Electronic Supplementary Information

Aromatic Phosphonate-Based Luminophores: Universal Building Blocks for Ultralong Room-Temperature Phosphorescence and Multifunctional Applications

Chunli Li, Zizhao Huang, Tao Li, Tengjiao Zhao, Lei Zhou, Zhenyi He*, He Tian, and Xiang Ma*

Key Laboratory for Advanced Materials and Feringa Nobel Prize Scientist Joint Research Center, Frontiers Science Center for Materiobiology and Dynamic Chemistry, Institute of Fine Chemicals, School of Chemistry and Molecular Engineering, East China University of Science and Technology, Meilong Road 130, Shanghai 200237, China.
E-mail: maxiang@ecust.edu.cn & zhenyiheh@qq.com

1. Materials, general procedures and synthesis.

1.1 Materials.

Biphenyl (BP), naphthalene (Na), phenanthrene (Phe), pyrene (Py), 1-methylnaphthalene (NaM) were purchased from Adamas beta. These reagents were used as supplied without further purification. Diethyl 1-naphthylmethylphosphonate (NaP) was purchased from Adamas beta and the purity was characterized by high-performance liquid chromatography (HPLC). All other reagents were commercially available and used as supplied without further purification. Ultrapure water was obtained using Direct-Pure UP UV 10 machine.

1.2 General methods. Reagents used for the synthesis and measurements were commercially available without further purification. The UV-Vis absorption spectra and PL spectra were obtained on a Varian Cray 500 spectrophotometer. Delayed emission spectra and lifetime decay spectra were obtained by an Agilent Cary Eclipse fluorescence spectrophotometer (Agilent Technologies). Quantum yields were measured by using an integrating sphere on a HAMAMATSU Quantaurus-QY C11347-11. ^{1}H nuclear magnetic resonance (NMR) and ^{13}C NMR spectra were recorded on Brüker AVANCE III 400 (400 MHz) spectrometers. Electro spray ionization (ESI) and direct analysis in real time (DART) high-resolution mass spectra (HRMS) were obtained using a Q Exactive Plus mass spectrometer (Thermo Fisher Scientific). The FT-IR were performed on INVENIO S+Hyperion3000. Scanning electron microcopy (SEM) images were obtained by using S-3400N (Hitachi) (droplets of the sample solution were applied to a silicon slice and dried in air at room temperature, and then coated with nano Pt in a vacuum). Density functional theory (DFT) and time-dependent (TD-DFT) calculations were performed with the Gaussian 09 (Revision E.01) software package. The ground-state (S_0) geometries were optimized with the B3LYP and 6- 311G* basis. The excitation energies in the singlet and triplet states were obtained using TD-DFT method based on the optimized S_0 molecular structure. All tensile tests were measured using a HY-0580 tension machine (HENGYI). The data were recorded in real time by a wire-connected computer system.

1.3 Preparation process of the doped systems

The poly(vinyl alcohol) macromolecule (PVA1799 (17 for degree of polymerization, 99 for degree of alcoholysis)) systems: Luminophores were dissolved in 1,4-Dioxane and PVA was dissolved in water. Then a fixed volume of 1,4-Dioxane solution of luminophore was thoroughly mixed with aqueous PVA solution (PVA1799 300 mg, water 15 mL). The resulting mixture was subjected to ultrasonic for about 60 min at 45 °C-55 °C, and then the solution was drop-cast in a glass petri dish, and baked at 80 °C for 2 h. After drying at 120 °C for 30 min, PVA film doped with different mass concentration of luminophore was obtained. The mass concentration of luminophore was controlled between 0.01 wt% and 10 wt%.

The polymethyl methacrylate (PMMA) systems: Luminophores and PMMA were dissolved separately in Dichloromethane (DCM). A fixed volume of luminophore solution and PMMA solution (300 mg, DCM 15 mL) were thoroughly mixed and subjected to ultrasonic for about 60 min at 45 °C-55 °C. Then the solution was drop-cast in a glass petri dish, and baked at 25 °C for 2 h. After drying at 120 °C for 30 min, PMMA film doped with different mass concentration of luminophore was obtained. The mass concentration of luminophore NaP was controlled at 0.3 wt% and that of PheP was controlled at 0.1 wt%.

The polyacrylonitrile (PAN) systems: Luminophores were dissolved in 1,4-Dioxane and PAN was dissolved in N, N-dimethylformamide (DMF). A fixed volume of luminophore solution and PAN solution (300 mg, DMF 20 mL) were thoroughly mixed and subjected to ultrasonic for about 60 min at 45 °C-55 °C. Then the solution was drop-cast in a glass petri dish, and baked at 80 °C for 6 h. After drying at 120 °C for 30 min, PAN film doped with different mass concentration of luminophore was obtained. The mass concentration of luminophore NaP was controlled at 0.3 wt% and that of PheP was controlled at 0.1 wt%.

The poly (vinyl chloride) (PVC) systems: Luminophores and PVC was dissolved in dichloromethane (DCM). A fixed volume of luminophore solution and PVC solution (300 mg, DCM 25 mL) were thoroughly mixed and subjected to ultrasonic for about 60 min at 45 °C-55 °C. Then the solution was drop-cast in a glass petri dish, and baked at 25 °C for 3 h. After drying at 120 °C for 30 min, PVC film doped with different mass concentration of luminophore was obtained. The mass concentration of luminophore NaP was controlled at 0.3 wt%.

The polyvinyl pyrrolidone (PVP) systems: Luminophores were dissolved in 1,4-Dioxane and PVP was dissolved in water. Then a fixed volume of 1,4-Dioxane solution of luminophore was thoroughly mixed with aqueous PVP solution (300 mg, water 17 mL). The resulting mixture was subjected to ultrasonic for about 60 min at 45 °C-55 °C, and then the solution was drop-cast in a glass petri dish, and baked at 80 °C for 2 h. After drying at 120 °C for 30 min, PVP system doped with different mass concentration of luminophore was obtained. The mass concentration of luminophore NaP was controlled at 0.3 wt%.

The poly (2-hydroxyethyl methacrylate) (HEMA) systems: Luminophores were dissolved in 1,4-Dioxane and HEMA was dissolved in water. Then a fixed volume of 1,4-Dioxane solution of luminophore was thoroughly mixed with aqueous PVP solution (300 mg, water 28 mL). The resulting mixture was subjected to ultrasonic for about 60 min at 45 °C-55 °C, and then the solution was drop-cast in a glass petri dish, and baked at 80 °C for 3 h. After drying at 120 °C for 30 min, HEMA system doped with different mass concentration of luminophore was obtained. The mass concentration of luminophore NaP was controlled at 0.3 wt%.

The *γ*-cyclodextrin (γ-CD) systems: Luminophores were dissolved in 1,4-Dioxane and γ-CD was dissolved in water. Then a fixed volume of 1,4-Dioxane solution of luminophore was thoroughly mixed with aqueous γ-CD solution (300 mg, water 20 mL). The resulting mixture was subjected to ultrasonic for about 60 min at 45 °C-55 °C, and then the solution was drop-cast in a glass petri dish, and baked at 80 °C for 3 h. After drying at 120 °C for 30 min, γ-CD system doped with different mass concentration of luminophore was obtained. The mass concentration of luminophore NaP was controlled at 0.3 wt% and that of PheP was controlled at 0.1 wt%.

The chitosan (CTS) systems: Luminophores were dissolved in 1,4-Dioxane and CTS was dissolved in water. Then a fixed volume of 1,4-Dioxane solution of luminophore was thoroughly mixed with aqueous CTS solution (300 mg, water 30 mL). The resulting mixture was subjected to ultrasonic for about 60 min at 45 ℃-55 ℃, and then the solution was drop-cast in a glass petri dish, and baked at 80 ℃ for 5 h. After drying at 120 ℃ for 30 min, doped system was obtained.

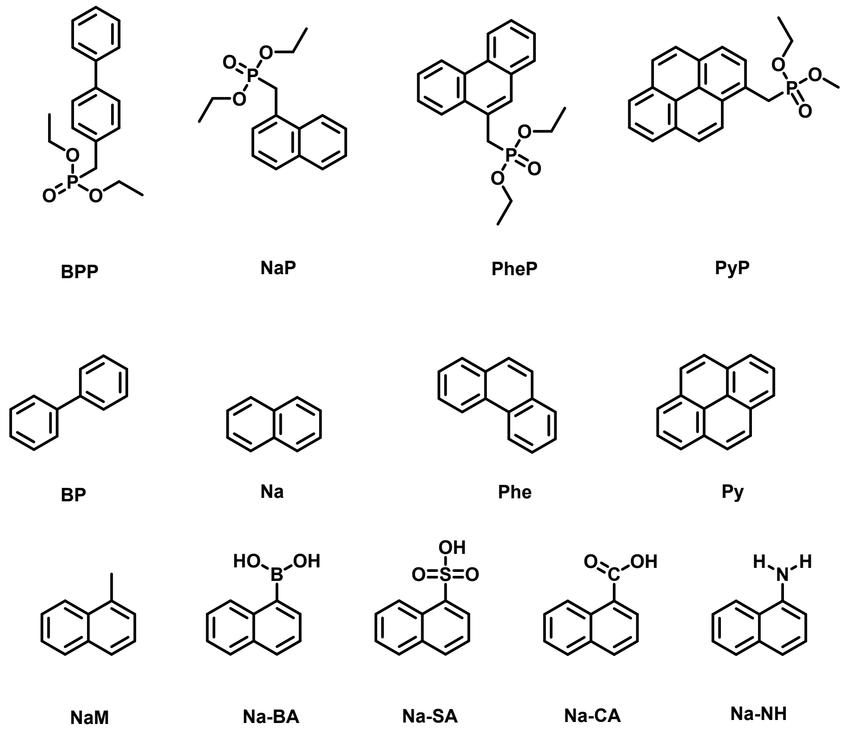
The D-Sorbitol (DS) systems: Luminophores were dissolved in 1,4-Dioxane and DS was dissolved in water. Then a fixed volume of 1,4-Dioxane solution of luminophore was thoroughly mixed with aqueous DS solution (300 mg, water 45 mL). The resulting mixture was subjected to ultrasonic for about 60 min at 45 ℃-55 ℃, and then the solution was drop-cast in a glass petri dish, and baked at 80 ℃ for 6 h. After drying at 120 ℃ for 30 min, doped system was obtained.

