乞
研究室内掲示

第 91 回・化学コロキウムの御案内

近年、機能性分子の自己集合の分野において顕著な業績を挙げられている Ajayaghosh 先生をお迎えして第 91 回化学コロキウムを開催いたします。

多数のご来場を、お待ちしております。

日時：2006 年 11 月 13 日 15：00～16：00
場所：12 号館（新理工講義棟 208 号室）

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“Molecular Self-assemblies of Linear π-Systems”

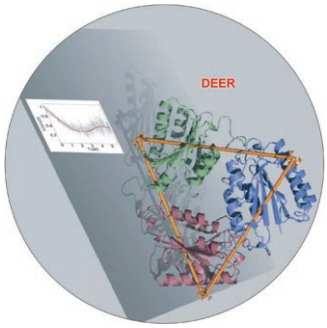
連絡先：化学コース・杉浦健一（内線 3574）

Cover Picture

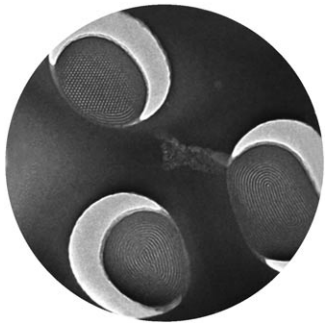
Ayyappanpillai Ajayaghosh,* Reji Varghese, Subi Jacob George, and Chakkooth Vijayakumar

Inversion of helicity and the formation of unusual fused supercoiled left and right helices of gel-forming linear π-conjugated molecules by a "sergeants and soldiers" approach, in which the achiral molecules (soldiers) mistake orders from the chiral molecules (sergeants), is described by A. Ajayaghosh et al. on page 1141 ff. The cover picture shows Janus, the double-faced Greek God, holding a left-handed DNA helix and a right-handed conch which epitomize the marvels of natural creations.

Natural Products Synthesis
Natural polyynes have a broad spectrum of biological activities on account of their structural diversity. R. R. Tykwinski and A. L. K. Shi Shun report on the isolation and synthesis of polyynes in their Review on page 1034 ff.



Protein Structures
In their Communication on page 1058 ff., G. Jeschke and co-workers show how pulsed DEER methods are used to measure an intermolecular distance of 6.15 nm between noncovalently interacting proteins.



Circles or Columns
T. Bein and co-workers describe in their Communication on page 1134 ff. how the structure of mesoporous silica can be controlled by carefully tuning the reaction conditions during its synthesis.

Helical Structures

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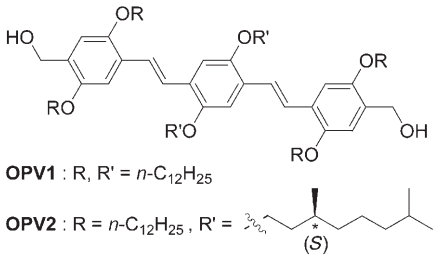
Transcription and Amplification of Molecular Chirality to Oppositely Biased Supramolecular π Helices**

Ayyappanpillai Ajayaghosh, Reji Varghese, Subi Jacob George, and Chakkooth Vijayakumar*

Nature has the amazing ability to create functional architectures with a preferred helicity over a wide range of scales: from nanoscopic DNA to macroscopic seashells. For example, the helical sense of biomacromolecules such as the DNA double helix and the collagen triple helix is determined by the configuration of the chiral centers present in their nucleotide or peptide backbone that bias the long-range overall order to a single handedness in a well-defined self-assembled architecture. The elegance and complexity of natural homochiral architectures has inspired chemists to explore noncovalent interactions, such as H bonding, π stacking, and van der Waals forces, between chiral building blocks to form a variety of aesthetically appealing helical supramolecular assemblies.[1–4] However, the control and prediction of the supramolecular chirality of artificial systems on the nano- to micrometer length scale continues to elude scientists.[5]

The amplification of chirality in polyisocyanates by Green et al. through the "sergeants and soldiers" approach was a clever step toward achieving macromolecular chirality in synthetic polymers.[6] The same principle was later independently applied by the research groups of Meijer and Reinhoudt to induce chirality in dynamic hydrogen-bonded assemblies.[7,8] These observations have prompted us to explore the viability of the "sergeants and soldiers" approach in organogel systems based on oligo(*p*-phenylenevinylene) (OPV).[9] Herein we show spectroscopic and microscopy evidence for the transcription and amplification of molecular chirality to supramolecular helicity through the unprecedented formation of right-handed (*P*) and left-handed (*M*) helices. These oppositely biased structures originate from the same stereogenic centers during the coassembly processes. Most surprisingly, we observed the formation of longitudinally fused *M* and *P* helices, which is a unique phenomenon.

