*nanomaterials*

MDPI

*Supporting information*

# Voltage-Dependent Emission Varying from Blue to Orange–Red from a Nondoped Organic Light-Emitting Diode with a Single Emitter

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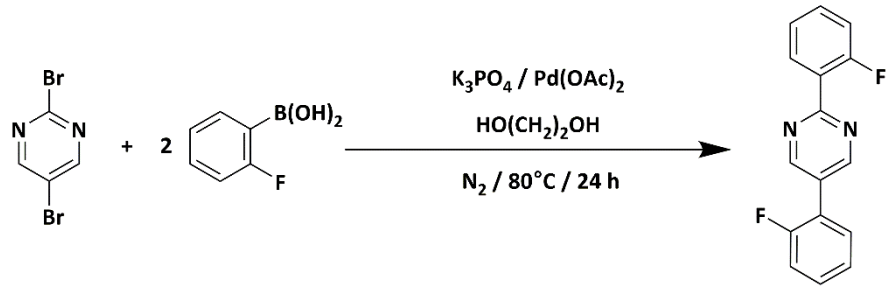
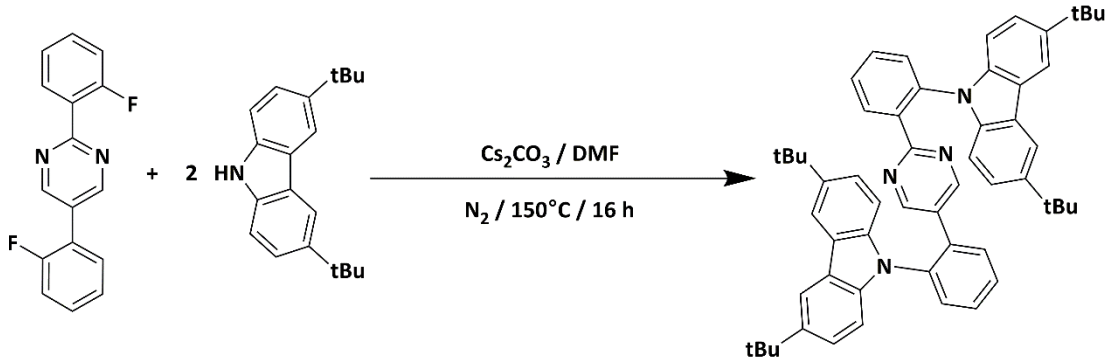
# 1. Synthetic schemes of Materials




