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Smectic liquid crystals based on hexaazatriphenylene: potential organic n-type semiconductor

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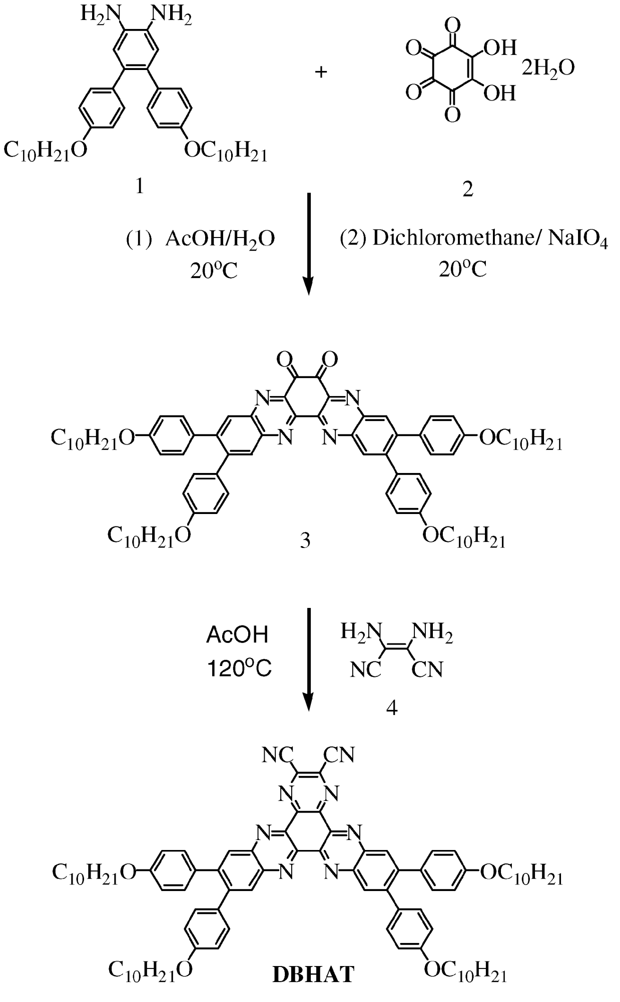
We report the synthesis of dibenzohexaazatriphenylene derivative DBHAT. The addition of electron-withdrawing groups on the dibenzohexaazatriphenylene core leads to a high electron-accepting capability. DBHAT exhibits reversible four-step reduction waves at half-wave potentials ($E_{1/2}$) of −0.42, −0.94, −1.35 and −1.80 V *vs.* Ag/AgCl. Furthermore, DBHAT is able to form a smectic liquid crystalline assembly over a wide temperature range. With strong dipole–dipole interactions, the smectic liquid crystals show extremely highly stabilized mesophases.

Organic conjugated materials that form liquid crystalline (LC) mesophases have attracted attention for applications in organic electronic devices.[1,2] These materials possess high intrachain charge carrier mobilities due to high degrees of order and extensive orbital overlap. Since these materials are typically composed of conjugated molecules, in which a central planar redox-active π-delocalised core is surrounded by flexible side chains,[3,4] they are more readily processed from solution or from an isotropic melt than π-stacked single-crystal materials. Therefore, extensive efforts have been directed towards developing and studying LC materials as hole (p-type) and electron (n-type) transport materials, and n-type organic conjugated materials, which are capable of transporting holes and electrons, respectively. However, most semiconducting LCs are good hole transporting materials (p-type), while only a limited number of electron transporting LC materials (n-type), such as heteroaromatic compounds,[5–10] and naphthalene and perylene diimides,[11,12] *etc.*, have been reported. Williams and co-workers have reported the self-assembly of n-type discotic pyrazine-containing conjugated molecules.[13–17] We also have studied the synthesis and characterization of a series of n-type pyrazine-containing conjugated molecules, and the self-assembling properties of n-type pyrazine semiconductors have been reported.[18,19]

Here, we have designed and synthesized the dibenzohexaazatriphenylene derivative **DBHAT**. The addition of electron-withdrawing groups onto the dibenzohexaazatriphenylene core leads to a high electron-accepting capability. Furthermore, **DBHAT** is able to form a smectic LC assembly over a wide temperature range. With strong dipole–dipole interactions, the smectic liquid crystals show extremely highly stabilized mesophases.

