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Supramolecular Chemistry

Asymmetric Induction in the Preparation of Helical Receptor–Anion Complexes: Ion-Pair Formation with Chiral Cations**

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A number of helical structures have been reported.[1] Foldamers form helical structures in response to chemical stimuli such as neutral molecules,[2] metal cations,[3] and anions.[4] The ability to prepare enantiomerically enriched helical foldamers is crucial for applying helical structures to functional materials with chiroptical properties.[5] One strategy for preparing enantiomerically enriched helices is the direct attachment of chiral moieties to the foldamers.[1] In addition, the introduction of a chiral guest species can also induce the preferential formation of one diastereomer of the resulting complex through specific noncovalent interactions between the guest and the host system.[4] Electrostatic interactions between oppositely charged species can occur in the absence of specific interactions.[6] Therefore, a challenging way to make a compound fold into an enantiomerically pure chiral structure is to use electrostatic interactions between an achiral ion and an enantiomerically pure chiral counterion. In fact, chiral anions have been used for the preparation of enantiomerically pure metal helicates.[7,8] Conversely, the association of chiral cations with helix-forming compounds that contain receptor and anionic moieties[9] has led to the formation of enantiomerically pure helical structures.[10] The chiroptical properties of receptor–anion helical complexes that form through hydrogen bonding can be difficult to examine because they can undergo more facile interconversion between enantiomeric helical forms compared to metal-based helices that form through coordination bonds. This fast interconversion is not a problem when one diastereomer of an ion pair consisting of a helical receptor–anion complexes and chiral counter cations is more stable than the other because then only one enantiomeric helix structure predominates in solution.

π-Conjugated molecules that form helical structures in the presence of anions include boron complexes of 1,3-dipyrrolyl-1,3-propanediones. These complexes, an example being **1a** (Scheme 1 a),[11] bind anions through dynamic conformational changes involving rotation of the bond between the carbonyl group and the pyrrole moiety, thus resulting in helical oligomers (e.g., **2a** and **2b**, Scheme 1 b).[11b,c,e] These helical oligomers were observed in the solid state and were comprised of alternately stacking negatively and positively charged species, that is, oligomer–anion complexes and counter cations, respectively.[11c,12] Anion complexes of the receptor-containing oligomers could be formed in enantiomerically enriched state in solution through ion pairing with optically active cations. In this paper, we report the preparation of enantiomerically enriched anionic helices that form electrostatic interactions with chiral counter cations; we also describe the chiroptical properties of these helices such as their circularly polarized luminescence (CPL).[11d,13]

Chiral π-conjugated cations are suitable candidates for inducing asymmetry in helix formation owing to their ability to form interactions with π-conjugated receptor–anion complexes. Therefore, we focused on the chiral binaphthylammonium Cl⁻ and Br⁻ salts, **RR**·X and **SS**·X (X = Cl and Br) (Scheme 1 c), which Ooi, Kameda, and Maruoka reported as being efficient phase-transfer catalysts in enantioselective reactions.[14] The formation of 1:1 receptor–anion complexes in solution can be followed by analyzing electronic spectra. Upon the addition of **RR**·Cl (1.5 equivalents) to **2b** in CH_2Cl_2 (1 mM) at 20 and −70 °C, the UV/Vis absorption bands associated with **2b** at 514 and 523 nm decreased and those at

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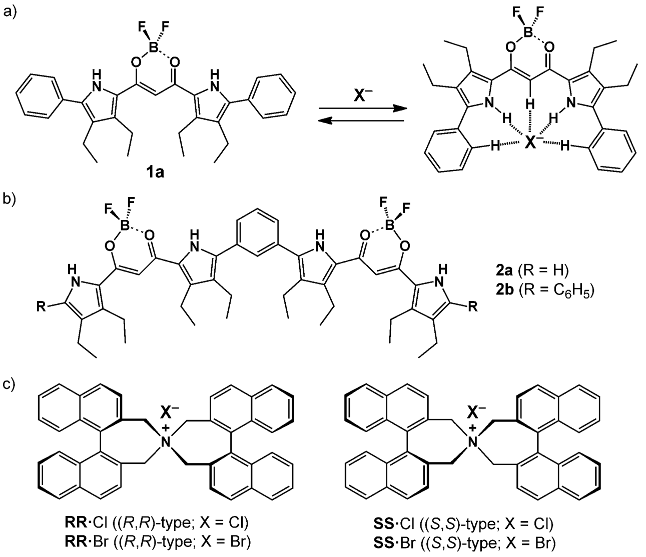

