Electronic Supplementary Information

Pure room temperature phosphorescence emission of organic host-guest doped system with quantum efficiency of 64%

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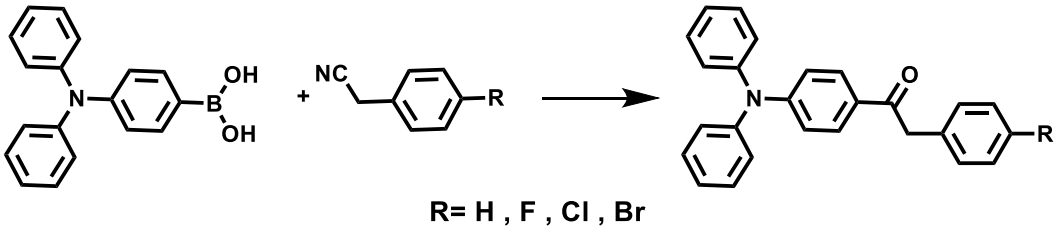
Contents:

1. Experimental

1.1 Measurements and materials

NMR spectra were determined on a Bruker DRX 500 NMR spectrometer using deuterated chloroform and dimethyl sulfoxide as a solvent and trimethylsilane as a reference. UV-vis absorption spectra were performed with a UV-3600 Shimadzu spectrophotometer. Fluorescence spectra were performed with a HITACHI F-7000 fluorometer. Phosphorescence spectra were measured by using FLS920 lifetime and steady state spectrometer. Solid-state emission quantum yields were collected by using FluoroMax-4 (Horiba Jobin Yvon) fluorimeter equipped with integrated sphere. The X-ray crystallographic analyses were conducted on a Bruker SMART II CCD area detector. The theoretical ground-state geometry and electronic structure were performed using the density functional theory (DFT) with B3LYP hybrid functional at the basis set level of 6-31+G (d, p). (4-(Diphenylamino)phenyl)boronic acid, 2-phenylacetonitrile, 2-(4-fluorophenyl)acetonitrile, 2-(4-chlorophenyl)acetonitrile, 2-(4-bromophenyl)- acetonitrile, and Ni(dppe)Cl_2 were obtained from the commercial suppliers. The 1-(4- (diphenylamino)phenyl)-2-phenylethan-1-one derivatives were synthesized by a similar synthetic method according to the previous literature.[1]



Scheme S1 Synthetic routes of the four guest molecules.

1.2 General procedure for the synthesis of the guest molecules

A mixture of (4-(diphenylamino)phenyl)boronic acid (20 mmol), the corresponding phenylacetonitrile derivative (10 mmol), Ni(dppe)Cl_2 (5.0 mol%), $ZnCl_2$ (15.0 mmol), H_2O (10.0 mL), and 1,4-dioxane (20.0 mL) was stirred at 80 °C for 8 h under nitrogen atmosphere. After the reaction solution was cooled to room temperature, Ni(dppe)Cl_2 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 1-(4-(diphenylamino)phenyl)-2-phenylethan-1-one derivative. Characterization data of the target compounds are listed as follows.

1-(4-(Diphenylamino)phenyl)-2-phenylethan-1-one (PAPO-H). White solid, 68% yield. ^{1}H NMR (500 MHz, $CDCl_3$): δ 4.20 (s, 2H), 6.97 (d, J = 8.0 Hz, 2H), 7.15 (d, J = 7.6 Hz, 6H), 7.24 (s, 1H), 7.30-7.34 (m, 8H), 7.86 (d, J = 8.0 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.9, 152.2, 146.4, 135.3, 130.3, 129.7, 129.4, 129.0, 128.6, 126.7, 126.1, 124.8, 119.5, 45.2 ppm.

1-(4-(Diphenylamino)phenyl)-2-(4-fluorophenyl)ethan-1-one (PAPO-F). White solid, 72% yield. ^{1}H

NMR (500 MHz, DMSO-d_6): δ 4.26 (s, 2H), 6.86 (d, J = 8.5 Hz, 2H), 7.11-7.21 (m, 8H), 7.26-7.29 (m, 2H), 7.40 (t, J = 7.5 Hz, 4H), 7.91 (d, J = 8.5 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.6, 162.8, 160.9, 152.3, 146.4, 131.0, 130.9, 130.8, 130.2, 129.7, 128.7, 126.1, 124.9, 119.4, 115.5, 115.4, 44.2 ppm.

2-(4-Chlorophenyl)-1-(4-(diphenylamino)phenyl)ethan-1-one (PAPO-Cl). White solid, 70% yield. ^{1}H NMR (500 MHz, DMSO-d_6): δ 4.27 (s, 2H), 6.86 (d, J = 8.5 Hz, 2H), 7.15-7.21 (m, 6H), 7.27 (d, J = 8.0 Hz, 2H), 7.35-7.41 (m, 6H), 7.90 (d, J = 8.5 Hz, 2H) ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.2, 125.4, 146.4, 133.7, 132.7, 130.8, 130.2, 129.7, 128.7, 126.2, 124.9, 119.4, 44.3 ppm.

2-(4-Bromophenyl)-1-(4-(diphenylamino)phenyl)ethan-1-one (PAPO-Br). White solid, 75% yield. ^{1}H NMR (500 MHz, DMSO-d_6): δ 4.26 (s, 2H), 6.85 (d, J = 9.0 Hz, 2H), 7.15-7.22 (m, 8H), 7.40 (t, J = 8.0 Hz, 4H), 7.49 (d, J = 8.5 Hz, 2H), 7.90 (d, J = 9.0 Hz, 2H), ppm. ^{13}C NMR (125 MHz, $CDCl_3$): δ 195.2, 152.4, 146.3, 134.2, 131.7, 131.2, 130.2, 129.6, 128.6, 126.2, 124.9, 120.8, 119.4, 44.4, ppm.

References:

1. Y. C. Wong, K. Parthasarathy, and C. H. Cheng. *Org. Lett.*, 2010, **12**, 1736-1739.

2. Figures and tables

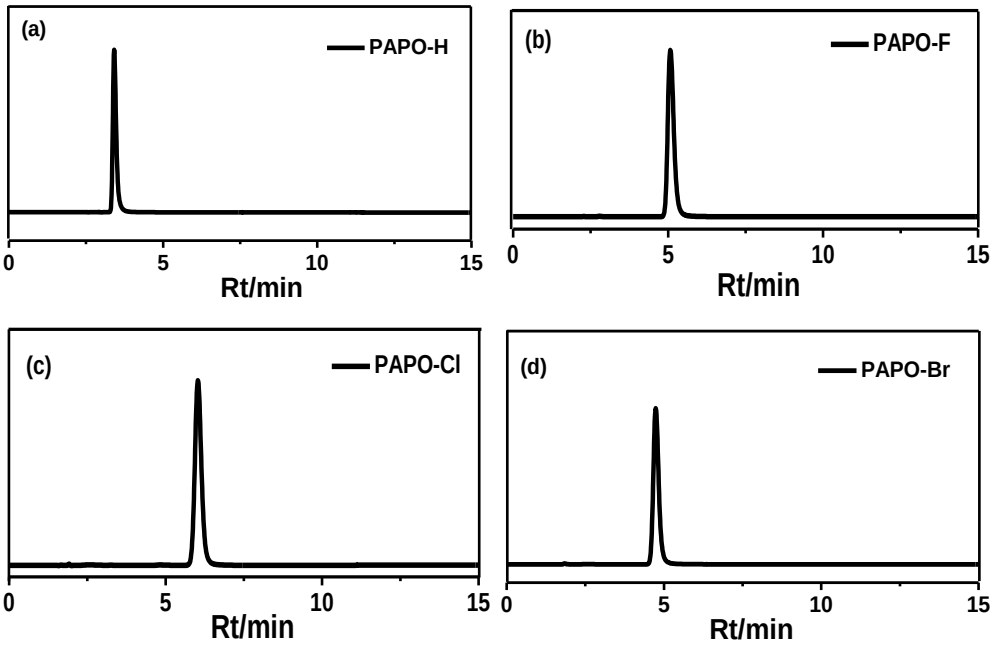


Figure S1. High performance liquid chromatography of PAPO-H (a), PAPO-F (b), PAPO-Cl (c), PAPO-Br (d). (CH_3OH/H_20= 80%: 20%)

