3-D Organic nanostructures from self-assembly of branched aromatic rods

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Self-assembling molecules based on branched aromatic rods, which are prepared by repeating of aromatic coupling reaction and substitution, and flexible dibranched ether-type coils were synthesized. Aggregation behavior could be investigated by optical polarized microscopy, differential scanning calorimetry, and X-ray diffraction. In contrast to the molecule **1** which shows an isotropic liquid state, the more elongated molecules **2** and **3** are observed to organize into a 3-D primitive monoclinic lattice with three distinct nanoscale dimensions, in which rods are tilted with respect to the layer normal.

Introduction

Discrete organic nanostructures have certainly become one of the most promising and creative research areas in recent years.[1] In spite of the high potential applications and processabilities, it is a field still unexplored because of the difficulty in accurately manipulating organic supramolecular structures. Discrete nanostructures can be prepared by copolymerization, thin film casting, and hybridization with inorganic materials.[2] In addition, organic materials consisting of well-defined nanostructures can be manipulated through rational molecular design of self-assembling molecules based on rigid rod building blocks. For example, it has been reported that, by increasing the volume fraction of the flexible coils, rod-coil molecules will change from lamellar or cylindrical structures to discrete bundle structures which organize themselves into a superlattice.[3] Incorporation of a bulky amorphous coil with a large cross-sectional area to the rod segments has also been reported to have a large impact on the ability of the system to self-organize into discrete organic nanostructures.[4] In addition, previous experiments from our laboratory have demonstrated that the rod-coil molecules based on topologically different flexible segments with almost identical molecular weights assemble into discrete bundles with tunable nano dimensions.[5]

The subsequent extension of research on supramolecular nanostructures increases the synthetic capabilities for designing the molecules based on various rods as well as on coil building blocks. A strategy to manipulate discrete supramolecular structures may be possible by introducing a branched aromatic rod building block into a rod-coil molecular architecture (Fig. 1). As the cross-sectional area of the rod end increases while maintaining the parallel order of rod building blocks, greater steric repulsion between adjacent rods could possibly cause frustration of the lamellar ordering to relieve repulsive forces. This implies that branched rods can give rise to the formation of well-defined discrete nanostructures. We report here on the synthesis and self-organization of the novel molecules based on branched rod block and flexible ether-type coils.

Experimental

Techniques

^{1}H-NMR spectra were recorded from $CDCl_3$ solutions on a Bruker AM 250 spectrometer. The purity of the products was checked by thin layer chromatography (TLC; Merck, silica gel 60). A Perkin Elmer DSC-7 differential scanning calorimeter equipped with a 1020 thermal analysis controller was used to determine the thermal transitions, which were reported as the maxima and minima of their endothermic or exothermic peaks. In all cases, the heating and cooling rates were 10 °C min^{-1}. A Nikon Optiphot 2-pol optical polarized microscope (magnification: 100×) equipped with a Mettler FP 82 hot-stage and a Mettler FP 90 central processor was used to observe the thermal transitions and to analyze the anisotropic texture. Microanalyses were performed with a Perkin Elmer 240 elemental analyzer. X-Ray scattering measurements were performed in transmission mode with synchrotron radiation at the 3C2 X-ray beam line at Pohang Accelerator Laboratory, Korea. Molecular weight distributions ($\bar{M}_w/\bar{M}_n$) were determined by gel permeation chromatography (GPC) with a Waters instrument equipped with Stragel HR 3, 4 and 4E columns, an M7725i manual injector, a column heating chamber and a 2010 Millennium data station. Measurements were made using a UV detector, $CHCl_3$ as eluent (1.0 ml min^{-1}) and a calibration plot constructed with polystyrene standards.

