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Side Chain Effect on the Double Helix Formation of Ethynylhelicene Oligomers

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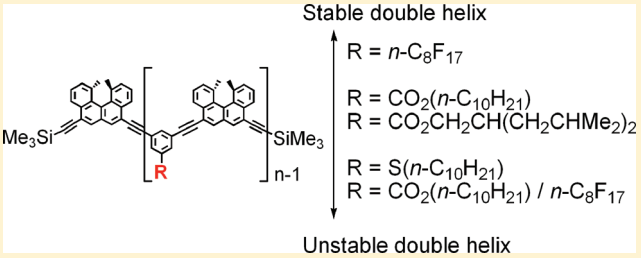
Supporting Information

ABSTRACT: Three series of ethynylhelicene oligomers with different side chains were synthesized: (*P*)-bD-***n*** (*n* = 2−6) with branched alkyloxycarbonyl side chains; (*P*)-S-***n*** (*n* = 2−7) with decylsulfanyl side chains; and (*P*)-DF-***n*** (*n* = 4, 6, 8, 10) with alternating decyloxycarbonyl and perfluorooctyl side chains. The double helix formation of these side chain derivatives was compared to that of (*P*)-D-***n*** with decyloxycarbonyl side chains. CD, UV−vis, and vapor pressure osmometry (VPO) studies showed that (*P*)-bD-***n*** formed double helices as well as (*P*)-D-***n***. CD studies in trifluoromethylbenzene at different temperatures and concentrations indicated that the stability of the aggregate of (*P*)-bD-**6** was similar to that of (*P*)-D-**6**. Bulkiness of side chains had little effect on aggregation, which indicated that π−π interactions of the aromatic moiety were essential for double helix formation. (*P*)-S-***n*** were random coils in all solvents examined except in trifluoromethylbenzene. Whereas (*P*)-D-**7** formed a double helix at 1×10^{-3} M in toluene, (*P*)-S-**7** was a random coil. This result indicated that the double helix forming ability of (*P*)-S-***n*** was substantially lower than that of (*P*)-D-***n***. Based on the previous observation that (*P*)-F-***n*** formed a more stable double helix than (*P*)-D-***n***, the order of stability may be summarized as follows: (*P*)-F-***n*** > (*P*)-D-***n*** and (*P*)-bD-***n*** > (*P*)-S-***n***. The lower stability of (*P*)-S-***n*** compared to that of (*P*)-F-***n*** was ascribed to the softness and/or the electron-rich nature at the *m*-phenylene moiety. (*P*)-DF-***n*** did not form a stable double helix. It was speculated that a regular alternating arrangement of soft/hard or electron-rich/deficient moieties is important for stable double helix formation. Side chains of ethynylhelicene oligomers can play significant roles in determining the stability of double helices.



INTRODUCTION

Synthetic oligomeric compounds that can form helical structures,[1] such as single helices,[2−17] double helices,[18−26] and multiple helices,[27−29] have recently attracted attention. In general, these organic compounds possess an array of aromatic moieties with long alkyl side chains, which are introduced to improve their solubility in organic solvents. In some cases, however, side chains affect helix formation.

In the case of a single helix, whereas the *m*-phenylene ethynylene oligomer with triethyleneglycoxycarbonyl [$CO_2CH_2(CH_2CH_2O)_3CH_3$] side chains forms a single helix in acetonitrile, which is a polar solvent, the oligomers with triethyleneglycoxy [$OCH_2(CH_2CH_2O)_3CH_3$] side chains or triethyleneglycoxymethyl [$CH_2OCH_2(CH_2CH_2O)_3CH_3$] side chains require solvents of higher polarity, such as a combination of acetonitrile and water, for helix formation.[30] A triblock oligomer with both triethyleneglycoxycarbonyl and triethyleneglycoxymethyl side chains shows intermediate aggregation. It has been discussed that electron-withdrawing groups strengthen π-stacking.[31]

The side chain effect on the double helix formation of aromatic oligoamides has also been discussed. The dimerization constant for the double helix formation of pyridine-dicarboxamide oligomers depends on the identity of the side chain.[4c,32] A heptamer with seven decyloxy side chains in $CDCl_3$ or C_6D_6 has a dimerization constant 3 orders of magnitude larger than that with three decyloxy side chains or one lacking a side chain. It was proposed that long side chains are involved in van der Waals interactions between strands. In $CDCl_3$, the dimerization constants of a pyridine-dicarboxamide heptamer[33] and a nonamer[34] with benzyloxy side chains on the pyridine rings are much higher than those with decyloxy or methoxy side chains. This result has been ascribed to the interstrand face-to-face and edge-to-face interactions between the benzyl groups. Similar dimerization constants, which were higher than those of unsubstituted oligomers, were obtained for the decyloxy and methoxy derivatives of the same oligomers.[33] These results were ascribed to the reduced unfavorable dipolar interactions by alkyloxy-substituted oligomers. These examples show that side chains affect the stability of helix formation by aromatic oligomers. However, systematic understanding of the effects of side chains remains insufficient, and thus further study is required.

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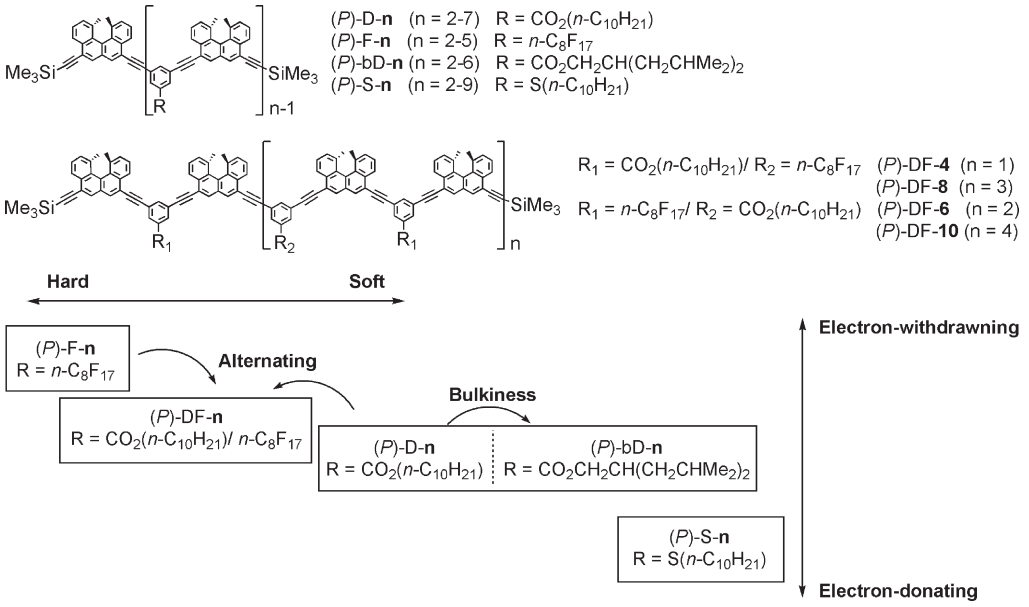
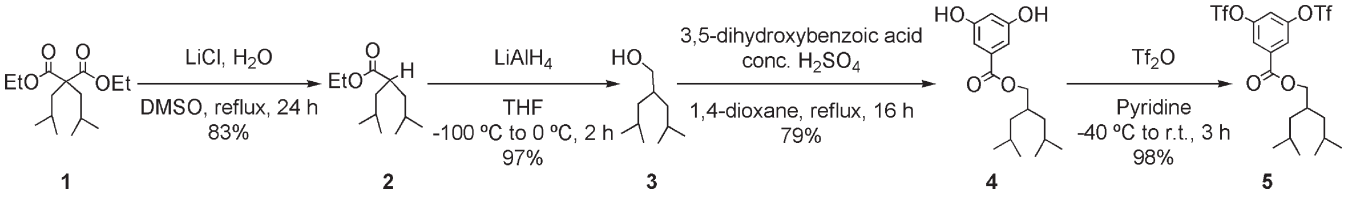


Figure 1. Side chain effect.

Scheme 1



Previously we reported double helix formation by optically active ethynylhelicene oligomers, in which (*P*)-5,8-diethynyl-1,12-dimethylbenzo[*c*]phenanthrene moieties were connected by *m*-phenylene spacers possessing decyloxycarbonyl side chains (Figure 1).[35,36] The circular dichroism (CD) spectrum obtained within 5 min after the dissolution of the heptamer (*P*)-D-7 in chloroform at 5×10^{-6} M was markedly different from the spectra of oligomers from the dimer to the hexamer and exhibited an extremely large Cotton effect between 300 and 400 nm. Hypochromic shifts were also observed in the UV−vis spectra. Vapor pressure osmometry (VPO) revealed a dimeric structure of (*P*)-D-7 when it showed the enhanced Cotton effect. The proton NMR of (*P*)-D-7 in chloroform at room temperature provided broad signals of aromatic protons shifted upfield, which indicated the formation of π-stacked structures. The results indicated the formation of a double helix by (*P*)-D-7. The double helix unfolded to random coils by heating, and investigations of the unfolding rate of (*P*)-D-7 revealed that the rate constant *k* was highly dependent on the type of aromatic solvents used. The *k* values differed by 7 orders of magnitude between iodobenzene and trifluoromethylbenzene, and log *k* exhibited a good correlation with the absolute hardness η:[37] higher unfolding rates were observed in soft arenes and lower rates in hard arenes.[36a] The results suggested the involvement of $\pi-\pi$ interactions in double helix formation and a notable relationship between the $\pi-\pi$ interactions and the HSAB principle: the $\pi-\pi$ interaction is a soft/soft interaction between arenes.

Later, we synthesized oligomers with perfluorooctyl side chains at the *m*-phenelene moiety (Figure 1).[38] Pentamer (*P*)-F-**5** formed a double helix in hard solvents such as trifluoromethylbenzene, *m*-difluorobenzene, and fluorobenzene as indicated by CD and VPO, and it was noted that (*P*)-F-**5** formed a more stable double helix than (*P*)-D-**5**. The CD spectra of (*P*)-F-**5** in trifluoromethylbenzene provided a mirror-image CD spectrum compared to that of (*P*)-D-**5**, which meant that their screw senses are inverted with respect to each other. (*P*)-F-**5** formed a heteroaggregate with (*M*)-D-**5** but not with (*P*)-D-**5**. The heteroaggregate also provided a CD spectrum similar to those of double helices of (*P*)-F-**5** and (*M*)-D-**5**. Significant chiral recognition in the aggregate formation can be explained by the formation of chiral ordered three-dimensional structures of double helices. In addition, the results indicated the crucial role of side chains in determining the structure and stability of double helices, which led us to further investigate side chain effects.

In this study, we synthesized a new series of ethynylhelicene oligomers with different side chains and examined their double helix formation (Figure 1). (*P*)-bD-***n*** (*n* = 2−6) with 4-methyl-2-(2-methylpropyl)-1-pentyloxy carbonyl side chains were synthesized to determine the effect of bulkiness at the side chain moiety. (*P*)-S-***n*** (*n* = 2−7) with decylsulfanyl side chains were synthesized to investigate the effect of soft and electron-donating side chains on *m*-phenylene moieties. (*P*)-DF-***n*** (*n* = 4, 6, 8, 10) with alternating decyloxycarbonyl and perfluorooctyl side chains

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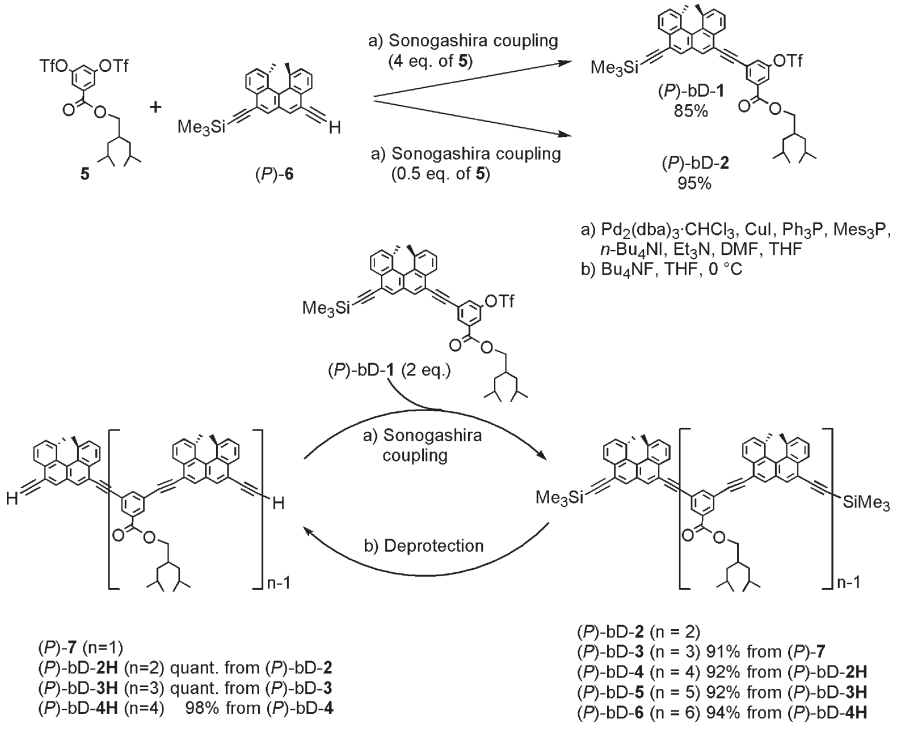
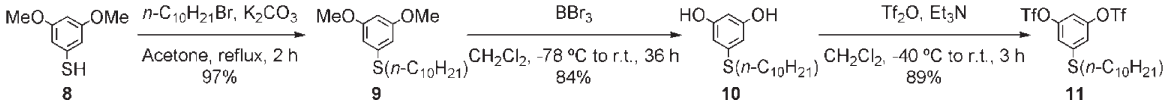
Scheme 2



Scheme 3



were synthesized to determine the effects of alternating arrangements.

For clarification, the names of oligomers are represented as follows. Decyloxycarbonyl compounds, perfluorooctyl compounds, and 4-methyl-2-(2-methylpropyl)-1-pentyloxycarbonyl compounds are denoted "D", "F", and "bD", respectively. Compounds with decylsulfanyl side chains are denoted "S", and compounds with alternating decyloxycarbonyl and perfluorooctyl side chains are denoted "DF". The bold-faced number represents the number of helicenes in an oligomer. Desilylated synthetic intermediates are denoted "H", for example, (*P*)-D-**2H**.

(*P*)-bD-***n*** showed double helix formation behavior similar to that of (*P*)-D-***n***, which indicated a small effect due to side chain bulkiness. The aggregate-forming ability of (*P*)-S-***n*** was substantially lower than those of (*P*)-F-***n*** and (*P*)-D-***n***. The results were explained by the importance of hardness and/or electron-deficient nature of the *m*-phenylene moiety to form stable aggregates. (*P*)-DF-***n*** did not form stable double helices. It was speculated that the arrangement of regular alternating soft/hard and/or electron-deficient/rich arrays is important for stable double helix formation.

RESULTS AND DISCUSSION

Synthesis. Ethynylhelicene oligomers were synthesized by repetitive deprotection and Sonogashira coupling in a two-directional method.[39a] (*P*)-bD-***n*** (n = 2−6) were synthesized starting from 4-methyl-2-(2-methylpropyl)pentyl-3,5-bis(trifluoromethanesulfonyloxy) benzoate **5**, which was obtained from diethyl-2,2-bis(2-methylpropyl)propanedionate **1** in four steps (Scheme 1). The coupling of monosilylated ethynylhelicene (*P*)-**6** and 4 equiv of **5** gave the building block (*P*)-bD-**1** (Scheme 2). The dimer (*P*)-bD-**2** was synthesized from **5** and (*P*)-**6** in 95% yield. The coupling of diethynylhelicene (*P*)-**7** and (*P*)-bD-**1** yielded the trimer (*P*)-bD-**3** in 91% yield, and subsequent deprotection and Sonogashira coupling converted (*P*)-bD-**3** to (*P*)-bD-**5** in 92% yield. The tetramer (*P*)-bD-**4** (n = 4) and the hexamer (*P*)-bD-**6** (n = 6) were synthesized starting from the deprotected dimer (*P*)-bD-**2H** in 92% and 94% yield, respectively.

The synthesis of (*P*)-S-***n*** (n = 2−7) employed 5-decylsulfanyl-1,3-bis(trifluoromethanesulfonyloxy)-benzene **11**, which was obtained from 3,5-dimethoxybenzenethiol **8** in three steps (Scheme 3). Coupling with **11** and (*P*)-**6** gave (*P*)-S-**1** in 94% yield (Scheme 4). The oligomers with odd numbers of helicenes, (*P*)-S-**3**, (*P*)-S-**5**, and (*P*)-S-**7**, were obtained starting from (*P*)-**7** by coupling with 2 equiv of (*P*)-S-**1** in 83%, 81%, and 55% yield, respectively. The dimer (*P*)-S-**2** was synthesized from **11** and 2 equiv of (*P*)-**6** in 89% yield. The subsequent deprotection and Sonogashira coupling converted (*P*)-S-**2** to (*P*)-S-**4** in 81% yield and then to (*P*)-S-**6** in 65% yield. Because of poor solubility,

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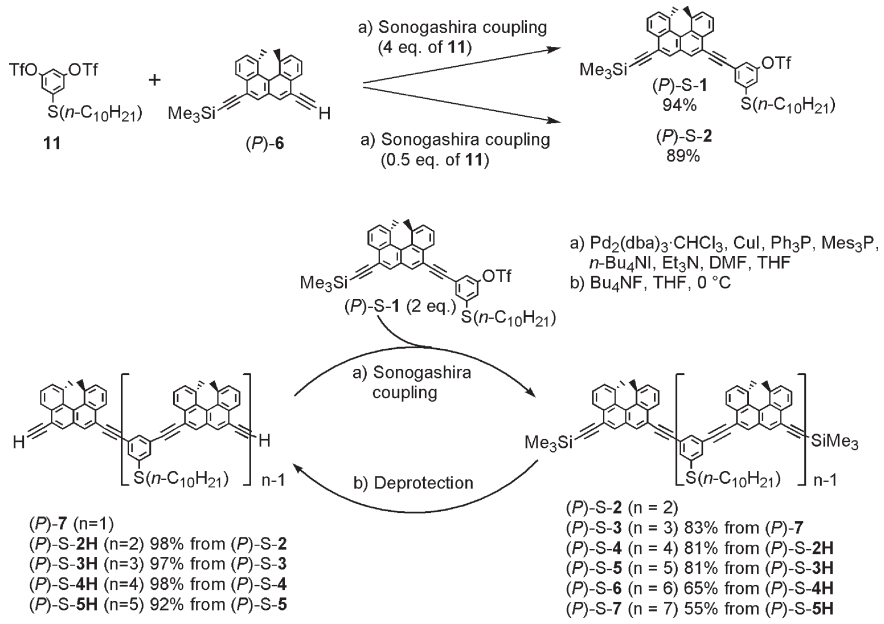
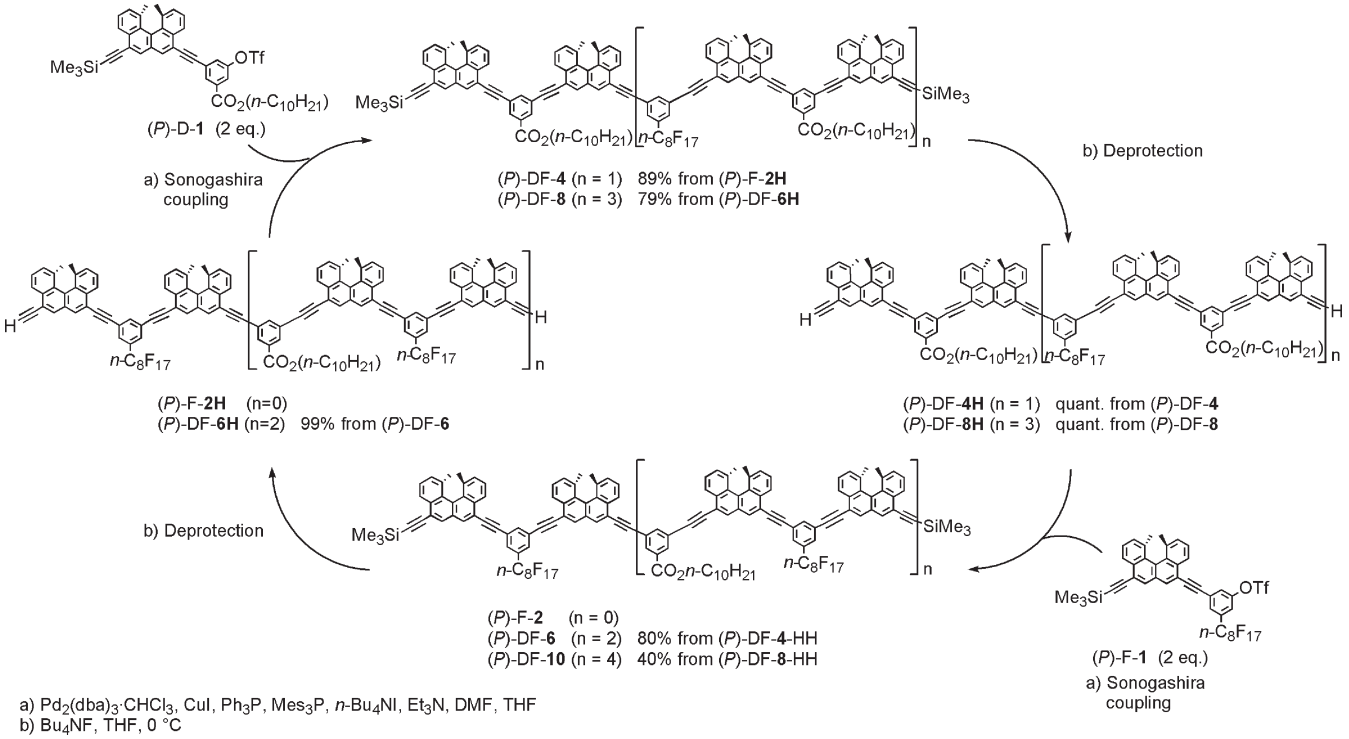
Scheme 4



Scheme 5



oligomers longer than (*P*)-S-**7** were not obtained in reasonable yields.