We chose to use an achiral molecule **OPV1**[9a] and a chiral analogue **OPV2** with two remote chiral handles[9c] (Scheme 1). **OPV2** tends to aggregate above a concentration



Scheme 1. Structures of the achiral and chiral molecules under investigation.

of 1.8×10^{-4} M in dodecane and leads to an exciton-coupled bisignate CD signal in the region of the π-π* transition which is characteristic of a left-handed helical assembly. However, it does not show any CD signal below this concentration, thus confirming that it is not possible to transfer chiral information from the stereogenic centers to the chromophore. In contrast, **OPV1** is inherently CD silent, although it forms aggregates and gels in dodecane.[9e] Mixing **OPV2** and **OPV1** together in dodecane (1.67 mol% of **OPV2**) at a total concentration of 7.5×10^{-4} M results in a CD signal with positive and negative Cotton effects, with the intensity of the signal increasing as the composition of **OPV2** increases up to 22 mol% (Figure 1a). The inversion of the CD spectrum with a near mirror image relationship at low compositions of **OPV2** indicates the formation of helices with opposite handedness, which was quite surprising (Figure 1a, inset). Increasing the mol% of **OPV2** further results in a decrease in the intensity of the CD

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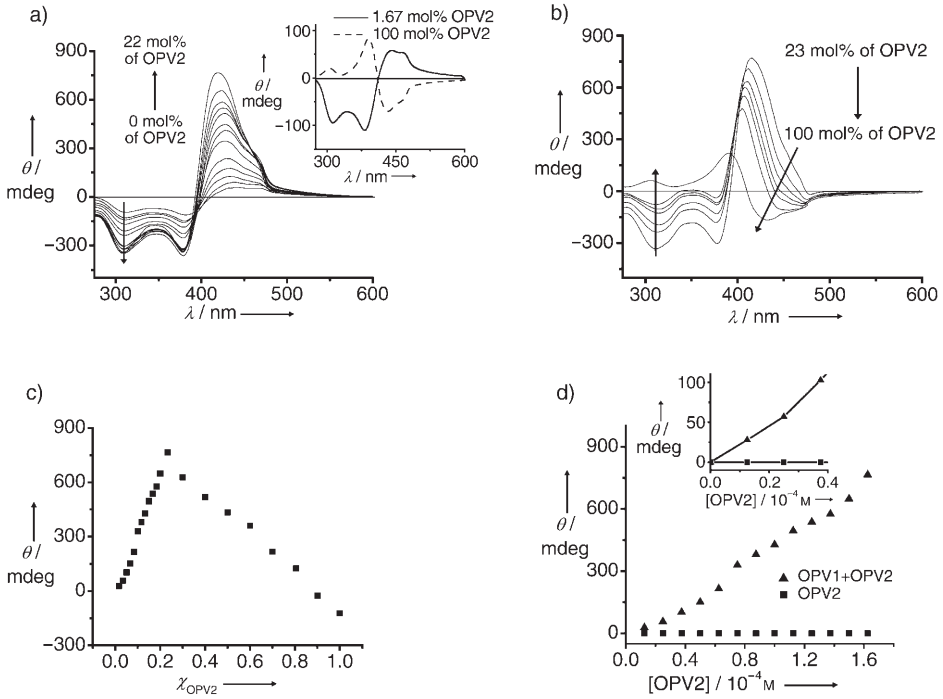

Figure 1. Changes in the CD spectrum during the coassembly of **OPV1**–**OPV2** in dodecane (7.5×10^{-4} M) at different compositions: a) 0–22 mol% of **OPV2**; the inset shows the mirror-image relationship of the CD spectra of **OPV2** and the **OPV1**–**OPV2** coassembly at 1.67 mol% of **OPV2**; b) 23–100 mol% of **OPV2**; c) variation of CD intensity at 420 nm with increasing mole fraction (χ) of **OPV2** at a total concentration of 7.5×10^{-4} M in dodecane; d) plots of CD intensity at 420 nm against the concentrations of **OPV2** in the homoassembly and coassembly; the inset shows the CD intensity variation up to 0.4×10^{-4} M. All measurements were carried out in a 1-mm cuvette at 278 K.

signal. A gradual blue-shift of the positive Cotton effect with concomitant weak growth of a negative signal is observed which tend to merge with the CD spectrum of pure **OPV2** (Figure 1b). This situation is clear from the plot of the CD intensity at 420 nm against the mole fraction of **OPV2** in the coassembly (Figure 1c). It is important to remember that **OPV2** on its own failed to give a CD signal up to a concentration of 1.6×10^{-4} M (Figure 1d). The observed CD spectrum, therefore, is the direct result of the formation of a coassembly and not the intrinsic property of the individual components. CD signals are observed even at very low concentrations (1.25×10^{-5} M, 1.67 mol%) of **OPV2** (Figure 1d, inset) during coassembly. This concentration is nearly 14 times less than that of pure **OPV2** which results in the onset of a CD signal, and reveals a remarkable induction and amplification of chirality as a result of the "sergeants and soldiers" effect during the coassembly process.

