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VIP Helical Structures

Formation of a Homo Double Helix of a Conjugated Polymer with Carboxy Groups and Amplification of the Macromolecular Helicity by Chiral Amines Sandwiched between the Strands**

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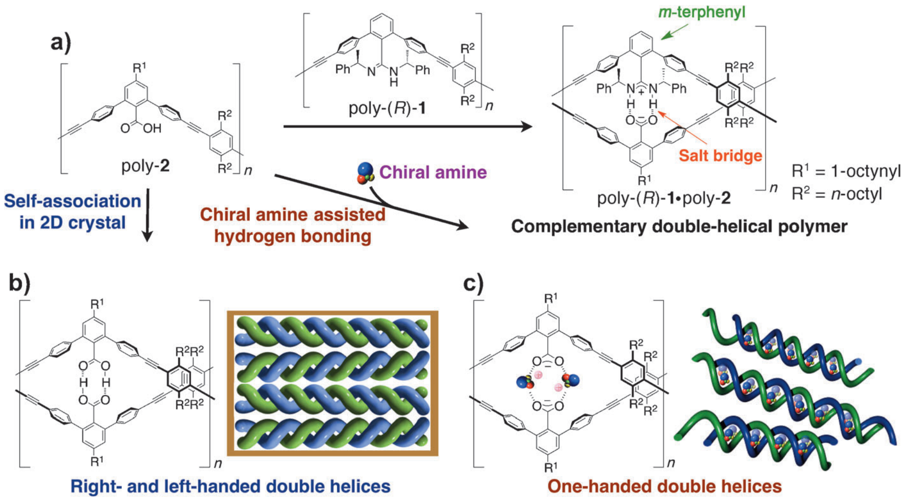

Figure 1. a) Formation of a double helix (poly-(*R*)-**1**·poly-**2**) from complementary strands of poly-(*R*)-**1** and poly-**2**. b) Formation of a racemic homo double helix of poly-**2** in the solid state. c) Formation of a preferred-handed homo double helix of poly-**2** in solution induced by optically active amines through inclusion complexation. Each strand of the homo double helix is drawn in different colors for clarity.

Since the discovery of the double-helical structure of DNA, enormous efforts have been made to mimic its structure based on synthetic and supramolecular approaches.[1] Until today, a few structural motifs have been proposed for the rational design and synthesis of artificial double helices[2] based on attractive interactions, such as metal coordinations,[2a,c,i] interstrand hydrogen-bonding,[2b,d,j,3] and aromatic–aromatic interactions.[2f,4]

We recently proposed a modular strategy to construct a series of artificial double-helical oligomers that are connected by various linkages. In this approach, complementary strands with crescent-shaped *m*-terphenyl-based rigid backbones that bear amidine and carboxy groups, respectively, assembled to a preferred-handed double-helical structure through the formation of amidinium–carboxylate salt bridges.[2e,h,5] Based on this modular strategy, a fully organic double-helical polymer (poly-(*R*)-**1**·poly-**2**) was also synthesized by employing complementary homopolymers composed of optically active amidine and achiral carboxylic acid units (Figure 1 a).[6] The double-helical structure was directly elucidated by high-resolution atomic force microscopy (AFM) of the two-dimensional (2D) crystals of the polymer deposited on a graphite substrate, which disclosed the helical pitch as well as its handedness.[6]

Here, we describe the synthesis and structure of a double-helical homopolymer (poly-**2**), which consists of identical carboxylic acid strands, with controlled helicity through noncovalent chiral acid–base interactions. We found that the achiral poly-**2** self-associated into a racemic double helix through hydrogen-bonding interactions in the solid state (Figure 1 b), while it formed a predominantly one-handed double helix with a chiral amine sandwiched between the strands, thus forming a unique cyclic hydrogen-bonding network (Figure 1 c).[7] The amplification of the helical chirality of the poly-**2** duplex was also investigated in terms of "the sergeants and soldiers"[8] principle and "majority rule".[9] For comparison, model carboxylic acid monomers and dimers were also synthesized.

