

Organic room-temperature phosphorescent polymers for efficient X-ray scintillation and imaging

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Experimental Section

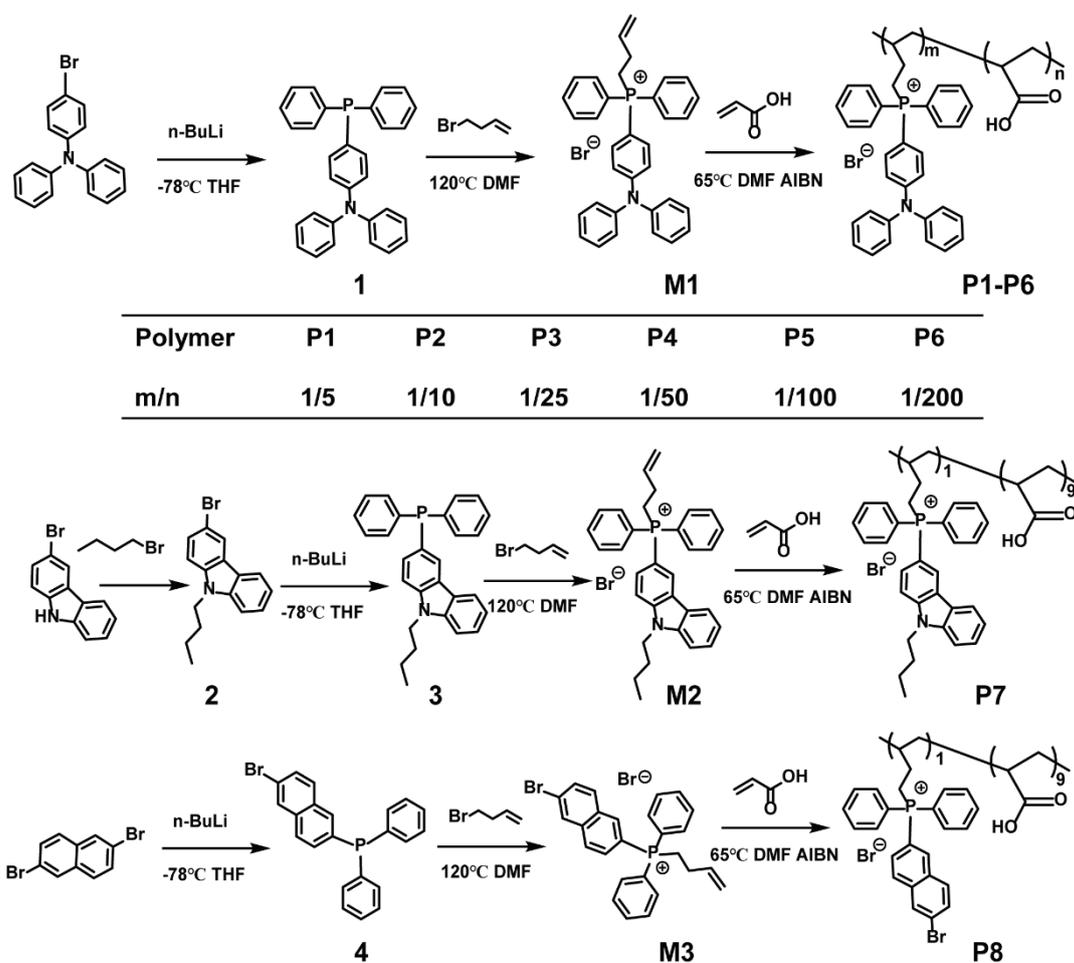
Reagents and Materials

Unless otherwise noted, all starting materials and reagents are commercially available and used without further purification. For column chromatography, silica gel with 200 ~ 300 mesh was used.

Measurements

^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded on a Bruker ACF400 spectrometer at 298 K using deuterated solvents ($\text{DMSO-}d_6$). The UV-visible absorption spectra were measured by Shimadzu UV-2600 UV-vis spectrophotometer. The steady-state fluorescence and phosphorescence spectra were measured using Hitachi F-4700. The lifetimes were obtained on an Edinburgh FLS980 fluorescence spectrophotometer equipped with a Xenon arc lamp (Xe900) and a microsecond flash-lamp (uF900). The powder X-ray diffraction patterns were collected by D8 Advanced (Bruker) using $\text{Cu-K}\alpha$ radiation. Aqueous gel permeation chromatography (GPC) was performed on a Series Samples used 0.05 mol/L THF as mobile phase at 1.0 mL min^{-1} flow rate. PMMA was used as the calibration standard.

Synthesis and characterization



Scheme S1. Synthetic route of **M1**, **M2**, **M3**, and **P1-P8**.

Synthesis of **M1**:

In nitrogen atmosphere, 4-bromotriphenylamine (5 g, 15.42 mmol) was added into the mixture *n*-BuLi (7.4 mL, 18.50 mmol) and dry THF (40 mL) at -78 °C for 2 h. Then chlorodiphenylphosphine (3.4 g, 15.42 mmol) was added into the mixture. The reaction at 25 °C for 24 h. **1** was purified through column chromatography, yield 58%. In nitrogen atmosphere, **1** (2 g, 4.66 mmol) was added into the mixture of 4-bromo-1-butene (0.77 g, 5.59 mmol) and DMF (20 mL). The reaction was at 120 °C for 24 h. The **M1** was purified through column chromatography, yield 85%. ¹H NMR (400 MHz, DMSO-*d*₆): δ 7.78 (s, 11H), 7.29 (s, 12H), 7.04 – 6.84 (m, 2H), 5.96 – 5.74 (m, 1H), 5.39 – 4.93 (m, 2H), 3.70 – 3.47 (m, 2H), 2.38 – 2.05 (m, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆, δ): 162.66, 153.25, 145.09, 135.43, 133.63, 130.42, 127.36, 126.48, 120.15, 119.60, 118.20, 117.07, 105.60, 104.20, 36.45, 31.24, 26.39, 20.04. ³¹P NMR (400 MHz, DMSO-*d*₆, δ): 40.16.

Synthesis of **P1-P6**:

Compound **M1** were copolymerized with acrylamide at the molar ratio of 200:1, 100:1, 50:1, 25:1, 10:1, 5:1 in order to prepare amorphous polymers (**P1–P6**). In view of the similarity of the synthesis method, **P2** was used as an example for demonstration. The polymer was prepared by copolymerization of the compound **M1** (200 mg, 0.44 mmol, 1 eq) and acrylamide (317.7 mg, 4.4mmol, 10 eq) by a radical polymerization with 2,2'-azobis(2-methylpropionitrile) (AIBN) (16 mg) as radical initiator at 65 °C under an argon atmosphere in toluene for 18 h. The resulting mixture was added into dichloromethane to precipitate polymeric materials. Precipitation was repeatedly washed with dichloromethane to give purified polymers.

Synthesis of **M2**:

First, a mixture of 3-Bromo-9H-Carbazole and 1-Bromobutane was stirred in tetrahydrofuran for 4 h. The product **2** was purified through column chroma-tography, yield 90%. In nitrogen atmosphere, 3-Bromo-9H-Carbazole (5 g, 16.56 mmol) was added into the mixture n-BiLi(7.9 mL, 19.87 mmol) and dry THF (40 mL) at -78 °C for 2 h. Then Chlorodiphenylphosphine(3.6 g, 15.56 mmol) was added into the mixture. The reaction at 25 °C for 24 h. **3** was purified through column chroma-tography, yield 60%.

