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ARTICLE

Pure hydrocarbon host materials based on spirofluorene with excellent performances for green phosphorescent light-emitting devices

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Four pure hydrocarbon molecules based on spirofluorene were synthesized and their optoelectronic properties were investigated. These four compounds (1-4) exhibited excellent optoelectronic properties with good thermal stabilities, favorable optical energy bandgaps and triplet energies, compatible HOMO-LUMO energy levels and so on. Green phosphorescent organic light emitting devices (PHOLEDs) in which these four compounds served as host materials have been fabricated, and compound 1 demonstrated the optimal electroluminescence (EL) performances with the maximum current efficiency, maximum power efficiency and external quantum efficiency (EQE) of 31.5 cd A⁻¹, 19.8 lm W⁻¹ and 9.0%, respectively, which make it promising candidate as host material for PHOLEDs.

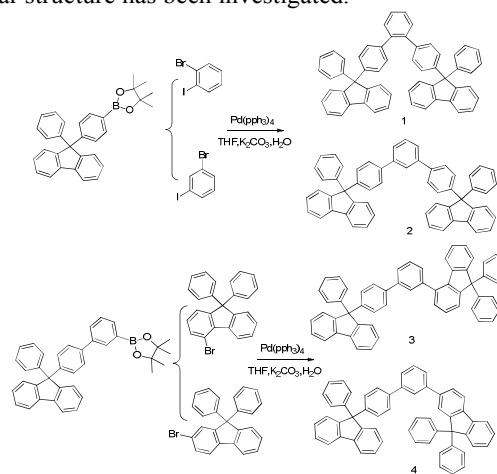
Introduction

Organic light-emitting diodes (OLEDs) have been aroused revolutionary changes in next-generation displays due to their superior features.¹⁻³ The device performances of OLEDs have been improved a lot in recent years, while there are still some critical problems to be solved, for example, efficiency and lifetime.⁴ An efficient way is to design novel and high-efficiency host materials. It is necessary for host materials that possess suitable optoelectronic characteristics.⁵⁻⁶

Nowadays, many effective strategies have been proposed to improve the optoelectronic properties of host materials. For example, molecular configurations with meso-, insulating or twisted linkage have been introduced to achieve high triplet energy levels and thermal properties.⁷⁻⁸ What is more, in order to obtain a balanced hole/electron transport material, many different heteroatom organic blocks, such as carbazole, pyridine, phosphine oxide, etc., are put forward to meet these requirements,⁹⁻¹² because the molecular structure of host materials can be delicately tuned with different groups. However, even though the benefit from multifunctional role of heteroatom compounds recognized, potential risks of the application of heteroatom exist. So it is essential to investigate the organic compound without heteroatom. Pure hydrocarbon (PHC) compounds have been emerged at the right time.¹³⁻¹⁴ Nevertheless, the performances of PHC compounds are still not comparable with that of heteroatom compounds. Tremendous

improvement of PHC compounds can be expected.¹⁵ It is urgent to explore the hydrocarbon blocks for high efficient compounds.

In this work, four PHC compounds (1-4) based on spirofluorene in different linkage ways have been designed and synthesized. In view of the excellent optoelectronic properties of spirofluorene, different molecular configurations without heteroatom were fabricated by introducing different linkage ways. Furthermore, just one step by Suzuki coupling reaction in high yield could obtain these four target compounds. The dependence of the EL performance on the compounds molecular structure has been investigated.



Scheme 1 Synthesis of compounds 1-4.

Results and discussion

Thermal properties

The thermogravimetric analyses (TGA) and differential scanning calorimetry (DSC) were applied to investigate the thermal properties of compounds 1-4. The glass transition (T_g) and decomposition (T_d) temperatures are summarized in Table 1. As shown by the TGA curves (Fig.1a), the decomposition temperatures (T_d), which correspond to 5% weight loss upon heating during TGA, were measured to be 406 °C, 429 °C, 402 °C and 406 °C for 1-4, respectively. In addition, Fig.1b showed the DSC heating curves of these four compounds, the corresponding glass transition temperatures (T_g) of 1-4 were determined to be 138 °C, 148 °C, 134 °C and 121 °C, respectively. These values were higher than those of mCP (65 °C) or other pure hydrocarbon materials,¹⁶ thus these excellent thermal properties are favorable to improve the OLED performances and lifetime during operation.