The Isoprene-styrene (SBS) systems: Luminophores and SBS were dissolved separately in Dichloromethane (DCM). A fixed volume of luminophore solution and SBS solution (300 mg, DCM 15 mL) were thoroughly mixed and subjected to ultrasonic for about 60 min at 45 ℃-55 ℃. Then the solution was drop-cast in a glass petri dish, and baked at 25 ℃ for 2 h. After drying at 120 ℃ for 30 min, doped system was obtained.

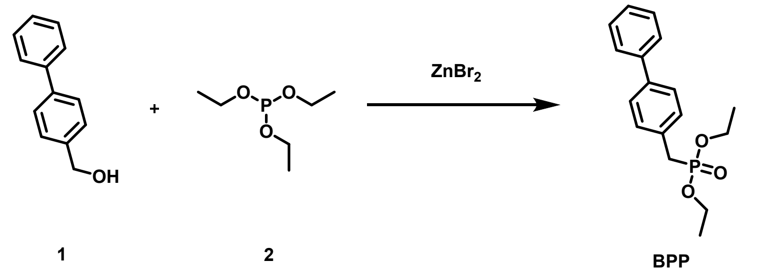
1.4 Preparation process of 3D printing materials

The 3D printed resin is composed of isobornyl acrylate (IBOA, 20 wt%), benzyl acrylate (BA, 40 wt%), aliphatic urethane diacrylate (AUD, 40 wt%), photoinitiator, 2,4,6-trimethylbenzoyldiphenyl phosphine oxide (TPO, 1.5 wt%) and luminophore NaP (0.2 wt%). The mixture was stirred for 6 h at 70 ℃, and then used in a commercial 3D printer (Anycubic Photon Mono M7) equipped with a 405 nm light source. The model was sliced by Anycubic Photon Workshop software.

1.5 Structural formula, synthesis and characterization of luminophores.



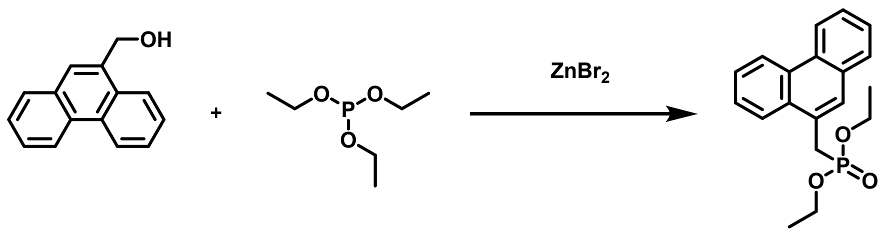
Structural formula and abbreviation of luminophores.



Scheme S1. Synthetic route of BPP.

Synthesis of BPP: Compound 1 (5.00 g, 0.03 mol) and compound 2 (23.00 mL, 0.15 mol) were added in a double-necked flask under Ar atmosphere. Then Zinc Bromide (6.20 g, 0.03 mol) was added into the flask, and the mixed solution was stirred for 6h at room temperature. The mixture was processed by rotary evaporator to remove extra compound 2, and extracted with dichloromethane three times (3 × 20 mL). After removing the solvent under reduced pressure, the crude product was purified by flash column chromatography on silica gel (n-Hexane/ethyl acetate = 2/1), and dried in a vacuum drying oven at 45 °C for 12 h to obtain product (4.93 g, 60% yield).

^{1}H NMR (400 MHz, $CDCl_3$, δ): 7.61 – 7.56 (m, 2H), 7.56 – 7.49 (m, 2H), 7.46 – 7.39 (m, 2H), 7.39 – 7.28 (m, 3H), 4.11 – 3.97 (m, 4H), 3.19 (d, J = 21.6 Hz, 2H), 1.26 (t, 6H); ^{13}C NMR (101 MHz, $CDCl_3$, δ): 140.70, 139.77, 130.39, 128.99, 128.59, 127.44, 127.09, 126.84, 77.46, 77.14, 76.82, 62.18, 34.10, 16.28. HRMS (ESI) m/z: $[M+H]^+$ calcd for $[C_{17}H_{22}O_3P]^+$: 305.1301, found: 305.1294.

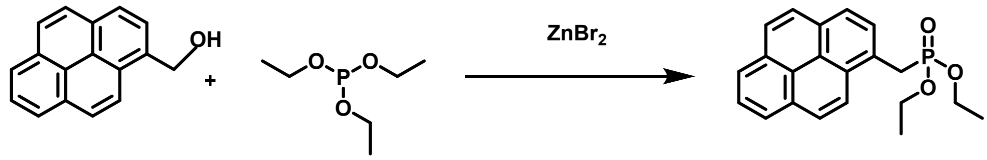


3 2 PheP

Scheme S2. Synthetic route of PheP.

Synthesis of PheP: Compound 3 (1.10 g, 0.005 mol) and compound 2 (4.30 mL, 0.025 mol) were added in a double-necked flask under Ar atmosphere. Then Zinc Bromide (1.16 g, 0.005 mol) was added into the flask, and the mixed solution was stirred for 6h at room temperature. The mixture was processed by rotary evaporator to remove extra compound 2, and extracted with dichloromethane three times (3 × 20 mL). After removing the solvent under reduced pressure, the crude product was purified by flash column chromatography on silica gel (n-Hexane/ethyl acetate = 2/1), and dried in a vacuum drying oven at 45 °C for 12 h to obtain product (1.09 g, 67% yield).

^{1}H NMR (400 MHz, $CDCl_3$, *δ*): 8.74 – 8.66 (m, 1H), 8.66 – 8.59 (m, 1H), 8.21 – 8.12 (m, 1H), 7.86 – 7.79 (m, 1H), 7.74 (d, *J* = 4.4 Hz, 1H), 7.69 – 7.52 (m, 4H), 4.04 – 3.84 (m, 4H), 3.66 (d, *J* = 21.9 Hz, 2H), 1.14 (t, 6H). ^{13}C NMR (101 MHz, $CDCl_3$, *δ*): 131.49, 130.94, 130.74, 130.01, 129.28, 129.22, 128.31, 126.77, 126.61, 126.51, 125.23, 123.07, 122.48, 77.26, 77.05, 76.84, 62.30, 62.26, 31.65, 16.36, 16.32. HRMS (DART) m/z: $[M+H]^+$ calcd for $[C_{19}H_{22}O_3P]^+$: 329.1301, found: 329.1281.



4 2 PyP

Scheme S3. Synthetic route of PyP.

Synthesis of PyP: Compound 4 (1.00 g, 0.004 mol) and compound 2 (3.60 mL, 0.020 mol) were added in a double-necked flask under Ar atmosphere. Then Zinc Bromide (1.00 g, 0.004 mol) was added into the flask, and the mixed solution was stirred for 6h at room temperature. The mixture was processed by rotary evaporator to remove extra compound 2, and extracted with dichloromethane three times (3 × 20 mL). After removing the solvent under reduced pressure, the crude product was purified by flash column chromatography on silica gel (dichloromethane /ethyl acetate = 2/1), and dried in a vacuum drying oven at 45 °C for 12 h to obtain product (1.17 g, 83% yield).

^{1}H NMR (400 MHz, DMSO-d_6, *δ*): 8.43 (d, *J* = 9.3 Hz, 1H), 8.33 – 8.25 (m, 3H), 8.25 – 8.20 (m, 1H), 8.17 (s, 2H), 8.08 (t, 1H), 8.05 – 8.00 (m, 1H), 4.02 (d, *J* = 22.2 Hz, 2H), 3.98 – 3.85 (m, 4H), 1.11 (t, 6H). ^{13}C NMR (101 MHz, DMSO-d_6, *δ*): 130.80, 130.32, 129.72, 128.85, 127.34, 126.97, 126.82, 126.19, 125.09, 124.91, 124.68, 124.08, 123.78, 61.51, 40.09, 39.88, 39.67, 39.46, 39.25, 39.04, 38.84, 30.82, 16.31. HRMS (DART) m/z: $[M+H]^+$ calcd for

$[C_{21}H_{22}O_3P]^+$: 353.1301, found: 353.1333.

