

Hexa-*peri*-hexabenzocoronenes – Controlling their Self-Assembly by Engineering the Lateral Substituents

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Abstract: Polycondensed aromatic hydrocarbons (PAH), which can be regarded as two-dimensional subsections of graphite, have begun to attract increasing interest in supramolecular chemistry. Substituted hexa-*peri*-hexabenzocoronenes (HBC), an outstanding class of PAH, are well-known to self-organize in solution into highly ordered columnar molecular stacks. The formed structures are very sensitive to any variation of the medium as well as the lateral substituents of the HBC derivatives. Various perfluoroalkylated HBC compounds have been prepared and investigated by powder XRD, DSC, fluorescence and cryo-SEM in order to gain certain control over the self-assembling behavior of this class of compounds.

Keywords: Liquid crystals · Perfluoroalkyl HBC · Polycondensed aromatic hydrocarbons (PAH) · Self-assembly · π -Stacking

1. Introduction

Supramolecular chemistry is a broad term that covers a new field of chemistry based on the synthesis and study of molecules that self-assemble through weak, non-covalent bonds.^[1] Such systems form well-defined supramolecular architectures, providing, therefore, novel properties with tailored functionalities. This interesting domain of research can be also considered as the most prominent imitation of nature that shows various examples emerging from co-operation between different constituents.^[2] The concepts developed in supramolecular chemistry are increasingly employed in the field of advanced materials science such as optoelectronic devices,^[3] sensor technology,^[4] biological applications,^[5] and nanotechnology.^[6]

Self-assembly of organic molecules in solution and in the solid state leading to supramolecular architectures has revealed the high importance of reversible weak non-covalent interactions in constructing and controlling materials down to the molecular level. These interactions comprise mainly hydrogen bonding,^[7] metal coordination^[8] and π -stacking,^[9] three different types of weak bonding whose stand-alone or combined presence^[10] affords outstanding properties to the supramolecular system. Self-organization relies upon complementarity of size, shape, and varying the number of chemical functionalities capable of performing non-covalent bonding^[5b] giving rise to new chemical and physical properties differing from the single building component. Furthermore, the reversibility of the non-covalent bonding excels that of covalent bonding, since the former can be restructured by simple changing of the medium parameters such as concentration, temperature, or the nature of solvent, when present in solution, and the substrate or the deposition technique, when engineered in the solid state to construct a variety of synthetic architectures.^[11] Thus, self-assembly by weak interactions offers a ‘self-healing’ network that can reassemble after being subjected to external influences.^[12]

Disc-shaped polyaromatic hydrocarbons (PAHs) are attracting increasing interest in many applied fields, especially in molecular electronics. This can be attributed to the strong π -interactions they exhibit, allowing

the formation of columnar structures^[13] of three-, four-, or six-fold rotational symmetry with relatively high charge carrier mobilities.^[14] It is noteworthy that the most prominent of these extended aromatic structures is hexa-*peri*-hexabenzocoronene (**1a**, R = H) depicted in Scheme 1. HBC derivatives exhibit the highest charge carrier mobility, in the bulk, recorded so far for any disc-shaped PAH molecule in the solid state and liquid crystalline mesophase,^[15] which opens the way for their potential employment in many electronic applications.^[16]

Müllen and coworkers have introduced a synthetic method which affords HBCs in few steps and in very good yields.^[17] The derivatization of the HBC molecule with aliphatic side chains makes the product soluble in common organic solvents and bestows it, generally, with a thermotropic liquid crystalline property over a wide temperature range depending on the length and on the nature of the side chains introduced.^[18]

Extensive studies on the stacking behavior of various substituted HBC species have been carried out. In solution, the molecules form columnar aggregates even at low concentration, the length of the stacks being increased by raising the concentration.^[19] The lateral aggregation of these columnar stacks affords in the solid state closely packed columnar arrays due to the high intercolumnar interaction based on the high degree of crystallization and packing order of the aliphatic side chains.^[20] Thus, characterization by electron emission mi-

