Supplementary information

Eu^{3+}-Crosslinked Polymers with Tunable Ultralong Phosphorescence for Time-Resolved Information Encryption

Xiao Yang,[a] Can Diao,[a] Pingru Su,*[a] Yu Tang*[ab]

a. State Key Laboratory of Natural Product Chemistry, Key Laboratory of Nonferrous Metal Chemistry and Resources Utilization of Gansu Province, College of Chemistry and Chemical Engineering, Lanzhou University, Lanzhou, 730000, P. R. China.
b. State Key Laboratory of Baiyunobo Rare Earth Resource Researches and Comprehensive Utilization, Baotou Research Institute of Rare Earths, Baotou 014030, P. R. China

*Correspondence to be done at: supr@lzu.edu.cn, tangyu@lzu.edu.cn

Contents

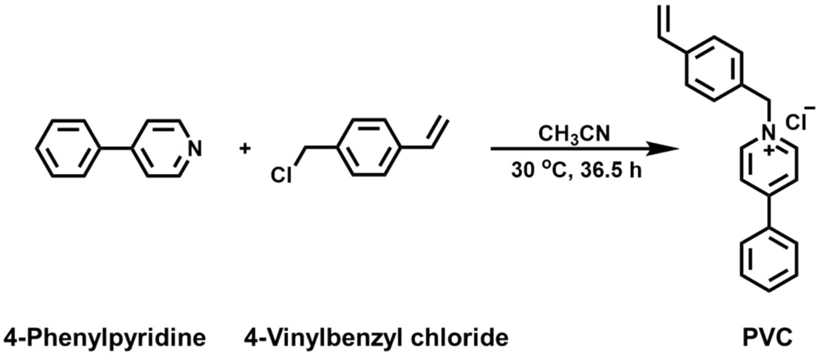
1. Chemical and Materials

P-Hydroxyacetophenone, 5-Bromo-1-pentene, Methyl benzoate, 4-Phenylpyridine, 4-Vinylbenzyl chloride, 2,2'-azobis(2-methylpropionitrile) (AIBN) and sodium hydride (NaH) are purchased from Energy Chemical with a purity of > 98.0% (NaH is 60% dispersion in mineral oil). And potassium carbonate is purchased from DAMAO. All solvents are of commercial grade and are used without further purification.

2. Characterization Methods

All fluorescence spectra (PL), fluorescence decay curves, and luminescence quantum yield data were collected using a FluoroLog-3 fluorescence spectrometer (HORIBA). Mass spectrometry data were obtained using an ACQUITY UPLC I-Class Plus-XEVO G3 QTOF mass spectrometer. ^{1}H NMR, ^{13}C NMR, spectrum data were recorded at 298 K on AVANCE NEO 600 and Bruker JNM-ECS 400M spectrometer operating at 600 /400 MHz nuclear magnetic resonance spectrometer using $CDCl_3$ and Acetonitrile-d_3 as the solvents with tetramethylsilane (TMS) as the internal standard. Chemical shifts are given in ppm with reference to the residual solvent peak of the deuterated solvents. Coupling constants (J) are presented in Hz. The Fourier transform infrared (FTIR) spectrum of the materials were recorded using a Nicolet 360 FTIR spectrometer in the wavenumber range of 4000–400 cm^{-1}. UV-Vis absorption spectrum were measured using a UV-Vis spectrophotometer (Shimadzu UV-2600). All steady-state and time-resolved photoluminescence measurements were performed at 298 K.

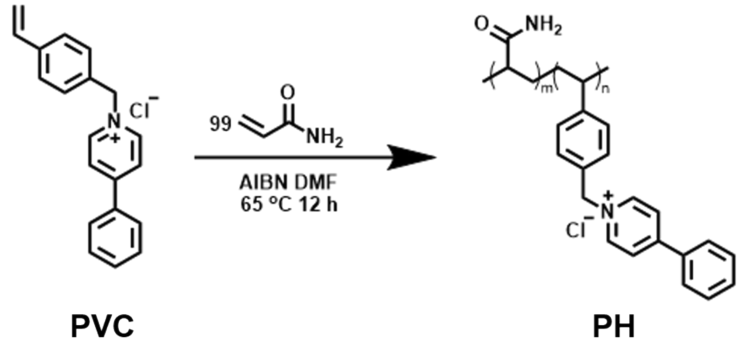
3. Synthesis of polymer



Scheme S1. Synthesis of **PVC**.