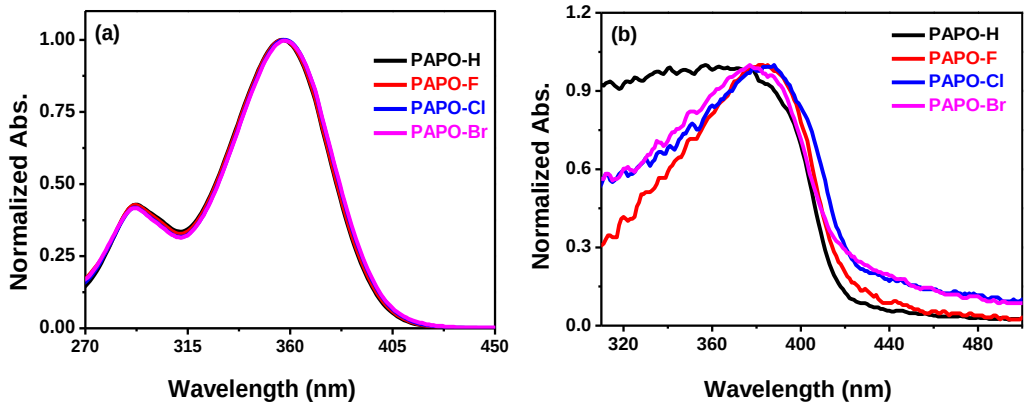


Fig. S2 (a) Normalized absorption spectra of the guests in THF solvent. Concentration: 1.0×10^{-5} mol/L. (b) Normalized absorption spectra of the guests in solid state.

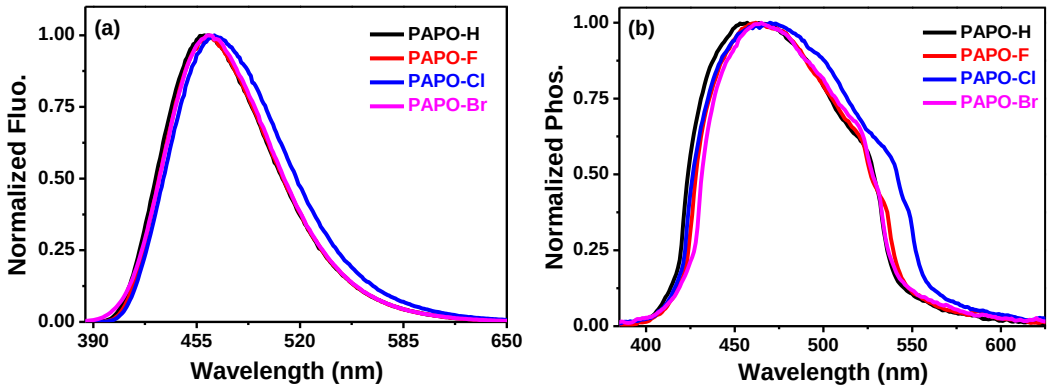


Fig. S3 (a) Normalized prompt emission spectra of the guests in THF solvent. Concentration: 1.0×10^{-5} mol/L. (b) Normalized delayed emission spectra of the guests in THF solvent. Concentration: 1.0×10^{-5} mol/L. Delayed time: 0.5 ms.

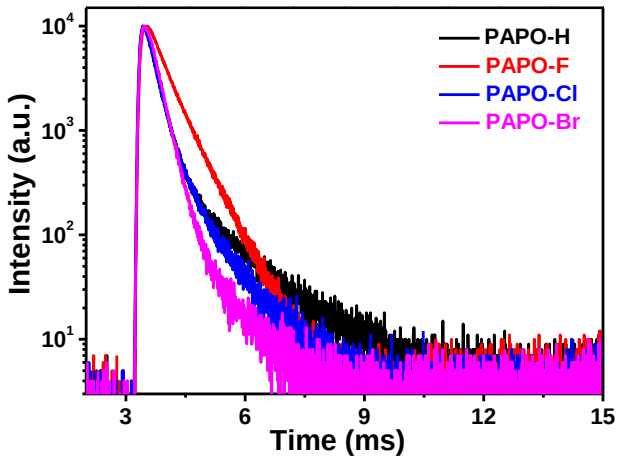


Fig. S4 Phosphorescence decay curves of four doped materials in solution state at 470 nm.

Table 1 Photophysical properties of the guest molecules.

Sample	Fluo. λ_{em} (nm)	Fluo. QY (%)	Fluo. τ (ns)	Phos. λ_{em} (nm)	Phos. QY (%)	Phos. τ (ms)
IPAPO-H	430[a]/463[b]	61.5[a]/44.3[b]	2.3[b]	570[a]/470[b]	6.5[a]/2.0[b]	32[a]/2.3[b]
IPAPO-F	432[a]/462[b]	65.3[a]/49.6[b]	3.1[b]	572[a]/471[b]	6.3[a]/1.6[b]	27[a]/4.6[b]
IPAPO-Cl	431[a]/464[b]	67.5[a]/42.8[b]	2.4[b]	570[a]/472[b]	9.1[a]/1.8[b]	35[a]/3.8[b]
IPAPO-Br	430[a]/463[b]	64.2[a]/47.2[b]	3.7[b]	570[a]/473[b]	13.2[a]/2.2[b]	31[a]/5.2[b]

[a] In the solid state. [b] In the solution state.

