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Synthesis, structure, and optoelectronic properties of a new twistacene 1,2,3,4,6,13-hexaphenyl-7 : 8,11 : 12-bisbenzo-pentacene†

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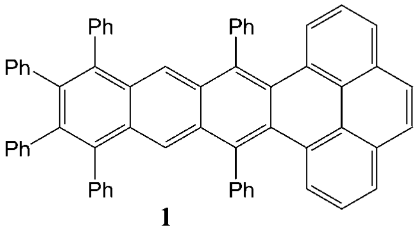
We report the synthesis, optical and electrochemical properties, as well as the fabrication of light-emitting devices for a new twistacene 1,2,3,4,6,13-hexaphenyl-7 : 8,11 : 12-bisbenzo-pentacene (HBP **1**). Its structure, determined by X-ray crystallography, confirmed that this material has a twisted topology with the torsion angle as high as 23.0°. HBP **1** showed bright green emission both in solution and solid state. The HOMO–LUMO gap of HBP **1** calculated from the difference between the half-wave redox potentials ($E_{1/2}^{ox} = +0.74$ eV and $E_{1/2}^{red} = -1.93$ eV) is 2.67 eV, which is in good agreement with the band gap, 2.64 eV, derived from the UV-Vis absorption data. Organic light emitting devices using HBP **1** as the emitters have been fabricated. The results revealed that twistacenes are promising materials to enhance the efficiency of OLEDs.

Introduction

Over past decades, organic electronics based on polycyclic aromatic hydrocarbons (**PAH**s) have received intensive scientific and technological interest because of their tunable electrical and optical properties by proper molecular design as well as their mechanical flexibility and capability for large-area processing with low cost, and improving performance.[1–5] As one member of **PAH**s, pyrene-based materials have been widely employed as active layers in organic semiconducting devices such as field-effect transistors, solar cells, and organic light-emitting devices (OLEDs).[6–8] Their excellent performance encourages us to examine a novel pyrene-based twistacene in OLEDs.

It is well-known that introducing bulky substituents on their conjugated framework can twist the **PAHs**[9,10] and create a more sterically hindered π-system and, in effect, decrease π···π attractions. Such a twist has negligible effect on the spectroscopic characteristics and electronic properties of **PAH**s when compared to their unsubstituted planar parent structures. These twisted π-systems provide an attractive molecular toolset for applications in OLEDs because non-twisted π-systems normally have strong π-stacking interactions, which will lead to **PAH**s concentration-quenching effect[11] and ultimately decrease the efficiency of the devices. Recently, an efficient white light-emitting diode based on a novel "twistacene" has been demonstrated by Wudl and Yang.[10] Our continuing pursuit of developing more effective emitters based on the twist concept led us to design and synthesize more bulky twistacenes. Herein, we reported the synthesis of a novel twistacene homologue 1,2,3,4,6,13-hexaphenyl-7 : 8,11 : 12-bisbenzo-pentacene (HBP **1**, Scheme 1) and its application in OLEDs.

1,2,3,4,6,13-Hexaphenyl-7 : 8,11 : 12-bisbenzo-pentacene (HBP **1**, Scheme 1) was prepared through benzyne-trapping chemistry between the aryne precursor **2** and dienenone **3** (Scheme 2). The single-crystal X-ray structural analysis of HBP **1** shows the anticipated twist topology in the dibenzopentacene scaffold. Taking advantage of this twist feature, several OLEDs using HBP **1** as emitters were fabricated and their light-emitting properties were studied.



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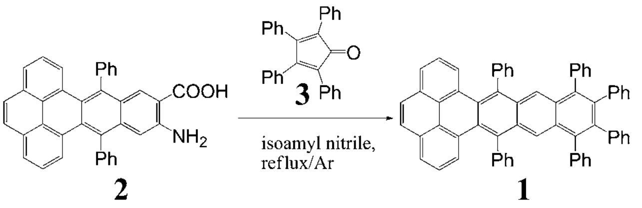
Scheme 1 The structure of 1,2,3,4,6,13-hexaphenyl-7 : 8,11 : 12-bisbenzo-pentacene (HBP **1**).



