

Polymer Chemistry

Accepted Manuscript



This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the [Information for Authors](#).

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard [Terms & Conditions](#) and the [Ethical guidelines](#) still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.



Polymer Chemistry

PAPER

Synthesis and Self-assembly of Amphiphilic Bent-Shaped Molecules Based on Dibenzo[a,c]Phenazine and Poly(ethylene oxide) Units

Received 7th July 2015,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

Yang Liu^{a†}, Keli Zhong^{b†}, Zhaohua Li^a, Yanqiu Wang^c, Tie Chen^a, Myongsoo Lee^{c*}, Long Yi Jin^{a*}

Bent-shaped amphiphilic molecules **1-5**, consisting of a dibenzo[a,c]phenazine unit and phenyl groups linked together as a rigid segment, and poly(ethylene oxide) (PEO) with a degree of polymerization (DP) of 6, 8 and 12 as a flexible chains were synthesized and characterized. Their aggregation behavior was investigated using DSC, POM, SAXS, CD, TEM, and AFM in the bulk and aqueous solutions. Molecules **1-4** with a various PEO coil chains self-organize into an oblique columnar structures in the solid state. In aqueous solution, molecule **1** (with a DP of 6) self-assembles into spherical aggregates, whereas molecules **2, 3**, and **5** (with coil chains longer than those of molecule **1**) exhibit a self-organizing capacity to form cylindrical micelles or diverse lengths of fibers, depending on the PEO chain lengths. Interestingly, CD experiments together with TEM investigations of molecules **4-5** incorporating lateral methyl groups at the interface of the rod and coil domains, showed that these molecules self-assemble into helical fibers. This indicates that lateral methyl groups lead to the formation of the helical arrangements of the rod segments.

Introduction

During the last decade, π -conjugated molecules have attracted a great deal of attention due to their outstanding self-assembling properties and applications in the field of biomimetic materials, medical technologies, supramolecular nano-reactors, nano-sensor and transport membranes, and so on.¹⁻¹⁰ Precise control of π -conjugated molecular nano-structures is achieved by tuning the molecular parameters (such as the volume fraction of rod to coil segments, coil cross-sectional area of flexible coils and the shape of rigid-flexible molecules) through non-covalent molecular interactions such as hydrophobic and hydrophilic effects, electrostatic interaction, π - π stacking, hydrogen bonding, and micro-phase separation.¹¹⁻¹⁴ Lee et al. and other research groups reported that K-, O-, Y-, and T-shaped conjugated rod-coil molecules spontaneously self-organized into spherical micelles, vesicles, nano-fibers, nano-sheets, toroids and nano-tubes. This was reported to occur via the controlling molecular driving force of rod-coil molecules based on the various lengths and types of the conjugated rods, and the linear or dendritic flexible poly(ethylene glycol)

units.¹⁵⁻²¹ We have constructed closed nanofiber and helical hollow tubular assemblies by self-assembly of the bent-shaped hydrophilic molecules consisting of a short bent-shaped conjugated rod segment incorporating an *m*-pyridine unit at the inner position and a dendritic oligo-ether with chiral groups at its apex.²² The hollow nanofiber is created via hydrogen-bonding interactions of the pyridine unit of the rod segment and an external guest molecule phenylphenol.

Recently, we have also reported the synthesis and self-assembling behavior of the T-shaped coil-rod-coil oligomers. These consist of a dibenzo[a,c]phenazine unit and phenyl groups as the rigid segment, and poly(ethylene glycol) as the coil segment.²³ We demonstrated that T-shaped molecules containing a lateral methyl group at the surface of the rod and poly(ethylene oxide) (PEO) coil segments, are able to organize into 2-D oblique columnar and 3-D body-centered tetragonal nano-structures in the solid state, for application in organic electro-photo materials. To our knowledge, many papers reported the self-assembly and applications of bent-shaped and other types molecules. However, there are only reports regarding the construction of nano-assemblies of bent-shaped amphiphilic rod-coil molecules incorporating the dibenzo[a,c]phenazine unit. For example, Williams et al. and co-workers reported the synthesis and phase behavior of some discotic mesogens formed by stacking of 2,7-dibromodibenzo[a,c]phenazine core building blocks, and constructed hexagonal and rectangular columnar nano-structures in the liquid crystalline phase.²⁴⁻²⁷ Therefore, it is of great interest to synthesize and self-assemble bent-shaped rod building block oligomers, containing the dibenzo[a,c] phenazine unit, that have skeletal rigidity, electron affinity, and thermal stability for use as organic electro-photo

^a Key Laboratory for Organism Resources of the Changbai Mountain and Functional Molecules, Ministry of Education, and Department of Chemistry, College of Science, Yanbian University, Jilin, Yanji 133002, China.

^b College of Chemistry, Chemical Engineering and Food Safety, Bohai University, Jinzhou, Liaoning 121013, P.R. China.

^c State Key Lab of Supramolecular Structure and Materials, College of Chemistry, Jilin University, Changchun 130012, China.

[†] Equally contribution to this work.

Electronic Supplementary Information (ESI) available: Experimental details, TEM and AFM images of molecule **5** and other data mentioned in the text. See DOI: 10.1039/x0xx00000x

PAPER

Polymer Chemistry

materials.