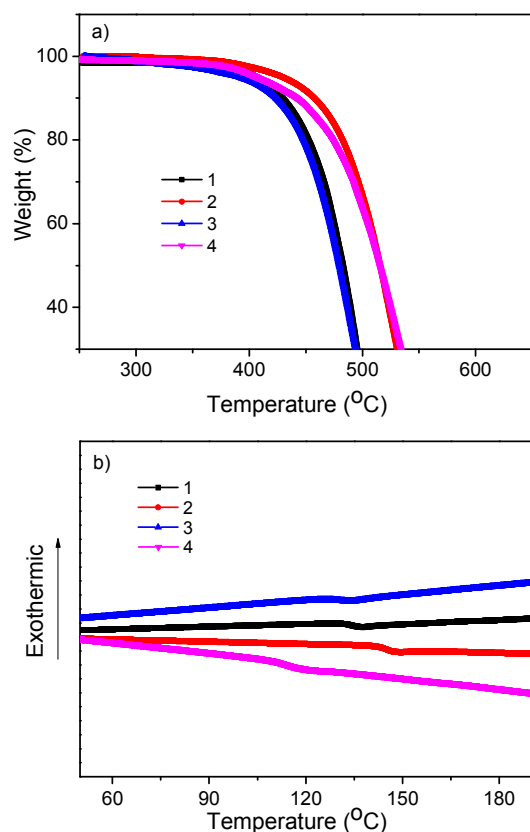


Fig.1 Thermal properties of compounds 1-4. (a) The thermogravimetric analyses (TGA) curves, the decomposition temperatures (T_d) corresponding to 5% weight loss upon heating during TGA; (b) Differential scanning calorimetry (DSC) heating curves of these four compounds.

Photophysical properties

The photophysical properties of compounds 1-4 were investigated by the UV-visible absorption, photoluminescence (PL) spectra (at room temperature in THF) and phosphorescence spectra (at 77 K in 2-methyl THF), which were shown in Fig.2 and the pertinent data were listed in Table 1. As shown in Fig.2a, the absorption spectra of 1-4

were analogous with the absorption bands in the range of 275-325 nm. The primary, strong absorption peaks of 1-4 are located at 275 nm that can be derived from $\pi \rightarrow \pi^*$ transitions of the peripheral phenyl ring.¹⁷ While the secondary, weak absorption peaks of 4 (323 nm) were different with that of 1-3 (309 nm), the reason may be ascribed to the difference of interaction with the two spirofluorene fragments. What is more, the secondary absorption bands can be attributed to $\pi \rightarrow \pi^*$ transitions of the fluorenyl part.¹⁸ The optical energy bandgaps (E_g) of 1-4 that obtained from the long wavelength absorption edges are determined to be 3.91 eV, 3.91 eV, 3.91 eV and 3.50 eV, respectively.

In terms of emission, the photoluminescence (PL) spectra of 1-4 are shown in Fig.2b with their maxima located at 326 nm, 342 nm, 371 nm and 348 nm, respectively. As for 1-3, the PL spectra are normally behaved with the extension of conjugation in the molecular structure, and the maximum of the PL spectrum are matching red-shifted. The PL performance of compound 4 is different from that of compounds 1-3. There are shoulder peaks in the PL spectra, which can be attributed to some low-energy transitions.¹⁹ Furthermore, by the measurement of the phosphorescence spectra in the frozen 2-methyl THF at 77 K (see Fig.2c), the triplet energies (E_T) were calculated on the basis of the short wavelength peak, i.e., 2.88 eV, 2.84 eV, 2.76 eV and 2.54 eV for compounds 1-4, respectively. Therefore, the high bandgaps and the high triplet energies make them good host materials candidates for green PHOLEDs.

