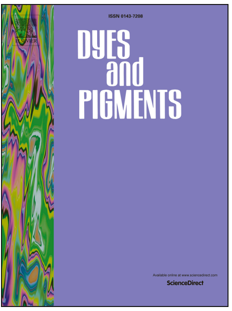

A novel spiro-annulated host based on carbazole with good thermal stability and high triplet energy for efficient blue and green phosphorescent organic light-emitting diodes

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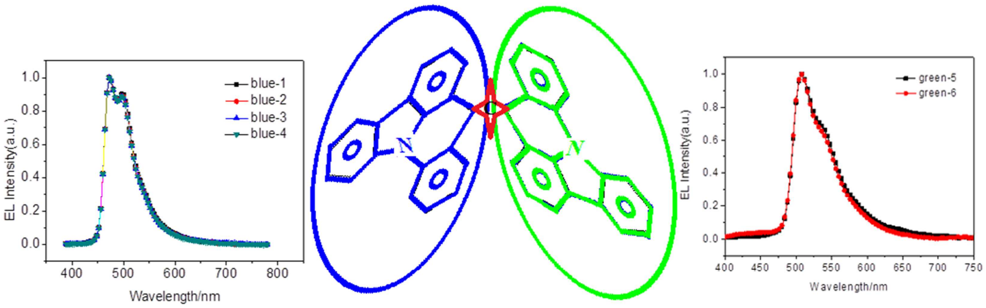

A novel spiro-annulated host material (H2) based on carbazole for efficient blue and green phosphorescent organic light-emitting diodes was synthesized and characterized. The devices based on H2 exhibit excellent performance due to its high triplet energy (2.90 eV) and good thermal stability. Four different blue devices were fabricated with the best performance of a maximum current efficiency of 12.2 cd A^{-1} and a maximum power efficiency of 8.8 lm W^{-1}. The performance of H2 was better than that of 4,4’-bis(9-carbazolyl)-biphenyl (CBP) which is a star host material in green devices.

A novel spiro-annulated host based on carbazole with good thermal stability and high triplet energy for efficient blue and green phosphorescent organic light-emitting diodes

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Abstract: A novel spiro-annulated host based on carbazole was synthesized and fully characterized. The thermal, photophysical and electrochemical properties of this host material were investigated. The host exhibited good thermal stabilities with a decomposition temperature of 427 ^{o}C and also exhibited excellent morphological properties. A high triplet energy (2.90 eV) was obtained for the host due to its spiro-annulated structure. This host was proved to be effective for both blue and green phosphorescent organic light-emitting diodes. Four different blue devices were fabricated with the best performance that a maximum current efficiency of 12.2 cd A^{-1}

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and a maximum power efficiency of 8.8 lm W^{-1}. The performance of the host was better than that of 4,4’-bis(9-carbazolyl)-biphenyl which is the benchmark host material in green PHOLED devices.

Keywords: Phosphorescent organic light-emitting diodes; spiro-annulated carbazole derivatives; amorphous materials; high triplet energy.

1. Introduction

Phosphorescent organic light-emitting diodes (PHOLEDs) have attracted tremendous attention for boosting the theoretical internal quantum efficiency (IQE) from 25% to 100% since the pioneering work by Forrest and Thompson in 1998 [1]. A series of blue/green/red PHOLEDs with high efficiency have been reported [2-5]. Host materials play a crucial role in the PHOLEDs, and an ideal host material should have the good thermal stability, a suitable HOMO-LUMO level, a high triplet energy (E_T) [6,7]. Therefore, developing novel promising host materials is important for the development of useable efficient PHOLEDs.

Nowadays, considerable attention has been directed to the design of novel hosts for effective PHOLEDs. In view of the above-mentioned key properties of host materials, spiro-annulated structures have been proven to be beneficial for improving the efficiency of PHOLEDs [8-10], because of the high thermal stability of the sprio-annulated structures which could be attributed to their bulky and orthogonal configuration [11,12]. Additionally, the perpendicular arrangements of the spiro-conformation give rise to a highly steric rigid structure, the conjugation of the two units in each side of the spiro-carbon is disconnected by the central sp^3-hybridized spiro-carbon, thus, preserving a high triplet energy (E_T) [13,14]. Therefore, these features make spiro-annulated structures highly attractive as potential host materials for fabricating effective PHOLEDs. Various spiro-annulated structures have been investigated as host materials for PHOLEDs [8-15].

It is well known that carbazole derivatives with excellent photophysical properties have been widely used as host materials were in OLEDs [16-18]. In this work, by combining the spiro-annulated structures and carbazole derivatives, we designed a novel small molecule (H2) based on spiro-annulated carbazole structure. It can be anticipated that H2 could keep the unique properties of carbazole with high triplet energy and good hole transport ability by introducing a spiro-annulated structure. The thermal, photophysical and electrochemical properties of H2 were fully investigated. Atomic force microscopy (AFM) was also applied to explore the intrinsic morphology of the thin film based on H2. Moreover, blue and green PHOLEDs with H2 as host materials were fabricated, a maximum current efficiency of 12.2 cd A^{-1} and a maximum power efficiency of 8.8 lm W^{-1} were obtained for blue PHOLEDs, the H2-based device exhibited a greatly improved performance as compared to a conventional 4,4’-bis(9-carbazolyl)-biphenyl (CBP)-based device for green PHOLEDs.

