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Oligomers of Hexa-*peri*-hexabenzocoronenes as "Super-oligophenylenes": Synthesis, Electronic Properties, and Self-assembly

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Hexa-*peri*-hexabenzocoronene (HBC) is a remarkable polycyclic aromatic hydrocarbon and is often called "superbenzene" because of its similarity to benzene. In this article we present the facile synthesis of oligomers of HBC, up to trimers (**3**, **4**, **5a**−**c**) with different modes of connection. UV−vis and fluorescence spectroscopy studies reveal that the oligomers are electronically decoupled. This arises from the small atomic orbital coefficients of the bridge-head carbon atoms, the large torsion angle between the HBC units, and the large distance of interacting transition dipoles due to the size of the HBC chromophore. For comparison, a methylene-bridged HBC dimer **6**, so-called "superfluorene", was prepared. The induced planarity improves π-conjugation and suppresses the geometrical relaxation of the backbone upon electronic excitation, leading to a prominent 0−0 transition band in the fluorescence spectra. The self-assembly of the oligomers and of superfluorene **6** was studied by wide-angle X-ray diffraction (WAXD) in the bulk state, and ordered columnar stacking occurs in the HBC dimer **3**, *p*-HBC trimer **4**, and superfluorene **6**. Measurements of shear-aligned samples show that, despite increasing aspects ratio by linear entrainment of disks, the anitropic element that is subject to alignment by shear is the supramolecular columns.

Introduction

Oligoarylenes have attracted great interest because they serve as (i) model compounds for related polyarylenes, (ii) active semiconducting materials in organic electronic devices, and (iii) "molecular wires" in molecular scale electronics.[1] Depending on the topology and geometry of the connected arylene units, the oligoarylenes are either electronically coupled[2] (such as oligophenylenes, oligothiophenes, oligopyrrols, etc.) or decoupled[3] (such as 2, 7-oligopyrene and 9,10-oligoanthrylenes). In the electronically coupled (conjugated) neutral and charged oligoarylenes, the electronic structure and optical properties such as the lowest-energy absorption onset strongly depend on the chain length and finally converge to those of related polymers.[4] The conjugation between the aromatic units is dramatically diminished when steric hindrance is induced between the units.[5,2k] In the oligo-(1, 4-naphthylene)s [3d−f] and oligo(9, 10-anthrylene)s,[3b] the larger size of the aromatic units in combination with the strong steric hindrance results in a very weak electronic coupling between the aromatic units, as convincingly proven by UV−vis spectroscopy and electrochemistry. Surprisingly, the 2,7-connected oligopyrenes show some

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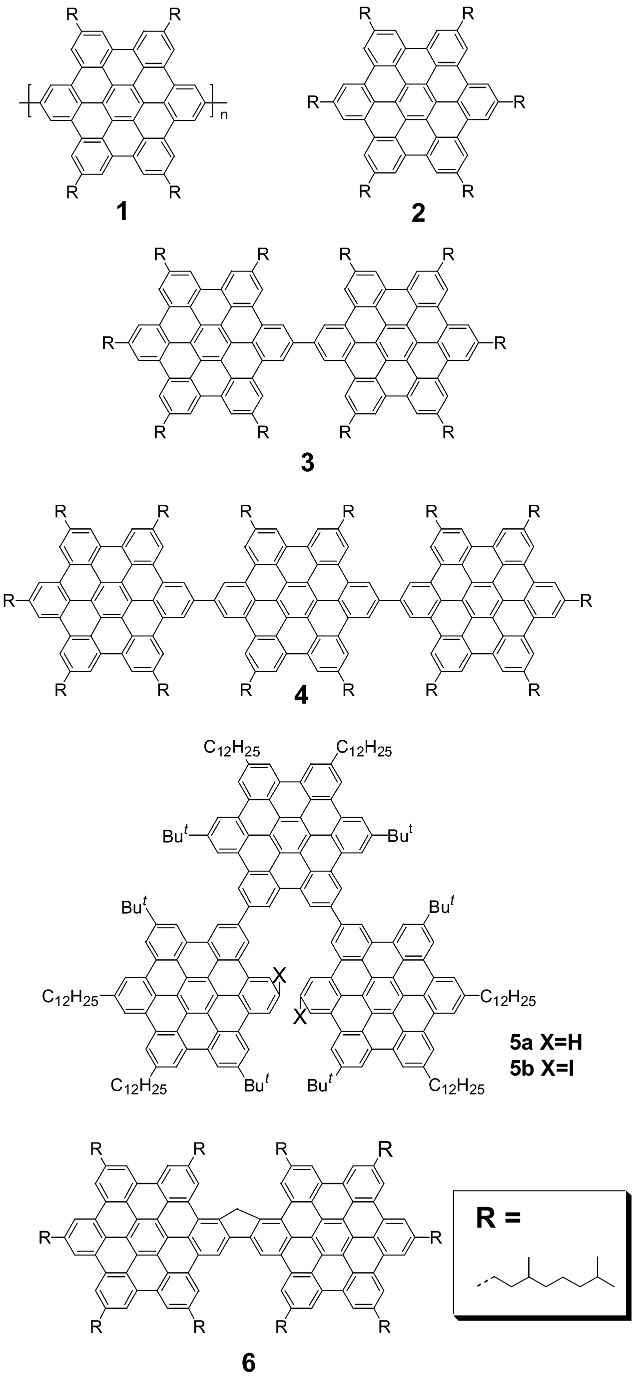
electronic decoupling of the subunits due to the small atomic orbital coefficients of C-2 and C-7 in the frontier orbitals.[3a] Oligoarylenes therefore lead to high spin states upon charging.

CHART 1. Molecular Structures of Oligo- and Polysuperphenylenes



Hexa-*peri*-hexabenzocoronenes (HBCs)[6] carrying solublizing alkyl chains are gaining increasing attention as discotic liquid crystalline materials for organic electronic devices such as field effect transistors (FETs),[7] photovoltaic cells,[8] and light-emitting diodes (LEDs)[9] as a result of their high tendency to form long-range ordered mesophases and very high charge carrier mobility along the columnar axis.[10] From an electronic point of view, HBC is regarded as an aromatic "superbenzene",[11] which suggests the synthesis of the corresponding oligomers as "super-oligophenylenes". Attempts to prepare poly-*p*-"superphenylenes" such as **1** (Chart 1) from the *p*-dibromo-substituted HBC by a Yamamoto coupling reaction, however, only gave an insoluble polymeric material.[12] The poor solubility even when branched solublizing alkyl chains are attached to the HBC core suggests strong interchain $\pi-\pi$ stacking. Interestingly, the UV−vis spectra of the soluble part of the polymers disclosed a spectrum similar to that of the HBC monomer **2** (Chart 1), indicating that the conjugation of the HBC units is interrupted. To understand the electronic properties of the HBC-containing polymers, we set out to make monodispersed oligomers such as the HBC dimer **3** and the *para*-connected HBC trimer **4** (Chart 1). The better solubilizing branched, racemic alkyl chains instead of *n*-alkyl chains were introduced in the hope of obtaining sufficient solubility and better resolved electronic absorption/emission spectra.[13] Two *ortho*-connected HBC trimers **5a,b** were also prepared and served as models for the corresponding poly-*o*-superphenylenes. The active iodo groups in compound **5b** were designed to facilitate an intramolecular coupling giving a fused tris-HBC **25** (Chart 2) or intermolecular coupling to afford higher oligomers. As an alternative of the twisted oliogmers, a nearly planar HBC dimer **6**, in which a methylene unit bridges the two neighboring disks, was synthesized. From an electronic and topological point of view **6** can be regarded as a "superfluorene". Our synthesis of HBCs[6] utilizes the oxidative cyclodehydrogenation of corresponding hexaphenylbenzene derivatives, and this concept has been extended here to the synthesis of HBC oligomers. The electronic and photophysical properties of the oligomers were studied by steady-state UV−vis absorption spectroscopy and fluorescence spectroscopy.

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(12) MALDI MS was conducted on the insoluble materials with TCNQ as matrix, and a series of peaks assigned to 4−18 HBC repeat units were observed. Synthetic details follow the literature: Yamamoto, T.; Morita, A.; Miyazaki, Y.; Maruyama, T.; Wakayama, H.; Zhou, Z.-H.; Nakamura, Y.; Kanbara, T.; Sasaki, S.; Kubota, K. *Macromolecules* **1992**, *25*, 1214−1223.

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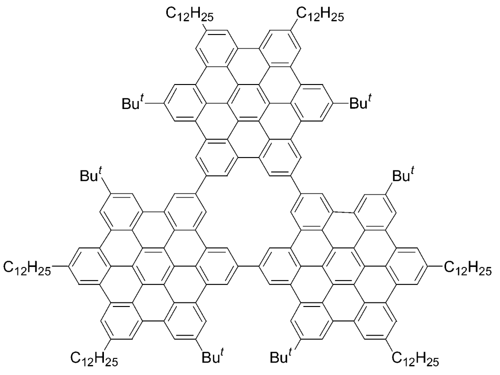
CHART 2. Molecular Structure of Fused HBC Trimer 25



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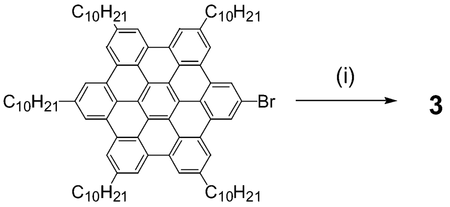
SCHEME 1[a]



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[a] (i) Ni(COD)$_2$, COD, 2,2′-bipyridine, toluene/DMF, 80 °C, 87%.

