

Supplementary Information

Construction of full-color room-temperature afterglow materials using dicyanomethylene-4*H*-pyrans based on alkene conjugated bridge as the third component

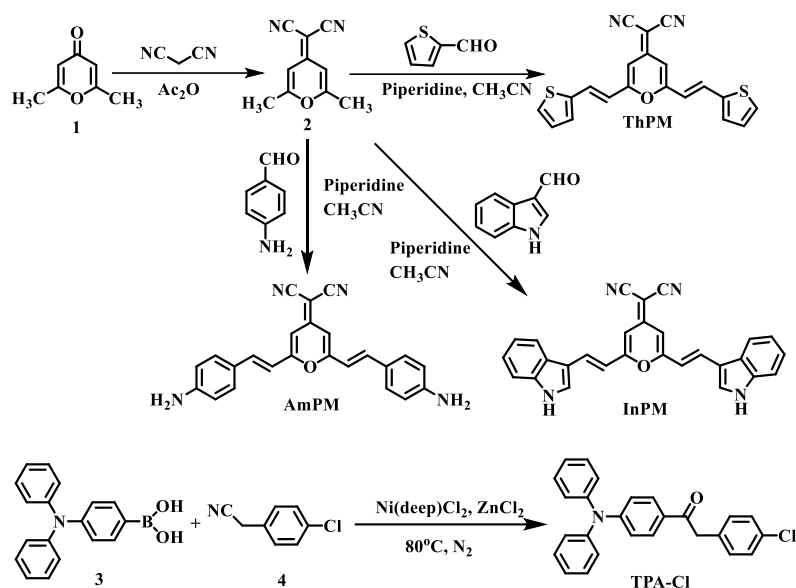
Jiayin Qian,^a Wenbo Dai,*^a Xiaoyu Qiu,^a Shuai Xia,^a Yunxiang Lei,^a Miaochang Liu,^a Yan Guan,*^b Xiaobo Huang*^a and Huayue Wu^a

^a College of Chemistry and Materials Engineering, Wenzhou University, Wenzhou 325035, P. R. China

^b College of Chemistry and Molecular Engineering, Peking University, Beijing 100871, P. R. China

E-mail: wbdai@wzu.edu.cn (W. Dai), yanguan@pku.edu.cn (Y. Guan), xiaobhuang@wzu.edu.cn (X. Huang)

Contents:



Scheme S1 Synthetic routes to TPA-Cl and dicyanomethylene-4H-pyran derivatives using an alkene bond as the conjugated bridge (ThPM, InPM, and AmPM).

1 Experimental

1.1 Measurements and materials

¹H NMR and ¹³C NMR spectra were conducted on a Bruker DRX 400/500 NMR spectrometer. Fluorescence spectra were conducted on a Cary Eclipse fluorescence spectrophotometer. Delayed emission spectra were conducted on a FLS920 lifetime and steady state spectrometer. Solid-state emission quantum yields were conducted on a FluoroMax-4 (Horiba Jobin Yvon) fluorimeter equipped with integrated sphere. UV-vis absorption spectra were collected on a UV-3600 Shimadzu spectrophotometer. 2,6-Dimethyl-4H-pyran-4-one (1), (4-(diphenylamino)phenyl)boronic acid (3), and 2-(4-chlorophenyl)acetonitrile (4) were purchased from commercial suppliers. 2-(2,6-Dimethyl-4H-pyran-4-ylidene)malononitrile (2),^[1] ThPM,^[2] InPM,^[3] AmPM,^[3] and TPA-Cl^[4] were synthesized according to the previous reports. The molecular weight of the polyvinylpyrrolidone (PVP) used in our experiments is 58000 g/mol (*M_w*).

1.2 Synthesis of dicyanomethylene-4H-pyran derivatives

A mixture of compound 2 (1.0 mmol), various aldehydes (6.0 mmol), piperidine (1.0 mL), and acetonitrile (10 mL) was refluxed under N₂ atmosphere for 24 h. The reaction mixture was poured into in methanol (50 mL) to precipitate out the crude product after being cooled to the room temperature. The crude product was washed with acetone and methanol three times, respectively, and then dried to afford the corresponding pure products.

2-(2,6-Bis((*E*)-2-(thiophen-2-yl)vinyl)-4H-pyran-4-ylidene)malononitrile (ThPM). Orange solid (266.4 mg, 74% yield). ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.00 (d, *J* = 16.0 Hz, 2H), 7.76 (d, *J* = 4 Hz, 2H), 7.58 (s, 2H), 7.22-7.19 (m, 2H), 7.11 (d, *J* = 16.0 Hz, 2H), 6.95 (s, 2H) ppm. ¹³C NMR (125 MHz,

Acetone- d_6): δ 158.6, 155.8, 140.6, 130.9, 130.8, 129.1, 128.5, 117.8, 114.9, 106.7 ppm. HRMS (ESI) m/z : $[M+H]^+$ calculated for $C_{20}H_{13}ON_2S_2$, 361.04638; found, 361.04625.

2-(2,6-Bis(*E*)-2-(1*H*-indol-3-yl)vinyl)-4*H*-pyran-4-ylidene)malononitrile (InPM). Red solid (285.4 mg, 67% yield). 1H NMR (400 MHz, DMSO- d_6): δ 11.88 (s, 2H), 8.25 (d, $J = 7.6$ Hz, 2H), 8.04 (s, 2H), 8.00 (d, $J = 16.0$ Hz, 2H), 7.50 (d, $J = 7.6$ Hz, 2H), 7.28-7.19 (m, 6H), 6.93 (s, 2H) ppm. ^{13}C NMR (125 MHz, DMSO- d_6): δ 160.9, 156.8, 138.1, 133.1, 133.0, 125.1, 123.2, 121.4, 121.3, 117.2, 113.8, 113.3, 112.9, 104.9, 53.2 ppm. HRMS (ESI) m/z : $[M+H]^+$ calculated for $C_{28}H_{19}ON_4$, 427.15534; found, 427.15555.

2-(2,6-Bis(*E*)-4-aminostyryl)-4*H*-pyran-4-ylidene)malononitrile (AmPM). Red solid (272.2 mg, 72% yield). 1H NMR (400 MHz, DMSO- d_6): δ 7.59 (d, $J = 15.6$ Hz, 2H), 7.51 (d, $J = 8.0$ Hz, 4H), 6.97 (d, $J = 15.6$ Hz, 2H), 6.64 (s, 2H), 6.60 (d, $J = 8.0$ Hz, 4H), 5.89 (s, 4H) ppm. ^{13}C NMR (125 MHz, DMSO- d_6): δ 160.5, 156.4, 152.0, 139.3, 130.8, 122.9, 116.8, 114.1, 112.9, 105.1, 53.6 ppm. HRMS (ESI) m/z : $[M+H]^+$ calculated for $C_{24}H_{19}ON_4$, 379.15534; found, 379.15491.

1.3 Synthesis of 2-(4-chlorophenyl)-1-(4-(diphenylamino)phenyl)ethan-1-one (TPA-Cl)

A mixture of compound **3** (10 mmol), compound **4** (5 mmol), Ni(dppe)Cl₂ (5.0 mol%), ZnCl₂ (7.5 mmol), H₂O (5.0 mL), and 1,4-dioxane (10.0 mL) was stirred at 80 °C for 8 h under nitrogen atmosphere. After the reaction solution was cooled to room temperature, Ni(dppe)Cl₂ was filtered. After the removal of solvent under reduced pressure, the crude products were purified by column chromatography (petroleum ether/ethyl acetate) to afford the pure compound. White solid (1.39 g, 70% yield). 1H NMR (400 MHz, DMSO- d_6): δ 7.91 (d, $J = 8.8$ Hz, 2H), 7.42-7.35 (m, 6H), 7.27 (d, $J = 8.4$ Hz, 2H), 7.22-7.14 (m, 6H), 6.86 (d, $J = 8.8$ Hz, 2H), 4.28 (s, 2H) ppm. ^{13}C NMR (125 MHz, CDCl₃): δ 195.3, 152.4, 146.3, 133.7, 132.7, 130.8, 130.2, 129.7, 128.8, 128.6, 126.2, 124.9, 119.4, 44.4 ppm.

1.4 Preparation of two-component doped materials

Dissolve the specific amount of PVP and TPA-Cl in dichloromethane, respectively. The solutions were treated with ultrasound for 20 min in the ultrasonic instrument. Different concentrations of TPA-Cl solution were dropped into PVP solution, and the two-component mixture was obtained by ultrasonication for 20 min. Then the two-component solution was slowly poured into the mold. Finally, thin and transparent film was obtained after drying the mixture at 100 °C for 4 h. Different mass ratio, such as 10:1, 50:1, 100:1, 200:1, 500:1, 1000:1, 2000:1, and 5000:1 is used for doping materials.