(*P*)-DF-***n*** (*n* = 4, 6, 8, 10) were synthesized using (*P*)-D-**1** with decyloxycarbonyl side chains[39a] and (*P*)-F-**1** with perfluorooctyl side chains (Scheme 5).[38] The tetramer (*P*)-DF-**4** was obtained in 89% yield by coupling (*P*)-F-**2H**[38] and (*P*)-D-**1**. After deprotection, (*P*)-DF-**4** was converted to the hexamer (*P*)-DF-**6** in 80% yield by coupling with (*P*)-F-**1**. Analogously, the octamer (*P*)-DF-**8** and the decamer (*P*)-DF-**10** were obtained in 79% and 40% yield, respectively.

Aggregation of (*P*)-D-*n*. Before conducting the study of the newly synthesized oligomers with different side chains, the

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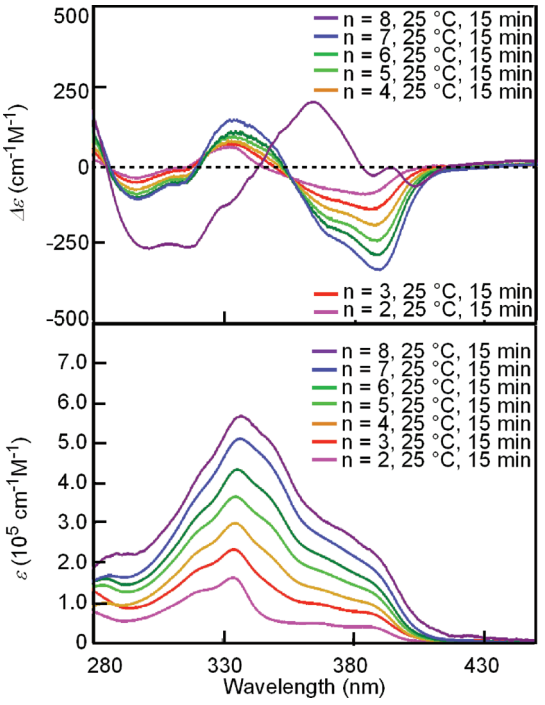

Figure 2. CD (top) and UV−vis (bottom) spectra (5×10^{-6} M, 25 °C) of (*P*)-D-***n*** ($n = 2-8$) in chloroform. Solutions were heated at 60 °C and then cooled to 25 °C. The spectra did not change between 15 and 30 min at 25 °C.

homoaggregation of (*P*)-D-***n*** ($n = 2-8$) was re-examined. CD and UV−vis analyses were conducted in chloroform and trifluoromethylbenzene, which are relatively weak and strong helix-forming solvents, respectively.[37a,b] In the previous work,[36a] spectroscopic studies were conducted within 5 min after dissolution at a concentration of 5×10^{-6} M to examine the unfolding rate. In this study, equilibrated states were examined by heating solutions at higher temperatures to unfold the double helix. Then the solutions were cooled to 25 °C, and the spectra after reaching a steady state were obtained.

In chloroform (5×10^{-6} M, 25 °C), the CD and UV−vis spectra of (*P*)-D-**2**, (*P*)-D-**3**, (*P*)-D-**4**, (*P*)-D-**5**, (*P*)-D-**6**, and (*P*)-D-**7** showed a monotonic increase in accordance with the number of helicenes (Figure 2). All spectra obtained after 15 min at 25 °C were unchanged after 30 min and were confirmed to be in an equilibrated state. The spectra were similar to those obtained in the previous study,[36a] which indicated random coil states for these compounds at equilibrium. (*P*)-D-**8** showed a slightly enhanced Cotton effect at 365 nm, and the spectrum was considered to reflect partial double helix formation. This explanation was supported by the observation that (*P*)-D-**8** provided a CD spectrum typical of a double helix at a higher concentration of 5×10^{-4} M in chloroform at 5 °C (Figure 3).

In trifluoromethylbenzene (5×10^{-6} M, 25 °C), the CD spectra of (*P*)-D-***n*** obtained after 15 min were confirmed to be equilibrated except for (*P*)-D-**6** and (*P*)-D-**7**, which reached steady state after 90 min and 2 h, respectively. The absolute CD values $|\Delta\varepsilon|$ at 335 and 385 nm for (*P*)-D-**2**, (*P*)-D-**3**, and (*P*)-D-**4** showed a monotonic increase in accordance with the number of helicenes. (*P*)-D-**5** showed a slightly different shape (Figure 4b), and (*P*)-D-**6**, (*P*)-D-**7**, and (*P*)-D-**8** showed quite different shapes; an increased $|\Delta\varepsilon|$ with maxima at 323 and

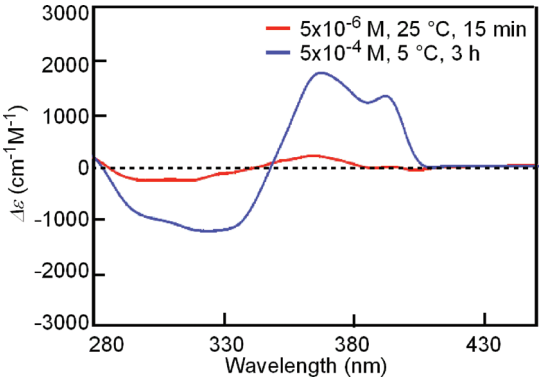

Figure 3. CD spectra (5×10^{-4} M) of (*P*)-D-**8** in chloroform. Solutions were heated at 60 °C and then cooled at 5 °C. The spectra did not change between 3 and 4 h at 25 °C. CD spectra of (*P*)-D-**8** (5×10^{-6} M, 25 °C) in chloroform are also shown.

365 nm (Figure 4a). The UV−vis spectra of the higher oligomers of (*P*)-D-***n*** ($n = 6-8$) showed a decrease in absorption and hypochromic shifts. The results of CD and UV−vis studies indicated stable double helix formation of (*P*)-D-**6**, (*P*)-D-**7**, and (*P*)-D-**8** in trifluoromethylbenzene at equilibrium.

At a higher concentration (1×10^{-3} M) in trifluoromethylbenzene, bimolecular aggregate formation was promoted, and even pentamer (*P*)-D-**5** exhibited the CD spectra of a double helix at 25 °C (Figure 5). At 10 °C, (*P*)-D-**4** also showed the enhanced Cotton effect of a double helix, while (*P*)-D-**2** and (*P*)-D-**3** did not (Figure 5). The dimeric aggregation of (*P*)-D-**4** at concentrations higher than 1×10^{-3} M was confirmed by VPO (trifluoromethylbenzene, 35 °C) (Figure S1).[40]

We previously reported that a cyclic ethynylhelicene oligomer containing three ethynylhelicenes and three *m*-phenylenes strongly forms a dimeric aggregate.[39] Taking account of this observation and the results obtained here, we assumed that one turn of the double helix contained three helicenes and three *m*-phenylenes, and at least four helicenes were required to form a helical conformation (Figure 6) in which one terminal helicene lay on the other.

In *m*-difluorobenzene and fluorobenzene, which are less hard aromatic solvents than trifluoromethylbenzene, (*P*)-D-**8** showed the CD spectra of a double helix (Figure 7). In soft solvents such as toluene, chlorobenzene, bromobenzene, and iodobenzene, (*P*)-D-**8** provided the CD spectra of random coils (Figure S2). In the following discussions, the stability of oligomers with different side chains is compared with that of the double helix formation of (*P*)-D-***n*** at equilibrium in these solvents.

Aggregation of (*P*)-bD-*n*. The CD and UV−vis spectra of (*P*)-bD-***n*** ($n = 2-6$) in chloroform (5×10^{-6} M, 25 °C) showed a monotonic increase in accordance with the number of helicenes and were similar to those of (*P*)-D-***n*** in the random coil state (Figure 8a).

In trifluoromethylbenzene, the CD spectra of (*P*)-bD-**6** reached equilibrium after 2 h and showed enhanced Cotton effects. Hypochromic shifts were observed in UV−vis spectra, which indicated double helix formation analogous to that of (*P*)-D-**6** (Figure 8b). A dimeric aggregate of (*P*)-bD-**6** was confirmed by VPO (trifluoromethylbenzene, 35 °C) (Figure 9).

In *m*-difluorobenzene and fluorobenzene, which are less hard aromatic solvents than trifluoromethylbenzene, (*P*)-bD-**6** showed CD spectra of random coils (Figure S3). In soft solvents

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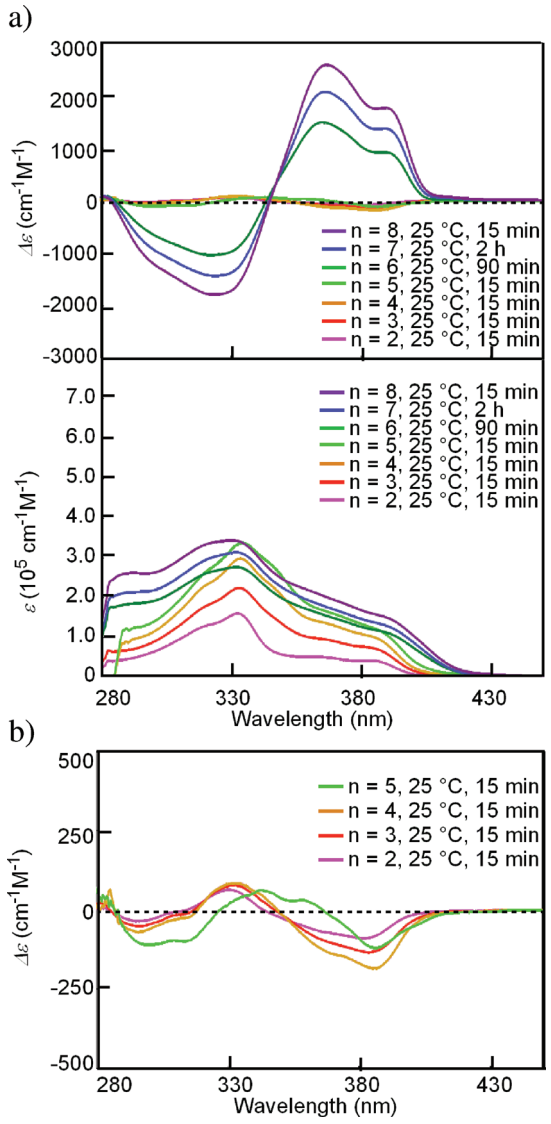

Figure 4. (a) CD (top) and UV−vis (bottom) spectra (5×10^{-6} M, 25 °C) of (*P*)-D-***n*** ($n = 2-8$) in trifluoromethylbenzene. Solutions were heated at 80 °C and then cooled to 25 °C. The spectra did not change between 15 and 30 min at 25 °C. As an exception to this, (*P*)-D-**6** and (*P*)-D-7 required 90 min and 2 h to reach the steady state at 25 °C, respectively. (b) Magnified CD spectra (5×10^{-6} M, 25 °C) of (*P*)-D-***n*** ($n = 2-5$) in trifluoromethylbenzene.

such as toluene, chlorobenzene, bromobenzene, and iodobenzene, (*P*)-bD-**6** showed CD spectra of random coils (Figure S4). The solvent effect on the aggregation of (*P*)-bD-**6** showed a tendency similar to that of (*P*)-D-**6**.

The stability of (*P*)-D-***n*** and (*P*)-bD-***n*** was compared on the basis of CD spectra in trifluoromethylbenzene. In both series, pentamers (*P*)-D-**5** and (*P*)-bD-**5** showed spectra of random coils at 5×10^{-6} M, and hexamers (*P*)-D-**6** and (*P*)-bD-**6** showed spectra of double helices (Figure 4 and Figure 8b). The aggregation was compared between (*P*)-D-**6** and (*P*)-bD-**6** at different temperatures and concentrations. A solution of (*P*)-D-**6** in trifluoromethylbenzene (5×10^{-6} M) was first heated at 60 °C, and the aggregate was unfolded to random coils and then cooled to 25, 5, and −10 °C. The CD spectrum of (*P*)-D-**6** showed double helix formation after 30 min at 25 °C, which did

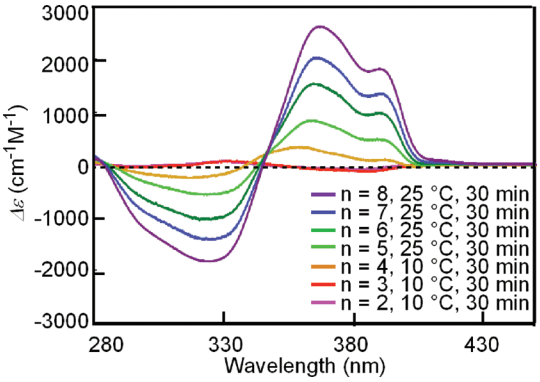

Figure 5. CD spectra (10 °C, 1×10^{-3} M) of (*P*)-D-***n*** ($n = 2-4$) and spectra (25 °C, 1×10^{-3} M) of (*P*)-D-***n*** ($n = 5-8$) in trifluoromethylbenzene. Solutions were heated at 60 °C and then cooled to 10 or 25 °C. The spectra did not change between 30 min and 1 h at each temperature.

Figure 6. Proposed model of the double helix structure. Two compounds that form a double helix are shown in different colors.

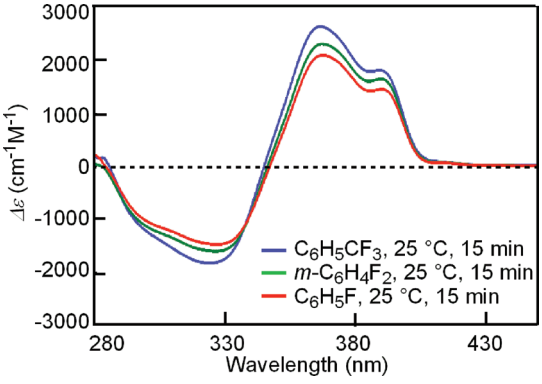

Figure 7. CD spectra (2.5×10^{-6} M, 25 °C) of (*P*)-D-**8** in trifluoromethybenzene, *m*-difluorobenzene, and fluorobenzene. Solutions were heated at 80 °C and then cooled to 25 °C. The spectra did not change between 15 and 30 min at 25 °C.

not change by cooling to 5 or −10 °C (Figure 10a). The same spectra were obtained at a higher concentration of 1×10^{-3} M at 5 °C (Figure 10a). Under the same conditions, (*P*)-bD-**6** showed CD spectra very similar to those of (*P*)-D-**6** (Figure 10b). The only exception was a slight decrease in the Cotton effect at a concentration of 5×10^{-6} M at 25 °C. The similar CD behavior of (*P*)-D-**6** and (*P*)-bD-**6** indicated that both compounds formed double helices with similar stabilities. The bulkiness at the side

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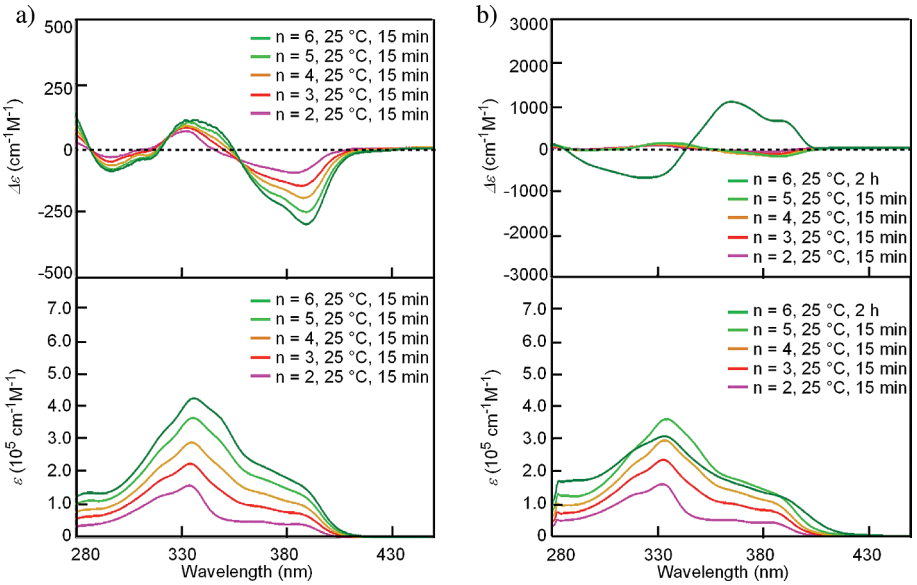

Figure 8. CD (top) and UV−vis (bottom) spectra (25 °C, 5×10^{-6} M) of (*P*)-bD-***n*** ($n = 2-6$), in (a) chloroform and (b) trifluoromethylbenzene. Solutions were heated at 60 °C in chloroform and at 80 °C in trifluoromethylbenzene and then cooled to 25 °C. The spectra did not change between 15 and 30 min at 25 °C. As an exception to this, (*P*)-D-**6** required 2 h to reach the steady state at 25 °C.