**Scheme S1** Synthetic route of 2,5-bis(2-fluorophenyl)pyrimidine




**Scheme S2** Synthetic route of 9-(2,3-bis((2-bromophenyl)thio)phenyl)-9*H*-carbazole (**PDPC**)

## 2. NMR Spectra

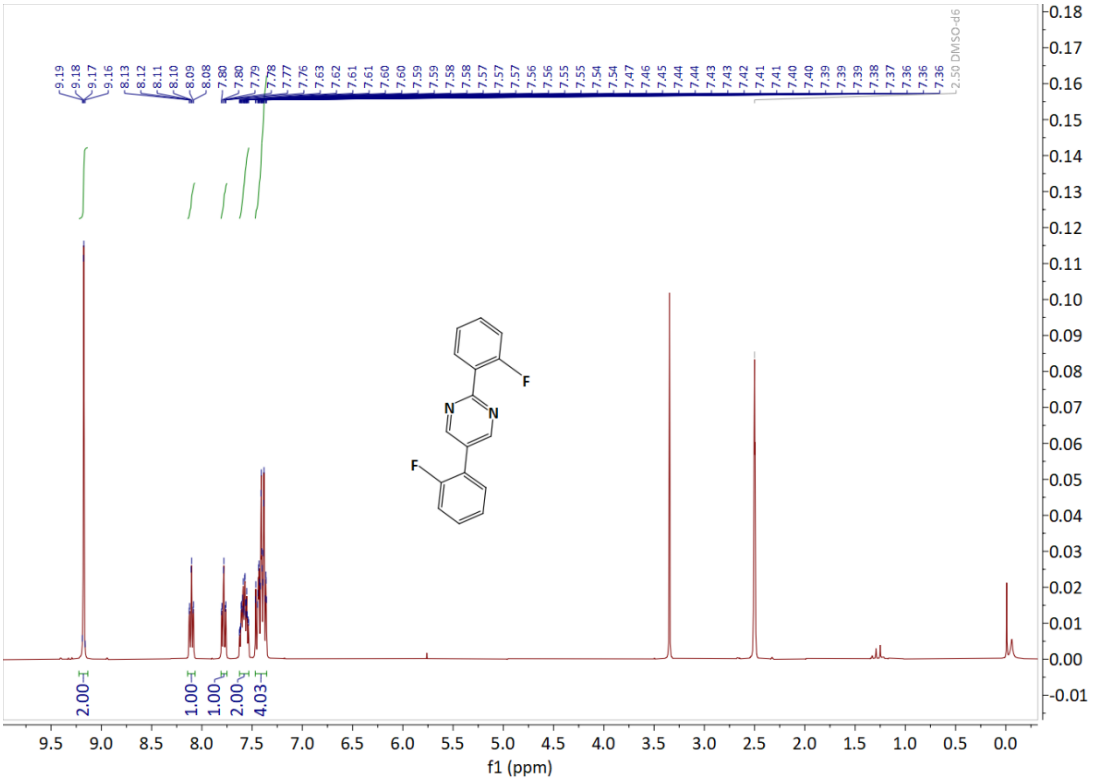



**Figure S1** $^{1}$H NMR spectrum of 2,5-bis(2-fluorophenyl)pyrimidine

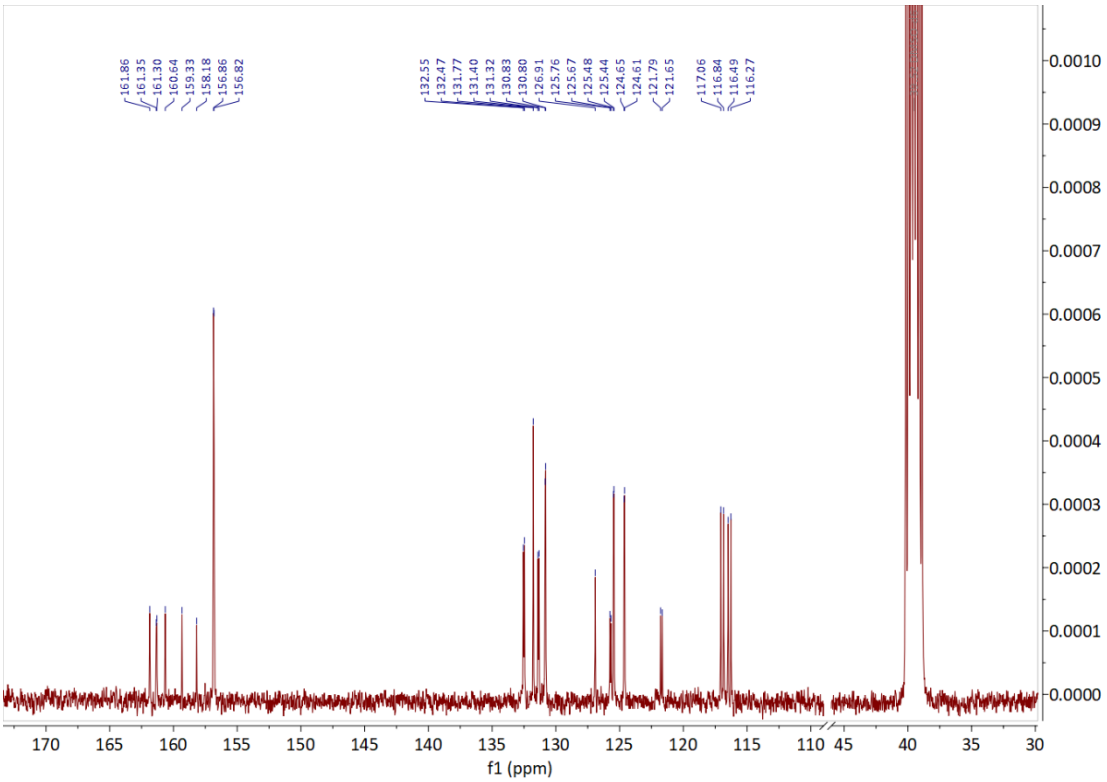



**Figure S2** $^{13}$C NMR spectrum of 2,5-bis(2-fluorophenyl)pyrimidine

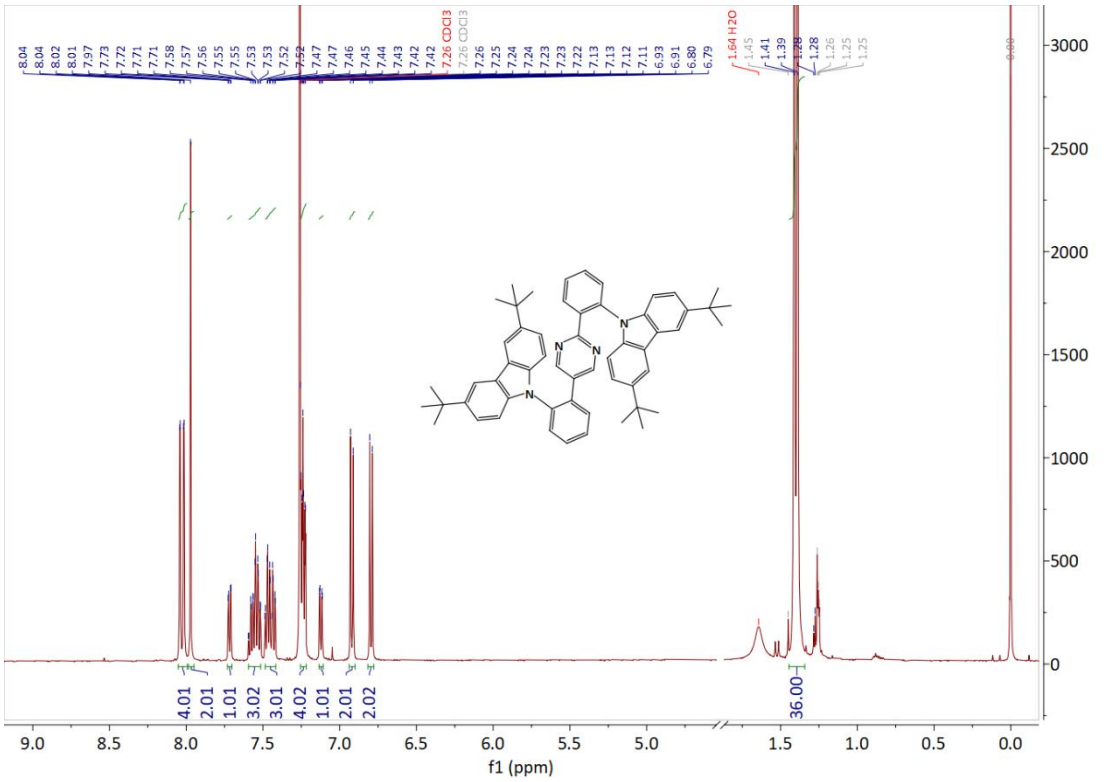



**Figure S3** $^{1}$H NMR spectrum of **PDPC**

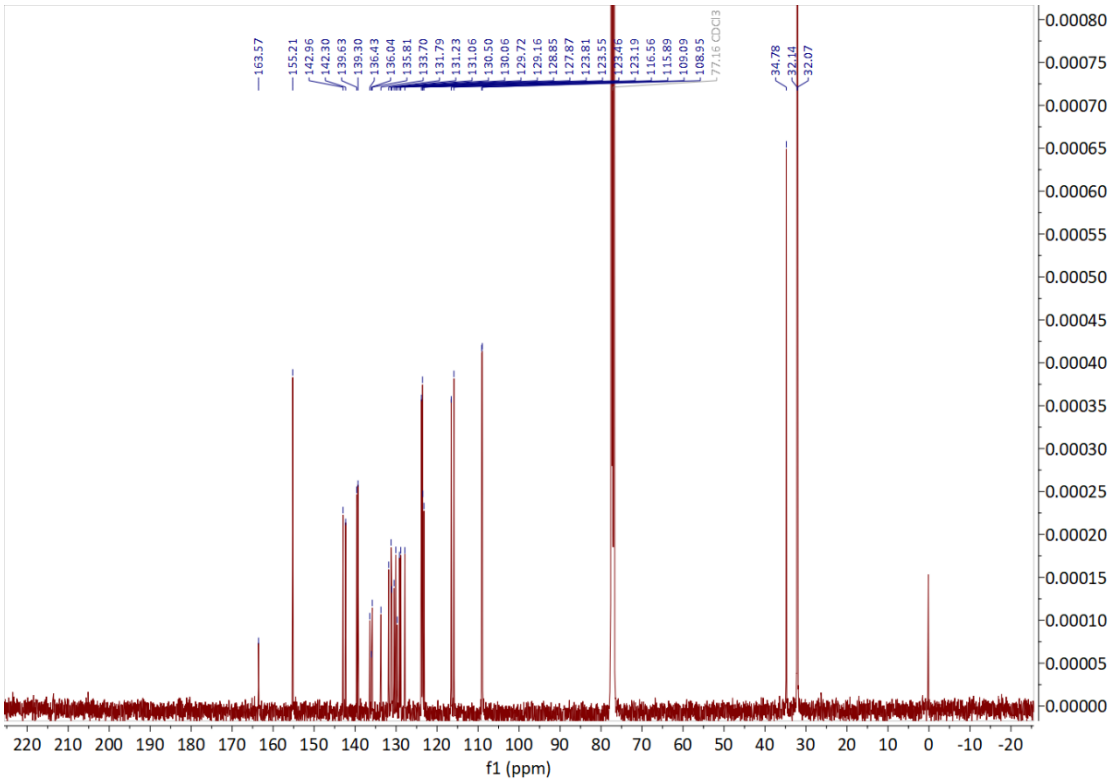



**Figure S4** $^{13}$C NMR spectrum of **PDPC**

## 3. Single Crystals Analysis

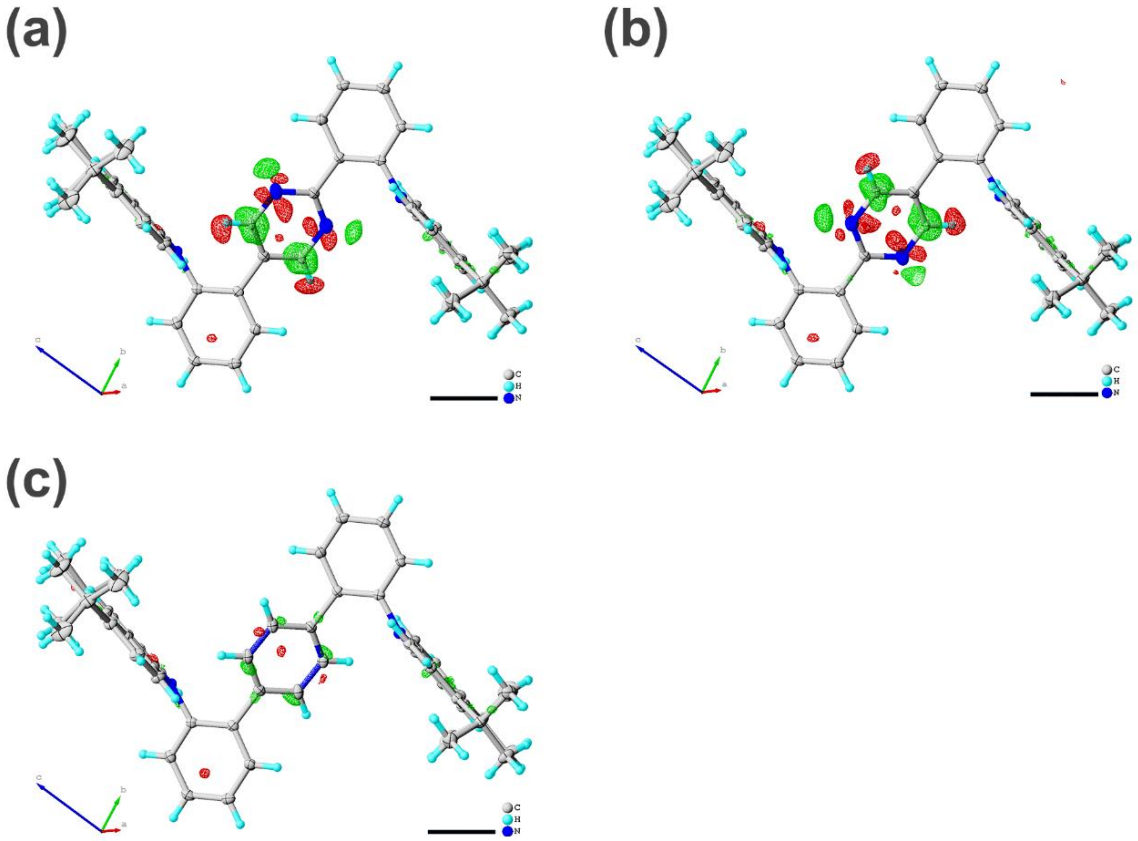



**Figure S5** Density residue for different denotations of pyrimidine ring, in which the wires in green color indicate positive and red negative. The N and C atoms are individual as for **(a)** and **(b)**, while 50% of C / N atoms are denoted in **(c)**

**Table S1** Single crystals data for **PDPC**

| Item | Value |
|---|---|
