JOURNAL OF
Materials
CHEMISTRY

Star-like substituted hexaarylbenzenes: synthesis and mesomorphic properties

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Received 5th February 2001, Accepted 22nd March 2001
First published as an Advance Article on the web 24th April 2001

A series of hexaarylbenzenes (**1–6**) with a variety of different aryl arms (*i.e.* phenyl, biphenylyl, mono-, bi-, and terthienylyl) around a benzene core, decorated with flexible dodecyl chains on the terminal positions, were synthesized. Their mesomorphic behaviors were studied by differential scanning calorimetry (DSC), polarizing optical microscopy (POM) and X-ray diffraction (XD) techniques. Compounds **1–3**, which have a hexaphenylbenzene core, form columnar mesophases. In particular **3**, in which the core is composed of hexaphenylbenzene surrounded by thiophene rings, shows a stable columnar mesophase (d-D_h) over a large temperature range compared to its phenyl analogs, hexakis(4-dodecylphenyl-4-yl)benzene (**1**) and hexakis(4′-dodecylbiphenylyl)benzene (**2**). Compounds **4–6**, hexa(oligo-α-thienylyl)benzenes, tend to form less ordered mesophases after annealing for a longer time. Compounds **4** and **5** form discotic nematic mesophases (N_d) at temperatures well below the decomposition temperature.

Introduction

Disc-like compounds have attracted considerable attention due to their intriguing self-assembly abilities to form supramolecular architectures. Since the first example of discotic liquid crystals was reported,[1] various discotic mesogens have been synthesized.[2,3] They are typically composed of flat or nearly flat cores surrounded by six or eight alkyl substituents. Benzene was the first aromatic core used for the construction of discotic mesogens. Two-dimensional aromatic cores, triphenylene (TP)[4] and hexabenzocoronene (HBC)[5,6] with more extended conjugation, were later employed as cores in succession. Especially in the case of the latter, its hexaalkyl substituted derivatives show stable hexagonal columnar mesophases over a wide temperature range.[5,6] Besides these large disc-like aromatic cores, some star-like cores were used to build discotic mesogens. For example, hexakis(4-heptylphenylethynyl)benzene and its hexakis(heptoxy) derivative were reported to form discotic nematic mesophases.[7] Depending on the length of flexible alkoxy chains, hexakis(4-alkoxyphenyl)benzenes have been shown to form a columnar mesophase or not be phase forming at all.[8,9] Thiophene is also often used as the aromatic unit in building calamitic mesogens because it possesses a strong lateral dipole within its structure due to the presence of lone electron pairs on the sulfur atom. In addition, it has been shown that it can further reduce the transition temperature of the material.[3,10,11] However, only a few reports on the mesomorphic behavior of discotic compounds containing a hetero-aromatic ring are reported in the literature.[11,12]

In this paper, a series of discotic molecules with hexaarylbenzene cores (**1**–**6**) were synthesized as depicted in Fig. 1. All of the prepared compounds are benzene derivatives, substituted by six radial aryl arms. They can be divided into three different classes, depending on their arms. The core of **1** and **2** is a hexaphenylbenzene moiety substituted by six alkyl arms or by six *p*-alkylphenyl arms, respectively. For compound **3**, the core is also composed of hexaphenylbenzene, which is surrounded by six thienyl groups. In comparison with the above three molecules, the core in **4–6** is a thienyl substituted benzene ring. For system **4** the periphery consists only of six pendant alkyl chains, whereas compounds **5** and **6** exhibit substitution with additional thienyl or bithienylyl rings, respectively. In all cases the length of the terminal alkyl chains (*i.e.* dodecyl chain) was not altered so that the effect on the mesomorphic behavior of the different aryl substituents for compounds **1–6** could be studied and compared.

Results

Synthesis

The synthesis of compounds **1** and **2** has been reported earlier.[5,6] Therefore, in this paper we only introduce compounds **3–6**. We employed a [2+2+2] cyclotrimerization of diarylacetylenes to synthesize compounds **3–6**, since this reaction had been used to synthesize many hexasubstituted benzene compounds with diverse substituents successfully in good yields,[5,6,8,9,13–16] even when the substituents were

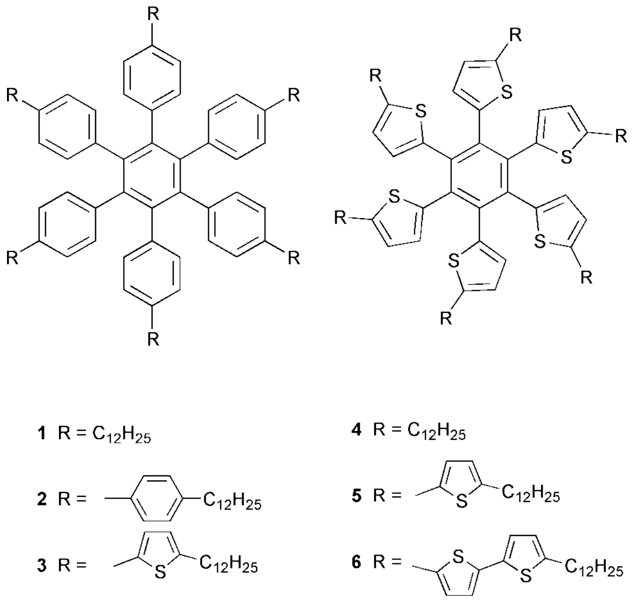


Fig. 1 Structures of hexaarylbenzenes (**1–6**).

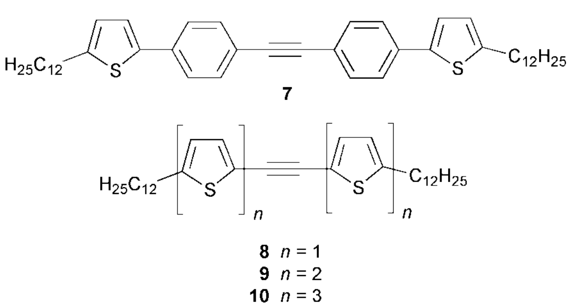


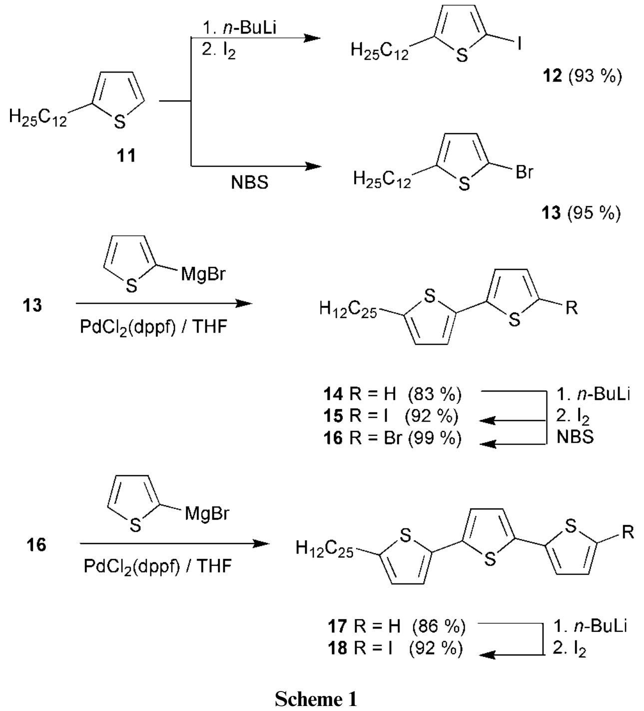
Fig. 2 Structures of diarylacetylenes (**7–10**).

dendrons with large volumes.[16] Following this reaction map the corresponding diarylacetylenes **7–10** (Fig. 2) were synthesized first.