After exposure to vapors of toluene at around 25 °C for 12 h, poly-**2** deposited from a dilute toluene/tetrahydrofuran (THF; 30/1, v/v) solution (ca. 0.0025 mg mL^{-1}) onto a highly oriented pyrolytic graphite (HOPG) self-associated into well-defined 2D helix bundles (Figure 2 a). The high-resolution AFM image (Figure 2 b) shows a number of periodic oblique stripes, which originate from the double-stranded helical structure of poly-**2**, consisting of right- and left-handed double-helical strands (green and red lines, respectively) with a helical pitch of around 1.6 nm.[10] The observed helical pitch is in good agreement with that of the hetero-double-

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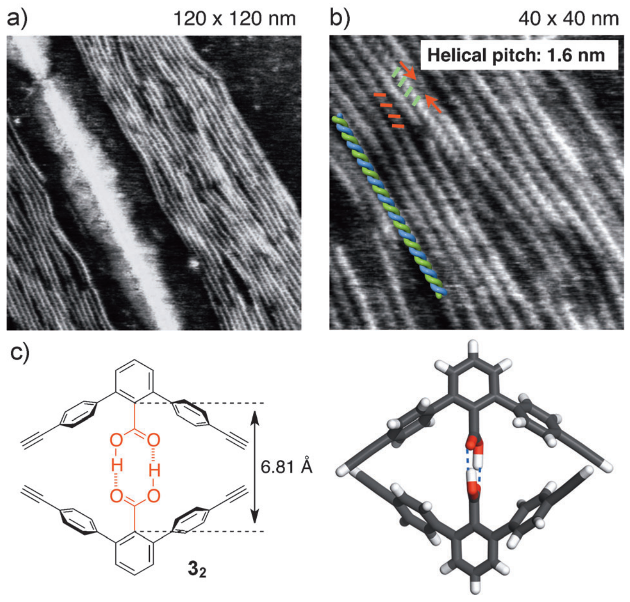

Figure 2. a) AFM phase image of self-associated double-stranded helical poly-**2** on HOPG. b) Magnification of (a). c) Crystal structure of $\mathbf{3}_2$.

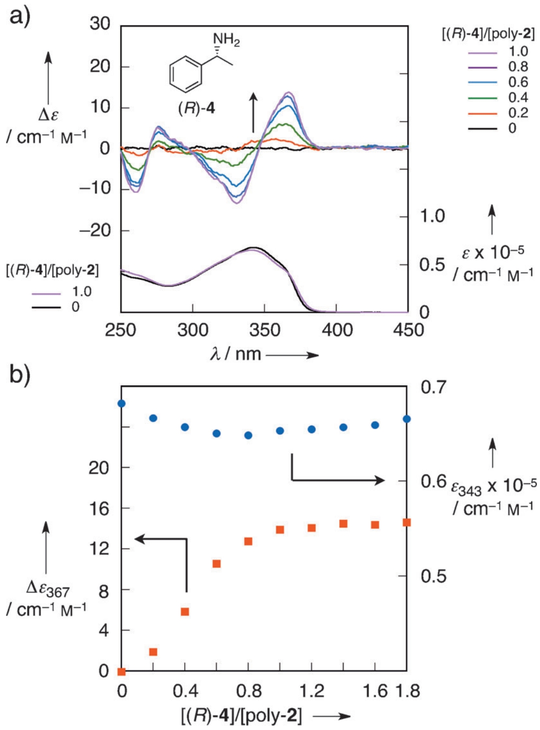

Figure 3. a) CD (left axis) and absorption (right axis) spectra of poly-**2** in the presence of varying amounts of (*R*)-**4** in $CHCl_3$/THF (98/2, v/v) at ambient temperature (ca. 23–25 °C). b) Plots of the CD signal intensity (left axis) at 367 nm ($\Delta\varepsilon_{367}$) and molar absorptivity (right axis) at 343 nm (ε_{343}) versus the molar ratio of (*R*)-**4** to poly-**2**. [poly-**2**] = 1.37 mM per monomer unit.