| Chemical formula | $C_{56}H_{58}N_4 \cdot 2(CH_2Cl_2)$ |
| Formula weight | 956.91 |
| Temperature / K | 100.01(15) |
| Crystal system | monoclinic |
| Space group | *P*21/*c* |
| a / Å | 11.3239(4) |
| b / Å | 13.6212(4) |
| c / Å | 32.8757(11) |
| $\alpha$ / ° | 90 |
| $\beta$ / ° | 90.735(3) |
| $\gamma$ / ° | 90 |
| Volume / Å$^3$ | 5070.5(3) |
| Z | 4 |
| $\rho_{calc}$ / g·cm$^{-3}$ | 1.254 |
| $\mu$ / mm$^{-1}$ | 2.438 |
| *F*(000) | 2024.0 |
| Crystal size / mm$^3$ | 0.15 × 0.18 × 0.2 |
| Radiation | Cu K$\alpha$ ($\lambda$ = 1.54184) |
| 2$\Theta$ range for data collection / ° | 7.024 to 146.95 |
| Index ranges | −11≤h≤14, −16≤k≤16, −40≤l≤32 |
| Reflections collected | 24234 |
| Independent reflections | 9961 [$R_{int}$ = 0.0302, $R_\sigma$ = 0.0369] |
| Data / restraints / parameters | 9961/10/608 |
| Goodness-of-fit on F$^2$ | 1.025 |
| Final R indexes [I>=2$\sigma$ (I)] | R1 = 0.0452, wR2 = 0.1164 |
| Final R indexes [all data] | R1 = 0.0642, wR2 = 0.1302 |
| Largest diff. peak/hole / e·Å$^{-3}$ | 0.51/−0.59 |