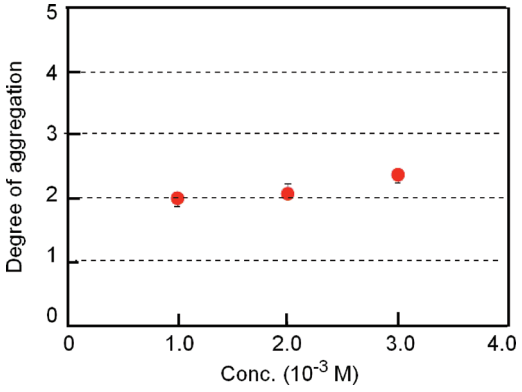

Figure 9. Degree of aggregation of (*P*)-bD-**6** obtained using VPO (trifluoromethylbenzene, 35 °C) at several concentrations. Circles represent an average of more than five measurements, and vertical lines represent a range of results.

chains did not affect the aggregation. The $\pi-\pi$ interactions of the aromatic array of helicenes and *m*-phenylenes, therefore, are crucial for double helix formation, and the interaction between side chains was unimportant. This observation is consistent with the double helix structure, in which the side chains occupy the outside of the double helix (Figure 6).

Aggregation of (*P*)-S-*n*. The aggregation of (*P*)-S-***n*** ($n = 2-7$) was examined using the same method described for (*P*)-bD-***n***. In chloroform (5×10^{-6} M, 25 °C), (*P*)-S-***n*** ($n = 2-7$) showed CD and UV−vis spectra of random coils with a monotonic increase as the number of helicenes increased (Figure 11a).

In trifluoromethylbenzene (5×10^{-6} M, 25 °C), the CD and UV−vis spectra of (*P*)-S-**2**, (*P*)-S-**3**, and (*P*)-S-**4** showed a monotonic enhancement of the Cotton effect indicating random coils. In contrast, the CD spectra of (*P*)-S-**6** and (*P*)-S-**7** showed a slow change at 25 °C, and reached a steady state after 7 and 18 h, respectively. The spectra at equilibrium were different from those of random coils, and significant hypochromic shifts were

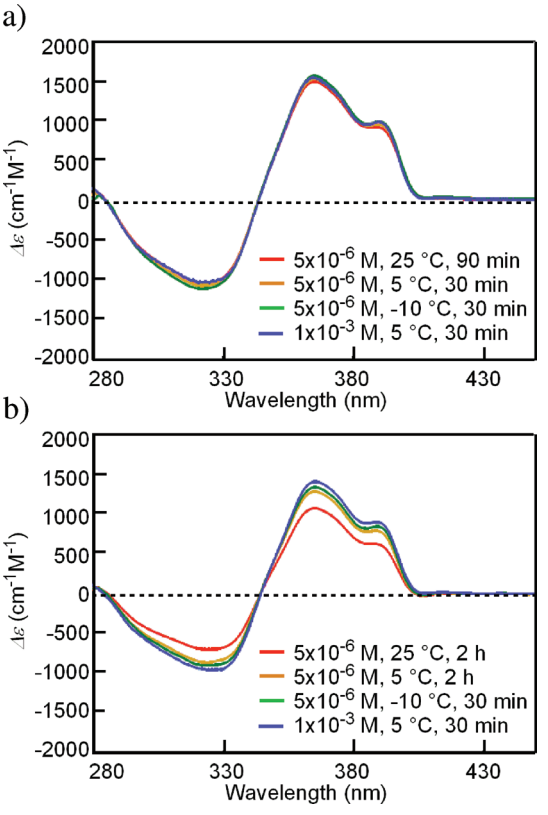

Figure 10. CD spectra (trifluoromethylbenzene) of (a) (*P*)-D-**6** and (b) (*P*)-bD-**6** at various temperatures and concentrations. Solutions at 5×10^{-6} M were heated at 60 °C and then cooled to 25, 5, and −10 °C. Solutions at 1×10^{-3} M were heated at 60 °C and then cooled to 5 °C. The spectra obtained under each set of conditions did not change after 30 min of each observation.

observed by UV−vis (Figure 11b). The results indicated aggregate formation by these longer oligomers. VPO analysis,

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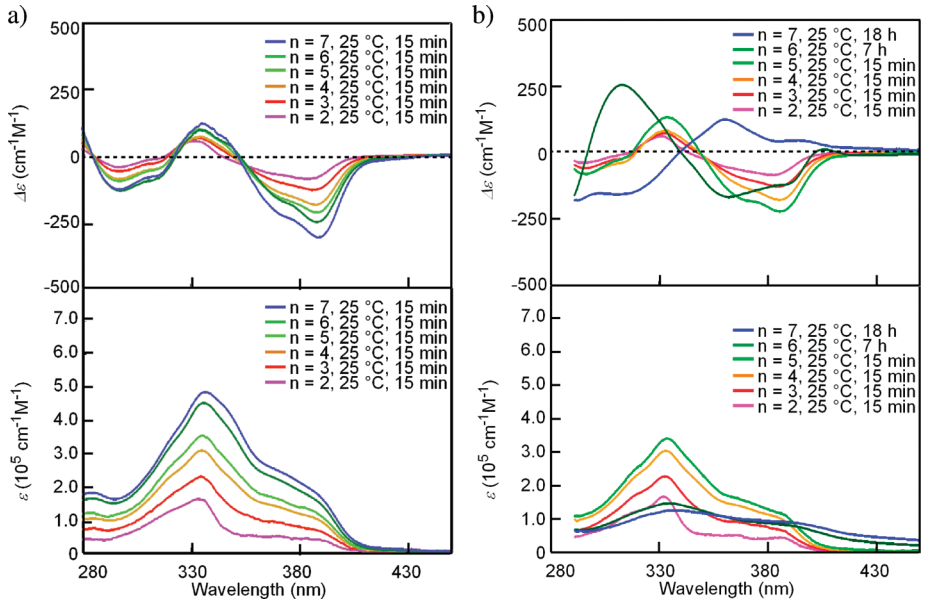

Figure 11. CD (top) and UV−vis (bottom) spectra (5×10^{-6} M, 25 °C) of (*P*)-S-***n*** ($n = 2-7$) in (a) chloroform and (b) trifluoromethylbenzene. Solutions were heated at 60 °C and then cooled to 25 °C. The spectra did not change between 15 and 30 min at 25 °C. As an exception to this, (*P*)-S-7 required 18 h to reach the steady state at 25 °C in trifluoromethylbenzene.

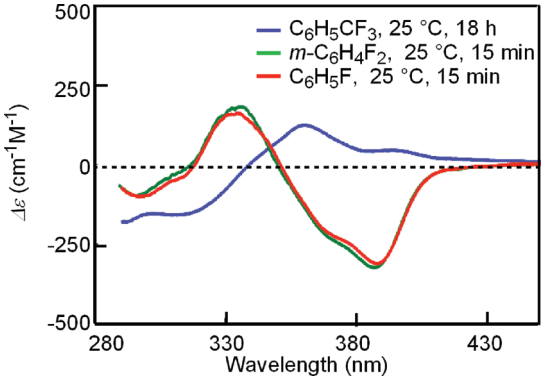

Figure 12. CD spectra (5×10^{-6} M, 25 °C) of (*P*)-S-7 in trifluoromethybenzene, *m*-difluorobenzene, and fluorobenzene. Solutions were heated at 60 °C and then cooled to 25 °C. The spectra did not change between 15 and 30 min at 25 °C. As an exception to this, (*P*)-S-7 required 18 h to reach the steady state at 25 °C in trifluoromethylbenzene.

however, could not be conducted because of their low solubility in trifluoromethylbenzene.

In less hard aromatic solvents such as *m*-difluorobenzene and fluorobenzene and soft solvents such as toluene, chlorobenzene, bromobenzene, and iodobenzene, (*P*)-S-7 gave the CD spectra (5×10^{-6} M, 25 °C) of random coils (Figures 12 and S5).

The aggregation of (*P*)-D-7 and (*P*)-S-7 in toluene was compared. The solutions of (*P*)-D-7 and (*P*)-S-7 in toluene were first heated at 60 °C to unfold to random coils and then cooled to 25 or 5 °C. Both (*P*)-D-7 and (*P*)-S-7 at 5×10^{-6} M showed CD spectra of random coils at 25 °C (Figure 13). At 1×10^{-3} M, (*P*)-S-7 was a random coil at 5 °C, while (*P*)-D-7 showed the CD spectrum of a double helix (Figure 13). The double helix of (*P*)-S-7 was less stable than that of (*P*)-D-7.

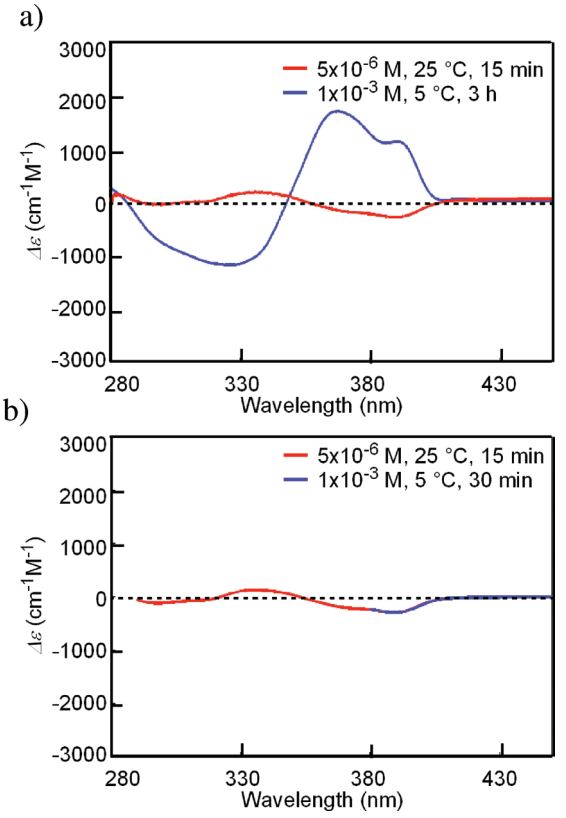

Figure 13. CD spectra (toluene) of (a) (*P*)-D-7 and (b) (*P*)-S-7 at various temperatures and concentrations. Solutions were heated at 60 °C and then cooled to 25 or 5 °C. The spectra (5×10^{-6} M) did not change between 15 and 30 min at 25 °C. The spectra (1×10^{-3} M) did not change after 30 min of each observation at25 °C. The spectrum of (*P*)-S-7 at 1×10^{-3} M was obtained at a wavelength region shorter than 380 nm because of UV−vis absorption of (*P*)-S-7.

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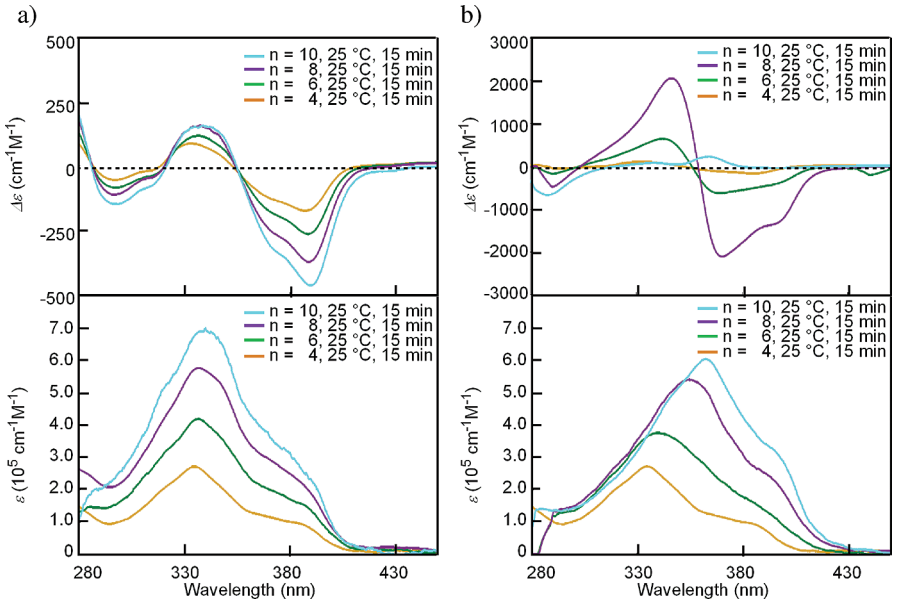

Figure 14. CD (top) and UV−vis (bottom) spectra (5×10^{-6} M, 25 °C) of (*P*)-DF-**4**, (*P*)-DF-**6**, (*P*)-DF-**8**, and (*P*)-DF-**10** (2.5×10^{-6} M for (*P*)-DF-**10**) in (a) chloroform and (b) trifluoromethylbenzene. Solutions were heated at 60 °C in chloroform and at 80 °C in trifluoromethylbenzene and then cooled to 25 °C. The spectra did not change between 15 and 30 min at 25 °C.

On the basis of our previous report[38] that (*P*)-F-**5** formed a more stable double helix than (*P*)-D-**5**, the order of stability was summarized as follows: (*P*)-F-***n*** > (*P*)-D-***n*** and (*P*)-bD-***n*** > (*P*)-S-***n***. This observation might be explained by the relation of double helix stability to the hardness of the *m*-phenylene moiety: (*P*)-F-***n*** possessing the harder *m*-phenylene formed a more stable double helix compared to that of (*P*)-S-***n***. The large π-electron systems of helicene moieties should be soft in nature.[36a] Then, (*P*)-F-***n*** has an alternating soft helicene moiety and hard *m*-phenylene moiety, whereas in contrast (*P*)-S-***n*** has soft arrays. The regular alternating arrangement of soft and hard moieties can form a rigid aggregate, which resulted in a stable double helix. Another explanation for the stability order can be related to the electronic nature of the *m*-phenylene moiety: electron-withdrawing side chains stabilized the aggregation. The tendency was experimentally supported by other groups[41,42] and our group[39d] in the case of arylene ethynylene macrocycles. We speculated in this study that the regular alternating arrangement of soft/hard and electron-rich/deficient moieties provides a rigid and stable double helix. Further systematic studies are required to examine this speculation.

Aggregation of (*P*)-DF-*n*. The aggregation of (*P*)-DF-***n*** (n = 4, 6, 8, 10) was examined in chloroform (5×10^{-6} M, 25 °C). CD and UV−vis showed spectra of random coil states with a monotonic increase with the number of helicenes (Figure 14a). In chloroform at 45 °C, (*P*)-DF-**4**, (*P*)-DF-**6**, and (*P*)-DF-**8** were monomeric by VPO at concentrations between 1×10^{-3} and 3×10^{-3} M (Figure S6). Thus, (*P*)-DF-**8** showed less tendency to form a double helix than (*P*)-D-**8**, which formed a partial double helix at 5×10^{-6} M in chloroform.

In trifluoromethylbenzene (5×10^{-6} M, 5 °C), (*P*)-DF-**4** showed a spectrum similar to that in chloroform (Figure 14b) and was monomeric at the concentrations from 1×10^{-3} to 3×10^{-3} M by VPO (45 °C) (Figure S7a).[40] Since (*P*)-D-**4** in the same solvent formed a double helix at concentrations higher than 2×10^{-3} M at 35 °C (Figure S1), (*P*)-DF-**4** showed less tendency to form a double helix than (*P*)-D-**4**. CD and UV−vis spectra of (*P*)-DF-**6** and (*P*)-DF-**8**, however, were different in trifluoromethylbenzene: the Cotton effects were considerably enhanced compared with those in chloroform (Figure 14b), and the absorption maxima in UV−vis shifted to the longer-wavelength region, 338 to 350 nm for (*P*)-DF-**6** and 339 to 358 nm for (*P*)-DF-**8**. The observations were different from (*P*)-D-***n***, which showed a regular increase in the Cotton effect for (*P*)-D-**4**, (*P*)-D-**5**, (*P*)-D-**6**, (*P*)-D-**7**, and (*P*)-D-**8** under the helix-forming conditions in trifluoromethylbenzene (Figure 4a, Figure 5). VPO analysis indicated that (*P*)-DF-**6** and (*P*)-DF-**8** formed aggregates higher than dimers (Figure S7b,c). The CD spectrum of (*P*)-DF-**10** in trifluoromethylbenzene (2.5×10^{-6} M, 25 °C) showed features different from those of (*P*)-DF-**6** and (*P*)-DF-**8** with weak Cotton effects. This may not be a random coil, because a significant shift of the UV−vis absorption maximum from 338 to 362 nm was observed, which was different from the UV−vis spectra in chloroform. The higher oligomers of (*P*)-DF-***n*** exhibited complex aggregation behavior in trifluoromethylbenzene.

In *m*-difluorobenzene, fluorobenzene, toluene, chlorobenzene, bromobenzene, and iodobenzene, (*P*)-DF-**8** showed spectra typical of random coils (Figures 15 and S8). The aggregation of (*P*)-DF-**8** was substantially less stable than that of (*P*)-D-**8**, which formed a double helix in *m*-difluorobenzene and fluorobenzene as well as in trifluoromethylbenzene.

The double helices of (*P*)-DF-***n*** were less stable than those of (*P*)-F-***n*** and (*P*)-D-***n***: (*P*)-F-***n*** and (*P*)-D-***n*** formed stable double helices, and (*P*)-DF-***n*** with alternating decyloxycarbonyl and perfluorooctyl side chains did not exhibit properties intermediate between (*P*)-F-***n*** and (*P*)-D-***n***. (*P*)-DF-***n*** possess a soft/electron-rich helicene moiety, a relatively soft/electron-deficient *m*-phenylene moiety with decyloxycarbonyl side chains, and a hard/electron-rich *m*-phenylene moiety with perfluorooctyl side chains. The low stability of (*P*)-DF-***n*** aggregates may be

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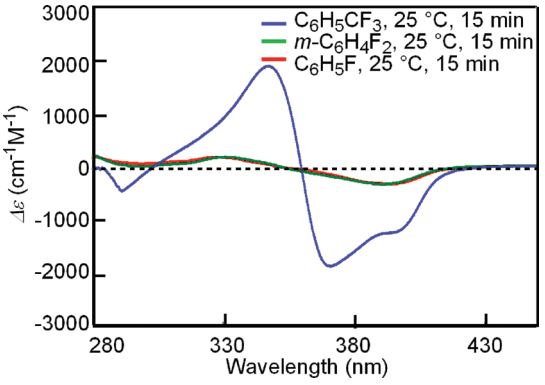

Figure 15. CD spectra (2.5×10^{-6} M, 25 °C) of (*P*)-DF-***8*** in trifluoromethybenzene, *m*-difluorobenzene, and fluorobenzene. Solutions were heated at 80 °C and then cooled to 25 °C. The spectra did not change between 15 and 30 min at 25 °C.

consistent with our speculation on the stable double helix formation with regular alternating arrangement of soft/hard and/or electron-rich/deficient moieties.

CONCLUSIONS

In summary, three series of ethynylhelicene oligomers with different side chains were synthesized: (*P*)-bD-***n*** with bulky alkyloxycarbonyl side chains; (*P*)-S-***n*** with decylsulfanyl side chains; and (*P*)-DF-***n*** with alternating decyloxycarbonyl and perfluorooctyl side chains. Double helix formation by these compounds was compared with that of (*P*)-D-***n***. (*P*)-bD-***n*** with bulky alkyloxycarbonyl side chains showed a double helix formation similar to that of (*P*)-D-***n***, which indicated bulkiness of side chains to be unimportant. It is considered that the side chains reside outside the double helix, and the aromatic rings aggregate via $\pi-\pi$ interactions. The double helix of (*P*)-S-***n*** was substantially less stable than that of (*P*)-D-***n***. The result indicated the important role of hardness and/or electron-deficient nature at *m*-phenylene moieties. (*P*)-DF-***n*** with alternating perfluorooctyl side chains and decyloxycarbonyl side chains did not form a stable double helix. It was speculated that the regular alternating soft/hard and/or electron-rich/deficient arrangement of helicenes and *m*-phenylenes is important for stable double helix formation. Further systematic studies are required to examine this speculation. Side chains of ethynylhelicene oligomers play significant roles in determining the stability of double helices.

