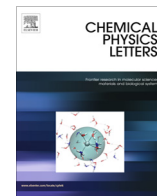




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Research paper

## Emissive nanotubes from templated self-assembly of small molecules

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## ABSTRACT

We report the use of supramolecular interactions to promote the AAO-templated formation of emissive nanotubes based on small organic molecules bearing complementary hydrogen-bonding sites. Nanotubes emitting blue, green, and red light were obtained using appropriate chromophores, whereas a mixture of blue and green chromophores afforded nanotubes emitting white light. Further characterization revealed that the emission from the nanotubes is polarized, indicating a preferential orientation of the chromophores. Aqueous dispersions of nanotubes showed that scrambling of the chromophores is minimal, and that it is possible to prepare samples in which many nanotubes of different colors are present in close proximity.

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## 1. Introduction

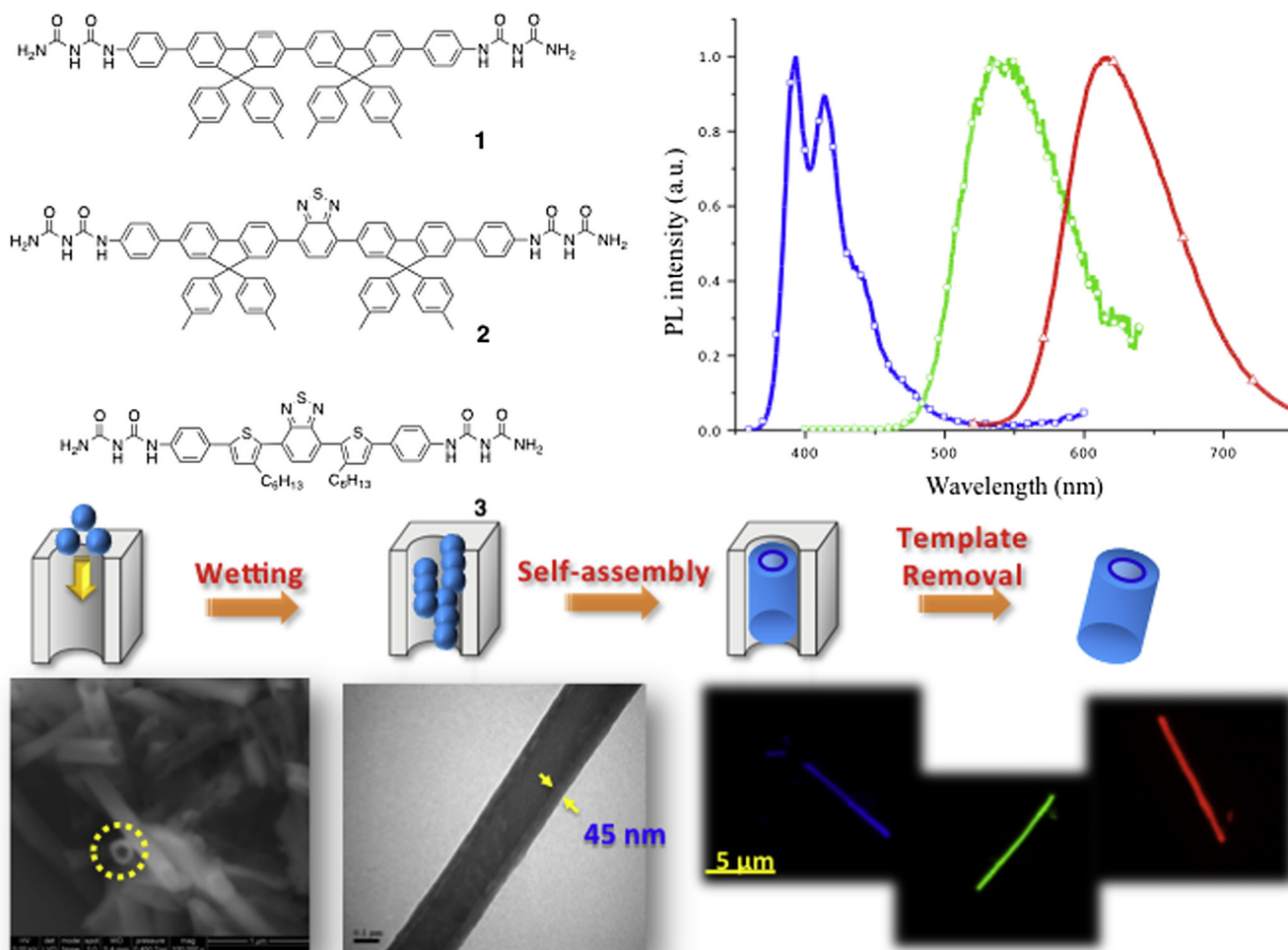
The design of molecular assemblies on the nanometer/sub-micron scale continues to represent a major challenge in bridging top-down and bottom-up fabrication strategies. In particular, molecular components endowed with self-assembly properties capable of inducing opto- and/or electro-active molecular components to form well-defined nano- or micron-sized architectures offers great potential to harness self-assembly in next-generation optoelectronic devices [1–4]. Sequential supramolecular self-assembly can be fine-tuned to control the composition of such structures and achieve the formation of e.g. tunable nanoparticles [5] or p-n junctions from hexabenzocoronene nanotubes [6]. In this regard, nanotubes (or nanorods) present certain advantages resulting from their high aspect ratio which may make them desirable in electronic devices such as solar cells [7]. For this reason numerous template-assisted fabrication methods employing polymer-based materials have been investigated [8–10], amongst which the use of anodic aluminum oxide (AAO) has been found to be particularly versatile [11–15]. The latter is composed of an array of ordered, vertically-aligned pores with a diameter typically on the order of 100–300 nm, and is commercially available as a membrane for applications in filtration. The formation of polymer nanotubes using an AAO template results from the evaporation of a solution of the polymer generating a viscous film that solidifies before

