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Synthesis and Controllable Self-Assembly of a Novel Coronene Bisimide Amphiphile

K. Venkata Rao and Subi J. George*

Supramolecular Chemistry Laboratory, New Chemistry Unit, Jawaharlal Nehru Centre for Advanced Scientific Research (JNCASR), Bangalore-560064, India

george@jncasr.ac.in

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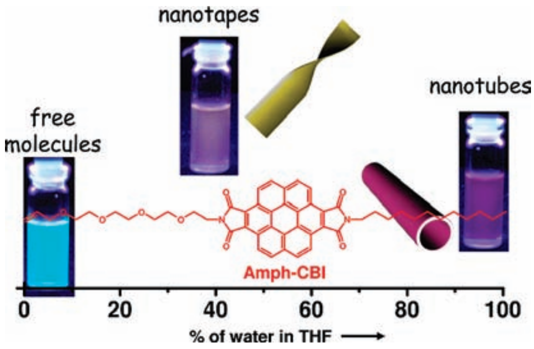
ABSTRACT



The synthesis of an amphiphilic coronene bisimide (Amph-CBI) and its self-assembly in THF/water through $\pi-\pi$ stacking and solvophobic interactions are reported. Spectroscopic and microscopic studies revealed a bilayer like self-assembly of the coronene amphiphile to different kinds of one-dimensional nanostructures, such as nanotubes and nanotapes, which can be controlled by solvent composition.

Ever since the advent of organic semiconductors in optoelectronic devices, the effect of structure and organization of the functional π-conjugated components on the performance of these devices has received continuous attention.[1] In this context, several attempts have been made in recent years to synthesize new π-conjugated systems and to control their self-assembly by utilizing various noncovalent interactions such as H-bonding, $\pi-\pi$ stacking and solvophobic interactions.[2] Although several efforts have been made to self-assemble electron-rich aromatic cores to generate *p*-type semiconducting supramolecular stacks,[3−8] only a limited number of electron-acceptor molecules, such as perylene bisimides[9] and fullerenes,[10] are exploited for the design of assemblies with *n*-type mobility.[11] Therefore, the synthesis and organization of novel *n*-type organic semiconductor materials is crucial for the development of organic and supramolecular electronics.[2a]

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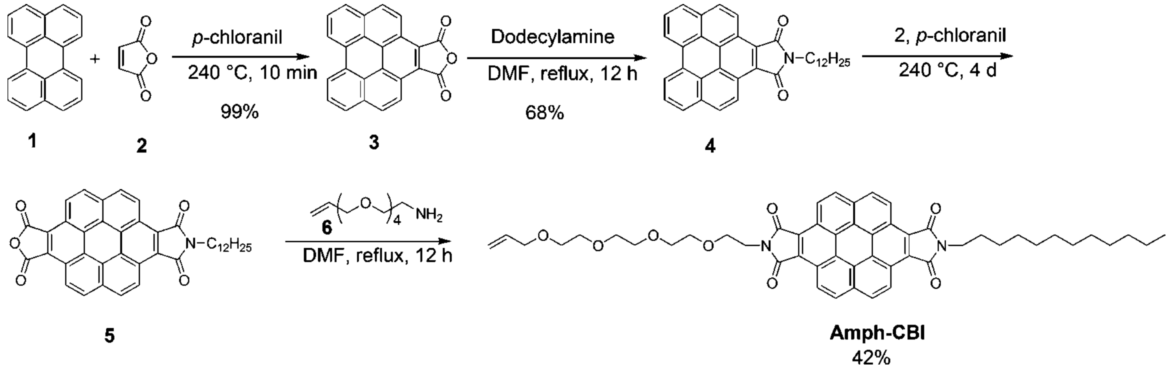
Scheme 1. Synthesis of Coronene Bisimide Amphiphile **Amph-CBI**