The self-assembly behavior of these oligomers is another important issue. Polyarylenes with flexible alkyl substituents can be regarded as "hairy-rod" polymers,[14] and depending on nature of the alkyl chains, two different packing models were observed: (i) layered structures via significant interchain $\pi-\pi$ stacking between the aryl units, if the polymers carry linear alkyl chains,[15] and (ii) a hexagonal packing, if the polymers carry short, branched alkyl chains that partially suppress the interchain $\pi-\pi$ interactions.[16] Poly-*p*-superphenylenes can be regarded as "hairy-rod-disc" polymers where strong interchain $\pi-\pi$ interaction of the HBC units could be more prominent. In this work, the self-assembly behavior of the mechanically aligned HBC oligomers and superfluorene was studied by wide-angle X-ray diffraction (WAXD) measurements in the bulk state.

Results and Discussion

Synthesis. The HBC dimer **3** was prepared by a Yamamoto[13] homocoupling of mono-bromo-substituted HBC **7** [6e] in 87% yield (Scheme 1). The key aspect for the synthesis of higher oligomers is the molecular design of branched oligophenylene precursors for the cyclodehydrogenation. Scheme 2 presents the synthesis of the *p*-HBC trimer **4**. A two-fold Suzuki coupling[17] between *p*-dibromo-substituted hexaphenylbenzene **8** [6e] and 4-(trimethysilyl)benzene boronic acid (**9**) gave the extended oligophenylene **10**, in which the trimethylsilyl (TMS) groups serve as precursors for iodo groups. After treatment with iodine monochloride, compound **10** was converted to the related iodide **11** in 94% yield. Standard Hagihara–Sonogashira coupling[18] between **11** and 4-(3,7-dimethyloctanyl)phenyacetylene[6e] provided the extended hexaphenylbenzene **12** with two diphenylacetylene arms. Diels–Alder cycloaddition of **12** with tetrakis[4-(3,7-dimethyloctanyl)phenyl]cyclopentadionene (**13**)[7e] afforded the branched oligophenylene **14** in 78% yield. The soluble precursor **14** was then fused to the related *p*-HBC trimer **4** by oxidative cyclodehydrogenation with $FeCl_3$ in nearly quantitative yield (Scheme 2). Compound **14** was obtained as a yellow powder after repeated washing with hot methanol and was slightly soluble in chloroform and THF.

The synthesis of the *ortho*-connected HBC trimers **5a,b** was based on a similar concept as shown in Scheme 3. An *o*-dibromo-substituted hexaphenylbenzene **17** was first synthesized by Diels–Alder cycloaddition between tetraphenylcyclopentadionene **15**[19] and 4,4′-dibromotolane (**16**) in 95% yield. After Suzuki coupling with 4-(trimethylsilyl)benzene boronic acid (**9**), compound **17** was converted in 82% yield to the extended hexphenylbenzene **18**, which was treated with iodine monochloride to afford the related di-iodide **19** in 92% yield. Compound **19** was subjected to Hagihara–Sonogashira coupling with either phenylacetylene or 4-(trimethylsilyl)phenylacetylene to afford compounds **20** and **21**, respectively. After Diels–Alder cycloaddition with **15**, compounds **20** and **21** were converted into the branched oligophenylenes **22** and **23**, respectively. The TMS groups of compound **23** were transformed to iodo groups with iodine monochloride, affording two potential coupling sites in compound **24**. Under the above cyclodehydrogenation conditions, precursors **22** and **24** were easily converted to the related *ortho*-connected HBC trimers **5a** and **5b**, respectively. The cyclodehydrogenation of compound **23** with $FeCl_3$, however, gave a mixture of HBC trimers with two TMS groups or one TMS group (i.e., one TMS was removed under the Lewis acidic conditions) and **5a** (loss of two TMS). The mixture was treated by tetrabutylammonium fluoride in hot THF overnight to afford clean compound **5a**. The identical spectroscopic properties of compound **5a** made from compound **23** and a sample prepared by direct cyclodehydrogenation of compound **22** suggests that **5a** is a twisted HBC trimer rather than a planar tris-HBC **25**, i.e., the possibility of intramolecular coupling in **5a** to planar molecule **25** during the cyclodehydrogentation of compound **22** can be excluded. It is of interest whether the planar tris-HBC **25** can be prepared by intramolecular coupling of compound **5b** in dilute solution, or if higher oligomers can be made by intermolecular coupling. Several attempts at Yamamoto coupling reactions of compound **5b** failed to give either compound **25** or higher oligomers but rather starting materials as well as some partially dehalogenated compounds. It seems that the intramolecular and intermolecular couplings meet with too strong steric interactions. The high

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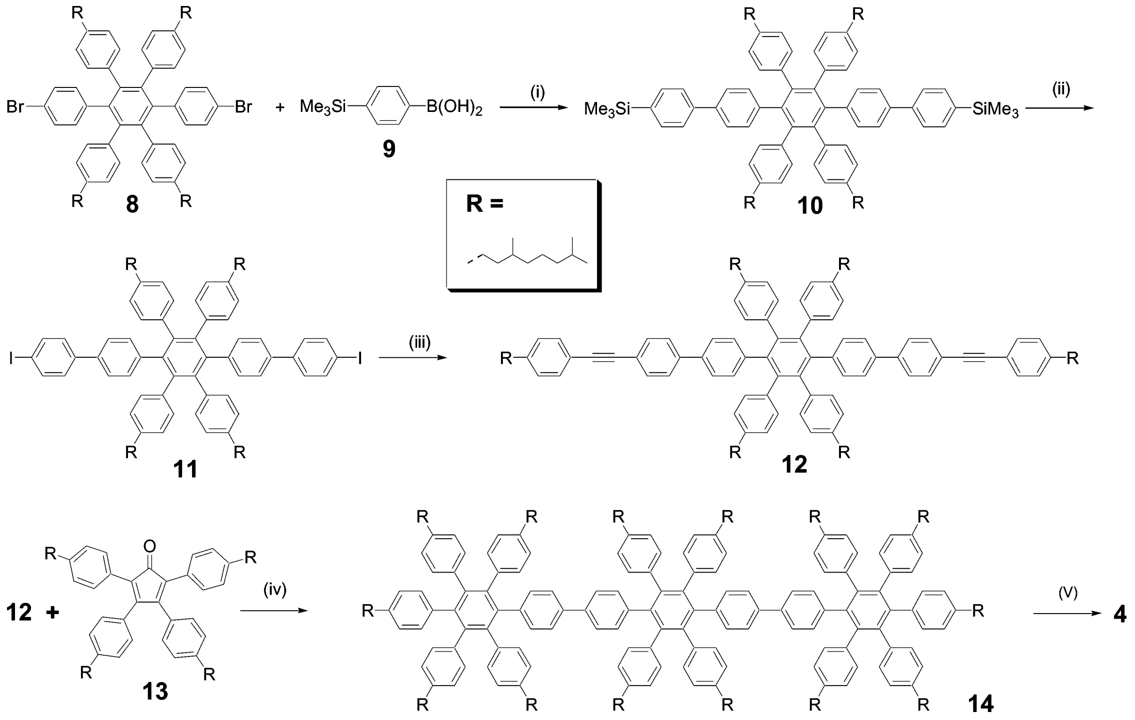
SCHEME 2[a]



[a] (i) Pd(PPh$_3$)$_4$, K$_2$CO$_3$, toluene, 95 °C, 87%; (ii) ICl, chloroform, room temperature, 94%; (iii) 4-(3,7-dimethyloctanyl)phenylacetylene, Pd(PPh$_3$)$_4$, CuI, piperidine, 92%; (iv) Ph$_2$O, reflux, 78%; (v) FeCl$_3$, CH$_3$NO$_2$/dichloromethane, 45 min, 83%.

solubility of **5a,b**, in contrast with that of their *para*-connected counterpart **4** suggests less aggregation in solution.

The methylene-bridged HBC trimer **6** was synthesized by similar cyclodehydrogenation of the oligophenylene precursor **28** as shown in Scheme 4. The synthesis started with a two-fold Hagihara−Sonogashira coupling reaction between commercially available 2,7-dibromofluorene and 4-(3,7-dimethyloctanyl)phenylacetylene[6e] to give compound **27**, which was followed by a two-fold Diels−Alder cyclodehydrogenation with compound **13** to afford precursor **28**.

All intermediate and target compounds were purified by standard column chromatography (except for compound **4** because of low solubility) and were fully characterized by mass spectroscopy (see Supporting Information), ^{1}H NMR and ^{13}C NMR spectroscopy, and elemental analysis.

UV−vis and Fluorescence Spectra in Solution. The UV−vis absorption and fluorescence spectra of the novel oligosuperphenylenes were measured in 1,2,4-trichlorobenzene. For comparison, the HBC unit concentration of the oligomers was controlled at 2.0×10^{-6}, 2.0×10^{-7}, and 2.0×10^{-8} M, respectively. Similar to other nonconjugated oligoarylenes,[3] the $\lambda_{\mathrm{max,ab}}$ values of the oligosuperphenylenes were shifted relative to one another by only a few wavelengths (0−8 nm) (Figure 1), suggesting that the HBC units are electronically decoupled.