helical poly-(*R*)-**1**·poly-**2** (1.7 nm).[6] The wide-angle X-ray diffraction (WAXD) measurements of uniaxially oriented films of poly-**2** and ^{1}H NMR studies of a dimeric model **5** (Scheme S1 and Figure S3 in the Supporting Information) in solution further support the self-associated double-helical structure. The structural features of poly-**2** resemble those observed for the poly-(*R*)-**1**·poly-**2** heteroduplex (Figure S1 c)[6] and an apparent nuclear Overhauser effect (NOE) cross-peak was observed between the interstrand protons of **5** in $CDCl_3$ (Figures S3–S6). In addition, the X-ray single-crystal analysis of **3**, a unit model for poly-**2**, showed the self-association of **3** to an entwined double helix through the hydrogen bonds between the two carboxy groups (Figure 2 c).

We anticipated that if poly-**2** could self-associate in solution, forming a racemic double helix, the sense of the helix in the double-helical poly-**2** could be biased in the presence of a chiral amine through acid–base interactions.[7] This possibility was first investigated using circular dichroism (CD) and absorption spectroscopies. Figure 3 a shows the CD and absorption spectra of poly-**2** in the presence of an increasing amount of (*R*)-1-phenylethylamine ((*R*)-**4**) in a mixture of $CHCl_3$/THF (98/2, v/v). A small amount of THF was used, because poly-**2** did not completely dissolve in $CHCl_3$ in the absence of THF. Poly-**2** exhibited a characteristic induced CD (ICD) signal in the absorption regions of the *p*-diethynylphenylene linkage chromophore (300–380 nm). The CD signal intensity gradually increased with an increased amount of (*R*)-**4** and reached a plateau value at around [(*R*)-**4**]/[poly-**2**] = 1 (Figure 3 b), thus indicating that poly-**2** formed a chiral main-chain structure, for instance, a preferred-handed double helix, induced by (*R*)-**4**.

The dynamic light scattering (DLS) measurements of the poly-**2**·(*R*)-**4** complex in $CHCl_3$/THF (98/2, v/v) indicated that the complex formed a chiral aggregate with a hydrodynamic diameter (d_H) of (243 ± 71) nm (Figure S2), whereas a solution of poly-**2** did not show any significant light scattering, thus suggesting that poly-**2** exists as a single strand in the absence of (*R*)-**4** in $CHCl_3$/THF (98/2, v/v); polar THF appears to hamper the interstrand hydrogen bonds.

Fortunately, we obtained single crystals from a solution of an equimolar mixture of **3** and a racemic amine **6** in CCl_4 suitable for X-ray analysis, while **5** produced only amorphous solids. The crystal structure of the **3**·**6** complex showed a unique double-stranded inclusion structure. The two carboxylate anions and the two *R* and *S* ammonium cations assemble to form a 2 + 2 ion-pair and the two *m*-terphenyl units sandwich a pair of the enantiomeric amines **6** through a cyclic hydrogen-bonding network with an average N•••O distance of 2.67 Å (Figure 4). Sada et al. reported similar hydrogen-bonded network complexes based on primary or secondary ammonium salts of a bulky carboxylic acid in nonpolar solvents and in the crystalline state.[11]

The formation of 2 + 2 ion-paired inclusion complexes ($\mathbf{3}_2$·$\mathbf{4}_2$ and $\mathbf{3}_2$·$\mathbf{6}_2$ as well as $\mathbf{13}_2$·$\mathbf{4}_2$ and $\mathbf{13}_2$·$\mathbf{6}_2$) between the monomer models of poly-**2** (**3** and **13**) and chiral amines (**4** and **6**) in solution were also supported by the positive-mode cold-spray ionization mass spectrometry (CSI-MS; Figure S7). These results combined with those of the CD titration indicated that poly-**2** likely forms a predominantly one-handed double-helical structure with a chiral amine in a cyclic hydrogen-bonding network.