With this in mind, in this study, we have designed and synthesized amphiphilic bent-shaped molecules **1-5**, consisting of a dibenzo[a,c]phenazine unit and phenyl groups linked together as a rigid segment and PEO with a degree of polymerization (DP) of 6, 8 and 12 as flexible chains. The self-assembly behavior of these molecules in bulk and aqueous solutions was investigated by using differential scanning calorimetry (DSC), thermal optical polarized microscopy (POM), small-angle X-ray scattering (SAXS), ultraviolet-visible and fluorescence spectroscopy (UV-vis and FL, respectively), transmission electron microscopy (TEM), circular dichroism (CD), and atomic force microscopy (AFM).

Experimental

Materials

9,10-phenanthrenequinone, liquid bromine, nitrobenzene, benzoyl peroxide (BPO), *o*-phenylenediamine, ethylene glycol, triethylamine (TEA), trimethylsilylacetylene (TMSA), bis(triphenylphosphine) palladium(II) chloride, copper iodide (CuI), tetrakis(triphenylphosphine) palladium(0), iodophenol, toluene-*p*-sulfonyl chloride (TsCl) and conventional reagents were used as received. Tetrahydrofuran (THF) was distilled from sodium metal in the presence of benzophenone and degassed prior to use. All manipulations involving air-sensitive reagents were performed under an atmosphere of dry nitrogen. Molecules **7** and **8** were prepared according to the references described in elsewhere (see Electronic supplementary information (ESI)).

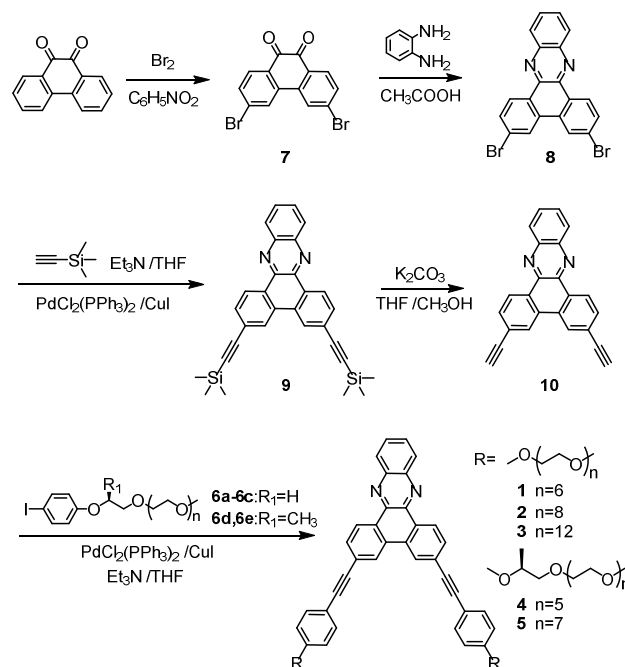
Techniques

Flash column chromatography was performed using silica gel (200-300 mesh). ¹H NMR (300 MHz) was recorded in CDCl₃ on Bruker AM-300 instruments. Chemical shifts were described in parts per million (ppm) (δ units) downfield of tetramethylsilane (TMS) as an internal standard and the coupling constants (*J* values) were reported in Hertz. A Perkin-Elmer Pyris Diamond differential scanning calorimeter was used to determine the thermal transitions, which were reported as the maxima and minima of their endothermic or exothermic peaks; the heating and cooling rates were controlled to 10 °C/min under N₂ atmosphere. The SAXS measurements were performed in transmission mode with synchrotron radiation at the 1W2A X-ray beam line at Beijing Accelerator Laboratory. A Nikon Optiphot 2-pol optical polarized micro scope, equipped with a Mettler FP 82 hot-stage and a Mettler FP90 central processor, was used to observe the thermal transitions and to analyze the anisotropic texture. MALDI-TOF-MS was performed on a perceptive Biosystems Voyager-DESTR using a 2-cyano-3-(4-hydroxyphenyl) acrylic acid (CHCA) as matrix. The UV-vis, FL and CD spectra were obtained from a Shimadzu UV-1650PC spectrometer, Hitachi F-4500 fluorescence spectrometer, and PMS 450 spectropolarimeter, respectively. Transmission electron microscopy (TEM) was performed with a JEOL JEM-2100F microscope. Atomic force microscope (AFM) images were obtained from an Agilent 5500 Atomic Force Microscope. A zetasizer Nano-ZS was used to analyze the size distributions of molecules **1-5** in aqueous solution.

Synthesis

Synthesis of compound 9

Compound **8** (1.31 g, 3.00 mmol), TMSA (1.77 g, 18.00 mmol), TEA (35 mL) and freshly distilled THF (100 mL) were added to 250 mL round bottom flask. Bis(triphenylphosphine)palladium (II) chloride (31.60 mg, 0.45 mmol) and CuI (0.17 mg, 0.89 mmol) were added. The mixture was degassed and then heated at reflux overnight with vigorous stirring under nitrogen. The solvent was removed in a rotary evaporator and the resulting mixture was poured into water and extracted with dichloromethane, dried over anhydrous magnesium sulfate. The solid was collected by filtration, and further purified by flash chromatography (5:1 and then 3:1 petroleum ether/dichloromethane) to give **9** as a yellow solid (1.09 g, 76.6%). ¹H NMR (300 MHz, CDCl₃, δ , ppm): 9.30 (d, *J* = 9.0 Hz, 2H), 8.64 (s, 2H), 8.42-8.29 (m, 2H), 7.87-7.79 (m, 4H), 0.35 (s, 18H).



Scheme 1 Synthetic route of molecules **1-5**.

