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Synthesis and Supramolecular Self-Assembly of Coil-Rod-Coil Molecules: The Relationship between Self-Assembled Nanostructures and Molecular Structures

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Abstract: Herein, the relationship between the supramolecularly self-assembled nanostructures and the chemical structures of coil-rod-coil molecules is discussed. A series of nonamphiphilic coil-rod-coil molecules with different alkyl chains, central mesogenic groups, and chemical linkers were designed and synthesized. The solvent-mediated supramolecular self-assembling of these coil-rod-coil molecules resulted in rolled-up nanotubes, nanofibers, submicron sized belts, needle-like microcrystals, and amorphous structures. The self-assembling behaviors of these coil-rod-coil molecules have been systematically investigated to reveal the relationship between the supramolecularly self-assembled nanostructures and their chemical structures. With respect to the formation of rolled-up nanotubes by self-assembly of coil-rod-coil molecules, we have systematically investigated the following three influencing structural factors: 1) the alkyl chain length; 2) the central mesogenic group; (3) the linker type. These studies disclosed the key structural features of coil-rod-coil molecules for the formation of rolled-up nanotubes.

Keywords: coil-rod-coil · nanotubes · self-assembly · superstructures · supramolecular chemistry

Introduction

The self-assembly of well-defined nanoscale architectures, especially tubular structures, by small organic molecules is of great current interest and a challenging topic in the areas of chemistry and material sciences.[1–6] In comparison with other nanostructures, such as ribbons and fibrils, the self-assembly of high-aspect nanotubes is considered most challenging as strict conditions are required and only a few examples have been reported.[7–12] In previous work, we have reported the hierarchically supramolecular self-assembly of a small organic nonamphiphilic coil-rod-coil molecule *p*-terphenylen-1,4″-ylenebis(dodecanamide) (**TB**) to form a new kind of rolled-up organic nanotube from its nanosheets precursor.[13] The nanotubes are micrometers in length and have diameters in the range of 90 to 120 nm, with approximately 20-nm-thick walls and an aspect ratio up to 300 with a novel scrolling pattern. Considering the importance of low-dimensional nanostructures, especially tubular structures, from both the academic and technologic standpoints,[1,2,14–20] these initial results inspired us to further explore what is the rational molecular design for the supramolecular self-assembly of low-dimensional nanostructures, especially tubular structures. The nonamphiphilic coil-rod-coil molecule **TB** is constituted of three parts: 1) a central rigid terphenylene segment; 2) two secondary amido functional groups; 3) two flexible alkyl chains. The central terphenylene segment has a strong tendency to aggregate through π–π overlapping; the two secondary amido groups can form the intermolecular translation-related hydrogen bonding. The synergistic effects of these two kinds of interactions make **TB** self-assemble to form one-layer supramolecular nanosheets. The one-layer nanosheets have a strong tendency to either stack to form lamellar sheets or to form rolled-up-type nanotubes.

To understand which parts play a key role in formation of rolled-up nanotubes by self-assembly of coil-rod-coil molecules, herein we report the design, synthesis, and self-assembly of three types of nonamphiphilic coil-rod-coil molecules. We have systematically investigated the following three influencing structural factors:[21–25] 1) the alkyl chain length; 2) the central mesogenic group; 3) the linker type. These studies disclosed the key structural features of coil-rod-coil molecules for the formation of rolled-up nanotubes.

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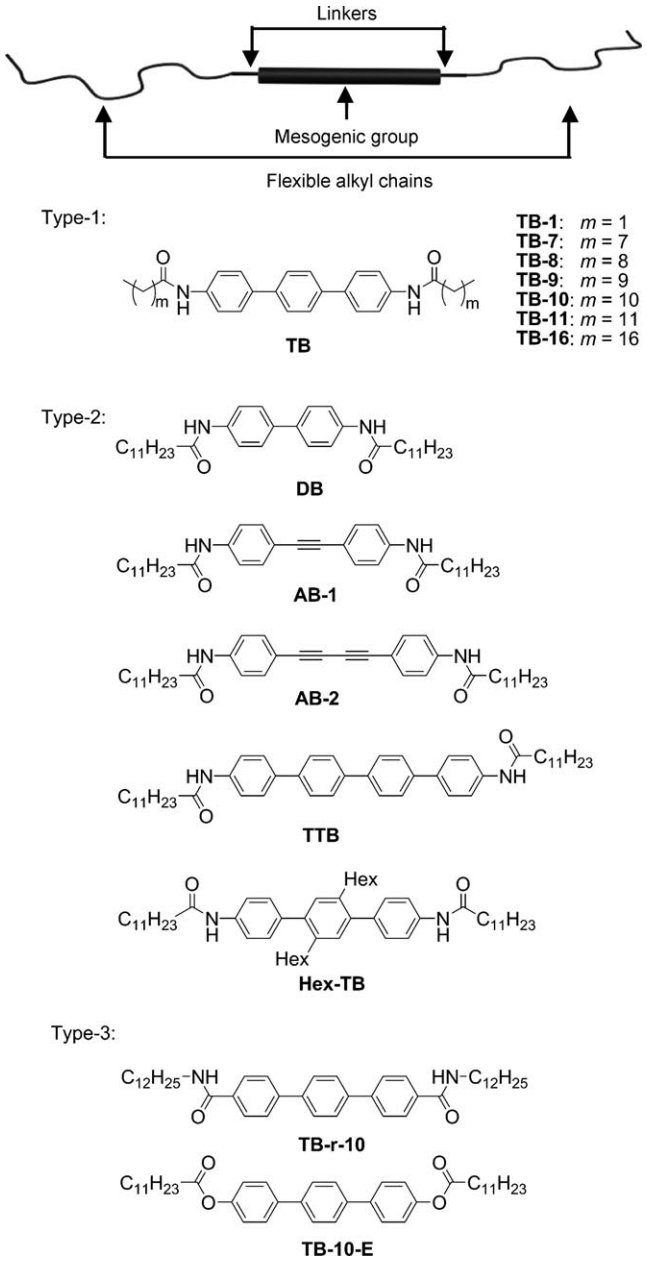
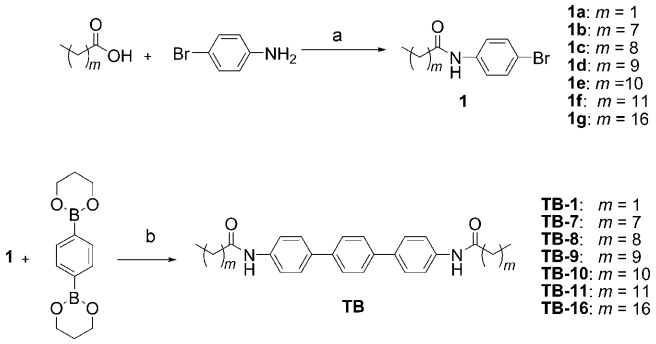
Results and Discussion