Scheme 1 outlines the synthesis of oligothiophenes which are then used in the synthesis of **7–10**. Deprotonation of 2-dodecylthiophene (**11**) with *n*-butyllithium followed by iodination with iodine gave 2-iodo-5-dodecylthiophene (**12**) in good yield. Its bromide analogue **13** was prepared by bromination of **11** with NBS in 95% yield according to the literature procedure.[24] Dimer **14** was synthesized by Kumada-type coupling reaction from **13** in 83% yield.[24] Iodination and bromination afforded dimers **15** and **16**, respectively. Trimer **17**[24] and its iodide analogue **18** were prepared in the same way as described for **14** and **15**.[24]

Diarylacetylenes **7–10** were prepared by two different methods as shown in Scheme 2. Acetylene **7** was also synthesized by a Kumada-type coupling reaction starting from 1,2-bis(4-bromophenyl)acetylene (**19**) in 84% yield. The preparation of acetylenes **8–10** was achieved *via* Sonogashira cross coupling using [$Pd(PPh_3)_2Cl_2$]–CuI as the catalyst. Reaction of **12**, **15** and **18** with (trimethylsilyl)acetylene yielded compounds **20**, **21** and **22**, respectively. Treatment of **20–22** with potassium carbonate afforded **23**, **24** and **25**, which then reacted with the corresponding iodo-substituted oligothiophenes **12**, **15** and **18** to yield acetylenes **8–10**.

Cyclotrimerization of acetylenes **7–10** was carried out using $Co_2(CO)_8$ as the catalyst which afforded compounds **3–6** in 77, 61, 47 and 32% yield, respectively. The yield decreased from **3** to **6**, which might be due to more side-reactions in the cyclotrimerization of dioligothienylacetylenes caused by their electron-rich characteristics and lower stability with increasing conjugated length.



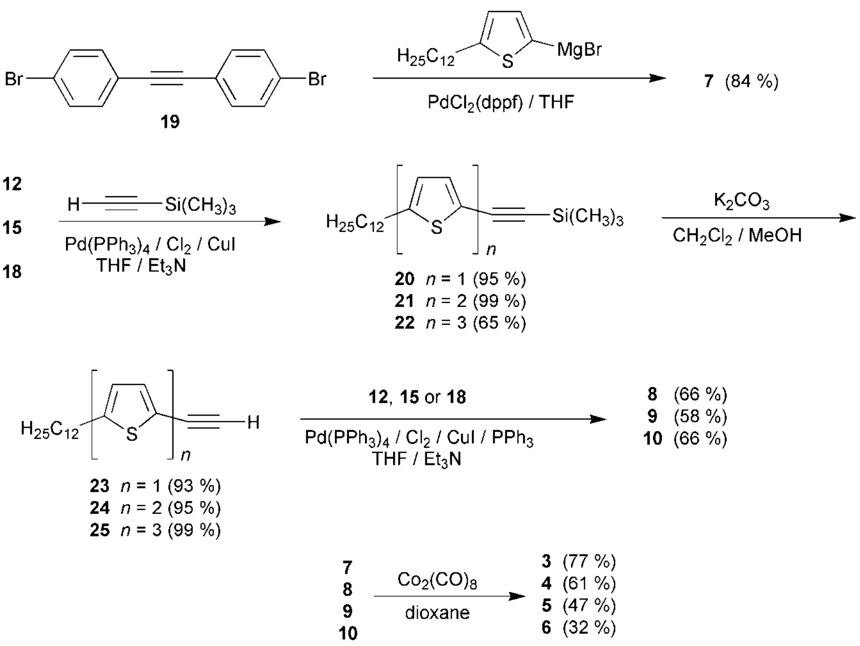
Scheme 1

Mesomorphic properties

Since all the above compounds are thermotropic liquid crystals, the thermal stability of these materials was checked by thermogravimetric analysis (TGA) at first. All other characterizations were then carried out below the decomposition temperature. The transition temperatures of compounds **1–3** were measured using differential scanning calorimetry (DSC). DSC traces and thermodynamic data are given in Fig. 3 and Table 1. In the first heating scan, **1** showed three endothermal peaks at 47.2, 56.5 and 66.6 °C (Fig. 3a). In the second heating scan, only one peak at 67.6 °C was observed. When the isotropic melt of **1** was cooled at a cooling rate of 4 K min^{-1}, a mesophase rapidly formed at 64 °C which was observed by polarizing optical microscopy (POM). The optical texture developed in a starburst shape and transformed into a texture as shown in Fig. 4, which is similar to some textures exhibited by columnar mesophases reported earlier.[17,18] The powder X-ray diffraction (XD) pattern of **1** recorded at room temperature prior to heating is that of a typical crystalline phase. XD patterns measured at 60 °C on heating, 60 °C on cooling and subsequently at room temperature are similar and exhibit a sharp reflection at small angles corresponding to a *d*-value of 38.4 Å (100) and several reflections in the wide angle region, the most prominent one corresponding to 4.8 and 4.3 Å, as shown in Fig. 5. These are suggesting the formation of an ordered columnar phase (D_x). The small reflection angles at 2θ between 5–17° should indicate the coexistence of unidentified crystal phase and columnar mesophase.[17] Therefore, the peaks at 56.5 and 66.6 °C in the DSC trace on the first heating scan are attributed to melting and clearing point, respectively.

In contrast to **1**, cooling **2** from the isotropic phase at the same cooling rate did not show the formation of any anisotropic phases by POM. This is in agreement with the DSC measurements, which showed one endothermal peak at 83.4 °C during the first heating cycle corresponding to the transition to the isotropic phase as depicted in Fig. 3b. In the following cooling and heating scans, no exo- or endothermal peaks were observed. After annealing the sample (compound **2**) at room temperature overnight, an optical schlieren texture appeared (Fig. 6), indicating the formation of a mesophase. The XD pattern of **2** (Fig. 7) shows a strong reflection at 34.0 Å (100) and a weak peak around 20.0 Å, which are in the ratio of $1:1.7$, which is close to $1:\sqrt{3}$, suggesting the formation of a hexagonal columnar mesophase (D_h).

