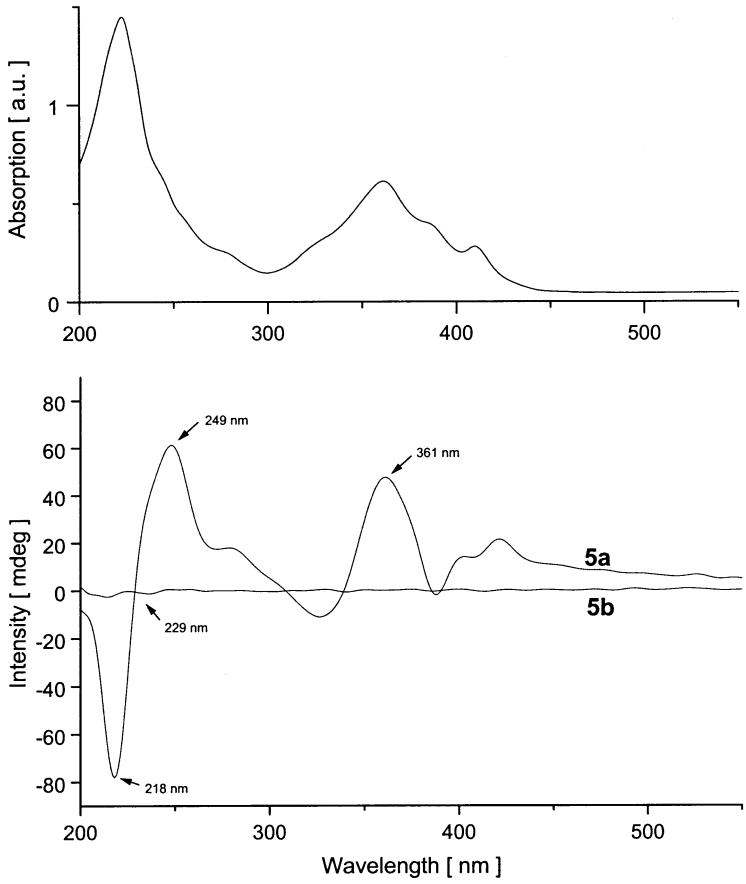


Figure 4. Circular dichroism spectra of **5a** and **5b** recorded from spincoated films.

solubility, as demonstrated for compounds **5a** and **5b** herein, we set out to prepare the *mono*-bromo-functionalized HBC **18**. The necessary functionalized hexaphenylbenzene precursor is prepared via the [4+2] cycloaddition of a suitably substituted diphenylacetylene, **16**, and 2,3,4,5-tetraarylcyclopenta-2,4-dien-1-one **11**. The cyclopentadieneone is synthesized via double Knoevenagel condensation between a 4,4′-substituted benzyl and a 1,3-diarylacetone (Scheme 3). The synthesis of a suitable 1,3-diarylacetone has until now, been the step with the lowest yields (47%) in the entire reaction sequence. For these reasons we chose a protection, deprotection route for the acetone derivative **9** (Scheme 2). At first, we protected 1,3-bis(4-bromophenyl)-2-propanone **6**[22] with ethylene glycol to give the acetal **7**. Next, under Kumada coupling conditions, the alkyl substituent was introduced in high yields. Just as in the herein reported synthesis of **3a** and **3b**, here we benefit from the advantage that the substituent 'R', which might be expensive monetarily or in terms of effort, is introduced after the low yielding process of synthesizing the dibromo functionalized acetone derivative **6**. The protected compound **8** proved to be extremely stable: quantitative deprotection could only be achieved by stirring **8** in concentrated sulfuric acid for several minutes.

While this procedure is acceptable for R=alkyl, the harsh deprotection will certainly limit the scope of functionalities which might be incorporated into this sequence. Therefore, we turned to the area of zinc chemistry, well known and widely applied in the field of organic- and natural product-chemistry.[61] As described in the literature,[62] zinc-alkyl compounds tolerate the ketone functional group and a wide range of other functionalities. Scheme 2 shows the direct alkyl functionalization of **6** via Pd-catalyzed coupling with 3,7-dimethyloctanylzincbromide, whereby 1,3-Bis-(4-(3,7-dimethyloctanyl)phenyl)-2-propanone (**9**) was obtained in good yields as a colorless oil. Oxidation of the above synthesized diphenylacetylene **3b** with iodine in DMSO at 155°C resulted in the 4,4′-alkylated benzil **10**. Twofold Knoevenagel condensation of **9** with **10** in *t*-butanol at 85°C afforded cyclopentadienone **11** in 84% yield (Scheme 3).

In order to obtain a *mono*-functionalized HBC derivative, an asymmetrically substituted diphenylacetylene is required (Scheme 4). 1-Bromo-4-trimethylsilylethinylbenzene (**12**) was alkylated similar to previous approaches with 3,7-dimethyloctanyl-magnesiumbromide and [$PdCl_2$(dppf)].[59] After quantitative deprotection of **13** in DMF with potassium fluoride, classical Hagihara–Sonogashira coupling[63] of the deprotected acetylene **14** with 1-bromo-4-iodobenzene (**15**) resulted in the bromine substituted diphenylacetylene **16**. [4+2] Diels–Alder reaction[22] of cyclopentadienone **11** and diphenylacetylene **16** in refluxing diphenylether afforded *mono*-bromo substituted hexaphenylbenzene **17** (Scheme 4). Planarization of **17** was carried out in the same manner as for compounds **5a** and **5b** and hexabenzocoronene **18** was obtained in high isolated yields (Scheme 5). As for hexabenzocoronenes **5a** and **5b**, the solubility and processability of **18** was dramatically

Table 1. Optical, thermal and thermodynamical data for compounds **5a**, **5b** and **18** (K=crystalline phase, Col_{ho}=ordered hexagonal columnar mesophase, I=isotropisation)

Compound	Transition	T (°C)	ΔH (J g^{-1})
5a	K→Col^{*}_{ho}	96	26
	Col^{*}_{ho}→I	430	
5b	K→Col_{ho}	81	31
	Col_{ho}→I	420	
18	K→Col_{ho}	32	
	Col_{ho}→I	>350	

enhanced with the introduction of the branched alkyl chains in place of the *n*-alkyl chains.

2.2. Spectroscopic characterization

NMR spectroscopy is an important tool for investigating aromatic stacking. It has been used to investigate the π–π aggregation of phenylacetylene macrocycles[64,65] and columnar structures formed by hexabenzocoronene derivatives[66] in the solid state. Here, the downfield signal at, e.g. δ=8.2 ppm for the core protons of compound **5a** clearly documents the diatropic character of these PAHs. These chemical shifts originate from a complex interplay of aromatic core size, perimeter type[28] and aggregation. We have utilized ^{1}H NMR spectra to qualitatively assess the strong influence that changes of concentration have on the aggregation of these aromatic compounds in solution. As depicted in Fig. 3, decreasing the concentration only from 12.36×10^{-3} to 0.82×10^{-3} mol L^{-1} results in a shift to lower field by $\Delta\delta$=0.33 ppm for the signals arising from the core protons. A less pronounced shift to lower field can be observed for the α-CH_2 protons of the alkyl side chains. We attribute these shifts to a decrease in aggregation number with decreasing concentration, a conclusion which finds support in theoretical calculations[67,68] in concert with solid-state NMR measurements.[26,29,69,70] Similar shifts to lower fields are observed with increasing temperature (for a constant concentration) and when carbon disulfide (a good solvent for the aromatic core) is added.