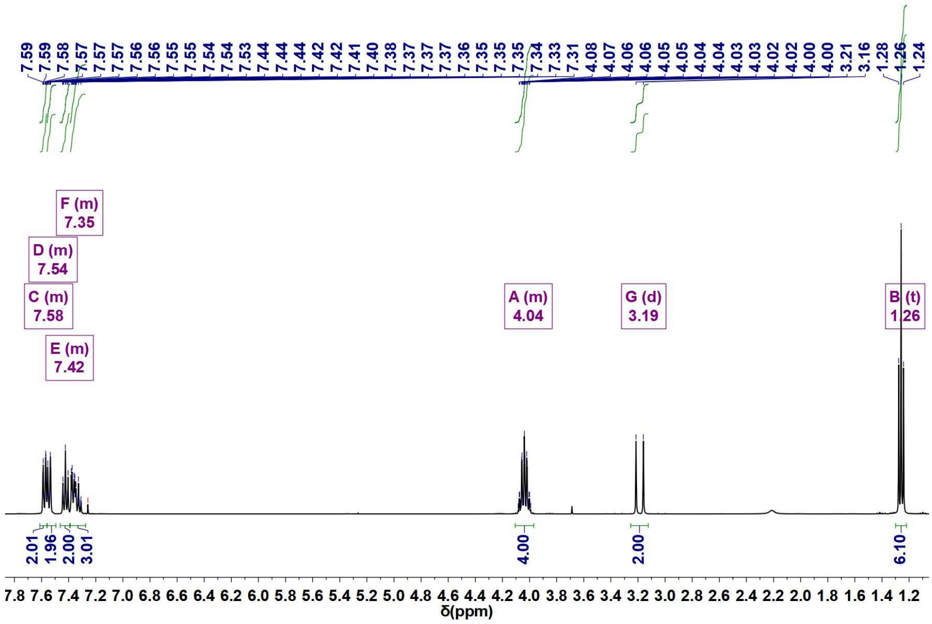


Fig. S1 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of BPP.

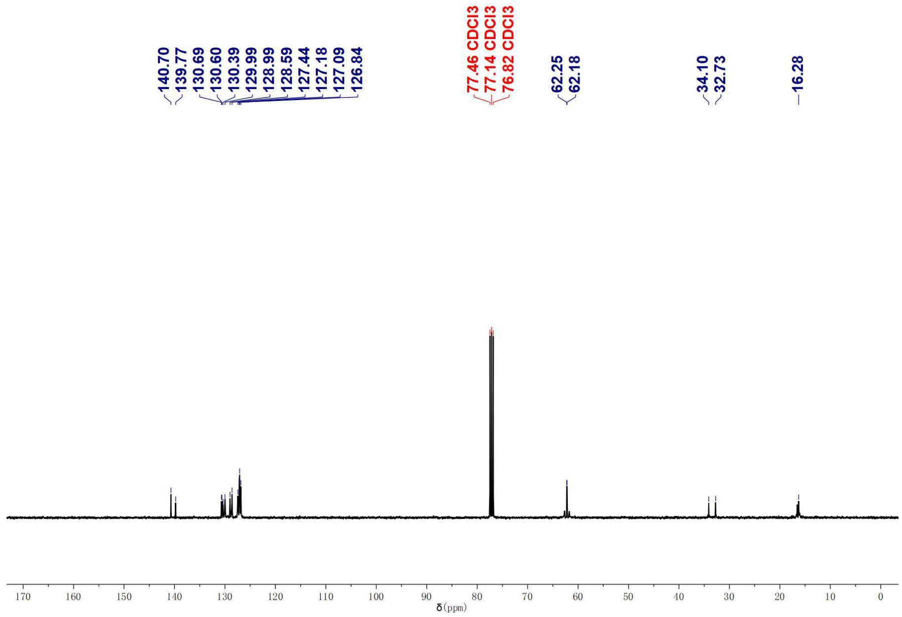


Fig. S2 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of BPP.

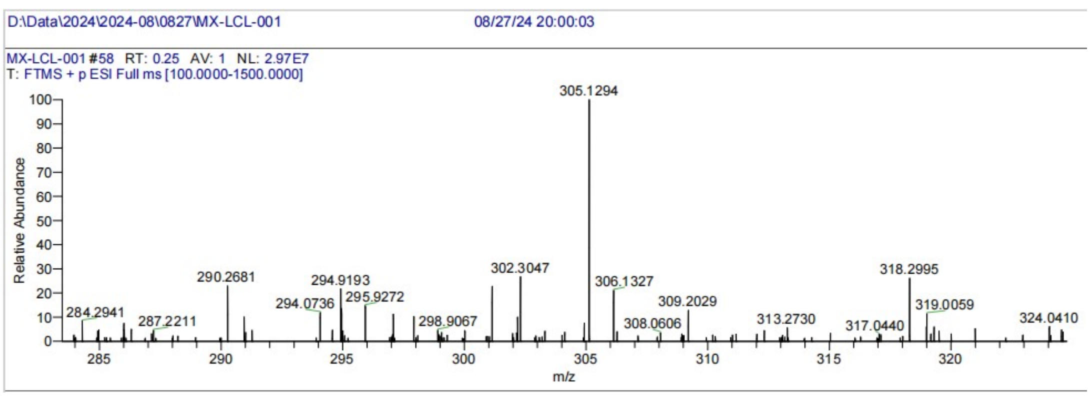


Fig. S3 HRMS (ESI) spectrum of BPP.

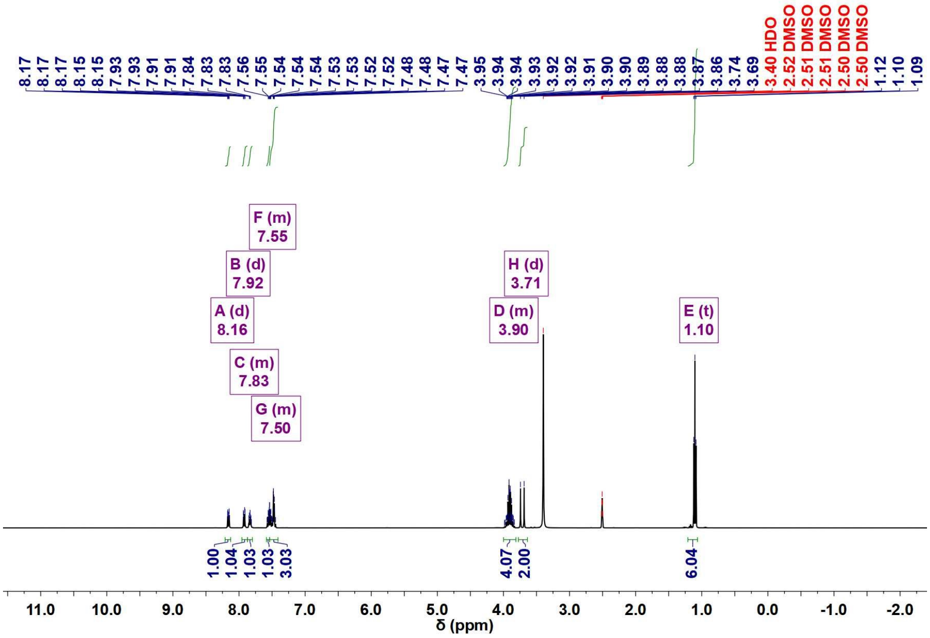


Fig. S4 ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of NaP.

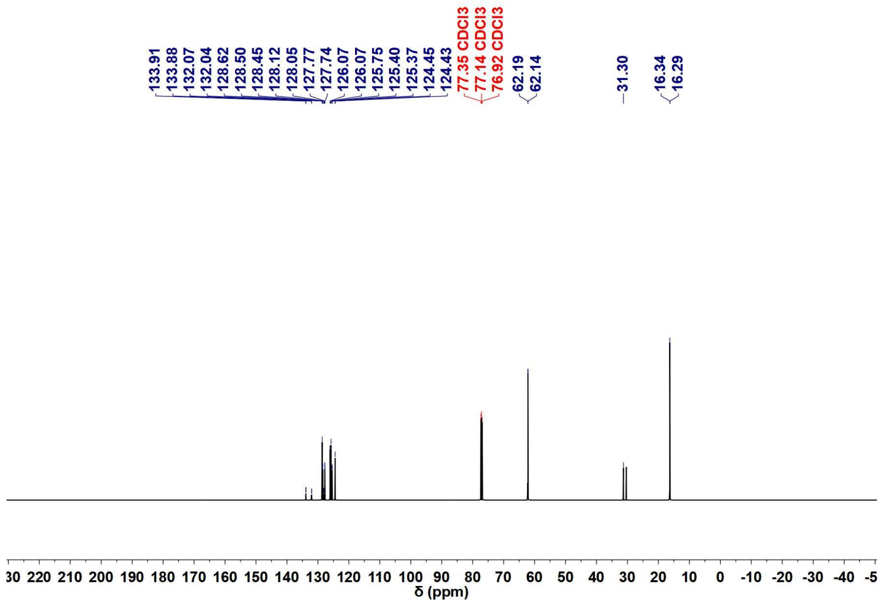


Fig. S5 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of NaP.