2. Experimental

2.1 General Information

All reagents that we have used in the route were purchased from Shanghai Taoe chemical technology Co., Ltd. and received without further purification. Carbazole and 1,2-dichlorobenzene were purchased from Adamas-beta.

The ^{1}H and ^{13}C NMR spectra were obtained using a Bruker AM 400 spectrometer, the mass spectra were recorded on a Waters LCT Premier XE spectrometer. The cyclic voltammograms were obtained using a Versastat II electrochemical workstation with conventional three electrodes containing an SCE reference electrode (the ferrocene/ferrocenium (Fc/F_C^+) redox couple as external standard), a glassy-carbon working electrodes and a platinum-wire counter electrode. The UV/Vis spectra and PL spectra were recorded on a Nicolet CARY 100 spectrophotometer and a Varian Cary fluorescence spectrophotometer, respectively. The differential scanning calorimetry (DSC) analysis and the thermogravimetric analysis (TGA) were performed under a nitrogen atmosphere on a NETZSCH STA 409 PC/PG instrument and a TGA instrument, respectively.

2.2. Synthesis

2.2.1. 9-(2-bromophenyl)-9H-carbazole (1)

In a one-neck flask, carbazole (3.3 g, 19.9 mmol), *o*-dibromobenzene (4.5 g, 19.9 mmol), CuI (0.8 g, 4.0 mmol), 1,10-phenanthroline monohydrate (0.8 g, 4.0 mmol) and KOH (2.3 g, 40 mmol)were dissolved in *o*-x1ylene (50 mL). The mixture was heated to reflux for 8 h under nitrogen. After the reaction had all reacted, the mixture was allowed to cool to room temperature and then CH_2Cl_2 (50 mL) was poured into the mixture. The organic layer was dried over anhydrous $MgSO_4$ and concentrated this by a rotary evaporator. The crude materials were purified by silica gel column chromatography (petroleum ether/CH_2Cl_2 = 4 : 1 v/v) to obtain a white solid 1.5 g, 39%. ^{1}H NMR (400 MHz, DMSO-d_6, TMS) δ: 8.25 (d, *J* = 7.6 Hz, 2 H), 8.00 (dd, *J* = 8.0, 1.2 Hz, 1 H), 7.68 (m, 2 H), 7.62 – 7.56 (m, 1 H), 7.45 – 7.38 (m, 2 H), 7.32 – 7.25 (m, 2 H), 7.00 (d, *J* = 8.0 H, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 140.84, 140.49, 134.25, 131.16, 130.64, 130.17, 129.78, 128.83, 125.94, 123.24, 120.36, 119.99, 110.14, 110.03. HRMS (m/z): $[M+H]^-$ calcd for $C_{18}H_{12}BrN$, 322.0231; found, 322.0250.

2.2.2 8H-indolo[3,2,1-de]acridin-8-one (3)

In a one-neck flask, carbazole (3.3 g, 19.9 mmol), methyl 2-iodobenzoate (5.7 g, 21.8 mmol), Cu (0.5 g, 7.1 mmol), CuI (0.34 g, 1.8 mmol) and K_2CO_3 (4.2 g, 30.4 mmol) were dissolved in 30 mL 1,2-dichlorobenzene, then heated the mixture to reflux for 12 h under nitrogen. After the reaction was completed fully, the mixture was allowed to cool to room temperature and then CH_2Cl_2 (50 mL) was poured into the mixture. Filtered the mixture and washed the cake with CH_2Cl_2, concentrated the filtrate by a rotary evaporator, then recrystallization the product from the concentrated solution by ethanol to obtain a pale yellow solid 5.4 g, 89%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ: 8.12 (t, *J* = 8.0 Hz, 3H), 7.75 (t, *J* = 7.6 Hz, 1H), 7.59 (t, *J* = 7.6 Hz, 2H), 7.37 (t, *J* = 7.6 Hz, 2H), 7.26 (t, *J* = 6.0 Hz, 2H), 7.12 (d, *J* = 8.2 Hz, 2H), 3.18 (s, 3H). Moreover, in a one-neck flask, put the previous product methyl 2-(9H-carbazol-9-yl)benzoate (2.0 g, 6.6 mmol) into polyphosphoric acid (10 mL), heated the mixture to 180 °C for 4 h. Cooled the mixture to about 80 °C after the reaction had full completed, poured H_2O (15 mL) into the mixture and extracted with

CH_2Cl_2 (20 mL × 3). The organic layer was dried over anhydrous $MgSO_4$ and concentrated this using a rotary evaporator. The crude materials were purified by silica gel column chromatography (petroleum ether/CH_2Cl_2 = 3 : 1 v/v) to obtain a pale yellow solid 1.2 g, 60%. ^{1}H NMR (400 MHz, $CDCl_3$, TMS) δ: 8.68 (dd, J = 8.0, 1.6 Hz, 1 H), 8.45 (dd, J = 7.6, 1.2 Hz, 2 H), 8.36 (dd, J = 7.6, 1.2 Hz, 1 H), 8.30 (d, J = 8.4 Hz, 1 H), 8.20 – 8.17 (m, 1 H), 7.90 – 7.84 (m, 1 H), 7.67 – 7.60 (m, 2 H), 7.50 – 7.44 (m, 2 H). ^{13}C NMR (126 MHz, $CDCl_3$) δ: 134.10, 129.18, 127.92, 125.24, 124.52, 123.46, 123.21, 123.12, 121.64, 115.66, 114.11. HRMS (m/z): $[M+H]^-$ calcd for $C_{19}H_{11}NO$, 270.0919; found, 270.0915.

