

Supplementary Information

Three-component color-tunable room temperature afterglow doped materials through Förster-Resonance Energy Transfer

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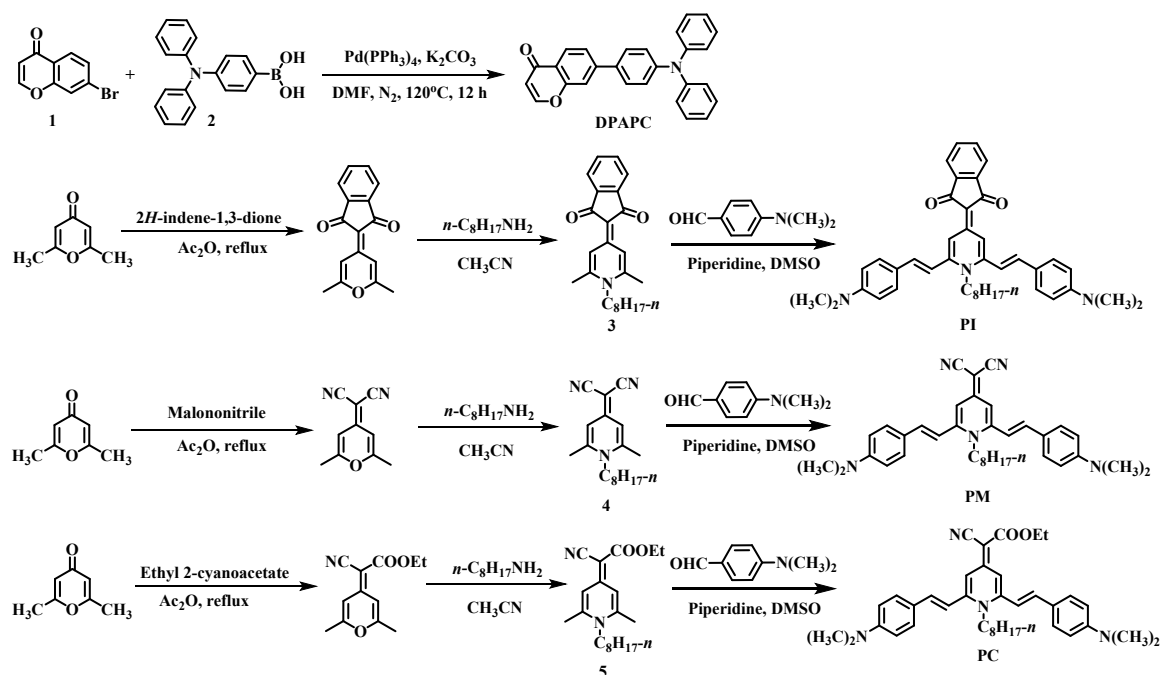
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Scheme S1 Synthetic routes to DPAPC, PI, PM, and PC.

1. Experimental

1.1 Measurements and materials

NMR spectra were determined on a Bruker DRX 400/500 NMR spectrometer. High-performance liquid chromatography was conducted on a Waters Alliance e2695. HRMS-ESI mass spectra were conducted on a Hitachi Nano Frontier LD spectrometer. Fluorescence spectra were conducted on a Cary Eclipse fluorescence spectrophotometer. Delayed emission spectra were conducted on a FLS920 lifetime and steady state spectrometer. The absolute emission quantum yields and emission lifetime decays were conducted on a Jobin Yvon Horiba FluoroMax-4 fluorometer. UV-vis absorption spectra were conducted on a UV-3600 Shimadzu spectrophotometer. 7-Bromo-4*H*-chromen-4-one (**1**), 4-(diphenylamino)phenylboronic acid (**2**), 2,6-dimethyl-4*H*-pyran-4-one, 2*H*-indene-1,3-dione, malononitrile, ethyl 2-cyanoacetate, 4-(dimethylamino)benzaldehyde, and piperidine were commercially available and used directly. Using 2,6-dimethyl-4*H*-pyran-4-one as the starting material, 2-(2,6-dimethyl-1-octylpyridin-4(1*H*)-ylidene)-1*H*-indene-1,3(2*H*)-dione (**3**), 2-(2,6-dimethyl-1-octylpyridin-4(1*H*)-ylidene)malononitrile (**4**), and ethyl 2-cyano-2-(2,6-dimethyl-1-octylpyridin-4(1*H*)-ylidene)acetate (**5**) were synthesized according to the previous reports.¹

1.2 Synthesis of 7-(4-(diphenylamino)phenyl)-4*H*-chromen-4-one (DPAPC)

Compound **1** (225 mg, 1 mmol), compound **2** (318 mg, 1.1 mmol), tetratriphenylphosphine palladium (90 mg), potassium carbonate (200 mg), and *N,N*-dimethylformamide (10 mL) were added to the Schlenk tube. The mixture was stirred at 120°C in N₂ atmosphere for 12 h. After being cooled to room temperature, the mixture was extracted with CH₂Cl₂ and dried with anhydrous Na₂SO₄. The organic solvent was removed under pressure. The residue was obtained by silica gel column chromatography (petroleum ether: ethyl acetate = 30:1) to produce a yellow solid (230 mg, 60% yield). ¹H NMR (CDCl₃, 500 MHz): δ 8.30 (d, *J* = 7.5 Hz, 1H), 8.05 (d, *J* = 10.5 Hz, 1H), 7.87 (s, 1H), 7.78-7.74 (m, 3H), 7.37-7.33 (m, 4H), 7.13-7.08 (m, 6H), 7.03 (d, *J* = 10.0 Hz, 1H), 6.35 (d, *J* = 7.0 Hz, 1H) ppm. ¹³C NMR (CDCl₃, 125 MHz): δ 177.5, 157.0, 155.3, 148.6, 147.3, 146.4, 132.0, 129.4, 128.1, 126.2, 125.0, 123.8, 123.6, 123.2, 123.0, 115.1, 113.1 ppm. HRMS (ESI) *m/z*: [M+H]⁺ calculated for C₂₇H₂₀NO₂, 390.1489; found, 390.1483.

1.3 Synthesis of 1,4-dihydropyridine derivatives

The mixture of **3/4/5** (1.5 mmol), 4-(dimethylamino)benzaldehyde (2.24 g, 15.0 mmol), piperidine (1.5 mL) and dimethyl sulfoxide (14 mL) was refluxed under argon for 48 h. After cooling to room temperature, the reaction mixture was poured into methanol (100 mL) and suction filtered to give the crude product. The crude product was washed with methanol three times and then dried to give the pure 1,4-dihydropyridine derivative.

2-(2,6-Bis((*E*)-4-(dimethylamino)styryl)-1-octylpyridin-4(1*H*)-ylidene)-1*H*-indene-1,3(2*H*)-dione (PI). Orange solids (638 mg), 68% yield. ¹H NMR (CDCl₃, 400 MHz): δ 9.03 (s, 2H), 7.61-7.59 (m, 2H), 7.47-7.45 (m, 2H), 7.42 (d, *J* = 8.8 Hz, 4H), 7.34 (d, *J* = 15.6 Hz, 2H), 6.76 (d, *J* = 15.6 Hz, 2H), 6.71 (d, *J* = 8.4 Hz, 4H), 4.11 (t, *J* = 8.0 Hz, 2H), 3.03 (s, 12H), 1.89-1.82 (m, 2H), 1.44-1.26 (m, 10H), 0.87 (t, *J* = 5.4 Hz, 3H). ¹³C NMR (CDCl₃, 125 MHz): δ 192.8, 151.3, 149.4, 149.2, 140.6,

139.6, 131.5, 129.0, 123.5, 119.6, 113.9, 113.8, 112.1, 102.8, 49.9, 40.2, 31.8, 29.5, 29.2, 29.0, 26.6, 22.6, 14.1 ppm. HRMS (ESI) m/z : $[M+H]^+$ calculated for $C_{42}H_{48}N_3O_2$, 626.3741; found, 626.3747.

2-(2,6-Bis((*E*)-4-(dimethylamino)styryl)-1-octylpyridin-4(*IH*)-ylidene)malononitrile (PM).

Orange solids (524 mg), 64% yield. 1H NMR ($CDCl_3$, 400 MHz): δ 7.39 (d, $J = 8.8$ Hz, 4H), 7.12 (d, $J = 15.6$ Hz, 2H), 6.91 (s, 2H), 6.71-6.65 (m, 6H), 4.02 (t, $J = 7.6$ Hz, 2H), 3.03 (s, 12H), 1.85-1.77 (m, 2H), 1.39-1.27 (m, 10H), 0.88 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 155.4, 151.5, 148.8, 139.8, 129.0, 122.9, 119.7, 113.2, 112.1, 110.4, 49.6, 44.9, 40.2, 31.7, 29.6, 29.1, 29.0, 26.5, 22.6, 14.1 ppm. HRMS (ESI) m/z : $[M+H]^+$ calculated for $C_{36}H_{44}N_5$, 546.3951; found, 546.3957.