The synthetic approach of **DBHAT** is outlined in Scheme 1. The synthesis of two-condensation intermediate **3** is a key step to obtain dibenzohexaazatriphenylene derivative **DBHAT**. The catechol derivative was successfully realized by adding **2** dropwise into an acetic acid solution of **1** at 20 °C, and then intermediate **3** was obtained by oxidising the catechol derivative in dichloromethane. **DBHAT** was prepared by the condensation coupling of **3** and **4**. The crude product was purified by column chromatography on silica gel with chloroform as



Scheme 1 Synthesis of **DBHAT**.

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the eluent to afford **DBHAT** as a red solid. The chemical structure of **DBHAT** was confirmed by NMR spectra, elemental analysis and mass spectra. The detailed synthetic procedure and structure characterization are described in the Experimental section.

The UV-vis absorption and fluorescence spectra of **DBHAT** in solution and in a film are shown in Fig. 1. In non-polar solvents, the absorption bands of **DBHAT** show a well-resolved vibrational fine structure at low concentration, which can be attributed to the vibronic transition of the **DBHAT** monomer. The absorption maximum appears at 459 nm, along with two higher vibronic transitions located at 360 and 323 nm, which are attributed to the hexaazatriphenylene core π–π* transition. A noticeable red shift of the absorption is observed in polar solvents and films. **DBHAT** exhibits a strong excited state solvatochromism. The λ_{em} value increases as the solvent polarity increases. The emission wavelength of **DBHAT** moves from 596 nm in toluene to 639 nm in dichloromethane, and the fluorescence quantum yield decreases from 61% in toluene to 43% in dichloromethane (Fig. 1). This clearly indicates a strong intramolecular charge transfer from the donor (decyloxy-benzene) to the acceptor (cyano groups).[20,21]

The redox properties of **DBHAT** were studied by cyclic voltammetry (CV) and differential pulse voltammetry (DPV). Fig. 2 shows the CV and DPV curves of **DBHAT**. The CV scan for **DBHAT** with anodic scanning from 0 to 2 V shows no peaks. Upon cathodic scanning, **DBHAT** exhibits four reversible reduction waves, which were further confirmed by the DPV scan, and the half-wave potentials ($E_{1/2}$) of these reduction waves are located at −0.42, −0.94, −1.35 and −1.80 V *vs.* Ag/AgCl. These results indicate the n-type nature of **DBHAT**. It is noteworthy that the multistep redox behavior of **DBHAT** is comparable with the results for C_{60} fullerene reported by Echegoyen and co-workers.[22] Furthermore, the first reduction of **DBHAT** occurs at a less negative potential than that of C_{60} fullerene, indicating the extremely high electron-accepting capability of **DBHAT**.

The LUMO (lowest unoccupied molecular orbital) energy levels and band gap of **DBHAT** can be estimated from the CV and UV/vis spectroscopic data. The LUMO energy level of **DBHAT**, estimated from the reduction onset potentials, was −3.98 eV, comparable to the well-known n-type perylene-tetracarboxylic acid diimide material.[23] Moreover, **DBHAT** showed a large band gap, 2.21 eV, which was estimated from the onset of UV-vis absorption in a solid film.

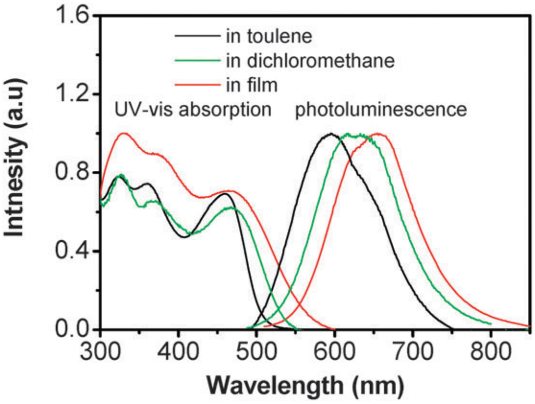

Fig. 1 UV-vis absorption and photoluminescence spectra of **DBHAT**.