Molecular Design and Synthesis

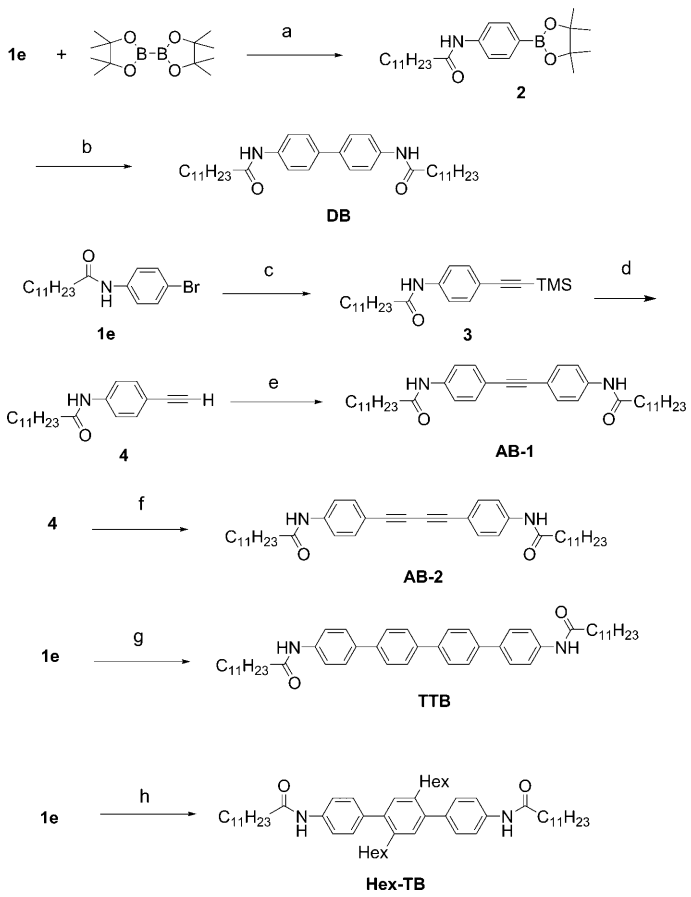
As shown in Scheme 1, the coil-rod-coil molecules used for supramolecular self-assembly can be categorized into three types according to their structural features. The first type (Type 1) includes molecules containing the central *p*-terphenylene core, two secondary amido functional groups, and alkyl chains with different lengths at two ends; the second one (Type 2) includes molecules containing two secondary amido functional groups, different central mesogenic groups, and two undecane chains at the two ends; the third one (Type 3) includes molecules containing a central *p*-terphenylene core, two undecane chains at two ends, and different linkers. The syntheses of Type-1 molecules (**TB-1**, **TB-7**, **TB-8**, **TB-9**, **TB-11**, and **TB-16**) are shown in Scheme 2. Starting from commercially available alkyl carboxylic acid and 4-bromoaniline, their coupling reaction was carried out by using 1-ethyl-3-(3-dimethylamino)propylcarbodiimide hydrochloride (EDC·HCl) and 1-hydroxybenzotriazole (HOBt) as mild coupling reagents to afford amides **1a–g** in yields of 35–97%. Suzuki–Miyaura cross-coupling of **1a–g** and benzene-1,4-diboronic acid 1,3-propanediol ester with $Pd(PPh_3)_4$ as the catalyst precursor afforded the desired molecules **TB-1**, **TB-7**, **TB-8**, **TB-9**, **TB-11**, and **TB-16**, respectively, in yields of 66–81%. The syntheses of Type-2 molecules (**AB-1**, **AB-2**, **DB**, **TTB**, and **Hex-TB**) are shown in Scheme 3. Miyaura cross-coupling of **1e** and bis(pinacolato)diboron with $Pd(dppf)_2Cl_2$ as the catalyst precursor afforded *N*-(4-*p*-inacolatoboronphenyl)dodecan amide (**2**) in a yield of 98%. The Suzuki–Miyaura cross-coupling of **2** and **1e** furnished *p*-diphenylen-1,4″-ylenebis(dodecanamide) (**DB**) in a yield of 83%. The synthesis of acetylene-containing compound **AB-1** started from amide **1e**, its reaction with trimethylsilyl acetylene under Sonogashira coupling conditions afforded TMS-protected acetylene, and followed by deprotection of the TMS group with tetrabutylammonium fluoride (TBAF), furnished the acetylene-terminated compound **4** in an overall yield of 83%. Sonogashira cross-coupling of **1e** and **4** afforded the acetylene-containing compound **AB-1** in a yield of 31%. The diacetylene-containing compound **AB-2** was synthesized in a yield of 63% by Glaser coupling of acetylene-terminated amide **4**. The *p*-tetraphenylen-1,4”-ylenebis(dodecanamide) (**TTB**) was synthesized in a yield of 79% by a Suzuki–Miyaura coupling of **1e** and 4,4′-biphenyldiboronic acid. Compound **Hex-TB** bearing two hexyl chains at the central benzene ring was obtained in 83% yield by Suzuki–Miyaura cross-coupling of **1e** and 2,5-dihexylbenzene-1,4-diboronic acid. The syntheses of Type-3 molecules are shown in Scheme 4. The coupling of dodecylamine and 4-bromobenzoic acid by using EDC·HCl and HOBt as mild coupling reagents afforded 4-bromo-*N*-dodecylbenzamide (**5**) in a yield of 98%. Suzuki–Miyaura cross-coupling



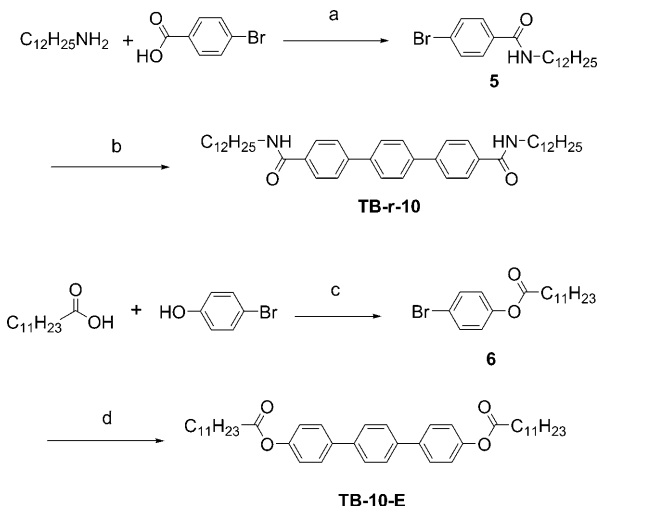
Scheme 1. Carton model of a coil-rod-coil molecule and the chemical structures of Type-1, Type-2, and Type-3 molecules.



Scheme 2. The synthetic routes for Type-1 molecules. Reaction conditions: a) EDC·HCl, HOBt, Et_3N, $CHCl_2$, RT, 24 h; b) $Pd(PPh_3)_4$, $NaHCO_3$, THF, H_2O, N_2, reflux, 24 h. THF = tetrahydrofuran.



Scheme 3. The synthetic routes for type-2 molecules. Reaction conditions: a) $Pd(dppf)Cl_2$, KOAc, DME, N_2, 80 °C, 24 h; b) **1e**, $Pd(PPh_3)_4$, $NaHCO_3$, THF, H_2O, N_2, reflux, 24 h; c) trimethysilylacetylene, $Pd(PPh_3)_2Cl_2$, CuI, $NH(iPr)_2$, THF, N_2, 80 °C, 24 h; d) TBAF, CH_2Cl_2; e) **1e**, $Pd(PPh_3)_2Cl_2$, CuI, $NH(iPr)_2$, THF, N_2, 80 °C, 24 h; f) $Pd(PPh_3)_2Cl_2$, CuI, $NH(iPr)_2$, THF, O_2, RT, 24 h; g) 1,4-biphenyldiboronic acid, $Pd(PPh_3)_4$, $NaHCO_3$, THF, H_2O, N_2, reflux, 24 h; h) 2,5-dihexylphenyldiboronic acid ester, $Pd(PPh_3)_4$, $NaHCO_3$, THF, H_2O, N_2, reflux, 24 h.