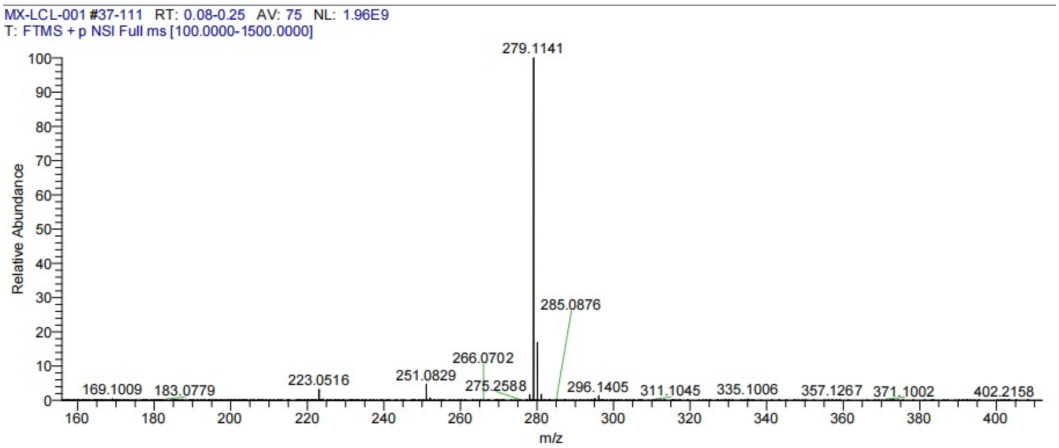


Fig. S6 HRMS (DART) spectrum of NaP.

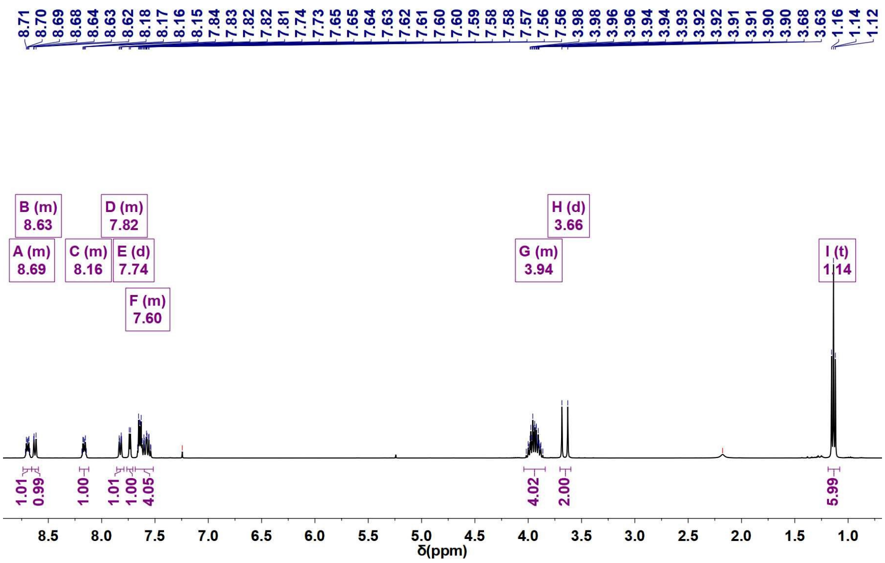


Fig. S7 ^{1}H NMR spectrum (400 MHz, $CDCl_3$) of PheP.

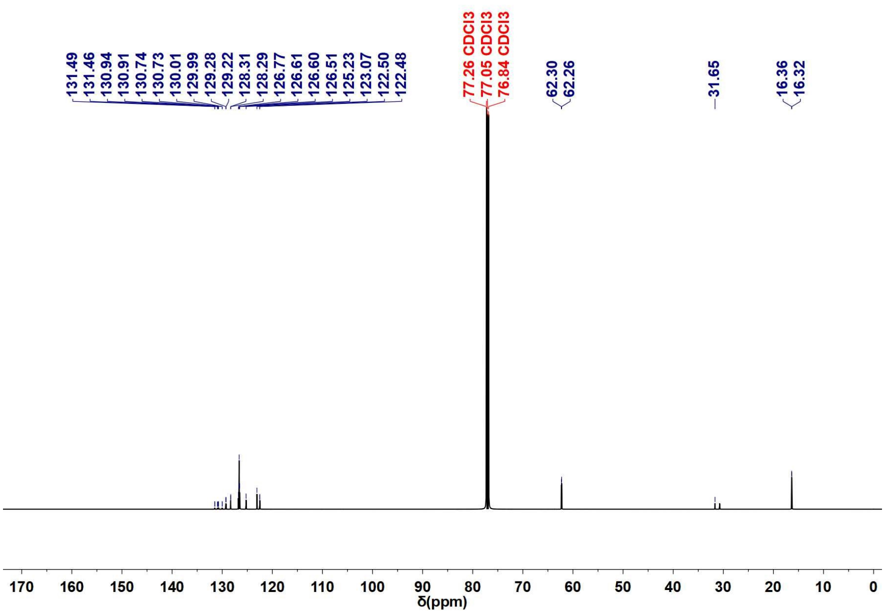


Fig. S8 ^{13}C NMR spectrum (101 MHz, $CDCl_3$) of PheP.

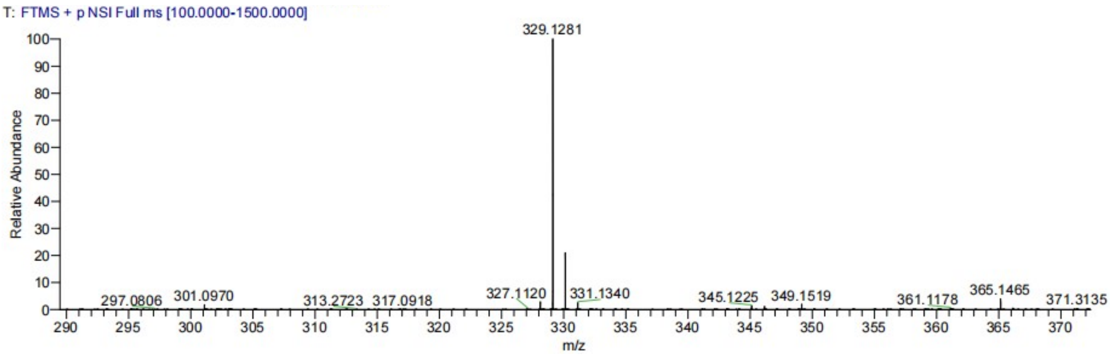


Fig. S9 HRMS (DART) spectrum of PheP.

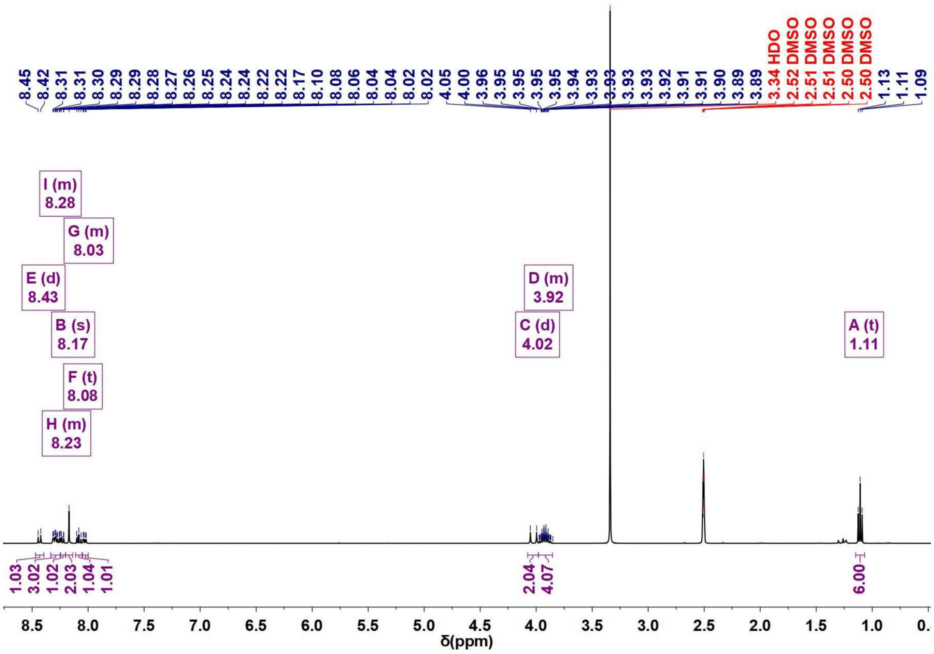


Fig. S10 ^{1}H NMR spectrum (400 MHz, DMSO-d_6) of PyP.

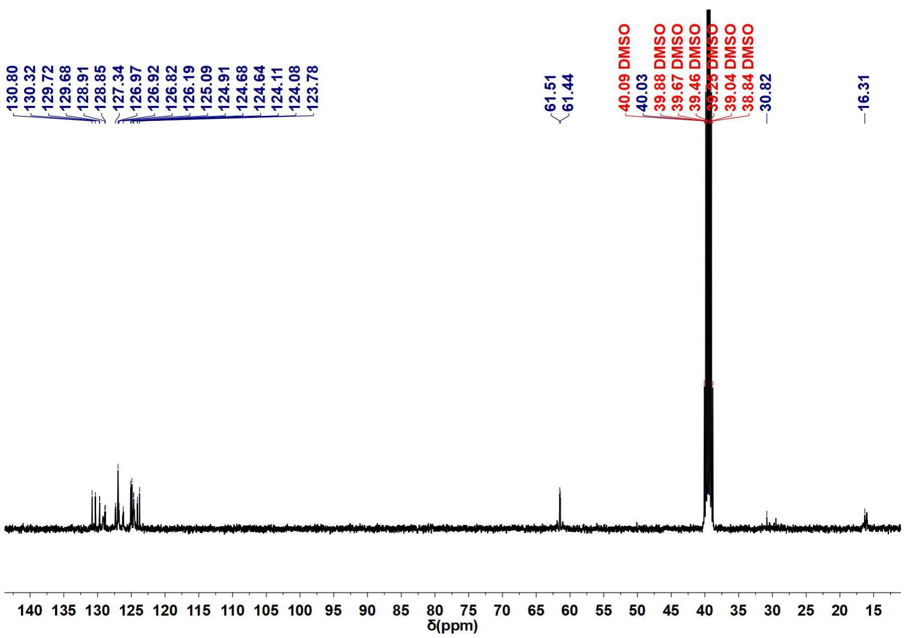


Fig. S11 ^{13}C NMR spectrum (101 MHz, DMSO-d_6) of PyP.

