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# Synthesis, Crystal Structure, Thermal Behavior and Optical Properties of An Organic Light-Emitting Diode Compound

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## Abstract

The title compound,  $C_{53}H_{36}N_5$ , was synthesized and characterized by IR and single-crystal X-ray diffraction analysis. The structure analysis indicates that the compound crystallizes in the triclinic space group  $P-1$  and employs  $C-H\cdots\pi$  and  $\pi\cdots\pi$  weak interactions to stabilize the structure. The compound exhibits good thermal stability, which can maintain the skeleton until 400 °C. It can be used for green organic light-emitting diode devices exhibiting good performance.

## Keywords

9-(3'-(4,6-diphenyl-1,3,5-triazin-2-yl)-[1,1'-biphenyl]-3-yl)-14-phenyl-9,14-dihydrodibenzo[2,3:6,7]azepino[4,5-*b*]indole; Crystalline structure; Organic light-emitting diode

## Introduction

Organic light-emitting diodes (OLEDs) are light-emitting diodes whose emission electroluminescent layer is a thin film of organic compounds that emit light under the action of an electric current<sup>[1]</sup>. They have many advantages, such as flexibility, low power consumption, low weight, high contrast, full-color capability, wide viewing angle, self-emitting property, high luminous efficiency and etc<sup>[2]</sup>. With these advantages, OLEDs have become a significant display technology and have been used in various electronic devices in our society, such as flat-panel displays for televisions and smartphones, replacing liquid-crystal displays (LCDs). In the near future, OLED displays will be used for a wide variety of applications. Therefore, over the past decades, many types of light emitting organic semiconductors have been designed and developed<sup>[3]</sup>, and these efforts are continuing in the search for materials that are easy to synthesize and exhibit improved solution processing capabilities and high efficiency<sup>[4]</sup>. The incorporation of heteroatoms result in considerable changes in the corresponding phases and/or in the physical properties of the observed phases, as most of the heteroatoms (S, O, and N) commonly introduced are more polarizable than carbon<sup>[5]</sup>.

To sum up, in the process of expanding OLED materials with good performance, in this paper we report the design, syntheses, crystal structure, thermal stability and optical properties of a novel OLED molecule 9-(3'-(4,6-diphenyl-1,3,5-triazin-2-yl)-[1,1'-biphenyl]-3-yl)-14-phenyl-9,14-dihydrodibenzo[2,3:6,7]azepino[4,5-*b*]indole (**1**) in which N heteroatoms are introduced in the structure. This new material exhibits good thermal stability and good green OLED performance.

## Experimental

All chemicals were of analytical reagent grade and used without further purification.

### Physical Measurements

The Infrared (IR) spectra were recorded as KBr pellets on a Bruker T27 FT-IR spectrometer.

Thermogravimetric analysis (TGA) was performed on a TA Q50 thermal analyzer with a heating rate of 10 K min<sup>-1</sup> under a nitrogen atmosphere. Optical properties were performed on the PR670 Spectrascan instrument, Keithley.