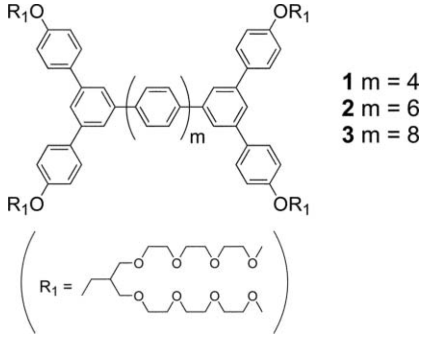

Fig. 1 Chemical structure of the molecules based on branched aromatic rod building blocks.

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MALDI-TOF-MS was performed on a Perspective Biosystems Voyager-DE STR using a 2,5-dihydroxybenzoic acid matrix. The molecular density (ρ) measurements were performed in aqueous sodium chloride solution at 25 °C.

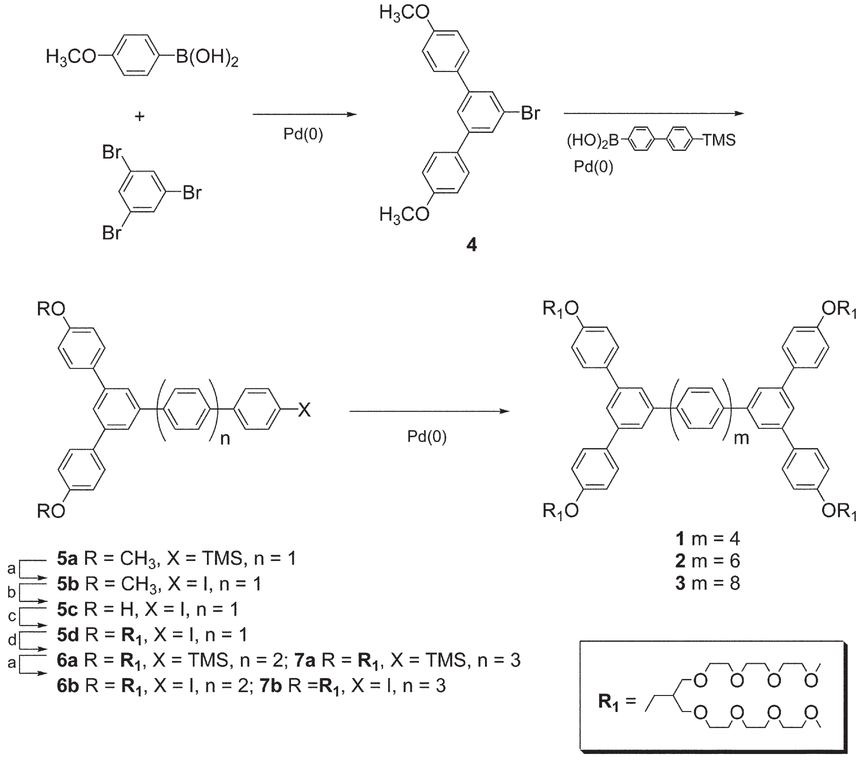
Synthesis

Chlorotrimethylsilane (98%), tetrakis(triphenylphosphine)-palladium(0) (99%), pentaerythritol (98%), *n*-butyllithium (1.6 M solution in *n*-hexane), 4,4′-dibromobiphenyl (98%), borane–THF complex (1.0 M solution in THF), boron tribromide (1.0 M solution in dichloromethane), 18-crown-6 (99%), potassium iodide (99%), *p*-toluenesulfonyl chloride (98%), triisopropyl borate (98+%), bisbenzonitrilepalladium(II) dichloride, tetradimethylaminoethylene (TDAE) (98%), iodine monochloride (1.0 M solution in dichloromethane), 4-bromoanisole (99%) (all from Aldrich) and the conventional reagents were used as-received. 4-Trimethylsilyl-4′-biphenylboronic acid, compounds **4**, **5a**–**c**, and ether-type dibranched coils (**R$_1$**) were prepared according to similar procedures described previously.[4,5] The general synthetic routes for **1**–**3** are shown in Scheme 1.