**Table S2** Selected bond lengths for **PDPC**

| Atom | Atom | Length / Å | Atom | Atom | Length / Å | Atom | Atom | Length / Å |
|---|---|---|---|---|---|---|---|---|
| N3A | C11A | 1.398(2) | C3 | N2 | 1.364(2) | C1 | N2A | 1.367(2) |
| N3A | C10A | 1.430(2) | C3 | N4 | 1.371(2) | C17 | C22 | 1.405(2) |
| N3A | C22A | 1.399(2) | C3 | C2A | 1.364(2) | C17 | C18 | 1.403(2) |
| N3 | C11 | 1.394(2) | C3 | C4A | 1.371(2) | C13 | C12 | 1.392(2) |
| N3 | C10 | 1.431(2) | C11A | C16A | 1.405(3) | C13 | C14 | 1.412(3) |
| N3 | C22 | 1.399(2) | C11A | C12A | 1.396(2) | C15 | C14 | 1.393(2) |
| C11 | C16 | 1.412(2) | C10A | C5A | 1.406(2) | C16A | C17A | 1.450(2) |
| C11 | C12 | 1.394(2) | C10A | C9A | 1.392(2) | C16A | C15A | 1.401(3) |

| Atom | Atom | Length / Å | Atom | Atom | Length / Å | Atom | Atom | Length / Å |
|---|---|---|---|---|---|---|---|---|
| C16 | C17 | 1.448(2) | C5A | C1 | 1.490(2) | C22 | C21 | 1.396(2) |
| C16 | C15 | 1.397(2) | C5A | C6A | 1.398(3) | C14 | C23 | 1.534(2) |
| C10 | C9 | 1.392(2) | C1 | C2 | 1.367(2) | C18 | C19 | 1.391(3) |
| C10 | C5 | 1.402(2) | C1 | C4 | 1.375(2) | C12A | C13A | 1.390(3) |
| C3 | C5 | 1.491(2) | C1 | N4A | 1.375(2) | C9 | C8 | 1.390(3) |

**Table S3** Selected bond angles for **PDPC**

| Atom | Atom | Atom | Angle/° | Atom | Atom | Atom | Angle/° |
|---|---|---|---|---|---|---|---|
| C11A | N3A | C10A | 125.02(14) | C21A | C22A | N3A | 129.33(16) |
| C11A | N3A | C22A | 107.78(14) | C21A | C22A | C17A | 121.22(16) |
| C22A | N3A | C10A | 124.39(14) | C7A | C6A | C5A | 121.72(17) |
| C11 | N3 | C10 | 124.96(14) | C15A | C14A | C13A | 118.20(16) |
| C11 | N3 | C22 | 108.02(14) | C15A | C14A | C23A | 122.06(16) |
| C22 | N3 | C10 | 124.36(14) | C13A | C14A | C23A | 119.68(15) |
| N3 | C11 | C16 | 109.11(15) | C14A | C15A | C16A | 120.03(17) |
| N3 | C11 | C12 | 129.90(16) | C20A | C21A | C22A | 117.48(17) |
| C12 | C11 | C16 | 120.98(16) | C7 | C6 | C5 | 121.47(17) |
| C11 | C16 | C17 | 106.73(15) | C21 | C20 | C19 | 123.10(17) |
| C15 | C16 | C11 | 120.13(16) | C20A | C19A | C27A | 118.83(17) |
| C15 | C16 | C17 | 133.09(16) | C18A | C19A | C20A | 118.09(17) |
| C9 | C10 | N3 | 117.90(16) | C18A | C19A | C27A | 123.06(17) |
| C9 | C10 | C5 | 119.98(16) | C21A | C20A | C19A | 123.24(17) |
| C5 | C10 | N3 | 122.12(16) | C29 | C27 | C30 | 108.56(18) |
| N2 | C3 | C5 | 122.29(16) | C28 | C27 | C29 | 108.12(19) |
| N2 | C3 | N4 | 120.40(16) | C28 | C27 | C30 | 109.21(19) |
| N4 | C3 | C5 | 117.32(16) | C19 | C27 | C29 | 111.90(16) |
| C2A | C3 | C5 | 122.29(16) | C19 | C27 | C30 | 109.46(17) |
| C2A | C3 | C4A | 120.40(16) | C19 | C27 | C28 | 109.55(17) |
| C4A | C3 | C5 | 117.32(16) | C19A | C27A | C28A | 108.89(18) |
| N3A | C11A | C16A | 109.12(15) | C29A | C27A | C19A | 112.01(17) |
| C12A | C11A | N3A | 129.67(17) | C29A | C27A | C28A | 108.3(2) |
| C12A | C11A | C16A | 121.20(16) | C29A | C27A | C30A | 108.6(2) |
| C5A | C10A | N3A | 121.99(15) | C30A | C27A | C19A | 109.98(18) |
| C9A | C10A | N3A | 117.94(16) | C30A | C27A | C28A | 109.0(2) |
| C9A | C10A | C5A | 120.07(16) | C6A | C7A | C8A | 119.51(17) |
| C10A | C5A | C1 | 123.21(16) | C12A | C13A | C14A | 123.16(16) |
| C6A | C5A | C10A | 118.12(16) | C14 | C23 | C24 | 108.65(15) |

