

Original article

Construction of supramolecular nanofibers through electrostatic interaction between perylene and cholesterol derivatives

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ABSTRACT

The self-assembly of cationic perylene diimide (PDI) and anionic cholesterol derivatives (CHOL) was conveniently achieved by the electrostatic attraction and π - π stacking interactions, exhibiting the well-defined supramolecular nanofibers ranging from hundreds of nanometers to micron dimension.

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1. Introduction

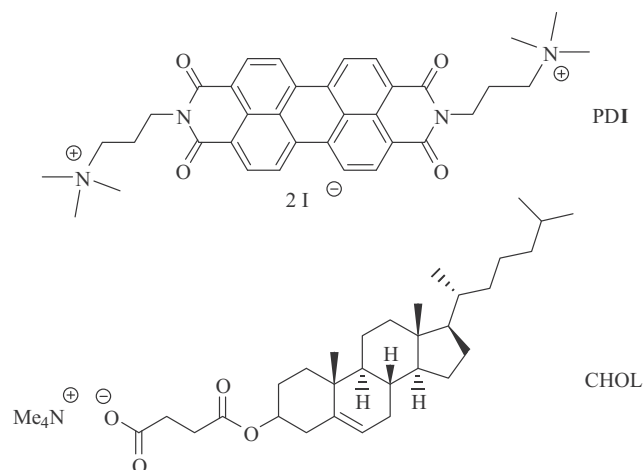
In recent years, supramolecular, one-dimensional (1D) nanostructures composed of electronically active constituents have stimulated increasing interest in the emerging fields of nanotechnology, mainly due to their promising applications in the construction of electronic and optoelectronic nanodevices [1]. In this regard, fibrous self-assembly by non-covalent interactions is a frequently observed feature in our biological and physiological events, and consequently, considerable effort has been devoted to mimicking the highly ordered fibrous morphologies with supramolecular characterization [2]. Particularly, in the numerous components that are available for the formation of 1D nanoarchitectures, perylene bisimide and its analogs are intensively studied as a photofunctional dye and n-type organic semiconductor with unique photo- and electroactive properties. A variety of multichromophoric assemblies based on perylene bisimide building blocks have been widely fabricated through covalent or non-covalent strategies [3]. For instance, Liu *et al.* have reported new types of fluorescence sensory material using perylene as the probing signal and cyclodextrin cavity

as the receptor unit, implementing an effective, reversible and selective solid state sensor for volatile aniline vapor [4]. Li and his co-workers have utilized *p*-phenylenevinylene-linked perylene diimides to construct the solvent-dependent molecular aggregates of nanospheres and vesicles, in which the fluorescence intensities were greatly enhanced upon laser irradiation [5].

Moreover, among all the non-covalent driving forces, the primary electrostatic attraction is considered as a reliable and flexible method to construct various supramolecular materials, by which some secondary interactions, such as hydrophobic, π - π stacking, van der Waals, and hydrogen bonding interactions, could be further stimulated to propagate the eventual formation of superstructures [6]. Therefore, inspired by this fascinating principle, we present herein the design and construction of 1D nanowires through the spontaneous self-assembly of cationic perylene derivative (Scheme 1, defined as PDI) and anionic cholesterol derivative (Scheme 1, defined as CHOL), taking both the amphiphilicity of cholesterol side chain and the highly affinitive π - π stacking of perylene cores into account. The spectroscopic and microscopic results jointly confirm that the formation of interior structures in PDI-CHOL assembly is driven by the strong π - π interaction between two adjacent rigid PDI units, whereas the amphiphilic moieties of CHOL are connected through the electrostatic attraction with PDI and interlace with each other via the side chains.

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Scheme 1. Structural illustration of cationic perylene diimide (PDI) and anionic cholesterol (CHOL) derivatives.

2. Experimental

All chemicals were commercially available unless noted otherwise. NMR data were recorded on Bruker AV400 spectrometer. UV/vis spectra were recorded in a quartz cell (light path 10 mm) on a Shimadzu UV-3600 spectrophotometer equipped with a PTC-348WI temperature controller. Fluorescence spectra and quantum yields were recorded in a conventional quartz cell (10 mm × 10 mm × 45 mm) at 25 °C on a spectrometer employing the single photon counting technique. SEM images were recorded on a HITACHI S-3500N scanning electron microscope.

AFM Measurements: A 1.0×10^{-5} mol/L of sample solution was dropped onto newly clipped mica and then dried in air. The samples were performed by using a Multimode Nanoscope-IIIa scanning probe microscope (Digital Instruments Co., Ltd.) in the tapping mode in air at room temperature.

