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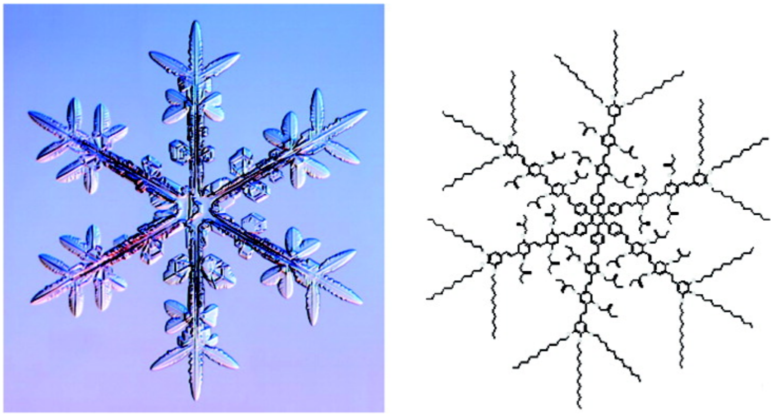

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Star-Shaped Oligo(*p*-phenylenevinylene) Substituted Hexaarylbenzene: Purity, Stability, and Chiral Self-assembly[†]

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Abstract: An oligo(*p*-phenylenevinylene) (OPV)-substituted hexaarylbenzene has been synthesized and fully characterized. Recycling gel permeation chromatography appeared to be a powerful technique to obtain the OPV molecules in a very pure form. X-ray analysis and polarization optical microscopy revealed that the OPV molecule is plastic crystalline at room temperature with an ordered columnar superstructure. In apolar solvents, the molecules self-assemble via a highly cooperative fashion into right-handed chiral superstructures, which are stable even at high temperatures and low concentration. Atomic force microscopy revealed right-handed fibers with a diameter of 6 nm, indicating π-stacked aggregates; on a silicon oxide substrate, supercoiled chiral structures were observed. STM studies on a liquid−solid interface showed that the star-shaped OPV molecule forms an organized monolayer having a chiral hexagonal lattice.

Introduction

The construction of supramolecular assemblies of π-conjugated systems in the 5−100 nm length scale offers an attractive bottom-up strategy to construct semiconducting wires in the nanometer range.[1] By using supramolecular chemistry, such nanowires can be created from almost any polymeric and oligomeric π-conjugated system. In some cases, these nanowires could be placed between electrodes and a current was measured for doped single wires and bundles of wires based on polymers and oligomers.[2,3] However, there are a large number of targets that should be reached before a single nanowire can serve as an attractive alternative for carbon nanotubes[4] and inorganic wires.[5] Two important issues concern the purity of the organic building blocks and the stability of the noncovalent interactions. Impurities will become important in single wires because they can act as traps for holes and electrons and thereby hamper the charge-carrier mobility properties. Noncovalent interactions are often temperature- and solvent-sensitive, and one of the challenges is to construct stable, robust self-assembled nano-objects. In the past, we studied a variety of π-conjugated oligo(*p*-phenylenevinylene) (OPV) derivatives, including H-bonded hexamers, which self-assemble into fibers by $\pi-\pi$ interactions.[6] In order to enhance the stability of these assemblies, we

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synthesized covalently linked OPV segments via amide linkages to yield C3-symmetrical discs[7] and showed that for the self-assembly of such disks, special demands must be taken into account to balance the topology, directionality and strength of multiple hydrogen bond and $\pi-\pi$ interactions. We now report on a star-shaped OPV-substituted hexaarylbenzene in which the number of OPV segments is increased to six, the hydrogen bond interactions are omitted, and the propeller-like structure results in more stable stacks.[8] Recycling gel permeation chromatography appeared to be an appropriate technique to obtain the π-conjugated OPV hexamer in a very pure form. Hexa-substituted chromophoric benzenes have been reported in literature;[9] however, the self-assembly properties have been scarcely addressed.