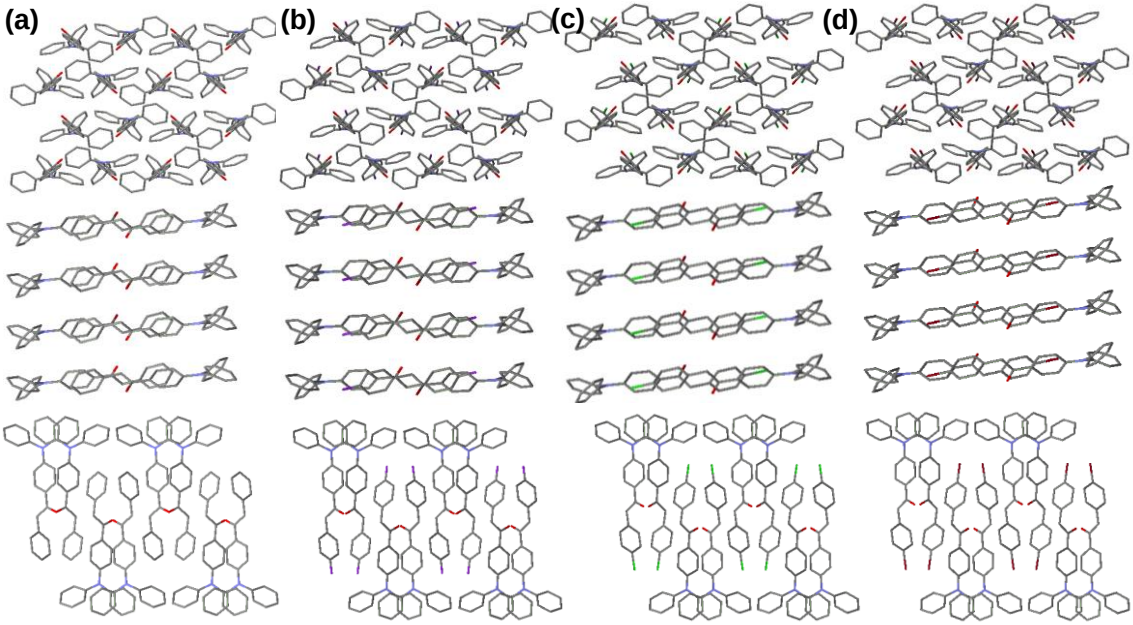


Fig. S5 Stacking arrangements of **PAPO-H** (a), **PAPO-F** (b), **PAPO-Cl** (c) and **PAPO-Br** (d) along *a*-axis (top), *b*-axis (middle), and *c*-axis (bottom).

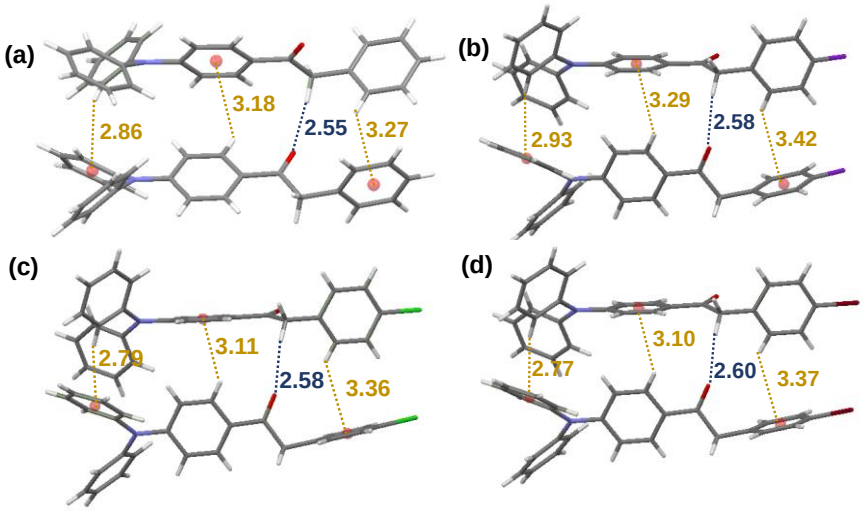


Fig. S6 Intramolecular interactions of **PAPO-H** (a), **PAPO-F** (b), **PAPO-Cl** (c) and **PAPO-Br** (d). (Orange line: C-H···π, blue line: C-H···O).

Table 2 Crystal data and details of collection and refinement for the guest molecules.

	PAPO-H	**PAPO-F**	**PAPO-Cl**	**PAPO-Br**
CCDC	2055990	2055992	2055994	2056001
Empirical formula	$C_{26}H_{21}NO$	$C_{26}H_{20}FNO$	$C_{26}H_{20}ClNO$	$C_{26}H_{20}BrNO$
Formula weight	363.44	381.43	397.88	442.34
Temperature (K)	153.15	293(2)	153.15	153.15
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	*P* 2(1)/c	*P* 2(1)/c	*P* 2(1)/c	*P* 2(1)/c
Z	4	4	4	4
D_{calcd} [Mg/m^3]	1.246	1.251	1.307	1.439
F (000)	768.0	800	832.0	904.0
θ range [°]	5.848-54.96	3.012-24.997	5.468-54.974	5.402-54.92
R_1 [I>2σ(I)]	0.0668	0.0921	0.0666	0.0618
wR_2 [I>2σ(I)]	0.1256	0.2363	0.1287	0.1072
a [Å]	20.928(4)	21.548(2)	22.361(5)	22.628(5)
b [Å]	10.831(2)	10.8853(11	10.757(2)	10.750(2)
c [Å]	8.5628(17)	8.6636(9)	8.4111(17)	8.3962(17)
α [deg]	90	90	90	90
β [deg]	93.09(3)	94.981(4)	92.09(3)	91.56(3)
γ [deg]	90	90	90	90
V [Å^3]	1938.1(7)	2024.4(4)	2021.9(7)	2041.7(7)
GOF	1.144	1.009	1.175	1.155
R(int)	0.0421	0.0821	0.0392	0.0460
No. of reflcns collect	12863	8516	13279	13536
No. of unique reflcns	4352	3526	4564	4644
R_1 (all data)	0.0794	0.1608	0.0766	0.0774
wR_2 (all data)	0.1322	0.2919	0.1340	0.1139

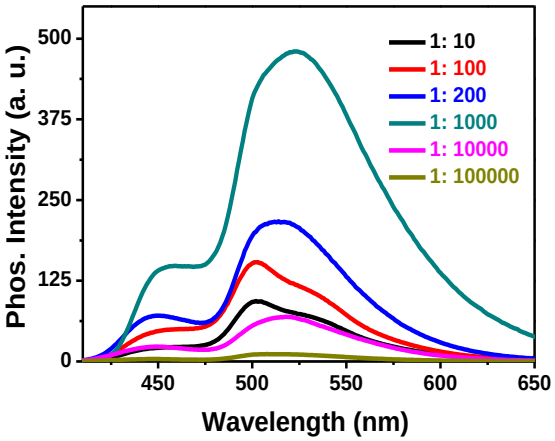


Fig. S7 Delayed emission spectra of the **PAPO-Br/BPO** doped materials with different amounts of **PAPO-Br** (Molar ratio). (Ex. = 380 nm)

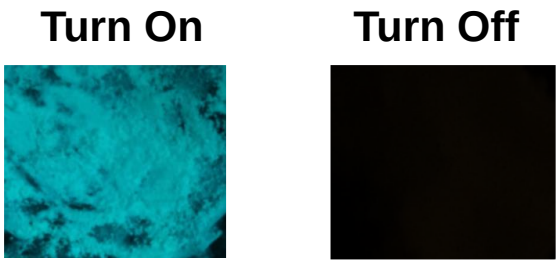


Fig. S8 Luminous pictures of host under different conditions.