In nitrogen atmosphere, **3** (2 g, 4.91 mmol) was added into the mixture of 4-Bromo-1-butene (0.81 g, 5.89 mmol).and DMF (20 mL). The reaction was at 120 °C for 24 h. The product **M2** was purified through column chroma-tography, yield 85%. ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.89 – 8.75 (m, 1H), 8.33 – 8.23 (m, 1H), 7.99 – 7.68 (m, 14H), 7.38 – 7.28 (m, 1H), 6.06 – 5.80 (m, 1H), 5.26 – 5.00 (m, 2H), 4.51 (s, 2H), 3.86 – 3.67 (m, 2H), 2.41 – 2.25 (m, 2H), 1.88 – 1.68 (m, 2H), 1.37 – 1.24 (m, 2H), 0.88 (t, J = 7.3 Hz, 3H). δ¹³C NMR (100 MHz, DMSO-*d*₆, δ):143.05, 141.59, 136.43, 135.04, 133.96, 130.38, 127.44, 123.53, 122.12, 120.88, 119.75, 177.14, 111.81, 110.59, 105.60, 31.26, 26.25, 20.38, 14.00. ³¹P NMR (400 MHz, DMSO-*d*₆, δ): 41.83.

Synthesis of **P7**:

Compound **M2** were copolymerized with acrylamide at the molar ratio of 10:1 in order to prepare amorphous polymers (**P7**). The polymer was prepared by copolymerization of the compound **M2** (200 mg, 0.43 mmol, 1 eq) and acrylic acid (312 mg, 4.3mmol, 10 eq) by a radical polymerization with 2,2'-azobis(2-methylpropionitrile) (AIBN) (16 mg) as radical initiator at 65 °C under an argon atmosphere in toluene for 18 h. The resulting mixture was added into dichloromethane to precipitate polymeric materials. Precipitation was repeatedly washed with dichloromethane to give purified polymers.

Synthesis of **M3**:

In nitrogen atmosphere, 2,6-Dibromonaphthalene (5 g, 17.48 mmol) was added into the mixture n-BiLi(8.4 mL, 20.97 mmol) and dry THF (40 mL) at -78 °C for 2 h. Then Chlorodiphenylphosphine(4.4 g, 20.32 mmol) was added into the mixture. The reaction at 25 °C for 24 h. Product **4** was purified through column chroma-tography, yield 60%.

In nitrogen atmosphere, Product **4** (2 g, 5.11 mmol) was added into the mixture of 4-Bromo-1-butene (1.35 g, 6.13 mmol).and DMF (20 mL). The reaction was at 120 °C for 24 h. The product **M3** was purified through column chroma-tography, yield 85%. ¹H NMR (400 MHz, DMSO-*d*₆): δ 8.67 – 8.54 (m, 1H), 8.53 – 8.39 (m, 1H), 8.32 – 8.24 (m, 1H), 8.16 – 8.11 (m, 1H), 7.94 – 7.76 (m, 13H), 6.04 – 5.80 (m, 1H), 5.27 – 5.03 (m, 2H), 3.90 – 3.69 (m, 2H), 2.42 – 2.22 (m, 2H). ¹³C NMR (100 MHz, DMSO-*d*₆, δ):140.61, 137.22, 136.12, 135.69, 134.11, 133.41, 130.70, 129.48, 128.19, 119.63, 118.78, 117.12, 116.35, 65.33, 26.08, 20.01, 19.44, 15.82, 14.20. ³¹P NMR (400 MHz, DMSO-*d*₆, δ): 42.23.

Synthesis of **P8**:

Compound **M3** were copolymerized with acrylamide at the molar ratio of 10:1 in order to prepare amorphous polymers (**P8**). The polymer was prepared by copolymerization of the compound **M3** (200 mg, 0.448 mmol, 1 eq) and acrylic acid (322mg, 4.48 mmol, 10 eq) by a radical polymerization with 2,2'-azobis(2-methylpropionitrile) (AIBN) (17 mg) as radical initiator at 65 °C under an argon atmosphere in toluene for 18 h. The resulting mixture was added into dichloromethane to precipitate polymeric materials. Precipitation was repeatedly washed with dichloromethane to give purified polymers.

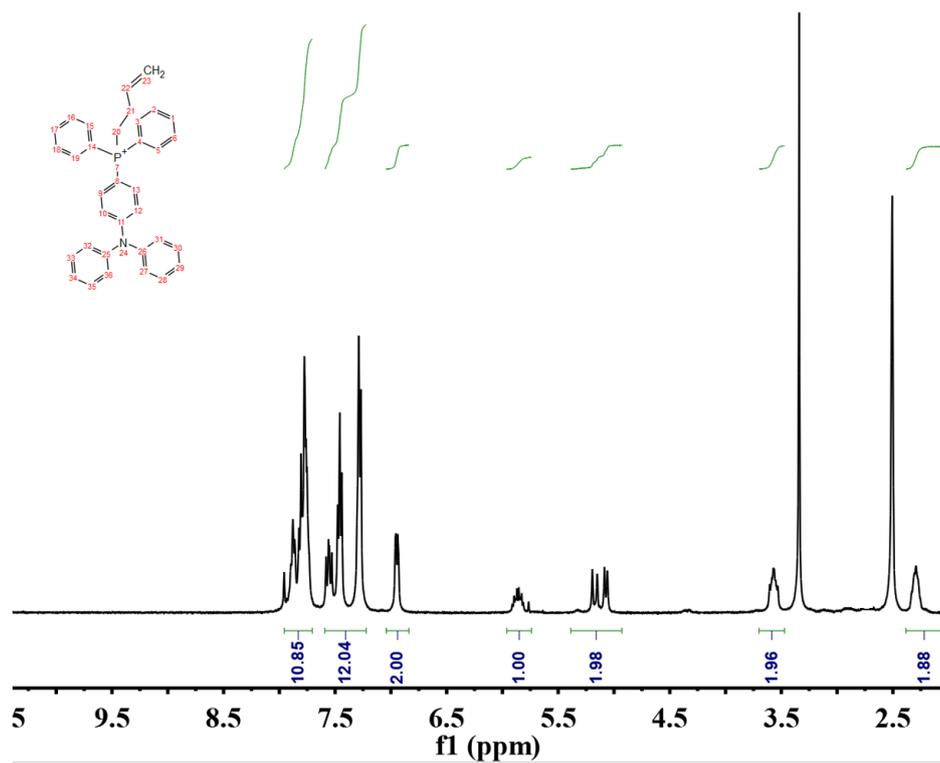


Fig.S1 ^1H NMR spectrum of M1 in $\text{DMSO-}d_6$.

