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Chiral Transcription and Retentive Helical Memory: Probing Peptide Auxiliaries Appended with Naphthalenediimides for Their One-Dimensional Molecular Organization

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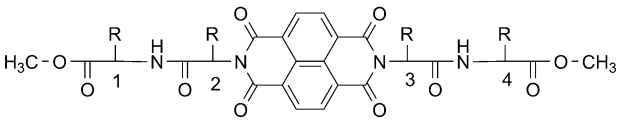
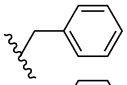
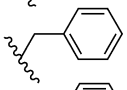
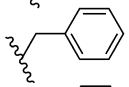
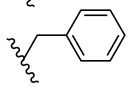
The single-handedness of biomolecular building blocks of life as in L-amino acids and D-sugars has been one of the greatest mysteries of the biotic world.[1] The biological macromolecules evolved from these chiral building blocks, such as DNA double helix and secondary α-helix of proteins, are exclusively homochiral. The origin of this homochirality has evoked enormous interest in the scientific community for several decades.[2,3] In this regard, pioneering work on synthetic covalent polymers by Green and co-workers led to the phenomenon of amplification of chirality.[4] The noncovalent interactions that drive supramolecular polymers are of interest as they offer modularity, tunability and reversibility. The Meijer and Reinhoudt groups independently developed various noncovalent systems to construct elegant chiral supramolecular assemblies.[5,6] Since then, supramolecular chirality has gained unprecedented importance from the fundamental science perspective and for practical applications in areas such as asymmetric catalysis, determination of absolute configuration, sensors, optoelectronics, materials science and biomedicine.[7,2f] Benefits of introducing chirality into synthetic covalent polymeric structures and the effects on function have been well documented.[8] However, supramolecular chirality is still in its infancy and will have a profound role in the development of fast emerging dynamic supramolecular polymers.

In particular, dedicated efforts towards chirogenesis and chiral enhancement have significantly influenced the structural and functional evolution of nano- and macroscale supramolecular polymeric materials through weak noncovalent-interaction-driven molecular self-assembly. However, the use of modular biomolecules as chiral auxiliaries, either freely or in conjugation with chromophores, is largely unknown and an unexplored area.[9] Thus, the study of chiral transcription and enhancement in the design of chiral supramolecular polymers could enable the production of novel hybrid materials with interesting functions as alternative to covalent polymers. These observations inspired us to design homochiral, heterochiral and achiral peptide auxiliaries appended with naphthalenediimides (NDIs) as shown in Scheme 1 (see the Supporting Information for synthesis and



NDI–peptide conjugate	Amino acid configuration				R
	1	2	3	4	
LL	L	L	L	L	
DD	D	D	D	D	
LD	D	L	L	D	
DL	L	D	D	L	
AA	-	-	-	-	

Scheme 1. Molecular structures of homochiral (**LL** and **DD**), heterochiral (**LD** and **DL**) and achiral (**AA**) peptide conjugates of NDI.

characterization details). Homochiral peptides appended with NDIs (**LL** and **DD**) comprised of identical L or D stereochemistry for the two α-phenylalanine units. Heterochiral peptides with appended NDIs (**LD** and **DL**) comprised of alternative L and D or D and L stereochemistry for the two α-phenylalanine units. The dipeptide auxiliary with two glycine units formulates the achiral peptide appended NDI (**AA**). The choice of phenylalanine was due to its favorable steric characteristics, which is expected to play a major role in the stereospecific orientation of supramolecular building units and to least sterically hinder conformation, and was partly inspired by the interesting results reported earlier.[10]

Organic chromophores were employed as an additional optical probe to study the process of chiral supramolecular assemblies. Herein we have employed NDI (n-type semiconductor) due to its versatile properties and potential applications ranging from electronics to biomedicine.[11–13] NDI

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chromophore not only serves as an optical probe but also facilitates a planar central aromatic core structure, and compliments the self-assembly characteristics of the peptide conjugates. Here, we report the induction of supramolecular chirality to achiral NDI with phenylalanine peptide auxiliaries. Chiral enhancement is demonstrated by using sergeants-and-soldiers and majority-rules experiments. Furthermore, we show that in case of the heterochiral peptide conjugates (**LD** and **DL**) the chirality of the first stereocenter (irrespective of the stereochemistry of second stereocenter) adjacent to the NDI core determines the supramolecular helicity; this is termed as retentive helical memory. Remarkably, morphological studies reveal that the homochiral **LL** and **DD** self-organize into 1D hierarchical supramolecular polymers with opposite helicity. Interestingly, the heterochiral peptide conjugates **LD** and **DL** form microspheres. The chiral enhancement experiments and the propensity of **LL** and **DD** conjugates to form 1D architectures, in principle can support the mechanism of both spontaneous deracemization and chiral enhancement pathways for biological homochirality.[10b]