Scheme 1. a) Anion-binding mode of anion receptor **1a**, b) anion receptor dimers **2a** and **2b**, and c) binaphthylammonium halides **RR**·X and **SS**·X (X = Cl and Br).

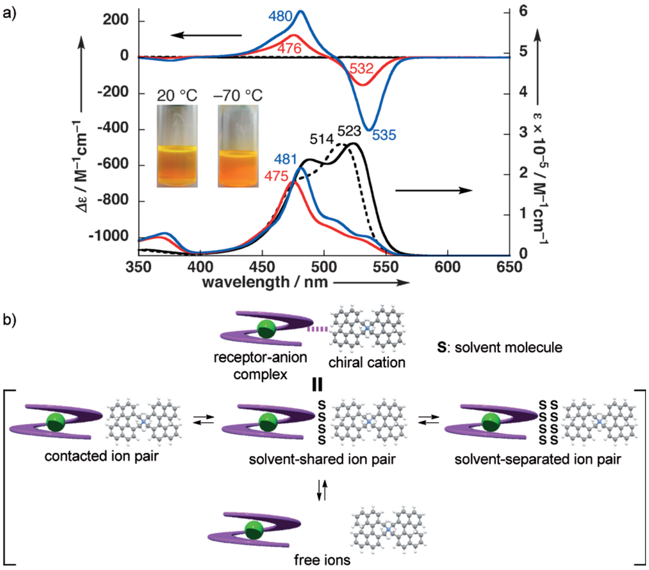

Figure 1. a) CD spectra (top) and UV/Vis spectra (bottom): **2b** in CH$_2$Cl$_2$ (1×10^{-3} M) at 20 °C (broken black line) and at −70 °C (solid black line); **2b** in CH$_2$Cl$_2$ (1×10^{-3} M) in the presence of **RR**·Cl (1.5 equiv), a mixture which forms **2b**·Cl$^-$···**RR**$^+$, at 20 °C (red line) and at −70 °C (blue line). Photographs of solutions of **2b**·Cl$^-$···**RR**$^+$ at 20 and −70 °C under visible light are given in the inset. b) Schematic models of a receptor–anion complex (as an *M*-type helix) in ion-pair forms and as a free ion (the representation of the ion-pair forms are schematic and do not represent the true form exactly).