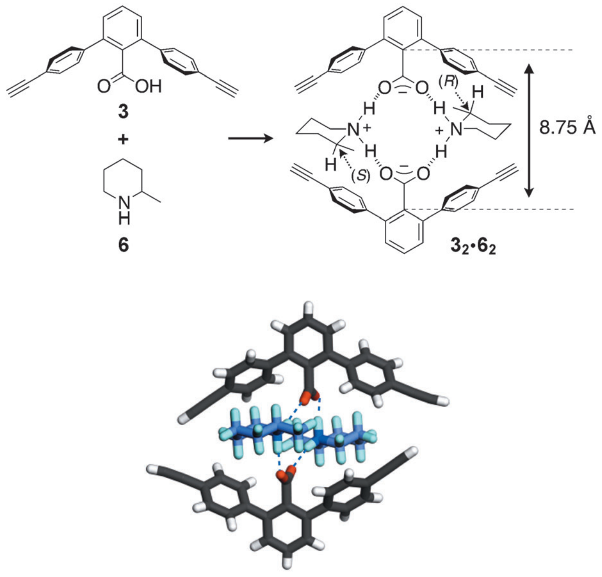

Figure 4. Complexation of **3** with **6** and the crystal structure of $\mathbf{3_2{\cdot}6_2}$ complex.

As a model study, the carboxylic acid dimer **5** was also subjected to the CD, MS, and 2D NMR experiments in the presence of (*R*)-**4** and/or (*S*)-**6**. Dimer **5** exhibited an ICD signal with (*R*)-**4** in the *p*-diethynylphenylene linkage chromophore region (300–370 nm), the signs of the Cotton effects of which were similar to those of poly-**2** complexed with (*R*)-**4**. The CD signal intensity gradually increased with an increase in the amount of (*R*)-**4** and reached a plateau value at around [(*R*)-**4**]/[COOH] = 2 (Figure 5a and b), thus indicating that dimer **5** also formed a similar preferred-handed double-stranded helical inclusion complex induced by (*R*)-**4**. The formation of such inclusion complexes of **5** with (*R*)-**4** and (*S*)-**6** was supported by CSI-MS (Figure 5c) and ^{1}H NMR spectra (Figures S8–S11 for **5**·(*R*)-**4** and Figures S12–S15 for **5**·(*S*)-**6** complexes). Clear interstrand and intermolecular NOE cross-peaks were observed for the aromatic protons of **5** with the terminal TMS groups, and the aromatic protons of **5** with the aromatic or aliphatic protons of (*R*)-**4** and (*S*)-**6** (Figures S11 and S15, respectively), thus indicating the homoduplex structure induced by the chiral amine (Figure 5d).

The effects of the structures of the chiral amines (primary (**4**, **9**, and **10**), secondary (**6** and **7**), and tertiary amines (**8**) with a different bulkiness, and primary amino alcohols (**11** and **12**)) on the induction of the preferred-handed helicity in poly-**2** (Figure S16) and its model dimer **5** (Figure S17) were then investigated. All the amines that were complexed with poly-**2** more or less induced the CD signals, but their spectral patterns and intensities significantly depended on the structures of the tested amines as anticipated (see the Supporting Information for more details).

We next investigated if the macromolecular helicity of the homoduplex of poly-**2** could be amplified in solution in the presence of nonracemic amines, such as **4**, by following the changes in the ICD signal intensity of poly-**2** with respect to the enantiomeric excess (*ee*) of **4** (*R*-rich; "majority rule",[9] Figure 6a). The formation of the complex of poly-**2** with nonracemic **4** displayed a positive nonlinear relationship (amplification of the helical chirality), that is, the observed Cotton effect intensity at 367 nm ($\Delta\varepsilon_{367}$) was nonlinearly increased with respect to the *ee* value of **4** during the homo-double-helix formation. The excess of enantiomers that are randomly sandwiched between the polymer strands might induce an excess of a one-handed double helix, in spite of its proportion, thus resulting in a more intense ICD signal than that expected from the *ee* value of **4**.

