
Electronic Supplementary Material (ESI) for Chemical Communications

Electronic Supplementary Information for

An Effective Host Material with Thermally Activated Delayed Fluorescence Formed by Confined Conjugation for Red Phosphorescent Organic Light-Emitting Diodes

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Fig. S6 Current density-voltage-luminance (*J*-V-L) characteristics and EL spectra at 5 mA cm^{-2} for PrDPhAc based device.

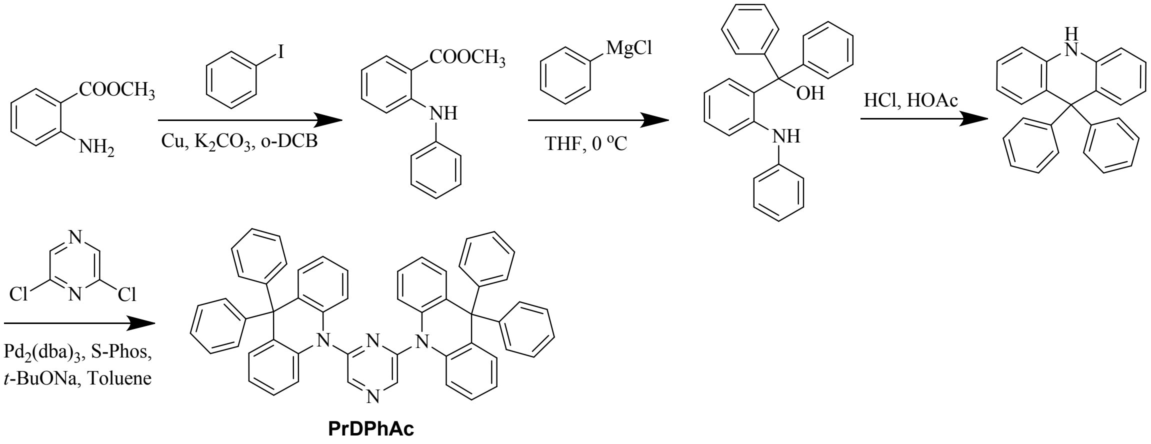
Table S3 Summary of electroluminescence data for red OLED.

Experimental Section

^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 spectrometer at room temperature. Mass spectra were recorded on a Thermo ISQ mass spectrometer using a direct exposure probe. UV-vis absorption spectra were recorded on a Perkin Elmer Lambda 750 spectrophotometer. PL spectra and phosphorescent spectra were recorded on a Hitachi F-4600 fluorescence spectrophotometer. Differential scanning calorimetry (DSC) was performed on a TA DSC 2010 unit at a heating rate of 10 ^{o}C min^{-1} under nitrogen. The glass transition temperatures (T_g) were determined from the second heating scan. Thermogravimetric analysis (TGA) was performed on a TA SDT 2960 instrument at a heating rate of 10 ^{o}C min^{-1} under nitrogen. Temperature at 5% weight loss was used as the decomposition temperature (T_d). Cyclic voltammetry (CV) was carried out on a CHI600 voltammetric analyzer at room temperature with ferrocenium-ferrocene (Fc$^+$/Fc) as the internal standard. Deaerated dichloromethane was used as solvent for oxidation scan with tetrabutylammonium hexafluorophosphate (TBAPF6) (0.1 M) as the supporting electrolyte. The cyclic voltammograms were obtained at scan rate of 0.1 V s^{-1}. Ultra-Violet Photoemission Spectroscopy (UPS) analysis was carried out with an unfiltered He I (21.22 eV) gas discharge lamp and a hemispherical analyzer, which was made by KRATOS ANALYTICAL SHIMADZU GROUP COMPANY. DFT calculations were performed using B3LYP/6-31g(d) basis set using Gaussian 09.

Fabrication and measurement of OLED devices

The OLEDs were fabricated on the indium-tin oxide (ITO) coated transparent glass substrates, the ITO conductive layer has a thickness of ca. 100 nm and a sheet resistance of ca. 30 Ω per square. The substrates was cleaned with ethanol, acetone and deionized water, and then dried in an oven, finally exposed to UV ozone for 30 min. All of the organic materials and metal layers under a vacuum of ca. 10^{-6} Torr. Four identical OLED devices were formed on each of the substrates and the emission area of 0.09 cm^2 for each device. The EL performances of the blue and white devices were measured with a PHOTO RESEARCH SpectraScan PR 655 PHOTOMETER and a KEITHLEY 2400 SourceMeter constant current source at room temperature.