475 and 481 nm increased, owing to the formation of the 1:1 complex **2b**·Cl$^-$ (Figure 1 a); these spectral changes were previously observed when Cl$^-$, in the form of an achiral tetrabutylammonium (TBA) salt, was added to **2b**.[11c,15] Furthermore, when chloride was added in the form of its **RR**$^+$ salt, CD signals associated with **2b**·Cl$^-$ that appeared at 535 nm (negative peak) and 480 nm (positive peak) were larger when the CD spectrum was acquired at −70 °C than when acquired at 20 °C (Figure 1 a), suggesting asymmetric formation of helical structures through diastereoselective ion-pair formation. The Cotton effects in the CD spectra, which are consistent with the formation of a helical structure, are associated with an excitonic interaction between the two receptor monomer units connected by an *m*-phenylene linkage. Time-dependent density functional theory (TD-DFT) calculations suggest that in the presence of **RR**$^+$, **2b**·Cl$^-$ should exist predominantly as the *M*-type helical structure.[16] The CD anisotropy factors g_{abs} of **2b**·Cl$^-$ and **2b**·Br$^-$ in the presence of **RR**$^+$ (1.5 equivalents) in CH$_2$Cl$_2$ (1 mM) at −70 °C were estimated to be 1.1×10^{-2} and 1.2×10^{-2}, respectively.[17] Under the same conditions, Cl$^-$ and Br$^-$ complexes of **2a** showed g_{abs} values of 2.4×10^{-3} and 1.4×10^{-3}, respectively, which are smaller than those of **2b**, thus suggesting that **2b** will lead to materials and compounds with better chiroptical properties. These g_{abs} values show significant correlation with the ratios of *M*- to *P*-type helical structures in solution, wherein the helical receptor–anion complexes exist as ion pairs, which include contacted, solvent-shared, and solvent-separated ion pairs, as well as free ions (Figure 1 b).[6] The ratio of *M*- to *P*-type helical structures depend on various factors such as the nature of the charged species, the solvent, temperature, and concentration. In fact, the addition of excess amounts of chiral halide salt to dilute solutions of **2b** (0.05 mM) provided increased CD signals, which allowed us to estimate that the $K_{\text{ion-pair}}$ values for the ion-pair formation for both **2b**·Cl$^-$ and **2b**·Br$^-$ with **RR**$^+$ at −70 °C, are 4×10^3 and 7×10^3 M^{-1}, respectively.

^{1}H NMR analysis afforded various insights into the solution-state anion-binding and ion-pair modes of the receptor oligomers. Upon the addition of 1.5 equivalents of TBACl to a solution of **2b** in CD$_2$Cl$_2$ (1 mM) at −50 °C, ^{1}H NMR signals at 9.58 (H^a), 9.49 (H^b), 7.62 (H^c), 7.52 (H^d), and 6.43 (H^e) ppm decreased in intensity with concurrent appearance of signals at 11.23 (H^a), 10.21 (H^b), 8.55 (H^c), 7.69 (H^e), and 7.24 (H^d) ppm, suggesting the formation of a stable 1:1 **2b**·Cl$^-$·**RR**$^+$ complex (spectra i and ii, Figure 2 a and Figure 2 b); additionally, the protons of β-ethyl CH$_2$ moieties show diastereotopic coupling because of the slow interconversion between helical enantiomers.[11c] On the other hand, upon the addition of 1.5 equivalents of **RR**·Cl to a solution of **2b** in CD$_2$Cl$_2$ at −50 °C,[18] ^{1}H NMR signals of **RR**·Cl decreased in intensity with the concurrent appearance of new signals at 11.08, 10.71, 10.22, and 9.88 ppm, which were assigned as the pyrrole NH groups, new signals at 8.47 and 8.14 ppm, which were assigned to H^c, new signals at 7.63 and 7.51 ppm, which were assigned to H^e, and new signals at 7.25 and 6.98 ppm, which were assigned to H^d. These sets of signals, an upfield-shifted set and downfield-shifted set (blue and red signals, respectively; Figure 2 a, iii) are consistent with the presence of two types of 1:1 complexes in a ratio of 1:0.62. These complexes could be diastereomeric ion pairs consisting of the *M* and *P* helices (**2b**^{M}·Cl$^-$ and **2b**^{P}·Cl$^-$, respectively) interacting with **RR**$^+$ (Figure 1 b and Figure 2 c, top two structures). It should be noted that the chemical shifts associated with each set of signals, represent an average of