EXPERIMENTAL SECTION

General Methods. ^{1}H NMR spectra were recorded on a 400 or 600 MHz spectrometer with tetramethylsilane as an internal standard (δ 0.00). ^{13}C NMR spectra were recorded on a 400 or 600 MHz spectrometer and calibrated using residual solvent $CDCl_3$ (δ 77.0). ^{19}F NMR spectra were recorded on a 400 or 600 MHz spectrometer with trifluoroacetic acid as an internal or external standard (δ −79.0). Chemical shifts are expressed in parts per million (ppm, δ). Coupling constants are expressed in hertz. FAB mass spectra were recorded using *m*-nitrobenzyl alchohol matrix. MALDI-TOF MS spectra were obtained using α-cyano-4-hydroxycinnamic acid as the matrix. Vapor pressure osmometry (VPO) was conducted using benzil as a standard. CD and UV−vis spectra were recorded using distilled or spectrophotomeric grade commercial solvents. The ratio of solvent mixture shows vol/vol.

4-Methyl-2-(2-methylpropyl)-pentanoic Acid Ethyl Ester, ***2***. Under an argon atmosphere, a mixture of diisobutylmalonic acid diethyl ester **1** (6.38 g, 23.4 mmol), lithium chloride (5.96 g, 0.141 mol), and water (2.50 mL, 0.140 mmol) in dimethyl sulfoxide (68 mL) was heated under reflux for 24 h. Then the mixture was cooled to room temperature, and saturated aqueous ammonium chloride was added. After being stirred for 1 h, the organic materials were extracted with ethyl acetate three times. The organic layer was washed with water and brine and dried over magnesium sulfate. The solvent was evaporated under reduced pressure, and separation by silica gel chromatography gave **2** as colorless oil (3.88 g, 19.4 mmol, 83%). LRMS (EI, 70 eV) *m*/*z*: 201 ($[M + H]^+$, 1.1%), 144 ($[M - C_4H_8]$, 81%), 101 ($[M - C_7H_{15}]^+$, 100%). HRMS *m*/*z* calcd for $C_{12}H_{25}O_2^+$: 201.1834. Found: 201.1855. IR (KBr) 2957, 2871, 1736, 1178 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.87 (6H, d, *J* = 6.4 Hz), 0.90 (6H, d, *J* = 6.4 Hz), 1.16−1.22 (2H, m), 1.25 (3H, t, *J* = 7.2 Hz), 1.49−1.51 (4H, m), 2.50 (1H, tt, *J* = 4.8 Hz), 4.13 (2H, q, *J* = 7.2 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.3, 22.0, 23.0, 26.1, 41.7, 42.2, 59.9, 176.9.

4-Methyl-2-(2-methylpropyl)-pentanol, ***3***. Under an argon atmosphere, to a suspension of lithium alminium hydride (878 mg, 23.1 mmol) in tetrahydrofuran (67 mL) was slowly added **2** (3.86 g, 19.3 mmol) in tetrahydrofuran (10 mL) at −100 °C. Then the mixture was warmed to 0 °C, and stirred for 2 h. At the temperature, sodium sulfate decahydrate was added slowly until formation of hydrogen stopped. Then, water (2−3 mL) was added, which was followed by excess sodium sulfate. After being stirred at room temperature overnight, insoluble materials were filtrated through Celite and washed with tetrahydrofuran three times. The solvent was evaporated under reduced pressure, and separation by silica gel chromatography gave **3** as colorless oil (2.95 g, 19.3 mmol, 97%). LRMS (EI, 70 eV) *m*/*z*: 140.15 ($[M - H_2O]$, 9.9%), 83 ($[C_5H_7O]^+$, 65%), 71 ($[C_4H_7O]^+$, 95%), 57 ($[C_4H_9]^+$, 100%), 43 ($[C_3H_7]^+$, 72%). HRMS (FAB) *m*/*z* calcd for $C_{20}H_{45}O_2^+$ ($[2M - H]^+$): 317.3414. Found: 317.3432. IR (KBr) 3325 (br), 2954, 2917, 2871, 1468, 1048 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.88 (6H, d, *J* = 6.4 Hz), 0.89 (6H, d, *J* = 6.4 Hz), 1.07 (2H, ddd, *J* = 12.8, 6.4 Hz), 1.22 (2H, ddd, *J* = 12.8, 6.4 Hz), 1.55−1.71 (3H, m), 1.71−1.83 (1H, m, br), 3.51 (2H, d, *J* = 4.8 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.8, 23.0, 25.2, 35.6, 41.1, 66.0.

4-Methyl-2-(2-methylpropyl)-pentyl Benzoate, ***4***. Under an argon atmosphere, a mixture of **3** (1.02 g, 6.43 mmol), 3,5-dihydroxybenzoic acid (1.04 g, 6.75 mmol), and conc sulfonic acid (0.01 mL) in dry 1,4-dioxane (13 mL) was heated under reflux for 22 h. After the mixture was cooled to room temperature, saturated aqueous ammonium chloride was added. The organic materials were extracted with ethyl acetate. The organic layer was washed with water and brine and dried over magnesium sulfate. The solvent was evaporated under reduced pressure, and separation by silica gel chromatography gave **4** as white solid (1.38 g, 4.68 mmol, 73%). Mp 98−100 °C (ethyl acetate−hexane). LRMS (EI, 70 eV) *m*/*z*: 294 ($[M]^+$, 24%), 154 ($[M - C_{10}H_{20}]$, 100%), 138 ($[M - C_{10}H_{20}O]$, 85%). HRMS *m*/*z* calcd for $C_{17}H_{26}O_4$: 294.1831. Found: 294.1840. IR (KBr) 3648 (br), 3304 (br), 2956, 1688, 1607, 1453, 1242, 1150 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.90 (6H, d, *J* = 6.4 Hz), 0.91 (6H, d, *J* = 6.4 Hz), 1.17 (2H, ddd, *J* = 12.8, 6.4 Hz), 1.28 (2H, ddd, *J* = 12.8, 6.4 Hz), 1.70 (2H, ddqq, *J* = 6.4 Hz), 1.85−1.94 (1H, m), 4.18 (2H, d, *J* = 5.2 Hz), 5.22 (2H, s), 6.58 (1H, t, *J* = 2.4 Hz), 7.11 (2H, d, *J* = 2.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.7, 23.0, 25.2, 32.9, 41.6, 68.7, 107.5, 109.1, 132.5, 156.9, 166.8.

4-Methyl-2-(2-methylpropyl)pentyl 3,5-Bis(trifluoromethanesulfoxy)-benzoate, ***5***. To a solution of **4** (1.15 g, 3.91 mmol) in pyridine (15 mL) was slowly added trifluoromethanesulfonic acid anhydride (1.6 mL, 9.7 mmol) at −30 °C. The mixture was gradually warmed to room temperature and stirred for 3 h. The reaction mixture was diluted with ethyl acetate, and saturated aqueous ammonium chloride was added. The organic materials were extracted with ethyl acetate. The organic layer was washed

with saturated aqueous sodium hydrogencarbonate, water, and brine and dried over magnesium sulfate. The solvent was evaporated under reduced pressure, and separation by silica gel chromatography gave **5** as white solid (2.15 g, 3.84 mmol, 98%). Mp 76−77 °C (hexane−methanol). LRMS (EI, 70 eV) *m*/*z*: 401 ($[M - C_{10}H_{21}O]^+$, 54%), 83 ($[C_6H_{11}]^+$, 100%). HRMS (FAB) *m*/*z* calcd for $C_{19}H_{23}F_6O_8S_2$ ($[M - H]^+$): 557.0733. Found: 557.0735. IR (KBr) 2960, 1719, 1434, 1250, 1224, 1138 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (6H, d, J = 6.8 Hz), 0.93 (6H, d, J = 6.8 Hz), 1.16−1.30 (4H, m), 1.67−1.74 (2H, m), 1.89−1.99 (1H, m), 4.26 (2H, d, J = 5.6 Hz), 7.44 (1H, t, J = 2.4 Hz), 7.98 (2H, d, J = 2.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.6, 23.0, 25.3, 32.9, 41.8, 70.0, 118.6 (q, J_{C-F} = 319 Hz), 119.6, 122.4, 134.7, 149.4, 162.9. ^{19}F NMR (376 MHz, $CDCl_3$, trifluoroacetic acid (δ −79.0) as an external standard) δ −75.3 (6F, s).

*(P)-Building Block with 4-Methyl-2-(2-methylpropyl)-pentanoxycarbonyl Side Chains, (P)-bD-**1***. Under an argon atmosphere, a mixture of **5** (1.23 g, 2.20 mmol), tris(dibenzylideneacetone)dipalladium(0) chloroform adduct (45.6 mg, 0.0440 mmol), cuprous iodide (101 mg, 0.0528 mmol), tris(2,4,6-trimethylphenyl)phosphine (103 mg, 0.264 mmol), triphenylphosphine (69.3 mg, 0.264 mmol), tetrabutylammonium iodide (1.30 g, 2.20 mmol), triethylamine (0.70 mL), *N*,*N*-dimethylformamide (6.6 mL), and tetrahydrofuran (2.6 mL) was freeze-evacuated three times in flask A. In flask B, a solution of monosilylated ethynylhelicene (*P*)-**6**[39a] (332 mg, 0.881 mmol) in tetrahydrofuran (4.0 mL) was freeze-evacuated three times, and the mixture was slowly added to flask A. The mixture was stirred at room temperature for 1 h. The reaction was quenched by adding saturated aqueous ammonium chloride, and the organic materials were extracted with toluene. The organic layer was washed with water and brine and dried over magnesium sulfate. The solvents were evaporated under reduced pressure, and separation by silica gel chromatography and recycling GPC gave (*P*)-bD-**1** as a yellow solid (588 mg, 0.749 mmol, 85%). Mp 64−66 °C (toluene−methanol). $[\alpha]^{27}_D$ −348 (*c* 0.50, $CHCl_3$). MALDI-TOF MS *m*/*z* calcd for $C_{45}H_{47}F_3O_5SSi$: 784.2866. Found: 784.4. UV−vis ($CHCl_3$, 5×10^{-6} M) λ_{max} (ε) 334 nm (7.3×10^4). CD ($CHCl_3$, 5×10^{-6} M) λ ($\Delta\varepsilon$) 261 nm (57), 295 nm (−19), 331 nm (27), 383 nm (−44). IR (KBr) 2956, 2148, 1729, 1429, 1248 cm^{-1}. Anal. ($C_{45}H_{47}F_3O_5SSi$) Calcd: C, 68.85; H, 6.03. Found: C, 68.82; H, 6.00. ^1H NMR (400 MHz, $CDCl_3$) δ 0.39 (9H, s), 0.94 (6H, d, J = 6.4 Hz), 0.96 (6H, d, J = 6.4 Hz), 1.24 (2H, ddd, J = 12.8, 6.4 Hz), 1.32 (2H, ddd, J = 12.8, 6.4 Hz), 1.70−1.80 (2H, m), 1.92 (6H, s), 1.93 (6H, s), 1.93−2.01 (1H, m), 4.28 (2H, d, J = 5.6 Hz), 7.45 (1H, d, J = 8.4 Hz), 7.47 (1H, d, J = 8.4 Hz), 7.67 (1H, dd, J = 8.4 Hz), 7.69 (1H, dd, J = 8.4 Hz), 7.76 (1H, dd, J = 1.6 Hz), 7.92 (1H, dd, J = 1.6, 1.2 Hz), 8.01 (1H,s), 8.06 (1H, s), 8.35 (1H, dd, J = 1.6, 1.2 Hz), 8.43 (2H, d, J = 8.4 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.097, 22.7, 23.06, 23.14, 23.2, 25.3, 33.0, 41.8, 69.5, 91.1, 91.4, 100.3, 102.9, 118.7 (q, J_{C-F} = 319 Hz), 118.9, 120.4, 121.9, 123.3, 123.7, 126.3, 126.9, 127.0, 128.1, 129.2, 129.3, 129.8, 130.3, 130.78, 130.82, 130.9, 131.9, 132.45, 132.53, 133.3, 136.8, 137.0, 137.1, 149.3, 164.2. ^{19}F NMR (376 MHz, $CDCl_3$, trifluoroacetic acid (δ−79.0) as an external standard) δ −75.5 (3F, s).

*(P)-Dimer with 4-Methyl-2-(2-methylpropyl)-pentanoxycarbonyl Side Chains, (P)-bD-**2***. Under an argon atmosphere, a mixture of tris(dibenzylideneacetone)dipalladium(0) chloroform adduct (8.52 mg, 0.00823 mmol), cuprous iodide (18.8 mg, 0.0988 mmol), tris-(2,4,6-trimethylphenyl)phosphine (19.2 mg, 0.0494 mmol), triphenylphosphine (13.0 mg, 0.494 mmol), tetrabutylammonium iodide (243 mg, 0.648 mmol), triethylamine (0.11 mL), *N*,*N*-dimethylformamide (1.1 mL), and tetrahydrofuran (0.2 mL) was freeze-evacuated three times in flask A. In flask B, a mixture of monosilylated ethynylhelicene (*P*)-**6**[39a] (56.7 mg, 0.151 mmol) and **5** (42.1 mg, 0.0753 mmol) in tetrahydrofuran (4.0 mL) was freeze-evacuated three times, and the mixture was slowly added to flask A. The mixture was stirred at 45 °C for 4 h. The reaction was quenched by adding saturated aqueous ammonium chloride, and the organic materials were extracted with toluene. The organic layer was washed with water and brine and dried over magnesium sulfate. The solvents were evaporated under reduced pressure, and separation by silica gel chromatography and recycling GPC gave (*P*)-bD-**2** as a yellow solid (72.4 mg, 0.715 mmol, 95%). Mp 158−160 °C (toluene−methanol). $[\alpha]^{27}_D$ −591 (*c* 0.50, $CHCl_3$). MALDI-TOF MS *m*/*z* calcd for $C_{71}H_{70}O_2Si_2$: 1010.5. Found: 1010.4. UV−vis ($CHCl_3$, 5×10^{-6} M) λ_{max} (ε) 334 nm (1.6×10^5). CD ($CHCl_3$, 5×10^{-6} M) λ ($\Delta\varepsilon$) 262 nm (115), 296 nm (−35), 333 nm (67), 385 nm (−87). IR (KBr) 2954, 2147, 1724, 1247 cm^{-1}. Anal. ($C_{71}H_{70}O_2Si_2$) Calcd: C, 84.31; H, 6.98. Found: C, 84.43; H, 7.24. ^1H NMR (400 MHz, $CDCl_3$) δ 0.40 (18H, s), 0.98 (6H, d, J = 6.8 Hz), 0.99 (6H, d, J = 6.8 Hz), 1.26 (6H, ddd, J = 13.6, 6.8 Hz), 1.38 (2H, ddd, J = 13.6, 6.8 Hz), 1.74−1.84 (2H, m), 1.92 (6H, s), 1.98−2.05 (1H, m), 4.31 (2H, d, J = 5.6 Hz), 7.43 (2H, d, J = 7.2 Hz), 7.46 (2H, d, J = 7.2 Hz), 7.65 (2H, dd, J = 8.0, 7.2 Hz), 7.70 (2H, dd, J = 8.0, 7.2 Hz), 8.01 (2H, s), 8.05 (2H, s), 8.19 (2H, t, J = 1.2 Hz), 8.35 (2H, d, J = 1.2 Hz), 8.44 (2H, d, J = 8.0 Hz), 8.54 (2H, d, J = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.14, 22.8, 23.16, 23.18, 25.4, 33.1, 41.8, 69.0, 89.4, 92.9, 100.2, 103.1, 119.6, 120.3, 123.5, 123.6, 124.3, 126.6, 126.9, 129.1, 129.8, 130.8, 130.9, 131.5, 132.1, 132.31, 132.35, 136.7, 136.8, 138.2, 165.5.

*Deprotected (P)-Dimer with 4-Methyl-2-(2-methylpropyl)-pentanoxycarbonyl Side Chains, (P)-bD-**2H** (Typical Procedure for Desilylation of (P)-bD-**n**)*. To a solution of (*P*)-bD-**2** (60.2 mg, 0.0595 mmol) in tetrahydrofuran (0.9 mL) was added 1.0 M tetrabutylammonium fluoride in tetrahydrofuran (0.18 mL, 0.18 mmol) at 0 °C. After 30 min of stirring at the temperature, saturated aqueous ammonium chloride was added. The organic materials were extracted with toluene. The organic layer was washed with water and brine and dried over magnesium sulfate. The solvents were evaporated under reduced pressure, and silica gel chromatography gave (*P*)-bD-**2H** (51.6 mg, 0.0595 mmol, quant). Mp 145−149 °C, decomp (toluene−methanol). $[\alpha]^{27}_D$ −582 (*c* 0.50, $CHCl_3$). MALDI-TOF MS *m*/*z* calcd for $C_{65}H_{54}O_2$: 866.4. Found: 866.6. UV−vis ($CHCl_3$, 5×10^{-6} M) λ_{max} (ε) 330 nm (1.5×10^5). CD ($CHCl_3$, 5×10^{-6} M) λ ($\Delta\varepsilon$) 264 nm (112), 297 nm (−37), 329 nm (64), 383 nm (−84). IR (KBr) 2952, 2205, 1719, 1240 cm^{-1}. Anal. ($C_{65}H_{54}O_2$) calcd for: C, 90.03; H, 6.28. Found: C, 89.88; H, 6.56. ^1H NMR (400 MHz, $CDCl_3$) δ 0.98 (6H, d, J = 6.4 Hz), 0.99 (6H, d, J = 6.4 Hz), 1.26 (6H, ddd, J = 13.6, 6.8 Hz), 1.38 (2H, ddd, J = 13.6, 6.8 Hz), 1.74−1.82 (2H, m), 1.94 (12H, s), 1.98−2.05 (1H, m), 3.56 (2H, s), 4.31 (2H, d, J = 5.6 Hz), 7.45 (2H, d, J = 7.2 Hz), 7.49 (2H, d, J = 7.2 Hz), 7.65 (2H, dd, J = 8.0, 7.2 Hz), 7.71 (2H, dd, J = 8.0, 7.2 Hz), 8.04 (2H, s), 8.07 (2H, s), 8.17 (2H, t, J = 1.6 Hz), 8.34 (2H, d, J = 1.6 Hz), 8.44 (2H, d, J = 8.0 Hz), 8.53 (2H, d, J = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.8, 23.16, 23.18, 25.4, 33.1, 41.8, 69.0, 81.8, 82.4, 89.3, 93.0, 119.4, 119.7, 123.5, 124.3, 126.8, 126.9, 127.0, 129.19, 129.24, 129.8, 130.4, 130.8, 130.9, 131.5, 132.1, 132.3, 132.4, 136.8, 136.9, 138.2, 165.5.