Structural information for an optically active compound such as **5a** can be obtained from circular dichroism (CD) spectroscopy which is an important method to study, e.g. the helical orientation of discotic liquid crystalline aggregates such as triphenylenes and phthalocyanines.[10,71] CD spectra can either be recorded from solution or films, i.e. Langmuir–Blodgett or spincoated films. Here, we studied thin films of the chiral HBC derivative **5a** and the racemic **5b**, prepared by spincoating concentrated solutions of **5a** and **5b** on quartz substrates. These samples were investigated by means of CD spectroscopy at room temperature and the resulting spectra are given in Fig. 4. As expected, the racemic HBC derivative **5b** did not show any CD effect at room temperature or after annealing in the mesophase at 90°C. Under the same experimental conditions, the *all* chiral HBC derivative **5a** showed two very strong, characteristic CD signals. A signal was observed at a wavelength of λ=361 nm, with a positive Cotton-effect in the CD spectra as depicted in Fig. 4. However, the most dominant signal in the spectra (Fig. 4) is a so-called CD-couplet that traverses the baseline at λ=229 nm. A CD-couplet is defined as the direct succession of two intensive Cotton-effects with reversed signs. Within this CD-couplet, compound **5a** exhibits a positive Cotton-effect at higher wavelength and a negative one at lower wavelength. In contrast to optically active phthalocyanine derivatives[10] the prepared films of **5a** did not have to be annealed at higher temperatures to achieve optical activity which is probably an indication of a very high degree of preorientation of the HBC discs before

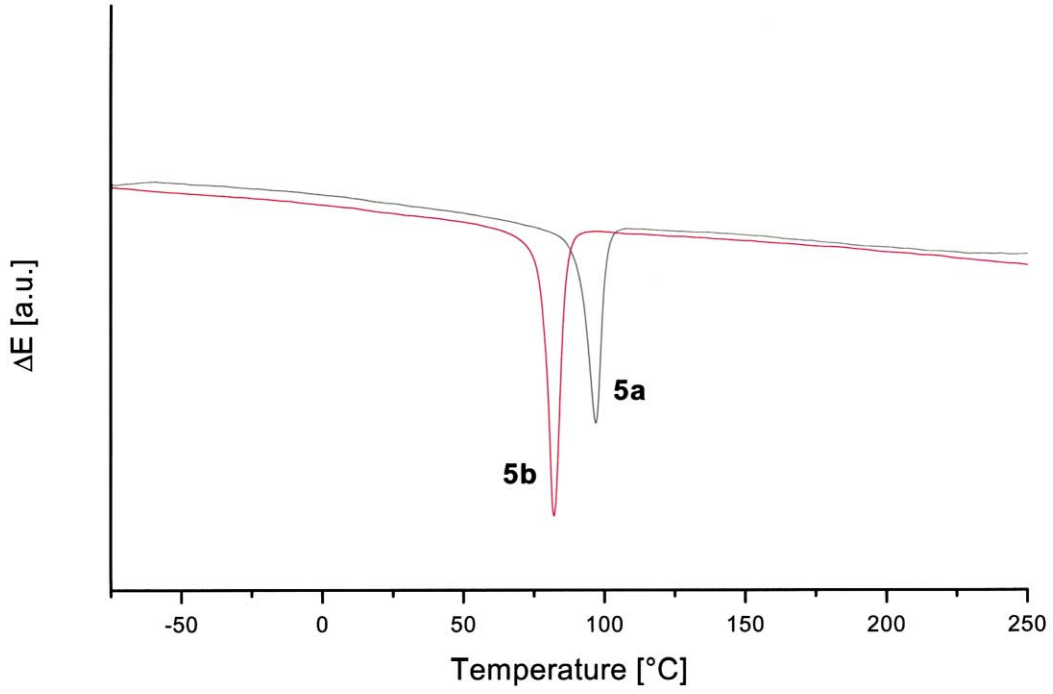


Figure 5. Differential scanning calorimetry traces of **5a**, **5b** and **18**.

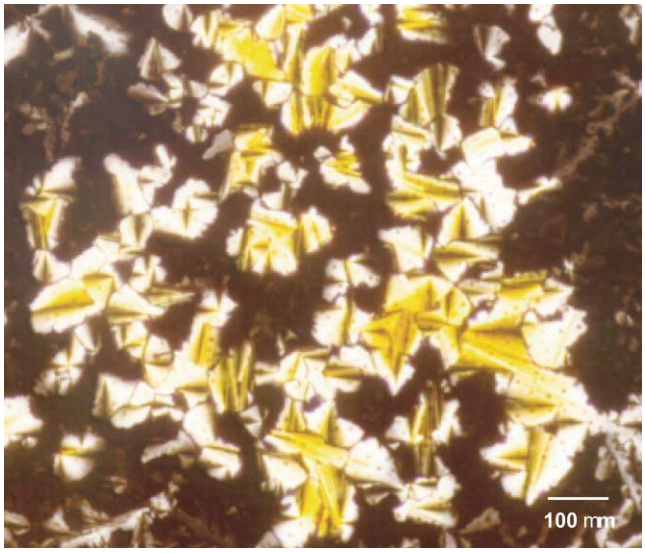


Figure 6. Optical textures of the hexagonal discotic mesophase of **5a** observed under polarized light.

or during the preparation of the films. However, artifacts due to linear dichroism can be excluded, since the identical spectrum was obtained from the same sample after rotating by 90° in the plane normal to the incident light. Further, temperature dependent CD measurements on thin films were conducted to probe the stability of the chiral superstructures. Here, the temperature was increased in steps of 20 K from −10°C up to 70°C. The recorded CD signals lost intensity on the order of 20% during the course of heating, but never faded completely.

2.3. Mesophase characterization

Preliminary differential scanning calorimetry (DSC) and optical polarization microscopy experiments were performed to study the phase behaviors of HBCs **5a**, **5b** and **18**. A summary of the thermal behavior derived from these measurements is shown in Table 1. At room temperature all compounds are yellow solids. Upon heating, all three compounds enter the columnar discotic mesophase Col_{ho} which is of chiral nature in the case of **5a**, as determined by CD spectroscopy, and therefore denoted as Col_{ho}^{*}. For the chiral HBC **5a**, a sharp endothermic peak at 96°C (Fig. 5) with a characteristic enthalpic value of 26 J g^{-1} indicates the transition from the solid phase into the chiral columnar mesophase. A phase transition 15°C lower, i.e. 81°C, as depicted in Fig. 5 is observed for the racemic compound **5b** with an enthalpic value of 31 J g^{-1}. The bromo-functionalized derivative **18** enters the mesophase at 32°C, almost 50°C lower than its analogue bearing 6 alkyl chains (**5b**). On heating, an additional reproducible first-order exotherm occurs just before this transition, which is absent in subsequent heating scans after annealing at its peak (−18°C). In all of the above cases, liquid crystallinity is maintained over a very large temperature range and no additional mesophase transitions were observed for any of the compounds.

Optical polarization microscopy studies were conducted for all the HBC derivatives introduced above, i.e. **5a**, **5b** and **18**, in order to study their thermal behavior as an addition to the DSC experiments. Drop-cast films were prepared from chloroform solutions. The films were heated at 10 K min^{-1} under a nitrogen atmosphere upon which the HBC samples changed from a crystalline to a liquid crystalline phase at temperatures reported in Table 1. The columnar hexagonal mesophases were preserved over large temperature ranges and finally entered the isotropic phase at above 400°C. Fig. 6 (compound **5a**) reveals textures which are typical for the columnar hexagonal mesophase formed from alkyl-substituted HBCs. These textures were observed after annealing the sample for a few minutes at the isotropisation temperature followed by cooling the sample to lower temperatures. These textures did not change until the sample temperature was decreased to the point of recrystallisation below 96°C.