Scheme 2 The synthetic route to 1,2,3,4,6,13-hexaphenyl-7 : 8,11 : 12-bisbenzo-pentacene (HBP **1**).

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Experimental

Materials

All starting materials were used as received without further purification. The compounds **2** and **3** were synthesized based on the reported procedures.[12,13]

1,2,3,4,6,13-Hexaphenyl-7 : 8,11 : 12-bisbenzopentacene (HBP 1). To a stirring solution of cyclopentadienone **3** (1 mmol) pre-heated at 90 °C, the corresponding acid **2** (1 mmol) (dispersed in DCE) and isoamyl nitrite (1 mL) in DCE (15 mL) were added alternately (the total addition time is 30 min). After addition, the solution was kept stirring at 90 °C overnight. The yellow–orange compound was filtered and washed with dichloromethane. Yield: 62% based on acid **2**; mp: >300 °C; ^{1}H NMR (ODCB, 500 MHz, δ ppm) 8.15(s, 2H), 7.73(d, 2H), 7.47(s, 2H), 7.43(d, 2H), 7.13(dd, 4H), 7.05–6.98(m, 10H), 6.87–6.75(m, 10H), 6.66–6.57(t, 4H), 6.48–6.47(t, 2H); ^{13}C NMR (CD_2Cl_2, 125 MHz, δ ppm)141.5, 140.6, 139.2, 138.37, 138.19, 136.4, 131.9, 131.2, 130.9, 130.62, 130.57, 130.54, 130.4, 128.9, 128.7, 128.4, 127.3, 127.0, 126.5, 126.3, 126.0, 125.8, 125.77, 125.5, 125.2, 124.6; IR (Drift, cm^{-1}) 3051, 3026, 2925, 2872, 1599, 1492, 1443, 1359, 1073, 1028, 902, 830, 728, 675, 603, 536, 448; EI exact mass 808.3119, calcd: 808.3130.

Cyclic voltammetry (CV) measurements

CV was performed with a three-electrode cell in an acetonitrile solution of tetrabutylammonium perchlorate (0.1 M, Bu_4NClO_4, abbreviated as TBAP) at a scan rate of 100 mV s^{-1}. A Pt wire, glassy carbon, and the Ag/AgCl electrode were used as a counter electrode, a working electrode, and a reference electrode, respectively. Its potential was corrected to the saturated calomel electrode (SCE) by measuring the ferrocene/ferrocenium couple in this system (0.44 V *versus* SCE).

X-Ray crystal structure

Single-crystal data[14] was collected at 150 K with graphite-monochromatized Mo-Kα radiation (λ = 0.71073 Å). The cell parameters were obtained from the least squares refinement of the spots using the SMART program. The structure was solved by the direct method using SHELXS-97, which revealed the positions of all non-hydrogen atoms. This is followed by several cycles of full-matrix least-squares refinement. Absorption corrections were applied by using SADABS.[15] Hydrogen atoms were included as fixed contributors to the final refinement cycles. The position of hydrogen atoms were calculated on the basis of idealized geometry and bond length. In the final refinement, all non-hydrogen atoms were refined with anisotropic thermal coefficients.

Fabrication and evaluation of OLEDs

The ITO (*I*ndium-*T*in-*O*xide) glass was cleaned using a routine cleaning procedure, which includes ultrasonication in acetone, followed by ethanol, and rinsing in de-ionized water. A clean ITO glass exhibited the resistance on the order of 50 Ω/square. Before deposition, the ITO was treated by oxygen plasma at 10 Pa for 2.5 min. Evaporation of organic materials and metals was carried out under high vacuum conditions (about 2 × 10^{-4} Pa). Electroluminescence spectra of the fabricated devices were measured with a PR650 Spectra Scan spectrometer. Current density–voltage characteristics were recorded by a Yokogawa source measurement unit. All measurements were carried out at room temperature under ambient conditions without any encapsulation.