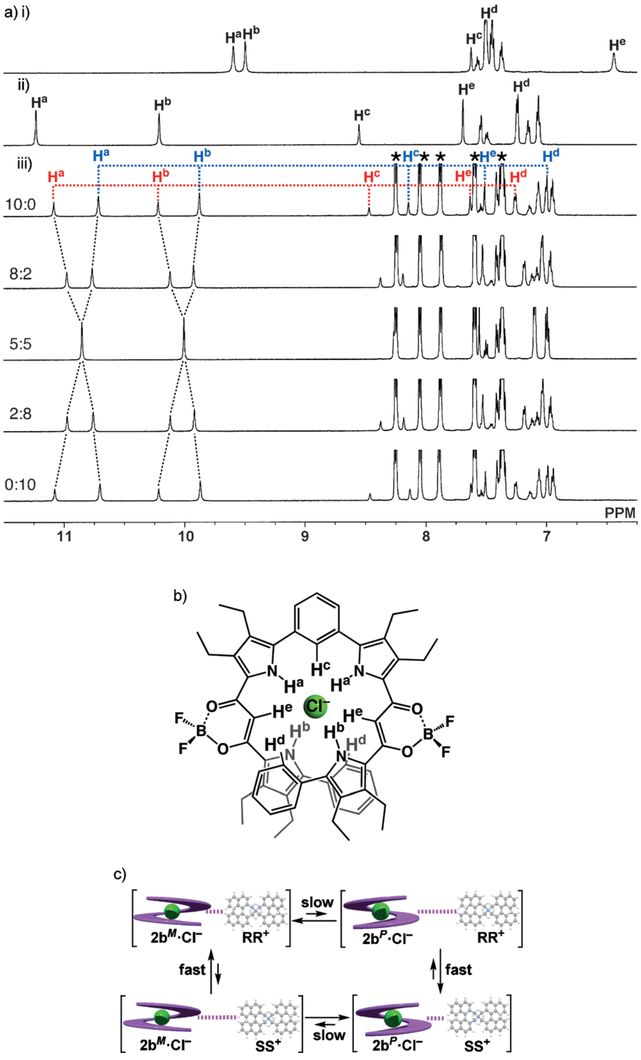

Figure 2. a) ^{1}H NMR spectra of i) **2b**, ii) **2b** with 1.5 equiv of TBACl, and iii) **2b** with mixtures of **RR**·Cl and **SS**·Cl in various ratios (1.5 equiv in total; ratios of salts **RR**·Cl:**SS**·Cl = 10:0, 8:2, 5:5, 2:8, and 0:10 from top to bottom) in CD$_2$Cl$_2$ (1 mM) at −50 °C (the signals that are indicated by an asterisk in iii are derived from the binaphthyl unit of **RR**$^+$). b) A schematic representation of $\mathbf{2b}^{M}$·Cl$^-$. c) Schematic models illustrating the interconversion between *M*- and *P*-type helices (horizontal equilibria) and where the ion pairs undergo cation exchange (vertical equilibria).

the shifts of the respective ion pair ($\mathbf{2b}^{M}$·Cl$^-$···**RR**$^+$ and $\mathbf{2b}^{P}$·Cl$^-$···**RR**$^+$) and the corresponding free ion ($\mathbf{2b}^{M}$·Cl$^-$ and $\mathbf{2b}^{P}$·Cl$^-$). The more stable diastereomer, $\mathbf{2b}^{M}$·Cl$^-$···**RR**$^+$, has signals that are in a more upfield region of the spectrum (blue signals; Figure 2 a, iii) owing to the greater shielding effect imparted by the chiral cation, which contains aromatic moieties. However, it is evident from the averaged NMR signals ascribable to several ion-pair modes in each diastereomer that the specific ion-pair modes of **2b**·Cl$^-$ and **RR**$^+$ cannot exist for a long time.

