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Efficient violet non-doped organic light-emitting device based on a pyrene derivative with novel molecular structure

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ABSTRACT

A novel pyrene derivative 1,6-bis[2-(3,5-diphenylphenyl)phenyl)pyrene (DPPP) was successfully designed and synthesized. X-ray analysis shows the pyrene core in this compound is fully protected by the introduced 3,5-diphenylphenyl groups, resulting no π - π stacking between pyrene units, and the dihedral angle between pyrene ring and adjacent benzene ring is as large as 80.1°. This structure character leads to DPPP achieving a violet emission both in solution and as a thin solid film. Furthermore, DPPP exhibits high thermal properties due to its non-coplanar structure and large molecular size. The nondoped electroluminescence device employing DPPP as emitting layer shows a stable and efficient violet emission with a maximum external quantum efficiency of 2.2% and a CIE coordinate of (0.16, 0.04), which is remarkable in reported violet devices.

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39 1. Introduction

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40 Organic light-emitting devices (OLEDs) have attracted much attention because of their applications in flat-panel displays and 41 solid-state lightings [1]. Efficient violet emitting materials play 42 an important role in OLEDs since violet emitters can be utilized 43 to generate light emission over the whole visible region and white 44 45 light emission [2–9]. Moreover, high-efficiency short-wavelength emission can effectively reduce the power consumption of full-46 color OLEDs [10]. In fact, violet OLEDs are also of great importance 47 in other fields, such as high-density information storage [11]. 48 Although many short-wavelength (blue-violet/violet) OLEDs have 49 50 been reported in recent years [12–25], violet OLEDs with emission peak below 400 nm and high color purity are still very rare to date 51 [22-24]. The molecular design of organic materials capable of effi-52 cient violet emission in OLEDs is highly challenging. To achieve a 53 54 violet emission, the extent of conjugation in molecule must be

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http://dx.doi.org/10.1016/j.orgel.2015.04.024 1566-1199/© 2015 Published by Elsevier B.V. confined, which in turn would usually impose constraints in molecular size. However, the resultant limited molecular size normally reduce the thermal stability of organic molecules and renders it more difficult to form stable and uniform amorphous thin films, which are detrimental for device operation. Furthermore, the confined conjugation length will cause decrease of chargetransporting ability and fluorescent quantum yield for organic molecules [26,27].

As a large conjugated aromatic system, pyrene not only has highly efficient violet emission around 390 nm, but also has high carrier mobility and excellent hole injection ability [28-30]. Nevertheless, pyrene itself is not suitable to act as violet-emitter in OLEDs due to its strong tendency to crystallize and form excimers by π - π stacking, which leads to a red-shifted emission above 480 nm as well as the decrease of fluorescence efficiency and make it incapable of forming stable amorphous thin film [28,29]. To suppress the π - π stacking, bulky groups generally are introduced to pyrene backbone at various positions, such as 1- and 6-positions, 2- and 7-positions, or 1-, 3-, 6-, and 8-positions [25,28,31-36]. In addition, incorporating pyrene with other chromophores also is a common strategy to design light-emitting materials for OLEDs [28,37-41]. As far as we know, numerous pyrene based lightemitting materials have been prepared through above mentioned methods, but only one violet OLED using pyrene derivative as

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79 emitting layer was reported by Kaafarani and co-workers, and this 80 device exhibits a low efficiency of 0.04 cd/A [12]. The important 81 reasons may be (i) introducing bulky rigid groups to pyrene back-82 bone increases the extent of conjugation in molecule resulting in a 83 longer emission wavelength, (ii) interactions between pyrene units 84 have not been fully suppressed in solid state, which leads to pyrene 85 derivatives exhibiting a obviously red-shifted emission in solid 86 state compared with in solution.