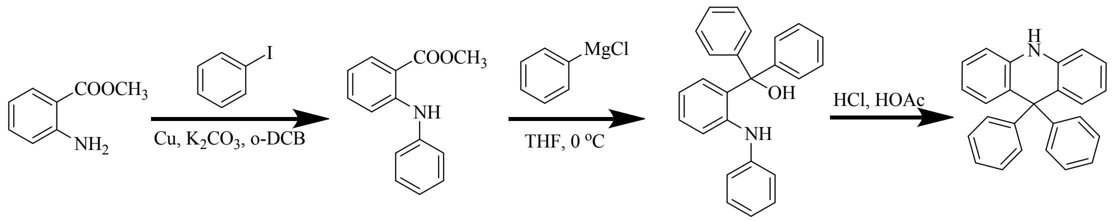


Scheme S1 Synthetic routes of PrDPhAc.

Preparation of 9,9-diphenylacridane and 2,6-bis(9,9-diphenylacridin-10(9H)-yl)pyrazine (PrDPhAc).

All chemicals and reagents were used as received from commercial sources without further purification. THF was purified by PURE SOLV (Innovative Technology) purification system. ^{1}H NMR and ^{13}C NMR spectra were recorded on a Bruker 400 spectrometer at room temperature. Mass spectra were recorded on a Thermo ISQ mass spectrometer using a direct exposure probe.

Preparation of 9,9-diphenylacridane[1]:

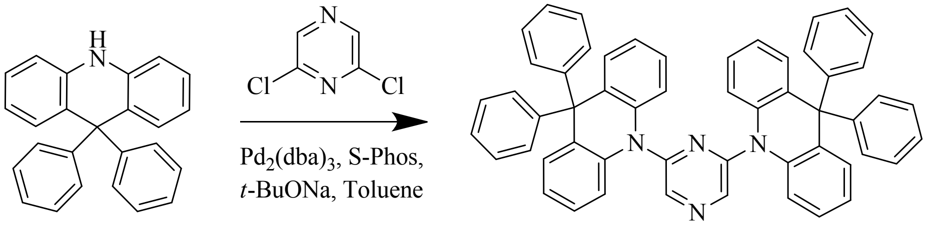


A mixture of methyl anthranilate (20 g, 132 mmol), iodobenzene (26.9 g, 132 mmol), K_2CO_3 (36.4 g, 264 mmol), and copper powder (0.17 g, 2.64 mmol) was scattered in 1,2-dichlorobenzene (*o*-DCB) and stirred for 10 hours at 180 °C under argon. After the reaction cooling to room temperature, filtered and washed with dichloromethane (DCM). Remove the solvent under reduced pressure and the crude product was purified by column chromatography using petroleum ether/dichloromethane (2/1, v/v) to afford the pure product as a colourless oil (23 g, 77%). This product used in the next step needn't to further purification.

The colourless oil (10 g, 44 mmol) was dissolved in 180 mL tetrahydrofuran (THF) in a 500 mL Schlenk tube under argon and cooled to 0 °C, and then phenylmagnesium chloride (PhMgCl, 2 M in THF, 66 mL, 132 mmol) was added dropwise under stirred. After 1 h reaction at 0 °C, the mixture was gradually warmed up to room temperature overnight. The reaction was quenched by water (5 mL). Put the mixture into 50 mL water, the product was extracted with EtOAc (3×50 mL), the combined organic layers were washed with brine and dried over anhydrous sodium sulfate ($NaSO_4$). Filtrated and evaporated under reduce pressure to afford a yellow oil or yellow soild (14 g), which was directly used in the next reaction without further purification.

