



## Synthesis of hexabenzocoronene-layered compounds



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### ABSTRACT

We report herein the synthesis and properties of  $\pi$ -stacked dimeric and polymeric compounds that consisted of hexabenzocoronene (HBC) and xanthene as the stacked  $\pi$ -electron system and the scaffold, respectively; the compounds were obtained by Sonogashira–Hagihara coupling. The obtained polymer was separated into three fractions, and the through-space conjugation effect was estimated. HBC units were layered in proximity (approximately 3.4 Å), leading to  $\pi$ - $\pi$  stacking in the ground and excited states.

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Recently, the construction of  $\pi$ -stacked structures of aromatic rings and  $\pi$ -electron systems in single polymer chains has been the subject of focus.<sup>1</sup> Their face-to-face structures enable transannular communication between the layered  $\pi$ -electron systems. In addition, such a  $\pi$ -stacked orientation is an important factor for effective charge transport and exciton diffusion. In this context, several rigid scaffolds have been developed for aligning  $\pi$ -electron systems in proximity to each other, such as naphthalene,<sup>2</sup> anthracene,<sup>3</sup> [2.2]paracyclophane,<sup>4</sup> bicyclo[4.4.1]undecane,<sup>5</sup> 2-substituted trimethylene,<sup>6</sup> norbornane,<sup>7</sup> and so on. As an unique approach, Nakano et al. and coworkers reported the synthesis of poly(dibenzofulvene)s, wherein the side chain dibenzofulvene groups are tightly stacked, that is, the  $\pi$ -electron systems are fully overlapped, resulting in a large Stokes shift as well as efficient hole transport.<sup>8</sup>

We have also studied the construction of  $\pi$ -stacked structures using a xanthene skeleton as the rigid scaffold.<sup>9</sup> Some xanthene compounds are commercially available, and various xanthene derivatives can be easily prepared through facile functionalizations at the 4- and 5-positions; thus, a variety of aromatic groups and  $\pi$ -electron systems can be introduced at these positions. The rotary motion of the substituted  $\pi$ -electron systems is suppressed by steric hindrance, which leads to layered structures for these  $\pi$ -electron systems.

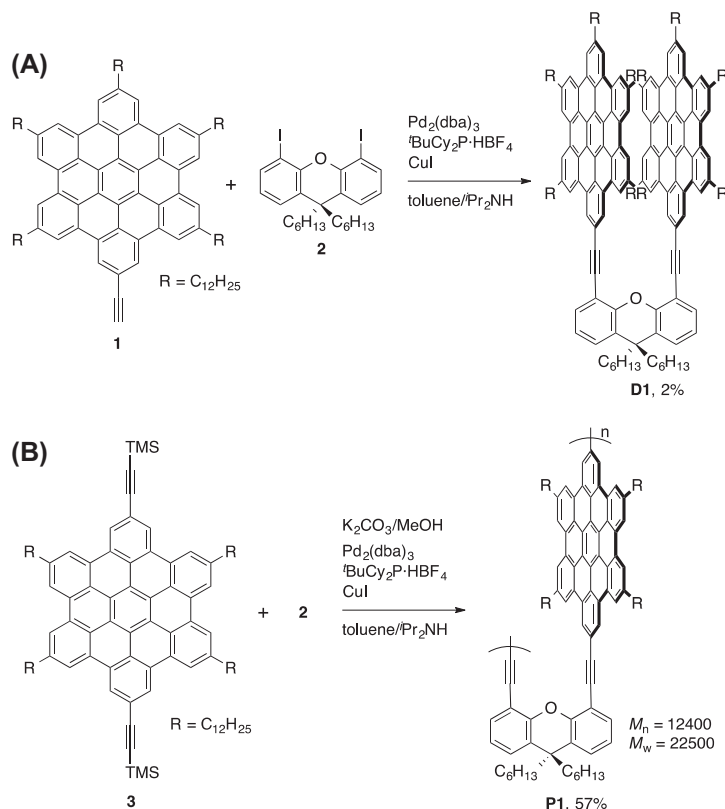
Further syntheses of novel aromatic-ring-layered compounds and investigations on the effect of the stacking on their properties are important for exploring their potential applications in opto-electronic devices. In this study, we selected