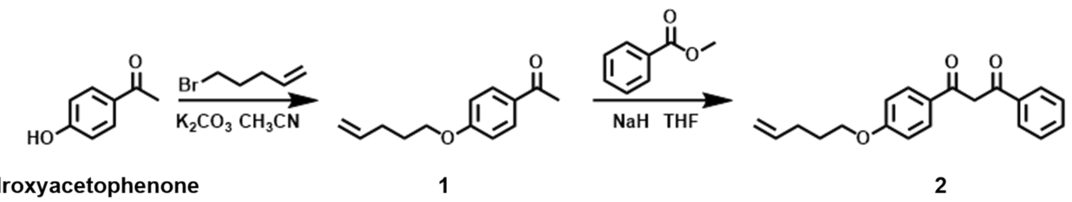
Synthesis of compound PVC. 4-Phenylpyridine (1.0 g, 6.4 mmol) was dispersed in 15 mL anhydrous acetonitrile at ice-bath under argon atmosphere for 1 h. Then, the ice-bath was removed after slow addition of 4-Vinylbenzyl chloride (1.4 mL, 9.6 mmol) by injection. The mixture was stirred at 30 °C for 36.5 h. Filtration was performed to get rid of solid impurity. Pouring anhydrous ether into the filtrate, the resulting precipitation was collected by filtration to afford compound PVC as light golden yellow, (1.05 g). Yield: 53.4%. ^{1}H NMR (600 MHz, Methanol-d_4, 298 K) δ 9.04 – 8.99 (m, 2H), 8.44 – 8.39 (m, 2H), 8.03 – 7.97 (m, 2H), 7.69 – 7.60 (m, 3H), 7.58 – 7.53 (m, 2H), 7.53 – 7.46 (m, 2H), 6.77 (dd, J = 17.6, 10.9 Hz, 1H), 5.85 (dd, J = 17.6, 0.8 Hz, 1H), 5.82 (s, 2H), 5.32 (dd, J = 11.0, 0.8 Hz, 1H). ^{13}C NMR (151 MHz, Methanol-d_4, 298 K) δ 144.39, 135.73, 132.16, 129.58, 129.07, 127.85, 126.96, 124.93, 114.57, 63.17, 48.04, 47.90, 47.76, 47.61, 47.47, 47.33, 47.19. Calcd. for $[C_{20}H_{18}NCl\text{-}Cl^{-}]^{+}$: 272.14, found: 272.13.

Synthesis of polymer PH General synthesis of the PH. In 6 mL anhydrous DMF under dark and argon atmosphere, PH was prepared by copolymerization of PVC (30.7 mg, 0.1 mmol, 1.0 eq) and acrylamide (703.8 mg, 9.9 mmol, 99.0 eq) with 2,2'-azobis(2-methylpropionitrile) (AIBN) (16.4 mg) as radical initiator at 65 °C for 12 h. After cooling, the crude solid obtained through filtration was dissolved by distilled water and the mixture was dialyzed (cut off = 8,000) against water for 5 d. The resulting solution was lyophilized and further dried under vacuum to obtain solid polymer. Similar method was performed to afford other polymers.

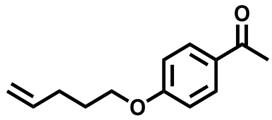


Scheme S2. Synthesis of the polymer **PH**.

4. Synthesis of Ligands and Eu^{3+} Complexes

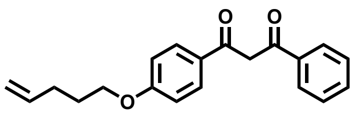


Scheme S3. Synthesis of the compound **2** (L).



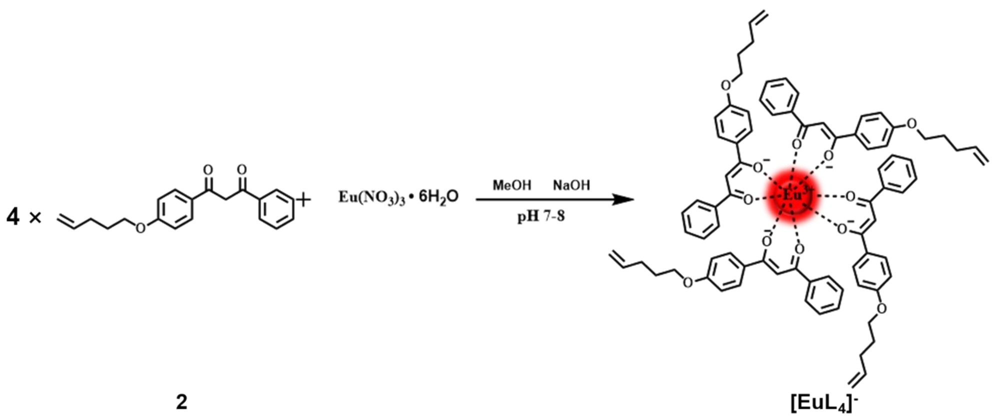
Synthesis of 1-[4-(4-Penten-1-yloxy)phenyl]ethanone (compound 1).