Results and Discussions

Synthesis. Star-shaped OPV-substituted hexaarylbenzene **3** was synthesized from bromo-substituted OPV derivative **1**, which was prepared according to a literature procedure (Figure 1).[10] Disubstituted acetylene **2** was isolated in 54% yield, after Stille-type coupling of **1** with commercially available bis-(tributylstannyl)acetylene in the presence of catalytic $Pd(PPh_3)_4$. Subsequent cyclotrimerization of **2** was carried out using $Co_2(CO)_8$ as catalyst in refluxing dioxane for 7 h, according to a literature procedure.[9a] The crude product was subjected to extensive column chromatography and gel permeation chromatography (GPC). After these purification steps, thin layer chromatography (TLC) and ^{1}H NMR did not show any impurities.[11] Mass spectrometry, however, apart from the molecular mass of **3** ($m/z = 7757$), showed two other mass peaks positioned at $m/z = 5203$ and $m/z = 2619$, which could originate from impurities or due to fragmentation during the mass analysis (Figure 2a). In order to analyze the purity of **3** in more detail, we decided to use recycling gel permeation chromatography (rGPC) on a preparative size-exclusion column. In the first cycle, only one peak was observed (Figure 2b); however, after three cycles, another peak appeared, indicating the presence of an impurity. After rGPC, star-shaped OPV **3** could be isolated in 57% yield, as a pure, soft, waxy material, soluble in common organic solvents (such as chloroform, dichloromethane, toluene, THF, hexane), and was characterized by MALDI-TOF mass spectrometry, IR spectroscopy, and ^{1}H and ^{13}C NMR spectroscopy.[11] During the purification, the main impurity could be isolated as well. The MALDI-TOF spectrum showed a mass peak at $m/z = 5203$, whereas infrared spectroscopy revealed a carbonyl vibration at 1707 cm^{-1}, pointing to a cyclopentadienone structure having four OPV units. This assignment is supported by scanning tunneling microscope (STM) images.[11] Cyclopentadienone has been reported as a side product in the trimerization of bulky alkynes in which insertion of carbon monoxide occurs instead of the insertion of the third alkyne.[12]

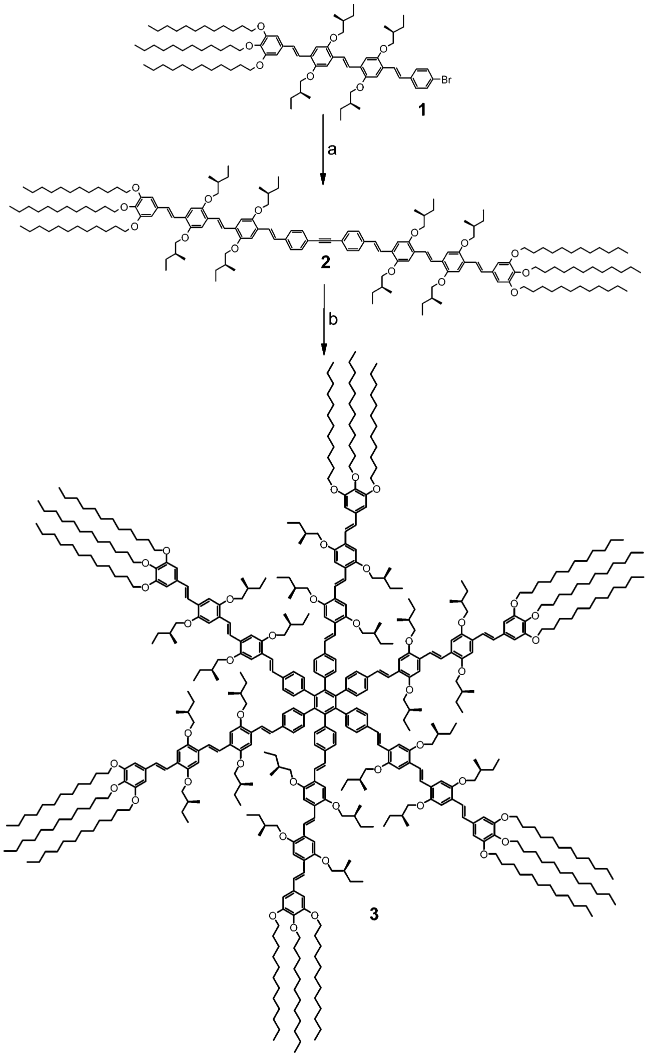

Figure 1. Synthesis of star-shaped OPV (**3**): (a) bis-(tributylstannyl)-acetylene, $Pd(PPh_3)_4$, toluene, 120 °C, 24 h, 54%; (b) $Co_2(CO)_8$, dioxane, 125 °C, 7 h, 57%.

