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Columnar Mesophase Formation of Cyclohexa-*m*-phenylene-Based Macrocycles

Wojciech Pisula, Marcel Kastler, Changduk Yang, Volker Enkelmann, and Klaus Müllen*[a]

Abstract: Two novel discotic macrocycles, substituted cyclohexa-*m*-phenylene (CHP) and cyclo-3,6-trisphenanthrylene (CTP), and the linear oligomer 3,3′:6′,3″-terphenanthrene (TP) as a model substance have been synthesized by repetitive cross-coupling reactions. To correlate the molecular design with the supramolecular architecture and the established macroscopic order, 2D wide-angle X-ray scattering experiments were performed on mechanically extruded filaments. At room temperature in their crystalline phases, all three compounds revealed columnar assemblies in which the macrocycles self-organized by π-stacking interactions. The degree of macroscopic order was found to depend upon the planarity and stiffness of the aromatic core. The flexible CHP ring showed a poor macroscopic order of the columnar structures and a low isotropization temperature, whereas the more-planar, less-flexible CTP self-assembled into well-defined superstructures. The larger π-stacking area and the more-pronounced intermolecular interactions for CTP led to the formation of a mesophase over a very large temperature range. The surprising columnar organization of the "open" TP system was explained by back-folding of the molecule into a ringlike structure.

Keywords: cross-coupling · macrocycles · mesophases · phase transitions · self-assembly

Introduction

Macrocycles with rigid, unsaturated hydrocarbon backbones have attracted great interest in the past few years, owing to their unique properties and their role as building blocks of three-dimensional nanostructures, discotic liquid crystals, extended tubular channels, guest–host complexes, and porous organic solids.[1–4] These molecules consist of a shape-persistent scaffold in a planar or nearly planar conformation, with minimal ring strain and a large diameter-to-thickness ratio.[5] The cyclic, stiff backbone of these macrocycles is typically decorated with solubilizing aliphatic side chains, which can contain various functionalities. The aliphatic substituents are mostly attached at the core periphery, but in some cases the side chains have been reported to fill the internal void of the macrocycle.[6,7] Due to π-stacking interactions, some of these building blocks self-assemble into discotic columnar superstructures.[8] The nanophase separation of the aliphatic part, which fills the columnar periphery, from the rather rigid aromatic cores further promotes thermotropic mesophase formation.[8–10] The liquid-crystalline state is reached by the input of thermal energy and is accompanied by a significant difference in the dynamics between the flexible substituents and the π-stacked, rigid building blocks.[6,11,12] The variation of the molecular architecture allows the control of these thermotropic properties, but requires appropriate synthetic methods for an efficient preparation of macrocycles.[13–15] Studies of the supramolecular organization of these macrocycles have provided a better understanding of the noncovalent driving force responsible for their self-assembly.[16–19]

Little is know about the correlation of the molecular structure of such macrocycles with the supramolecular packing and the phase behavior. In particular, the effect of the core planarity and architecture on thermotropic behavior has not been investigated extensively. Therefore, in this study, the long-range self-assembly in the solid state of alkyl-substituted phenylene-based macrocycles cyclohexa-*m*-phenylene (CHP) and cyclo-3,6-trisphenanthrylene (CTP)

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[a] Dr. W. Pisula,+ Dr. M. Kastler, Dr. C. Yang, Dr. V. Enkelmann,
Prof. Dr. K. Müllen
Max-Planck-Institut für Polymerforschung
Ackermannweg 10, D-55128 Mainz (Germany)
Fax: (+49) 6131-379-350
E-mail: muellen@mpip-mainz.mpg.de

[+] Present address: Degussa AG, Process Technology & Engineering
Process Technology—New Processes
Rodenbacher Chaussee 4, D-63457 Hanau-Wolfgang (Germany)

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(Figure 1) were compared, whereby both molecules differed significantly in their core planarity. Two-dimensional wide-angle X-ray scattering (2D WAXS) experiments indicated that the lower the core planarity, the poorer the interaction between the building blocks, and thus the lower the degree of macroscopic order of the columnar structures. Furthermore, for the organization of an open-ring structure, 3,3′:6′,3″-terphenanthrene (TP) was investigated as a model system. Remarkably, TP showed a columnar arrangement identical to that of the closed macrocycle CTP. These packing similarities were attributed to a back-folding of TP into a ringlike molecular structure supported by the nanophase separation between alkyl side chains and the aromatic core. This is the first example in which a conformational change of a low-molecular-weight oligomer into a "quasi" macrocycle structure results in columnar superstructures. The change of molecular conformation may be considered as an additional tool, besides the introduction of noncovalent interactions, to control the supramolecular organization and finally the macroscopic properties.

