

Evolution from Lyotropic Liquid Crystal to Helical Fibrous Organogel of an Achiral Fluorescent Twin-Tapered Bi-1,3,4-oxadiazole Derivative

Songnan Qu,^[a] Lijun Wang,^{*[a]} Xingyuan Liu,^[a] and Min Li^{*[b]}

Abstract: We report an unprecedented hierarchical self-assembly of an achiral twin-tapered bi-1,3,4-oxadiazole derivative (2,2-bis(3,4,5-trioctoxyphenyl)-bi-1,3,4-oxadiazole, BOXD-T8). This molecule can form a layer-structured lyotropic liquid crystal and further forms a helical fibrous organogel in DMF at concentrations above 0.6 wt %. The self-assembly process of BOXD-

T8 in DMF is accompanied by a change in its fluorescence. The pitches of the helical fibers are non-uniform, and both left- and right-handed helical fibers are observed in equal quantities.

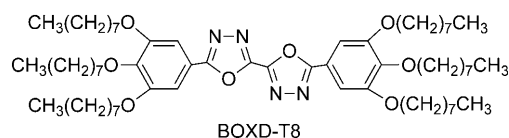
Intermolecular π - π interactions between aromatic segments have been demonstrated to be the driving force for aggregate formation. This helical structure of BOXD-T8 is dependent on the solvent, concentration, and the layer-structured intermediate liquid-crystalline state.

Keywords: helical structures · liquid crystals · organogels · oxadiazoles · self-assembly

Introduction

Chirality is one of the most fascinating features commonly found in nature, which appears hierarchically at both molecular and supramolecular levels.^[1] By introducing chirality into functional materials, new properties can be created.^[2] Chiral assemblies are generally obtained through noncovalent interactions between chiral molecules or between chiral building blocks. In some cases, achiral molecules can be induced to form various chiral architectures by chiral molecules or a chiral matrix.^[3] The preparation of functional chiral architectures from achiral molecules without the introduction of any chiral species and understanding the origin of the chirality of these peculiar chiral assemblies is a current “hot topic”.^[4–8] Among the most interesting chiral architectures derived from achiral molecules are those based on achiral bent-core liquid crystals (LC), the chirality of which is thought to originate from tilting of the molecule with respect to the layer normal producing the mirror image, or twisting of the layers to counteract spontaneously induced polarization.^[5] Ribó et al. reported achiral diprotonated porphyrins that formed homoassociates in aqueous solution, thereby leading to spontaneous chiral symmetry

breaking.^[6] The authors proposed that the achiral dye molecules form supramolecular fibers during unidirectional stirring, and the presence of a vortex in the stirring solution was suggested to induce chirality in the originally achiral system. Liu et al. reported that by compressing Langmuir films spread at an air/water interface, symmetry breaking can occur in some molecular films composed of achiral molecules.^[7] Lu et al. reported that by tuning the length of alkoxy side chains, achiral discotic π -conjugated triphenylbenzene derivatives can form helical fibrous organogels.^[8] The authors proposed that the helices originated from a propeller-like conformation and defects in the molecular packing.



Lyotropic LCs, which typically consist of self-assembled amphiphilic associated structures, have been well documented and are widely used in the fields of materials synthesis, biology and life sciences, pharmaceuticals, foods, cosmetics, and so on.^[9] Organogels are materials in which 3D networks are formed by the self-assembly of low-molecular-weight gelators (LMWGs) through noncovalent interactions, and these networks can absorb large amounts of solvents.^[10] Great efforts have been made to fabricate fluorescent or LC organogels with attractive optical, electronic, or sensing properties.^[11] For example, Ajayaghosh and co-workers reported a series of oligo(*p*-phenylenevinylene)-derived LMWGs with tunable emissions, utilizing the absorption spectral shifts after gelation and an effective fluorescence resonance energy transfer (FRET) process in the organogel

[a] Dr. S. Qu, Prof. L. Wang, Prof. X. Liu
Key Laboratory of Excited State Processes
Changchun Institute of Optics, Fine Mechanics and Physics
Chinese Academy of Sciences, Changchun 130033 (P.R. China)
Fax: (+86)431 86176341
E-mail: ljwang.ciomp@gmail.com

[b] Prof. M. Li
Key Laboratory of Automobile Materials (Jilin University)
Ministry of Education, Institute of Materials Science and
Engineering, Jilin University, Changchun 130012 (P.R. China)
Fax: (+86)431 85168444
E-mail: minli@mail.jlu.edu.cn

scaffold.^[11a-g] Ajayaghosh, Kato, and co-workers reported the preparation of aligned LC physical gels with polarized photoluminescent properties by the simple mixing of an oligo(*p*-phenylenevinylene)-based gelator (OPV) with nematic and smectic liquid crystals.^[11h] Park and co-workers described the emission tuning of organogels by light irradiation rather than heating through the incorporation of a photochromic compound.^[11i] It is considered to be very difficult to find low molecular weight compounds that are capable of gelling solvents and displaying lyotropic and thermotropic mesomorphic behaviors.^[12]

In our previous work, we reported a series of fluorescent liquid-crystalline bi-1,3,4-oxadiazole derivatives.^[13] Among these bi-1,3,4-oxadiazole derivatives, an achiral fluorescent twin-tapered bi-1,3,4-oxadiazole derivative (BOXD-T8) was found to exhibit a thermotropic LC phase and various self-assembled structures in solution, such as nanoparticles, helical nanobelts, and flat nanobelts.^[13b] In this work, we report an unprecedented hierarchical self-assembly of achiral BOXD-T8, which forms layer-structured lyotropic liquid crystals, and these in turn form a helical fibrous organogel in DMF at concentrations above 0.6 wt%. The novelty of this work is that the helical structure of BOXD-T8 is dependent on the solvent, the concentration, and the intermediate layer-structured lyotropic liquid-crystalline state, which provides an interesting case for investigating the chiral phenomena.