## 4. UV-Vis Analysis and Thermogravimetry

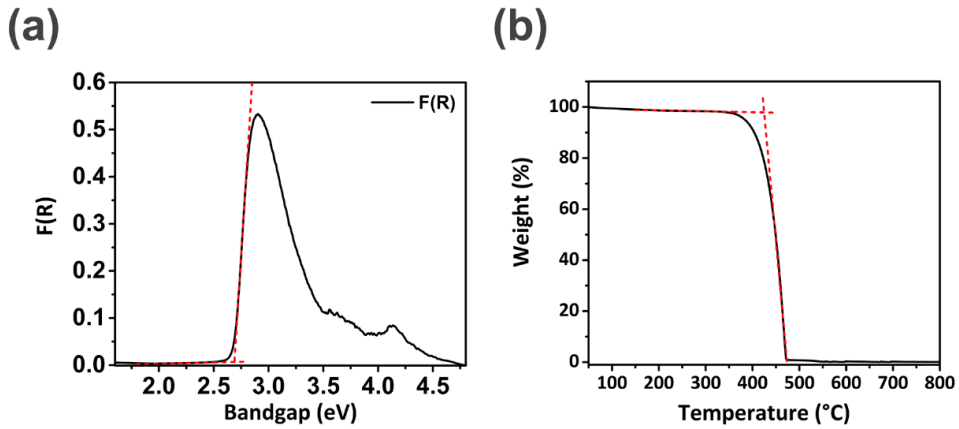



**Figure S6 (a)** UV-vis absorption spectrum of solid state **PDPC**; **(b)** TGA curve of **PDPC**

## 5. Photophysical Properties

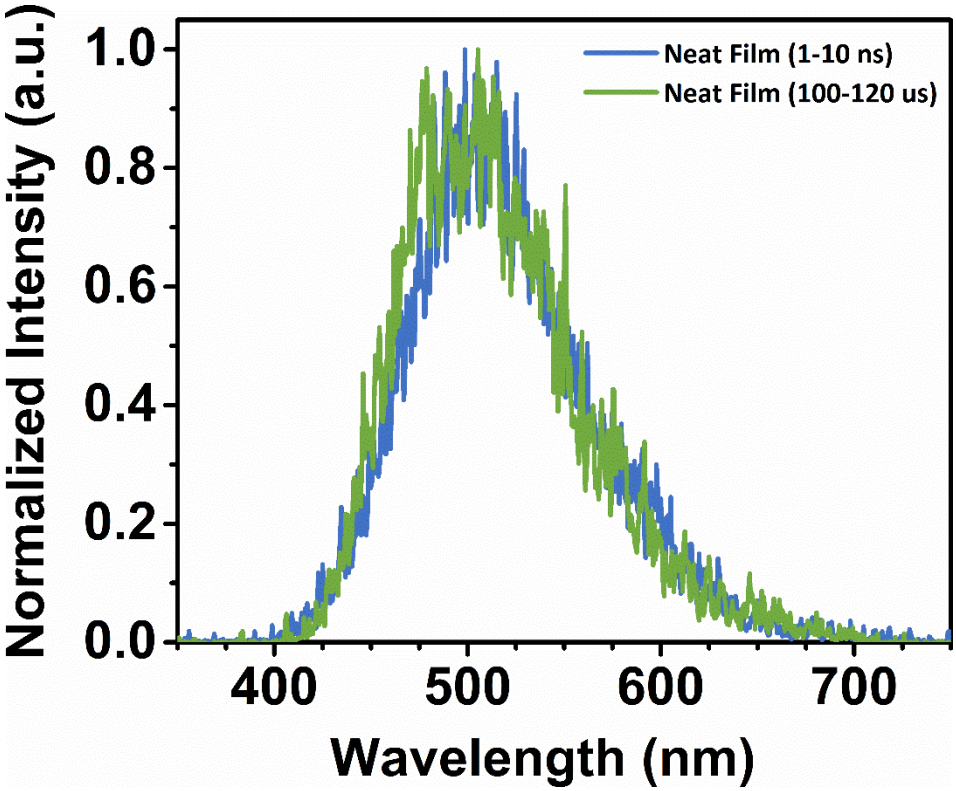



**Figure S7** The normalized time-resolved photoluminescent spectra of neat film **PDPC** in different time ranges under ambient temperature