The normalized fluorescence spectra of HBC monomer **2**, dimer **3**, and trimer **4** at [HBC] = 2×10^{-8} M in 1,2,4-TCB are presented in Figure 2a. The HBC dimer **3** has emission bands similar to those of HBC monomer **2** with a small red-shift, further proving the very weak coupling interaction between two HBCs. The *para*-connected HBC trimer **3** also has similar emission bands with lower fluorescence quantum yield. At the same time, the bands are broadened with a long wavelength emission tail. The *ortho*-connected HBC trimer **5a** shows an emission band similar to that of *para*-connected HBC trimer **4** (Figure 4b), however, with a small blue-shift. Omitting the issue of the band broadening and red-shift due to intermolecular stacking, the similarity of emission bands of these oligomers further supports the electronic decoupling of the oligosuperphenylenes.

Alkylated HBC are known to show a strong tendency to aggregate even in very dilute solution (to 10^{-9} M in toluene),[20] and thus the spectroscopic properties of HBC materials strongly depend on the concentration and solvents.[21] Herein upon increasing the concentration, the extinction coefficients (ϵ) of **2**, **3**, **4**, **5a,b**, and **6** gradually decrease (see S-Figure 3 in Supporting Information), a consequence of intermolecular π-stacking of HBC units.[21] On the other hand, upon increasing the number of the HBC units, i.e., upon going from monomer to the *para*-connected trimer, the UV−vis absorption spectra recorded at the same HBC unit concentration became broad and showed smaller extinction coefficients, suggesting that the tendency to aggregate becomes stronger (Figure 1a). Compared to the *para*-connected HBC trimer **4**, the *ortho*-connected HBC trimer **5a,b** has larger ϵ values at the same concentration (Figure 1b), which can be explained by the more twisted conformation in **5a,b**. The interchain $\pi-\pi$ interactions also led to broadening and

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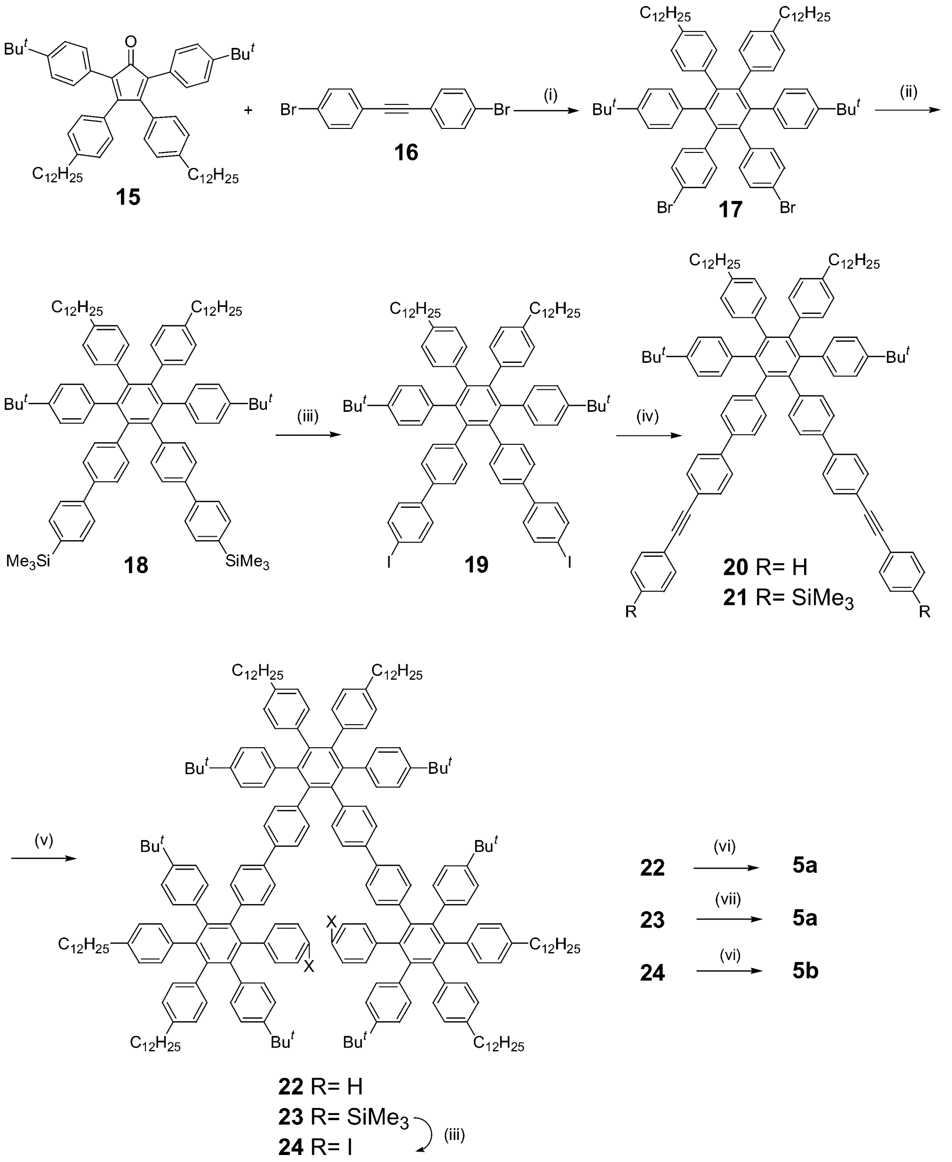
SCHEME 3[a]



[a] (i) Ph_2O, reflux, 95%; (ii) $Pd(PPh_3)_4$, K_2CO_3, toluene, 95 °C, 86%; (iii) ICl, chloroform, room temperature, 92%; (iv) phenylacetylene or 4-trimethylsilylphenylacetylene, $Pd(PPh_3)_4$, CuI, piperidine, 88% and 91%, respectively; (v) **15**, Ph_2O, reflux, 72% for **22** and 94% for **23**; (vi) $FeCl_3$, CH_3NO_2/dichloromethane, 45 min, 92% for **5a** and 80% for **5b**; (vii) (a) $FeCl_3$, CH_3NO_2/dichloromethane; (b) TBAF, THF, 60 °C, overnight.

red-shift of the fluorescence band (Figure 2a), and this phenomenon was usually observed in conjugated polymers and oligomers in which strong interchain interactions exist.[22,23] The strongly twisted conformation in the *ortho*-connected HBC trimers **5a,b** diminishes the interchain interactions, leading to a blue-shift of the emission bands with respect to their *para*-connected counterpart **4**.

It is also known that the parent poly-*p*-phenylenes adopt a twisted conformation with a distortion angle of 23° between adjacent building blocks in solution, and the substituted derivatives display even larger torsional angle of 60−80°.[23] As a result of the twisted structure, only a weak π-conjugation among the rings was observed.[24] The ground-state geometric optimization of the oligomers of HBC by different calculation methods (e.g., pcff 3.00 force field level, AM1, or B3LYP 6-31G**) disclosed that the HBC dimer **2** and trimers (**4** and **5a**)

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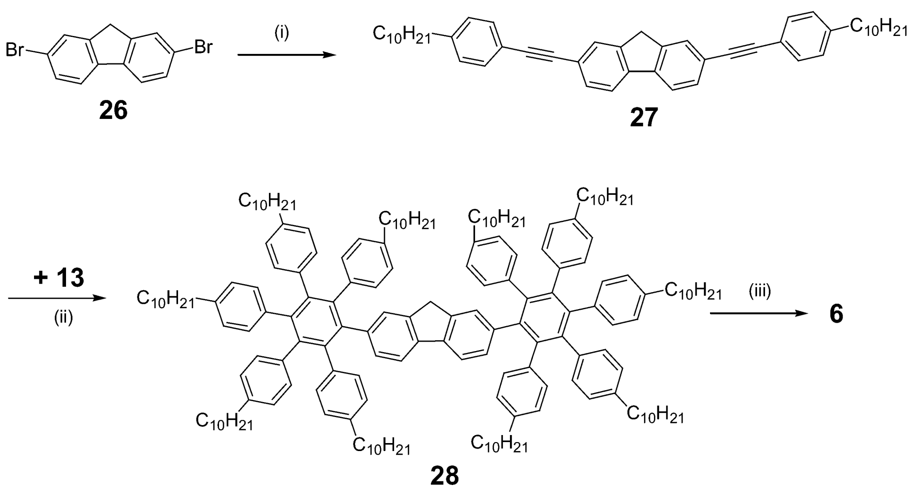
SCHEME 4[a]



[a] (i) 4-(3,7-Dimethyloctanyl)phenylacetylene, Pd(PPh$_3$)$_4$, CuI, piperidine, 78%; (ii) Ph$_2$O, reflux, 27%; (iii) FeCl$_3$, CH$_3$NO$_2$/dichloromethane, 55%.

