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Modulating supramolecular helicity and electrical conductivity of perylene dyes through an achiral alkyl chain[†]

Yongwei Huang,*^a Junchao Wang^{ab} and Zhixiang Wei*^b

Here we have shown that it is possible to modulate hydrophobic and hydrophilic interactions to further adjust the supramolecular helicity by changing the length of an alkyl chain. These modulated supramolecular interactions have been translated to and observed in electrical conductivity, and provide a new pathway to construct a high-performance nanodevice.

The helix is a basic structural motif in natural biomacromolecules. Such distinct helical structures of biomacromolecules motivated chemists to construct various types of artificial helical supramolecular nanostructures from small molecules with controlled helicity that mimic the structure and function of biological helices.¹ Many studies on helical aggregations have unveiled various fascinating phenomena, among them, a reversible helix inversion between right-handed and left-handed has been discovered to be one of the most interesting and unique features of dynamic helical aggregation.² Generally for synthetic organic molecules, an external stimulus causes reversible helix inversion.² However, chiroptical inversion is a particularly intriguing phenomenon, and the relationship between the higher order structure and the chiroptical characteristics needs to be fully understood.

Alkyl chains are the most widely used solubilizing groups in organic materials.³ On the one hand, alkyl chains can improve the solubility of organic molecules in some organic solvent. On the other hand, especially for π -conjugated organic semiconductors, alkyl chains possess strong hydrophobic interactions in polar solvent that can tune solute–solvent interactions to determine the self-assembled process and aggregation morphology. Hence, it is expected that chiral amphiphiles with various lengths of alkyl chains may adopt right-handed and/or left-handed aggregation mode by the modulation of the hydrophilic and hydrophobic interactions. However, reports concerning the effect of an achiral alkyl chain on the

modulation of aggregate chirality of chiral amphiphiles are scarce,⁴ although it has been well-known that a small modification of the achiral group may cause significant variations in the generation and morphologies of chiral assemblies.⁵

In the present study, we designed a series of sugar-based perylenediimide derivatives (PTCDIs) bearing various achiral alkyl chains (Scheme 1). The aggregation behaviour in THF–H₂O solvent systems and the electrical conductivity of the corresponding aggregates were investigated. The combination here with a hydrophilic carbohydrate residue⁶ and a hydrophobic alkyl chain provides, at the same time, a source of supramolecular chirality and driving forces for the self-assembly of PTCDI molecules. Moreover, Density Functional Theory (DFT) calculations revealed that the length of the alkyl chain is also affected by the rotation angle of a stacked dimer that ultimately leads to a difference in changing electrical conductivity.

To discuss the structural dependence of the aggregate chirality clearly, it is helpful to first consider the solution-state characteristics. The absorption spectra of OBAG, DBAG and HBAG in dilute THF (a good solvent) show three pronounced peaks in the range 450–525 nm (Fig. S1 in ESI†). This is a typical spectrum of individual PTCDI molecules in solution (*i.e.*, in a non-aggregated form), and corresponds to the electronic π - π * transition superimposed with vibrational transitions.⁷ Accordingly, no obvious Cotton effect in circular dichroism (CD) spectra was observed in THF solution (Fig. S1 in ESI†), which fits well with absorption spectra.

However, THF solution of OBAG, DBAG and HBAG containing H_2O (a poor solvent) shows remarkable bisignate CD signals. Fig. 1 shows the CD and UV-vis spectra at various THF/H₂O volume ratios. When H_2O was gradually added into the THF solution,





^a Medical College, Henan University, Kaifeng 475004, China.

E-mail: hywei79@126.com

^b National Center for Nanoscience and Technology, Beijing 100190, China. E-mail: weizx@nanoctr.cn

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Fig. 1 (a, c, e) CD and (b, d, f) UV-vis spectra for OBAG, DBAG and HBAG, respectively, at different volume ratios of THF/H₂O (0.05 mg mL⁻¹).