The changes in the ICD signal intensity of poly-**2** induced by (*R*)-**4** in the presence of achiral benzylamine at different molar ratios ("the sergeants and soldiers" effect)[8] were also investigated (Figure 6b). The formation of the complex of poly-**2** with (*R*)-**4** and benzylamine displayed a large positive nonlinear relationship between the molar fractions of (*R*)-**4** and the observed intensities of the Cotton effect at 330 nm ($\Delta\varepsilon_{330}$) and 366 nm ($\Delta\varepsilon_{366}$) (Figure 6b), thus indicating the amplification of the helical chirality because of the strong cooperativity during the homoduplex formation. In other

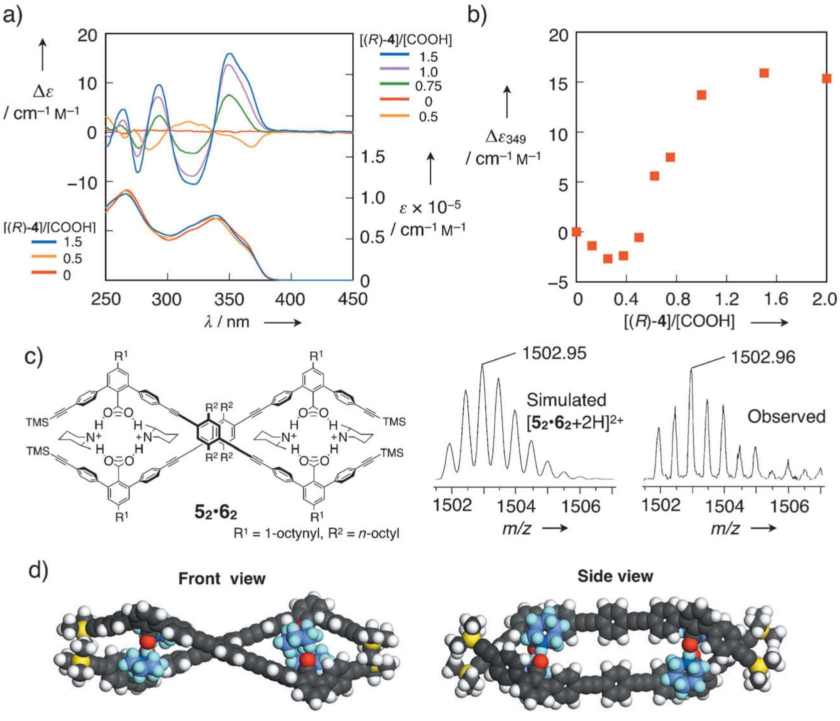

Figure 5. a) CD and absorption spectra of **5** in the absence and presence of (*R*)-**4** in $CHCl_3$ at ambient temperature (ca. 23–25 °C). b) Plots of the CD signal intensity at 349 nm ($\Delta\varepsilon_{349}$) versus the molar ratio of (*R*)-**4** to the carboxy groups of **5**. [**5**] = 2.0 mM. c) Positive-mode CSI-MS spectrum of $\mathbf{5_2{\cdot}6_2}$ ($CHCl_3$/MeOH = 4/1 (v/v) at −20 °C). d) Energy-minimized structures of the $\mathbf{5_2}$·(piperidine)$_2$ inclusion duplex.