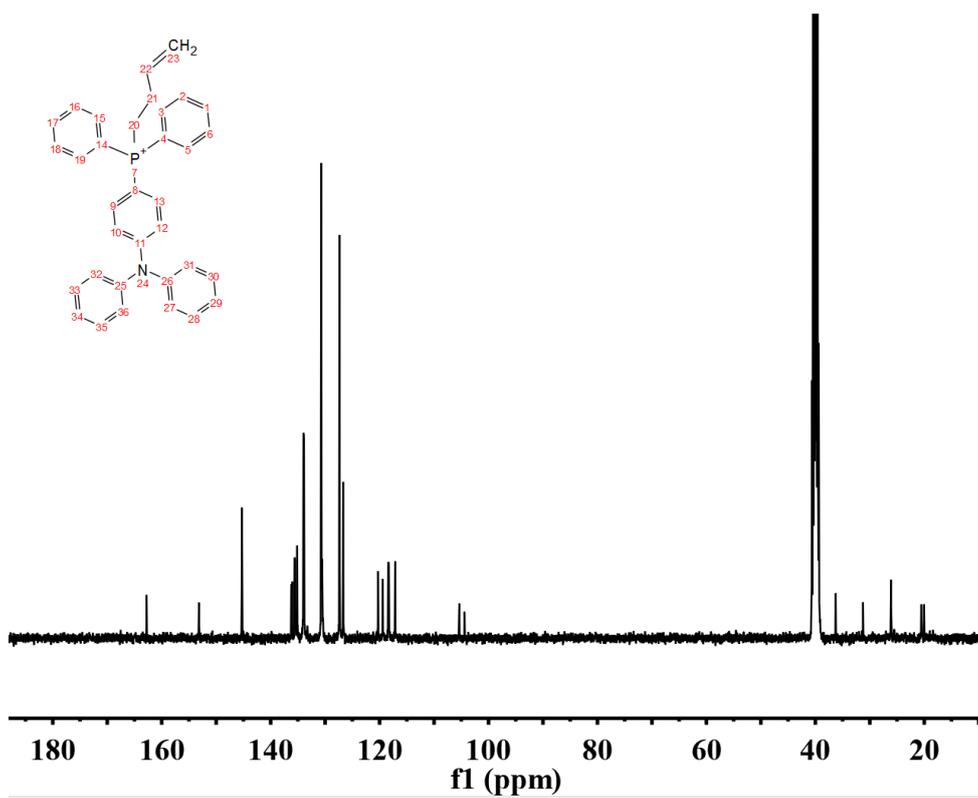


Fig. S2 ^{13}C NMR spectrum of M1 in $\text{DMSO-}d_6$.

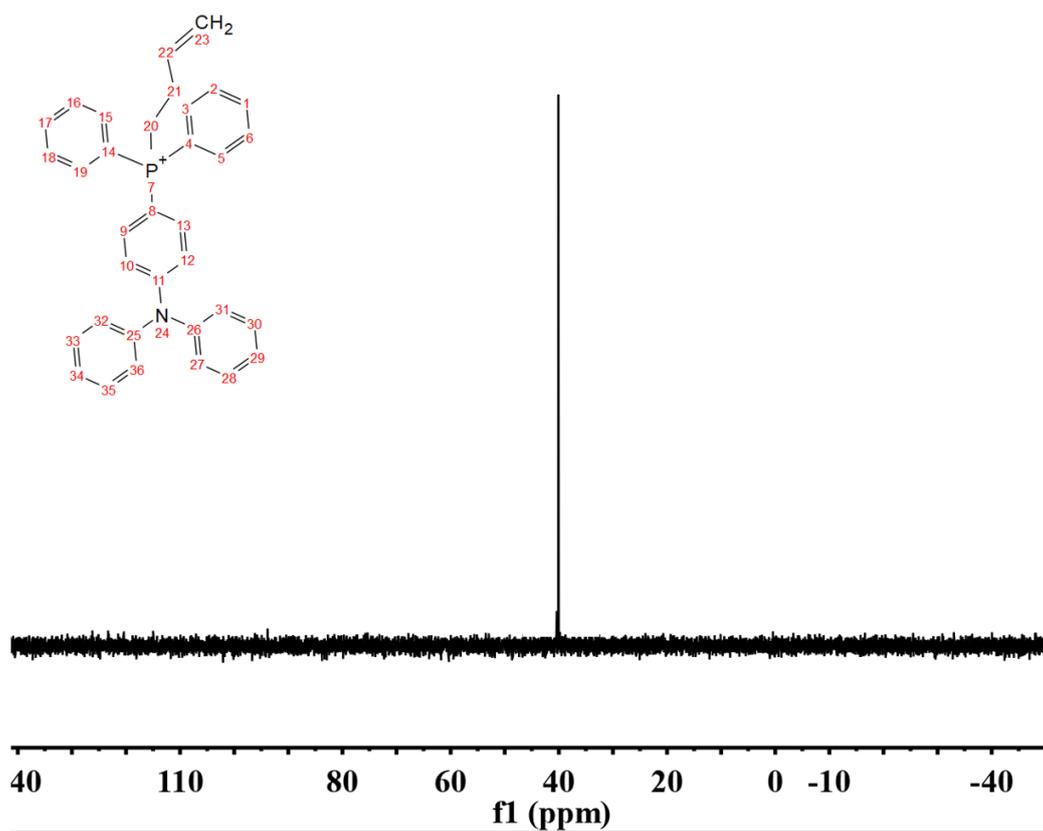


Fig. S3 ^{31}P NMR spectrum of M1 in DMSO- d_6 .

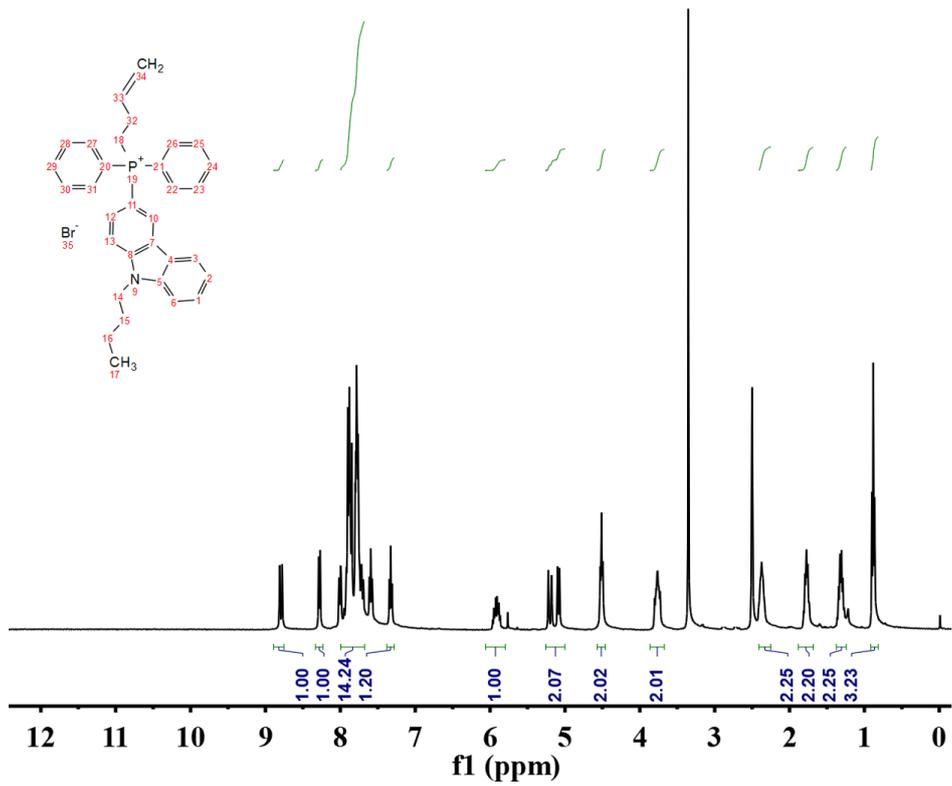


Fig. S4 ^1H NMR spectrum of M2 in $\text{DMSO-}d_6$.