Thermotropic Properties. The bulk properties of star shaped OPV molecule **3** were investigated by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), polarized optical microscopy (POM), and wide-angle X-ray scattering

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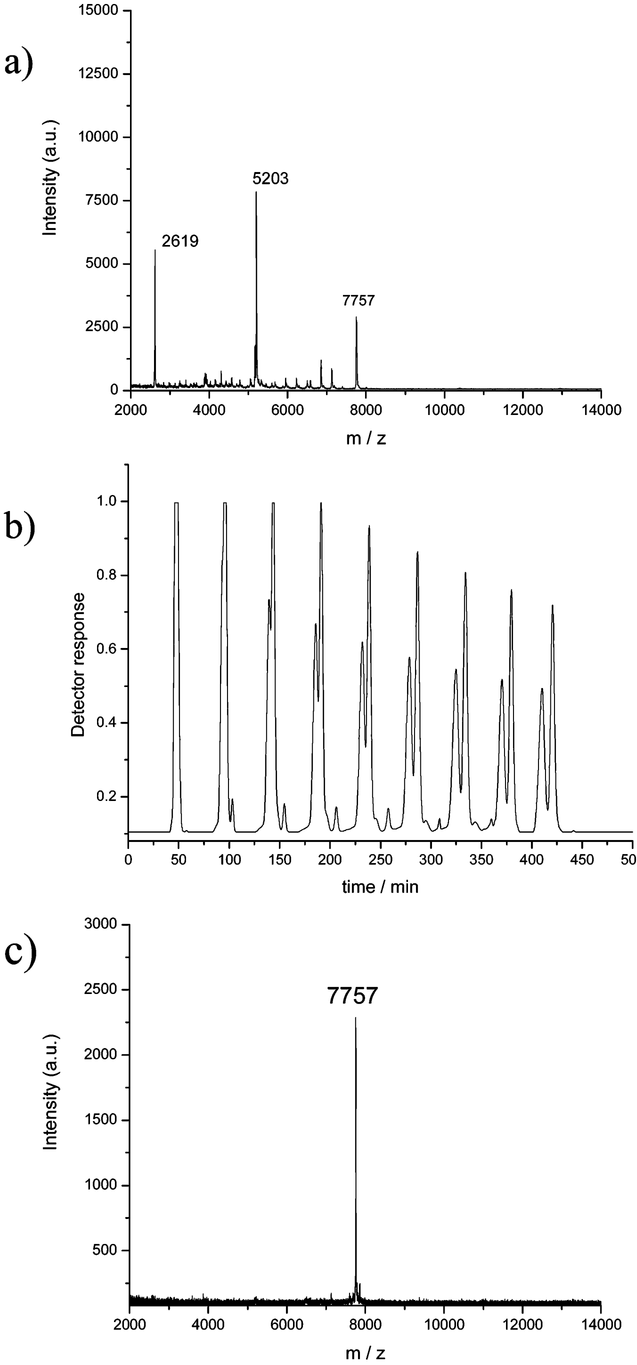

Figure 2. (a) MALDI-TOF mass spectrum of **3** before purification by rGPC. (b) rGPC trace of impure **3** (9 cycles). (c) MALDI-TOF mass spectrum of **3** after purification (calculated average mass of **3**: 7758).

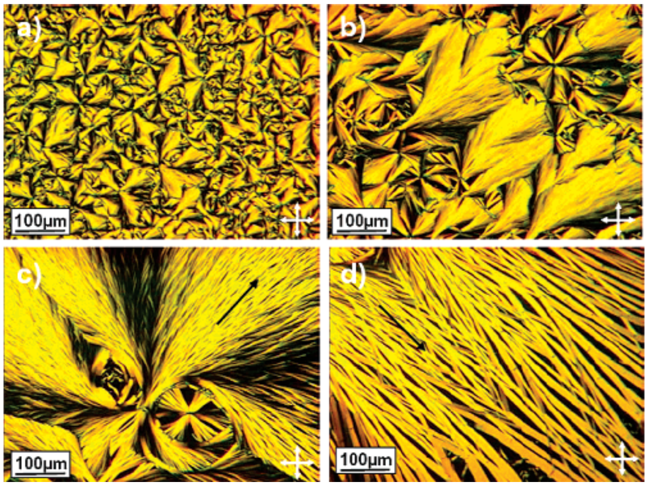

Figure 3. Images from polarized optical microscopy of the star-shaped OPV (**3**) obtained by cooling from the isotropic phase at rates of (a) 10 °C/min, (b) 2 °C/min, and (c,d) 0.2 °C/min.

(WAXS). TGA experiments showed a stability of **3** up to 300 °C. DSC revealed an exothermic peak at 260 °C (ΔH = 76.8 kJ/mol), which we ascribe to the isotropization temperature, while no other thermal transitions were observed between −100 and 260 °C.[11] POM micrographs of **3** by cooling the sample from the melt exhibited fan-shaped domains of which the size increased with decreasing the cooling rate (Figure 3). The domain sizes exceeded several hundred micrometers, consisting of fibers oriented along the solidification direction, especially at low cooling rates. This morphology exemplifies the pronounced tendency of the star-OPV molecules to self-assemble in well-ordered macroscopic structures (vide infra).[13] The fan-shaped highly birefringent textures are characteristic for a crystalline phase, indicating a high degree of order, as later specified by X-ray scattering results. Alternatively, due to the waxy and soft consistency of the compound, the phase was assigned as plastic crystalline.