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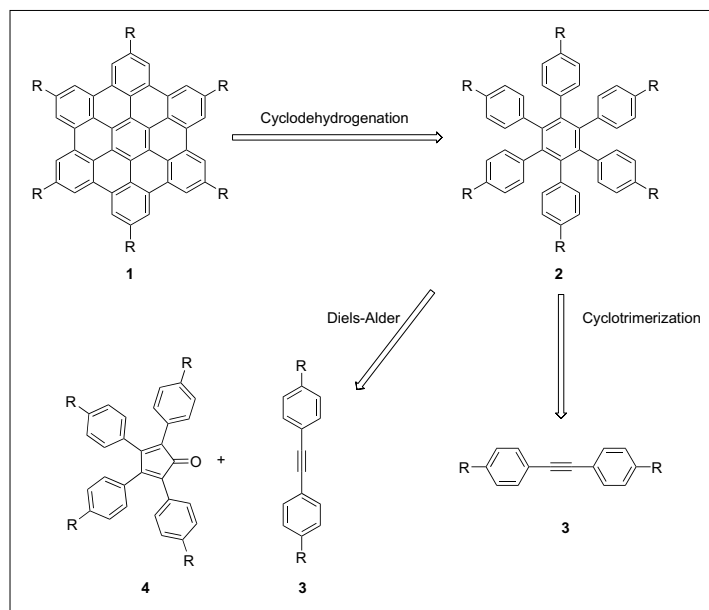
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Scheme 1. General strategies to produce hexa-*peri*-hexabenzocoronene bearing alkyl or perfluoroalkyl chains

scopy of ultrathin layers of unsubstituted HBC **1a** (5–8 molecules in thickness) on Cu(111) or Au(111) surfaces revealed that the columns are perfectly aligned with little translation.^[21] Moreover, Aida and co-workers prepared amphiphilic HBC derivatives that self-assemble into large uniform nanotubes with a diameter of ~20 nm.^[22] In spite of the large number of publications dealing with the self-assembling behavior of HBC derivatives under various conditions, full control of the self-assembly has not yet been achieved.

2. Preparation of Hexa-*peri*-hexabenzocoronene Derivatives

The key step in the synthesis of hexa-*peri*-hexabenzocoronene (HBC) derivatives is the oxidative cyclodehydrogenation^[23] of a corresponding hexaphenylbenzene (HPB, **2**) precursor (Scheme 1). In turn hexaphenylbenzene derivatives are generally obtained by one of two pathways: the cyclotrimerization approach involving an acetylene derivative (**3**), favorable for target molecules bearing the same lateral functional group at all positions.^[18a,24] The second strategy, generally used to produce asymmetrical HBC moieties, employs a double Knoevenagel condensation between a benzil and dibenzylidene acetone derivative yielding a cyclopentadienone building block (**4**) followed by a Diels-Alder cycloaddition reaction with again an acetylene derivative (**3**) as a third component.^[17a,18b,d]

2.1. The Cyclotrimerization Approach

As a consequence of its symmetrical structure, the synthetic approach in our

work is based on first preparing the *para*-substituted tolane derivative **3**, followed by its trimerization using a suitable catalyst^[25] to yield the HPB species **2**, which is oxidized subsequently to the desired HBC derivative **1**. The synthesis of the tolane species **3** is achieved *via* three different techniques: firstly by the dehydrohalogenation of a 1,2-diphenyl dihaloethane derivative,^[26] secondly by a step-by-step Sonogashira cross-coupling,^[27] and thirdly by the same cross-coupling reaction but in a one-pot procedure.^[28]

2.2. The Diels-Alder Approach

This synthetic route is generally used when an HBC bearing different terminal groups is needed. In this case the hexaphenylbenzene **2** derivative is produced, in a fairly good yield, after a [4+2]-cycloaddition reaction of tetraarylcyclopentadienone **4** and tolane **3**. Nonetheless, product **4** is only obtained after a series of different multistep reactions.^[18b,29] It is worth noting that each of these starting materials could bear different functional groups at their ends yielding, thereby, an HBC having a maximum of four different side chains. The advantage of this synthetic strategy is that it allows the decoration of the HBC moieties **1** with different functional groups, which consequently widens the prospect of obtaining HBC products with different symmetries. Nevertheless, this approach requires additional steps and more starting materials to be synthesized.