A temperature-dependent CD signal and the changes in the UV spectra (not shown) indicate a sharp transition above 45 °C for compositions up to 22 mol% of **OPV2**. However, at least two transitions are observed over a wide range of temperatures with greater than 22 mol% of **OPV2**. The composition-dependent variation of the CD spectra and the plots of the temperature-dependent changes in the CD intensity transition are complementary, and reveal the formation of helical aggregates that differ in stability at higher mole ratios of **OPV2** (>22 mol%). The observations from the CD studies are unequivocally confirmed by AFM analysis of the coassembly.

The tapping mode AFM height image (Figure 2a) of the **OPV2** homoassembly showed left-handed helical tapes, in agreement with the observed CD spectrum. The width of the tapes varies from 78 ± 1 to 176 ± 1 nm and they are several micrometers in length, with an average helical pitch length of 156 ± 1 nm. The thickness of these tapes varied from 9 ± 1 to 20 ± 1 nm. The AFM image of the coassembly of **OPV1** with 9 mol% of **OPV2** showed the presence of *P*-helical tapes along with a few oppositely biased *M*-helical tapes (Figure 2b). The width of the smallest fiber obtained in this case is 106 ± 1 nm and the thickness is 4 ± 1 nm. The number of *M* helices increase as the mol% of **OPV2** in the coassembly is increased. The AFM image of the coassembly of **OPV1** with 60 mol% **OPV2** shows the presence of mainly *M* helices along with a few *P* helices (Figure 2c), which is in agreement with the CD spectral changes.

Surprisingly, in addition to the oppositely biased individual helices, longitudinally fused *M* and *P* helices were also observed (Figure 3). These unusual structures are formed in large numbers at around 20 mol% of **OPV2** (Figure 3a, $c=9\times10^{-5}$ M). This observation supports the initial formation of individual nonhelical stacks of **OPV1**, left-handed stacks of **OPV2**, and a right-handed coassembly of **OPV1** and **OPV2**,

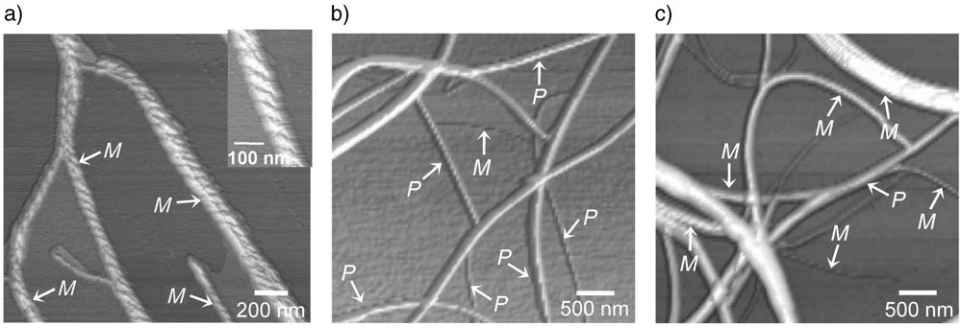

Figure 2. AFM height images of: a) **OPV2** homoassembly, b) coassembly of **OPV1** with 9 mol% of **OPV2**, and c) coassembly of **OPV1** with 60 mol% of **OPV2**. Samples were prepared in dodecane ($c=9\times10^{-5}$ M) and transferred to freshly cleaved mica by drop-casting under ambient conditions.

