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Protonation-Induced Dual Fluorescence of a Blue Fluorescence Material with Twisted A-π-D-π-A Configuration

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1. ^{1}H NMR, ^{13}C NMR and mass spectra of CzPA-F-PD in $CDCl_3$

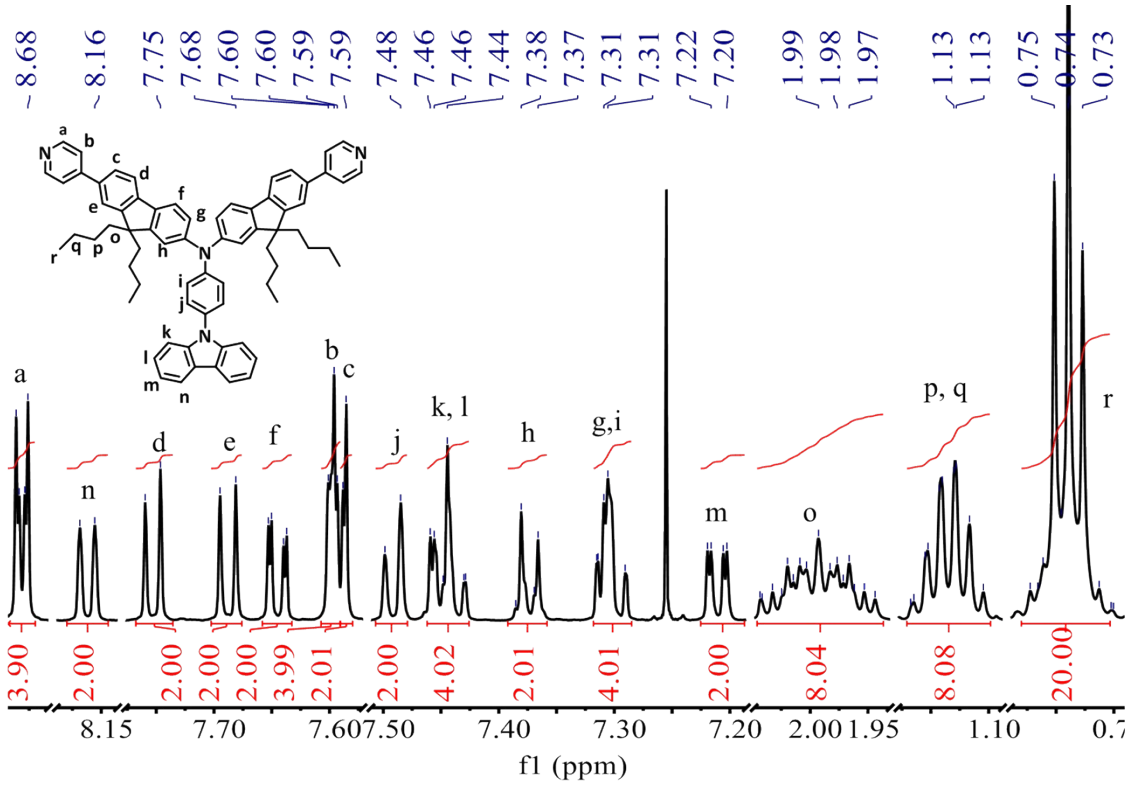


Fig. S1 ^{1}H NMR spectrum of **CzPA-F-PD** in $CDCl_3$.