Several HBC derivatives bearing pendant chains were synthesized during the past few years (Table), most of which were produced using the two synthetic approaches mentioned above. From these

HBCs we note the ones with straight alkyl chains,^[17c,d,18b] branched alkyl chains,^[30] as well as with straight and branched perfluoroalkylated chains.^[31] It is worthwhile mentioning that other HBC structures were also synthesized, ranging from those bearing heteroatoms^[32] and/or aromatic intercalators,^[18b,33] to the unsymmetrical trisubstituted HBCs.^[34] In addition, more exotic HBC derivatives were also synthesized like ones capable of forming hollow self-assembled nanotubes^[22] and those whose self-assembly is reinforced through attaching a polymeric chain,^[18c] or hydrogen-bonded substituents.^[35]

3. Reducing the Lateral Aggregation by a 'Fluorine Mantle'

Introduction of fluorine into a molecule tends to generate novel, sometimes hardly predictable properties, and holds potential for phase separation. Fluorine combines the highest electronegativity with lowest polarizability. Furthermore, fluorine and

Table. Summary of synthesized hexasubstituted HBCs with alkyl and perfluoroalkyl chains

HBC	R =	abbreviation
<i>alkyl chains</i>		
1b	<i>t</i> -C ₄ H ₉	tBu
1c	<i>n</i> -C ₁₀ H ₂₁	C ₁₀
1d	<i>n</i> -C ₁₂ H ₂₅	C ₁₂
1e	<i>n</i> -C ₁₄ H ₂₉	C ₁₄
1f	-CH ₂ CH(C ₂ H ₅)(C ₄ H ₉)	C _{2,6}
1g	-CH ₂ CH(C ₆ H ₁₃)(C ₈ H ₁₇)	C _{6,10}
1h	-CH ₂ CH(C ₁₀ H ₂₁)(C ₁₂ H ₂₅)	C _{10,14}
<i>perfluoroalkylated chains</i>		
1i	-(CH ₂) ₂ (CF ₂) ₆ F	Rf _{2,6}
1j	-(CH ₂) ₂ (CF ₂) ₈ F	Rf _{2,8}
1k	-(CH ₂) ₃ (CF ₂) ₆ F	Rf _{3,6}
1l	-(CH ₂) ₃ (CF ₂) ₈ F	Rf _{3,8}
1m	-(CH ₂) ₄ (CF ₂) ₄ F	Rf _{4,4}
1n	-(CH ₂) ₄ (CF ₂) ₆ F	Rf _{4,6}
1o	-(CH ₂) ₄ (CF ₂) ₈ F	Rf _{4,8}
1p	-(CH ₂) ₄ (CF ₂) ₁₀ F	Rf _{4,10}
1q	-(CH ₂) ₅ (CF ₂) ₆ F	Rf _{5,6}
1r	-(CH ₂) ₅ (CF ₂) ₈ F	Rf _{5,8}
1s	-(CH ₂) ₆ (CF ₂) ₆ F	Rf _{6,6}
1t	-(CH ₂) ₆ (CF ₂) ₈ F	Rf _{6,8}
1u	-(CH ₂) ₈ (CF ₂) ₄ F	Rf _{8,4}
1v	-(CH ₂) ₈ (CF ₂) ₆ F	Rf _{8,6}
1w	-(CH ₂) ₈ (CF ₂) ₈ F	Rf _{8,8}
<i>branched perfluoroalkylated chains</i>		
1x	-(CH ₂) ₃ CH[CH ₂ (CF ₂) ₄ F] ₂	Rf _{3,3,4,4}
1y	-(CH ₂) ₃ CH[CH ₂ (CF ₂) ₆ F] ₂	Rf _{3,3,6,6}

hydrogen differ considerably in their Van der Waals radii (1.47 vs. 1.20 Å, respectively). Perfluorinated compounds are known to be sterically more demanding and much stiffer than their alkyl counterparts.^[36] The cross-section of a perfluoroalkyl chain (30 Å²) differs strongly from an alkyl chain (20 Å²).^[37] Moreover, the typical planar 'zig-zag' structure of alkanes becomes rather helical and much more rigid in perfluorinated analogues.^[38] Furthermore, perfluorinated chains have a much more hydrophobic character than alkyl chains, but are fairly lipophobic as well.^[39]