2.2.3 8,8'-spirobi[indolo[3,2,1-de]acridine] (H2)

In a dry three-neck flask, 1.6 M n-BuLi in hexane (3.9 mL, 6.2 mmol, 15%solution) was added dropwise to a solution of 9-(2-bromophenyl)-9H-carbazole (2.0 g, 6.2 mmol) in THF at -78 ^{o}C under nitrogen. After stirring the mixture for 1 h at this temperature, 8H-indolo[3,2,1-de]acridin-8-one (1.7 g, 6.2 mmol) was added dropwise into the mixture with stirring for 2 h and then stirred the mixture for 12 h at the room temperature, which was poured into water and extracted with CH_2Cl_2 (20 mL × 3). The organic layer was dried over anhydrous $MgSO_4$ and concentrated this to obtain the crude materials by a rotary evaporator. Moreover, put the crude compound into acetic acid (20 mL) with a little HCl and heated the mixture to reflux for 4 h. Then, poured water (30 mL) into the mixture and extracted with CH_2Cl_2 (20 mL × 3). Dried the organic layer over anhydrous $MgSO_4$ and concentrated this using a rotary evaporator. The crude materials were purified by silica gel column chromatography (petroleum ether/CH_2Cl_2 = 6 : 1 v/v) to obtain a white solid 1.2 g, 60%. ^1H NMR (400MHz, $CDCl_3$, TMS) δ: 8.23 (d, *J* = 8.4 Hz, 2 H), 8.18 – 8.11 (m, 4 H), 7.79 (d, *J* = 7.6 Hz, 2 H), 7.57 (t, *J* = 7.6 Hz, 2 H), 7.34 (t, *J* = 7.6 Hz, 2 H), 7.26 (t, *J* = 7.2 Hz, 2 H), 7.04 (t, *J* = 8.0 Hz, 4 H), 6.83 (t, *J* = 8.8 Hz, 4 H).^{13}C NMR (126 MHz, $CDCl_3$) δ: 138.42, 135.11, 134.98, 134.00, 133.64, 130.00, 127.64, 126.75, 126.57, 126.26, 123.62, 122.99, 122.04, 121.26, 120.99, 117.78, 113.84, 113.45, 47.80. HRMS (m/z): $[M+H]^-$ calcd for $C_{37}H_{22}N_2$, 495.1861; found, 495.1886.

3. Results and discussion

3.1. Synthesis

The synthetic routes of target materials were illustrated in **Scheme 1**. It was easy to obtain the key intermediates 9-(2-bromophenyl)-9H-carbazole and 8H-indolo[3,2,1-de]acridin-8-one. The final product H2 resulted from the addition of the anion derived from the action of n-butyllithium on 1 to 3. All of the isolated intermediates and the target materials in the synthesis were characterised by ^1H NMR, ^{13}C NMR and HRMS.

3.2. Thermal properties

The thermal properties of H2 were investigated by the differential scanning calorimetry (DSC) analysis and the thermogravimetric analysis (TGA) in **Fig. S1** (ESI †). The endothermic glass transition (T_g) of H2 was determined to be 150 ^oC in the second scan by the DSC, whereas the melting point of H2 was determined to be 321 ^oC in the first scan by the DSC. From the TGA of H2, it was obvious that H2 exhibited high thermal stability with a decomposition temperature (T_d, corresponding to 5% weight loss) of 427 ^{o}C. In view of the spirocycle induced steric hindrance of the carbazole unit of H2, these thermal data were higher than those for other small molecules based on the carbazole unit, which implied that H2 was favorable for high efficient OLED device due to its good thermal stability.

3.3. Morphology property

Atomic force microscopy (AFM) was employed to investigate the possible effect of morphology on the device performance. The AFM images of the thin films of CBP and H2 were exhibited in **Fig. 2**. As shown in **Fig. 2**, the root-mean-square (R_{RMS}) surface roughness of CBP and H2 thin films were determined to be 13.61 and 3.72 nm, respectively. Moreover, it can be seen clearly from the AFM images that, both the crystallinity and homogeneity of H2 are much better than CBP, which would facilitate the carrier mobility and increase the recombination of electrons and holes, and thus guarantee H2 to be an effective host material [19].

3.4. Photophysical properties

The UV-vis absorption, photoluminescence spectra (at room temperature in THF) and phosphorescence spectrum (at 77 K in 2-methyl THF) of H2 are shown in **Fig. 3**. There are two absorption peaks for H2, the stronger absorption peak at around 290 nm could be assigned to carbazole $\pi\rightarrow\pi^*$ transitions and the weaker absorption peak at 346 nm was ascribed to the $n\rightarrow\pi^*$ transitions derived from the extended phenylcarbazole conjugation. The optical energy bandgap (E_g) of H2 was determined to be 3.22 eV from the threshold of the absorption spectra in THF. From the PL spectrum of H2, the emission peak was located at 366 nm, which was similar to that of phenylcarbazole derivatives [20-23]. According to the phosphorescence spectrum of H2 at 77 K in 2-methyl THF, the triplet energy level (E_T) was determined to be 2.90 eV, which was higher than that of CBP [16]. The E_T value of H2 was considerable high due to its limited variation, which qualify it to be a potential host material for blue and green PHOLEDs, because the high E_T value could effectively prevent the energy transfer from the dopant to host material.