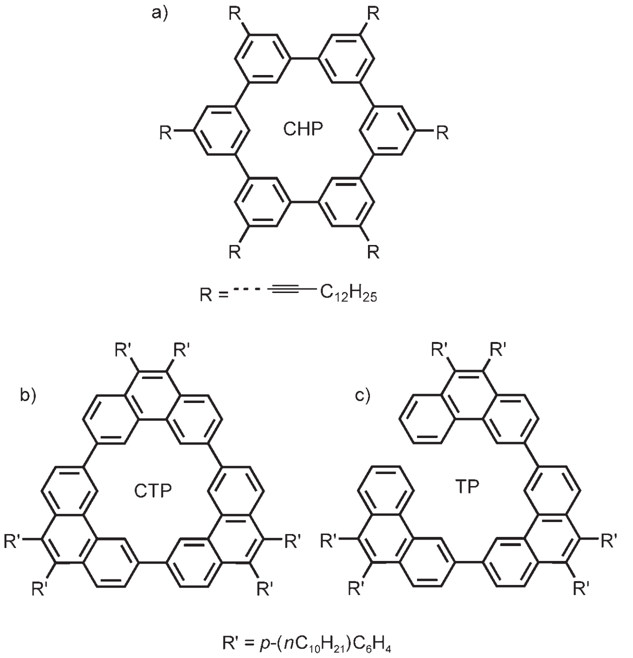


Figure 1. Chemical structures of the investigated compounds. a) Cyclohexa-*m*-phenylene (CHP), b) cyclo-3,6-trisphenanthrylene (CTP), c) 3,3′:6′,3″-terphenanthrene (TP).

Results and Discussion

Synthesis and Characterization

The synthesis of the hexaalkyl CHP was performed in a stepwise fashion by using Suzuki reactions (Scheme 1). Commercially available 1,3,5-tribromobenzene was converted into the trimethylsilyl-substituted **4**.[20] This compound was lithiated with *tert*-butyllithium and subsequently converted into the bis-iodo analogue **5** as the first building block. Compound **4** was also converted into the boronic acid **6**. The Suzuki cross-coupling reaction of **5** with **6** was conducted selectively at room temperature to yield the *m*-terphenyl derivative **7**. The most-critical step concerned the dimerization of the *m*-terphenyl unit **7** according to the Yamamoto protocol. Expectedly, the concentration influenced the yield to a great extent, and the reaction conditions had to be tested to produce the substituted hexa-*m*-phenylene **8** in 58% yield. The single-crystal structure study of **8** indicated that the *m*-connected ring has enough flexibility to establish a chair conformation of the macrocycle analogous to cyclohexane (Figure 2).[21] The trimethylsilyl groups of **8** were converted in an *ipso* substitution into the macrocycle with six iodine atoms as reactive groups in an overall yield of 32% over five steps, which is far higher than that reported for the synthesis of the unsubstituted analogue.[22] Although **9** is sparingly soluble, the subsequent six-fold Hagihara–Sonogashira cross-coupling with tetradec-1-yne yielded the alkyl-substituted ring molecule CHP.