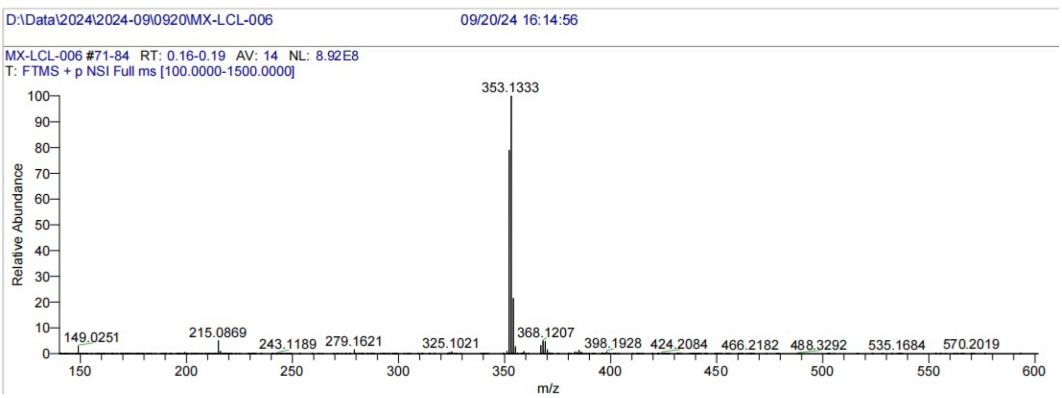


Fig. S12 HRMS (DART) spectrum of PyP.

2. Supplementary explanations for photoluminescent properties.

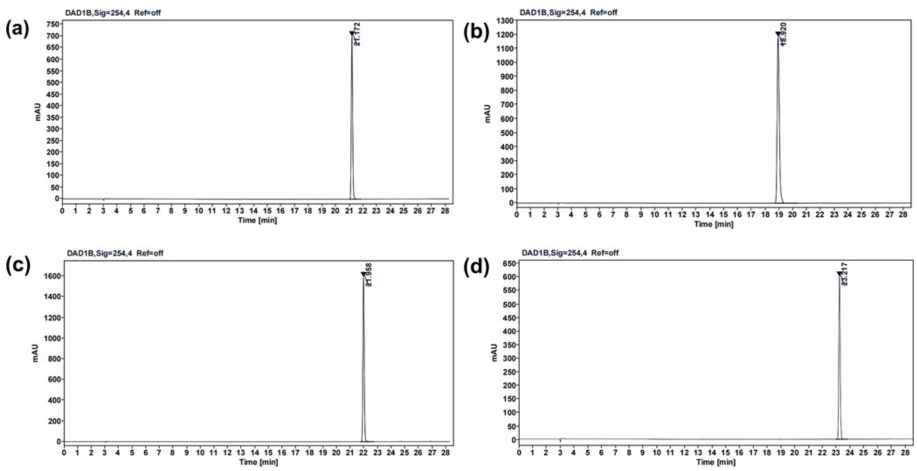


Fig. S13 High-performance liquid chromatography (HPLC) of (a) BPP, (b) NaP, (c) PheP and (d) PyP.

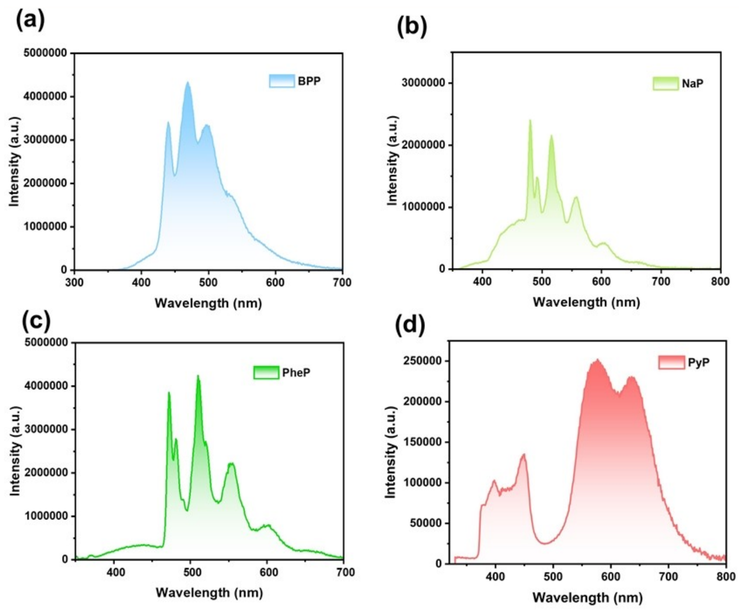


Fig. S14 The delayed spectra of 2-methyltetrahydrofuran solution of (a) BPP (λ_{ex} = 254 nm), (b) NaP (λ_{ex} = 280 nm) and (c) PheP (λ_{ex} = 250 nm); (d) The delayed spectrum of 1,4-Dioxane solution of PyP (λ_{ex} = 310 nm) (delay time = 0.1 ms).

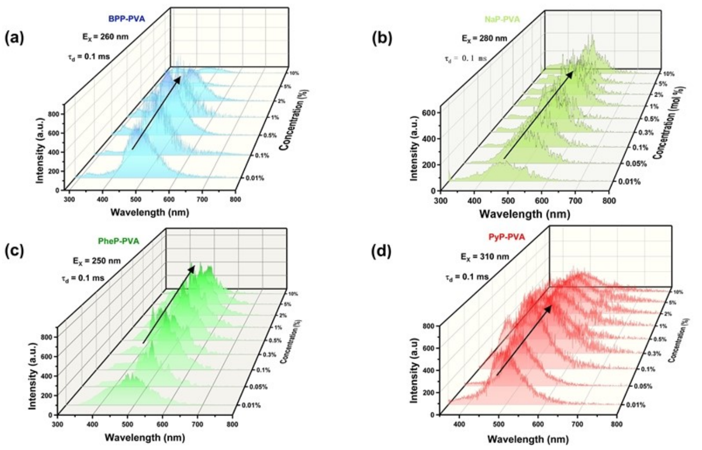


Fig. S15 Delayed emission spectra of the four doped films with different concentration (a) BPP-PVA; (b) NaP-PVA; (c) PheP-PVA; (d) PyP-PVA.

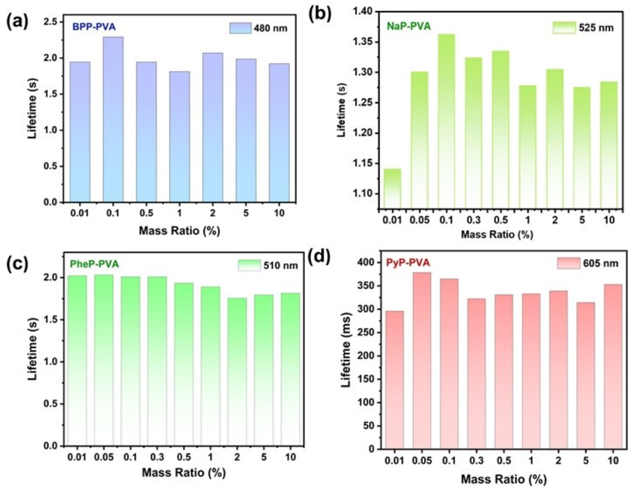


Fig. S16 Lifetime decay curves of the four doped films with different concentration: (a) BPP-PVA (λ_{ex} = 254 nm); (b) NaP-PVA (λ_{ex} = 280 nm); (c) PheP-PVA (λ_{ex} = 250 nm); (d) PyP-PVA (λ_{ex} = 305 nm).

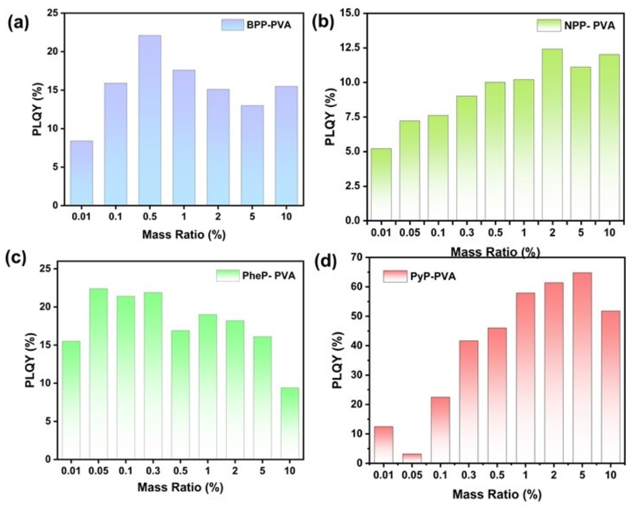


Fig. S17 The PLQY of the four doped films with different concentration: (a) BPP-PVA (λ_{ex} = 254 nm); (b) NaP-PVA (λ_{ex} = 280 nm); (c) PheP-PVA (λ_{ex} = 250 nm); (d) PyP-PVA (λ_{ex} = 305 nm).