87 In this paper, we designed and synthesized a novel violet-light-88 emitting material 1,6-bis[2-(3,5-diphenylphenyl)phenyl]pyrene 89 (DPPP) employing pyrene as the chromophore (Scheme 1). In this 90 compound, two 3,5-diphenylbenzene groups are connected with 91 pyrene backbone by two benzene rings, respectively, and the bulky 92 3,5-diphenylbenzene group and pyrene unit locate at the adjacent 93 positions of benzene ring. The structural characteristic of DPPP has 94 significant advantages. Firstly, it can increase the dihedral angles 95 between pyrene ring and adjacent benzene rings to confine the 96 extent of conjugation in molecule through improving steric hin-97 drance. Secondly, the bulky 3,5-diphenylbenzene groups can cap the pyrene core from both sides to prohibit the strong interactions 98 99 between pyrene units. In addition, the bulky substituents at pyrene 100 backbone can increase the molecular size to improve the high thermal stability. We characterized the structure and physical 101 102 properties of DPPP, as we desired, it exhibits high-efficiency violet 103 emission and high thermal stability. The non-doped electrolumi-104 nescence device using DPPP as emitting layer achieved an efficient 105 and stable violet emission (λ_{max} = 396 nm, EQE_{max} = 2.2%).

106 2. Experimental

107 2.1. General information

108 Commercially available reagents were used without purification unless otherwise stated. The $^1\mathrm{H}$ NMR spectra and $^{13}\mathrm{C}$ NMR 109 spectrum were recorded on Bruker Avance 400 spectrometer. 110 Elemental analysis was performed on a Vario III elemental 111 analyzer. Mass spectra were obtained on a Bruker Microflex spec-112 trometer. The absorption and photoluminescence spectra were 113 recorded on a Hitachi U-3010 UV-Vis spectrophotometer and a 114 Hitachi F-4500 fluorescence spectrophotometer, respectively. 115 Photoluminescence quantum yield of solid film was measured by 116 117 a combined measurement system for infrared fluorescence 118 (Nanolog^R FluoroLog-3-2-iHR320) equipped with F-3018 integrat-119 ing sphere. Cyclic voltammetry was performed on a CHI620C elec-120 trochemical analyzer, and the electrolytic cell is a conventional 121 three-electrode cell consisting of a Pt working electrode, a Pt wire 122 counter electrode and an Ag/AgCl reference electrode. Thermal 123 gravimetric analysis (TGA) and differential scanning calorimetry 124 (DSC) were performed on a TA instrument TGA2050 and a TA 125 instrument DSC2910, respectively, with a heating rate of 126 10 °C/min under the nitrogen atmosphere. DFT calculations 127 were performed using Gaussian 03 with the B3LYP/6-31G(d) 128 method [42].

129 2.2. Synthesis

130 2.2.1. Compound **3**

1-Iodo-2-bromobenzene 2 (1.41 g, 5.0 mmol), 3,5-diphenylphe-131 132 nyl boronic acid 1 (1.37 g, 5.0 mmol), and tetrakis(triphenylphos-133 phine)palladium [Pd(PPh₃)₄] (80 mg) were mixed in toluene 134 (35 ml), then Na₂CO₃ (2 M, 10 mL) and ethanol (10 mL) were added 135 under the nitrogen atmosphere. The mixture reacted at 80 °C under 136 the nitrogen atmosphere over night. After cooling, the resulting 137 solution was extracted with CH₂Cl₂ three times, then the combined 138 organic solution was dried over anhydrous MgSO₄ and evaporated

with a rotary evaporator. The crude product was puried by column139chromatography (eluent = petroleum ether 60–90 °C) to give a140white powder (yield: 1.56 g, 82%). ¹H NMR (400 MHz, CDCl₃) δ 141(ppm): 7.83 (1H, s), 7.72–7.69 (5H, m), 7.63 (2H, s), 7.48–7.44 (5H,142t, J = 8.0), 7.35–7.40 (3H, q, J = 6.7), 7.24 (1H, s). TOF-MS: 384.126.143

2.2.2. Compound 4

n-Butyl lithium (1.6 M, 1.5 mL) was added dropwise to the solution of compound **3** (1.5 g, 4 mmol) in anhydrous THF (20 mL) at -80 °C over half an hour, and the mixture was stirred for another 1 h at this temperature. Then trimethylborate (0.6 mL, 5.2 mmol) was added to the reaction mixture at -80 °C, and stirred for 12 h at room temperature. Then HCl (2 M, 10 mL) was added, and stirred for 1 h. The resulting solution was extracted with CH₂Cl₂ three times, then the combined organic solution was dried over anhydrous MgSO₄ and evaporated with a rotary evaporator. The crude product was puried by column chromatography (eluent = dichloromethane/petroleum ether, 1:3 v/v) to give a white powder (yield: 0.82 g, 58%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 7.94 (1H, d, *J* = 8.0), 7.85 (1H, s), 7.65–7.68 (4H, m), 7.62 (2H, s), 7.28–7.52 (9H, m), 4.66 (2H, s).