3.5. Electrochemical properties

The cyclic voltammetry (CV) was performed to investigate the electrochemical property of H2. **Fig. 4** shows the irreversible oxidation process of H2, which is accorded with the feature of carbazole derivatives. The HOMO and LUMO energy level of H2 were obtained by calculation with the formula of $E_{HOMO} = -(4.7+E_{onset\text{-}ox})$ eV and $E_{LUMO} = E_{HOMO} + E_g$, respectively. The onset oxidation potential of H2 was calculated to be 0.88 eV from **Fig. 4**, so the corresponding HOMO and LUMO values were determined to be -5.58 eV and -2.36 eV. These data were similar to the values of CBP [12], the relatively high-lying HOMO level of H2 could facilitate the hole injection to the emitting layer and the favorable LUMO level may facilitate the electron injection, so the carrier recombination in the device could be more balanced to some degree [24].

3.6. Eletrophosphorescent PHOLEDs

In view of the above favorable properties of H2, blue and green phosphorescent devices based on H2 were fabricated. Four contrastive blue phosphorescent devices based on H2 were investigated with the different hole injection layers (HIL) and the hole transport layers (HTL). The device structures were as follow: 1) ITO/Pedot:PSS(50nm)/NPB(40nm)/H2:FIrpic(8wt%)(70nm)/TPBI(40nm)/LiF(1nm)/Al; 2) ITO/Pedot:PSS(50nm)/DY(40nm)/H2:FIrpic(8wt%)(70nm)/TPBI(40nm)/LiF(1nm)/Al; 3) ITO/MoO_3(3nm)/NPB(40nm)/H2:FIrpic(8wt%)(70nm)/TPBI(40nm)/LiF(1nm)/Al; 4) ITO/MoO_3(3nm)/DY(40nm)/H2:FIrpic(8wt%)(70nm)/TPBI(40nm)/LiF(1nm)/Al. H2 was doped with 8 wt% FIrpic to form an emitting layer (EML). Pedot:PSS and MoO_3 were used as the hole injection layers (HIL). NPB and DY were served as the hole transport layers (HTL). TPBI and LiF were used as the electron transport layers (ETL) and the electron injection layers (EIL), respectively. On the other hand, two green phosphorescent devices were studied with CBP as a contrastive host material, the corresponding structures were 5) ITO/Pedot:PSS(50nm)/DY(40nm)/H2:Ir(ppy)$_3$(8wt%)(50nm)/TPBI(40nm)/LiF(1nm)/Al; 6) ITO/Pedot:PSS(50nm)/DY(40nm)/CBP:Ir(ppy)$_3$(8wt%)(50nm)/TPBI(40nm)/LiF(1nm)/Al. H2 and CBP were doped with 8 wt% Ir(ppy)$_3$ to form an emitting layer (EML), the other materials served their corresponding roles in the green device as mentioned above.

It was important for the hole injection and transport material in a phosphorescent device due to its critical role in charge-carrier balance, so four different hole injection and transport materials were introduced to study the performance of H2 as a blue phosphorescent host material. The pertinent performances and data of blue phosphorescent devices were shown in **Fig. 6** and **Table 1**, respectively. As shown in **Fig. 6**, the maximum luminance for device 1-4 were 19283, 19058, 20856 and 17612 cd m^{-2}, the corresponding maximum current density were 756, 818, 940 and 836 mA cm^{-2}. On the one hand, the maximum current efficiency for devices 1-4 were 10.8, 12.2, 10.5 and 8.9 cd A^{-1}, the maximum power efficiency were 6.8, 8.8, 7.3 and 6.5 lm W^{-1}, respectively. On the other hand, allowing for the overall performances for device 1-4, device 2 was the best device with the maximum current efficiency (12.2 cd A^{-1}) and power efficiency (8.8 lm W^{-1}), these values for blue small-molecule-PHOLEDs were quite larger than that of some small molecules [25], and were attributed to the excellent thermal stability, good film-forming ability and favorable triplet energy (E_T) of H2. The color coordinate of the blue PHOLEDs device for 1-4 were determined to be (0.16, 0.28), (0.17, 0.27), (0.16, 0.26) and (0.17, 0.28), respectively, the relevant electroluminescence spectra of 1-4 were shown in **Fig. 6d**, which were also analogous due to the same emitting layers of these devices. In terms of the relationship between eletrophosphorescent efficiency and structure for device 1-4, the group of Pedot:PSS(50nm)/DY(40nm) as hole transport material was better than others, the reason may be the charge-carrier was more balanced in this group. Due to the limitation of device-optimization, just four different hole transport materials were used in fabricating blue PHOLEDs, provided conducting optimization fully, PHOLEDs with further optimization studies better performance could be confidently obtained.

