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Novel 9,9-Dimethylfluorene-bridged D–π–A-type Fluorophores with Hybridized Local and Charge-transfer Excited State for Deep-blue Electroluminescence with CIE$_y$ ~ 0.05

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Cotents

SI-1. Theoretical calculations

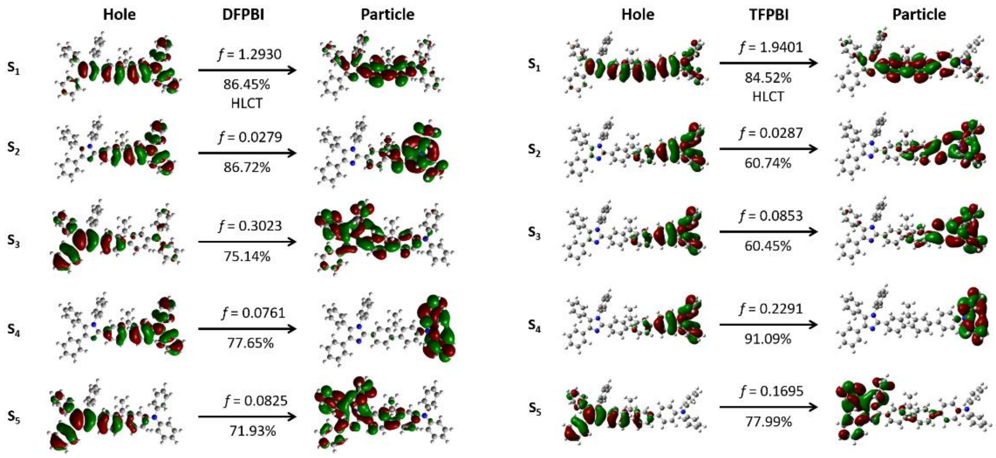


Fig. S1 Natural transition orbitals of first-five singlet excited states of DFPBI and TFPBI.

SI-2. Photophysical properties

1. Lippert-Mataga calculation

The properties of ground state (S_0) and the lowest singlet excited state (S_1) can be better understood through solvatochromic experiment. We use the Lippert-Mataga equation to explore the influence of solvent environment on the optical property of our materails, the model can describes the interaction between the solvent and the dipole moment of solute:

$$hc(\mathrm{v}_a - \nu_f) = hc(\nu_a^0 - \nu_f^0) - \frac{2(\mu_e - \mu_g)^2}{a^3} f(\varepsilon, n)$$

where f is the orientational polarizability of the solvent, $\nu_a^0 – \nu_f^0$ corresponds to the Stokes shifts when f is zero, μ_e is the excited state dipole moment, μ_g is the ground-state dipole moment; a is the solvent cavity (Onsager) radius, derived from the Avogadro number (N), molecular weight (M), and density (d = 1.0 g cm^{-3}); ε and n are the solvent dielectric and the solvent refractive index, respectively; $f(\varepsilon, n)$ and a can be calculated respectively as follows:

$$f(\varepsilon, n) = \frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}$$

$$a = \left(\frac{3\mathrm{M}}{4N\pi\mathrm{d}}\right)^{1/3}$$

The relationships between stokes shift and solvent polarity are presented in Fig. 5, the corresponding μ_e was estimated to be 10.1 D (Slope = 3947, R = 0.92) and 18.3 D (Slope = 11660, R = 0.93) for DFPBI, 10.4 D (Slope = 3744, R = 0.95) and 20.7 D (Slope = 12922, R = 0.91) for TFPBI. The detailed data are listed in Table S1 and Table S2.