1.5 Preparation of three-component doped materials

Dissolve the specific amount of PVP, TPA-Cl, and guest molecule (ThPM/InPM/AmPM) in dichloromethane, respectively. The solutions were treated with ultrasound for 20 min in the ultrasonic instrument. The TPA-Cl solution was dropped into the PVP solution, and the two-component mixture was obtained by ultrasonication for 20 min. The solution of different guest molecules was dropped into the two-component mixture in proportion, and a fully mixed three-component solution was

obtained after ultrasonication for 20 min. Then the three-component solution was slowly poured into the mold. Finally, thin and transparent film was obtained after drying the mixture at 100 °C for 4 h. Different mass ratio, such as 500:1:0.1, 500:1:0.2, 500:1:0.5, 500:1:0.7, 500:1:1.0, 500:1:1.5, and 500:1:2.0 is used for doping materials.

1.6 Preparation of four-component doped materials

Dissolve the specific amount of **RhB** and **Cy5** in water, respectively. The **RhB/Cy5** solution was dropped into the three-component solution in proportion, and the fully mixed four-component solution was obtained by ultrasonication for 20 min. The four-component mixture was dried at 100 °C for 4 h.

1.7 Computational details

DFT and TD-DFT calculations were performed on Gaussian 09 program (Revision D.01).^[5] The S_0 geometry optimizations were calculated using DFT at the cam-B3LYP/6-311G level. TD-DFT method was used to investigate the characteristics of electron excitation for S_n and T_n . According to the specific optimized geometries, the excited state energies for S_n and T_n were calculated using TD-DFT with cam-B3LYP/6-311G level. The excited state energy for S_1 of Cy5 was calculated by the experiment: $E_{S_1} = 1240/\lambda_{\text{peak}}$ (eV) (Where λ_{peak} was maximum emission peak of fluorescence in tetrahydrofuran solution at 77 K).

References

- [1] L. L. Woods, *J. Am. Chem. Soc.* **1958**, *80*, 1440–1442.
- [2] Q. Li, Z. Y. Liu, L. J. Liu, Z. F. Li, W. D. Cheng, H. Li, P. F. Li, Z. J. Li, C. J. Guan, Y. L. Jia and W. J. Tian, *Chem. J. Chin. Univ.* **2012**, *33*, 182–187.
- [3] X. Zhang, D. Wang, H. Shen, S. Wang, Y. Zhou, Y. Lei, W. Gao, M. Liu, X. Huang and H. Wu, *Org. Chem. Front.* **2021**, *8*, 856–867.
- [4] X. Liu, W. Dai, J. Qian, Y. Lei, M. Liu, Z. Cai, X. Huang, H. Wu and Y. Dong, *J. Mater. Chem. C* **2021**, *9*, 3391–3395.
- [5] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, T. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz,

2 Figures and tables

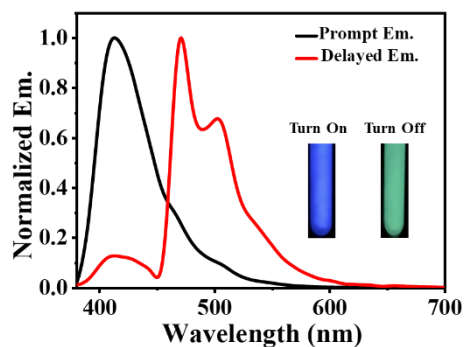


Fig. S1 Prompt and delayed spectra of **TPA-Cl** in tetrahydrofuran solvent (1×10^{-5} mol/L) at 77 K. (λ_{ex} = 360 nm, delay time: 0.5 ms). Inset: photos of the luminescence before and after turning off the 365 nm lamp.

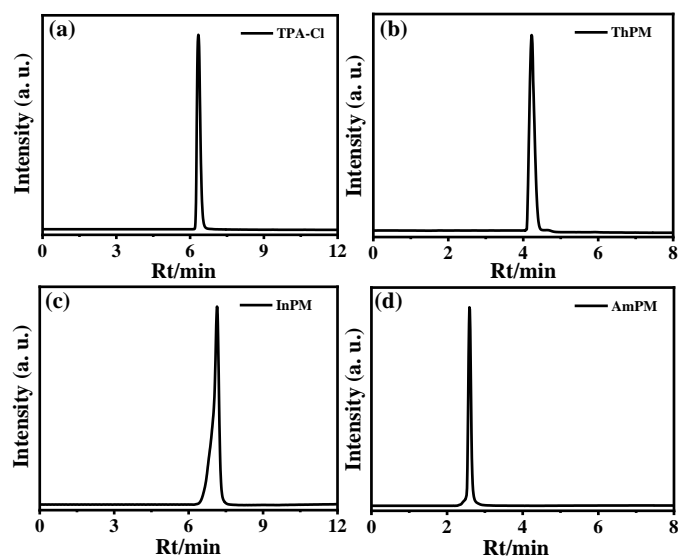


Fig. S2 High performance liquid chromatography of **TPA-Cl** (a), **ThPM** (b), **InPM** (c), and **AmPM** (d). Condition: $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ = 80%:20% for **TPA-Cl**; $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ = 90%:10% for **ThPM**; $\text{CH}_3\text{OH}/\text{H}_2\text{O}$ = 80%:20% for **InPM**; $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ = 70%:30% for **AmPM**.

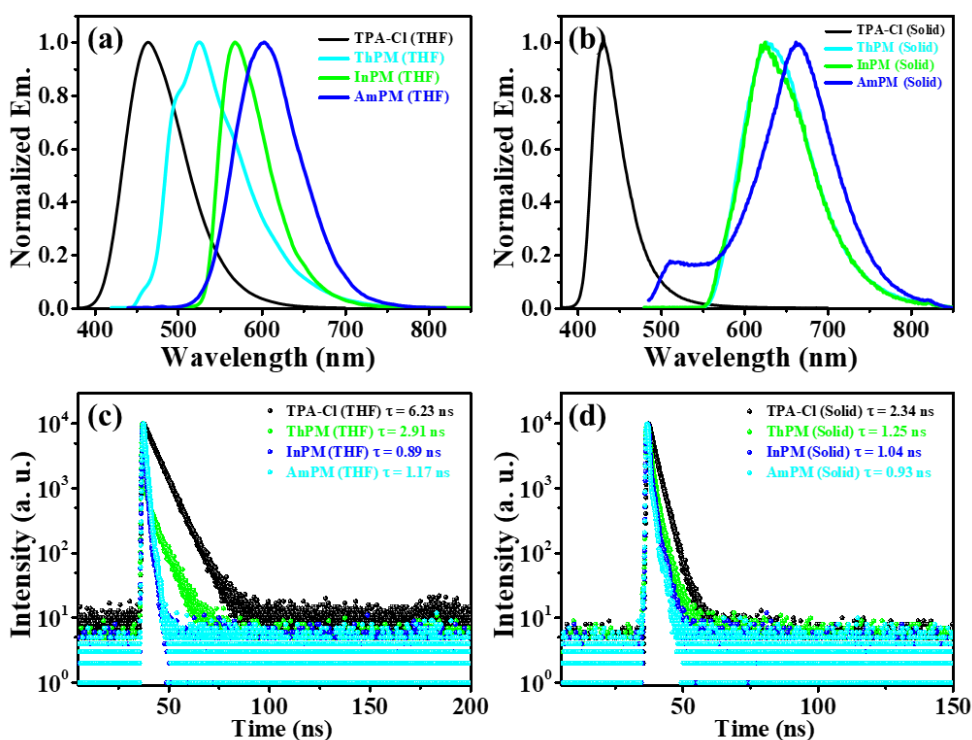


Fig. S3 Normalized prompt PL spectra of the guests in (a) THF solution (1.0×10^{-5} mol/L) and (b) solid states. The decay curves of the fluorescence of the guests in (c) THF solution (1.0×10^{-5} mol/L) and (d) solid states.

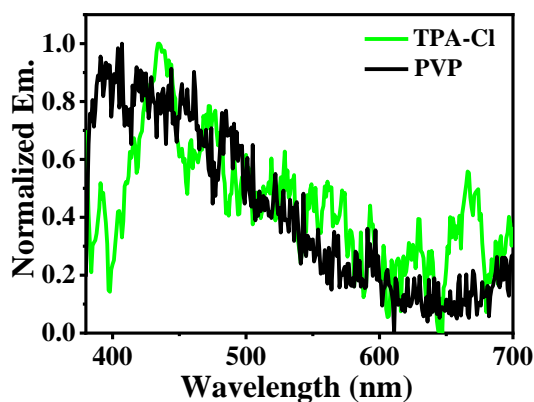


Fig. S4 Delayed spectra of the host molecule PVP and the guest molecule TPA-Cl in solid state at room temperature ($\lambda_{ex} = 360$ nm, delay time: 0.5 ms).