Electrochemical properties

The electrochemical properties of compounds 1-4, namely the highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO), were determined by cyclic voltammetry (CV). Fig.3 show the corresponding cyclic voltammograms, measured in CH_2Cl_2 (0.1 M TBAPF₆ as the supporting electrolyte at a scan rate of 100 mV s^{-1} , with an SCE reference electrode (ferrocene/ferrocenium (Fc/Fc^+) redox couple as the external standard), a glassy-carbon working electrode and a platinum-wire counter electrode. As shown in Fig.3, the HOMO values of compounds 1-4 could be obtained to be -6.20 eV, -6.11 eV, -5.89 eV and -5.75 eV, respectively. With the formula $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g$, the corresponding LUMO values of compounds 1-4 could be calculated to be -2.29 eV, -2.20 eV, -1.98 eV and -2.25 eV, respectively. These data could guarantee the compatible alignment of the energy levels of the green PHOLEDs that we pursued for efficient carriers injection.²⁰

Table 1 The physical properties of the compounds 1-4.

Compound	$\lambda_{\text{abs}}^{\text{max}}$ (nm) ^a	$\lambda_{\text{em}}^{\text{max}}$ (nm) ^d	E_{g} (eV) ^b	HOMO (eV) ^c	LUMO (eV) ^d	E_{T} ^e	T_{g} ^f	T_{d} ^f
1	309	326	3.91	-6.20	-2.29	2.88	138	406
2	309	342	3.91	-6.11	-2.20	2.84	148	429
3	309	371	3.91	-5.89	-1.98	2.76	134	402
4	323	348	3.50	-5.75	-2.25	2.54	121	406

^aMeasured in tetrahydrofuran. ^bEstimated from onset of the absorption spectra ($E_{\text{g}} = 1240/\lambda_{\text{onset}}$). ^cCalculated from cyclic voltammetry. ^dCalculated by the equation $E_{\text{HOMO}} = E_{\text{LUMO}} - E_{\text{g}}$. ^eCalculated by the first peak of phosphorescence spectra measured at 77k. ^fMeasured by TGA and DSC.

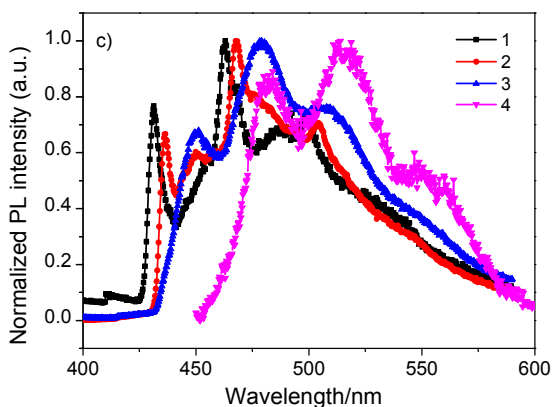
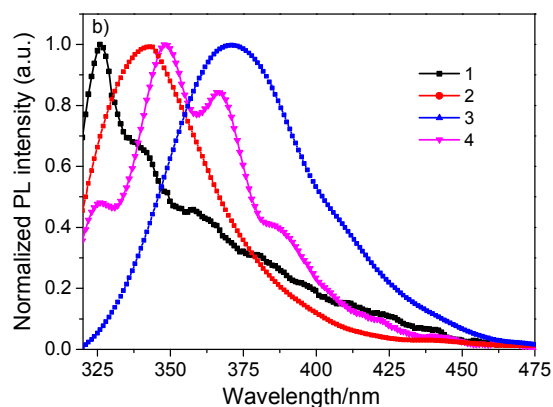
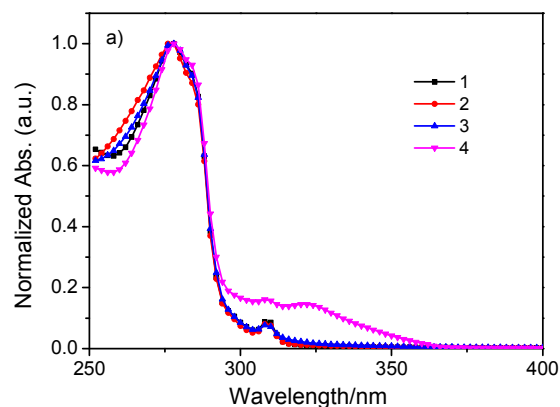


Fig.2 Absorption (a), photoluminescence spectra (at room temperature in THF) (b) and phosphorescence spectra (at 77 K in 2-methylTHF) (c) of compounds 1-4 at 1.0×10^{-5} mol/L.