Ethyl 2-(2,6-bis((*E*)-4-(dimethylamino)styryl)-1-octylpyridin-4(*IH*)-ylidene)-2-cyanoacetate (PC).

Orange solids (414 mg), 70% yield. 1H NMR ($CDCl_3$, 400 MHz): δ 8.58 (d, $J = 2.0$ Hz, 1H), 7.39 (d, $J = 8.8$ Hz, 4H), 7.24 (d, $J = 15.5$ Hz, 1H), 7.16-7.12 (m, 2H), 6.72-6.67 (m, 6H), 4.23 (q, $J = 6.8$ Hz, 2H), 4.02 (t, $J = 8.0$ Hz, 2H), 3.026 (s, 6H), 3.022 (s, 6H), 1.85-1.77 (m, 2H), 1.37-1.26 (m, 13H), 0.87 (t, $J = 7.2$ Hz, 3H). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 168.0, 154.0, 151.31, 151.28, 148.27, 148.15, 139.2, 139.0, 128.9, 123.5, 123.3, 122.9, 114.3, 113.9, 112.8, 112.08, 112.06, 111.8, 67.8, 59.0, 49.5, 40.2, 31.7, 29.6, 29.1, 29.0, 26.5, 22.6, 14.8, 14.1 ppm. HRMS (ESI) m/z : $[M+H]^+$ calculated for $C_{38}H_{49}N_4O_2$, 593.3850; found, 593.3852.

1.4 Preparation of two-component doped materials

Put the corresponding amount of host and guest molecules together, and heat the mixture to 40-50°C in air atmosphere. After the guests are completely dissolved in the molten hosts, the mixed materials are cooled to room temperature, and the mixed materials are crystallized to obtain the two-component doped materials. The two-component doped materials with high guest-host molar ratio (1:50, 1:100, 1:500, 1:1000) are using direct weighing method, while for low guest-host molar ratio (1:5000, 1:10000, 1:100000) doped materials, we use the indirect dilution method.

1.5 Preparation of three-component doped materials

Put the corresponding amount of host, guest and third component molecules together, and heat the mixture to 40-50°C in air atmosphere. After the guests are completely dissolved in the molten hosts, the mixed materials are cooled to room temperature, and the mixed materials are crystallized to obtain the three-component doped materials. All three-component doped materials were prepared by direct weighing method.

1.6 Theoretical calculations

All chemical structures were optimized at the level of B3LYP/6-311G* and the excited energies were calculated by the time-dependent density functional theory (TD-DFT) method at the level of M062X/6-311G*. All the calculations were performed within Gaussian 09 software package.

References

1 Y. Lei, D. Yang, H. Hua, C. Dai, L. Wang, M. Liu, X. Huang, Y. Guo, Y. Cheng, H. Wu, *Dyes Pigm.* **2016**, *133*, 261–272.

2. Figures and tables

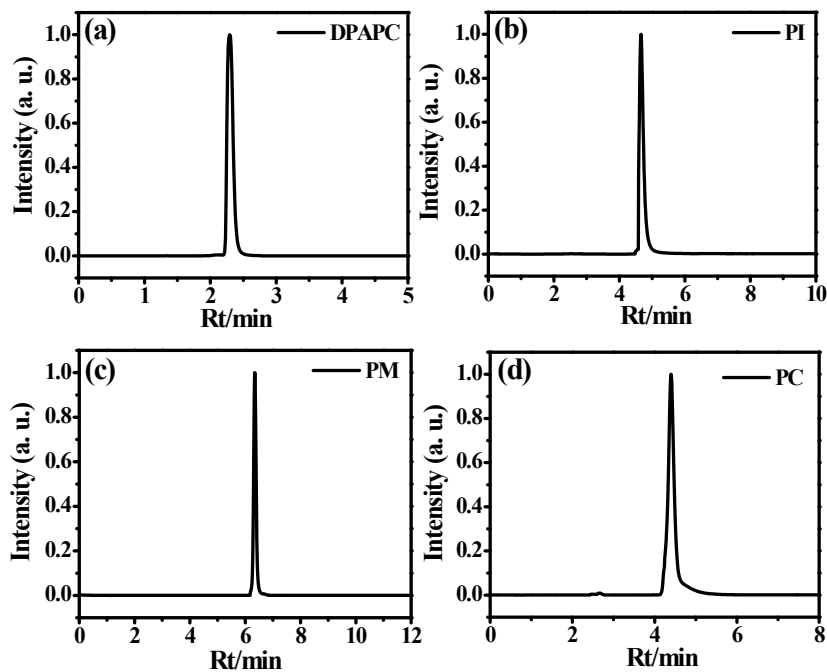


Fig. S1 High performance liquid chromatography of **DPAPC** (a), **PI** (b), **PM** (c), and **PC** (d). Condition: CH₃CN/MeOH = 60%:40% for **DPAPC**; CH₃CN/MeOH = 20%:80% for **PI**; CH₃CN/MeOH = 60%:40% for **PM**; CH₃CN/MeOH = 99%:1% for **PC**.

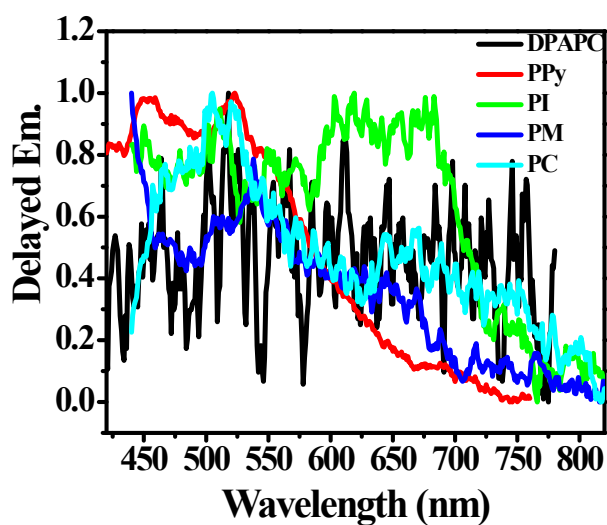


Fig. S2 Delayed spectra of host molecule **PPy**, guest molecule **DPAPC**, and third components **PI**, **PM**, and **PC** in solid state at room temperature ($\lambda_{\text{ex}} = 365$ nm, delay time: 0.5 ms).

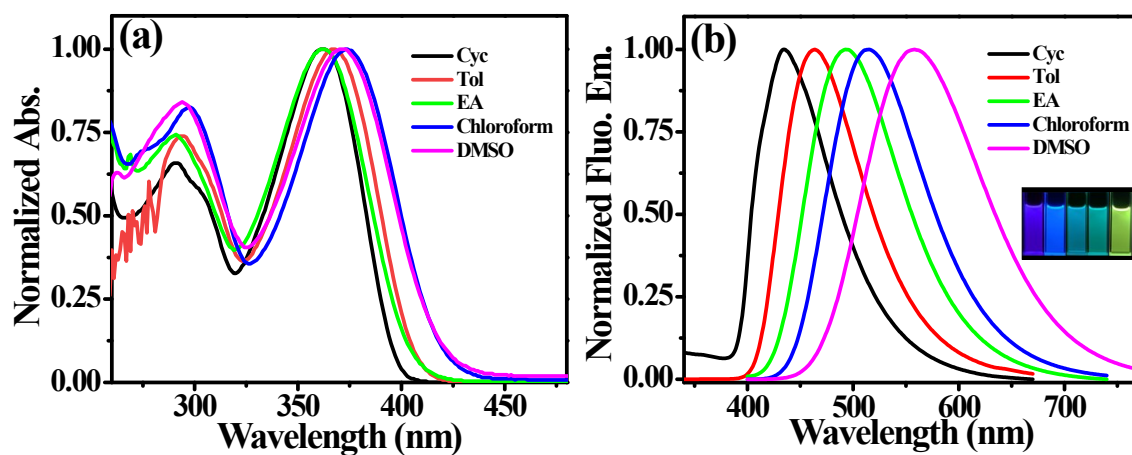


Fig. S3 Normalized UV-vis absorption (a) and fluorescence (b) spectra of **DPAPC** in various solvents (1×10^{-5} mol/L) ($\lambda_{\text{ex}} = 320$ nm). Inset: fluorescence pictures in cyclohexane (Cyc), toluene (Tol), ethyl acetate (EA), chloroform, and dimethyl sulfoxide (DMSO) from left to right.

