specific properties. Studies with OMs should therefore provide insight into the molecular basis of novel properties of reversible polymeric systems, for example, at surfaces and interfaces.[8]

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Molecular Clips that Undergo Heterochiral Aggregation and Self-Sorting**

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Biological systems offer exquisite examples of the ways in which spatially and temporally controlled self-processes—self-organization, self-assembly, and self-recognition—can lead to the creation of higher order functional structures.[1] To approach the design of supramolecular systems that display complex biomimetic behavior, chemists have developed metal coordination, donor-acceptor interaction, and hydrogen-bond-driven self-assembly to a level of sophistication that has allowed these assemblies to be endowed with desirable chemical or physical properties.[2] Within the area of self-assembly driven by hydrogen bonds, these activities have resulted in intriguing discoveries including quadruple hydrogen bonding modules[3] that form the basis of supramolecular polymers,[4] molecular capsules,[5] systems that display enantiomeric self-recognition,[6] and complete asymmetric induction.[7] The use of hydrogen bonding as a tool in these applications depended on the design of robust, functionalizable, and tightly associated H-bonding modules. The further implementation of H-bonding modules as instructed components[1] in self-organizing systems additionally requires systems capable of self-sorting.[8] Such systems display high levels of discrimination between self and non-self species and consequently operate simultaneously and orthogonally within complex mixtures. One strategy to create robust H-bonding modules relies on increasing the number of hydrogen bonds and tailoring their geometrical arrangement. In this paper we employ a strategy using molecular clips,[9,10] based on molecular shape and chirality. We report that compounds **1a**, **1b**, (±)-**2a**, and (±)-**2b** form tightly self-associated dimers in $CDCl_3$ driven by the simultaneous formation of π–π interactions and two hydrogen bonds. The dimers possess a confluence of properties—tight binding, high levels of chiral discrimination, and self-sorting—that make them prime modules for use in advanced applications.

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Figure 1 shows the chemical structures of the four molecular clips described in this paper. Compounds **1a** and **1b** are C_s-symmetric achiral meso forms, whereas (±)-**2a** and (±)-**2b** are chiral C_2-symmetric compounds. All four compounds

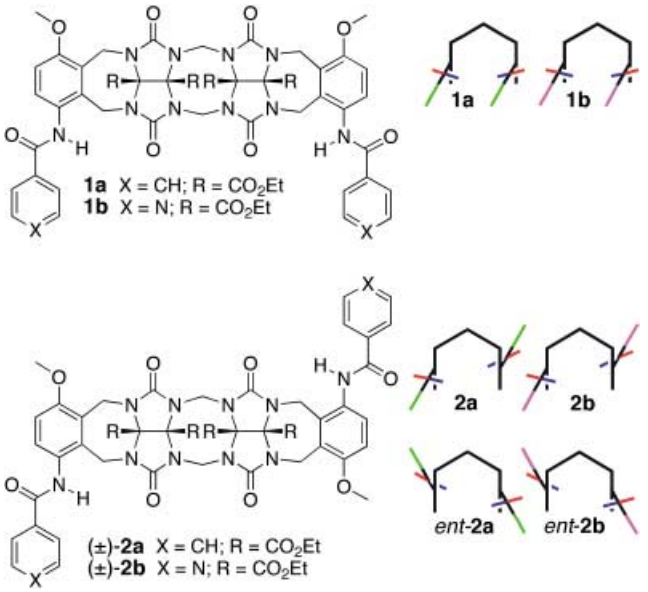

Figure 1. Structures of **1a**, **1b**, (±)-**2a**, and (±)-**2b**, and schematic representations of their three dimensional shapes; phenyl rings (green), pyridyl rings (purple), carbonyl oxygen atoms (red), amide NH groups (blue).

display remarkable self-association properties. In particular, the ^{1}H NMR spectra of **1a**, **1b**, (±)-**2a**, and (±)-**2b** (Figure 2a, b, e, and f) displayed two sets of resonances for the amide NH groups and the protons on substituted *o*-xylylene side-walls. These observations suggested the formation of kinetically and thermodynamically stable dimeric aggregates in $CDCl_3$.[11]