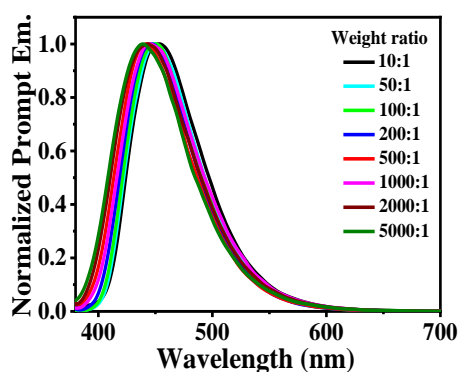


Fig. S5 Prompt spectra of PVP/TPA-CI with different host/guest weight ratios ($\lambda_{\text{ex}} = 360 \text{ nm}$).

Table S1 Photophysical properties of guest molecules in THF and solid state.

Sample	λ_{THF} [nm]	Φ_{THF} [%]	τ_{THF} [ns]	λ_{Solid} [nm]	Φ_{Solid} [%]	τ_{Solid} [ns]
TPA-CI	464	85.58	6.23	432	10.50	2.34
ThPM	525	3.93	2.91	627	2.05	1.25
InPM	568	6.42	0.89	625	2.06	1.04
AmPM	603	23.23	1.17	662	1.70	0.93

Table S2 Photophysical properties of the doped materials

Sample	Prompt Em.		Delayed Em.		
	Weight ratio	λ_{em} (nm)	λ_{em} (nm)	Φ_{DE} (%)	τ (ms)
PVP/TPA-CI	500:1	444	516	20.3	231
PVP/TPA-CI/ThPM	500:1:0.1	468/519	525	10.6	229
	500:1:0.2	468/526	522	9.8	205
	500:1:0.5	543	524	11.8	198
	500:1:0.7	543	530	14.7	190
	500:1:1.0	548	535	8.5	186
	500:1:1.5	549	537	5.1	162
	500:1:2.0	551	533	4.3	129
PVP/TPA-CI/InPM	500:1:0.1	445/571	501/570	8.5	212
	500:1:0.2	442/587	493/584	6.5	174
	500:1:0.5	439/595	591	14.2	125
	500:1:0.7	437/602	593	10.3	92
	500:1:1.0	441/604	602	5.6	48
	500:1:1.5	443/608	601	3.2	37
	500:1:2.0	437/613	600	2.0	35
PVP/TPA-CI/AmPM	500:1:0.1	441/626	521/631	3.6	214
	500:1:0.2	439/634	526/632	2.9	198
	500:1:0.5	436/652	533/648	4.1	154
	500:1:0.7	438/647	531/650	4.6	130
	500:1:1.0	441/651	531/666	2.2	103
	500:1:1.5	437/663	532/672	2.1	75
	500:1:2.0	442/677	531/684	1.1	41
PVP/TPA-CI/ThPM/RhB	500:1:0.7:0.5	531/593	530/586	5.4	178
	500:1:0.7:1.0	527/599	522/596	3.5	127
	500:1:0.7:2.0	605	508/604	2.5	93
	500:1:0.7:4.0	606	506/610	1.2	75
PVP/TPA-CI/InPM/Cy5	500:1:0.5:0.5	580/719	569/733	1.1	50
	500:1:0.5:1.0	579/741	564/740	0.8	27
	500:1:0.5:2.0	578/743	571/744	0.6	25
	500:1:0.5:4.0	580/743	544/745	0.2	23

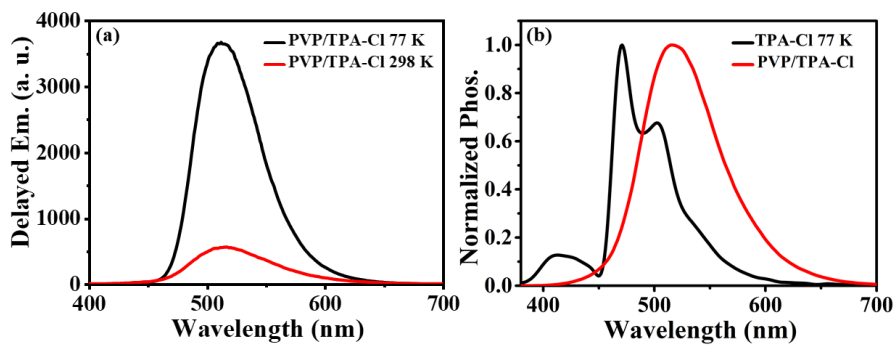


Fig. S6 (a) Delayed emission of **PVP/TPA-CI** at 77 K and 298 K at a weight ratio of 500:1 ($\lambda_{\text{ex}} = 360$ nm, delay time: 0.5 ms). (b) Delayed spectrum of **TPA-CI** at 77 K in tetrahydrofuran solution (1×10^{-5} mol/L) and delayed spectrum of **PVP/TPA-CI** at room temperature ($\lambda_{\text{ex}} = 360$ nm, delay time: 0.5 ms).

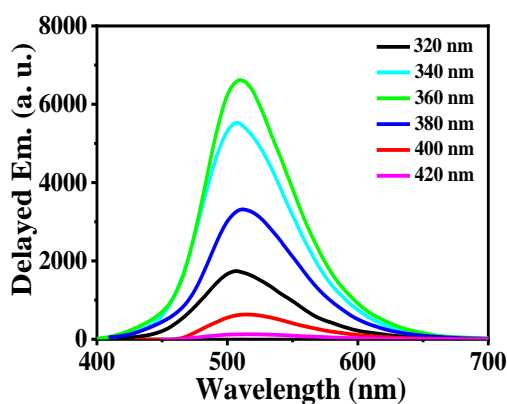


Fig. S7 Delayed spectra of **PVP/TPA-CI** with different excitation wavelengths (delay time: 0.5 ms).

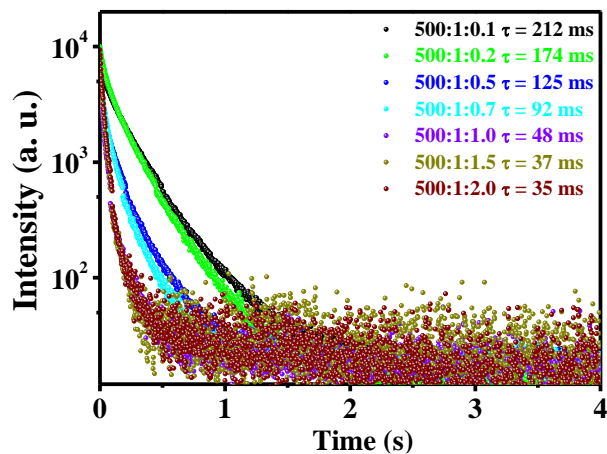


Fig. S8 Delayed emission lifetimes of **PVP/TPA-CI/InPM** with different weight ratios.

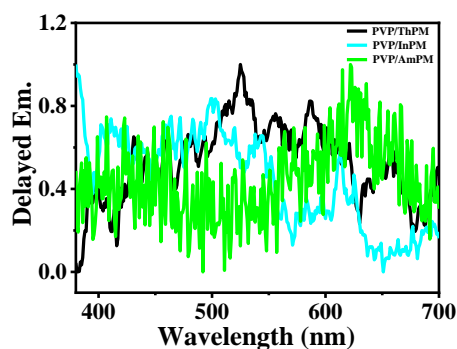


Fig. S9 Delayed spectra of **PVP/ThPM**, **PVP/InPM**, and **PVP/AmPM** at room temperature ($\lambda_{\text{ex}} = 360$ nm, delay time: 0.5 ms).