Thus, the decoration of HBCs with perfluoroalkyl chains instead of alkyl ones, whose crystallization leads to the undesired lateral aggregation of the HBC stacks,^[40] should greatly reduce the tendency for lateral interaction without altering the desired π - π -stacking. This may also be a possible reason why perfluoroalkylated HBCs have much higher transition temperatures to the mesophase when compared to their purely *n*-alkylated homologues.^[31b] As decomposition occurs before the isotropization point of perfluoroalkylated HBC derivatives is reached, no statement on the width of the mesophase temperature span can be made. Nevertheless, it is highly probable that the stability and the mesophase range are higher for perfluorinated HBC derivatives than for the alkylated ones, as observed for other compounds as well.^[41]

Aliphatic spacers, placed between the HBC core and the perfluoroalkyl side chain, turned out to be crucial not only for synthetic reasons^[42] as they shield the HBC core from the electron-withdrawing effect of the perfluorinated substituents, but also for the stacking behavior of the molecules. Preliminary investigations showed that the perfluoro/alkyl ratio is a critical parameter affecting the lateral aggregation.^[31b,43,44a] Probable reasons are the solubility and/or the phase segregation between the different constituents, *i.e.* the aromatic core, the paraffin-like alkyl part, and the perfluorinated part. It has to be noted that the length and the ratio of the perfluorinated parts influence the morphology of the derivatives much more than the variation in length of a pure alkyl chain does.^[45] The Table illustrates the large variety of different semi-perfluorinated derivatives reported to date.^[31]

3.1. Investigation Techniques for Semi-perfluorinated HBC Derivatives

The self-assembling behavior of HBC derivatives can be investigated by a series of different techniques, such as: scanning tunneling microscopy (STM),^[46] wide-angle X-ray scattering (WAXS),^[47] nuclear magnetic resonance (NMR),^[48] UV/Vis and fluorescence spectroscopy,^[49] Langmuir-Blodgett techniques,^[50] to mention only the

most important ones. Due to the inherently low volatility and the relatively low solubility of perfluorinated HBC derivatives in common organic solvents, some of the before-mentioned techniques are not applicable for these compounds. To overcome this difficulty, an insight into the formation of nanostranded columns may be gained by using solid-state and low-concentration-demanding techniques such as powder XRD, cryo-SEM and fluorescence spectroscopy. Cryo-SEM, a variant of SEM, is the technique favored by biologists to investigate cryogenated biological cell samples.^[51] Self-assembled HBC structures show a dynamic equilibrium of various aggregates in solution, which are very sensitive to concentration variations occurring during the standard deposition techniques used in SEM, such as spin coating or drop casting. Cryo-SEM in contrast involves shock freezing of solutions containing the desired self-assembled structures in liquid nitrogen, which preserves formed aggregates and allows their observation under the microscope after the solvent has been partially removed by sublimation.^[44]

3.2. Solvent, Concentration and Temperature Influence on Self-aggregation

The hexasubstituted HBC derivative with perfluoroalkyl chains carrying four aliphatic spacers and six fluorinated carbons (**1n**), was extensively studied. Fig. 1 shows the fluorescence spectra and the cryo-SEM micrographs of a 10⁻⁴ M solu-

tion of HBC-Rf_{4,6} (**1n**) in three halogenated solvents in order of increasing dissolution capacity: 1,2,4-trichlorobenzene (TCB), α,α,α -trifluorotoluene (BTF), and hexafluorobenzene (HFB). At this concentration the compound shows no traces of the typical monomeric HBC fluorescence in TCB,^[48] indicating that only laterally aggregated monostranded HBC stacks are present, which yield a typical featureless broad emission at longer wavelength. This finding is corroborated by the corresponding cryo-SEM micrograph (Fig. 1B) which shows long ribbons extending over several micrometers. The low solubility of the compound both in the monomeric and stacked form is responsible for this behavior as the formation of highly extended structures is enabled. As compared to TCB, BTF is a much better solvent. Accordingly in BTF solutions, a dynamic equilibrium of single HBC moieties (revealed by the typical fluorescence), monostranded HBC stacks and laterally aggregated HBC stacks (as shown in the cryo-SEM micrographs) is observed. Finally, the fluorescence spectrum in HFB solution shows the typical monomer emission only, even at concentrations, where the cryo-SEM indicated the presence of monostranded HBC stacks with a uniform diameter of about 35 nm (it has to be noted that this apparent thickness is nearly entirely due to the platinum coating). The lower number of observed structures (as compared to BTF solutions) as well as their very much reduced length corroborates our assumption of a pronounced π - π -complexation of HBC