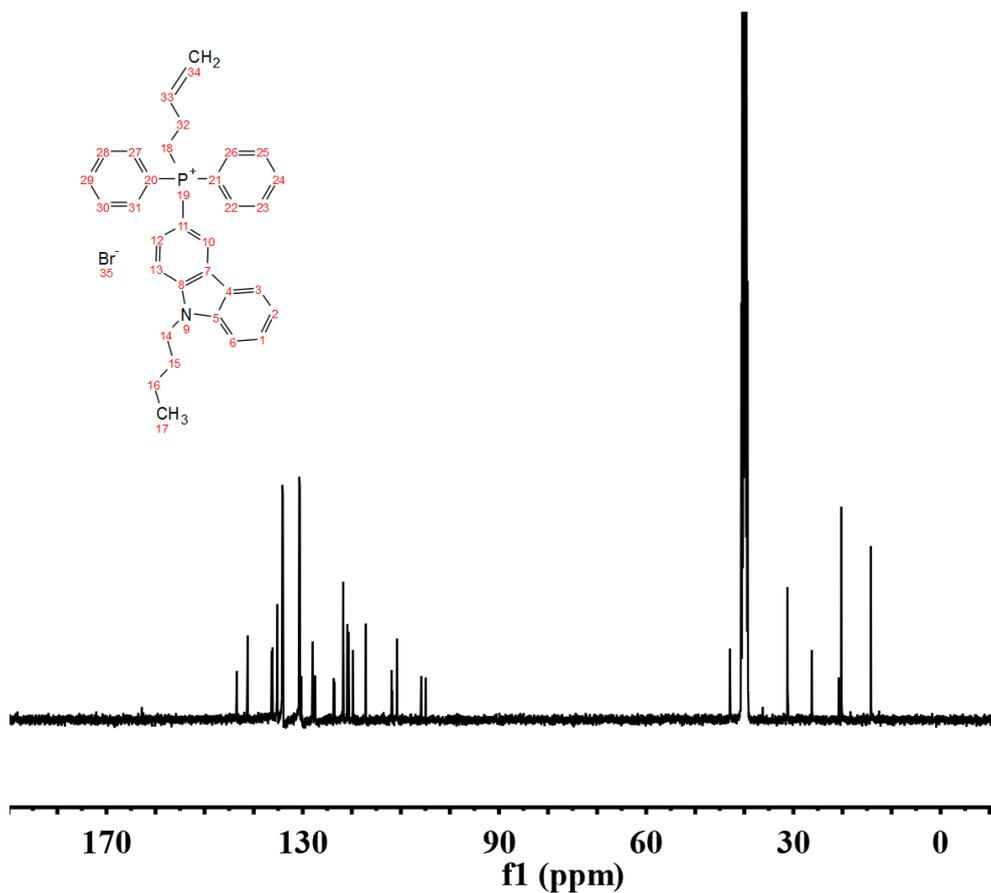


Fig. S5 ^{13}C NMR spectrum of M2 in $\text{DMSO-}d_6$.

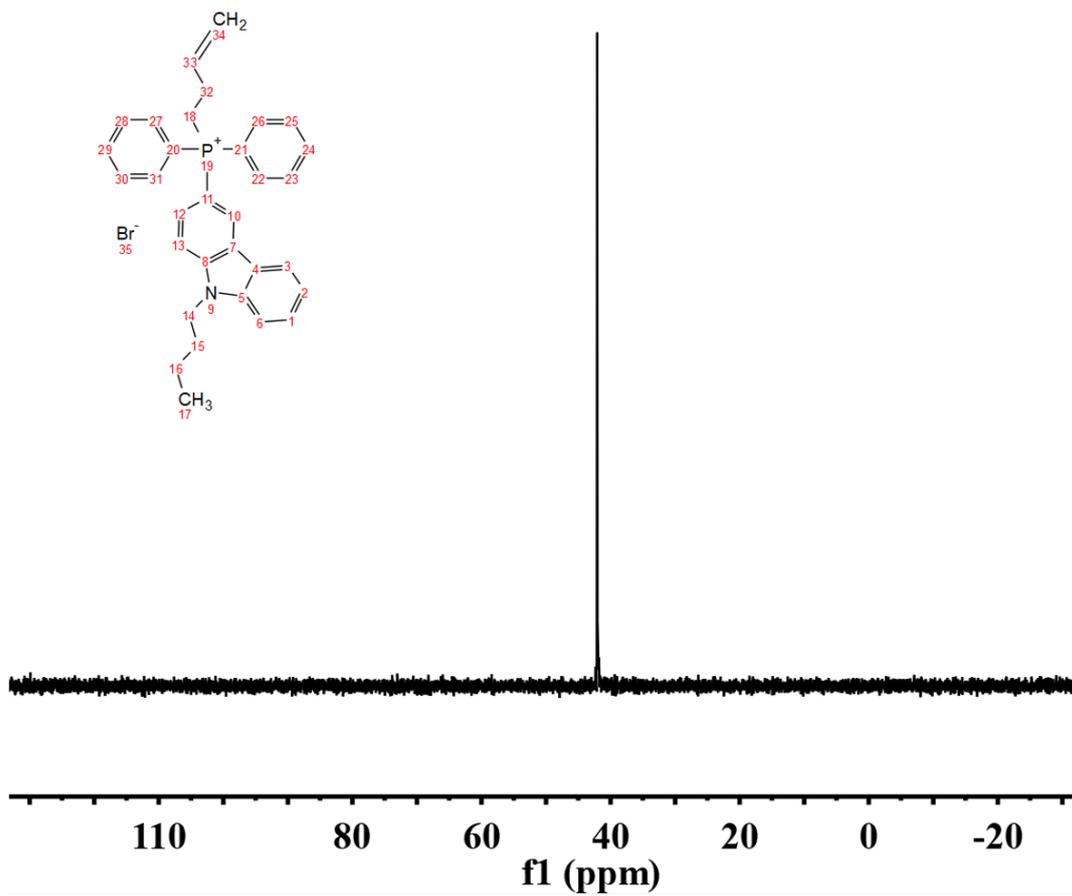


Fig. S6 ^{31}P NMR spectrum of M2 in DMSO- d_6 .

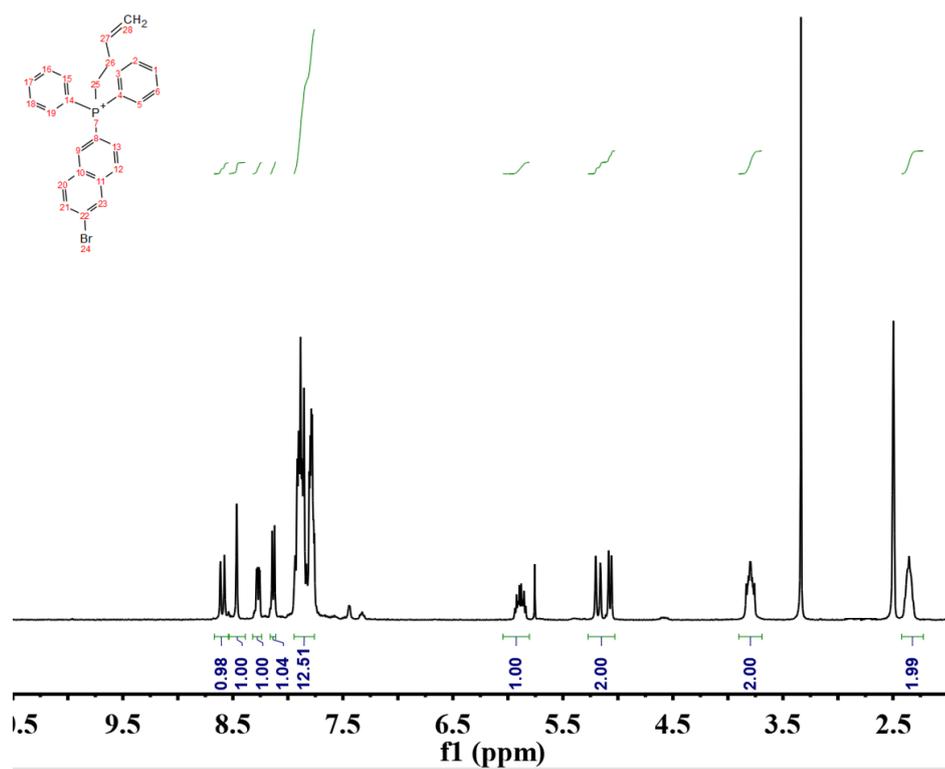


Fig. S7 ^1H NMR spectrum of **M3** in $\text{DMSO-}d_6$.