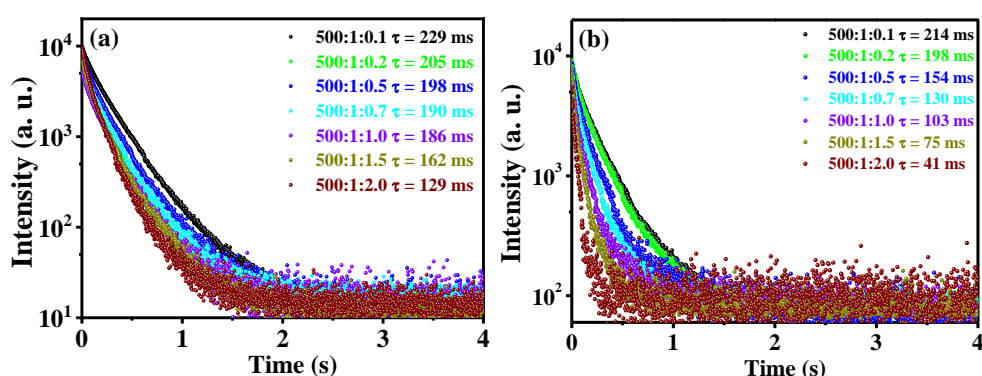


Fig. S10 Delayed emission lifetimes of **PVP/TPA-CI/ThPM** ($\lambda_{\text{em}} = 530$ nm) and **PVP/TPA-CI/AmPM** ($\lambda_{\text{em}} = 650$ nm) with different weight ratios.

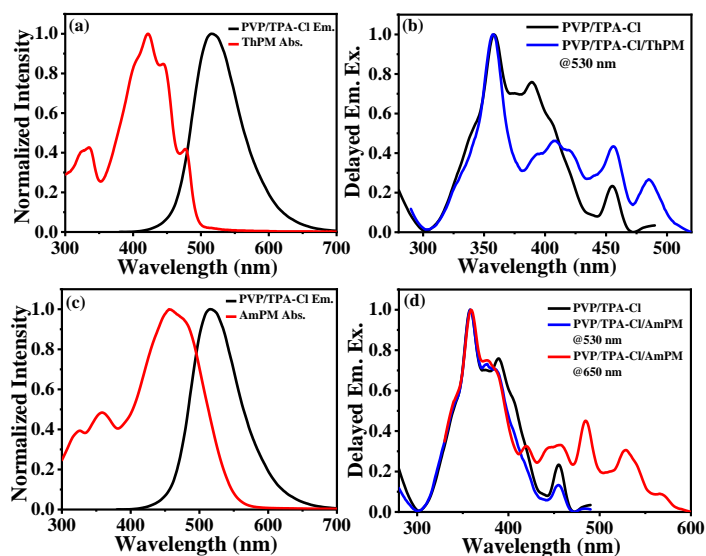


Fig. S11 (a) Delayed spectrum of **PVP/TPA-CI** (500:1) and absorption spectra of **ThPM** ($\lambda_{\text{ex}} = 360$ nm, delay time: 0.5 ms). (b) Excitation spectra of delayed emissions of **PVP/TPA-CI** (500:1) and **PVP/TPA-CI/ThPM** (500:1:0.7). (c) Delayed spectrum of **PVP/TPA-CI** (500:1) and absorption spectra of **AmPM** ($\lambda_{\text{ex}} = 360$ nm, delay time: 0.5 ms). (d) Excitation spectra of delayed emissions of **PVP/TPA-CI** (500:1) and **PVP/TPA-CI/AmPM** (500:1:0.7).

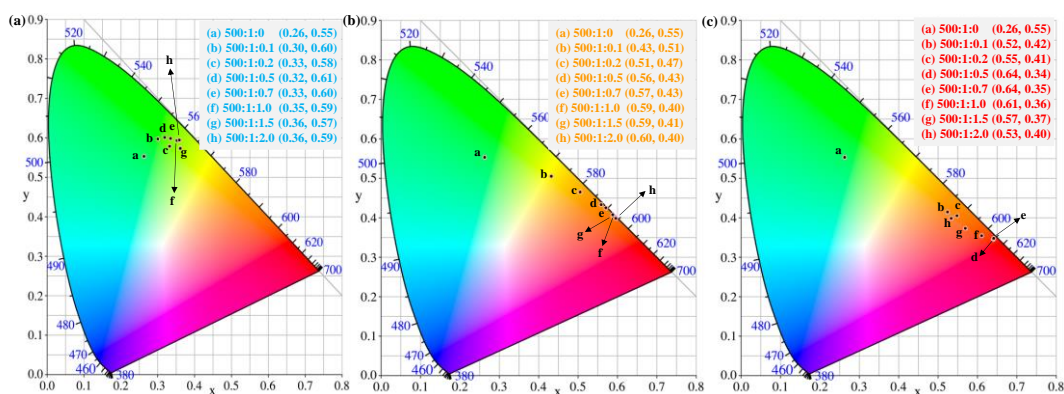


Fig. S12 CIE coordinates of the doped materials **PVP/TPA-CI/ThPM**, **PVP/TPA-CI/InPM**, and **PVP/TPA-CI/AmPM**.

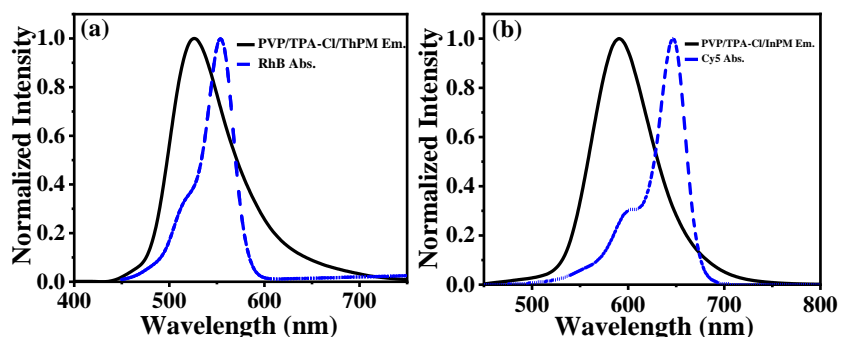


Fig. S13 (a) Delayed spectrum of **PVP/TPA-CI/ThPM** and absorption spectra of **RhB** ($\lambda_{\text{ex}} = 360$ nm, delay time: 0.5 ms). (b) Delayed spectrum of **PVP/TPA-CI/InPM** and absorption spectra of **Cy5** ($\lambda_{\text{ex}} = 360$ nm, delay time: 0.5 ms).

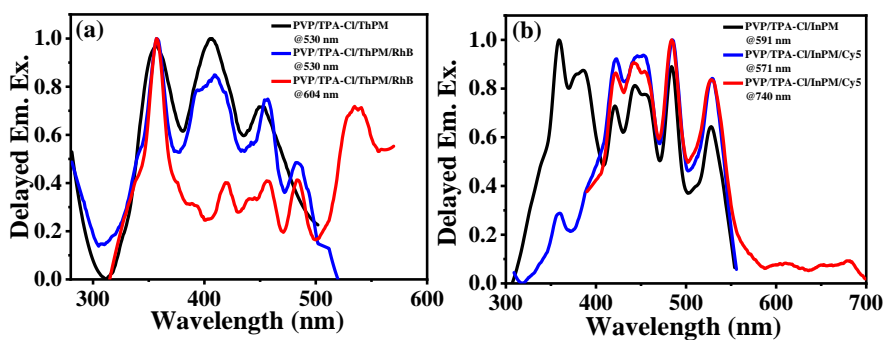


Fig. S14 (a) Excitation spectra of delayed emissions of **PVP/TPA-CI/ThPM** and **PVP/TPA-CI/ThPM/RhB**. (b) Excitation spectra of delayed emissions of **PVP/TPA-CI/InPM** and **PVP/TPA-CI/InPM/Cy5**.

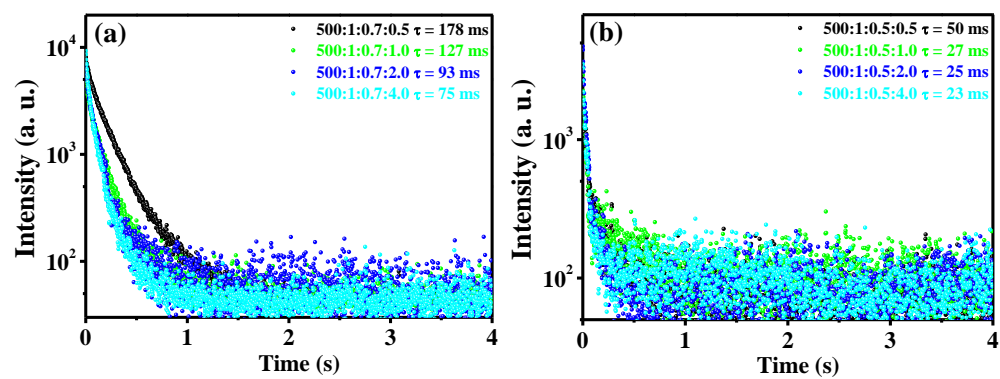


Fig. S15 (a) Delayed emission lifetimes of **PVP/TPA-CI/ThPM/RhB** at $\lambda_{em} = 604$ nm. Delayed emission lifetimes of **PVP/TPA-CI/InPM/Cy5** at $\lambda_{em} = 740$ nm.

