Two-level self-assembly from nanowires to microrods based on a heterotriangulene derivative

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ABSTRACT

Compound **1** was synthesized by a palladium-catalyzed Sonogashira cross-coupling reaction of heterotriangulene derivative **3** with three equiv. of 1-dodecyloxy-4-ethynylbenzene **2** in good yield. After the dichloromethane solution of **1** was mixed with methanol, two-level self-assembly from nanowires to microrods based on **1** was obtained and characterized with scanning electron microscopy (SEM), transmission electron microscopy (TEM) and X-ray diffraction (XRD). The driving force of the two-level self-assembly is attributed to the strong π–π stacking interactions of heterotriangulene cores and the hydrophobic interactions of alkyl chains with solvent molecules.

1. Introduction

In the past decades, one dimensional (1D) nanomaterials including wires [1], tubes [2], rods [3], and belts [4] have attracted extensive investigations, due to their unique properties and applications in nanoscale devices. However, most researches have focused on inorganic compounds [1–4] and polymers [5]. Recently, organic nanomaterials based on small molecules have attracted more and more attention, owing to their special properties for use in electronic and optoelectronic nanodevices [6]. Scientists have successfully constructed 1D organic nanostructures with the help of hydrogen-bonding [7–9], π–π stacking [10,11], electronstatic interactions [12,13] and other noncovalent interactions [14]. Among them, self-assembly of π-conjugated molecules is of extreme importance, and π–π stacking is considered as one of the main driving forces for the formation of 1D assembly [15]. This is particularly evident in the large discotic molecules such as perylene tetracarboxylic diimide (PTCDI) based derivatives [16,17], which form a unique class of *n*-type semiconductors. The *n*-type semiconductors are indispensable for diodes and complementary circuits with high operation speed and low power consumption, but their development lags a lot in comparison to the more common *p*-type counterparts in organic electronics [18]. As a part of our efforts toward synthesizing new organic *n*-type materials, we have identified heterotriangulene **A** (Chart 1) as a promising candidate in our previous work [19]. The three carbonyl groups of **A** greatly reduce the electron density of the aromatic core, a feature that has been shown to effectively promote π–π interaction [20],

which is important for the conduction of electrons in *n*-type materials. The electron deficient aromatic core of **A** and its C_3 symmetry also provide us with an excellent platform to investigate the self-assembly of 1D nanostructures, which may show potential applications for supramolecular assembly based electronic devices [21]. But there has so far been no example of a supramolecular assembly based on **A** or its derivative. In this Letter, we wish to report two level self-assembly from nanowires to macrorods based on a heterotriangulene derivative **1** (Chart 1).
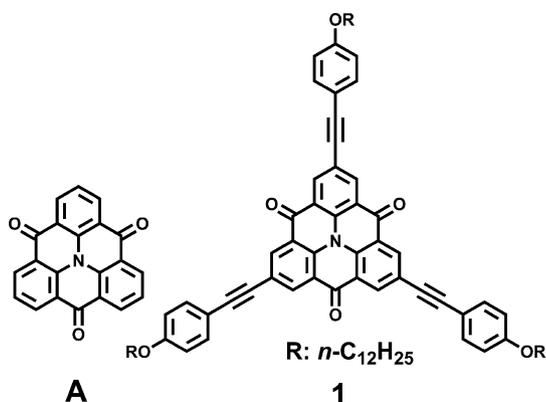
2. Experimental

Unless stated otherwise, all chemicals and reagents were purchased reagent grade and used without further purification. Solvents were purified by standard methods. All manipulations were performed under a dry Argon atmosphere using standard Schlenk techniques.

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker AC-300 Spectrometer. Chemical shifts δ, were reported in parts per million relative to the internal standard TMS. FT-IR spectra were recorded on Bruker–Tensor 27 spectrometer and measured as KBr pellets. High resolution mass spectra (HRMS) were recorded on a VG ZAB-HS mass spectrometer. Scanning electron microscopy (SEM) analysis was carried on a Hitachi S-3500 N scanning electron microscope at an accelerating voltage of 20 kV. Transmission electron microscopy (TEM) images were performed using a Tecnai 20 at an accelerating voltage of 200 kV. A 200 kV JEOL 2010F was used for elemental mapping. X-ray diffraction (XRD) experiment was performed on a Rigaku D/max-2500 X-ray powder diffractometer with Cu Kα radiation (λ = 1.5406 Å) at a generator voltage of 40 kV and a current of 100 mA. Small angle X-ray scattering (SAXS)

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Chart 1. Molecular structures of **A** and **1**.
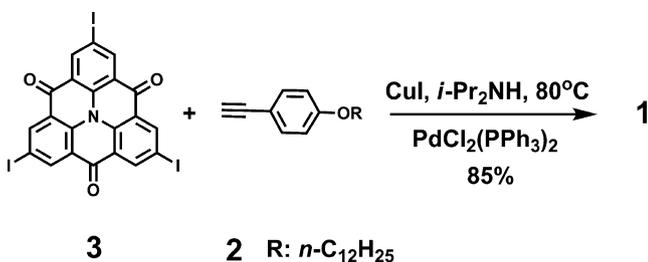
experiments were performed on a Bruker NanoStar SAXS system (Cu Kα radiation source at a voltage of 40 kV and a current of 35 mA).