*(P)-Trimer with 4-Methyl-2-(2-methylpropyl)-pentanoxycarbonyl Side Chains, (P)-bD-**3** (Typical Procedure for the Sonogashira Coupling Reaction of (P)-bD-**n**)*. Under an argon atmosphere, a mixture of tris(dibenzylideneacetone)dipalladium(0) chloroform adduct (13.2 mg, 0.0127 mmol), cuprous iodide (29.1 mg, 0.1529 mmol), tris(2,4,6-trimethylphenyl)phosphine (29.7 mg, 0.764 mmol), triphenylphosphine (20.1 mg, 0.0764 mmol), tetrabutylammonium iodide (376 mg, 0.255 mmol), triethylamine (0.12 mL), *N*,*N*-dimethylformamide (1.2 mL), and tetrahydrofuran (0.2 mL) was freeze-evacuated three times in flask A. In flask B, a mixture of diethynylhelicene (*P*)-**7**[39a] (38.8 mg, 0.127 mmol) and (*P*)-bD-**1** (200 mg, 0.255 mmol) in tetrahydrofuran (1.0 mL) was freeze-evacuated three times, and the mixture was slowly added to flask A. The mixture was stirred at 45 °C for 4 h. The reaction was quenched by adding saturated aqueous ammonium chloride, and the organic materials were extracted with toluene three times. The combined organic layer was washed with water and brine and dried over

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magnesium sulfate. The solvents were evaporated under reduced pressure, and separation by silica gel chromatography and recycling GPC gave (*P*)-bD-**3** as a yellow solid (182 mg, 0.116 mmol, 91%). Mp 175−177 °C (toluene−methanol). $[\alpha]^{27}_{D}$ −592 (*c* 0.50, $CHCl_3$). MALDI-TOF MS *m*/*z* calcd for $C_{112}H_{108}O_4Si_2$: 1572.8. Found: 1572.4. UV−vis ($CHCl_3$, 5×10^{-6} M) λ_{max} (ε) 335 nm (2.5×10^5). CD ($CHCl_3$, 5×10^{-6} M) λ ($\Delta\varepsilon$) 264 nm (174), 296 nm (−52), 333 nm (81), 387 nm (−146). IR (KBr) 2954, 2148, 1724, 1242 cm^{-1}. Anal. ($C_{112}H_{108}O_4Si_2$) Calcd: C, 85.45; H, 6.91. Found: C, 85.56; H, 6.90. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.40 (18H, s), 0.99 (12H, d, *J* = 6.4 Hz), 1.00 (12H, d, *J* = 6.4 Hz), 1.26 (4H, ddd, *J* = 12.8, 6.4 Hz), 1.39 (4H, ddd, *J* = 12.8, 6.4 Hz), 1.75−1.85 (4H, m), 1.93 (6H, s), 1.95 (6H, s), 1.99 (6H, s), 1.99−2.05 (2H, m), 4.32 (4H, d, *J* = 5.6 Hz), 7.44 (2H, d, *J* = 7.2 Hz), 7.47 (2H, d, *J* = 7.2 Hz), 7.50 (2H, d, *J* = 7.2 Hz), 7.66 (2H, dd, *J* = 8.0, 7.2 Hz), 7.71 (2H, dd, *J* = 8.0, 7.2 Hz), 7.73 (2H, dd, *J* = 8.0, 7.2 Hz), 8.02 (2H, s), 8.06 (2H, s), 8.11 (2H, s), 8.20 (2H, dd, *J* = 1.6, 1.2 Hz), 8.35 (2H, dd, *J* = 1.2 Hz), 8.36 (2H, dd, *J* = 1.6 Hz), 8.44 (2H, d, *J* = 8.0 Hz), 8.54 (2H, d, *J* = 8.0 Hz), 8.56 (2H, d, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.13, 22.8, 23.16, 23.23, 25.4, 33.1, 41.9, 69.0, 89.3, 89.4, 92.9, 93.0, 100.2, 103.1, 119.6, 119.8, 120.3, 123.5, 123.6, 123.7, 124.3, 124.4, 126.6, 126.8, 126.9, 127.0, 129.1, 129.2, 129.3, 129.9, 130.8, 130.9, 131.0, 131.5, 132.1, 132.2, 132.4, 136.7, 136.86, 136.92, 138.3, 165.5.

*Deprotected (P)-Trimer with 4-Methyl-2-(2-methylpropyl)-pentanoxycarbonyl Side Chains, (P)-bD-**3H***. The compound (76.7 mg, 0.0536 mmol, quant) was prepared from (*P*)-bD-**3** (84.5 mg, 0.0536 mmol). Mp 167−170 °C, decomp (toluene−methanol). $[\alpha]^{21}_{D}$ −603 (*c* 0.50, $CHCl_3$). MALDI-TOF MS *m*/*z* calcd for $C_{106}H_{92}O_4$: 1428.7. Found: 1428.9. UV−vis ($CHCl_3$, 5×10^{-6} M) λ_{max} (ε) 331 nm (2.1×10^5). CD ($CHCl_3$, 5×10^{-6} M) λ ($\Delta\varepsilon$) 264 nm (175), 297 nm (−51), 330 nm (71), 387 nm (−136). IR (KBr) 2954, 2208, 1724, 1240 cm^{-1}. Anal. ($C_{106}H_{92}O_4$) Calcd: C, 89.04; H, 6.49. Found: C, 89.04; H, 6.43. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.98 (12H, d, *J* = 6.8 Hz), 0.99 (12H, d, *J* = 6.4 Hz), 1.26 (4H, ddd, *J* = 14.7, 7.0 Hz), 1.39 (4H, ddd, *J* = 13.6, 6.8 Hz), 1.75−1.85 (4H, m), 1.95 (12H, s), 1.99 (6H, s), 1.99−2.05 (2H, m), 3.56 (2H, s), 4.31 (4H, d, *J* = 5.6 Hz), 7.45−7.51 (6H, m), 7.66 (2H, dd, *J* = 8.0, 7.2 Hz), 7.72 (2H, dd, *J* = 8.0, 7.2 Hz), 7.73 (2H, dd, *J* = 8.0, 7.2 Hz), 8.05 (2H, s), 8.08 (2H, s), 8.12 (2H, s), 8.19 (2H, dd, *J* = 1.6 Hz), 8.34 (2H, dd, *J* = 1.6 Hz), 8.36 (2H, dd, *J* = 1.6 Hz), 8.44 (2H, d, *J* = 8.0 Hz), 8.54 (2H, d, *J* = 8.0 Hz), 8.55 (2H, d, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.8, 23.17, 23.19, 23.24, 25.4, 33.1, 41.9, 69.0, 81.8, 82.4, 89.3, 92.96, 93.01, 119.4, 119.75, 119.83, 123.5, 124.3, 126.8, 126.86, 126.94, 126.99, 127.03, 129.2, 129.25, 129.31, 129.8, 129.9, 130.4, 130.8, 130.9, 131.0, 131.1, 131.5, 132.1, 132.2, 132.4, 136.8, 136.9, 137.0, 138.3, 165.5.

*(P)-Tetramer with 4-Methyl-2-(2-methylpropyl)-pentanoxycarbonyl Side Chains, (P)-bD-**4***. The compound (86.2 mg, 0.0403 mmol, 92%) was prepared from (38.0 mg, 0.0438 mmol) and (*P*)-bD-**1** (68.8 mg, 0.0877 mmol) as a yellow solid. Mp 187−189 °C (toluene−methanol). $[\alpha]^{27}_{D}$ −566 (*c* 0.50, $CHCl_3$). MALDI-TOF MS *m*/*z* calcd for $C_{153}H_{146}O_6Si_2$: 2135.1. Found: 2135.6. UV−vis ($CHCl_3$, 5×10^{-6} M) λ_{max} (ε) 335 nm (2.9×10^5). CD ($CHCl_3$, 5×10^{-6} M) λ ($\Delta\varepsilon$) 264 nm (237), 296 nm (−66), 333 nm (87), 387 nm (−193). IR (KBr) 2953, 2146, 1724, 1239 cm^{-1}. Anal. ($C_{153}H_{146}O_6Si_2$) Calcd: C, 85.99; H, 6.89. Found: C, 85.97; H, 7.00. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.40 (18H, s), 0.98−1.02 (36H, m), 1.23−1.31 (6H, m), 1.36−1.44 (6H, m), 1.75−1.84 (6H, m), 1.94 (6H, s), 1.95 (6H, m), 2.00 (12H, s), 2.00−2.05 (3H, m), 4.32−4.34 (6H, m), 7.45 (2H, d, *J* = 7.2 Hz), 7.48 (2H, d, *J* = 7.2 Hz), 7.51 (4H, d, *J* = 7.2 Hz), 7.66 (2H, dd, *J* = 8.0, 7.2 Hz), 7.70−7.76 (6H, m), 8.02 (2H, s), 8.06 (2H, s), 8.12 (4H, s), 8.21 (2H, dd, *J* = 1.6 Hz), 8.22 (1H, dd, *J* = 1.6 Hz), 8.35 (2H, dd, *J* = 1.6 Hz), 8.37 (4H, dd, *J* = 1.6 Hz), 8.44 (2H, d, *J* = 7.2 Hz), 8.54−8.58 (6H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.13, 22.8, 23.15, 23.25, 25.4, 33.1, 41.8, 69.0, 89.3, 89.4, 92.9, 93.0, 100.2, 103.1, 119.6, 119.8, 120.3, 123.5, 123.59, 123.64, 124.3, 124.34, 124.4, 126.6, 126.8, 126.9, 127.0, 129.1, 129.2, 129.3, 129.8, 130.8, 130.9, 130.93, 131.0, 131.5, 132.1, 132.2, 132.3, 136.7, 136.86, 136.92, 138.2, 165.5.

*Deprotected (P)-Tetramer with 4-Methyl-2-(2-methylpropyl)-pentanoxycarbonyl Side Chains, (P)-bD-**4H***. The compound (45.5 mg, 0.0228 mmol, 98%) was prepared from (*P*)-bD-**4** (50.0 mg, 0.0234 mmol) as a yellow solid. Mp 205−208 °C, decomp (toluene−methanol). $[\alpha]^{27}_{D}$ −572 (*c* 0.50, $CHCl_3$). MALDI-TOF MS *m*/*z* calcd for $C_{147}H_{130}O_6$: 1991.0. Found: 1990.3. UV−vis ($CHCl_3$, 5×10^{-6} M) λ_{max} (ε) 332 nm (2.7×10^5). CD ($CHCl_3$, 5×10^{-6} M) λ ($\Delta\varepsilon$) 265 nm (235), 297 nm (−51), 330 nm (83), 387 nm (−184). IR (KBr) 2953, 2205, 1724, 1240 cm^{-1}. Anal. ($C_{147}H_{130}O_6$) Calcd: C, 88.61; H, 6.58. Found: C, 88.33; H, 6.83. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.97−1.01 (36H, m), 1.23−1.30 (6H, m), 1.35−1.43 (6H, m), 1.76−1.83 (6H, m), 1.94 (12H, s), 1.99 (12H, s), 1.99−2.04 (3H, m), 3.56 (2H, s), 4.31−4.33 (6H, m), 7.45 (2H, d, *J* = 6.8 Hz), 7.48 (2H, d, *J* = 7.2 Hz), 7.51 (4H, d, *J* = 6.8 Hz), 7.66 (2H, dd, *J* = 8.0, 7.2 Hz), 7.69−7.76 (6H, m), 8.05 (2H, s), 8.08 (2H, s), 8.13 (4H, s), 8.19 (2H, dd, *J* = 1.6 Hz), 8.22 (1H, dd, *J* = 1.6 Hz), 8.34 (2H, dd, *J* = 1.6 Hz), 8.35−8.36 (4H, m), 8.44 (2H, d, *J* = 8.0 Hz), 8.53−8.57 (6H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 22.8, 23.16, 23.24, 25.4, 33.1, 41.9, 69.0, 81.8, 82.4, 89.3, 92.95, 93.01, 119.4, 119.7, 119.8, 123.5, 123.6, 124.3, 126.8, 126.87, 126.94, 126.99, 127.04, 129.19, 129.24, 129.3, 129.8, 129.9, 130.4, 130.82, 130.84, 130.9, 131.0, 131.1, 131.5, 132.1, 132.2, 132.4, 136.8, 136.9, 137.0, 138.3, 165.5.

*(P)-Pentamer with 4-Methyl-2-(2-methylpropyl)-pentanoxycarbonyl Side Chains, (P)-bD-**5***. The compound (133 mg, 0.0494 mmol, 92%) was prepared from (*P*)-bD-**3H** (76.7 mg, 0.0536 mmol) and (*P*)-bD-**1** (84.2 mg, 0.107 mmol) as a yellow solid. Mp 189−191 °C (toluene−methanol). $[\alpha]^{21}_{D}$ −550 (*c* 0.50, $CHCl_3$). MALDI-TOF MS *m*/*z* calcd for $C_{194}H_{184}O_8Si_2$: 2697.4. Found: 2696.9. UV−vis ($CHCl_3$, 5×10^{-6} M) λ_{max} (ε) 336 nm (3.7×10^5). CD ($CHCl_3$, 5×10^{-6} M) λ ($\Delta\varepsilon$) 264 nm (304), 297 nm (−83), 334 nm (101), 389 nm (−248). IR (KBr) 2954, 2150, 1726, 1240 cm^{-1}. Anal. ($C_{194}H_{184}O_8Si_2$) Calcd: C, 86.31; H, 6.87. Found: C, 86.37; H, 7.10. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.39 (18H, s), 0.97−1.01 (48H, m), 1.22−1.30 (8H, m), 1.35−1.43 (8H, m), 1.74−1.83 (8H, m), 1.93 (6H, s), 1.94 (6H, s), 1.99 (12H, s), 2.00 (6H, s), 2.00−2.04 (4H, m), 4.30−4.33 (8H, m), 7.44 (2H, d, *J* = 6.8 Hz), 7.47 (2H, d, *J* = 7.2 Hz), 7.49−7.52 (6H, m), 7.66 (2H, dd, *J* = 8.0, 7.2 Hz), 7.69−7.76 (8H, m), 8.01 (2H,s), 8.06 (2H, s), 8.11−8.12 (6H, m), 8.20 (2H, dd, *J* = 1.6, 1.2 Hz), 8.21 (2H, dd, *J* = 1.6, 1.2 Hz), 8.34 (2H, dd, *J* = 1.6, 1.2 Hz), 8.35−8.36 (6H, m), 8.43 (2H, d, *J* = 7.6 Hz), 8.53−8.57 (8H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.12, 22.8, 23.16, 23.23, 25.4, 33.1, 41.9, 69.0, 89.3, 89.4, 92.9, 93.0, 100.2, 103.1, 119.6, 119.8, 120.3, 123.5, 123.58, 123.65, 124.3, 126.6, 126.8, 126.9, 127.0, 129.1, 129.2, 129.3, 129.9, 130.8, 130.9, 131.0, 131.47, 131.48, 132.1, 132.2, 132.3, 136.7, 136.86, 136.93, 138.2, 165.5.

*(P)-Hexamer with 4-Methyl-2-(2-methylpropyl)-pentanoxycarbonyl Side Chains, (P)-bD-**6***. The compound (147 mg, 0.0451 mmol, 94%) was prepared from (*P*)-bD-**4H** (96.0 mg, 0.0482 mmol) and (*P*)-bD-**1** (75.6 mg, 0.0964 mmol) as a yellow solid. Mp 190−193 °C (toluene−methanol). $[\alpha]^{27}_{D}$ −506 (*c* 0.50, $CHCl_3$). MALDI-TOF MS *m*/*z* calcd for $C_{235}H_{222}O_{10}Si_2$: 3259.6. Found: 3260.5. UV−vis ($CHCl_3$, 5×10^{-6} M) λ_{max} (ε) 336 nm (4.3×10^5). CD ($CHCl_3$, 5×10^{-6} M) λ ($\Delta\varepsilon$) 264 nm (354), 297 nm (−88), 336 nm (111), 389 nm (−295). IR (KBr) 2954, 2148, 1724, 1239 cm^{-1}. Anal. ($C_{235}H_{222}O_{10}Si_2$) Calcd: C, 86.52; H, 6.86. Found: C, 86.35; H, 7.11. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.39 (18H, s), 0.97−1.01 (60H, m), 1.23−1.35 (10H, m), 1.36−1.43 (10H, m), 1.74−1.85 (10H, m), 1.92 (6H, s), 1.94 (6H, s), 1.98−2.06 (29H, m), 4.30−4.32 (10H, m), 7.44 (2H, d, *J* = 7.2 Hz), 7.46−7.51 (10H, m), 7.66 (2H, dd, *J* = 8.0, 7.2 Hz), 7.69−7.75 (10H, m), 8.01 (2H, s), 8.05 (2H, s), 8.10 (4H, s), 8.11 (4H, m), 8.19 (1H, dd, *J* = 1.6 Hz), 8.20−8.22 (4H, m), 8.33 (2H, dd, *J* = 1.6 Hz), 8.34−8.36 (8H, m), 8.43 (2H, d, *J* = 8.0 Hz), 8.53−8.57 (10H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.12, 22.8, 23.16, 23.25, 25.4, 29.7, 33.1, 41.8, 69.0, 89.3, 89.4, 92.9,

93.0, 100.2, 103.0, 119.6, 119.8, 120.3, 123.5, 123.57, 123.64, 124.3, 126.6, 126.8, 126.9, 127.0, 129.1, 129.2, 129.3, 129.8, 130.8, 130.9, 131.0, 131.4, 132.1, 132.2, 132.3, 136.7, 136.87, 136.92, 138.2, 165.5.

5-Decylsulfanyl-1,3-dimethoxybenzene, ***9***. Under an argon atmosphere, a mixture of potassium carbonate (3.90 g, 28.2 mmol), 3,5-dimethoxybenzenethiol **8** (2.67 g, 15.7 mmol), acetone (64 mL), and 1-bromodecane (6.6 mL, 31.4 mmol) was heated under reflux for 2 h. After insoluble materials were filtered, the solvent was evaporated under reduced pressure. Separation by silica gel chromatography gave **9** as colorless oil (4.71 g, 15.2 mmol, 97%). LRMS (EI, 70 eV) *m*/*z*: 310 ($[M]^+$, 27%), 170 ($[M - C_{10}H_{20}]^+$, 100%). HRMS *m*/*z* calcd for $C_{18}H_{30}O_2S$: 310.1966. Found: 310.1945. IR (neat) 2923, 1585, 1455, 1417, 1204, 1157 cm^{-1}. Anal. ($C_{18}H_{30}O_2S$) Calcd: C, 69.63; H, 9.74. Found: C, 69.67; H, 9.71. ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 6.8 Hz), 1.26−1.30 (12H, m), 1.37−1.45 (2H, m), 1.66 (2H, quint, *J* = 7.2 Hz), 2.90 (2H, t, *J* = 7.2 Hz), 3.77 (6H, s), 6.26 (1H, t, *J* = 2.0 Hz), 6.46 (2H, d, *J* = 3.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.6, 28.9, 29.0, 29.1, 29.3, 29.48, 29.51, 31.8, 33.1, 55.3, 97.8, 106.0, 139.2, 160.8.