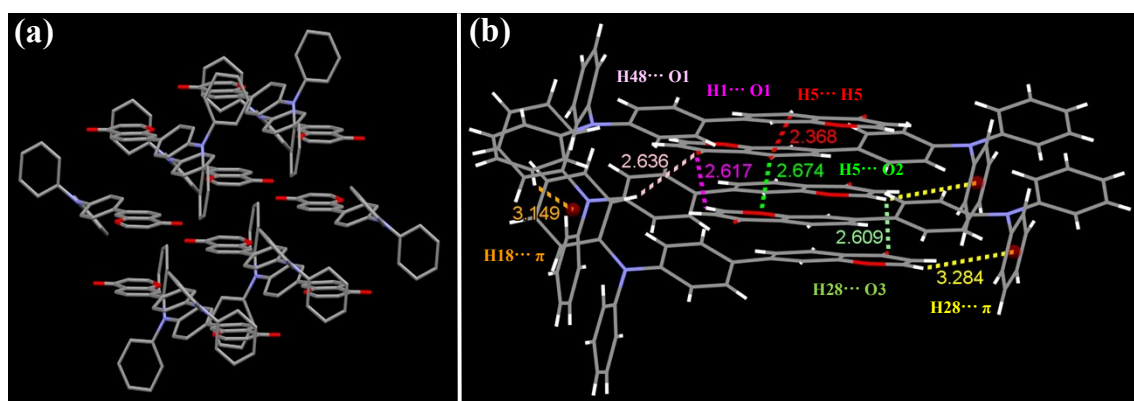


Fig. S4 (a) Stacking arrangement of **DPAPC**. (b) Intermolecular interactions in the crystal structure of **DPAPC**.

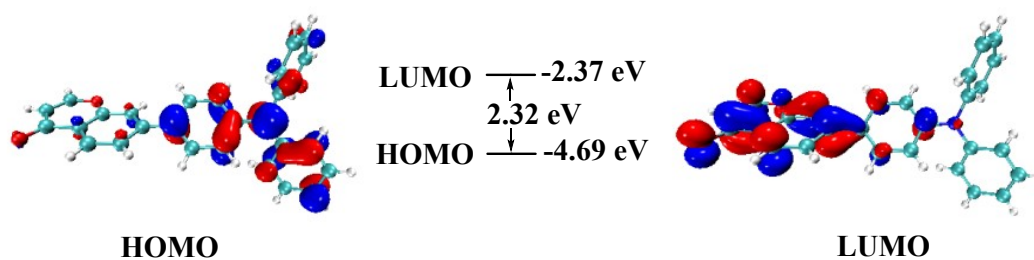


Fig. S5 HOMO/LUMO orbitals and energy gap of **DPAPC** based on DFT calculation.

Table S1 Crystal data and details of collection and refinement for **DPAPC**.

Compound	DPAPC
CCDC (no.)	2265625
Empirical formula	C ₂₇ H ₁₉ NO ₂
Formula weight	389.43
Temperature (K)	293(2)
Crystal system	Triclinic
Space group	<i>P</i> $\bar{1}$
<i>Z</i>	4
<i>D</i> _{calcd} [Mg/m ³]	1.282
<i>F</i> (000)	816
θ range [°]	2.572-25.999
<i>R</i> ₁ [<i>I</i> >2 σ (<i>I</i>)]	0.0611
<i>wR</i> ₂ [<i>I</i> >2 σ (<i>I</i>)]	0.1492
<i>a</i> [Å]	6.5009(2)
<i>b</i> [Å]	14.8557(6)
<i>c</i> [Å]	21.2715(7)
α [deg]	80.4050(10)
β [deg]	88.7850(10)
γ [deg]	85.1330(10)
<i>V</i> [Å ³]	2018.21(12)
GOF	1.015
<i>R</i> (int)	0.0700
No. of reflns collected	40188
No. of unique reflns	7885
<i>R</i> ₁ (all data)	0.0959
<i>wR</i> ₂ (all data)	0.1779

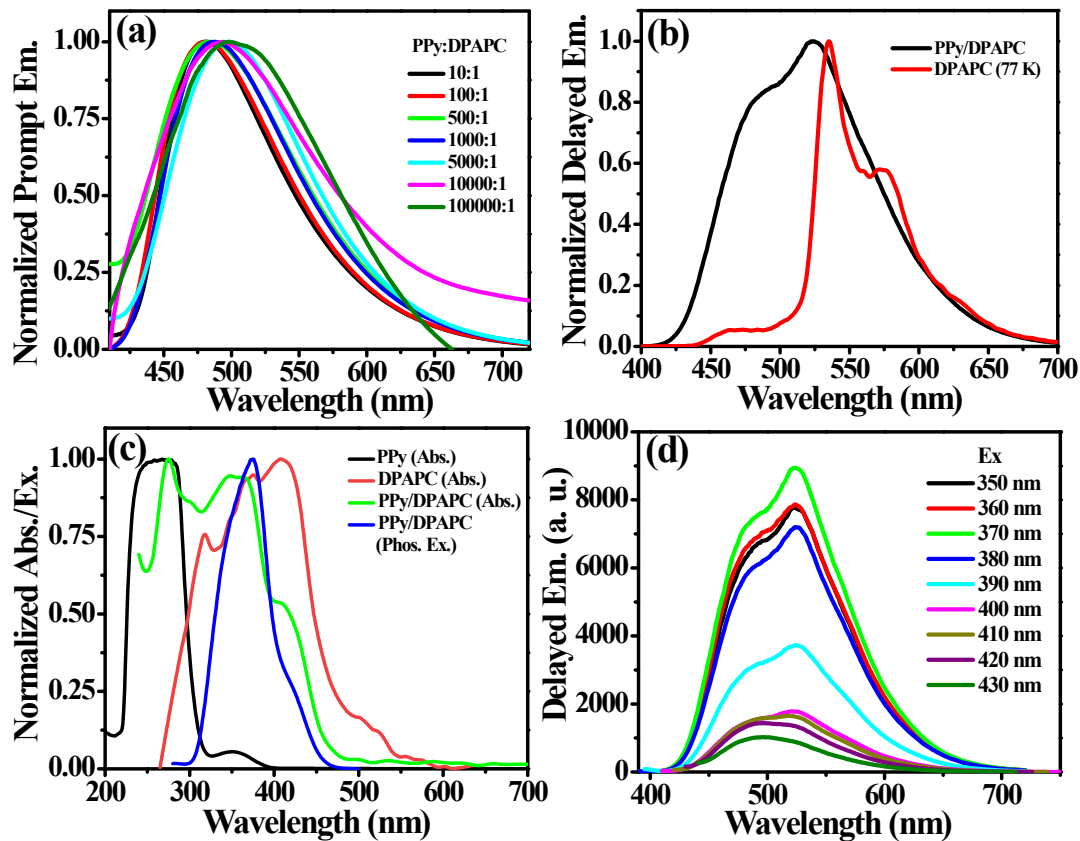


Fig. S6 (a) Prompt spectra of PPy/DPAPC materials with different molar ratios ($\lambda_{\text{ex}} = 400$ nm). (b) Phosphorescence spectra of DPAPC at 77 K in tetrahydrofuran solution (1×10^{-5} mol/L) and delayed spectrum of PPy/DPAPC ($\lambda_{\text{ex}} = 370$ nm, delay time: 0.5 ms). (c) Absorption spectra of PPy, DPAPC, and PPy/DPAPC, and the excitation spectrum for the phosphorescent emission of PPy/DPAPC. (d) Phosphorescence spectra of PPy/DPAPC under different excitation wavelengths.

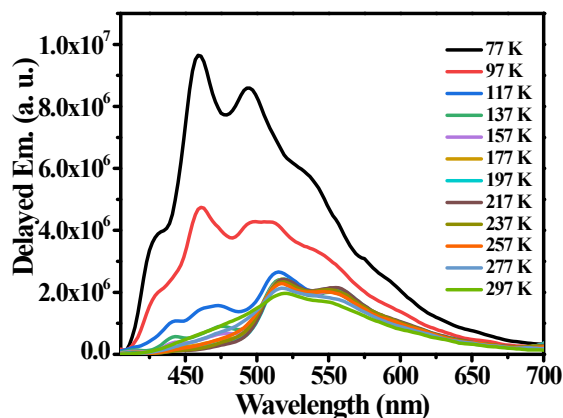


Fig. S7 Temperature-dependent delayed emission of the PPy/DPAPC material at a molar ratio of 1000:1 ($\lambda_{\text{ex}} = 370$ nm, delay time: 0.5 ms).

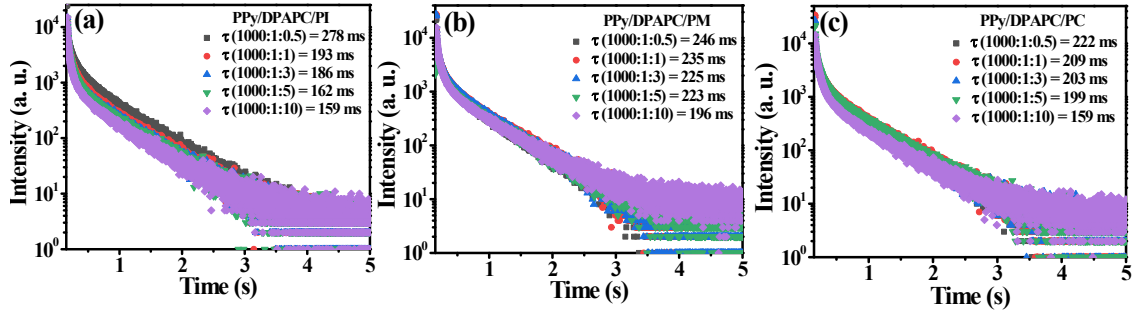


Fig. S8 Delayed emission lifetimes of the doped materials PPy/DPAPC/PI (a), PPy/DPAPC/PM (b), and PPy/DPAPC/PC (c) with different molar ratios.