The molecular aggregation behavior of peptide conjugates **LL**, **DD**, **LD** and **DL** were explored through absorption and fluorescence spectroscopic studies. All the NDI–peptide conjugates in dimethylsulfoxide (DMSO) exhibited strong absorption bands in the region of 300–400 nm (band I), which is attributed to the characteristic π–π* transitions of NDI chromophore polarized along the *z* axis (see the Supporting Information). In aqueous DMSO (water/DMSO, 85:15) slight bathochromic shift of band I was observed. However, a weak fluorescent emission was observed for NDI chromophores in DMSO (Figure 1a). Interestingly, in aqueous DMSO (water/DMSO, 85:15) a very broad band centered at 475 nm with a shoulder at 530 nm appeared. This red-shifted fluorescence is attributed to excimer-like emission due to the formation of ground state aggregates as reported earlier.[14] The inset in Figure 1a shows the excimer-like emission of **LL** upon UV irradiation.

In order to probe the induction of molecular chirality on achiral NDI chromophores, circular dichroism (CD) spectroscopic measurements were performed. The CD spectrum of **LL** shows negative excitonic Cotton effects between 300–400 nm, corresponding to the π–π* transitions of NDI chromophore (Figure 1b). Thus, L-phenylalanyl-L-phenylalanine methylester based peptide auxiliaries transcript their stereochemical information to achiral NDI chromophore. The negative Cotton effect indicates M-type supramolecular helical assembly for **LL**. On the other hand, **DD** exhibits positive Cotton effect suggesting P-type helicity (Figure 1b). Surprisingly, in aqueous DMSO (water/DMSO, 85:15) both **LL** and **DD** undergo a bathochromic shift with an enhanced Cotton effect. The observed bathochromic shift in CD was attributed to the π–π stacking as revealed in absorption studies. Previous reports have shown that the amplitude of CD signal depends on molar extinction coefficient, length of the helical polymer, angle and the intermolecular distance between the chromophores.[15] Therefore, the enhanced CD

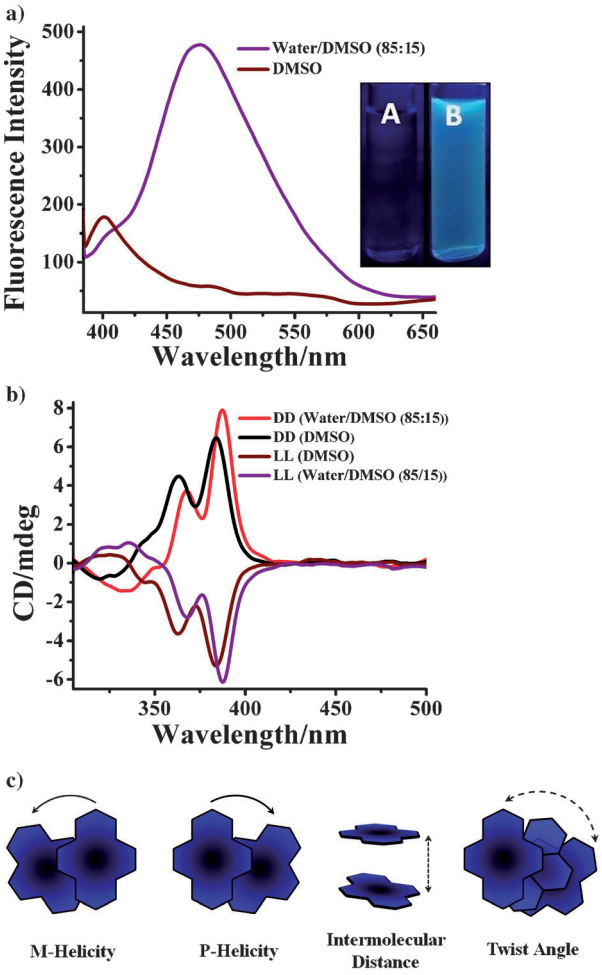

Figure 1. a) Fluorescence emission spectra of **LL**. Inset: photographs of **LL** in DMSO (A) and in water/DMSO (85:15) under UV light (B). b) CD spectra of NDI–peptide conjugates. c) Schematic representation of the transition of the angles and distance between the *z* polarized transition moments of stacked NDI chromophores.

signal in aqueous DMSO can arguably be attributed, predominantly due to modifications in the angle and intermolecular distance between the NDI chromophores by hydrophobic effect.