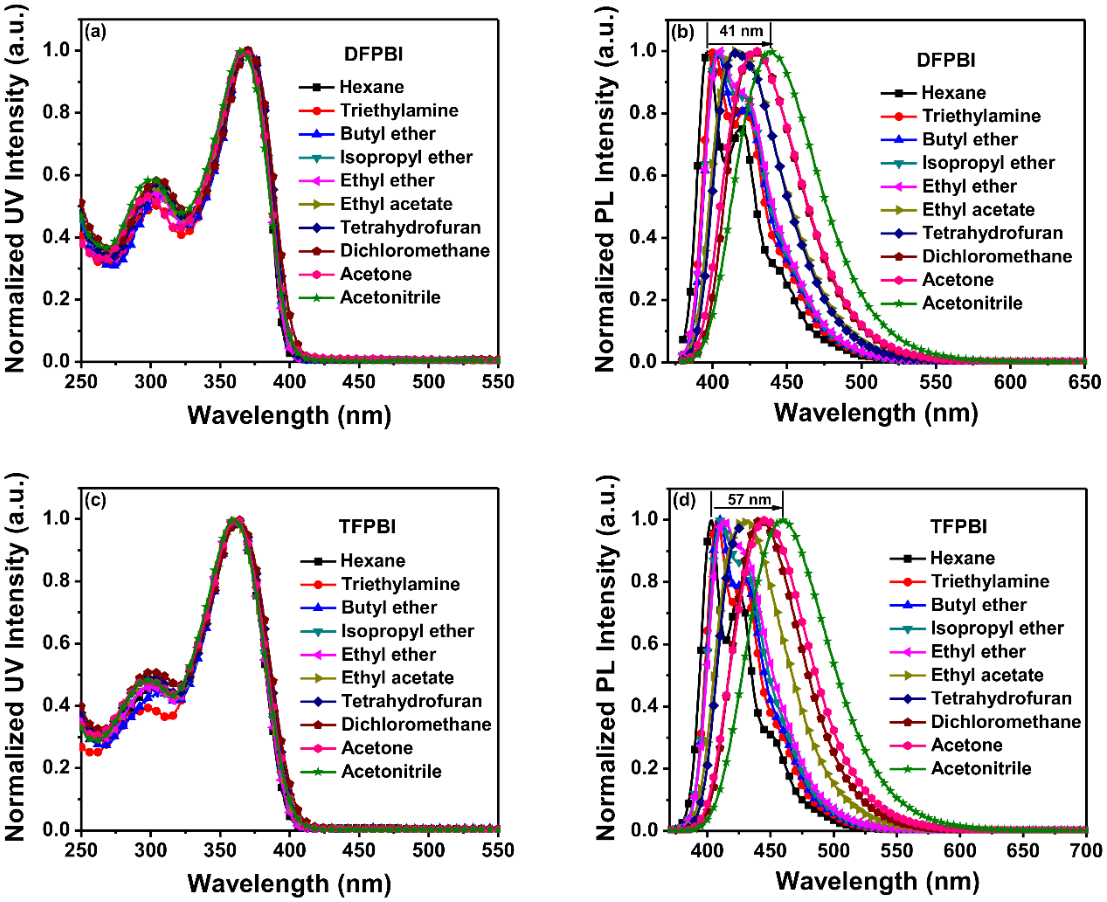


Fig. S2 UV-vis and PL spectra of DFPBI (a, b) and TFPBI (c, d), measured in different solvents with increasing polarity.

Table S1 Detailed absorption and emission peak positions, fluorescence quantum efficiency and emission full-width at half-maximum of DFPBI in different solvents.

Solvents	n	$f(\varepsilon, n)$	DFPBI				
			λ_{abs} (nm)	λ_{em} (nm)	ν_a-ν_f (cm^{-1})	Φ_F (%)	FWHM (nm)
Hexane	1.375	0.0012	371	396	1702	57	40
Triethylamine	1.401	0.048	370	401	2089	65	43
Butyl ether	1.399	0.096	370	403	2213	62	45
Isopropyl ether	1.368	0.145	369	404	2348	64	46
Ethyl ether	1.352	0.167	369	405	2409	65	47
Ethyl acetate	1.372	0.200	368	415	3078	68	55
Tetrahydrofuran	1.407	0.210	370	416	2989	70	54
Dichloromethane	1.424	0.217	371	428	3590	68	56
Acetone	1.359	0.284	367	428	3883	65	60
Acetonitrile	1.344	0.305	366	437	4439	72	64

λ_{abs} = absorption maximum, λ_{em} = emission maximum, Φ_F = fluorescence quantum yield, FWHM = full-width at half-maximum

Table S2 Detailed absorption and emission peak positions, fluorescence quantum efficiency and emission full-width at half-maximum of TFPBI in different solvents.