The crude product was dissolved in 100 mL acetic acid (HOAc) under 70 °C and 10 mL hydrochloric acid (HCl) was added dropwise under stirred. The mixture was reaction overnight at 70 °C. After the reaction cooling to room temperature, filtered and washed with absolute ethyl alcohol, and dried under vacuum to give 9,9-diphenylacridane as white powder (12 g, ~90%)

Preparation of 2,6-bis(9,9-diphenylacridin-10(9H)-yl)pyrazine (PrDPhAc):



9,9-diphenylacridane (10 g, 30 mmol), 2,6-dichloropyrazine (4.47 g, 30 mmol), tris(dibenzylideneacetone)dipalladium(0) ($Pd_2(dba)_3$, 0.27 g, 0.3 mmol), 2-dicyclohexylphosphino-2',6'-dimethoxy-1,1'-biphenyl (S-Phos, 0.37 g, 0.9 mmol), sodium t-butoxide (*t*-BuONa, 5.76 g, 60 mmol) were dissolved in toluene under argon and heated to 110 °C. After 20 h reaction under stirring, the reaction was cooled to room temperature and 200 mL water was added. The product was extracted with dichloromethane (DCM, 3×100 mL), the combined organic layers were washed with brine and dried over anhydrous sodium sulfate ($NaSO_4$). Filtered and evaporated under reduced pressure. The crude product was purified by column chromatography using petroleum ether/dichloromethane (2/1, v/v) to give 2,6-bis(9,9-diphenylacridin-10(9H)-yl)pyrazine (PrDPhAc) as a yellow powder (7.4 g, 65%). ^1H NMR (400 MHz, $CDCl_3$): δ 7.48 (m, 4H), 7.30-7.26 (m, 6H), 7.19-7.11 (m, 16H), 6.97 (m, 4H), 6.92-6.87 (m, 8H) ppm. ^{13}C NMR (100 MHz, $CDCl_3$): δ 149.65, 144.66, 140.80, 139.82, 130.43, 129.19, 128.44, 127.66, 126.66 (d, J = 6.3 Hz), 123.66, 122.80, 58.11 ppm. MS m/z: 742.33. Anal. Calcd for $C_{54}H_{38}N_4$ (%): C 87.30, H 5.16, N 7.54; found: C 87.46, H 5.52, N 7.36.

Figures

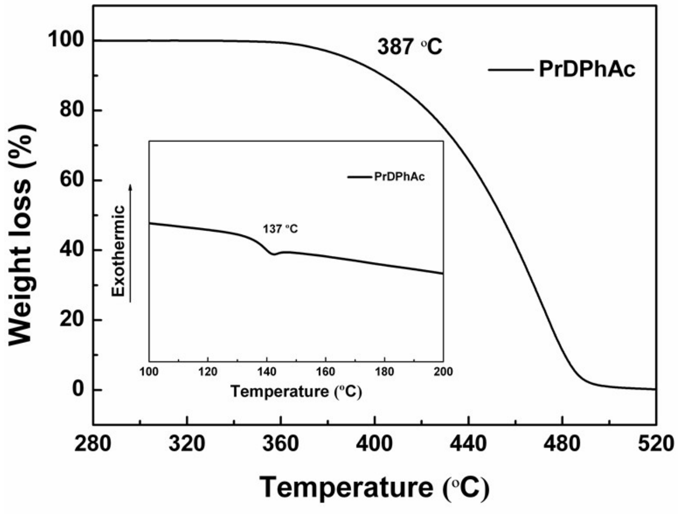


Fig. S1 TGA and DSC (inset) curves of PrDPhAc.

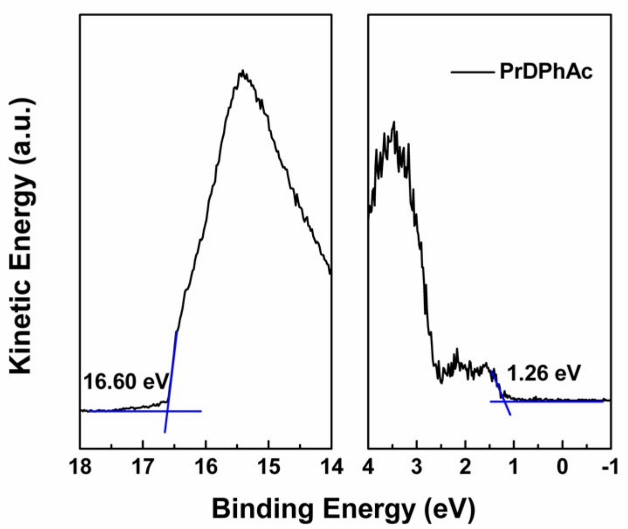


Fig. S2 UPS spectrum of PrDPhAc.