### **X-ray crystallography and structure solution**

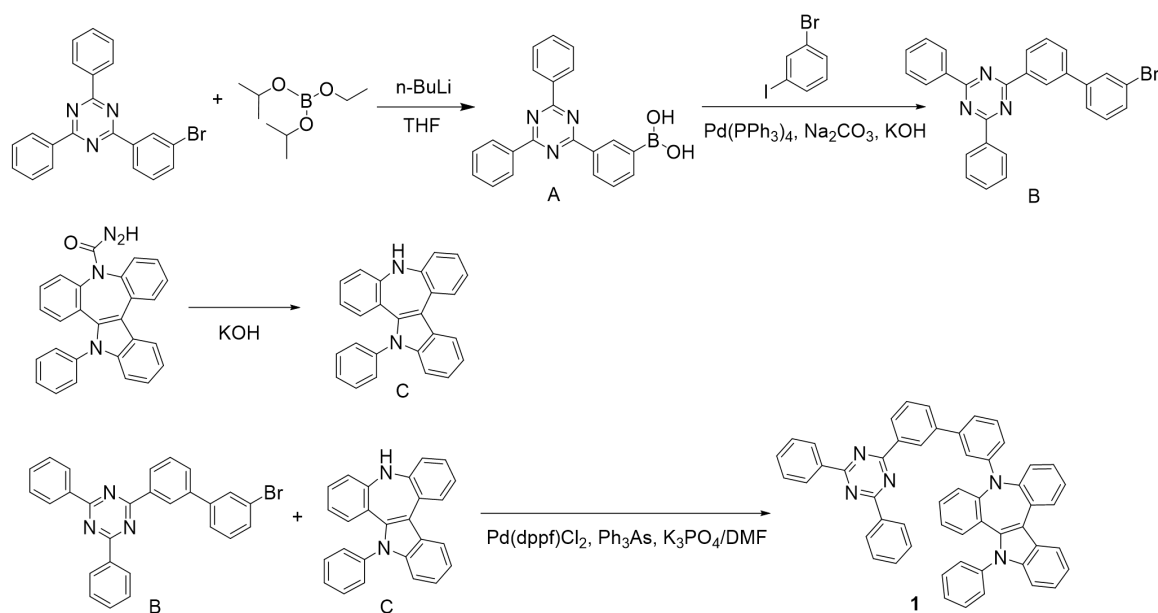
Single-crystal X-ray diffraction data for **1** were collected on a Bruker Smart Apex II diffractometer, equipped with 1 K CCD instrument, using a graphite monochromator with Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) at room temperature. Cell parameters were determined using SMART software. Data reduction and correction were performed using SAINTPlus. Absorption corrections were made via SADABS program<sup>[6]</sup>.

The structures were solved by direct methods with the program SHELXS-2014 package<sup>[7]</sup>. All non-H atoms were refined anisotropically. The H atoms attached to C and N atoms were added theoretically and treated as riding on the concerned atoms. The final cycle of full-matrix least-squares refinement was based on observed reflections and variable parameters.

## **Results and Discussion**

### **The synthesis of compound 1**

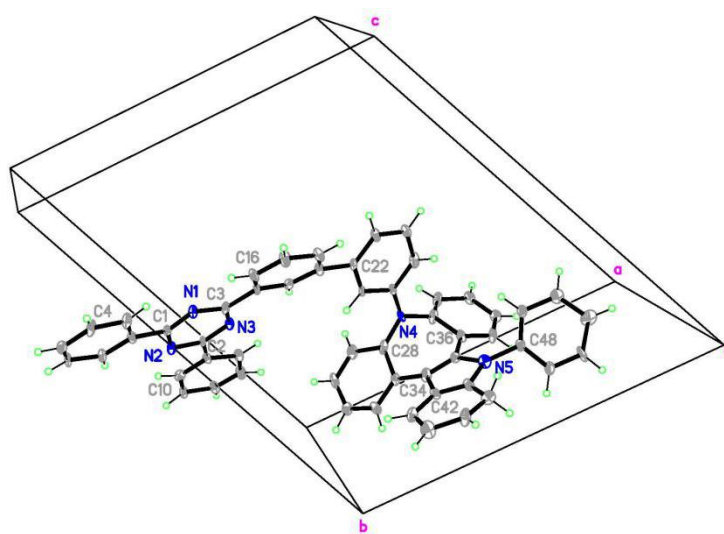
Scheme 1. Diagram showing the synthesis of compound **1**.