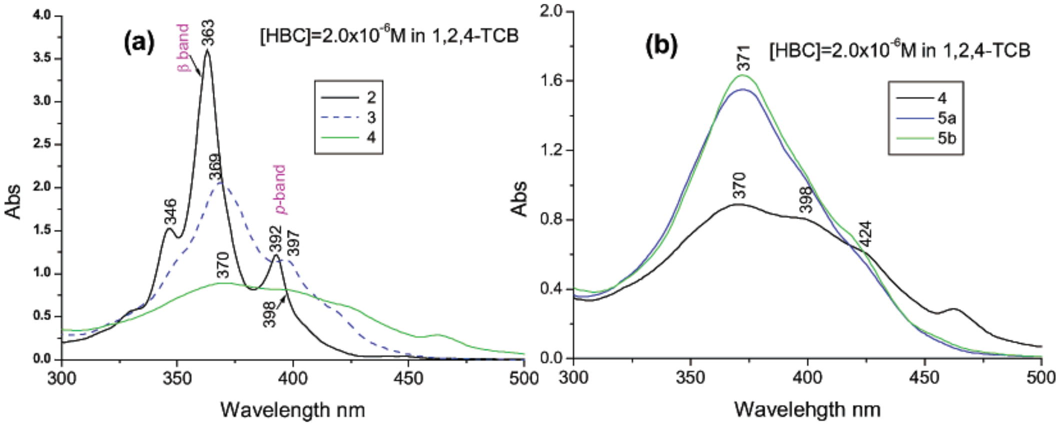


FIGURE 1. UV−vis spectra of **2, 3, 4, 5a,b** in 1,2,4-trichlorobenzene with [HBC] = 2 × 10^{-6} M.

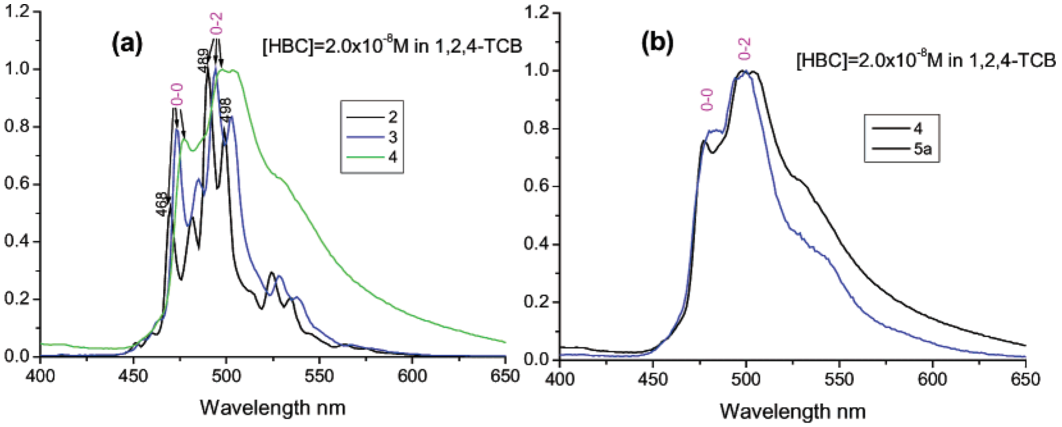


FIGURE 2. Fluorescence spectra of **2**, **3**, **4**, **5a** in 1,2,4-trichlorobenzene with [HBC] = 2 × 10^{-8} M. All are excited at 370 nm.

possessed a large dihedral angle (above 40°) between the HBC units. The large torsional angle induced by the repulsion between 2,2′-hydrogens as well as the alkyl chains of the neighboring HBC units is thus one important reason explaining the weak electronic coupling in the oligosuperphenylenes. Another possible reason for the weak electronic coupling in the oligosuperphenylenes is the large size of HBC building blocks, which results in a large distance of the interacting transition dipoles.

The atomic orbital coefficients of the bridged-head atoms in the oligoarylenes also play an important role.[3] Calculations (AM1 method) disclose that the atomic orbital coefficients (ρ) of the bridge-head carbon atoms in the HBC dimer **2** are very small (ρ = 0.13), and on

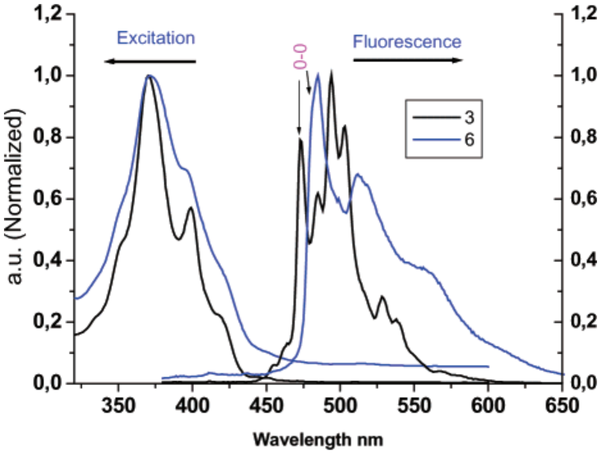


FIGURE 3. Emission (exited at 370 nm) and excitation spectra (excited at 480 nm) of compound **3** and **6** in 1,2,4-trichlorobenzene with [HBC] = 2×10^{-8} M.

the basis of the calculated torsional angle of about 45° in the HBC dimer **2** (comparable to that of biphenyl[22]), the interaction between the HBC units, expressed by $\rho^2 \cos \theta$, is very weak.[25]

Significant improvement of conjugation in poly-*p*-phenylenes came from the synthesis of "stepladder" and "ladder" polymers.[26,27] The induced planarity in molecule **6** significantly changes the optical properties of the HBC dimer as shown in Figure 3. The fluorescence spectra of the molecule **6** are obviously different from that of molecule **2**. The forbidden 0−0 transition in the HBC dimer **2**[28] is now allowed and becomes prominent in superfluorene **6**. The bathochromic shift and broadening of the UV−vis absorption and fluorescence spectra of superfluorene **6** compared to those of HBC dimer **2** suggest an improved conjugation induced by the increased planarity.

WAXD Studies on the HBC Oligomers in the Bulk State. The above UV−vis and fluorescence measurements clearly show that the HBC oligomers have a high tendency to aggregate by π−π interactions. Another point of interest is to understand how these oligomers stack in the bulk state and whether they can still form a columnar stacking as the normal alkyl-substituted HBCs. The phase behavior of the oligomers was investigated by differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXD). The DSC curves of HBC dimer **3** showed a second-order (probably glass) transition at 57 °C and a first-order endothermic (on heating) transition at 238 °C. Both transitions were reversible and were observed on the cooling scan with a hysteresis of 70 °C for the first-order transition. For the other oligomers as well as superfluorene, however, no phase transitions were observed even up to 300 °C, suggesting either a thermally stable ordered phase for the *para*-connected HBC trimer and superfluorene due to strong π−π interaction or an amorphous state in the *ortho*-connected HBC trimer.

The WAXD measurements[29] were conducted on extruded fibers of the oligomers and compound **6**. Figure 4 presents a 2D diffractogram together with the intensity distribution in the equatorial direction for the HBC-dimer **3** at room temperature. The wide-angle reflection peaks between the meridian and equator leave no doubt that HBC dimer **3** forms a columnar phase, and that it is the columns, not the molecules themselves, that are aligned in the direction of shear. The disks in the columns are tilted at arcos (0.37 nm/0.53 nm) = 45° with respect to the fiber axis. The main repeating distance along the fiber (0.53 nm) corresponds to the distance between tilted disks in the column. As indicated by the above model calculation, an intracolumnar coplanar conformation seems to be unlikely because of steric hindrance, so column formation is only possible if the dimer molecules are stacked on top of each other, i.e., if a face-to-face double-column stack is formed (Figure 4). As a result of the twist of the two HBC disks, the columnar axes of the two stacked HBC columns are also tilted to each other. Integration in the equatorial direction reveals a strong two-dimensional correlation in directions lateral to the columnar axes, and the observed reflexes can be matched relatively well to an orthorhombic 2D unit cell with cell parameters $a = 2.74$ nm, $b = 2.17$ nm.

The *p*-HBC trimer **4** shows a similar diffractogram (Figure 5). The reflex along the meridian and equator again implies a tilted columnar stacking and can be correlated to the intracolumn disc−disk distance (0.38 nm, i.e., the disks are tilted by 24° with respect to the fiber axis). Integration along the equatorial direction reveals a series of reflection maxima that could approximately be fitted to a monoclinic 2D unit cell with the cell parameters $a = 4.27$ nm, $b = 2.99$, and $\gamma = 60°$.

The 2D WAXD patterns of an oriented fiber of superfluorene **6** also reveal a tilted columnar phase; however, only one obvious reflex on the equatorial direction was observed (see Supporting Information), making the elucidation of a 2D unit cell difficult. The *ortho*-connected HBC trimers **5a,b** cannot form a columnar phase on the basis of their 2D WAXD measurement, possibly because the twisted conformation prohibits columnar stacking. When compared to the twisted dimer, **3**, it is particular surprising that the supposed nearly planar superfluorene does not form a more ordered columnar phase.