Synthesis of compound 5d. Compound **5c** (0.6 g, 1.1 mmol), **R$_1$**OTs (0.67 g, 1.2 mmol) and K_2CO_3 (1.5 g, 11 mmol) were dissolved in CH_3CN (70 ml). The reaction mixture was refluxed for 72 h under nitrogen. Cooled to room temperature, water (100 ml) was added and the aqueous layer was washed twice with ethyl acetate. The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. The solvent was removed in a rotary evaporator. The crude product was purified by column chromatography (silica gel, ethyl acetate followed by THF to yield 1.1 g (70%) of a colorless oil; ^{1}H-NMR (250 MHz, $CDCl_3$, δ/ppm) 2.41–2.44 [m, 2H, $C(CH_2)_3H$], 3.36 (s, 12H, OCH_3), 3.50–3.66 (m, 56H, OCH_2), 4.09 (m, 4H, CH_2OPh, J = 5.6 Hz), 7.01 (d, 4Ar-H, *o* to OCH_2, J = 8.7 Hz), 7.40 (d, 2Ar-H, *o* to I, J = 8.4 Hz), 7.60–7.81 (m, 13Ar-H).

Synthesis of compounds 6a and 7a. Compounds were synthesized using the same procedure. A representative example is described for **7a**. Compound **5d** (2.3 g, 1.8 mmol) and 4-trimethylsilyl-biphenyl-4′-boronic acid (0.5 g, 1.9 mmol) were dissolved in degassed THF (50 ml). Degassed 2 M aqueous Na_2CO_3 (50 ml) was added to the solution and then tetrakis(triphenylphosphine)palladium(0) (10 mg, 9 μmol) was added. The mixture was refluxed for 24 h with vigorous stirring under nitrogen. Cooled to room temperature, the layers were separated, and the aqueous layer was washed twice with ethyl acetate. The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel, ethyl acetate followed by THF) to yield 2.0 g (81%) of a light yellow oil; ^{1}H-NMR (250 MHz, $CDCl_3$, δ/ppm) 0.31 [s, 9H, $(CH_3)_3Si$], 2.41–2.44 [m, 2H, $C(CH_2)_3H$], 3.36 (s, 12H, OCH_3), 3.50–3.66 (m, 56H, OCH_2), 4.09 (m, 4H, CH_2OPh, J = 5.6 Hz), 7.01 (d, 4Ar-H, *o* to OCH_2, J = 8.7 Hz), 7.61–7.80 (m, 23Ar-H).

Compound **6a**. Yield 60%; ^{1}H-NMR (250 MHz, $CDCl_3$, δ/ppm) 0.32 [s, 9H, $(CH_3)_3Si$], 2.41–2.44 [m, 2H, $C(CH_2)_3H$], 3.36 (s, 12H, OCH_3), 3.50–3.66 (m, 56H, OCH_2), 4.09 (m, 4H,



Scheme 1 Synthesis of molecules **1**, **2**, and **3**: a) ICl; b) BBr_3; c) **R$_1$**OTs, K_2CO_3; d) Pd(0), 4-trimethylsilylbenzeneboronic acid or 4-trimethylsilyl-4′-biphenylboronic acid.

CH_2OPh, $J = 5.6$ Hz), 7.01 (d, 4Ar-H, *o* to OCH_2, $J = 8.8$ Hz), 7.64–7.79 (m, 19Ar-H).

Synthesis of compounds 6b and 7b. Compounds were synthesized using the same procedure. A representative example is described for **7b**. To a solution of compound **7a** (2.0 g, 1.43 mmol) in CH_2Cl_2 at −78 °C was added dropwise a 1.0 M solution of ICl in CH_2Cl_2 (3 ml). The reaction mixture was stirred over 1 h under nitrogen. 1 M aqueous $Na_2S_2O_5$ solution was added and stirred over 1 h. The layers were separated, and the aqueous layer was washed twice with CH_2Cl_2. The combined organic layer was dried over anhydrous $MgSO_4$ and filtered. The solvent was removed in a rotary evaporator, and the crude product was purified by column chromatography (silica gel, ethyl acetate followed by THF) to yield 1.5 g (72%) of a colorless oil; ^{1}H-NMR (250 MHz, $CDCl_3$, δ/ppm) 2.40–2.44 [m, 2H, $C(CH_2)_3H$], 3.36 (s, 12H, OCH_3), 3.50–3.66 (m, 56H, OCH_2), 4.09 (m, 4H, CH_2OPh, $J = 5.6$ Hz), 7.00 (d, 4Ar-H, *o* to OCH_2, $J = 8.7$ Hz), 7.41 (d, 2Ar-H, *o* to I, $J = 8.4$ Hz), 7.60–7.81 (m, 21Ar-H).