2.2.3. DPPP

1,6-Dibromopyrene (0.36 g, 1 mmol), compound **3** (0.77 g, 160 2.2 mmol) and tetrakis(triphenylphosphine)palladium $[Pd(PPh_3)_4]$ 161 (25 mg) were mixed in toluene (15 ml), then Na₂CO₃ (2 M, 3 mL) 162 and ethanol (5 mL) were added under the nitrogen atmosphere. 163 The mixture reacted at 110 °C under the nitrogen atmosphere over 164 night. After cooling, the resulting solution was extracted with 165 CH₂Cl₂ three times, then the combined organic solution was dried 166 over anhydrous MgSO₄ and evaporated with a rotary evaporator. 167 The crude product was puried by column chromatography (elu-168 ent = dichloromethane/petroleum ether, 1:8 v/v) to give a white 169 powder (yield: 0.37 g, 46%). ¹H NMR (400 MHz, CDCl₃) δ (ppm): 170 8.20 (1H, d, J=4), 8.15-8.07 (4H, m), 8.04-7.98 (3H, m), 7.81 171 (1H, d, J = 4), 7.76 (1H, d, J = 8), 7.68 - 7.65 (3H, m), 7.61 - 7.56 (3H, m)172 m), 7.51–7.48 (3H, m), 7.42 (1H, d, *J* = 8), 7.33 (1H, S), 7.24 (4H, 173 s), 7.17–7.13 (7H, m), 7.08–7.04 (4H, m), 6.96–6.94 (6H, m). ¹³C 174 NMR (100 MHz, CDCl₃) δ (ppm): 142.12, 141.97, 141.09, 141.05, 175 141.02, 140.09, 140.00, 137.60, 132.08, 130.49, 130.21, 129.91, 176 128.82, 128.57, 128.48, 128.27, 127.72, 127.22, 127.15, 127.07, 177 127.03, 125.62, 124.55, 124,27. TOF-MS: 811.232. Anal. Calcd. for 178 C₆₄H₄₂: C, 94.78; H, 5.22. Found: C, 94.62; H, 5.26. 179

2.3. X-ray structure determination

The single crystal suitable for X-ray diffraction analysis was 181 obtained by slowly evaporating the CDCl₃ solution of DPPP. 182 Crystal data were collected on a Bruker SMART APEX-II CCD 183 diffractometer with Mo K α radiation (λ = 0.071073 Å) at 296 K. 184 The data were corrected for Lorentz-polarization factors as well 185 as for absorption. Structures were solved by direct methods and 186 refined by full-matrix least squares methods on F^2 with the 187 SHELX-97 program. All nonhydrogen atoms were refined 188 anisotropically, while hydrogen atoms were placed in geometri-189 cally calculated positions. Crystal data for DPPP: C₆₄H₄₂, 190 M = 810.98, Monoclinic, P2(1)/c, a = 9.201(4) Å, b = 11.487(5) Å, 191 c = 21.142(10) Å, $\alpha = \gamma = 90^{\circ}$, $\beta = 94.410(6)^{\circ}$. V = 2228.1(18) Å³, 192 Z = 2, $D_{Calc} = 1.209 \text{ Mg/m}^3$, 16535 reflections measured, 4128 193 unique reflections with $I > 2\sigma(I)$, $R_1 = 0.0459$, w $R_2 = 0.1049$. CCDC 194 1008121. 195

2.4. OLED fabrication and measurements

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Indium-tin-oxide (ITO) coated glass substrates were cleaned 197 with isopropyl alcohol and deionized water, then dried in an oven 198

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Scheme 1. Synthesis and structure of DPPP.

at 120 °C, and finally treated with UV-ozone. The devices were 199 prepared in a vacuum at a pressure of about 1×10^{-6} Torr. 200 Organic layers were deposited on to the substrate at a rate of 201 202 0.1-0.2 nm/s. After the organic film deposition, LiF and aluminum were thermally evaporated onto the surface of organic layer. 203 204 Electroluminescence (EL) spectra, luminance and 1931 CIE color 205 coordinates were measured with a PR650 spectrascan photometer 206 and the current-voltage characteristic was measured with a 207 computer-controlled Keithley 2400 SourceMeter under ambient 208 atmosphere.