Results

Self-assembly process in DMF:

The lyotropic LC phase of BOXD-T8 is formed upon cooling of its solutions in DMF at concentrations above 0.4 wt%. The lyotropic LC of BOXD-T8 is not stable, and can evolve into an organogel at concentrations above 0.6 wt%. The procedure for lyotropic LC formation and lyotropic LC to organogel transition of BOXD-T8 in DMF (1.0 wt%) is outlined in Figure 1. We have used optical microscopy, polarized optical microscopy (POM), photoluminescence microscopy (PLM), and scanning electron microscopy (SEM) to investigate the self-assembly process of BOXD-T8 in DMF at 1.0 wt%. Upon cooling of the isotropic solution in DMF, circular domains with birefringence were observed under POM observation, which are characteristic of lyotropic LC phase formation (Figure 2a). Under PLM observation, the circular lyotropic LC domains exhibit

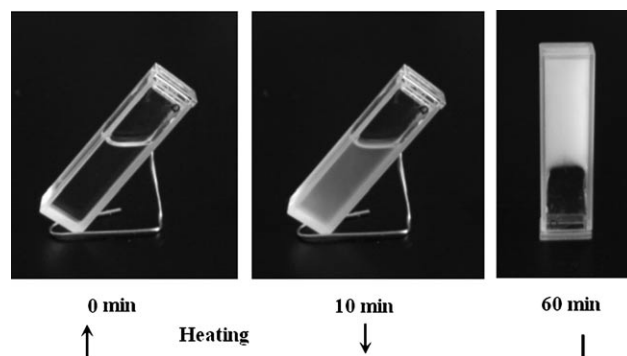


Figure 1. Photographs showing the progressive formation of lyotropic liquid crystal and organogel from BOXD-T8 in DMF at 1.0 wt% upon heating to obtain an isotropic solution and holding at room temperature for different time periods.

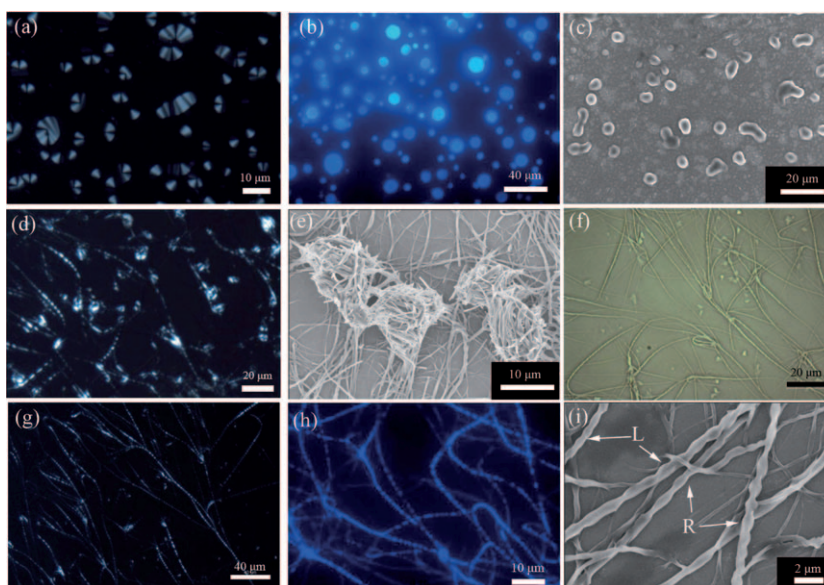


Figure 2. Images of BOXD-T8 in DMF at 1.0 wt% upon cooling from an isotropic solution and holding at room temperature for 10 min: a) POM image, b) PLM image, and c) SEM image; 20 min: d) POM image, e) SEM image; and 30 min: f) optical image, g) POM image, and h) PLM image; i) SEM image of BOXD-T8 xerogel from a 1.0 wt% gel in DMF. Black areas in the POM and PLM images correspond to the solvent DMF.

ed blue fluorescence (Figure 2b). The LC phase can be obtained by quickly evaporating the solvent in this situation. We refer to it as the “solvent-free lyotropic LC phase”. Upon holding for more than 15 min, helical fibers began to develop from the lyotropic LC phase, as identified by POM observation,^[14] in which the single fibers exhibited periodical repetitions of strongly birefringent regions and dark regions (Figure 2d). On quickly evaporating the solvent in this situation, in preparation for SEM observation, the circular lyotropic LC domains became balls of entwisted helical nanobelts (Figure 2e). Upon further holding for more than 30 min, a stable organogel composed of helical fibers developed, which could be observed by optical and polarized optical microscopies (Figure 2f, g). Under PLM observation, the individual fibers exhibited periodical spots of deep-blue fluorescence (Figure 2h). The BOXD-T8 xerogel from DMF

was seen to exhibit both right- and left-handed helical fibers of widths 0.3–1 μm under SEM observation (Figure 2i). The helical pitches in these samples were non-uniform. Furthermore, left- and right-handed helical fibers were present in equal quantities, thus resulting in overall racemic mixtures without any CD signals. At concentrations below 0.4 wt %, the lyotropic LC was not formed, but a flocculent precipitate appeared during storage. For example, a BOXD-T8 solution in DMF at a concentration of 0.15 wt % was isotropic at room temperature. During storage at 4 °C for more than 2 h, a flocculent precipitate developed. Under SEM observation, this flocculent precipitate was seen to consist of entangled flat fibers of widths 0.2–0.4 μm (Figure 3). The formation of elongated fibrous aggregates indicates that the self-assembly of BOXD-T8 is driven by strong directional intermolecular interactions. It can be concluded that the helical structure of BOXD-T8 in DMF is dependent on the concentration and the intermediate lyotropic liquid-crystalline state.