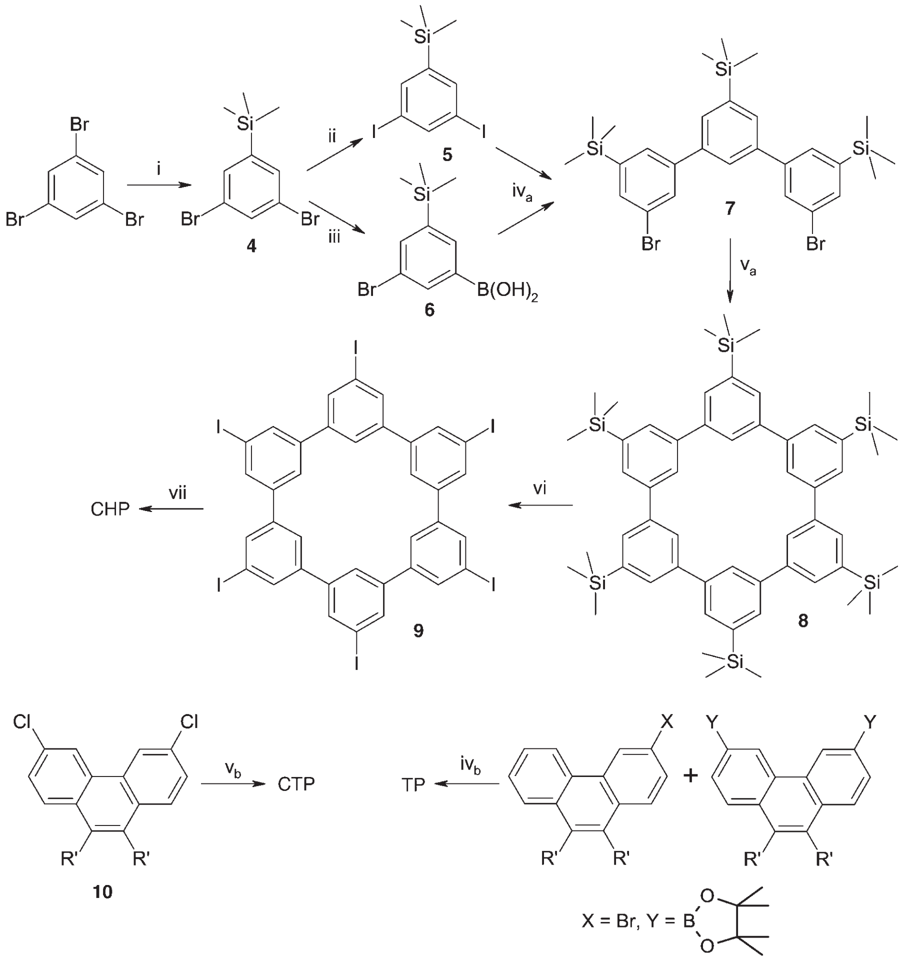
The Yamamoto-type polycondensation of 3,6-dihalophenanthrenes was found to lead predominantly to the formation of a macrocyclic trimer owing to the intrinsic angle of the 3,6-phenanthryl unit. Staab and Neunhoef reported the synthesis of a hardly soluble, not processable macrocyclic trimer by Ullmann reaction of 3,6-diiodophenanthrene.[19] The introduction of solubilizing alkylaryl groups at the 9,10-positions of the phenanthrene building block allowed the synthesis of TP, which revealed excellent solubility.[23] Hence, nickel(0)-mediated Yamamoto-type coupling of dichlorophenanthrene **10** in dilute solution led to the formation of CTP (Scheme 1), which was isolated by column chromatography (12%) and fully characterized.

Temperature-dependent ^{1}H NMR spectroscopy of the cyclohexaphenylene derivatives and the linear terphenanthrene (CHP, CTP, and TP) in solution revealed only a small change of the chemical shift for all observed protons of only 0.1 ppm, thus indicating a weak π-stacking interaction in solution.[24,25]

Thermal Characterization

To correlate the molecular design with the phase formation and stability, it is important to determine the phase-transition temperatures of all three derivatives (CHP, CTP, and TP) by using differential scanning calorimetry (DSC) (Figure 3).

A relatively low melting point of 45 °C directly from the crystalline phase and the absence of a mesophase were found for the ring molecule CHP. For CTP, the DSC trace showed two endothermic peaks: one minor peak at 46 °C relating to the reorganization of alkyl side chains at higher temperatures, and a more pronounced one at 148 °C corresponding to a transition to the mesophase.[11] The open-ring structure TP revealed a small peak at 43 °C in the DSC trace, which could not be assigned to a phase transition. No



Scheme 1. Synthetic routes to CHP, CTP, and TP. i) *n*BuLi, TMSCl, 79%; ii) *t*BuLi, I_2, 82%; iii) *n*BuLi, $B(OiPr)_3$, 97%; iv) a) K_2CO_3, $[Pd(PPh_3)_4]$, 81%; b) 71%; v) a) cod, bipy, $[Ni(cod)_2]$, 58%; b) 12%; vi) ICl, 84%; vii) tetradec-1-yne, PPh_3, CuI, $[Pd(PPh_3)_4]$, 51%. bipy = 2,2′-bipyridine, cod = 1,5-cyclooctadiene, TMS = trimethylsilyl.