3. Discussion

The production of materials on large scale becomes more and more important when the targeted compound is being tested for possible device applications. The availability of hexaalkyl-substituted HBCs on a multi gram scale has become more facile with the incorporation of [$PdCl_2$-(dppf)][59] for the alkyl functionalization of 4,4′dibromodiphenylacetylenes. However, the $Co_2(CO)_8$ catalyzed cyclotrimerization of a functionalized diphenylacetylene only gives access to molecules with C_6 symmetry. It has the advantage of a fast and easy access to soluble alkylated HBCs, but has the disadvantage of not providing single site functionalization or break of symmetry in any controlled manner. Alternately, Ito et al. presented a synthetic strategy that allows *mono*-, *ortho*-di-, and *para*-di-functionalization of the hexabenzocoronene discs.[22] The sp^2 C–Br bond of bromo-functionalized HBC's served as a reactive site for coupling reactions leading to a number of new functionalized HBC's. These syntheses met with varying levels of success, which were no doubt limited in some cases by low solubility. For this reason, we prepared the highly soluble compound **18**, via a similar but simpler route to that of Ito. Utilization of Pd-catalyzed aryl halide–zincate coupling reactions not only simplified the synthesis of compound **18**, but also opens the way to prepare an endless number of other functionalized derivatives by more direct means. In principle, HBCs with each substitution pattern shown in Fig. 1, and with a broad range of functionalities, can now be prepared via coupling reactions starting just from the dibromo compounds **2**, **6** and **10** (R=Br).

Further, the fact that branching of the introduced alkyl chains has a positive impact on the processability of the described compounds has been demonstrated. Not only has the solubility been increased dramatically compared to HBCs substituted with *n*-alkyl chains (e.g. 1a R=*n*-$C_{12}H_{25}$)[20,21] but also the phase transition temperature into the columnar hexagonal mesophase was reduced by up to 27°C,[23] without compromising the stability of the mesophase ($T_{isotrop}$>400°C).

The fact that compound **5a** is substituted with 6 chiral alkyl chains and is optically active gives hope for increased one-dimensional charge carrier mobility, as was reported

for the helical mesophase of a hexa hexylthiotriphenylene derivative.[5,31] Before the introduction of liquid-crystalline hexabenzocoronenes, this material was the previous record holder for the mobility of charge carriers in organic liquid crystals.[23,27] The synthesis of the racemic derivative **5b** was important for several reasons. The mesophase formation of an optically pure material (**5a**) can be documented properly only if the racemic version (**5b**) of this compound is also subjected to similar characterization. DSC results showed that **5a** enters the columnar hexagonal mesophase at 96°C whereas **5b** already shows a phase transition at 81°C (Table 1).

These results are in contrast to those which van Nostrum and co-workers reported for chiral and racemic derivatives of phthalocyanines.[10] They determined a higher phase transition temperature for the racemic than for the optically pure material, which lacks a crystalline phase, and only shows amorphous behavior at low temperatures. This was not expected and could also not be explained in the course of their experiments. As depicted in Fig. 4 spincoated films of **5a** give very strong signals during CD measurements even without annealing whereas spincoated films of **5b** do not show any signal (as expected). In a similar experiment, films of chiral phthalocyanines had to be annealed before CD signals could be recorded.[10] While in that case, the identical alkyl chains were utilized, they were separated from the core by an oxygen (ether linkage) spacer. This not only increases the distance between the core and the stereogenic center, but also the added rotational freedom associated with an ether linkage may serve to further diminish the effect of the optically active center on the packing behavior of the core. In the case of the HBC **5a**, the stereogenic center is very close to the center and therefore has a stronger, more direct influence on the packing behavior. The reported signals in the CD spectra (Fig. 4) can be assigned as follows: Since compound **5a** is per definition chiral, with six alkyl chains, each carrying a stereogenic center, the signal at $\lambda=361$ nm is resulting from the individual discotic molecule **5a**. A similar signal is observed by UV–Vis spectroscopy, also at $\lambda=361$ nm, assigned as the β-band according to Clar's nomenclature.[72] The presence of a CD-couplet as shown in Fig. 4 is an indication for the coexistence of two electronic excited states with individual transition dipole moments. These two dipole moments are assigned to two HBC-C_8^* monomers. A splitting of the energy levels occurs, since the antiparallel orientation of dipole moments is energetically preferred. This gives rise to the two absorptions at different wavelengths ($\lambda=249$ and 218 nm) in the CD-spectra. The energy difference is calculated to be $\Delta\lambda=31$ nm (249–218 nm). This phenomena is commonly addressed as exciton-coupling or Davydov-coupling.[73] This coupling is occurring at a wave length where the UV–Vis spectra shows a presumed aggregation band, suggesting that the columnar superstructure formed by the individual HBC-C_8^* molecules (compound **5a**) might have a helical orientation. These assumptions were made in analogy to the conclusions drawn from detailed experiments with triphenylenes[71] and phthalocyanines.[10]

From the initial temperature-dependent CD experiments, it can be concluded that the chiral aggregates formed must be relatively stable since the intensity only dropped by a factor of 20% while the temperature was raised from −10 up to 70°C. The loss of intensity is attributed to higher mobility of the alkyl side-chains leading to the formation of more mobile, but still chiral, aggregates. Upon entry into the discotic mesophase at 96°C the uni-axial rotation should drastically increase, and whether the helical orientation of the molecules is still preserved will be investigated at a later time. The preliminary characterization presented here does not permit assignment of the helical arrangement of **5a** to one of the three arrangements suggested by van Nostrum and co-workers.[10] More detailed morphological studies are underway including X-ray analysis, solid state NMR, and more detailed temperature-dependant CD measurements. To investigate the aggregation of the HBC discs in solution and the possible resulting optical activity of the aggregates, CD measurements in a range of solvents are planned as well as temperature dependent CD experiments for both solution and film samples.

4. Conclusions

Dramatically enhanced solubility and processability are imparted when branched alkyl chains (3,7-dimethyloctanyl) are employed in place of *n*-alkyl chains at the periphery of hexabenzocoronene. Preliminary characterization by CD measurements revealed a distinct effect upon introduction of chiral side groups, which was tentatively assigned to a helical arrangement within the discotic columnar mesophase. An HBC carrying these chains as well as a single bromo-function attached to the core was also prepared. The high solubility of this compound in a range of organic solvents has facilitated further functionalization and the buildup of oligomers and polymers, all of which will be the subject of forthcoming publications.

5. Experimental

5.1. General methods

^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ and $C_2D_2Cl_4$ on a Bruker DPX 250, Bruker AMX 300 and Bruker DRX 500 with use of the solvent proton or carbon signal as internal standard. Melting points were determined on a Büchi hot stage apparatus and are uncorrected. Infrared spectra were recorded on a Nicolet FT-IR 320 spectrophotometer as KBr pellets or as film between NaCl discs. Mass spectra were obtained on a VG Instruments ZAB 2-SE-FPD by using FD. Elemental analyses were carried out on a Foss Heraeus Vario EL.

Differential scanning calorimetry (DSC) was measured on a Mettler DSC 30 with heating and cooling rates of $10\ K\ min^{-1}$. First order transition temperatures were reported as the minima of their endothermic peaks during heating. A Zeiss Axiophot with a nitrogen flushed Linkam THM 600 hot stage was used to characterize the optical textures under cross polars.

5.2. Materials

(*S*)-1-Bromo-3,7-dimethyloctane was synthesized according to standard literature procedure[74] using commercially available (3*S*)-(+)-3,7-dimethyl-6-octene-1-ylbromide from Aldrich. 4,4′-Dibromodiphenylacetylene (**2**)[58] and 1,3-bis(4-bromophenyl)-2-propanone (**6**)[22] were synthesized as previously described in the literature. [$PdCl_2$(dppf)], $Pd(PPh_3)_4$ were used as received from Strem. THF (A.C.S. reagent, Riedel-de Haen) was refluxed over potassium and distilled freshly before use. All other materials were used as received.