a well-resolved bisignate CD signal with a positive Cotton effect at 430 nm and negative at 460 nm was observed at a THF/H₂O volume ratio of 40/60 (Fig. 1a). The bisignate positive/negative Cotton effect with increasing wavelength indicates that the OBAG molecules adopt a left-handed helical arrangement during aggregation.⁷ With a further increase of the H₂O content to 80%, OBAG aggregation exhibited the opposite behaviour in terms of chirality, which indicated a right-handed helical arrangement in 20/80 THF/H₂O.⁷ Similar experimental results were also observed in the CD spectra of HBAG in THF-H₂O solutions in spite of a longer length of an alkyl chain substituted at the imide nitrogen (Fig. 1e). In contrast, no chiroptical inversion effect was found for DBAG in THF-H2O solutions, and a bisignate negative/positive Cotton effect suggests that HBAG molecules adopted a right-handed helical arrangement (Fig. 1c). The results were further supported by TEM examination, and nanowires or nanofibers with corresponding helicity are shown in Fig. S2 (ESI⁺). Comparing CD data and molecular structures among these PTCDIs showed that only the length of the alkyl chain changes, which indicates that a unique alkyl chain lengthdependent chiroptical inversion effect was achieved.

A significant difference was also observed in UV-vis spectra. As shown in Fig. 1b, the intensity ratio of the absorption peak at 450 nm to that at 520 nm faintly increased in 40/60 THF/H₂O solution compared to that in THF (Fig. S1 is ESI†), indicating the weak aggregation occurring between OBAG molecules.⁷ But, the intensity ratio was dramatically increased compared to OBAG for DBAG and HBAG in 40/60 THF/H₂O solution (Fig. 1d and f), implying the onset of strong aggregation. Moreover, a new peak was observed at approximately 580 nm for HBAG, suggesting effective π - π stacking in the cofacial PTCDI molecules (Fig. 1f). With a further increase of

the H₂O content to 80 vol%, the absorption peak at 520 nm disappeared and a new shoulder peak at 580 nm was observed for OBAG and DBAG, indicating strong π - π stacking between PTCDI molecules in 20/80 THF/H₂O solution. Strong π - π stacking was also found in X-ray diffraction (XRD) patterns of OBAG, DBAG and HBAG nanowires/fibers obtained from 20/80 THF/H₂O (v/v). As shown in Fig. S3 (ESI†), a diffraction peak was observed for all PTCDI molecules in the wide angle region at $2\theta = \sim 25.4^{\circ}$ with a *d*-spacing of 3.5 Å, which is characteristic of the π - π stacking between π -conjugated molecules.⁸ Extended π - π stacking along the long-axis of the nanowire/fiber has been proven to be effective for mediating charge transfer through π -electron delocalization.⁹ Indeed, a dramatic increase in conductivity was found for OBAG, DBAG and HBAG nanowires/fibers in hydrazine vapour (see the discussion below).

To gain more insight into the origin and mechanism of the helix inversion, it is crucial to examine the effect of alkyl chains on the induction of helical sense. DFT calculations were performed to investigate the thermodynamic process to form such chiral architectures. Due to the steric hindrance of the galactosyl groups and alkyl chains, the adjacent molecules should rotate a certain angle to reach the conformation with the minimal system energy. With most energetically preferable molecules (Fig. S4 in ESI[†]) coaxially arranged, the energy dependence on the rotation angle was calculated and is presented in Fig. 2.

As shown in Fig. 2, the binding energy of the system changes from negative to positive with the rotation angle changing from 0° to 90° and from 0° to -90° . The positive binding energy means that the system is unstable, whereas the negative binding energy means that the system is stable. Detailed analysis reveals that the molecule of OBAG, DBAG and HBAG with the right-handed rotation angle of 32°, 28° and 30° , respectively, has a lower binding energy (partially enlarged image in Fig. S5 in ESI⁺), indicating that such a structure is most stable. It is interesting to note that a rotation angle of -32° , -30° and -31° (left-handed) for OBAG, DBAG and HBAG, respectively, was also revealed, and the system has a less stable local minimum with a positive binding energy. This result suggests that although it is not the most thermodynamically preferred state, it still can occur kinetically. Compared to DBAG, the energy difference in the right-handed and left-handed state is smaller for OBAG and HBAG, implying that left-handed aggregation was more easily achieved.



Fig. 2 Simulations to investigate the energy dependence on rotation of the OBAG, DBAG and HBAG in a stacked dimer. The upper molecule rotates with the rotation angle changing from 0° to 90° (right-handed) and from 0° to -90° (left-handed). The binding energy equals the total energy of the dimer minus the energy of the two separate molecules.



