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PAPER

Spirobifluorene derivative: a pure blue emitter ($\text{CIE}_y \approx 0.08$) with high efficiency and thermal stability

Xing Xing, Lixin Xiao,* Lingling Zheng, Shuangyuan Hu, Zhijian Chen, Bo Qu and Qihuang Gong*

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A spirobifluorene derivative containing phenanthrene moiety, 2,7-di(phenanthren-9-yl)-9,9'spirobifluorene (DPSF), has been synthesized. It shows absorption peaks at 254 nm, 310 nm, and 327 nm and a fluorescence peak at 383 nm in CHCl₃ that shifts to 398 nm in the film state. The quantum yield is 0.79 calibrated with a standard of coumarin 102 (0.93). A pure blue emission at Commission Internationale de l'Éclairage (CIE) (0.15, 0.08), has been achieved using DPSF as the emitter, poly(3,4ethylene dioxythiophene) : poly(styrene sulfonic acid) (PEDOT : PSS) as the hole injecting layer, 4,4'bis[*N*-(1-naphthyl)-*N*-phenyl-amino] biphenyl (NPB) as the hole transporting layer, and 1,3,5-tris(*N*phenylbenzimidazol-2-yl)-benzene (TPBI) mixing with 2-*tert*-butylphenyl-5-biphenyl-1,3,4-oxadiazole (PBD) (2 : 1) as the electron transporting material. The maximum current efficiency (CE) and power efficiency (PE) of the DPSF device are 3.24 cd A⁻¹ and 2.54 lm W⁻¹, corresponding to 5.41% of maximum external quantum efficiency (EQE). The spirobifluorene derivative show high thermal stabilities, 178 °C for the glass transition temperature (T_g) and 503 °C for the decomposition temperature (T_d). The synthesized spirobifluorene derivative shows potential application as a highly efficient pure blue emitter for organic light emitting devices (OLED).

1. Introduction

Although organic light-emitting devices (OLED) have been commercialized since 1997, a pure blue emitter with high efficiency is still a challenge for full colour display. In addition, 100% internal quantum efficiency of sky-blue electrophosphorescence has been obtained,^{1,2} however, highly efficient, stable deep-blue phosphorescence is still under developed.^{3,4} Therefore, many efforts have been paid on highly efficient stable blue fluorescent emitters which can be listed as single-cyclic aromatics;^{5,6} e.g. 4,4'-bis(2,2-diphenylvinyl)biphenyl (DPVBi),⁵ anthracene derivatives;7-11 e.g. 9,10-di-(2-naphthyl) anthracene (ADN),⁸ fluorene and spirobifluorenes;¹²⁻²¹ multi-cyclic aromatic;²²⁻²⁴ aromatic amines;²⁵⁻²⁸ nitrogen-containing heterocyclic blue emitters;^{11,29,30} other hetero-atom compounds.³¹ Among them, there have been reported a few emissions with a high external quantum efficiency (EQE) and Commission Internationale de l'Éclairage (CIE) coordinates in the range of (CIE_x <0.15, CIE_y <0.15) which was usually defined as a deepblue colour.^{7,11,12,16,22,24,28,32} However, a saturated deep-blue (CIE_x <0.15, CIE_y <0.10) emitter with high efficiency is a pressing concern for the development of full-colour saturated displays.³³⁻³⁸ C. H. Chien et al. reported a saturated deep blue emitter of 2-tert-butyl-9,10-bis[40-(diphenylphosphoryl) phenyl]

anthracene (POAn) at a saturated deep-blue CIE (0.15, 0.07) although the fluorescence quantum yield (Φ) of POAn in dilute cyclohexane reached as high as 0.98, the Φ in the solid state reduced to 0.71. The glass transition temperature (T_{o}) of it was 146 °C.33 Recently, T. Peng et al. reported a fluorescent beryllium complex of bis(2-(2-hydroxyphenyl)-4-methyl-pyridine)beryl- $\lim (Be(4-mpp)_2)$ with a saturated deep blue emission by CIE (0.14, 0.09) and EQE of 5.4%, however the quantum yield of $Be(4-mpp)_2$ was as low as 0.37, moreover beryllium is poisonous.³⁴ Kwon et al. reported a pure blue emission with a National Television Standards Committee (NTSC) standard blue at CIE (0.14, 0.08) from 9, 10-bis[(2",7"-di-t-butyl)-9',9"spirobifluorenyl] anthracene (TBSA), however the power efficiency (PE) needed to be improved (PE, 0.54 lm W⁻¹).³⁵ Therefore, it is more desirable to develop a highly efficient pure blue emitter with $\text{CIE}_{v} \approx 0.08$ and higher thermal stability.