Results and discussion

Synthesis

HBP **1** was prepared through a [4 + 2] cycloaddition involving *in situ* aryne as dienophile and cyclopentadienone **3** as diene (Scheme 2). The intermediate aryne precursor **2** was synthesized according to our previous procedure,[13] through the intermediate step-by-step bisbenzyne precursor. To avoid the nucleophilic displacement of the nitro group by the hydroxyl group, the aryne precursors **2** were introduced slowly as a 1,2-dichloroethane (DCE) suspension to an awaiting cyclopentadienone **3** with isoamyl nitrite in refluxing DCE. These conditions afforded the HBP **1** in 62% yield without any evidence of phenol formation.

Crystal structure

Single crystals were obtained in 1,2,4-trichlorobenzene. The molecular structure of HBP **1** with atomic labeling is illustrated in Fig. 1a and crystal data given in Table 1. As shown in Fig. 1b, there is a significant twist in the bisbenzo-pentacene π-system. The terminal pyrene moiety and anthracene component are not coplanar due to the interaction between the phenyl substituents and the corner benzo groups. The torsional angles measured at

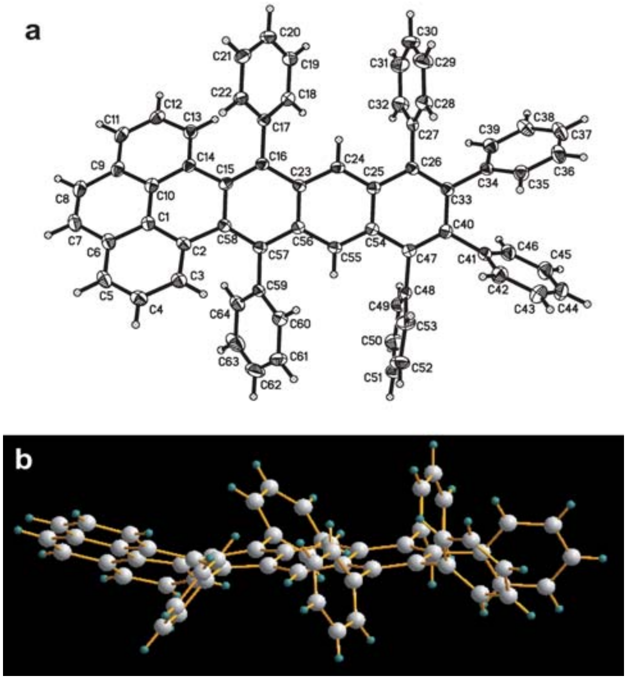

Fig. 1 (a) X-Ray structure of **1** showing the crystallographic numbering scheme. (b) Side-view of the structure of HBP **1**.

Table 1 Crystal data and structure refinement for HBP **1**

Identification code	HBP **1**·2(1,2,4-trichlorobenzene)
Empirical formula	$C_{76}H_{46}Cl_6$
Formula weight	1171.83
Temperature	150(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	$P2_1/n$
Unit cell dimensions	$a = 8.0402(4)$ Å, $\alpha = 90°$ $b = 18.3260(9)$ Å, $\beta = 91.2270(10)°$ $c = 38.1833(18)$ Å, $\gamma = 90°$
Volume	5624.8(5) Å^3
Z	4
Density (calculated)	1.384 Mg m^{-3}
Absorption coefficient	0.353 mm^{-1}
$F(000)$	2416
Crystal size	$0.40 \times 0.20 \times 0.20$ mm^3
2θ	1.54 to 28.31°
Index ranges	$-10 \leq h \leq 10$, $-24 \leq k \leq 24$, $-50 \leq l \leq 50$
Reflections collected	50371
Independent reflections	13704 [R(int) = 0.0696]
Completeness	97.8%
Max/min transmission	0.9927 and 0.9215
Goodness-of-fit on F^2	1.010
Final R indices $I > 2\sigma(I)$	$R_1 = 0.0556$, w$R_2 = 0.1051$
R indices (all data)	$R_1 = 0.1708$, w$R_2 = 0.1368$

