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Original article

Synthesis, properties, and self-assembly of 2,3-bis(*n*-octyl)hexaazatriphenylene

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ABSTRACT

A hexaazatriphenylene (HAT) derivative that bears two *n*-octyl chains was designed and synthesized. Its photophysical and electrochemical properties have been investigated. SEM study revealed that it could self-assemble into well-ordered 1D nanoribbons or 2D microsheets, which depends on the polarity of the solvents used.

1. Introduction

The construction of novel π-conjugated molecules has drawn considerable attention in the past decades due to their potential applications in fabricating optic and electronic devices [1]. In most cases the devices were fabricated from aggregates consisting of a large amount π-conjugated molecules, except those used as single-molecular devices. In this context, arranging π-conjugated molecules into well-defined structures with certain shape, size, and dimensions is highly desired. As a basic tool for the ‘‘bottom-up’’ approach, molecular self-assembly, a process that individual molecules are drawn together by noncovalent interactions, is a powerful technique to fabricate well-defined objects of micro- and nano-scales [2]. However, for π-conjugated molecules with large planar structures, their high tendency of aggregation driven by strong π–π stacking between the planar skeletons frequently results in poor solubility in organic solvents, which sometimes is adverse to the self-assembly process. To overcome this obstacle, peripheral substitutents are usually introduced, which can not only enhance the solubility of the resulting derivatives, but also manipulate the morphologies of their self-assembled structures.

Hexaazatriphenylene (HAT) is a disc-like heterocycle. Thanks to its C_3 symmetry and six nitrogen atoms that exhibit excellent coordination ability to transition metal ions, HAT has been widely used as a ligand in coordination chemistry to construct metal-organic architectures with various structures [3]. The electron-withdrawing imine nitrogens also endow HAT an electron-deficient feature, which makes it and its derivatives potential *n*-type (electron-accepting) organic materials [4]. Herein, we report the synthesis of a novel HAT derivative, that is, 2,3-bis(*n*-octyl)hexaazatriphenylene (**1**), and its photophysical and electrochemical properties and self-assembly behavior.

2. Experimental

2.1. General procedure for hexaaminobenzene trihydrochloride (3)

To a stirred solution of $SnCl_2 \cdot 2H_2O$ (20.2 g, 90 mmol) and concentrated HCl (30 mL) was added a suspension of 1,3,5-triamino-2,4,6-trinitrobenzene **2** [5] (1.12 g, 4.3 mmol) in ethyl acetate (120 mL) at room temperature. The mixture was heated under reflux for 5 h and then cooled to room temperature. The resulting precipitate was filtered, washed with ethyl acetate (30 mL), methanol (30 mL) and diethyl ether (30 mL) and dried in vacuo to afford compound **3** as a yellow solid (0.91 g, 75%). FT-IR (KBr, cm^{-1}): ν 3348, 3218, 2877, 2604, 1674, 1651, 1624, 1539, 1486, 1218, 1178, 1110, 729, 698. MS (ESI): *m/z* 169 $[M-3HCl+H]^+$.

2.2. General procedure for 9,10-diamino-1,4,5,8-tetraazaphenanthrene (4)

To a stirred solution of **3** (0.45 g, 1.61 mmol) in 100 mL ethanol/water (1/2, v/v) at 50 °C was added a solution of glyoxal (0.47 g, 40% aqueous solution) in ethanol (40 mL) dropwise. The mixture was stirred at 50 °C for 1 h and then cooled and extracted with chloroform (50 mL). The organic phase was washed with water (25 mL × 3) and brine (25 mL) and dried over magnesium sulfate.

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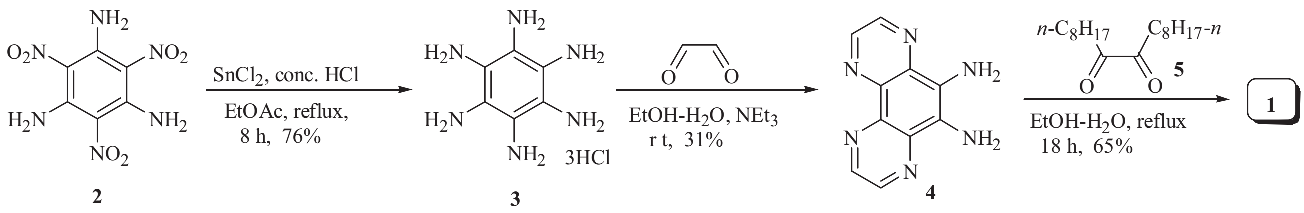

Scheme 1. The synthesis of compound **1**.