The X-ray crystal structures obtained for **1a** and (±)-**2b** provide corroborating evidence for the dimerization of **1a**, **1b**, (±)-**2a**, and (±)-**2b** and suggest plausible geometries for these aggregates in $CDCl_3$ (Figure 3).[12] The geometrical features of these dimers are dictated by the formation of only two C=O···HN hydrogen bonds.[13] Their high thermodynamic stability, however, is likely to be caused by favorable interactions between the four aromatic rings that occur as the aromatic side-walls penetrate deep into the cleft of the opposing molecular clip.[9a,b] One consequence of this geometry is the parallel orientation of the four amide groups, a feature which may prove valuable in the preparation of dynamic functional group arrays.[14] In the dimerization of (±)-**2b**, three outcomes are theoretically possible: enantiomeric self-recognition ((+)-**2b**)$_2$ and (−)-**2b**)$_2$), formation of a heterochiral aggregate ((+)-**2b**·(−)-**2b**), or a mixture of the two processes. In reality, the heterochiral aggregate (+)-**2b**·(−)-**2b** is formed exclusively. The origin of this highly diastereoselective process is simple to explain; in the heterochiral dimer the simultaneous formation of π–π interactions and two hydrogen bonds is possible, whereas the hypothetical homochiral dimer benefits from π–π interactions and only a single hydrogen bond.

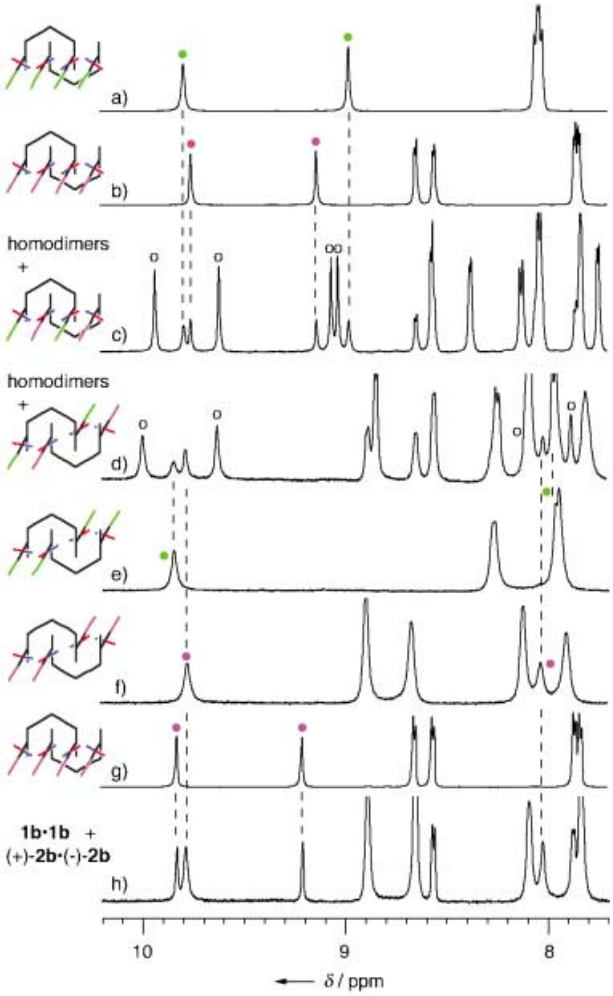

Figure 2. Hydrogen bonding region of the ^{1}H NMR spectra ($CDCl_3$, 500 MHz, 2 mM) recorded for a) **1a**·**1a** (298 K), b) **1b**·**1b** (298 K), c) a mixture of **1a**·**1a**, **1b**·**1b**, and (±)-**1a**·**1b** (298 K), d) a mixture of (+)-**2a**·(−)-**2a**, (+)-**2b**·(−)-**2b**,(+)-**2a**·(−)-**2b**, and (−)-**2a**·(+)-**2b** (263 K), e) (+)-**2a**·(−)-**2a** (263 K), f) (+)-**2b**·(−)-**2b** (263 K), g) **1b**·**1b** (263 K), and h) a mixture of **1b**·**1b** and (+)-**2b**·(−)-**2b** (263 K). The schematic representations depict the species present in solution and their geometries. The resonances for amide NH groups of the homodimers are identified with green (●) and purple (●) bullets, whereas those of the heterodimers are marked with open bullets (○). The unmarked resonances arise from the appended pyridyl and phenyl rings.