In order to achieve this goal, we designed and synthesized a spirobifluorene derivative through considering the high thermal stability of the spirobifluorene moiety. Although anthracene derivatives are highly efficient emitters, it is still a challenge to get a highly efficient saturated deep-blue emission with them. Considering anthracene is more conjugated than phenanthrene, we introduced highly efficient emitting phenanthrene moieties to improve its colour purity and obtained 2,7-di(phenanthren-9-yl)-9,9'-spirobifluorene (DPSF) with a higher T_g of 178 °C than that of POAn³³ and a higher Φ of 0.79 than that of Be(4-mpp)₂.³⁴ A pure blue emission at CIE (0.15, 0.08) with a maximum EQE of 5.41% has been achieved by using DPSF as the emitter.

State Key Laboratory for Mesoscopic Physics and Department of Physics, Peking University, Beijing, 100871, P. R. China. E-mail: lxxiao@pku.edu. cn; qhgong@pku.edu.cn

2. Experimental sections

General

The ¹H NMR spectra were recorded on a JEOL 270 (270 MHz) spectrometer. Mass spectra were obtained using a JEOL JMS-K9 mass spectrometer. Ultraviolet-visible (UV-vis) absorption and photoluminescence spectra were obtained on an Agilent UV-vis Spectroscopy System (8453E). The electrochemical properties of DPSF was studied through cyclic voltammetry (CV) with a threeelectrode configuration with a Pt disk as the working electrode, Pt wire as the counter electrode, and a saturated calomel electrode (SCE) as the reference electrode in an acetonitrile solution containing 0.1 M of tetrabutylammonium perchlorate as the supporting electrolyte. Differential scanning calorimetry (DSC) was performed on a Perkin-Elmer Diamond DSC Pvris instrument under nitrogen atmosphere at a heating rate of 20 °C min⁻¹. Thermogravimetric analysis (TGA) was undertaken using a SEIKO EXSTAR 6000 TG/DTA 6200 unit under nitrogen atmosphere at a heating rate of 10 °C min⁻¹. HOMO levels were determined by atmospheric ultraviolet photoelectron spectroscopy (Rikken Keiki AC-2).

Synthesis of DPSF

A standard Suzuki-Miyaura cross-coupling reaction procedure was followed to synthesize DPSF. To a solution of 2,7-dibromo-9,9-spirobifluorene (1.314 g, 2.773 mmol) and phenanthrene-9boronic acid (1.353 g, 6.097 mmol) in toluene (200 mL) was added ethanol (100 mL) and a Na₂CO₃ solution (2 M, 100 mL) under nitrogen and agitation, followed by the addition of Pd(PPh₃)₄ (710 mg, 0.614 mmol). The resultant solution was refluxed for 24 h. Water was added to guench the reaction, then extracted with CH₂Cl₂, finally purified by column chromatography eluting with: CH_2Cl_2 : hexane (1:4), a solid was obtained with a yield of 46.7%. ¹H NMR (270 MHz, CDCl₃) δ : 8.70 (d, J = 8.31 Hz, 2H), 8.65 (d, J = 8.19 Hz, 2H), 8.05 (d, J = 7.82 Hz, 2H), 7.81 (d, J = 8.05 Hz, 4H), 7.75 (d, J = 7.60 Hz, 2H), 7.54–7.63 (m, 10H), 7.44 (t, J = 7.92 Hz, 2H), 7.34 (t, J = 7.72Hz, 2H), 7.19 (t, J = 7.33 Hz, 2H), 7.00 (d, J = 3.77 Hz, 2H), 6.96 (s, 2H). MS (EI, *m/z*): calcd for C₅₃H₃₂, 668.8; found, 669.3. Anal. calcd for C53H32: C 95.17%, H, 4.83%; found: C 95.10%, H 5.07%.

