

Hierarchical Superstructures with Control of Helicity from the Self-Assembly of Chiral Bent-Core Molecules

Shih-Chieh Lin,^[a] Rong-Ming Ho,^{*[a]} Chin-Yen Chang,^[b] and Chain-Shu Hsu^{*[b]}

Abstract: Herein, two asymmetric chiral bent-core molecules, 3-[(4-[[4-(heptyloxy)benzoyl]oxy]benzoyl)oxy]-phenyl-4-[(4-[[1*R*]-1-methylheptyl]oxy)benzoyl]oxy] benzoate (BC7R) and 3-[(4-[[4-(heptyloxy)benzoyl]oxy]benzoyl)oxy]-phenyl-4-[(4-[[1*S*]-1-methylheptyl]oxy)benzoyl]oxy] benzoate (BC7S), were synthesized to demonstrate control of the helicity of their self-assembled hierarchical superstructures. Mirror-imaged CD spectra showed a split-type Cotton effect after

the formation of self-assembled aggregates of BC7R and BC7S, thereby suggesting the formation of intermolecular exciton couplets with opposite optical activities. Both twisted and helical ribbons with preferential helicity that corresponded to the twisting character of the intermolecular exciton couplet

were found in the aggregates. The formation of helical ribbons was attributed to the merging of twisted ribbons through an increase in width to improve morphological stability. As a result, control of the helicity of hierarchical superstructures from the self-assembly of bent-core molecules could be achieved by taking advantage of the transfer of chiral information from the molecular level onto the hierarchical scale.

Keywords: aggregation • bent-core molecules • chirality • helical structures • self-assembly

Introduction

Nature uses self-assembly as a convenient tool to construct materials into highly ordered structures through cooperative secondary interactions, such as hydrogen bonding, amphiphilic effects, electrostatic interactions, metal coordination, van der Waals interactions, π - π stacking, steric hindrance, and chirality.^[1-4] Biological molecules and macromolecules can form different kinds of self-assembled superstructures that have specific functions through the interplay of these non-covalent bonding forces.^[5] Among the biological architectures that are constructed by self-assembly in nature, the helical morphology is perhaps the most-fascinating texture.^[6,7] Molecular chirality is considered to be one of the most-important driving forces for the formation of helical morphologies of different lengths.^[8-41] In contrast to the formation of helical morphologies from the self-assembly of in-

trinsic chiral compounds, unique phase-chirality could also be acquired from the self-assembly of achiral bent-core molecules.^[42-44] The macroscopic chirality of the achiral bent-core molecules could be built on the basis of their characteristic mesophases, such as the B₂ phase (also named the SmCP phase, it is a smectic structure with layered chirality that is determined by the direction of polarity and the tilting of the molecular director with respect to the layer normal),^[45,46] the B₄ phase (a helical structure in which the helical axis lies parallel to the smectic layer as the twisted-grain-boundary (TGB) phase),^[47-49] and the B₇ phase (a spiral filament and more-complicated chiral textures with polarization-modulated/undulated-layer (PM/UL) structures).^[50-53] Watanabe and co-workers suggested that the formation of phase chirality from achiral bent-core molecules was attributed to the asymmetric twist conformation that resulted from the ester linkages that connected the central phenyl ring to the side wings.^[54-64] Moreover, the twisting power that was induced by an offset to the macroscopic polarization and an enantiomorphous structure that was constructed by tilting the molecules with respect to the layer normal were proposed as the origins of phase chirality.^[65-67] More recently, in contrast to the unique chiral mesophases that were formed from achiral bent-core molecules, Hough, Clark, and co-workers also studied the B₄ phase, and found helical nanofilament phases with right- and left-handedness from twisted smectic layers.^[68]

Although the mechanism for the formation of helical phases of bent-core molecules from the molecular level have been well-studied and rationalized, the control of helicity in these helical morphologies remains challenging.^[69-72] Thus, the development of methods to control the helicity of

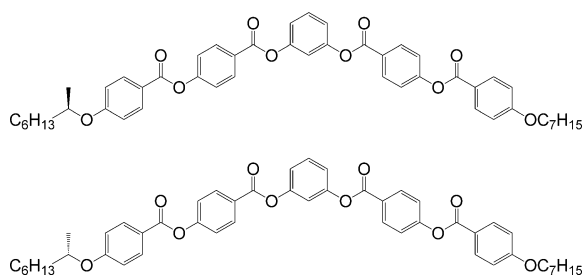
[a] S.-C. Lin, Prof. R.-M. Ho
Department of Chemical Engineering
National Tsing Hua University
No. 101, Section 2, Kuang-Fu Road
Hsinchu, Taiwan 30013 (R.O.C)
Fax: (+886)3-571-5408
E-mail: rmho@mx.nthu.edu.tw

[b] C.-Y. Chang, Prof. C.-S. Hsu
Department of Applied Chemistry
National Chiao Tung University
No. 1001, University Road, Hsinchu
Taiwan 30013 (R.O.C.)
Fax: (+886)3-572-3764
E-mail: cshsu@mail.nctu.edu.tw

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helical superstructures is attracting much attention. Recently, by taking advantage of the ferroelectric-switching property of the B_2 phase, the formation of one-handed helical phases in achiral bent-core molecules was achieved by applying an electronic field to induce a symmetry-breaking transition.^[73–81] Moreover, helical phases with preferential helicity were obtained by introducing small amounts of enantiomerically pure chiral dopants into an achiral host.^[82–87] Watanabe and co-workers synthesized a series of bent-core molecules to clarify the B_4 phase and they demonstrated the formation of helical structures.^[82] Two different domains with opposite optical rotations, which gave intense CD peaks at around 430 nm with opposite signs, were found under uncrossed polarizers, thus suggesting that right- and left-handed helical phases could be formed simultaneously. Most interestingly, one-handed helical structures could be selectively formed by introducing chiral dopants into the host compound. Although controlling the helicity of hierarchical superstructures and phases from the self-assembly of achiral bent-core molecules could be achieved by using physical and external approaches, the formation of one-handed helical morphologies by the directly assembly of bent-core molecules remains challenging. In our previous work, we formed both left- and right-handed helical superstructures from the self-assembly of achiral bent-core molecule 1,3-phenylene bis[4-(4-*n*-heptyloxybenzoyloxy)benzoates] (BC7).^[88]