For the 2D-WAXS experiments, mechanically aligned samples were prepared by filament extrusion.[14] In agreement with the DSC analysis, no change in the 2D-WAXS pattern was observed up to the isotropic phase, and a characteristic 2D-WAXS pattern of **3** is shown in Figure 4a. The distinct and sharp reflections in the equatorial plane of the pattern indicated the formation of columnar superstructures, which were well-oriented along the shearing direction, and thus along the extruded filament. Furthermore, the large number of higher-order reflections was typical for a pronounced degree of columnar order,[11] whereby the analysis of the positions of the scattering intensities revealed a two-dimensional lateral hexagonal unit cell describing the intercolumnar arrangement with a packing parameter of 5.47 nm, which was in agreement with the molecular architecture. The meridional reflections were assigned to the molecular packing within the columnar stacks. The off-meridional scattering intensities were characteristic for a tilting of the single OPV building blocks toward the columnar axis.[15] As schematically illustrated in Figure 4b,c, the star-shaped OPV stack on top of each other, whereby each of the single OPVs is rotated out of the molecular plane, giving rise to the off-meridional reflections, correlated to a relatively long π-stacking distance of 0.45 nm and a tilting angle of ~35°. Due to this tilting, an intracolumnar period of 0.55 nm was determined. The 2D-WAXS results indicate a self-organization of the star-shaped OPV molecules into highly ordered columnar superstructures, which are oriented along the alignment direction during extrusion.

Self-Assembly in Solution. The absorption spectrum of **3** in chloroform shows an absorption maximum at λ_{max} = 436 nm, which is typical for molecular dissolved OPVs (Figure 5).[10,11] Fluorescence measurements reveal an emission maximum at λ_{em} = 501 nm with a shoulder at λ_{em} = 537 nm.

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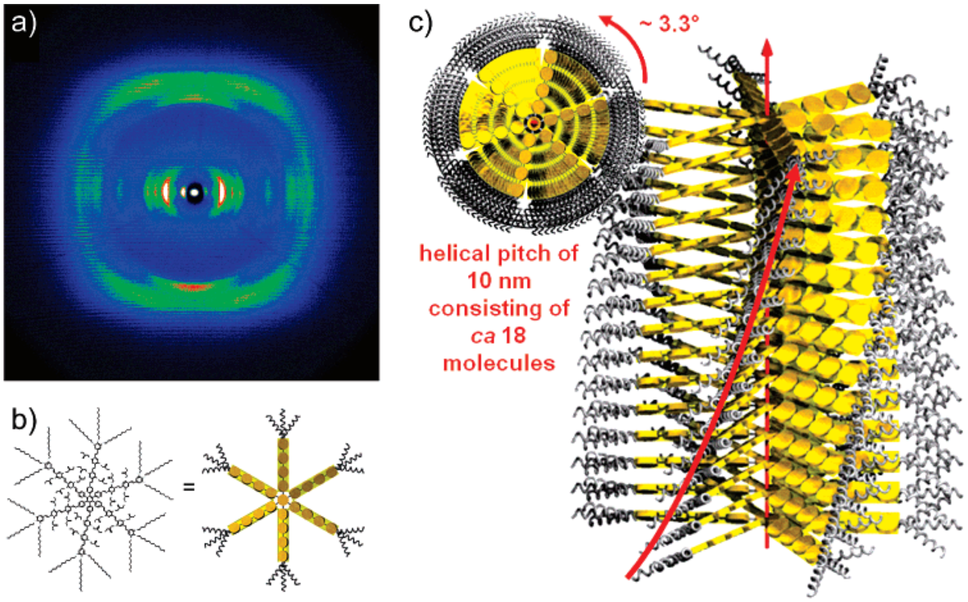

Figure 4. (a) 2D-WAXS pattern recorded at 30 °C of **3** prepared as an extruded filament, (b) schematic representation of **3**, and (c) schematic illustration of the helical columnar packing based on X-ray, CD and AFM data.