The single-crystal structures of parent *p*-oligophenylenes reveal a planar conformation in the main chain with a herringbone-type packing at room temperature.[30] The alkyl-substituted PPPs, however, adopt twisted conformations due to the induced steric hindrance and the main chains are separated by a layer of side chains, suggesting less importance of the interchain π−π inter-

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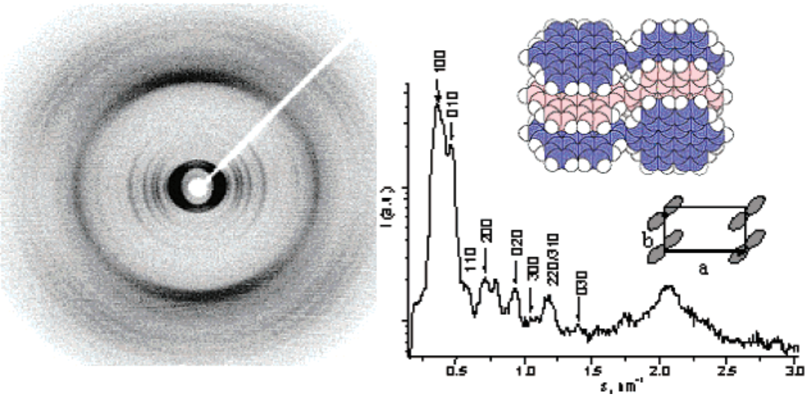

FIGURE 4. 2D X-ray diffractogram of an extruded fiber of HBC dimer **3** at room temperature. The integrated reflex along the equatorial direction reveals an orthorhombic 2D unit cell. Insert is the proposed top-to-top packing of the HBC disks to form a dimeric column.

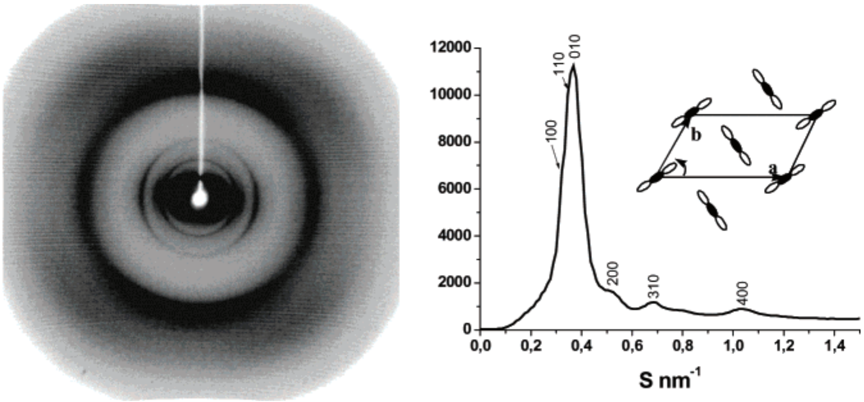

FIGURE 5. Room temperature 2D X-ray diffractogram of an extruded fiber of HBC trimer **4**. Integration along the equatorial direction discloses an approximate monoclinic 2D unit cell (insert).

actions.[31] In the present cases, the strong intermolecular interactions between the HBC disks drive the *para*-connected oligomers of HBC and molecule **6** into a stable columnar stacking in a microcrystalline phase. The self-assembled dimeric or trimeric columns form multiple hole-transfer tunnels, thus making them promising electronic materials for organic devices.

Conclusion

Oligomers of "superbenzene" (HBC) up to a trimer with different geometries were successfully prepared by either Yamamoto coupling or oxidative cycodehydrogenation from corresponding branched oligophenylenes. These oligomers represent a new kind of electronically decoupled oligoarylenes and serve as model compounds of corresponding poly-*p*-(*o*-)"superphenylenes". The reduction of these oligomers by an active metal such as potassium offers the possibility toward high-spin oligoradical anion formation.[32] The strong aggregation tendency of HBC leads to a columnar stacking of the HBC dimer **3**, trimer **4**, and superfluorene **6** in the bulk state, allowing one to study the charge carrier transport along the HBC multi-columns. Although poly-*p*-superphenylenes and poly-*o*-superphenylenes are not readily available by transition-metal-catalyzed polymerization of the corresponding monomers as a result of either their poor solubility or the strong steric hindrance between the HBC units, the *meta*-connected polysuperphenylenes and related oligo-*m*-superphenylenes could be made by a similar synthetic strategy based on *m*-dibromo-substituted HBC. The weaker steric hindrance between the HBC units in poly-*m*-superphenylenes is expected to allow formation of high molecular weight polymers, and the remaining twisted conformation could diminish the intermolecular π-stacking, thus leading to good solubility. Synthesis and characterization of such kind of polymers and oligomers is a subject of future research.

Experimental Section

General Experimental Methods. ^{1}H NMR and ^{13}C NMR spectra were recorded in deuterated solvents such as CD_2Cl_2 and 1,2-dichlorobenzene-d^4. UV−vis and fluorescence spectra of the oligomers were recorded in dilute solution at room temperature. FD mass spectra were obtained with a working voltage of 8 KV. MALDI TOF mass spectra were recorded using a 337 nm nitrogen laser with TCNQ as matrix. Differential scanning calorimetry (DSC) was measured with heating and cooling rate of 10 K/min. 2D wide-angle X-ray diffraction measurements of oriented fibers were conducted using a rotating anode (Rigaku, 18 kw) X-ray beam (CuKα, pinhole collimation, double graphite monochromator) and a CCD camera.

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Unless otherwise noted, all starting materials were used as received. Toluene for water-free reactions was refluxed over potassium under argon and freshly distilled before use.

HBC Dimer 3. To a deoxygenated mixture of 1,5-cyclooctadiene (COD, 3 mL) in toluene (25 mL) were added Ni(COD)$_2$ (116 mg, 0.42 mmol) and 2,2′-dipyridyl (68 mg, 0.42 mmol). After the mixture was stirred at room temperature for 1 h, a deoxygenated solution of 2-bromo-5,8,11,14,17-penta(3,7-dimethyloctanyl)-hexa-*peri*-hexabenzocoronene (**7**) (0.45 g, 0.35 mmol) in toluene (50 mL) was added. The resulting mixture was heated at 60 °C for 20 h. The mixture was allowed to cool to room temperature, and the precipitated product was filtered and washed with toluene, dibromoethane, and methanol. The product was purified by recrystallization from toluene to give **3** as a yellow solid in 87% yield. MALDI TOF MS (TCNQ as matrix): *m*/*z* (%) = 2444.57 (100%), calcd 2445.92. ^{1}H NMR (500 MHz, 1,2-dichlorobenzene-*d*,^{4} 443 K): δ ppm 9.78 (s, 4H), 9.19 (s, 4H), 8.92 (s, 4H), 8.84 (s, 4H), 8.81 (s, 4H), 8.76(s, 4H), 3.39−3.25 (m, 20H, α-CH$_2$), 2.30−0.73 (m, 190H). ^{13}C NMR (125 MHz, C$_2$D$_2$Cl$_4$, 413 K): δ ppm 141.9, 141.8, 141.4, 131.8, 131.5, 131.3, 131.2, 125.9, 125.0, 124.7, 122.9, 122.8, 122.7, 122.6, 122.4, 121.3, 121.0, 120.7, 41.0, 40.8, 40.7, 39.1, 38.9, 36.3, 36.1, 36.0, 34.8, 34.7, 34.5, 29.4, 29.1, 26.3, 26.2, 26.1, 24.0, 23.9, 23.7, 23.7, 21.3, 21.2. Elemental analysis: found C 90.21, H 9.34; calcd C 90.36, H 9.64.

1,2,4,5-Tetrakis[4′-(3″,7″-dimethyloctanyl)phenyl]-3,6-bis[4′-(trimethylsilyl)biphenyl] Benzene (10). A 1.25-g portion of *p*-dibromo-substituted hexaphenylbenzene **8**, 775 mg of 4-trimethylsilylbenzene boronic acid (**9**), and 58 mg of catalyst Pd(PPh$_3$)$_4$ were dissolved in 15 mL toluene, and then 10 mL 1 M K$_2$CO$_3$ aqueous solution was added. The mixture was degassed by two freeze-pump-thaw cycles and heated to reflux for 24 h. After cooling, 150 mL of acetyl acetate was added to extract the product. The organic layer was washed with water three times and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (silica gel, PE/DCM = 10:1) to afford 1.45 g of compound **10** as a white solid in 87% yield. FD MS (8kv): *m*/*z* (%) = 1392.4 (100%), calcd 1392.35. ^{1}H NMR (CD$_2$Cl$_2$, 250 MHz): δ ppm 7.51 (d, J = 8.2 Hz, 4H), 7,41 (d, J = 8.2 Hz, 4H), 7.14 (d, J = 8.2 Hz, 4H), 6.90 (d, J = 8.2 Hz, 4H), 6.77 (d, J = 7.9 Hz, 8H), 6.70 (d, J = 7.9 Hz), 2.42 (m, 8H), 1.56−0.80 (m, 76H), 0.27(s, 18H). ^{13}C NMR (CD$_2$Cl$_2$, 62.5 MHz): δ ppm 140.7, 140.2, 139.9, 139.8, 138.6, 137.8, 137.0, 133.4, 131.7, 131.1, 126.3, 125.6, 124.6, 39.1, 38.5, 36.9, 32.6, 31.9, 27.7, 24.4, 22.2, 22.2, 19.1, −1.7. Elemental analysis: found C 86.06, H 9.62; calcd C 86.26, H 9.70, Si 4.03.