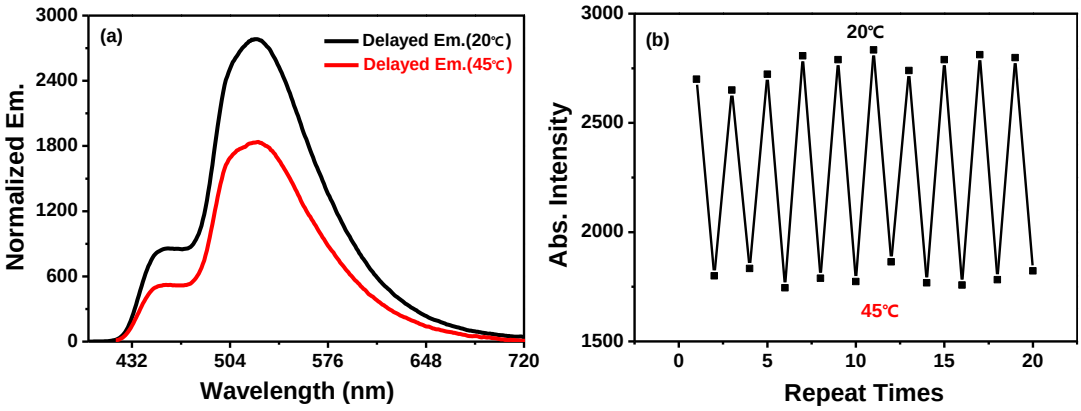


Fig. S9. (a) Delayed spectra of **PAPO-Br/BPO** at different temperatures. (b) Recycling of the heating process of **PAPO-Br/BPO** (emission peak intensity).

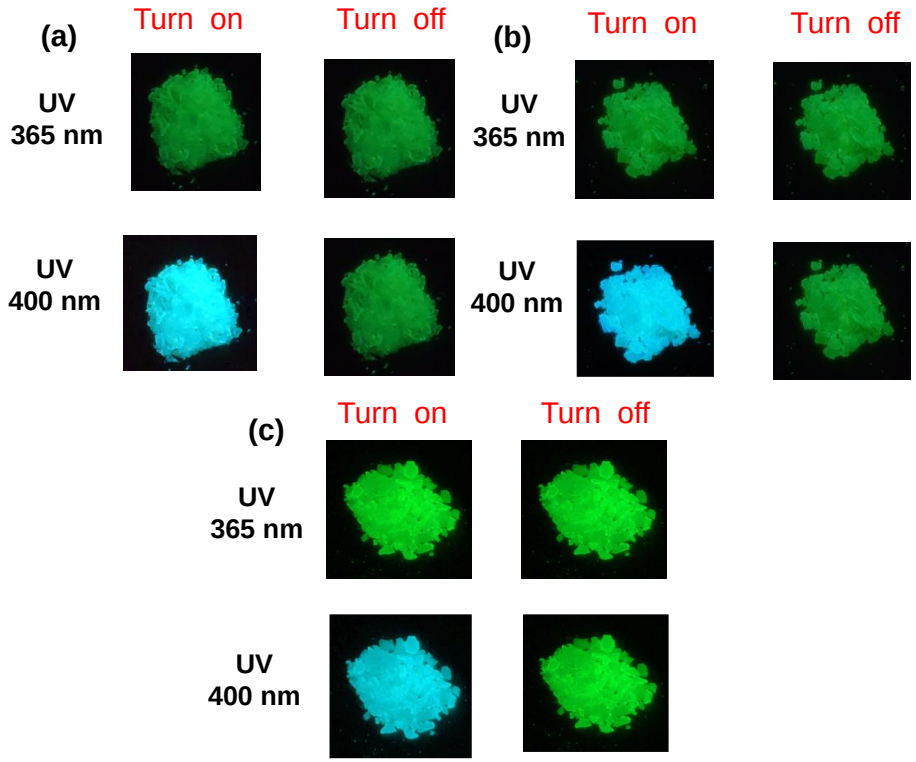
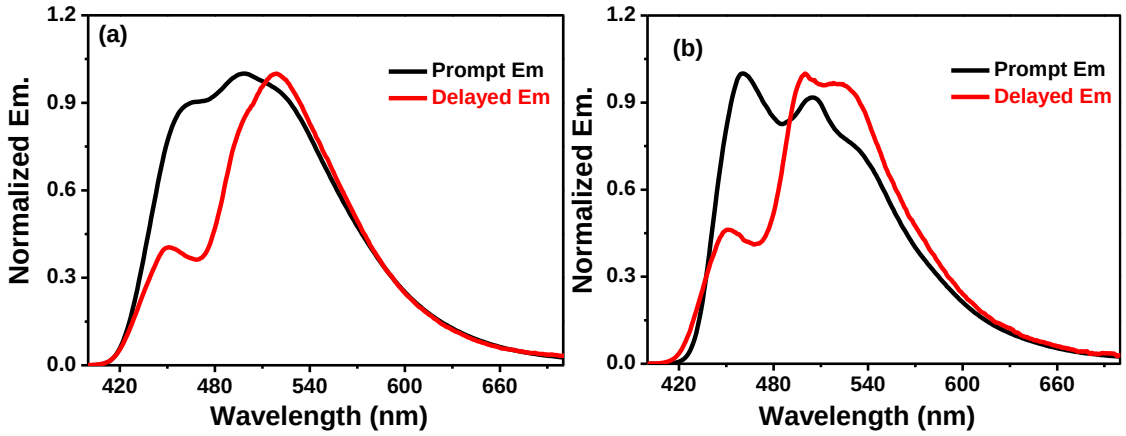


Fig. S10 Luminous pictures of **PAPO-H/BPO** (a), **PAPO-F/BPO** (b), and **PAPO-Cl/BPO** (c) under different conditions.



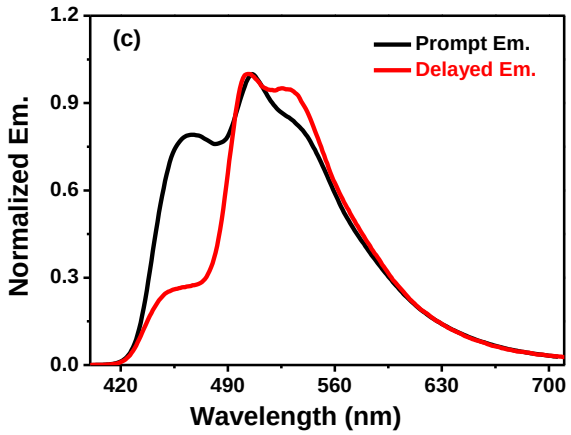


Fig. S11 Emission spectra of **PAPO-H/BPO** (a), **PAPO-F/BPO** (b), **PAPO-Cl/BPO** (c) under 365 nm excitation wavelength.