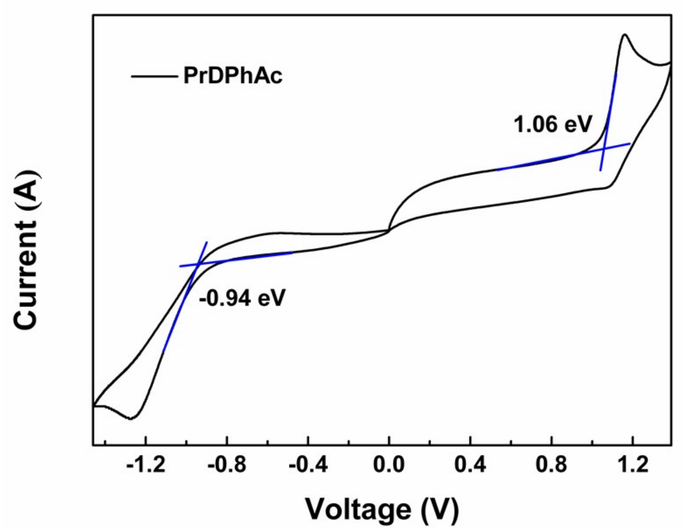


Fig. S3 Cyclic voltammograms of PrDPhAc.

The electrochemical properties of PrDPhAc was measured by cyclic voltammetry (CV) using typically tri-electrode configuration method with ferrocene as the internal standard in dichloromethane solution with 0.1 M n-Bu_4NPF_6 as the supporting electrolyte. We calculated the HOMO level of PrDPhAc is -5.36 eV, from the onset of the first oxidation wave. The LUMO of PrDPhAc can be gained from the onset of the reduction wave, is 3.36 eV.

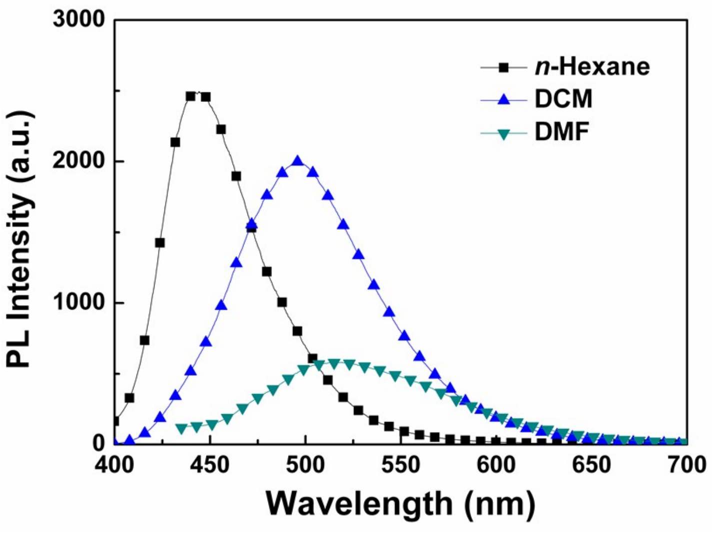


Fig. S4 Fluorescence spectra of PrDPhAc in different solvents (10^{-5} M).

Table S1 Summary of the physical properties of PrDPhAc.

Host	Abs λ_{max}^{a}	PL λ_{max}^{a}	T_g^{b}	T_d^{c}	E_g^{d}	E_T^{e}	HOMO^f	LUMO^g	ΔE_{ST}
	[nm]	[nm]	[°C]	[°C]	[eV]	[eV]	[eV]	[eV]	[eV]
PrDPhAc	375	495	137	387	3.07	2.48	-5.88	-2.81	0.08^h/0.07^i

[a] Measured in CH_2Cl_2 solution at room temperature. [b] T_g: Glass transition temperature. [c] T_d: Decomposition temperature. [d] E_g: Band gap energies were calculated from the corresponding absorption onset in CH_2Cl_2 solution. [e] E_T: Measured in 2-MeTHF glass matrix at 77 K. [f] HOMO levels were calculated from UPS date. [g] LUMO levels, calculated from the HOMO and E_g. [h] ΔE_{ST}: singlet-triplet energy difference, based on DFT calculations. [i] ΔE_{ST}: estimated from the difference of onsets of the PL and Phos.