To further study the properties of H2, green PHOLEDs based on H2 as host material was fabricated and in comparison with conventional star host material CBP. **Fig. 7** exhibits the relevant performance of these two green PHOLEDs. The maximum luminance of device 5 (3679 cd m^{-2}) was bigger than that of device 6 (2542 cd m^{-2}), while the current density was 147 and 156 mA cm^{-2}, respectively. It was obvious that the performance of device 5 was better than that of device 6, which was further confirmed from the current efficiency (device5 *vs* device 6 = 11.2 cd A^{-1} *vs* 6.0 cd A^{-1}) and power efficiency (device5 *vs* device 6 = 5.0 lm W^{-1} *vs* 2.0 lm W^{-1}). These properties could be derived from the thermal and morphology property of H2 and CBP, as mentioned above, H2 was better than CBP in terms of thermal stability, film-forming property and crystallinity. The triplet energy (E_T) of H2 was 2.90 eV, which was high enough for effective triplet exciton blocking [26,27]. The color coordinate of the green PHOLED devices 5 and 6 were (0.27, 0.61) and (0.26, 0.60), respectively, the corresponding electroluminescence spectra were shown in **Fig. 7d**. By comparing with the performance of CBP, H2 could be a promising host material for its excellent properties.

4. Conclusion

A novel small molecule (H2) based on spiro-annulated carbazole was synthesized and characterized. It exhibits excellent properties such as good thermal stability (T_d = 427 ^{o}C), film-forming ability, suitable HOMO-LUMO level and high triplet energy (E_T = 2.90 eV), which eventually allow H2 to be competent for blue and green phosphorescent devices. Four different hole transport materials were introduced to fabricate blue devices, the best-performing device with the group of Pedot:PSS(50nm)/DY(40nm) as hole transport material exhibited a maximum current efficiency of 12.2 cd A^{-1} and a maximum power efficiency of 8.8 lm W^{-1}, these values were high as compared to those values of other small molecule based blue emitting devices. Moreover, the performance of the H2-based green device was better than that of CBP-based green device. Given the favorable properties of H2 achieved, other potential application such as use in white PHOLEDs is under further study.

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Table 1 Electroluminescence characteristics of the devices.

Device	Max brightness(cd m^{-2})	Current efficiency(cd A^{-1})[a]	Power efficiency(lm W^{-1})[a]	CIE(x,y)[b]
Blue-1	19283	10.8	6.8	(0.16,0.28)
Blue-2	19058	12.2	8.8	(0.17,0.27)
Blue-3	20856	10.5	7.3	(0.16,0.26)
Blue-4	17612	8.9	6.5	(0.17,0.28)
Green-5	3679	11.2	5.0	(0.27,0.61)
Green-6	2542	6.0	2.0	(0.26,0.60)

[a] Estimated at the luminance of 100 cdm^{-2}. [b] Measured from the EL spectra by inverting into chromaticity coordinates on the CIE 1931 diagram.

Fig. S1(ESI†). The differential scanning calorimetry (DSC) analysis and the thermogravimetric analysis (TGA) spectra of H2.

Fig. 2. AFM images of the thermally evaporated thin films of CBP (a) and H2 (b).

Fig. 3. Absorption, photoluminescence spectra (at room temperature in THF) and phosphorescence spectrum (at 77 K in 2-methyl THF) of H2.

Fig. 4. Cyclic voltammogram of H2 in dichloromethane with tetra(n-butyl)ammonium hexafluorophosphate(0.1 M) as a supporting electrolyte for the oxidation scan.

Fig. 5. Energy-level diagram of blue and green PHOLEDs.

Fig. 6. a) Current density-voltage-luminance data of blue PHOLEDs; b) Current efficiency-current density curves of blue PHOLEDs; c) Power efficiency-luminance curves of blue PHOLEDs; d) Electroluminescence spectra of blue PHOLEDs.

Fig. 7. a) Current density-voltage-luminance data of green PHOLEDs; b) Current efficiency-current density curves of green PHOLEDs; c) Power efficiency-luminance curves of green PHOLEDs; d) Electroluminescence spectra of green PHOLEDs.

Scheme 1. The Synthetic routes of compound H2.