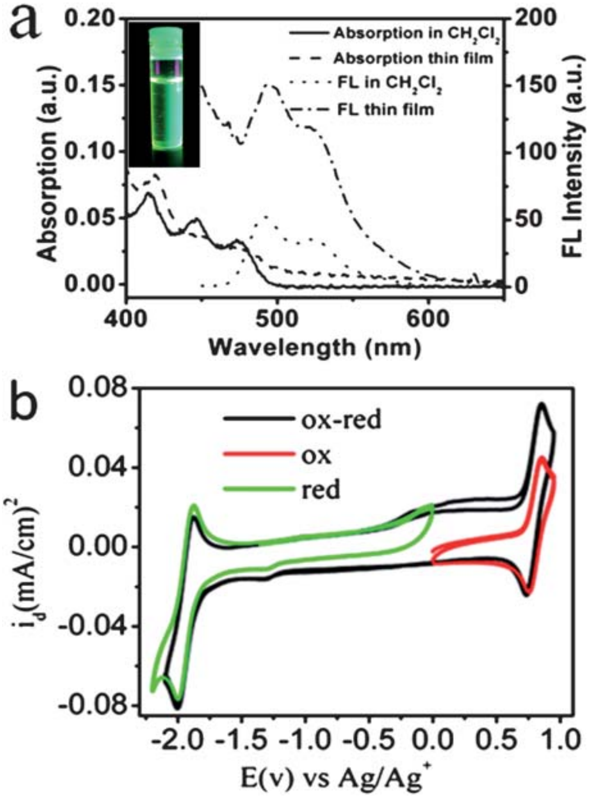

Fig. 2 (a) UV-Vis and fluorescence spectra of HBP **1** in DCM and in solid films. Inset: the fluorescence picture of HBP **1**. (b) Cyclic voltammogram of 10^{-5} M HBP **1** in 0.1 M TBAP/CH_3CN (first three cycles, *vs.* Ag/AgCl).

C57–C56–C2–C3 and C13–C14–C15–C16 in **1** are 20.6° and 23.0°, respectively.

Optical properties and electrochemical characterization

The spectroscopic properties of HBP **1** were recorded at room temperature in dichloromethane (DCM) solution. As shown in Fig. 2a, HBP **1** displays a broad absorption band between 400 and 500 nm due to π–π* transition derived from the conjugated framework. The emission spectrum shows two peaks at 491 nm and 521 nm. The film fluorescence (prepared by drop coating) shows an obvious red-shift comparing to that in DCM solution. The PL quantum yield of HBP **1** in DCM solution was calculated to be 0.69 by using 9,10-diphenylanthracene as a reference standard (ethanol solution $\Phi_f = 0.95$).[16]

Cyclic voltammetry (CV) of **1**, measured at room temperature in CH_3CN solution containing 0.1 M tetrabutylammonium perchlorate (TBAP), shows that both oxidation and reduction processes are chemically and electrochemically reversible (Fig. 2b). The HOMO–LUMO gap calculated from the difference between the half-wave redox potentials ($E_{1/2}^{ox} = +0.74$ eV and $E_{1/2}^{red} = -1.93$ eV) is 2.67 eV. This value is in good agreement with the band gap, 2.64 eV, derived from the UV–Vis absorption data.