Compound **6b**. Yield 68%; ^{1}H-NMR (250 MHz, $CDCl_3$, δ/ppm) 2.38–2.44 [m, 2H, $C(CH_2)_3H$], 3.36 (s, 12H, OCH_3), 3.50–3.67 (m, 56H, OCH_2), 4.09 (m, 4H, CH_2OPh, $J = 5.6$ Hz), 7.03 (d, 4Ar-H, *o* to OCH_2, $J = 8.5$ Hz), 7.40 (d, 2Ar-H, *o* to I, $J = 8.1$ Hz), 7.58–7.80 (m, 17Ar-H).

Synthesis of compounds 1, 2, and 3. Compounds were synthesized using the same procedure. A representative example is described for **3**. Compound **7b** (0.7 g, 0.48 mmol), and TDAE (0.2 g 1.0 mmol) were dissolved in DMF (30 ml). And then $Pd(PhCN)_2Cl_2$ (10 mg, 25 μmol) was added. The mixture was heated at 50 °C for 4 h with stirring under nitrogen. After being cooled to room temperature, the DMF solvent was removed under vacuum distillation, and the crude product was purified by column chromatography (silica gel, ethyl acetate followed by THF) and precipitated by CH_2Cl_2 and *n*-hexane to yield 0.48 g (75%) of a waxy solid: mp > 300 °C; GPC $\bar{M}_w/\bar{M}_n = 1.04$; ^{1}H-NMR (250 MHz, $CDCl_3$, δ/ppm) 2.43–2.48 [m, 4H, $C(CH_2)_3H$], 3.37 (s, 24H, OCH_3), 3.52–3.66 (m, 112H, OCH_2), 4.11 (d, 8H, CH_2OPh, $J = 5.5$ Hz), 7.03 (d, 8Ar-H, *o* to OCH_2, $J = 8.7$ Hz), 7.62–7.80 (m, 46Ar-H). MALDI-TOF-MS *m*/*z* $(M + H + Na)^+$ 2675.35; Calc. 2675.40; Anal. calc. for $C_{156}H_{202}O_{36}$: C, 70.62; H, 7.67. Found C, 70.60; H, 7.54%.

Compound **1**. Yield 60%; GPC $\bar{M}_w/\bar{M}_n = 1.04$; ^{1}H-NMR (250 MHz, $CDCl_3$, δ/ppm) 2.44–2.48 [m, 4H, $C(CH_2)_3H$], 3.37 (s, 24H, OCH_3), 3.52–3.66 (m, 112H, OCH_2), 4.11 (d, 8H, CH_2OPh, $J = 5.5$ Hz), 7.03 (d, 8Ar-H, *o* to OCH_2, $J = 8.6$ Hz), 7.54–7.90 (m, 30Ar-H). MALDI-TOF-MS *m*/*z* $(M + H + Na)^+$ 2371.66; Calc. 2371.27; Anal. calc. for $C_{132}H_{186}O_{36}$: C, 67.50; H, 7.98. Found C, 67.46; H, 7.95%.