Fabrication of organic electrophosphorescent devices and the measurements

Organic layers were deposited by high-vacuum (10^{-6} Torr) thermal evaporation as previously reported.³⁹ First, a 30 nm layer of PEDOT : PSS (10 : 1 by weight) was coated *via* a dichloroethane solution as the hole injecting layer, before it was loaded into the evaporation system. After this the hole transporting, emitting, and electron transporting layers were sequentially deposited on the surface *via* thermal evaporation in a vacuum of 10^{-6} Torr. Finally, 0.5 nm of LiF together with 100 nm of Al were deposited as the cathode. The emitting area was defined by using a cyclic shadow mask. EQE was determined based on luminance, electroluminescence spectra, and current densities.

3. Results and discussions

DPSF was synthesized through a Suzuki–Miyaura crosscoupling reaction⁴⁰ by 2,7-dibromo-spirobifluorene with 9boronic acid phenanthrene as shown in Scheme 1.

The absorption spectra of DPSF in CHCl₃ and as a film which was deposited by high-vacuum (10^{-6} Torr) thermal evaporation on quartz are shown in Fig. 1. The absorption peaks at around 254 nm, 310 nm, and 327 nm for DPSF in solution, shift to 257 nm, 313 nm, and 336 nm for DPSF in its film state. The 254 nm absorption peak can be assigned to the π - π * transitions of the molecule. The peaks at 310 nm and 327 nm can be attributed to the absorption nature of the phenanthrene moiety.⁴¹ The emission peak of DPSF at around 400 nm is more red shifted than phenanthrene at around 350 nm⁴² in solution due to the larger conjugated system of DPSF. According to the absorption edges, the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) energy gap (E_{σ}) of DPSF can be calculated as 3.5 eV. The energy gap of DPSF is even wider than those of ADN (3.2 eV), DPVBi (3.1 eV), Be(4-mpp)₂ (3.1 eV), POAn (3.1 eV), and TBSA (2.8 eV) which are listed in Table 1. A fluorescence peak at 383 nm in CHCl₃ shifts to 398 nm in the film state. The quantum yield of DPSF in CHCl₃ is 0.79 calibrated with a standard of coumarin 102 (ϕ , 0.93).

The electrochemical properties of DPSF are shown in Fig. 2. Two reduction peaks were observed, the first peak located at 0.70 V (*vs.* SCE) was referred to monoanion formation (X/X^{-1}), and the second peak located at 0.98 V (*vs.* SCE) was the dianion (X^{-1}/X^{-2}) as reported.⁴³ The formation of dianion indicates that the monoanion is quite stable, which should be a benefit for a long time operation under charge transporting. The unsymmetrical redox processes may be due to the protonation reaction induced by the reactivity of the supporting electrolyte.⁴³

The thermal properties of the spirobifluorene derivative were measured by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) (Table 1). The T_g of DPSF is 178 °C, much higher than 64 °C for that of DPVBi. The decomposition temperature (T_d) of DPSF is 503 °C. The highly thermal stability of DPSF can be attributed to the existence of high thermal stability of the spirobifluorene moiety.⁴⁴

To study the emitting properties of the spirobifluorene derivative, devices were fabricated by using a 30 nm layer of 10 : 1 (wt) of poly(3,4-ethylene dioxythiophene) : polystyrene sulfonic acid (PEDOT : PSS) as the hole injecting material, a 30 nm layer of 4,4'-bis[N-(1-naphthyl)-N-phenyl-amino]biphenyl (NPB) as the hole transporting material, a 30 nm layer of DPSF or DPSF : N,N'-dicarbazolyl-3,5-benzene (mCP) (4 : 1 by weight) as the emitter and a 30 nm layer of 1,3,5-tris(N-phenyl-benzimidazol-2-yl)-benzene (TPBI) or TPBI : 2-tert-butyl-phenyl-5-biphenyl-1,3,4-oxadiazole (PBD) (2 : 1 by weight) as the electron transporting (ET) material. Finally, 0.5 nm of LiF together with 100 nm of Al was deposited as the cathode. The



Scheme 1 Synthesis of the spirobifluorene derivative.



Fig. 1 Absorption and PL spectra of DPSF.

 Table 1
 Physical properties of the blue emitters

Materials	$T_{\rm g}$ (°C)	$E_{\rm a}~({\rm eV})$	Ip (eV)	$E_{\rm g}~({\rm eV})$	Ref.
DPSF	178	2.3	5.8	3.5	This work
ADN		2.6	5.8	3.2	13
DPVBi	64	2.8	5.9	3.1	5, 45
POAn	146	2.5	5.6	3.1	33
$Be(4-mpp)_2$		2.6	5.7	3.1	34
TBSA	207	3.0	5.8	2.8	35



Fig. 2 CV curves of DPSF at a scan-rate of $10 \text{ mV} \cdot \text{s}^{-1}$.

emitting area was defined by using a shadow mask with 2 mm diameter opening. The device architecture and their energy levels are shown in Fig. 3.