3 ^1H NMR and ^{13}C NMR spectra

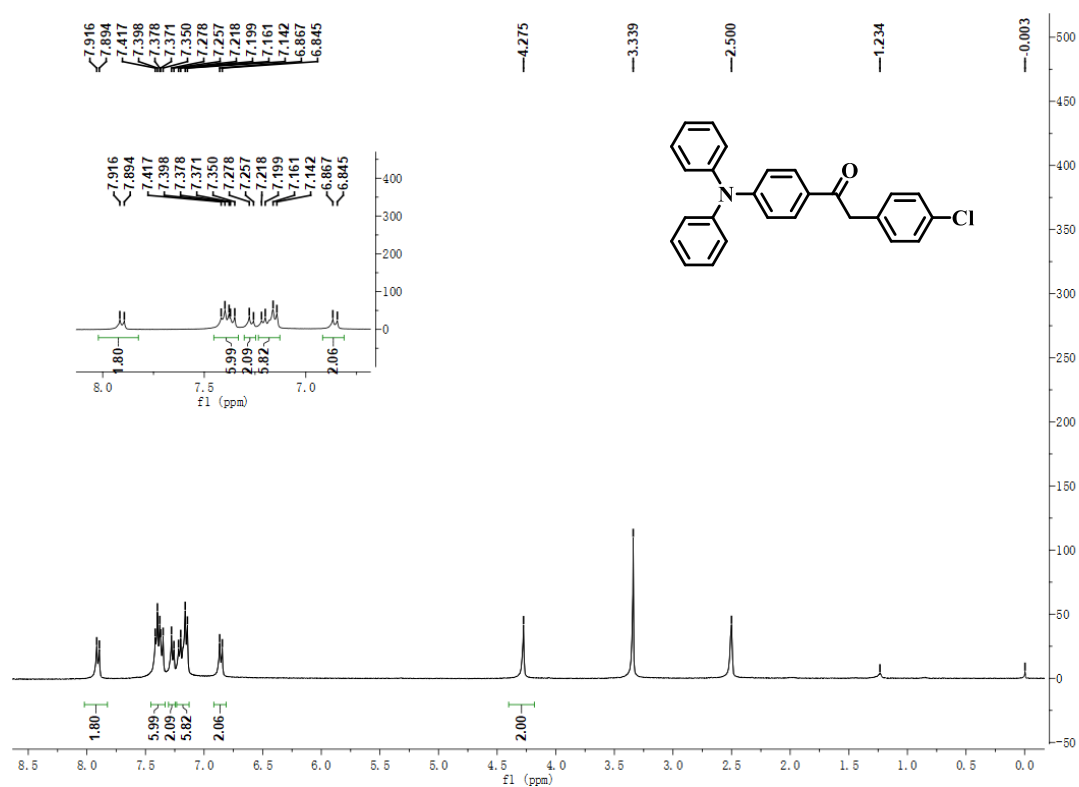


Fig. S16 ^1H NMR of TPA-Cl ($\text{DMSO-}d_6$, 400 MHz).

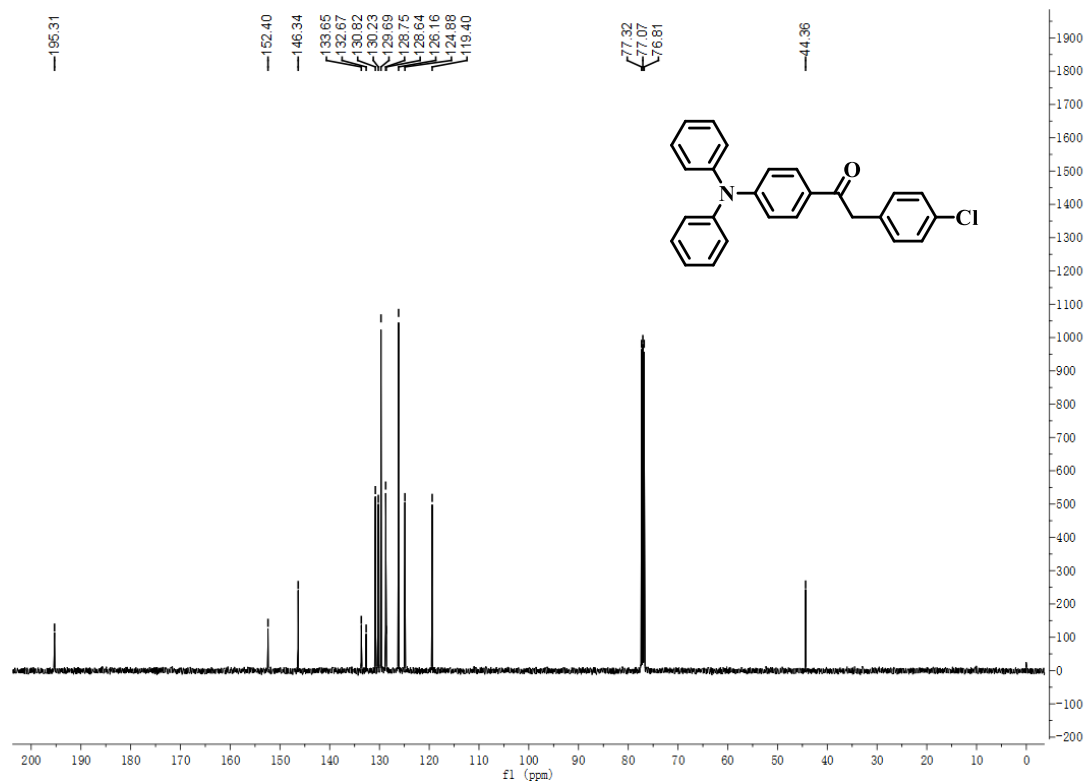


Fig. S17 ^{13}C NMR of TPA-Cl (CDCl_3 , 125 MHz).

TPA-Cl #9 RT: 0.11 AV: 1 NL: 2.20E8
T: FTMS (1,1) + p APCI corona Full ms [100.00-1000.00]

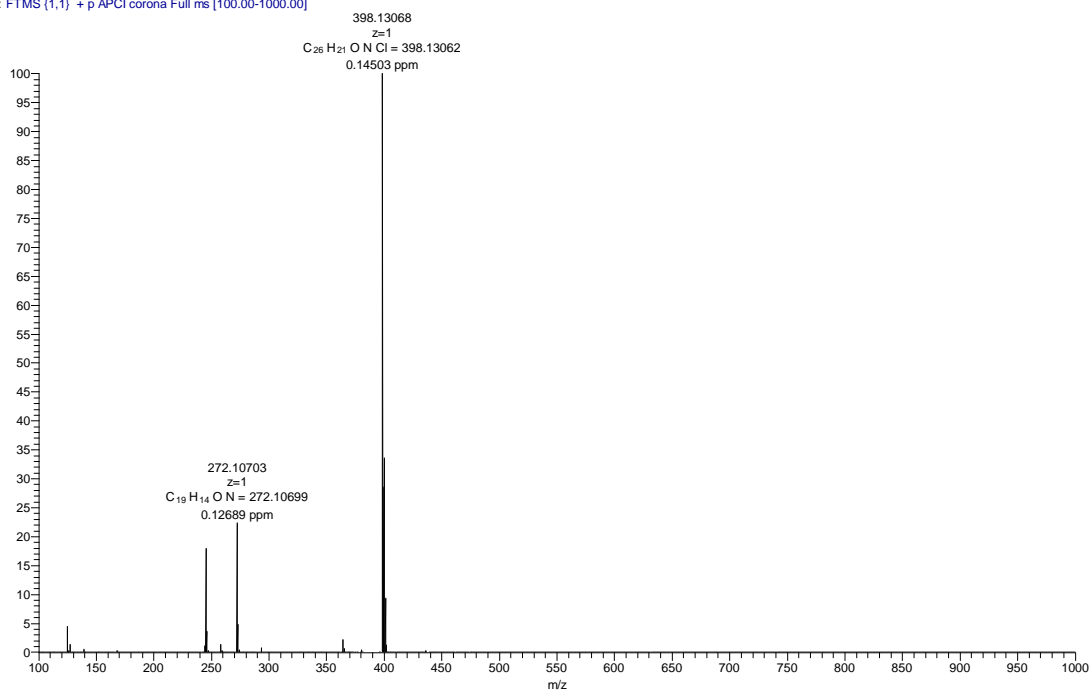


Fig. S18 The high-resolution mass spectrum of TPA-Cl.