209 3. Results and discussion

210 3.1. Synthesis and crystal structure

Synthetic route for DPPP is shown in Scheme 1. Firstly, the 211 Suzuki coupling reaction of 3,5-diphenylphenyl boronic acid 1 212 213 and 1-iodo-2-bromobenzene 2 afforded 1-(3,5-diphenylphenyl)-2-bromobenzene 3. This Suzuki coupling reaction was carried out 214 215 at a lower temperature of about 80 °C to protect the bromine atom 216 in compound 2. Then compound 3 was translated to 1-(3,5-diphe-217 nylphenyl)phenyl-2-boronic acid **4** with the aids of n-butyl 218 lithium, trimethylborate and HCl. Finally, the designed material DPPP was obtained by Suzuki coupling reaction between 219 compound **4** and 1,6-dibromopyrene **5**. The structure of DPPP 220 was characterized by ¹H NMR, ¹³C NMR, TOF-MS, and elemental 221 222 analysis (EA).

The molecular structure of DPPP was further confirmed by X-ray diffraction analysis (Fig. 1). This compound has a symmetrical



Fig. 1. Single crystal structure of DPPP (H atoms are omitted for clarity).

molecular structure, the important bond lengths and dihedral 225 angles are listed in Table 1. The bond lengths of C4-C9 and C14-226 C15 are longer than those of C17-C21 and C19-C27, which should 227 be caused by steric hindrance from the bulky substituents at 1- and 228 6-positions of pyrene backbone. The adjacent aromatic rings are 229 twisted each other to a larger angle from 37.0° to 80.1°, which indi-230 cates DPPP has a highly non-coplanar molecular structure. 231 Especially the two benzene rings at 1- and 6-positions of pyrene 232 backbone are highly twisted toward the pyrene ring to an angle 233

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The important bond lengths and dihedral angles.

Bond lengths (Å)		Dihedral angles ^a (°)	
C4-C9	1.501(2)	Pr-B1	80.1
C14-C15	1.500(2)	B1-B2	66.5
C17-C21	1.484(3)	B2-B3	37.0
C17-C21	1.484(3)	B2-B4	42.4

^a Pr denotes the pyrene ring, B1, B2, B3 and B4 denote the benzene rings C9-C14, C15-C20, C21-C26 and C27-C32 orderly (Fig. 1).

234 of 80.1°, such large dihedral angle can strictly confine the extent of conjugation in DPPP to reduce the emission wavelength. Fig. 1 235 shows the pyrene core is capped from both sides by two 236 3,5-diphenylbenzene groups, this structure arrangement can pro-237 hibit the strong π - π interactions between pyrene units, which is 238 239 confirmed by the packing diagram of DPPP (Fig. 2). It can be found that the pyrene units in adjacent DPPP molecules do not overlap 240 241 each other, it suggests there is no π - π stacking between pyrene units which usually leads to red-shifted emission [43]. As shown 242 243 in Fig. 2, the intramolecular and intermolecular C–H $\cdots\pi$ interac-244 tions exit in DPPP, the distances are measured to be 2.783 (Å) and 2.746 (Å), respectively, which should affect the photophysical 245 properties of DPPP in solid state. 246