The thermal behavior of **3** is remarkably different from that of **1**, **2** and of hexakis(4-alkoxylphenyl)benzene.[8,9] Compound **3** formed a mesophase in a wide temperature range observed by both POM and DSC. In the first heating scan three endothermal maxima at 29.2, 35.7 and 155.5 °C have been observed. The first cooling scan showed two exothermal peaks at 103.3 and 27.8 °C. The second heating scan showed similar features to the first heating scan. The peaks at 35.7 and 155.9 °C are attributed to melting and clearing point, respectively. The peaks at 29.2 °C should be attributed to a transition between incomplete crystalline phases. The clearing point of **3** is higher than that of **1** and **2**. In the observation of POM, while cooling isotropic **3** to 130 °C at a cooling rate of 4 °C min^{-1}, a typical optical texture for columnar hexagonal mesophases,[19–22] was observed as shown in Fig. 8. While further cooling the sample to room temperature, the texture broke slowly, indicative of the formation of a crystalline phase. This is in agreement with the DSC measurement. In order to determine the mesophase structure of **3**, its XD was measured at 100 °C. As shown in Fig. 9, at small angles, there are three peaks at 26.8 Å (100), 15.5 Å (110) and 13.4 Å (200) in the ratio of $1:1.7:2$, the typical diffraction of columnar hexagonal



Scheme 2

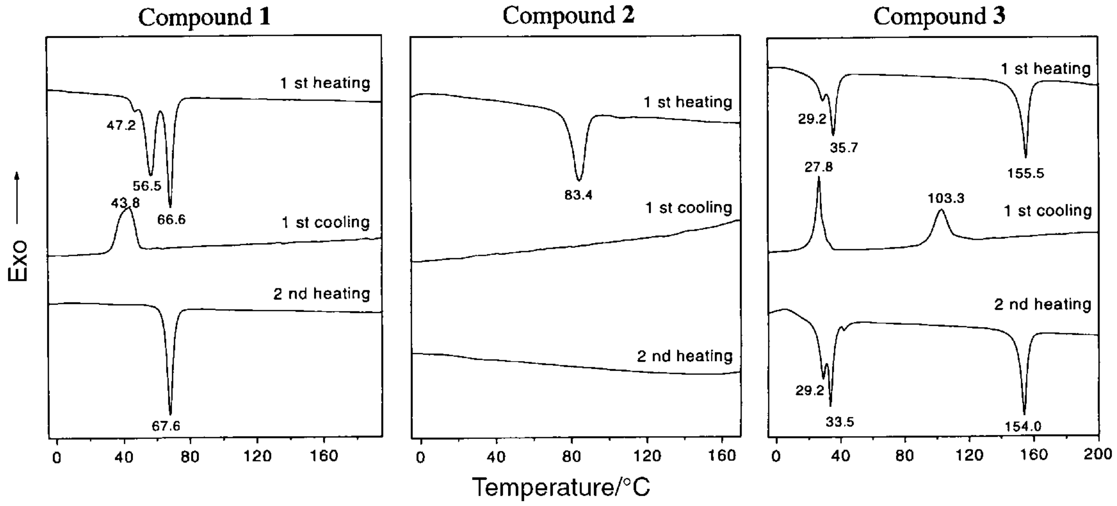


Fig. 3 DSC thermograms of **1**, **2** and **3**, heating and cooling rate: 10 K min^{-1}.

mesophases. The broad halo at about 20° is attributed to the melting of the disorderd alkyl side chains. It is superimposed by some reflections originating probably from the intracolumnar packing of discotic molecules.[5] Considering that a shoulder peak appears at 28.5 Å and the peak around 15.5 Å is broad, we assign the mesophase to be a disordered hexagonal columnar phase (d-D$_h$).

In comparison to compound **3**, compounds **4**–**6**, whose aryl arms are oligo-α-thiophenes, did not form anisotropic phases on cooling from their isotropic phases, no matter how low the employed cooling rates were. Upon cooling the isotropic melt of **4**, only a black field under POM was observed throughout the cooling process even when the temperature was below −40 °C. However, anisotropic phases were formed while

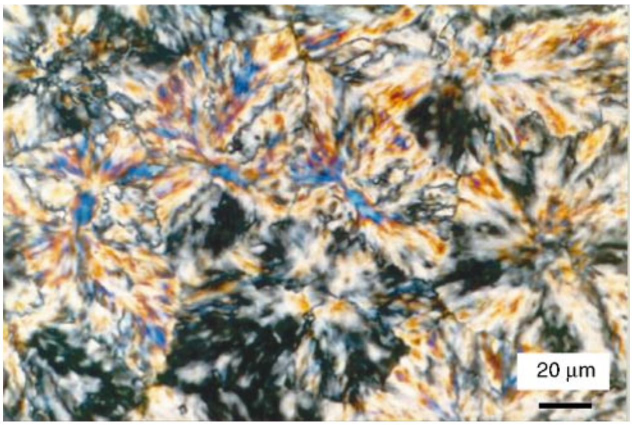


Fig. 4 Optical textures of **1** at 64 °C on cooling between crossed polarizers, magnification: ×50.

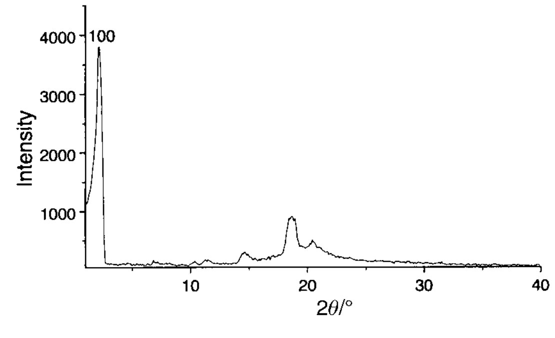


Fig. 5 X-Ray diffractions of **1** at 60 °C upon cooling.

Table 1 Thermal transitions and thermodynamic data of compounds **1–3**, heating and cooling rate: 10 °C min^{-1}

	Phase transitions (°C) and corresponding enthalpies (kJ mol^{-1}, in parentheses)^{a}	
Compound	Heating scan	Cooling scan
1	K 47.2, 56.5 D 66.6 (92.45)^{b} I	I 43.8 (38.12) D
2	D$_{h}$ 83.4 (21.58) I	—
3	K 29.2, 35.7 (58.19)^{b} D$_{ho}$ 155.5 (41.14) I	I 103.3 (33.64) D$_{ho}$ 27.8. (47.52) K

^{a}K = crystalline; D = columnar mesophase; I = isotropic. ^{b}Overlapped with a previous transition.

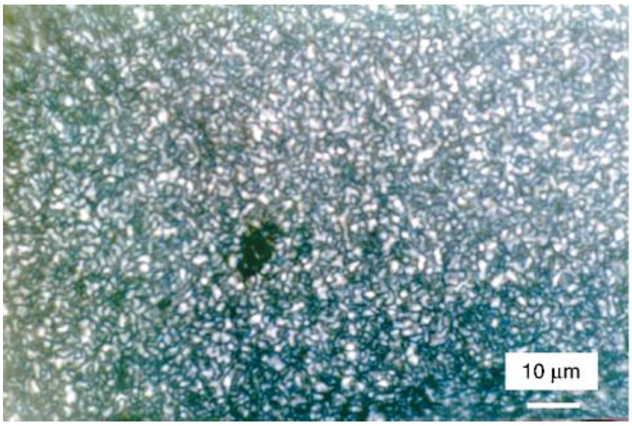


Fig. 6 Optical textures of **2** after annealing at room temperature for 2 days, magnification: × 100.

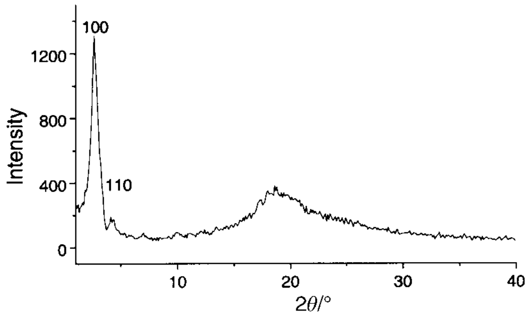


Fig. 7 X-Ray diffractions of **2** at room temperature.