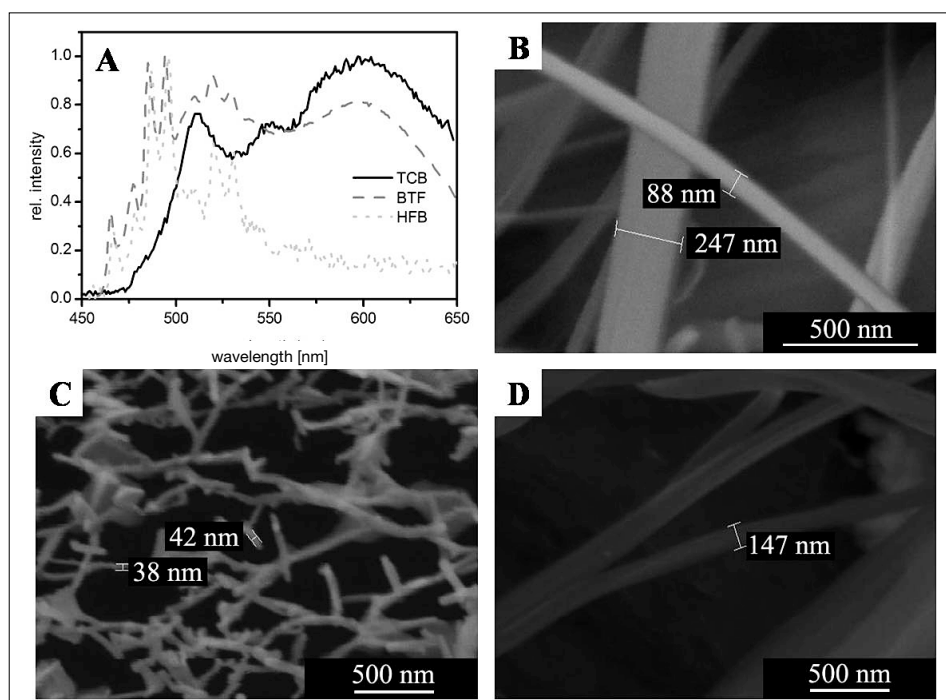


Fig. 1. A: Luminescence spectra of HBC-Rf_{4,6} **1n** ($\lambda_{\text{ex}} = 360$ nm) in TCB, BTF and HFB (10⁻⁴ M solutions), the spectra are arbitrarily normalized. B–D: Cryo-SEM micrographs prepared from 10⁻⁴ M solutions in TCB (B), HFB (C), and BTF (D). From ref. [44a], reproduced with permission of the Royal Society of Chemistry.

with HFB, leading to efficient end-capping of the formed structures and hence resulting in shorter filaments. Noteworthy is the absence of any fluorescence emission from aggregates despite their presence in solution as shown by cryo-SEM. Variation of the concentration or the temperature was also reported^[44] and influenced the self-aggregation behavior of perfluoroalkylated HBC derivatives analogously.