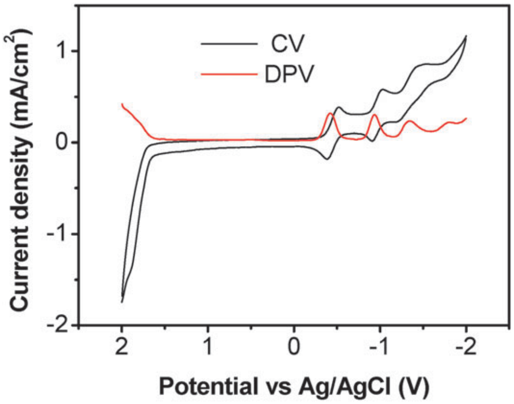

Fig. 2 Cyclic voltammograms of **DBHAT** in dichloromethane at a scan rate of 0.1 V s^{-1}.

Thermogravimetric analysis (TGA) performed under nitrogen revealed that **DBHAT** is thermally stable with a weight loss temperature beyond 350 °C. The differential scanning calorimetry (DSC) traces of **DBHAT** are illustrated in Fig. 3, and the transition temperatures and enthalpies are summarized. The first heating trace is significantly different from the second, but no further changes were observed upon subsequent cooling and heating. There is only one endothermic transition at 144 °C, and the corresponding transition enthalpy is 8.55 KJ mol^{-1}. It corresponds to the crystal phase to LC phase transition, based on polarized light microscopy (PLM) observations.

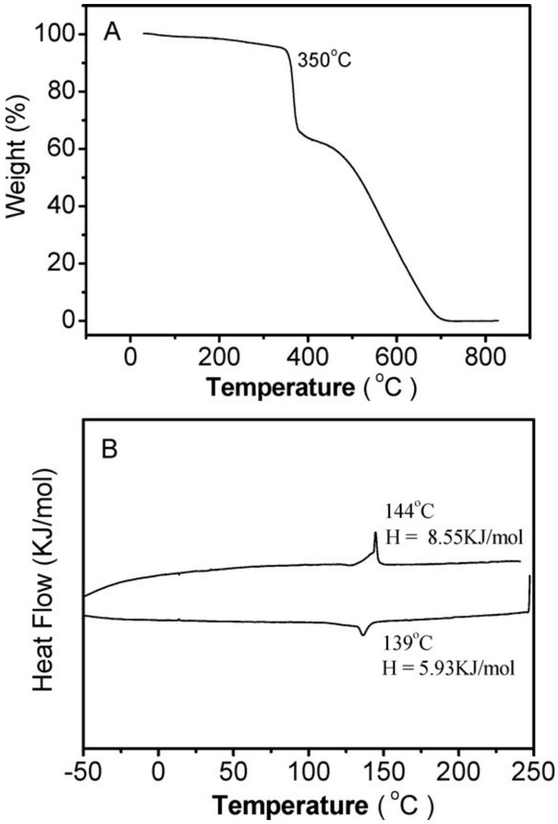

Fig. 3 Thermogravimetric (A) and DSC (B) curves of **DBHAT**.

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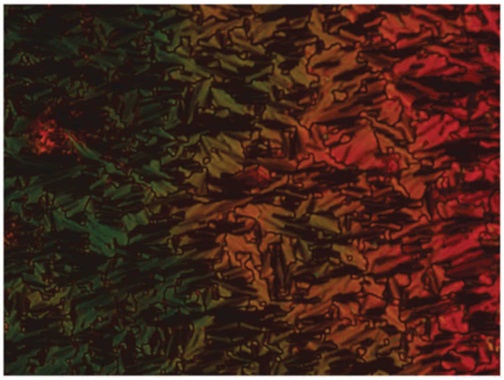

Fig. 4 Polarized optical micrographs of **DBHAT** at 200 °C.