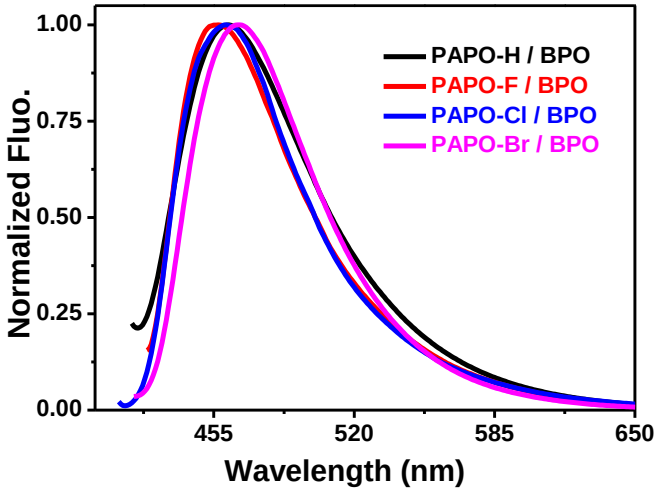
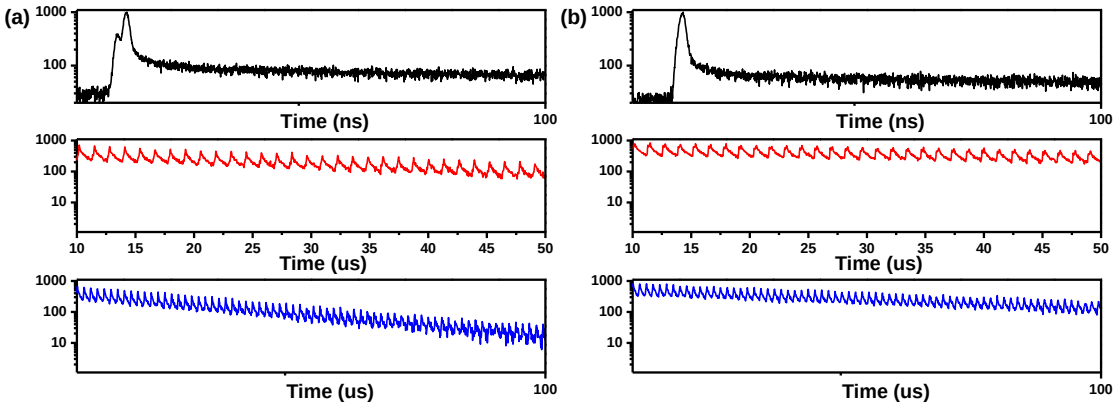


Fig. S12 Prompt emission spectra of the doped materials under 400 nm excitation wavelength.



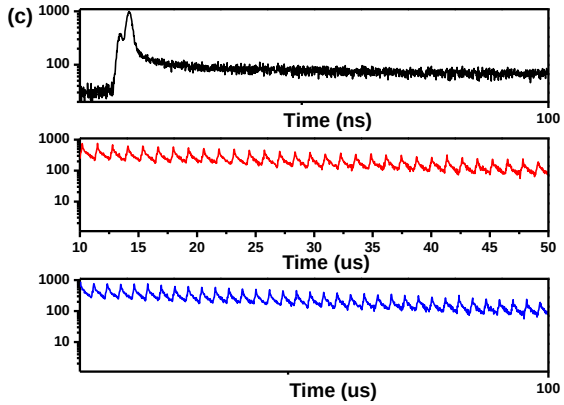


Fig. S13 Time-resolved prompt emission decay curves of **PAPO-H/BPO** (a), **PAPO-F/BPO** (b), and **PAPO-Cl/BPO** (c) in different decay range.

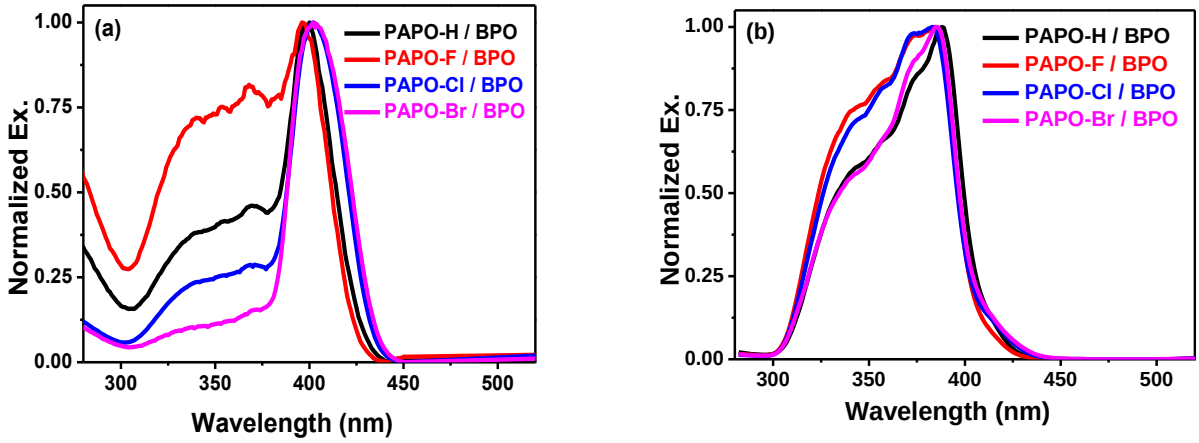


Fig. S14 (a) The excitation spectra of fluorescence of the doped materials. (b) The excitation spectra of phosphorescence of the doped materials.

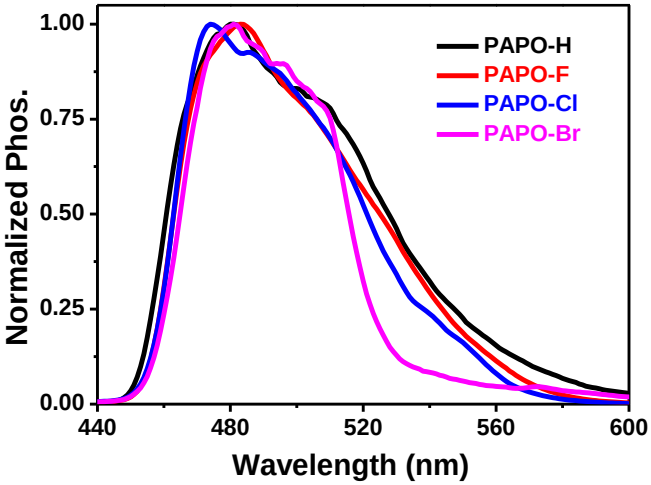


Fig. S15 Phosphorescence emission spectra of four guests in the solution state (Concertation: 1.0×10^{-5} mol/L, 77K).

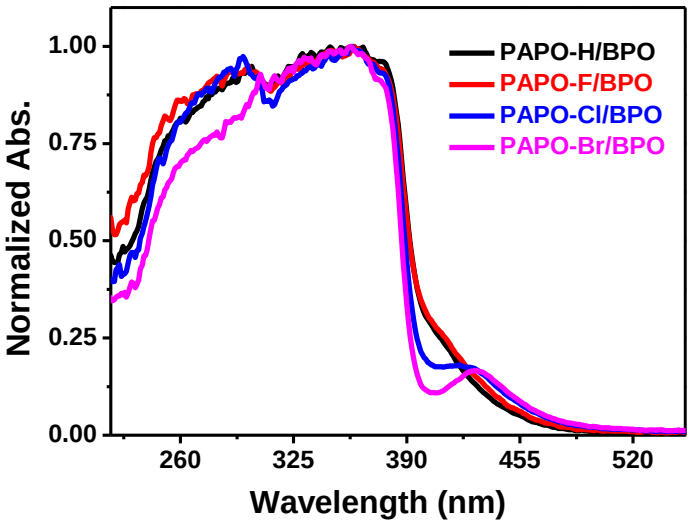


Fig. S16 UV-visible absorption spectra of the doped materials under 400 nm excitation wavelength.

