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Modulating helicity through amphiphilicity—tuning supramolecular interactions for the controlled assembly of perylenes†

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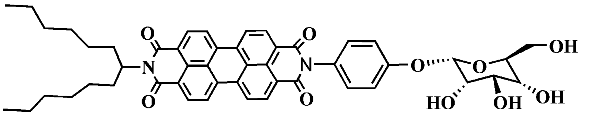
Here we show that it is possible to modulate the supramolecular assembly of designed H-bonding amphiphilic perylene-based materials through simple solvent interactions. These modulated supramolecular interactions have been translated to and observed in macroscopic properties, and provide new pathways to the preparation of switchable interfaces based on designed supramolecular interactions.

Helical self-assembly by noncovalent interactions is a widely observed feature of natural biomacromolecules that directs the formation of highly ordered structures, *e.g.*, the spontaneous self-assembly of DNA into a double helix and assembly of proteins and polysaccharides into α-helices. Inspired by the unique features of fascinating biological superstructures, chemists have been able to design a variety of aesthetically appealing helical supramolecular assemblies by elegantly utilizing cooperative noncovalent and covalent forces, such as hydrogen bonding, π–π stacking, van der Waals and chirality.[1] In this context, the control of the supramolecular organization of π-conjugated systems into helices of nanoscopic dimensions is of fundamental importance,[2–4] as the resulting structures could find application in the emerging area of (supramolecular) electronics and photonics because of their unique electronic and optical properties.

Chiral amphiphiles provide a rich library of chiral building blocks, which make them attractive candidates for application in the design of functional self-assembled materials, even more so if they exhibit biocompatibility.[5] Chiral amphiphilic molecules often assemble in solution to form aggregates with high aspect ratios such as rods, tapes, or tubes, suggesting that chirality is intimately associated with growth and stability of self-assembled fibers of small organic molecules.[6] However, the aggregate morphologies of the amphiphile molecules are often influenced by environmental parameters such as the nature of the solvent, the ratio of the good/poor solvent, or temperature,[7] with slight changes leading to different aggregate morphologies. Understanding and tuning of these factors should therefore lead to pathways for the controlled production of chiral superstructures.



Scheme 1 Chemical structure of the **PTCDI–HAG** amphiphile molecule.

In the present study, a new sugar-based amphiphilic perylene diimide derivative *N*-(1-hexylheptyl)-*N*′-((4-aminophenyl)-α-D-glucopyranoside)–perylene-3,4,9,10-tetracarboxylbisimide (**PTCDI–HAG**, Scheme 1) was synthesized and its aggregate morphologies in different solvents studied (see ESI† for the synthesis and characterization of **PTCDI–HAG**). **PTCDI** was selected as the central building block for self-assembly on the basis of geometry (strong, well-studied π–π interactions),[4] function (optoelectronic activity),[8] and the possibility to produce asymmetric molecular structures.[8,9] The combination here with carbohydrates provides, at the same time, a source of chirality and biocompatibility for functional supramolecular materials.[10] Although the self-assembly of perylene diimide amphiphilic molecules into nanofibers in solution has been extensively studied,[11] limited investigations have been performed on the control of helical morphologies.[12] Therefore, it was expected that the aggregate morphologies of the amphiphilic perylene moieties could be tuned by solvents with different polarities.

To trace the effect of the solvents on the aggregation behavior and elucidate the self-assembly mechanism of the helical nanowires, CD, UV-Vis and fluorescence measurements were conducted to monitor the self-assembly process. Binary solutions with a final **PTCDI–HAG** concentration of 0.1 mg·mL^{-1} were prepared by injecting the selected poor solvents (*n*-octane or water) into good solvent (chloroform or THF) solutions of **PTCDI–HAG**, respectively. After vigorous stirring for 10 minutes, the samples were left to stand overnight at room temperature.

Fig. 1a and b show the CD and UV-Vis spectra of the **PTCDI–HAG** aggregates at various chloroform/*n*-octane volume ratios, respectively. When *n*-octane was gradually added into the chloroform solution, a well-resolved bisignate

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† Electronic supplementary information (ESI) available: Experiments for the synthesis and characterization of **PTCDI–HAG** and additional XRD, TEM and PL data. See DOI: 10.1039/c1cc10220f

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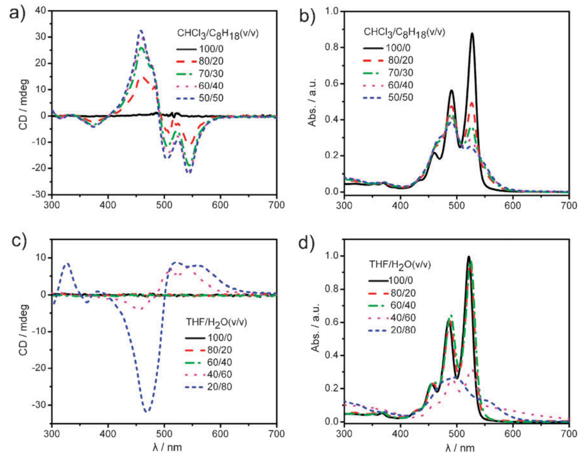

Fig. 1 (a, c) CD and (b, d) UV-Vis spectra of the **PTCDI–HAG** molecules in different volume ratios of $CHCl_3$/n-C_8H_{18} or THF/H_2O.