Scheme 4. The synthetic routes for Type-3 molecules. Reaction conditions: a) EDC·HCl, HOBt, Et_3N, $CHCl_2$, RT, 24 h; b) 1,4-phenyldiboronic acid ester, $Pd(PPh_3)_4$, $NaHCO_3$, THF, H_2O, N_2, reflux, 24 h; c) DCC, DMAP, $TsSO_3H{\cdot}H_2O$, CH_2Cl_2, RT, 24 h; d) 1,4-phenyldiboronic acid ester, $Pd(PPh_3)_4$, $NaHCO_3$, THF, H_2O, N_2, reflux, 24 h.

of **5** and benzene-1,4-diboronic acid 1,3-propanediol ester afforded the desired coil-rod-coil molecule **TB-r-10** in a yield of 92%. Ester-linked molecule **TB-10-E** was acquired by a Suzuki–Miyaura coupling of benzene-1,4-diboronic acid 1,3-propanediol ester and 4-bromophenyl dodecanoate (**6**), which was prepared by coupling 4-bromophenol and dodecanoic acid with 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS) and DCC as mild coupling agents. All intermediates were unambiguously characterized by ^1H and ^{13}C NMR spectroscopy and elemental analysis. With the exception of **Hex-TB** and **TB-10-E**, all the coil-rod-coil molecules are almost insoluble in any organic solvent at room temperature, thus making routine NMR spectroscopic characterization impossible. These coil-rod-coil molecules precipitated from the solvent mixture during the reaction. The precipitates were thoroughly washed with THF and water to remove the soluble impurities and inorganic salts, the residue was dissolved in hot THF and filtrated, and the resulting precipitate from the hot THF filtrates were collected by filtration to afford the desired products as a colorless solid. The high purity of the products was confirmed by combustion analysis. Compound **TB-10** was selected for solid-state ^{13}C NMR characterization (Figure S1 in the Supporting Information), and the result confirmed the expected structure. The introduction of two hexyl chains on the central benzene ring significantly improved the solubility of **Hex-TB** in common organic solvents. ^1H and ^{13}C NMR spectra of **Hex-TB** and **TB-10-E** also confirmed the expected structures.

Self-Assembly of Coil-Rod-Coil Molecules

The solvent-mediated supramolecular self-assembly experiments were performed by following the previously reported procedures.[13] Typically, a suspension of coil-rod-coil molecules in THF (0.1 mg mL^{-1}) was heated to reflux until all solids were completely dissolved to form a clear solution. The solution was allowed to cool gradually to room temperature, and it turned cloudy after about 1 hour. A drop of the suspension was deposited onto the silicon substrate and copper-grid coated with carbon film for SEM and TEM investigations, respectively. Owing to the extremely poor solubility of compounds **TTB** and **TB-r-10** in THF, only about 0.02 mg mL^{-1} was used to ensure that these two compounds could be completely dissolved in refluxing THF. However, owing to the good solubility of **DB** and **TB-10-E** in THF, a higher concentration (1.0 mg mL^{-1}) was used for the self-assembly study. **Hex-TB** exhibited very good solubility in THF at room temperature; its self-assembling experiment was therefore carried out with xylene as the solvent.

Influence of the Alkyl Chain Length on the Self-Assembly Behavior

To investigate the influence of the coil part on the self-assembly behavior, type-1 series molecules (**TB-1**, **TB-7**, **TB-8**, **TB-9**, **TB-11**, and **TB-16**) with alkyl chain length from C2 to C17 were synthesized and used for supramolecular self-as-

sembling. There was a common feature for type-1 series molecules, they all exhibited a concentration-dependent self-assembling behavior as reported in our previous paper,[13] namely, the self-assembly of the type-1 series molecules at low concentration afforded exclusively rolled-up nanotubes, at high concentration afforded thick layered sheets, and in between afforded a mixture of nanotubes and layered sheets. We have investigated the self-assembly of rolled-up nanotubes by type-1 series molecules in details. Following standard procedures, the supramolecular self-assembly of type-1 series molecules in THF at a concentration of $0.1\,mg\,mL^{-1}$ furnished exclusively rolled-up nanotubes.[13,26–28] SEM images of nanotubes formed by solvent-mediated supramolecular assembly of type-1 series molecules (**TB-1**, **TB-7**, **TB-8**, **TB-9**, **TB-11**, and **TB-16**) are shown in Figure 1. Even **TB-1**, which has a very short coil

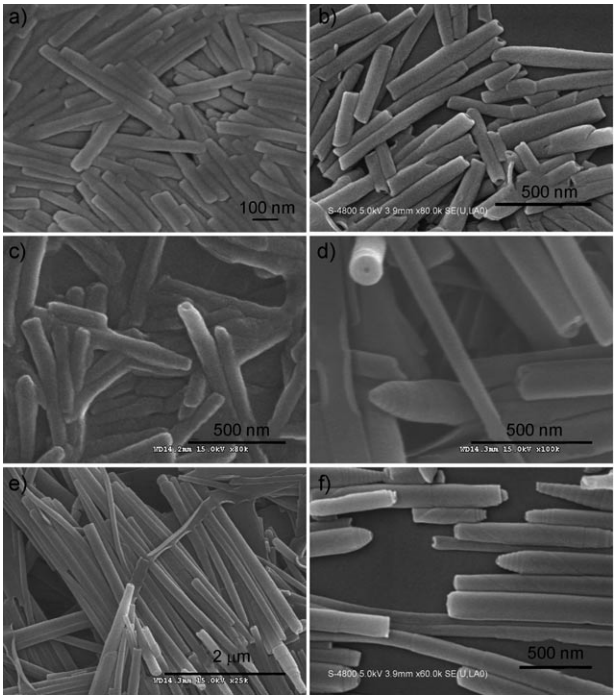


Figure 1. SEM images of a) **TB-1**; b) **TB-7**; c) **TB-8**; d) **TB-9**; e) **TB-11**; f) **TB-16** nanotubes on silicon substrates.

part (C2), can self-assemble to form nanotubes. As observed by SEM and TEM (Figure 2), the nanotubes formed by the self-assembly of **TB-1** are several hundreds of nanometers long and about 60 nanometers in diameter. The TEM image revealed that **TB-1** nanotubes have a very small inner hollow space and a thick tube wall. The self-assembled nanotubes with **TB-7**, **TB-8**, **TB-9**, and **TB-11** have a large diameter distribution ranging from about 100 to 200 nm and a large length distribution ranging from about one to tens of micrometers. As observed by SEM and TEM, the self-assembly of coil-rod-coil molecules (**TB-16**) carrying long flexible alkyl chains afforded high aspect ratio nanotubes. From the above-mentioned results, we could find that the variation of the length of the flexible alkyl chains can cause the change of the diameter and length of the self-assembled nanotubes. These results indicated that the flexible alkyl chain part did not play a key role in the hierarchical supramolecular assembly of nanotubes.