3. NMR Spectra

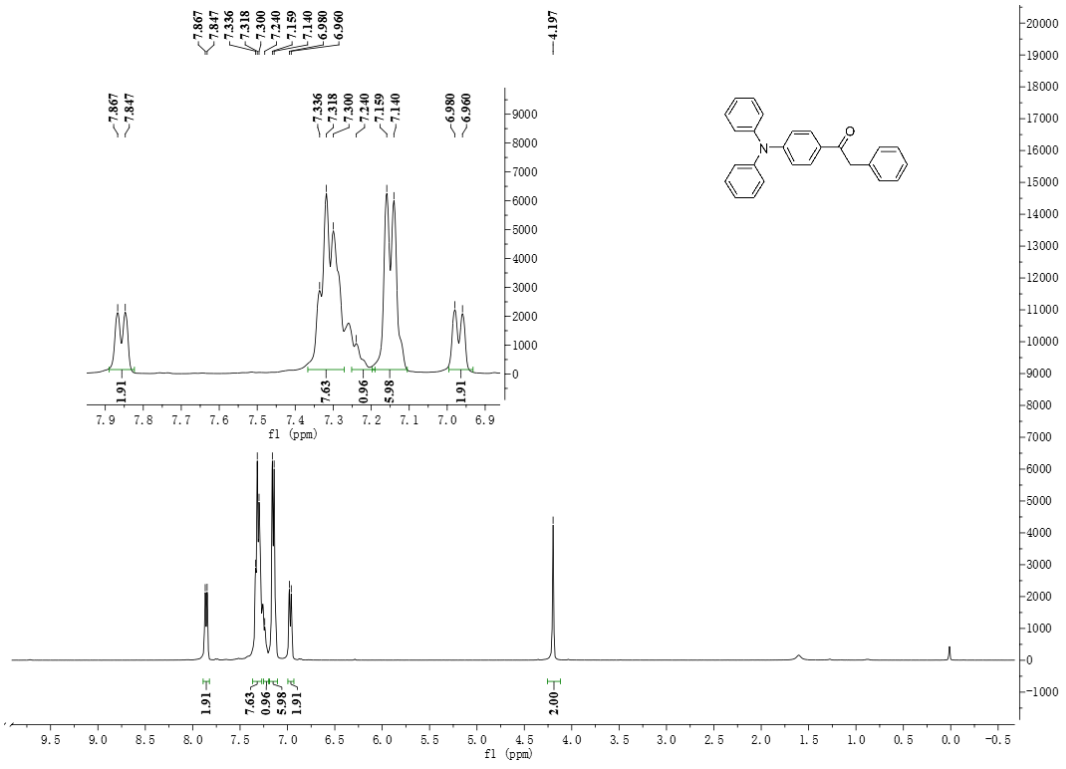


Fig. S17 ^{1}H NMR of **PAPO-H** ($CDCl_3$, 500 MHz).

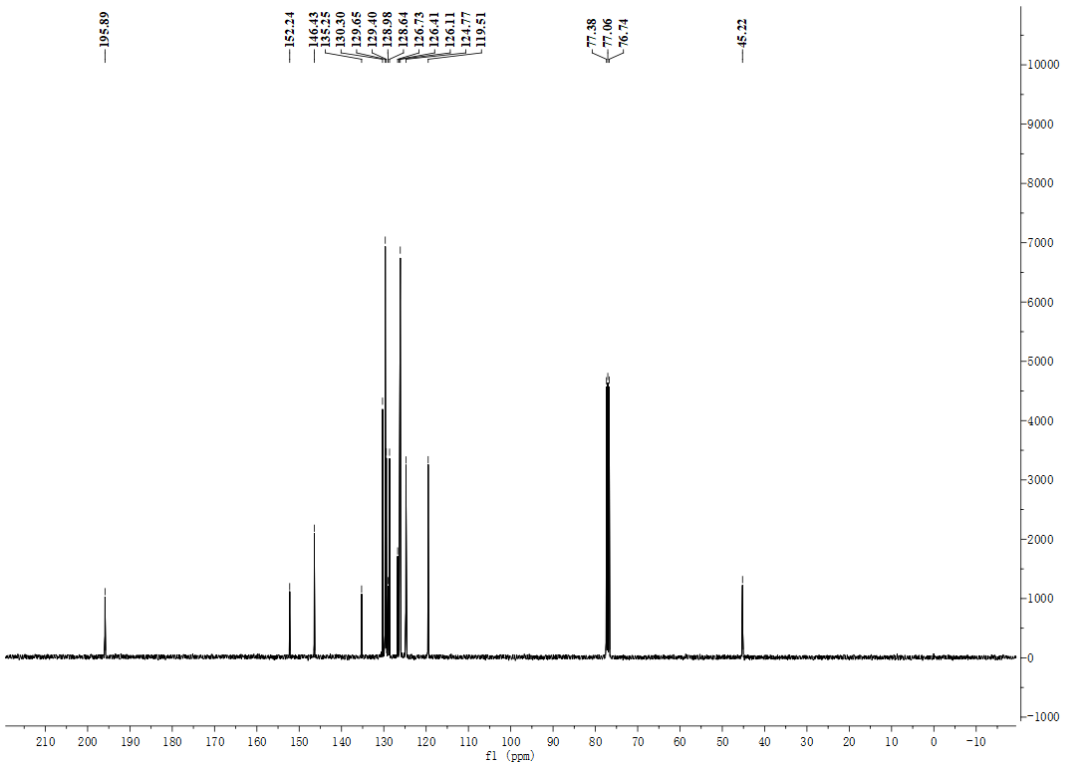


Fig. S18 ^{13}C NMR of **PAPO-H** ($CDCl_3$, 125 MHz).

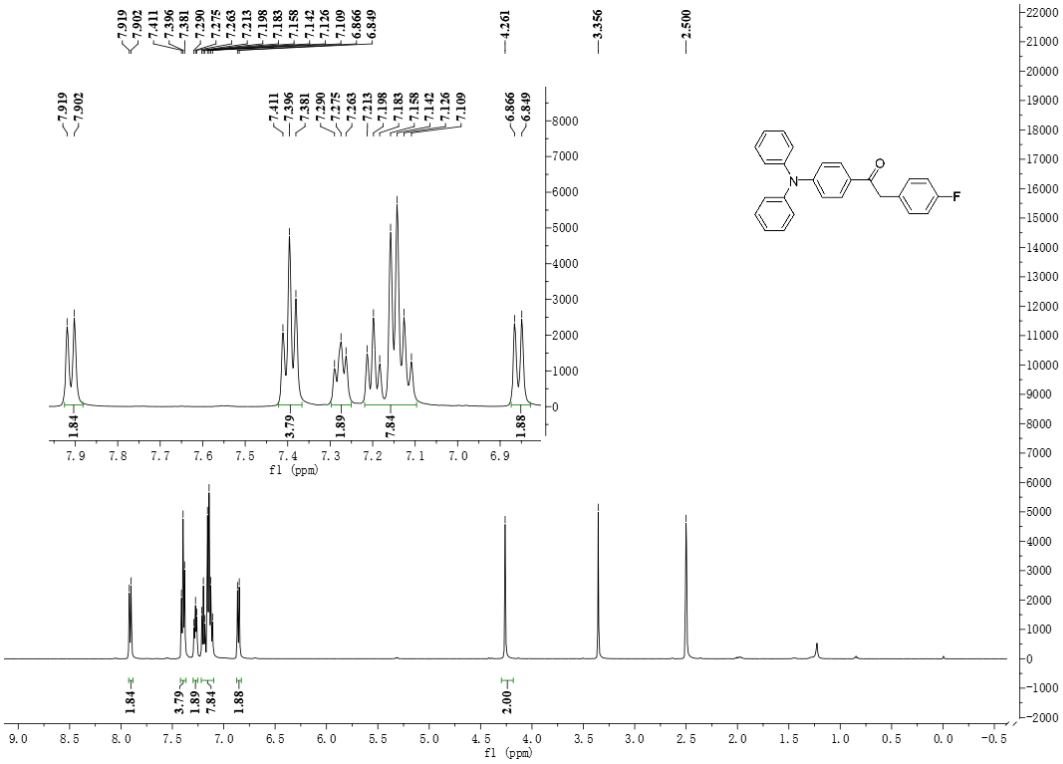


Fig. S19 ^{1}H NMR of **PAPO-F** (DMSO-d_6, 500 MHz).