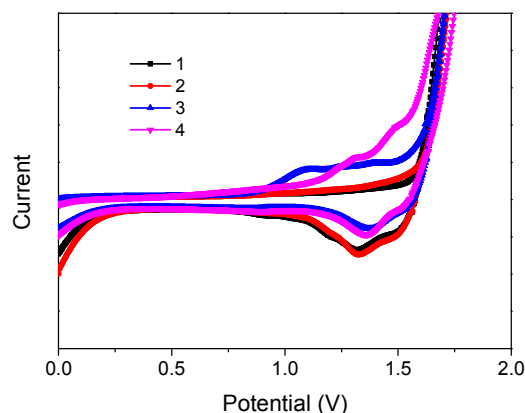


Fig.3 Cyclic voltammograms of compounds 1-4 in dichloromethane with tetra(n-butyl)ammonium hexafluorophosphate (0.1 M) as the supporting electrolyte for the oxidation scan.

Electroluminescence (EL) of PHOLEDs

To evaluate the capabilities of compounds 1-4 as host materials in device performance, green PHOLEDs based on compounds 1-4 were fabricated. The device structures were: ITO/MoO₃ (3 nm)/CBP (15 nm)/host: Ir(ppy)₃ (15 nm, 5 wt%)/TPBi (40 nm)/LiF (0.6 nm)/Al (80 nm). The emitting layer (EML) was composed of 5 wt% Ir(ppy)₃ doped into the host materials (compounds 1-4). LiF was employed as the electron injection layer (EIL) and TPBi served as the electron transport layer (ETL). MoO₃ and CBP were acted as the hole injection layers (HIL), the hole transport layers (HTL), respectively. Fig.4 exhibited the related HOMO and LUMO energy levels of these materials in the device. The green phosphorescent devices based on these four host materials were fabricated successfully according to previous procedure.²¹

The relevant electrical performances are shown in Fig.5 and the data are listed in Table 2. From the current density-voltage-luminance curves, it was apparent that the onset voltages of these four devices were small and be 4V, 3.8V, 3.9V and 3.6V, respectively. The maximum current efficiency for compounds 1-4 based devices were 31.5, 26.1, 19.4 and 25.2 cd A⁻¹, respectively, and the corresponding maximum power efficiency were 19.8, 16.4, 13.5 and 17.6 lm W⁻¹. Furthermore, the external quantum efficiency (EQE) was also determined to be 9.0%, 7.5%, 5.6% and 7.2%, for compounds 1-4 based devices, respectively. These values demonstrated that these four host

materials were competitive with currently available small pure hydrocarbon hosts.^{6,13,22} As for the pure hydrocarbon hosts, their excellent performances can be ascribed to their: (i) electron-predominant characteristic for carrier balance, (ii) favorable molecular configurations, and (iii) high thermal properties and triplet energies. For compounds 1-4, with different linkage ways of spirofluorene units, they exhibited excellent optoelectronic properties such as good thermal stabilities, favorable optical energy bandgaps and triplet energies, compatible HOMO-LUMO energy levels and so on, which result in such excellent device performances. Therefore, the molecular structure plays an important role in device performance.

The EL spectra of device based on these four compounds severed as hosts were also investigated, the color coordinates of these four green phosphorescent devices were determined to be (0.31, 0.62), (0.32, 0.61), (0.31, 0.62) and (0.32, 0.62), respectively, according to the normalized EL spectra (Fig.5d) of compounds 1-4 based devices.