5.3. Syntheses

5.3.1. (*S*)-4,4′-Bis(3,7-dimethyloctanyl)diphenylacetylene (3a). (As an example for the synthesis of substituted diphenyl acetylenes.) In a 250 mL two-necked round bottom flask, 60 mL of a 1 M solution of (*S*)-3,7-dimethyloctanyl-1-magnesiumbromide (prepared immediately prior to use from (*S*)-1-bromo-3,7-dimethyloctane and magnesium) was added dropwise to 5 g (14.9 mmol) 4,4′-dibromodiphenylacetylene (**2**) dissolved in 150 mL of dry THF. Then, 500 mg of [$PdCl_2$(dppf)] catalyst was added to this solution. The resulting mixture was stirred under reflux in an inert atmosphere overnight. The reaction was quenched with methanol and the solvent removed under reduced pressure. Purification using column chromatography on silica gel with petrol ether as the eluent afforded 5.8 g **3a** as a colorless oil. Yield: 85%. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$): δ=7.42 (d, ^3J(H,H)=7.9 Hz, 4H; CH), 7.15 (d, ^3J(H,H)=7.9 Hz, 4H; CH), 2.63 (m, 4H; α-CH_2), 1.63 (m, 4H; β-CH_2), 1.55 (m, 2H; CH), 1.47 (m, 4H; CH_2), 1.37–1.24 (m, 6H; CH, CH_2), 1.81 (m, 4H; CH_2), 0.94 (d, ^3J(H,H)=6.1 Hz, 6H; CH_3) 0.91 (d, ^3J(H,H)=6.1 Hz, 12H; CH_3); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$): δ=140.12, 128.11.40, 124.89, 117.35, 85.75, 35.95, 35.06, 33.76, 29.99, 29.13, 24.45, 21.17, 19.16, 19.10, 16.17; MS (FD, 8 kV): *m/z* (%)=458.1 (100) [M^+] (calcd for $C_{34}H_{50}$=458.77).

5.3.2. 4,4′-Bis(3,7-dimethyloctanyl)diphenylacetylene (3b). Prepared as described above for compound **3a**. Colorless oil, yield: 86%. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$): δ=7.38 (d, ^3J(H,H)=7.9 Hz, 4H; CH), 7.11 (d, ^3J(H,H)=7.9 Hz, 4H; CH), 2.54 (m, 4H; α-CH_2), 1.55 (m, 2H; CH), 1.47 (m, 2 H; CH), 1.37 (m, 4H; CH_2), 1.25 (m, 4H; CH_2), 1.11–1.05 (m, 8H; CH_2), 0.87 (d, ^3J(H,H)=6.1 Hz, 6H; CH_3) 0.82 (d, ^3J(H,H)=6.7 Hz, 12H; CH_3); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$): δ=143.96, 131.85, 128.75, 120.72, 89.35, 39.62, 38.98, 37.43, 33.73, 32.79, 28.25, 25.01, 23.09, 23.00, 19.94; MS (FD, 8 kV): *m/z* (%)=458.5 (100) [M^+] (calcd for $C_{34}H_{50}$=458.77).

5.3.3. (*S*)-Hexa-4-(3,7-dimethyloctanyl)hexaphenylbenzene (4a). (As an example for the cyclotrimerization reaction.) 230 mg (0.68 mmol) [$Co_2(CO)_8$] was added under argon to a degassed solution of 2 g (4.36 mmol) (*S*)-4,4′-bis(3,7-dimethyloctanyl)diphenylacetylene (**3a**) in 100 mL of dioxane in a 250 mL round bottom flask equipped with a reflux condenser. After refluxing for 3 h, the solvent was evaporated under vacuum, and the residue was purified using column chromatography on silica gel with petrol ether/CH_2Cl_2 (9/1) as the eluent, yielding 1.8 g **4a** as colorless oil. Yield: 90%. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$): δ=6.61 (d, ^3J(H,H)=7.9 Hz, 12H; CH), 6.56 (d, ^3J(H,H)=7.9 Hz, 12H; CH), 2.29 (m, 12H; α-CH_2), 1.47 (m, 6H; CH), 1.35 (m, 6H; CH), 1.20–0.98 (m, 48H; CH_2), 0.82 (d, ^3J(H,H)=6.7 Hz, 36H; CH_3), 0.75 (d, ^3J(H,H)=6.1 Hz, 18H; CH_3); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$): 136.58, 135.52, 134.91, 130.0, 122.84, 35.92, 35.24, 33.68, 29.46, 28.52, 24.49, 21.26, 19.36, 19.29, 16.22; MS (FD, 8 kV): *m/z* (%)=1377.0 (100) [M^+] (calcd for $C_{102}H_{150}$=1376.31).

5.3.4. Hexa-4-(3,7-dimethyloctanyl)hexaphenylbenzene (4b). Prepared as described above for compound **4a**. Colorless oil, yield: 88%. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$): δ=6.58 (d, ^3J(H,H)=7.6 Hz, 12H; CH), 6.53 (d, ^3J(H,H)=7.9 Hz, 12H; CH), 2.26 (m, 12H; α-CH_2), 1.45 (m, 6H; CH), 1.32 (m, 6H; CH), 1.19–1.10 (m, 36H; CH_2), 1.05–0.97 (m, 12H; CH_2), 0.80 (d, ^3J(H,H)=6.7 Hz, 36H; CH_3); 0.73 (d, ^3J(H,H)=5.5 Hz, 18H; CH_3); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$): 139.45, 138.41, 137.78, 130.87, 125.71, 38.79, 38.15, 36.56, 32.34, 31.34, 27.37, 24.14, 22.23, 22.16, 19.09; MS (FD, 8 kV): *m/z* (%)=1375.9 (100) [M^+] (calcd for $C_{102}H_{150}$=1376.31).

5.3.5. (*S*)-Hexa(3,7-dimethyloctanyl)hexa-*peri*-hexabenzocoronene (5a). (As an example for the cyclodehydrogenation reaction.) A 250 mL two necked round bottom flask was charged with 0.50 g (0.36 mmol) of (*S*)-hexa-4-(3,7-dimethyloctanyl)hexaphenylbenzene (**4a**) and 100 mL of CH_2Cl_2. Using a glass capillary, a constant stream of argon was bubbled through the solution. Then, 1.12 g (6.9 mmol) of $FeCl_3$ dissolved in CH_3NO_2 (13 mL) was added dropwise using a syringe. After 30 min, the mixture was quenched with a large excess of methanol and the precipitate was filtered. The resulting yellow solid was redissolved in dichloromethane and filtered through a short pad of silica gel and dried under vacuum to yield 0.39 g **5a** as a yellow powder. Yield: 80%; ^{1}H NMR (500 MHz, $C_2D_2Cl_4$): δ=8.09 (s, 12H; CH), 2.96 (m, 12H; α-CH_2), 2.01 (m, 6H; CH), 1.8 (m, 12H; CH_2), 1.64 (m, 12H; CH_2), 1.54 (m, 6H; CH), 1.43 (m, 12H; CH_2), 1.33 (m, 12H; CH_2), 1.23 (d, ^3J(H,H)=6.1 Hz, 18H; CH_3), 0.97 (d, ^3J(H,H)=6.7 Hz, 36H; CH_3); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 100°C): δ=140.36, 129.98, 123.41, 121.42, 119.56, 40.01, 39.96, 37.95, 35.12, 33.69, 28.42, 25.32, 23.13, 23.05, 20.36; mp>300°C MS (FD, 8 kV): *m/z* (%)=1364.0 (100) [M^+] (calcd for $C_{102}H_{138}$=1364.21) EA: Anal. Calcd (%) for $C_{102}H_{138}$: C 89.80, H 10.20; found: C 89.77, H 10.17.