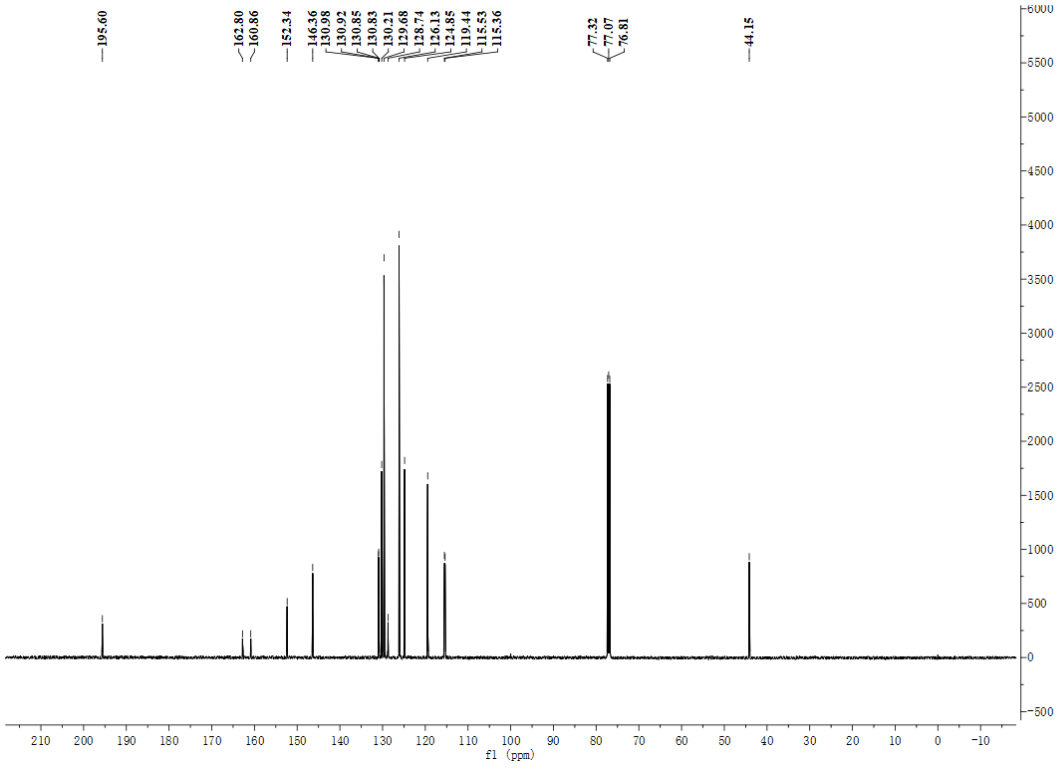


Fig. S20 ^{13}C NMR of **PAPO-F** ($CDCl_3$, 125 MHz).

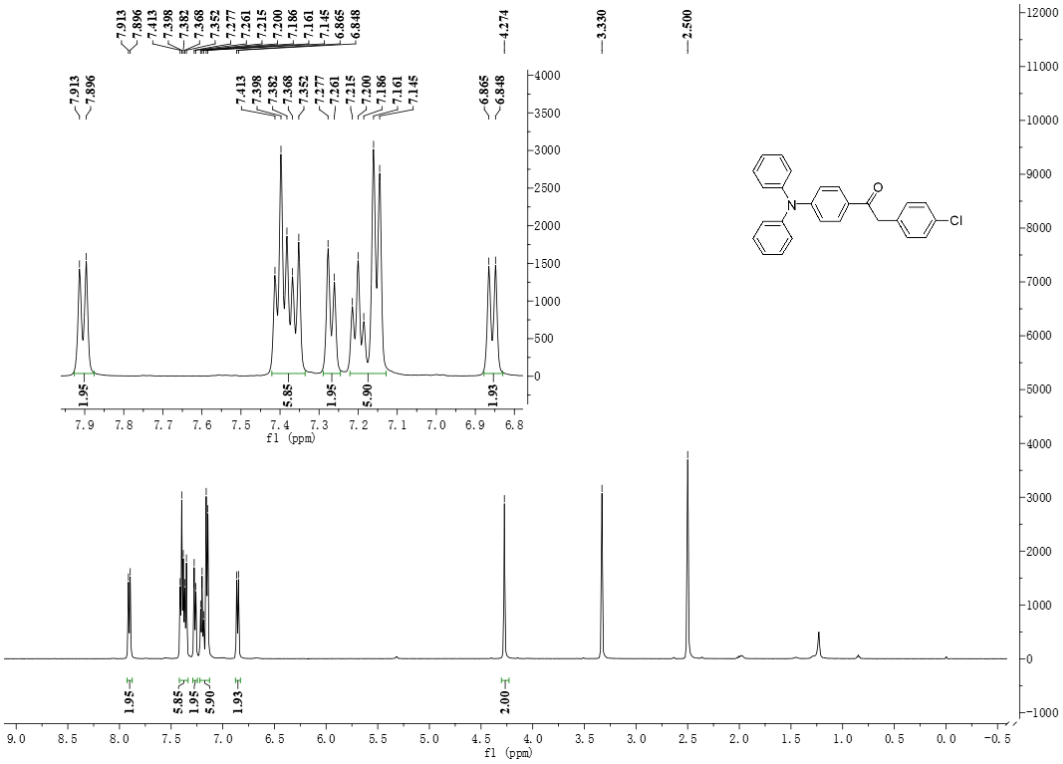


Fig. S21 ^{1}H NMR of **PAPO-Cl** (DMSO-d_6, 500 MHz).