Upon heating from room temperature to 200 °C, typical conical fan-shaped textures characteristic of a smectic phase are observed for **DBHAT** under a polarizing microscope, as shown in Fig. 4. Within the temperature range from 150 °C to the decomposition temperature (350 °C), the fan-shaped textures of the smectic phase do not change, suggesting that the smectic liquid crystals show extremely highly stabilized mesophases.

Fig. 5 shows the XRD scan collected for the birefringent phase of **DBHAT** at 200 °C. The birefringent phase of **DBHAT** was confirmed as a smectic phase through assignment of the reflections. In the small-angle region, the XRD profile of **DBHAT** shows two reflection peaks corresponding to *d*-spacings of 25.94 and 12.91 Å, which were indexed in sequence as (100) and (200). No sharp peaks are observed in the wide-angle region, although one diffuse halo is centered around *d*-spacings of *ca.* 5 Å, which is attributed to liquid-like correlations between adjacent molecules. The data indicate that **DBHAT** adopts a smectic mesophase.

In summary, we have reported the dibenzohexaazatriphenylene derivative **DBHAT**. The addition of electron-withdrawing groups onto the dibenzohexaazatriphenylene core leads to a high electron-accepting capability. **DBHAT** exhibits four reversible reduction waves at half-wave potentials ($E_{1/2}$) of −0.42, −0.94, −1.35 and −1.80 V *vs.* Ag/AgCl. The LUMO energy level of **DBHAT** was −3.98 eV, comparable to the well-known n-type perylenetetracarboxylic acid diimide material. Furthermore, **DBHAT** is able to form a smectic LC assembly over a wide temperature range. With strong dipole–dipole interactions, the smectic liquid crystals showed extremely high stabilized mesophases. These results suggest that dibenzohexaazatriphenylene derivative **DBHAT** is a potential organic n-type semiconductor.

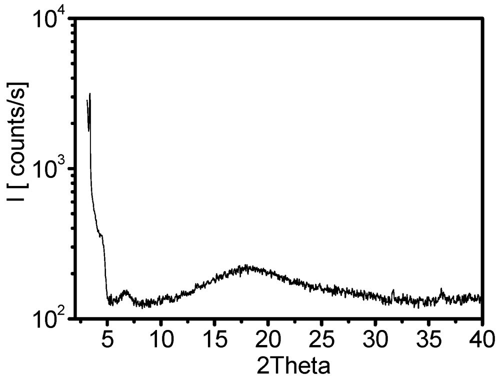

Fig. 5 X-Ray diffraction patterns of **DBHAT** at 200 °C.

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Experimental

General information

The starting materials, diaminomaleonitrile, rhodizonic acid dihydrate and solvents were purchased from Acros and used without any further purification. Compound **1** was synthesized according to a reported method.[18] ^{1}H NMR spectra were recorded at 25 °C on a 300 MHz NMR spectrometer (Bruker). Chemical shifts are reported in ppm at room temperature using $CDCl_3$ as the solvent and tetramethylsilane as the internal standard unless indicated otherwise. Abbreviations used for splitting patterns are s = singlet, d = doublet, t = triplet and m = multiplet. Mass spectra were carried out using MALDI-TOF/TOF matrix assisted laser desorption ionization mass spectrometry with an autoflexIII smartbeam (Bruker Daltonics Inc.). Elemental analyses were carried out on an Eager 300 elemental analyzer.

Cyclic voltammetry (CV) was performed on a CHI660b electrochemical analyzer with a three-electrode cell in a 5.0×10^{-4} mol L^{-1} **DBHAT** dichloromethane solution with 0.1 M tetrabutylammonium perchlorate at a scan rate of 100 mV s^{-1}. A glass carbon disk (2 mm diameter) was used as a working electrode with a Pt wire as the counterelectrode and an Ag/AgCl electrode as the reference electrode. The redox potential was calibrated with ferrocene/ferrocenium (0.44 V *vs.* Ag/AgCl in DCM). LUMO energy levels were calculated according to LUMO = $(4.4 + E_{\mathrm{onset}}^{\mathrm{red}})$.