Synthesis of compound 10

Compound **9** (1.09 g, 3.32 mmol) was dissolved in a mixture of methanol (30 mL) and THF (30 mL) and then anhydrous potassium carbonate (3.20 g, 23.00 mmol) was added to the solution. The reaction mixture was stirred at room temperature overnight under nitrogen. The solvent was removed in a rotary evaporator. Hydrochloric acid (10%) and water were added into the resulting mixture and filtered. Filter cake was washed by water and obtained a yellow solid. Then the filtrate was extracted with ethyl acetate and dichloromethane, the combined organic layer was dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated to dryness. The crude product and the yellow solid were combined and then purified by column chromatography (silica gel) using petroleum ether / dichloromethane (5:1 and then 3:1 v/v) as eluent to yield a light yellow solid (0.36 g, 44.1%). ¹H NMR (300 MHz, CDCl₃, δ , ppm): 9.38 (d, *J* = 9.0 Hz, 2H), 8.69 (s, 2H), 8.35-8.33 (m, 2H), 7.91-7.85 (m, 4H), 3.33 (s, 2H).

Synthesis of molecules 1-5

A representative example is described for **1**. Compound **10** (164 mg, 0.50 mmol) and compound **6a** (622 mg, 1.25 mmol) were added to freshly distilled THF (30 mL). TEA (20 mL) was added and then tetrakis(triphenyl-phosphine) palladium (0) (115.6 mg, 0.1 mmol) and CuI (38.1 mg, 0.2 mmol) were added. The mixture was degassed and then heated at reflux for 35 hours with vigorous stirring under nitrogen. The solvent was removed in a rotary evaporator and the resulting mixture was poured into water and extracted with dichloromethane, dried over anhydrous magnesium sulfate and filtered. The solvent was evaporated to dryness. The crude product was purified by column chromatography (silica gel) using methylene dichloride / methanol (60:1 v/v) as eluent to yield a luminous yellow solid (88 mg, 16.5%).

^1H NMR (300 MHz, CDCl_3 , δ , ppm): 9.32 (d, $J = 9.0$ Hz, 2H), 8.68 (s, 2H), 8.31-8.28 (m, 2H), 7.86-7.83 (m, 4H), 7.58 (d, $J = 8.6$ Hz, 4H), 6.96 (d, $J = 8.6$ Hz, 4H), 4.19 (t, $J = 6.0$ Hz, 4H), 3.91 (t, $J = 6.0$ Hz, 4H), 3.75-3.56 (m, 42H), 3.38 (s, 6H). MALDI-TOF-MS: m/z ($\text{M}+\text{H}$) $^+$ 1070, ($\text{M}+\text{Na}$) $^+$ 1092.

Molecule **2**: luminous yellow solid (16.2%). ^1H NMR (300 MHz, CDCl_3 , δ , ppm): 9.41 (d, $J = 8.4$ Hz, 2H), 8.72 (s, 2H), 8.41-8.38 (m, 2H), 7.90-7.86 (m, 4H), 7.57 (d, $J = 8.7$ Hz, 4H), 6.95 (d, $J = 8.7$ Hz, 4H), 4.20 (t, $J = 6.0$ Hz, 4H), 3.89 (t, $J = 6.0$ Hz, 4H), 3.76-3.57 (m, 54H), 3.36 (s, 6H). MALDI-TOF-MS: m/z ($\text{M}+\text{H}$) $^+$ 1245, ($\text{M}+\text{Na}$) $^+$ 1268, ($\text{M}+\text{K}$) $^+$ 1284.

Molecule **3**: luminous yellow solid (10.7%). ^1H NMR (300 MHz, CDCl_3 , δ , ppm): 9.41 (d, $J = 8.4$ Hz, 2H), 8.75 (s, 2H), 8.42-8.39 (m, 2H), 7.92-7.89 (m, 4H), 7.58 (d, $J = 8.7$ Hz, 4H), 6.99 (d, $J = 8.7$ Hz, 4H), 4.21 (t, $J = 6.0$ Hz, 4H), 3.92 (t, $J = 6.0$ Hz, 4H), 3.77-3.57 (m, 90H), 3.37 (s, 6H). MALDI-TOF-MS: m/z (M) $^+$ 1598.

Molecule **4**: orange solid (24%). ^1H NMR (300 MHz, CDCl_3 , δ , ppm): 9.31 (d, $J = 9.0$ Hz, 2H), 8.66 (s, 2H), 8.30-8.27 (m, 2H), 7.86-7.82 (m, 4H), 7.57 (d, $J = 9.0$ Hz, 4H), 6.96 (d, $J = 8.8$ Hz, 4H), 4.66-4.61 (m, 2H), 3.75-3.52 (m, 54H), 3.37 (s, 7H), 1.36 (d, $J = 6.0$ Hz, 6H). MALDI-TOF-MS: m/z ($\text{M}+\text{H}$) $^+$ 1088, ($\text{M}+\text{Na}$) $^+$ 1110, ($\text{M}+\text{K}$) $^+$ 1136.

Molecule **5**: red liquid (18.7%). ^1H NMR (300 MHz, CDCl_3 , δ , ppm): 9.39-9.36 (d, $J = 9.0$ Hz, 1H), 8.73 (s, 1H), 8.35-8.32 (m, 2H), 7.87 (d, $J = 12.0$ Hz, 4H), 7.57 (d, $J = 9.0$ Hz, 4H), 6.96 (d, $J = 9.0$ Hz, 3H), 4.68-4.59 (m, 2H), 3.75-3.52 (m, 71H), 3.37 (s, 7H), 1.35 (d, $J = 6.0$ Hz, 6H). MALDI-TOF-MS: m/z (M) $^+$ 1273.