Herein, we wanted to control the helicity of hierarchical superstructures from the self-assembly of two asymmetric chiral bent-core molecules, 3-[(4-[[4-(heptyloxy)benzoyl]oxy]benzoyl)oxy]-phenyl-4-[(4-[[*(1R)*-1-methylheptyl]oxy]benzoyl)oxy] benzoate (BC7R) and 3-[(4-[[4-(heptyloxy)benzoyl]oxy]benzoyl)oxy]-phenyl-4-[(4-[[*(1S)*-1-methylheptyl]oxy]benzoyl)oxy] benzoate (BC7S; Scheme 1). Unlike



Scheme 1. Chemical structures of chiral bent-core molecules BC7R (top) and BC7S (bottom).

the control of helicity through physical and external approaches, the control of helicity during the forming of helical superstructures from BC7R and BC7S was achieved by directly introducing chiral entities into the chemical structures of the bent-core molecules for self-assembly; therefore, one-handed helical superstructures were formed with control of their helicity through the transfer of chiral information from the molecular level onto the hierarchical scale.

Results and Discussion

Self-assembly of chiral bent-core molecules: Figure 1 shows the UV/Vis and CD spectra of dilute solutions of BC7R and BC7S in isopropyl alcohol (IPA). According to the chemical

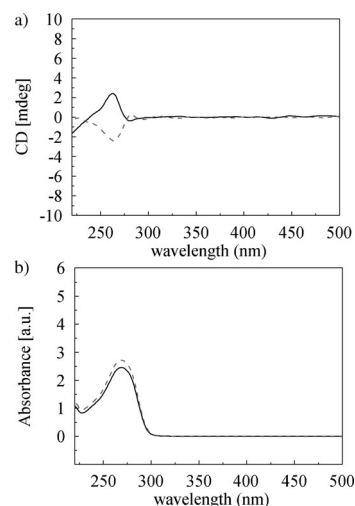


Figure 1. a) CD and b) UV/Vis spectra of BC7R (solid line) and BC7S (dashed line) in dilute IPA solutions (1 mg/4 mL, 0.032 wt.%, 3.1×10^{-4} M).

structures of BC7R and BC7S, which were composing of several *para*-substituted benzoate groups in a bent-core structure, the main absorption in the UV/Vis spectra was attributed to the π - π^* transitions in the benzoate chromophore. In the CD spectra, a positive Cotton effect was clearly identified in the BC7R solution at the same wavelength (263 nm), which corresponded to the absorption band in the UV/Vis spectrum, whereas a negative Cotton effect was found in the BC7S solution, thereby suggesting the existence of the opposite chiral entity in each enantiomer. In contrast to the specific Cotton effect from the configurational chirality of the chiral bent-core molecules in dilute solution, mirror-imaged CD spectra with a significant split-type Cotton effect (Figure 2a) were observed for BC7R and BC7S after their aggregation from IPA solutions. The IPA solvent played a role as the theta-solvent for BC7R and BC7S, that is, the solubility of the chiral bent-core molecules in IPA largely decreased on lowering the temperature so as to result in the formation of self-assembled chiral aggregates. Thus, it was reasonable to suggest that the significant changes and enhancement in the CD signals were due to intermolecular incorporation. Comparing the CD and UV/Vis spectra of the self-assembled chiral aggregates, the theoretical anastatic point, which was calculated from the splitting between the doubly intense CD bands at 247 nm and 289 nm, was located at 268 nm, which corresponded well with the maximum absorption band in the UV/Vis spectra (Figure 2b), thereby indicating that the CD signals were indeed due to the molecular absorption of the constituent

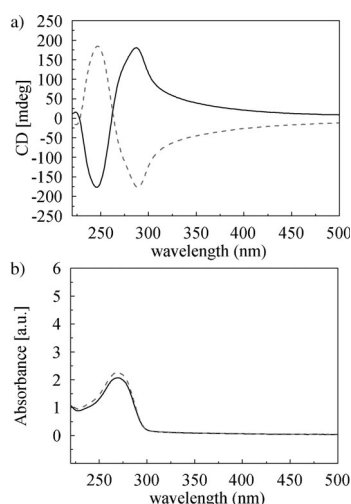


Figure 2. a) CD and b) UV/Vis absorption spectra of self-assembled aggregates of BC7R (solid line) and BC7S (dashed line) in IPA (1 mg/2 mL, 0.064 wt. %, 6.2×10^{-4} M).

chiral bent-core molecules and that the splitting of the Cotton effect was mainly due to intermolecular interactions.

To further investigate the above-mentioned intermolecular incorporation into self-assembled chiral aggregates of BC7R and BC7S, the split-type Cotton effect was rationalized by using the exciton-chirality method.^[89] Typically, the benzoate chromophore exhibited three kinds of $\pi-\pi^*$ transitions in the UV region: ${}^1A_{1g}-{}^1B_{2u}$ (1L_b), an intramolecular charge-transfer transition, and ${}^1A_{1g}-{}^1B_{1u}$ (1L_a).^[90,91] The first and second absorption bands were due to the electronic-transition dipoles along the short and long axis of the benzoate chromophore, respectively. The dibenzoate Cotton effect that was due to $\pi-\pi^*$ intramolecular charge-transfer transitions may have been red-shifted owing to the influence of *para* substituents.^[92] Consequently, by considering the type of *para* substitution in the benzoate chromophore examined herein and by calculating the ϵ value from the UV/Vis spectra, the absorption at 263 nm was attributed to intramolecular charge-transfer transitions. Moreover, this electronic-transition dipole was approximately parallel to the alcoholic (C–O) bond so that the dihedral angle between the transition dipoles of the adjacent benzoate chromophores was too small to result in the occurrence of an exciton couplet.^[90] As a result, we suggested that the formation of the split-type Cotton effect (Figure 2a) was mainly due to intermolecular interactions. The aggregation of self-assembled BC7S gave rise to the formation of dipole–dipole interactions between the benzoate chromophores at which the electronic-transition dipoles would be perpendicular to the helical axis of self-assembled superstructure so as to result in the occurrence of an exciton couplet (Figure 3).