UV/vis spectra were recorded by a Shimadzu WV-2550 spectrophotometer. TGA measurements were performed on a Perkin-Elmer TGA7 thermal analyzer. Differential scanning calorimetry (DSC) was carried out using a Perkin-Elmer differential scanning calorimeter (DSC7) with heating and cooling rates of 10 K min^{-1}. Phase transitions were also examined by a polarization optical microscope (POM) Olympus BX51 with a T95-PE temperature-controlled THMS-600 hot stage. X-Ray diffraction measurements were performed on a D8 Advance instrument (Bruker AXS Inc.) with Cu-Kα1: 1.54051 Å.

Synthesis and characterization of DBHAT

Into a stirred solution of **1** (1.140 g, 2.0 mmol) in 80 mL acetic acid was added compound **2** dropwise (0.206 g, 1.0 mmol) in 10 mL water at 20 °C. The mixture was stirred overnight and the precipitated product filtered. The precipitated product was dissolved in 100 mL dichloromethane, 2.50 g $NaIO_4$ in 30 mL water was added and the mixture stirred overnight. The organic layer was washed with water (100 mL × 2) and

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brine (100 mL × 2), dried over anhydrous Na_2SO_4 and evaporated *in vacuo* to dryness. The crude product was dried under vacuum and purified by column chromatography on silica gel with chloroform as the eluent to afford compound **3** as a red solid (0.72 g, 58%). ^{1}H NMR (300 Hz, $CDCl_3$, 298 K): δ (ppm) 8.53 (s, 2 H), 8.42 (s, 2 H), 7.23 (t, J = 7.5 Hz, 8 H), 6.88 (m, 8 H), 4.00 (t, J = 6.2 Hz, 8 H), 1.88–1.79 (m, 8 H), 1.50–1.32 (m, 28 H), 0.92 (t, J = 6.5 Hz, 12 H). Anal. calc. for $C_{84}H_{104}N_4O_6$: C, 79.32; H, 8.44; N, 4.51. Found: C, 79.03; H, 8.65; N, 4.82. m/z [MALDI-TOF]: 1241.9 (MH^+).

A mixture of compound **3** (0.620 g, 0.5 mmol) and compound **4** (0.108 g 1.0 mmol) in 60 mL acetic acid was heated to 120 °C for 24 h under a nitrogen atmosphere. After the reaction mixture had cooled to room temperature, it was poured into water (200 mL) and extracted with dichloromethane (30 mL × 3). The organic layer was washed with saturated aqueous sodium hydrogen carbonate solution (100 mL × 2) and brine (100 mL × 2), dried over anhydrous Na_2SO_4 and evaporated *in vacuo* to dryness. The residue was purified by column chromatography on silica gel with dichloromethane as the eluent to afford **DBHAT** as a deep red solid (0.58 g, 88%). ^{1}H NMR (300 Hz, $CDCl_3$, 298 K): δ (ppm) 8.73 (s, 2 H), 8.64 (s, 2 H), 7.32 (d, J = 7.5 Hz, 8 H), 6.93 (d, J = 8.7 Hz, 8 H), 4.03 (t, J = 6.6 Hz, 8 H), 1.88–1.81 (m, 8 H), 1.38–1.33 (m, 28 H), 0.93 (t, J = 6.3 Hz, 12 H). ^{13}C NMR (75 Hz, $CDCl_{3,}$ 298 K): δ (ppm) 159.28, 145.94, 143.99, 143.21, 132.60, 131.53, 131.35, 114.67, 68.45, 32.31, 29.98, 29.85, 29.74, 26.51, 23.08, 14.50. Anal. calc. for $C_{86}H_{104}N_8O_4$: C, 78.62; H, 7.98; N, 8.53. Found: C, 78.53; H, 7.74; N, 8.76. m/z [MALDI-TOF]: 1314.7 (MH^+).

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