Synthesis of Compound 1: **3** (700 mg, 1 mmol), **2** (1.15 g, 4 mmol), CuI (38 mg, 0.2 mmol), $PdCl_2(PPh_3)_2$ (70 mg, 0.1 mmol) were added to a mixture of i-Pr_2NH and toluene (v/v = 1:3) (30 mL). The mixture was stirred at 80 °C for 24 h. After cooling to room temperature, the black mixture was filtered through a thin pad of silica gel and the solid on silica gel was washed thoroughly with CH_2Cl_2. The filtrate was evaporated under vacuum. The residue was purified by flash chromatography on silica (CH_2Cl_2/Hexane = 1:2) to obtain the pure compound as orange brown solid (0.99 g, 85%). ^1H NMR (300 MHz, $CDCl_3$, ppm) δ 8.997 (s, 2H, ArH), 7.502 (d, ^3J = 8.7 Hz, 2H, ArH), 6.882 (d, ^3J = 8.7 Hz, 2H, ArH), 3.978 (t, 2H, OCH_2), 1.835–0.87 (m, 23H, $(CH_2)_{10}CH_3$); ^{13}C NMR (75 MHz, $CDCl_3$, ppm) δ 173.9, 159.5, 135.9, 134.9, 134.3, 134.1, 133.3, 128.5 128.4, 122.6, 121.8, 114.3, 113.9, 93.2, 85.2, 68.0; IR (KBr) v_{max} 3433, 2924, 2854, 2212, 1655, 1510, 1464, 1294, 1250, 1173, 1107, 1028 cm^{-1}. HRMS (MALDI) m/z 1176.7083 ($C_{81}H_{94}NO_6$ [M+H]$^+$ requires 1176.7081).
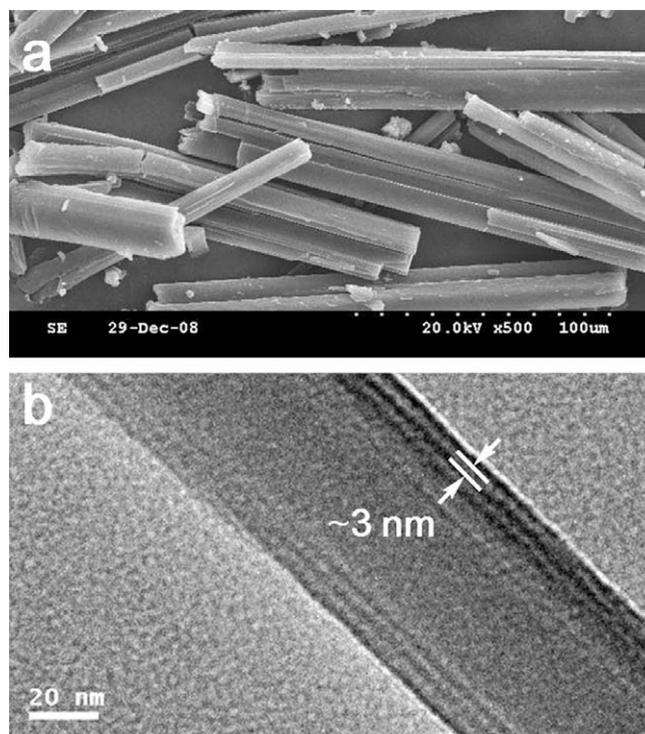
Results and discussion

Compound **1** was synthesized by a palladium-catalyzed Sonogashira cross-coupling reaction [22] of core derivative **3** [19] with three equiv of 1-dodecyloxy-4-ethynylbenzene **2** [23] in 85% yield (Scheme 1). As expected, **1** was readily soluble in common organic solvents such as toluene, CH_2Cl_2, and THF.