In this study, the ratio between prompt and delayed components was calculated from transient PL measurements. The intensity ratio between prompt (r_1) and delayed (r_2) components were determined using emission life time (τ_1, τ_2) and fitting parameter (A_1, A_2) as follow.

$$I(\mathrm{t}) = A_1 \mathrm{e}^{-\frac{1}{\tau_1}} + A_2 \mathrm{e}^{-\frac{1}{\tau_2}}$$

$$r_1 = \frac{A_1\tau_1}{A_1\tau_1 + A_2\tau_2}$$

$$r_2 = \frac{A_2\tau_2}{A_1\tau_1 + A_2\tau_2}$$

And then, prompt fluorescence efficiency (Φ_{PF}) and delayed fluorescence efficiency (Φ_{DF}) were determined using intensity ratio (r_1, r_2) and total emission quantum yield (Φ_{total}).[2]

$$\Phi_{total} = \Phi_{PF} + \Phi_{DF}$$

$$\Phi_{PF} = r_1 \times \Phi_{total}$$

$$\Phi_{\mathrm{DF}} = r_2 \times \Phi_{\mathrm{total}}$$

It is known that the TADF is significant only if the two following conditions are met: (i) reasonably high probability of $S_1 \rightarrow T_1$ intersystem crossing, i.e., high quantum yield of triplet formation η_{ISC}, where

$$\eta_{\mathrm{ISC}} = \frac{k_{\mathrm{ISC}}}{k_{\mathrm{ISC}} + k_{\mathrm{r}}^{\mathrm{S}} + k_{\mathrm{nr}}^{\mathrm{S}}} = \frac{k_{\mathrm{ISC}}}{k_{\mathrm{S}}}\text{, in which, } k_{\mathrm{S}} = k_{\mathrm{r}}^{\mathrm{S}} + k_{\mathrm{nr}}^{\mathrm{S}} + k_{\mathrm{ISC}}\text{, therefore}$$

$$k_{\mathrm{ISC}} = k_{\mathrm{S}} \times \eta_{\mathrm{ISC}} = \frac{\eta_{\mathrm{ISC}}}{\tau_{\mathrm{S}}};$$

and (ii) sufficiently high probability of subsequent RISC, i.e., high quantum yield of singlet formation, η_{RISC}, which is defined as

$$\eta_{\mathrm{RISC}} = \frac{k_{\mathrm{RISC}}}{k_{\mathrm{RISC}} + k_{\mathrm{r}}^{\mathrm{T}} + k_{\mathrm{nr}}^{\mathrm{T}}} = \frac{k_{\mathrm{RISC}}}{k_{\mathrm{T}}}\text{, in which, } k_{\mathrm{T}} = k_{\mathrm{r}}^{\mathrm{T}} + k_{\mathrm{nr}}^{\mathrm{T}} + k_{\mathrm{RISC}}\text{, hence}$$

$$k_{\mathrm{RISC}} = k_{\mathrm{T}} \times \eta_{\mathrm{RISC}} = \frac{\eta_{\mathrm{RISC}}}{\tau_{\mathrm{T}}}$$

Thus, the product of η_{ISC} and η_{RISC}, and $\eta_{\mathrm{ISC}}{*}\eta_{\mathrm{RISC}}$, is an important factor to dictate the what the degree of TADF process is, and the ratio of delayed fluorescence (DF) to prompt fluorescence (PF) is given by Φ