Results and discussion

Synthesis

The rigid-flexible block molecules **1-5** with bent-shaped rigid building blocks and PEO with a number of repeating units of 6, 8, and 12 connected with the phenyl unit as a coil segment were synthesized using phenanthrenequinone as the starting material. 3,6-diethynyl dibenzo[a,c]phenazine (molecule **10**) was obtained via radical bromination, Sonogashira and detrimethylsilylation reactions. The resulting molecules **1-5** were successfully synthesized by Sonogashira coupling reactions of molecule **10** and compounds **6a-6e**, respectively. The molecular structures were characterized with ^1H NMR and matrix-assisted laser desorption ionization time-of-flight (MALDI-TOF) mass spectroscopy. These were shown to be in full agreement with the structures presented in Scheme 1.

Structure analysis of 1-4 in bulk state

The self-assembling behavior of rigid-flexible block molecules **1-4** was investigated by means of DSC, POM, and SAXS. Fig. 1 shows the DSC heating/cooling traces of **1-4**. The transition temperatures of **1-4** obtained from the DSC heating and cooling scans are summarized in Table 1.

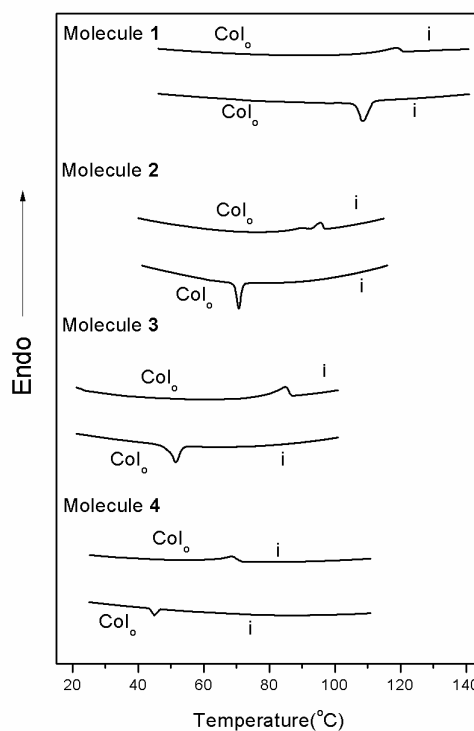


Fig. 1 DSC traces (10 °C/min) recorded during the heating and cooling scans of **1-4** (Col_o: oblique columnar phase; i: isotropic phase).

Table 1 Thermal transitions of **1-5** (data are from the second heating and the first cooling scans).

Molecule	f_{coil}	Phase transition (°C)	
		Heating	Cooling
1	0.55	Col _o 118 i	i 108 Col _o
2	0.62	Col _o 96 i	i 71 Col _o
3	0.70	Col _o 85 i	i 51 Col _o
4	0.56	Col _o 69 i	i 45 Col _o
5	0.62	—	—

f_{coil} : volume fraction of coil to rod-coil molecule, molecule **5** is liquid state at room temperature.

As shown in Table 1, the melting transition temperatures of the coil-rod-coil molecules decrease as the PEO coil length increases. Molecules **4** and **5** were designed and synthesized to investigate the variation of self-assembling behavior when the methyl group was attached to the surface between the rod and coil segments. Molecule **5**, with a longer PEO coil than molecule **4**, is a liquid at room temperature. The melting point of **4**, composed of a PEO coil segment incorporating methyl groups between the rod and coil segment, was significantly less than those of **1-3**. This is indicative of methyl groups at the surface of the rod and coil segment that lead

to the loose stacking of the molecules forming the supramolecular structures. On slow cooling from the optically isotropic phase, molecules **3** and **4** are formed. These are homogeneously grey with small spherulitic textures and correspond to a typical columnar mesophase (Fig. 2).²⁸ To confirm the self-assembly nano-structures of **1-4**, the SAXS experiments were performed at various temperatures. In the crystalline phases of **1**, the SAXS patterns display three sharp reflections which can be indexed as the (100), (010), (120) reflections of a 2D oblique columnar phase with lattice parameters $a = 4.4$ nm, $b = 3.6$ nm and $\gamma = 79^\circ$. Similar to **1**, coil-rod-coil molecules **2** and **3**, based on the longer coil length, displayed an oblique columnar structure with a characteristic angle of $\gamma = 70^\circ$ and $\gamma = 68^\circ$, respectively. The X-ray scatterings are shown in Fig. 3. These can be indexed as the (100), (010), (220) and (100), (010), (200) reflections for **2** and **3**, respectively. Also, the lattice constants of the oblique columnar structures of **2** and **3** are calculated to be $a = 6.1$ nm, $b = 4.6$ nm and $a = 6.3$ nm, $b = 4.9$ nm, respectively. The rigid rod segments of all the molecules are identical. Hence, the diverse volume fractions of the flexible chains lead to the attributed construction of the different supramolecular nano-structures.²⁹

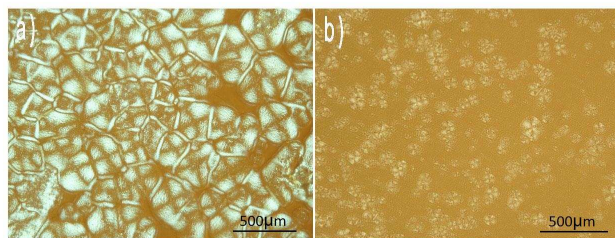


Fig. 2 Representative optical polarized micrographs (40 \times) of the textures exhibited by (a) oblique columnar structure for **3** and (b) oblique columnar structure for **4**.