The self-assembly of star-shaped OPV **3** was first studied in heptane solution. The UV−vis absorption spectrum of **3** (1×10^{-6} M) shows a blue-shifted (relative to chloroform) absorption band at 422 nm with a red-shifted onset, whereas the fluorescence spectrum reveals a quenched red-shifted maximum at $\lambda_{em} = 550$ nm with two shoulders at $\lambda_{em} = 514$ nm and $\lambda_{em} = 590$ nm, indicating aggregated OPVs (Figure 5a). Circular dichroism measurements show a bisignated CD effect with a positive sign at long wavelengths and a negative sign at short wavelengths with a zero-crossing at 421 nm, indicating that the chiral packing of the *S*-2-methylbutoxy side chains causes a helical packing of the OPV segment, suggesting right-handed helical aggregates (Figure 5b). Temperature-dependent CD measurements showed no transitions, indicating extremely stable chiral aggregates. Even at a concentration of 2×10^{-7} M and 90 °C, the chiral aggregates could not be broken. This behavior is a remarkable increase in stability with respect to our previously reported hydrogen-bonded hexamers having similar OPV segments that form stacks in heptane solution that can be melted at 25 °C at a concentration of 5×10^{-5} M.[16]

We also studied the self-assembly of **3** in methylcyclohexane (MCH). The UV−vis absorption spectrum of **3** (2.5×10^{-6} M) shows a structureless band at 424 nm, with a shoulder at higher wavelengths (Figure 5c), whereas in CD, a bisignated CD effect was observed having a positive sign at long wavelengths and a negative sign at short wavelengths (Figure 5e), indicating helical aggregated OPVs. The fluorescence spectrum reveals a similar behavior as found in heptane, a quenched red-shifted maximum at $\lambda_{em} = 550$ nm with two shoulders at $\lambda_{em} = 514$ nm and $\lambda_{em} = 590$ nm. Concentration-dependent PL measurements show that **3** is still aggregated at room temperature at a concentration of 10^{-9} M. Temperature-dependent UV−vis, CD, and PL measurements showed a transition from aggregated to molecularly dissolved species upon heating (Figure 5c−e). The vibronic shoulder in UV−vis and the CD-effect disappeared, whereas the fluorescence shifted toward a spectrum similar to the one recorded in chloroform with a maximum at $\lambda_{em} = 491$ nm and shoulder at λ_{em} 522 nm, typically for molecularly dissolved **3**. Temperature-dependent CD measurements, made by monitoring the appearance of the Cotton effect at 390 nm, reveal a highly cooperative self-assembly process; the melting curve is not sigmoidal, and a steep rise in the CD signal occurs at the elongation temperature at which the self-assembly starts (Figure 5f).[17] Temperature-dependent UV spectroscopic measurements by following the absorption intensity at 500 nm yield the same elongation temperature as that obtained by CD, suggesting that helical aggregates are formed without an intermediate non-helical state.[11] The CD melting curve was fitted with the nucleation-growth model to characterize the cooperative self-assembly in more detail.[17] An enthalpy of release of $h_e = -184$ kJ/mol was determined while the elongation temperature (T_e) = 331 K (Figure 5, parts g and h). The enthalpy value is higher than that found previously for stacks composed of hydrogen-bonded OPV dimers, which could be due to the higher number of OPV segments in compound **3**. The high degree of cooperativity is reflected in the small value of the equilibrium constant K_a of the nucleation step, which was determined to be 3×10^{-5}. The stacks at T_e, which are an indication of the size of the nucleus, contain 32 molecules, on average, whereas stacks at room-temperature enclose more than 10 000 molecules. The latter value would imply that, by assuming an intracolumnar distance of 0.55 nm (2D WAXS data), the stacks are micrometers long.

Self-Assembly at Surfaces. The solutions, in which the star-shaped OPV (**3**) is self-assembled, were further studied in the solid state by scanning force microscopy operated in Tapping mode. A heptane solution of **3** (1.1×10^{-5} M) was deposited on a silicon wafer, and the sample was allowed to dry for 24 h in a saturated atmosphere of heptane. Typical Tapping mode images show long fibrils (few micrometers, Figure 6, parts a