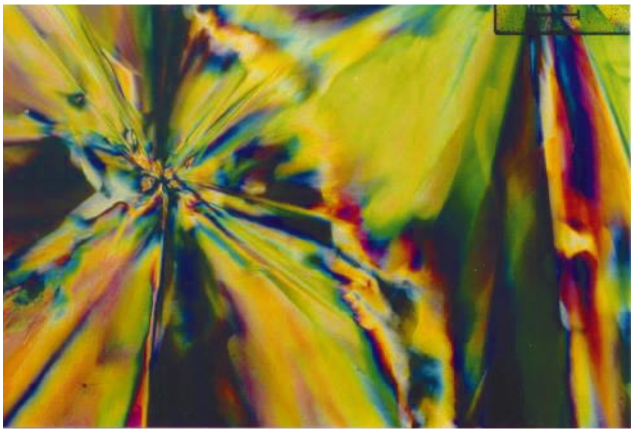


Fig. 8 Optical textures of **3** at 100 °C upon cooling between crossed polarizers, magnification: × 20.

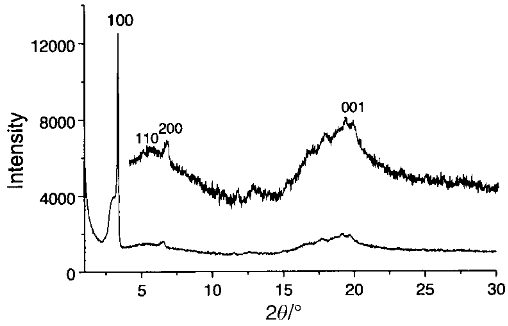


Fig. 9 X-Ray diffractions of **3** at 100 °C upon cooling.

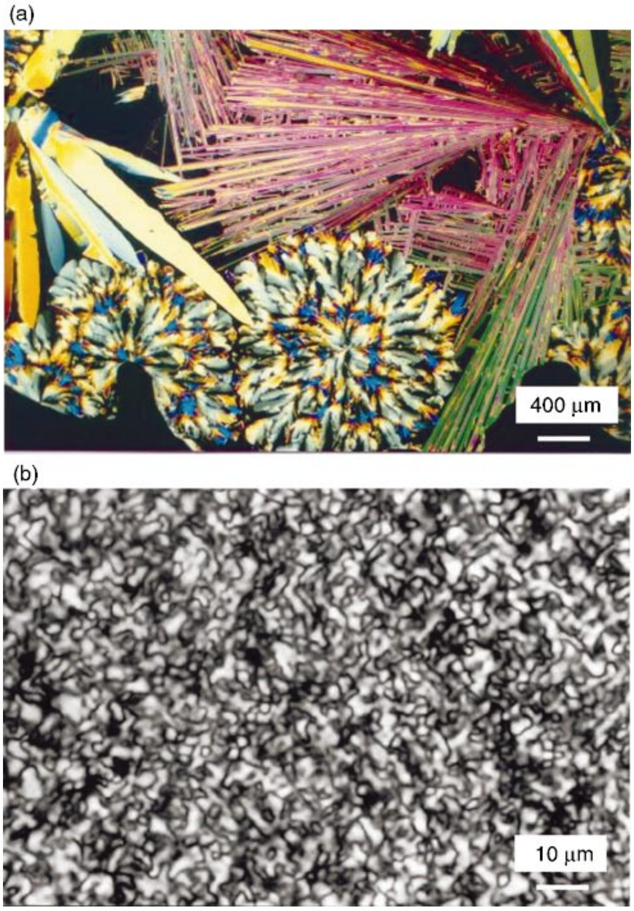


Fig. 10 Optical textures of **4** after annealing the isotropic phase at room temperature for 2 days (a, magnification: × 2.5) and at −20 °C for 1 day (b, magnification: × 100) between crossed polarizers.

annealing the sample for a long time. The structure of the anisotropic phase depends on the annealing temperature. As shown in Fig. 10, annealing the sample at 20 °C gave crystalline phases composed of flower- and fiber-like crystals (Fig. 10a), which melted at 30 and 35 °C, respectively. While annealing the sample at −20 °C, a schlieren optical texture was observed (Fig. 10b). Its XD pattern only exhibits broad peaks in both small and wide angle, indicative of the formation of a discotic nematic mesophase (N$_{d}$).

Compound **5** is isotropic at room temperature. While annealing the viscous liquid at room temperature, some anisotropic bright droplets distributed in a dark field were observed by POM (Fig. 11). Its XD pattern only shows broad reflections, pointing to the formation of nematic mesophase

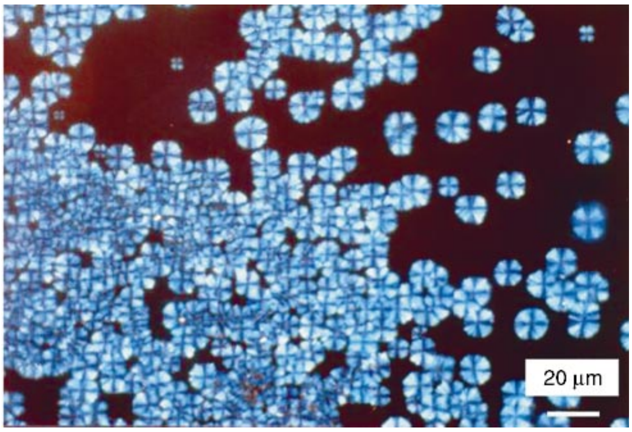


Fig. 11 Optical textures of **5** after annealing at room temperature for 3 days, magnification: ×50.

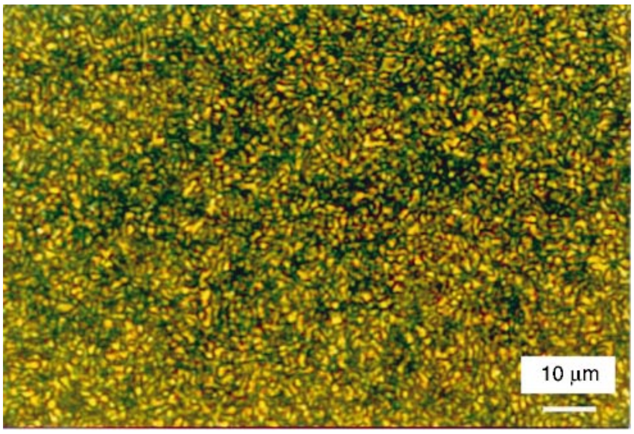


Fig. 12 Optical textures of **6** after annealing at room temperature for 1 month, magnification: ×100.

(N_d). Terthienyl derivative **6** is a waxy solid at room temperature. Formation of an anisotropic phase from isotropic **6** is quite slow and it took over 1 month annealing at room temperature. Its optical texture (Fig. 12) is similar to that of **2** (Fig. 6). The XD pattern of aged **6** exhibits several weak sharp reflections at small angles and a halo in the wide angle region. It is difficult to determine its mesophase structure based on the above observations. We can only assume that its mesophase is less ordered than those of compounds **1–3**.

Discussion

From the above results, we can conclude that the incorporation of a thiophene layer around a hexaphenylbenzene core (compound **3**) results in a stable mesophase over a wide temperature range as well as remarkable enhancement of the clearing point of the compound. Compound **3** forms a columnar hexagonal mesophase between 35.7 and 155.9 °C. In contrast to **3**, compounds **1** and **2** become isotropic liquids already at 66.6 and 83.4 °C, respectively. Furthermore, **3** forms a mesophase rapidly upon cooling its isotropic liquid, whereas its phenyl analog, **2**, remained a supercooled liquid during all cooling procedures at a cooling rate of 4 °C $\min^{-1}$. The mesophase could only be formed after annealing for a long time at room temperature. These phenomena are quite different from those in calamitic liquid crystals, in which introduction of the thiophene ring normally has an inferior effect on the formation of the mesophase and reduces the transition temperature including both melting and clearing points due to a reduction in packing efficiency of the molecules.[3,10,11] In contrast to **3**, compounds **4** and **5**, analogs of **1** and **2**, exhibit a behavior similar to that of calamitic liquid crystals. They show lower melting or clearing points and form less ordered mesophases than **1** and **2**.