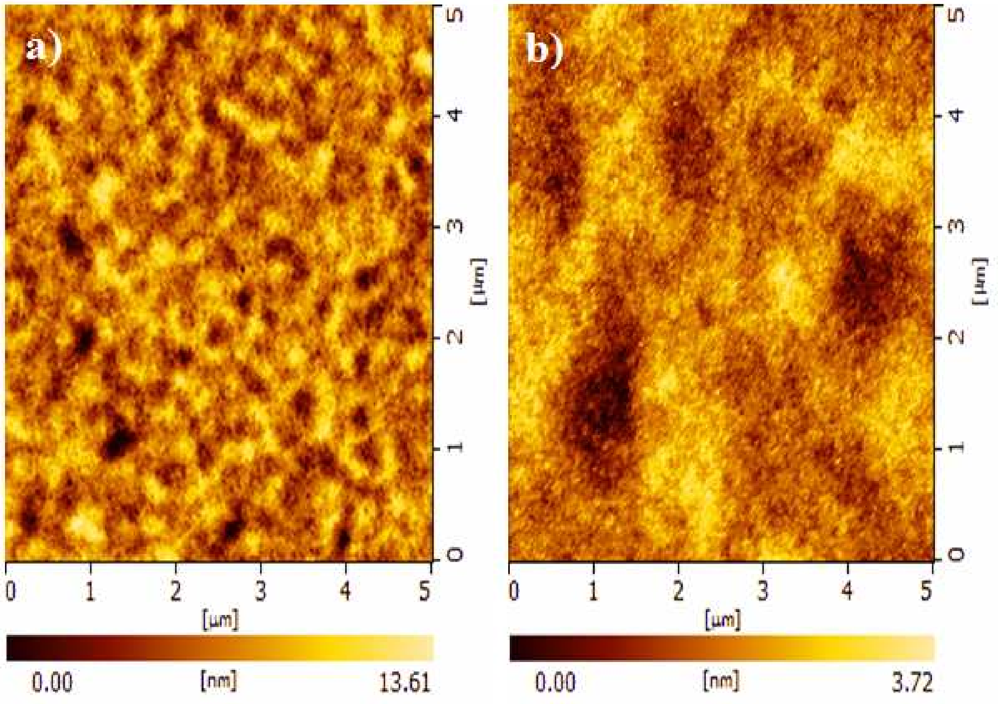


Fig. 2. AFM images of the thermally evaporated thin films of CBP (a) and H2 (b).

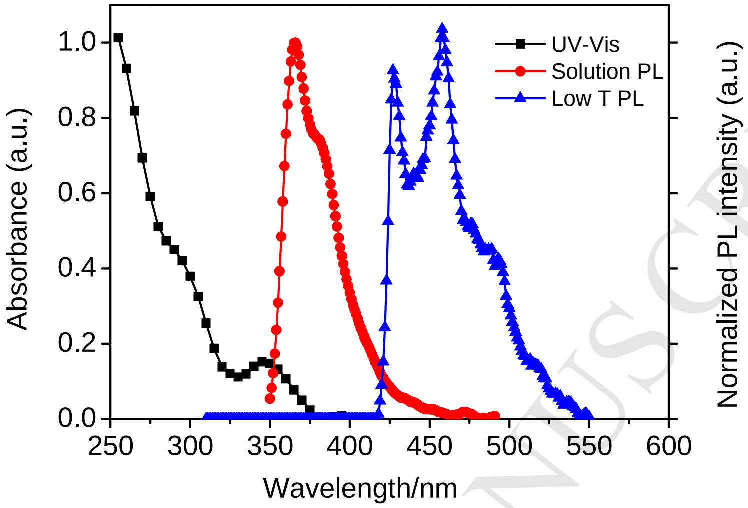


Fig. 3. Absorption, photoluminescence spectra (at room temperature in THF) and phosphorescence spectrum (at 77 K in 2-methyl THF) of H2.

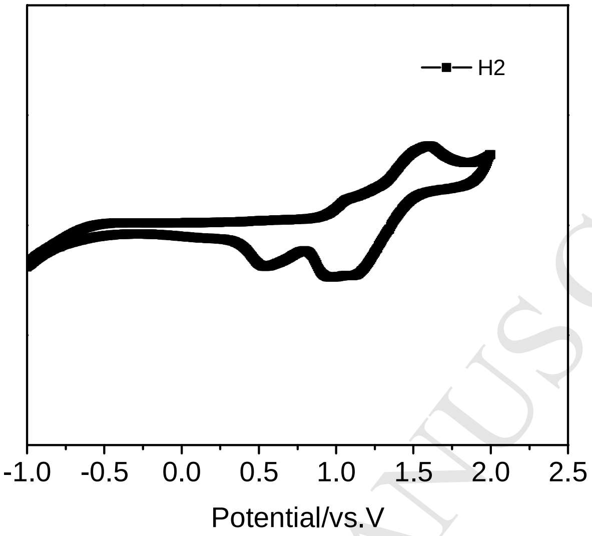


Fig. 4. Cyclic voltammogram of H2 in dichloromethane with tetra(n-butyl)ammonium hexafluorophosphate(0.1 M) as a supporting electrolyte for the oxidation scan.