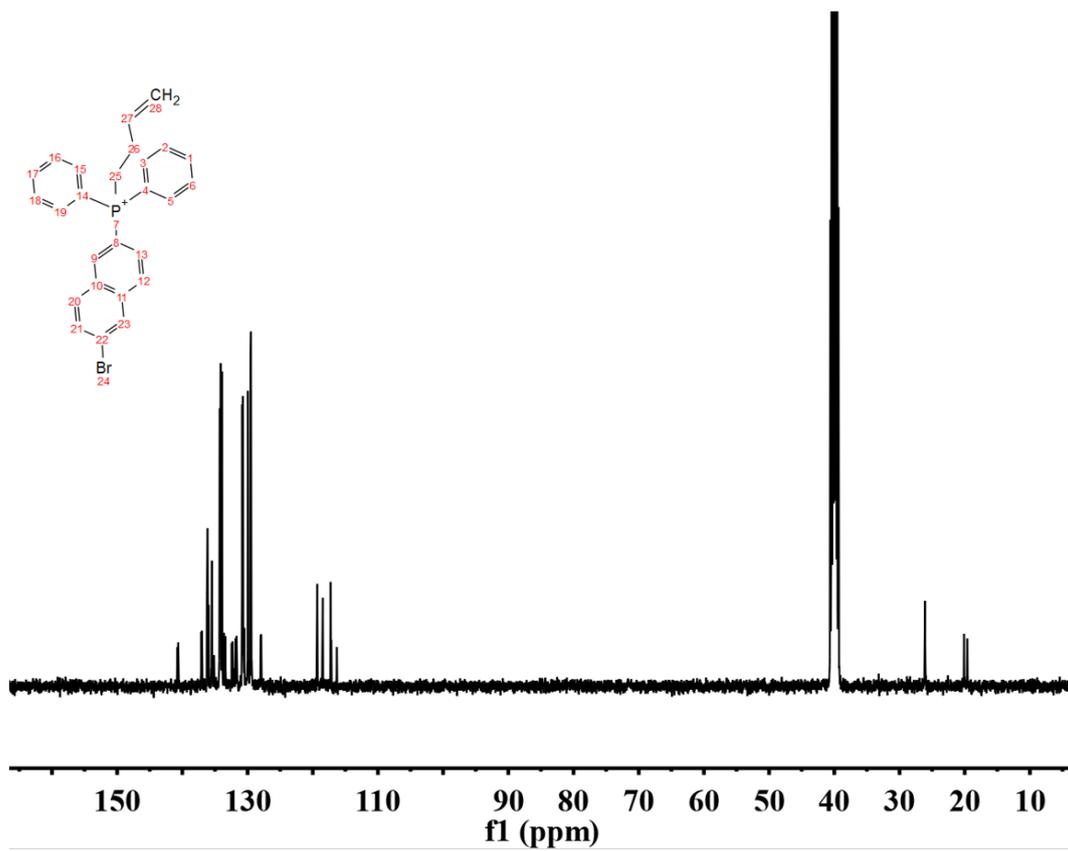


Fig. S8 ^{13}C NMR spectrum of M3 in $\text{DMSO-}d_6$.

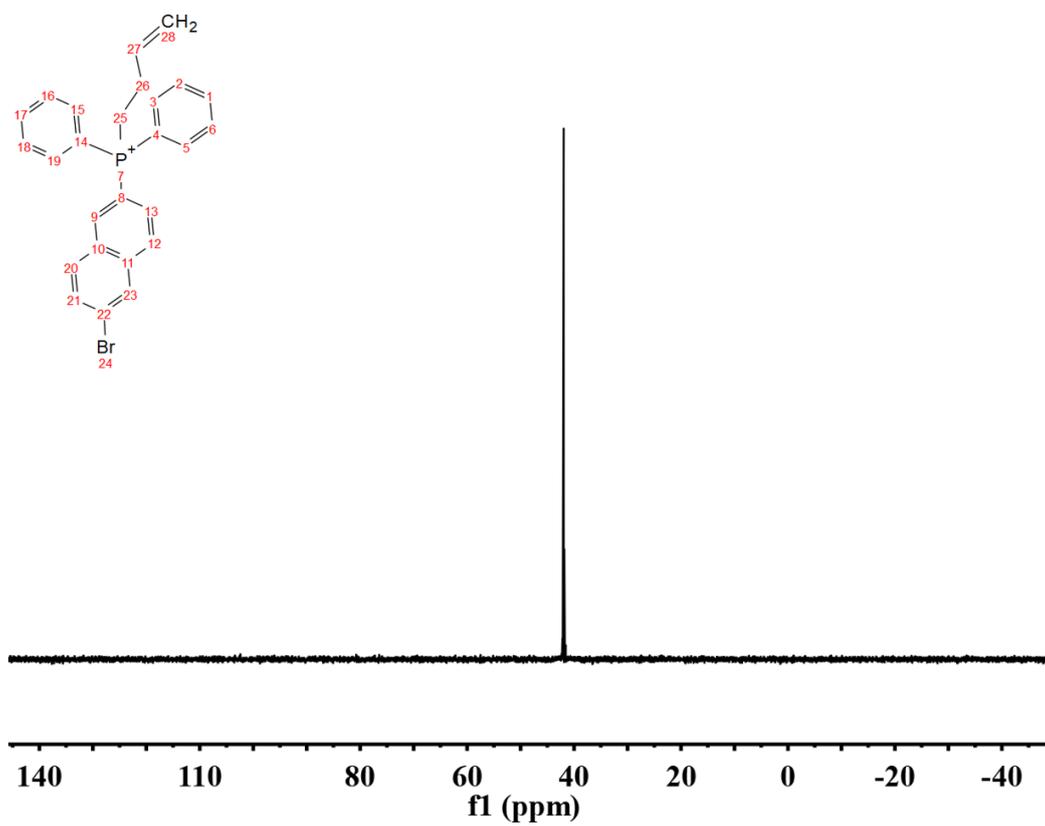


Fig. S9 ^{31}P NMR spectrum of M3 in $\text{DMSO-}d_6$.

Table S1. Characterizations of polymers **P1-P8**.

Samples	Mw (Da)	Mn (Da)	PDI
P1	23241	19036	1.21950
P2	27166	24956	1.08855
P3	31585	24956	1.06591
P4	36587	32632	1.12113
P5	40035	38949	1.02788
P6	43992	42328	1.15632
P7	25376	24383	1.04072
P8	29537	26109	1.13129

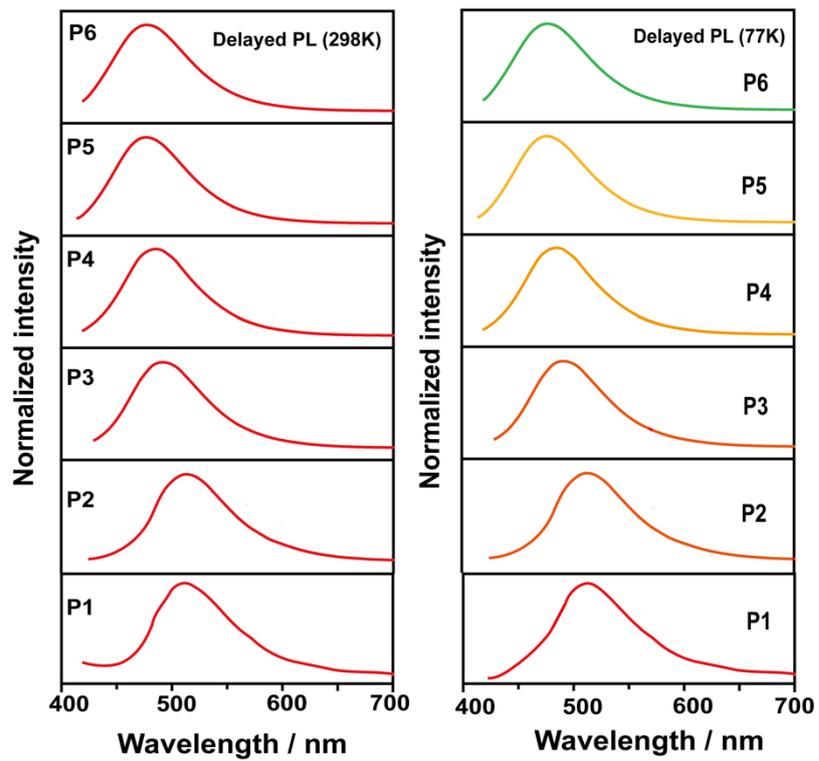


Fig. S10 The delayed PL spectra of **P1-P6** at room temperature and 77 K.