hexa-*peri*-hexabenzocoronene (HBC)<sup>10</sup> as the layered aromatic ring; HBC is chemically stable, and functionalized HBCs are readily obtained. The HBC-layered monomeric, dimeric, and polymeric compounds were synthesized using the xanthene skeleton as the scaffold, and their optical properties were investigated.

The HBC-layered dimeric compound **D1** and polymer **P1** with xanthene were synthesized by the Sonogashira–Hagihara coupling<sup>11</sup> using the Pd<sub>2</sub>(dba)<sub>3</sub> (dba = dibenzylideneacetone)/<sup>t</sup>ByCy<sub>2</sub>P·HBF<sub>4</sub>/CuI catalytic system (Scheme 1A and B, respectively). The reaction of HBC monoacetylene **1**<sup>12</sup> with xanthene compound **2**<sup>13</sup> afforded the corresponding crude compound **D1**, which was purified using a silica gel column and by recycling preparative high-performance liquid chromatography (HPLC) using gel permeation columns (GPC). Most of the products were lost during column chromatography, because of strong  $\pi$ - $\pi$  interactions among the molecules, and pure **D1** was obtained in 2% yield. As shown in Scheme 1B, polymerization was carried out by the treatment of trimethylsilyl-protected HBC diacetylene **3** with **2** in the presence of K<sub>2</sub>CO<sub>3</sub>, using the same catalytic system as Scheme 1A. The trimethylsilyl group of **3** was removed in situ because terminal alkynes are unstable towards oxidation. The obtained polymer **P1** was purified by reprecipitation from THF and MeOH (good and poor solvents, respectively). The number-average ( $M_n$ ) and weight-average ( $M_w$ ) molecular weights of **P1** were estimated, by GPC in CHCl<sub>3</sub> eluent using a calibration curve of polystyrene standard calibration curve, to be 12,400 and 22,500, respectively. Polymer **P1** was soluble in common organic solvents such as THF, CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub> and toluene; it was separated by HPLC into three fractions (Fig. S9 in the Supporting information); **P1a** ( $M_n$  = 8700,  $M_w/M_n$  = 1.09, degree of polymerization (DP) = 5.5), **P1b** ( $M_n$  = 13,600,  $M_w/M_n$  = 1.11, DP = 8.6), and **P1c** ( $M_n$  = 17,500,  $M_w/M_n$  = 1.25, DP = 11). The structures of the

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**Scheme 1.** Synthesis of (A) dimeric compound **D1** and (B) polymer **P1**.

obtained compounds **D1** and **P1** were characterized by  $^1\text{H}$  NMR spectroscopy and/or matrix assisted laser desorption/ionization-time of flight (MALDI-TOF) mass spectrometry. In the  $^1\text{H}$  NMR spectra of **D1** and **P1**, all the signals were broadened because of the restricted mobility of the HBC moieties; for example, the  $^1\text{H}$  NMR spectrum of **D1** is shown in Figure 1. The MALDI-TOF mass spectrum of **D1** exhibited only one signal corresponding to the  $[\text{M}^+]$  ion of **D1** (Fig. 1B), supporting the formation of **D1**. It was difficult to obtain MALDI-TOF mass and  $^{13}\text{C}$  NMR spectra of **P1**. Although, thus, the existence of diyne units in **P1** by Sonogashira–Hagihara coupling could not be denied, stacked structure of the coronene moieties can be discussed in any cases.