Solvents	n	$f(\varepsilon, n)$	TFPBI				
			λ_{abs} (nm)	λ_{em} (nm)	ν_a-ν_f (cm^{-1})	Φ_F (%)	FWHM (nm)
Hexane	1.375	0.0012	360	402	2902	68	42
Triethylamine	1.401	0.048	362	407	3054	83	45
Butyl ether	1.399	0.096	362	409	3174	64	47
Isopropyl ether	1.368	0.145	361	411	3370	70	50
Ethyl ether	1.352	0.167	360	413	3565	76	53
Ethyl acetate	1.372	0.200	361	429	4391	72	61
Tetrahydrofuran	1.407	0.210	362	431	4422	76	59
Dichloromethane	1.424	0.217	363	442	4924	74	63
Acetone	1.359	0.284	361	445	5229	71	70
Acetonitrile	1.344	0.305	360	459	5991	75	74

λ_{abs} = absorption maximum, λ_{em} = emission maximum, Φ_F = fluorescence quantum yield, FWHM = full-width at half-maximum

2. Lifetime of the DFPBI and TFPBI in four solutions.

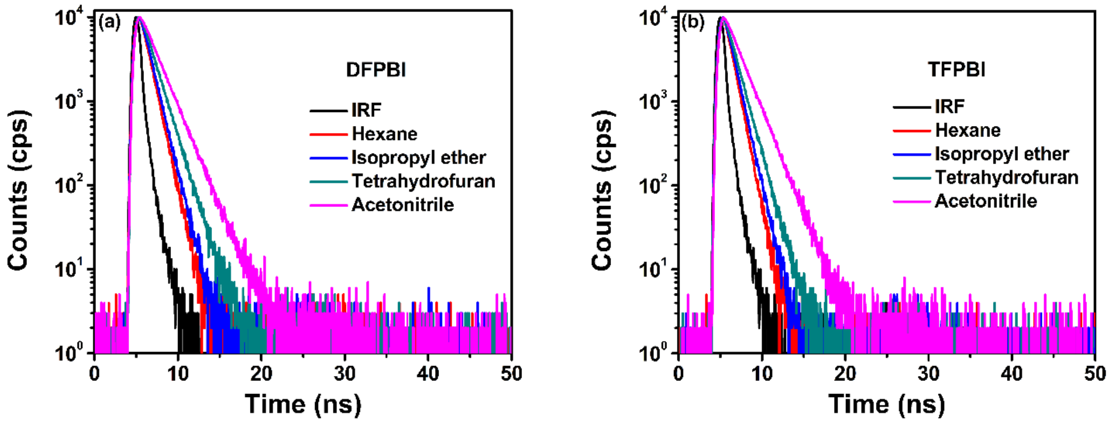


Fig. S3 Lifetime measurement of the DFPBI (a) and TFPBI (b) in hexane, isopropyl ether, tetrahydrofuran and acetonitrile solutions. (The concentrations of the solutions are 1×10^{-5} mol L^{-1}.)

Table S3 Lifetime of DFPBI and TFPBI in different solutions.

	Hexane	Isopropyl ether	Tetrahydrofuran	Acetonitrile
DFPBI (τ/ns)	1.01	1.10	1.38	1.83
TFPBI (τ/ns)	0.91	1.03	1.22	1.78

SI-3. Eletroluminescence properties

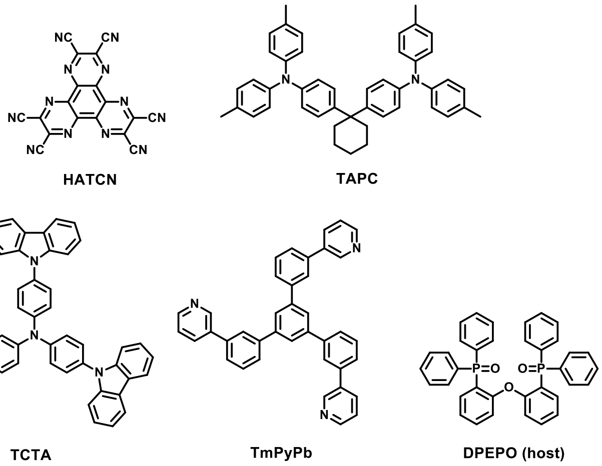


Fig. S4 Chemical structures of the materials used in OLEDs devices.