3. Results and discussion

3.1. UV/vis and fluorescence spectroscopy

The molecular structures of PDI and CHOL are shown in Scheme 1. PDI was synthesized by the condensation reaction with perylene tetracarboxylic bisanhydride [7]. Then, CHOL was modified with carboxylic groups to endow the cholesterol backbone with

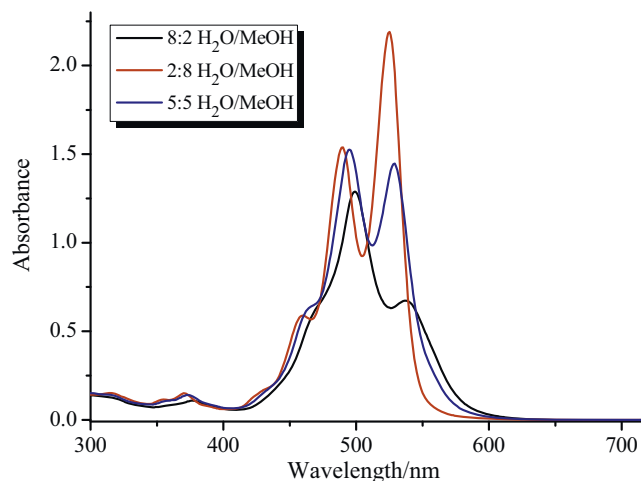


Fig. 1. UV/vis spectra of PDI (5.0×10^{-5} mol/L) in different ratios of solvents at 25 °C.

amphiphilicity [8]. It is expected that the combination of cationic PDI with anionic CHOL could confer suprastructural characteristics upon the mutual electrostatic attraction. Moreover, due to the broad optical transparency of the CHOL skeleton in the UV/vis region, the photophysical properties of the PDI-CHOL complex can be conveniently monitored by the spectral changes of PDI, as described below.

It is well established that the π - π stacking of PDI is critically solvent-dependent [9]. Therefore, we primarily studied the aggregation behaviors of PDI in MeOH/H₂O mixed solvents of various compositions. As shown in Fig. 1, the UV/vis spectra of PDI in organic solvents show three clear absorption bands in the range from 400 nm to 600 nm with the maximal absorptivity of the first band around 525 nm, which could be assigned to the typical non-aggregated or low-aggregated state of PDI²⁺. Comparatively, the spectrum of PDI dramatically decreases as the proportion of water increases, with the maximal absorptivity of the second band around 500 nm, indicative of the pronounced π - π stacking aggregation of PDI moieties in aqueous media. Therefore, considering the aggregation ability of PDI and the water solubility of CHOL, a 1:1 ratio of MeOH/H₂O was established as the optimal solvent system for the following studies of the photophysical behavior of the PDI-CHOL complex.

As illustrated in Fig. 2, the apparent absorption of PDI at 528 nm and 493 nm decreased upon addition of CHOL, but with

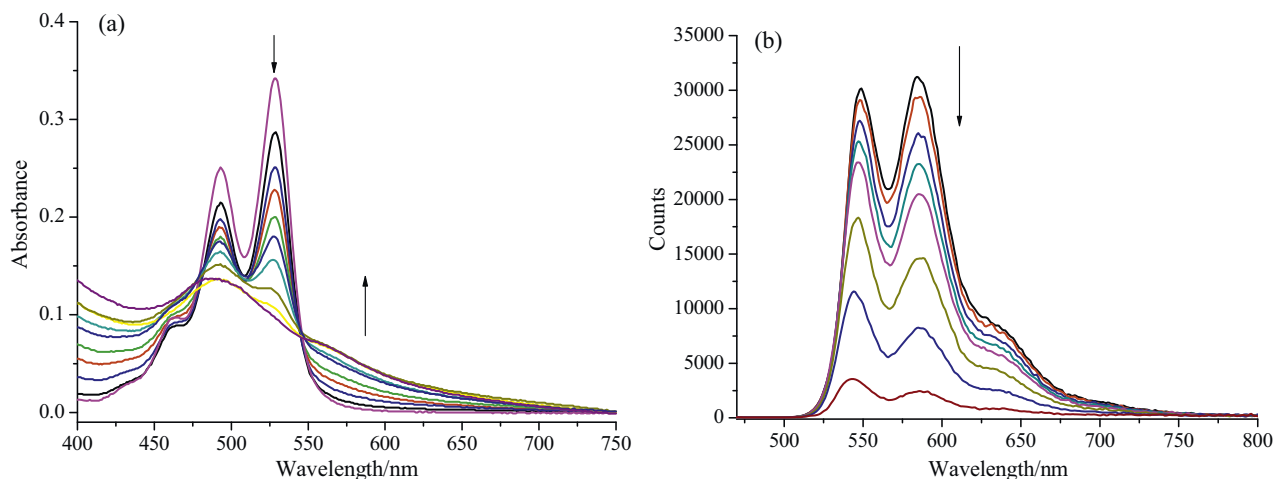


Fig. 2. UV/vis spectral (a) and fluorescence spectral (b) changes of PDI upon addition of CHOL from 0 to 1×10^{-4} mol/L in 1:1 MeOH/H₂O ([PDI] = 1×10^{-5} mol/L) at 25 °C.

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