de-wetting the surface of the template [13]. In the case of AAO, the template can be dissolved in a solution of aqueous base, thereby freeing the nanotubes. Although numerous reports of using AAO as a template for functional polymers have been reported, its use in templating the assembly of small organic molecules using supramolecular interactions is, to the best of our knowledge, undocumented. In this regard, the propensity for small-molecule systems to precipitate rather than forming a homogeneous film upon concentration of the solution is a serious hurdle which might be overcome through the use of supramolecular interactions to control how the molecules assemble in the solid. We now report the formation and investigation of the electronic properties of nanotubes prepared using an AAO template applied to a supramolecular small-molecule system devoid of poly- or oligomeric side-chains that instead relies on complementary hydrogen-bonding (H-B).

Our interest in employing supramolecular interactions to control the electronic properties of material led us to engineer a series of compounds based on the well-known fluorene or thiophene chromophores appended with biuret H-B motifs [16]. The latter present a unique combination of binding sites due to the formation of an intramolecular H-B and, because of this, these compounds undergo spontaneous self-assembly into hollow spheres with a diameter of 200–500 nm upon dissolution in aprotic solvents such as THF [17,18]. By altering the composition of the chromophore, the absorption and emission of the aggregates in solution or in the solid can be adjusted to cover the entire visible portion of the spectrum. We have previously shown that these materials

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**Fig. 1.** Chemical structure emission spectra ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ) of nanotubes of compounds **1–3** formed using an AAO template as illustrated below. Bottom: Transmission electron microscopy of nanotubes of **1** and fluorescence optical microscopy ( $\lambda_{\text{ex}} = 365 \text{ nm}$ ) of nanotubes of **1–3**.

can be included in the fabrication of sandwich OLED devices in which the size of the emissive domains is determined by the dimensions of the spherical aggregates, thus demonstrating the potential of this system [19]. An interesting aspect of self-assembled materials is their capability of responding to their environment. The biuret motifs in compounds **1–3** (Fig. 1) induce the formation of vesicles in solution, but may also lead to the formation of H-B sheets and pearl-necklace structures [18]. Therefore, we surmised that it might be possible to direct the formation of nanotubes whose length and diameter are controlled by the mesoporous material. The modular approach of the self-assembly process further allows different chromophores to be combined to permit the formation of single nanotubes emitting e.g. white light through energy transfer processes. We show that the nanotubes exhibit polarized emission and light-guiding properties, thereby demonstrating that the mesoscopic architecture of the assembly directly affects the electronic properties of the molecular constituents.

## 2. Results and discussion

The synthesis of compounds **1–3** has been described previously [17]. To fabricate the nanotubes, solutions of each compound ( $10^{-4} \text{ M}$  THF) were spin cast onto AAO and allowed to evaporate.

As illustrated in Fig. 1, the deposition of a film inside the pores of the template results in the formation of a hollow tube of organic material. The latter can be freed from the inorganic matrix by dissolution of the AAO template in aqueous base. The nanotubes thus obtained were collected by centrifugation, washed with water, and then re-dispersed in aqueous media.

Transmission electron microscopy images show that the nanotubes are indeed hollow, and that the thickness of the wall is ca. 45 nm. Using this approach, nanotubes of compounds **1**, **2**, or **3**, emitting in the blue<sup>1</sup>, green, and red region of the spectrum can be obtained. Optical microscopy images (Fig. 1,  $\lambda_{\text{ex}} = 365 \text{ nm}$ , see Figs. S1–S3 for additional images, emission spectra, and chromatic diagrams of nanotubes) confirm the color of the emission of the individual nanotubes. Energy transfer has been shown to be particularly efficient in supramolecular aggregates and is often used as tool to tune the emission of individual particles. Interestingly, spherical aggregates formed in solution by mixing compounds **1–3** are homogeneous in their emission, which results from the linear combination of the emission of the individual chromophores. Even small quantities of **2** or **3** (0.5–2%) dispersed in aggregates of **1** are sufficient to completely modify the emission spectrum, confirming efficient energy transfer. By employing a solution whose compositions

<sup>1</sup> For interpretation of color in Fig. 1, the reader is referred to the web version of this article.

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