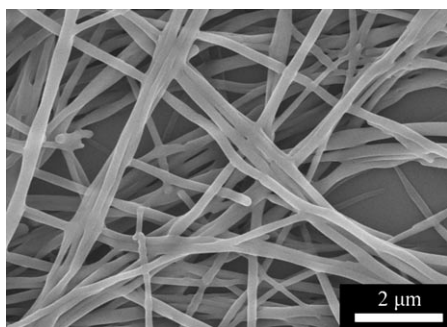


Figure 3. SEM image of BOXD-T8 precipitate from a 0.15 wt % solution in DMF.

XRD investigations: To reveal the structure of the lyotropic LC phase, a drop of BOXD-T8 solution in the lyotropic LC state was placed on a glass slide and the solvent was quickly evaporated under vacuum. The residue was then subjected to XRD investigation. The XRD profile of BOXD-T8 in the solvent-free lyotropic LC phase consists of one strong (100) ($d=23.2$ Å) peak and one weak (200) ($d=11.8$ Å) peak in the small-angle region and no additional peak in the wide-angle region, which is similar to the profile of its thermotropic LC columnar phase, suggesting a lamellar structure (Figure 4a). The solvent-free lyotropic LC phase of BOXD-T8 proved to be unstable, and crystallization was observed upon storage at room temperature for more than one day. The XRD profile of the BOXD-T8 crystalline phase that developed from the solvent-free lyotropic LC phase consists of one strong ($d=20.5$ Å) peak and several peaks in both the small- and wide-angle regions (Figure 4b), which is similar to the profile of its crystalline phase developed from the thermotropic columnar LC phase,^[13a] indicating similar crystalline structures. In contrast, the XRD profile of the BOXD-T8 helical fibrous xerogel that developed from the lyotropic LC phase consists of three peaks ($d=17.6$, 13.1,

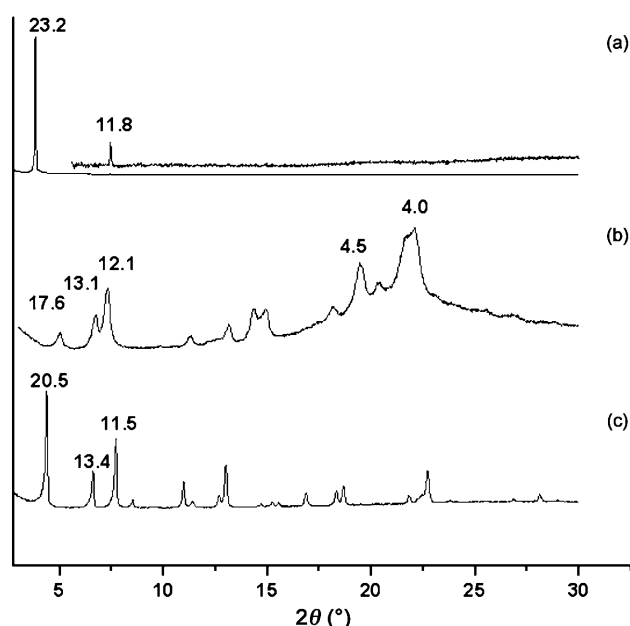


Figure 4. XRD patterns of BOXD-T8: a) solvent-free lyotropic LC from DMF, b) xerogel from a solution in DMF (1.0 wt %), and c) crystalline phase from solvent-free lyotropic LC.

and 12.1 Å) in the small-angle region and several peaks in the wide-angle region (Figure 4c).

Fluorescence and fluorescence lifetime decay spectral investigations: The self-assembly process of BOXD-T8 in DMF is accompanied by a change in its fluorescence. The fluorescence properties of BOXD-T8 in DMF (1.0 wt %) in the various aggregation states are summarized in Table 1. At

Table 1. Fluorescence and fluorescence lifetime characteristics of BOXD-T8 in DMF (1.0 wt %) and different aggregation states.

	$\lambda_{\text{em,max}}$ [nm]	τ [ns] ^[a]	χ^2 ^[b]
isotropic state in DMF	480	2.96	1.06
holding at RT for 5–10 min	465	2.56 (66 %) 6.11 (34 %)	1.02
holding at RT for 10–15 min	460	2.41 (56 %) 5.91 (44 %)	1.00
gel from DMF	403	1.52	1.10
xerogel from DMF	397	1.36	0.87
solvent-free lyotropic LC	432	2.12 (41 %) 5.1 (59 %)	1.01
crystals from solvent-free lyotropic LC	396	0.93	1.10

[a] τ [ns]=fluorescence lifetime in nanoseconds; [b] χ^2 =fitting parameter.

1.0 wt %, the maximum emission of BOXD-T8 in isotropic DMF solution was observed at 480 nm. During storage at room temperature, the maximum emission was blue shifted to about 460 nm in the lyotropic LC state, and was further enhanced and blue shifted to 403 nm during formation of the organogel (Figure 5). The maximum emissions of the

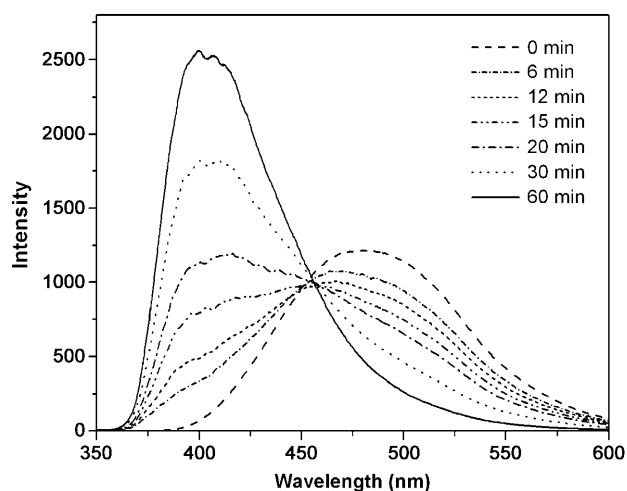


Figure 5. Fluorescence emission spectra of BOXD-T8 in DMF (1.0 wt%) upon heating to obtain an isotropic solution and then holding at room temperature for different time periods.

solvent-free lyotropic LC and the xerogel from DMF (1.0 wt%) were observed at 432 and 397 nm, respectively. The maximum emission of the crystals derived from the solvent-free lyotropic LC was observed at 396 nm (Figure 6).