Compound **2**. Yield 78%; mp 105 °C; GPC $\bar{M}_w/\bar{M}_n = 1.03$; ^{1}H-NMR (250 MHz, $CDCl_3$, δ/ppm) 2.42–2.46 [m, 4H, $C(CH_2)_3H$], 3.36 (s, 24H, OCH_3), 3.52–3.64 (m, 112H, OCH_2), 4.10 (d, 8H, CH_2OPh, $J = 5.4$ Hz), 7.02 (d, 8Ar-H, *o* to OCH_2, $J = 8.5$ Hz), 7.46–7.80 (m, 38Ar-H). MALDI-TOF-MS *m*/*z* $(M + H + Na)^+$ 2523.24; Calc. 2523.33; Anal. calc. for $C_{144}H_{194}O_{36}$: C, 69.15; H, 7.82. Found C, 69.10; H, 7.86%.

Results and discussion

The synthesis of molecules with branched aromatic rods was outlined in Scheme 1. A flexible ether-type dibranched coil was prepared according to the procedures described previously.[5] The synthesis of a branched rod building block was performed by using an aromatic coupling reaction with a Pd(0) catalyst.[6] Commercially available 1,3,5-tribromobenzene, which was selected as an aromatic branching point, was coupled with 2 equiv. of anisole boronic acid by a Suzuki aromatic coupling reaction. The resulting terphenylene compound **4** was elongated by coupling with 4-trimethylsilyl-4′-biphenylboronic acid and yielded compound **5a**. The silyl group of **5a** was subsequently substituted into iodine which is the most active group for the next aromatic coupling. To increase the solubility, flexible coil should be attached to the rod building blocks at the penta phenylene step prior to further extension of the rod block. However, through treatment with boron tribromide, compound **5b** was demethylated to **5c** and then coupled with the flexible coil $\mathbf{R_1}$ in acetonitrile in the presence of potassium carbonate to give rise to **5d**, which shows good solubility in common organic solvents such as chloroform, ethyl acetate and ethanol. The molecule **1** with a short branched aromatic rod was obtained by aromatic homo coupling of precursor molecule **5d** in a catalytic amount of Pd. Also, **5d** could be elongated further by repeating the Suzuki coupling reaction with a boronic acid derivative and consecutive substitution with iodine monochloride. For example, **6a** was prepared from the Suzuki coupling reaction of **5d** with 4-trimethylsilylphenylboronic acid. The trimethylsilyl group was substituted with iodide, and then the subsequent homo aromatic coupling reaction of **6b** produced **2**. Compound **3** could be synthesized by using a similar procedure, except that 4-trimethylsilyl-4′-biphenylboronic acid was used in place of 4-trimethylsilylphenylboronic acid. All of the resulting molecules were purified by column chromatography (silica gel) and subsequent recrystallization, and characterized by ^{1}H-NMR spectroscopy, gel permeation chromatography, elemental analysis and MALDI-TOF mass spectroscopy, and were shown to be in full agreement with the structures presented.

The thermotropic phase behavior of the molecules was studied by a combination of thermal optical polarized microscopy (OPM), differential scanning calorimetry (DSC), and X-ray diffraction (XRD). Molecule **1** exists only as an isotropic liquid, most probably due to relatively weak interactions between the short rod blocks. In contrast, **2**, based on an elongated rod block, shows an ordered bulk-state structure with bright birefringence which transforms it into an isotropic liquid at 105 °C [Fig. 2(a)]. On slow cooling from the isotropic liquid the formation of unique domains, which grow in four directions and coalesce into a mosaic texture, could easily be observed under OPM [Fig. 2(b)]. The DSC curves and optical texture preliminarily confirmed the presence of an ordered phase, which could be attributed to the rigidity of elongated phenylene rod segments. To identify the detailed aggregation structures, X-ray scattering studies were performed. Small-angle X-ray scattering (SAXS) in the ordered state of **2** revealed a number of well-resolved reflections, as