3.3. Variation of the Fluorine Ratio of the Lateral Chain

The study of HBC derivatives bearing alkyl-perfluoroalkyl side chains of different lengths and ratios, between the aliphatic and the perfluorinated parts, revealed that the equilibrium between monomers, monostranded stacks and laterally aggregated columns was not only affected by the medium, but it was also highly influenced by the length of the alkyl spacer and the perfluorinated tail, which exerts a considerable effect on self-aggregation. Surprisingly, a dramatic variation of the self-aggregation behavior could be observed when a minor change was made to the lateral chain such as changing the number of CH₂ spacers or the length of the perfluorinated tail, besides the introduction of a branching point to the side chain. For illustration, two series of HBC derivatives were synthesized, each of which has a constant number of perfluorinated carbons (six or eight CF₂) but whose number of CH₂ groups was changed. Fig. 2 summarizes the result of the luminescence and cryo-SEM data collected for these HBC derivatives at a fixed concentration of 10⁻⁴ M in BTF solutions, where all HBC-Rf_{n,6} (**1i**, **1k**, **1n**, **1q**, **1s**, and **1v**) and HBC-Rf_{n,8} (**1j**, **1l**, **1o**, **1r**, **1t**, and **1w**) derivatives are shown with respect to their lateral aggregation tendency. In summary, the experimental data reveal that the lateral aggregation is rather strong when using short alkyl spacers (two or three CH₂). The derivatives bearing slightly longer alkyl parts (four, five or six CH₂), however, show a dynamic equilibrium between monomers and aggregated structures in the examined concentration range. By increasing the alkyl spacer even more (eight CH₂) the lateral aggregation dominates once more. Fig. 2 clearly shows that the derivatives carrying four, five or six CH₂ spacer groups yield the smallest lateral aggregation. Though their overall behavior is quite comparable, the HBCs bearing longer perfluorinated chains show a slightly more pronounced effect than the shorter ones. On the other hand, when taking a constant butyl spacer and varying the length of the perfluorinated tail (4 (**1m**), 6 (**1n**), 8 (**1o**) and 10 (**1p**) perfluorinated carbon atoms), we found that only the HBCs with six and eight CF₂ groups yield thin filaments, while the ones with 4 or 10 perfluorinated

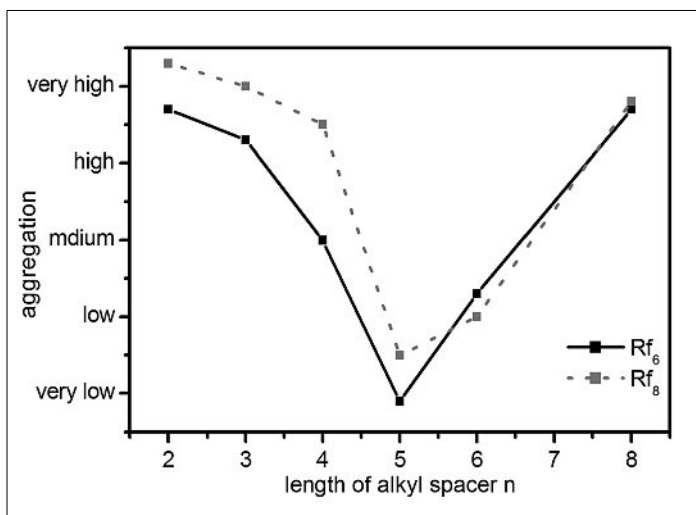


Fig. 2. Lateral aggregation as function of the alkyl spacer for two types of compounds: HBC-Rf_{n,6} (solid line) and HBC-Rf_{n,8} (dashed line). The aggregation was determined in BTF solution from fluorescence and cryo-SEM data.^[44]

carbon atoms produce predominantly laterally aggregated structures.^[44] This clearly shows how subtle the HBC self-assembly depends on the exact nature of the side chains: only a balanced combination of the flexibility of the alkyl spacer and the rigidity of the perfluorinated tail results in the formation of long monostranded filaments with minimized lateral aggregation.

Branched perfluoroalkylated HBCs (**1x**, **1y**) were also studied because they present another way to increase the fluorine coating as compared to HBC-Rf_{4,10} (**1p**) without decreasing the solubility further. Fluorescence spectroscopy of these derivatives revealed no or only very little lateral aggregation, even at concentrations up to 10⁻³ M in BTF. The steric hindrance around the central HBC core seems to be exceedingly large as cryo-SEM shows only very few monostranded filaments.

3.4. Morphology of Perfluorinated HBCs in the Bulk

The thermal behavior and the structural modification upon heating were investigated by a combination of DSC and XRD. All derivatives bearing linear semi-perfluorinated chains with the exception of HBC-Rf_{8,6} (**1v**) were found to exhibit a liquid-crystalline mesophase, after several crystal-to-crystal phase transitions, most probably due to small rearrangements of the lateral chains. No isotropization temperature could be reached for most of these derivatives below 250 °C; a temperature limit where decomposition started. Generally short alkyl spacers led to higher transition temperatures (up to 180 °C), an observation which agrees well with the reduced flexibility of the lateral chain. It is worth noting that the HBC bearing branched side

chains behave amorphously, except for the case with perfluorobutyl tails (**1x**).