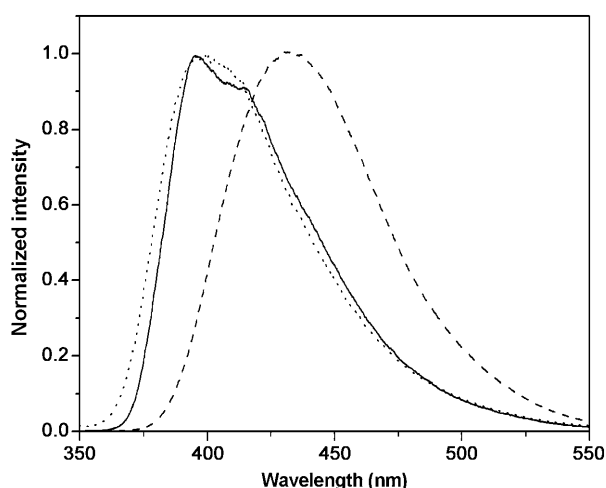


Figure 6. Fluorescence emission spectra of BOXD-T8 in solvent-free lyotropic LC (dashed line), xerogel from DMF (1.0 wt%; dotted line), and crystals from solvent-free lyotropic LC (solid line).

Fluorescence lifetime decay spectra were measured to obtain further information about the self-assembly process of BOXD-T8 in DMF (Figure 7) and the various solid states (Figure 8). The fluorescence decay profile of BOXD-T8 in the isotropic state in DMF (1.0 wt%) showed a monoexponential decay with a lifetime of 3.0 ns. After holding at room temperature for 10–15 min, the fluorescence decay profile of BOXD-T8 in the lyotropic LC state showed a double-exponential decay with an average lifetime of about 3.2 ns. The fluorescence decay profile of BOXD-T8 in the

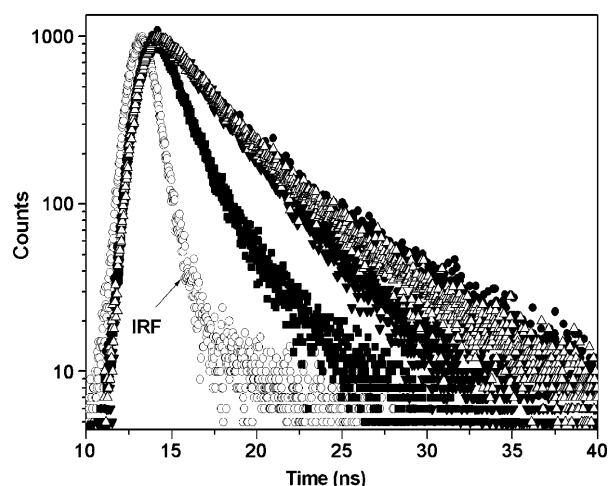


Figure 7. Fluorescence lifetime decay profiles ($\lambda_{\text{ex}}=340$ nm) of BOXD-T8 in DMF (1.0 wt%) in the isotropic state (∇ ; emission monitored at 480 nm), after holding at room temperature for 5–10 min (Δ ; emission monitored at 460 nm) and for 10–15 min (\bullet ; emission monitored at 460 nm), and in the gel state (\blacksquare ; emission monitored at 400 nm). IRF = instrument response function.

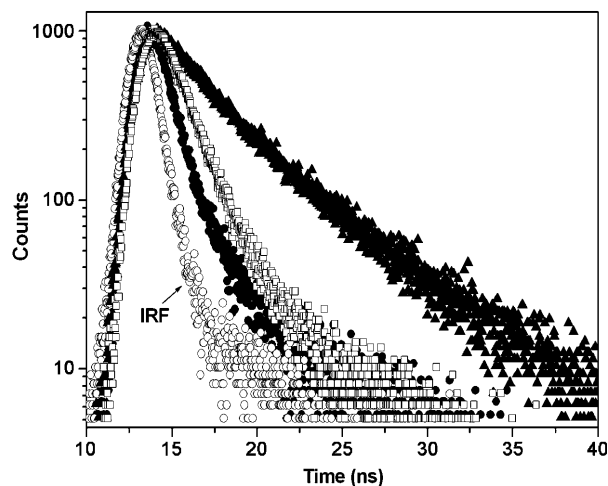


Figure 8. Fluorescence lifetime decay profiles ($\lambda_{\text{ex}}=340$ nm) of BOXD-T8 in solvent-free lyotropic LC (\blacktriangle ; emission monitored at 430 nm), xerogel from DMF (1.0 wt%; \square ; emission monitored at 400 nm), and crystals from solvent-free lyotropic LC (\bullet ; emission monitored at 400 nm).

solvent-free lyotropic LC state showed a double-exponential decay with an average lifetime of 3.5 ns. The profile of BOXD-T8 organogel in DMF (1.0 wt%) showed a monoexponential decay with a lifetime of 1.5 ns, whereas that of its xerogel showed a monoexponential decay with a lifetime of 1.4 ns. The profile of BOXD-T8 crystals from the solvent-free lyotropic LC showed a monoexponential decay with a lifetime of 0.9 ns. The different fluorescence lifetimes in the various aggregation states indicated different aggregation patterns.