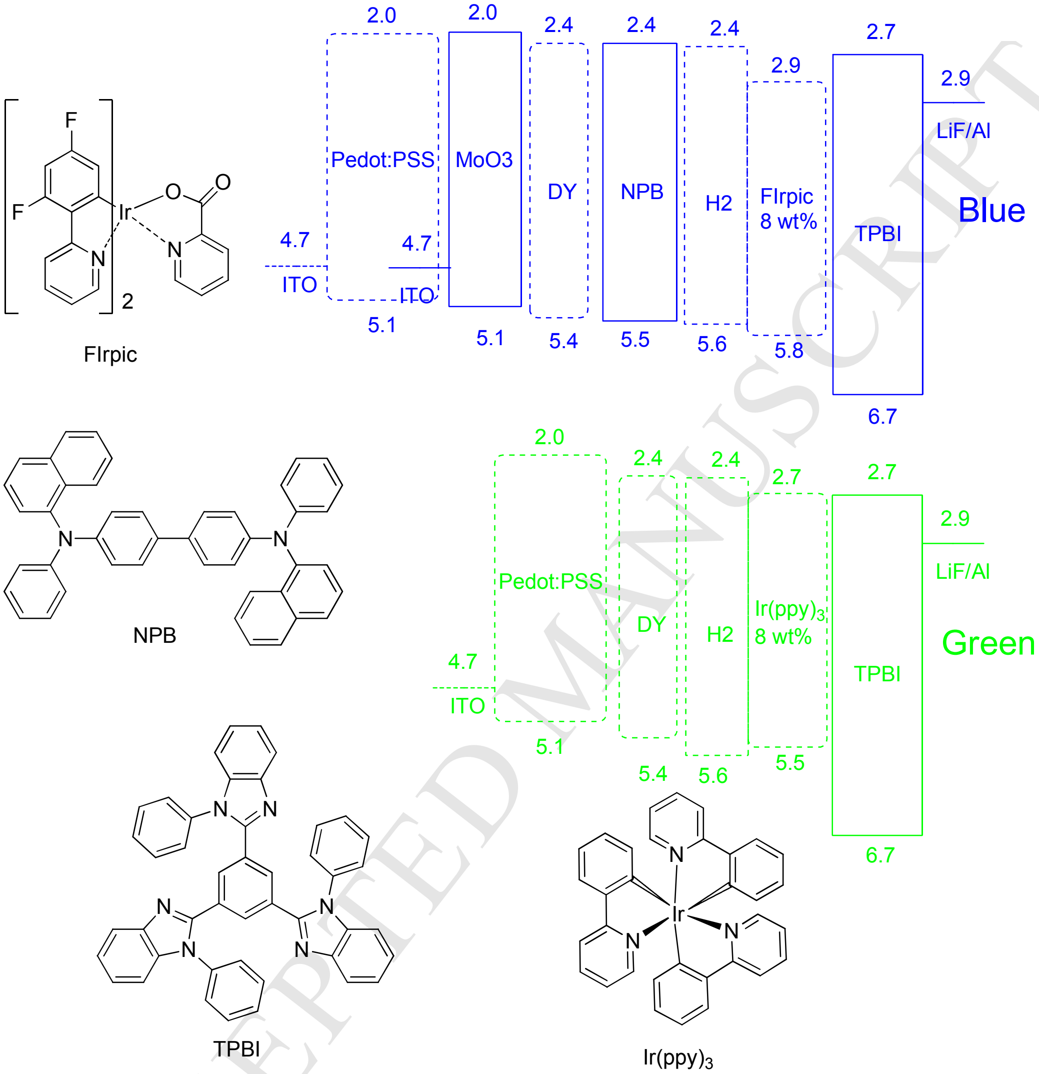


Fig. 5. Energy-level diagram of blue and green PHOLEDs.

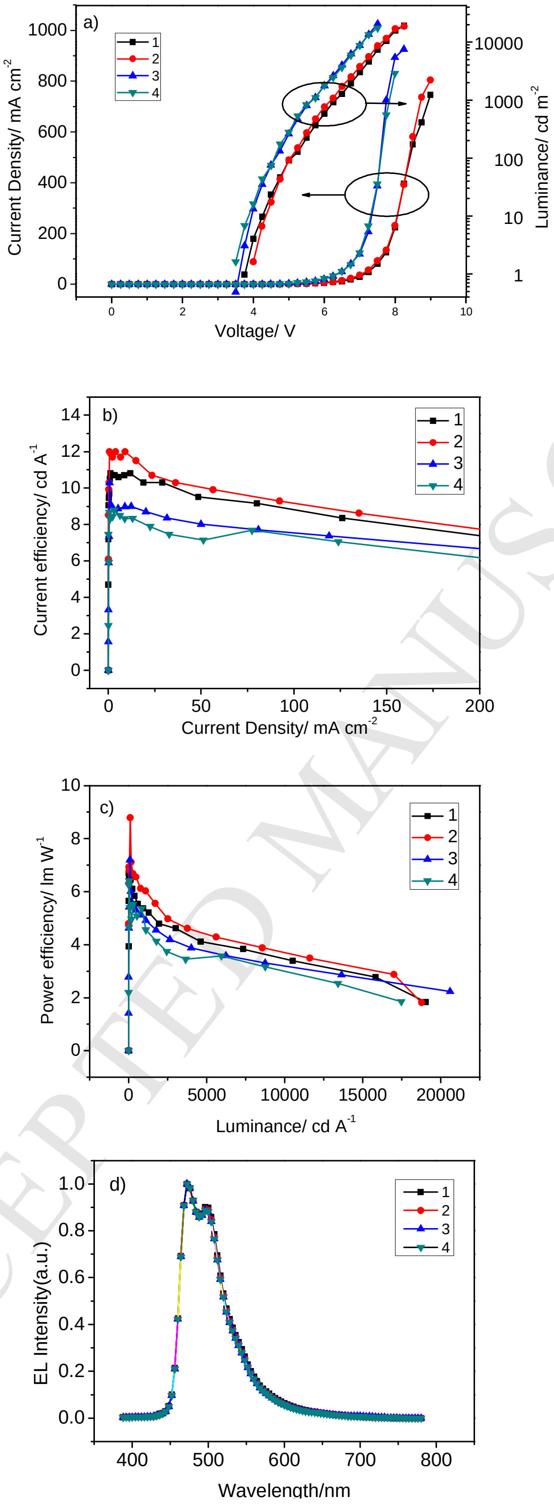


Fig.6. a) Current density-voltage-luminance data of blue PHOLEDs; b) Current efficiency-current density curves of blue PHOLEDs; c) Power efficiency-luminance curves of blue PHOLEDs; d) Electroluminescence spectra of blue PHOLEDs.