Here, we present the synthesis and self-assembly of a novel class of soluble *n*-type coronene bisimide amphiphiles. Diimide, tetraester, and imidoester derivatives of coronene are known to be liquid crystalline with high charge carrier mobilities.[12] Although various *p*-type coronene derivatives such as hexabenzocoronenes (HBCs) have been exploited for the design of supramolecular one-dimensional nanostructures,[5] there is no report pertaining to *n*-type coronene self-assembly. We have rendered the coronene bisimide (CBI) molecule amphiphilic (**Amph-CBI**), with a dodecyl and a tetraethylene glycol chain, in order to promote a surfactant-like self-assembly in water.[13] Furthermore, it has been shown that an amphiphilic π-conjugated design would result in closely $\pi-\pi$ stacked aromatics as a result of stronger hydrophobic interactions in water, leading to less dynamic, stable self-assembled stacks.[14] Strong intermolecular interactions between the extended planar aromatic cores of these derivatives are expected to result in higher charge carrier mobility and hence can emerge as an alternative to the well-studied class of *n*-type perylene bisimide (PBI) molecules for potential electron transport materials. Moreover, here we show that the optical properties and the morphology of the self-assembled coronene diimide nanostructures could be controlled by the solvent composition.

The unsymmetrical amphiphilic coronene was synthesized by a stepwise benzogenic Diels−Alder reaction starting with perylene (**1**) as shown in Scheme 1. We preferred a stepwise reaction compared to statistical reactions reported for the perylene bisimide amphiphilic derivatives because of the difficulty to purify the corresponding coronene dianhydride. An overnight reaction of the monoanhydride derivative (**3**), formed by the Diels−Alder reaction between perylene (**1**) and maleic anhydride (**2**), with dodecylamine in DMF gave the dodecyl monoimide derivative (**4**). A second benzogenic Diels−Alder reaction of **4** with maleic anhydride yielded the monoanhydride derivative **5**, and its subsequent reaction with glycolamine (**6**) gave **Amph-CBI** in 42% yield.[15,16] The product was purified by a combination of column

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(15) See the Supporting Information.

chromatography on silica gel and size-exclusion chromatography (Biobeads, SX-3, chloroform). **Amph-CBI** has been fully characterized by ^{1}H and ^{13}C NMR spectroscopy, matrix-assisted laser desorption/ionization mass spectrometry (MALDI-TOF-MS), and elemental analysis.[15]

The UV/vis absorption as well as fluorescence spectra of molecularly dissolved **Amph-CBI** in THF (1×10^{-5} M) show all of the typical spectral features of substituted coronene bisimides reported in the literature.[12,15] An absorption band with a vibronic fine structure between 425 and 500 nm was observed for **Amph-CBI**, whereas the absorption maxima appear at 339 nm ($\varepsilon = 1.5 \times 10^{5}$ M^{-1} cm^{-1}) and the fluorescence emission maxima appear at 486 nm.

The self-assembly behavior of amphiphilic coronene dye in solution was first probed by optical spectroscopic studies in THF−water solvent mixtures.[17] Absorption and emission spectra of **Amph-CBI** in THF−water mixtures of different compositions showed significant changes, consistent with the presence of aggregates at higher water percentages (Figure 1). For example, addition of an increasing amount of water (20−90%) to a molecularly dissolved solution of **Amph-CBI** in THF ($c = 1 \times 10^{-5}$ M) led to a gradual decrease in the intensities of the absorption bands at 339, 452, and 481 nm with a simultaneous increase in the intensity of the red-shifted bands at 355, 474, and 502 nm. In addition, a gradual decrease in fluorescence intensity at 450−550 nm with the appearance of a new red-shifted, broad, and structureless band with maxima at 590 nm was observed upon the addition of the "bad solvent", water, into the THF solution of **Amph-CBI** ($\lambda_{\text{exc}} = 450$ nm). These features are diagnostic of the $\pi-\pi$ interactions of the CBI chromophores as a result of the self-assembly of the amphiphiles and are similar to the J-aggregation of analogous perylene bisimide dyes.[9] Self-assembly induced changes in fluorescence could also be monitored by the naked eye, which showed different emissions ranging from the green emission of molecularly dissolved chromophores in 100% THF to the orange-red emission of the aggregates in solvent mixtures containing 90% water (inset, Figure 1). UV/vis spectra of **Amph-CBI** at intermediate THF−water compositions (30−70%) showed significant scattering characteristic of large aggregates which gradually disappeared at higher water percentages (80−98%), indicating the presence of two-different self-assembled structures (vide infra). The occurrence of different aggregates was further supported by a two-stage transition in the composition-dependent absorption changes.[15]