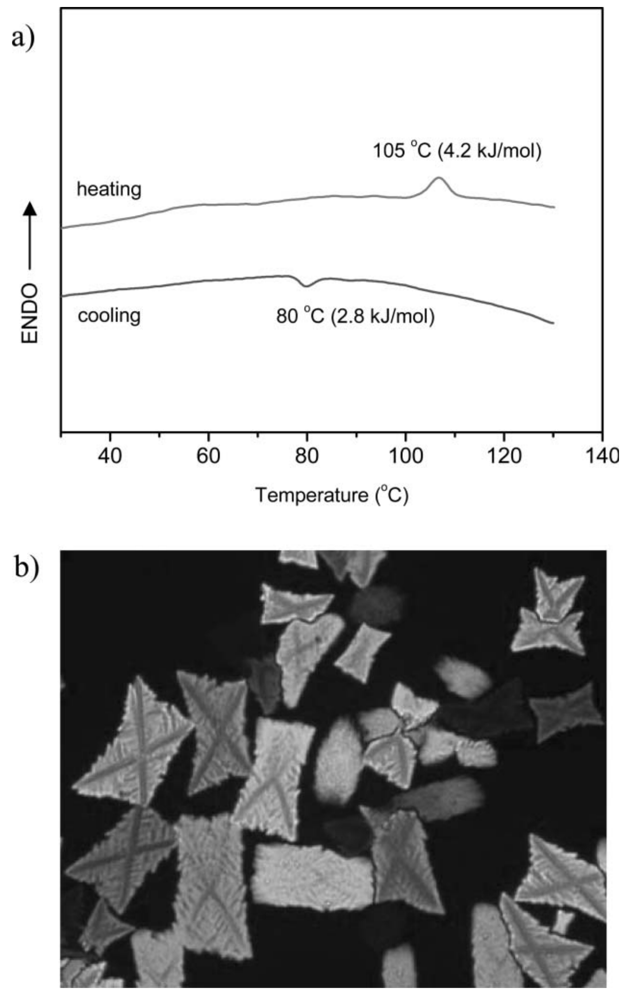


Fig. 2 (a) DSC curves of molecule **2** and (b) representative optical polarized micrograph (100 ×) of the texture exhibited by a primitive monoclinic structure of **2** at the transition from the isotropic liquid state.

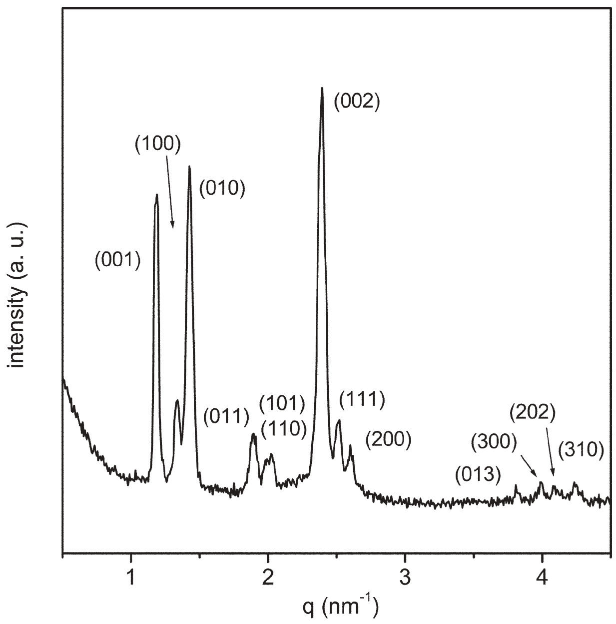


Fig. 3 Small-angle X-ray pattern of **2** at room temperature.

Table 1 Small-angle X-ray diffraction data for the primitive monoclinic structure for **2**

h	k	l	$q_{\mathrm{obs}}/\mathrm{nm}^{-1}$	$q_{\mathrm{calc}}/\mathrm{nm}^{-1}$
0	0	1	1.196	1.196
1	0	0	1.324	1.324
0	1	0	1.424	1.424
0	1	1	1.865	1.879
1	1	0	1.951	1.979
1	0	1	2.022	2.022
0	0	2	2.393	2.392
1	1	1	2.477	2.485
2	0	0	2.648	2.613
0	2	3	3.858	3.837
3	0	0	3.971	3.986
2	0	2	4.057	4.078
3	1	0	4.227	4.228