A 250 mL three-neck round-bottom flask was charged with p-hydroxyacetophenone (6.13 g, 45 mmol), 5-bromo-1-pentene (6.29 g, 42 mmol), potassium carbonate (11.06 g, 80 mmol) and anhydrous acetonitrile (100 mL) with a condensing reflux apparatus and a magnetic stirring system. After the reaction was complete, the acetonitrile solvent was removed by vacuum concentration using a rotary evaporator. The residue was dissolved in 100 mL of dichloromethane. The resulting organic layer was sequentially washed with saturated saline solution (3 × 50 mL) to remove inorganic salt impurities. After drying over anhydrous sodium sulfate, the mixture was filtered and concentrated to yield the crude product. The crude product was purified by column chromatography on silica gel eluted with (PE/ EA 20:1, v/v) to give the compound 2 (7.64 g). Yield 88.07% as a colorless transparent liquid. ^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ 7.95 – 7.91 (m, 2H), 6.94 – 6.90 (m, 2H), 5.85 (ddt, J = 16.9, 10.2, 6.7 Hz, 1H), 5.10 – 4.99 (m, 2H), 4.04 (t, J = 6.4 Hz, 2H), 2.55 (s, 3H), 2.28 – 2.22 (m, 2H), 1.91 (dt, J = 13.5, 6.6 Hz, 2H).^{13}C NMR (151 MHz, $CDCl_3$, 298 K) δ 196.78, 163.03, 137.53, 130.59, 130.21, 115.44, 114.15, 67.38, 30.01, 28.24, 26.34.



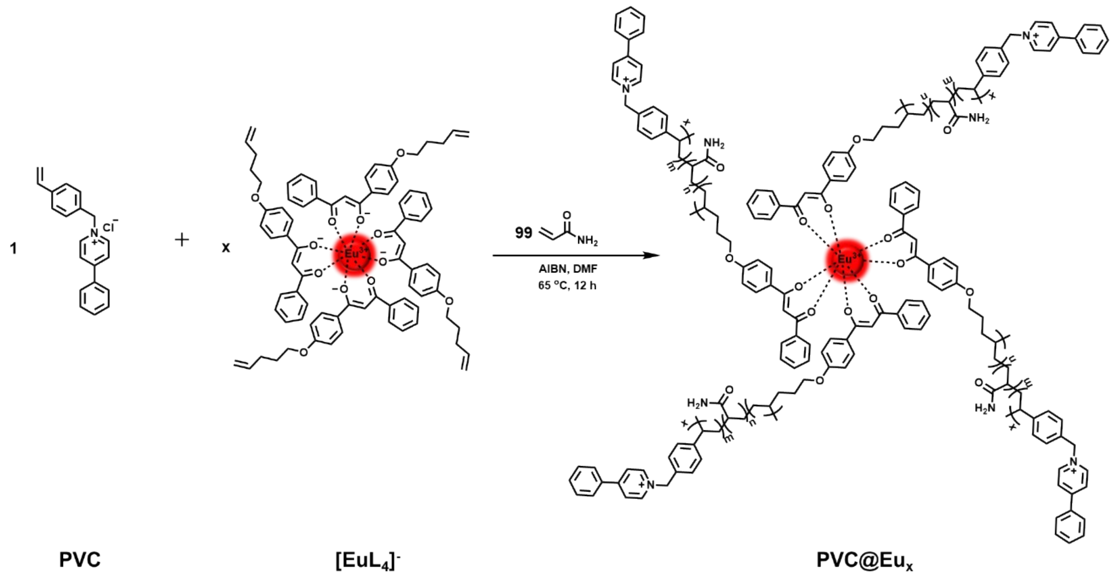
Synthesis of 1-(4-(pent-4-en-1-yloxy)phenyl)-3-phenylpropane-1,3-dione (compound 2).