Variable-temperature ^1H NMR spectral investigations: To investigate the intermolecular interactions of BOXD-T8 in

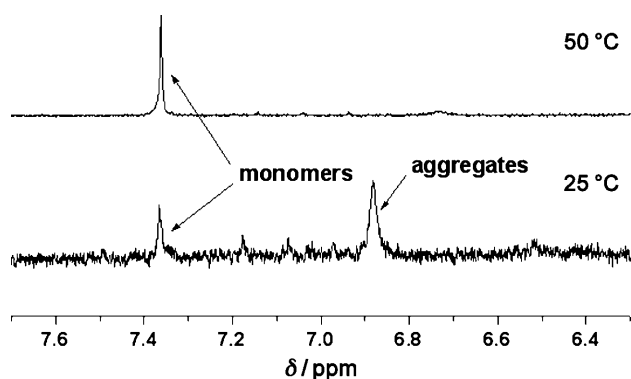


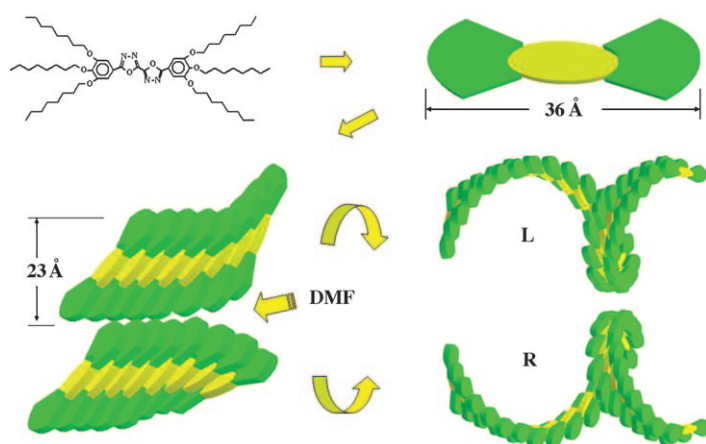
Figure 9. Temperature-dependent ^1H NMR spectra of BOXD-T8 in $[\text{D}_6]\text{DMSO}$ at $5 \times 10^{-5} \text{ mol L}^{-1}$.

polar aprotic solvents, temperature-dependent ^1H NMR experiments were performed on a $5 \times 10^{-5} \text{ mol L}^{-1}$ solution of BOXD-T8 in $[\text{D}_6]\text{DMSO}$ (Figure 9). At 50°C , a sharp peak at $\delta = 7.37 \text{ ppm}$, attributable to the protons of the aromatic rings (Ar-H) of the BOXD-T8 monomers. Upon cooling to 25°C , 30% of the Ar-H signal was observed at $\delta = 7.37 \text{ ppm}$ and 70% of the Ar-H signal was observed at $\delta = 6.88 \text{ ppm}$, indicating the coexistence of another species in slow exchange with the monomeric entity on the NMR time scale. It was concluded that the Ar-H signal observed at higher magnetic field ($\delta = 6.88 \text{ ppm}$) corresponded to the aggregates, the upfield shift resulting from π -stacking interactions between the aromatic segments of BOXD-T8.^[15]

Discussion

In our previous work, we reported the formation of an organogel consisting of straight fibers from fluorescent BOXD-T8 in ethanol and an evolution from nanoparticles to helical fibers.^[13b] The XRD profile of BOXD-T8 xerogel derived from ethanol indicated a lamellar structure, which is similar to those of its thermotropic LC columnar phase and the solvent-free lyotropic LC phase. The XRD profile of the BOXD-T8 helical fibrous precipitate that developed from nanoparticles in DMSO is different from that of the BOXD-T8 helical fibrous xerogel from DMF, indicating different aggregation patterns, although the morphology is similar. Considering the differences between the XRD profiles of the stable helical fibrous xerogel developed from the lyotropic LC phase in DMF and the stable crystalline phase developed from the solvent-free lyotropic LC phase, it could be concluded from these peculiar self-assembly processes of BOXD-T8 that the helical self-assembly process is dependent on the intermediate metastable state and the nature of the solvent molecules. Thus, it would seem that the helical assembly not only originates from a chiral conformation of BOXD-T8 molecules, but might also be due to the solvent participating in crystalline transitions from the intermediate

metastable states. We have attempted to predict the aggregation patterns based on the XRD profiles by computational calculations, but this approach has not yet produced a reasonable aggregation pattern. It is truly difficult to delineate the underlying mechanism responsible for the formation of the helical fibers from achiral BOXD-T8. Computational calculations indicate that the rigid backbone of the BOXD-T8 molecule is coplanar and fully conjugated, which might be beneficial for self-assembly of these molecules to supramolecules through intermolecular π - π interactions between the aromatic segments. A possible packing motif of BOXD-T8 in the lyotropic LC and a mechanism for the formation of the helical fibers in DMF are illustrated in Scheme 1. In



Scheme 1. A possible packing motif of BOXD-T8 in the lyotropic LC and a mechanism for the formation of helical nanofibers in DMF.

the lyotropic LC phase, BOXD-T8 molecules are tilted by a large angle to form a layered structure through intermolecular π - π interactions between aromatic segments and van der Waals interactions between the alkyl chains. During storage, DMF solvent molecules penetrate into the interfaces between the layers that are sustained by the weak van der Waals interactions between alkyl chains in adjacent layers, and separate these layers. Considering the different strengths of interactions in continuous parts and separated parts of the layers following the inclusion of some DMF solvent molecules, helical twisting would seem to be a reasonable means of balancing the stresses in the separated single or multiple layers. This, together with the further formation of helical fibers through intermolecular π - π interactions between the aromatic segments, might be the origin of the helical structure. At lower concentrations ($< 0.4 \text{ wt } \%$) in DMF, BOXD-T8 molecules directly aggregate into straight fibers through directional intermolecular π - π interactions during storage.