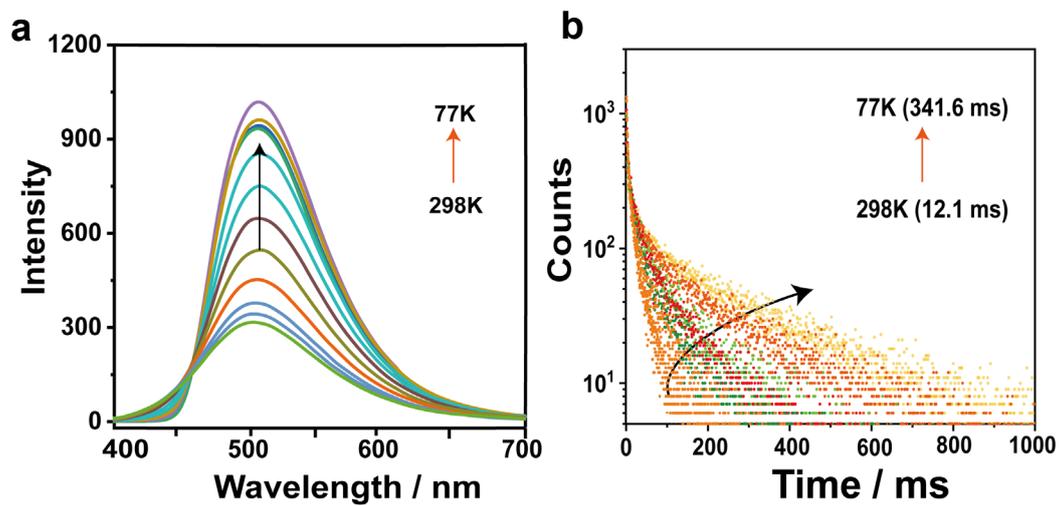


Fig. S11 **a** The delayed PL spectra at different temperatures (77 to 298 K). **b** Phosphorescence lifetimes at different temperatures (77 to 298 K).

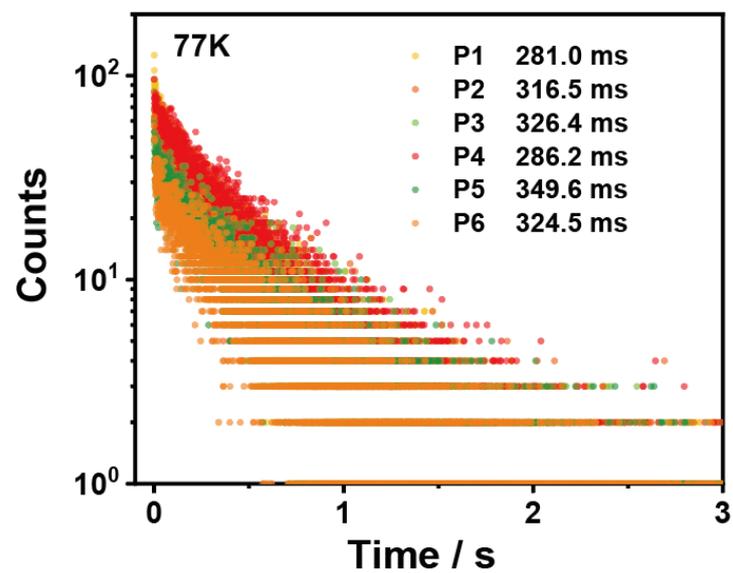


Fig. S12 Phosphorescence decay profiles of **P1-P6** at 77K.

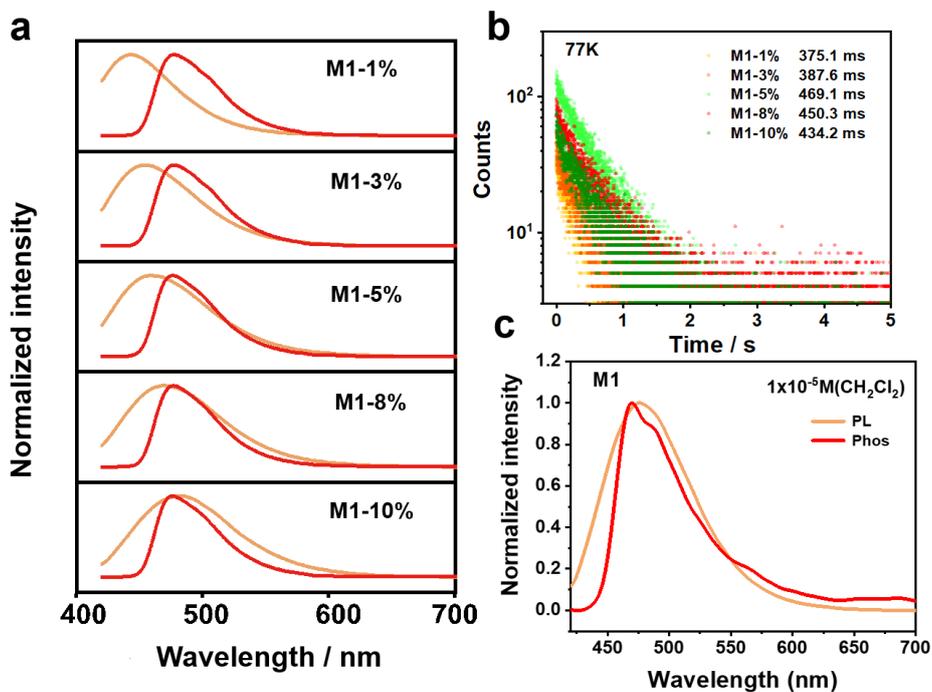


Fig. S13 a The PL (yellow line) and delayed PL (red line) spectra of **M1**-doped PMMA films with concentrations from 1.0 wt% to 10.0 wt%. **b** Lifetime decay curves of the phosphorescence emission for **M1**-doped PMMA films with concentrations from 1.0 wt% to 10.0 wt% at 77 K. **c** The PL and delayed phosphorescence spectra of **M1** in CH_2Cl_2 solution.