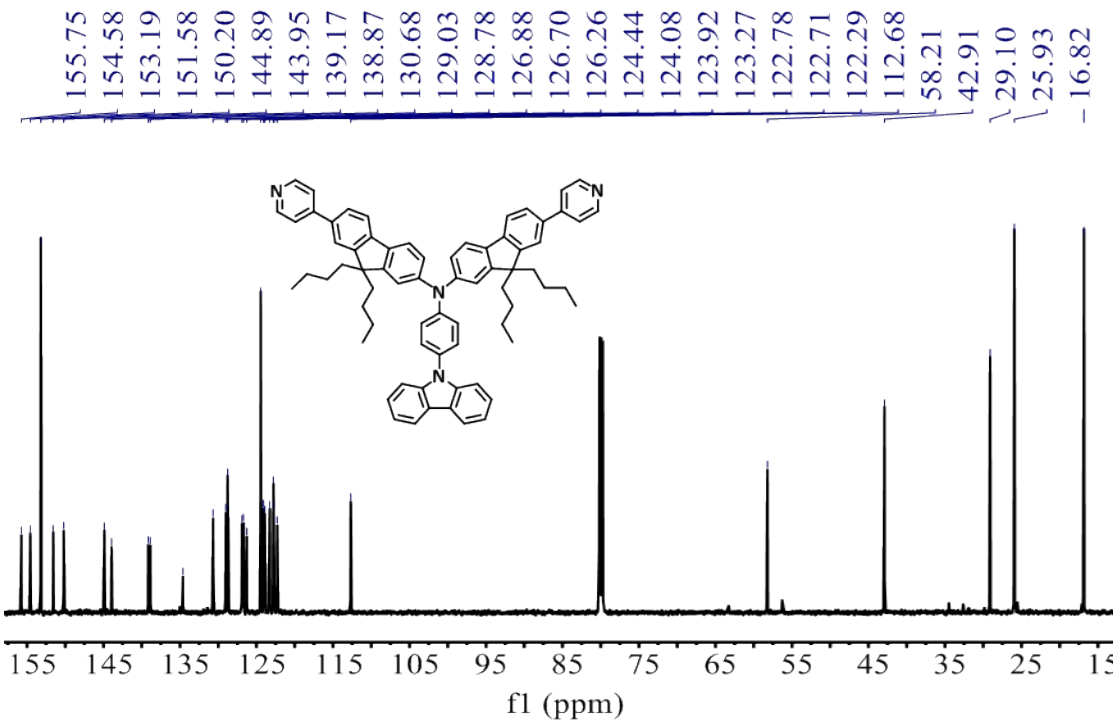


Fig. S2 ^{13}C NMR spectrum of **CzPA-F-PD** in $CDCl_3$.