5.3.6. Hexa(3,7-dimethyloctanyl)hexa-*peri*-hexabenzocoronene (5b). Prepared as described above for compound **5a**. Yellow powder, yield: 83%. ^{1}H NMR (500 MHz, $C_2D_2Cl_4$): δ=8.26 (s, 12H; CH), 3.05 (m, 12H; α-CH_2), 2.06 (m, 6H; CH), 1.83 (m, 12H; CH_2), 1.65 (m, 12H; CH_2), 1.56–1.43 (m, 18H; CH, CH_2), 1.35 (m, 12H; CH_2), 1.23 (d, ^3J(H,H)=6.3 Hz, 18H; CH_3), 0.97 (d, ^3J(H,H)=6.6 Hz, 36H; CH_3); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$, 100°C): δ=140.07, 129.68, 123.10, 121.18, 119.25, 39.93, 39.87, 37.81, 35.00, 33.57, 28.31, 25.21, 23.06, 22.97, 20.25; mp >300°C, MS (FD, 8 kV): *m/z* (%)=1363.5 (100) [M^+] (calcd for $C_{102}H_{138}$=1364.21), EA: Anal. Calcd (%) for $C_{102}H_{138}$: C 89.80, H 10.20; found: C 89.83 H 10.11.

5.3.7. 1,3-Bis(4-(3,7-dimethyloctanyl)phenyl)-2-propanone (9): three step protection, Grignard coupling, deprotection route: 1,3-bis(4-bromophenyl)-2-propanone ethylene acetal (7)—protection. A mixture of 1,3-Bis(4-bromophenyl)-2-propanone (**6**) (16 g, 43.5 mmol), ethylene glycol (3.77 g, 60.9 mmol), and *p*-toluenesulfonic acid (Ts-OH, 4.35 mg) in 50 mL of dry toluene was refluxed in a round-bottomed flask fitted with a Dean–Stark for 12 h. The reaction mixture was cooled to room temperature and washed with 10% $NaHCO_3$ and water. The organic phase was dried ($MgSO_4$) and concentrated under reduced pressure to give a white solid, which was recrystallized from *n*-heptane to give pure **6** as white crystals. Yield: 99%. ^{1}H NMR (250 MHz, $C_2D_2Cl_4$): δ=7.32 (d, ^3J(H,H)=8.3 Hz, 4H; CH), 7.06 (d, ^3J(H,H)=8.39 Hz, 4H; CH), 3.37 (s, 4H, CH_2), 2,78 (s, 4H, CH_2). ^{13}C NMR (125 MHz, $C_2D_2Cl_4$): 135.79, 132.82, 131.25, 120.71, 110.51, 65.76, 44.19. MS (FD, 8 kV): *m/z* (%)=412.2 (100) [M^+] (calcd for $C_{17}H_{16}{\cdot}Br_2O_2$=412.12).

5.3.8. 1,3-Bis(4-(3,7-dimethyloctanyl)-phenyl)-2-propanone ethylene acetal (8)—Grignard coupling. Compound **8** was prepared utilizing a procedure identical to that used for preparation of **3a**, starting from dibromo compound **7**. The reaction was quenched with methanol and the solvent removed under reduced pressure. Purification using column chromatography on silica with petrolether as the eluent, afforded 5.9 g of **8** as a colorless oil. Yield: 75%. ^{1}H NMR (250 MHz, $C_2D_2Cl_4$): δ=7.09 (d, ^3J(H,H)=8.01 Hz, 4H; CH), 7.02(d, ^3J(H,H)=8.01 Hz, 4H; CH), 3.41(s, 4H, CH_2), 2,80 (s, 4H, CH_2), 2.50 (m, 4H; α-CH_2), 1.55–1.07 (m, 20H), 0.82 (d, ^3J(H,H)=6.11 Hz, 6H; CH_3) 0.79 (d, ^3J(H,H)=6.49 Hz, 12H; CH_3); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$): 141.44, 133.92, 130.92, 128.15, 111.21, 65.61, 44.30, 39.59, 39.19, 37.44, 33.38, 32.84, 28.22, 24.99, 23.07, 22.98, 19.98. MS (FD, 8 kV): *m/z* (%)=537.9 (55%) [M^+] (calcd for $C_{37}H_{58}O_2$=534.84); *m/z*=305.0 (100%) [$M^+-CH_2-C_6H_4-C_{10}H_{21}$]; *m/z*=232.7 (65%) [$CH_2-C_6H_4-C_{10}H_{21}$].

5.3.9. 1,3-Bis(4-(3,7-dimethyloctanyl)phenyl)-2-propanone (9)—deprotection. To 5 g (10 mmol) of **8**, 10 mL of concentrated sulfuric acid was added. The reaction mixture was stirred for 5 min, then poured into water. The product was extracted with toluene, washed with 10% of $NaHCO_3$, H_2O, dried with $MgSO_4$ and filtered through silica gel to give 3.9 g of **9** as a colorless oil. Yield: 80%. ^{1}H NMR (250 MHz, $C_2D_2Cl_4$): δ=7.35 (d, ^3J(H,H)=8.01 Hz, 4H; CH), 6.96 (d, ^3J(H,H)=8.01 Hz, 4H; CH), 3.61(s, 4H, CH_2), 2.51 (m, 4H; α-CH_2), 1.57–1.05 (m, 20H), 0.84 (d, ^3J(H,H)=6.49 Hz, 6H; CH_3) 0.79 (d, ^3J(H,H)=6.48 Hz, 12H; CH_3); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$): 142.34, 131.27, 129.75, 128.94, 49.01, 39.6, 39.12, 37.42, 33.36, 32.86, 28.23, 24.98, 23.07, 22.98, 19.95. MS (FD, 8 kV): *m/z* (%)=490.8 (100%) [M^+] (calcd for $C_{35}H_{54}O$=490.82)

5.3.10. 1,3-Bis(4-(3,7-dimethyloctanyl)-phenyl)-2-propanone (9)—direct route. A 50 mL, three-necked flask was charged with Mg (0.396 g, 16.3 mmol) and THF (16 mL). Under an Ar atmosphere, the Grignard reaction was started by adding a 3,7-dimethyloctanyl-1-bromide (3.6 g, 16.3 mmol) and a one drop of CH_2Br_2 with stirring and gentle heating. The reaction mixture was stirred for 1 h at room temperature. $ZnBr_2$ (3.6 g, 16.3 mmol) was dissolved in dry THF (8 mL) in a 50 mL three-necked flask with stirring and under argon. After cooling this solution to below 0°C, the Grignard solution was added dropwise, accompanied by precipitation and exothermic reaction. After stirring for an additional 15 min at 0°C, the reaction mixture was cooled to −78°C, and $PdCl_2$(dppf) (20 mg, 0.027 mmol) and 1,3-bis(4-bromophenyl)-2-propanone (**6**) (solution in 8 mL of THF) were added consecutively. The cooling bath was removed, and the reaction mixture was stirred overnight. After the reaction was quenched with 10% HCl, extracted with CH_2Cl_2, dried with $MgSO_4$ and evaporated. The residue was purified by column chromatography, eluent PE/CH_2Cl_2(50:50), to give **9** as a colorless oil. Yield: 75%.

5.3.11. 4,4′-(3,7-Dimethyloctanyl)benzil (10). 15.2 g (32.7 mmol) of 4,4′-bis(3,7-dimethyloctanyl)diphenylacetylene (**3b**) and 4.15 g (16.35 mmol) iodine were dissolved in 130 mL of DMSO and stirred overnight at 155°C under an Ar atmosphere. After cooling, the reaction mixture was poured into 150 mL of 4% solution of $NaSO_3$ and stirred 30 min. The product was extracted with PE, concentrated and purified by column chromatography with PE as eluent. Yield: 71%. ^{1}H NMR (250 MHz, $C_2D_2Cl_4$): δ=7.79 (d, ^3J(H,H)=8.01 Hz, 4H; CH), 7.25 (d, ^3J(H,H)=8.39 Hz, 4H; CH), 2.61 (m, 4H; α-CH_2), 1.54–1.06 (m, 20H), 0.84 (d, ^3J(H,H)=6.11 Hz, 6H; CH_3) 0.78 (d, ^3J(H,H)=6.87 Hz, 12H; CH_3); ^{13}C NMR (125 MHz, $C_2D_2Cl_4$): 194.90, 151.91, 130.93, 130.38, 129.39, 39.56, 38.67, 37.33, 34.10, 32.81, 28.22, 24.95, 23.06, 22.97, 19.87.