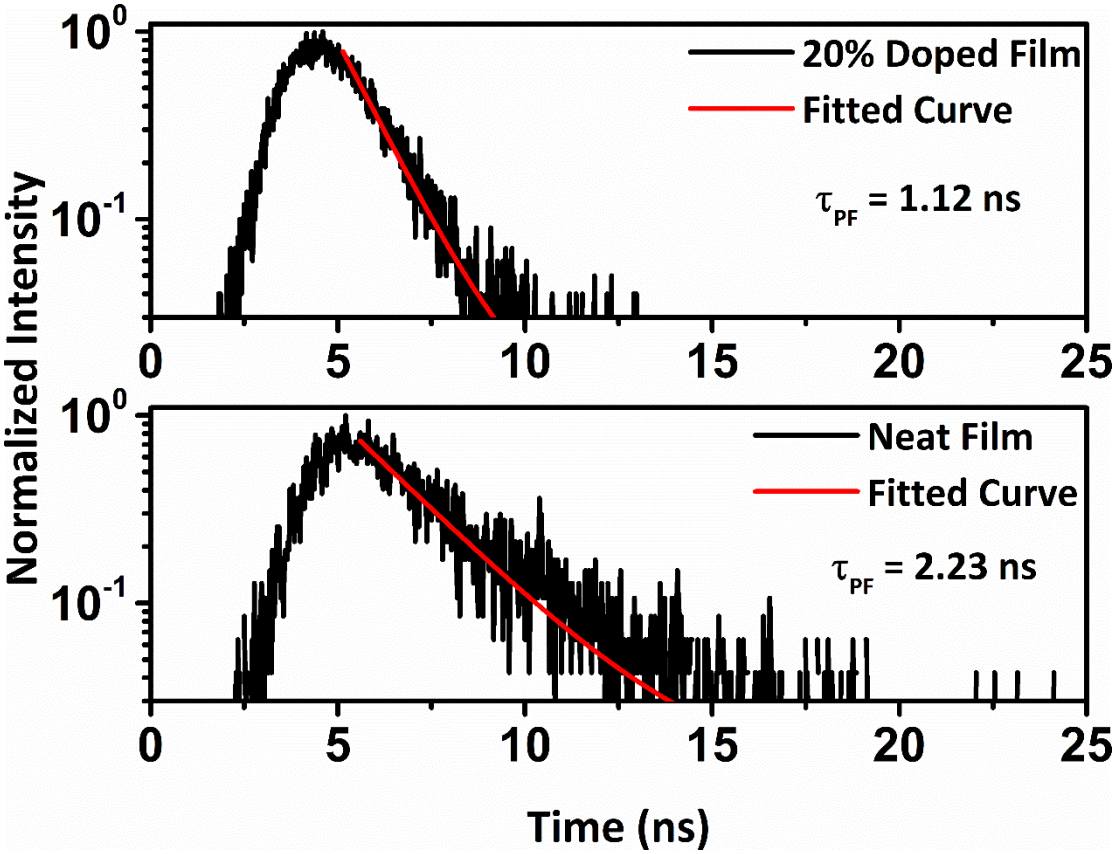



**Figure S8** The transient decay spectra of doped and neat film **PDPC** at room temperature

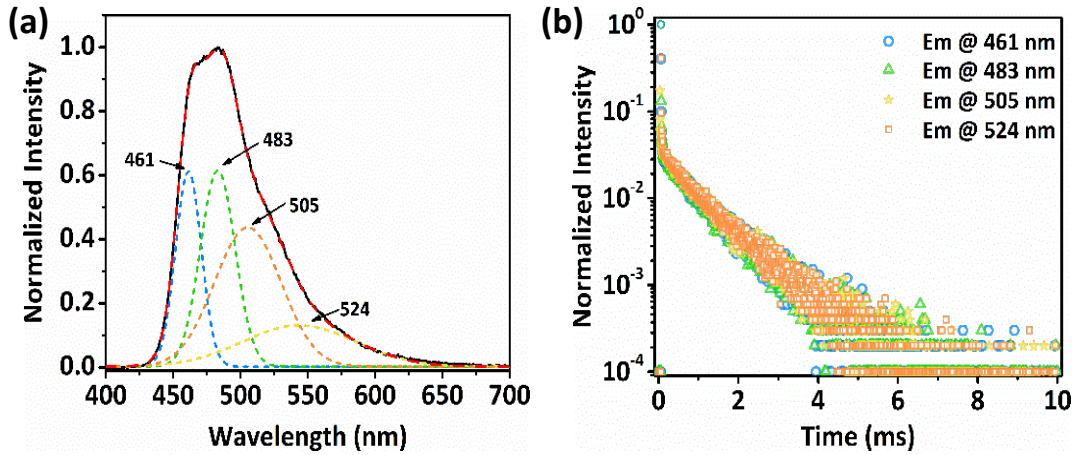



**Figure S9** The **(a)** photoluminescence spectra and **(b)** transient decay curve of PDPC powder. The solid black line in **(a)** is the original spectrum, while the short-dashed lines in blue, green, orange and yellow represent the fitted gaussian peaks, and the sum of the fitted peaks was plotted in red dashed line. The colors in **(b)** corresponds to that in **(a)**. The peak fitting was proceeded through "Peak Analyzer" function in OriginPro software [1] ,and the fitted curves comply to "Area version of Gaussian Function":

$$y = y_0 + \frac{Ae^{\frac{-4\ln(2)(x-x_c)^2}{w^2}}}{w\sqrt{\frac{\pi}{4\ln(2)}}}$$

In which $A$, $x_c$ and $w$ indicated the area, center x value, and FWHM, respectively.

**Table S4** Photoluminescent lifetimes and percentages (*A*) of crystalline **PDPC**

| **Wavelength(nm)** | $\tau_1$ **(μs)** | $A_1$ **(%)** | $\tau_2$ **(μs)** | $A_2$ **(%)** | $\bar{\tau}$**(μs)** |
|---|---|---|---|---|---|
| 461 | 188.87 | 8.11 | 995.16 | 91.89 | 929.76 |
| 483 | 130.24 | 5.34 | 968.94 | 94.66 | 924.15 |
| 524 | 179.16 | 8.17 | 1003.61 | 91.83 | 936.25 |

# 6. Theoretical Calculation

**Table S5** Component analysis of the excited-state **PDPC** monomer and dimer

| | States | Energy (eV) | Transition Contributions [a] (%) | Oscillator Strength |
|---|---|---|---|---|
| Monomer | $S_1$ | 3.2736 | H→L(97.97%) | 0.0164 |
| | $S_2$ | 3.4785 | H-1→L(97.72%) | 0.0130 |
| | $S_3$ | 3.6437 | H→L+1(97.33%) | 0.0241 |
| | $S_4$ | 3.6856 | H-2→L(94.48%) | 0.0078 |
| | $S_5$ | 3.7402 | H-1→L+1(95.88%) | 0.0291 |
| | $S_6$ | 3.8607 | H-3→L(96.05%) | 0.0021 |
| | $S_7$ | 3.9438 | H-2→L+1(41.31%), H-7→L+1(16.95%), H-4→L+1(14.99%), H-7→L(4.97%), H-4→L(4.91%) | 0.0053 |
| | $S_8$ | 4.0128 | H→L+3(82.95%), H-4→L(3.35%) | 0.0472 |
| | $S_9$ | 4.0273 | H-4→L(26.28%), H-7→L(23.85%), H-2→L+1(22.53%), H→L+3(8.69%), H-5→L(5.72%), H-6→L(3.61%) | 0.0106 |
| | $S_{10}$ | 4.0530 | H-1→L+2(83.95%), H-3→L+1(8.49%), H-3→L+7(3.06%) | 0.0301 |
| Dimer | $S_1$ | 3.2620 | H→L+1(55.04%), H→L(38.49%) | 0.0128 |
| | $S_1$* | 3.2693 | H-1→L(65.25%), H-1→L+1(30.58%) | 0.0165 |
| | $S_3$ | 3.4084 | H-2→L(53.11%), H-2→L+1(21.53%), H→L(13.77%), H→L+1(9.08%) | 0.0084 |
| | $S_4$ | 3.4753 | H-3→L+1(59.25%), H-3→L(37.24%) | 0.0135 |
| | $S_5$ | 3.4873 | H→L(43.32%), H→L+1(31.41%), H-2→L(15.39%), H-2→L+1(7.07%) | 0.0024 |
| | $S_6$ | 3.5470 | H-1→L+1(58.28%), H-1→L(27.99%), H-1→L+2(10.77%) | 0.0040 |
| | $S_7$ | 3.6471 | H-2→L+1(24.68%), H-2→L+2(21.24%), H-4→L+1(16.23%), H-4→L(12.13%), H-2→L(9.74%), H→L+2(3.07%) | 0.0148 |
| | $S_8$ | 3.6611 | H→L+3(67.28%), H→L+2(10.84%), H-1→L+2(7.17%) | 0.0047 |
| | $S_9$ | 3.6662 | H-1→L+2(56.73%), H→L+3(11.41%), H-5→L(11.02%), H-1→L+1(5.44%), H-5→L+1(4.56%), H-4→L+1(3.17%) | 0.0231 |
| | $S_{10}$ | 3.6738 | H-5→L(41.06%), H-5→L+1(20.19%), H-4→L(12.11%), H→L+3(5.84%), H-2→L+2(5.39%), H-4→L+1(4.16%), H-1→L+2(3.99%) | 0.0298 |

[a] H: HOMO; L: LUMO

* Degenerated orbital.