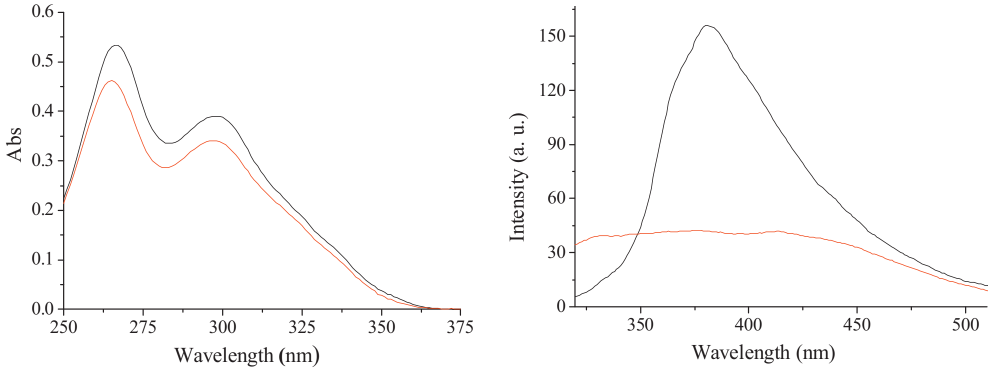

Fig. 1. UV–vis (left) and fluorescence (right, λ_{ex} = 267 nm) spectra of **1** in $CHCl_3$ (black) and methanol (red). The concentration for the UV–vis and fluorescence experiments was 1.3×10^{-5} mol/L and 2.5×10^{-6} mol/L, respectively. (For interpretation of the references to color in this text, the reader is referred to the web version of the article.)

Upon removal of the solvent with a rotavapor, the resulting residue was subjected to column chromatography (chloroform/ethanol = 50/1, v/v) to give compound **4** as a reddish brown solid (0.17 g, 31%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 4.75 (s, 4H), 8.91 (s, 2H), 8.94 (s, 2H). MS (ESI): *m/z* 213 $[M+H]^+$, 235 $[M+Na]^+$.

2.3. General procedure for 2,3-bis(n-octyl)hexaazatriphenylene (1)

A mixture of **4** (58 mg, 0.27 mmol) and octadecane-9-10-dione **5** (77 mg, 0.27 mmol) in anhydrous ethanol (9 mL) and acetic acid (1 mL) was refluxed for 18 h and then cooled. Upon removal of the solvent with a rotavapor, the resulting residue was dissolved in dichloromethane (30 mL). The solution was washed with water (10 mL) and saturated sodium bicarbonate solution (10 mL), water (10 mL), and brine (10 mL × 2) and then dried over sodium sulfate. The solvent was then removed with a rotavapor and the resulting crude product was subjected to column chromatography (CH_2Cl_2/acetone = 15:1, v/v) to give **1** as a pale yellow solid (80 mg, 65%), mp 177–179 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 0.88 (t, 6H, *J* = 6.9 Hz), 1.24–1.39 (m, 16H), 1.50–1.55 (m, 4H), 1.88–1.93 (m, 4H), 3.28 (t, 4H, *J* = 8.1 Hz), 9.23 (d, 2H, *J* = 2.1 Hz), 9.30 (d, 2H, *J* = 2.1 Hz); ^{13}C NMR (75 MHz, $CDCl_3$): δ 160.0, 147.1, 146.3, 142.8, 141.9, 139.8, 36.1, 32.1, 30.3, 30.1, 29.7, 29.4, 22.9, 14.3. MS (ESI): *m/z* 459.3 $[M+H]^+$; Anal. Calcd. for $C_{28}H_{38}N_6$: C 73.33, H 8.35, N 18.32; Found: C 73.51, H 8.26, N 18.47.