The self-aggregation of molecules to higher ordered mesophases is strongly influenced by intermolecular forces such as dipole–dipole or steric interactions. Therefore, the different phase forming properties can be explained as follows. In **3**, the broader mesophase is a consequence of the stronger intermolecular interactions induced by the presence of a dipole resulting from the lone electron pairs on the sulfur atom. However, the case in **4–6** is different. The significant difference between **1–3** on the one hand and **4–6** on the other hand is an exchange of the inner core from a hexaphenylbenzene to a hexathienylbenzene system. This results in a distortion of the conventional packing behavior usually associated with cores surrounded by a 1,4-substituted phenylene unit.[10] Thus, **4–6** exhibit lower transition temperatures and tend to form less ordered mesophases.

Conclusions

A variety of star-like hexaarylbenzenes (**1–6**) have been synthesized by [2+2+2] cyclotrimerization of diarylsubstituted acetylenes. All of them form mesophases, with structures that depend on the compositions and lengths of the aryl arms. Hexakis(4-dodecylphenyl)benzene (**1**), hexakis(4′-dodecylbiphenylyl)benzene (**2**) and hexakis[4-(5′-dodecyl-2′-thienyl)phenyl]benzene (**3**) form ordered columnar mesophases. In particular, compound **3** exhibits a much higher clearing point than **1** and **2**. This indicates that the introduction of six thiophene rings around a hexaphenylbenzene core is advantageous for the formation of higher ordered mesophases. Replacement of the phenyl or biphenyl linker in **1** and **2** with thienyl or bithienyl segments as in **4** and **5**, results in lower transition temperatures and less ordered mesophases.

Further attempts will be made to convert the hexaphenylbenzene core of **3** to a two-dimensional extended aromatic disc carrying six thiophene arms on its outer periphery.[5] Resulting from this extended aromatic center the material might exhibit interesting optical and electrical properties which could be investigated by scanning tunneling microscopy (STM) and charge carrier mobility experiments.[6]

Experimental

THF was distilled from sodium benzophenone ketyl immediately prior to use. Other solvents were used as obtained. 2-Dodecylthiophene (**11**) was synthesized following reported methods.[23] Other chemicals were used as obtained without further purification.

The ^{1}H and ^{13}C NMR spectra were measured on a Bruker AMX-250, Bruker Avance-400 or Bruker AMX-500 spectrometers using chloroform-d or tetrachloroethane-d_2 as solvents. The chemical shifts are reported in ppm and deuterated solvents were used as internal reference. Mass spectra were recorded on HP MS 5973 or ZAB2-SE-FPD equipment. UV-Vis spectra were recorded on a Perkin–Elmer Lambda 15 UV-Vis spectrometer using chloroform as solvent.

Under a nitrogen atmosphere, TGA was performed on a Mettler TGA 50 at a heating rate of 10 °C $\min^{-1}$, and the DSC thermograms were recorded on a Mettler DSC 30 at a heating or cooling rate of 10 K $\min^{-1}$. A ZEISS Axiophot polarizing optical microscope (POM) equipped with a THM 600 hot stage was used to observe the thermal behavior of the materials. In the cell the sample was protected by a nitrogen atmosphere in both heating and cooling procedure. X-Ray patterns were recorded on a Siemens D-500 powder diffractometer (Cu-Kα: 1.541 angstrom) with scan rate of 0.1°/20 s.

Preparation of Grignard reagents

To magnesium (1.2 eq.) in THF (20 ml) was added dropwise 2-bromothiophene or 2-bromo-5-dodecylthiophene (**13**) (1 eq.) at room temperature maintaining a mild reflux. The resulting mixture was stirred at 55 °C for another 30 min. While cooling the mixture to room temperature, THF was added until a clear solution was obtained. All the Grignard reagents were freshly prepared and transferred to the reaction flasks using a syringe.

2-Iodo-5-dodecylthiophene (12)

n-Butyllithium (1.6 M in hexane, 7.4 ml, 11.9 mmol) was added to a solution of 2-dodecylthiophene (**11**, 3.00 g, 11.9 mmol) in THF (20.0 ml) at 0 °C. The mixture was stirred at room temperature for 20 min and then cooled to −78 °C. Iodine (3.02 g, 11.9 mmol) in THF (10.0 ml) was added dropwise. The resulting mixture was allowed to warm to room temperature slowly and then poured into 200 ml petroleum ether. The solution was washed with NaCl–$Na_2S_2O_3$ dilute aqueous solution and the organic phase was dried over $MgSO_4$. After the solvent was removed, the residue was purified on a short silica gel column to afford 4.15 g (92.4%) product as a light-brown liquid.

^1H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.01 (d, $J = 3.48$ Hz, 1 H), 6.45 (d, $J = 3.48$ Hz, 1 H), 2.77 (t, $J = 7.25$ Hz, 2 H), 1.61 (quin., 2 H), 1.4–1.1 (m, 18 H), 0.86 (t, $J = 6.60$ Hz, 3 H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): 152.21, 136.52, 125.77, 69.29, 31.91, 31.51, 30.20, 29.61, 29.51, 29.34, 29.30, 28.98, 22.68, 14.11. MS (EI): *m*/*z* (%): 377 (73) [M^+], 222 (100) [$M^+-I-C_2H_5$] ($C_{16}H_{27}IS$: 378.1).

5-Iodo-5′-dodecyl-2,2′-bithiophene (15)

Compound **15** was prepared from **14** (1.88 g, 5.64 mmol) using an identical procedure as in **12**. After workup, the crude product was recrystallized with hexane to afford 2.43 g (91.8%) pure product as a white crystal.

^1H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.10 (d, $J = 3.78$ Hz, 1 H), 6.90 (d, $J = 3.45$ Hz, 1 H), 6.74 (d, $J = 3.78$ Hz, 1 H), 6.64 (d, $J = 3.45$ Hz, 1 H), 2.75 (t, $J = 7.50$ Hz, 2 H), 1.64 (quin., 2 H), 1.4–1.1 (m, 18 H), 0.86 (t, $J = 6.59$ Hz, 3 H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): 146.02, 143.91, 137.52, 133.57, 124.76, 124.31, 123.86, 70.92, 31.91, 31.56, 30.12, 29.62, 29.52, 29.34, 29.06, 22.68, 14.11. MS (EI): *m*/*z* (%): 460 (100) [M^+] ($C_{20}H_{29}IS_2$: 460.1).

5-Bromo-5′-dodecyl-2,2′-bithiophene (16)

Compound **16** was prepared from **14** (4.50 g, 13.45 mmol) using an identical procedure as in **13**. After workup, the crude product was purified by column chromatography on silica gel with petroleum ether to give 5.56 g (98.9%) pure product as a white solid.