We further investigated sergeants-and-soldiers effect in the case of homochiral **LL** and **DD**. In a conventional sergeants-and-soldiers experiment the chiral **LL** was mixed with achiral **AA** in different proportions by keeping the overall concentration (500 μM) constant. In order to induce self-organization, the mixture of **LL** and **AA** in DMSO was sonicated for 15 min (for homogeneity) and was followed by the addition of deionized water (44%) prior to recording the CD spectra (see the Supporting Information). The plot of fraction chiral with net helicity reveals a complex chiral behavior (Figure 2a). For a clear visualization of chiral enhancement, we performed another experiment in which an increasing amount of achiral **AA** (0, 100, 200 and 300 μM) was added to a fixed concentration of chiral **LL** or **DD** (100 μM). The obtained CD spectra after sonication and ad-

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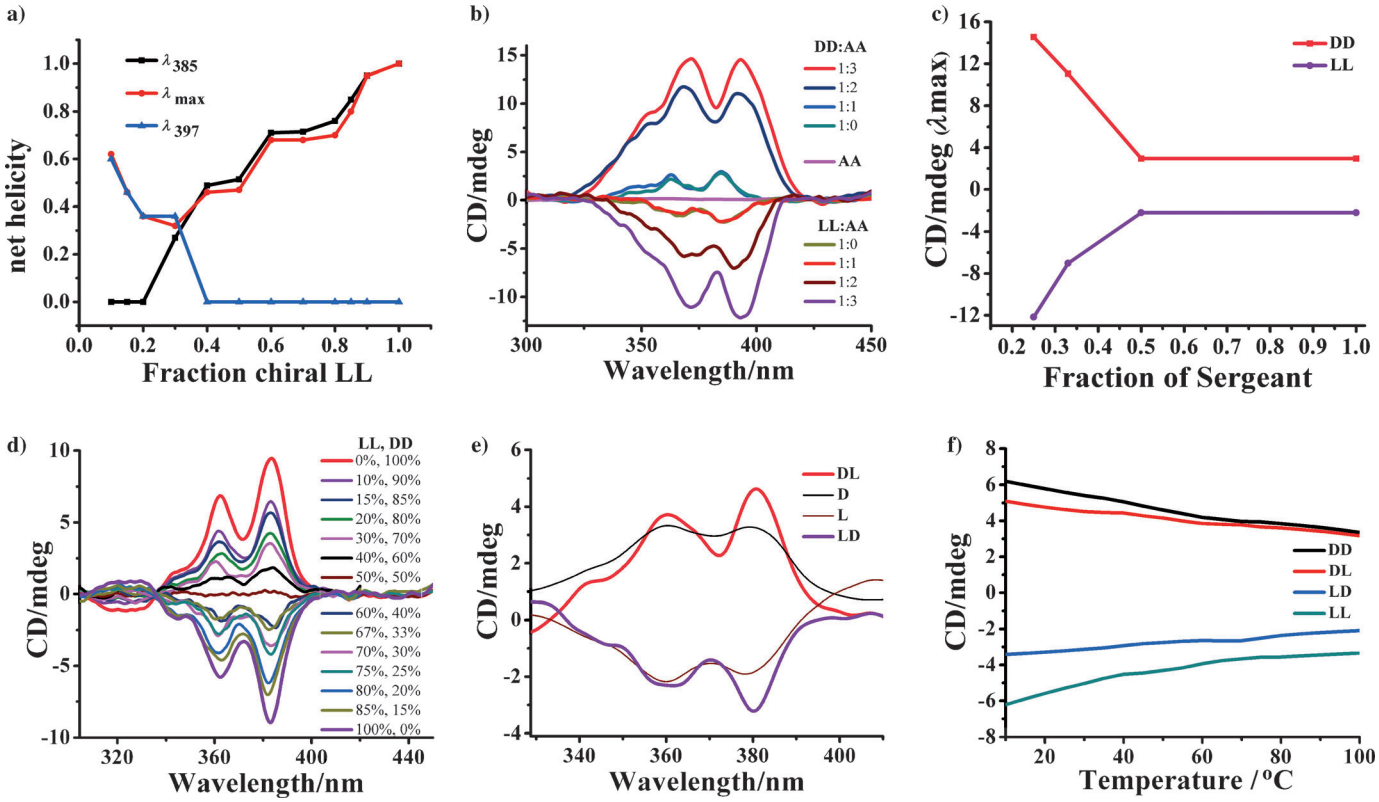