## 7. Electroluminescence Properties

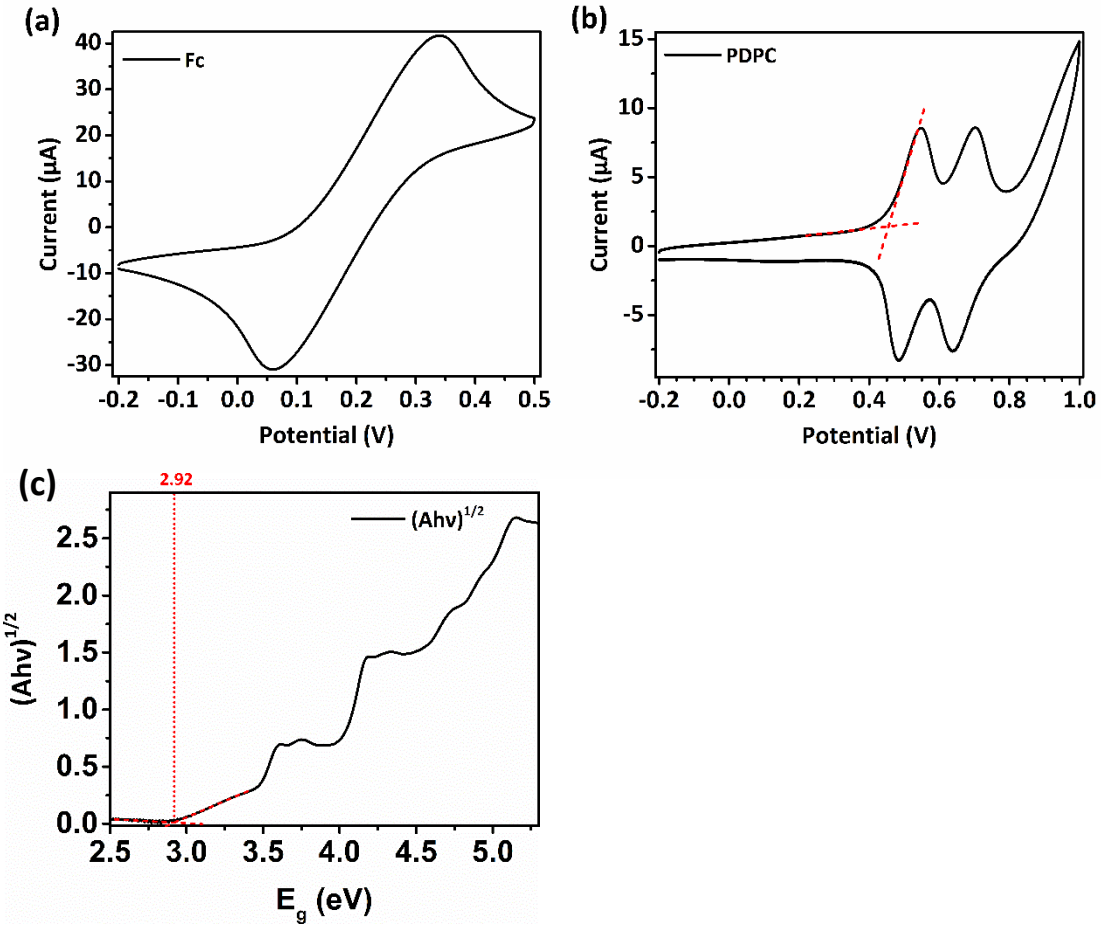



**Figure S10** The cyclic voltametric plots for **(a)** ferrocene and **(b) PDPC**; **(c)** Tauc plot for UV-vis absorption of **PDPC** solution (c.a. $10^{-5}$ mol/L)