5.3.12. 2,3,4,5-Tetrakis(4-(3,7-dimethyloctanyl)phenyl)-cyclopentadienone (11). 5.2 g (10.7 mmol) of 1,3-bis-(4-(3,7-dimethyloctanyl)-phelyl)-2-propanone (**9**) and 5.2 g (10.7 mmol) of 4,4′-(3,7-dimethyloctanyl)benzil (**10**) were dissolved in 13 mL of *t*-butanol under Ar atmosphere and stirred at 85°C. A solution prepared from 7.4 mL of 0.8 M tetrabutylammoniumhydroxide in methanol and 3.3 mL of *t*-butanol was added. After 10 min, the reaction mixture was quenched by addition of 50 mL H_2O. The product was extracted with CH_2Cl_2, concentrated, and purified by column chromatography, eluent PE/CH_2Cl_2 (4:1). Yield: 8.6 g, (84%). ^{1}H NMR (250 MHz, $C_2D_2Cl_4$): δ=7.07(d, ^3J(H,H)=8.01, 4H, CH), 7.00 (d, ^3J(H,H)=8.39, 4H, CH), 6.91 (d, ^3J(H,H)=8.01, 4H, CH), 6.72(d, ^3J(H,H)=8.39, 4H, CH), 2.49 (m, 8H, α-CH_2), 1.51–1.07 (m, 40H, CH_2), 0.84 (d, ^3J(H,H)=6.48 Hz, 12H, CH_3), 0.79 (d, ^3J(H,H)=6.87 Hz, 24H, CH_3). ^{13}C NMR (125 MHz, $C_2D_2Cl_4$): 154.74, 143.83, 142.64, 130.56, 130.25, 129.65, 128.56, 128.31, 128.04, 124.77, 39.60, 38.94, 38.71, 37.44, 33.57, 32.91, 32.64, 28.22, 25.04, 24.99, 23.07, 22.99, 19.95. MS (FD, 8 kV): *m/z* (%)=945.5 (100%) [M^+] (calcd for $C_{69}H_{100}O$=945.57).

5.3.13. 4-(3,7-Dimethyloctanyl)-trimethylsilylethinylbenzene (13). In round bottom flask, 60 mL of a 1 M solution of (*S*)-3,7-dimethyloctanyl-1-magnesiumbromide was added dropwise to 3 g (12 mmol) 1-bromo-4-trimethylsilylethinylbenzene (**12**) dissolved in 30 mL of dry THF. Then 350 mg of [$PdCl_2$(dppf)] catalyst was added to this solution. The resulting mixture was refluxed under argon over night.

The reaction was quenched with methanol and the solvent removed under reduced pressure. Purification using column chromatography on silica gel with petrolether as the eluent, afforded 3.2 g **13** as a colorless oil. Yield: 85%. ^{1}H NMR (250 MHz, $C_2D_2Cl_4$): δ=7.3 (d, ^3J(H,H)=8.01 Hz, 2H, CH), 7.04 (d, ^3J(H,H)=8.01, 2H, CH), 2.52 (m, 2H, α-CH_2), 1.47 (m, 3H, β-CH_2,CH), 1.34–1.1 (m, 7H, CH_2), 0.83 (d, ^3J(H,H)=6.11 Hz, 3H, CH_3), 0.79 (d, ^3J(H,H)=6.4 Hz, 6H, CH_3), 0.17 (s, 9H, CH_3). ^{13}C NMR (125 MHz, $C_2D_2Cl_4$): 144.40, 132.38, 128.62, 120.47, 105.58, 93.98, 39.61, 38.94, 37.41, 33.71, 32.73, 28.24, 24.99, 23.08, 22.99, 19.91, 0.44. MS (FD, 8 kV): *m/z* (%)=314.7 (100%) [M^+] (calcd for $C_{21}H_{34}Si$=314.59).

5.3.14. 4-(3,7-Dimethyloctanyl)-phenylacetylene (14). 3 g (9.5 mmol) of 4-(3,7-dimethyloctanyl)-trimethylsilylethinylbenzene (**13**) was dissolved in 20 mL of DMF, together with 1.1 g (19 mmol) KF. The reaction mixture was stirred for 4 h at rt, then quenched with water and extracted with toluene. The solvent was removed under reduced pressure. Purification using column chromatography on silica gel with petrol ether as the eluent, afforded 2 g **14** as a white solid, yield 90%. ^{1}H NMR (250 MHz, $CDCl_3$): δ=7.38 (d, ^3J(H,H)=8.39 Hz, 2H, CH), 7.11 (d, ^3J(H,H)=8.01, 2H, CH), 2.55 (m, 2H, α-CH_2), 1.61–1.12 (m, 10H, CH_2), 0.9 (d, ^3J(H,H)=6.49 Hz, 3H, CH_3), 0.85 (d, ^3J(H,H)=6.87 Hz, 6H, CH_3). ^{13}C NMR (125 MHz, $CDCl_3$): 144.67, 132.48, 128.77, 119.63, 84.30, 76.79, 39.72, 39.06, 37.52, 33.85, 32.87, 28.37, 25.07, 23.08, 23.00, 19.97. MS (FD, 8 kV): *m/z* (%)=242.4 (100%) [M^+] (calcd for $C_{18}H_{26}$=242.41).

5.3.15. 4-Brom-4′-(3,7-dimethyloctanyl)diphenylacetylene (16). To the solution of 6.5 g (27 mmol) 4-(3,7-dimethyloctanyl)-phenylacetylene (**14**), 12 g (54 mmol) 4-bromiodobenzene, 0.51 g (2.7 mmol) CuI and 0.7 g (2.7 mmol) triphenylphosphine in 100 mL dry THF, 35 mL triethylamine and 0.94 g (1.35 mmol) bis(triphenylphosphine)palladium(II)chloride were added consecutively under argon. The reaction mixture was stirred overnight at room temperature, quenched with 2 M HCl, and extracted with CH_2Cl_2. The extract was concentrated under reduced pressure and purified by column chromatography with petrol ether as eluent to afford 8.8 g of **16** as a white solid. Yield: 82%. ^{1}H NMR (250 MHz, $C_2D_2Cl_4$): δ= 7.43–7.30 (m, 6H, CH), 7.1 (d, ^3J(H,H)=8.39, 2H, CH), 2.54 (m, 2H, α-CH_2), 1.52 (m, 2H, β-CH_2), 1.45 (m, 1H, CH), 1.35–1.1 (m, 7H, CH_2), 0.85 (d, ^3J(H,H)=6.1 Hz, 3H, CH_3), 0.79 (d, ^3J(H,H)=6.5 Hz, 6H, CH_3). ^{13}C NMR (125 MHz, $C_2D_2Cl_4$): 145.98, 134.81, 133.38, 130.30, 124.19, 124.01, 121.56, 92.67, 89.56, 41.07, 40.40, 38.87, 35.22, 34.25, 29.71, 26.47, 24.55, 24.47, 21.40. MS (FD, 8 kV): *m/z* (%)=398.2 (100%) [M^+] (calcd for $C_{24}H_{29}$·Br=397.8).