CD signal (positive Cotton effect at 450 nm, negative at 503 nm and 543 nm) was observed for an 80/20 chloroform/*n*-octane ratio, and became more pronounced until a 50/50 ratio was reached. The bisignate CD intensities changed continuously until reaching a 50/50 ratio, with more *n*-octane causing rapid precipitation. The bisignate positive/negative Cotton effect with increasing wavelength indicates that the **PTCDI–HAG** molecules adopt a left-handed or counter-clockwise helical arrangement during aggregation.[13] The shape of the UV-Vis spectra in chloroform/*n*-octane also change with an increase in the *n*-octane ratio. The isosbestic point at 540 nm suggests that the monomeric amphiphile molecules self-assemble into aggregates,[12] which was further supported by fluorescence spectra (Fig. S2 in ESI†). The results of the CD and UV-Vis analysis show clearly that the **PTCDI–HAG** molecules, while optically inactive in good solvents, formed optically active left-handed helical aggregates in a mixed chloroform/*n*-octane solvent system.

However, when dissolved in a tetrahydrofuran/water (THF/H_2O) solution, **PTCDI–HAG** aggregation exhibited exactly the opposite behaviour in terms of chirality, and produced mirror image Cotton effects, as shown in Fig. 1c and d. No optical activity was observed in pure THF, with a CD signal appearing with the addition of water as a poor solvent. When a THF/H_2O volume ratio of 40/60 was reached, well-resolved bisignate CD signals were observed (negative Cotton effect at 470 nm, positive at 520 nm and 560 nm). This indicated that the **PTCDI–HAG** molecules adopted a right-handed helical arrangement.[13] The CD spectra of the **PTCDI–HAG** molecules in solution were also consistent with the TEM observations, as will be discussed below.

Samples for TEM investigations were prepared by dropping 1 μL of the aged solution onto carbon-film-covered copper grids, followed by evaporation of the solvent in air at room temperature. Fig. 2a and b present the typical TEM images of **PTCDI–HAG** obtained from the two binary solvent mixtures at volume ratios of 80/20, respectively. Nanofibers were formed in both mixtures, and at 80/20 THF/H_2O a left-handed helical morphology was observed. Since almost no aggregation of **PTCDI–HAG** was observed by CD and UV-Vis in these solutions, these nanofibers were formed by a dynamic controlled process during solvent evaporation. The sample obtained from the 50/50 chloroform/*n*-octane binary solution consists of a high concentration of left-handed nanowires with an average diameter of *ca.* 40 nm and several micrometres in length. However, the nanostructures obtained from a 50/50 THF/H_2O solution exhibited right-handed super-helical morphologies with an average diameter of approximately 100 nm (Fig. 2c and d and enlarged images in Fig. S3 in ESI†). Closer investigation of these larger fibers indicated they are constructed of bundles of helical nanowires. The obvious difference in handedness of the nanowires indicates that the solvent plays a critical role in determining the packing architecture of the amphiphile molecules. The handednesses of the nanostructures are consistent with that in solution, indicating they are formed by a thermodynamic process.

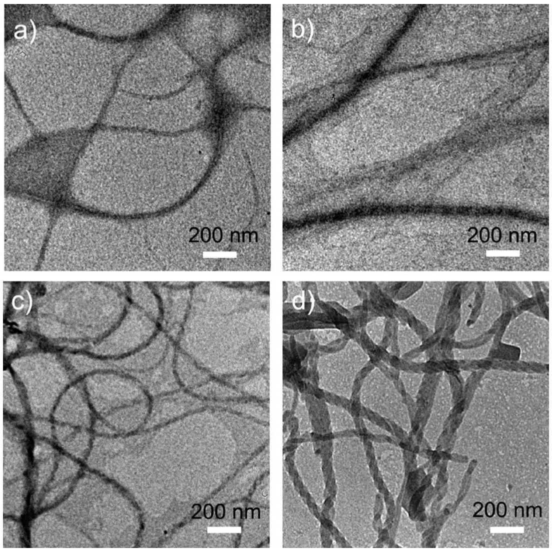

Fig. 2 TEM images of the **PTCDI–HAG** helical nanowires obtained from (a) chloroform/*n*-octane (80/20, v/v), (b) THF/H_2O (80/20, v/v), (c) chloroform/*n*-octane (50/50, v/v) and (d) THF/H_2O (50/50, v/v).