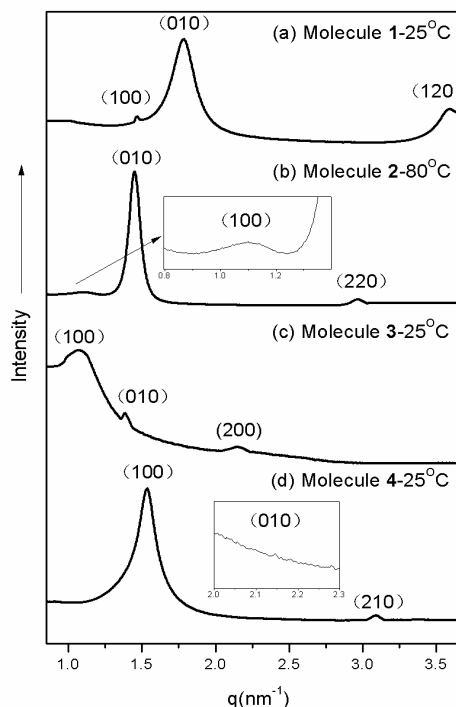
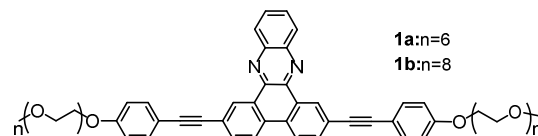


Fig. 3 Small-angle X-ray diffraction patterns of **1-4** plotted against q .

It is worth mentioning that bent-shaped molecules **1** or **2** have the same chemical formula, but a different substituent position of the dibenzo[a,c]phenazine unit as T-shaped molecules **1a** or **1b** (Scheme 2). These were obtained from the Sonogashira coupling reaction of 2,7-diethynyl-dibenzo[a,c]phenazine and compounds **6a-6b**, respectively as reported in our previous work.²³ Molecules **1a** and **1b** self-organize into lamellar and rectangular columnar structures in the solid state, while molecules **1** and **2** self-assemble into oblique columnar structures. The self-assembling behavior of these isomers reveals that the sequence of rod segments is also an important factor for the self-assembling rod-coil molecular architecture, which is consistent with the results reported by our team.³⁰



Scheme 2 The structures of molecules **1a** and **1b**.

Similar to molecules **1-3**, molecule **4**, incorporating the methyl groups at the surface of the rod and coil domains, self-assembles into an oblique columnar phase. The SAXS pattern of **4** shows a sharp, high intensity reflection at a low angle together with two reflections of low intensity [Fig. 3(d)]. These reflections can be indexed as the (100), (010), (210) planes of an oblique columnar structure with lattice parameters $a = 4.4$ nm, $b = 3.1$ nm and $\gamma = 70^\circ$. On the basis of the data presented so far, a summary of the SAXS data is illustrated in Table 2.

Table 2 Data of small-angle X-ray diffraction for molecules **1-4**.

Molecule	Crystalline phase			
	Oblique columnar structure (Col _o)			
	<i>a</i> (nm)	<i>b</i> (nm)	γ	<i>n</i>
1	4.4	3.6	79	4
2	6.1	4.6	70	4
3	6.3	4.9	68	4
4	4.4	3.1	70	4

a, *b*, lattice constant (nm); γ , characteristic angle; *n*, the average number of molecules per cross-sectional slice of the column.

Aggregation behavior in aqueous solution

Bent-shaped molecules **1-5** can self-assemble into aggregate nanostructures in aqueous solution because of their amphiphilic characteristics. The aggregation behaviors of these molecules were subsequently studied in dichloromethane and aqueous solutions using UV-vis and fluorescence spectra. The absorption spectra of **1-5** in aqueous solution (2×10^{-5} M) exhibit a red-shift of the absorption maxima when compared to that of dichloromethane solution (Figs. 4 and S1, respectively). These observations may be caused by the cooperative effect between the hydrophilic and hydrophobic interactions and the π - π stacking interactions between the aromatic segments.^{31,32} The fluorescence spectrum of **1** in dichloromethane solution (2×10^{-5} M) exhibits a strong emission maximum at 481 nm. However, the emission maximum in aqueous solution is red-shifted with respect to that observed in dichloromethane solution, and the fluorescence is significantly quenched [Fig. 4(a)]. This is indicative of an aggregation of the conjugated rod core segments.²⁴ The same phenomena were also found for **2-5** in their UV-vis and FL studies [Figs. 4(b) and S1, respectively]. DLS experiments further corroborated this; the DLS data showed that molecules **1-5** self-assembled into nano-aggregates with an average hydrodynamic diameters ranging from 12 nm to 396 nm, respectively (Fig. S2).

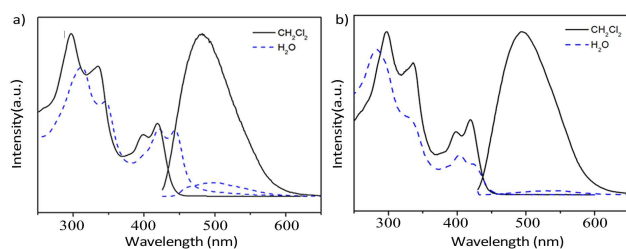


Fig. 4 (a) Absorption and emission spectra of **1** in dichloromethane and aqueous solution (2×10^{-5} M), (b) Absorption and emission spectra of **4** in dichloromethane and aqueous solution (2×10^{-5} M).