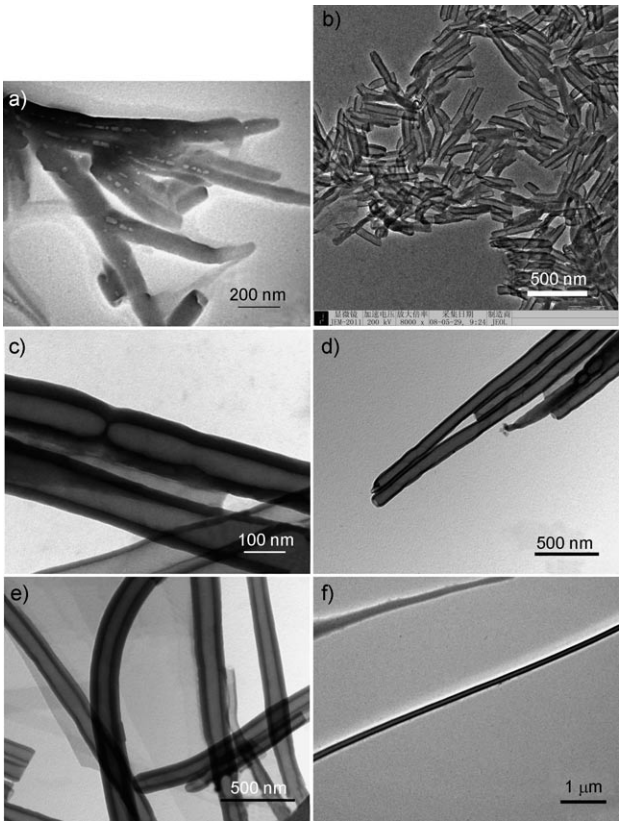


Figure 2. TEM images of a) **TB-1**; b) **TB-7**; c) **TB-8**; d) **TB-9**; e) **TB-11**; f) **TB-16** nanotubes.

Influence of the Central Mesogenic Group on the Self-Assembling Behavior

To investigate the influence of the central mesogenic group on the self-assembly behavior, Type-2 series molecules (**DB**, **AB-1**, **AB-2**, **TTB**, and **Hex-TB**) were synthesized and used for supramolecular self-assembling. In contrast with Type-1 series molecules, Type-2 series molecules showed quite different self-assembling behaviors from one another. An air-dried suspension of **DB** displayed ill-defined aggregates, with only the quasi-1D assemblies (Figure 3a). Owing to the weaker π–π attractive forces between the biphenyl units, the supramolecular assembly of **DB** only afforded less-ordered nanostructures. For **TTB**, the tetraphenylene scaffold has an extremely strong tendency to aggregate through π–π overlap. As shown in Figure 3b, the self-assembly of **TTB** in THF afforded 2D crystals. It is worth noting that a recent paper has already reported a helical structure formed by supramolecular assembly of phenylen-1,4-ylenebis (dodecanamide).[29] The supramolecular self-assembly of coil-rod-

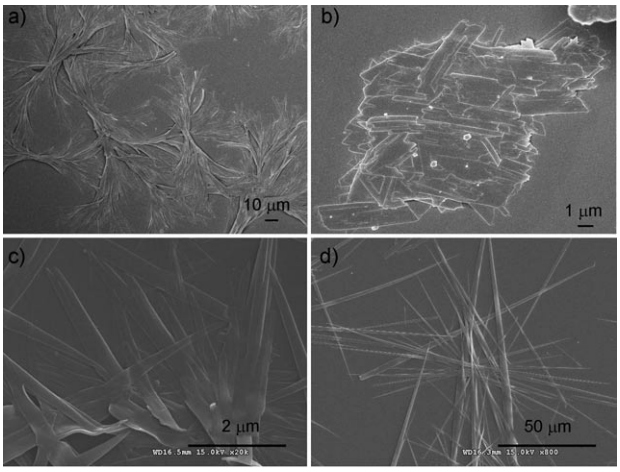


Figure 3. SEM images of self-assembled nanostructures of a) **DB**; b) **TTB**; c) **AB-1**; d) **AB-2**.

coil molecules **AB-1** and **AB-2** in THF only afforded irregular nanobelts as shown in Figure 3c and 3d.

We also studied the steric effect on the supramolecular assembly behavior. Compound **Hex-TB** carrying two lateral hexyl chains at the center phenyl group was also synthesized and used for supramolecular self-assembly. The two bulky lateral hexyl chains can prevent the central terphenylene unit from close packing. As expected, **Hex-TB** is soluble in THF and formed organogel in xylene. SEM and AFM images of **Hex-TB** gel displayed a network structure composed of nanoscale fibrous aggregates with a high aspect ratio. These fibers are several micrometers long and with diameters in the range of 50 to 300 nm, thereby reflecting the hierarchical self-organization (Figure S2 in the Supporting Information).

These experimental results revealed that the central terphenylene segment of coil-rod-coil molecules played a very crucial role for the formation of rolled-up nanotubes.

Influence of the Linker Type on the Self-Assembling Behavior

To investigate the influence of the linker on the self-assembly behavior, Type-3 series molecules (**TB-10-E** and **TB-r-10**) were synthesized and used for supramolecular self-assembly. Coil-rod-coil molecule (**TB-10-E**) with ester linkers between the central *p*-terphenylene unit and the two flexible alkyl chains was also designed and synthesized. In comparison with Type-1 and Type-2 series molecules with amide linkers, **TB-10-E** shows much better solubility in common organic solvents such as THF, chloroform, and methylene chloride. As observed by SEM, the self-assembly of **TB-10-E** in THF only afforded an amorphous film on silicon substrate (Figure S3 in the Supporting Information). Coil-rod-coil molecule **TB-r-10**, which has a central *p*-terphenylene unit, two flexible alkyl chains, and two amide linkers with a nitrogen atom on the alkyl chain, was also used for supramolecular self-assembly. By using similar conditions for the

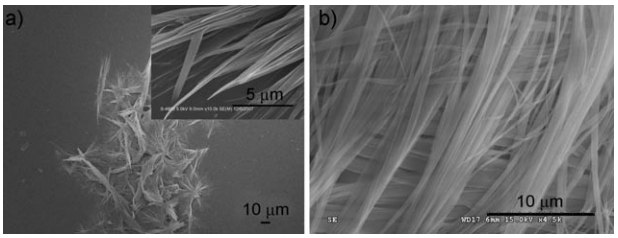


Figure 4. SEM images of a) irregular needle-like microcrystals from the self-assembly of **TB-r-10** at low concentration; b) high aspect ratio microfibrils from the self-assembly of **TB-r-10** at a higher concentration.

self-assembly of Type-1 molecules, the self-assembly of **TB-r-10** in THF with a concentration of 0.02 mg mL^{-1} only afforded irregular needle-like microcrystals[25] (Figure 4a); whereas the supramolecular self-assembly of **TB-r-10** at a higher concentration afforded high aspect ratio microfibrils (Figure 4b). These experiments revealed that the linker between the central terphenylene unit and the two flexible alkyl chains is also very crucial for the formation of rolled-up nanotubes.