5-Decylsulfanyl-1,3-dihydroxybenzene, ***10***. Under an argon atmosphere, to a solution of **9** (4.63 g, 16.4 mmol) in dichloromethane (42 mL) was slowly added boron tribromide (1 M dichloromethane solution, 33 mL, 32.8 mmol) at −78 °C. Then the mixture was warmed to room temperature and stirred for 36 h. The reaction was quenched by slowly adding water (84 mL) at 0 °C, and the organic materials were extracted with ethyl acetate. The organic layer was washed with water and brine and dried over magnesium sulfate. The solvents were evaporated under reduced pressure, and separation by silica gel chromatography gave **10** as white solid (3.91 g, 13.8 mmol, 84%). Mp 94−96 °C (ethyl acetate). LRMS (EI, 70 eV) *m*/*z*: 282 ($[M]^+$, 29%), 142 ($[M - C_{10}H_{20}]^+$, 100%). HRMS *m*/*z* calcd for $C_{16}H_{26}O_2S$: 282.1653. Found: 282.1644. IR (KBr) 3252, 2920, 1624, 1594, 1485, 1471 cm^{-1}. Anal. ($C_{16}H_{26}O_2S$) Calcd: C, 68.04; H, 9.28. Found: C, 67.97; H, 9.14. ^1H NMR (400 MHz, $CDCl_3$−CD_3OD) δ 0.89 (3H, t, *J* = 6.8 Hz), 1.23−1.34 (12H, m), 1.38−1.46 (2H, m), 1.65 (2H, quint, *J* = 7.6 Hz), 2.88 (2H, t, *J* = 7.6 Hz), 6.13 (1H, t, *J* = 2.0 Hz), 6.32 (2H, d, *J* = 2.0 Hz) 7.56 (2H, s). ^{13}C NMR (100 MHz, $CDCl_3$−CD_3OD) δ 13.2, 22.1, 28.3, 28.59, 28.63, 28.7, 29.0, 31.3, 32.3, 99.7, 106.2, 138.2, 157.6.

5-Decylsulfanyl-1,3-bis(trifluoromethanesulfonyloxy)benzene, ***11***. Under an argon atmosphere, to a mixture of **10** (3.75 g, 13.3 mmol), dichloromethane (13 mL), and triethylamine (13 mL) was slowly added trifluoromethanesulfonic acid unhydride (7.4 mL, 43.8 mmol) at −40 °C. The reaction mixture was warmed to room temperature, and was stirred for 3 h. The reaction was quenched by adding saturated aqueous ammonium chloride, and the organic materials were extracted with ethyl acetate. The organic layer was washed with saturated aqueous sodium hydrogencarbonate, brine, and dried over magnesium sulfate. The solvent was evaporated under reduced pressure, and separation by silica gel chromatography gave **11** as colorless oil (6.44 g, 11.8 mmol, 89%). LRMS (EI, 70 eV) *m*/*z*: 546 ($[M]^+$, 100%), 406 ($[M - C_{10}H_{20}]^+$, 69%), 149 ($[CF_3O_3S]^+$, 28%). HRMS *m*/*z* calcd for $C_{18}H_{24}F_6O_6S_3$: 546.0639. Found: 546.0628. IR (neat) 2928, 1604, 1578, 1431, 1213, 1139 cm^{-1}. Anal. ($C_{18}H_{24}F_6O_6S_3$) Calcd: C, 39.55; H, 4.43. Found: C, 39.79; H, 4.46. ^1H NMR (400 MHz, $CDCl_3$) δ 0.88 (3H, t, *J* = 7.2 Hz), 1.23−1.34 (12H, m), 1.41−1.48 (2H, m), 1.70 (2H, quint, *J* = 7.2 Hz), 2.97 (2H, t, *J* = 7.2 Hz), 6.96 (1H, t, *J* = 2.0 Hz), 7.16 (2H, d, *J* = 2.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.0, 22.7, 28.3, 28.8, 29.1, 29.3, 29.4, 29.5, 31.9, 32.6, 111.3, 118.6 (q, J_{C-F} = 319.2 Hz), 119.3, 144.3, 149.5. ^{19}F NMR (376 MHz, $CDCl_3$) δ −75.6 (6F, s).

*(P)-Building Block with Decylthio Side Chains, (P)-S-****1***. Under an argon atmosphere, a mixture of tris(dibenzylidenacetone)dipalladium-(0)-chloroform adduct (24.1 mg, 0.0232 mmol), cuprous iodide (53.1 mg, 0.279 mmol), trimesitylphosphine (54.2 mg, 0.139 mmol), triphenylphosphine (36.6 mg, 0.139 mmol), tetrabutylammonium iodide (687 mg, 1.86 mmol), triethylamine (0.78 mL), and *N*,*N*-dimethylformamide (7.8 mL) was freeze-evacuated three times in flask A. In flask B, a solution of monosilylated ethynylhelicene (*P*)-***6***[39a] (350 mg, 0.930 mmol) and **11** (1.02 g, 1.86 mmol) in *N*,*N*-dimethylformamide (7.8 mL) was freeze-evacuated three times, and the mixture was slowly added to flask A. The mixture was stirred at room temperature for 1 h. The reaction was quenched by adding saturated aqueous ammonium chloride, and the organic materials were extracted with toluene. The organic layer was washed with water and brine and dried over magnesium sulfate. The solvents were evaporated under reduced pressure, and separation by silica gel chromatography and recycling GPC gave (*P*)-S-**1** as a yellow solid (635 mg, 0.821 mmol, 88%). Mp 58−59 °C. (diethyl ether−methanol). $[\alpha]^{26}_D$ −297 (*c* 0.10, $CHCl_3$). LRMS (EI, 70 eV) *m*/*z*: 772 ($[M]^+$, 100%). HRMS *m*/*z* calcd for $C_{44}H_{47}F_3O_3S_2Si$: 772.2688. Found: 772.2674. IR (KBr) 2925, 2210, 2148, 1596, 1246, 1215 1139 cm^{-1}. Anal. ($C_{44}H_{47}F_3O_3S_2Si$) Calcd: C, 68.36; H, 6.13. Found: C, 68.28; H, 6.21. ^1H NMR (400 MHz, $CDCl_3$) δ 0.38 (9H, s), 0.87 (3H, t, *J* = 7.2 Hz), 1.23−1.36 (12H, m), 1.43−1.51 (2H, m), 1.72 (2H, quint, *J* = 7.2 Hz), 1.927 (3H, s), 1.931 (3H, s), 3.01 (2H, t, *J* = 7.2 Hz), 7.17 (1H, t, *J* = 2.0 Hz), 7.33 (1H, dd, *J* = 2.0 Hz, 1.6 Hz), 7.45 (1H, d, *J* = 6.8 Hz), 7.46 (1H, d, *J* = 6.8 Hz), 7.57 (1H, t, *J* = 1.6 Hz), 7.65 (1H, dd, *J* = 8.0, 6.8 Hz), 7.69 (1H, dd, *J* = 8.0, 6.8 Hz), 8.01 (1H, s), 8.04 (1H, s), 8.42 (1H, d, *J* = 8.0 Hz), 8.43 (1H, d, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.37, 14.1, 22.7, 23.13, 23.14, 28.6, 28.8, 29.1, 29.3, 29.46, 29.51, 31.9, 33.0, 90.1, 92.0, 100.3, 103.0, 118.7 (q, J_{C-F} = 318.3 Hz), 119.2, 120.0, 120.4, 120.7, 123.4, 123.5, 123.7, 125.9, 126.8, 126.9, 127.0, 129.16, 129.24, 129.8, 130.0, 130.3, 130.8, 130.92, 130.94, 131.9, 132.4, 136.8, 136.9, 141.5, 149.4. ^{19}F NMR (376 MHz, $CDCl_3$) δ −75.4 (3F, s).

*(P)-Dimer with Decylthio Side Chains, (P)-S-****2***. Under an argon atmosphere, a mixture of tris(dibenzylidenacetone)dipalladium(0)-chloroform adduct (7.8 mg, 0.0076 mmol), cuprous iodide (17.3 mg, 0.0908 mmol), trimesitylphosphine (17.6 mg, 0.0454 mmol), triphenylphosphine (11.9 mg, 0.0454 mmol), tetrabutylammonium iodide (224 mg, 0.605 mmol), triethylamine (0.18 mL), and *N*,*N*-dimethylformamide (1.3 mL) was freeze-evacuated three times in flask A. In flask B, a solution of monosilylated ethynylhelicene (*P*)-***6***[39a] (114 mg, 0.303 mmol) and **11** (82.6 mg, 0.151 mmol) in *N*,*N*-dimethylformamide (2.3 mL) was freeze-evacuated three times, and the mixture was slowly added to flask A. The mixture was stirred at the room temperature for 1 h. The reaction was quenched by adding saturated aqueous ammonium chloride, and the organic materials were extracted with toluene. The organic layer was washed with water and brine and dried over magnesium sulfate. The solvents were evaporated under reduced pressure, and separation by silica gel chromatography and recycling GPC gave (*P*)-S-**2** as a yellow solid (135 mg, 0.135 mmol, 89%). Mp 126−128 °C. (chloroform−methanol). $[\alpha]^{27}_D$ −629 (*c* 0.10, $CHCl_3$). HRMS (FAB) *m*/*z* calcd for $C_{70}H_{70}SSi_2$: 998.4737. Found: 998.4723. UV−vis ($CHCl_3$, 5×10^{-6} M) λ_{max} (ε) 333 nm (1.6×10^5). CD ($CHCl_3$, 5×10^{-6} M) λ ($\Delta\varepsilon$) 297 nm (−44), 332 nm (54), 384 nm (−88). IR (KBr) 2925, 2147, 1248 cm^{-1}. Anal. ($C_{70}H_{70}SSi_2$) Calcd: C, 84.11; H, 7.06. Found: C, 83.92; H, 7.05. ^1H NMR (400 MHz, $CDCl_3$) δ 0.39 (18H, s), 0.86 (3H, t, *J* = 7.2 Hz), 1.23−1.38 (12H, m), 1.46−1.54 (2H, m), 1.75 (2H, quint, *J* = 7.2 Hz), 1.93 (6H, s), 1.94 (6H, s), 3.06 (2H, t, *J* = 7.2 Hz), 7.45 (2H, d, *J* = 7.2 Hz), 7.47 (2H, d, *J* = 7.2 Hz), 7.64 (2H, d, *J* = 1.6 Hz), 7.66 (2H, dd, *J* = 8.0, 7.2 Hz), 7.70 (2H, dd, *J* = 8.0, 7.2 Hz), 7.82 (1H, t, *J* = 1.6 Hz), 8.03 (2H, s), 8.06 (2H, s), 8.43 (2H, d, *J* = 8.0 Hz), 8.52 (2H, d, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.13, 14.1, 22.7, 23.15, 23.18, 28.9, 29.0, 29.2, 29.3, 29.5, 29.6, 31.9, 33.4, 88.8, 93.5, 100.1, 103.1, 119.9, 120.3, 123.6, 123.7, 124.3, 126.6, 126.9, 129.1, 129.2, 129.7, 129.9, 130.9, 130.97, 131.00, 131.1, 132.1, 132.3, 136.7, 136.9, 138.5.

*Deprotected (P)-Dimer with Decylthio Side Chains, (P)-S-****2H*** *(Typical Procedure for Desilylation of (P)-S-****n****)*. To a solution of (*P*)-S-**2** (106 mg, 0.106 mmol) in tetrahydrofuran (3.5 mL) was added

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tetrabutylammonium fluoride (1.0 M tetrahydrofuran solution, 0.32 mL, 0.32 mmol) at 0 °C, and the mixture was stirred at the temperature for 30 min. The reaction was quenched by adding saturated aqueous ammonium chloride, and the organic materials were extracted with toluene. The organic layer was washed with water and brine and dried over magnesium sulfate. The solvents were evaporated under reduced pressure, and separation by silica gel chromatography gave (*P*)-S-**2H** as a yellow solid (89.2 mg, 0.104 mmol, 98%). Mp 115−117 °C (chloroform−methanol). $[\alpha]^{27}_{D}$ −612 (*c* 0.10, $CHCl_3$). HRMS (FAB) *m*/*z* calcd for $C_{64}H_{54}S$: 854.3946. Found: 854.3948. IR (KBr) 3290, 2924 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 0.85 (3H, t, *J* = 6.8 Hz), 1.24−1.36 (12H, m), 1.46−1.54 (2H, m), 1.76 (2H, quint, *J* = 7.2 Hz), 1.95 (12H, s), 3.06 (2H, t, *J* = 7.2 Hz), 3.56 (2H, s), 7.46 (2H, d, *J* = 7.2 Hz), 7.48 (2H, d, *J* = 7.2 Hz), 7.64 (2H, d, *J* = 1.6 Hz), 7.66 (2H, dd, *J* = 7.6, 7.2 Hz), 7.71 (2H, dd, *J* = 7.6, 7.2 Hz), 7.82 (1H, t, *J* = 1.6 Hz), 8.06 (2H, s), 8.08 (2H, s), 8.45 (2H, d, *J* = 7.6 Hz), 8.52 (2H, d, *J* = 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 23.2, 28.9, 29.0, 29.2, 29.3, 29.5, 29.6, 31.9, 33.4, 81.8, 82.4, 88.7, 93.5, 119.3, 120.0, 123.5, 123.6, 124.3, 126.7, 126.9, 127.0, 129.19, 129.22, 129.6, 130.4, 130.87, 130.90, 130.94, 131.2, 131.8, 132.2, 132.3, 136.8, 136.9, 138.6.

*(P)-Trimer with Decylthio Side Chains, (P)-S-**3** (Typical Procedure for the Sonogashira Coupling Reaction of (P)-S-**n**).* Under an argon atmosphere, a mixture of (*P*)-S-**1** (147 mg, 0.190 mmol), tris(dibenzylidenacetone)dipalladium(0)-chloroform adduct (9.8 mg, 0.0095 mmol), cuprous iodide (21.7 mg, 0.114 mmol), trimesitylphosphine (22.1 mg, 0.0570 mmol), triphenylphosphine (14.9 mg, 0.0570 mmol), tetrabutylammonium iodide (281 mg, 0.760 mmol), triethylamine (0.11 mL), *N*,*N*-dimethylformamide (0.77 mL), and tetrahydrofuran (0.39 mL) was freeze-evacuated three times in flask A. In flask B, a solution of diethynylhelicene (*P*)-7[39a] (28.9 mg, 0.0950 mmol) in tetrahydrofuran (1.2 mL) was freeze-evacuated three times, and the mixture was slowly added to flask A. The mixture was stirred at 45 °C for 1.5 h. The reaction was quenched by adding saturated aqueous ammonium chloride, and the organic materials were extracted with toluene three times. The combined organic layer was washed with water and brine and dried over magnesium sulfate. The solvents were evaporated under reduced pressure, and separation by silica gel chromatography and recycling GPC gave (*P*)-S-**3** as a yellow solid (123 mg, 0.0792 mmol, 83%). Mp 137−139 °C (chloroform−methanol). $[\alpha]^{27}_{D}$ −624 (*c* 0.10, $CHCl_3$). MALDI-TOF MS *m*/*z* calcd for $^{12}C_{109}{}^{13}CH_{108}S_2Si_2$: 1549.7. Found: 1550.2. UV−vis ($CHCl_3$, 5 × 10^{-6} M) λ_{max} (ε) 334 nm (2.3 × 10^5). CD ($CHCl_3$, 5 × 10^{-6} M) λ ($\Delta\varepsilon$) 297 nm (−60), 334 nm (64), 386 nm (−129). IR (KBr) 2923, 2146, 1248 cm^{-1}. Anal. ($C_{110}H_{108}S_2Si_2$) Calcd: C, 85.22; H, 7.02. Found: C, 85.04; H, 7.16. ^1H NMR (400 MHz, $CDCl_3$) δ 0.39 (18H, s), 0.86 (6H, t, *J* = 7.2 Hz), 1.23−1.40 (24H, m), 1.47−1.54 (4H, m), 1.76 (4H, quint, *J* = 7.2 Hz), 1.94 (6H, s), 1.95 (6H, s), 1.99 (6H, s), 3.07 (4H, t, *J* = 7.2 Hz), 7.45 (2H, d, *J* = 7.2 Hz), 7.47 (2H, d, *J* = 7.2 Hz), 7.50 (2H, d, *J* = 7.2 Hz), 7.64−7.75 (10H, m), 7.83 (2H, t, *J* = 1.6 Hz), 8.03 (2H, s), 8.06 (2H, s), 8.12 (2H, s), 8.43 (2H, d, *J* = 7.6 Hz), 8.52 (2H, d, *J* = 7.6 Hz), 8.54 (2H, d, *J* = 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.13, 14.1, 22.7, 23.15, 23.18, 23.23, 28.9, 29.0, 29.2, 29.3, 29.5, 29.6, 31.9, 33.4, 88.7, 88.8, 93.4, 93.5, 100.1, 103.1, 119.8, 120.0, 120.2, 123.57, 123.64, 124.30, 124.32, 126.5, 126.6, 126.87, 126.94, 129.1, 129.16, 129.24, 129.7, 129.9, 130.8, 130.96, 130.99, 131.1, 131.8, 132.1, 132.2, 132.3, 136.7, 136.8, 136.9, 138.5.

*Deprotected (P)-Trimer with Decylthio Side Chains, (P)-S-**3H**.* The compound (266 mg, 189 mmol, 97%) was prepared from (*P*)-S-**3** (302 mg, 0.195 mmol) as a yellow solid. Mp 123−125 °C (chloroform−methanol). $[\alpha]^{27}_{D}$ −670 (*c* 0.10, $CHCl_3$). MALDI-TOF MS *m*/*z* calcd for $^{12}C_{103}{}^{13}CH_{92}S_2$: 1405.7. Found: 1406.4. IR (KBr) 3290, 2924 cm^{-1}. Anal. ($C_{104}H_{92}S_2$) Calcd: C, 88.84; H, 6.60. Found: C, 88.67; H, 6.49. ^1H NMR (400 MHz, $CDCl_3$) δ 0.86 (6H, t, *J* = 7.2 Hz), 1.22−1.38 (24H, m), 1.46−1.53 (4H, m), 1.75 (4H, quint, *J* = 7.2 Hz), 1.94 (12H, s), 1.98 (6H, s), 3.06 (4H, t, *J* = 7.2 Hz), 3.56 (2H, s), 7.45 (2H, d, *J* = 7.2 Hz), 7.47 (2H, d, *J* = 7.2 Hz), 7.49 (2H, d, *J* = 7.2 Hz), 7.62−7.74 (10H, m), 7.83 (2H, t, *J* = 1.6 Hz), 8.04 (2H, s), 8.06 (2H, s), 8.08 (2H, s), 8.44 (2H, d, *J* = 8.0 Hz), 8.53 (2H, d, *J* = 8.0 Hz), 8.54 (2H, d, *J* = 8.0 Hz). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 23.18, 23.24, 28.9, 29.0, 29.2, 29.3, 29.5, 29.6, 31.9, 33.4, 81.8, 82.4, 88.7, 88.8, 93.5, 119.3, 119.96, 119.99, 123.5, 123.6, 124.3, 126.6, 126.7, 126.90, 126.94, 129.17, 129.21, 129.24, 129.6, 129.7, 130.4, 130.8, 130.88, 130.92, 131.0, 131.1, 131.8, 132.2, 132.3.