Dynamic light scattering (DLS) further proved the self-assembly of **Amph-CBI** in THF−water solvent mixtures.[15] In 50% THF−water mixtures, large aggregate species with an average diameter of 7 μm were obtained, consistent with the scattering observed in the absorption spectra. However, the increase in water composition resulted in significant decrease in the size of the aggregate, thus showing an average diameter of 75 nm in 97% of water.[15] Since the increase of water composition is generally expected to result in more efficient and higher-order self-assembly, and therefore an increase in the aggregate size, the unexpected decrease in the DLS dimensions at higher water percentages could be attributed to a completely different self-assembly (vide infra).

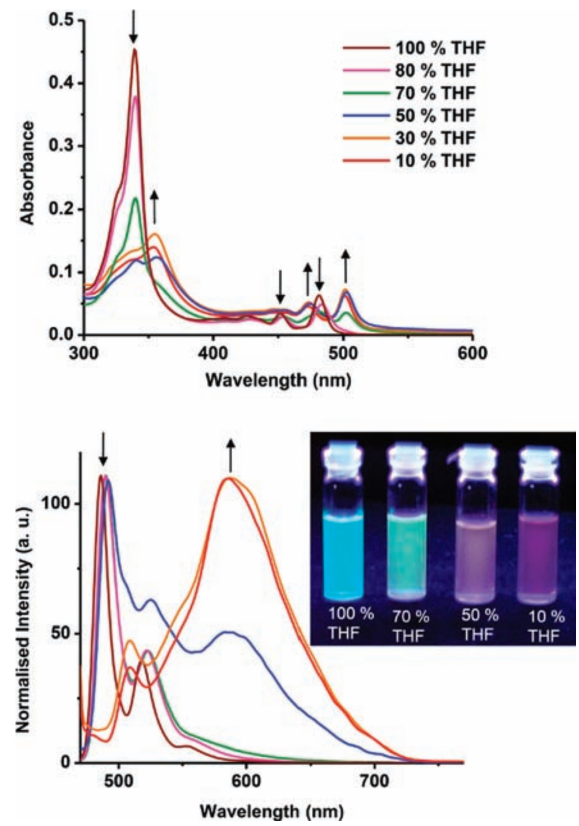

Figure 1. Changes in (top) absorption and (bottom) emission spectra of **Amph-CBI** ($c = 1 \times 10^{-5}$ M, $\lambda_{\text{exc}} = 450$ nm) in THF−water mixtures of different compositions. The inset shows the photograph of **Amph-CBI** in THF−water mixtures under UV-light irradiation.

To get insight into the morphology of the self-assembled **Amph-CBI**, detailed microscopic studies have been preformed. Remarkably, FE-SEM studies of the **Amph-CBI** from a 50% THF−water solvent mixture showed long twisted nanotapes of 30−150 nm width and several micrometers length, suggesting a highly directional one-dimensional self-assembly (Figure 2a). The presence of supramolecular nanotapes is further evident from the AFM and TEM studies.[15] The self-assembly can be envisaged to involve the stacking of bilayers of the CBI amphiphile along the $\pi-\pi$ stacking direction of the chromophore, characteristic of surfactant-like molecules.

Detailed AFM investigation of the nanotapes showed a thickness of 30−40 nm, which could be due to the presence of multibilayers along the height of the tapes.[15] The presence of multibilayers is further supported by the TEM analysis of the self-assembled tapes that are negatively stained with uranyl acetate and that showed a clear contrast for different layers with a thickness of 3.5 nm at the twisted edges of the nanotapes (Figure 2b). These dimensions are in good

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(16) Alkene functionality on the ethylene glycol chain would help to perform further chemistry on the surface of self-assembled coronene bisimide nanostructures.

(17) All the self-assembled samples were prepared by the injection of the THF solution of **Amph-CBI** into water.