A 250 mL three-neck round-bottom flask was charged with compound 1 (4.76 g, 35 mmol) and anhydrous tetrahydrofuran (100 mL) with a constant-pressure dropping funnel and condenser. Slowly add sodium hydride (2.00 g, 50 mmol) in portions under ice bath conditions, maintaining the system temperature below 10 °C throughout the addition. Subsequently, remove the ice bath and raise the reaction system to 70 °C, refluxing for 5 minutes. Slowly add a solution of methyl benzoate (5.11 g, 25 mmol) in tetrahydrofuran (20 mL) via a constant-pressure dropping funnel, controlling the addition rate to maintain the reaction temperature at 70 °C. Continue stirring the reaction at 70°C for 24 hours, monitoring the reaction progress via thin-layer chromatography. Upon completion, remove the tetrahydrofuran solvent using a rotary evaporator. The reaction mixture was quenched by the addition of 100 mL ice water, the pH was adjusted to around 1 by progressively adding 3M hydrochloric acid solution. The mixture obtained from the hydrochloric acid solution was extracted with dichloromethane (3 × 50 mL). The organic layers were combined and washed with saturated sodium chloride solution (3 × 50 mL). After drying over anhydrous sodium sulfate, the mixture was filtered and concentrated under reduced pressure to yield the crude product. The crude product was purified by column chromatography on silica gel eluted with (PE/ EA 30:1, v/v) to give the compound 2 (7.64 g, 88.07%) as a white crystalline compound 2 (4.84 g). Yield 58.96%.^{1}H NMR (600 MHz, $CDCl_3$, 298 K) δ 7.97 (d, J = 9.0 Hz, 4H), 7.54 (t, J = 7.3 Hz, 1H), 7.48 (t, J = 7.5 Hz, 2H), 6.97 (d, J = 8.8 Hz, 2H), 6.80 (s, 1H), 5.86 (ddt, J = 16.9, 10.2, 6.6 Hz, 1H), 5.08 (d, J = 17.1 Hz, 1H), 5.02 (d, J = 10.2 Hz, 1H), 4.05 (t, J = 6.4 Hz, 2H), 2.26 (q, J = 7.4 Hz, 2H), 1.92 (p, J = 6.7 Hz, 2H). ^{13}C NMR (151 MHz, $CDCl_3$, 298 K) δ 186.26, 183.98, 162.81, 137.57, 135.61, 133.63, 132.16, 131.29, 129.33, 128.92, 128.74, 128.65, 128.06, 127.01, 115.49, 115.44, 114.48, 114.40, 92.36, 67.43, 30.04, 29.99, 28.28. ESI-MS (m/z): Calcd. for $[C_{20}H_{20}O_3-H^+]^-$: 307.13, found: 307.14.



Scheme S4. Synthesis of $[EuL_4]^-$.

Synthesis of Eu^{3+}-complex ($[EuL_4]^-$). The complex $[EuL_4]^-$ was synthesized according to previous work. Compound 2 (0.4 M, 0.1233 g) was dissolved in 5 mL MeOH. The solution was adjusted pH to 8.0 with 1 M NaOH (400 μL), resulting a clear solution. And then, the solution of $Eu(NO_3)_3 \cdot 6H_2O$ (0.1 M, 0.0446 g) was dropped into the above solution, forming a light yellow turbid solution, which was stirred at 60 °C for another 12 h. The product was vacuum dried after filtering and washing with water and Ethanol for several times. Yield 90%. 1H NMR (600 MHz, DMSO-*d*$_6$) δ 6.58 (t, J = 7.1 Hz, 1H), 6.22 (d, J = 7.0 Hz, 1H), 5.76 – 5.69 (m, 2H), 5.45 (s, 1H), 4.93 – 4.86 (m, 1H), 4.12 – 4.08 (m, 1H), 4.08 (s, 11H), 3.80 (t, J = 6.4 Hz, 2H), 3.57 (t, J = 6.4 Hz, 1H), 2.66 (q, J = 7.2 Hz, 16H), 2.12 – 2.05 (m, 1H), 1.98 – 1.92 (m, 1H), 1.72 – 1.64 (m, 1H), 1.53 (dt, J = 8.1, 6.6 Hz, 1H), 1.03 (t, J = 7.2 Hz, 23H). Calcd. for $[C_{80}H_{80}EuO_{12}\text{-}4H^{+}]^{-}$: 1381.45, found: 1381.48.



Scheme S5. Synthesis of **PVC@Eu$_x$** polymer.