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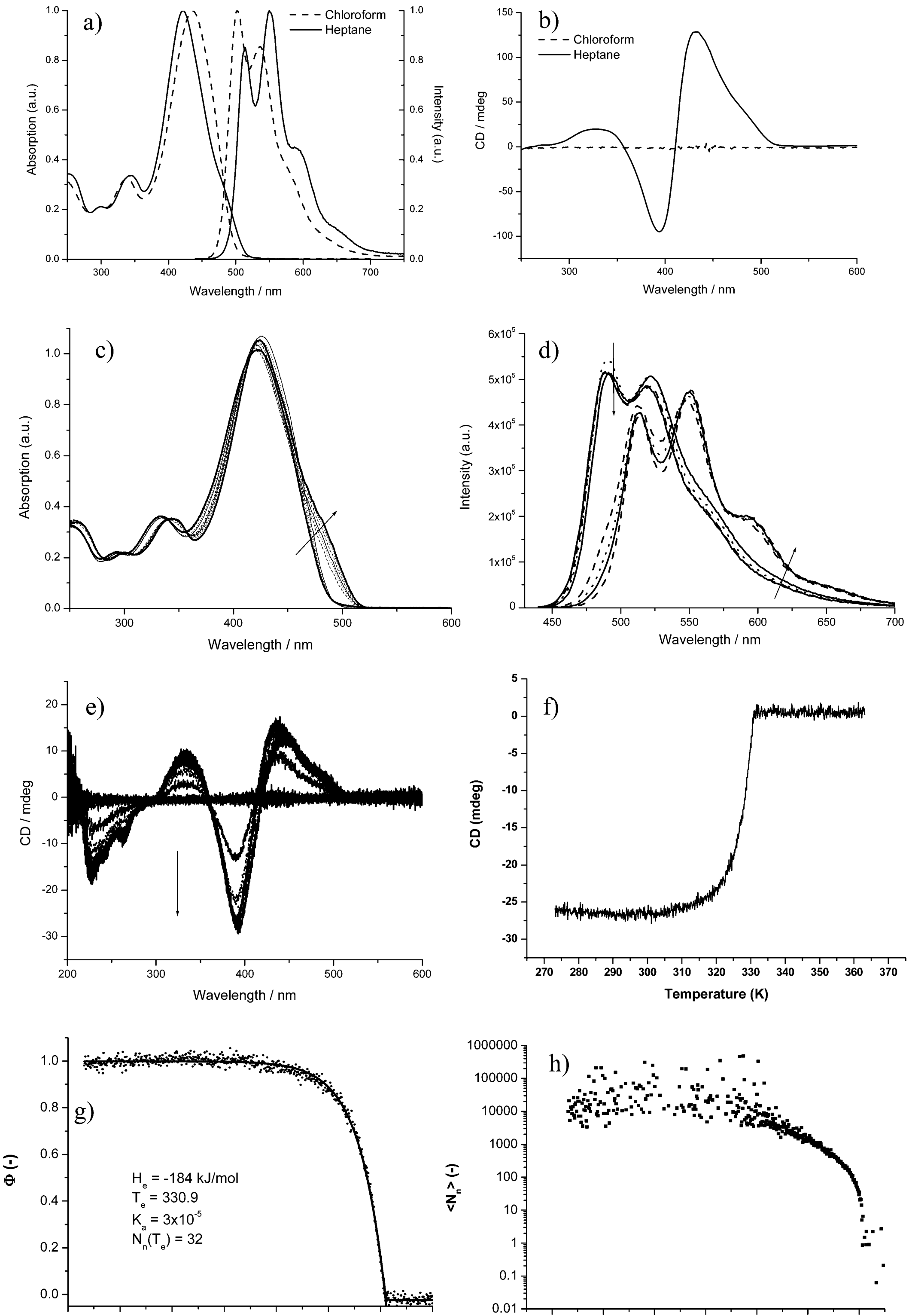

Figure 5. (a) Normalized absorption and fluorescence spectra of **3** in chloroform and heptane (1.1 × 10^{-6} M), (b) CD spectra of **3** in chloroform (5.0 × 10^{-5} M) and heptane (5.4 × 10^{-5} M), (c−e) Temperature-dependent UV−vis (c) PL (d) and CD (e) spectra of **3** in MCH (2.5 × 10^{-6} M) (from 90 to 0 °C with intervals of 10 °C, arrow indicates the changes upon cooling), (f) cooling curve of **3** in MCH (2.5 × 10^{-6} M) obtained by monitoring CD signal at 390 nm ($dT/dt = -12$ °C/hr), (g) fit of the normalized melting curve using the nucleation-growth model, (h) calculation of the number of molecules in the stacks using the nucleation-growth model.

and b) with a constant diameter of 6 nm. Remarkably, at places where the fibrils are densely packed, they leave the surface and form a supercoiled organization with a right-handed helix. This phenomena was previously observed for chiral oligo(thiophene)s,[18] but in the present case, there is less side-by-side interactions leading to the supramolecular chiral nanoribbons. When a more diluted sample is used (1.1 × 10^{-6} M), the fibrils are shorter (about 100 nm, Figure 6c) and have right-handed