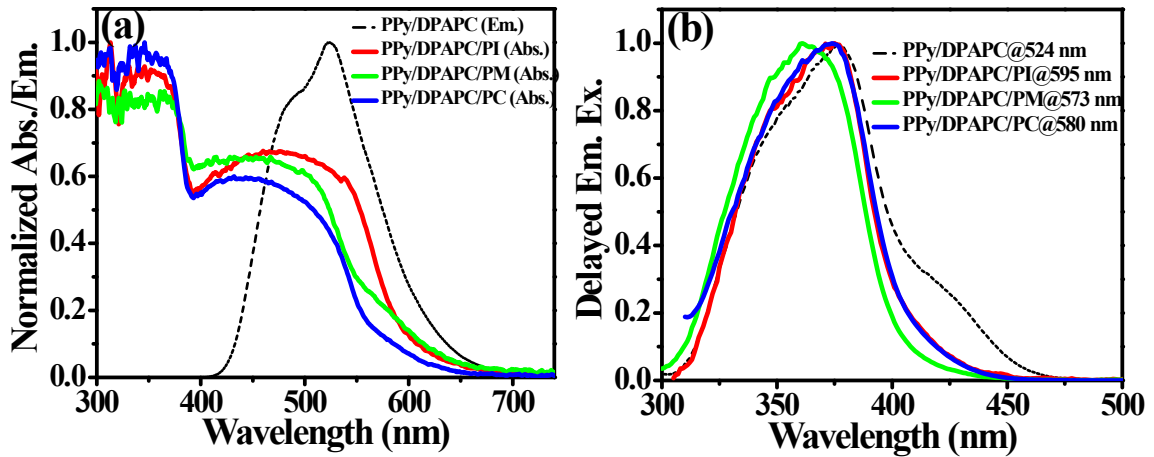


Fig. S9 (a) Delayed spectrum of PPy/DPAPC (1000:1) and absorption spectra of PPy/DPAPC/PI (1000:1:10), PPy/DPAPC/PM (1000:1:10), and PPy/DPAPC/PC (1000:1:10) ($\lambda_{\text{ex}} = 370$ nm, delay time: 0.5 ms). (b) Excitation spectra of delayed emissions of PPy/DPAPC (1000:1), PPy/DPAPC/PI (1000:1:10), and PPy/DPAPC/PM (1000:1:10), PPy/DPAPC/PC (1000:1:10).

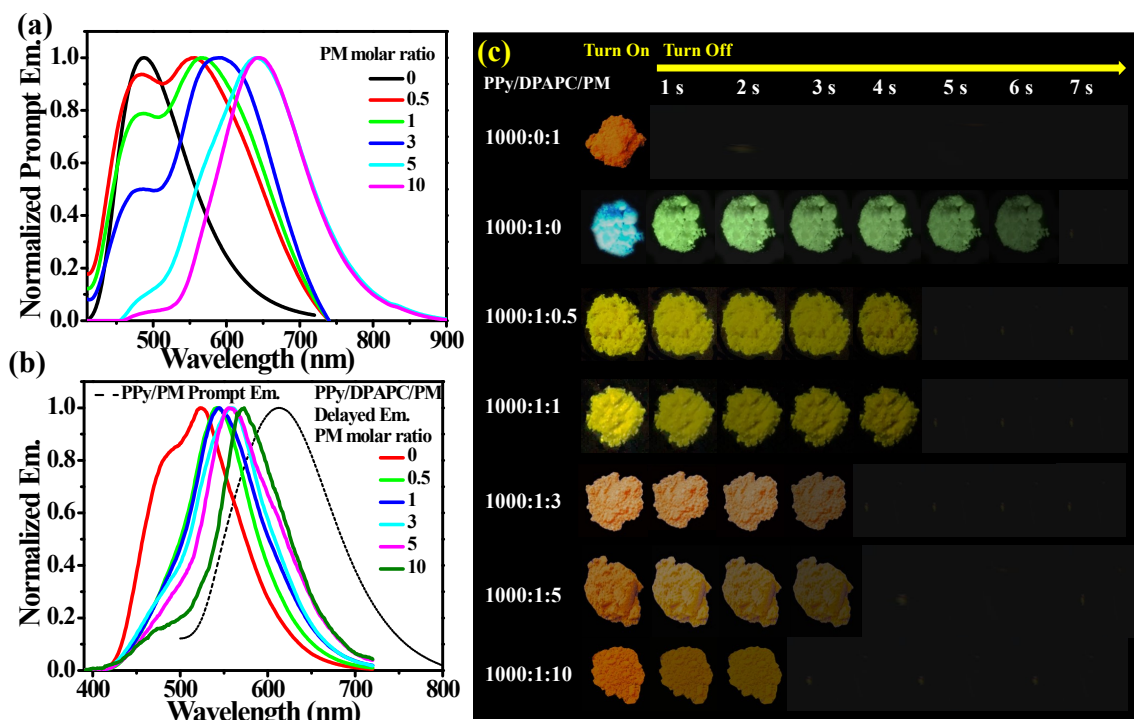


Fig. S10 Prompt (a) and delayed (b) spectra of **PPy/DPAPC/PM** materials with different molar ratios ($\lambda_{\text{ex}} = 390$ nm for prompt emission and $\lambda_{\text{ex}} = 370$ nm for delayed emission, delay time: 0.5 ms). (c) Luminescence images of **PPy/DPAPC/PM** materials with different molar ratios before and after turning off the 365 nm excitation.

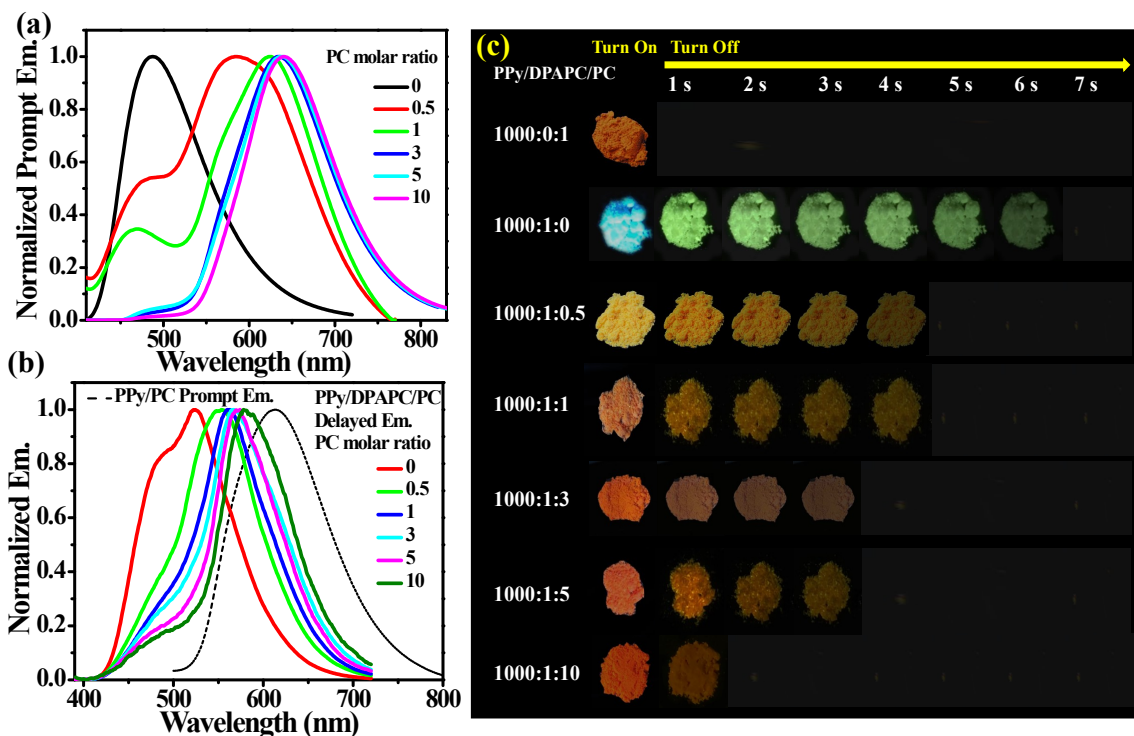


Fig. S11 Prompt (a) and delayed (b) spectra of **PPy/DPAPC/PC** materials with different molar ratios ($\lambda_{\text{ex}} = 390$ nm for prompt emission and $\lambda_{\text{ex}} = 370$ nm for delayed emission, delay time: 0.5 ms). (c) Luminescence images of **PPy/DPAPC/PC** materials with different molar ratios before and after turning off the 365 nm excitation.