The ratio (0.62:0.38) of *M*- and *P*-type helical structures at −50 °C represents a diastereomeric excess (*de*) value of 24 %. Similar to the g_{abs} values, the *de* values are also affected by the experimental conditions. Temperature can be used to control the *de* value; lowering the temperature leads to the formation of more tightly associated ion pairs and an increase in the *de* value; in fact, the *de* value of **2b**·Cl$^-$···**RR**$^+$ in CD$_2$Cl$_2$ (1 mM) increased to 29 % when the temperature was lowered to −70 °C, as observed in the increase of the CD signals. The nature of the anions bound in the helical structure can also control the *de* value; for example, when the anion is changed from chloride to bromide, as in **2b**·Br$^-$···**RR**$^+$, the *de* value, as measured at −70 °C, increases to 43 % in favor of the *M*-type helix.[19] The higher $K_{\text{ion-pair}}$ value associated with the mixture of **2b**·Br$^-$ and **RR**$^+$ is one of the factors that explain the higher *de* value. When **2b** in CH$_2$Cl$_2$ (1 mM) is treated with 1.5 equivalents of chiral salt at −70 °C, the resulting $K_{\text{ion pair}}$ values represent 74 % and 82 % conversion into **2b**·Cl$^-$···**RR**$^+$ and **2b**·Br$^-$···**RR**$^+$, respectively, suggesting that the ideal *de* values based on mixtures of just ion pairs, rather than that associated with mixtures of ion pairs and free ions, were estimated as being 40 % and 52 %, respectively. The selectivity in helical direction in CD$_2$Cl$_2$ may be correlated with the nature of the helical structure. Furthermore, solvents can control the *de* values. When **2b** in CD$_2$Cl$_2$/octane-d_{18} (1:1, 1 mM) is treated with 1.5 equivalents of chiral salt at −70 °C, the resulting ion pairs, **2b**·Cl$^-$···**RR**$^+$ and **2b**·Br$^-$···**RR**$^+$, were formed with a higher but similar *de* value of 70 % together with g_{abs} values of 1.9×10^{-2} and 2.3×10^{-2}, respectively; this increase in *de* value is presumably due to increased stabilization of the ion pairs in less polar solvent. Considering the ideal *de* values in CH$_2$Cl$_2$, diastereoselectivity in the formation of the helical structures can be controlled not only by the degree of ion-pair formation but also by the state of the ion pairs, that is, whether they are tightly bound or relaxed, for example.

Furthermore, the ROESY spectrum of a sample of **2b**·Cl$^-$···**RR**$^+$ in CD$_2$Cl$_2$ (1 mM) at −50 °C showed a correlation between the signals associated with the *M*- and *P*-type helices, thus suggesting interconversion between *M*- and *P*-type helices. When **2b** (1 mM), is treated with the chiral salt (1.5 equivalents) in CD$_2$Cl$_2$ the interconversion between *M*- and *P*-type helices in **2b**·Cl$^-$ is slower than that in **2b**·Br$^-$, as suggested by their coalescence temperatures, which are approximately 20 and −30 °C, respectively. In both cases, the interconversion between helices is faster than the anion binding/folding and unfolding/anion releasing processes. For the transition of the helix from *M*-type to *P*-type in **2b**·Cl$^-$···**RR**$^+$ at −50 °C, EXSY[20] experiments provided a rate constant $k_{M \rightarrow P}$ of 3.8 s^{-1}. In contrast to the ion pairs derived from **2b**, those derived from **2a**, either as Cl$^-$ or Br$^-$ complexes, did not show two sets of signals associated with diastereomers in the ^{1}H NMR spectrum, which was acquired at −50 °C, owing to fast interconversion between the helical structures; this fast interconversion is probably due to the absence of terminal phenyl moieties.

The diastereoselective formation of the ion pair between **2b**·Cl$^-$ and the chiral cation depends on the configuration of the cation, that is, whether it is **RR**$^+$ or **SS**$^+$; of course, the ion pairs of **2b**·Cl$^-$ with each cation afford identical ^{1}H NMR spectra, which exhibit the same ratio of diastereomers and the same chemical shifts (Figure 2 a, iii, 10:0 and 0:10). The slow interconversion between the diasteromeric *M*- and *P*-type helical structures (top and bottom horizontal equilibria,