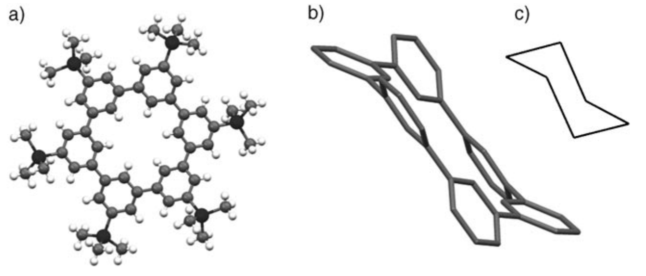


Figure 2. Crystal structure of **8**. a) Top view (silicon atoms in dark grey, carbon in grey, hydrogen in white; solvent molecules not shown), b) side view (TMS groups and hydrogen atoms omitted for clarity), c) chair conformation of cyclohexane.

isotropization of TP, which was characterized as crystalline, was found within the investigated temperature range. Thermogravimetric analysis (TGA) showed a high thermal stability for both CTP and TP with onset decomposition temperatures (T_d, 5% weight loss) of 420–450 °C under nitrogen.

Structure Investigation by 2D WAXS

The supramolecular organization and macroscopic order of the three compounds were analyzed on the basis of the 2D WAXS data obtained for mechanically extruded filaments and the phase-transition temperatures found by DSC measurements.[26] The 2D WAXS pattern of CHP exhibited only anisotropic reflections at room temperature in the crystalline phase, indicating a poor macroscopic alignment of the sample (Figure 4a). The small-angle reflections in the corresponding range of 2.34 nm implies a columnar structure formed by the ring-shaped molecules, whereby wide-angle reflections correlate to a stacking distance of 0.41 nm for the single building blocks within the columns. The intracolumnar organization of CHP is illustrated in Figure 4a. However, the residual flexibility and the nonplanarity of the central ring weaken the molecular interactions, leading to a poor macroscopically ordered self-assembly. This is in accordance with the low melting point of 45 °C, confirming the poor intermolecular attractive forces in the case of CHP.

In contrast, the orientation of the columnar structures in the extruded samples was more pronounced for CTP and

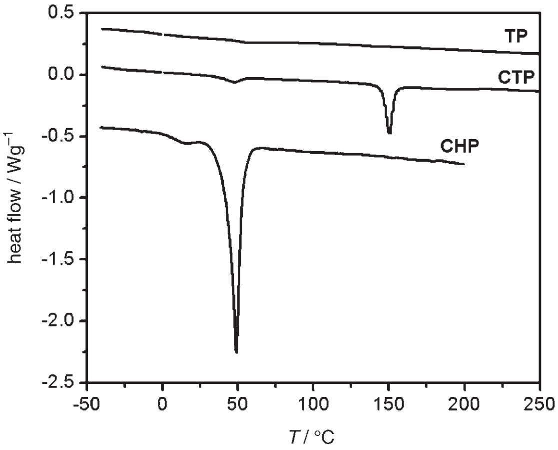


Figure 3. Differential scanning calorimetry (DSC) of CHP, CTP, and TP.

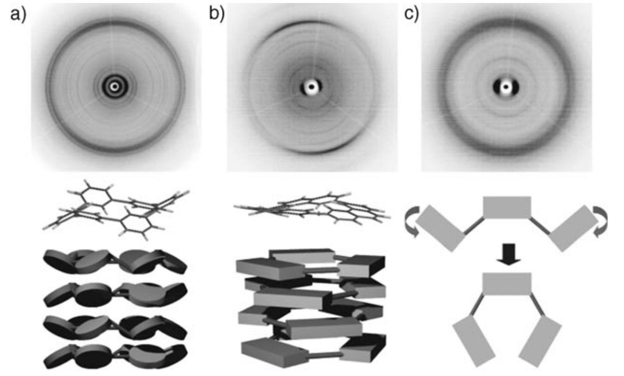


Figure 4. Room-temperature 2D WAXS patterns, calculated molecular geometries using SPARTAN PRO, and schematic illustrations of the intracolumnar organization of a) CHP, b) CTP, and c) TP.