Synthesis of PVC@Eu$_x$ polymer. PVC@Eu-0.5 was prepared as a model. In 6 mL anhydrous DMF under dark and argon atmosphere, PVC@Eu-0.5 was prepared by copolymerization of PVC (30.7 mg, 0.1 mmol, 1.0 eq), Eu(PED)$_4$ (69.1 mg, 0.05 mmol, 0.5 eq) and acrylamide (703.8 mg, 9.9 mmol, 99.0 eq) with 2,2'-azobis(2-methylpropionitrile) (AIBN) (16.4 mg, 0.1 mmol, 1.0 eq) as radical initiator at 65 °C for 12 h. After cooling, the crude solid obtained through filtration was dissolved by distilled water and the mixture was dialyzed (cut off = 8,000) against water for 5 d. The resulting solution was lyophilized and further dried under vacuum to obtain solid polymer. Similar method was performed to afford other polymers.

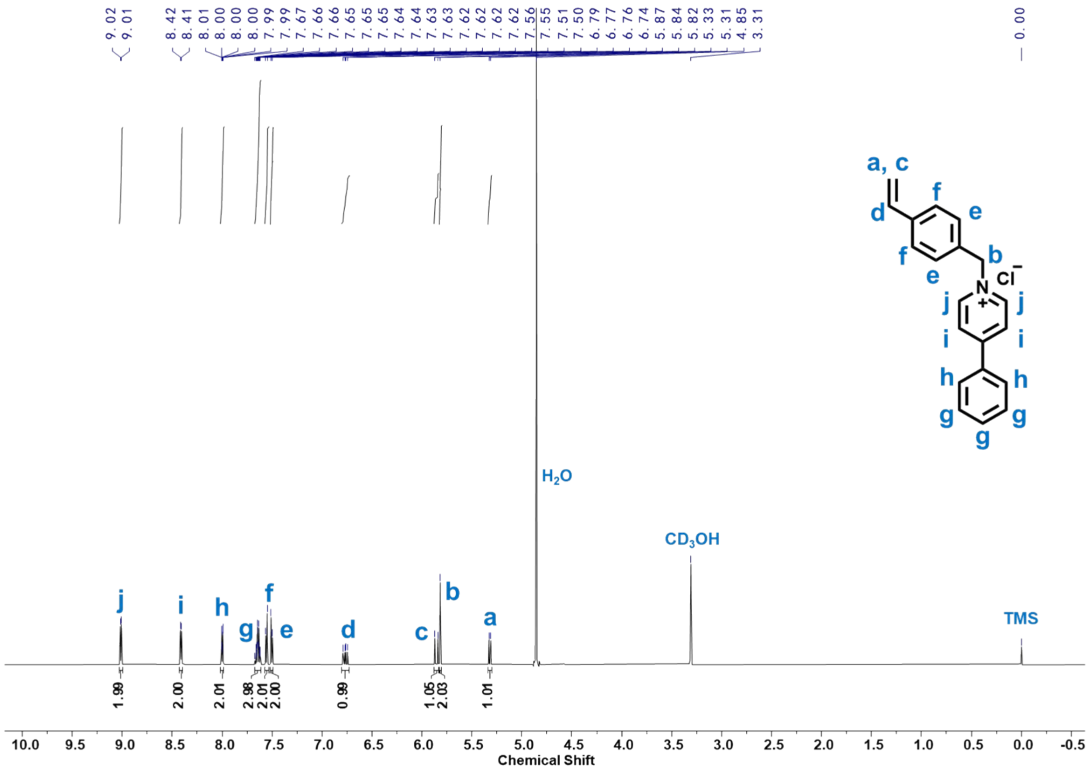


Figure S1. ^{1}H NMR (600 MHz, Methanol-d_4, 298 K) spectrum of PVC.