5.3.16. 1-(4-Bromophen-1yl)-2,3,4,5,6-pentakis(3,7-dimethyloctanylphen-1-yl)benzene (17). 8.5 g (8.95 mmol) of 2,3,4,5-tetrakis(4-(3,7-dimethyloctanyl)-phenyl)cyclopentadienone (**11**) and 3.56 g (8.95 mmol) of 4-brom-4′-(3,7-dimethyloctanyl)diphenylacetylene (**16**) were suspended in a minimal amount of diphenylether and refluxed for 5 h under Ar atmosphere. After cooling, diphenylether was removed under reduced pressure and the residue was purified by column chromatography with PE/CH_2Cl_2=20:1 as eluent to afford 6.2 g of **17**, as a yellow oil. Yield: 53%. ^{1}H NMR (250 MHz, $C_2D_2Cl_4$): δ=6.85 (d, ^3J(H,H)= 8.39 Hz, 2H, Ar-H), 6.57 (m, 22H, Ar-H), 2.3–2.24 (m, 10H, α-CH_2), 1.49–1.04 (m, 50H), 0.78 (d, ^3J(H,H)= 6.87 Hz, 30H, CH_3), 0.71 (m, 15H, CH_3). ^{13}C NMR (125 MHz, $C_2D_2Cl_4$): 140.12, 139.71, 139.41, 138.74, 138.27, 138.12, 133.59, 131.59, 129.64, 126.89, 126.61, 39.63, 38.98, 38.85, 37.38, 34.45, 33.17, 32.26, 32.18, 28.21, 24.97, 23.07, 23.01, 19.92. MS (FD, 8 kV): *m/z* (%)=1315.2 (100%) [M^+] (calcd for $C_{92}H_{129}Br$=1314.96).

5.3.17. 2-Bromo-5,8,11,14,17-penta (3,7-dimethyloctanyl)-hexa-*peri*-hexabenzo-coronene (18). Compound **18** was prepared from **17** as described for **5a** to give an orange solid. Yield: 80%. ^{1}H NMR (250 MHz, $C_2D_2Cl_4$): δ=7.85 (bs, 2H, Ar-H), 7.74 (bs, 2H, Ar-H), 7.57 (bs, 4H, Ar-H), 7.46 (bs, 2H, Ar-H), 7.28 (bs, 2H, Ar-H), 2.83–2.62 (m, 10H, α-CH_2), 2.61–1.14 (m, 65H), 0.99–0.93 (m, 30H, CH_3). ^{13}C NMR (125 MHz, $C_2D_2Cl_4$): 139.18, 130.24, 129.01, 128.77, 128.55, 128.39, 127.26, 122.76, 121.97, 121.93, 121.82, 121.74, 121.18, 120.75, 120.58, 120.50, 120.10, 118.39, 118.02, 117.83, 117.02, 40.44, 40.25, 39.89, 39.87, 39.73, 37.82, 35.12, 34.99, 33.80, 33.72, 28.39, 25.35, 25.33, 23.19, 23.08, 20.35, 20.30, 20.24. MS (FD, 8 kV): *m/z* (%)=1302.9 (100%) [M^+] (calcd for $C_{92}H_{117}Br$=1302.86)

Acknowledgements

This research was supported by the TMR European Research Program through the SISITOMAS project and the Volkswagen-Stiftung. We thank Petra Räder for conducting 'last-minute' DSC and TGA experiments. The help and advice from Professor Dr E. W. Meijer and his group, especially from Luc Brunsveld, during the CD experiments is gratefully acknowledged.

References

1. Demus, D.; Goodby, J. W.; Gray, G. W.; Spiess, H. W.; Vill, V. *Handbook of Liquid Crystals*; Wiley-VCH: Weinheim, 1998.
2. Chandrasekhar, C. *Liquid Crystals*; 2nd ed.; Cambridge University: Cambridge, 1992.
3. Chandrasekhar, S.; Prasad, S. K. *Contemop. Phys.* **1999**, *40*, 237–245.
4. Adam, D.; Closs, F.; Frey, T.; Funhoff, D.; Haarer, D.; Ringsdorf, H.; Schuhmacher, P.; Siemensmeyer, K. *Phys. Rev. Lett.* **1993**, *70*, 457–460.
5. Adam, D.; Schuhmacher, P.; Simmerer, J.; Häussling, L.; Siemensmeyer, K.; Etzbach, K. H.; Ringsdorf, H.; Haarer, D. *Nature* **1994**, *371*, 141–143.
6. Bao, Z.; Lovinger, A. J.; Dodabalapur, A. *Adv. Mater.* **1997**, *9*, 42–44.
7. Christ, T.; Glüsen, B.; Greiner, A.; Kettner, A.; Sander, R.; Stümpflen, V.; Tsukruk, V.; Wendorff, J. H. *Adv. Mater.* **1997**, *9*, 48–51.
8. Chandrasekhar, S.; Sadashiva, B. K.; Suresh, K. A. *Pramana* **1977**, *7*, 471.
9. Cammidge, A. N.; Busby, R. J. In *Handbook of Liquid*