Fig. 3 Current modulation (///_0)-time (t) curves of OBAG, DBAG and HBAG devices obtained from THF/H_2O (20/80, V/V) in hydrazine vapor.

This provides theoretical support for our experimental observation of the left-handed aggregation for OBAG and HBAG in 40/60 THF/ H₂O solution. Keeping the presented data in mind, we can now proceed to detailed analyses of remarkable differences in CD spectra by the following arguments. As shown in Scheme 1, the amphiphiles in our study are unique in that their amphiphilic structure consists of a perylene scaffold with a hydrophobic alkyl chain and a hydrophilic galactosyl residue on either side. When dissolved in THF, the alkyl chain, with addition of H2O, will aggregate due to its hydrophobic effect in the latter solvent. In contrast, the hydrophilic interactions that root in multiple O-H···O hydrogen bonds between the OH groups from the galactosyl residue and water molecules will be enhanced. Concerning the OBAG in 40/60 THF/H₂O solution, the hydrophilic interaction will be dominant due to a shorter alkyl chain that cannot lead a strong hydrophobic effect. This is supported by the UV-vis spectrum and it suggests that weak aggregation was achieved in 40/60 THF/H₂O solution. In contrast, the hydrophobic effect may direct the aggregation of HBAG in 40/60 THF/H₂O solution because of the longer alkyl chain that was also consistent with the corresponding UV-vis spectrum. Hence, it is inferred that a single dominated driving force, namely the hydrophilic or hydrophobic effect, may induce the kinetically controlled aggregation process of OBAG and HBAG in 40/60 THF/H2O solution and ultimately lead to left-handed helical stacking. While the equilibrium between hydrophobic and hydrophilic effects leads to a thermodynamically controlled aggregation process of DBAG with the right-handed helix in 40/60 THF/H2O solution. With the increasing H₂O content to 80 vol%, both hydrophobic and hydrophilic effects can dramatically enhance, a new equilibrium is achieved and a energetically preferred right-handed helical arrangement is obtained for OBAG, DBAG and HBAG in 20/80 THF/H₂O solution.

The conductivity of nanowire or nanofiber bundles formed at 40/60 and 20/80 THF/H₂O was also examined in hydrazine vapor using a two-probe method in order to reveal the structure– function relationship. As shown in Fig. 3, compared to the conductivity in vacuum, an approximately 5-orders-of-magnitude increase in current is observed for DBAG nanofiber bundles formed in 20/80 THF/H₂O solution upon exposure to hydrazine vapor (10 ppm), which is 1.5 and 3 times higher than that of HBAG wire and OBAG nanofiber bundles. Similar changes in current were also found for OBAG, DBAG and HBAG nanostructures formed in 40/60 THF/H₂O solution (Fig. S6 in ESI†). The large electrical modulation thus observed is largely due to the electron donation from

hydrazine through electron donor-acceptor complexation with PTCDIs, followed by efficient long range electron transport through the π - π delocalization (see Fig. S7 in ESI[†]).¹⁰ It is should be noted that π - π overlap of vicinal PTCDI molecules also affects the electron transport mobility, and evidence suggests that charge carrier mobility is usually maximized along the direction of cofacial π - π stacking of PTCDI molecules (i.e., the rotation angle between vicinal perylene molecules is equal to zero).¹¹ As revealed by DFT calculations, DBAG molecules possess a smaller rotation angle between vicinal perylene molecules compared to OBAG and HBAG. The smaller rotation angle for DBAG (28° or -30°) implies that a larger π - π overlap of the vicinal perylene core is expected to enhance electron mobility and lead to the most dramatic increase in conductivity (about 5 orders). While a larger rotation angle for OBAG (32° or -32°) and HBAG (30° or -31°) will reduce the π - π overlap of the vicinal perylene core so as to weaken electron transport mobility and ultimately lead to approximately 3 and 1.5 times smaller mobility for OBAG and HBAG with increasing magnitude of conductivity than that of DBAG.

In summary, we have shown that it is possible to modulate hydrophobic and hydrophilic interactions to further adjust the supramolecular helicity by simply changing the length of the alkyl chain. These modulated supramolecular interactions have been translated to and observed in electrical conductivity, and provide new pathways to construct a high-performance nanodevice based on designed supramolecular interactions.

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