TP, as shown by sharper and more-distinct reflections in the patterns at room temperature for their crystalline phases (Figure 4b, c). The 2D WAXS patterns showed scattering intensities at identical positions, which suggest a quite-similar organization for both CTP and TP. Equatorial reflections indicate the self-assembly of both types of molecules into columnar assemblies that are well-aligned in the shearing direction. Such supramolecular organization was expected for CTP, but the columnar arrangement of TP is rather surprising, as the conformation of the molecule was not predicted to be ringlike. Typically, linear conjugated oligomers align along the shearing direction owing to their great aspect ratio, giving rise to π-stacking reflections in the equatorial plane of the 2D pattern. It is assumed that the nanophase separation between the aromatic core and the flexible side chains of TP results in a conformational change to the ringlike arrangement as shown schematically in Figure 4c. An identical back-folding effect was only reported for ribbon-shaped oligo(*m*-phenylene ethynylene)s, which adopt a helical columnar conformation at a sufficient oligomer length.[27,28] The effect reported herein is the first example of a conformational change of a low-molecular-weight species. This shape modification is even more surprising, as TP consists of a more-rigid core than oligo(*m*-phenylene ethynylene)s. However, because the nonclosed structure TP did not reveal core planarity as did CTP, the packing and macroscopic order of TP was less pronounced. Indeed, sharper and more-anisotropic meridional reflections were observed for CTP (π-stacking distance of 0.44 nm) in comparison to TP. Additional meridional reflections appeared for both CTP and TP at corresponding distances of 0.62 and 1.2 nm (for CTP) and are related to correlations between each 4th molecule along the columnar structures. Thus, the macrocycles are rotated successively by $120°/4=30°$ leading to a helical pitch that contains three molecules as shown schematically in Figure 4b. The phenyl groups attached to the macrocycle CTP are most probably rotated out of plane towards the macrocycle and thus induce the helical packing.[29]

Heating of CTP at 148 °C (above the phase-transition temperature) to the mesophase was accompanied by a significant change of the intracolumnar arrangement (the 2D WAXS pattern is shown in the Supporting Information). The helical packing disappeared owing to greater molecular dynamics, what is characteristic for different types of columnar mesogenes.[30] In the mesophase, CTP is arranged with its molecular plane perpendicular to the columnar axes with an intracolumnar distance of 0.37 nm, whereby the columns are organized in a hexagonal array with a packing parameter of 3.2 nm. This columnar mesophase was stable up to 500 °C, at which temperature the isotropic phase was not yet reached. This is by far the highest isotropization temperature observed for a macrocycle.[5]

The introduction of flexible side chains attached to the cyclo-*m*-hexaphenylene-based macrocycles enhanced the solubility of the compounds, but also opened the opportunity for controlling the thermal behavior and thus the supramolecular self-assembly. All three investigated compounds showed a columnar organization due to the π interaction between the aromatic cores and a nanophase separation between the aliphatic chains and the better-ordered ring-shaped skeletons. The structural analysis revealed a pronounced influence of the core planarity on the supramolecular long-range order. The less-planar flexible cyclic oligomer CHP has a weak organization, whereas the cyclic compound CTP revealed an excellent columnar formation and a stable discotic mesophase up to high temperatures. Similar results have been reported only for porphyrin octaesters, for which the transition temperatures to the mesophase and the isotropic state were strongly influenced by the planarity of the porphyrin core.[31] The CTP core was clearly rigidified by the additional C2 units relative to the CHP. Furthermore, an identical intracolumnar packing was observed for the nonclosed TP as for the macrocycle CTP, which suggests a conformational change of the molecule by back-folding during the self-assembly into columnar structures.

Conclusions

Two cyclo-*m*-hexaphenylene-based macrocycles with a different core planarity or stiffness, cyclohexa-*m*-phenylene (CHP) and cyclo-3,6-trisphenanthrylene (CTP), have been synthesized. An oligomer, 3,3′:6′,3′′-terphenanthrene (TP), has been prepared as a noncyclic model system. The introduction of alkyl side chains allowed the solubility and the thermal behavior to be controlled. The propensity of all the synthesized molecules to associate in solution was weak. In the bulk state, the structural investigations of extruded samples revealed a poor macroscopic ordering of the less-planar CHP, whereas the stiffer macrocycle CTP formed well-oriented columnar superstructures with a striking thermal stability. CTP also has a larger π-stacking area than CHP, resulting in a more-pronounced intermolecular interaction. Therefore, CTP showed mesophase formation with a transition window ranging from 148 to 500 °C, at which point thermal decomposition set in. To our knowledge, this is one of the highest observed mesophase stabilities. For discotics, it has been shown that helical packing is an additional reason for the high isotropization temperature.[32] In this study, the helicity along the columnar structures of CTP and TP supported the pronounced solid-state stability within the investigated temperature for both compounds. Surprisingly, the linear model system TP formed similar columnar superstructures, which, however, were less well-organized. This can be attributed to back-folding into a ringlike molecular structure, which is the first example so far for a low-molecular-weight species that self-assembles into columnar structures. This gives a further possibility not only of controlling the supramolecular organization by noncovalent interactions, but also by the change in molecular conformation during structure formation. The study also revealed the importance of π-stacking interactions as attractive intermolecular forces, which allow well-defined superstructures to be established. In other words, more-planar disklike molecules form better-organized structures.