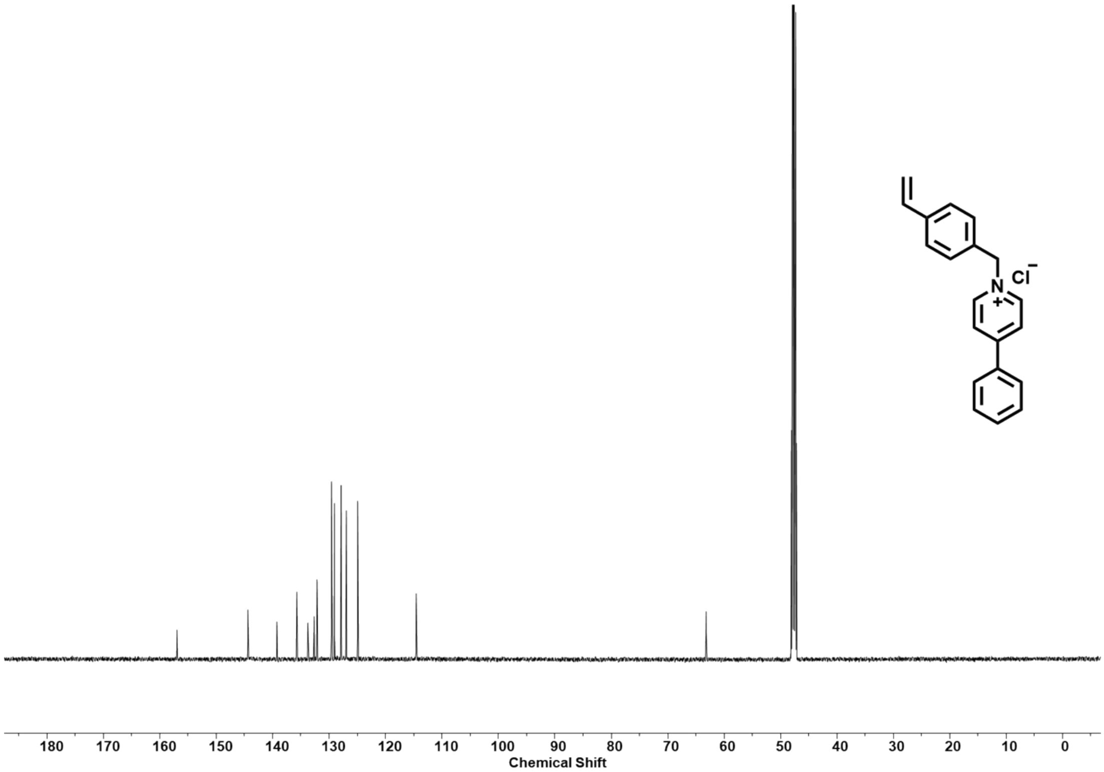


Figure S2. ^{13}C NMR (600 MHz, Methanol-d_4, 298 K) spectrum of PVC.

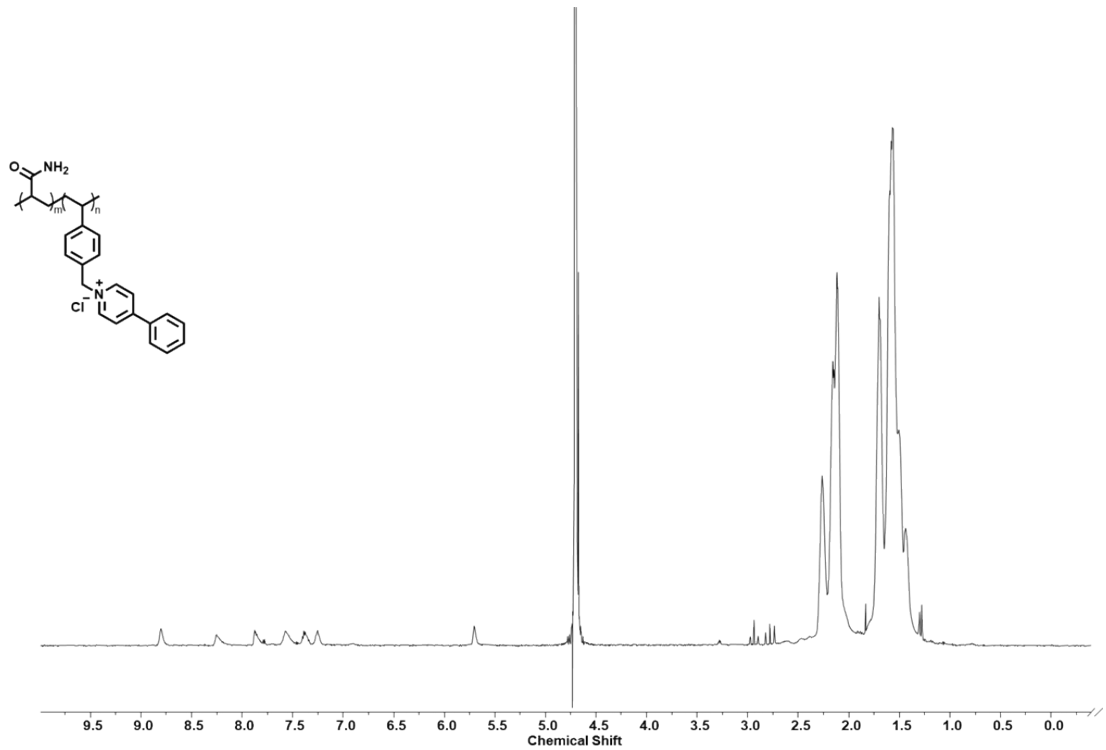


Figure S3. ^{1}H NMR (600 MHz, D_2O, 298 K) spectrum of PH.