1,2,4,5-Tetrakis[4′-(3″,7″-dimethyloctanyl)phenyl]-3,6-bis(4′-iodobiphenyl)Benzene (11). A 1.10-g portion of compound **10** was dissolved in 200 mL of fresh chloroform. The solution was degassed by bubbling argon for 15 min, and 3.16 mL of iodine monochloride solution in dichloromethane (1 M) was added. After stirring at room temperature for 45 min, the reaction was quenched by adding 100 mL of 2 M aqueous sodium sulfite. The organic layer was washed with water three times and dried over magnesium sulfate. The solvent was removed, and the residue was purified by column chromatography (silica gel, PE/DCM = 9:1) to give 1.4 g of compound **11** as a colorless solid in 94% yield. FD MS (8kv): *m*/*z* (%) = 1499.40 (100%), calcd 1499.78. ^{1}H NMR (CD$_2$Cl$_2$, 250 MHz): δ ppm 7.65 (d, J = 8.5 Hz, 4H), 7.16(d, J = 8.5 Hz, 4H), 7.07 (d, J = 8.5 Hz, 4H), 6.88 (d, J = 8.5 Hz, 4H), 6.73 (d, J = 8.2 Hz, 8H), 6.67 (d, J = 8.2 Hz, 8H), 2.34 (m, 8H), 1.42(m, 4H), 1.2−0.74(m, 72 H). ^{13}C NMR (CD$_2$Cl$_2$, 62.5 MHz): δ ppm 141.4, 140.9, 140.7, 140.6, 140.5, 138.5, 138.1, 136.59, 132.57, 131.8, 128.9, 127.1, 125.2, 39.9, 39.2, 37.6, 33.3, 32.6, 28.4, 25.1, 23.0, 23.0, 19.9. Elemental analysis: found C 75.18, H 7.86; calcd C 75.28, H 7.80, I 16.92.

1,2,4,5-Tetrakis[4′-(3″,7″-dimethyloctanyl)phenyl]-3,6-bis[4′-(3″,7″-dimethyloctanyl)diphenylethynyl] Benzene (12). A 500-mg portion of compound **11**, 242 mg of 4-(3,7-dimethyloctanyl)phenylene acetylne, 20 mg of Pd(PPh$_3$)$_4$, 6.3 mg of CuI, and 4 mL of piperidine were mixed together. The mixture was degassed by two freeze-pump-thaw cycles and was stirred at room temperature for 16 h. The reaction was quenched with 20 mL of saturated aqueous ammonium chloride, and the product was extracted by diethyl ether. The organic layer was washed with water three times and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the residue was purified by column chromatography (silica gel, PE/DCM = 8:1) to give 530 mg of compound **12** as a colorless solid in 92% yield. ^{1}H NMR (CD$_2$Cl$_2$, 250 MHz): δ ppm 7.42−7.33 (m, 12H), 7.10 (d, J = 8.8 Hz, 4H), 7.07 (d, J = 8.8 Hz, 4H), 6.83 (d, J = 8.8 Hz, 4H), 6.68 (d, J = 8.2 Hz, 8H), 6.61 (d, J = 8.2 Hz, 8H), 2.53 (m, 4H), 2.28 (m, 8H), 1.47−0.75(m, 72 H). ^{13}C NMR (CD$_2$Cl$_2$, 62.5 MHz): δ ppm 143.8, 140.7, 140.3, 140.2, 139.9, 137.8, 136.2, 131.9, 131.6, 131.2, 128.3, 126.4, 126.3, 124.6, 121.8, 120.2, 89.9, 88.4, 39.2, 38.5, 36.9, 33.2, 32.7, 32.4, 31.9, 27.8, 24.5, 22.3, 22.2, 19.2. FD MS (8kv): *m*/*z* (%) = 1728.5 (100%), calcd 1728.77. Elemental analysis: found C 90.24, H 9.60; calcd C 90.32, H 9.68.

***para*-Connected Hexaphenylbenzene Trimer 14.** A 500-mg portion of compound **12** and 820 mg of tetra[4-(3,7-dimethyloctanyl)phenyl]cyclopentadienone (**13**) were dissolved in 2.0 mL of diphenyl ether. The mixture was degassed under vacuum, filled back with argon, and heated to reflux for 19 h. After cooling, the diphenyl ether was removed under high vacuum, and the residue was purified by column chromatography (PE/DCM = 8:1) to afford 803 mg of compound **14** as a colorless waxy product in 78% yield. MALDI-TOF MS (dithranol as matrix): *m*/*z* (%) = 3562.11 (100%), calcd 3563.88. ^{1}H NMR (CD$_2$Cl$_2$, 500 MHz): δ ppm 6.91 (d, J = 7.6 Hz, 8H), 6.78 (d, J = 7.6 Hz, 8H), 6.66 (m, 56H), 2.39−2.32 (m, 28H), 1.40−0.78 (m, 266H). ^{13}C NMR (CD$_2$Cl$_2$, 125 MHz): δ ppm 140.9, 140.8, 140.6, 140.4, 140.3, 140.2, 140.1, 140.0, 138.6, 138.4, 132.2, 131.6, 126.9, 126.7, 124.8, 39.7, 39.2, 37.4, 33.2, 32.6, 32.5, 28.4, 25.1, 22.9, 22.8, 19.8, 19.7, Elemental analysis: found C 89.57, H 10.21; calcd C 89.65, H 10.35.

***para*-Connected HBC Trimer 4.** A 220-mg portion of precursor **14** was dissolved in 60 mL of fresh dichloromethane, and the solution was degassed by bubbling argon for 20 min. Then 720 mg of FeCl$_3$ dissolved in 5 mL of nitromethane was slowly added by syringe. The mixture was bubbled through argon over 35 min and then quenched by adding 200 mL of methanol. The yellow precipitate was collected and washed by methanol until the filtrate is colorless. The powder was further stirred in hot methanol (50 °C) overnight to remove residual iron inside. After filtering and drying, 180 mg of yellow powder was obtained (83% yield, MALDI-TOF mass spectra of crude compound indicate quantitative conversion, the low yield here because of the loss of product during purification). MALDI-TOF MS (TCNQ as matrix): *m*/*z* (%) = 3528.11 (100%), calcd [M$^+$] 3527.60. ^{1}H NMR (1,2-dichlorobenzene-*d*$_4$, 500 MHz, 443 K): δ ppm 9.86 (s, 6H), 9.18−8.67 (m, 28H), 3.54−3.28 (m, 28H), 2.28−0.76 (m, 266H). Elemental analysis: found C 90.02, H 9.34; calcd C 90.57, H 9.43.

1,2-Bis(4′-bromophenyl)-4,5-bis(4′-dodecylphenyl)-3,6-bis(4′-*tert*-butylphenyl) Benzene (17). A 2.6-g portion of compound **15**, 1.05 g of 4,4′-dibromotolane (**16**), and 3 mL of diphenyl ether were mixed together. The mixture was degassed under vacuum, filled back with argon, and heated to reflux for 17 h. After cooling, 50 mL of methanol was added to precipitate the product. The white precipitate was washed by methanol to remove diphenyl ether, dried under vacuum, and afforded 3.4 g of pure compound **17** as a pale yellow solid (95%). FD MS (8 kV): *m*/*z* (%) = 1141.2 (100%), calcd [M$^+$] 1141.37. ^{1}H NMR (CD$_2$Cl$_2$, 250 MHz): δ ppm 6.95 (d, J = 8.5 Hz, 4H), 6.89 (d, J = 8.2 Hz, 4H), 6.73−6.66 (m, 16H), 2.35 (t, J = 7.6 Hz, -CH_2-C$_{11}$H$_{23}$, 4H), 1.27 (m, -CH$_2$-(CH_2)$_{10}$-CH$_3$, 20H), 1.14 (s, *tert*-butyl, 18H), 0.89(t, -(CH$_2$)$_{11}$-CH_3, 6H). ^{13}C NMR (CD$_2$Cl$_2$, 125 MHz): δ ppm 148.7, 141.5, 140.8, 140.3, 140.1, 139.0, 138.3, 137.8, 133.5, 131.5, 131.4, 130.1, 126.9, 123.8, 119.72, 35.70, 34.4, 32.3, 31.8, 31.3, 30.1, 30.0, 29.9, 29.8, 29.3, 23.1, 14.3. Elemental analysis: found C 77.86, H 8.13; calcd C 77.87, H 8.12, Br 14.00.

1,4-Bis(4′-*tert*-butylphenyl)-2,3-bis(4′-dodecylphenyl)-5,6-bis[4′-(trimethylsilyl)biphenyl] Benzene (18). Following the procedure of the synthesis of **10**, compound **18** was obtained in 86% yield after purification with column chromatography (silica gel, PE/DCM = 9:1). FD MS (8 kV): *m/z* (%) = 1281.0 (100), calcd 1281.1. ^{1}H NMR (CD_2Cl_2, 250 MHz): δ ppm 7.19 (d, J = 8.2 Hz, 4H), 7.14 (d, J = 8.2 Hz, 4H), 7.12−6.71 (m, 24H), 2.42 (t, J = 7.2 Hz, $-CH_2-C_{11}H_{23}$, 4H), 1.34 (m, $CH_2-(CH_2)_{10}-CH_3$, 20H), 1.25 (s, *tert*-butyl, 18H), 0.95 (t, $-(CH_2)_{11}-CH_3$, 6H), 0.29 (s, $SiMe_3$, 18H). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ ppm 141.3, 141.0, 140.8, 140.3, 140.0, 139.2, 138.7, 138.3, 137.9, 134.1, 132.5, 131.8, 131.6, 130.2, 127.0, 126.4, 125.5, 123.8, 123.7, 119.3, 35.8, 34.5, 32.4, 31.9, 31.5, 30.2, 30.1, 30.0, 29.9, 29.4, 23.2, 14.4, −1.0. Elemental analysis: found C 85.78, H 8.85; calcd C 86.32, H 9.29, Si 4.39.