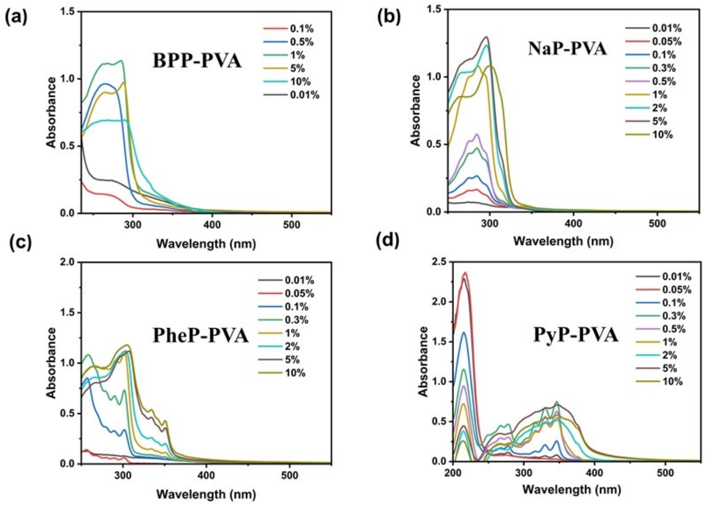


Fig. S18 The UV-vis absorbance spectra of the four doped films with different concentration: (a) BPP-PVA; (b) NaP-PVA; (c) PheP-PVA; (d) PyP-PVA

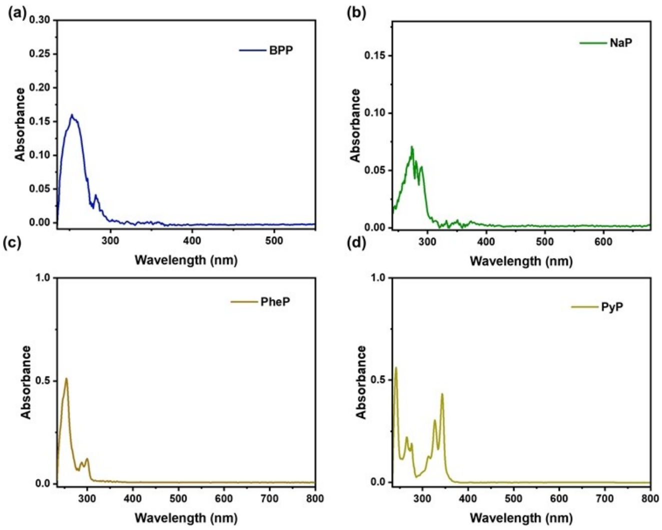


Fig. S19 The UV-vis absorbance spectra of four luminophores in tetrahydrofuran solution: (a) BPP; (b) NaP; (c) PheP; (d) PyP (10 μM).

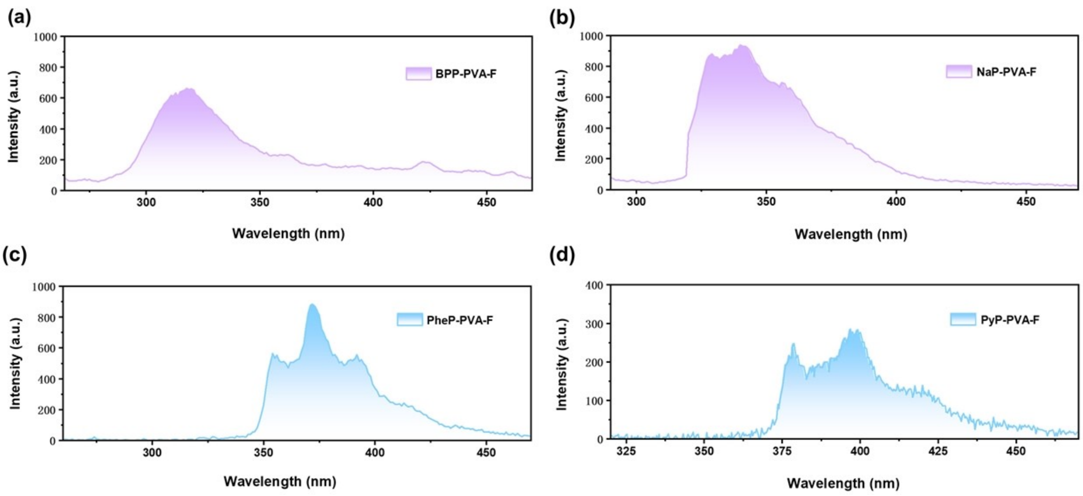


Fig. S20 The fluorescence spectra of the four doped films: (a) BPP-PVA (λ_{ex} = 254 nm); (b) NaP-PVA (λ_{ex} = 280 nm); (c) PheP-PVA (λ_{ex} = 250 nm); (d) PyP-PVA (λ_{ex} = 305 nm).

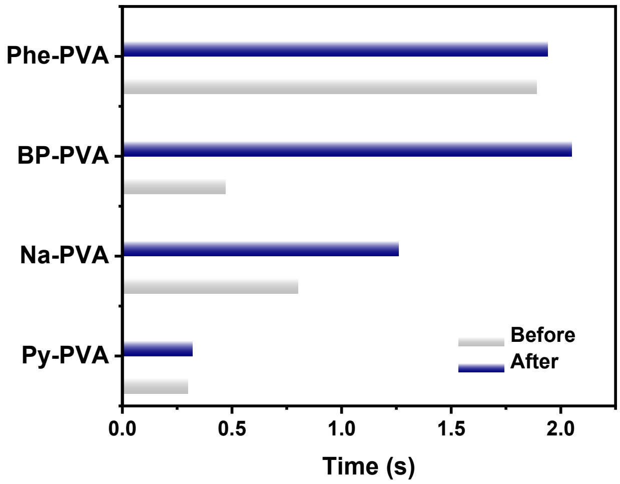


Fig. S21 Phosphorescence lifetime of doped systems before and after diethyl phosphite functionalization.

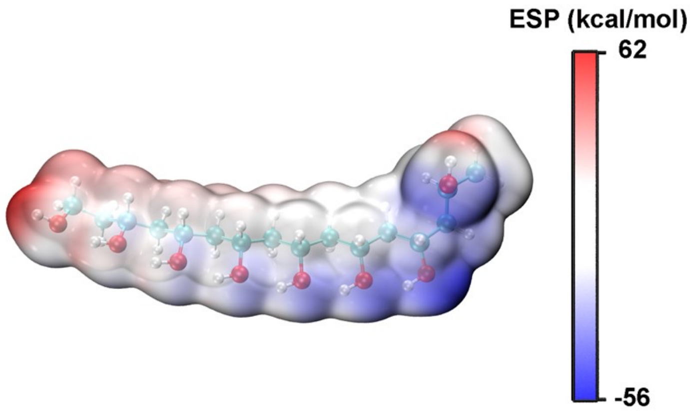


Fig. S22 ESP distribution of pure PVA.

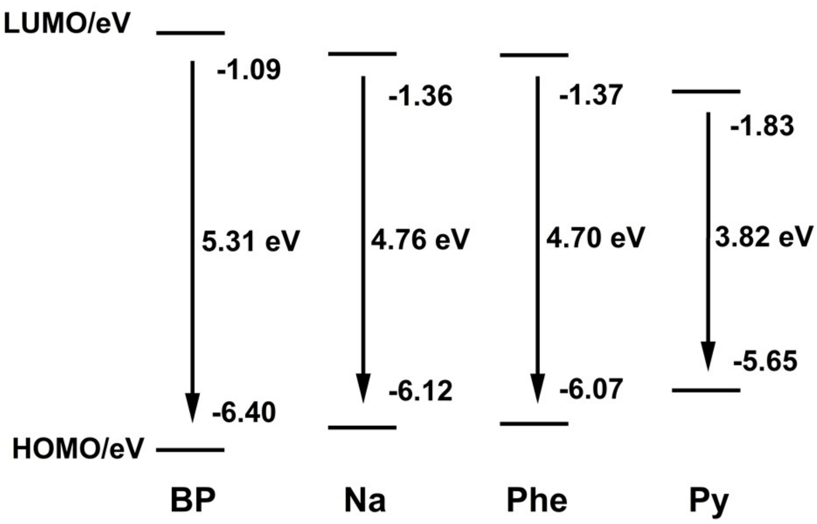


Fig. S23 Frontier molecular orbital analysis of four luminophores BP, Na, Phe and Py.