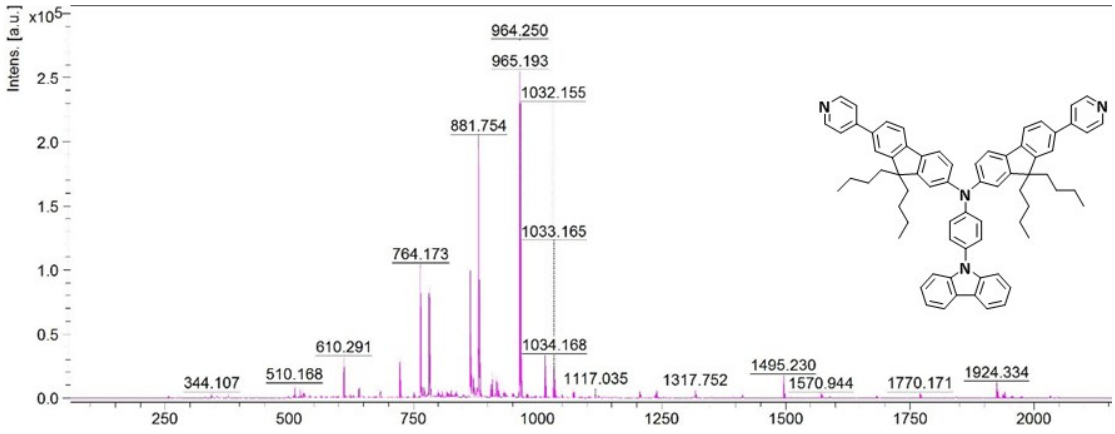


Fig. S3 Mass spectrum of **CzPA-F-PD.**

2. Thermogravimetric analysis

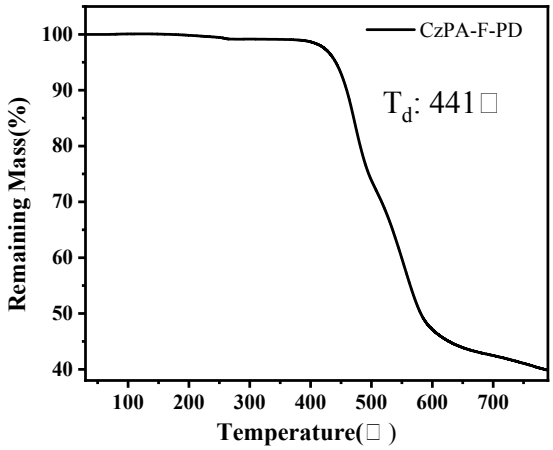


Fig. S4 TGA curve of **CzPA-F-PD**.

3. Electrochemical properties

The HOMO/LUMO level is calculated according to the following formalism:

$$E_{HOMO} = -4.8 - e(E_C^{OX} - E_f^{OX})V \quad (1)$$

$$E_g = 1240/\lambda_{onset} \quad (2)$$

$$E_{LUMO} = E_{HOMO} + E_g \quad (3)$$

where E_C^{OX} is the onset of oxidation potential of CV measurements, and E_f^{OX} is the oxidation peak of ferrocene. E_g is estimated from the onset of the absorption spectra.

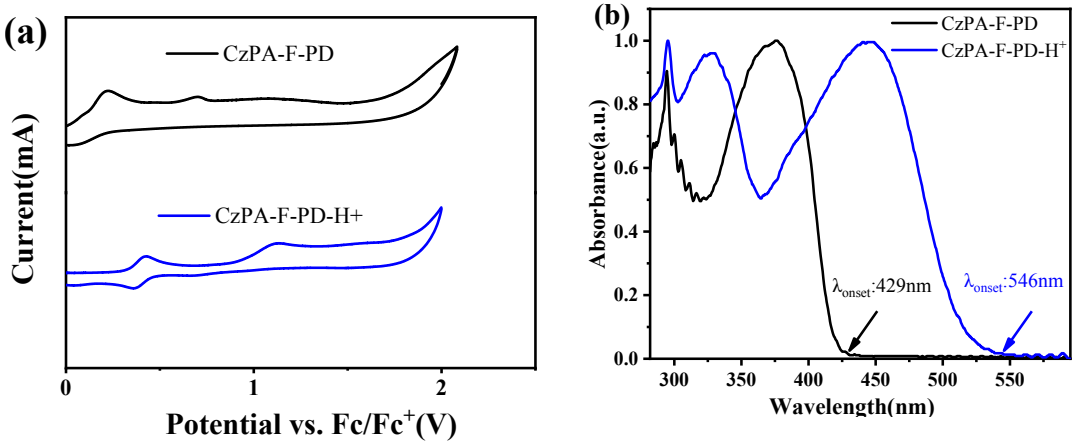


Fig. S5 (a) Cyclic voltammograms curve of **CzPA-F-PD** and **CzPA-F-PD-H$^+$** in DCM solution; (b) UV-vis absorption spectrum of **CzPA-F-PD** and **CzPA-F-PD-H$^+$**.