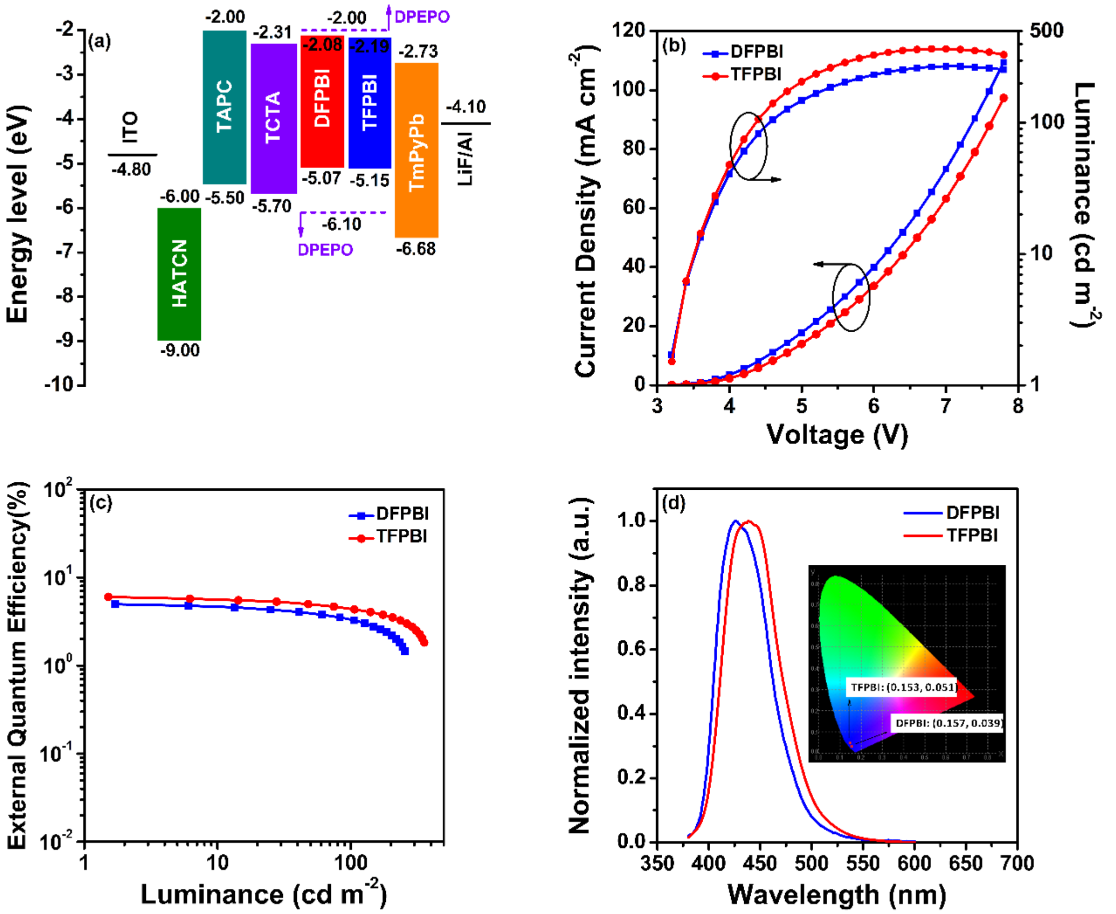


Fig. S5 (a) Schematic energy level diagram, (b) current density–voltage–luminance (*J*–*V*–*L*) characteristics and (c) external quantum efficiency–luminance curves of doped devices. (d) EL spectra of doped devices based on DFPBI and TFPBI 10 wt% doped in DPEPO as the emitters (the inset graph shows CIE coordinates at 5 V).