Having established that **1a**, **1b**, (±)-**2a**, and (±)-**2b** form strong homodimeric aggregates, we decided to investigate the formation of heterodimers. When **1a** and **1b** were dissolved in $CDCl_3$, a roughly statistical mixture of the homodimers **1a**·**1a** and **1b**·**1b** and the heterodimer **1a**·**1b** was observed (Figure 2c). Unlike the homodimers, the heterodimer (±)-**1a**·**1b** does not possess a C_2-axis, and each of the four amide NH groups give rise to separate resonances in the ^{1}H NMR spectrum. Similarly, when a mixture of (+)-**2a**·(−)-**2a** (Figure 2e) and (+)-**2b**·(−)-**2b** (Figure 2f) was analyzed by ^{1}H NMR (Figure 2d) we observed a mixture of the two heterochiral homodimers and a racemic mixture of heterodimers ((+)-**2a**·(−)-**2b** and (−)-**2a**·(+)-**2b**). These heterodimers are noteworthy as, for example, (+)-**2a** exhibits complete enantioselective discrimination between (+)-**2b** and (−)-**2b**.

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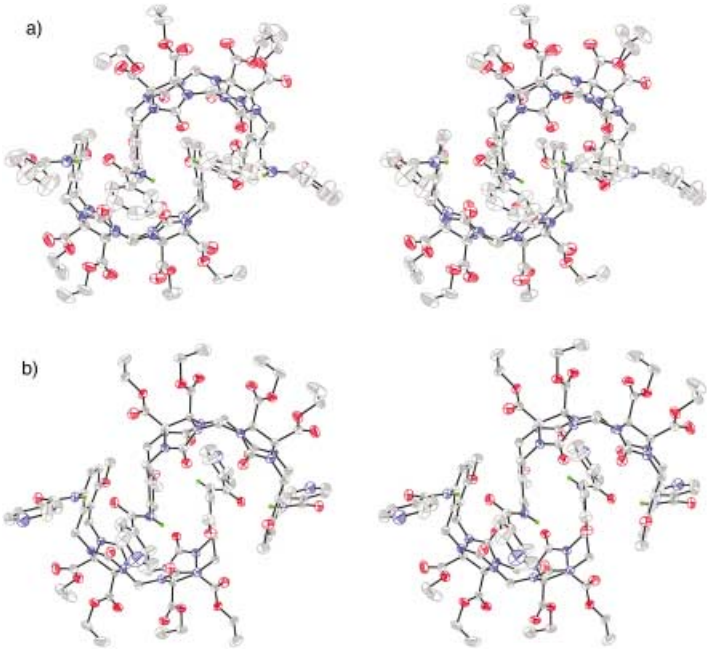

Figure 3. Cross-eyed stereoscopic ORTEP plots of the crystal structures of a) **1a**·**1a** and b) (+)-**2b**·(−)-**2b**. The solvating $PhCH_3$ and $CHCl_3$ molecules in these complexes, as well as H atoms not bonded to amide N atoms have been removed for clarity. Two of the CO_2Et groups of **1a** adopt two orientations in the crystal structure; here, the major orientation component is depicted. Colors: C (grey), O (red), N (blue), and H (green).

The high level of enantioselectivity exhibited by **2a** and **2b** based on molecular shape and chirality led us to consider the behavior of a solution containing mixtures of achiral and chiral molecular clips. For example, upon mixing solutions containing **1b**·**1b** (Figure 2g) and (+)-**2b**·(−)-**2b** (Figure 2f) we observed a simple superposition of the ^{1}H NMR spectra (Figure 2h) of the two homodimeric aggregates, a result which indicates that this class of compounds is self-sorting.[8,15] The constraints placed on the system by the arrangement of the H-bonding groups, relative to the cleft of the molecular clip, dictate that optimal noncovalent interactions are achieved only through self-sorting.

In summary, we have developed two tightly self-associated H-bonding modules that are driven by the formation of only two hydrogen bonds, reinforced by π–π interactions. The relative geometry of the two H-bonding groups with respect to the cleft of the molecular clip controls the self-association process by favoring aggregates that simultaneously form both H-bonds and participate in π–π interactions. These aggregates display high levels of chiral discrimination and self-sorting. We anticipate that these characteristics will make them desirable for a variety of applications including noncovalent polymer chemistry, enantioselective recognition and catalysis, and as an instructed component in supramolecular chemistry.