*(P)-Tetramer with Decylthio Side Chains, (P)-S-**4**.* The compound (154 mg, 0.0731 mmol, 81%) was prepared from (*P*)-S-**2H** (77.7 mg, 0.0909 mmol) and (*P*)-S-**1** (141 mg, 0.182 mmol) as a yellow solid. Mp 139−141 °C (chloroform−methanol). $[\alpha]^{27}_{D}$ −604 (*c* 0.10, $CHCl_3$). MALDI-TOF MS *m*/*z* calcd for $^{12}C_{149}{}^{13}CH_{146}S_3Si_2$: 2100.0. Found: 2100.9. UV−vis ($CHCl_3$, 5 × 10^{-6} M) λ_{max} (ε) 335 nm (3.1 × 10^5). CD ($CHCl_3$, 5 × 10^{-6} M) λ ($\Delta\varepsilon$) 297 nm (−90), 335 nm (70), 387 nm (−186). IR (KBr) 2923, 2146, 1248 cm^{-1}. Anal. ($C_{150}H_{146}S_3Si_2$) Calcd: C, 85.74; H, 7.00. Found: C, 85.70; H, 7.19. ^1H NMR (400 MHz, $CDCl_3$) δ 0.39 (18H, s), 0.85 (9H, t, *J* = 7.2 Hz), 1.22−1.40 (36H, m), 1.47−1.54 (6H, m), 1.72−1.80 (6H, m), 1.93 (6H, s), 1.94 (6H, s), 1.99 (12H, s), 3.07 (4H, t, *J* = 7.2 Hz), 3.08 (2H, t, *J* = 7.2 Hz), 7.45 (2H, d, *J* = 7.2 Hz), 7.47 (2H, d, *J* = 7.2 Hz), 7.50 (4H, d, *J* = 7.2 Hz), 7.64−7.75 (14H, m), 7.83 (2H, t, *J* = 1.6 Hz), 7.85 (1H, t, *J* = 1.6 Hz), 8.03 (2H, s), 8.06 (2H, s), 8.12 (4H, s), 8.43 (2H, d, *J* = 8.0 Hz), 8.50−8.56 (6H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.12, 14.1, 22.7, 23.15, 23.18, 23.24, 28.9, 29.0, 29.2, 29.3, 29.5, 29.6, 31.9, 33.4, 88.8, 93.45, 93.54, 100.1, 103.1, 119.8, 120.0, 120.2, 123.57, 123.64, 124.3, 126.5, 126.6, 126.86, 126.93, 129.1, 129.16, 129.24, 129.67, 129.69, 129.9, 130.8, 130.95, 130.98, 131.1, 131.8, 132.1, 132.2, 132.3, 136.7, 136.8, 136.9, 138.5.

*Deprotected (P)-Tetramer with Decylthio Side Chains, (P)-S-**4H**.* The compound (140 mg, 0.0715 mmol, 98%) was prepared from (*P*)-S-**4** (154 mg, 0.0732 mmol) as a yellow solid. Mp 126−128 °C (chloroform−methanol). $[\alpha]^{26}_{D}$ −566 (*c* 0.10, $CHCl_3$). MALDI-TOF MS *m*/*z* calcd for $^{12}C_{143}{}^{13}CH_{130}S_3$: 1955.9. Found: 1955.6. IR (KBr) 3292, 2924 cm^{-1}. Anal. ($C_{144}H_{130}S_3$) Calcd: C, 88.39; H, 6.70. Found: C, 88.21; H, 6.54. ^1H NMR (400 MHz, $CDCl_3$) δ 0.85 (9H, t, *J* = 7.2 Hz), 1.22−1.38 (36H, m), 1.46−1.53 (6H, m), 1.72−1.79 (6H, m), 1.95 (12H, s), 1.98 (12H, s), 3.06 (4H, t, *J* = 7.2 Hz), 3.07 (2H, t, *J* = 7.2 Hz), 3.56 (2H, s), 7.45−7.51 (8H, m), 7.63−7.74 (14H, m), 7.83 (2H, t, *J* = 1.2 Hz), 7.84 (1H, t, *J* = 1.2 Hz), 8.05 (2H, s), 8.07 (2H, s), 8.11 (4H, s), 8.44 (2H, d, *J* = 8.0 Hz), 8.51−8.56 (6H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 23.19, 23.24, 28.9, 29.0, 29.2, 29.3, 29.5, 29.6, 31.9, 33.4, 81.8, 82.4, 88.7, 93.5, 119.3, 119.97, 120.01, 123.5, 123.6, 124.3, 126.67, 126.70, 126.9, 127.0, 129.18, 129,21, 129.24, 129.6, 129.7, 130.4, 130.86, 130.89, 130.93, 131.0, 131.1, 131.8, 132.2, 132.3, 136.8, 136.9, 138.6.

*(P)-Pentamer with Decylthio Side Chains, (P)-S-**5**.* The compound (198 mg, 0.0745 mmol, 81%) was prepared from (*P*)-bD-**3H** (130 mg, 0.0925 mmol) and (*P*)-bD-**1** (143 mg, 0.185 mmol) as a yellow solid. Mp 143−145 °C (chloroform−methanol). $[\alpha]^{27}_{D}$ −617 (*c* 0.10, $CHCl_3$). MALDI-TOF MS *m*/*z* calcd for $^{12}C_{188}{}^{13}C_2H_{184}S_4Si_2$: 2651.3. Found: 2650.5. UV−vis ($CHCl_3$, 5 × 10^{-6} M) λ_{max} (ε) 335 nm (3.5 × 10^5). CD ($CHCl_3$, 5 × 10^{-6} M) λ ($\Delta\varepsilon$) 297 nm (−97), 334 nm (97), 388 nm (−214). IR (KBr) 2924, 2146, 1248 cm^{-1}. Anal. ($C_{190}H_{184}S_4Si_2$) Calcd: C, 86.05; H, 6.99. Found: C, 85.81; H, 6.93. ^1H NMR (400 MHz, $CDCl_3$) δ 0.39 (18H, s), 0.85 (12H, t, *J* = 7.2 Hz), 1.22−1.38 (48H, m), 1.46−1.54 (8H, m), 1.72−1.80 (8H, m), 1.93 (6H, s), 1.94 (6H, s), 1.98 (18H, s), 3.06 (4H, t, *J* = 7.2 Hz), 3.07 (4H, t, *J* = 7.2 Hz), 7.43−7.52 (10H, m), 7.63−7.75 (18H, m) 7.83 (2H, t, *J* = 1.6 Hz), 7.85 (2H, t, *J* = 1.6 Hz), 8.02 (2H, s), 8.06 (2H, s), 8.11 (6H, s), 8.43 (2H, d, *J* = 7.2 Hz), 8.50−8.57 (8H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.11, 14.1, 22.7, 23.1, 23.18, 23.23, 28.9, 29.0, 29.2, 29.3, 29.5, 29.6, 31.9, 33.4, 88.7, 93.4, 93.5, 100.1, 103.1, 119.9, 120.0, 120.3, 123.57, 123.64, 124.3, 126.6, 126.7, 126.9, 127.0, 129.1, 129.2, 129.3,

129.7, 129.9, 130.9, 130.97, 131.00, 131.1, 131.2, 131.8, 132.1, 132.2, 132.3, 136.7, 136.86, 136.91, 138.5, 138.6.

*Deprotected (P)-Pentamer with Decylthio Side Chains, (P)-S-**5H**.* The compound (157 mg, 0.0626 mmol, 92%) was prepared from (*P*)-S-**5** (181 mg, 0.0682 mmol) as a yellow solid. Mp 133−135 °C (chloroform−methanol). $[\alpha]^{27}_{D}$ −595 (*c* 0.10, $CHCl_3$). MALDI-TOF MS *m*/*z* calcd for $^{12}C_{182}{}^{13}C_2H_{168}S_4$: 2507.2. Found: 2506.7. IR (KBr) 3290, 2922 cm^{-1}. Anal. ($C_{184}H_{168}S_4$) Calcd: C, 88.13; H, 6.75. Found: C, 87.85; H, 6.92. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.85 (12H, t, *J* = 7.2 Hz), 1.20−1.40 (48H, m), 1.46−1.58 (8H, m), 1.72−1.80 (8H, m), 1.95 (12H, s), 1.96−2.00 (18H, m), 3.06 (4H, t, *J* = 7.2 Hz), 3.07 (4H, t, *J* = 7.2 Hz), 3.56 (2H, s), 7.44−7.52 (10H, m), 7.63−7.76 (18H, m), 7.83 (2H, t, *J* = 1.2 Hz), 7.85 (2H, t, *J* = 1.2 Hz), 8.06 (2H, s), 8.08 (2H, s), 8.12 (4H, s), 8.13 (2H, s), 8.44 (2H, d, *J* = 8.0 Hz), 8.51−8.57 (8H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 14.1, 22.7, 23.18, 23.23, 28.9, 29.0, 29.2, 29.3, 29.5, 29.6, 31.9, 33.4, 81.8, 82.4, 88.7, 88.8, 93.5, 119.3, 119.98, 120.00, 123.5, 123.61, 123.64, 124.3, 126.66, 126.69, 126.90, 126.94, 129.17, 129.21, 129.24, 129.6, 129.7, 130.4, 130.8, 130.88, 130.93, 131.0, 131.1, 131.2, 131.8, 132.2, 132.3, 136.8, 136.9, 138.6.

*(P)-Hexamer with Decylthio Side Chains, (P)-S-**6**.* The compound (16.2 mg, 0.00506 mmol, 65%) was prepared from (*P*)-S-**4H** (15.2 mg, 0.0078 mmol) and (*P*)-S-**1** (12.0 mg, 0.0156 mmol) as a yellow solid. Mp 148−150 °C (chloroform−methanol). $[\alpha]^{26}_{D}$ −624 (*c* 0.10, $CHCl_3$). MALDI-TOF MS *m*/*z* calcd for $^{12}C_{228}{}^{13}C_2H_{222}S_5Si_2$: 3201.6. Found: 3201.9. UV−vis ($CHCl_3$, 5 × 10^{-6} M) λ_{max} (ε) 336 nm (4.5 × 10^5). CD ($CHCl_3$, 5 × 10^{-6} M) λ ($\Delta\varepsilon$) 298 nm (−132), 334 nm (95), 388 nm (−250). IR (KBr) 2922, 2146, 1248 cm^{-1}. Anal. ($C_{230}H_{222}S_5Si_2$) Calcd: C, 86.25; H, 6.99. Found: C, 86.48; H, 7.07. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.38 (18H, s), 0.85 (15H, t, *J* = 7.2 Hz), 1.22−1.38 (60H, m), 1.46−1.55 (10H, m), 1.72−1.80 (10H, m), 1.93 (6H, s), 1.94 (6H, s), 1.98 (24H, s), 3.04−3.09 (10H, m), 7.43−7.52 (12H, m), 7.63−7.75 (22H, m), 7.83 (2H, t, *J* = 1.6 Hz), 7.84−7.86 (3H, m), 8.02 (2H, s), 8.05 (2H, s), 8.09−8.13 (8H, m), 8.42 (2H, d, *J* = 7.6 Hz), 8.50−8.56 (10H, m). ^{13}C NMR (100 MHz, $CDCl_3$) δ 0.11, 14.1, 22.7, 23.16, 23.19, 23.24, 28.9, 29.0, 29.2, 29.3, 29.5, 29.6, 31.9, 33.4, 88.7, 93.4, 93.5, 100.1, 103.1, 119.8, 120.0, 120.2, 123.57, 123.64, 124.3, 126.5, 126.7, 126.9, 127.0, 129.1, 129.2, 129.3, 129.7, 129.9, 130.9, 131.0, 131.1, 131.8, 132.1, 132.2, 132.3, 136.7, 136.86, 136.91, 138.6.

*(P)-Heptamer with Decylthio Side Chains, (P)-S-**7**.* The compound (31.6 mg, 0.00841 mmol, 55%) was prepared from (*P*)-S-**5H** (38.6 mg, 0.0154 mmol) and (*P*)-S-**1** (23.8 mg, 0.0308 mmol) as a yellow solid. Mp 155−157 °C (chloroform−methanol). $[\alpha]^{26}_{D}$ −574 (*c* 0.05, $CHCl_3$). MALDI-TOF MS *m*/*z* calcd for $^{12}C_{268}{}^{13}C_2H_{260}S_6Si_2$: 3751.8. Found: 3751.2. UV−vis ($CHCl_3$, 5 × 10^{-6} M) λ_{max} (ε) 336 nm (4.9 × 10^5). CD ($CHCl_3$, 5 × 10^{-6} M) λ ($\Delta\varepsilon$) 297 nm (−128), 335 nm (119), 388 nm (−308). IR (KBr) 2924, 2148, 1248 cm^{-1}. Anal. ($C_{270}H_{260}S_6Si_2$) Calcd: C, 86.40; H, 6.98. Found: C, 86.74; H, 7.13. ^{1}H NMR (400 MHz, $CDCl_3$) δ 0.38 (18H, s), 0.85 (18H, t, *J* = 7.2 Hz), 1.22−1.38 (72H, m), 1.46−1.55 (12H, m), 1.71−1.80 (12H, m), 1.92 (6H, s), 1.94 (6H, s), 1.97 (30H, s), 3.04−3.09 (12H, m), 7.43−7.52 (14H, m), 7.62−7.75 (26H, m), 7.82 (2H, t, *J* = 1.6 Hz), 7.83−7.85 (4H, m), 8.01 (2H, s), 8.04 (2H, s), 8.08−8.12 (10H, m), 8.42 (2H, d, *J* = 8.0 Hz), 8.50−8.56 (12H, m). ^{13}C NMR(100 MHz, $CDCl_3$) δ 0.11, 14.1, 22.7, 23.15, 23.18, 23.23, 28.9, 29.0, 29.2, 29.3, 29.5, 29.6, 30.9, 31.9, 33.4, 88.7, 93.4, 93.5, 100.1, 103.1, 119.8, 120.0, 120.2, 123.6, 124.3, 126.5, 126.7, 126.87, 126.94, 129.1, 129.16, 129.24, 129.7, 129.9, 130.8, 131.0, 131.1, 131.8, 132.1, 132.2, 132.3, 136.7, 136.85, 136.90, 138.6.

*(P)-Tetramer with Alternating Perfluorooctyl Side Chains and Decyloxycarbonyl Side Chains, (P)-DF-**4** (Typical Procedure for the Sonogashira Coupling Reaction of (P)-DF-**n**).* Under an argon atmosphere, a mixture of (*P*)-D-**1**[39a] (114 mg, 0.145 mmol), tris(dibenzylideneacetone)dipalladium(0) chloroform adduct (15.1 mg, 0.0145 mmol), cuprous iodide (33.2 mg, 0.174 mmol), tris(2,4,6-trimethylphenyl)phosphine (33.9 mg, 0.0872 mmol), triphenylphosphine (22.9 mg, 0.0872 mmol), tetrabutylammonium iodide (429 mg, 1.16 mmol), triethylamine (0.26 mL), *N*,*N*-dimethylformamide (1.3 mL), and tetrahydrofuran (1.0 mL) was freeze-evacuated three times in flask A. In flask B, a solution of (*P*)-F-**2H**[38] (80.0 mg, 0.0727 mmol) in tetrahydrofuran (2.9 mL) was freeze-evacuated three times, and the mixture was slowly added to flask A. The mixture was stirred at 45 °C for 2 h. The reaction was quenched by adding saturated aqueous ammonium chloride, and the organic materials were extracted with toluene three times. The combined organic layer was washed with water and brine and dried over magnesium sulfate. The solvents were evaporated under reduced pressure, and separation by silica gel chromatography and recycling GPC gave (*P*)-DF-**4** as a yellow solid (153 mg, 0.0646 mmol, 89%). Mp 228−230 °C (toluene−methanol). $[\alpha]^{22}_{D}$ −473 (*c* 0.10, $CHCl_3$). MALDI-TOF MS *m*/*z* calcd for $^{12}C_{149}{}^{13}CH_{125}F_{17}O_4Si_2$: 2369.9. Found: 2370.3. UV−vis ($CHCl_3$, 5 × 10^{-6} M) λ_{max} (ε) 336 nm (2.8 × 10^5). CD ($CHCl_3$, 5 × 10^{-6} M) λ ($\Delta\varepsilon$) 297 nm (−54), 333 nm (89), 387 nm (−175). IR (KBr) 2924, 2148, 1724, 1240, 1207 cm^{-1}. Anal. ($C_{150}H_{125}F_{17}O_4Si_2$) Calcd: C, 75.99; H, 5.31; F, 13.62. Found: C, 75.77; H, 5.48; F, 13.58. ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.39 (18H, s), 0.86 (6H, t, *J* = 6.6 Hz), 1.26−1.42 (24H, m), 1.50 (4H, quin, *J* = 7.2 Hz), 1.85 (4H, quin, *J* = 7.2 Hz), 1.93 (6H, s), 1.95 (6H, s), 2.00 (12H, s), 4.42 (4H, t, *J* = 6.6 Hz), 7.44 (2H, d, *J* = 7.2 Hz), 7.47 (2H, d, *J* = 7.2 Hz), 7.50−7.52 (4H, m), 7.65 (2H, dd, *J* = 7.2 Hz), 7.70−7.75 (6H, m), 7.92 (2H, s), 8.00 (2H, s), 8.05 (2H, s), 8.08 (2H, s), 8.09 (2H, s), 8.18 (2H, s), 8.22 (1H, s), 8.35 (2H, s), 8.36 (2H, s), 8.43 (2H, d, *J* = 7.8 Hz), 8.53−8.56 (6H, m). ^{13}C NMR (150 MHz, $CDCl_3$) δ 0.12, 14.1, 22.7, 23.1, 23.17, 23.23, 26.1, 28.8, 29.31, 29.33, 29.6, 31.9, 65.8, 89.3, 89.4, 90.2, 92.3, 92.9, 93.1, 100.2, 103.1, 119.5, 119.7, 120.0, 120.4, 123.5, 123.6, 123.7, 124.3, 124.4, 124.9, 126.7, 126.9, 127.0, 127.108, 127.12, 129.1, 129.2, 129.36, 129.37, 129.5, 129.8, 129.9, 130.1, 130.9, 130.98, 131.02, 131.5, 132.1, 132.3, 132.38, 132.40, 136.8, 136.9, 136.97, 137.02, 137.8, 138.3, 165.4. ^{19}F NMR (565 MHz, $CDCl_3$) δ −127.4 (2F, s, br), −124.0 (2F, s, br), −123.1 (2F, s, br), −123.0 (2F, s, br), −122.6 (2F, s, br), −122.4 (2F, s, br), −122.3 (2F, t, *J* = 13.3 Hz), −82.1 (3F, t, *J* = 9.9 Hz).

*Deprotected (P)-Tetramer with Alternating Perfluorooctyl Side Chains and Decyloxycarbonyl Side Chains, (P)-DF-**4H** (Typical Procedure for Desilylation of (P)-DF-**n**).* To a solution of (*P*)-DF-**4** (150 mg, 0.0634 mmol) in tetrahydrofuran (1.8 mL) was added 1.0 M tetrabutylammonium fluoride in tetrahydrofuran (0.16 mL, 0.16 mmol) at 0 °C. After 30 min of stirring at the temperature, the reaction was quenched by adding saturated aqueous ammonium chloride. The organic materials were extracted with toluene. The organic layer was washed with water and brine and dried over magnesium sulfate. The solvents were evaporated under reduced pressure, and silica gel chromatography gave (*P*)-DF-**4H** as a yellow solid (141 mg, 0.0634 mmol, quant). Mp 175 °C, decomp (chloroform−methanol). $[\alpha]^{23}_{D}$ −523 (*c* 0.10, $CHCl_3$). MALDI-TOF MS *m*/*z* calcd for $^{12}C_{143}{}^{13}CH_{109}F_{17}O_4$: 2225.8. Found: 2226.3. UV−vis ($CHCl_3$, 5 × 10^{-6} M) λ_{max} (ε) 333 nm (2.4 × 10^5). CD ($CHCl_3$, 5 × 10^{-6} M) λ ($\Delta\varepsilon$) 297 nm (−73), 329 nm (62), 387 nm (−166). IR (KBr) 2924, 2207, 1723, 1240, 1207 cm^{-1}. Anal. ($C_{144}H_{109}F_{17}O_4$) Calcd: C, 77.68; H, 4.93; F, 14.51. Found: C, 77.44; H, 5.18; F, 14.24. ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.85 (6H, t, *J* = 7.2 Hz), 1.26−1.43 (24H, m), 1.50 (4H, quin, *J* = 7.2 Hz), 1.85 (4H, quin, *J* = 7.2 Hz), 1.95 (12H, s), 1.99 (12H, s), 3.56 (2H, s), 4.42 (4H, t, *J* = 7.2 Hz), 7.45 (2H, d, *J* = 7.2 Hz), 7.48 (2H, d, *J* = 7.2 Hz), 7.50−7.52 (4H, m), 7.66 (2H, dd, *J* = 7.8 Hz), 7.70−7.76 (6H, m), 7.92 (2H, s), 8.04 (2H, s), 8.07 (2H, s), 8.11 (2H, s), 8.12 (2H, s), 8.18 (2H, t, *J* = 1.5 Hz), 8.22 (1H, s), 8.35 (2H, t, *J* = 1.5 Hz), 8.36 (2H, t, *J* = 1.5 Hz), 8.44 (2H, d, *J* = 7.8 Hz), 8.53 (4H, d, *J* = 7.8 Hz), 8.55 (2H, d, *J* = 7.8 Hz). ^{13}C NMR (150 MHz, $CDCl_3$) δ 14.1, 22.7, 23.17, 23.23, 26.1, 28.7, 29.3, 29.5, 29.6, 31.9, 65.8, 81.8, 82.4, 89.27, 89.31, 90.1, 92.3, 92.9, 93.1,

119.4, 119.5, 119.8, 119.9, 123.5, 123.55, 123.57, 123.6, 124.29, 124.32, 124.9, 126.8 126.95, 127.00, 127.10, 127.12, 129.0, 129.2, 129.25, 129.35, 129.4, 129.5, 129.8, 130.1, 130.4, 130.86, 130.94, 130.97, 130.99, 131.02, 131.5, 132.1, 132.2, 132.3, 132.4, 136.8, 136.9, 136.98, 137.02, 137.8, 138.3, 165.4. ^{19}F NMR (565 MHz, $CDCl_3$) δ −127.2 (2F, s, br), −123.8 (2F, s, br), −123.0 (2F, s, br), −122.9 (2F, s, br), −122.4 (2F, s, br), −122.2 (2F, s, br), −122.1 (2F, t, J = 13.6 Hz), −81.9 (3F, t, J = 9.9 Hz).