To further investigate the aggregation structure in aqueous solution, TEM experiments have been performed with film prepared from an aqueous solution of molecules **1-5**. When a sample of molecule **1** was cast from an aqueous solution (0.01 wt%) and then negatively stained with sodium phosphotungstate, the image showed spherical objects with a uniform diameter of ~12 nm [Fig. 5(a)] that is consistent with the DLS result. In contrast to **1**, molecule **2** exhibits short-length cylindrical micelles with a uniform diameter of ~5.8 nm [Fig. 5(b)]. Considering that the fully extended molecular length is 5.6 nm for **2** (by CPK: Corey-Pauling-Koltun), the core of the cylindrical micelles consists of an aromatic segments in aqueous

solution, which are fully interdigitated with each other.³³⁻³⁵ Similar to **2**, molecule **3** (from a 0.01 wt% solution) self-assembles into longer nanofibers with a uniform diameter of ~6.9 nm and lengths of several micrometers [Fig. 5(c)]. Interestingly, we have precisely controlled the morphology of molecular aggregates from spherical and cylindrical micelles to nanofibers, via the tuning of the systematic variation of rod-coil molecular architectures. This variation of micellar structures can be rationalized by considering the relative volume fraction of hydrophilic head groups to hydrophobic segments. The π - π stacking and hydrophobic interactions increase as the volume fraction of the PEO coil decreases. Thus, the interface between the hydrophilic and hydrophobic domains changes from a highly curved to a more flat interface, causing a small interfacial area and resulting in the increase of the aggregate size, from spherical to cylindrical.

TEM investigation of **4** and **5** with methyl groups between rod and coil segments, revealed that molecules spontaneously self-assemble into relatively short and long cylindrical micelles with a uniform diameter of ~6.7 nm and ~7.3 nm [Figs. 5(d) and S3], respectively. The diameters of the cylindrical aggregates correspond to less than twice the extended molecular length. Also, for molecules **4** and **5**, the indicative rod building blocks are fully interdigitated with each other. Molecule **5** displays a fibroid bundle with a length of over several micrometers. The fibroid bundle may form because of the tendency of the molecules to stack along the axial and radial directions of the cylindrical micelles, to increase the stability of the micelles. All the nanofibers described above consist of hydrophobic aromatic inner cores surrounded by hydrophilic flexible segments that are exposed to the aqueous environment (Fig. 7).

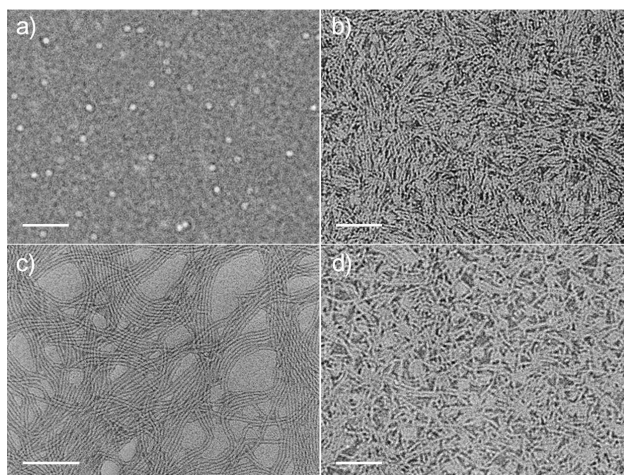


Fig. 5 TEM images of negatively stained nanoaggregates obtained from pure (a) **1**, (b) **2**, (c) **3** and (d) **4** (0.01 wt% in aqueous solution). Scale bar: 100 nm.

To further investigate the effect of the methyl groups attached at the surface of rod and coil domains for self-assembly of rod-coil molecular systems, we performed CD experiments on molecules **4** and **5**. The CD spectra of **4** and **5** show a significant Cotton effect over the absorption ranges (Fig. 6), indicating the formation of supramolecular aggregates with a preferred handedness.³⁶⁻³⁸ Further

PAPER

Polymer Chemistry

distinct evidence is obtained from the AFM images of **5** that are in accord with a helical arrangement (Fig. S4). Interestingly, no CD signals could be detected for molecules **1-3** with a lack of methyl groups, indicating that the helical stacks of the rod segments were caused by the chiral groups at the surface of the rod and coil segments. Incorporating chiral methyl groups drives the bent-shaped aromatic segments to be packed more loosely. This is attributed to the enhanced steric constraints imposed by the closer packing of bent-shaped aromatic segments. To fit more closely together, the aromatic segments are aligned with each other in a slight tilting arrangement, and consequently, the tilted stacks of the aromatic segments lead to the formation of helical fibers.

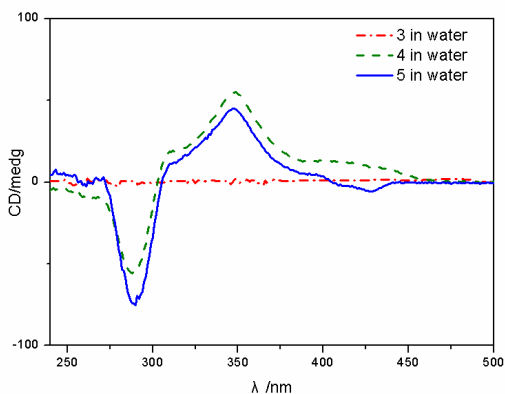


Fig. 6 CD spectra of molecules **3**, **4** and **5** in aqueous solution (2×10^{-5} M).