Self-assembled superstructures with control over their helicity: To further examine the hierarchical superstructures of BC7R and BC7S from the self-assembly of the chiral bent-core molecules in IPA solution, the self-assembled chiral ag-

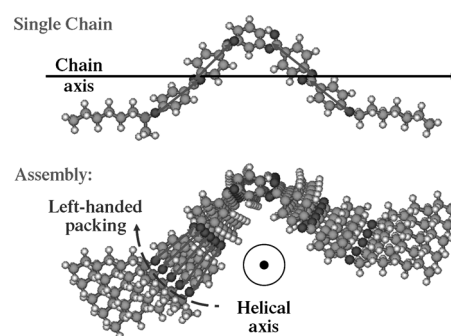


Figure 3. Electronic-transition dipoles along the long axis of the benzoate chromophores (shown as arrows) in BC7S and its aggregates.

gregates were examined by TEM. Figure 4 shows TEM images of chiral superstructures that resulted from the self-assembly of BC7R and BC7S into right- and left-handed

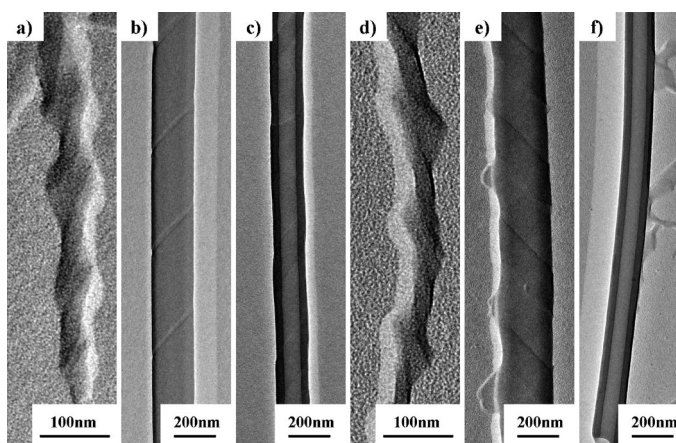


Figure 4. TEM images of self-assembled superstructures of BC7R (a–c) and BC7S (d–f) in IPA (1 mg/2 mL): a) Right- and d) left-handed twisted ribbons; b) right- and e) left-handed helical ribbons; c, f) tubular structures.

twisted ribbons (Figure 4a,d), right- and left-handed helical ribbons (Figure 4b,e), and tubular superstructures with specific helical trace lines on the exterior (Figure 4c,f). The handedness of the helical superstructure corresponded well with the sign of the exciton couplet of the benzoate chromophores (i.e., positive or negative chirality), thus indicating a correlation between the sign of intermolecular exciton coupling and the helicity of the formed helical superstructure. That is, the helicity of the self-assembled morphologies could be controlled by introducing a chiral entity onto the chemical structure of the bent-core molecules. These spectra showed the successful transfer of chirality from configurational chirality on the molecular level into superstructural chirality on the hierarchical scale through self-assembly.

Interestingly, the morphological evolution from twisted ribbons into helical ribbons was occasionally observed by TEM (Figure 5). Morphological transition owing to the fusion of one-handed twisted ribbons onto helical ribbons

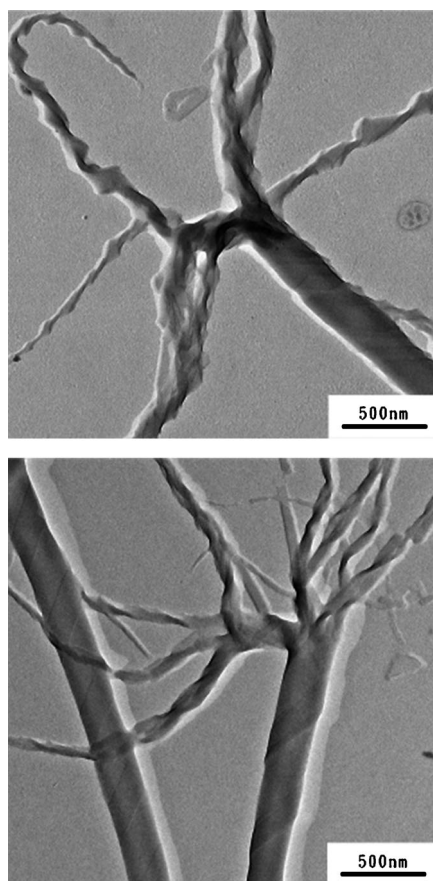


Figure 5. TEM images of the morphological transition from the fusion of one-handed twisted ribbons to the helical ribbon with same helicity to afford self-assembled aggregates of BC7R (top) and BC7S (bottom) in IPA.

with the same helicity was identified for the self-assembled aggregates of BC7R (left) and BC7S (right) in IPA. That is, the formation of helical ribbons was attributed to the merging of twisted ribbons so as to reach a morphological state with higher thermodynamic stability.^[93–95] This morphological transformation from the self-assembly of chiral bent-core molecules was in line with the predictions of tilted chiral lipid bilayer (TCLB) theory.^[96–98] By considering the morphological stability, the spherical vesicles that were organized with chiral lipid molecules may have transformed into twisted strips and further become wound-ribbon helical structures that eventually formed the tubular texture through a scrolling mechanism for the reduction of lateral surface free energy. To investigate the molecular dispositions in each chiral superstructure, SAED experiments were performed to examine the structural packing of the self-assembled morphologies. Figure 6a shows a TEM image of the twisted ribbons of self-assembled BC7R aggregates from which a [00L] zonal SAED pattern was obtained (Figure 6b). The basal unit-cell dimensions were $a=1.02$ nm and $b=0.80$ nm with an orthorhombic lattice, which was close to the previously reported unit-cell dimensions of the achiral bent-core molecule (i.e., BC7).^[88] These ED results

suggested that the molecular packing in the aggregates was due to the bent-core structure and that the chiral entity on the terminal chain would determine the twist direction of the packing. Similar diffraction results were found in the helical ribbon (Figure 6d,f), regardless of enantiomeric character; the unit cell possessed the same dimensions as that of the twisted ribbon, thus indicating that the molecular packing in the crystalline state of the aggregates was identical, regardless of the assembled hierarchical morphologies. Moreover, the SAED pattern exhibited symmetrical arcs that consisted of a series of reflections. This arc-like diffraction pattern, which was comprised of a series of single-crystalline-like reflections (i.e., diffraction spots) was possible evidence to support the twisting and bending mechanisms for the formation of helical superstructures, similar to our previous studies in BC7.^[88]

Proposed mechanism for the formation of helical architectures:

Figure 7 shows a hypothetical model for the formation of helical superstructures from the self-assembly of chiral bent-core molecules. On the basis of the geometry optimization of the bent-core molecules, the adjacent benzoate groups should rotate at different angles with respect to each other by twisting the ester linkages so as to result in the formation of the optimum molecular geometry with a twist (Figure 7a). Subsequently, the solvophobic interactions would result in the formation of closely packed molecules as crystallites with higher stability, as confirmed by the scattering results (Figure 6). Furthermore, the packing of these bent-core molecules would give rise to significant intermolecular interactions between adjacent benzoate chromophores (Figure 8) and would also result in the accumulation of free energy in the molecular packing. Consequently, the twisting driving force for ordering would be triggered by a lowering of the steric hindrance so as to form the twisted crystallite, that is, the twisted-ribbon superstructures (Figure 7b). With the increase in the population of twisted ribbons during aggregation, these twisted ribbons would begin to merge together and fuse into a wide ribbon with continuous growth. However, the increase in the width of the ribbon would cause instability in the energetic state owing to the saddle-like curvature with double twists in the twisted ribbon (Figure 7c). Consequently, a wide ribbon should transform into a helical ribbon with cylindrical curvature for improved morphological stability.^[99–102] The formation of helical ribbons was attributed to these twisting and bending mechanisms owing to the combination of width-growth and chiral effects. Eventually, consistent with the predictions of TCLB theory, the helical ribbon may further scroll to form tubular superstructures, which would be the most-stable morphology, to lower the energetic penalty from the lateral surfaces.

Co-assembly of enantiomeric chiral mixtures and the racemate:

To further demonstrate that the control over the helicity of helical superstructures was based on the configurational chirality of the self-assembly of bent-core molecules,

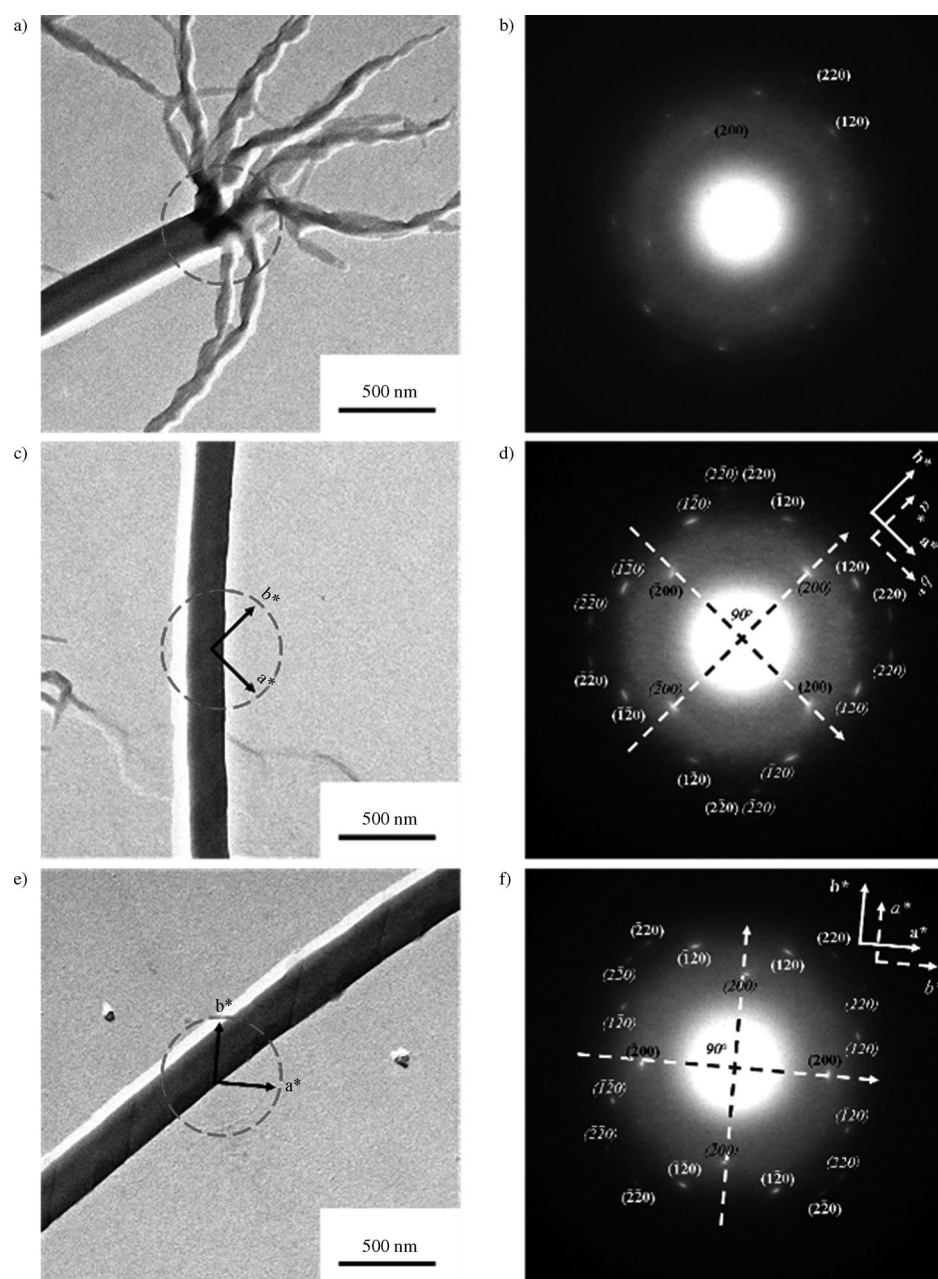


Figure 6. TEM images of a) right-handed twisted ribbons, c) right-handed helical ribbon from BC7R, and e) left-handed helical ribbon from BC7S in IPA. b,d,f) Selected area electron diffraction (SAED) patterns of the circled regions in (a), (c), and (e), respectively. Straight lines and dashed lines in (d) and (f) indicate the coordinates of the upper and lower layers of the helical superstructure in (c) and (e), respectively.