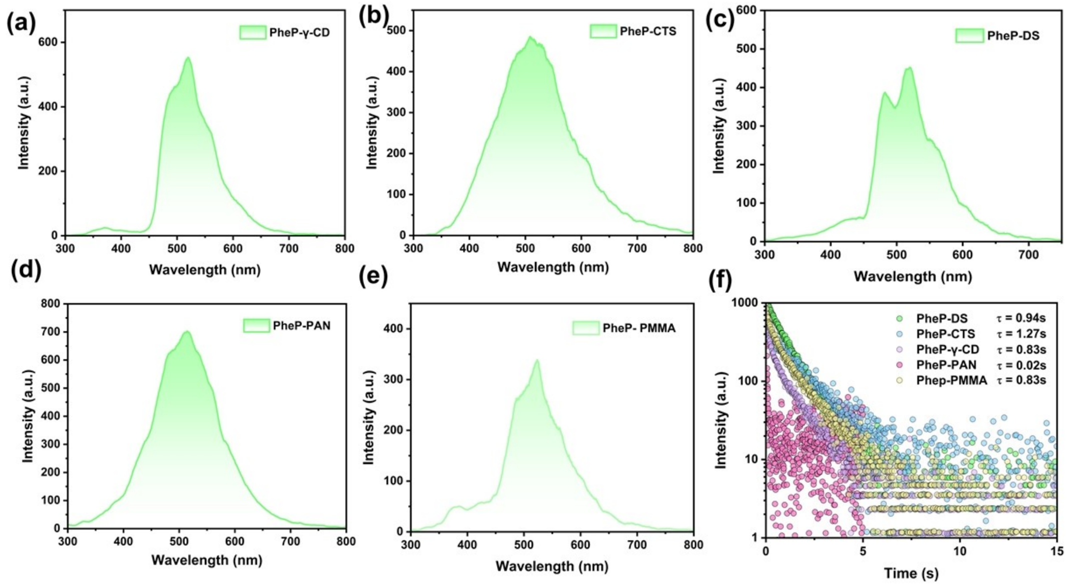


Fig. S24 Delayed emission spectra of (a) PheP-γ-CD, (b) PheP-CTS, (c) PheP-DS, (d) PheP-PAN and (e) PheP-PMMA (under UV irradiation for 15 s); (f) Lifetime decay curves of the doped systems (λ_{ex} = 250 nm), (delay time = 10 ms).

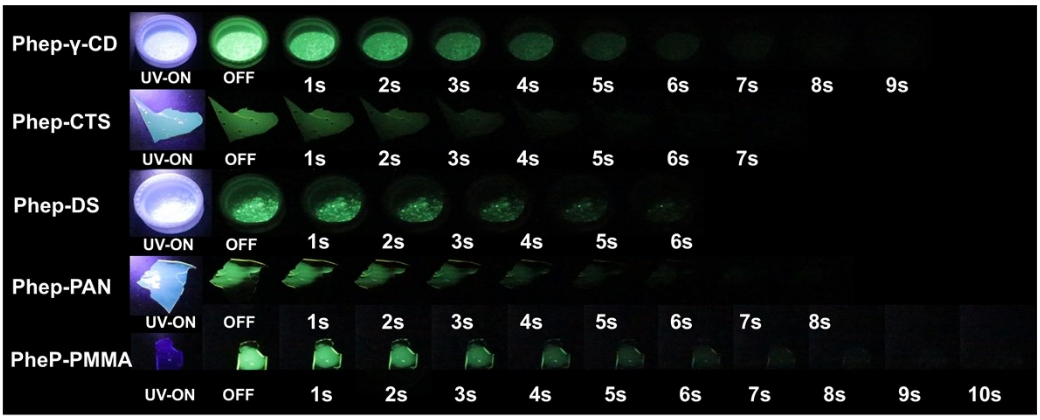


Fig. S25 Photographs of the luminescence of doped systems. (λ_{ex} = 254 nm).

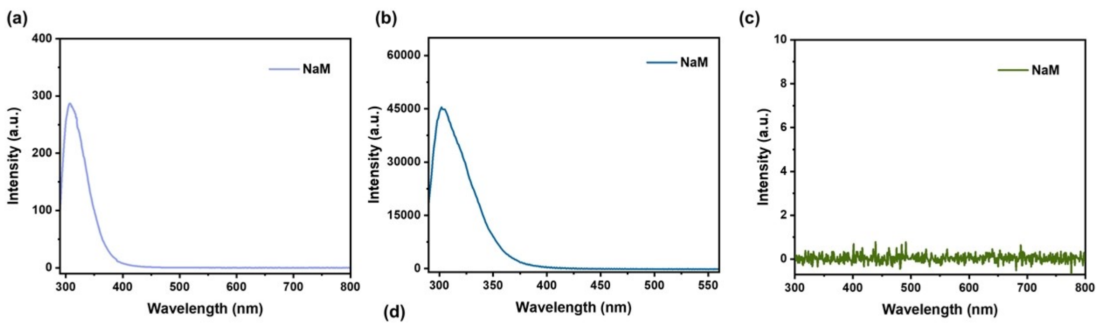


Fig. S26 The (a) fluorescence spectra, (b) photoluminescence spectra and (c) delayed emission spectra of NaM in tetrahydrofuran solution (λ_{ex} = 280 nm), (delay time = 0.1 ms).

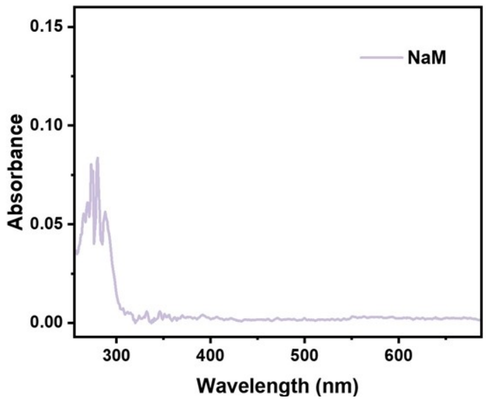


Fig. S27 The UV-vis absorbance spectra of NaM in tetrahydrofuran solution (10 μM).

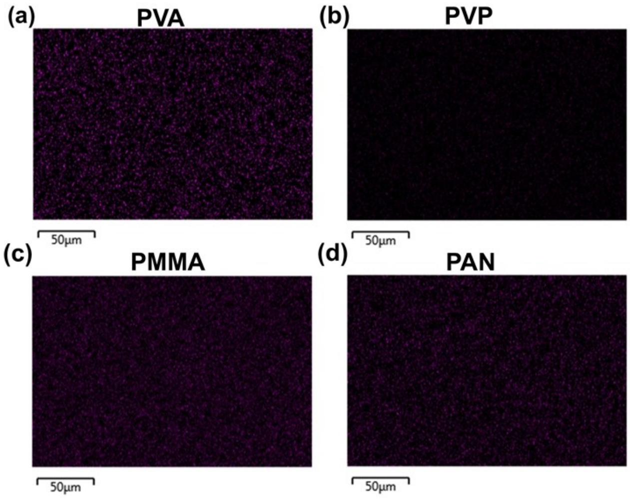


Fig. S28 EDS mapping of P element in (a) NaP-PVA, (b) NaP-PVP, (c) NaP-PMMA and (d) NaP-PAN.

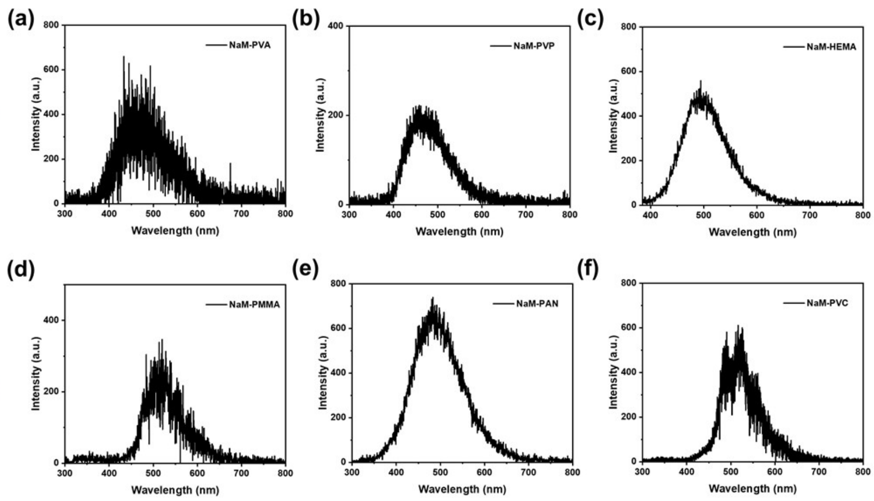


Fig. S29 Delayed emission spectra of (a) NaM-PVA, (b) NaM-PVP, (c) NaM-HEMA, (d) NaM-PMMA, (e) NaM-PAN and (f) NaM-PVC (λ_{ex} = 280 nm, delay time = 0.10 ms).

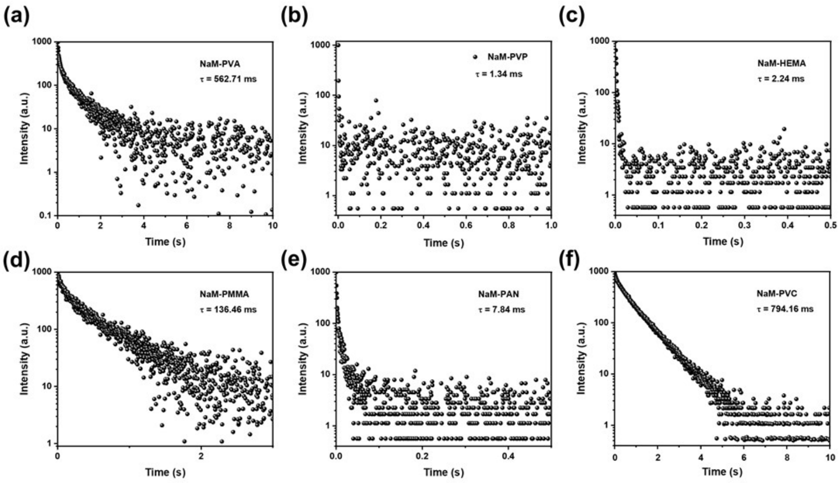


Fig. S30 Lifetime decay curves of (a) NaM-PVA, (b) NaM-PVP, (c) NaM-HEMA, (d) NaM-PMMA, (e) NaM-PAN and (f) NaM-PVC (λ_{ex} = 280 nm, delay time = 0.10 ms).