II. Supplemental Experimental Figures and Tables

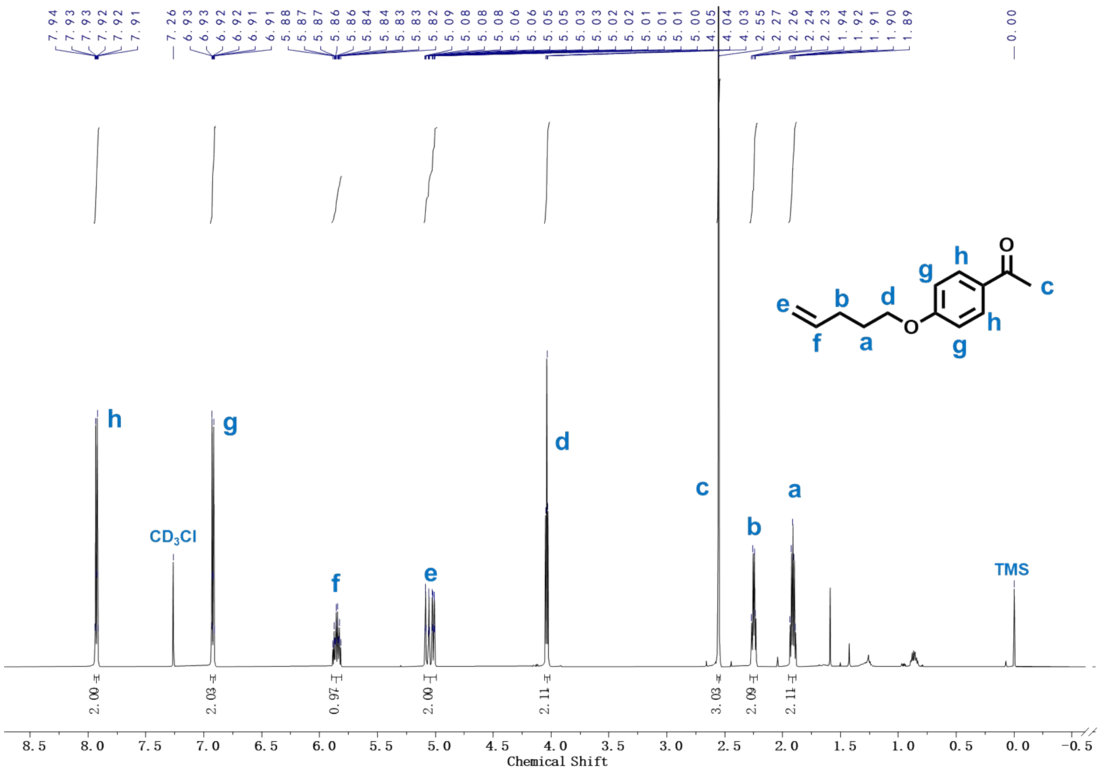


Figure S4. ^{1}H NMR (600 MHz, Chloroform-*d*, 298 K) spectrum of compound 1.