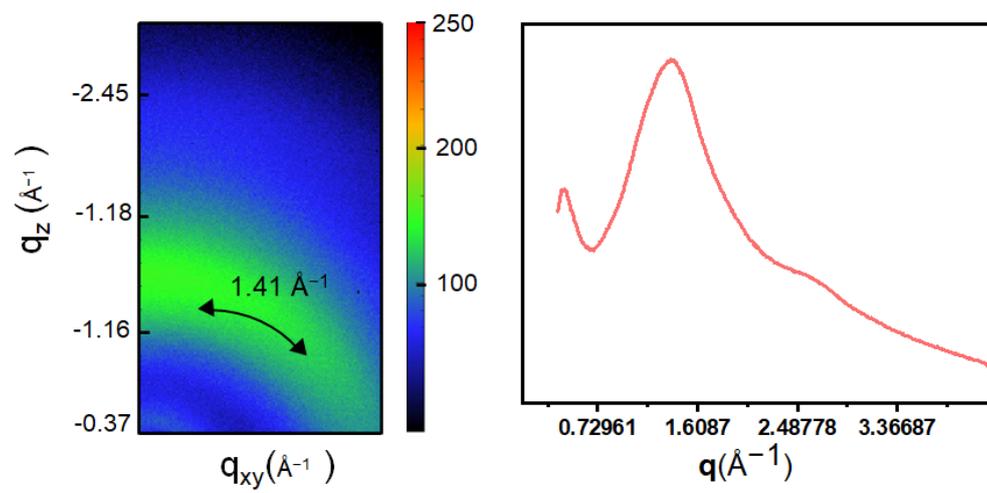


Fig. S14 Wide angle X-ray scattering patterns of polymer film **P2**.

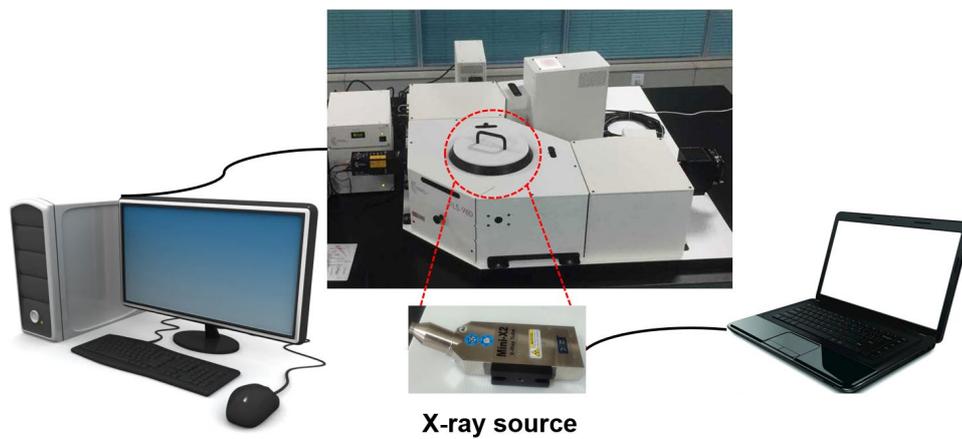


Fig. S15 Schematic illustration of the testing system for radioluminescence intensity measurement.

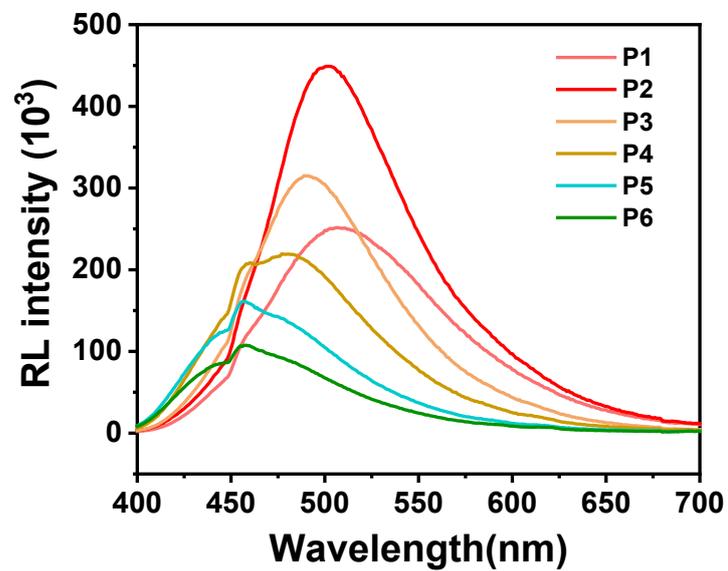


Fig. S16 RL spectra of P1-P6 under X-ray irradiation.

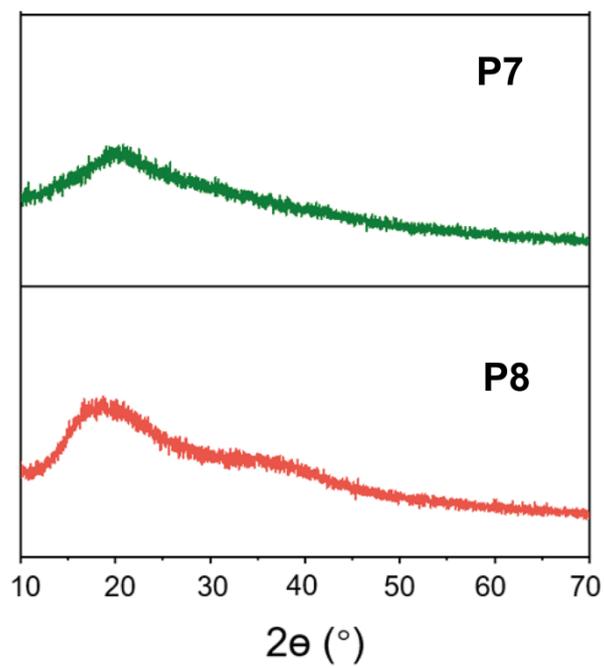


Fig. S17. PXRD patterns of **P7** and **P8**

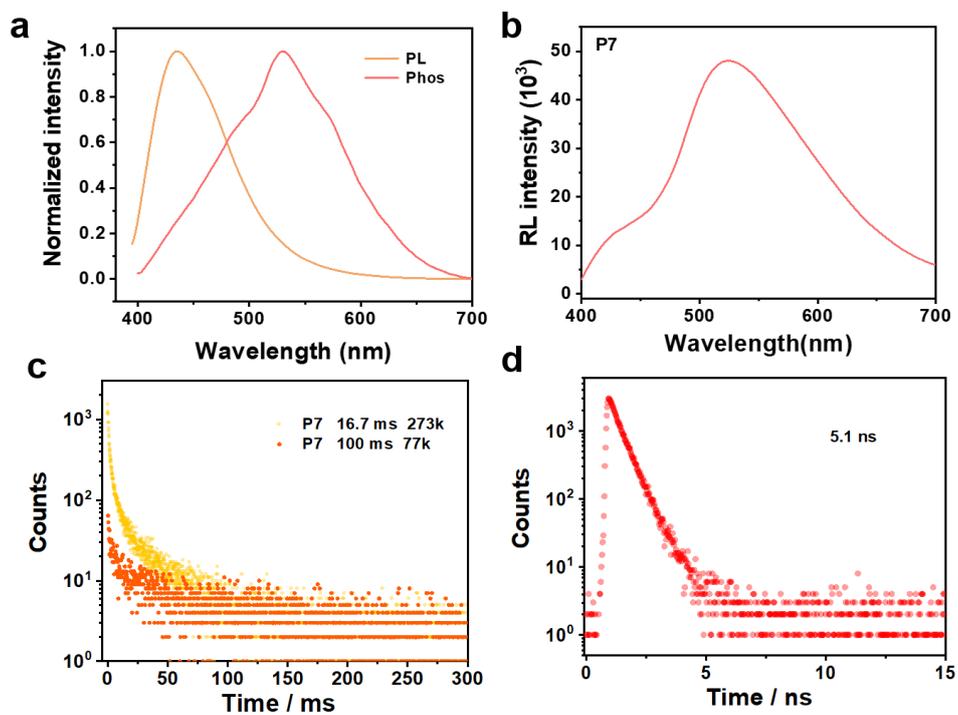


Fig. S18 **a** The normalized PL (yellow line) and delayed PL (red line) spectra of **P7**. **b** The RL spectra **P7** under the irradiation of X-ray. **c** Lifetime decay curves of the phosphorescence emission of **P7** at 273K and 77 K. **d** The steady-state photoluminescence emission lifetime profile of **P7**.