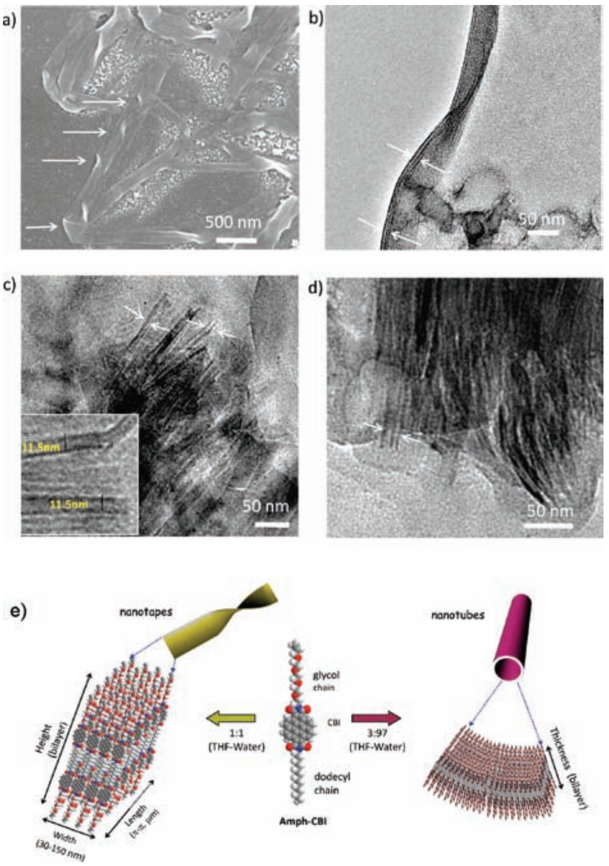

Figure 2. Microscopic images of the **Amph-CBI** self-assembly in THF−water solvent mixtures ($c = 1 \times 10^{-4}$ M): (a) FE-SEM and (b) TEM images of the nanotapes formed in 1:1 THF−water. TEM sample was stained with uranyl acetate (1 wt % in water). Parts (c) and (d) are TEM images of nanotubes formed in 3:97 THF−water measured on carbon-coated copper grids without staining. (e) Schematic representation of the bilayer self-assembly of the coronene amphiphile to nanotapes (left) and nanotubes (right).

correlation with the bilayer packing of the amphiphiles (excluding the hydrophilic part), in which the two hydrophobic chains are fully interdigitated at the interior, implying that the CBI amphiphiles are positioned with its long axis perpendicular to the $\pi-\pi$ direction in the bilayer. Based on these observations, the proposed molecular organization in single-layer supramolecular tapes is schematically shown in Figure 2e, in which the CBI amphiphiles are arranged with their short-axis along the width and long axis (bilayer direction) along the height of the nanotapes. Since optical spectroscopy clearly showed a J-type aggregation of the chromophores, we expect a slipped packing for the adjacent $\pi-\pi$ stacked bilayers along the length of the tapes (Figure 2e), instead of a perfect face-to-face arrangement characteristic of H-aggregates. Interestingly, TEM of the self-assembled **Amph-CBI** in high percentages of water (90−99%) showed the presence of uniform nanotubes having an average diameter of 12 nm (Figure 2c,d). The thickness of the nanotube side walls is approximately 3.8 nm, which also matches with the interdigitated bilayer arrangement of **Amph-CBI** (4 nm), indicating that most of the nanotubes are single-walled (Figure 2e). These nanotubes might have been formed by the rolling of CBI bilayer sheets, as frequently observed in the case of surfactant molecules.[13] It is evident that the morphology of the self-assembled **Amph-CBI** depends on THF−water solvent composition, although the molecular arrangement in both cases favors typical bilayers.

In conclusion, we have reported on the synthesis and self-assembling properties of a new coronene bisimide amphiphilic chromophore, decorated with polar glycol and nonpolar dodecyl chains. The amphiphilic nature of **Amph-CBI** triggered a bilayer self-assembly, supported by the strong π-interactions of the large coronene aromatic surface, in water to result in stable, one-dimensional nanotapes and nanotubes. The interesting feature of the present system is the diverse optical properties and morphology of the self-assembly, which can be fine-controlled by the solvent-composition. The coronene bisimide self-assembled nanostructures could be exploited for efficient energy- and electron-transfer processes, as already shown for perylene bisimide stacks, and are promising functional components for mesoscopic scale opto-electronics.

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Supporting Information Available: Detailed synthetic procedures and characterization, general procedures, and supporting spectroscopic and microscopic images. This material is available free of charge via the Internet at http://pubs.acs.org.

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