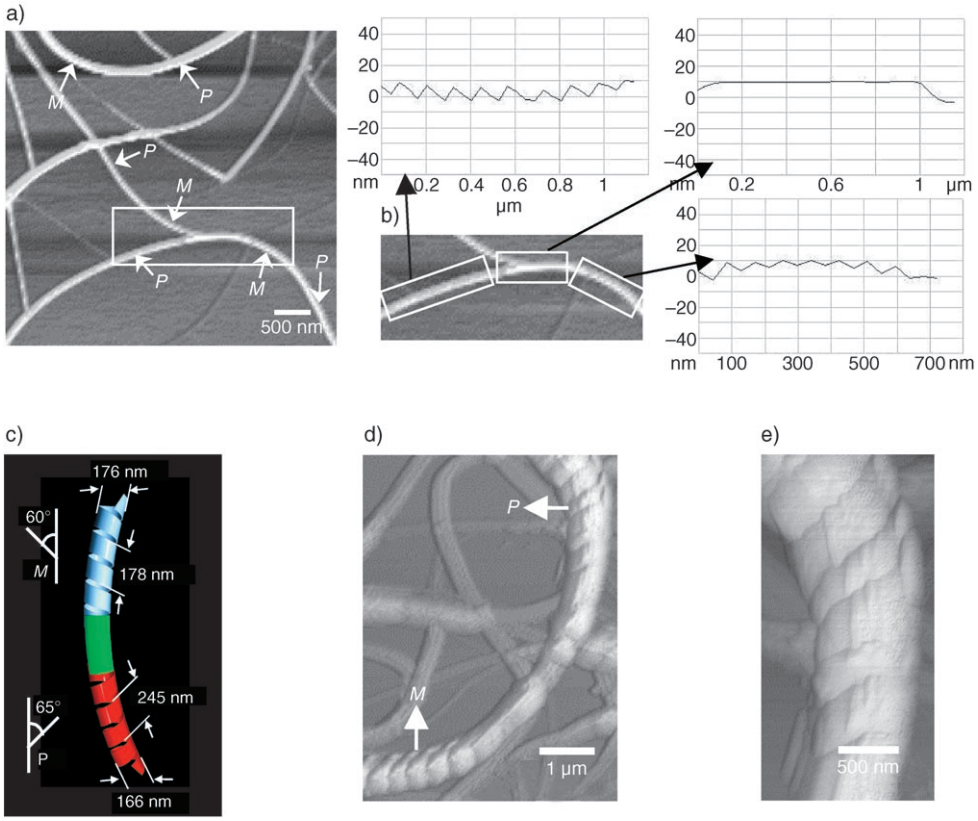

Figure 3. a) AFM image of fused helices at 20 mol% **OPV2**. b) Cross-sectional analysis of *P*-, *M*-, and nonhelical zones. c) A schematic representation of the fused helical tape showing the morphological parameters. d) An enlarged image of the coassembly showing the *M*- and *P*-supercoiled segments. e) A right-handed coiled-coil super structure formed from left-handed coiled tapes.

which at a later stage self-associate, thus resulting in fused superstructures. *M* helices predominate above 20 mol% of **OPV2**. The sign of the CD signal changes dramatically at these compositions (Figure 1b). Detailed section analysis of a fused helix showed a thickness of 13 ± 2 nm and a width of 166–176 nm. Cross-sectional analysis along the length of a fused assembly showed a uniform corrugated height profile for the *P*- and *M*-helical portions. The nonhelicity of the fused zone is clear from the linear profile (Figure 3b). AFM analysis of dried gels of the coassembly formed in dodecane (20 mol% of **OPV2**) showed micrometer-sized fused helices (Figure 3d). The enlarged image of the *P*-helical zone shows right-handed coiled-coil superstructures formed from the winding of left-handed helical tapes in the opposite screw sense (Figure 3e). Such artificial helical assemblies are reminiscent of the collagen triple helix in which three left-handed helices are wound to form a right-handed supercoil, but are rarely found in artificial assemblies.[5a]

Insights from the CD and AFM studies reveal that a helical bias of supramolecular chirality is possible within OPV coassemblies without changing the chiral handle attached to the chromophore. This result is in analogy to some of the previous reports on chirality inversion[10] and stereomutation[11] in polymers and in molecular excitons.[12] In these studies, other than CD spectral evidence, no morphological support of inverted or stereomutated helicity was reported. However, Würthner and coworkers have recently shown inversion of helicity in merocyanine dye aggregates, as evidenced by the changes in the exciton-coupled Cotton effect. However, AFM studies did not show the formation of opposite supramolecular helices.[13] In our case, $M \rightarrow P$ helix inversion and the associated changes could be unambiguously proved by CD and AFM techniques. It is interesting to note that in the "sergeants and soldiers" approach reported previously, the soldiers strictly follow the chiral instructions of the sergeants. In the present case, however, the soldiers mistake orders from the sergeants and behave in an opposite sense, which is a unique phenomenon in coassembled supramolecular architectures.

In conclusion, shown here is the hitherto unknown phenomenon of transcription of molecular chirality by inverted helicity. This process leads to supramolecular π helices with longitudinally fused *M* and *P* helices (originating from common stereogenic centers) during the coassembly of linearly π-conjugated organogelators. Apart from the exotic appeal, helical assemblies of such molecules may have implications in the emerging field of supramolecular electronics.[14]

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