3. NMR spectra

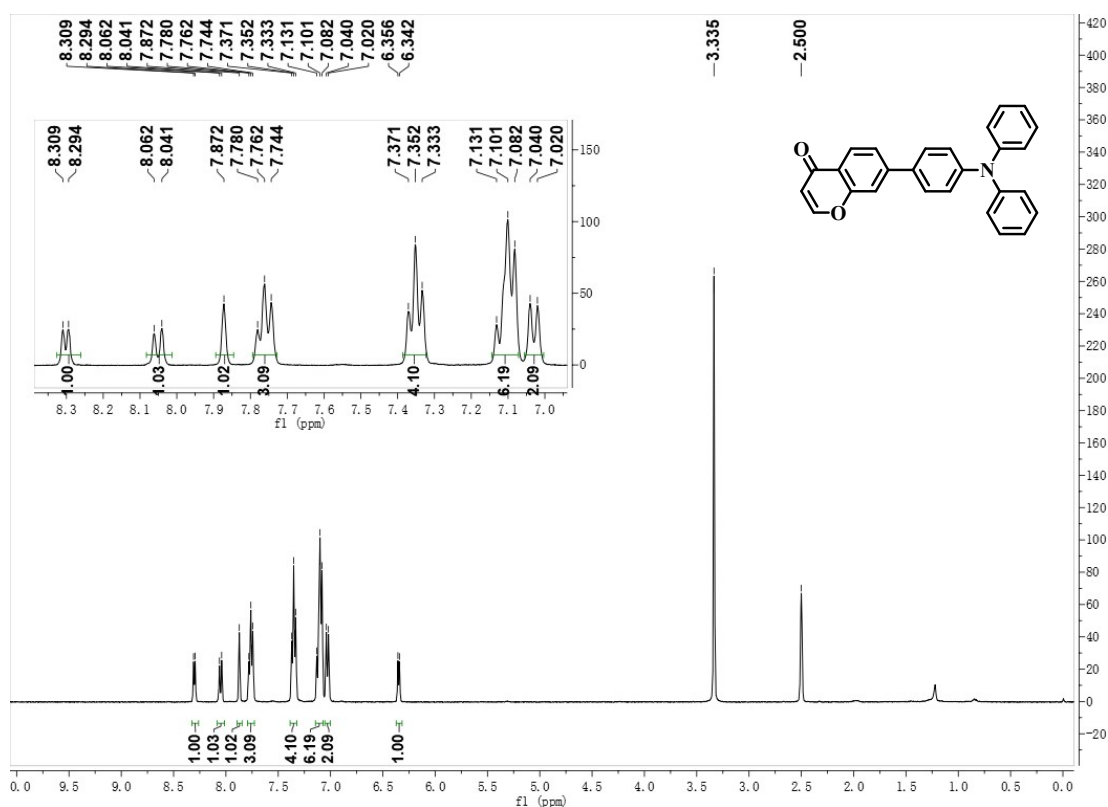


Fig. S12 ¹H NMR of DPAPC (DMSO-*d*₆, 500 MHz).

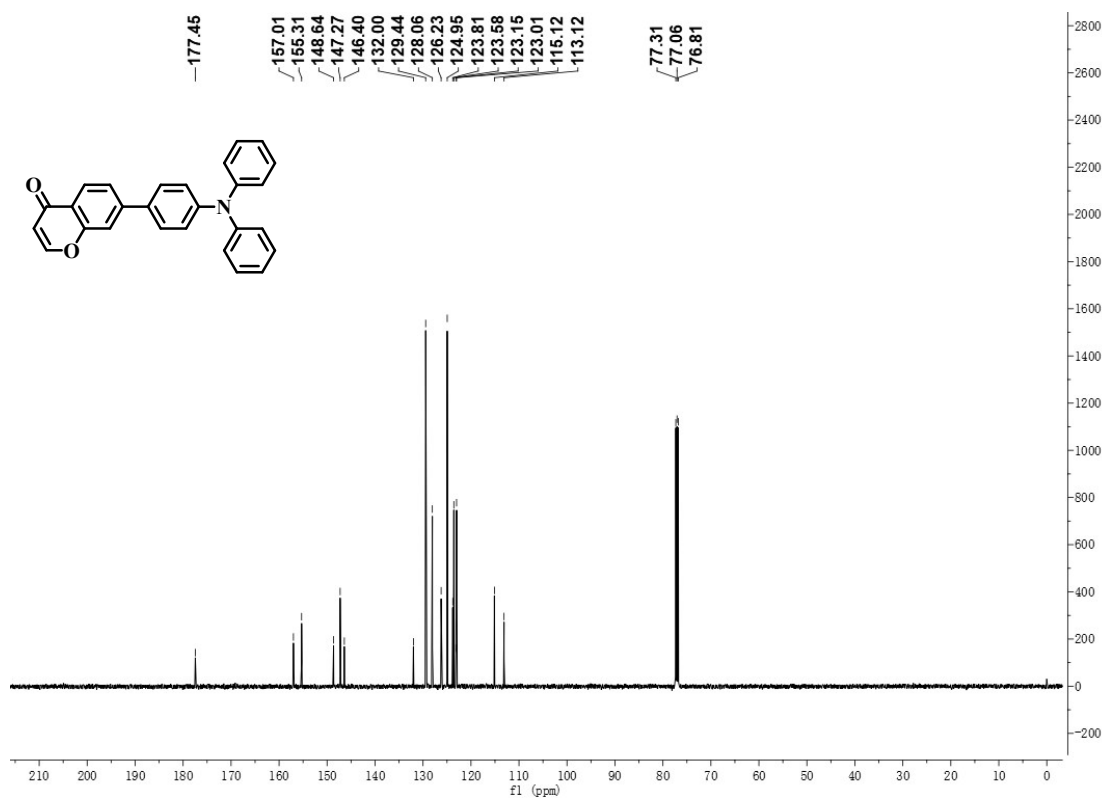


Fig. S13 ¹³C NMR of DPAPC (CDCl₃, 125 MHz).

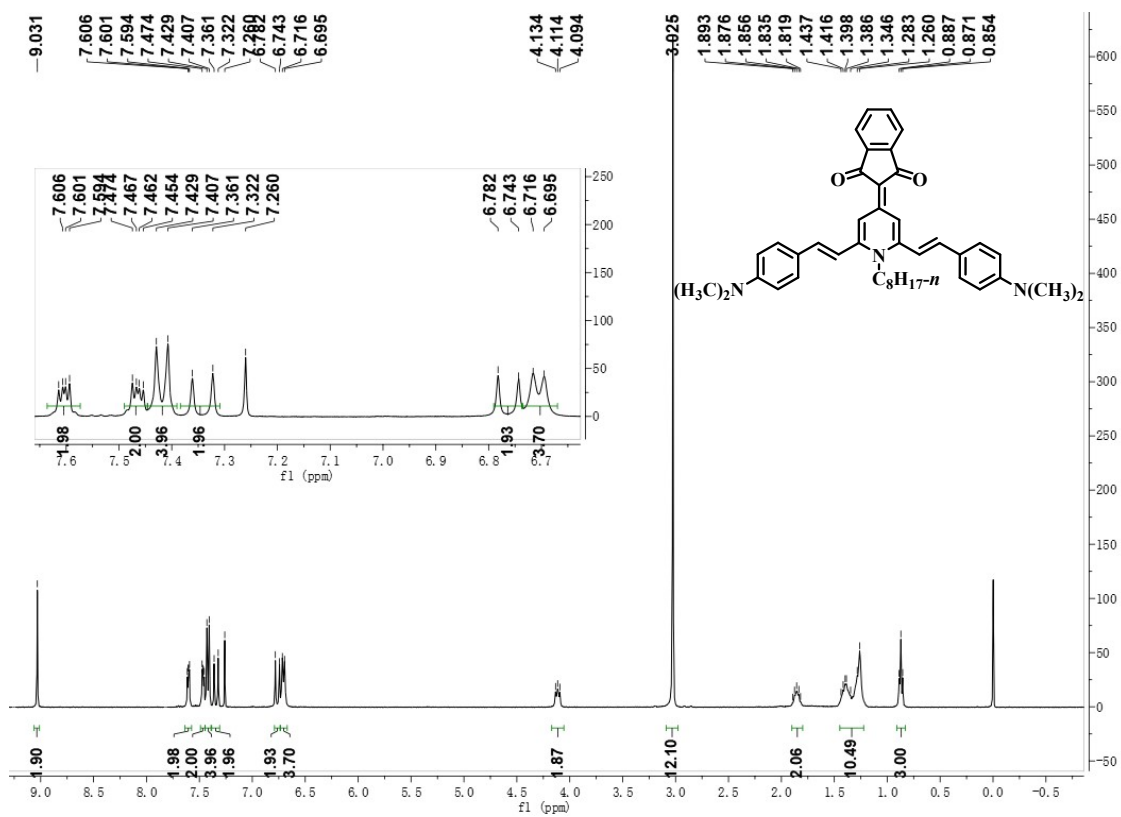


Fig. S14 ¹H NMR of PI (CDCl₃, 400 MHz).