4. Crystal data of CzPA-F-PD

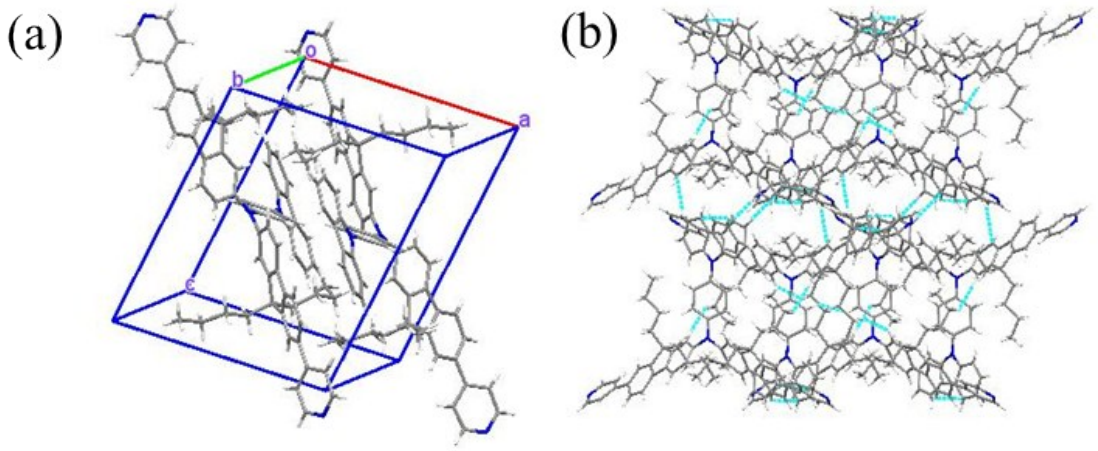


Fig. S6 (a) Unit cell diagrams for the crystal of **CzPA-F-PD**. (b) Crystal packing diagram of **CzPA-F-PD.**

Table S1 Crystal data and structure refinement for **CzPA-F-PD**

Identification code	**CzPA-F-PD**
Empirical formula	C70H68N4
Formula weight	965.28
Temperature/K	220.00(13)
Crystal system	triclinic
Space group	P-1
a/Å	12.27610(10)
b/Å	14.6350(2)
c/Å	16.8615(2)
α/°	110.1380(10)
β/°	103.3260(10)
γ/°	92.4780(10)
Volume/Å^3	2742.54(6)
Z	2
ρ_{calc}g/cm^3	1.169
μ/mm^{-1}	0.513
F(000)	1032.0
Crystal size/mm^3	0.285 × 0.125 × 0.038
Radiation	CuKα (λ = 1.54184)
2Θ range for data collection/°	5.784 to 151.022
Index ranges	-15 ≤ h ≤ 15, -18 ≤ k ≤ 17, -15 ≤ l ≤ 21
Reflections collected	34996
Independent reflections	10851 [R_{int} = 0.0227, R_{sigma} = 0.0222]
Data/restraints/parameters	10851/0/671
Goodness-of-fit on F^2	1.040
Final R indexes [I>=2σ (I)]	R_1 = 0.0417, wR_2 = 0.1065
Final R indexes [all data]	R_1 = 0.0469, wR_2 = 0.1129

Largest diff. peak/hole / e Å^{-3}	0.22/-0.19

5. Solvatochromic effect

Lippert-Mataga equation can be used to understand the influence of solvent environment on the optical properties of our compounds. The equation describes the interaction between solvent and solute dipole moments:

$$hc(v_a - v_f) = hc(v_a^0 - v_f^0) - \frac{2(\mu_e - \mu_g)^2}{\alpha^3} f(\varepsilon,n) \quad (4)$$

where $f(\varepsilon,n)$ is the orientational polarizability of the solvent, and $f(\varepsilon,n) = [\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}]$, ε and n are the solvent dielectric and the solvent refractive index, respectively; $v_a^0 - v_f^0$corresponds to the Stokes shifts when $f(\varepsilon,n)$ is zero, $\mu_e$is the excited state dipole moment, $\mu_g$is the ground-state dipole moment. α is the solvent cavity (Onsager) radius, derived from the Avogadro number (N), molecular weight (M), and density (d=1.0 g/cm^3) and $\alpha = (\frac{3M}{4N\pi d})^{1/3}$

The detailed data are listed in Table S2.