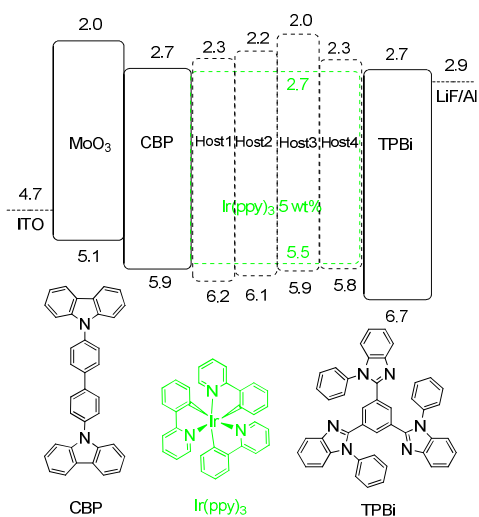


Fig.4 Energy-level diagram of the green PHOLEDs.

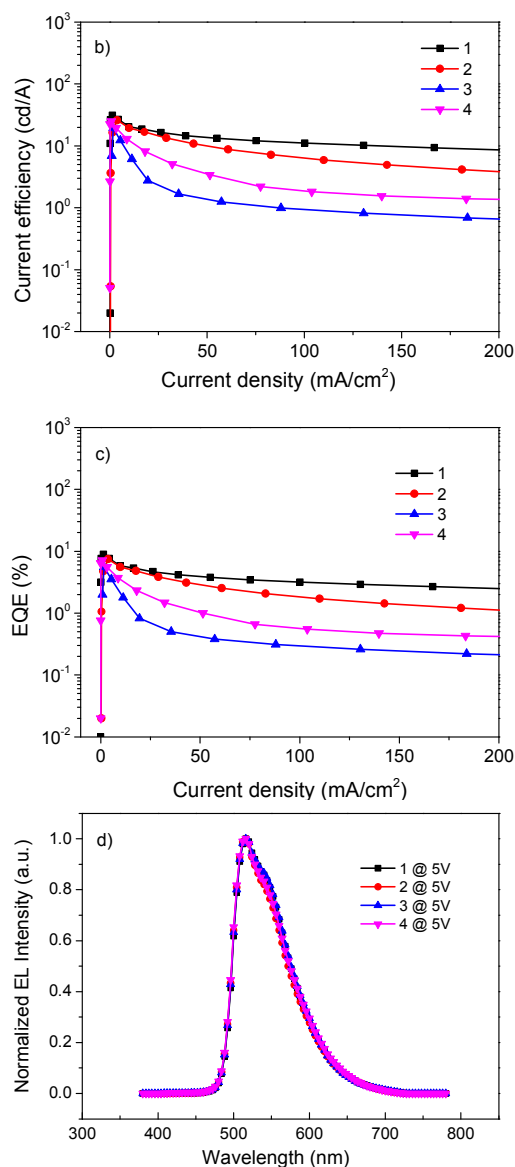
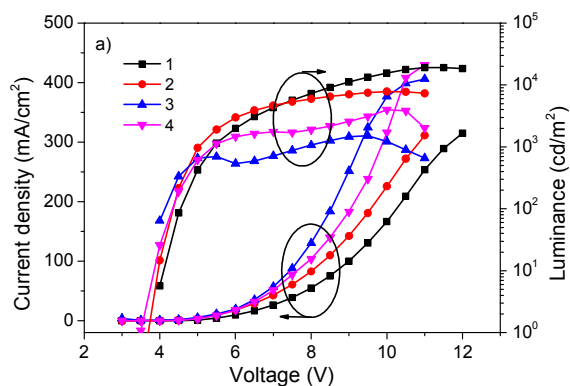


Fig.5 (a) Current density–voltage–luminance curves; (b) current efficiency–current density curves; (c) external quantum efficiency – luminance curves of green PHOLEDs; (d) electroluminescence spectra of green PHOLEDs.