Through the above investigations, we could find that the rolled-up nanotubes are closely related to 2D sheets. Coil-rod-coil molecules that can self-assemble to form 2D sheets at a high concentration always form rolled-up nanotubes at a low concentration. If the self-assembly of coil-rod-coil molecules forms nanobelts or nanofibrils, no rolled-up nanotubes can be formed. The rolled-up nanotubes always coexist with 2D sheets, but never with nanofibrils or nanobelts.

Conclusions

Herein, we have described the design and synthesis of a series of non-amphiphilic coil-rod-coil molecules. We have systematically investigated the influence of the following three factors (the length of alkyl chains at two ends, the type of central mesogenic group, and the linker between the central mesogenic group and the alkyl chains) on the self-assembling behaviors. We have found that the central mesogenic group and the linkers play a key role in the self-assembly of rolled-up nanotubes. Only coil-rod-coil molecules with a *p*-terphenylene mesogenic group and two amide linkers with nitrogen atoms at the central *p*-terphenylene unit can form rolled-up nanotubes through supramolecular self-assembling. Variation of the length of alkyl chains at the two ends (from C2 to C17) can modulate the diameter and the length of the self-assembled nanotubes. The self-assembly of other types of coil-rod-coil molecular structures can only afford nanofibrils or nanobelts, but not rolled-up nanotubes. These studies disclosed the key structural features of coil-rod-coil molecules for the formation of rolled-up nanotubes.

Experimental Section

General Methods: The catalyst precursor, $Pd(PPh_3)_4$, was prepared according to the literature[30] and stored in a Schlenk tube under nitrogen. Benzene-1,4-diboronic acid 1,3-propanediol ester[31] and 2,5-dihexylbenzene-1,4-diboronic acid[32] were prepared according to literature procedures. 1,4-Biphenyldiboronic acid was purchased from Lancaster Synthesis. 1-Hydroxybenzotrizole (HOBt), 1-ethyl-3-(3-(dimethylamino) propyl) carbodiimide hydrochloride (EDC·HCl) and dicyclohexylcarbodiimide (DCC) were purchased from Shanghai Medpep. Other chemicals were purchased from Aldrich or Acros and used without further purification. Solvents were dried according to standard procedures. All reactions were performed under an atmosphere of nitrogen and monitored by TLC with silica gel 60 F254 (Merck, 0.2 mm). Column chromatography was carried out on silica gel (200–300 mesh).

Characterization: ^1H and ^{13}C NMR spectra were recorded on an AV400 spectrometer in $CDCl_3$. Elemental analyses were performed on a Flash EA 1112 analyzer. Scanning electron microscopy (SEM) was performed on a JEOL model JSM-6700F FE-SEM and a Hitachi S-4800 FE-SEM operating at 5 kV. Samples for SEM measurement were prepared by dropping a THF suspension onto a silicon substrate followed by air drying and coating with platinum. Transmission electron microscopy (TEM) was performed on a Hitachi H-800 electron microscope operating at 100 kV and a JEOL model JEM-2011 electron microscope operating at 200 kV. Samples for TEM measurement were prepared by dropping the THF suspension (0.1 mg mL^{-1}) onto 200-mesh copper grids followed by air drying. AFM images were recorded under ambient conditions by using a Digital Instrument Multimode Nanoscope IIIA operating in the tapping mode. Samples for AFM measurement were prepared by dipping a silicon wafer into the gel phase for 15 min.

General Procedure for Amide Synthesis: A mixture of amine, acid, HOBt, EDC·HCl, dry CH_2Cl_2, and triethylamine was stirred at room temperature for 24 h. Water was added; the organic layer was separated, washed successively with aqueous HCl (5 M) solution and water, dried over anhydrous Na_2SO_4, and evaporated to dryness. The crude product was purified by silica gel chromatography.

General Procedure for Suzuki Cross-Coupling: A mixture of aryl bromide, diboronic acid or diboronic acid ester, $Pd(PPh_3)_4$, $NaHCO_3$, H_2O, and THF were charged sequentially in a Schlenk flask under a nitrogen atmosphere and heated to reflux for 24 h. The precipitated white solid was filtered, and washed with water and THF. The crude product was then dissolved in refluxing THF, and followed by hot filtration.

N-(4-bromophenyl)propanamide (1a): The general procedure for amide synthesis was followed. 4-Bromoaniline (2.0 g, 11.6 mmol), propanoic acid (0.57 g, 7.7 mmol), HOBt (1.26 g, 9.3 mmol), EDC·HCl (2.67 g, 13.9 mmol), dry CH_2Cl_2 (50.0 mL), and triethylamine (2.0 mL) were used. Chromatography on silica gel eluting with CH_2Cl_2/*n*-hexane (4:1) afforded **1a** as a white solid (1.7 g, 97%). ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.41$ (s, 4H, ArH), 7.30 (s, 1H, NH), 2.38 (m, 2H, CH_2), 1.23 ppm (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 172.51$, 137.17, 132.06, 121.64, 116.92, 30.80, 9.77 ppm. Anal calcd for $C_9H_{10}NBrO$: C 47.39, H 4.42, N 6.14; found: C 47.49, H 4.43, N 5.94.

***N*-(4-bromophenyl)nonanamide (1b)**: The general procedure for amide synthesis was followed. 4-Bromoaniline (2.0 g, 11.6 mmol), nonanoic acid (1.23 g, 7.8 mmol), HOBt (1.26 g, 9.3 mmol), EDC·HCl (2.67 g, 13.9 mmol), dry CH_2Cl_2 (50.0 mL), and triethylamine (2.0 mL) were used. Chromatography on silica gel eluting with CH_2Cl_2/*n*-hexane (4:1) afforded **1b** as a white solid (2.0 g, 82%). ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.41$ (s, 4H, ArH), 7.31 (s, 1H, NH), 2.34 (t, 2H, CH_2), 1.69 (m, 2H, CH_2), 1.28–1.26 (m, 10H, CH_2), 0.87 ppm (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 171.80$, 137.16, 132.07, 121.55, 116.89, 37.91, 31.96, 29.48, 29.42, 29.29, 25.73, 22.79, 14.25 ppm. Anal calcd for $C_{15}H_{22}NBrO$: C 57.70, H 7.10, N 4.49; found: C 57.84, H 7.23, N 4.58.

***N*-(4-bromophenyl)decanamide (1c)**: The general procedure for amide synthesis was followed. 4-Bromoaniline (1.5 g, 8.7 mmol), decanoic acid (1.0 g, 5.8 mmol), HOBt (0.94 g, 7.0 mmol), EDC·HCl (2.0 g, 10.4 mmol), dry CH_2Cl_2 (50.0 mL), and triethylamine (2.0 mL) were used. Chromatography on silica gel eluting with CH_2Cl_2/*n*-hexane (3:1) afforded **1c** as a white solid (1.5 g, 79%). ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.42$ (s, 4H, ArH), 7.15 (s, 1H, NH), 2.34 (t, 2H, CH_2), 1.71 (m, 2H, CH_2), 1.33–1.26 (m, 12H, CH_2), 0.88 ppm (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta =$ 171.60, 136.95, 131.89, 121.34, 116.72, 37.73, 31.82, 29.40, 29.34, 29.23, 25.54, 22.63, 14.08 ppm. Anal calcd for $C_{16}H_{24}NBrO$: C, 58.90; H, 7.41; N, 4.29; found: C 59.02, H 7.47, N 4.34.