Experimental Section

General

Commercially available materials were used as received unless otherwise noted. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker 300 AMX, Bruker DRX 500, or Bruker DRX 700 MHz spectrometer and referenced to the solvent peak. UV/Vis absorption spectra were recorded on a Perkin–Elmer Lambda 15 spectrophotometer. Photoluminescence spectra were recorded on a SPEX Fluorolog 2 Type F212 steady-state fluorometer, with a 450-W xenon arc lamp as excitation source and a PMT R 508 photomultiplier as detector system. Crystals of CHP suitable for structure determination were obtained by slow evaporation of a solution in hexane/CH_2Cl_2. The crystals contained two molecules of hexane per ring and were mounted in a closed capillary. Data collection was carried out at 120 K with $Mo_{K\alpha}$ radiation on a Nonius KCCD diffractometer. Crystal parameters: orthorhombic, Ccmb (No. 64 Int. Tables), $a=11.8698(4)$, $b=21.1929(6)$, $c=26.2232(7)$ Å, $V=6596.6(2)$ Å^3, $Z=16$, $D_x=1.069$ g cm^{-3}, $\mu=0.163$ mm^{-1}. 27962 reflections were measured ($\theta_{max}=30°$) of which 4781 were unique ($R_{int}=0.0459$) and 3026 were considered observed ($I>3\sigma(I)$). The structure was solved by direct methods and refined on F with anisotropic temperature factors for C and Si. The H atoms were refined in the riding mode with fixed isotropic temperature factors; $R=0.0506$, $R_w=0.0370$. TGA and DSC measurements were carried out on a Mettler 500 thermogravimetric analyser and Mettler DSC 30 calorimeter, respectively. The 2D WAXS experiments were performed by means of a rotating anode (Rigaku 18 kW) X-ray beam with a pinhole collimator and a 2D Siemens detector. A double graphite monochromator for the $Cu_{K\alpha}$ radiation ($\lambda=0.154$ nm) was used.

Syntheses

5: 1,3-Dibromo-5-(trimethylsilyl)benzene (10.5 g, 34 mmol) was dissolved in anhydrous diethyl ether (350 mL) and carefully degassed. The solution was cooled to −78 °C, and *tert*-butyllithium (1.7 M in pentane, 80 mL, 136 mmol) was slowly added. After 30 min, the reaction mixture was stirred for one hour at room temperature before the solution was again brought to −78 °C. A solution of iodine (36 g, 142 mmol) in diethyl ether (200 mL) was added, and the reaction was stirred overnight at room temperature. The organic phase was washed with water, aqueous sodium bisulfite, and ammonium chloride, and dried with magnesium sulfate. After solvent removal in vacuo, the residue was filtered over a short silica pad with hexane to afford 11.2 g of the desired product (82 %, 28 mmol) as a colorless, crystalline material. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta=8.05$ (t, $J=1.71$ Hz, 1H), 7.77 (d, $J=1.53$ Hz, 2H), 0.25 ppm (s, 9H); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta=147.4$, 145.5, 141.3, 96.0, −1.4 ppm; FDMS: *m*/*z* calcd for $C_9H_{12}I_2Si$: 402.09 [*M*·]$^+$; found: 402.1; elemental analysis: calcd (%) for $C_9H_{12}I_2Si$: C 26.88, H 3.01; found: C 27.56, H 3.05.