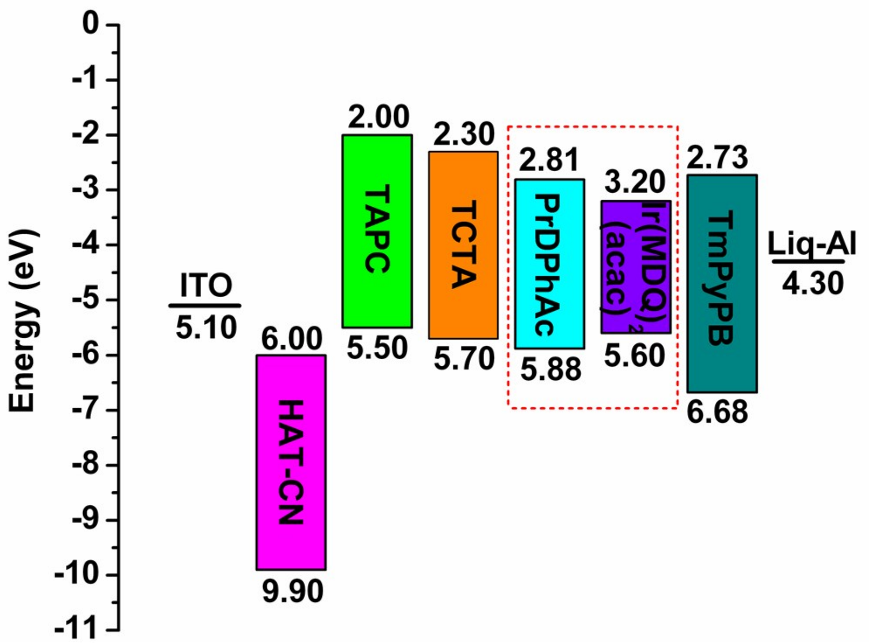
$$\Phi = \frac{I_{\mathrm{DF}}}{I_{\mathrm{PF}}} = \frac{\Phi_{\mathrm{DF}}}{\Phi_{\mathrm{PF}}} = \frac{1}{\frac{1}{\Phi_{\mathrm{S}}\Phi_{\mathrm{T}}} - 1}$$

In this case, the PrDPhAc showed evident delayed fluorescence with $\eta_{\mathrm{ISC}}{*}\eta_{\mathrm{RISC}} = 67\%$, which means about two thirds of electron-generated excitons is back-transferred to singlet states via up-conversion pathway because of its small ΔE_{ST}. In other words, the density of triplet excitons was thus reduced obviously. With the disturbance of triplet oxygen molecule, by the way, the $\eta_{\mathrm{ISC}}{*}\eta_{\mathrm{RISC}}$ dropped drastically to ~6%, indicating only a few triplet excitons can enter the singlet orbital because of the oxygen quenching effect. The Φ_{DF}:Φ_{PF} was estimated as 2:1, indicating the singlet excitons increased by three times in TADF process. All the time-dependent data are summarized in Table S2.

Table S2 Data extracted from the transient characterization of PrDPhAc solution.

k_{PF}(s^{-1})^{a}	k_{DF}(s^{-1})^{b}	τ_{PF} (s)^{c}	τ_{DF} (s)^{d}	k_{S}(s^{-1})^{e}	k_{T}(s^{-1})^{f}	k_{ISC}*k_{RISC}(s^{-2})	η_{ISC}*η_{RISC}
1.19×10^{8}	2.65×10^{5}	8.38×10^{-9}	3.77×10^{-6}	1.19×10^{8}	7.99×10^{5}	6.34×10^{13}	0.67

[a)] Delayed fluorescence rate constant; [b)] Prompt fluorescence rate constant; [c)] Delayed fluorescence lifetime; [d)] Prompt fluorescence lifetime; [e)] Fluorescence rate constant; [f)] Phosphorescence rate constant.