These remarkable differences can be explained by the following arguments: it is well known that both possible helical conformations (*i.e.* M for right handed and P for left handed) necessarily have equal intermolecular interaction energies in molecules in the absence of chiral units, therefore, a racemic mixture of the helical assemblies can be expected. By means of the chiral galactosyl moiety, the M/P chemical equilibrium can be biased and the aggregate may adopt a preferential screw sense helical conformation owing to side chain interactions. However, solvent molecules often influence P–M helical inversion, and solvent–solute interactions profoundly affect the stability of conformationally flexible molecules and their higher-order assemblies.[14,15]

The amphiphilic molecules in our study are unique in that their amphiphile structure consists of a hydrophobic perylene diimide scaffold with a 1-hexylheptyl group and hydrophilic galactosyl residue on either side. When dissolved in chloroform, the galactosyl group, with addition of octane, will aggregate due to its low solubility in the latter solvent. The chiral group will induce the arrangement of the perylene diimide scaffold with a left-handed screw sense. In contrast, the multiple O–H···O hydrogen bonds between the OH groups from the galactosyl

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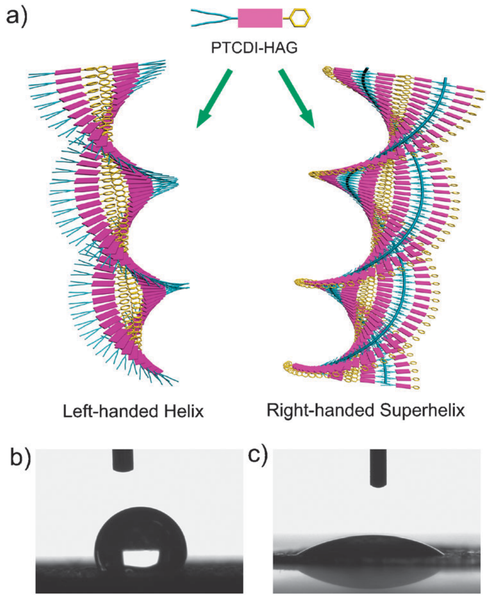

Fig. 3 (a) Schematic representation of the self-assembly process of the **PTCDI–HAG** helical nanowires; (b) contact angles of the film that consists of the helical nanowires obtained from (b) chloroform/*n*-octane (126 ± 5°) and (c) THF/H_2O (35 ± 5°).

residue and water molecules will weaken the interaction between the amphiphile molecules in THF/H_2O. Right-handed helical aggregates were formed until the addition of a large volume of water (*i.e.*, 80%) due to the hydrophobic nature of the 1-hexylheptyl and perylene diimide groups. However, significant differences lie in the arrangement of the molecules in the two oppositely handed nanowire systems. As far as the left-handed nanowires obtained from chloroform/*n*-octane are concerned, the galactosyl group is buried inside the aggregates to form a hydrophilic core that is sheltered from octane. The 1-hexylheptyl chains tend to gather on the outside to stabilize the aggregates in octane. Compared to the molecular arrangement in the chloroform/*n*-octane, the amphiphile molecules have an opposite arrangement in polar THF/H_2O, that is, galactosyl groups are presented to the outside of the amphiphilic aggregates. The hydrogen-bonding interactions between galactosyl groups induce further aggregation of the nanofibers, consequently leading to the formation of a super-helical structure. Solvent molecules can therefore modulate the supramolecular arrangement of the perylene amphiphiles in the nanowires, as shown in the schematic representation in Fig. 3a. XRD investigations showed a lamellar structure for the nanofibers obtained from THF/H_2O. The fibers from chloroform/octane however did not show any pronounced internal structure (Fig. S1 in ESI†).

To further validate our arguments, the contact angles of films consisting of the helical nanowires were examined. The contact angle of the helical nanowires from chloroform/*n*-octane is 126 ± 5° (Fig. 3b), clearly indicating its hydrophobic nature. On the other hand, the contact angle of nanowires prepared from THF/H_2O was 35 ± 5° (Fig. 3c), indicating its hydrophilic nature. These results further confirm the supramolecular arrangement as suggested in Fig. 3a, and provide new pathways to the preparation of switchable interfaces based on designed supramolecular interactions.

In conclusion, we have shown that it is possible to modulate the supramolecular assembly of H-bonding amphiphilic perylene-based materials through simple solvent interactions. These modulated supramolecular interactions have been translated to and observed in macroscopic properties, and provide new pathways to the preparation of switchable interfaces based on designed supramolecular interactions.

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