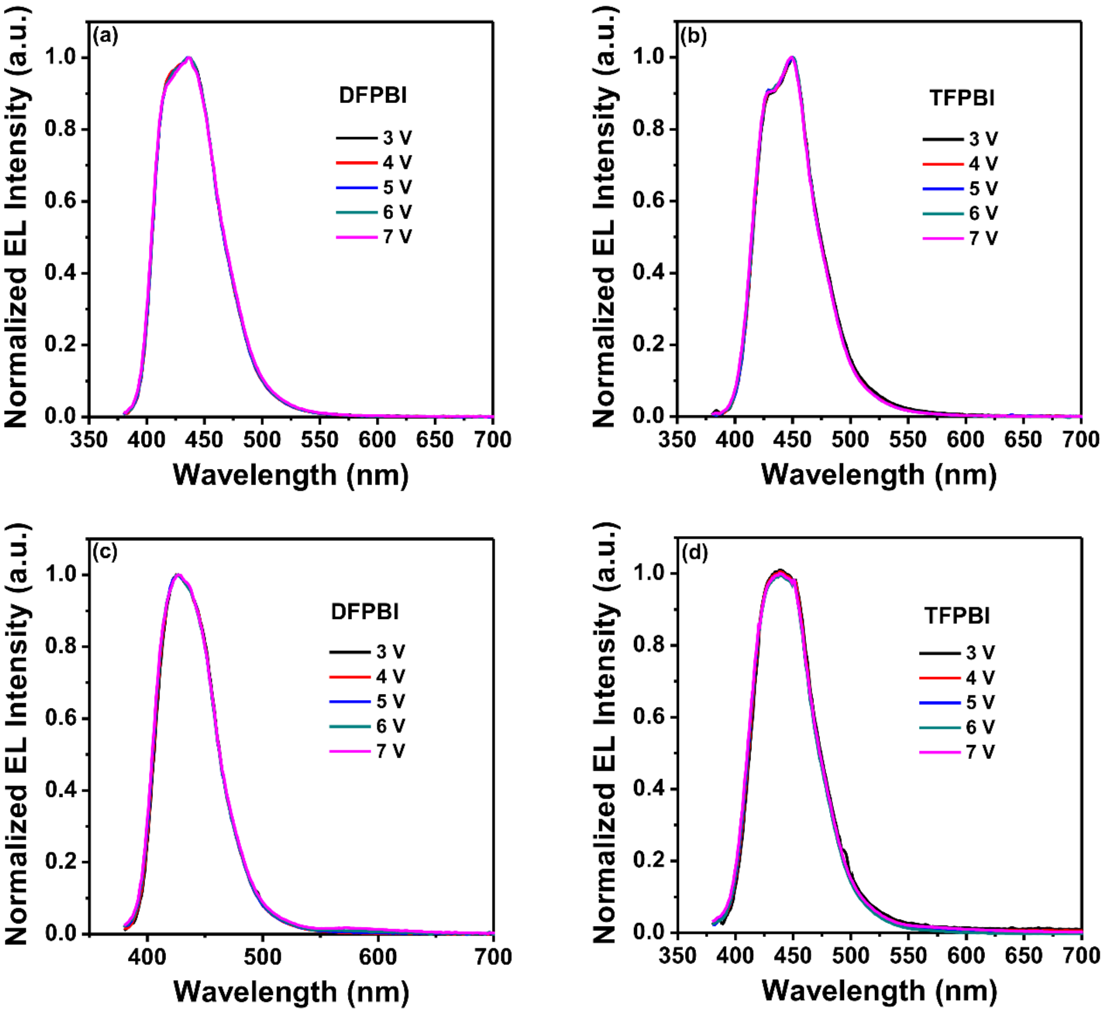


Fig. S6 Normalized EL spectra of the non-doped (a, b) and doped (c, d) devices from 3 V to 7 V.