Conclusion

An unprecedented hierarchical self-assembly of achiral fluorescent twin-tapered BOXD-T8 from lyotropic liquid crystal to helical fibrous organogel was demonstrated in DMF at concentrations above 0.6 wt %. The self-assembly process of BOXD-T8 in DMF is accompanied by a change in its fluorescence. The pitches of the helical fibers are non-uniform, and both left- and right-handed helical fibers are observed in equal quantities. Intermolecular π - π interactions between aromatic segments were identified as the driving force for the aggregation. The helical structure of BOXD-T8 is dependent on the solvent, the concentration, and the intermediate liquid-crystalline state. The peculiar helical self-assemblies of BOXD-T8 provide an interesting case to investigate chiral phenomena.

Experimental Section

Experimental details: BOXD-T8 was prepared according to our previously published procedure.^[12] PL spectra were collected using a Hitachi F-4500 spectrometer. FE-SEM observations were made with a Hitachi S-4800 apparatus. Optical, polarized optical, and fluorescence microscopy images were acquired with an Olympus BX51TRF microscope. The light source for fluorescence microscopy observation was a mercury lamp with a fluorescent filter cube, which provided excitation in the range 330–385 nm and collected the emission at >420 nm. The intensity of the fluorescence emission was measured using a built-in CCD camera in conjunction with the associated software. Fluorescence lifetimes were measured using an FL920 time-corrected single-photon counting (TCSPC) system. XRD analysis was carried out with a Bruker Advance D8 X-ray diffractometer. ¹H NMR spectra were recorded with a Bruker Avance 500 MHz spectrometer with [D₆]DMSO as the solvent and tetramethylsilane (TMS) as an internal standard (δ = 0.00 ppm).

Acknowledgements

This work has been supported by the CAS Innovation Program, the Jilin Province Science and Technology Research Project (Nos.: 20050108, 20090346, and 20100570), the National Science Foundation Committee of China (project No. 50873044), and the Open Fund of Key Laboratory of Automobile Materials (Jilin University).