The synthesis route of compound **1** was given in Scheme 1. As shown in Scheme 1, compound **1** was prepared by the reaction of B and C. Firstly, 2-(3-bromophenyl)-4,6-diphenyl-1,3,5-triazine (1 mol) and ethyl diisopropyl borate (1 mol) were reacted in THF at  $-78\text{ }^{\circ}\text{C}$  with the addition of n-BuLi (1 mol), then flavescens powder of (3-(4,6-diphenyl-1,3,5-triazin-2-yl)phenyl)boronic acid (A) was obtained with the yield of 80%. Secondly, added 1-bromo-3-iodobenzene (0.8 mol) and Pd(PPh<sub>3</sub>)<sub>4</sub> (0.004 mol) to A (0.8 mol) with the addition of Na<sub>2</sub>CO<sub>3</sub> (1 mol) and KOH (1 mol), kept the reaction at room temperature, then flavescens powder of 2-(3'-bromo-[1,1'-biphenyl]-3-yl)-4,6-diphenyl-1,3,5-triazine (B) was obtained with the yield of 65%. Thirdly, 14-phenyl-9,14-dihydrodibenzo[2,3:6,7]azepino[4,5-b]indole (C) was obtained by the reaction of diazenyl(14-phenyldibenzo[2,3:6,7]azepino[4,5-b]indol-9(14H)-yl)methanone in KOH at  $80\text{ }^{\circ}\text{C}$  with the yield of 93%. Lastly, compound **1** can be obtained by the reaction of B and C in DMF at  $80\text{ }^{\circ}\text{C}$  with the addition of Pd(dppf)Cl<sub>2</sub> (1 mol), Ph<sub>3</sub>As (1 mol) and K<sub>3</sub>PO<sub>4</sub> (1 mol) in 98% yield. Single crystals in the form of block were obtained by slow evaporation from mother solution, with 65% yield. IR ( $\nu/\text{cm}^{-1}$ , s for strong, m medium, w weak): 3433w, 3062m, 1595m, 1516s, 1446m, 1398w, 1368s, 1319m, 1265w, 1176w, 1090w, 1027w, 845m, 763s, 719w, 693s, 645m, 617w, 557w, 501w.

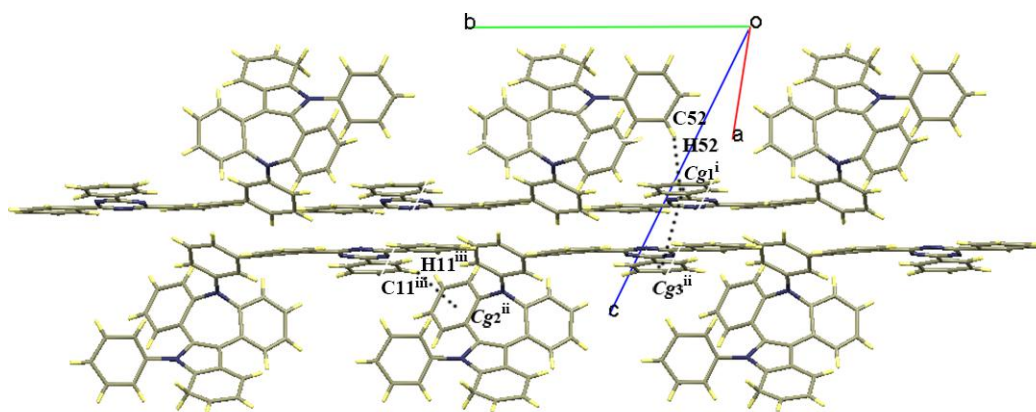
### Description of the structure of compound **1**

Single-crystal X-ray diffraction revealed that compound **1** crystallized in the triclinic with *P*-1 space group. The asymmetric unit consisted of one crystallographically independent organic molecule of **1**. The whole molecular structure was shown in Figure 1. The whole molecule contains five nitrogen atoms employed in the triazine, azepine and indole rings respectively. The 2,4,6-triphenyl-1,3,5-triazine part is almost in a plane, while the azepine ring is twisted. The dihedral angles between the triazine and indole rings, and the benzene rings on both sides of the azepine are 49.9 and 57.8° respectively. All C-C and C-N bond distances and the bond angles are typical and comparable to those observed in the heterocyclic compounds [8-10].



**Figure 1.** The whole molecular structure of compound **1** and displacement ellipsoids are drawn at the 10% probability.