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[11] The NMR spectra for **1a**·**1a** and **1b**·**1b** were measured at 298 K, as the complexes are kinetically stable on the chemical shift timescale at this temperature. In contrast, it was necessary to record the NMR spectra of (+)-**2a**·(−)-**2a** and (+)-**2b**·(−)-**2b** at 263 K to achieve kinetic stability. We attempted to determine the thermodynamic stability of these aggregates by ^{1}H NMR dilution experiments in $CDCl_3$, but did not observe any changes in chemical shift upon dilution to 100 μM. Isothermal titration calorimetry yielded thermodynamic parameters for dimerization (C_6H_6/DMSO 95:5, 298 K, **1a**·**1a**: $K_a = 5550 \pm 1230\,M^{-1}$, $\Delta H = -15.7 \pm 0.9\,kJ\,mol^{-1}$).

[12] CCDC-187956 (**1a**·**1a**) and CCDC-187957 ((+)-**2b**·(−)-**2b**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.ac.uk).

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[15] The observed self-sorting phenomenon can be explained based on either kinetic or thermodynamic arguments. The lifetimes of the kinetically more stable dimers determined by ^{1}H EXSY NMR measurements (**1a**·**1a**: 13.6 s^{-1}; **1b**·**1b**: 6.3 s^{-1}) indicate that a fast exchange occurs, which rules out a kinetically controlled process and implies a thermodynamic preference for self-sorting in this system.

Novel Liquid-Crystalline Phases with Layerlike Organization**

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Investigation of the driving forces of molecular self-organization is one of the most exciting and most rapidly growing areas of chemical research. In this respect, ordered structures with liquid-crystalline (LC) properties are of special interest, because they are reversibly formed under thermodynamic equilibrium conditions and combine order and mobility on molecular, supramolecular, and macroscopic levels. The mobility enables them to respond to different external stimuli by changing their configuration, which in turn determines their importance in biological systems and technical applications.[1] In conventional LC materials rod- or disklike anisometric rigid units, which provide long-range orientational order, are connected to flexible alkyl chains, which are largely responsible for positional order and mobility. This design principle leads to the well-known nematic, smectic, and columnar LC phases.[2] A characteristic feature of such LC materials is a molecular topology in which rigid cores and flexible chains are connected in such a manner that the parallel organization of the rigid segments and the segregation of the incompatible molecular parts enhance each other.

Exciting new mesophase morphologies can be realized if rodlike (calamitic) rigid units are combined with two incompatible subunits in a competitive and nonlinear manner.[3,4] Examples are bolaamphiphilic biphenyl derivatives carrying a long lateral alkyl chain.[4] In such bolaamphiphiles, the strongest attractive forces (hydrogen bonding) act at the two termini of a rigid calamitic core. The lateral alkyl chains represent a third group of units that are incompatible with both the polar terminal diol groups[5] and the rigid biphenyl cores. As a consequence, each of these units segregates into its own subspace, and a series of unusual columnar mesophases results. They are built up by networks of cylinders, formed by ribbons of the biphenyl cores which are held together by ribbons of hydrogen-bonding networks (see Figure 1). The

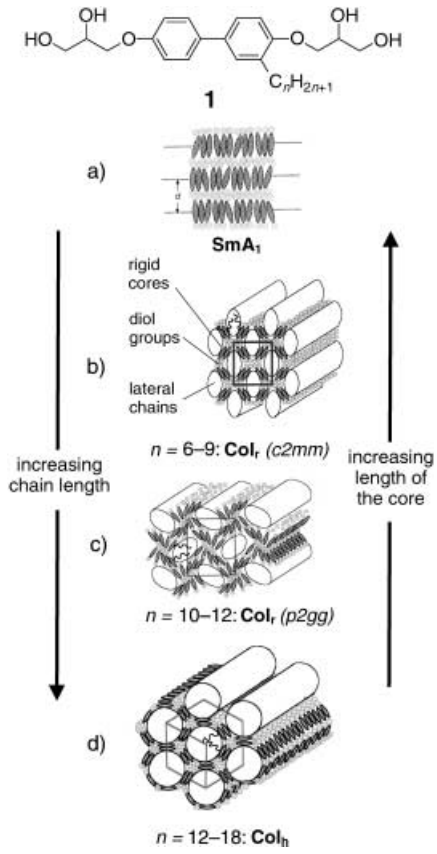

Figure 1. Molecular organization of compounds **1** in their mesophases in dependence on the molecular structure.[4]

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