The self-assembly of **1** was performed using diffusion process in a binary solvent of dichloromethane/methanol, which enables effective molecular aggregation into well-organized nanowires and microrods, as evidenced by the optical spectral measurements below. In SEM image (Fig. 1a), self-assembly of **1** was observed to exist as many microrods, with average diameters of 10 µm and lengths of several millimeters. TEM imaging gave a deeper insight about the structure of the microrods. From the TEM image (Fig. 1b),

**Fig. 1.** SEM image of microrods (a) and TEM image of nanowires (b) based on self-assembly of **1**.

we could find that the microrods are composed of straight nanowires packed side by side. It is very interesting to note that the typical width of these nanowires (ca. 3 nm) is consistent with the diameter of 1D assembly columns (ca. 2.9 nm) (from the XRD results below). Thus, a two-level self-assembly process may exist in the formation of the microrods based on **1**. The first level is due to the strong intermolecular π–π interactions between the large **A** cores, where the molecules assemble along the axis direction of the nanowires. Then, these nanowires assemble in the orthogonal direction of the axis to form the microrods. The driving force for the second level assembly is believed to come from the hydrophobic interactions of the long alkyl chains with solvent molecules [24]. These arguments are supported by the following XRD results.

Identification and unequivocal assignment of the self-assembly of **1** was finally achieved by X-ray diffraction (XRD) (Fig. 2) and

Scheme 1. The synthesis of **1**.
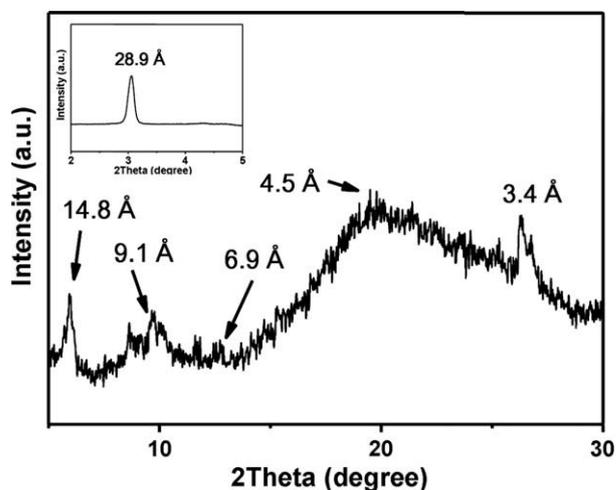
Fig. 2. XRD and SAXS (inset) patterns of self-assembly of **1** at room temperature.
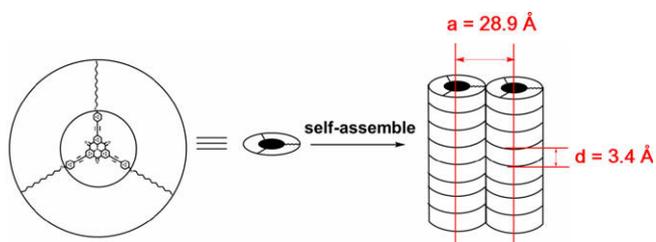
Fig. 3. Schematic illustration of possible molecular arrangements for self-assembly of **1**.

small angle X-ray scattering (SAXS) (inset of Fig. 2). In the wide-angle region, features have been observed corresponding to various short-range interactions. First, at $d = 3.4$ Å, a slightly diffuse scattering was observed, corresponding to the π-stacking distance of the large flat **A** cores along the 1D assembly columnar axis. This is also supported by the single crystal X-ray data of the parent compound heterotriangulene **A**, where the molecules pack into 1D column with a stacking distance of 3.5 Å [20,25]. The broadening peak at 3.4 Å suggests that either the stacking is less regular or that the **A** cores are slightly tilted with respect to the columnar axis [26]. Then, a large broad and diffuse scattering centered at around 4.5 Å was visible, which reflects the short-range correlations of the alkyl chains. Finally, a very weak signal at 6.9 Å, which corresponds to about twice the π-stacking distance ($\sim$2d), may be due to some kind of dimerization. In the slightly lower angle region, another weak diffuse scattering peak corresponding to a distance of ca. 9.1 Å was attributed to some correlations of alkyl chains between neighboring molecules. In the small-angle region, a sharp reflection peak at $2\theta = 3.06°$ was detected, from which a spacing of $a = 28.9$ Å was estimated. This value corresponds to the spacing between the lateral 2D arrays. Its second-order reflection ($28.9/n$, $n = 2$) appeared at approximately 14.8 Å. The sharpness and intensity of the small-angle reflection at $2\theta = 3.06°$ indicate clearly the long-range second level assembly between the 1D assembly columns, which is formed by the first-level assembly of **1** due to the intermolecular π–π interactions of **A** cores. Overall, the two-level self-assembly process can be illustrated in Fig. 3.

3. Conclusions

Due to the π–π stacking interactions of **A** cores and the hydrophobic interactions of alkyl chains with solvent molecules, compound **1** could self-assemble into supramolecular organizations from straight nanowires to well-organized microrods through a two-level self-assembly process in a binary solvent of methanol/dichloromethane. This process may well be used for other molecules to fabricate new nanomaterials in the field of photoelectric devices.

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