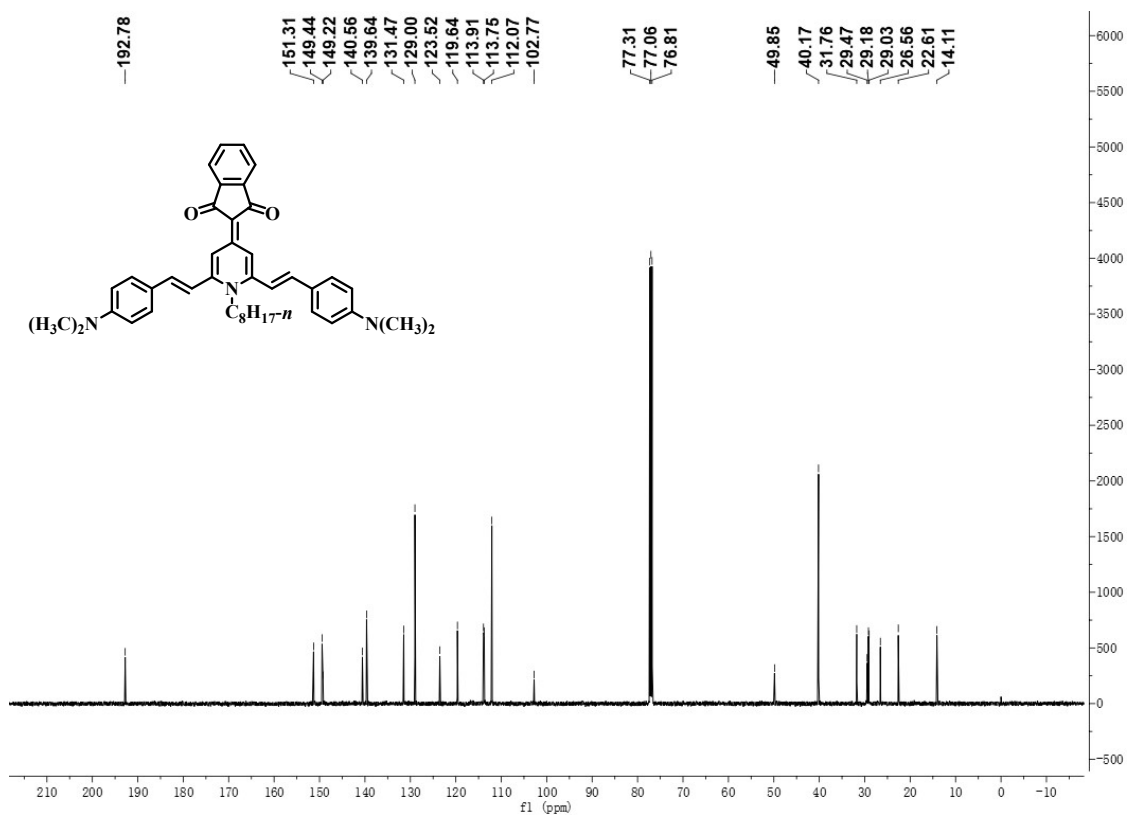


Fig. S15 ¹³C NMR of PI (CDCl₃, 125 MHz).

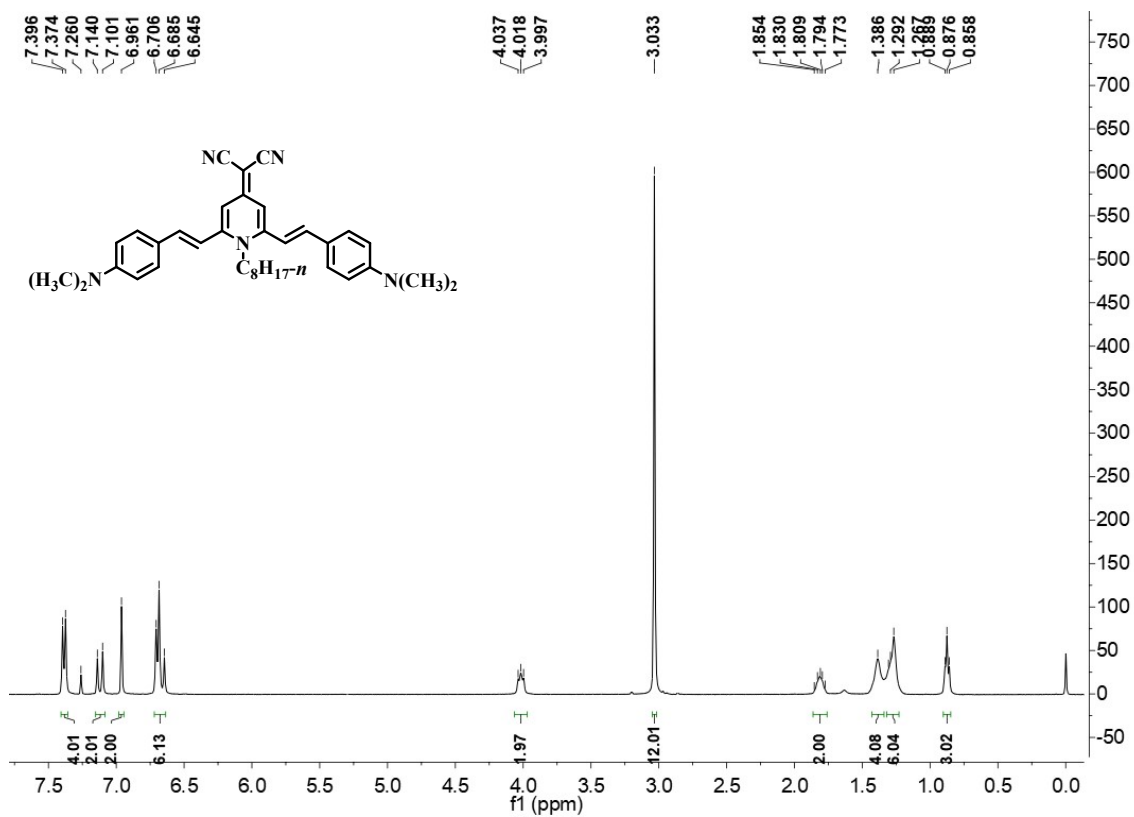


Fig. S16 ^1H NMR of PM (CDCl_3 , 400 MHz).