3. Results and discussion

The synthesis of compound **1** is shown in Scheme 1. Thus, **2** was first reduced by $SnCl_2$ in concentrated hydrochloride acid to give **3** in 76% yield. The hexaamine was then condensed with glyoxal to generate **4** in 31% yield. Refluxing a mixture of diamine and **5** in ethanol and water for 18 h afforded **1** in 65% yield (Scheme 1).

The UV–vis spectroscopy of **1** in chloroform exhibited two absorption peaks at 266 nm and 298 nm, respectively (Fig. 1). The first one was assigned to the π–π^* transition of the conjugated structure and the second one to n–π^* transition. From the tangent of the absorption edge, the HOMO–LUMO energy gap was estimated to be 3.41 eV [6]. The absorption intensity decreased in methanol, reflecting that π–π stacking of the HAT cores was enhanced in more polar solvents. The fluorescence spectrum of **1** in chloroform displayed an emission peak centered at 381 nm, which was weakened noticeably in methanol (Fig. 1), also evidencing the

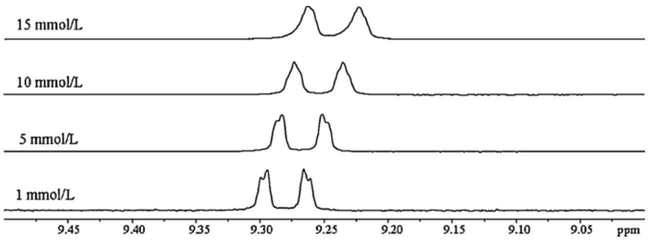

Fig. 2. Partial ^{1}H NMR spectra of **1** at different concentrations in methanol-d_4 at 25 °C.

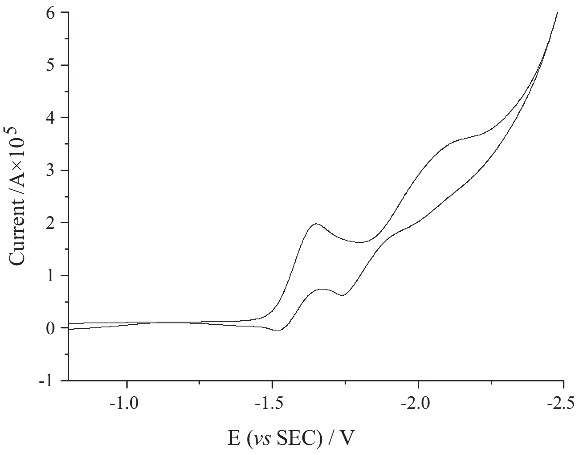

Fig. 3. Cyclic voltammogram for the reduction of compound **1** in CH_2Cl_2 (0.15 mmol/L). Tetrabutyl ammonium hexafluorophosphate (0.1 mol/L) was used as electrolyte.

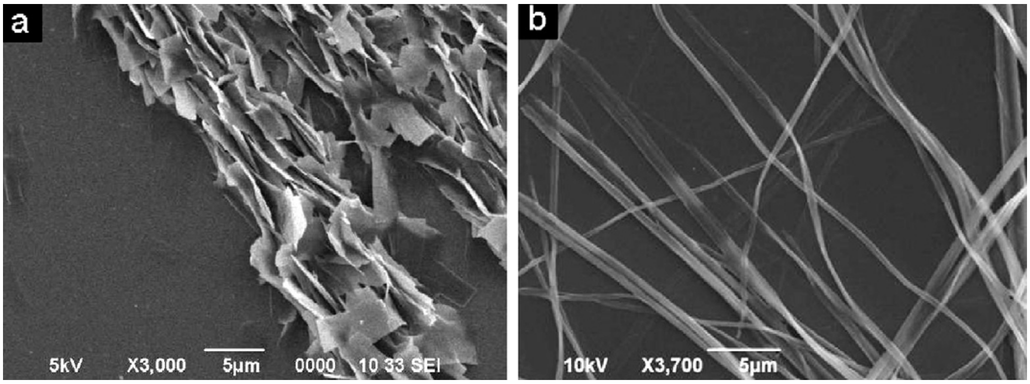

Fig. 4. SEM images of the samples (0.5 mmol/L) of **1** in (a) methanol and (b) methano/water (4/1, v/v) on mica surfaces after the solvent was evaporated.

existence of π–π stacking of the HAT cores. ^{1}H NMR dilution experiment in CD_3OD was carried out (Fig. 2). The signals of the aromatic protons of **1** shifted downfield with the decrease of its concentration, suggesting again intermolecular stacking of the HAT cores in high polar solvent.