***N*-(4-bromophenyl)undecanamide (1d)**: The general procedure for amide synthesis was followed. 4-Bromoaniline (1.38 g, 8.0 mmol), undecanoic acid (1.0 g, 5.4 mmol), HOBt (0.87 g, 6.4 mmol), EDC·HCl (1.85 g, 9.7 mmol), dry CH_2Cl_2 (50.0 mL), and triethylamine (2.0 mL) were used. Chromatography on silica gel eluting with CH_2Cl_2/*n*-hexane (3:1) afforded **1d** as a white solid (1.2 g, 66%). ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.41$ (s, 4H, ArH), 7.22 (s, 1H, NH), 2.34 (t, 2H, CH_2), 1.71 (m, 2H, CH_2), 1.31–1.25 (m, 14H, CH_2), 0.88 ppm (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 172.07$, 137.13, 132.05, 121.68, 116.98, 37.84, 32.04, 29.72, 29.64, 29.53, 29.46, 25.78, 22.83, 14.27 ppm. Anal calcd for $C_{17}H_{26}NBrO$: C 60.00, H 7.70, N 4.12; found: C 60.01, H 7.70, N, 4.35.

***N*-(4-bromophenyl)dodecanamide (1e)**: The general procedure for amide synthesis was followed. 4-Bromoaniline (1.93 g, 11.2 mmol), lauric acid (1.5 g, 7.5 mmol), HOBt (1.22 g, 9.0 mmol), EDC·HCl (2.58 g, 13.4 mmol), dry CH_2Cl_2 (60.0 mL), and triethylamine (2.0 mL) were used. The crude product was precipitated in *n*-hexane and then filtrated. Flash chromatography on silica gel eluting with CH_2Cl_2 afforded **1e** as a white solid (1.9 g, 72%). ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7$ .42 (s, 4H, ArH), 7.18 (s, 1H, NH), 2.34 (t, 2H, CH_2), 1.71 (m, 2H, CH_2), 1.32–1.25 (m, 16H, CH_2), 0.88 ppm (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta =$ 171.87, 137.20, 132.06, 121.58, 116.89, 37.91, 32.07, 29.78, 29.65, 29.54, 29.50, 29.43, 25.75, 22.85, 14.29 ppm. Anal calcd for $C_{18}H_{28}NBrO$: C 61.34, H 7.99, N 4.21; found: C 61.02, H 7.97, N, 4.52.

***N*-(4-bromophenyl)tridecanamide (1f)**: The general procedure for amide synthesis was followed. 4-Bromoaniline (1.2 g, 7.0 mmol), tridecanoic acid (1.0 g, 4.6 mmol), HOBt (0.76 g, 5.6 mmol), EDC·HCl (1.61 g, 8.4 mmol), dry CH_2Cl_2 (50.0 mL), and triethylamine (2.0 mL) were used. Chromatography on silica gel eluting with CH_2Cl_2/*n*-hexane (3:1) afforded **1f** as a white solid (0.9 g, 52%). ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7$ .42(s, 4H, ArH), 7.09 (s, 1H, NH), 2.34(t, 2H, CH_2), 1.71 (m, 2H, CH_2), 1.33–1.25 (m, 18H, CH_2), 0.88 ppm (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 171.81$, 137.12, 132.05, 121.54, 116.89, 37.88, 32.05, 29.76, 29.61, 29.48, 29.40, 25.71, 22.82, 14.26 ppm. Anal calcd for $C_{19}H_{30}NBrO$: C 61.95, H 8.21, N 3.80; found: C 61.92, H 8.29, N 3.58.

***N*-(4-bromophenyl)stearicamide (1g)**: The general procedure for amide synthesis was followed. 4-Bromoaniline (1.36 g, 7.9 mmol), stearic acid (1.5 g, 5.3 mmol), HOBt (0.86 g, 6.4 mmol), EDC·HCl (1.8 g, 9.4 mmol), dry CH_2Cl_2 (50.0 mL), and triethylamine (2.0 mL) were used. The crude product was recrystallized with CH_2Cl_2 to afford a white solid (0.8 g, 35%). ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.42$(s, 4H, ArH), 7.14(s, 1H, NH), 2.34(t, 2H, CH_2), 1.71(m, 2H, CH_2), 1.43–1.25 (m, 28H, CH_2), 0.88 ppm (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 171.53$, 137.02, 131.97, 121.34, 116.74, 37.84, 33.68, 31.95, 29.72, 29.49, 29.38, 29.28, 29.10, 25.56, 24.77, 22.72, 14.14 ppm. Anal calcd for $C_{24}H_{40}BrNO$: C 65.74, H 9.19, N 3.19; found: C 65.81, H 9.35, N 3.48.

***N*-(4-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)phenyl)dodecanamide (2)**: A Schlenk tube was charged with **1e** (0.45 g, 1.27 mmol), KOAc (0.75 g, 7.6 mmol), bis(pinacolato)diboron (0.645 g, 2.54 mmol), Pd(dppf)Cl_2 (0.03 g, 0.038 mmol) and DMF (30 mL) and flushed with nitrogen. The mixture was stirred at 80 °C for 24 h under nitrogen. Ethyl acetate (80 mL) was added and the mixture was washed with water (3× 50 mL) to remove DMF from the organic layer. The organic layer was separated, dried over anhydrous Na_2SO_4, and evaporated to dryness. The crude product was purified by flash silica gel chromatography eluting with CH_2Cl_2 to afford **2** as a white solid (0.50 g, 98%). ^1H NMR ($CDCl_3$, 400 MHz): $\delta = 7.76$ (d, 2H, ArH), 7.52 (d, 2H, ArH), 7.17 (s, 1H, NH), 2.35 (t, 2H, CH_2), 1.71 (m, 2H, CH_2), 1.33 (s, 12H, CH_3), 1.29–1.25 (m, 16H, CH_2), 0.88 ppm (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta =$ 171.59, 140.68, 135.79, 118.56, 83.72, 37.90, 31.90, 29.60, 29.47, 29.38, 29.32, 29.27, 25.56, 25.16, 24.84, 22.68, 14.11 ppm. Anal calcd for $C_{24}H_{40}NBO_3$: C 71.81, H 10.04, N 3.49; found: C 71.27, H 10.06, N, 3.59.