Table S2 Detailed absorption and emission peak positions of **CzPA-F-PD** in different solvents

solvents	f(ε,n)	**CzPA-F-PD**			
		$v_a^{a)}$ [nm]	$v_f^{b)}$ [nm]	$v_a - v_f^{c)}$ [cm^{-1}]	FWHM [nm]
Hexane	0.0012	379	422	2689	46
Benzene	0.0026	381	433	3152	51
Toluene	0.012	381	431	3045	49
Triethylamine	0.048	376	427	3177	49
Butyl ether	0.096	379	435	3397	57
Ethyl ether	0.167	375	436	3731	57
Ethyl acetate	0.2	374	455	4760	71
Tetrahydrofuran	0.21	377	462	4845	73
Dimethyl formamide	0.276	378	511	6886	104
Acetone	0.28	380	500	6316	101
Acetonitrile	0.305	377	529	7622	118

[a)] Absorption maximum. [b)] Emission maximum. [c)] Stokes shifts in different solvents. [d)] Full-width at half-maximum.

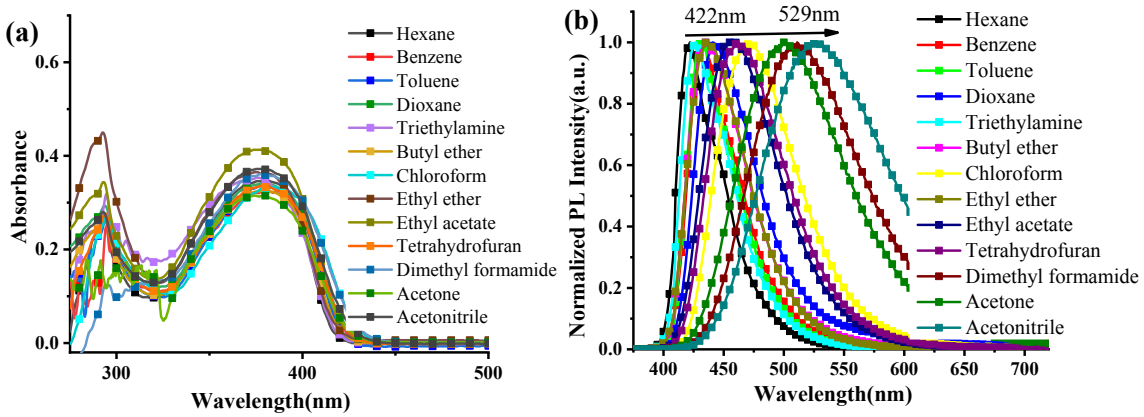


Fig. S7 (a) UV-vis absorption and (b) PL spectra of **CzPA-F-PD** in different solutions (10^{-5} mol/L).

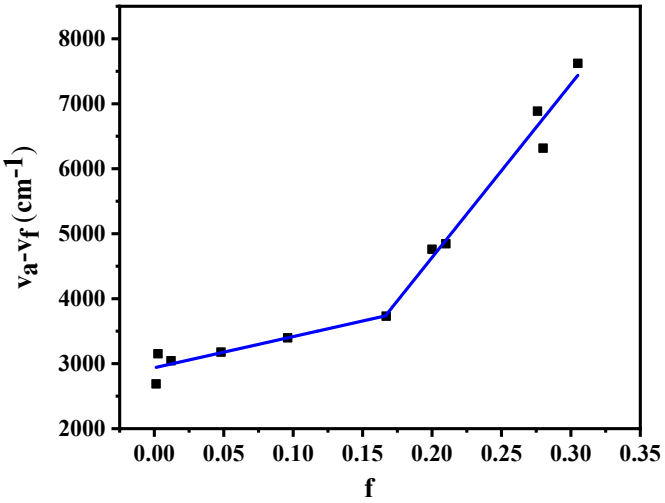
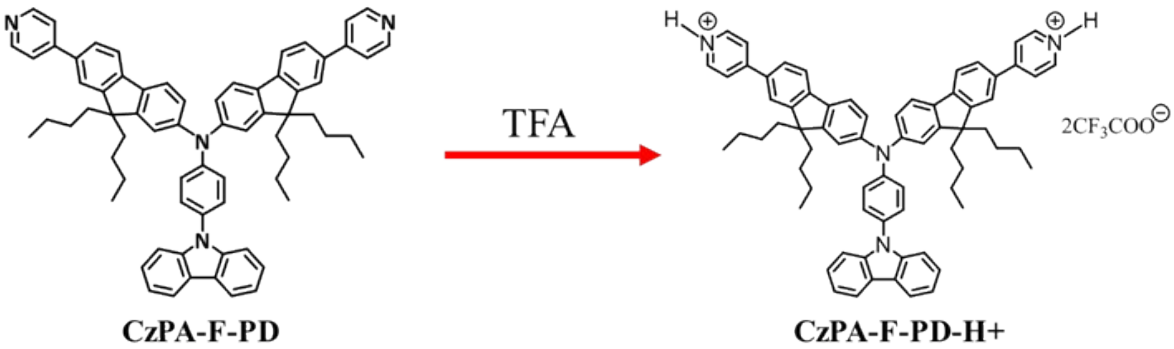