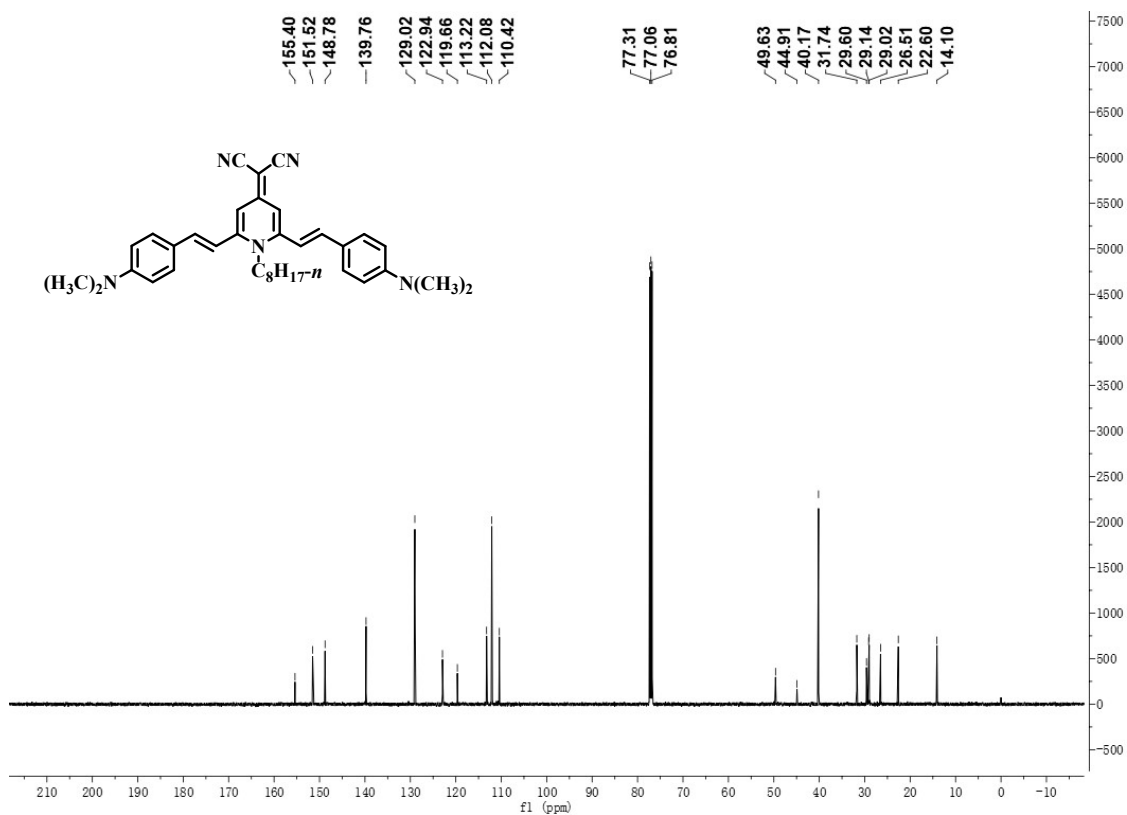
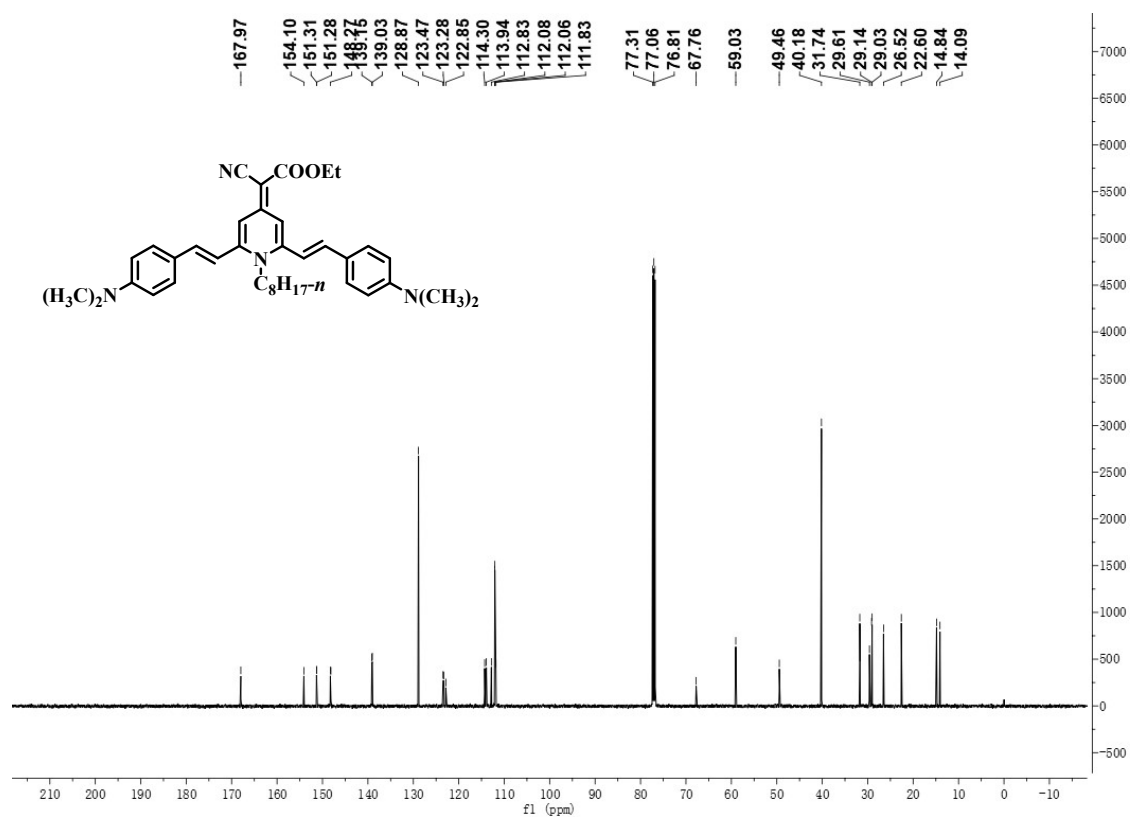
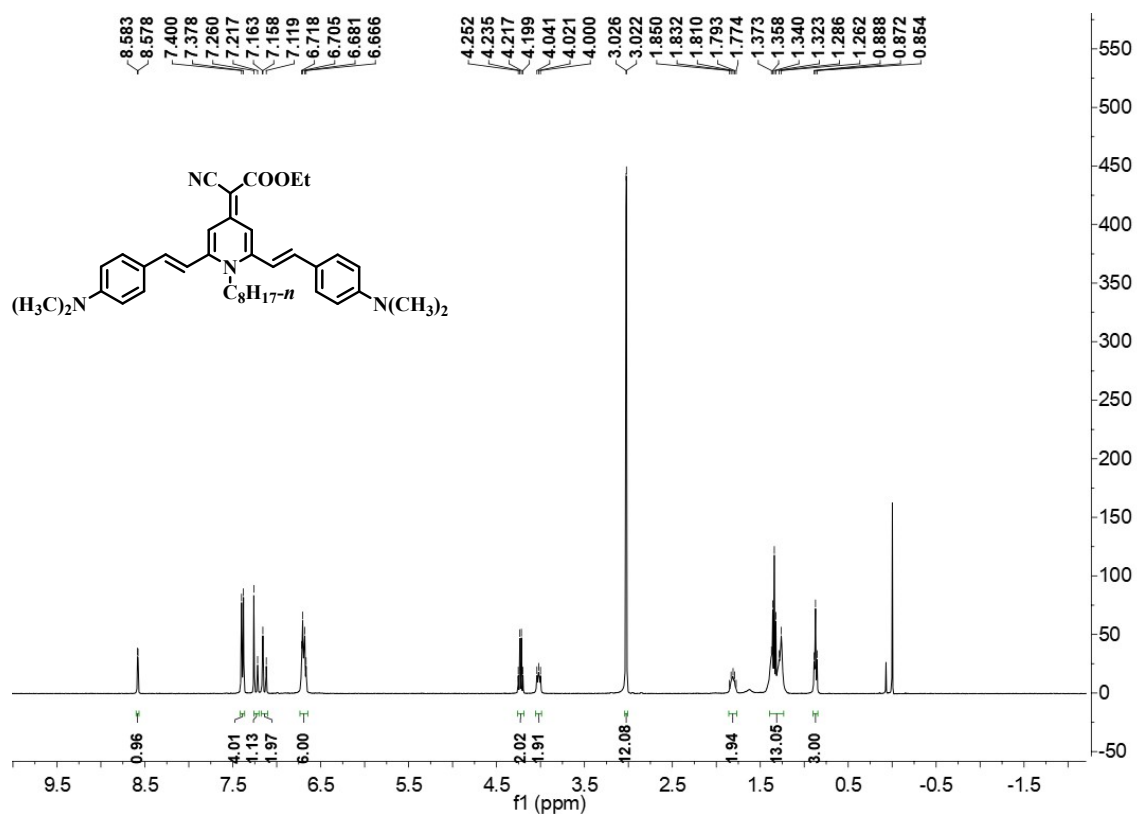


Fig. S17 ^{13}C NMR of PM (CDCl_3 , 125 MHz).



4. HRMS spectra

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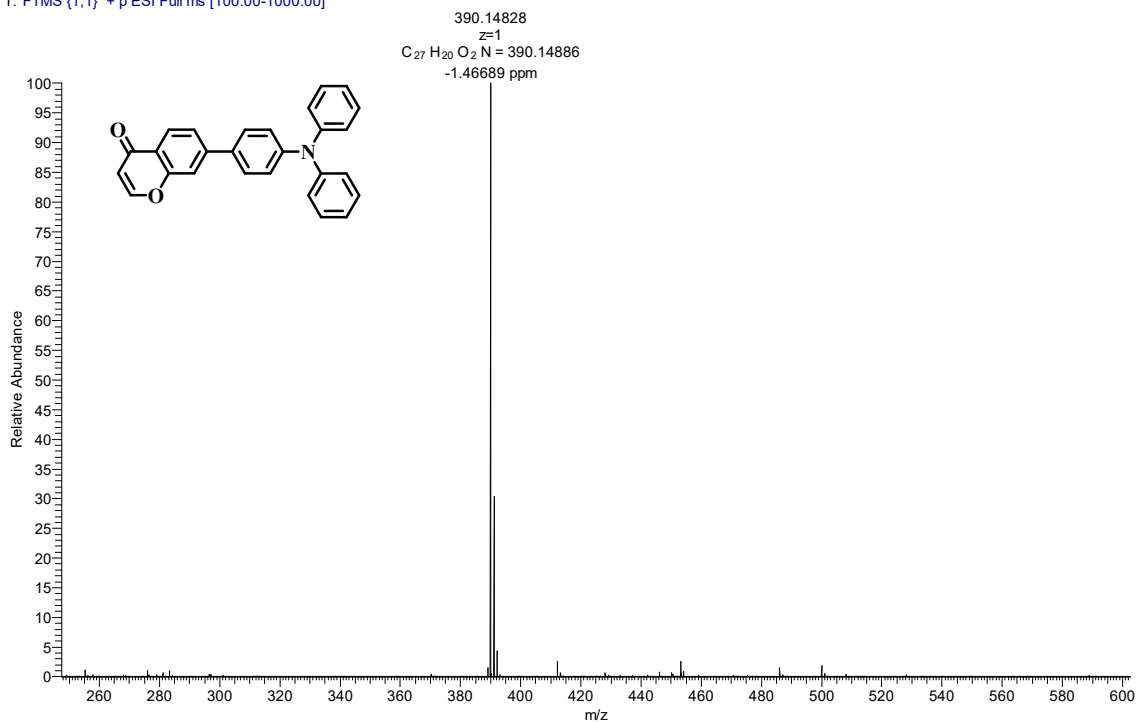


Fig. S20 HRMS spectrum of DPAPC.