***N*-(4-ethylene phenyl)dodecanamide (4)**: $Pd(PPh_3)_2Cl_2$ (36 mg, 0.050 mmol) and CuI (19.3 mg, 0.01 mmol) were added to a dry Schlenk flask, which was degassed and purged with nitrogen, **1e** (1.8 g, 5.08 mmol), THF (12 mL) and $HN(i\text{Pr})_2$ (8 mL), and trimethysilylacetylene (0.87 mL, 6.09 mmol) were added by using a syringe. The mixture was heated to 80 °C and stirred for 24 h. The solvent was removed under vacuum, the residue was dissolved in CH_2Cl_2 and purified by flash silica gel chromatography eluting with CH_2Cl_2 to give **3** as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.47$ (d, 2H, ArH), 7.41 (d, 2H, ArH), 7.13 (s, 1H, NH), 2.34 (t, 2H, CH_2), 1.71 (m, 2H, CH_2), 1.33–1.25 (m, 16H, CH_2), 0.88 (t, 3H, CH_3), 0.24 ppm (s, 9H, CH_3). Tetrabutylammonium fluoride (1.69 g, 6.46 mmol) was added dropwise to a solution of compound **3** in 25 mL of CH_2Cl_2 at 0 °C. The mixture was stirred for 10 min and purified by flash silica gel chromatography eluting with CH_2Cl_2 to afford **4** as a white solid (1.26 g, 83 %). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta =$ 7.49 (d, 2H, ArH), 7.43 (d, 2H, ArH), 7.31 (s, 1H, NH), 3.03 (s, 1H, CH), 2.34 (t, 2H, CH_2), 1.71 (m, 2H, CH_2), 1.33–1.25 (m, 16H, CH_2), 0.88 ppm (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 171.45$, 138.39, 132.89, 119.23, 117.49, 83.34, 37.83, 31.86, 29.56, 29.43, 29.32, 29.28, 29.22, 25.50, 22.64, 14.07 ppm. Anal calcd for $C_{20}H_{29}NO$: C 80.22, H 9.76, N, 4.68; found: C 80.04, H 9.68, N 4.66.

4-Bromo-*N*-dodecylbenzamide (5): The general procedure for amide synthesis was followed. 4-Bromobenzoic acid (2.0 g, 9.95 mmol), dodecanamine (2.2 g, 11.9 mmol), HOBt (1.6 g, 11.8 mmol), EDC·HCl (3.4 g, 17.7 mmol), dry CH_2Cl_2 (60.0 mL), and triethylamine (2.0 mL) were used. Chromatography on silica gel eluting with CH_2Cl_2/*n*-hexane (3:1) afforded **5** as a white solid (3.6 g, 98 %). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.62$ (d, 2H, ArH), 7.55 (d, 2H, ArH), 6.13 (s, 1H, NH), 3.43 (m, 2H, CH_2), 1.60 (m, 2H, CH_2), 1.33–1.25 (m, 18H, CH_2), 0.88 ppm (t, 3H, CH_3). ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 166.60$, 133.66, 131.71, 128.53, 125.93, 40.26, 31.91, 29.64, 29.63, 29.59, 29.55, 29.34, 27.01, 22.68, 14.11 ppm; Anal calcd for $C_{19}H_{30}NBrO$: C 61.95, H 8.21, N, 3.80; found: C 62.02, H 8.19, N, 3.98.

4-Bromophenyl dodecanoate (6): A mixture of lauric acid (1.0 g, 5.0 mmol), 4-bromophenol (1.3 g, 7.5 mmol), 4-(dimethylamino)pyridinium 4-toluenesulfonate (DPTS)[33] (1.76 g, 6 mmol), and CH_2Cl_2 (30 mL) was stirred at room temperature for 1 h. A solution of DCC (1.8 g, 9.0 mmol) in CH_2Cl_2 (20 mL) was slowly added to this mixture. After the addition was complete, the mixture was stirred at room temperature for 24 h. The urea precipitate was filtered off and the obtained solution was evaporated to dryness. The residue was purified by chromatography on silica gel eluting with CH_2Cl_2/*n*-hexane (1:2) to afford **6** as a white solid (1.6 g, 90 %). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.48$ (d, 2H, ArH), 6.97 (d, 2H, ArH), 2.54 (t, 2H, CH_2), 1.74(m, 2H, CH_2), 1.41–1.19 (m, 16H, CH_2), 0.89 ppm (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 171.92$, 149.82, 132.41, 123.39, 118.74, 34.94, 34.34, 31.91, 29.60, 29.45, 29.33, 29.24, 29.09, 24.88, 22.68, 14.10 ppm. Anal calcd for $C_{18}H_{27}BrO_2$: C 60.85, H 7.66, found: C 61.21, H 7.65.

Terphenylene-bispropanamide (TB-1): The general procedure for Suzuki cross-coupling was followed. **1a** (0.200 g, 0.88 mmol), 1,4-phenyldiboronic acid ester (0.087 g, 0.35 mmol), $Pd(PPh_3)_4$ (16 mg, 0.014 mmol), $NaHCO_3$ (1.23 g, 14.6 mmol), H_2O (5 mL) and THF (10 mL) were used. **TB-1** was obtained as a white solid (0.10 g, 76 %). Anal calcd for $C_{24}H_{24}N_2O_2$: C 77.39, H 6.49, N 7.52; found: C 77.01, H 7.50, N 6.47.

Terphenylene-bisnonanamide (TB-7): The general procedure for Suzuki cross-coupling was followed. **1b** (0.200 g, 0.64 mmol), 1,4-phenyldiboronic acid ester (0.065 g, 0.26 mmol), $Pd(PPh_3)_4$ (12 mg, 0.010 mmol), $NaHCO_3$ (0.9 g, 10.7 mmol), H_2O (5 mL), and THF (10 mL) were used. **TB-7** was obtained as a white solid (0.10 g, 70 %). Anal calcd for $C_{36}H_{48}N_2O_2$: C 79.96, H 8.95, N 5.18; found: C 79.88, H 8.99, N 5.27.

Terphenylene-bisdecanamide (TB-8): The general procedure for Suzuki cross-coupling was followed. **1c** (0.15 g, 0.46 mmol), 1,4-phenyldiboronic acid ester (0.047 g, 0.19 mmol), $Pd(PPh_3)_4$ (8.8 mg, 0.0076 mmol), $NaHCO_3$ (0.64 g, 7.6 mmol), H_2O (5 mL), and THF (10 mL) were used to afford **TB-8** as a white solid (0.072 g, 66 %). Anal calcd for $C_{38}H_{52}N_2O_2$: C 80.24, H 9.21, N 4.92; found: C 79.80, H 9.00, N 5.06.

Terphenylene-bisundecanamide (TB-9): The general procedure for Suzuki cross-coupling was followed. **1d** (0.200 g, 0.59 mmol), 1,4-phenyldiboronic acid ester (0.06 g, 0.244 mmol), $Pd(PPh_3)_4$ (11 mg, 0.0095 mmol), $NaHCO_3$ (0.82 g, 9.8 mmol), H_2O (5 mL), and THF (10 mL) were used to afford **TB-9** as a white solid (0.11 g, 76 %). Anal Calcd for $C_{40}H_{56}N_2O_2$: C 80.49, H 9.46, N 4.69; found: C 79.99, H 9.38, N 4.69.

Terphenylene-bisdodecanamide (TB-10): The general procedure for Suzuki cross-coupling was followed. **1e** (0.200 g, 0.56 mmol), 1,4-phenyldiboronic acid ester (0.058 g, 0.23 mmol), $Pd(PPh_3)_4$ (11 mg, 0.0095 mmol), $NaHCO_3$ (0.79 g, 9.4 mmol), H_2O (5 mL), and THF (10 mL) were used to afford **TB-10** as a white solid (0.115 g, 78 %). Anal calcd for $C_{42}H_{60}N_2O_2$: C 80.72, H 9.68, N 4.48; found: C 80.43, H 9.59, N 4.41.