6: 1,3-Dibromo-5-(trimethylsilyl)-benzene (10 g, 32.4 mmol) was dissolved in anhydrous diethyl ether (150 mL), degassed, and cooled to −78 °C. *n*-Butyllithium (1.6 M in hexane, 20.3 mL, 32.4 mmol) was added dropwise to the mixture. The resulting solution was allowed to stir at room temperature for an additional hour. Again at −78 °C, triisopropyl borate (15 mL, 64.9 mmol) was quickly added, and the mixture was stirred at room temperature overnight. The reaction was stopped by adding 10 % aqueous HCl. The organic phase was separated, washed with water, and dried with magnesium sulfate. After solvent removal in vacuo, 8.6 g product (97 %, 31.5 mmol) was obtained as a colorless, amorphous solid, which was used without further purification. NMR analysis was difficult owing to the many signals that arose due to oligomerisation. FDMS: *m*/*z* calcd for: 273.01 [*M*·]$^+$; found: 273.1; elemental analysis: calcd (%) for $C_9H_{14}BBrO_2Si$: C 39.60, H 5.17; found: C 41.95, H 5.06.

7: 3-Bromo-5-(trimethylsilyl)phenylboronic acid (4 g, 14.65 mmol), 1,3-diiodo-5-(trimethylsilyl)benzene (2.94 g, 7.31 mmol), and potassium carbonate (32 g) were dissolved in a mixture of toluene (240 mL), water (120 mL), and ethanol (18 mL) and carefully degassed. Tetrakis(triphenylphosphanyl)palladium(0) (426 mg, 0.37 mmol, 2.5 mol % per iodo functionality) was added, and the mixture was stirred at room temperature for 48 h. The organic phase was separated, washed with water, and dried with magnesium sulfate. After the removal of the solvent, the residue was purified by preparative column chromatography (silica gel, hexane, $R_f=0.50$) to afford 3.6 g of the desired product (81 %, 6 mmol) as a colorless solid. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta=7.77$ (dd, $J=1.92$ Hz, 2H), 7.69 (s, 3H), 7.67 (dd, $J=1.52$ Hz, 2H), 7.65 (dd, $J=1.92$ Hz, 2H), 0.36 (s, 9H), 0.32 ppm (s, 18H); ^{13}C NMR (75 MHz, CD_2Cl_2): $\delta=144.8$, 143.3, 142.7, 140.5, 135.2, 132.0, 131.2, 130.9, 127.2, 123.4, −1.2 ppm; FDMS: *m*/*z* calcd for $C_{27}H_{36}Br_2Si_3$: 604.65 [*M*·]$^+$; found: 602.4; elemental analysis: calcd (%) for $C_{27}H_{36}Br_2Si_3$: C 53.63, H 6.00; found: C 53.95, H 5.91.

8: Bipy (218 mg, 1.40 mmol), cod (152 mg, 1.40 mmol, 173 μL), and [Ni(cod)$_2$] (386 mg, 1.40 mmol) were placed in a well-dried Schlenk flask, dissolved in anhydrous *N*,*N*-dimethylformamide (DMF; 30 mL), and stirred for 30 min at 80 °C in the absence of light. A solution of 5,3′′-dibromo-3,5′,5′′-tris-trimethylsilyl-1,1′;3′,1′′-terphenyl (423 mg, 0.70 mmol) in dry and degassed toluene (150 mL) was added quickly, and the resulting mixture was stirred for three days at 80 °C. The reaction was stopped by adding 10 % aqueous HCl. The organic phase was separated, washed with water, and dried with magnesium sulfate. After solvent removal in vacuo, the residue was purified by preparative column chromatography (silica gel, low-boiling petroleum ether/dichloromethane = 20:1, $R_f=0.29$) to obtain 180 mg (58 %, 0.20 mmol) of the desired product as a colorless, crystalline solid. ^{1}H NMR (700 MHz, CD_2Cl_2): $\delta=8.28$ (s, 6H), 7.92 (s, 12H), 0.43 ppm (s, 54H); ^{13}C NMR (175 MHz, CD_2Cl_2): $\delta=142.6$, 141.3, 130.9, 128.5, −0.9 ppm; FDMS: *m*/*z* calcd for $C_{54}H_{72}Si_6$: 889.69 [*M*·]$^+$; found: 888.2; elemental analysis: calcd (%) for $C_{54}H_{72}Si_6$: C 72.90, H 8.16; found: C 73.15, H 8.17.