Figure 2. CD spectroscopy. a) The plot (line+symbol) of fraction chiral with net helicity in a conventional sergeants-and-soldiers experiment expressed as absorptions at 385, 397 nm and absorption maxima. The chiral **LL** was mixed with achiral **AA** in different proportions by keeping the overall concentration constant (500 μM). The mixture was sonicated for 15 min (for homogeneity) followed by the addition of deionized water (44%, water/DMSO 44:56) prior to CD measurements. b) Achiral **AA** (0, 100, 200 and 300 μM) was added to a fixed concentration of chiral **LL** or **DD** (100 μM) in DMSO followed by the addition of deionized water (44%). c) The plot (line+symbol) of fraction chiral with net helicity for (b). d) Majority-rule experiment. e) Spectra of **LD**, **DL** and monophenylalanine methylester (L or D isomer) conjugated NDI. f) Summary of temperature-dependant studies of **LL**, **DD**, **LD** and **DL**.

dition of water are shown in Figure 2b. The chiral enhancement clearly shows that the achiral "soldier", **AA**, undergoes chiral supramolecular assembly as guided by the helicity of the "sergeant", **LL** or **DD**. The plot of fraction chiral with net helicity confirms the nonlinear behavior with a remarkable chiral enhancement (Figure 2c). To further elucidate the effect of incorporating homochiral NDI–peptide conjugates of mismatched chirality into a single column, a majority-rules experiment was performed. Subsequently, homochiral NDI–peptide conjugates were mixed in different ratios by keeping the overall concentration constant (500 μM; Figure 2d). The net helicity was determined as a function of enantiomeric excess (*ee*) at 383 nm (see the Supporting Information). The marginal nonlinear dependence of net helicity on the enantiomeric excess suggests minimal chiral enhancement in the majority-rules experiments.

We further investigated the effect of heterochirality of peptide auxiliary on supramolecular chirality. The CD spectrum of **LD** showed negative Cotton effect, indicating M-helicity similar to that of **LL** (Figure 2e). On the contrary, **DL** showed P-helicity similar to that of **DD** (Figure 2e). Conjugates **LD** and **DL** exhibited relatively low induced chirality compared to **LL** and **DD**, respectively. Furthermore, the amplitude of the CD signal observed in **LD** and **DL** were almost similar to monophenylalanine methylester appended NDI (Figure 2e). These results clarified that the supramolecular helicity is determined by the first stereocenter adjacent to NDI core whereas the second regulates chiral enhancement. This ability of the stereocenter to retain the memorized stereochemical information in supramolecular chirogenesis even in the presence of neighbors with opposite chirality is termed as retentive helical memory. The retentive helical memory of the stereocenter is attributed to its direct connection with the achiral NDI chromophore. A similar helical retention behavior has very recently been observed with dendritic dipeptides,[10b] whereas a reverse helical retention was observed in case of benzenetricarboxamides.[9a] The reverse retentive helical memory observed in the latter was attributed to peripheral mesogen-driven aggregation. Unlike covalent polymers, chiral supramolecular assemblies are strongly dependant on temperature, as it determines the strength of intermolecular, noncovalent interactions. Temperature-dependent CD spectra for both homochiral and heterochiral NDI–peptide conjugates were carried out from 10 to 100 °C (see the Supporting Information). The summary of the temperature-dependant CD data is shown in Fig-

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ure 2 f. Even though noncovalent interactions are weak in nature, approximately 55 % of the CD intensity was retained at 100 °C; this strongly emphasizes the strength of the peptide auxiliaries-driven chiral supramolecular assembly.