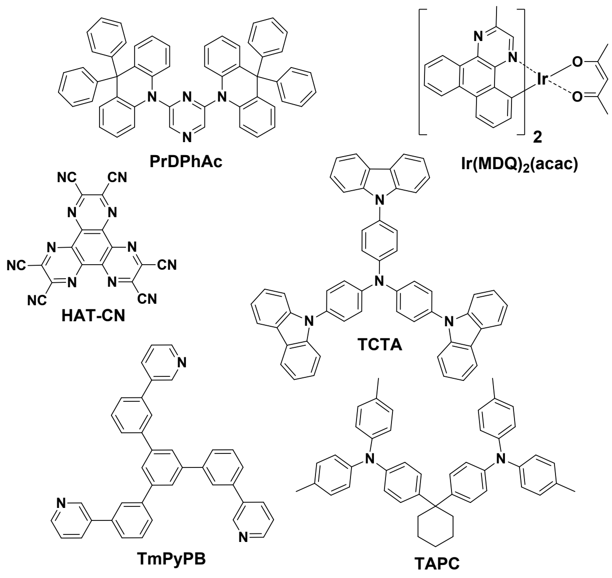
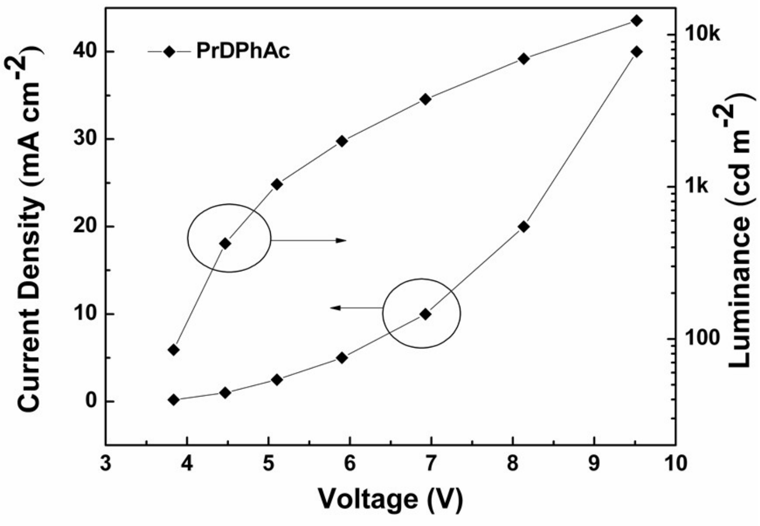


Fig. S5 Molecular structures and representative energy level diagram of the materials.



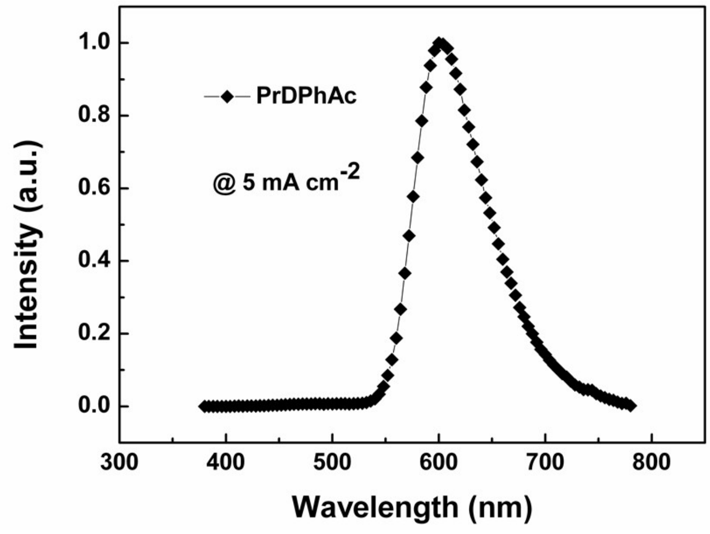


Fig. S6 Current density–voltage–luminance (*J*-V-L) characteristics and EL spectra at 5 mA cm^{-2} for PrDPhAc based device.

Table S3 Summary of electroluminescence data for red OLED.

Device	V^a	□$\eta_{CE}{}^b$	□$\eta_{PE}{}^b$	□$\eta_{ext}{}^b$	CIE^c
	V	cd A^{-1}	lm W^{-1}	%	x, y
R	3.9	42.5, 42.3	34.8, 25.2	25.8, 25.3	0.61, 0.39

[a)] Voltages at 100 cd m^{-2}. [b)] Efficiencies in the order of maximum and at 1000 cd/m^2. [c)] Measured at 5 mA cm^{-2}.

References

1 X.-Y. Liu, F. Liang, L.-S. Cui, X.-D. Yuan, Z.-Q. Jiang, L.-S. Liao, *Chem. Asian J.*, 2015, **10**, 1402-1409.

2 T. Nakagawa, S.-Y. Ku, K.-T. Wong, C. Adachi, *Chem. Commun.*, 2012, **48**, 9580-9582.