a racemic mixture was also prepared for co-assembly. There was no optical activity in a racemic mixture. The absence of a CD signal for the racemic mixture was attributed to the co-existing of equal amount of enantiomers in the solution so as to result in an equal population of helical morphologies with opposite handedness (i.e., the equal and opposite signs of the intermolecular exciton couplets) owing to the lack of preferential chirality (i.e., chiral bias from the enantiomers). TEM analysis further confirmed that these co-assembled aggregates exhibited twisted ribbons with both

right- and left-handedness (Figure 9). No helical ribbons were formed from the self-assembly of the racemic mixture. We speculated that, for enantiomerically pure chiral bent-core molecules, the twist character of the intermolecular interactions (i.e., exciton couplet) could be executed by following the same chirality of the bent-core molecules, which would result in the lowest energetic penalty in molecular packing so as to form the same handed twisted ribbons and eventually develop as helical ribbons, as predicted by TCLB theory. However, the energetic penalty in molecular packing would have become significant owing to the incompatible steric hindrance that would have been caused by the enantiomer with an opposite twist in its molecular geometry. Consequently, it would be much more difficult to reach the most-stable morphology (i.e., helical ribbons) for the chiral superstructures that consisted of the enantiomers. That is, the minor enantiomer played the role of a defective unit for the formation of the co-assembled chiral superstructures by the transformation of their optimum molecular geometry into the opposite one for packing.

Conclusion

The helicity of hierarchical superstructures of bent-core molecules could be control by simply introducing a chiral entity onto the chemical structure. Both twisted and helical ribbons with preferential one-handed helicity were obtained through the self-assembly of BC7R and BC7S. Helical ribbons were formed from the merging of twisted ribbons with increasing width so as to afford higher morphological stability. In contrast, both right- and left-handed twisted ribbons with equal populations could be observed as a racemic mixture. The lack of preferential helicity was attributed to the presence of equal amounts of the enantiomers so as to result in equivalent an opposite signs in the intermolecular

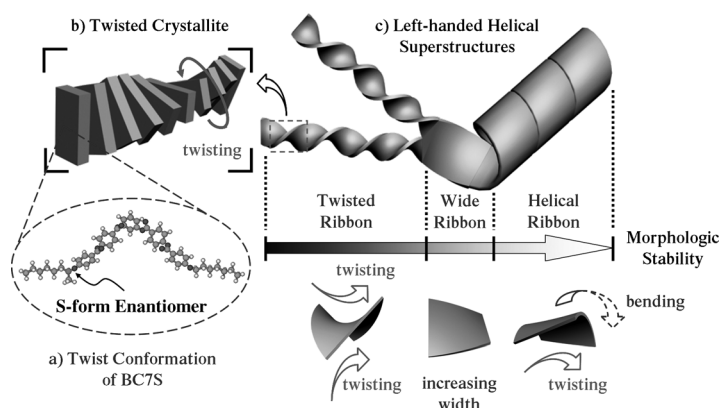


Figure 7. Hypothetic formation of left-handed helical superstructures in the self-assembly of BC7S: a) optimal molecular geometry with a twist of the chiral bent-core molecule, that is, the conformational chirality, results in the formation of one-handed twisted-ribbon superstructures (b). Once the twisted ribbons merge together, a wide ribbon is formed and further scrolls into a helical ribbon with the same helicity through twisting and bending mechanisms to afford higher morphological stability (c).

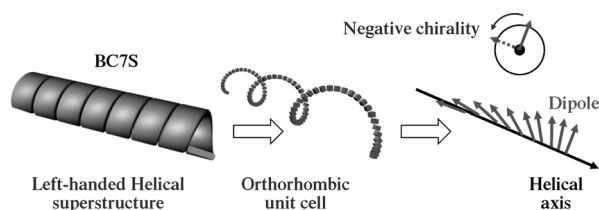


Figure 8. Correlation between the sign of intermolecular exciton coupling and the helicity of the helical superstructure.

exciton couplet. The absence of the formation of helical ribbon superstructures may have been due to higher morphological instability because of the energetic penalty for the molecular packing of the enantiomers.

Experimental Section

Characterization: UV/Vis absorption and CD spectra were obtained simultaneously on a JASCO J-815 spectrometer in a cylindrical quartz cuvette with 1 mm light path. TEM was carried out on a JEOL JEM-2100 LaB₆ at an accelerating voltage of 200 kV. Bright-field TEM images were obtained by using the mass-thickness contrast from shadowing with Pt/Pb = 4:1 at a tilt angle of 30° to the sample surface. Molecular simulations were carried out by using HyperChem 7 with the OPLS force field to execute the geometric optimization of the bent-core molecules.

Sample preparation: The syntheses of chiral bent-core molecules BC7R and BC7S are described in detail in the Supporting Information. For the self-assembly studies, a sample of the bent-core molecule (1 mg) was added to isopropyl alcohol (IPA) with 2 mL and 4 mL for dilute and self-assembled aggregates of solution, respectively. The solution was heated until the solution became transparent (approximately 80 °C for 5 min). After complete dissolution, the solution was cooled to ambient temperature to induce aggregation (i.e., either self-assembly or co-assembly). To prepare the dilute solutions for the single-chain measurements, the transparent solution was left under ambient conditions for 30 min to eliminate the temperature fluctuation for absorption and then the solution was examined by CD spectroscopy (i.e., the experiment was carried out in

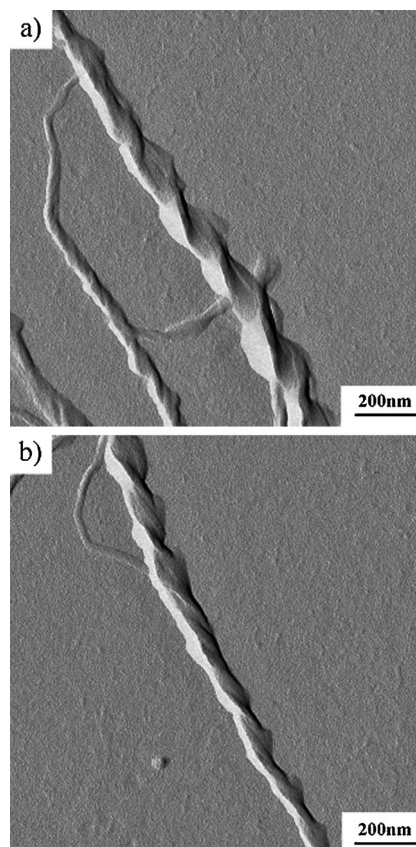


Figure 9. TEM images of a) right- and b) left-handed twisted ribbons from a racemic mixture of BC7R and BC7S in IPA solution.

a transparent state). To acquire fully aggregated samples with more-stable morphologies owing to self-assembly, the solution was left to stand under ambient conditions for about 1 month before the aggregates were collected for UV/Vis and CD spectroscopic measurements and TEM analysis.