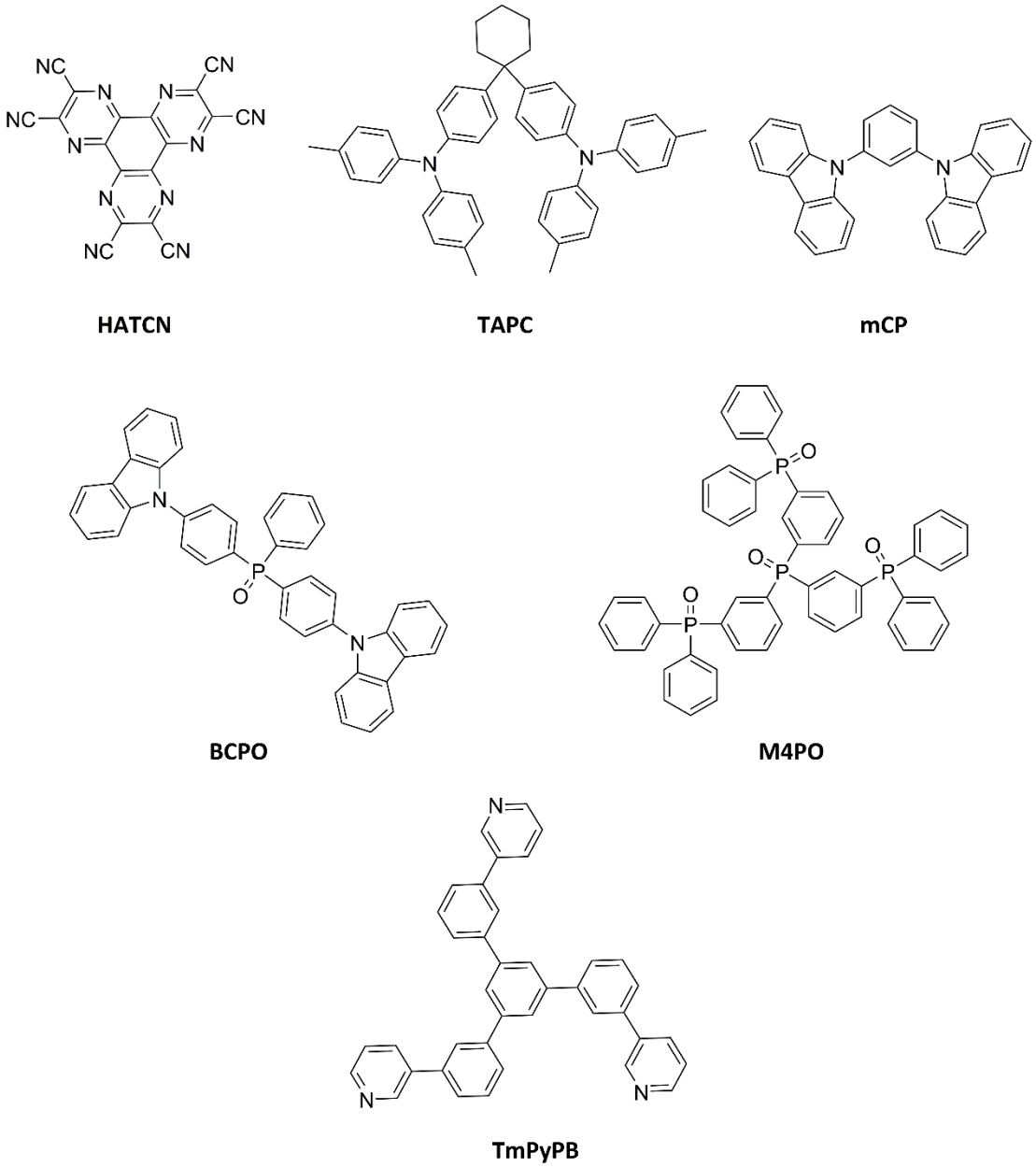



**Figure S11** Chemical formula to the abbreviations in the fabricated device

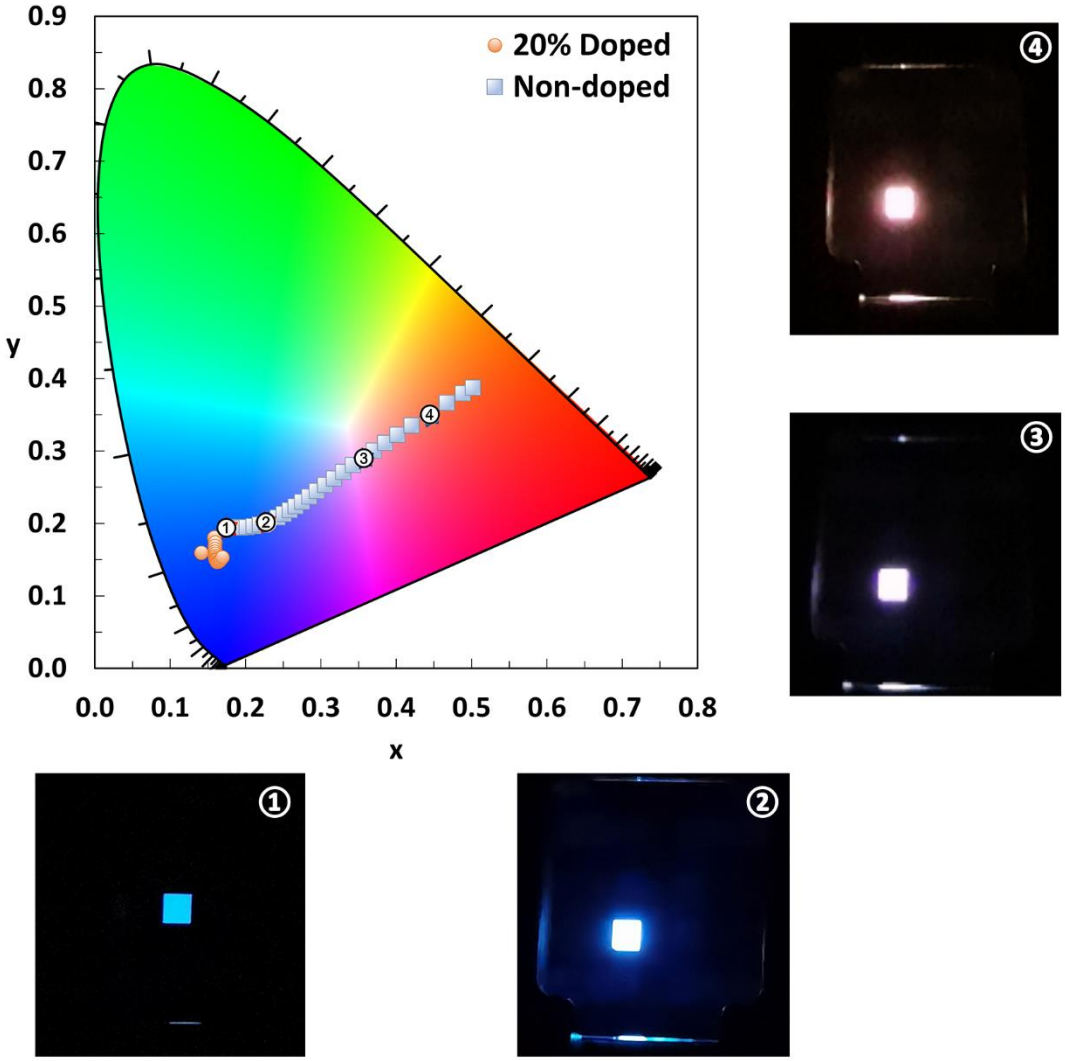



**Figure S12** Enlarged photo shots for nondoped device

**Table S6** Parameters for doped and nondoped device

| Emitter | $\lambda_{EL}$ a) (nm) | CIE b) (x, y) | $CRI_{max}$ c) | $L_{max}$ d) (cd / m²) | $CE_{max}$ e) (cd / A) | $PE_{max}$ f) (lm / W) | $EQE_{max}$ g) |
|---|---|---|---|---|---|---|---|
| Nondoped | 454 / 588 | (0.35, 0.29) | 93 | 278.4 | 1.22 | 0.77 | 0.81 |
| 20% Doped | 454 | (0.16, 0.17) | – | 133.6 | 2.16 | 1.94 | 1.53 |

a) Wavelength of emission peaks; b) CIE coordinate nearest to (0.33, 0.33); c) The optimum Color Rendering Index; d)–g) The maximum luminance, current efficiency, power efficiency and external quantum efficiency.

**Reference**

1. OriginPro, Learning Edition. OriginLab Corporation: Northampton, MA, USA. Available online: https://www.originlab.com/originprolearning.aspx (accessed on 6 June 2022).