^1H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.0–6.85 (m, 2 H), 6.82 (d, $J = 3.75$ Hz, 1 H), 6.65 (d, $J = 3.45$ Hz, 1 H), 2.77 (t, $J = 7.53$ Hz, 2 H), 1.67 (quin., 2 H), 1.5–1.1 (m, 18 H), 0.90 (t, $J = 6.42$ Hz, 3 H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): 145.85, 139.47, 133.69, 130.40, 124.71, 123.61, 122.91, 110.07, 31.92, 31.54, 30.12, 29.63, 29.54, 29.35, 29.07, 22.68, 14.11. MS (EI): *m*/*z* (%): 414 (80) [M^+], 258 (100) [$M^+-Br-C_2H_5$] ($C_{20}H_{29}BrS_2$: 413.5).

5″-Dodecyl-5-iodo-2,2′:5′,2″-terthiophene (18)

Compound **18** was prepared from **17** using an identical procedure as in **12** (2.50 g, 6.00 mmol). After the reaction was completed, the mixture was poured into 400 ml CH_2Cl_2. The resulting solution was washed with NaCl–$Na_2S_2O_3$ dilute aqueous solution and the organic phase was dried over $MgSO_4$. While the solvent was distilled to *ca.* 50 ml, 200 ml hexane was added. The solid was collected by filtration to give 3.11 g (91.8%) of the light yellow product.

^1H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.13 (d, $J = 3.75$ Hz, 1 H), 7.1–6.9 (m, 3 H), 6.80 (d, $J = 3.75$ Hz, 1 H), 6.66 (d, $J = 3.45$ Hz, 1 H), 2.76 (t, $J = 7.54$ Hz, 2 H), 1.65 (quin., 2 H), 1.4–1.1 (m, 18 H), 0.86 (t, $J = 6.59$ Hz, 3H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): 145.95, 143.21, 137.68, 137.41, 134.18, 134.15, 124.86, 124.77, 124.71, 123.60, 123.48, 71.63, 31.92, 31.57, 30.18, 29.61, 29.53, 29.34, 29.06, 22.68, 14.11. MS (EI): *m*/*z* (%): 542 (100) [M^+] ($C_{24}H_{31}IS_3$: 542.1).

1,2-Bis[4′-(5-*n*-dodecyl-2-thienyl)phenyl]acetylene (7)

The Grignard reagent in THF (*ca.* 40 ml), freshly prepared from **13** (6.00 g, 18.1 mmol) was added to a mixture of 1,2-bis(4-bromophenyl)acetylene (**19**, 0.833 g, 2.48 mmol) and [$PdCl_2$(dppf)] (17 mg, 0.024 mmol) in THF (40 ml). The resulting mixture was refluxed for 3 d. While cooling the mixture to room temperature, the solid was filtrated and washed with hot THF. After drying under vacuum at room temperature, 1.41 g (83.8%) product as a light-yellow crystal was obtained.

^1H NMR (500 MHz, $C_2D_2Cl_4$, 403 K) δ (ppm): 7.50 ($\frac{1}{2}$ ABq, $J = 7.90$ Hz, 4 H), 7.47 ($\frac{1}{2}$ ABq, $J = 8.05$ Hz, 4 H), 7.12 (d, $J = 3.35$ Hz, 2 H), 6.73 (d, $J = 3.70$ Hz, 2 H), 2.81 (t, $J = 7.48$ Hz, 4 H), 1.71 (quin., 4 H), 1.50–1.20 (m, 36 H), 0.88 (t, $J = 6.55$ Hz, 6 H). EA: anal. calcd. (%) for $C_{46}H_{62}S_2$: C 81.35, H 9.20; found: C 81.17, H 9.32. MS (MALDI-TOF): *m*/*z* (%) = 678.47 [M^+] (calcd for $C_{46}H_{62}S_2 = 679.12$)

2-Trimethylsilylethynyl-5-*n*-dodecylthiophene (20)

A mixture of **12** (3.00 g, 7.94 mmol), $Pd(PPh_3)_2Cl_2$ (147 mg, 0.209 mmol) and CuI (79 mg, mmol) was degassed. Then, THF (20.0 ml) and triethylamine (5.0 ml) were added. After the mixture was stirred for 5 min, trimethylsilylacetylene (1.4 ml, 0.966 g, 9.83 mmol) was added dropwise. The resulting mixture was stirred at room temperature overnight and poured into 200 ml petroleum ether. The precipitate was removed by filtration and then the solvent was distilled under reduced pressure. The residue was purified by column chromatography on silica gel with petroleum ether. 2.61 g (94.5%) product as colorless oil was obtained.

^1H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.03 (d, $J = 3.45$ Hz, 1 H), 6.58 (d, $J = 3.45$ Hz, 1 H), 2.74 (d, $J = 7.52$ Hz, 2 H), 1.62 (quin., 2 H), 1.4–1.1 (m, 18 H), 0.86 (t, 6.60 Hz, 3 H), 0.21 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 148.32, 132.62, 123.90, 120.36, 98.10, 97.62, 31.88, 31.50, 30.11, 29.59, 29.49, 29.31, 29.28, 28.94, 22.65, 14.08, −0.13. MS (EI): *m*/*z* (%): 348 (72) [M^+], 193 (100) [$M^+-C_{11}H_{23}$] ($C_{21}H_{36}SSi$: 348.2).

2-Ethynyl-5-*n*-dodecylthiophene (23)

2.0 g K_2CO_3 was added into a solution of **20** (2.60 g, mmol) in methanol (100.0 ml). The resulting mixture was stirred at room temperature for 2 hours and poured into water. The mixture was extracted with petroleum ether (3 ×). The organic extracts were washed with brine and dried over $MgSO_4$. After the solvent was removed, 1.93 g (93.0%) product as light-yellow liquid was obtained, which was used in the next step without further purification.

^1H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.07 (d, $J = 3.45$ Hz, 1 H), 6.61 (d, $J = 3.45$ Hz, 1 H), 3.26 (s, 1 H), 2.74 (d, $J = 7.52$ Hz, 2 H), 1.62 (quin., 2 H), 1.4–1.1 (m, 18 H), 0.86 (t, 6.60 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 148.54, 133.04, 123.88, 119.15, 80.31, 77.44, 31.89, 31.50, 30.09, 29.60, 29.50, 29.32, 29.28, 28.99, 22.66, 14.08. MS (EI): *m*/*z* (%): 276 (24) [M^+], 121 (100) [$M^+-C_{11}H_{23}$] ($C_{18}H_{28}S$: 276.2).

1,2-Bis(5-*n*-dodecyl-2-thienyl)acetylene (8)

A mixture of **23** (1.93 g, mmol), **12** (2.90 g, mmol), Pd(PPh_3)$_2$$Cl_2$ (123 mg, mmol), CuI (16 mg, mmol) and PPh3 (23 mg, mmol) in THF (20.0 ml) and triethylamine (5.0 ml) was stirred at room temperature overnight and then poured into 200 ml petroleum ether. The mixture was washed with brine. The organic phase was dried over $MgSO_4$. After the solvent was removed, the residue was purified by column chromatography on silica gel with petroleum ether to give 2.42 g (65.9%) product as a white solid.

^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.04 (d, $J = 3.78$ Hz, 2 H), 6.64 (d, $J = 3.78$ Hz, 2 H), 2.76 (d, $J = 7.52$ Hz, 4 H), 1.62 (quin., 4 H), 1.4–1.1 (m, 36 H), 0.87 (t, $J = 6.42$ Hz, 6 H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): 148.50, 131.90, 124.18, 120.39, 89.90, 31.92, 31.54, 30.22, 29.62, 29.53, 29.34, 29.32, 29.03, 22.68, 14.11. EA: anal. calcd. (%) for $C_{34}H_{54}S_2$: C 77.50, H 10.33, S 12.17; found: C 77.41, H 10.54. MS (MALDI-TOF): *m*/*z* (%) = 526.42 [M$^+$] (calcd for $C_{34}H_{54}S_2 = 526.92$).