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- [1] G. M. Whitesides, J. P. Mathias, C. T. Seto, *Science* **1991**, *254*, 1312–1319.
- [2] M. Muthukumar, C. K. Ober, E. L. Thomas, *Science* **1997**, *277*, 1225–1232.
- [3] J.-M. Lehn, *Science* **2002**, *295*, 2400–2403.
- [4] G. M. Whitesides, B. Grzybowski, *Science* **2002**, *295*, 2418–2421.
- [5] D. Philp, J. F. Stoddart, *Angew. Chem.* **1996**, *108*, 1242–1286; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1154–1196.
- [6] J. D. Watson, F. H. C. Crick, *Nature* **1953**, *171*, 737–738.
- [7] S. H. Kim, G. J. Quigley, F. L. Suddath, A. McPherson, D. Sneden, J. J. Kim, J. Weinzierl, A. Rich, *Science* **1973**, *179*, 285–288.
- [8] J. J. L. M. Cornelissen, J. J. J. M. Donners, R. Gelder, W. S. Graszwinckel, G. A. Metselaar, A. E. Rowan, N. A. J. M. Sommerdijk, R. J. M. Nolte, *Science* **2001**, *293*, 676–680.
- [9] J.-S. Park, H.-S. Lee, J. R. Lai, B. M. Kim, S. H. Gellman, *J. Am. Chem. Soc.* **2003**, *125*, 8539–8545.
- [10] P. Wittung, P. E. Nielsen, O. Buchardt, M. Egholm, B. Nordén, *Nature* **1994**, *368*, 561–563.