To further verify the difference in the carriers transport of compounds 1-4, hole and electron only devices were fabricated with the structure: hole only, ITO/MoO₃ (3 nm)/CBP (15 nm)/host (15 nm)/CBP (15 nm)/MoO₃ (3 nm)/Al; electron only, ITO/LiF (0.6 nm)/TPBi (40 nm)/host (15 nm)/TPBi (40 nm)/LiF (0.6 nm)/Al, in which compounds 1-4 served as the hosts of the structure. As shown in Fig.6, the carriers transport of compounds 1, 2 and 4 were proved to be efficient, especially for compound 1 and 2, their hole current densities could be comparable to some classic hosts. Meanwhile, compound 1 also exhibited the capability of electron transport. Therefore, the ambipolar property of compound 1 may be beneficial to balanced carrier injection resulting in excellent device performance.²³ For compound 2, the hole transport was excellent while the electron transport was recessive, compound 3 was similar with compound 2 that the hole transport was recessive and the

electron transport was excellent, so their device performances were not very good. It was noteworthy that the performance of hole only and electron only device for compound 1 and 4 due to their excellent hole and electron transport properties. In general, such abovementioned carriers transport behavior was in good agreement with the green PHOLEDs EL performances.

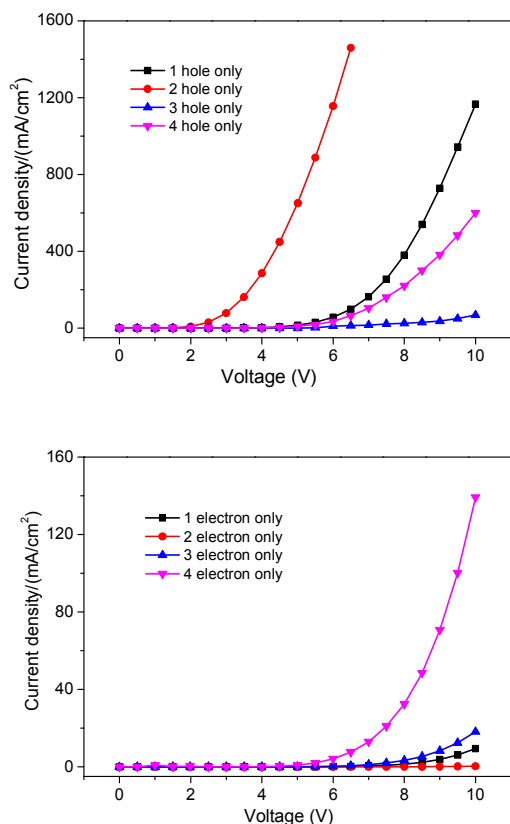


Fig.6 Current density versus voltage characteristics of the hole-only and electron-only devices based on compounds 1-4.

Table 2 Electroluminescent characteristics of the devices.

Device	Voltage ^a (V)	$\eta_{c,max}$ (cd/A)	$\eta_{p,max}$ (lm/W)	η_{ext}^b (%)	CIE(x,y) ^c
1	4.0	31.5	19.8	9.0	0.31,0.62
2	3.8	26.1	16.4	7.5	0.32,0.61
3	3.9	19.4	13.5	5.6	0.31,0.62
4	3.6	25.2	17.6	7.2	0.31,0.62

^a Operating voltage of onset. ^b Maximum of external quantum efficiency

(η_{ext}). ^c Measured at 5V.

Conclusions

Four pure hydrocarbon (PHC) compounds based on spirofluorene have been synthesized, and their optoelectronic

properties and EL performances were investigated. Good thermostability with the endothermal glass transitions over 120°C for all four compounds was demonstrated. As for the green phosphorescent light-emitting devices (PHOLEDs), compound 1 exhibited the best EL performances with the maximum current efficiency, maximum power efficiency and the external quantum efficiency (EQE) of 31.5 cd A⁻¹, 19.8 lm W⁻¹ and 9.0%, respectively, which were superior compared with those of pure hydrocarbon compounds reported elsewhere. Given the excellent optoelectronic properties of spirofluorene, pure hydrocarbon compounds combining spirofluorene derivatives might be employed as promising host materials in phosphorescent light-emitting devices (PHOLEDs) and further investigation is underway.

Experimental

General information

All reagents of the route were purchased from Shanghai Taochemical technology Co., Ltd and received without further purification.

The ¹H and ¹³C NMR spectra were obtained by a Bruker AM 400 spectrometer, the mass spectra were recorded on a Waters LCT Premier XE spectrometer. 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. The cyclic voltammograms were obtained by a Versastat II electrochemical workstation with conventional three electrodes containing an SCE reference electrode (the ferrocene/ferrocenium(Fc/Fc⁺) redox couple as external standard), a glassy-carbon working electrodes and a platinum-wire counter electrode.