Fig. S8 Fitted linear correlation of the orientation polarization of solvent media with the stokes shift for **CzPA-F-PD**.

6. Photophysical properties



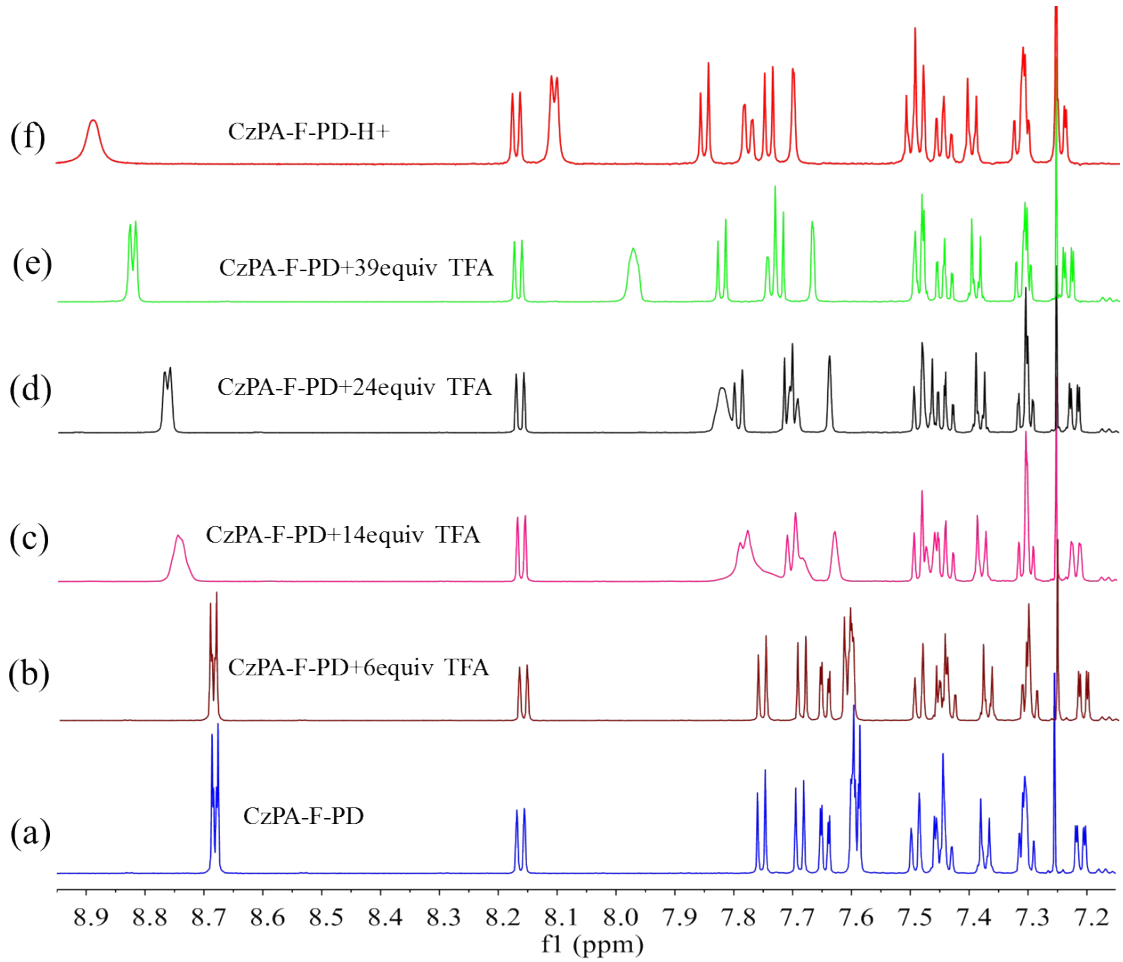


Fig. S9 Partial ^{1}H NMR spectra in $CDCl_3$ solution: (a) **CzPA-F-PD**; (b) **CzPA-F-PD** + 6 equiv. TFA; (c) **CzPA-F-PD** + 