- [1] a) N. Berova, K. Nakanishi, R. W. Woody (Eds.), *Circular Dichroism: Principles and Applications*, 2nd ed., Wiley-VCH, New York, **2000**; b) D. Clines (Ed.), *The Physical Origin of Homochirality in Life*, AIP Press, Woodbury, New York, **1996**; c) J.-M. Lehn, *Supramolecular Chemistry: Concepts and Perspectives*, Wiley-VCH, Weinheim, **1995**; d) A. Guijarro, M. Yus, *The Origin of Chirality in the Molecules of Life*, RSC, Cambridge, **2009**; e) E. L. Eliel, S. H. Wilen, L. N. Mander, *Stereochemistry of Organic Compounds*, Wiley, New York, **1994**; f) H. G. Kuball, T. Höfer, *Chirality* **2000**, *12*, 278; g) L. Pérez-García, D. B. Amabilino, *Chem. Soc. Rev.* **2002**, *31*, 342; h) M. Quack, *Angew. Chem.* **2002**, *114*, 4812; *Angew. Chem. Int. Ed.* **2002**, *41*, 4618; i) R. Lemieux, *Acc. Chem. Res.* **2001**, *34*, 845; j) R. Holzwarth, R. Bartsch, Z. Cherkaoui, G. Solladie, *Chem. Eur. J.* **2004**, *10*, 3931; k) A. Brizard, R. Oda, I. Huc, *Top. Curr. Chem.* **2005**, *256*, 167.
- [2] a) C. C. Lee, C. Grenier, E. W. Meijer, A. P. H. J. Schenning, *Chem. Soc. Rev.* **2009**, *38*, 671; b) F. Vera, J. L. Serrano, T. Sierra, *Chem. Soc. Rev.* **2009**, *38*, 781; c) Z. Chen, A. Lohr, C. R. S. Möller, F. Würthner, *Chem. Soc. Rev.* **2009**, *38*, 564; d) J. H. Ryu, D. J. Hong, M. Lee, *Chem. Commun.* **2008**, 1043; e) H. Frauenrath, E. Jahnke, *Chem. Eur. J.* **2008**, *14*, 2942; f) G. A. Hembury, V. V. Borovkov, Y. Inoue, *Chem. Rev.* **2008**, *108*, 1; g) S. Yagai, H. Aonuma, Y. Kikkawa, S. Kubota, T. Karatsu, A. Kitamura, S. Mahesh, A. Ajayaghosh, *Chem. Eur. J.* **2010**, *16*, 8652; h) V. K. Praveen, S. S. Babu, C. Vijayakumar, R. Varghese, A. Ajayaghosh, *Bull. Chem. Soc. Jpn.* **2008**, *81*, 1196.
- [3] a) K. Tang, M. M. Green, K. S. Cheon, J. V. Selinger, B. A. Garetz, *J. Am. Chem. Soc.* **2003**, *125*, 7313; b) J. van Gestel, A. R. A. Palmans, B. Titulaer, J. A. J. M. Vekemans, E. W. Meijer, *J. Am. Chem. Soc.* **2005**, *127*, 5490; c) M. M. J. Smulders, A. P. H. J. Schenning, E. W. Meijer, *J. Am. Chem. Soc.* **2008**, *130*, 606; d) Y. Li, T. Wang, M. Liu, *Soft Matter* **2007**, *3*, 1312; e) T. Miyagawa, M. Yamamoto, R. Muraki, H. Onouchi, E. Yashima, *J. Am. Chem. Soc.* **2007**, *129*, 3676; f) K. Morino, N. Watase, K. Maeda, E. Yashima, *Chem. Eur. J.* **2004**, *10*, 4703; g) D. Ogata, T. Shikata, K. Hanabusa, *J. Phys. Chem. B* **2004**, *108*, 15503; h) M. Waki, H. Abe, M. Inouye, *Angew. Chem.* **2007**, *119*, 3119; *Angew. Chem. Int. Ed.* **2007**, *46*, 3059; i) R. M. Meudtner, S. Hecht, *Angew. Chem.* **2008**, *120*, 5004; *Angew. Chem. Int. Ed.* **2008**, *47*, 4926; j) W. Cai, G. T. Wang, P. Du, R. X. Wang, X. K. Jiang, Z. T. Li, *J. Am. Chem. Soc.* **2008**, *130*, 13450.
- [4] a) E. D. Sone, E. R. Zubrarev, S. I. Stupp, *Angew. Chem.* **2002**, *114*, 1781; *Angew. Chem. Int. Ed.* **2002**, *41*, 1705; b) U. Siemeling, I. Schepplmann, B. Neumann, A. Stammel, H. G. Stammer, J. Frelek, *Chem. Commun.* **2003**, 2236; c) K. Köhler, G. Föester, A. Hauster, B. Dobner, U. F. Heiser, F. Ziethe, W. Richter, F. Steiniger, M. Drechsler, H. Stettin, A. Blume, *J. Am. Chem. Soc.* **2004**, *126*, 16804; d) G. Pelzl, S. Diele, W. Weissflog, *Adv. Mater.* **1999**, *11*, 707; e) K. U. Jeong, S. Jin, J. J. Ge, B. S. Knapp, M. J. Graham, J. Ruan, M. Guo, H. Xiong, F. W. Harris, S. Z. D. Cheng, *Chem. Mater.* **2005**, *17*, 2852; f) U. Jeong, B. S. Knapp, J. J. Ge, S. Jin, M. J. Graham, F. W. Harris, S. Z. D. Cheng, *Chem. Mater.* **2006**, *18*, 680; g) Y. Qiu, P. Chen, P. Guo, Y. Li, M. Liu, *Adv. Mater.* **2008**, *20*, 2908; h) Y. Qiu, P. Chen, M. Liu, *J. Am. Chem. Soc.* **2010**, *132*, 9644; i) D. M. Walba, E. Korblova, C. C. Huang, R. Shao, M. Nakata, N. A. Clark, *J. Am. Chem. Soc.* **2006**, *128*, 5318; j) O. Arteaga, C. Escudero, G. Oncins, Z. El-Hachemi, J. Llorens, J. Crusats, A. Canillas, J. M. Ribó, *Chem. Asian J.* **2009**, *4*, 1687; k) Z. El-Hachemi, C. Escudero, O. Arteaga, A. Canillas, J. Crusats, G. Mancini, R. Purrello, A. Sorrenti, Al. D'Urso, J. M. Ribó, *Chirality* **2009**, *21*, 408; l) R. Lauceri, A. Raudino, L. M. Sclaro, N. Micali, R. Purrello, *J. Am. Chem. Soc.* **2002**, *124*, 894.
- [5] a) T. Sekine, T. Niori, J. Watanabe, T. Furukawa, S. W. Choi, H. Takezoe, *J. Mater. Chem.* **1997**, *7*, 1307; b) D. R. Link, G. Natale, R. Shao, J. E. MacLennan, N. A. Clark, E. Korblova, D. M. Walba, *Science* **1997**, *278*, 1924; c) D. A. Coleman, J. Fernsler, N. Chattham, M. Nakata, Y. Takanishi, E. Korblova, D. R. Link, R.-F. Shao, W. G. Jang, J. E. MacLennan, O. Mondainn-Monval, C. Boyer, W. Weissflog, G. Pelzl, L.-C. Chien, J. Zasadzinski, J. Watanabe, D. M. Walba, H. Takezoe, N. A. Clark, *Science* **2003**, *301*, 1204; d) H. N. Shreenivasa Murthy, B. K. Sadashiva, *J. Mater. Chem.* **2003**, *13*, 2863; e) R. Amaranatha Reddy, M. W. Schröder, M. Bodyagin, H. Kresse, S. Diele, G. Pelzl, W. Weissflog, *Angew. Chem.* **2005**, *117*, 784; *Angew. Chem. Int. Ed.* **2005**, *44*, 774; f) R. A. Reddy, C. Tschierske, *J. Mater. Chem.* **2006**, *16*, 907; g) V. Görtz, J. W. Goodby, *Chem. Commun.* **2005**, 3262; h) J. Thisayukta, Y. Nakayama, S. Kawachi, H. Takezoe, J. Watanabe, *J. Am. Chem. Soc.* **2000**, *122*, 7441; i) J. Etxebarria, M. B. Ros, *J. Mater. Chem.* **2008**, *18*, 2919.
- [6] a) J. M. Ribó, J. Crusats, F. Sagués, J. Claret, R. Rubires, *Science* **2001**, *292*, 2063; b) J. Crusats, J. Claret, I. Díez-Pérez, Z. El-Hachemi, H. García-Ortega, R. Rubires, F. Sagués, J. M. Ribó, *Chem. Commun.* **2003**, 1588; c) J. Crusats, Z. El-Hachemi, J. M. Ribó, *Chem. Soc. Rev.* **2010**, *39*, 569.
- [7] a) J. Yuan, M. Liu, *J. Am. Chem. Soc.* **2003**, *125*, 5051; b) L. Zhang, Q. Lu, M. H. Liu, *J. Phys. Chem. B* **2003**, *107*, 2565; c) X. Huang, C. Li, S. Jiang, X. Wang, B. Zhang, M. Liu, *J. Am. Chem. Soc.* **2004**, *126*, 1322; d) P. Guo, M. Liu, *Langmuir* **2005**, *21*, 3410.