shown in Fig. 3. This indicates the existence of a highly ordered nanoscopic structure. These reflections can be very well indexed as a 3-D primitive monoclinic structure with lattice parameters a = 5.0 nm, b = 4.4 nm, c = 5.5 nm, and β = 73° (Table 1). The parallel arrangement would cause the greater steric hindrance and consequently make the structure unstable. Considering that the fully extended molecular length of **2** is about 5.6 nm, the molecules are likely to be tilted with respect to the c-axis. Furthermore, several peaks observed between q = 1.5–4.5 nm^{-1} were well explained with the occasion of a tilted orientation with respect to the c-axis rather than the parallel arrangement. The discrete structure with nano dimensions would come from branched phenyl moieties, which cause crowding at the ends of the rod segments and frustrate the lamellar packing. In addition, the molecules are most likely to be tilted for taking up so much space at the rod ends while simultaneously maintaining π–π interactions between the phenylene stems.[7] This result demonstrates that the molecular orientation as well as the nanostructure of self-assembling molecules based on rigid segments can be manipulated by the incorporation of branched architecture in rigid rod segments. A wide-angle X-ray scattering (WAXS) pattern of **2** showed only a broad halo centered at approximately 4.4 Å, which is indicative of the lateral distance between rod segments (Fig. 4). The lack of crystallinity within the rod domains is most probably due to packing frustration between the branched rods. From the experimental values of the unit cell parameters (a, b, c, and β) and the density (ρ), the average number of molecules per bundle of **2** can be calculated according to eqn. 1, where M is the molecular mass and N_A is Avogadro's number. Using eqn. 1, the average number (n) of molecules in each bundle is estimated to be about 28:

$$n = \frac{abc \sin \beta}{M/N_A \rho} \tag{1}$$

Molecule **3**, which is based on the most elongated rod, has a birefringent waxy state that is retained at an elevated temperature up to the decomposition temperature of approximately 300 °C without any significant change in optical

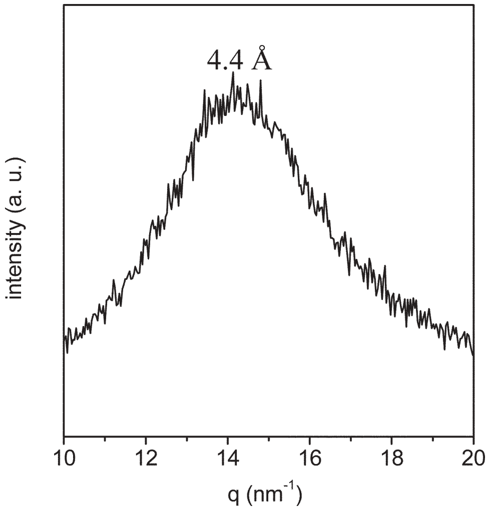


Fig. 4 Wide-angle X-ray pattern of **2** at room temperature.

texture. The SAXS pattern of this molecule is shown to be similar to that of **2** recorded at room temperature, indicating the presence of a 3-D primitive monoclinic superlattice with lattice constants a = 5.4 nm, b = 5.2 nm, c = 6.2 nm, and β = 73°, which are slightly larger than those of **2**. The average number of molecules in each supramolecular aggregate is estimated to be about 37. However, **3**, which has stronger π–π interactions caused by more extended rod segments, could stand well against the frustration of packing by branched parts and goes on to aggregate into a larger nanostructure. On the basis of the XRD, OPM, and above calculations, schematic representations can be constructed as shown in Fig. 5.

In summary, molecules consisting of a branched rod block and flexible coil segments were synthesized, characterized, and their self-assembling behavior investigated. In contrast to **1**, which shows only an isotropic liquid state, molecules **2** and **3** were observed to self-assemble into discrete nanostructures that self-organized into a primitive monoclinic structure with the characteristic angle of 73°. These results demonstrate that the introduction of a branched aromatic architecture into rod-coil systems can lead to the formation of a well-defined discrete organic nanostructure by frustration of the parallel packing of rod segments.