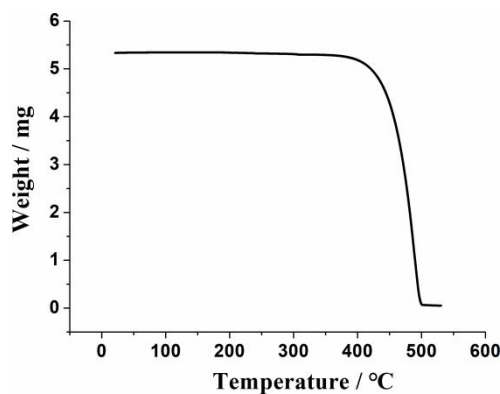
It is interesting that the structure of **1** is further stabilized by extensive intermolecular C–H $\cdots$  $\pi$  hydrogen bonds and weak  $\pi\cdots\pi$  interactions between aromatic rings, giving rise to a 3D network structure. As shown in Figure 2, atom H52 and H11<sup>iii</sup> are involved in the C–H $\cdots$  $\pi$  interactions with the centroids (*Cg*) of the C10 – C15 and C36 – C42 aromatic rings respectively; the H $\cdots$ *Cg* distances are 2.835(2) and 2.873(2) Å and the C–H $\cdots$ *Cg* angles are 140.8(2) and 147.9(9)° [symmetry codes: (i) *x*, *y*–1, *z*; (ii) –*x*+1, –*y*+1, –*z*+1; (iii) –*x*+1, –*y*+2, –*z*+1]. Moreover, the interatomic distance of  $\pi\cdots\pi$  interaction between aromatic rings is about 3.632(4) Å.



**Figure 2.** The packing diagram of complex **1**. Dashed lines represent the C–H $\cdots$  $\pi$  hydrogen bonds and  $\pi\cdots\pi$  interactions between aromatic rings.

### Thermal analysis

TGA was performed in the range of 20–530 °C. As shown in Figure 3, compound **1** can maintain the skeleton until 400 °C, showing extremely high thermal stability. After that, as the temperature rises, the framework begins to decompose rapidly.



**Figure 3.** TGA plots of compound **1**.

### Optical properties

The compound **1** can be used as a hole-barrier material and has good performance in green phosphorescent devices. Figure 4 shows the Efficiency-Current density curve and the emission spectra of the optical devices with different hole-barrier film thickness of **1**. With the increase of the hole-barrier film thickness, the device efficiency increases, and the device efficiency is the best when the thickness is 25 nm.

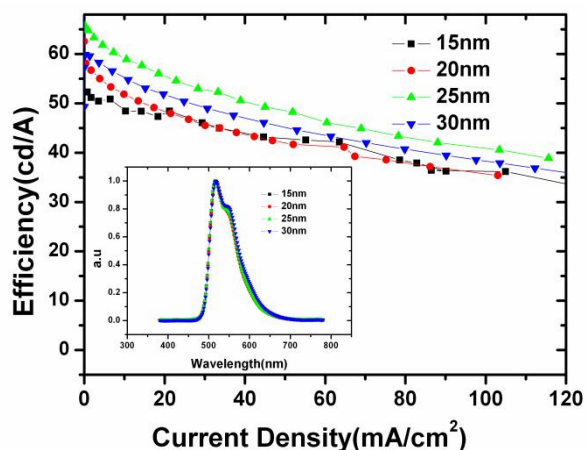


Figure 4. Efficiency-Current density curve and the emission spectra (inserted) of the optical devices with different hole barrier film thickness (15-30 nm) of 1.

## Conclusions

We have synthesized and structurally characterized a novel organic light-emitting diode compound

9-(3'-(4,6-diphenyl-1,3,5-triazin-2-yl)-[1,1'-biphenyl]-3-yl)-14-phenyl-9,14-dihydrodibenzo[2,3:6,7]azepino[4,5-*b*]indole. The crystal structure showed that it is a carboheterocyclic aromatic compound with intermolecular C–H $\cdots\pi$  hydrogen bonds and weak  $\pi\cdots\pi$  interactions between aromatic rings, giving rise to a 3D network structure. The research indicates that the compound has good thermal stability and good performance in green phosphorescent devices. It is a potential green organic light-emitting diode material.

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