Figure 2c) explains the observation of two independent sets of signals in the ^{1}H NMR spectrum. On the other hand, the ^{1}H NMR spectrum of a mixture of **2b**, **RR**·Cl, and **SS**·Cl showed interesting behavior, which was dependent on the ratios of the chiral cations. Upon addition of a 1:1 mixture of **RR**·Cl and **SS**·Cl (1.5 equivalents in total) to a solution of **2b** in CD_2Cl_2 (1 mM) at −50 °C, a single set of signals, assigned as a 1:1 complex, was observed. Furthermore, when the ratio of enantiomeric cations was increased or decreased from 1:1, the set of ^{1}H NMR signals split into two sets of signals with changes in the relative integrations of the signals associated with the diastereomeric ion pairs (Figure 2a, iii). This observation suggested that the presence of unequal amount of the chiral cations, **RR**$^{+}$ and **SS**$^{+}$, leads to different amounts of **2b**^{M}·Cl^{-}···**XX**$^{+}$ and **2b**^{P}·Cl^{-}···**XX**$^{+}$ (**XX** = **RR** and **SS**), which consist of both ion pairs and free ions. In addition, the ^{1}H NMR spectra are consistent with fast cation exchange between **2b**^{M}·Cl^{-}···**RR**$^{+}$ and **2b**^{M}·Cl^{-}···**SS**$^{+}$ and between **2b**^{P}·Cl^{-}···**RR**$^{+}$ and **2b**^{P}·Cl^{-}···**SS**$^{+}$ (left and right perpendicular equilibria, Figure 2c). That is, cation exchange between diastereomeric ion pairs is faster than racemization of the helix, a flipping process that involves inversion of the pyrrole moieties.

The ion pairs composed of **2b**·Cl^{-} or **2b**·Br^{-} helices are highly fluorescent. When a solution of either **2b**·Cl^{-} or **2b**·Br^{-} in the presence of **RR**$^{+}$ (1.5 equivalents) in CH_2Cl_2 (1 mM) at −70 °C was excited with light at 483 nm, which was the isosbestic point in the corresponding UV/Vis absorption spectrum, the resulting fluorescence spectrum exhibited a maximum emission wavelength (λ_{em}) of 559 nm (Figure 3 bottom).[21] The ion pairs formed from **2b**·X^{-} (X = Cl and Br) and the chiral cations exhibit CPL.[13] In fact, ion-pair-induced CPL was observed in solutions of **2b**·Cl^{-}···**RR**$^{+}$ and **2b**·Br^{-}···**RR**$^{+}$ (Figure 3 top), under the conditions described above, and the CPL anisotropy factors g_{lum} were 8.4×10^{-3} and 1.3×10^{-2}, respectively. Furthermore, the g_{lum} values increased to 1.8×10^{-2} and 2.1×10^{-2}, respectively, when the ion pairs were formed in CH_2Cl_2/octane (1:1, 1 mM) at −70 °C. On the other hand, smaller g_{lum} values were observed at 20 °C. As was observed above in the context of g_{abs} values, larger g_{lum} values were also obtained under conditions that engendered helical anion complexes with relatively high *de* values. Notably, CPL is induced through ion-pair formation involving helical charged species and counter ions in solution.

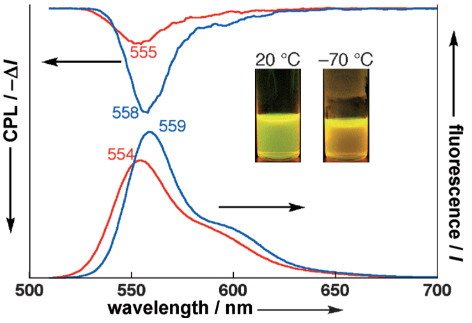

Figure 3. CPL (top) and fluorescence (bottom) spectra (excited at 483 nm) of **2b** in CH_2Cl_2 (1 mM) with **RR**·Cl salt (1.5 equiv) at 20 (red) and −70 °C (blue), along with photographs of **2b**·Cl^{-}···**RR**$^{+}$ at 20 and −70 °C under UV$_{365\,nm}$ light (inset). These spectra, which were measured under their respective optimized conditions, are represented using arbitrary units.