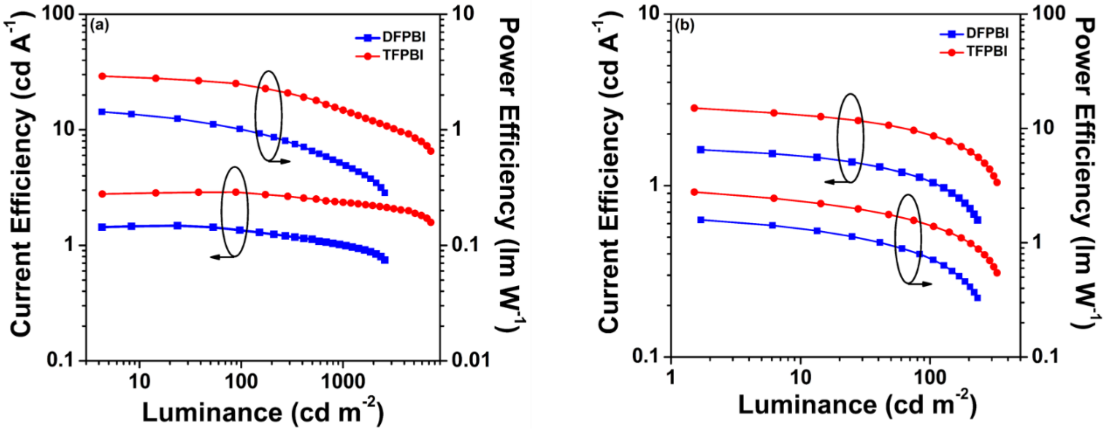


Fig. S7 The current efficiency–luminance–power efficiency characteristics of (a) non-doped devices and (b) doped devices.

The lifetime of the non-doped device based on TFPBI is measured as an example with a device structure: ITO/HATCN (15 nm)/TAPC (55 nm)/TCTA (5 nm)/TFPBI (20 nm)/TmPyPb (40 nm)/LiF

(1 nm)/Al (100 nm). The relative luminance-time curves of TFPBI-based non-doped OLED device at 100 cd m^{-2} as initial luminance are shown in **Fig. S8**. The device exhibits a half-life (LT50) value of 0.55 h with an initial luminance of 100 cd m^{-2}, indicating the device is unstable. The lifetimes of OLEDs were determined by many factors, such as the unbalanced charge transporting and the oxidation of metal electrodes. For the material TFPBI itself, the π-conjugated bridge 9,9-dimethylfluorene may be an instable moiety, which is usually oxidized on the C-9 position of the fluorene.[1,2]

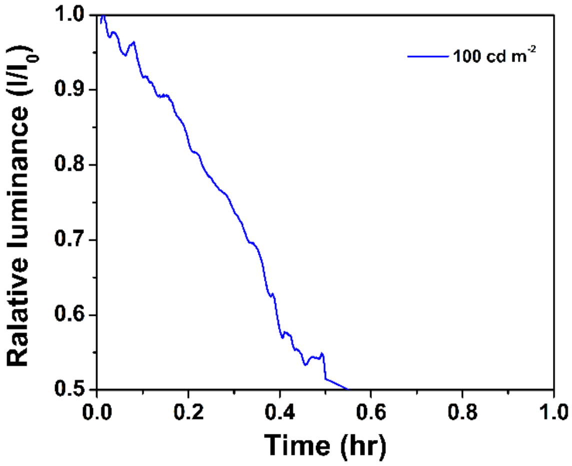
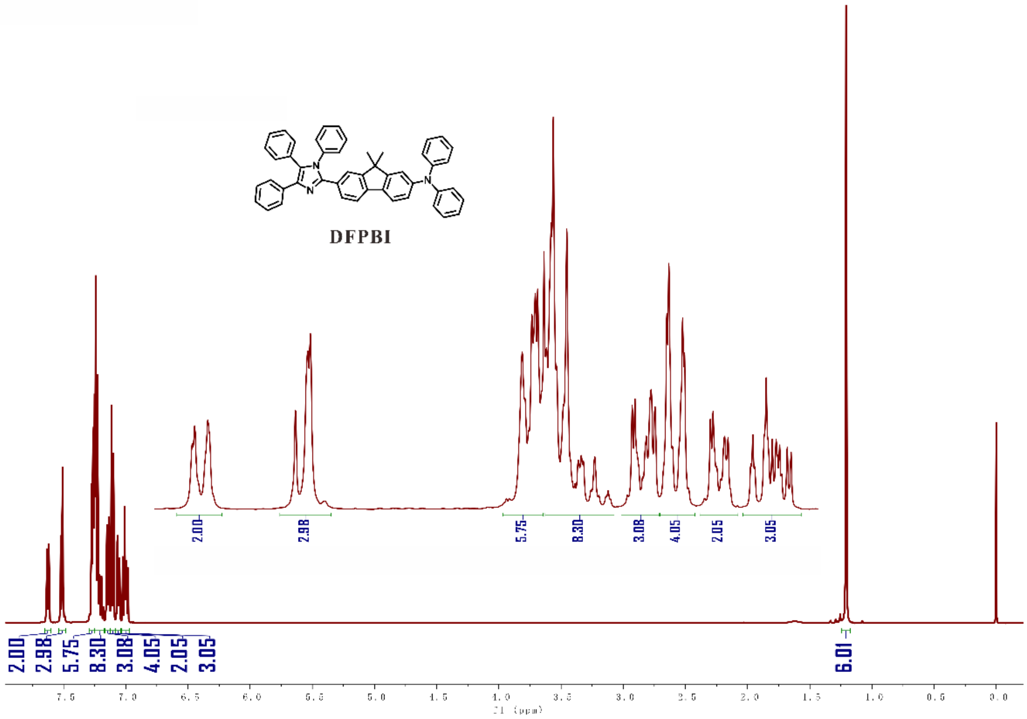