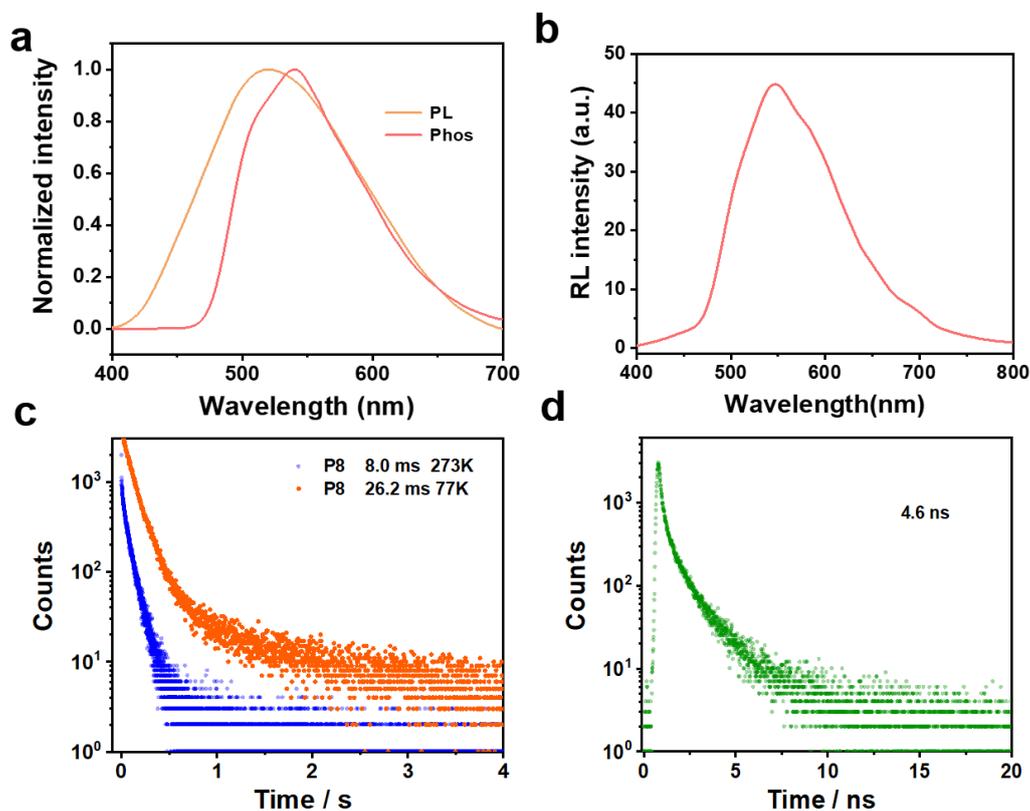


Fig. S19 **a** The normalized PL (yellow line) and delayed PL (red line) spectra of **P8**. **b** The RL spectra **P8** under the irradiation of X-ray. **c** Lifetime decay curves of the phosphorescence emission of **P8** at 273K and 77 K. **d** The steady-state emission lifetime profile of **P8**.

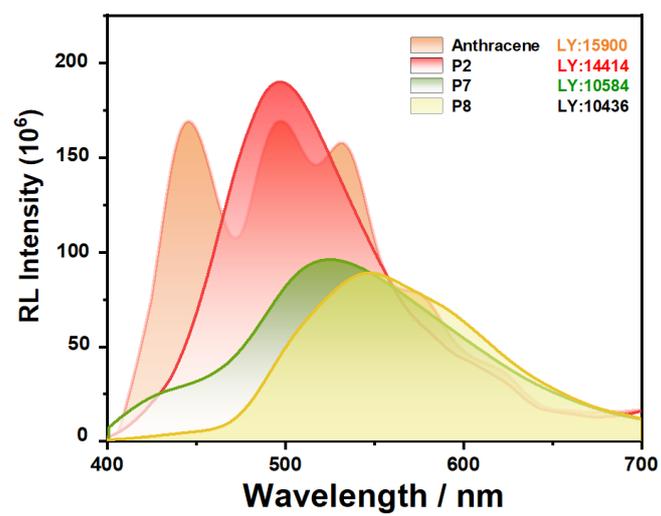


Fig.S20 RL spectra of anthracene, P2, P7, and P8 with light yields

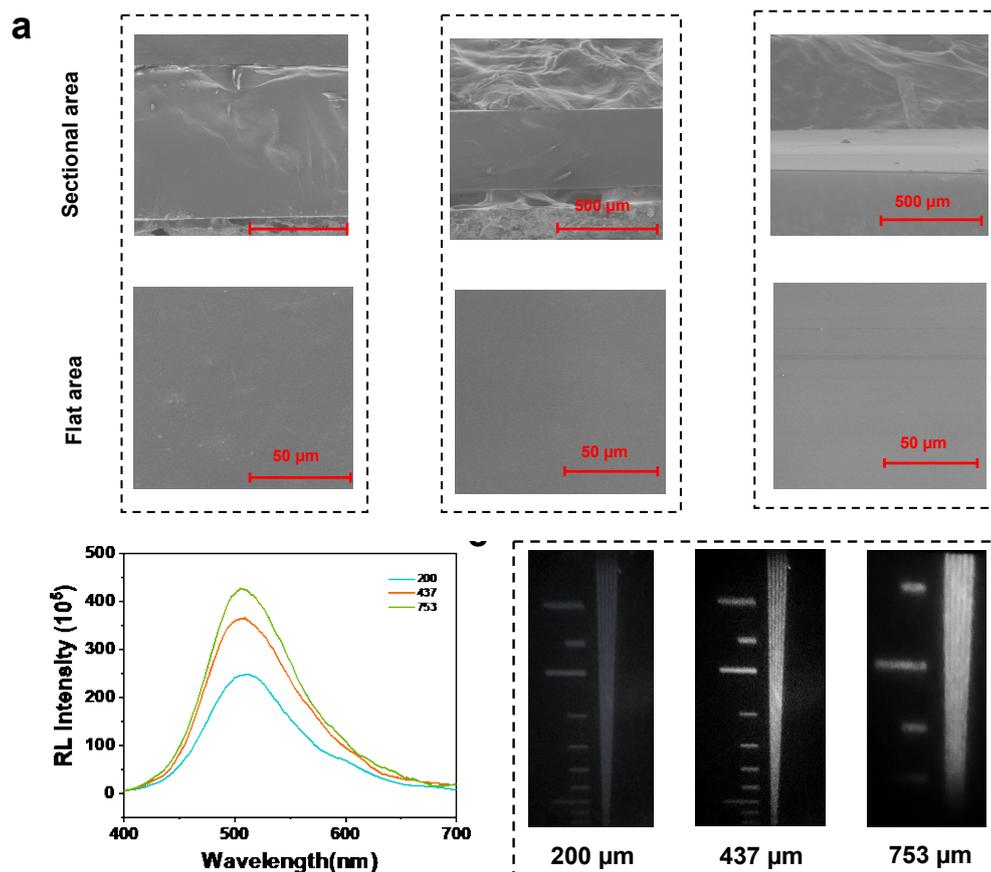


Fig. S21 a The SEM images of **P2** scintillator screens with different thickness 753 μm, 437μm and 200μm. **b** The RL intensity of **P2** thin films, **c** X-ray images of a standard X-ray test pattern plate with different thickness.