Crystals; Demus, D., Goodby, J. W., Gray, G. W., Spiess, H. W., Vill, V., Eds.; Wiley-VCH: Weinheim, 1998.
10. van Nostrum, C. F.; Bosman, A. W.; Gelinck, G. H.; Schouten, P. G.; Warman, J. M.; Kentgens, A. P. M.; Devillers, M. A. C.; Meijerink, A.; Picken, S. J.; Sohling, U.; Schouten, A.-J.; Nolte, R. J. M. *Chem. Eur. J.* **1995**, *1*, 171–182.
11. Eichhorn, H. *J. Porphyr. Phthalocya.* **2000**, *4*, 88–102.
12. Frampton, C. S.; MacNicol, D. D.; Rowan, S. J. *J. Mol. Struct.* **1997**, *405*, 169–178.
13. Henderson, P.; Ringsdorf, H.; Schuhmacher, P. *Liq. Cryst.* **1995**, *18*, 191–195.
14. Musgrave, O. C.; Webster, C. J. *J. Chem. Soc. C* **1971**, 1397–1401.
15. Yatabe, T.; Harbison, M.; Brand, J. D.; Wagner, M.; Müllen, K.; Samori, P.; Rabe, J. P. *J. Mater. Chem.* **2000**, *10*, 1519–1525.
16. Bock, H.; Helfrich, W. *Liq. Cryst.* **1995**, *18*, 387–399.
17. Uznanski, P.; Marguet, S.; Markovitsi, D.; Schumacher, P.; Ringsdor, H. *Mol. Cryst. Liq. Cryst.* **1997**, *293*, 123–133.
18. Müller, G. R. J.; Meiners, C.; Enkelmann, V.; Geerts, Y.; Müllen, K. *J. Mater. Chem.* **1998**, *8*, 61–64.
19. van de Craats, A. M.; Warman, J. M.; Schlichting, P.; Rohr, U.; Geerts, Y.; Müllen, K. *Synth. Met.* **1999**, *102*, 1550–1551.
20. Stabel, A.; Herwig, P.; Müllen, K.; Rabe, J. P. *Angew. Chem.* **1995**, *107*, 1768–1770.
21. Herwig, P.; Kayser, C. W.; Müllen, K.; Spiess, H. W. *Adv. Mater.* **1996**, *8*, 510–513.
22. Ito, S.; Wehmeier, M.; Brand, J. D.; Kübel, C.; Epsch, R.; Rabe, J. P.; Müllen, K. *Chem. Eur. J.* **2000**, *6*, 4327–4342.
23. van de Craats, A. M.; Warman, J. M.; Fechtenkötter, A.; Brand, J. D.; Harbison, M. A.; Müllen, K. *Adv. Mater.* **1999**, *11*, 1469–1472.
24. Herwig, P. T.; Enkelmann, V.; Schmelz, O.; Müllen, K. *Chem. Eur. J.* **2000**, *6*, 1834–1839.
25. Thünemann, A. F.; Ruppelt, D.; Ito, S.; Müllen, K. *J. Mater. Chem.* **1999**, *9*, 1055–1057.
26. Brown, S. P.; Schnell, I.; Brand, J. D.; Müllen, K.; Spiess, H. W. *J. Am. Chem. Soc.* **1999**, *121*, 6712–6718.
27. van de Craats, A. M.; Warman, J. M.; Müllen, K.; Geerts, Y.; Brand, J. D. *Adv. Mater.* **1998**, *10*, 36–38.
28. Dötz, F.; Brand, J. D.; Ito, S.; Gherghel, L.; Müllen, K. *J. Am. Chem. Soc.* **2000**, *122*, 7707–7717.
29. Fechtenkötter, A.; Saalwächter, K.; Harbison, M. A.; Müllen, K.; Spiess, H. W. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 3039–3042.
30. Zander, M. *Polycyclische Aromaten*; Teubner: Stuttgart, 1995.
31. van de Craats, A. M.; Warman, J. M.; de Haas, M. P.; Adam, D.; Simmerer, J.; Haarer, D.; Schuhmacher, P. *Adv. Mater.* **1996**, *8*, 823–826.
32. van de Craats, A. M.; Siebbeles, L. D. A.; Bleyl, I.; Haarer, D.; Berlin, Y. A.; Zharikov, A. A.; Warman, J. M. *J. Phys. Chem. B* **1998**, *102*, 9625–9634.
33. van de Craats, A. M.; de Haas, M. P.; Warman, J. M. *Synth. Met.* **1997**, *86*, 2125–2126.
34. Brown, A.; Wilkinson, F. *J. Chem. Soc., Faraday Trans.* **1979**, 75.
35. Markovitsi, D.; Germain, A.; Millie, P.; Lecuyer, P.; Gallos, L. K.; Argyrakis, P.; Bengs, H.; Ringsdorf, H. *J. Phys. Chem.* **1995**, *99*, 1005–1017.
36. Simmerer, J.; Glüsen, B.; Paulus, W.; Kettner, A.; Schuhmacher, P.; Adam, D.; Etzbach, K. H.; Siemensmeyer, K.; Wendorff, J. H.; Ringsdorf, H.; Haarer, D. *Adv. Mater.* **1996**, *8*, 815–819.
37. Boden, N.; Bushby, R. J.; Cammidge, A. N.; Clements, J.; Luo, R. *Mol. Cryst. Liq. Cryst.* **1995**, *261*, 251–257.
38. Haarer, D.; Adam, D.; Simmerer, J.; Closs, F.; Funhoff, D.; Häusling, L.; Siemensmeyer, K.; Ringsdorf, H.; Schumacher, P. *Mol. Cryst. Liq. Cryst.* **1994**, *252*, 155–164.
39. Kumar, S.; Schuhmacher, P.; Henderson, P.; Rego, J.; Ringsdorf, H. *Mol. Cryst. Liq. Cryst.* **1996**, *288*, 211–222.
40. Vaes, A.; Van der Auweraer, M.; De Schryver, F. C.; Laguitton, B.; Jonas, A.; Henderson, P.; Ringsdorf, H. *Langmuir* **1998**, *14*, 5250–5254.
41. Walba, D. M.; Stevens, F.; Clark, N. A.; Parks, D. C. *Acc. Chem. Res.* **1996**, *29*, 591–597.
42. Charra, F.; Cousty *J. Phys. Rev. Lett.* **1998**, *80*, 1682–1685.
43. Ikeda, S.; Takanishi, Y.; Ishikawa, K.; Takezoe, H. *Mol. Cryst. Liq. Cryst.* **1999**, *329*, 589–595.
44. Kreuder, W.; Ringsdorf, H.; Tschirner, P. *Macromol. Chem., Rapid Commun.* **1985**, *6*, 367–373.
45. Wenz, G. *Macromol. Chem., Rapid Commun.* **1985**, *6*, 577–584.
46. Boden, N.; Bushby, R. J.; Martin, P. S.; Evans, S. D.; Owens, R. W.; Smith, D. A. *Langmuir* **1999**, *15*, 3790–3797.
47. Kranig, W.; Hüser, B.; Spiess, H. W.; Kreuder, W.; Ringsdorf, H.; Zimmermann, H. *Adv. Mater.* **1990**, *2*, 36–40.
48. Bachmann, C. *J. Am. Chem. Soc.* **1927**, *49*, 2093–2094.
49. Destrade, C.; Mondon, M. C.; Malthete, J. *J. Phys. Colloq.* **1979**, *C3*, 17–21.
50. Boden, N.; Borner, R. C.; Bushby, R. J.; Cammidge, A. N.; Jesudason, M. V. *Liq. Cryst.* **1993**, *15*, 851–858.
51. Kumar, S.; Varshney, S. K. *Liq. Cryst.* **1999**, *26*, 1841–1843.
52. Iyer, V. S.; Wehmeier, M.; Brand, J. D.; Keegstra, M. A.; Müllen, K. *Angew. Chem.* **1997**, *109*, 1675–1679.
53. Iyer, V. S.; Yoshimura, K.; Enkelmann, V.; Epsch, R.; Rabe, J. P.; Müllen, K. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2696–2699.
54. Ito, S.; Herwig, P. T.; Böhme, T.; Rabe, J. P.; Rettig, W.; Müllen, K. *J. Am. Chem. Soc.* **2000**, *122*, 7698–7706.
55. Brand, J. D.; Kübel, C.; Ito, S.; Müllen, K. *Chem. Mater.* **2000**, *12*, 1638–1647.
56. Thünemann, A. F.; Ruppelt, D.; Burger, C.; Müllen, K. *J. Mater. Chem.* **2000**, *10*, 1325–1329.
57. Reitzel, N.; Hassenkamp, T.; Balashev, K.; Jensen, T. R.; Howes, P. B.; Kjaer, K.; Fechtenkötter, A.; Ito, S.; Müllen, K.; Bjornholm, T. *Chem.-Eur. J.* **2001**, submitted.
58. Barber, H. J.; Slack, R. *J. Chem. Soc.* **1944**, 612.
59. Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158.
60. Strukelj, M.; Papadimitrakopoulos, F.; Miller, T. M.; Rothberg, L. J. *Science* **1995**, *267*, 1969.
61. Knochel, P.; Singer, D. *Chem. Rev.* **1993**, *93*, 2117–2188.
62. Baumgarth, M.; Beier, N.; Gericke, R. *J. Med. Chem.* **1997**, *40*, 2017–2034.
63. Taskahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627.
64. Shetty, A. S.; Zhang, J.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 1019–1027.
65. Shetty, A. S.; Fischer, P. R.; Storck, K. F.; Bohn, P. W.; Moore, J. S. *J. Am. Chem. Soc.* **1996**, *118*, 9409–9414.
66. Brand, J. D. *Supramolekulare Strukturen Polycyclischer Aromatischer Kohlenwasserstoffe Synthese*; Charakterisierung, Eigenschaften: Mainz, 2000.
67. Ochsenfeld, C. *Phys. Chem., Chem. Phys.* **2000**, *2*, 2153–2159.

68. Ochsenfeld, C.; Brown, S. P.; Schnell, I.; Gauss, J.; Spiess, H. W. *J. Am. Chem. Soc.* **2000**, submitted for publication.
69. Brown, S. P.; Schnell, I.; Brand, J. D.; Müllen, K.; Spiess, H. W. *Phys. Chem., Chem. Phys.* **2000**, *2*, 1735–1745.
70. Brown, S. P.; Schnell, I.; Brand, J. D.; Müllen, K.; Spiess, H. W. *J. Mol. Struct.* **2000**, *521*, 179–195.
71. Green, M. M.; Ringsdorf, H.; Wagner, J.; Wüstefeld, R. *Angew. Chem.* **1990**, *102*, 1525–1528.
72. Clar, E. *Ber. Dtsch. Chem. Ges.* **1936**, *69*, 607.
73. Rodger, A.; Norden, B. *Circular Dichroism and Linear Dichroism*; University: Oxford, 1997.
74. Schouten, P. G.; van der Pol, J. F.; Zwikker, J. W.; Drenth, W.; Picken, S. J. *Mol. Cryst. Liq. Cryst.* **1991**, *195*, 291–305.