247 3.2. Photophysical properties

The UV-vis absorption and photoluminescence (PL) spectra of 248 DPPP were measured in dilute CH₂Cl₂ solution. The absorption 249 spectrum shows two prominent bands at 250 nm and 358 nm, 250 251 respectively (Fig. 3 and Table 2), which are the characteristic vibra-252 tion pattern of pyrene derivatives [32,36,43–46]. When the dilute 253 CH₂Cl₂ solution of DPPP is excited at either 250 nm or 358 nm, 254 the same PL spectrum with a structureless emission peak at 398 nm is observed, which also shows a very narrow FWHM 255 256 (full-width at half-maximum) of about 41 nm (Table 2). Quantum chemical calculations show that the highest occupied molecular 257 orbital (HOMO) and the lowest unoccupied molecular orbital 258 (LUMO) mainly locate on pyrene core, which implies that the 259 260 absorption and emission of DPPP were controlled mostly by pyrene 261 unit (Fig. 4). In addition, The HOMO and LUMO contain a certain amount of contributions from the substituents at 1- and 6-posi-262 tions of pyrene backbone, which make the PL spectrum of DPPP 263 lost vibronic structure and red-shift about 15 nm with respect to 264 265 that of pyrene monomer (Fig. 3). Fortunately, the red-shift makes



Fig. 2. Packing diagram of DPPP (All H atoms except H1 and H22 are omitted for clarity).



Fig. 3. Absorption and photoluminescence of DPPP in CH₂Cl₂ solution and solid film, photoluminescence of pyrene in CH₂Cl₂ solution.

Table 2

Photophysical properties of DPPP in CH₂Cl₂ solution and solid film.

	Absorption (nm)	Emission (nm)	FWHM (nm)	Quantum yield	
Solution	250, 358	398	41	0.68 ^a	
Film	254, 368	410	50	0.37 ^b	

^a Measured using DPA as the reference standard.

^b Absolute quantum yield.



Fig. 4. Calculated HOMO and LUMO of DPPP.

most of the PL spectrum of DPPP fall in the visible violet light region above 380 nm. The fluorescence quantum yield (Φ_f) of DPPP in dilute CH₂Cl₂ solution was measured to be 0.68 by using 9,10-diphenylanthracene (DPA) as the reference standard.

The solid film of DPPP was fabricated by vacuum vapor deposition on a quartz disc. The shape of the absorption spectrum of DPPP in thin film is almost identical to that of in CH_2Cl_2 solution except a red-shift <10 nm. The PL spectrum of DPPP in thin film exhibits an emission peak at 410 nm with a FWHM of about 50 nm (Fig. 3 and Table 2). It can be found that the absorption and PL spectra measured from solid film only shows slight difference compared to those acquired from CH_2Cl_2 solution. This suggests that the strong interactions between pyrene units do not occur in thin solid film, which is in accord with the results of single crystal analysis. In addition, the $C-H\cdots\pi$ interactions is probably another important reason for the slight change besides the difference of dielectric constant of the environment [47].

3.3. Thermal properties and electrochemical properties

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Thermal gravimetric analysis (TGA) and differential scanning 284 calorimetry (DSC) show that DPPP has an excellent thermal 285

286 stability. The decomposition temperature (T_d) of DPPP was mea-287 sured to be 442 °C (Fig. 5). DSC measurements were performed 288 from 30 to 375 °C under the nitrogen atmosphere (Fig. 6). DPPP melted at 312 °C ($T_{\rm m}$) upon the first heating process, and then 289 the liquid sample was rapidly cooled to form an amorphous glassy 290 state. When the amorphous glassy sample was heated again, a 291 glass transition occurred at 148 °C (T_g). The high glass transition 292 temperature is presumably due to the non-coplanar structure 293 and large molecular weight, and implies DPPP can form stable 294 amorphous film in the devices. Upon further heating beyond T_{g} , 295 an exothermic peak due to crystallization was observed at around 296 297 204 °C.

The electrochemical property of DPPP was investigated by 298 cyclic voltammetry in CH₂Cl₂ solution containing tetrabutylammo-299 300 nium hexauorophosphate (0.1 M) with a scan rate of 50 mV/s. As 301 shown in Fig. 7. DPPP exhibits a reversible oxidation process with 302 half-wave oxidation potential of 1.25 V, and shows a quasireversible oxidation process at a higher potential. The HOMO 303 energy level was calculated to be -5.65 eV by using the energy 304 level value of -4.8 eV for ferrocene (Fc) with respect to zero vac-305 306 uum level. The LUMO energy level was estimated to be -2.55 eV 307 according to the HOMO energy level value in combination with 308 the band gap derived from the absorption band edge.