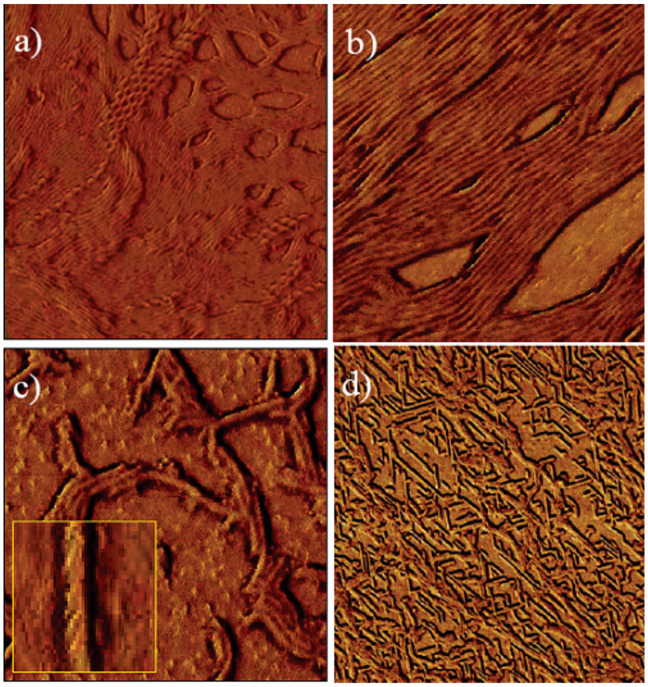

Figure 6. Tapping mode phase images of **3** deposited from heptane solutions on silicon wafer (a) 1.1 × 10^{-5} M (scan size = 500 nm); (b) 1.1 × 10^{-5} M (scan size = 200 nm); (c) 1.1 × 10^{-6} M (scan size = 250 nm), inset: enlargement of one of the fibers (image size = 30 nm); (d) Tapping mode phase images of **3** deposited from heptane solutions on HOPG (1.1 × 10^{-5} M, scan size = 1.0 μm).

helical structure. The pitch of these chiral fibrils is about 10 nm (Figure 6c) and the handedness is in agreement with the that found in solution (vide supra). Taking into account an intracolumnar period of 0.55 nm between individual molecules along the columnar structures, as determined by 2D-WAXS, this indicates that ∼18 building blocks within one helical pitch. This leads to a lateral rotation angle of ∼3.3° between molecules which is rather small (Figure 4c). However, it was not possible to confirm this helical arrangement by 2D small-angle X-ray scattering measurements (SAXS) in the corresponding scattering range. The supramolecular order in this kind of assembly systems is probably too weak to contribute to long-range correlations of ∼10 nm between single molecules along the stacking direction.

When the heptane solution of **3** (1.1 × 10^{-5} M) is deposited on a highly oriented pyrolytic graphite (HOPG) substrate, the observed morphology is once again fibrillar (Figure 6d). The diameter is about 6 nm showing that the molecules are π-stacked. Compared to the silicon surface, the fibrils are shorter and tend to orient along a 3-fold symmetry of HOPG. The chirality of individual fibrils is difficult to observe by AFM even when the sample solution is diluted.

Self-Assembly at the Liquid−Solid Interface. The self-assembly properties of **3** were also probed at the liquid (liquid 1-phenyloctane−solid HOPG substrate interface by scanning tunneling microscopy (STM).[19,20] Typical STM images (Figure 7) show six-armed stars: the tunneling efficiency through the OPV units is higher compared to the alkyl chains,[21] and therefore, the former ones appear bright. In some images, submolecular features appear along the rods that we tentatively assign to the phenyl rings of the OPV arms. The alkyl chains can under favorable measuring conditions be discriminated as faint gray lines (Figure 7a), which run parallel to one of the main symmetry axes of graphite, a phenomenon which is typical for alkyl chains.[19,22] In addition, the STM images show that **3** assembles into a hexagonal lattice. The unit cell vectors *a* and *b* are identical in length (5.56 ± 0.07 nm) and the angle between both unit cell vectors measures 61 ± 2° (Figure 7c). The STM images are two-dimensionally chiral,[23−26] and the molecules appear as stars, which belong to the crystallographic plane point group 6*mm* (the combination of a mirror with a hexad). Neglecting the intrinsic chirality[27] of the molecules, these stars can only order into an achiral pattern if their "arms" are oriented parallel or perpendicular to the unit cell vectors. This is, however, not the case, and this has an effect on the relative distance between parallel oriented OPV-units of adjacent molecules. Consider, for instance, the orientation of the longer dashed and shorter solid white lines that connect the terminal