To characterize the optical properties of **D1** and **P1**, model compounds **M1** and **M2** were synthesized for comparison, as shown in Scheme 2A and B, respectively. Figure 2A shows the UV–vis absorption and fluorescence spectra of **D1** and model compound **M1** in dilute  $\text{CHCl}_3$  solution ( $1.0 \times 10^{-5}$  and  $1.0 \times 10^{-6}$  M for the absorption and fluorescence spectra, respectively). In addition, the UV–vis absorption and fluorescence spectra of **D1**, **P1c** and the model compound **M2** are shown in Figure 2B. In the absorption spectra of **D1** and **M1** (Fig. 2A), the absorption edge of **D1** was red-shifted in comparison with that of **M1** because of  $\pi$ – $\pi$  interactions between two HBC units in the ground state of **D1**. The fluorescence spectrum of **M1** in dilute  $\text{CHCl}_3$  solution ( $1.0 \times 10^{-6}$  M) appeared at around 500 nm with a clear vibrational structure, while that of **D1** was observed at 515 nm as a broad and featureless signal. We confirmed that this concentration ( $1.0 \times 10^{-6}$  M) was sufficiently dilute; thus, each spectrum exhibits fluorescence from a single molecule. These results suggest that the stacked HBC units in **D1** exhibit  $\pi$ – $\pi$  interactions in the excited state, which leads to the excimer-like emission.

The peak tops of the absorption spectra of **D1** and **P1c** were identical and appeared at 367 nm, whereas that of **M2** was observed at 370 nm, which was slightly red-shifted in comparison

with those of **D1** and **P1c**. In **M2**, two anisoyl groups combine with an HBC unit to form a planar structure, because of which its  $\pi$ -conjugation length is expected to be well extended. Therefore, the absorption peak top appeared in a longer wavelength region than those of **D1** and **P1c**, wherein the twisting of the HBC rings suppresses the extension of the conjugation length. On the other hand, the absorption edges of **D1** and **P1c** were bathochromically shifted relative to that of **M2**, indicating  $\pi$ – $\pi$  interactions between HBC units in the ground state of **D1** and **P1c**. The energy band gaps of all compounds were calculated by the absorption edges, and the energy levels were estimated by cyclic voltammetry, as shown in Figure S10 and Table S1. The HOMO levels of all compounds were found to be approximately  $-5.0$  eV; thus, there were no noticeable differences by the stacked structure. Figure 2B shows their fluorescence spectra in dilute  $\text{CHCl}_3$  solution ( $1.0 \times 10^{-6}$  M). Despite the sufficiently dilute condition, the fluorescence spectra of **D1** and **P1c** were broad without any vibrational structures. Thus, in the excited state, the HBC rings in the polymer were interacting with one another even as single molecules. The molar extinction coefficient ( $\epsilon/\text{M}^{-1} \text{cm}^{-1}$ ) and photoluminescence quantum efficiency ( $\Phi_{\text{PL}}$ ) are listed in Table S1.

According to the absorption and fluorescence spectra of the polymers (Fig. 3), **P1b** ( $M_n = 13600$ ,  $M_w/M_n = 1.11$ ,  $\text{DP} = 8.6$ ) and **P1c** ( $M_n = 17,500$ ,  $M_w/M_n = 1.25$ ,  $\text{DP} = 11$ ) exhibited almost identical optical profiles. It is considered that, in both ground as well as excited states, the bathochromic shift of the HBC-stacked compound saturates upon reaching nine to eleven HBC units. The  $\pi$ – $\pi$  interactions of the stacked aromatic units in the  $\pi$ -stacked polymer have been studied. The electronic interactions of 7,7-diphenylnorbornane-based polymers<sup>7</sup> and poly(dibenzofulvene)<sup>8</sup> are effective through approximately five aromatic moieties in the ground state, whereas [2.2]paracyclophane-based through-space conjugated polymer exhibits the electronic interactions through at least ten  $\pi$ -electron systems due to the fixed  $\pi$ -stacked conformation.<sup>4h</sup>

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