Synthesis, Structure, and Physical Properties of 5,7,14,16-Tetraphenyl-8:9,12:13-bisbenzo-hexatwistacene

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Abstract: A novel compound, 5,7,14,16-tetraphenyl-8:9,12:13-bisbenzo-hexatwistacene (**TBH**), has been successfully synthesized through a retro-Diels–Alder reaction. Single-crystal structure analysis indicated that **TBH** has a twisted configuration with a torsion angle of 27.34°. The HOMO– LUMO gap of **TBH** calculated from

the difference between the half-wave redox potentials ($E_{1/2}^{ox} = +0.40 \text{ eV}$ and $E_{1/2}^{red} = -1.78 \text{ eV}$) is 2.18 eV, which is in good agreement with the band gap

Keywords: OLED • semiconductors • structure elucidation • synthetic methods • twistacene (2.19 eV) derived from the UV/Vis absorption data. In addition, organic light-emitting devices using **TBH** as emitter have been fabricated. The results revealed that **TBH** is a promising red light-emitting candidate for applications in organic light-emitting diodes.

Introduction

During the past decades, organic semiconductors have attracted considerable attention due to fundamental and technological interests.^[1] Compared to inorganic semiconductors, the possibility of flexible, low-cost, and large-area processing makes organic materials more suitable for many applications of devices such as light-emitting diodes (LEDs), field-effect transistors (FETs), biosensors, lasers, memory devices, and photovoltaic cells.^[2] Recently, several promising results have been reported in developing novel organic materials for OLEDs.^[3] However, many OLEDs suffer from the lower emission intensity of organic materials caused by an aggregation quenching effect. This problem could be solved

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into π systems to enlarge the distance between neighboring molecules and to reduce π -stacking interactions.^[4] Because polycyclic aromatic hydrocarbons (PAHs)^[5] have been demonstrated to be a promising system for OLEDs and their properties can be tuned through the precise design of molecules, it should be very interesting to integrate the twist concept into PAHs.^[6,7] Such integration could produce a novel type of compounds, twistacenes. The twisted π -system in such compounds should have a negligible effect on spectroscopic characteristics and electronic properties but reduce the π -stacking interactions. Practically, a twistacene can be realized by introducing bulky substituents on a conjugated framework to create a more sterically hindered π -system. Recently, an efficient white light-emitting diode based on a novel "twistacene" has been demonstrated by Wudl and Yang.^[8]

through molecular designs by introducing the twist concept

In our continued work,^[7] we focus on extending twistacenes that contain only one pyrene unit at the end. Here, we report the synthesis, structure, and physical properties of a novel compound, 5,7,14,16-tetraphenyl-8:9,12:13-bisbenzohexatwistacene (**TBH**, Scheme 1), and its application in OLEDs.



Scheme 1. Molecular structure of 5,7,14,16-tetraphenyl-8:9,12:13-bisben-zo-hexatwistacene (**TBH**).

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Results and Discussion

The synthetic route of **TBH** is presented in Scheme 2. The precursors 1 and 2 were prepared according to reported methods.^[7a, b, 9, 10] The intermediate bridge compound 3 was



Scheme 2. Route for the synthesis of TBH.

obtained in 54% yield by injecting a solution of **1** in dichloroethane (DCE) and isoamyl nitrile alternately into a solution of **2** in DCE under nitrogen atmosphere at reflux temperature. Compound **3** was then heated at 240°C under vacuum for 4 h to afford a red product (**TBH**), which was characterized by FT-IR, ¹H NMR, ¹³C NMR, MALDI-TOF and HRMS spectroscopies (see the Supporting Information). The synthesized twistacene **TBH** is soluble in common organic solvents such as methylene chloride, chloroform, tetrahydrofuran, and *N*,*N*-dimethylformamide.

A single crystal of twistacene **TBH** was grown by slowly evaporating a solution of **TBH** in methylene chloride/methanol (1:1) under nitrogen atmosphere at room temperature (Figure 1). The twistacene **TBH** adopts a triclinic unit cell, space group $P\overline{1}$ (CCDC number: 841858).^[11] The parameter data are: a=7.7160 Å, b=11.1718 Å, c=22.5538 Å, a=92.110°, $\beta=99.101°$, and $\gamma=102.127°$. As shown in Figure 1 a, the crystal structure displayed molecules with a twisted topology with a torsion angle of 27.34°. Figure 1b shows the packing diagram along the *a* axis. Only the pyrene units are involved in π -stacking interactions; the tetracene moieties do not show any $\pi-\pi$ interactions. Compounds with such a twisted structure could be very interesting as materials in OLEDs.

