
Yuanyuan Sun
Xi'an Manareco New Material Co., Ltd., Affiliated 71#, 2nd Jinye Rd, Gaoxin District, Xi'an, Shanxi, People’s Republic of China.
E-mail: syy@xarlm.com

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···π and π···π 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\(^1\). 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\(^2\). 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\(^3\), and these efforts are continuing in the search for materials that are easy to synthesize and exhibit improved solution processing capabilities and high efficiency\(^4\). 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\(^5\).

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\(^{-1}\) 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 (\(\lambda = 0.71073\) Å) 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\(^6\).

The structures were solved by direct methods with the program SHELXS-2014 package\(^7\). 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 °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(PPh₃)₄ (0.004 mol) to A (0.8 mol) with the addition of Na₂CO₃ (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-phenyl)dibenzo[2,3:6,7]azepino[4,5-b]indol-9(14H)-yl)methanone in KOH at 80 °C with the yield of 93%. Lastly, compound 1 can be obtained by the reaction of B and C in DMF at 80 °C with the addition of Pd(dpdpf)Cl₂ (1 mol), Ph₃As (1 mol) and K₃PO₄ (1 mol) in 98% yield. Single crystals in the form of block were obtained by slow evaporation from mother solution, with 65% yield. IR (υ/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⋯π hydrogen bonds and weak π⋯π interactions between aromatic rings, giving rise to a 3D network structure. As shown in Figure 2, atom H52 and H11\(^{iii}\) are involved in the C–H⋯π interactions with the centroids (\( Cg \)) of the C10 – C15 and C36 – C42 aromatic rings respectively; the H⋯\( Cg \) distances are 2.835(2) and 2.873(2) Å and the C–H⋯\( Cg \) angles are 140.8(2) and 147.9(9)° \([\text{symmetry codes: (i) } x, y-1, z; (\text{ii}) -x+1, -y+1, -z+1; (\text{iii}) -x+1, -y+2, -z+1]\). Moreover, the interatomic distance of π⋯π interaction between aromatic rings is about 3.632(4) Å.
Figure 2. The packing diagram of complex 1. Dashed lines represent the C–H···π hydrogen bonds and π···π 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.
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⋯π hydrogen bonds and weak π⋯π 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.

References