1,4-Bis(4′-*tert*-butylphenyl)-2,3-bis(4′-dodecylphenyl)-5,6-bis(4′-iodobiphenyl) Benzene (19). Following the synthetic procedure for compound **11**, compound **19** was obtained as a slightly yellow solid in 92% yield. FD MS (8 kV): *m/z* (%) = 1388.1 (100), calcd 1387.56. ^{1}H NMR (CD_2Cl_2, 250 MHz): δ ppm 7.63 (d, J = 8.5 Hz, 4H), 7.12 (d, J = 8.2 Hz, 4H), 7.09 (d, J = 7.6 Hz, 4H), 6.95 (d, J = 8.2 Hz, 4H), 6.89 (d, J = 8.2 Hz, 4H), 6.79−6.86 (m, 12H), 2.37 (t, J = 7.2 Hz, $-CH_2-C_{11}H_{23}$, 4H), 1.28 (m, $CH_2-(CH_2)_{10}-CH_3$, 20H), 1.11 (s, *tert*-butyl, 18H), 0.90 (t, $-(CH_2)_{11}-CH_3$, 6H). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ ppm 140.6, 140.0, 139.9, 138.5, 138.2, 138.0, 136.7, 132.5, 131.6, 131.5, 130.1, 128.9, 126.9, 125.2, 123.7, 35.7, 34.4, 32.4, 31.8, 31.4, 30.1, 30.0, 29.9, 29.8, 29.3, 23.1, 14.3. Elemental analysis: found C 74.02, H 7.42; calcd C 74.44, H 7.26, I 18.29.

1,4-Bis(4′-*tert*-butylphenyl)-2,3-bis(4′-dodecylphenyl)-5,6-bis(4′-diphenylethynyl) Benzene (20). A mixture of 556 mg of compound **19**, 13.8 mg of $Pd(PPh_3)_4$, and 4.6 mg of CuI in 4 mL of piperidine was degassed by two freeze-pump-thaw cycles, and then 122 mg of phenyl acetylene was added. The mixture was stirred at 40 °C for 2 h. After cooling, the mixture was poured into saturated aqueous ammonium chloride and extracted by diethyl ether. The organic layer was washed with water three times and dried over magnesium sulfate. The solvent was removed under vacuum, and the residue was purified by column chromatography (silica gel, PE/DCM = 4:1) to give 470 mg of compound **20** as a pale yellow powder (88%). FD MS (8 kV): *m/z* (%) = 1335.8 (100%), calcd 1336.01. ^{1}H NMR (CD_2Cl_2, 250 MHz): δ ppm 7.55−7.54 (m, 4H), 7.49 (d, J = 8.5 Hz, 4H), 7.41 (d, J = 8.8 Hz, 4H), 7.38−7.34 (m, 4H), 7.17 (d, J = 8.5 Hz, 4H), 6.99 (d, J = 8.2 Hz, 4H), 6.91 (d, J = 8.5 Hz, 4H), 6.80 (d, J = 8.5 Hz, 4H), 6.76 (d, J = 8.2 Hz, 4H), 6.69 (d, J = 8.2 Hz, 4H), 2.38 (t,, J = 7.3 Hz, $-CH_2-C_{11}H_{23}$, 4H), 1.29 (m, $CH_2-(CH_2)_{10}-CH_3$, 20H), 1.13 (s, *tert*-butyl, 18H), 0.91 (t, $-(CH_2)_{11}-CH_3$, 6H). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ ppm 140.9, 140.0, 138.6, 138.2, 137.0, 132.5, 132.2, 131.9, 131.7, 131.5, 128.8, 128.7, 126.9, 125.4, 123.8, 123.7, 122.1, 90.2, 89.7, 35.8, 34.4, 32.4, 31.8, 31.4, 30.5, 30.1, 29.9, 29.8, 29.4, 23.1, 14.3. Elemental analysis: found C 91.65, H 8.32; calcd C 91.70, H 8.30.

4-Trimethylsilyphenyl Acetylene. A 6.88-g portion of 1-brom-4-trimethylsilylbenzene, 315 mg of $Pd(PPh_3)_2Cl_2$, and 172 mg of CuI were mixed together with 50 mL of piperidine. The mixture was degassed by two freeze-pump-thaw cycles, and then 4.42 g of trimethylsilylacetylene was added. The mixture was heated to 80 °C overnight (ca. 16 h). The solvent was removed under vacuum, and the residue was stirred in 60 mL of methanol with 12.4 g of K_2CO_3 for 1 h. The mixture was poured into 200 mL of water and extracted with 50 mL of diethyl ether. Under standard workup and column chromatography (silica gel, PE), 5.0 g of pale yellow liquid was obtained in 95% yield. ^{1}H NMR (CD_2Cl_2, 250 MHz): δ ppm 7.58 (m, 4H), 3.21 (s, $-CCH$, 1H), 0.37(s, $SiMe_3$,9H). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ ppm 142.4, 133.8, 131.7, 122.9, 84.3, 78.1(-CCH), −1.0 ($SiMe_3$). Elemental analysis: found C 75.65, H 8.21; calcd C 75.79, H 8.10, Si 16.11.

1,4-Bis(4′-*tert*-butylphenyl)-2,3-bis(4′-dodecylphenyl)-5,6-bis[4′- (trimethylsilyl) diphenylethynyl] Benzene (21). Following the synthetic procedure for compound **20**, Hagihara coupling between compound **19** and 4-(trimethylsilyl)phenyl acetylene gave compound **21** as a pale yellow solid in 91% yield after column chromatography (silica gel, PE/DCM = 4:1). FD MS (8 kV): *m/z* (%) = 1480.5 (100%), calcd 1480.38. ^{1}H NMR (CD_2Cl_2, 250 MHz): δ ppm 7.55−7.51 (m, 8H), 7.48 (d, J = 8.5 Hz, 4H), 7.39 (d, J = 8.5 Hz, 4H), 7.16 (d, J = 8.5 Hz, 4H), 6.99 (d, J = 8.2 Hz, 4H), 6.92 (d, J = 8.2 Hz, 4H), 6.81 (d, J = 8.5 Hz, 4H), 6.77 (d, J = 8.5 Hz, 4H), 6.69 (d, J = 8.2 Hz, 4H), 2.38 (t, J = 7.2 Hz, $-CH_2-C_{11}H_{23}$, 4H), 1.30 (m, $CH_2-(CH_2)_{10}-CH_3$, 20H), 1.13 (s, *tert*-butyl, 18H), 0.91 (t, $-(CH_2)_{11}-CH_3$, 6H), 0.29 (s, $SiMe_3$, 18H).^{13}C NMR (CD_2Cl_2, 125 MHz): δ ppm 147.9, 141.1, 140.7, 140.6, 140.4, 140.3, 139.4, 138.0, 137.6, 136.4, 133.1, 131.9, 131.6, 131.1, 130.9, 130.3, 126.4, 126.3, 124.7, 123.3, 123.1, 121.5, 35.1, 33.8, 31.8, 31.2, 30.8, 29.5, 29.4, 29.3, 29.2, 28.7, 22.5, 13.7, −1.8. Elemental analysis: found C 87.16, H 8.64; calcd C 87.63, H 8.58, Si 3.79.

***ortho*-Connected Hexaphenylbenzene Trimer 22.** A 200-mg portion of compound **20** and 500 mg of compound **15** were dissolved in 1 mL of diphenyl ether. The mixture was degassed under vacuum, filled back with argon, and heated to reflux for 4 h. After cooling, 10 mL of methanol was added, and the precipitate was further purified by column chromatography (silica gel, PE/DCM = 4:1) to give 320 mg of pure compound **22** as a pale yellow solid in 72% yield. MALDI-TOF MS (dithranol as matrix): *m/z* (%) = 2945.82 (100), calcd 2946.68. ^{1}H NMR (CD_2Cl_2, 250 MHz): δ ppm 6.84−6.63 (m, aromatic rings, 74H), 2.36 (t, J = 7.3 Hz, $-CH_2-C_{11}H_{23}$, 12H), 1.28 (m, $CH_2-(CH_2)_{10}-CH_3$, 60H), 1.13−1.11 (overlapped, *tert*-butyl, 54H), 0.90 (t, $-(CH_2)_{11}-CH_3$, 18H). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ ppm 140.2, 140.1, 139.9, 138.6, 138.2, 137.4, 132.2, 131.9, 131.7, 131.5, 126.8, 125.0, 123.6, 35.7, 34.4, 32.4, 31.8, 31.4, 30.1, 30.0, 29.9, 29.8, 29.3, 23.1, 14.3. Elemental analysis: found C 89.44, H 9.61; calcd C 90.49, H 9.51.