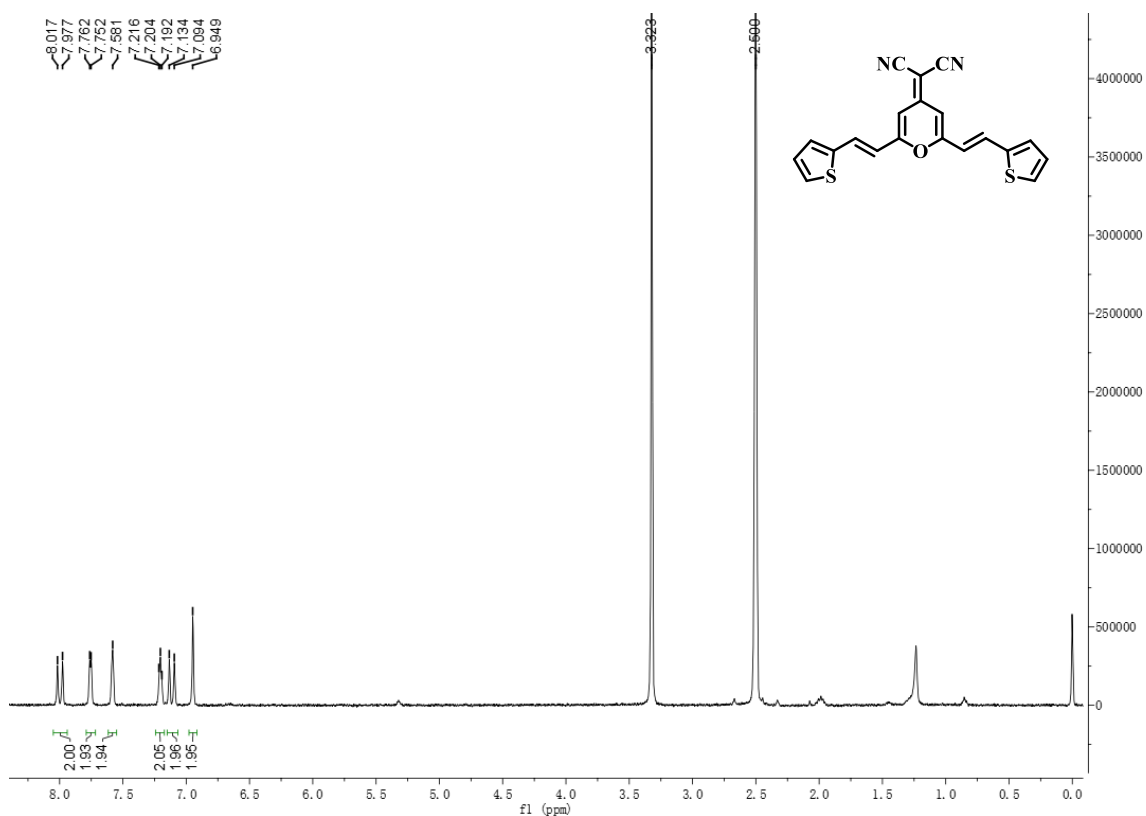


Fig. S19 ¹H NMR of ThPM (DMSO-*d*₆, 400 MHz).

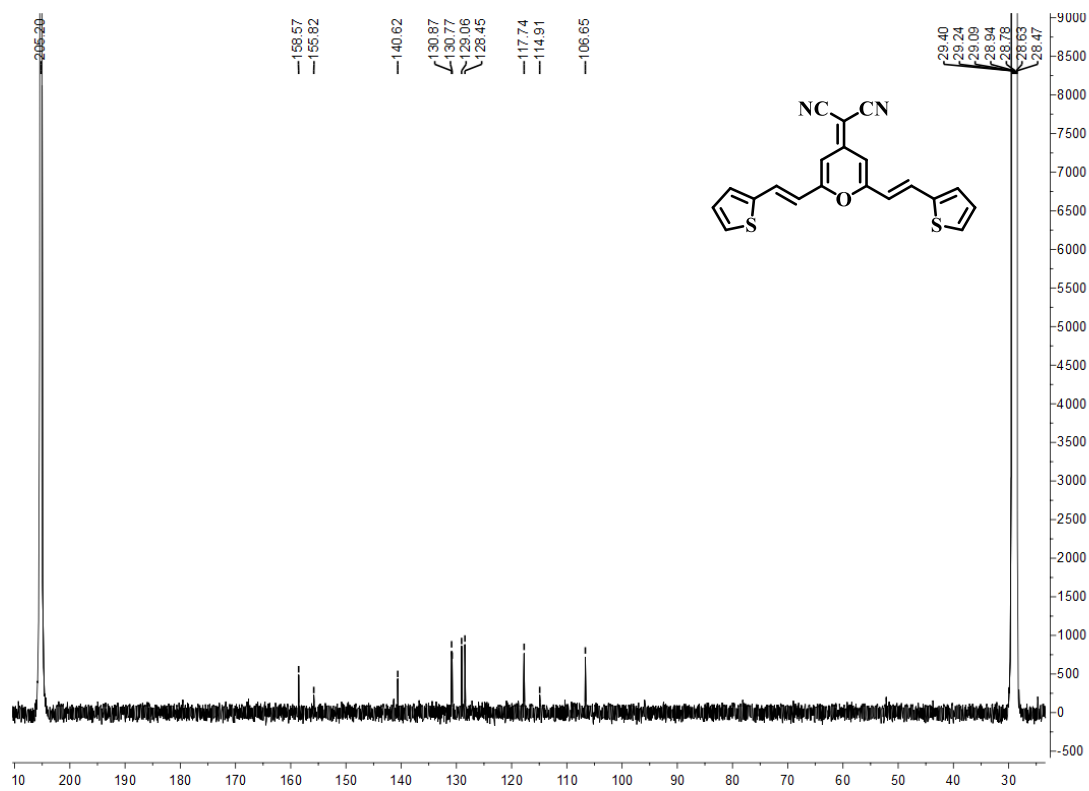


Fig. S20 ^{13}C NMR of ThPM (Acetone- d_6 , 125 MHz).

ThPM #3 RT: 0.04 AV: 1 SB: 46 0.01-0.02, 0.31-1.04 NL: 3.48E6
 T: FTMS (1.1) + p APCI corona Full ms [100.00-1000.00]

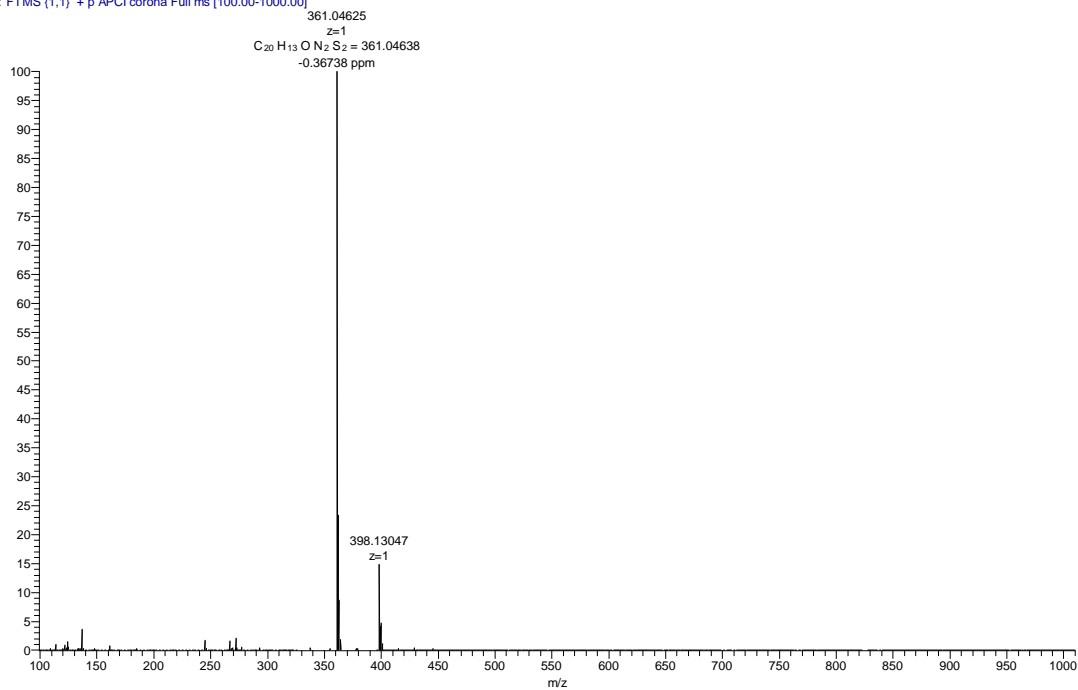


Fig. S21 The high-resolution mass spectrum of ThPM.