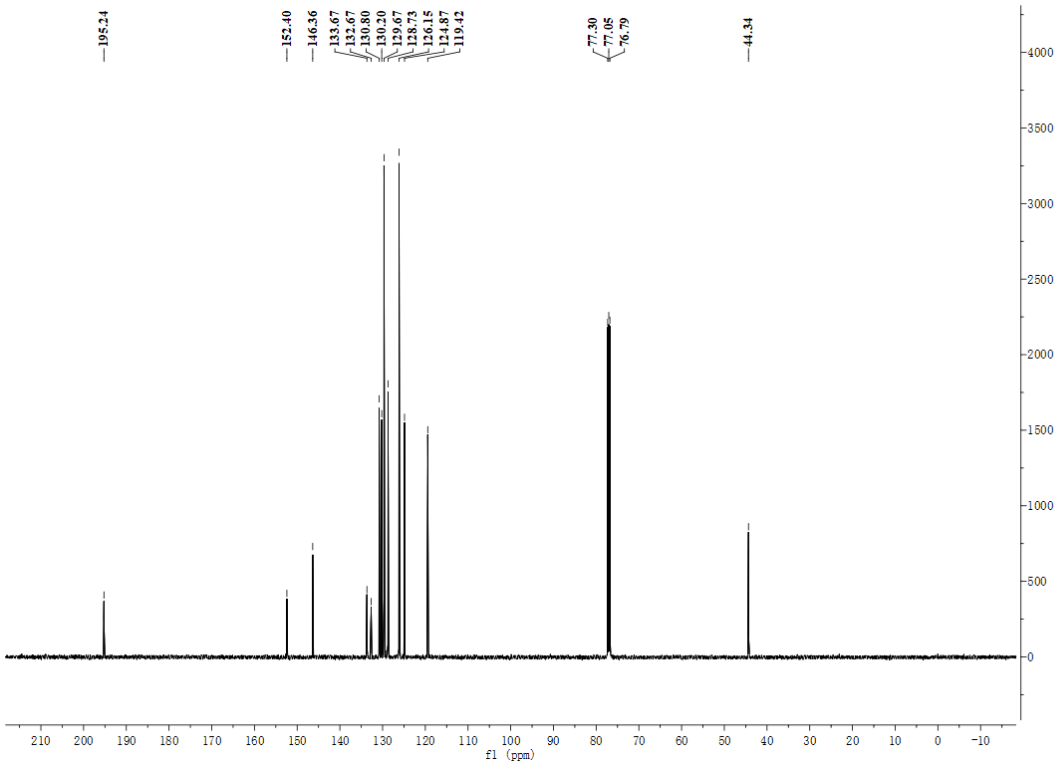


Fig. S22 ^{13}C NMR of **PAPO-Cl** ($CDCl_3$, 125 MHz).

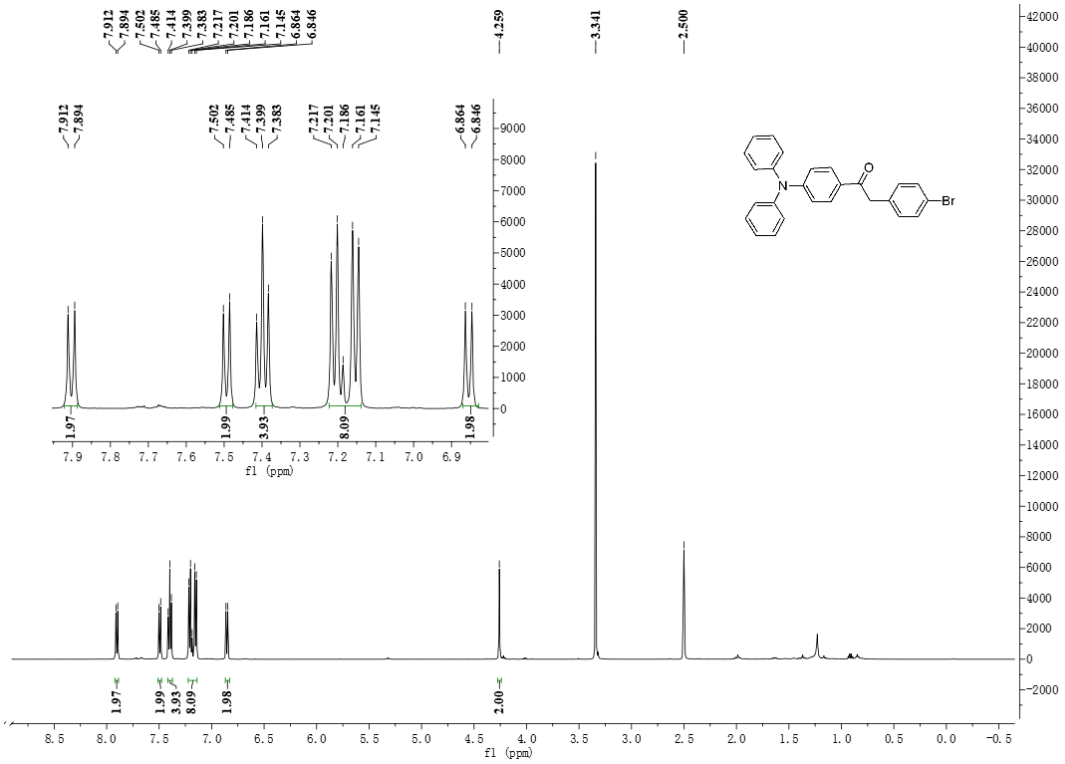


Fig. S23 ^{1}H NMR of **PAPO-Br** (DMSO-d_6, 500 MHz).

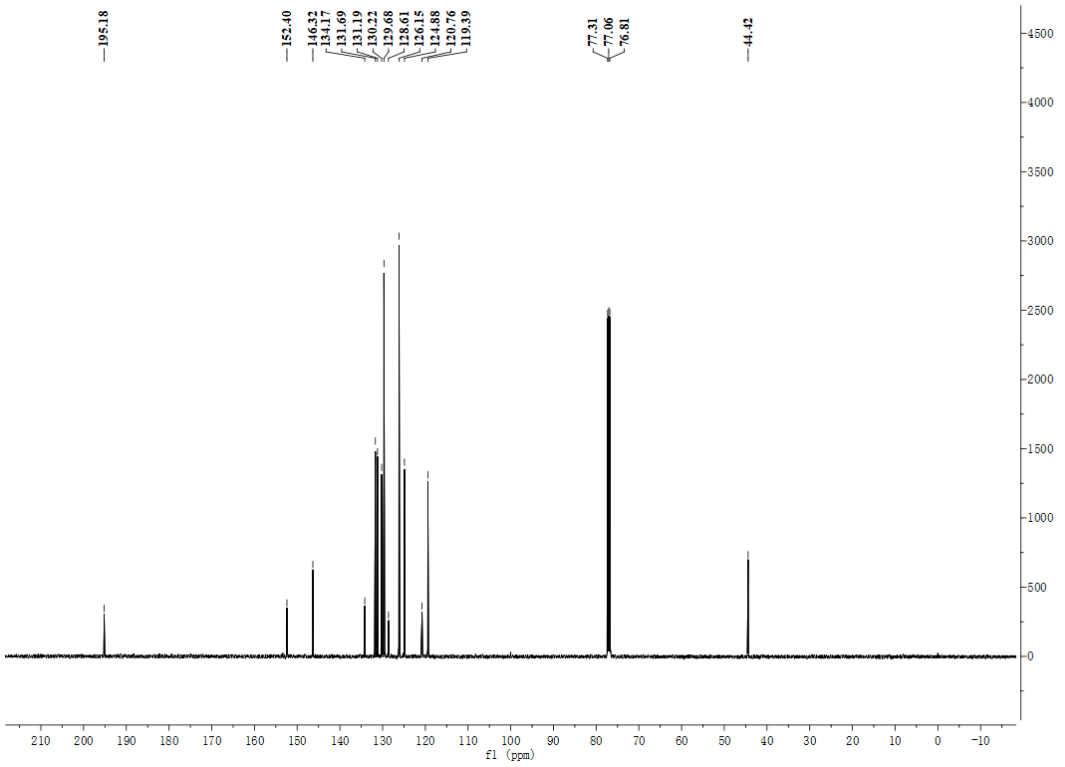


Fig. S24 ^{13}C NMR of **PAPO-Br** ($CDCl_3$, 125 MHz).