14 equiv. TFA; (d) **CzPA-F-PD** + 24 equiv. TFA; (e) **CzPA-F-PD** + 39 equiv. TFA; (f) **CzPA-F-PD-H^{+}**.

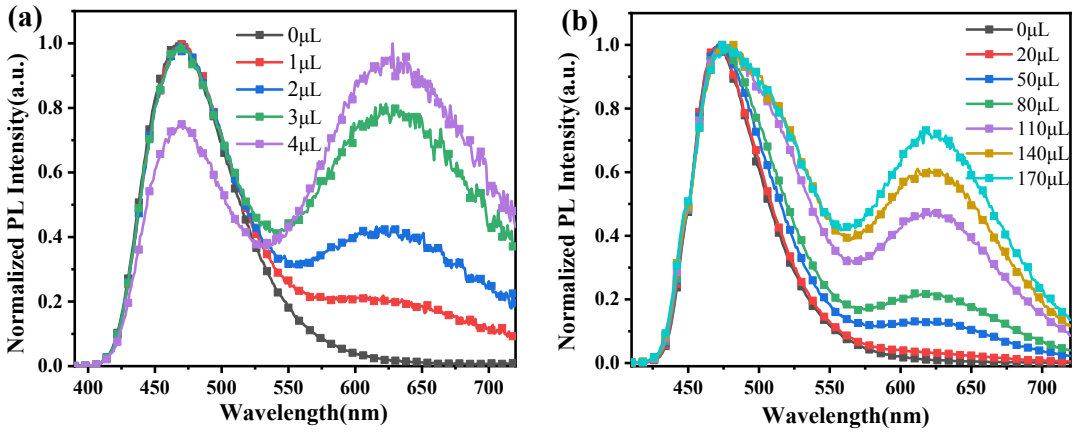


Fig. S10 The PL spectra of **CzPA-F-PD** in $CHCl_3$ solution (10^{-5} mol/L) after treated with different equivalents of a) HOAc and b) HCl (0.03 mol/L).