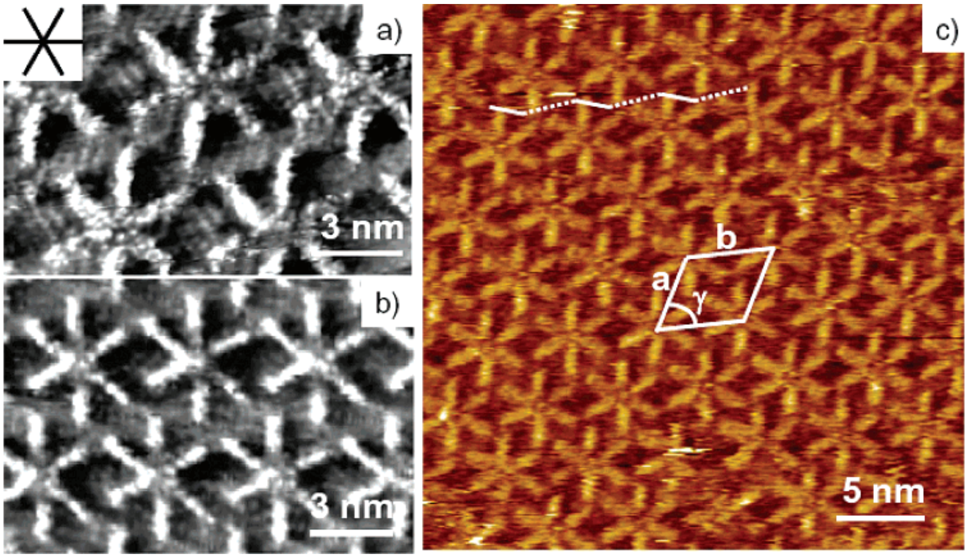

Figure 7. (a and b) Small scale STM images of **3** at the 1-phenyloctane−HOPG interface. The bright rods are the OPV-units. Alkyl chains can clearly be identified as the gray stripes between the OPV-rods of adjacent molecules. Insert: the orientation of the main symmetry axes of graphite (<11 −2 0>). c) Large scale image. The unit cell is indicated. The longer dashed and shorter solid white lines connect the terminal phenyl groups of similarly oriented OPV units along unit cell vector *b*.

phenyl groups of similarly oriented OPV units along unit cell vector *b* in Figure 7c. Note that these dashed and solid marker lines are not in line. Their relative orientation can be described as dashed-up and solid-down: **3** self-assembles into a chiral pattern in accordance with the plane group *p*6. Mirror plane images are never observed for this molecule,[11] as expected for an enantiopure molecule.[28]

In contrast to other systems, the chirality at the level of the monolayer is not or only very weakly expressed in terms of the monolayer orientation with respect to the substrate. The alkyl chains run parallel to the main symmetry axes of graphite (inset in Figure 7a), and also the unit cell vectors run within error parallel to the main symmetry axes of graphite. It is interesting to note that the surface pattern formed by this covalent star shows many similarities with our previous reported hydrogen-bonded hexamers having the similar OPV segments that further organize into a hexagonal lattice (the plane group is *p*6, Figure S15 of the Supporting Information).[11,16,29] In addition, the same chirality aspects also apply to the surface organization of this OPV-oligomer which carries the same (*S*)-2-methylbutoxy substituents.

Conclusions

We have synthesized a star-shaped oligo(*p*-phenylenevinylene) (OPV) substituted hexaarylbenzene which could be purified by recycling GPC. This separation method can serve as a very helpful technique to purify π-conjugated molecules to a high extent. The star-shaped molecule is a plastic crystalline at room temperature, in which highly ordered columnar superstructures are formed. These properties make these molecules attractive to apply in electronic devices in which the mesoscopic order can possibly be aligned.[30] Interestingly, in apolar solution, chiral fibers are formed which still do not disassemble at 90 °C at a very low concentration. This shows that the stability of π-stacked fibers can be greatly enhanced by using a hexaarylbenzene scaffold in which the number of π-conjugated segments is increased without using other non-covalent interactions such as hydrogen bonding. The star-shaped OPV molecule also forms organized monolayers at the liquid−solid interface having a chiral hexagonal lattice. All of these properties make the star-shaped oligo(*p*-phenylenevinylene) (OPV)-substituted hexaarylbenzene potentially useful in the field of supramolecular electronics.[1]

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Supporting Information Available: Experimental details, synthetic procedures, characterization data and complete reference 6b. This material is available free of charge via the Internet at http:// pubs.acs.org.

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