- [8] C. Bao, R. Lu, M. Jin, P. Xue, C. Tan, T. Xu, G. Liu, Y. Zhao, *Chem. Eur. J.* **2006**, *12*, 3287.
- [9] a) L. L. Cheng, Y. Y. Luk, C. J. Murphy, B. A. Israel, N. L. Abbott, *Biomaterials* **2005**, *26*, 7173; b) S. V. Shiyanovskii, T. Schneider, I. I. Smalyukh, T. Ishikawa, G. D. Niehaus, K. J. Doane, C. J. Woolverton, O. D. Lavrentovitch, *Phys. Rev. E* **2005**, *71*, 020702; c) W. C. Pomerantz, N. L. Abbott, S. H. Gellman, *J. Am. Chem. Soc.* **2006**, *128*, 8730; d) I. W. Hamley, M. J. Krysmann, V. Castelletto, L. Noirez, *Adv. Mater.* **2008**, *20*, 4394.
- [10] a) N. M. Sangeetha, U. Maitra, *Chem. Soc. Rev.* **2005**, *34*, 821; b) M. George, R. G. Weiss, *Acc. Chem. Res.* **2006**, *39*, 489; c) A. Ajayaghosh, V. K. Praveen, *Acc. Chem. Res.* **2007**, *40*, 644; d) P. Dastidar, *Chem. Soc. Rev.* **2008**, *37*, 2699.
- [11] a) C. Vijayakumar, V. K. Praveen, A. Ajayaghosh, *Adv. Mater.* **2009**, *21*, 2059; b) S. S. Babu, V. K. Praveen, S. Prasanthkumar, A. Ajayaghosh, *Chem. Eur. J.* **2008**, *14*, 9577; c) A. Ajayaghosh, V. K. Praveen, C. Vijayakumar, S. J. George, *Angew. Chem.* **2007**, *119*, 6376; *Angew. Chem. Int. Ed.* **2007**, *46*, 6260; d) A. Ajayaghosh, V. K. Praveen, S. Srinivasan, R. Varghese, *Adv. Mater.* **2007**, *19*, 411; e) A. Ajayaghosh, R. Varghese, V. K. Praveen, S. Mahesh, *Angew. Chem.* **2006**, *118*, 3339; *Angew. Chem. Int. Ed.* **2006**, *45*, 3261; f) V. K. Praveen, S. J. George, R. Varghese, C. Vijayakumar, A. Ajayaghosh, *J. Am. Chem. Soc.* **2006**, *128*, 7542; g) A. Ajayaghosh, C. Vijayakumar, V. K. Praveen, S. S. Babu, R. Varghese, *J. Am. Chem. Soc.* **2006**, *128*, 7174; h) Y. Hirai, S. S. Babu, V. K. Praveen, T. Yasuda, A. Ajayaghosh, T. Kato, *Adv. Mater.* **2009**, *21*, 4029; i) J. W. Chung, S. J. Yoon, S. J. Lim, B. K. An, S. Y. Park, *Angew. Chem.* **2009**, *121*, 7164; *Angew. Chem. Int. Ed.* **2009**, *48*, 7030; j) B. K. An, D. S. Lee, J. S. Lee, Y. S. Park, H. S. Song, S. Y. Park, *J. Am. Chem. Soc.* **2004**, *126*, 10232; k) K. Sugiyasu, N. Fujita, S. Shinkai, *Angew. Chem.* **2004**, *116*, 1249; *Angew. Chem. Int. Ed.* **2004**, *43*, 1229; l) P. C. Xue, R. Lu, G. J. Chen, Y. Zhang, H. Nomoto, M. Takafuji, H. Ihara, *Chem. Eur. J.* **2007**, *13*, 8231; m) Q. Chen, D. Zhang, G. Zhang, X. Yang, Y. Feng, Q. Fan, D. Zhu, *Adv. Funct. Mater.* **2010**, *20*, 3244.
- [12] a) R. Ziessel, G. Pickaert, F. Camerel, B. Donnio, D. Guillon, M. Cesario, T. Prange, *J. Am. Chem. Soc.* **2004**, *126*, 12403; b) G. C. Kuang, Y. Ji, X. R. Jia, Y. Li, E. Q. Chen, Y. Wei, *Chem. Mater.* **2008**, *20*, 4173.
- [13] a) S. Qu, M. Li, *Tetrahedron* **2007**, *63*, 12429; b) S. Qu, L. Zhao, Z. Xiu, M. Li, *Langmuir* **2009**, *25*, 1713; c) S. Qu, X. Chen, X. Shao, F. Li, H. Zhang, H. Wang, P. Zhang, Z. Yu, K. Wu, Y. Wang, M. Li, *J. Mater. Chem.* **2008**, *18*, 3954; d) P. Zhang, S. Qu, H. Wang, B. Bai, M. Li, *Liquid Crystals* **2008**, *35*, 389.
- [14] a) J. van Esch, S. D. Feyter, R. M. Kellogg, F. D. Schryver, B. L. Feringa, *Chem. Eur. J.* **1997**, *3*, 1238; b) S. Qu, H. Wang, Z. Yu, B. Bai, M. Li, *New J. Chem.* **2008**, *32*, 2023.
- [15] a) R. B. Martin, *Chem. Rev.* **1996**, *96*, 3043; b) F. Huang, H. W. Gibson, *J. Am. Chem. Soc.* **2004**, *126*, 14738; c) S. Qu, F. Li, H. Wang, B. Bai, C. Xu, L. Zhao, B. Long, M. Li, *Chem. Mater.* **2007**, *19*, 4839; d) S. Qu, M. Li, *Tetrahedron* **2008**, *64*, 10890.

Received: November 3, 2010
Published online: February 15, 2011