The illustrated XRD pattern of HBC-Rf_{4,6} (**1n**) was measured at 200 °C in the liquid crystalline phase and exhibits several sharp reflections with the spacings being in the ratio 1:√3:√4:√7:√12:√13. These reflections were assigned as the (10), (11), (20), (21), (22), and (31) indices typical for a hexagonal 2D lattice ($a = 31.4$ Å). Two broad signals were observed in the wide angle part, being a broad halo (h_{ch}) as well as the stacking periodicity (h_0) corresponding to the liquid-like order of the molten fluorinated chains (5.65 Å) as well as the stacking of the central polyaromatic cores in the third dimension (3.5 Å).

The columnar cross section (S), deduced from the X-ray pattern (*cf.* Fig. 3) together with the molecular volume (V_{mol}), which is calculated theoretically (*cf.* Fig. 3) allows the stacking periodicity h ($h = V_{mol}/S$) to be determined. The knowledge of h and h_0 permits the arrangement of the individual disks in the columnar stacks to be determined as illustrated in Fig. 4.^[52] For HBC-Rf_{4,6} (**1n**) h_0 and h being 3.5 Å and 3.6 Å, respectively, an almost perpendicular and not a tilted arrangement with respect to the columnar axis was found. The only possible way to accommodate the much thicker perfluorinated chains (5.65 Å) in this arrangement consists of a 30° rotation of each subsequent HBC core allowing therefore the fluorinated chains to extend out of the center through the gaps left by the previous molecule. This requires a minimum length of the alkyl spacer, but a too long spacer will counteract as well, since it allows for too much flexibility in the arrangement of the perfluorinated parts and hence favors intercolumnar interactions.

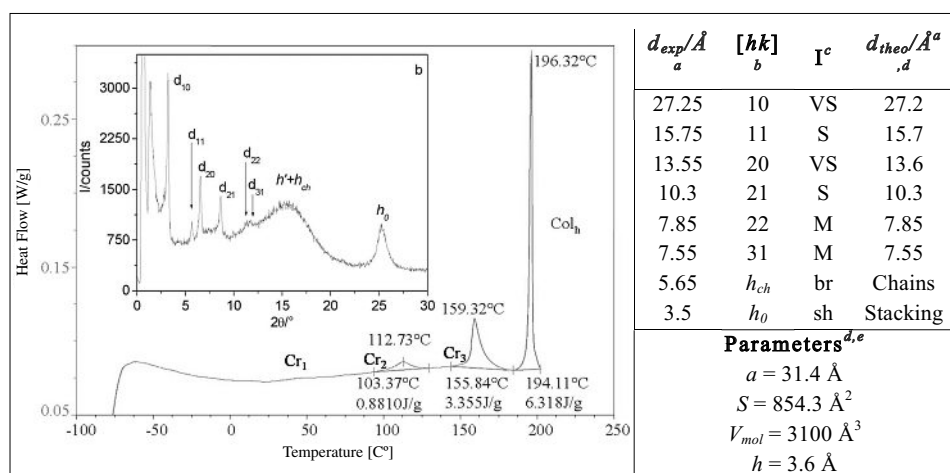


Fig. 3. DSC trace of HBC-Rf_{4,6} (**1n**) (second heating), inset: XRD pattern of HBC-Rf_{4,6} at 200 °C. Table: XRD parameters for HBC-Rf_{4,6}: ^a d_{exp} and d_{theo} are the experimentally measured and theoretical diffraction spacings at 200 °C. The distances are given in Å. ^b $[hk]$ are the indexation of the reflections, and h_0 and h_{ch} are the short range periodicities determined by XRD corresponding to the molecular stacking distance (h_0) and to the liquid-like order of the molten chains (h_{ch}) respectively. ^cIntensity of the reflections: VS: very strong, S: strong, M: medium; br and sh stand for broad and sharp (diffuse) reflections, respectively. ^d d_{theo} and the lattice parameter a are deduced from the following mathematical expressions: $\langle d_{10} \rangle = 1/N_{hk}[\sum_{hk} d_{hk}^2(h^2+k^2+hk)^{1/2}]$ where N_{hk} is the number of hk reflections and $a = 2\langle d_{10} \rangle/\sqrt{3}$. ^e Col_h : hexagonal columnar phase, Cr_i : crystalline solids, I : isotropic liquid. S is the lattice area: $S = a^2\sqrt{3}/2$. V_{mol} is the molecular volume: $V_{mol} = V_{HBC} + 6(nV_{CH_2} + mV_{CF_2})$, where $V_{HBC} = 650$, $V_{CH_2} = 26.5616 + 0.02023T$, and $V_{CF_2} = 40.815 + 0.03318T$; h is the intracolumnar repeating distance, deduced directly from the measured molecular volume and the columnar cross-section according to $h = V_{mol}/S$.^[52]