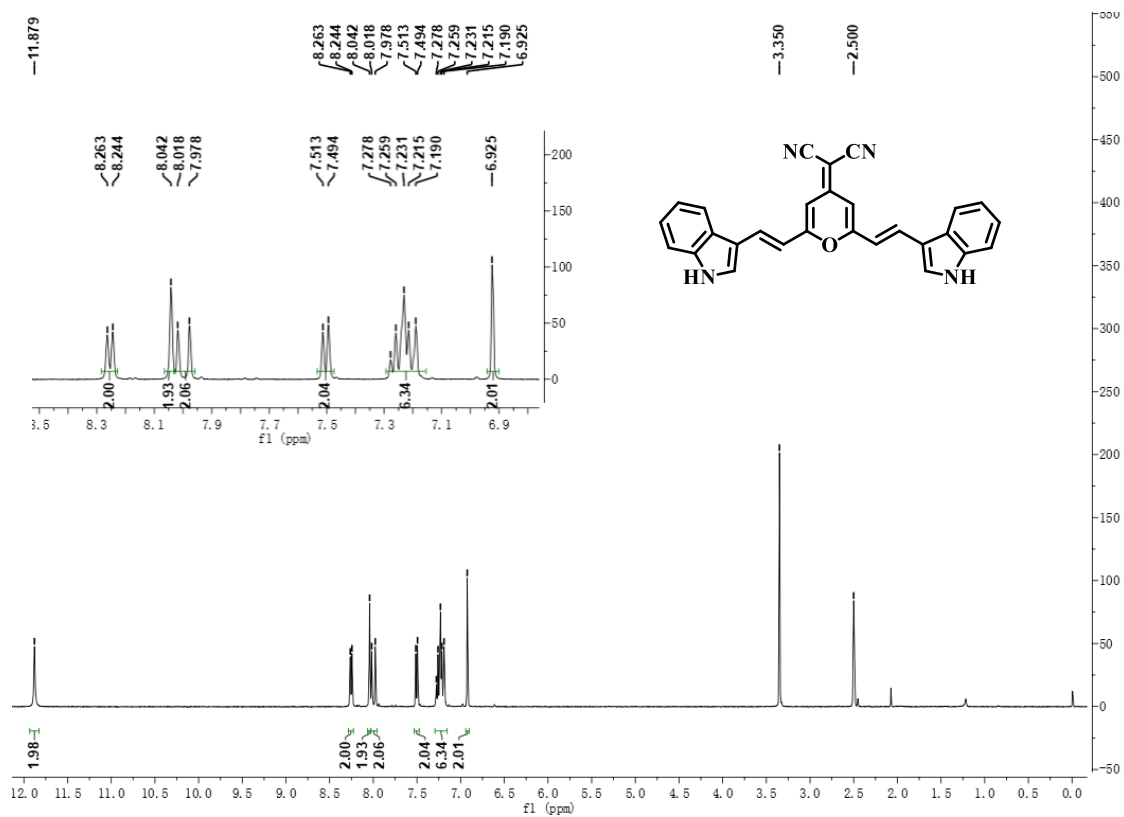


Fig. S22 ¹H NMR of InPM (DMSO-*d*₆, 400 MHz).

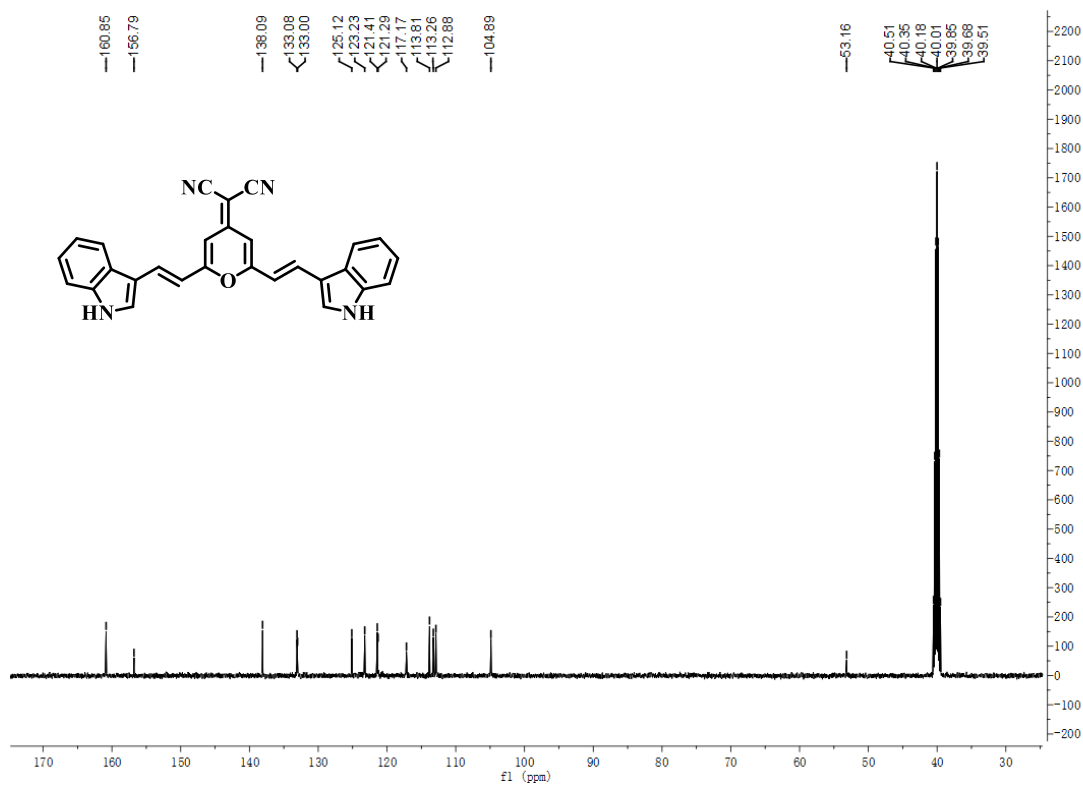


Fig. S23 ¹³C NMR of InPM (DMSO-*d*₆, 125 MHz).

InPM #3 RT: 0.04 AV: 1 NL: 6.51E5
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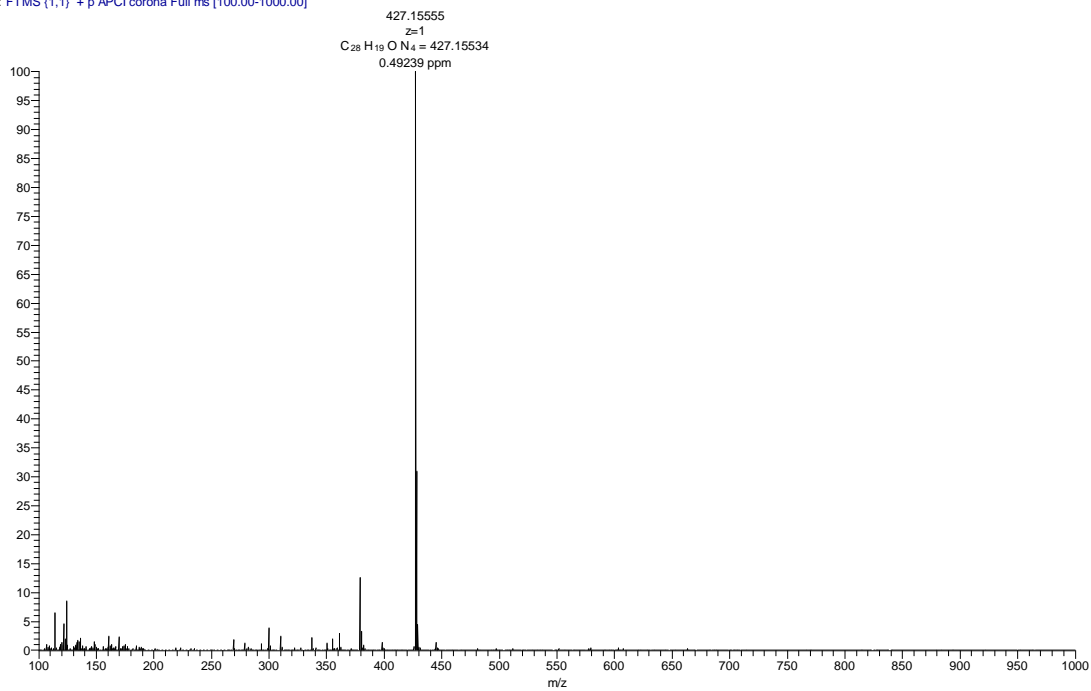


Fig. S24 The high-resolution mass spectrum of InPM.