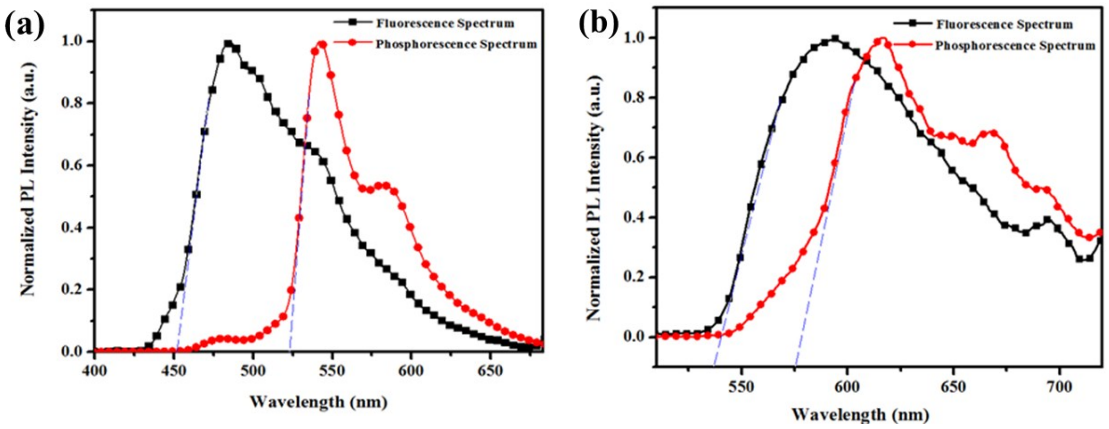


Fig. S11 The PL spectra of (a) **CzPA-F-PD** and (b) **CzPA-F-PD-H**$^+$ in the $CHCl_3$ solution under 77K (delayed 1ms).

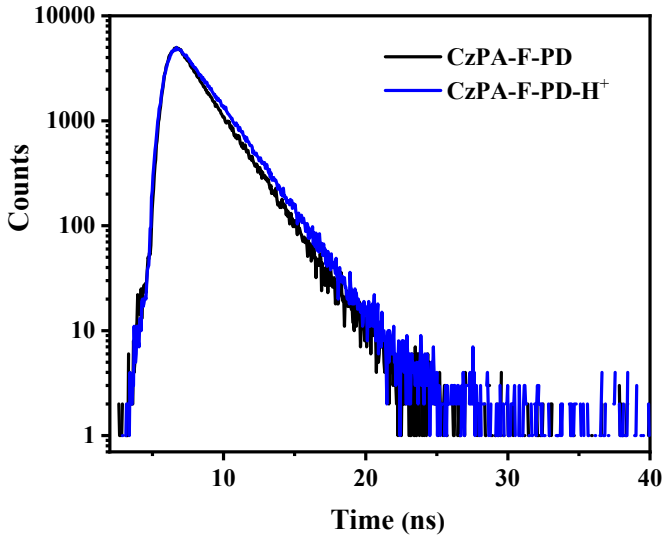


Fig. S12 Time-resolved fluorescence of **CzPA-F-PD** and **CzPA-F-PD-H**$^+$ in $CHCl_3$ solution (The concentrations of the solutions are 10^{-5} mol /L).

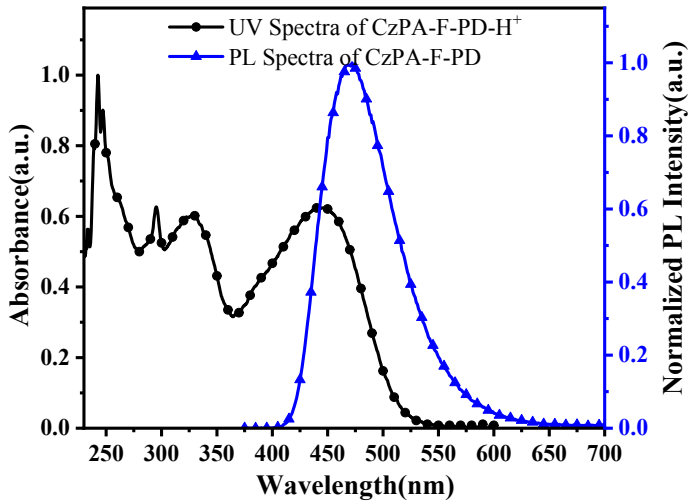


Fig. S13 The PL spectrum of **CzPA-F-PD** and UV spectrum of **CzPA-F-PD-H**$^+$ in the $CHCl_3$ solution with the concentration of 10^{-5} mol/L.