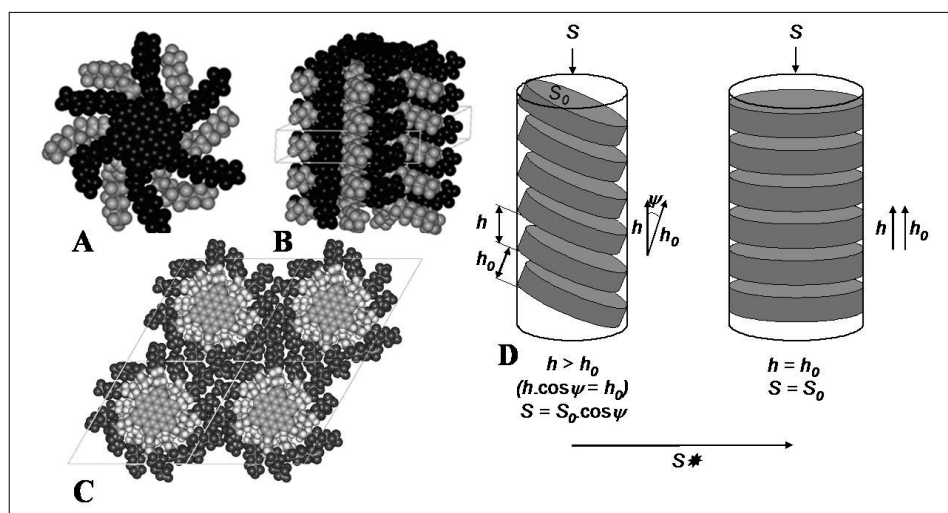


Fig. 4. (A): View of the stacking of neighboring molecules (top view); (B): side view of the stacking within the column (side view); (C): Snapshot showing the molecular self-assembly of HBC-Rf_{4,6} (**1n**) into the hexagonal lattice of the Col_h phases polar central core in light grey, aliphatic spacers in white-grey, fluorinated segments in dark grey. (D): representation of two types of stacking of discs within the column and the different parameters h , h_0 , S and S_0 (obtained from X-ray diffraction and dilatometry) allowing for their discrimination. ψ is the angle between the columnar axis and the molecular disc normal. From ref. [44a], reproduced with permission of the Royal Society of Chemistry.

The dense packing of individual discs discussed above forming monostranded stacks as well as laterally aggregated structures is supported by molecular dynamics simulation. This model of the packing explains why HBCs carrying branched perfluorinated chains are amorphous, as in this case the lateral chains are too bulky to be accommodated within the cross-section of the HBC cores. This supports clearly that

both disc–disc interaction as well as micro-segregation is needed in order to observe mesomorphism.

4. Conclusion

The synthesis of a series of symmetrical HBC derivatives bearing straight and branched perfluoroalkylated side chains of

different ratios between the alkyl intercalator and the outer fluorinated part allowed a systematic investigation of a structure–property relationship. The careful analysis of fluorescence spectroscopy, powder XRD, and cryo-SEM data showed that the introduction of this particular type of side chains reduces the undesired intercolumnar interactions and provides better self-assembling properties to the HBCs as compared to their alkylated homologues, both in solution and in the solid state. These data revealed the crucial role of external factors on self-assembly such as the type of solvent, the concentration, and the temperature. In addition, the tuning of the CH_2/CF_2 ratio in the side chains allows an even better control of the self-assembly at the molecular level, pointing to interesting design perspectives in supramolecular chemistry.

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