OLEDs

HBP **1** is incorporated as an emitter in an organic light-emitting diode (OLED). The OLED has a structure of ITO/NPB (70 nm)/CBP: HBP **1** (x% wt) (30 nm)/BCP (20 nm)/Alq_3 (30 nm), where ITO is indium-tin-oxide; NPB is *N*,*N*′-bis(naphthalen-1-yl)-*N*,*N*′-bis(phenyl)-benzidine, a common hole-transporting layer; CBP is 4,4′-bis(carbazol-9-yl)biphenyl, a common host material; BCP is 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, a common hole-blocking layer; Alq_3 is tris(8-hydroxy-quinolinato) aluminium, a common electron-transporting layer. The doping concentration was 2 and 10 wt% for HBP **1** in CBP. Fig. 3

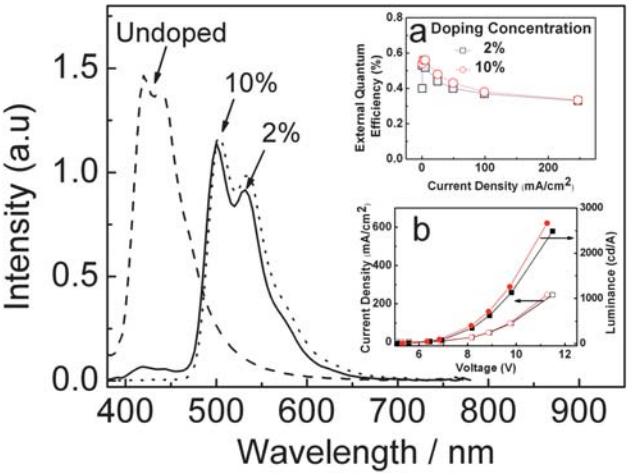

Fig. 3 Emission spectra for devices with different concentration of doping of HBP **1** at a current density of 25 mA cm^{-2} and the undoped device with a structure of NPB/CBP/BCP/Alq_3. Inset: (a) the EQE as a function of current density and (b) current density *versus* voltage for devices with different concentration of doping of HBP **1**.

shows the emission spectra for devices measured at a constant current density of 25 mA cm^{-2}. HBP **1** emits a green color with a peak emission at 500 nm. The inset (a) of Fig. 3 shows the external quantum efficiency (EQE) as a function of current density. The EQE is the highest (0.56% photons/electron) measured for any devices with a doping concentration of 10%. For the device with a doping concentration of 2%, the EQE drops slightly to 0.52% photons/electron. This EQE drop is followed by the appearance of a blue peak at 420 nm, which corresponds to the host emission, indicating an incomplete host (CBP) to guest (HBP **1**) energy transfer. It can also be seen that the EQE drops significantly as the current density increases. The EQE drops from 0.66% (at current density of 2.5 mA cm^{-2}) to 0.33% photons/electron (at current density of 250 mA cm^{-2}), corresponding to a 50% drop. This result indicates that the biexcitonic annihilation processes, such as the singlet–singlet, singlet–polaron annihilations, which are responsible for the EQE roll-off with current density,[17] are significant. Inset (b) of Fig. 3 shows the current density and brightness *versus* voltage for the corresponding devices. It demonstrates that there is no significant difference in term of carrier transport for all devices. The brightness (luminance) of the device with doping concentration of 10% is slightly higher than that with doping concentration of 2%. The maximum brightness of 2700 cd m^{-2} [Commission Internationale de l'éclairage (CIE) coordinate of ($x = 0.26$, $y = 0.61$)] and 2500 cd m^{-2} [CIE coordinate of ($x = 0.25$, $y = 0.54$)] were achieved for doping concentration of 10% and 2%, respectively.

Conclusions

A new twistacene 1,2,3,4,6,13-hexaphenyl-7 : 8, 11 : 12-bisbenzo-pentacene (HBP **1**) was designed and synthesized. Its single crystal structure clearly shows that this material has a twist structure topology with the torsion angles as high as 23.0°. The material performs very well in OLEDs with a green light emission. Our results greatly support twistacenes as promising candidates for enhancing the efficiency of OLEDs.

Acknowledgements

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