Synthesis

4,4''-bis(9-phenyl-9H-fluoren-9-yl)-1,1':2',1''-terphenyl (1)

4,4,5,5-tetramethyl-2-(4-(9-phenyl-9H-fluoren-9-yl)phenyl)-1,3,2-dioxaborolane (1.0g, 2.3mmol), 1-bromo-2-iodobenzene (0.3g, 1.1 mmol), 2M K₂CO₃ (20mL), Pd(pph₃)₄ (20mg) and THF (60mL) were added to a 100 mL one-necked flask under nitrogen and heated to reflux for 6h. After the reaction was completed, the reaction mixture was diluted with dichloromethane and the organic phase was washed with water. Then drying over MgSO₄, the solvent was removed. The resulting crude product was passed through a flash column chromatograph to remove impurities and recrystallized from methanol to obtain a white solid product. Yield: 86%. ¹H NMR (400 MHz, DMSO, TMS) δ : 7.95 (t, *J* = 6.2 Hz, 4H), 7.48 (t, *J* = 7.6 Hz, 2H), 7.40 (m, 6H), 7.34 (m, 5H), 7.24 (t, *J* = 7.2 Hz, 10H), 7.15 (m, 2H), 7.07 (m, 3H), 6.92 (d, *J* = 1.6 Hz, 6H). ¹³C NMR (100 MHz, CDCl₃) δ : 151.26, 145.93, 144.09, 140.25,

140.15, 139.68, 130.20, 129.76, 128.22, 128.06, 127.68, 127.51, 127.46, 127.38, 126.76, 126.63, 126.18, 120.15, 99.99, 65.24. MALDI-TOF (m/z): M calcd for C₅₆H₃₈, 710.2974; found, 710.2976. Anal. Cald for C₅₆H₃₈: C, 94.61; H, 5.39. Found: C, 94.55; H, 5.41.

4,4''-bis(9-phenyl-9H-fluoren-9-yl)-1,1':3',1''-terphenyl (2)

Compound 2 was synthesized by the similar procedure as described above for 1 using 4,4,5,5-tetramethyl-2-(4-(9-phenyl-9H-fluoren-9-yl)phenyl)-1,3,2-dioxaborolane and 1-bromo-3-iodobenzene. Yield: 82%. ¹H NMR (400 MHz, DMSO, TMS) δ: 7.95 (d, *J* = 7.4 Hz, 4H), 7.79 (s, 1H), 7.62 (d, *J* = 8.4 Hz, 4H), 7.57 (d, *J* = 7.2 Hz, 2H), 7.51 - 7.46 (m, 5H), 7.42 (t, *J* = 8.0 Hz, 4H), 7.33 (t, *J* = 7.6 Hz, 4H), 7.26 (m, 6H), 7.17 (m, 8H). ¹³C NMR (100 MHz, CDCl₃) δ: 151.11, 145.85, 145.17, 141.23, 140.18, 139.41, 130.04, 129.09, 128.58, 128.26, 128.16, 127.79, 127.55, 127.00, 126.70, 126.21, 125.86, 120.23, 100.04, 65.27. MALDI-TOF (m/z): M calcd for C₅₆H₃₈, 710.2974; found, 710.2975. Anal. Cald for C₅₆H₃₈: C, 94.61; H, 5.39. Found: C, 94.56; H, 5.40.

9,9-diphenyl-4-(4'-(9-phenyl-9H-fluoren-9-yl)-[1,1'-

biphenyl]-3-yl)-9H-fluorene (3)