Fig. S8 Relative luminance–time curves of TFPBI-based non-doped OLED device at 100 cd m^{-2} as initial luminance.

SI-4. Structure characterizations



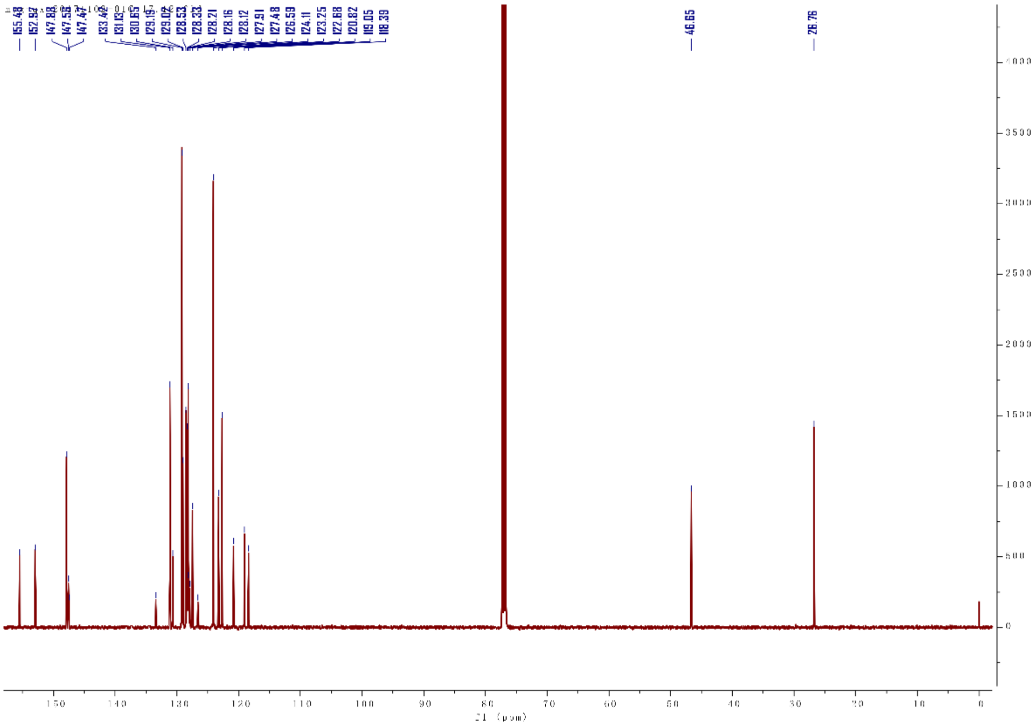
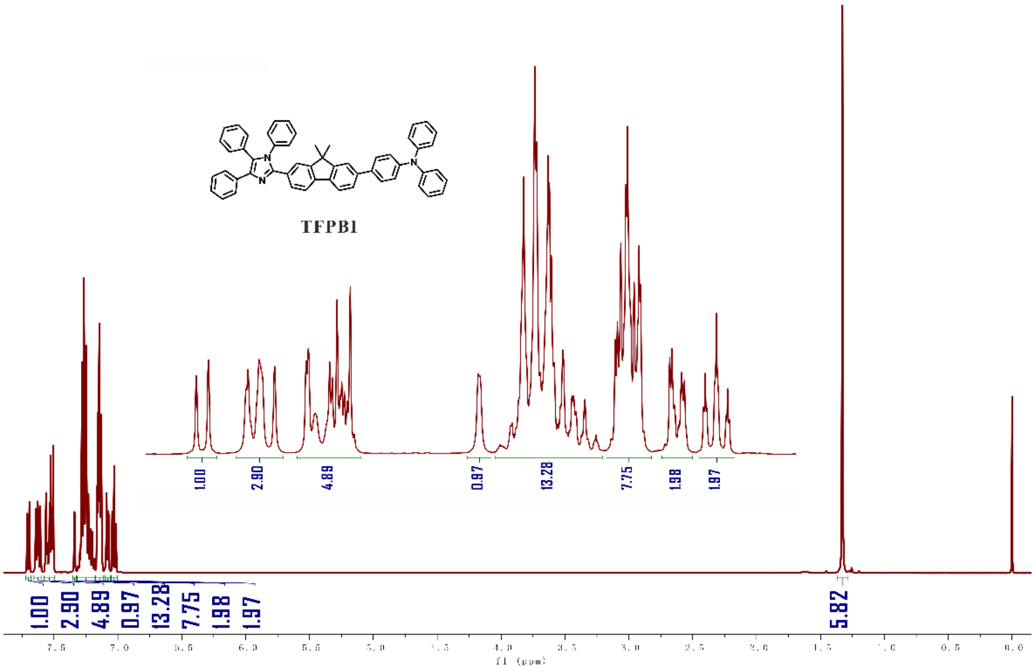