5-Trimethylsilylethynyl-5′-*n*-dodecyl-2,2′-bithiophene (21)

Compound **21** was prepared from **15** (1.0 g, 2.17 mmol) in an identical procedure as for **20**. After workup, the crude product was purified by column chromatography on silica gel with petroleum ether to give 0.93 g (99.4%) product as a white solid.

^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.08 (d, $J = 3.78$ Hz, 1 H), 6.96 (d, $J = 3.45$ Hz, 1 H), 6.89 (d, $J = 3.78$ Hz, 1 H), 6.64 (d, $J = 3.45$ Hz, 1 H), 2.76 (d, $J = 7.52$ Hz, 2 H), 1.64 (quin., 2 H), 1.4–1.1 (m, 18 H), 0.86 (t, $J = 6.42$ Hz, 3 H), 0.22 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 146.21, 139.49, 133.98, 133.39, 124.83, 123.90, 122.38, 120.94, 99.55, 97.54, 31.86, 31.53, 30.12, 29.58, 29.48, 29.29, 29.00, 22.64, 14.07, −0.19. MS (EI): *m*/*z* (%): 430 (100) [M$^+$] ($C_{25}H_{38}S_2Si$: 430.2).

5-Ethynyl-5′-*n*-dodecyl-2,2′-bithiophene (24)

Compound **24** (0.73 g, 94.5%) as a light-yellow solid was prepared from **21** (0.93 g, 2.16 mmol) in an identical procedure as for **23**.

^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.13 (d, $J = 3.75$ Hz, 1 H), 6.97 (d, $J = 3.75$ Hz, 1 H), 6.91 (d, $J = 3.78$ Hz, 1 H), 6.66 (d, $J = 3.45$ Hz, 1 H), 3.36 (s, 1 H), 2.76 (d, $J = 7.50$ Hz, 2 H), 1.65 (quin., 2 H), 1.4–1.1 (m, 18 H), 0.86 (t, $J = 6.60$ Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 146.35, 139.81, 133.84, 133.78, 124.85, 124.07, 122.35, 119.74, 81.85, 77.02, 31.89, 31.54, 30.13, 29.61, 29.51, 29.32, 29.03, 22.66, 14.09. MS (EI): *m*/*z* (%): 358 (20) [M$^+$], 83 (100) [$C_4H_2S^+$] ($C_{22}H_{30}S_2$: 358.2).

1,2-Bis(5′-*n*-dodecyl-2,2′-bithienyl-5-yl)acetylene (9)

Compound **9** was prepared from **24** (0.73 g, 2.04 mmol) and **15** (1.0 g, 2.17 mmol) in an identical procedure as **8**. After the reaction was completed, the crude product was collected by filtration and washed with a little CH_2Cl_2. Recrystallization of the crude product gave 0.82 g (58.1%) product as orange crystals.

^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.12 (d, $J = 3.78$ Hz, 2 H), 6.98 (d, $J = 3.45$ Hz, 2 H), 6.96 (d, $J = 3.78$ Hz, 2 H), 6.66 (d, $J = 3.45$ Hz, 2 H), 2.77 (d, $J = 7.52$ Hz, 4 H), 1.66 (quin., 4 H), 1.4–1.1 (m, 36 H), 0.86 (t, $J = 6.59$ Hz, 6 H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): 146.35, 139.94, 134.02, 132.89, 124.94, 124.02, 122.78, 120.73, 87.24, 31.92, 31.58, 30.19, 29.65, 29.62, 29.53, 29.34, 29.06, 22.68, 14.11. EA: anal. calcd. (%) for $C_{42}H_{58}S_4$: C 72.98, H 8.46, S 18.52; found: C 72.74, H 8.52. MS (MALDI-TOF): *m*/*z* (%) = 690.30 [M$^+$] (calcd for $C_{42}H_{58}S_4 = 691.17$).

5-Trimethylsilylethynyl-5″-*n*-dodecyl-2,2′:5′,2″-terthiophene (22)

Compound **22** (0.635 g, 65.1%) as a light-yellow crystal was prepared from **18** (1.0 g, 1.84 mmol) in an identical procedure to **20**.

^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.10 (d, $J = 3.75$ Hz, 1 H), 7.03 (d, $J = 3.78$ Hz, 1 H), 7.00–6.90 (m, 3 H), 6.66 (d, $J = 3.45$ Hz, 1 H), 2.76 (d, $J = 7.52$ Hz, 2 H), 1.65 (quin., 2 H), 1.4–1.1 (m, 18 H), 0.86 (t, $J = 6.90$ Hz, 3 H), 0.23 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 145.92, 138.70, 137.54, 134.59, 134.15, 133.46, 124.83, 124.76, 123.58, 123.51, 122.89, 121.55, 100.06, 97.39, 31.88, 31.54, 30.14, 29.60, 29.50, 29.31, 29.03, 22.65, 14.08, −0.20. MS (EI): *m*/*z* (%): 512 (100) [M$^+$] ($C_{29}H_{40}S_3Si$: 512.2).

5-Ethynyl-5″-*n*-dodecyl-2,2′:5′,2″-terthiophene (25)

1.5 g K_2CO_3 was added into a solution of **22** (0.635 g, 1.24 mmol) in CH_2Cl_2–MeOH (120.0 : 20.0 ml). The resulting mixture was stirred at room temperature for 3 hours and then treated in an identical procedure as for **23** to give 0.538 g (98.7%) product as yellow crystals.

^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.15 (d, $J = 3.78$ Hz, 1 H), 7.04 (d, $J = 3.78$ Hz, 1 H), 7.00–6.90 (m, 3 H), 6.66 (d, $J = 3.45$ Hz, 1 H), 3.38 (s, 1 H), 2.77 (t, $J = 7.52$ Hz, 2 H), 1.68 (quin., 2 H), 1.4–1.1 (m, 18 H), 0.86 (t, $J = 6.60$ Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 145.98, 139.04, 137.70, 134.36, 134.10, 133.92, 124.93, 124.84, 123.62, 123.50, 122.85, 120.31, 82.23, 76.87, 31.88, 31.54, 30.15, 29.60, 29.50, 29.31, 29.03, 22.65, 14.08. MS (EI): *m*/*z* (%): 440 (100) [M$^+$] ($C_{26}H_{32}S_3$: 440.2).

1,2-Bis(5″-*n*-dodecyl-2,2′:5′,2″-terthienyl-5-yl)acetylene (10)

Compound **10** was prepared from **23** (0.538 g, 1.22 mmol) and **16** (0.93 g, 1.71 mmol) in an identical procedure as for **8**. After the reaction was completed, the crude product was collected by filtration and washed with CH_2Cl_2 to afford 0.682 g (65.6%) product as an orange solid.

^{1}H NMR (500 MHz, $C_2D_2Cl_4$, 403 K) δ (ppm): 7.16 (d, $J = 3.65$ Hz, 2 H), 7.07 (d $J = 3.70$ Hz, 2 H), 7.04 (d, $J = 3.65$ Hz, 2 H), 7.01–6.95 (m, 4 H), 6.69 (d, $J = 3.05$ Hz, 2 H), 2.80 (t, $J = 7.48$ Hz, 4 H), 1.71 (quin., 4 H), 1.5–1.2 (m, 36 H), 0.90 (t, $J = 6.58$ Hz, 6 H). EA: anal. calcd. (%) for $C_{50}H_{62}S_6$: C 70.20, H 7.31, S 22.49; found: C 71.21, H 7.67. MS (MALDI-TOF): *m*/*z* (%) = 854.27 [M$^+$] (calcd for $C_{50}H_{62}S_6 = 855.42$).