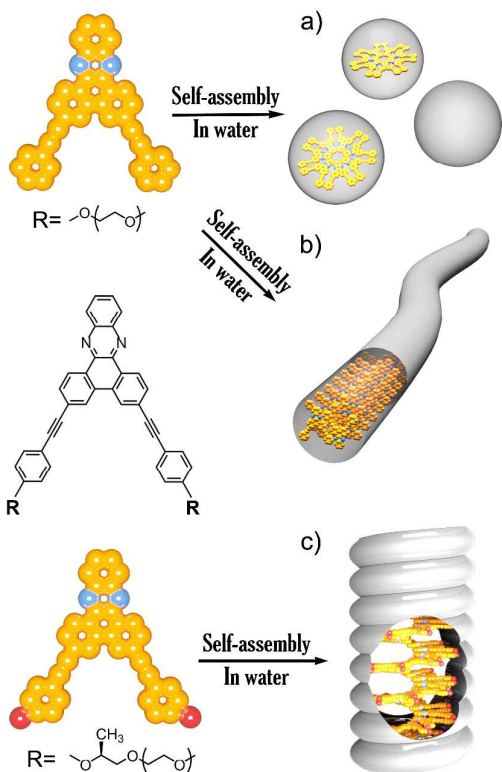


Fig. 7 Schematic representation of the proposed self-assembly of molecules in aqueous solution (a) a spherical micelle for **1**, (b) a cylindrical micelle for **2** and (c) a helical fiber for **4**.

Conclusions

Bent-shaped amphiphilic molecules consisting of a dibenzo[a,c]phenazine unit and phenyl groups linked together with acetylenyl bonds at the 3,6-position of dibenzo[a,c]phenazine as a rigid segment, and PEO with a degree of polymerization of 6, 8, 12 as the coil segment, were synthesized. Molecules **1-4** with diverse chain lengths, self-assemble into oblique columnar structures. This phenomenon may be caused by the powerful π - π stacking interactions between the adjacent aromatic units in the solid state. Control of the flexible chain length and the chiral groups attached to the surface between the rod and coil segments, can tune the supramolecular nano-structures. In aqueous solution, the amphiphilic molecules based on relatively long PEO coils were observed to self-assemble into fibrous structures, whereas the molecules with shorter PEO coils self-organized into a spherical aggregate. Interestingly, molecules with chiral groups at the surface of the rod and coil segments, self-assembled into helical nano-fibers, revealing that chiral groups are an important factor for the construction of helical nano-structures in rod-coil molecular systems. The study of these amphiphilic molecules may prospectively be used for the development of various drug delivery systems and biological applications.

Acknowledgements

This work was supported by the National Natural Science Foundation of China (grant numbers: 21164013, 21304009), the Open Projects of the State Key Laboratory of Elemento-organic Chemistry (201410), Nankai University, China and the Program for Liaoning Excellent Talents in University (No. LJQ2014125). We are grateful to Beijing Synchrotron Radiation Facility (BSRF), Institute of High Energy Physics, Chinese Academy of Sciences for help with the X-ray scattering measurements of molecular structures.

Notes and references

- (a) X. Tan, L. Yang, Z. Huang, Y. Yu, Z. Wang and X. Zhang, *Polym. Chem.*, 2015, **6**, 681-685; (b) V. Percec, M. R. Imam, M. Peterca and P. Leowanawat, *J. Am. Chem. Soc.*, 2012, **134**, 4408-4420.
- (a) L. Wang, L.-L. Li, H. L. Ma and H. Wang, *Chin. Chem. Lett.*, 2013, **24**, 351-358; (b) G. Yu, M. Xue, Z. Zhang, J. Li, C. Han, and F. Huang, *J. Am. Chem. Soc.*, 2012, **134**, 13248-13251; (c) G. Yu, K. Jie, and F. Huang, *Chem. Rev.*, 2015, **15**, DOI: 10.1021/cr5005315.
- (a) J. Yang, G. Yu, D. Xia and F. Huang, *Chem. Commun.*, 2014, **50**, 3993-3995; (b) Y. Yao, X. Chi, Y. Zhou and F. Huang, *Chem. Sci.*, 2014, **5**, 2778-2782.
- A. Tena, Á. Marcos-Fernández, M. de la Viuda, L. Palacio, P. Prádanos, Á. E. Lozano, J. de Abajo and A. Hernández, *Eur. Polym. J.*, 2015, **62**, 130-138.
- V. Percec, P. Leowanawat, H.-J. Sun, O. Kulikov, C. D. Nusbaum,