Fig. S9 ^{1}H NMR and ^{13}C NMR spectra of DFPBI in CDCl$_3$.



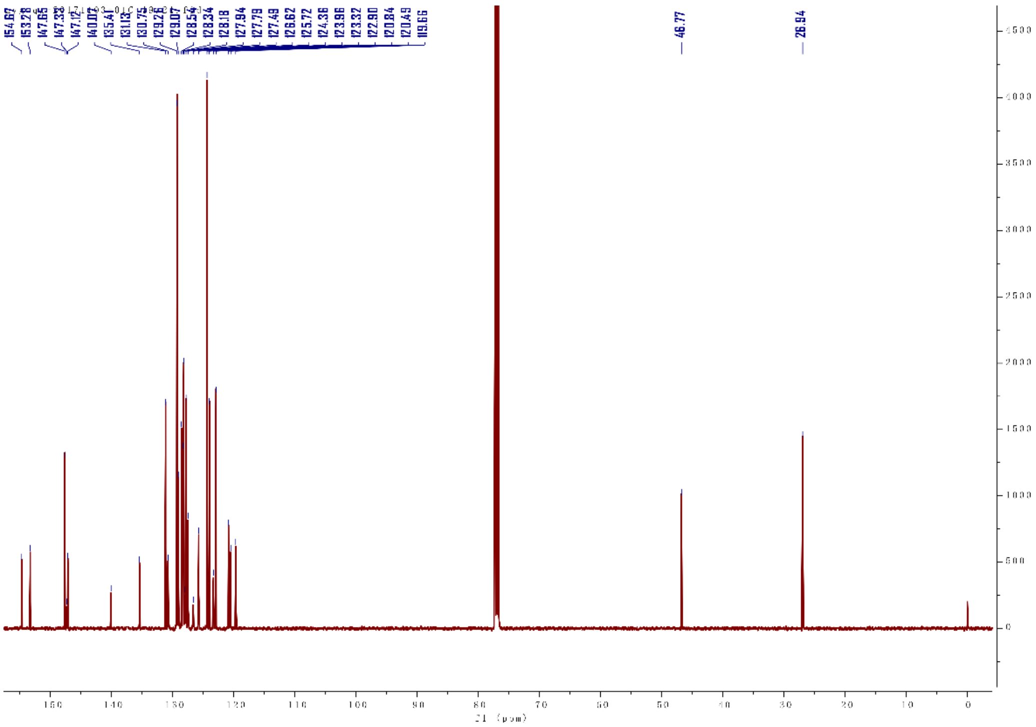


Fig. S10 ^{1}H NMR and ^{13}C NMR spectra of TFPBI in $CDCl_3$.

References

1. S. Y. Cho, A. C. Grimsdale, D. J. Jones, S. E. Watkins, and A. B. Holmes, *J. Am. Chem. Soc.*, 2007, **129**, 11910–11911.
2. L. Romaner, A. Pogantsch, P. Scandiucci de Freitas, U. Scherf, M. Gaal, E. Zojer and E.J.W. List, *Adv. Funct. Mater.*, 2003, **13**, 597–601.