The photophysical properties of compound **TBH** were studied by UV/Vis and fluorescence spectroscopy. In methylene chloride, **TBH** presents three low-energy absorption peaks at 491, 527, and 567 nm (Figure 2 a), a typical characteristic of polycyclic aromatic hydrocarbons.^[4,7] **TBH** emits red light, and the maximum emission peak is at 577 nm with a shoulder at 623 nm under excitation at 491 nm (Figure 2 a). The quantum yield (Φ_f) of **TBH** in methylene chloride was recorded as 0.02 using rhodamine 6G (ethanol solution, Φ_f = 0.95) as the reference at room temperature.^[12] It should be noted that the Stokes shift was very small (10 nm), which indicates that the excited molecules have a small structural deformation. In the film, the absorbance of **TBH** was red-shifted by 5–10 nm (peaks at 496, 537, and 575 nm, see Figure S1 in the Supporting Information). The emission spectrum of



Figure 1. a) Single-crystal structure of **TBH** and b) molecule stacking along the a axis. Carbon atoms are shown as spheres and hydrogen atoms are omitted.



Figure 2. a) UV/Vis and fluorescence spectra of **TBH** in CH_2Cl_2 . b) Cyclic voltammogram of **TBH** in TBAP/ODCB at a scan rate of 100 mV s⁻¹.

TBH in the thin film shows two peaks at 589 and 632 nm, which are slightly red-shifted compared to those in solution. The bathochromic effect might result from a higher percentage of aggregation in the solid state compared to that in dilute solution.

The electrochemical behavior of **TBH** was measured at room temperature in dry *ortho*-dichlorobenzene (ODCB) containing 0.1 M tetrabutylammonium perchlorate (TBAP) as the supporting electrolyte. As shown in Figure 2b, the oxidation and reduction processes were found to be chemically and electrochemically reversible. The HOMO–LUMO gap of **TBH** calculated from cyclic voltammetry measurements was 2.18 eV, a value very similar to the optical band gap (2.19 eV) determined from the UV/Vis data. The thermal gravimetric analysis shows that **TBH** is stable up to 390 °C (Figure 3).



Figure 3. Thermal gravimetric analysis (TGA) of **TBH** under nitrogen atmosphere at a heating rate of 10 °C min⁻¹.

Considering that the twisted structure could decrease the π -stacking interactions, the OLED performance using **TBH** molecules as emitting material was investigated. The devices were fabricated by the physical vapor deposition method (PVD), and the configurations of the OLED devices are as follows: ITO/**TBH** (50 nm)/Alq₃ (50 nm)/LiF (0.6 nm)/Al (100 nm) (OLED-1) and ITO/**TBH** (50 nm)/BCP (10 nm)/Alq₃ (50 nm)/LiF (0.6 nm)/Al (100 nm) (OLED-2), in which ITO is indium tin oxide, Alq₃ is tris(8-hydroxyquinolinato)a-luminum, and BCP is 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline.

The only difference between OLED-1 and OLED-2 is the BCP layer at the **TBH**/Alq₃ interface. BCP and Alq₃ have a LUMO value of approximately 2.9 eV and 3.2 eV, respectively. As a result, the additional barrier for electron injection is smaller in OLED-2. One could see that the current efficiency of OLED-2 (0.04 cd A^{-1}) was smaller than that of OLED-1 (0.06 cd A^{-1}), which suggested that **TBH** had a very low quantum yield, consistent with the results of the fluorescence test experiments.

The electroluminescence (EL) spectra of both OLEDs displayed peaks at 596 and 655 nm; OLED-1 exhibited an additional peak at 524 nm (Figure 4a). The latter peak belongs to Alq₃, thereby further confirming that the electroluminescence results from the **TBH** layer in OLED-2 and that the higher efficiency of OLED-1 is due to light emission from the Alq₃ side. The current efficiency (CE_{max}) and external quantum efficiency (EQE) of device OLED-2 were 0.04 cd A⁻¹ and 0.07 %, respectively, at a current density of 20 mA cm⁻². The maximum luminance (L_{max}) was 262 cd m⁻². These experimental results also indicate that the performance of the device was moderate; thus, an optimization of the device fabrication is needed.

Conclusions

In summary, a novel conjugated molecule, 5,7,14,16-tetraphenyl-8:9,12:13-bisbenzo-hexatwistacene (**TBH**), has been successfully synthesized and characterized. The reduced π - π interactions caused by the twisted structure makes **TBH** an interesting compound for applications in OLEDs. The characteristics of the as-prepared OLED devices suggest that



Figure 4. Characteristics of OLED-1 and OLED-2. a) EL spectra. b) V-L and I-L curves. c) EQE-L and CE-L curves.

TBH is a promising red light-emitting candidate for such applications.

Experimental Section

Materials

All chemical reagents were purchased from Alfa Aesar (VWR Singapore Pte. Ltd., Singapore) or Sigma–Aldrich (Singapore) and used without any further purification. The solvents were purified by standard methods.