Device A: ITO/PEDOT : PSS 30 nm/NPB 30 nm/DPSF 30 nm/TPBI 30 nm/LiF 0.5 nm/Al 100 nm.

Device **B**: ITO/PEDOT : PSS 30 nm/NPB 30 nm/DPSF 30 nm/ TPBI : PBD (2 : 1) 30 nm/LiF 0.5 nm/A1 100 nm.

Device C: ITO/PEDOT : PSS 30 nm/NPB 30 nm/DPSF : mCP (4 : 1) 30 nm/TPBI 30 nm/LiF 0.5 nm/A1 100 nm.

Device **D**: ITO/PEDOT : PSS 30 nm/NPB 30 nm/ DPSF : mCP (4 : 1) 30 nm/TPBI : PBD (2 : 1) 30 nm/LiF 0.5 nm/ Al 100 nm.

Current density–voltage curves of the devices are shown in Fig. 4, in which the current density of device **B** with TPBI : PBD as the electron transporting material is higher than that of device **A** where only TPBI functions as the electron transporting material. Accordingly, the turn-on voltage of device **B** (4.1 V) is lower than that of device **A** (4.5 V). This is due to the slightly lower electron mobility of TPBI (10^{-6} to 10^{-5} cm² V s⁻¹)⁴⁶ than 1.9×10^{-5} cm² V s⁻¹ for PBD.⁴⁷ The deeper HOMO of PBD (6.5 eV)⁴⁸ might also be the reason for the higher efficiency for device **B**. The holes should be more effectively blocked by PBD



Fig. 3 Chemical structures and energy levels of the organic materials used in the OLEDs.



Fig. 4 Current density and luminance–voltage curves of device A: ITO/ PEDOT : PSS 30 nm/NPB 30 nm/DPSF 30 nm/TPBI 30 nm/LiF/A1 (△); device B: ITO/PEDOT : PSS 30 nm/NPB 30 nm/DPSF 30 nm/ TPBI : PBD (2 : 1) 30 nm/LiF/A1 (▲); device C: ITO/PEDOT : PSS 30 nm/NPB 30 nm/DPSF : mCP (4 : 1) 30 nm/TPBI 30 nm/LiF/A1 (○); device D: ITO/PEDOT : PSS 30 nm/NPB 30 nm/DPSF : mCP (4 : 1) 30 nm/TPBI : PBD (2 : 1) 30 nm/LiF/A1 (●).

than TPBI. Accordingly, the current efficiency (CE) and PE of device **B**, 3.26 cd A^{-1} and 2.27 lm W^{-1} , respectively, are higher than those of device **A** as shown in Fig. 5. Device **B** achieved a



Fig. 5 CE and PE-current density curves of device A: ITO/ PEDOT : PSS 30 nm/NPB 30 nm/DPSF 30 nm/TPBI 30 nm/LiF/Al (Δ); device B: ITO/PEDOT : PSS 30 nm/NPB 30 nm/DPSF 30 nm/ TPBI : PBD (2 : 1) 30 nm/LiF/Al (Δ); device C: ITO/PEDOT : PSS 30 nm/NPB 30 nm/DPSF : mCP (4 : 1) 30 nm/TPBI 30 nm/LiF/Al (\bigcirc); device D: ITO/PEDOT : PSS 30 nm/NPB 30 nm/DPSF : mCP (4 : 1) 30 nm/TPBI : PBD (2 : 1) 30 nm/LiF/Al (\bigcirc).

higher EQE of 4.99%. The device performances are listed in Table 2.