Fig. 9. EL spectra of the DPPP based device under different luminance. Inset: comparison of EL and PL spectra of DPPP solid film.

3.4. Electroluminescence

To investigate the electroluminescence (EL) performance of 310 DPPP, the non-doped OLED was fabricated with a configuration of 311 ITO/NPB (25 nm)/TCTA (5 nm)/DPPP (30 nm)/TPBI (40 nm)/LiF 312 (1.5 nm)/Al (100 nm). In this device, ITO (indium tin oxide) and 313 LiF/Al are the anode and the cathode, respectively; NPB 314 (4,4'-bis[N-(1-naphthyl)-N-phenylamino]biphenyl) is the hole transporting layer; TCTA (4,4',4''-tris(N-carbazolyl)triphenylamine)

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is used as the exciton blocking layer; TPBI (1,3,5-tris(phenyl-2-benzimidazolyl)benzene) is the electron transporting layer and exciton blocking layer simultaneously; DPPP is used as the emitting layer. Relative energy level alignment of the device is shown in Fig. 8.

Fig. 9 shows the EL spectra of the device under different luminance, which are not fully measured since the ultraviolet emission below 380 nm cannot be detected by PR650 spectrascan photometer. From the EL spectra, the DPPP based device shows a violet emission with an emission peak at 396 nm and a narrow FWHM of about 50 nm, similar to the PL spectra of DPPP. The 1931 CIE coordinates of the device under different luminance are all about (0.16, 0.04), which is located in the violet area of the CIE chromaticity diagram and rarely reported in OLEDs to our knowledge [13,17,22]. Furthermore, the high color purity and stable violet emissions also confirm that the non-coplanar molecular structure of DPPP can effectually hinder intermolecular aggregation.

333 The current density-voltage-luminance characteristic of the device is shown in Fig. 10. The device has a low turn-on voltage 334 below 4 V at a brightness of 1 cd/m^2 , and exhibits a maximum 335 luminance of 1890 cd/m^2 at 9 V with a current density of 336 337 446 mA/cm². Such low turn-on voltage is due to the high carrier 338 mobility and excellent hole injection ability of the pyrene deriva-339 tives and the small injection barriers in the devices (HOMO: 340 -5.7/-5.65 eV at TCTA/DPPP interface; LUMO: -2.55/-2.7 eV at 341 DPPP/TPBI interface). As shown in Fig. 11, the maximum current



Fig. 10. Current density-voltage-luminance characteristic of the DPPP based device.





Table 3

EL performance of the device based on DPPP.

V _{on} ^a	Max CE	Max EQE	λ _{max}	Max luminance	$CIE(x, y)^{b}$
(V)	(cd/A)	(%)	(nm)	(cd/m ²)	
4.0	0.74	2.2	396	1890	(0.160, 0.041)

^a Recorded at 1 cd/m².

^b Recorded at 100 cd/m².

efficiency of the device is 0.74 cd/A at a luminance of 69.3 cd/m², 342 corresponding a maximum external quantum efficiency (EQE) of 343 2.2%. Moreover, this violet device exhibits a lower efficiency roll-344 off, remaining a high EQE of 1.56% at the practical luminance of 345 1000 cd/m^2 , which is highly desirable for OLEDs. EL performance 346 of the device was summarized in Table 3. As far as we know, the 347 comprehensive performance of the device is the best result for 348 violet OLEDs with λ_{max} < 400 nm considering the FWHM of EL 349 spectrum, color purity, EL efficiency and stability [22-24]. 350

4. Conclusions

In summary, a novel high-efficiency violet-light-emitting 352 material DPPP has been successfully developed employing pyrene 353 as the chromophore. In this compound, the introduced functional 354 groups play three important roles, (i) protect pyrene unit to 355 prohibit π - π stacking, (ii) confine the extent of conjugation in 356 molecule utilizing the steric hindrance, (iii) enlarge the molecular 357 size to improve the thermal stabilities. The non-doped violet 358 OLED based on DPPP achieved an excellent performance: high effi-359 ciency (EQE_{max} = 2.2%), high color purity (CIE, x = 0.16, y = 0.04). 360 lower efficiency roll-off, which indicates DPPP is a promising violet 361 material for OLEDs. 362

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