Terphenylene-bistridecanamide (TB-11): The general procedure for Suzuki cross-coupling was followed. **1f** (0.200 g, 0.54 mmol), 1,4-phenyldiboronic acid ester (0.056 g, 0.23 mmol), $Pd(PPh_3)_4$ (10 mg, 0.0086 mmol), $NaHCO_3$ (0.76 g, 9.0 mmol), H_2O (5 mL), and THF (10 mL) were used to afford **TB-11** as a white solid (0.12 g, 81 %). Anal calcd for $C_{44}H_{64}N_2O_2$: C 80.93, H 9.88, N 4.29; found: C 80.24, H 9.75, N 4.16.

Terphenylene-bisstearicamide (TB-16): The general procedure for Suzuki cross-coupling was followed. **1g** (0.15 g, 0.34 mmol), 1,4-phenyldiboronic acid ester (0.035 g, 0.14 mmol), $Pd(PPh_3)_4$ (6.6 mg, 0.0057 mmol), $NaHCO_3$ (0.48 g, 5.7 mmol), H_2O (5 mL), and THF (10 mL) were used to afford **TB-16** as a white solid (0.076 g, 67 %). Anal calcd for $C_{54}H_{84}N_2O_2$: C 81.76, H 10.67, N 3.53 ; found: C 81.06, H 10.50, N 3.54.

DB: The general procedure for Suzuki cross-coupling was followed. **1e** (0.094 g, 0.265 mmol), **2** (0.1 g, 0.249 mmol), $Pd(PPh_3)_4$ (5.4 mg, 0.0047 mmol), $NaHCO_3$ (0.4 g, 4.7 mmol), H_2O (5 mL), and THF (10 mL) were used to afford **DB** as a white solid (0.113 g, 83 %). Anal calcd for $C_{36}H_{56}N_2O_2$: C 78.78, H 10.28, N 5.10; found: C 78.63, H 10.38, N 5.09.

TTB: The general procedure for Suzuki cross-coupling was followed. **1e** (0.200 g, 0.56 mmol), 1,4-biphenyldiboronic acid (0.056 g, 0.23 mmol), $Pd(PPh_3)_4$ (10 mg, 0.0086 mmol), $NaHCO_3$ (0.79 g, 9.4 mmol), H_2O (5 mL), and THF (15 mL) were used to afford **TTB** as a white solid (0.131 g, 79 %).

Hex-TB: The general procedure for Suzuki cross-coupling was followed. **1e** (0.42 g, 1.18 mmol), 2,5-dihexylphenyldiboronic acid ester (0.2 g, 0.48 mmol), $Pd(PPh_3)_4$ (12 mg, 0.01 mmol), $NaHCO_3$ (1.66 g, 19.8 mmol), H_2O (9 mL) and THF (25 mL) were used. The organic layer was separated, the aqueous layer was extracted with Et_2O (2×30 mL), and the combined organic layers were dried over anhydrous Na_2SO_4 and evaporated to dryness. Chromatography on silica gel eluting with CH_2Cl_2/*n*-hexane (2:1) afforded **Hex-TB** as a white solid (0.32 g, 83 %). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.58$ (d, 4H, ArH), 7.48 (s, 2H, NH), 7.30 (d, 4H, ArH), 7.08 (s, 2H, ArH), 2.54 (t, 4H, CH_2), 2.41 (t, 4H, CH_2), 1.76 (m, 4H, CH_2), 1.45–1.17 (m, 48H, CH_2), 0.88 (t, 6H, CH_3), 0.81 ppm (t, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 171.79$, 140.21, 138.08, 137.65, 136.73, 131.03, 129.99, 119.57, 37.99, 32.73, 32.04, 31.67, 31.51, 29.75, 29.64, 29.54, 29.47, 29.35, 25.90, 22.82, 22.64, 14.25, 14.17 ppm; Anal calcd for $C_{54}H_{84}N_2O_2$: C 81.76, H 10.67, N 3.53; found: C 81.43, H 10.51, N 3.73.

AB-1: **4** (0.217 g, 0.72 mmol) and **1e** (0.31 g, 0.87 mmol) were dissolved in a solvent mixture of THF (6 mL) and diisopropylamine (4 mL) in a Schlenk tube. The mixture was degassed and purged with nitrogen, $Pd(PPh_3)_2Cl_2$ (5.1 mg, 0.0073 mmol) and CuI (2.8 mg, 0.01 mmol) were then added. After the mixture was further carefully degassed and recharged with nitrogen, it was heated to 80 °C and stirred for 24 h. The precipitate was filtered and washed thoroughly with CH_2Cl_2, water, and THF to afford **AB-1** as a gray solid (0.13 g, 31 %). Anal calcd for $C_{38}H_{56}N_2O_2$: C 79.67, H 9.85, N 4.89; found: C 79.40, H 9.45, N 4.90.

AB-2: **4** (0.24 g, 0.80 mmol), $Pd(PPh_3)_2Cl_2$ (6 mg, 0.0085 mmol), and CuI (55 mg, 0.289 mmol) were dissolved in pyridine (8 mL) and filled with O_2. The mixture was then stirred for 24 h. The precipitate was filtered and washed thoroughly with CH_2Cl_2, water, and THF to afford **AB-2** as a gray solid (0.15 g, 63 %). Anal calcd for $C_{40}H_{56}N_2O_2$: C, 80.49, H 9.46, N 4.69; found: C 80.22, H 9.46, N 4.62.

TB-r-10: The general procedure for Suzuki cross-coupling was followed. **5** (0.400 g, 1.08 mmol), 1,4-phenyldiboronic acid ester (0.111 g, 0.45 mmol), $Pd(PPh_3)_4$ (21 mg, 0.018 mmol), $NaHCO_3$ (1.52 g, 18.1 mmol), H_2O (10 mL) and THF (30 mL) were used and afforded **TB-r-10** as a white solid (0.27 g, 92%). Anal calcd for $C_{44}H_{64}N_2O_2$: C 80.93, H 9.88, N 4.29; found: C 80.56, H 9.83, N 4.27.

TB-10-E: The general procedure for Suzuki cross-coupling was followed. **6** (0.2 g, 0.56 mmol), 1,4-phenyldiboronic acid ester (0.054 g, 0.22 mmol), $Pd(PPh_3)_4$ (5.4 mg, 0.0047 mmol), $NaHCO_3$ (0.79 g, 9.4 mmol), H_2O (5 mL), and THF (10 mL) were used. The precipitated white solid was filtered and washed with water and THF to afford **TB-10-E** as a white solid (0.09 g, 65%). ^{1}H NMR ($CDCl_3$, 400 MHz): $\delta = 7.64$ (s, 4H, ArH), 7.63 (d, 4H, ArH), 7.17 (d, 4H, ArH), 2.59 (t, 4H, CH_2), 1.78 (m, 4H, CH_2), 1.46–1.28 (m, 32H, CH_2), 0.89 ppm (t, 6H, CH_3); ^{13}C NMR ($CDCl_3$, 100 MHz): $\delta = 172.38$, 150.32, 139.39, 138.28, 128.02, 127.49, 121.94, 34.47, 31.92, 29.62, 29.48, 29.35, 29.28, 29.14, 24.99, 22.70, 14.12 ppm. Anal calcd for $C_{42}H_{58}O_4$: C 80.47, H 9.33; found: C 80.44, H 9.30.

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