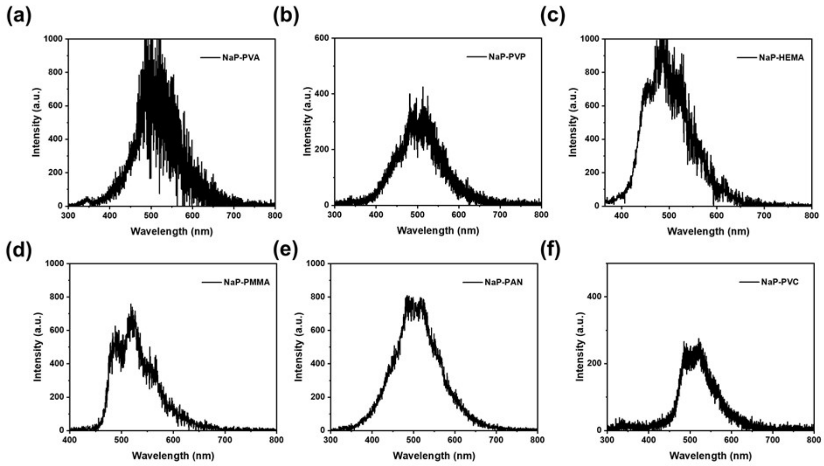


Fig. S31 Delayed emission spectra of (a) NaP-PVA, (b) NaP-PVP, (c) NaP-HEMA, (d) NaP-PMMA, (e) NaP-PAN and (f) NaP-PVC (λ_{ex} = 280 nm, delay time = 0.10 ms).

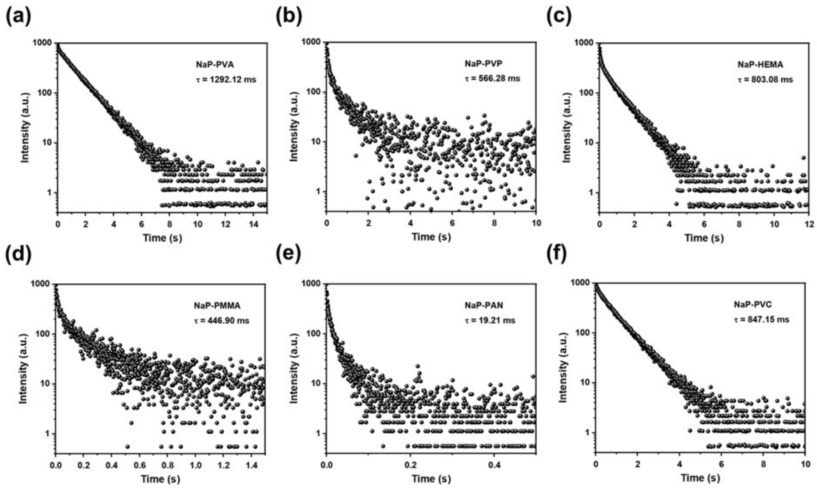


Fig. S32 Lifetime decay curves of (a) NaP-PVA, (b) NaP-PVP, (c) NaP-HEMA, (d) NaP-PMMA, (e) NaP-PAN and (f) NaP-PVC (λ_{ex} = 280 nm, delay time = 0.10 ms).

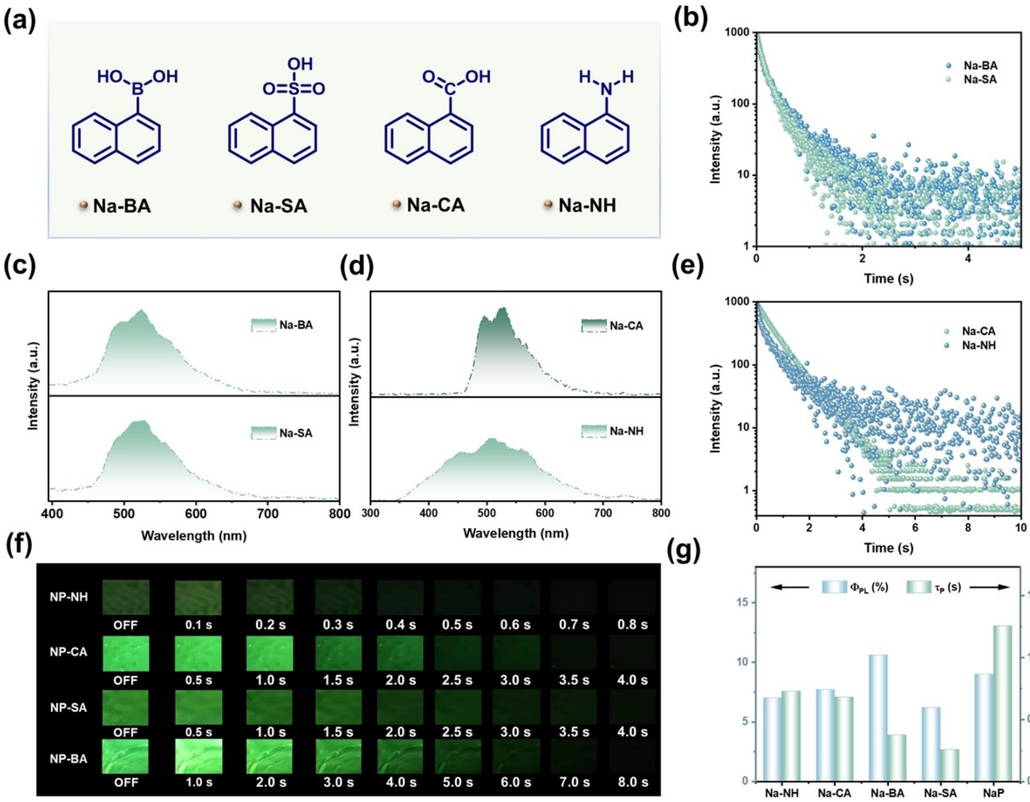


Fig. S33 (a) Chemical structure of luminophores; (b) and (e) Lifetime decay curves of doped systems; (c) and (d) Delayed emission spectra of doped systems; (f) Photographs of luminescence of doped systems; (g) Photoluminescence quantum yield and lifetime of doped systems. (λ_{ex} = 280 nm, delay time = 0.10 ms)

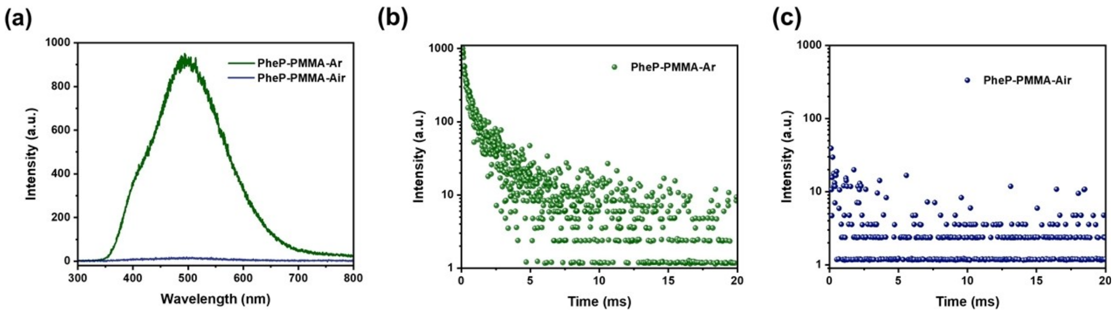


Fig. S34 (a) Delayed emission spectra of PheP-PMMA in Ar and Air (λ_{ex} = 254 nm, slit width = 20 nm, voltage = 680 V, delay time = 0.10 ms); (b) Lifetime decay curves of PheP-PMMA in Ar and Air. (λ_{ex} = 254 nm, delay time = 0.10 ms).

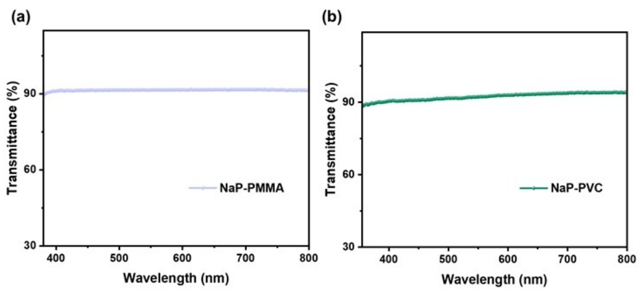


Fig. S35 Transmittance spectra of NaP-PMMA (thickness = 0.10 mm) and NaP-PVC (thickness = 0.10 mm).

Table S1. The theoretical calculation parameters of luminophores.

	ΔE_{ST}/eV[a]	SOC/cm^{-1}[b]
BPP	S_1-T_7 = 0.0936	S_1-T_7 = 0.445
NaP	S_1-T_3 = 0.0995	S_1-T_3 = 0.437
PheP	S_1-T_2 = 0.4619	S_1-T_2 = 0.041
PyP	S_1-T_3 = 0.0414	S_1-T_3 = 0.253
BP	S_1-T_7 = 0.1789	S_1-T_7 = 0.150
Na	S_1-T_3 = 0.1572	S_1-T_3 = 0.060
Phe	S_1-T_2 = 0.4962	S_1-T_2 = 0.000
Py	S_1-T_4 = 0.086	S_1-T_4 = 0.040

[a] ΔE_{ST} was based on theoretical calculations. [b] SOC is for spin-orbit coupling.