General procedure of cyclotrimerization

A suspension of acetylene (1 eq.) in dioxane was degassed several times with argon. Then [$Co_2(CO)_8$] catalyst (0.15 eq.) was added. The resulting mixture was refluxed for 1.5 to 4 hours until starting materials disappeared, as detected by TLC. While cooling to room temperature, the mixture was poured into water and extracted with CH_2Cl_2 (3 ×). The organic extracts was washed with brine and dried over $MgSO_4$. After the solvent was removed under reduced pressure, the residue was purified by column chromatography on silica gel.

Hexakis[4-(5′-*n*-dodecyl-2′-thienyl)phenyl]benzene (3)

[$Co_2(CO)_8$] (100 mg, 0.292 mmol) was added to a suspension of **7** (1.29 g, 1.90 mmol) in dioxane (60.0 ml). The resulting mixture was refluxed for 3 hours and treated as described in the general procedure. Purification by column chromatography on silica gel with petroleum ether–CH_2Cl_2 (9 : 1 then 6 : 1) gave 0.99 g (76.9%) **3** as a waxy white solid.

^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 7.08 ($\frac{1}{2}$ ABbq, $J = 8.48$ Hz, 12 H), 6.92 (d, $J = 3.45$ Hz, 6 H), 6.80 ($\frac{1}{2}$ ABbq, $J = 8.18$ Hz, 12 H), 6.60 (d, $J = 3.45$ Hz, 6 H), 2.71 (t, $J = 7.38$ Hz, 12 H), 1.60 (quin., 12 H), 1.4–1.1 (m, 108 H), 0.87 (t, $J = 6.44$ Hz, 18 H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): 145.05, 141.60, 140.14, 139.16, 131.78, 131.56, 124.73, 123.72, 122.19, 31.91, 31.66, 30.18, 29.63, 29.52, 29.34, 29.06, 22.67, 14.11. EA: anal. calcd. (%) for $C_{138}H_{186}S_6$: C 81.35, H 9.20, S 9.44; found: C 81.40, H 9.40. UV-Vis: λ_{max} ($CHCl_3$): 320 nm (lg ε: 5.30). MS (FD, 8 kV): *m*/*z* (%): 2037.1 (100) [M^+] ($C_{138}H_{186}S_6$: 2035.29).

Hexakis(5-*n*-dodecyl-2-thienyl)benzene (4)

[$Co_2(CO)_8$] (150 mg, 0.438 mmol) was added to a suspension of **8** (1.50 g, 2.85 mmol) in dioxane (40.0 ml). The resulting mixture was refluxed for 1.5 hours and treated as described in the general procedure. Purification by column chromatography on silica gel with petroleum ether–CH_2Cl_2 (100 : 0 then 95 : 5) gave 0.90 g (60.5%) product as a colorless oil, which formed a waxy white solid slowly at room temperature.

^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 6.30 (s, 12 H), 2.57 (t, $J = 7.21$ H, 12 H), 1.44 (quin., 12 H), 1.4–1.1 (m, 108 H), 0.86 (t, $J = 6.59$ Hz, 18 H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): 146.32, 138.86, 136.92, 128.41, 122.66, 31.94, 31.81, 29.83, 29.76, 29.69, 29.42, 29.39, 28.72, 22.70, 14.11. EA: anal. calcd. (%) for $C_{102}H_{162}S_6$: C 77.50, H 10.33, S 12.17; found: C 77.41, H 10.35. UV-Vis: λ_{max} ($CHCl_3$): 305 nm (lg ε: 4.74). MS (FD, 8 kV): *m*/*z* (%): 1580.5 (100) [M^+] ($C_{102}H_{162}S_6$: 1579.10).

Hexakis(5′-*n*-dodecyl-2,2′-bithienyl-5-yl)benzene (5)

[$Co_2(CO)_8$] (50 mg, 0.14 mmol) was added to a suspension of **9** (0.60 g, 0.87 mmol) in dioxane (30.0 ml). The resulting mixture was refluxed for 2 hours and treated as described in the general procedure. Purification by column chromatography on silica gel with petroleum ether–CH_2Cl_2 (8 : 1) gave 0.28 g (46.7%) **5** as a brown–yellow solid.

^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 6.76 (d, $J = 3.45$ Hz, 6 H), 6.68 (d, $J = 3.75$ Hz, 6 H), 6.54 (d, $J = 3.78$ Hz, 6 H), 6.48 (d, $J = 3.78$ Hz, 6 H), 2.69 (t, $J = 7.52$ Hz, 12 H), 1.60 (quin., 12 H), 1.4–11.1 (m, 108 H), 0.86 (t, $J = 6.59$ Hz, 18 H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): 144.98, 138.99, 138.64, 136.82, 134.87, 129.92, 124.48, 123.06, 122.16, 31.92, 31.65, 30.12, 29.64, 29.53, 29.34, 29.10, 22.68, 14.11. EA: anal. calcd. (%) for $C_{126}H_{174}S_{12}$: C 72.98, H 8.46, S 18.56; found: C 72.74, H 8.52. UV-Vis: λ_{max} ($CHCl_3$): 346 nm (lg ε: 5.11). MS (FD, 8 kV): *m*/*z* (%): 2072.1 (100) [M^+] ($C_{126}H_{174}S_{12}$: 2071.02).

Hexakis(5″-*n*-dodecyl-2,2′:5′,2″-terthienyl-5-yl)benzene (6)

[$Co_2(CO)_8$] (38 mg, 0.11 mmol) was added into a suspension of **10** (0.60 g, 0.70 mmol) in dioxane (30.0 ml). The resulting mixture was refluxed for 2 hours and treated as described in general procedure. Purification by column chromatography on silica gel with petroleum ether–CH_2Cl_2 (8 : 1 then 6 : 1) gave 0.19 g (31.6%) of **6** as a yellow–brown solid.

^{1}H NMR (250 MHz, $CDCl_3$) δ (ppm): 6.90–6.82 (m, 18 H), 6.78 (d, $J = 3.78$ Hz, 6 H), 6.6 (d, $J = 3.75$ Hz, 6 H), 6.55 (d, $J = 3.78$ Hz, 6 H), 2.73 (t, $J = 7.52$ Hz, 12 H), 1.62 (quin., 12 H), 1.4–1.1 (m, 108 H), 0.85 (t, $J = 6.59$ Hz, 18 H). ^{13}C NMR (62.5 MHz, $CDCl_3$) δ (ppm): 145.44, 139.10, 138,58, 136.79, 136.61, 135.47, 134.52, 130.23, 124.71, 124.10, 123.44, 123.27, 122.77, 31.91, 31.55, 30.16, 29.62, 29.53, 29.34, 29.08, 22.68, 14.11. EA: anal. calcd. (%) for $C_{150}H_{186}S_{18}$: C 70.20, H 7.31, S 22.49; found: C 70.96, H 7.46. UV-Vis: λ_{max} ($CHCl_3$): 387 nm (lg ε: 5.27). MS (FD, 8 kV): *m*/*z* (%): 2563.6 (100) [M^+] ($C_{150}H_{186}S_{18}$: 2562.95).

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