9: 5,5′,5′′,5′′′,5′′′′,5′′′′′-Hexatrimethylsilylhexa-*m*-phenylene (110 mg, 120 μmol) was dissolved in chloroform (20 mL) and degassed. A solution of iodomonochloride (1 M, 1.5 mL, 1.50 mmol) in dichloromethane was added in the absence of light. The resulting mixture was stirred at room temperature for seven hours, before the reaction was stopped with concentrated, aqueous sodium thiosulfate (5 mL). The precipitate was filtered off, washed extensively with chloroform, THF, and water, and dried in vacuo to afford 122 mg of the desired product (84 %, 100 μmol) as a hardly soluble colorless material. The compound was used without further purification. FDMS: *m*/*z* calcd for $C_{36}H_{18}I_6$: 1211.97 [*M*·]$^+$; found: 1212.2.

CHP: 5,5′,5′′,5′′′,5′′′′,5′′′′′-Hexaiodohexa-*m*-phenylene (50 mg, 41.0 μmol), tetradec-1-yne (96 mg, 0.49 mmol), triphenylphosphine (1.6 mg, 6.20 μmol), and copper(I) iodide (1.2 mg, 6.20 μmol) were dissolved in piperidine (8 mL) and degassed with three freeze–vacuum–thaw cycles. Afterwards, [Pd(PPh$_3$)$_4$] (7.1 mg, 6.2 μmol, 1.1 mol % per iodide) was added under an argon atmosphere, and the mixture was stirred overnight at 55 °C. The solvent was removed in vacuo, and the residue was purified by preparative column chromatography (silica gel, low-boiling petroleum ether/dichloromethane = 1:1, $R_f = 0.67$) to afford 34 mg of the desired product (51 %, 21.1 μmol) as a colorless oil. ^{1}H NMR (300 MHz, CD_2Cl_2): $\delta = 8.05$ (s, 6 H), 7.68 (s, 12 H), 2.48 (t, $J = 6.78$ Hz, 12 H), 1.8–1.1 (m, 120 H), 0.88 ppm (t, $J = 6.78$ Hz, 18 H); ^{13}C NMR (125 MHz, CD_2Cl_2): $\delta = 140.6$, 129.1, 126.0, 125.7, 91.7, 80.7, 32.4, 30.1, 30.1, 30.0, 29.8, 29.7, 29.5, 29.3, 23.1, 19.9, 14.3 ppm; FDMS: m/z calcd for $C_{120}H_{168}$: 1610.68 $[M\cdot]^+$; found: 1610.9.

CTP: Bipy (244 mg, 1.58 mmol), cod (0.171 mg, 1.58 mmol, 192 μL), and $[Ni(cod)_2]$ (430 mg, 1.58 mmol) were placed in a well-dried Schlenk flask, dissolved in anhydrous toluene (40 mL) and anhydrous DMF (20 mL), and stirred for 20 min at 60 °C in the absence of light. A solution of **10** (448 mg, 0.66 mmol) in dry and degassed toluene (10 mL) was added quickly, and the resulting mixture was stirred for two days at 80 °C. The reaction was stopped by adding 10 % aqueous HCl. The organic phase was separated, washed with water, and dried with magnesium sulfate. After solvent removal in vacuo, the residue was purified by preparative column chromatography (silica gel, hexane/dichloromethane = 5:1, $R_f = 0.25$) to afford 50 mg of the desired product (12 %, 27 μmol) as a colorless solid. ^{1}H NMR (300 MHz, $CDCl_3$): $\delta = 9.83$ (s, 6 H), 8.18 (d, $J = 8.8$ Hz, 6 H), 7.80 (d, $J = 8.6$ Hz, 6 H), 7.10 (q, $J = 8.3$ Hz, 24 H), 2.60 (t, $J = 7.6$ Hz, 12 H), 1.71–1.61 (m, 12 H), 1.39–1.25 (m, 84 H), 0.90 ppm (t, $J = 6.7$ Hz, 18 H); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 140.5$, 136.7, 136.1, 135.1, 131.6, 130.6, 130.0, 127.1, 35.2, 31.5, 31.0, 29.3, 29.2, 29.0, 28.8, 22.3, 13.7 ppm; FDMS: m/z calcd for $C_{138}H_{168}$: 1826.88 $[M\cdot]^+$; found: 1825.0; elemental analysis: calcd (%) for $C_{138}H_{168}$: C 90.73, H 9.27; found: C 90.57, H 9.53.

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