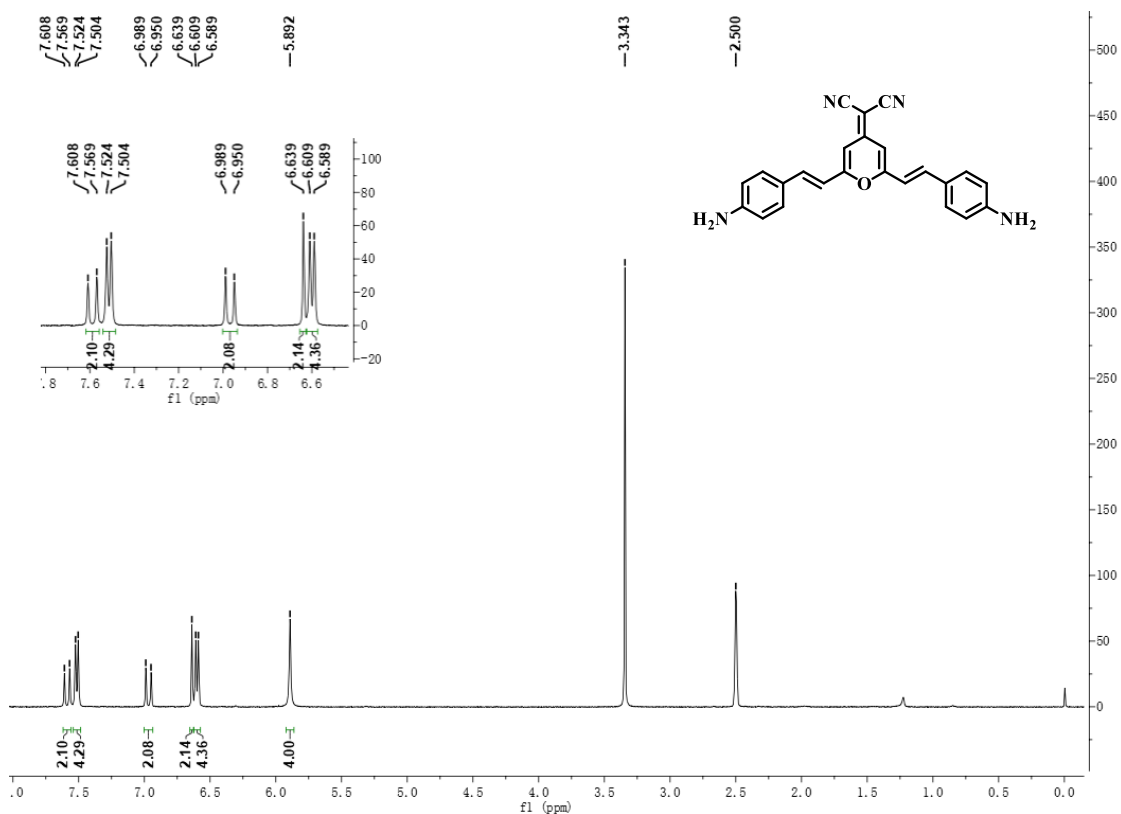


Fig. S25 ¹H NMR of AmPM (DMSO-*d*₆, 400 MHz).

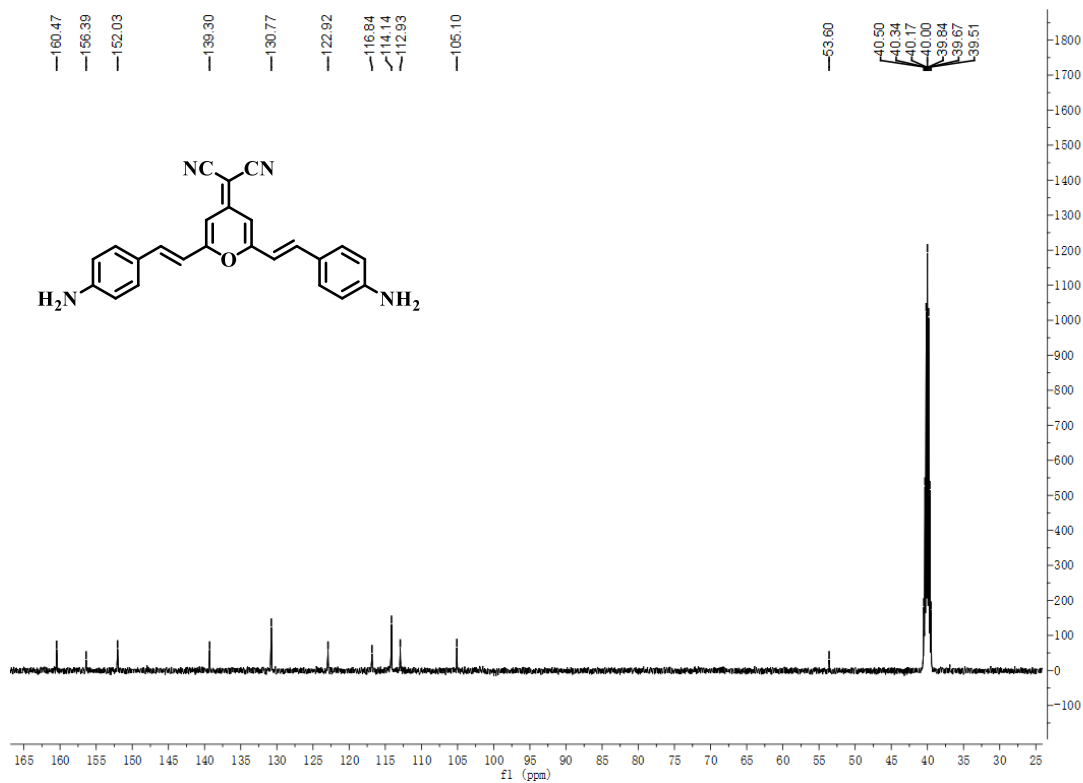


Fig. S26 ^{13}C NMR of AmPM (DMSO- d_6 , 125 MHz).

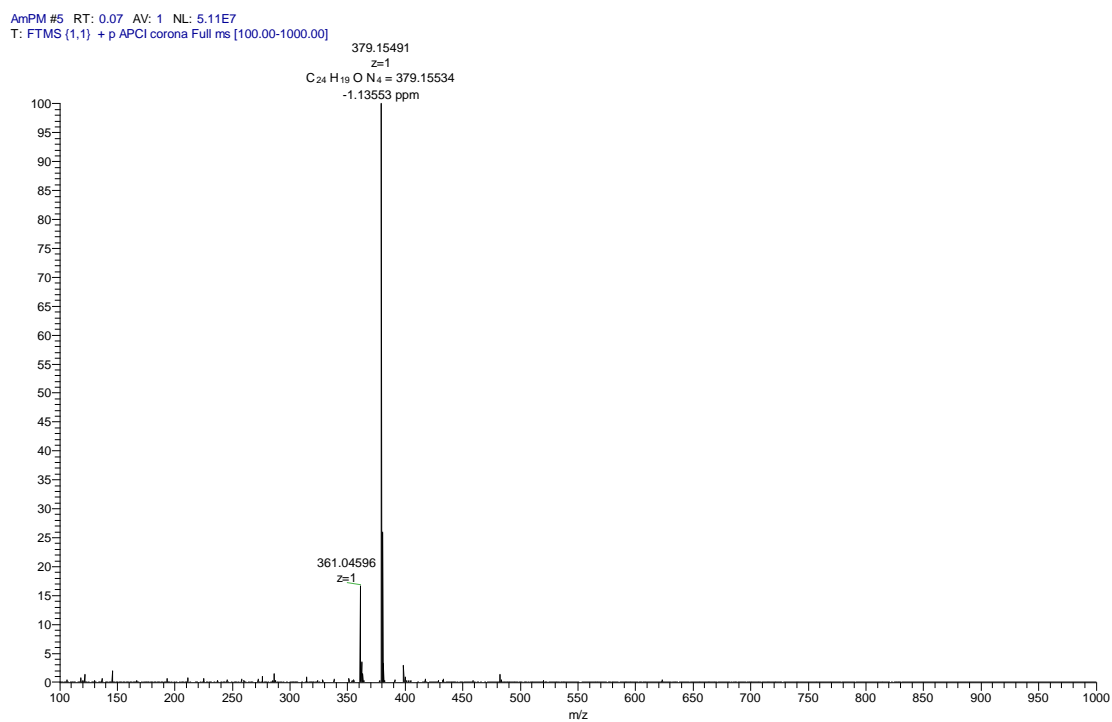


Fig. S27 The high-resolution mass spectrum of AmPM.