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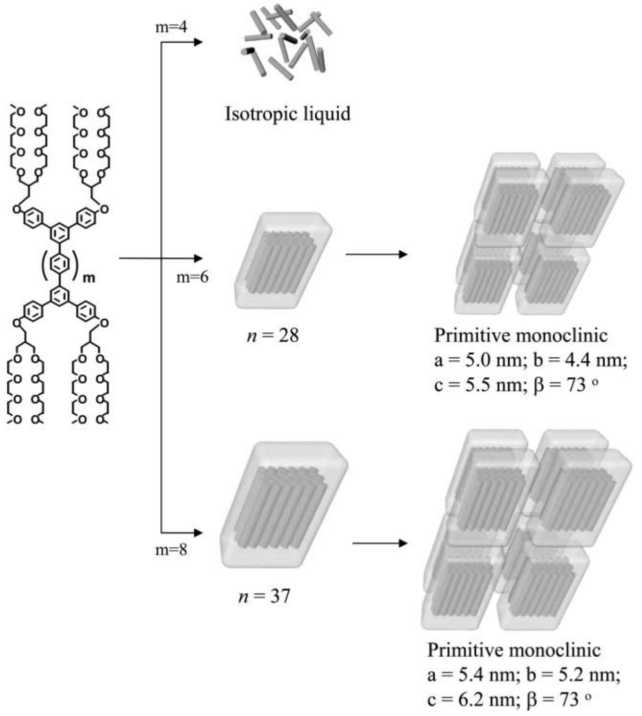

Fig. 5 Schematic representation of the supramolecular structure from molecules **1**, **2**, and **3**; n is the number of molecules per aggregate.

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References

1 J. M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, Germany, 1995; C. Tschierske, *J. Mater. Chem.*, 2001, **11**, 2647; G. Ungar, Y. Liu, X. Zeng, V. Percec and W.-D. Cho, *Science*, 2003, **299**, 1208; A. T. Cate, H. Kooijman, A. L. Spek, R. P. Sijbesma and E. W. Meijer, *J. Am. Chem. Soc.*, 2004, **126**, 3801; J. W. Goodby, G. H. Mehl, I. S. Saez, R. P. Tuffin, G. Mackenzie, R. Auzély-Velty, T. Benvegnu and D. Plusquellec, *Chem. Commun.*, 1998, 2057.
2 J. A. Osaheni and S. A. Jenekhe, *J. Am. Chem. Soc.*, 1995, **117**, 7389; R. Sasai, H. Itoh, I. Shindachi, T. Shichi and K. Takagi, *Chem. Mater.*, 2001, **13**, 2012; W. Li, D. Hooks, P. Chiarelli, Y. Jiang, H. Xu and H.-L. Wang, *Langmuir*, 2003, **19**, 4639; D. Horn and J. Rieger, *Angew. Chem., Int. Ed.*, 2001, **40**, 4330.
3 M. Lee, B.-K. Cho and W.-C. Zin, *Chem. Rev.*, 2001, **101**, 3869; M. Lee and Y.-S. Yoo, *J. Mater. Chem.*, 2002, **12**, 2161; Y.-S. Yoo, J.-H. Choi, J.-H. Song, N.-K. Oh, W.-C. Zin, S. Park, T. Chang and M. Lee, *J. Am. Chem. Soc.*, 2004, **126**, 6294.
4 S. I. Stupp, V. LeBonheur, K. Walker, L. S. Li, K. Huggins, M. Keser and A. Amstutz, *Science*, 1997, **276**, 384; G. N. Tew, M. U. Pralle and S. I. Stupp, *Angew. Chem., Int. Ed.*, 2000, **39**, 517.
5 M. Lee, Y.-S. Jeong, B.-K. Cho, N.-K. Oh and W.-C. Zin, *Chem. Eur. J.*, 2002, **8**, 876.
6 N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457.
7 A. Halperin, *Macromolecules*, 1990, **23**, 2724.