To reduce exciton quenching in the emitting layer, doping is an effective way. In device **C**, we introduced mCP as the diluter because of its large gap which may prevent the energy transfer from DPSF to the dopant and its deep HOMO to confine excitons in the emitting layer. The doping ratio is 4:1 by weight of DPSF : mCP, which is quite high for the content of DPSF, thus it is quite easy to fabricate. This results in the reduced exciton quenching effect in the emitter of DPSF. The maximum luminance of device **C** is 4430 cd m⁻², 64% higher than that of device **A**. The efficiencies of device **C** are also accordingly increased to 2.75 cd A⁻¹ and 1.73 lm W⁻¹ from 1.97 cd A⁻¹ and 1.23 lm W⁻¹ for those of device **A**. The sum that of device **C** is higher than that of device **A**. The sum that of device **C** is higher than that of device **A**. The sum that of device **C** is higher than that of device **A**. The sum that of device **C** is higher than that of device **A**. The sum that of device **C** is higher than that of device **A**. The sum that of device **C** is higher than that of device **A**. The sum that of device **C** is higher than that of device **A**. The sum that of device **C** is higher than that of device **A**. The sum that of device **C** is higher than that of device **A**. The sum that of 2.3 eV for the emitter of DPSF and



Fig. 6 EQE-current density of device **A**: ITO/PEDOT : PSS 30 nm/NPB 30 nm/DPSF 30 nm/TPBI 30 nm/LiF/Al (\triangle); device **B**: ITO/PEDOT : PSS 30 nm/NPB 30 nm/DPSF 30 nm/TPBI : PBD (2 : 1) 30 nm/LiF/Al (\blacktriangle); device **C**: ITO/PEDOT : PSS 30 nm/NPB 30 nm/DPSF : mCP (4 : 1) 30 nm/TPBI 30 nm/LiF/Al (\bigcirc); device **D**: ITO/PEDOT : PSS 30 nm/NPB 30 nm/DPSF : mCP (4 : 1) 30 nm/TPBI 30 nm/DPSF : mCP (4 : 1) 30 nm/LiF/Al (\blacklozenge).



Fig. 7 EL spectra of the devices: ITO/PEDOT : PSS 30 nm/NPB 30 nm/ DPSF 30 nm/TPBI 30 nm/LiF/Al (\triangle); ITO/PEDOT : PSS 30 nm/NPB 30 nm/DPSF 30 nm/TPBI : PBD (2 : 1) 30 nm/LiF/Al (\blacktriangle); ITO/ PEDOT : PSS 30 nm/NPB 30 nm/DPSF : mCP (4 : 1) 30 nm/TPBI 30 nm/LiF/Al (\bigcirc); ITO/PEDOT : PSS 30 nm/NPB 30 nm/DPSF : mCP (4 : 1) 30 nm/TPBI : PBD (2 : 1) 30 nm/LiF/Al (\spadesuit).

much closer to the LUMO level of TPBI, therefore the electrons should transfer more easily from the electron transporting layer to the emitting layer.

By combining the advantages of device **B** and device **C**, we prepared device **D** by using a mixture of TPBI and PBD as the electron transporting and hole blocking layer, and DPSF doped with mCP as the emitting layer. Thus we get not only a high luminance of 4745 cd m⁻², but also the highest EQE of 5.41% (Fig. 6), corresponding to nearly 100% of internal quantum efficiency obtained by using doped DPSF as the emitter. All the devices of **A**, **B**, **C**, and **D** show an electroluminescence at around

Table 2 The performance of devices with different electron transporting layers

Device	Turn-on voltage (V@1 cd m^{-2})	Max luminance (cd m ⁻²)	Max PE (lm W ⁻¹)	Max CE (cd A ⁻¹)	Max EQE (%)	$\operatorname{CIE}\left(x,y\right)$
Α	4.5	2711	1.23	1.97	3.41	0.15, 0.08
В	4.1	2632	2.27	3.26	4.99	0.15, 0.08
С	4.5	4430	1.73	2.75	4.82	0.15, 0.08
D	3.5	4745	2.54	3.24	5.41	0.15, 0.08

435 nm (Fig. 7), and pure blue emission at CIE (0.15, 0.08) has been achieved using DPSF as the emitter. The synthesized spirobifluorene derivative shows a potential application as a highly efficient pure blue emitter for OLEDs.

4. Conclusions

In summary, a highly thermally stable spirobifluorene derivative, DPSF, with a $T_{\rm g}$ of 178 °C was synthesized and its emitting properties in deep blue devices were investigated. The maximum CE and PE of the DPSF device are 3.24 cd A⁻¹ and 2.54 lm W⁻¹, corresponding to 5.41% of maximum EQE has been obtained. A pure blue emission at CIE (0.15, 0.08) has been achieved using DPSF as the emitter. The spirobifluorene derivative showed high thermal stabilities and exhibits potential application as an emitter for pure blue devices.

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