***ortho*-Connected Hexaphenylbenzene Trimer 23.** Following the synthetic procedure for compound **22**, Diels−Alder cycloaddition between compound **21** and **15** gave compound **23** as a slightly yellow solid in 94% yield after column chromatography (silica gel, PE/DCM = 5:1). FD MS (8 kV): *m/z* (%) = 3091.2 (100), calcd 3091.06. ^{1}H NMR (CD_2Cl_2, 250 MHz): δ ppm 7.35−6.61 (m, aromatic rings, 72H), 2.35 (t, J = 7.3 Hz, $-CH_2-C_{11}H_{23}$, 12H), 1.27 (m, $CH_2-(CH_2)_{10}-CH_3$, 60H), 1.11−1.10 (overlapped, *tert*-butyl, 54H), 0.89 (t, $-(CH_2)_{11}-CH_3$, 18H), 0.10 (s, $SiMe_3$, 18H). ^{13}C NMR (CD_2Cl_2, 125 MHz): δ ppm 140.9, 139.9−137.72(m), 132.2−131.1(m), 130.1, 126.8, 125.1, 124.6, 123.6, 123.5, 35.7, 34.4, 32.3, 31.8, 31.4, 31.3, 30.1, 30.0, 29.9, 29.8, 29.3, 23.1, 14.3, −1.1. Elemental analysis: found C 88.42, H 9.61; calcd C 88.60, H 9.59, Si 1.82.

***ortho*-Connected Hexaphenylbenzene Trimer 24.** Following the synthetic procedure for compound **11**, compound **24** as a pale yellow solid was obtained in 92% yield after column chromatography (silica gel, PE/DCM = 5:1). FD MS (8 kV): *m/z* (%) = 3198.2 (100), calcd 3198.48. ^{1}H NMR (CD_2Cl_2, 250 MHz): δ ppm 7.35−6.57 (m, aromatic rings, 72H), 2.35 (t, J = 7.2 Hz, $-CH_2-C_{11}H_{23}$, 12H), 1.27 (m, $CH_2-(CH_2)_{10}-CH_3$, 60H), 1.15−1.11 (overlapped, *tert*-butyl, 54H), 0.89 (t, $-(CH_2)_{11}-CH_3$, 18H. ^{13}C NMR ($CD_2Cl_{2,}$ 125 MHz): δ ppm 140.2, 140.0, 139.9, 139.8, 139.5, 139.3, 138.6, 138.4, 138.3, 138.1, 138.0, 137.8, 137.5, 137.3, 137.1, 136.0, 134.8, 133.9, 132.3, 132.2, 131.6, 131.4, 130.1, 126.9, 126.3, 125.3, 125.1, 125.0, 124.3, 123.8, 123.7, 123.2, 119.2, 35.7, 34.4, 32.3, 31.8, 31.4, 30.1, 30.0, 29.9, 29.8, 29.3, 23.1, 14.3. Elemental analysis: found C 83.28, H 8.62; calcd C 83.37, H 8.70, I7.94.

***ortho*-Connected HBC Trimer 5a.** Following the synthetic procedure for compound **4**, cyclodehydrogenation of **22** with 72 equiv of $FeCl_3$ over 35 min gave compound **5a** as a yellow-to-orange solid in 92% yield after column chromatography (silica gel, PE/DCM = 2:1). MALDI-TOF MS (TCNQ as matrix): *m/z* (%) = 2909.32 (100%), calcd 2910.37. ^{1}H NMR (1,2-dichlorobenzene-d_4, 443 K, 700 MHz): δ ppm 10.43, 9.61, 9.37, 9.06, 8.79, 8.59, 8.41, 7.65 (overlapped, Ar−H, 38H), 3.47−3.37 (overlapped, -CH_2-C$_{11}$H$_{23}$, 12H), 2.37−1.27 (overlapped, 174H), 0.88 (t, J = 7.6 Hz, -(CH$_2$)$_{11}$-CH_3,18H). ^{13}C NMR (1,2-dichlorobenzene-d_4, 403 K, 700 MHz): δ ppm 147.8 (br), 139.5 (br), 136.0−117.6 (br), 36.6 (br), 35.0, 34.5, 31.1−29.1 (br), 21.8, 12.9. Elemental analysis: found C 91.14, H 8.67; calcd C 91.62, H 8.38.

***ortho*-Connected HBC Trimer 5b.** Following the synthetic procedure for compound **4**, cyclodehydrogenation of **24** with 36 equiv of FeCl$_3$ for 35 min gave compound **5b** as a yellow-to-orange solid in 80% yield after column chromatography (silica gel, PE/DCM = 2:1). MALDI-TOF-MS (TCNQ as matrix): *m/z* (%) = 3161.53 (100), calcd 3162.20. ^{1}H NMR (1,2-dichlorobenzene-d_4, 443 K, 700 MHz): δ ppm 10.5−7.45 (overlapped, Ar−H, 36H), 3.48−3.32 (overlapped, -CH_2-C$_{11}$H$_{23}$, 12H), 2.32−1.22 (overlapped, 174H), 0.85 (t, J = 7.6 Hz, -(CH$_2$)$_{11}$-CH_3,18H). ^{13}C NMR (1,2-dichlorobenzene-d_4, 403 K, 125 MHz): δ ppm 148.0 (br), 139.6 (br), 136−118.0 (br), 36.5 (br), 34.3 (br), 34.3−228.2 (br), 21.5, 12.6. Elemental analysis: found C 83.91, H 7.71; calcd C 84.32, H 7.65, I 8.03.

2,7-Bis[4′-(3″,7″-dimethyloctanyl)phenylethynyl]fluorene (27). A mixture of 500 mg of 2,7-dibromofluorene (**26**, 1.54 mmol), 785 mg of 4-(3,7-dimethyloctyl)phenylacetylene (3.24 mmol), 178 mg of Pd(PPh$_3$)$_4$ (5 mol % per Br), 31 mg of CuI, and 10 mL of piperidine was degassed by bubbling argon for 20 min and heated to reflux (80 °C in bath) overnight. After cooling, the mixture was poured into saturated NH$_4$Cl aqueous solution and extracted by dichloromethane three times. The organic layer was washed with water and dried over magnesium sulfate. After removing the solvent, the residue was purified by column chromatography (silica gel, PE/DCM = 10:1) to give 778 mg of compound **27** as a colorless solid in 78% yield. FD MS (8 kV): *m/z* (100) = 647.1, calcd 647.01. ^{1}H NMR (CD$_2$Cl$_2$, 250 MHz): δ ppm 7.75 (d, J = 7.9 Hz, 2H), 7.70 (s, 2H), 7.56 (d, J = 7.9 Hz, 2H), 7.48 (d, J = 8.2 Hz, 4H), 7.21 (d, J = 8.2 Hz, 4H), 3.91 (s, 2H), 2.66 (m, 4H), 1.65−1.14 (m, 20H), 0.98−0.89 (m, 18H, CH$_3$). ^{13}C NMR (CD$_2$Cl$_2$, 62.5 MHz): δ ppm 144.4, 144.2, 141.5, 131.8, 130.9, 128.9, 128.4, 122.3, 120.8, 120.4, 111.4, 90.3, 89.7, 39.7, 39.1, 37.5, 37.0, 33.8, 32.95, 28.4, 25.1, 22.9, 22.8, 19.8. Elemental analysis: found C 90.84, H 8.86; calcd C 90.96, H 9.04.

2,7-Bis{2′,3′,4′,5′,6′-penta[4”-(3‴,7‴-dimethyloctanyl)-phenyl]phenyl} Fluorene 28. Following the synthetic procedure for compound **14**, Diels−Alder cycloaddition between compound **27** (200 mg, 0.31 mmol) and **13** (585 mg, 0.62 mmol) in 1 mL of diphenyl ether afforded 210 mg of compound **28** as a slightly yellow solid in 27% yield after column chromatography (silica gel, PE/DCM = 85:15). FD MS (8 kV): *m/z* (%) = 2482.6 (100), calcd 2482.12. ^{1}H NMR (CD$_2$Cl$_2$, 250 MHz): δ ppm 7.06−6.65 (br, Ar−H, 46H), 3.15 (s, bridged methylene, 2H), 2.39−2.33 (br, 20H), 1.53−0.78 (overlapped, 166H). ^{13}C NMR (CD$_2$Cl$_2$, 62.5 MHz): δ ppm 140.5, 140.2, 140.0, 139.7, 138.7, 138.6, 138.5, 131.7, 130.7, 128.7, 128.5, 126.9, 126.8, 117.9, 39.8, 39.2, 39.0, 37.5, 33.2, 32.6, 28.4, 25.1, 22.8, 19.8. Elemental analysis: found C 89.38, H 10.37; calcd C 89.52, H 10.48.

Superfluorene 6. Following the synthetic procedure for compound **4**, cyclodehydrogentation of **28** (120 mg, 0.048 mmol) with 565 mg of FeCl$_3$ (24 equiv) in 30 mL of dichloromethane gave 65 mg of pure product (55%) after column chromatography (silica gel, toluene). MALDI-TOF MS (TCNQ as matrix): *m/z* (%) = 2457.56 (100), calcd 2457.93. ^{1}H NMR (1,2-dichlorobenzene-d_4, 448 K, 500 MHz): δ ppm 9.59, 9.30−8.70 (br, Ar-H), 5.23, 3.86−3.37 (br), 2.45−0.96 (br, alkyl chains). Elemental analysis: found C 89.52, H 9.36; calcd C 90.40, H 9.60.

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Supporting Information Available: Selected MALDI-TOF MS and NMR spectra of the oligomers; concentration-dependent UV−vis spectra of compound **2**, **3**, **4** and **5a,b** in 1,2,4-TCB solution; WAXD diffractogram for compound **6** in the solid state. This material is available free of charge via the Internet at http://pubs.acs.org.

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