*(P)-Hexamer with Alternating Perfluorooctyl Side Chains and Decyloxycarbonyl Side Chains, (P)-DF-**6***. The compound (214 mg, 0.0539 mmol, 80%) was prepared from (*P*)-DF-**4H** (150 mg, 0.0674 mmol) and (*P*)-F-**1**[38] (137 mg, 0.135 mmol) as a yellow solid. Mp > 240 °C (chloroform−methanol). $[\alpha]^{22}_D$ −433 (*c* 0.10, $CHCl_3$). MALDI-TOF MS *m*/*z* calcd for $^{12}C_{225}{}^{13}CH_{159}F_{51}O_4Si_2$: 3962.1. Found: 3962.2. UV−vis ($CHCl_3$, 2.5 × 10^{-6} M) λ_{max} (ε) 338 nm (4.2 × 10^5). CD ($CHCl_3$, 5 × 10^{-6} M) λ ($\Delta\varepsilon$) 297 nm (−85), 336 nm (118), 388 nm (−265). IR (KBr) 2925, 2205, 1726, 1241, 1207 cm^{-1}. Anal. ($C_{226}H_{159}F_{51}O_4Si_2$) Calcd: C, 68.48; H, 4.04; F, 24.44. Found: C, 68.12; H, 4.26; F, 24.51. ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.39 (18H, s), 0.85 (6H, t, J = 7.2 Hz), 1.26−1.42 (24H, m), 1.49 (4H, quin, J = 7.2 Hz), 1.85 (4H, quin, J = 7.2 Hz), 1.93 (6H, s), 1.94 (6H, s), 1.99 (24H, s), 4.42 (4H, t, J = 7.2 Hz), 7.45 (2H, d, J = 7.2 Hz), 7.48 (2H, d, J = 7.2 Hz), 7.50−7.51 (8H, m), 7.66 (2H, dd, J = 7.8, 7.2 Hz), 7.70−7.75 (10H, m), 7.90−7.92 (6H, m), 8.00 (2H, s), 8.06 (2H, s), 8.09 (4H, s), 8.10 (4H, s), 8.19 (2H, s), 8.20 (2H, s), 8.22 (1H, s), 8.36 (4H, s), 8.43 (2H, d, J = 7.8 Hz), 8.53−8.56 (10H, m). ^{13}C NMR (150 MHz, $CDCl_3$) δ 0.19, 14.2, 22.8, 23.23, 23.25, 23.32, 26.2, 28.8, 29.4, 29.7, 29.8, 32.0, 65.9, 89.4, 90.22, 90.23, 90.3, 92.3, 92.4, 93.1, 100.4, 103.1, 115.5−118.4 (m, br), 119.4, 119.6, 120.0, 120.5, 123.5, 123.6, 123.7, 123.8, 124.4, 124.98, 125.00, 125.02, 126.9, 127.06, 127.10, 127.2, 129.3, 129.4, 129.5, 129.46, 129.54, 129.9, 130.2, 130.3, 130.4, 130.9, 131.0, 130.07, 131.10, 131.6, 132.1, 132.2, 132.4, 132.5, 136.9, 137.0, 137.07, 137.10, 137.8, 138.4, 165.5. ^{19}F NMR (565 MHz, $CDCl_3$) δ −127.3 (6F, s, br), −123.9 (6F, s, br), −123.0 (6F, s, br), −122.9 (6F, s, br), −122.5 (6F, s, br), −122.3 (6F, s, br), −122.2 (6F, t, J = 14.1 Hz), −82.1 (9F, t, J = 9.3 Hz).

*Deprotected (P)-Hexamer with Alternating Perfluorooctyl Side Chains and Decyloxycarbonyl Side Chains, (P)-DF-**6H***. The compound (92.0 mg, 0.0241 mmol, 99%) was prepared from (*P*)-DF-**6** (96.1 mg, 0.0242 mmol) as a yellow solid. Mp 185 °C, decomp (chloroform−methanol). $[\alpha]^{23}_D$ −437 (*c* 0.10, $CHCl_3$). MALDI-TOF MS *m*/*z* calcd for $^{12}C_{218}{}^{13}C2H_{143}F_{51}O_4$: 3819.0. Found: 3818.7. UV−vis ($CHCl_3$, 2.5 × 10^{-6} M) λ_{max} (ε) 336 nm (3.8 × 10^5). CD ($CHCl_3$, 5 × 10^{-6} M) λ ($\Delta\varepsilon$) 296 nm (−104), 332 nm (88), 389 nm (−259). IR (KBr) 2925, 2207, 1725, 1241, 1208 cm^{-1}. Anal. ($C_{220}H_{143}F_{51}O_4$) Calcd: C, 69.18; H, 3.77; F, 25.37. Found: C, 68.86; H, 4.17; F, 25.29. ^{1}H NMR (600 MHz, $CDCl_3$, observed at 40 °C) δ 0.85 (6H, t, J = 7.2 Hz), 1.26−1.36 (24H, m), 1.41 (4H, quin, J = 7.2 Hz), 1.85 (4H, quin, J = 7.2 Hz), 1.95 (12H, s), 1.99 (24H, s), 3.54 (2H, s), 4.42 (4H, t, J = 7.2 Hz), 7.45 (2H, d, J = 7.2 Hz), 7.48 (2H, d, J = 7.2 Hz), 7.49−7.51 (8H, m), 7.65 (2H, dd, J = 7.8 Hz), 7.70−7.74 (10H, m), 7.89 (2H, s), 7.90 (2H, s), 7.91(2H, s), 8.04 (2H, s), 8.08 (2H, s), 8.11 (4H, m), 8.12 (4H, m), 8.19 (4H, s), 8.22 (1H, s), 8.35−8.36 (4H, m), 8.44 (2H, d, J = 7.8 Hz), 8.50−8.56 (10H, m). ^{13}C NMR (150 MHz, $CDCl_3$, observed at 40 °C) δ 14.0, 22.7, 23.1, 23.2, 26.1, 28.8, 29.31, 29.34, 29.6, 31.9, 65.9, 81.8, 82.4, 89.4, 90.2, 92.3, 92.4, 93.1, 105.0−119.0 (m, br), 119.5, 119.56, 119.59, 120.0, 123.5, 123.55, 123.62, 123.7, 124.4, 125.0, 127.03, 127.05, 127.07, 127.09, 127.12, 127.2, 129.25, 129.33, 129.36, 129.38, 129.4, 129.5, 129.9, 130.08, 130.14, 130.3, 130.4, 130.5, 130.87, 130.90, 131.0, 131.05, 131.08, 131.7, 132.1, 132.2, 132.4, 132.46, 132.52, 136.9, 137.0, 137.1, 137.8, 138.3, 165.4. ^{19}F NMR (565 MHz, $CDCl_3$, observed at 40 °C) δ −127.1 (6F, s, br), −123.7 (6F, s, br), −122.9 (6F, s, br), −122.7 (6F, s, br), −122.3 (6F, s, br), −122.1 (6F, s, br), −122.0 (6F, t, J = 12.7 Hz), −81.9 (9F, t, J = 8.5 Hz).

*(P)-Octamer with Alternating Perfluorooctyl Side Chains and Decyloxycarbonyl Side Chains, (P)-DF-**8***. The compound (51.8 mg, 0.0102 mmol, 79%) was prepared from (*P*)-DF-**6H** (49.0 mg, 0.0128 mmol) and (*P*)-D-**1** (20.4 mg, 0.0259 mmol) as a yellow solid. M*p* > 240 °C (chloroform -methanol). $[\alpha]^{23}_D$ −487 (*c* 0.10, $CHCl_3$). MALDI-TOF MS *m*/*z* calcd for $^{12}C_{308}H_{235}F_{51}O_8Si_2$: 5085.7. Found: 5085.9. UV−vis ($CHCl_3$, 2.5 × 10^{-6} M) λ_{max} (ε) 339 nm (5.4 × 10^5). CD ($CHCl_3$, 5 × 10^{-6} M) λ ($\Delta\varepsilon$) 297 nm (−112), 336 nm (155), 389 nm (−374). IR (KBr) 2958, 2208, 1724, 1241, 1207 cm^{-1}. Anal. ($C_{308}H_{235}F_{51}O_8Si_2$) Calcd: C, 72.69; H, 4.65; F, 19.04. Found: C, 72.37; H, 4.95; F, 18.78. ^{1}H NMR (600 MHz, $CDCl_3$) δ 0.38 (18H, s), 0.85 (12H, t, J = 7.2 Hz), 1.26−1.34 (40H, m), 1.34−1.47 (8H, m), 1.49−1.53 (8H, m), 1.82−1.88 (8H, m), 1.93 (6H, s), 1.94 (6H, s), 1.98 (36H, s), 4.40−4.43 (8H, m), 7.44 (2H, d, J = 7.2 Hz), 7.47 (2H, d, J = 7.2 Hz), 7.50−7.51 (12H, m), 7.66 (2H, t, J = 7.8 Hz), 7.70−7.75 (14H, m), 7.90−7.91 (6H, m), 8.01 (2H, s), 8.05 (2H, s), 8.10−8.11 (12H, m), 8.18 (2H, s), 8.19 (2H, s), 8.22 (3H, s), 8.33−8.35 (8H, m), 8.42 (2H, d, J = 7.8 Hz), 8.52−8.55 (14H, m). ^{13}C NMR (150 MHz, $CDCl_3$) δ 0.11, 14.1, 22.6, 23.1, 23.16, 23.21, 26.1, 28.8, 29.31, 29.33, 29.6, 29.65, 29.70, 31.9, 65.8, 89.28, 89.30, 89.4, 90.2, 92.3, 92.9, 93.1, 100.2, 103.1, 108.3−118.1 (m, br), 119.5, 119.7, 119.9, 120.4, 123.5, 123.6, 123.66, 123.68, 124.3, 124.4, 124.9, 126.7, 126.9, 127.0, 127.1, 129.1, 129.2, 129.4, 129.5, 129.8, 129.9, 130.0, 130.1, 130.2, 130.9, 131.0, 131.5, 132.1, 132.3, 132.4, 136.8, 136.9, 136.98, 137.02, 137.8, 138.3, 165.4. ^{19}F NMR (565 MHz, $CDCl_3$) δ −127.3 (6F, s, br), −123.9 (6F, s, br), −123.0 (6F, s, br), −122.9 (6F, s, br), −122.4 (6F, s, br), −122.3 (6F, s, br), −122.2 (6F, t, J = 13.0 Hz), −82.1 (9F, t, J = 9.0 Hz).

*Deprotected (P)-Octamer with Alternating Perfluorooctyl Side Chains and Decyloxycarbonyl Side Chains, (P)-DF-**8H***. The compound (61.7 mg, 0.0125 mmol, quant) was prepared from (*P*)-DF-**8** (63.5 mg, 0.0125 mmol) as a yellow solid. Mp 212 °C, decomp (chloroform−methanol). $[\alpha]^{23}_D$ −453 (*c* 0.10, $CHCl_3$). MALDI-TOF MS *m*/*z* calcd for $^{12}C_{301}{}^{13}CH_{219}F_{51}O_8$:.4942.6. Found: 4942.5. UV−vis ($CHCl_3$, 2.5 × 10^{-6} M) λ_{max} (ε) 337 nm (4.9 × 10^5). CD ($CHCl_3$, 5 × 10^{-6} M) λ ($\Delta\varepsilon$) 297 nm (−133), 337 nm (158), 389 nm (−374). IR (KBr) 2924, 2207, 1725, 1240, 1207 cm^{-1}. Anal. ($C_{302}H_{219}F_{51}O_8$) Calcd: C, 73.35; H, 4.46; F, 19.59. Found: C, 73.10; H, 4.72; F, 19.34. ^{1}H NMR (600 MHz, $CDCl_3$, observed at 50 °C) δ 0.85 (12H, t, J = 6.6 Hz), 1.26−1.35 (48H, m), 1.39−1.42 (8H, m), 1.82−1.87 (8H, m), 1.95 (12H, s), 1.98 (36H, s), 3.53 (2H, s), 4.40−4.43 (8H, m), 7.44 (2H, d, J = 6.6 Hz), 7.46−7.50 (14H, m), 7.64 (2H, d, J = 7.2 Hz), 7.69−7.72 (14H, m), 7.90 (6H, s), 8.03 (2H, s), 8.06 (2H, s), 8.10−8.11 (12H, m), 8.16 (2H, s), 8.18 (2H, s), 8.21 (3H, s), 8.32 (2H, s), 8.35 (6H, m), 8.43 (2H, d, J = 7.8 Hz), 8.50−8.55 (14H, m). ^{13}C NMR (150 MHz, $CDCl_3$, observed at 50 °C) δ 15.4, 26.6, 33.5, 33.89, 33.92, 36.3, 38.5, 38.8, 38.9, 39.1, 40.9, 68.1, 80.9, 81.3, 86.92, 86.94, 87.6, 89.3, 89.8, 89.9, 95.4, 111.0, 111.1, 111.3, 111.5, 114.2, 114.3, 114.4, 114.9, 115.4, 116.9, 116.98, 117.02, 117.10, 117.12, 118.77, 118.81, 118.9, 118.98, 119.01, 119.3, 119.5, 119.7, 119.8, 120.2, 120.3, 120.8, 121.20, 121.24, 121.3, 121.37, 121.41, 124.9, 125.0, 125.05, 125.08, 125.6, 126.0, 147.7. ^{19}F NMR (565 MHz, $CDCl_3$) δ −127.3 (6F, s, br), −123.9 (6F, s, br), −123.1 (6F, s, br), −122.9 (6F, s, br), −122.5 (6F, s, br), −122.3 (6F, s, br), −112.2 (6F, s, br), −82.0 (9F, t, J = 9.6 Hz).

*(P)-Decamer with Alternating Perfluorooctyl Side Chains and Decyloxycarbonyl Side Chains, (P)-DF-**10***. The compound (17.4 mg, 0.00260 mmol, 40%) was prepared from (*P*)-DF-**8H** (32.0 mg, 0.00647 mmol) and (*P*)-F-**1** (13.2 mg, 0.0129 mmol) as a yellow solid. Mp >240 °C (chloroform−methanol). $[\alpha]^{23}_D$ −394 (*c* 0.10, $CHCl_3$). MALDI-TOF MS *m*/*z* calcd for $C_{384}H_{269}F_{85}O_8Si_2$: 6677.9. Found: 6678.4. UV−vis ($CHCl_3$, 2.5 × 10^{-6} M) λ_{max} (ε) 338 nm (6.9 × 10^5). CD ($CHCl_3$, 2.5 × 10^{-6} M) λ ($\Delta\varepsilon$) 296 nm (−147), 338 nm (158), 390 nm (−466). IR (KBr) 2924, 2208, 1725, 1241, 1208 cm^{-1}. Anal. ($C_{384}H_{269}F_{85}O_8Si_2$) Calcd: C, 69.02; H, 4.06; F, 24.17. Found: C, 68.68; H, 4.37; F, 23.92. ^{1}H NMR (600 MHz, $CDCl_3$, observed at

50 °C) δ 0.38 (18H, s), 0.85 (12H, t, J = 6.6 Hz), 1.26−1.34 (48H, m), 1.38−1.43 (8H, m), 1.82−1.87 (8H, m), 1.93 (6H, s), 1.94 (6H, s), 1.98−1.99 (48H, s), 4.42 (8H, t, J = 6.6 Hz), 7.44 (2H, d, J = 7.2 Hz), 7.46−7.50 (18H, m), 7.65 (2H, t, J = 7.2 Hz), 7.69−7.73 (18H, m), 7.89−7.90 (10H, m), 8.00 (2H, s), 8.07 (2H, s), 8.11−8.13 (16H, m), 8.18−8.21 (9H, m), 8.34−8.35 (6H, m), 8.35 (2H, s), 8.42 (2H, d, J = 7.8 Hz), 8.49−8.55 (18H, m). ^{13}C NMR (150 MHz, $CDCl_3$, observed at 55 °C) δ 0.12, 14.0, 22.6, 22.7, 23.0, 23.06, 23.08, 23.13, 23.9, 26.1, 28.8, 29.0, 29.29, 29.34, 29.4, 29.6, 29.67, 29.71, 30.5, 31.9, 32.0, 36.4, 39.0, 65.9, 89.4, 90.28, 90.30, 92.4, 93.2, 100.0, 103.2, 119.5, 119.7, 120.1, 120.6, 123.5, 123.6, 123.73, 123.74, 123.75, 123.81, 124.5, 125.08, 125.10, 125.13, 126.9, 127.0, 127.13, 127.14, 127.16, 127.17, 127.19, 129.2, 129.28, 129.29, 129.37, 129.39, 129.45, 129.47, 129.48, 129.87, 129.88, 130.17, 130.18, 130.19, 131.05, 131.12, 131.13, 131.14, 131.8, 132.2, 132.3, 132.46, 132.48, 132.50, 132.6, 136.6, 136.7, 136.8, 136.9, 137.02, 137.05, 137.07, 137.10, 137.13, 137.76, 137.78, 137.80, 138.3, 165.4. ^{19}F NMR (565 MHz, $CDCl_3$, observed at 40 °C) δ −127.2 (10F, s, br), −123.8 (10F, s, br), −123.0 (10F, s, br), −122.9 (10F, s, br), −122.4 (10F, s, br), −122.2 (10F, s, br), −112.1 (10F, s, br), −82.0 (15F, t, J = 8.8 Hz).

■ ASSOCIATED CONTENT

Supporting Information. CD spectra of (*P*)-D-**8**, (*P*)-S-**7**, and (*P*)-DF-**8**, VPO results of (*P*)-DF-**8**, and copies of ^{1}H and ^{13}C NMR spectra of all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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