Instrumentation

FT-IR spectra were measured on a Perkin–Elmer Spectrum GX spectrophotometer using KBr pellets of compounds. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker 300 MHz spectrometer. MALDI-TOF mass spectrometric measurements were performed on a Shimadzu Biotech AXIMA-TOF^{2TM} instrument. UV/Vis and fluorescence spectra of **TBH** in CH₂Cl₂ and in thin film were recorded on an UV-2501 and an RF-5301 spectrophotometer (Shimadzu), respectively. X-ray crystallographic data were collected at 293 K using a Bruker APEX II CCD diffractometer and graphite-monochromatic Mo_{Ka} radiation (λ =0.71073 Å). Empirical absorption was done, and the structure was solved by the direct method and refined with the aid of the SHELX-TL program package. All hydrogen atoms were calculated and refined with a riding model.

Synthesis of 3

2-Methyl-1,4-diphenylisoquinolin-3-one (**2**, 170 mg, 0.54 mmol) was preheated at 90 °C in degassed 1,2-dichloroethane (DCE). Subsequently, a solution of compound **1** (281 mg, 0.54 mmol) in DCE and isoamyl nitrile (1 mL) were alternately added during 1 h under a nitrogen atmosphere. The mixture was kept overnight at reflux temperature. After that, the reaction mixture was cooled to room temperature, washed with water, and extracted with methylene chloride (40 mL×3). The organic phase was concentrated under reduced pressure, and the crude product was purified by column chromatography (silica gel) with methylene chloride/petrole-um ether (5:4, v/v) to afford the intermediate **3** as a light-yellow solid (225 mg, 54%). FT-IR (KBr): $\bar{\nu}$ =3056, 2926, 2871, 1689, 1455, 1440, 1311, 1184, 828, 751, 704, 539 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, 298 K): δ =8.23–8.20 (m, 2H), 7.92 (s, 1H), 7.88–7.83 (m, 6H), 7.78–7.76 (m, 2H), 7.70 (s, 1H), 7.57–7.29 (m, 16H), 7.11–7.08 (m, 2H), 6.97 (m, 1H), 6.75 (m, 1H), 2.84 ppm (s, 3H); ¹³C NMR (75 MHz, CDCl₃, 298 K): δ =

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178.24, 143.59, 142.20, 141.83, 141.68, 139.22, 138.96, 136.85, 136.65, 134.42, 134.04, 131.94, 131.90, 131.69, 131.50, 130.71, 130.67, 130.48, 130.17, 130.12, 130.08, 129.69, 129.56, 129.23, 129.03, 128.98, 128.73, 128.58, 128.48, 127.97, 127.87, 127.36, 127.31, 127.22, 126.98, 126.87, 126.81, 126.32, 125.86, 125.80, 125.74, 125.44, 124.69, 124.65, 124.49, 123.95, 121.35, 70.92, 61.75, 35.65 ppm; MALDI-TOF MS: calcd for $C_{s8}H_{37}NO$ [*M*]: 763.29, found [*M*-(Me–N=C=O)] 706.06. HR-MS: calcd for $C_{s8}H_{37}NO$ [*M*+1], 764.2953; found, 764.2961.

5,7,14,16-tetraphenyl-8:9,12:13-bisbenzo-hexatwistacene (TBH)

The intermediate **3** (120 mg, 0.16 mmol) was purged three times with nitrogen gas and then gradually heated at 240 °C for 4 h to form a red powder. The crude product was washed thrice with ether, affording **TBH** as a red solid (87 mg, 78%). FT-IR (KBr): $\bar{\nu}$ =3056, 3022, 1600, 1483, 1435, 1394, 1305, 1168, 1072, 1024, 825, 756, 701, 543 cm⁻¹; ¹H NMR (300 MHz, CDCl₃, 298 K): δ =8.36 (s, 2H), 7.82–7.74 (m, 9H), 7.51–7.23 ppm (m, 23 H); ¹³C NMR (75 MHz, CDCl₃, 298 K): δ =141.77, 138.82, 137.34, 136.44, 132.12, 131.25, 130.76, 130.72, 130.63, 129.45, 129.26, 128.88, 128.56, 128.27, 127.21, 127.14, 126.72, 126.25, 126.11, 125.83, 124.91, 124.79 ppm; MALDI-TOF MS: calcd for C₅₆H₃₄ [*M*+1], 707.2739; found, [*M*], 706.17. HR-MS: calcd for C₅₆H₃₄ [*M*+1], 707.2739; found, 707.2742.

Device Fabrication

First, the ITO glass substrates were treated using routine cleaning procedures, such as washing in detergent and subsequent ultrasonication in acetone, isopropyl alcohol, and deionized water, respectively. After drying in an oven, the ITO substrates were treated using O_2 plasma to remove possible organic residues. Subsequently, the substrates were loaded into the deposition chamber where all materials were deposited using a thermal evaporation method; details were described previously.^[13]

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