The electrochemical property of **1** was further investigated by cyclic voltammetry (CV). As shown in Fig. 3, **1** displayed two reduction waves in the range of 0 to −2 V with the first half-wave potential ($E_{1/2}^{\text{red}-1}$) at −1.56 V. On the basis of the first half-wave potential and the band gap obtained from the UV–vis spectrum, the HOMO and LUMO energies of **1** were calculated to be −6.29 and −2.88 eV, respectively [7]. The energies of the frontier orbitals of **1** were estimated, using DFT calculations at the B3LYP/6-31G* level, to be −6.69 eV for HOMO and −2.02 eV for LUMO. The values are close to the experimental results, suggesting that **1** might be further exploited as a *n*-type organic semi-conductor.

In contrast to the parent HAT that exhibits a poor solubility, **1** was soluble in common organic solvents. Its self-assembling behavior in different solvents was then investigated using SEM. The samples were prepared by drop-casting the solutions of **1** on freshly cleaved mica substrates. It was found that, in solvents of low and medium polarity, such as *n*-hexane, dichloromethane, chloroform, acetone, tetrahydrofuron, and acetyl acetate, **1** did not give rise to any well-defined aggregates. However, using methanol as solvent, sheet-like structures (named as micro-sheets) with lateral sizes of several microns were observed (Fig. 4a), reflecting a two dimensional (2D) growing process. It is anticipated that the driving force for the self-assembly of **1** should mainly come from the π–π stacking between the planar HAT core. Therefore, more polar water was added into the methanol solution to promote the aggregation. The SEM images of a sample prepared from a solution of **1** in methanol/water (4/1, v/v) displayed ribbon-like structures (named as nanoribbons, Fig. 4b), which supported a one-dimensional (1D) growing process. The widths of the ribbons were several hundred of nanometers and the lengths were more than dozens of microns, with salient twisting being observed. The different morphology of the aggregates in different solvents should reflect different stacking patterns. To shed light on this phenomenon, powder X-ray diffraction (XRD) experiments were carried out for both the microsheets and nanoribbons. As can be seen in Fig. 5, the two species shared some common diffraction peaks in the 2θ range of 5−17.5°. However, the patterns appearing after 17.5° displayed different diffraction peaks, which should correspond to different stacking manners, although the exact arrangement in the two aggregates is unknown at this stage. The result reflected that the solvophobic interaction plays a crucial role in dictating the self-assembly of this type of large conjugated systems.

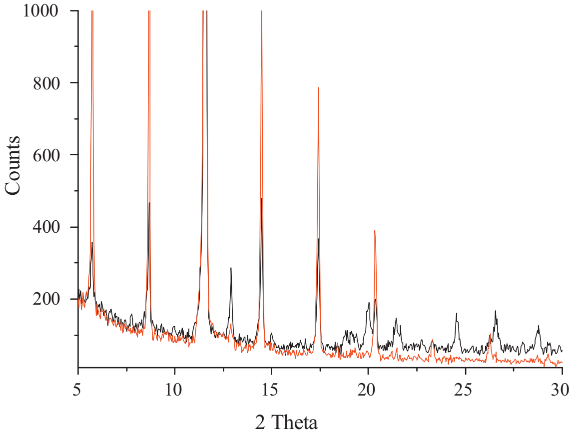

Fig. 5. Powder XRD patterns of the samples prepared from **1** in methanol (black) and methanol–water (4:1, v/v, red). (For interpretation of the references to color in this text, the reader is referred to the web version of the article.)

4. Conclusions

We have described the synthesis of a novel HAT derivative. Its optical and electrochemical properties have been investigated, which reveals an *n*-type organic semiconducting character. It is also revealed that in solvents of different polarity, the molecule can self-assemble into well-ordered 1D or 2D morphology. We believe this study should provide valuable information for the future construction of organic devices for electronics through molecular self-assembly of conjugated systems derived from the HAT skeleton.

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