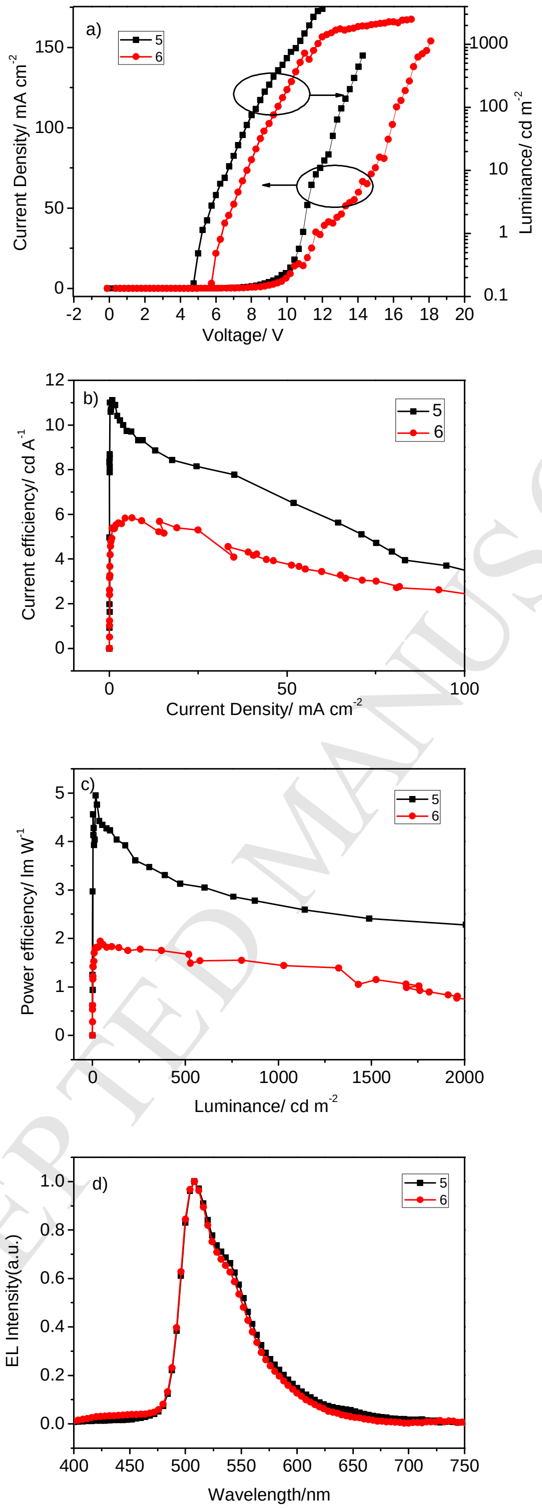
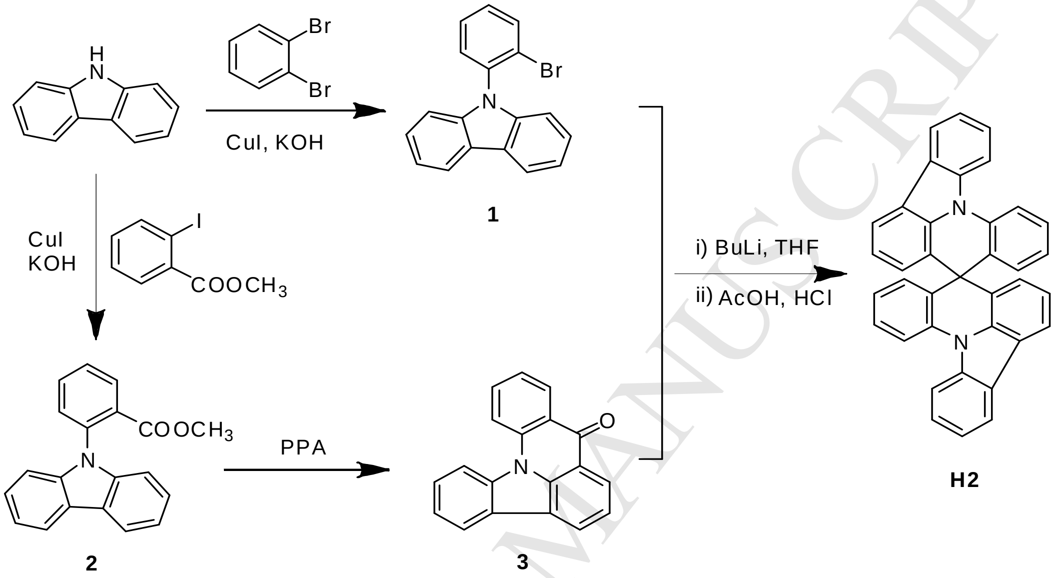


Fig. 7. a) Current density-voltage-luminance data of green PHOLEDs; b) Current efficiency-current density curves of green PHOLEDs; c) Power efficiency-luminance curves of green PHOLEDs; d) Electroluminescence spectra of green PHOLEDs.



Scheme 1. The Synthetic routes of compound H2.

Highlights

- A novel spiro-annulated host based on carbazole has been synthesized and characterized.
- The dye exhibits good thermal stability and high triplet energy.
- Efficient blue and green phosphorescent organic light-emitting diodes based on the dye have been fabricated.