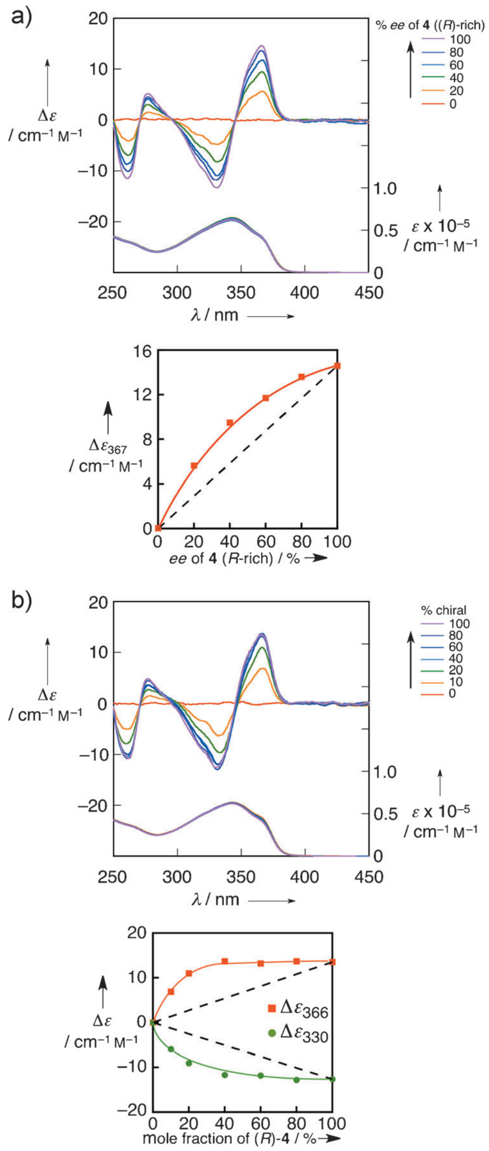

Figure 6. a) CD (left axis) and absorption (right axis) spectra of poly-**2** in the presence of **4** (1 equiv) with different *ee* values ((*R*)-rich) in $CHCl_3$/THF (98/2, v/v) at ambient temperature (ca. 23–25 °C). Underneath, the changes in CD signal intensity ($\Delta\varepsilon_{367}$) of poly-**2** versus the *ee* value of **4** are shown. [Poly-**2**] = 1.37 mM per monomer unit. b) CD (left axis) and absorption (right axis) spectra of poly-**2** in the presence of (*R*)-**4** and benzylamine in different molar ratios (([(*R*)-**4**] + [benzylamine])/[poly-**2**] = 1) in $CHCl_3$/THF (98/2, v/v) at ambient temperature (ca. 23–25 °C). Underneath, the changes in CD signal intensities ($\Delta\varepsilon_{330}$ and $\Delta\varepsilon_{366}$) of poly-**2** versus mole fractions of (*R*)-**4** are shown. [poly-**2**] = 1.37 mM per monomer unit.

words, once an appropriate amount of (*R*)-**4** was incorporated as a "sergeant" between the poly-**2** strands, the achiral benzylamine appears to behave as a "soldier" to maintain the one-handedness of the polymer duplex induced by (*R*)-**4**, thus resulting in a more intense ICD signal than that expected from the molar fractions of (*R*)-**4**.

In sharp contrast, dimer **5** showed almost no chiral amplification in the presence of **4** with different *ee* values, and (*R*)-**4** and benzylamine with different molar ratios at 20 °C, and even at low temperatures (−10–10 °C; Figures S18 and S19). These results demonstrate that the right- and left-handed double helices of **5** assisted by the chiral and/or achiral amines are dynamic in nature and the excess of the handedness is completely governed by the chirality of the amines that are sandwiched between the strands under thermodynamic equilibrium.[5d,12]

The unique features of the amplification of the macromolecular helicity are now available in a variety of polymeric and supramolecular helical systems through covalent and noncovalent bonding interactions,[13,14] but the present results may be the first example of the amplification of the helical chirality in double-helical polymers through noncovalent acid–base interactions.[15]