- T. M. Tran, A. Bertin, D. A. Wilson, M. Peterca and S. Zhang, *J. Am. Chem. Soc.*, 2013, **135**, 9055-9077.
6. X. Yan, F. Wang, B. Zheng and F. Huang, *Chem. Soc. Rev.*, 2012, **41**, 6042-6065.
7. H. J. Kim, D. R. Whang, J. Gierschner, C. H. Lee and S. Y. Park, *Angew. Chem. Int. Ed.*, 2015, **54**, 4330-4333.
8. S. S. Jeon, H. H. An, C. S. Yoon and S. S. Im, *Polymer*, 2011, **52**, 652-657.
9. N. Li and M. D. Guiver, *Macromolecules*, 2014, **47**, 2175-2198.
10. H. Shamsipur, B. A. Dawood, P. M. Budd, P. Bernardo, G. Clarizia and J. C. Jansen, *Macromolecules*, 2014, **47**, 5595-5606.
11. Y. Yao, H. Dong and W. Hu, *Polym. Chem.*, 2013, **4**, 5197-5205.
12. L. Tian, K.-L. Zhong, Y. Liu, Z. Huang, L. Y. Jin and L. S. Hirst, *Soft Matter*, 2010, **6**, 5993-5998.
13. Y. I. Park, Y.-S. Park, J. Gao, J. K. Grey, C.-C. Wang, M. A. Johal, J. Park, H. Y. Woo and H.-L. Wang, *Polymer*, 2014, **55**, 855-859.
14. X. Cheng, F. Liu, X. Zeng, G. Ungar, J. Kain, S. Diele, M. Prehm and C. Tschierske, *J. Am. Chem. Soc.*, 2011, **133**, 7872-7881.
15. Y. b. Lim, E. Lee and M. Lee, *Macromol. Rapid Commun.*, 2011, **32**, 191-196.
16. L. Gao, J. Yao, Z. Shen, Y. Wu, X. Chen, X. Fan and Q. Zhou, *Macromolecules*, 2009, **42**, 1047-1050.
17. M. S. Rahman, S. Samal and J.-S. Lee, *Macromolecules*, 2006, **39**, 5009-5014.
18. J.-H. Ryu, D.-J. Hong and M. Lee, *Chem. Commun.*, 2008, 1043-1054.
19. K. Zhong, T. Chen and L. Y. Jin, *Prog. Chem.*, 2012, **24**, 1353-1358.
20. H.-J. Kim, T. Kim and M. Lee, *Acc. Chem. Res.*, 2010, **44**, 72-82.
21. M. Peterca, V. Percec, P. Leowanawat and A. Bertin, *J. Am. Chem. Soc.*, 2011, **133**, 20507-20520.
22. Y. Wang, Z. Huang, Y. Kim, Y. He and M. Lee, *J. Am. Chem. Soc.*, 2014, **136**, 16152-16155.
23. Z. Wang, J. Cui, Y. Liang, T. Chen, M. Lee, B. Yin and L. Y. Jin, *J. Polym. Sci., Part A: Polym. Chem.*, 2013, **51**, 5021-5028.
24. E. J. Foster, C. Lavigueur, Y.-C. Ke and V. E. Williams, *J. Mater. Chem.*, 2005, **15**, 4062-4068.
25. E. J. Foster, R. B. Jones, C. Lavigueur and V. E. Williams, *J. Am. Chem. Soc.*, 2006, **128**, 8569-8574.
26. E. Voisin, E. Johan Foster, M. Rakotomalala and V. E. Williams, *Chem. Mater.*, 2009, **21**, 3251-3261.
27. C. Lavigueur, E. J. Foster and V. E. Williams, *J. Am. Chem. Soc.*, 2008, **130**, 11791-11800.
28. F. Bouchama, M. B. Thathagar, G. Rothenberg, D. H. Turkenburg and E. Eiser, *Langmuir*, 2004, **20**, 477-483.
29. K.-L. Zhong, Q. Wang, T. Chen and L. Y. Jin, *Eur. Polym. J.*, 2013, **49**, 3244-3250.
30. J. Zhu, T. Chen, G. Jin, J. Xu, K. Zhong, B. Yin and L. Y. Jin, *Polym. Int.*, 2014, **63**, 1070-1075.
31. A. Ajayaghosh and S. J. George, *J. Am. Chem. Soc.*, 2001, **123**, 5148-5149.
32. F. J. Hoeben, I. O. Shklyarevskiy, M. J. Pouderoijen, H. Engelkamp, A. P. Schenning, P. Christianen, J. C. Maan and E. Meijer, *Angew. Chem.*, 2006, **118**, 1254-1258.
33. E. Lee, J. K. Kim and M. Lee, *Angew. Chem.*, 2008, **120**, 6475-6478.
34. Y. He, Z. Li, P. Simone and T. P. Lodge, *J. Am. Chem. Soc.*, 2006, **128**, 2745-2750.
35. J. K. Kim, E. Lee and M. Lee, *Angew. Chem. Int. Ed.*, 2006, **45**, 7195-7198.
36. E. Yashima, K. Maeda and O. Sato, *J. Am. Chem. Soc.*, 2001, **123**, 8159-8160.
37. K. Maeda, H. Mochizuki, M. Watanabe and E. Yashima, *J. Am. Chem. Soc.*, 2006, **128**, 7639-7650.
38. J. K. Hirschberg, L. Brunsveld, A. Ramzi, J. A. Vekemans, R. P. Sijbesma and E. Meijer, *Nature*, 2000, **407**, 167-170.

Graphical Abstract

Synthesis and Self-assembly of Amphiphilic Bent-Shaped Molecules Based on Dibenzo[a,c]Phenazine and Poly(ethylene oxide) Units

Yang Liu^{a†}, Keli Zhong^{b†}, Zhaohua Li^a, Yanqiu Wang^c, Tie Chen^a, Myongsoo Lee^{c*}, Long Yi Jin^{a*}

Rod-coil molecules consisting of a dibenzo[a,c]phenazine unit and different lengths of PEO coils were synthesized, and their self-assembling behavior in both bulk and aqueous solutions was investigated.