- [11] H. Nakako, Y. Mayahara, R. Nomura, M. Tabata, T. Masuda, *Macromolecules* **2000**, *33*, 3978–3982.
- [12] M. Fujiki, *J. Am. Chem. Soc.* **1994**, *116*, 6017–6018.
- [13] E. Yashima, T. Matsushima, Y. Okamoto, *J. Am. Chem. Soc.* **1995**, *117*, 11596–11597.
- [14] E. Yashima, K. Maeda, Y. Okamoto, *Nature* **1999**, *399*, 449–451.
- [15] N. Nakashima, S. Asakuma, T. Kunitake, *J. Am. Chem. Soc.* **1985**, *107*, 509–510.
- [16] J.-H. Fuhrhop, P. Schnieder, E. Boekema, W. Helfrich, *J. Am. Chem. Soc.* **1988**, *110*, 2861–2867.
- [17] J. H. Jung, G. John, K. Yoshida, T. Shimizu, *J. Am. Chem. Soc.* **2002**, *124*, 10674–10675.
- [18] C.-H. Sung, L.-R. Kung, C.-S. Hsu, T.-F. Lin, R.-M. Ho, *Chem. Mater.* **2006**, *18*, 352–359.
- [19] T.-F. Lin, R.-M. Ho, C.-H. Sung, C.-S. Hsu, *Chem. Mater.* **2006**, *18*, 5510–5519.
- [20] T.-F. Lin, R.-M. Ho, C.-H. Sung, C.-S. Hsu, *Chem. Mater.* **2008**, *20*, 1404–1409.
- [21] T.-F. Lin, R.-M. Ho, C.-H. Sung, M.-S. Ho, C.-S. Hsu, *Chem. Eur. J.* **2010**, *16*, 7385–7388.
- [22] J. Song, Q. Cheng, S. Kopta, R. C. Stevens, *J. Am. Chem. Soc.* **2001**, *123*, 3205–3213.
- [23] B. W. Messmore, P. A. Sukerkar, S. I. Stupp, *J. Am. Chem. Soc.* **2005**, *127*, 7992–7993.
- [24] Y. Lin, A. Wang, Y. Qiao, C. Gao, M. Drechsler, J. Ye, Y. Yan, J. Huang, *Soft Matter* **2010**, *6*, 2031–2036.
- [25] C. Y. Li, D. Yan, S. Z. D. Cheng, F. Bai, T. He, L.-C. Chien, F. W. Harris, B. Lotz, *Macromolecules* **1999**, *32*, 524–527.
- [26] C. Y. Li, S. Z. D. Cheng, X. Weng, J. J. Ge, F. Bai, J. Z. Zhang, B. H. Calhoun, F. W. Harris, L.-C. Chien, B. Lotz, *J. Am. Chem. Soc.* **2001**, *123*, 2462–2463.
- [27] J. J. L. M. Cornelissen, M. Fischer, N. A. J. M. Sommerdijk, R. J. M. Nolte, *Science* **1998**, *280*, 1427–1430.
- [28] K. T. Kim, M. A. Winnik, I. Manners, *Soft Matter* **2006**, *2*, 957–965.
- [29] C.-K. Chen, S.-C. Lin, R.-M. Ho, Y.-W. Chiang, B. Lotz, *Macromolecules* **2010**, *43*, 7752–7758.
- [30] D. Pijper, M. G. M. Jongejan, A. Meetsma, B. L. Feringa, *J. Am. Chem. Soc.* **2008**, *130*, 4541–4552.
- [31] D. Maillard, R. E. Prud'homme, *Macromolecules* **2006**, *39*, 4272–4275.
- [32] K. L. Singfield, J. M. Klass, G. R. Brown, *Macromolecules* **1995**, *28*, 8006–8015.
- [33] R.-M. Ho, Y.-W. Chiang, C.-C. Tsai, C.-C. Lin, B.-T. Ko, B.-H. Huang, *J. Am. Chem. Soc.* **2004**, *126*, 2704–2705.
- [34] R.-M. Ho, C.-K. Chen, Y.-W. Chiang, *Macromol. Rapid Commun.* **2009**, *30*, 1439–1456.
- [35] R.-M. Ho, Y.-W. Chiang, C.-K. Chen, H.-W. Wang, H. Hasegawa, S. Akasaka, E. L. Thomas, C. Burger, B. S. Hsiao, *J. Am. Chem. Soc.* **2009**, *131*, 18533–18542.
- [36] C.-C. Chao, C.-K. Chen, Y.-W. Chiang, R.-M. Ho, *Macromolecules* **2008**, *41*, 3949–3956.
- [37] R.-M. Ho, Y.-W. Chiang, S.-C. Lin, C.-K. Chen, *Prog. Polym. Sci.* **2011**, *36*, 376–453.
- [38] S. J. George, A. Ajayaghosh, P. Jonkheijm, A. P. H. J. Schenning, E. W. Meijer, *Angew. Chem. Int. Ed.* **2004**, *43*, 3422–3425.
- [39] A. Ajayaghosh, C. Vijayakumar, R. Varghese, S. J. George, *Angew. Chem.* **2006**, *118*, 470–474; *Angew. Chem. Int. Ed.* **2006**, *45*, 456–460.
- [40] A. Ajayaghosh, R. Varghese, S. Mahesh, V. K. Praveen, *Angew. Chem.* **2006**, *118*, 7893–7896; *Angew. Chem. Int. Ed.* **2006**, *45*, 7729–7732.
- [41] V. K. Praveen, S. S. Babu, C. Vijayakumar, R. Varghese, A. Ajayaghosh, *Bull. Chem. Soc. Jpn.* **2008**, *81*, 1196–1211.
- [42] G. Pelzl, S. Diele, W. Weissflog, *Adv. Mater.* **1999**, *11*, 707–724.
- [43] R. A. Reddy, C. Tschierske, *J. Mater. Chem.* **2006**, *16*, 907–961.
- [44] H. Takezoe, Y. Tahanishi, *Philipp. J. Vet. Med. Jap. J. Appl. Phys.* **2006**, *45*, 597–625.
- [45] D. R. Link, G. Natale, R. Shao, J. E. MacLennan, N. A. Clark, E. Körblová, D. M. Walba, *Science* **1997**, *278*, 1924–1927.
- [46] D. M. Walba, E. Körblová, R. Shao, J. E. MacLennan, D. R. Link, M. A. Glaser, N. A. Clark, *Science* **2000**, *288*, 2181–2184.
- [47] F. Araoka, N. Y. Ha, Y. Kinoshita, B. Park, J. W. Wu, H. Takezoe, *Phys. Rev. Lett.* **2005**, *94*, 137801.
- [48] D. M. Walba, L. Eshdat, E. Körblová, R. K. Shoemaker, *Cryst. Growth Des.* **2005**, *5*, 2091–2099.
- [49] S.-W. Choi, S. Kang, Y. Takanishi, K. Ishikawa, J. Watanabe, H. Takezoe, *Angew. Chem.* **2006**, *118*, 6653–6656; *Angew. Chem. Int. Ed.* **2006**, *45*, 6503–6506.
- [50] G. Pelzl, S. Diele, A. Jäkli, Ch. Lischka, I. Wirth, W. Weissflog, *Liq. Cryst.* **1999**, *26*, 135–139.
- [51] A. Jäkli, C. Lischka, W. Weissflog, G. Pelzl, A. Saupe, *Liq. Cryst.* **2000**, *27*, 1405–1409.
- [52] H. N. S. Murthy, B. K. Sadashiva, *Liq. Cryst.* **2003**, *30*, 1051–1055.
- [53] D. A. Coleman, J. Fernsler, N. Chattham, M. Nakata, Y. Takanishi, E. Körblová, 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*, 1204–1211.
- [54] T. Sekine, T. Niori, M. Sone, J. Watanabe, S.-W. Choi, Y. Takanishi, H. Takezoe, *Jpn. J. Appl. Phys.* **1997**, *36*, 6455–6463.
- [55] E. Gorecka, M. Nakata, J. Mieczkowski, Y. Takanishi, K. Ishikawa, J. Watanabe, H. Takezoe, S. H. Eichhorn, T. M. Swager, *Phys. Rev. Lett.* **2000**, *85*, 2526–2529.
- [56] T. Imase, S. Kawachi, J. Watanabe, *J. Mol. Struct.* **2001**, *560*, 275–281.
- [57] J. Thisayukta, H. Niwano, H. Takezoe, J. Watanabe, *J. Am. Chem. Soc.* **2002**, *124*, 3354–3358.
- [58] H. Kurosu, M. Kawasaki, M. Hirose, M. Yamada, S. Kang, J. Thisayukta, M. Sone, H. Takezoe, J. Watanabe, *J. Phys. Chem. A* **2004**, *108*, 4674–4678.
- [59] H. Niwano, M. Nakata, J. Thisayukta, D. R. Link, H. Takezoe, J. Watanabe, *J. Phys. Chem. B* **2004**, *108*, 14889–14896.
- [60] R. Y. Dong, J. Xu, G. Benyei, K. Fodor-Csorba, *Phys. Rev. E* **2004**, *70*, 011708.
- [61] J. Xu, R. Y. Dong, V. Domenici, K. Fodor-Csorba, C. A. Veracini, *J. Phys. Chem. B* **2006**, *110*, 9434–9441.
- [62] D. M. Walba, E. Körblová, C.-C. Huang, R. Shao, M. Nakata, N. A. Clark, *J. Am. Chem. Soc.* **2006**, *128*, 5318–5319.
- [63] R. Y. Dong, A. Marini, *J. Phys. Chem. B* **2009**, *113*, 14062–14072.
- [64] H. S. Jeong, S. Tanaka, D. K. Yoon, S.-W. Choi, Y. H. Kim, S. Kawachi, F. Araoka, H. Takezoe, H.-T. Jung, *J. Am. Chem. Soc.* **2009**, *131*, 15055–15060.
- [65] T. Sekine, T. Niori, J. Watanabe, T. Furukawa, S. W. Choi, H. Takezoe, *J. Mater. Chem.* **1997**, *7*, 1307–1309.
- [66] J. Watanabe, T. Niori, T. Sekine, H. Takezoe, *Jpn. J. Appl. Phys.* **1998**, *37*, L139–L142.
- [67] G. Heppke, D. Moro, *Science* **1998**, *279*, 1872–1873.
- [68] L. E. Hough, H. T. Jung, D. Krücker, M. S. Heberling, M. Nakata, C. D. Jones, D. Chen, D. R. Link, J. Zasadzinski, G. Heppke, J. P. Rabe, W. Stocker, E. Körblová, D. M. Walba, M. A. Glaser, N. A. Clark, *Science* **2009**, *325*, 456–460.
- [69] E. Gorecka, D. Pocięcha, F. Araoka, D. R. Link, M. Nakata, J. Thisayukta, Y. Takanishi, K. Ishikawa, J. Watanabe, H. Takezoe, *Phys. Rev. E* **2000**, *62*, R4524–R4527.
- [70] J. P. F. Lagerwall, F. Giesselmann, M. D. Wand, D. M. Walba, *Chem. Mater.* **2004**, *16*, 3606–3615.
- [71] R. A. Reddy, B. K. Sadashiva, U. Baumeister, *J. Mater. Chem.* **2005**, *15*, 3303–3316.
- [72] C. V. Yelamaggad, I. S. Shashikala, G. Liao, D. S. S. Rao, S. K. Prasad, Q. Li, A. Jäkli, *Chem. Mater.* **2006**, *18*, 6100–6102.
- [73] M. Zennyoji, Y. Takanishi, K. Ishikawa, J. Thisayukta, J. Watanabe, H. Takezoe, *J. Mater. Chem.* **1999**, *9*, 2775–2778.
- [74] D. Shen, A. Pegenau, S. Diele, I. Wirth, C. Tschierske, *J. Am. Chem. Soc.* **2000**, *122*, 1593–1601.
- [75] G. Dantlgraber, A. Eremin, S. Diele, A. Hauser, H. Kresse, G. Pelzl, C. Tschierske, *Angew. Chem.* **2002**, *114*, 2514–2518; *Angew. Chem. Int. Ed.* **2002**, *41*, 2408–2412.