In summary, we have found that a *m*-terphenyl-based conjugated polymer that bears carboxy groups self-associates to form a racemic double helix through interstrand hydrogen bonds between the carboxy groups in the solid state and in solution. With chiral amines in solution, the polymer forms a unique double helix in which the two *m*-terphenyl units sandwich a pair of chiral amines through a cyclic hydrogen-bonding network, resulting in a preferred-handed double-helical inclusion complex. An excess of the one-handed double helix was induced in the presence of nonracemic amines and also chiral/achiral amine mixtures during the duplex formation, thus resulting in the amplification of the helical chirality. This result suggests that the chiral information of chiral amines, which are trapped between the polymer strands through acid–base interactions, can be transferred to the main chain and further amplified in the double-helical polymer backbone with a great cooperativity as an excess of a one-handed helical sense. The present findings of the formation of a metal-free homoduplex imply that more sophisticated supramolecular homoduplexes assisted by metal coordination may also be formed by taking advantage of the recently developed and emerging concept of metal–organic frameworks (MOFs), because carboxylic acids have been extensively utilized as one of the most popular building blocks for constructing supramolecular MOF materials with specific functions.[16] Work along this line is now ongoing in our laboratory.

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[14] For examples of the sergeants and soldiers effects, see: a) R. B. Prince, J. S. Moore, L. Brunsveld, E. W. Meijer, *Chem. Eur. J.* **2001**, *7*, 4150–4154; b) L. J. Prins, P. Timmerman, D. N. Reinhoudt, *J. Am. Chem. Soc.* **2001**, *123*, 10153–10163; c) A. Saxena, G. Guo, M. Fujiki, Y. Yang, A. Ohira, K. Okoshi, M. Naito, *Macromolecules* **2004**, *37*, 3081–3083; d) J. P. Deng, J. Tabei, M. Shiotsuki, F. Sanda, T. Masuda, *Macromolecules* **2004**, *37*, 9715–9721; e) J. J. D. de Jong, T. D. Tiemersma-Wegman, J. H. van Esch, B. L. Feringa, *J. Am. Chem. Soc.* **2005**, *127*, 13804–13805; f) M. M. J. Smulders, A. P. H. J. Schenning, E. W. Meijer, *J. Am. Chem. Soc.* **2008**, *130*, 606–611; g) T. Yamamoto, T. Fukushima, A. Kosaka, W. Jin, Y. Yamamoto, N. Ishii, T. Aida, *Angew. Chem.* **2008**, *120*, 1696–1699; *Angew. Chem. Int. Ed.* **2008**, *47*, 1672–1675; h) F. Helmich, M. M. J. Smulders, C. C. Lee, A. P. H. J. Schenning, E. W. Meijer, *J. Am. Chem. Soc.* **2011**, *133*, 12238–12246. For reviews, see: i) K. Maeda, E. Yashima, *Top. Curr. Chem.* **2006**, *265*, 47–88; j) A. R. A. Palmans, E. W. Meijer, *Angew. Chem.* **2007**, *119*, 9106–9126; *Angew. Chem. Int. Ed.* **2007**, *46*, 8948–8968; k) D. Pijper, B. L. Feringa, *Soft Matter* **2008**, *4*, 1349–1372.

[15] We attempted to visualize the helical structure of poly-**2** complexed with (*R*)-**4** or benzylamine by high-resolution AFM under various conditions, according to the procedure for visualizing the helical structure of the poly-**2** duplex on HOPG (Figure 2). However, we could not obtain 2D crystals of the poly-**2**·amine complexes on HOPG suitable for the observation of the helical structures, because the poly-**2** duplex most likely expands upon complexation of the amines between the strands as anticipated from the crystal structure of the $\mathbf{3}_2\cdot\mathbf{6}_2$ and $\mathbf{3}_2\cdot$(piperidine)$_2$ inclusion complex (Figure 4). Therefore, we could not determine the helical structure of the poly-**2**·amine duplex (see Figures S21 and S22 in more detail), although we presume that the poly-**2**·(*R*)-**4** duplex may possess a right-handed double-helical structure, by comparing the first Cotton effect sign to that of the right-handed double-helical poly-(*R*)-**1**·poly-**2**, the helical sense of which was determined by direct AFM observation.[6]

[16] For reviews, see: a) M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319–330; b) S. Beer, O. B. Berryman, D. Ajami, J. Rebek, Jr., *Chem. Sci.* **2010**, *1*, 43–47; c) J.-R. Li, J. Sculley, H.-C. Zhou, *Chem. Rev.* **2012**, *112*, 869–932.