H1 #7 RT: 0.09 AV: 1 NL: 1.38E7
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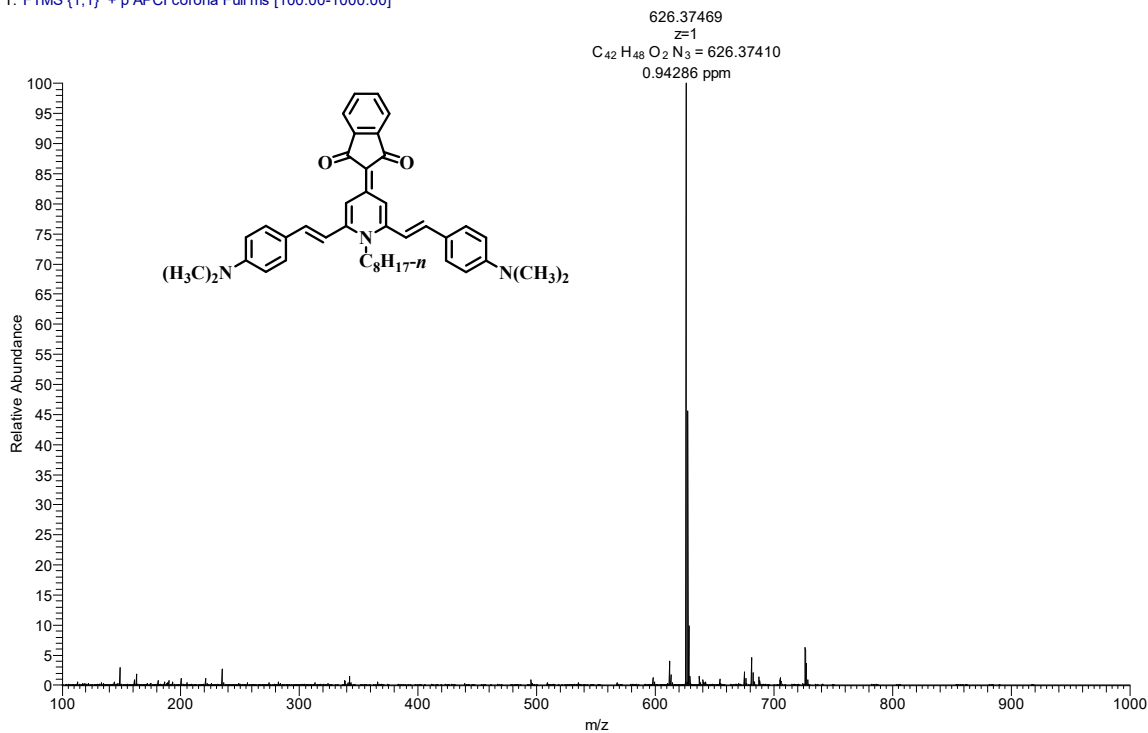


Fig. S21 HRMS spectrum of PI.

H2 #23 RT: 0.27 AV: 1 NL: 3.69E7
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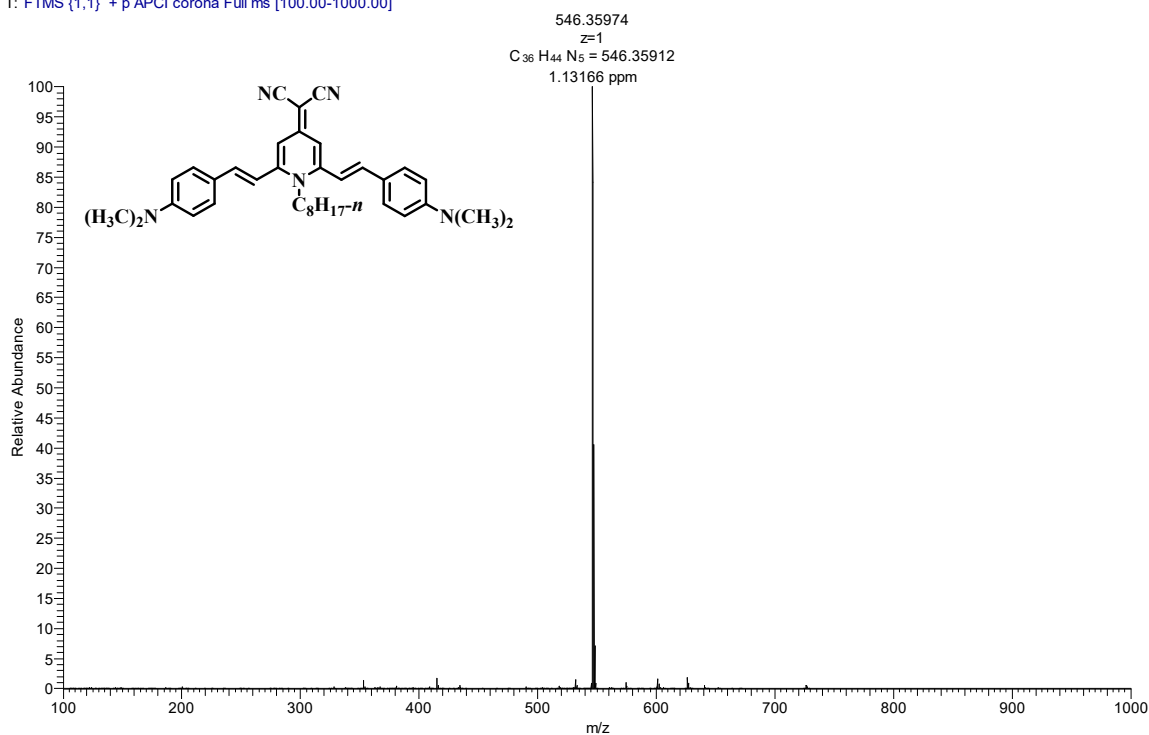


Fig. S22 HRMS spectrum of PM.

H3 #7 RT: 0.09 AV: 1 SB: 37 0.01-0.02, 0.52-1.03 NL: 6.28E7
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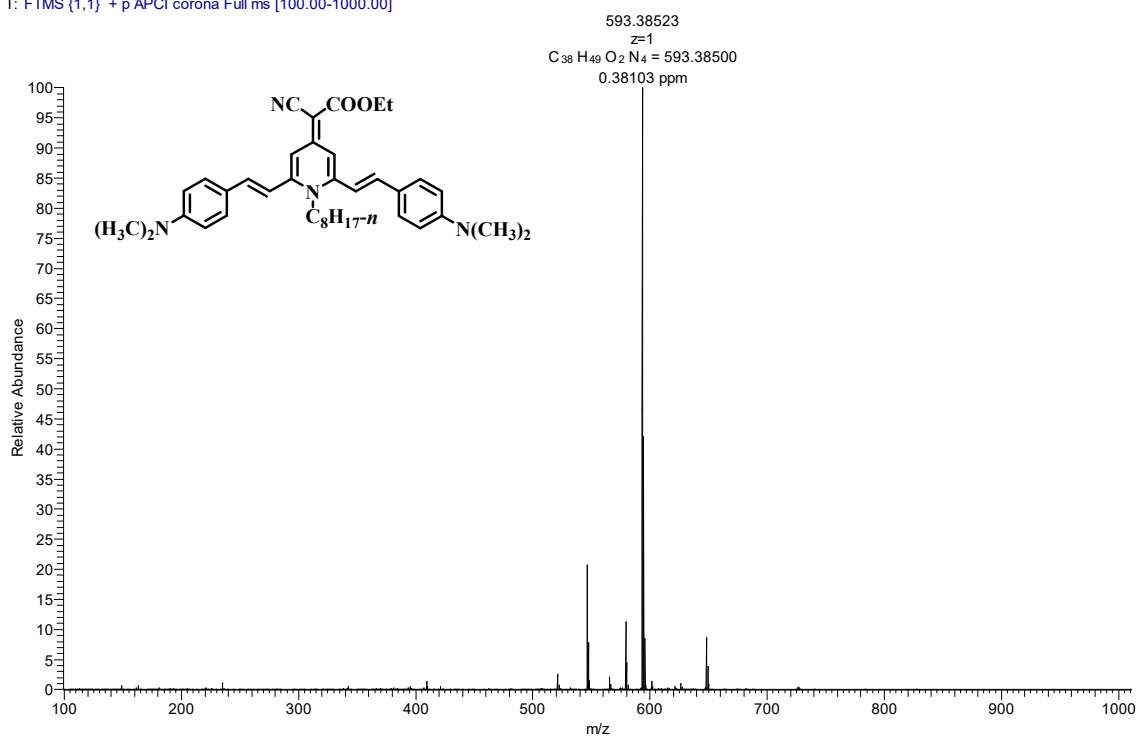


Fig. S23 HRMS spectrum of PC.