The homochiral peptide auxiliaries-driven supramolecular helical polymerization led to 1D assembly of NDI chromophores (Figure 3 a–c) in aqueous DMSO (water/DMSO, 85:15). Both peptide conjugates **LL** (Figure 3 a and b) and

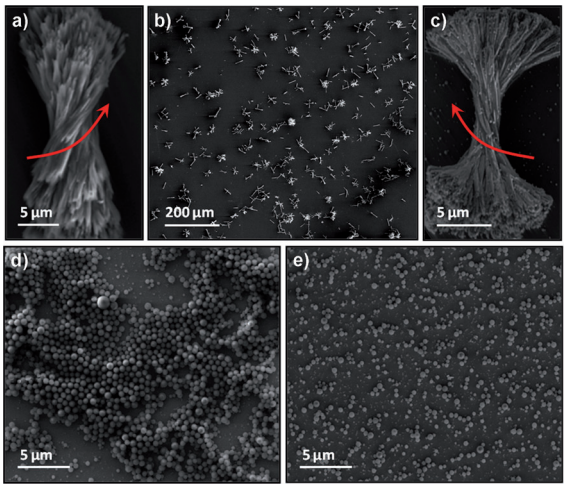

Figure 3. Field emission scanning electron microscopy (FESEM) images of self-assembled structures from water/DMSO (85:15); a), b) **LL**, c) **DD**, d) **LD** and e) **DL**.

DD (Figure 3 c) formed 1D belt-like nanostructures of over 50 μm in length. These 1D belts pile up to form hierarchical structures with helical signatures. Such morphological helicity in a hierarchical structure is rarely observed, to the best of our knowledge.[16] However, **LD** (Figure 3 d) and **DL** (Figure 3 e) formed mesospheres in aqueous DMSO (water/DMSO, 85:15). These morphological studies strongly emphasize that the formation of 1D single-handed supramolecular helical polymers are more favorable in homochiral NDI–peptide conjugates (**LL** and **DD**) than in heterochiral NDI–peptide conjugates (**LD** and **DL**). A model is proposed to explain the supramolecular chirality observed in the solution and self-assembled structures of **LL**, **DD**, **LD** and **DL** (Figure 4 a). Figure 4 b depicts the induction of supramolecular chirality to achiral soldiers, **AA**, by either of the chiral sergeants **LL** or **DD**, as seen in the sergeants-and-soldiers experiment.

In conclusion, we have successfully demonstrated chirality transcription and enhancement by employing the homochiral, heterochiral and achiral peptide conjugates of NDI. An unprecedented enhancement of chirality was observed in sergeants-and-soldiers experiments. Temperature-dependent CD data showed high thermal stability of the peptide auxiliaries-driven chiral supramolecular assembly of NDI conjugates. Moreover, an interesting phenomenon, coined as retentive helical memory, is reported. Remarkably, the homochiral **LL** and **DD** showed 1D molecular organization, unlike

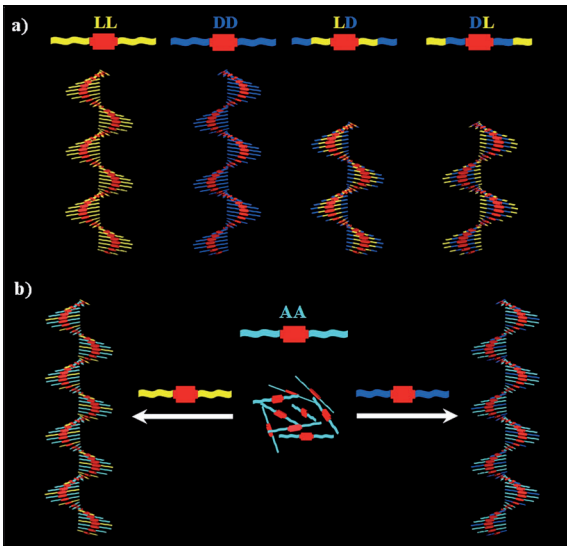

Figure 4. Proposed models. a) Schematic representation of left-handed (**LL** and **LD**) and right-handed (**DD** and **DL**) chiral supramolecular assemblies. b) Schematic illustration of sergeants-and-soldiers effect in which the achiral soldier **AA** follows the chiral sergeant, **LL** or **DD**.

the zero dimensional organization of heterochiral **LD** and **DL**. These observations in principle could support the mechanism of both spontaneous deracemization and enhancement pathways for biological homochirality. This work is significant from the fundamental science perspective as well as envisioned potential applications of NDI–peptide conjugates in chiral optoelectronics, biomaterials and chiral technology.

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Keywords: chirality · enhancement · memory · naphthalenediimide · peptides

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