- [76] M. W. Schröder, S. Diele, G. Pelzl, W. Weissflog, *ChemPhysChem* **2004**, *5*, 99–103.
- [77] R. A. Reddy, M. W. Schröder, M. Bodyagin, H. Kresse, S. Diele, G. Pelzl, W. Weissflog, *Angew. Chem.* **2005**, *117*, 784–788; *Angew. Chem. Int. Ed.* **2005**, *44*, 774–778.
- [78] R. A. Reddy, V. A. Raghunathan, B. K. Sadashiva, *Chem. Mater.* **2005**, *17*, 274–283.
- [79] C. Keith, R. A. Reddy, A. Hauser, U. Baumeister, C. Tschierske, *J. Am. Chem. Soc.* **2006**, *128*, 3051–3066.
- [80] C. Keith, R. A. Reddy, M. Prehm, U. Baumeister, H. Kresse, J. L. Chao, H. Hahn, H. Lang, C. Tschierske, *Chem. Eur. J.* **2007**, *13*, 2556–2577.
- [81] Y. Zhang, M. J. O’Callaghan, U. Baumeister, C. Tschierske, *Angew. Chem.* **2008**, *120*, 6998–7002; *Angew. Chem. Int. Ed.* **2008**, *47*, 6892–6896.
- [82] J. Thisayukta, Y. Nakayama, S. Kawauchi, H. Takezoe, J. Watanabe, *J. Am. Chem. Soc.* **2000**, *122*, 7441–7448.
- [83] J. Thisayukta, H. Niwano, H. Takezoe, J. Watanabe, *J. Mater. Chem.* **2001**, *11*, 2717–2721.
- [84] M. Nakata, D. R. Link, J. Thisayukta, Y. Takanishi, K. Ishikawa, J. Watanabe, H. Takezoe, *J. Mater. Chem.* **2001**, *11*, 2694–2699.
- [85] A. Jákli, G. Liao, I. Shashikala, U. S. Hiremath, C. V. Yelamaggad, *Phys. Rev. E* **2006**, *74*, 041706.
- [86] M. Lee, S.-T. Hur, H. Higuchi, K. Song, S.-W. Choi, H. Kikuchib, *J. Mater. Chem.* **2010**, *20*, 5813–5816.
- [87] S. Taushanoff, K. V. Le, J. Williams, R. J. Twieg, B. K. Sadashiva, H. Takezoe, A. Jákli, *J. Mater. Chem.* **2010**, *20*, 5893–5898.
- [88] S.-C. Lin, T.-F. Lin, R.-M. Ho, C.-Y. Chang, C.-S. Hsu, *Adv. Funct. Mater.* **2008**, *18*, 3386–3394.
- [89] K. Nakanishi, N. Berova, *Circular Dichroism: Principles and Applications* (Eds: K. Nakanishi, N. Berova, R. W. Woody) VCH, New York **1994**, Ch. 13.
- [90] J. Tanaka, *Bull. Acad. Vet. Fr. Bull. Chem. Soc. Jap.* **1963**, *36*, 833–847.
- [91] N. Harada, K. Nakanishi, *Acc. Chem. Res.* **1972**, *5*, 257–263.
- [92] N. Harada, K. Nakanishi, *J. Am. Chem. Soc.* **1968**, *90*, 7351–7352.
- [93] H. Cui, T. Muraoka, A. G. Cheetham, S. I. Stupp, *Nano Lett.* **2009**, *9*, 945–951.
- [94] I. A. Nyrkova, A. N. Semenov, A. Aggeli, N. Boden, *Eur. Phys. J. B* **2000**, *17*, 481–497.
- [95] A. Aggeli, I. A. Nyrkova, M. Bell, R. Harding, L. Carrick, T. C. B. McLeish, A. N. Semenov, N. Boden, *Proc. Natl. Acad. Sci. USA* **2001**, *98*, 11857–11862.
- [96] O.-Y. Zhong-can, L. Ji-xing, *Phys. Rev. Lett.* **1990**, *65*, 1679–1682.
- [97] O.-Y. Zhong-can, L. Ji-xing, *Phys. Rev. A* **1991**, *43*, 6826–6836.
- [98] J. V. Selinger, J. M. Schnur, *Phys. Rev. Lett.* **1993**, *71*, 4091–4094.
- [99] R. Oda, I. Huc, M. Schmutz, S. J. Candau, F. C. MacKintosh, *Nature* **1999**, *399*, 566–569.
- [100] A. Brizard, C. Aimé, T. Labrot, I. Huc, D. Berthier, F. Artzner, B. Desbat, R. Oda, *J. Am. Chem. Soc.* **2007**, *129*, 3754–3762.
- [101] E. T. Pashuck, S. I. Stupp, *J. Am. Chem. Soc.* **2010**, *132*, 8819–8821.
- [102] L. Ziserman, H.-Y. Lee, S. R. Raghavan, A. Mor, D. Danino, *J. Am. Chem. Soc.* **2011**, *133*, 2511–2517.

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