In summary, we have herein described the first example of solution-state asymmetric induction in the formation of helical π-conjugated-receptor–anion complexes, which form electrostatic interactions with chiral π-conjugated cations. The asymmetric induction in the formation of the helical structures led to enhanced CD signals together with an increase in CPL. This fascinating observation can be attributed to the characteristic properties of electronically neutral anion-responsive molecules that form helical anion complexes. Further oligomerization should afford enantiomerically enriched macromolecular systems comprised of anionic helical structures and appropriate counter cations, which form ion pairs.[22] Further investigation into more functional materials based on these types of ion pairs is currently underway.

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[15] Binding constants (K_a) of **2b** with Cl$^-$ and Br$^-$ as **RR**$^+$ salts were estimated as being 30000000 and 930000 M^{-1}, respectively, based on UV/Vis spectral changes. These values are higher than those of the corresponding TBA salts, 12000000 and 24000 M^{-1}, respectively (Ref. [11c]), a fact that may be attributed to the difference in the stabilities of ion pairs comprised of halide anions and counter cations.

[16] a) Gaussian 09 (Revision B.01), M. J. Frisch, et al. Gaussian, Inc., Wallingford CT, **2009**; b) ZINDO calculations provided evidence that longer helical pitches will afford larger CD intensities; c) It is challenging to estimate exactly the arrangement of components in the ion pairs.

[17] a) Difference in the g_{abs} values of the anion complexes might be attributed to the slightly different conformations of the associated species in solution (Ref. [16b]); b) The observed CD signals can be considered to be derived from the chromophores of excess amounts of enantiomeric helical structures in the form of diastereomeric ion pairs.

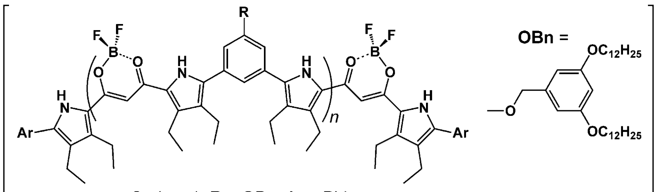
[18] Based on the estimated K_a values (Ref. [15]), > 99.9% of **2b** exists as 1:1 complexes (1 mM) in CH$_2$Cl$_2$ at 20 °C in the presence of 1.5 equivalent of Cl$^-$ and Br$^-$ salts.

[19] a) The exact *de* value of **2b**·Br$^-$···**RR**$^+$ at −50 °C could not be determined; b) In a preliminary examination, the addition of **RR**$^+$ as an I$^-$ salt showed a faster interconversion between *M*- and *P*-type helices as unstable 1:1 complexes.

[20] A selected review and article on EXSY spectroscopy: a) C. L. Perrin, T. J. Dwyer, *Chem. Rev.* **1990**, *90*, 935–967; b) D. Zuccaccia, L. Pirondini, R. Pinalli, E. Dalcanale, A. Macchioni, *J. Am. Chem. Soc.* **2005**, *127*, 7025–7032.

[21] The emission quantum yields for **2b**·Cl$^-$···**RR**$^+$ and **2b**·Br$^-$···**RR**$^+$ were 0.65 and 0.33, respectively, in CH$_2$Cl$_2$ (1 mM) at 20 °C (λ_{ex} = 479 nm).

[22] Anion receptor dimer **2c** and tetramers **4a** and **4b** in CD$_2$Cl$_2$ formed 1:1, 1:2, and 1:2 single helices, respectively, in racemic form upon the addition of TBACl. However, the addition of **RR**·Cl to these oligomers afforded complicated NMR signals in CD$_2$Cl$_2$ at −50 °C owing to the existence of several diastereomeric ion pairs involving the chiral cation.



2c (*n* = 1, R = OBn, Ar = Ph)
4a (*n* = 3, R = Ar = H)
4b (*n* = 3, R = OBn, Ar = H)