Compound 3 was synthesized by the similar procedure as described above for 1 using 4,4,5,5-tetramethyl-2-(4'-(9-phenyl-9H-fluoren-9-yl)-[1,1'-biphenyl]-3-yl)-1,3,2-dioxaborolane and 4-bromo-9,9-diphenyl-9H-fluorene. Yield: 87%. ¹H NMR (400 MHz, CDCl₃, TMS) δ: 7.78 (d, *J* = 7.6 Hz, 2H), 7.70 (s, 1H), 7.64 (d, *J* = 8.0 Hz, 1H), 7.53 (dd, *J* = 15.6, 8.0 Hz, 3H), 7.46 - 7.42 (m, 4H), 7.39 (d, *J* = 7.6 Hz, 1H), 7.36 (d, *J* = 7.6 Hz, 3H), 7.31 - 7.27 (m, 4H), 7.25 - 7.22 (m, 16H), 7.14 - 7.11 (m, 1H), 6.99 (t, *J* = 8.0 Hz, 2H). ¹³C NMR (100 MHz, CDCl₃) δ: 151.11, 143.41, 140.17, 136.00, 128.98, 128.65, 128.60, 128.31, 128.25, 128.20, 128.16, 127.78, 127.55, 127.54, 127.36, 127.23, 127.08, 127.00, 126.69, 126.64, 126.47, 126.44, 126.21, 126.13, 123.14, 120.21, 99.99. MALDI-TOF (m/z): M calcd for C₅₆H₃₈, 710.2974; found, 710.2977. Anal. Cald for C₅₆H₃₈: C, 94.61; H, 5.39. Found: C, 94.55; H, 5.39.

9,9-diphenyl-2-(4'-(9-phenyl-9H-fluoren-9-yl)-[1,1'-

biphenyl]-3-yl)-9H-fluorene (4)

Compound 4 was synthesized by the similar procedure as described above for 1 using 4,4,5,5-tetramethyl-2-(4'-(9-phenyl-9H-fluoren-9-yl)-[1,1'-biphenyl]-3-yl)-1,3,2-dioxaborolane and 2-bromo-9,9-diphenyl-9H-fluorene. Yield: 82%. ¹H NMR (400 MHz, CDCl₃, TMS) δ: 7.75 (d, *J* = 8.0 Hz, 1H), 7.72 (d, *J* = 6.6 Hz, 4H), 7.69 (d, *J* = 2.8 Hz, 1H), 7.63 (s, 1H), 7.58 - 7.53 (m, 2H), 7.50 (s, 1H), 7.47 (d, *J* = 9.6 Hz, 1H), 7.41 (d, *J* = 5.4 Hz, 1H), 7.40 - 7.37 (m, 4H), 7.35 (t, *J* = 3.2 Hz, 1H), 7.32 (d, *J* = 1.6 Hz, 2H), 7.30 (d, *J* = 7.2 Hz, 3H), 7.27 (s, 1H), 7.24 (d, *J* = 3.2 Hz, 1H), 7.22 (m, 4H), 7.17 (d, *J* = 3.2 Hz, 8H), 7.09 - 7.05 (m, 1H), 6.93 (s, 1H). ¹³C NMR (100 MHz, CDCl₃) δ: 159.21, 153.65, 150.41, 143.98, 128.59, 128.29, 128.27, 128.18, 128.17, 127.80, 127.78, 127.72, 127.56, 127.53, 127.06, 126.76, 126.70, 126.68, 126.26, 126.23, 126.21, 126.09, 124.81, 120.49, 120.34, 120.23, 100.00. MALDI-TOF (m/z): M calcd for C₅₆H₃₈,

710.2974; found, 710.2978. Anal. Cald for C₅₆H₃₈: C, 94.61; H, 5.39. Found: C, 94.52; H, 5.46.

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Notes and references

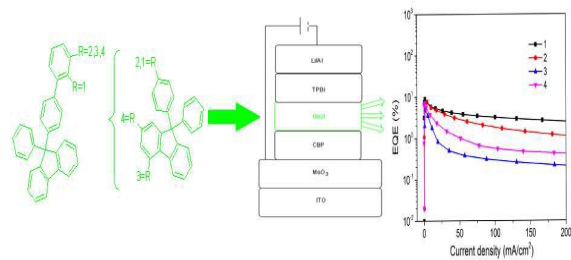
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Electronic Supplementary Information (ESI) available: [The spectra (¹H NMR, ¹³C NMR, MALDI-TOF) for compounds 1-4].

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Four novel pure hydrocarbon spirofluorene-based compounds were fully investigated for green electrophosphorescent devices.