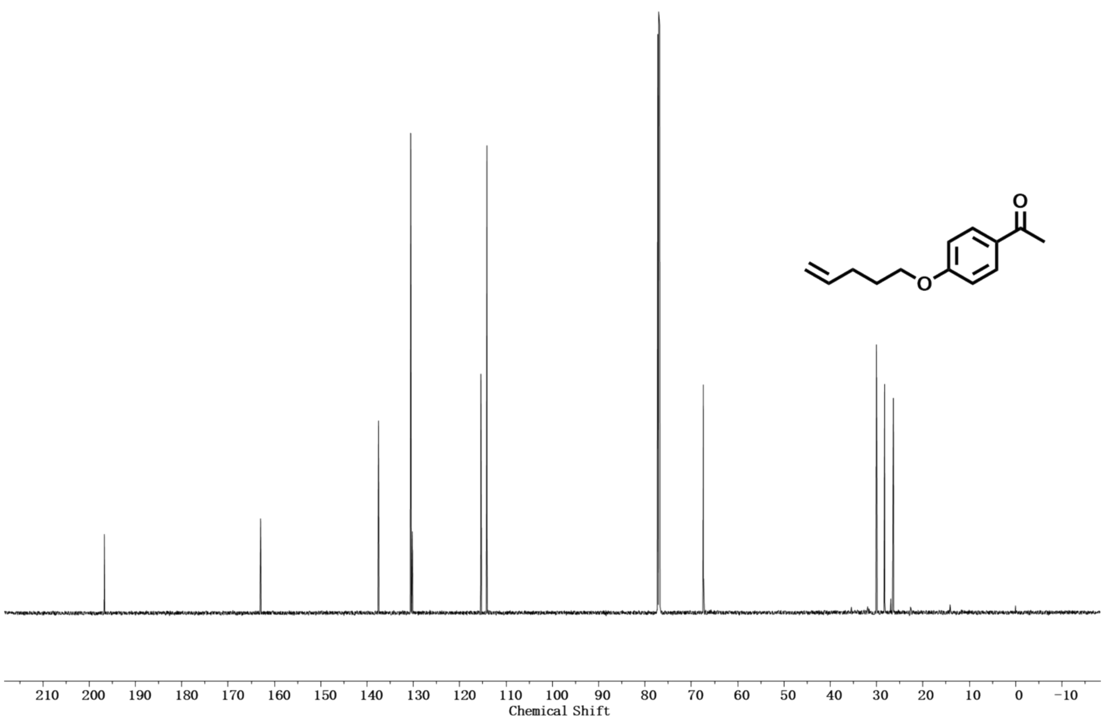


Figure S5. ^{13}C NMR (600 MHz, Chloroform-*d*, 298 K) spectrum of compound 1.

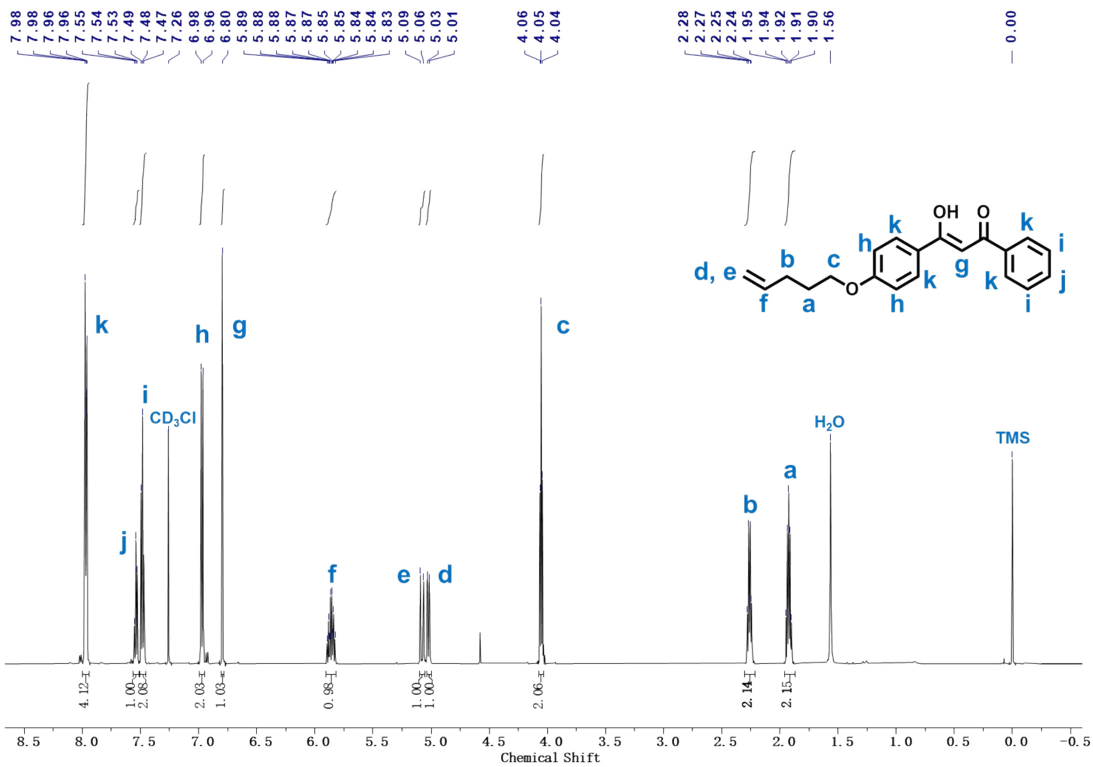


Figure S6. ^{1}H NMR (600 MHz, Chloroform-*d*, 298 K) spectrum of compound 2.

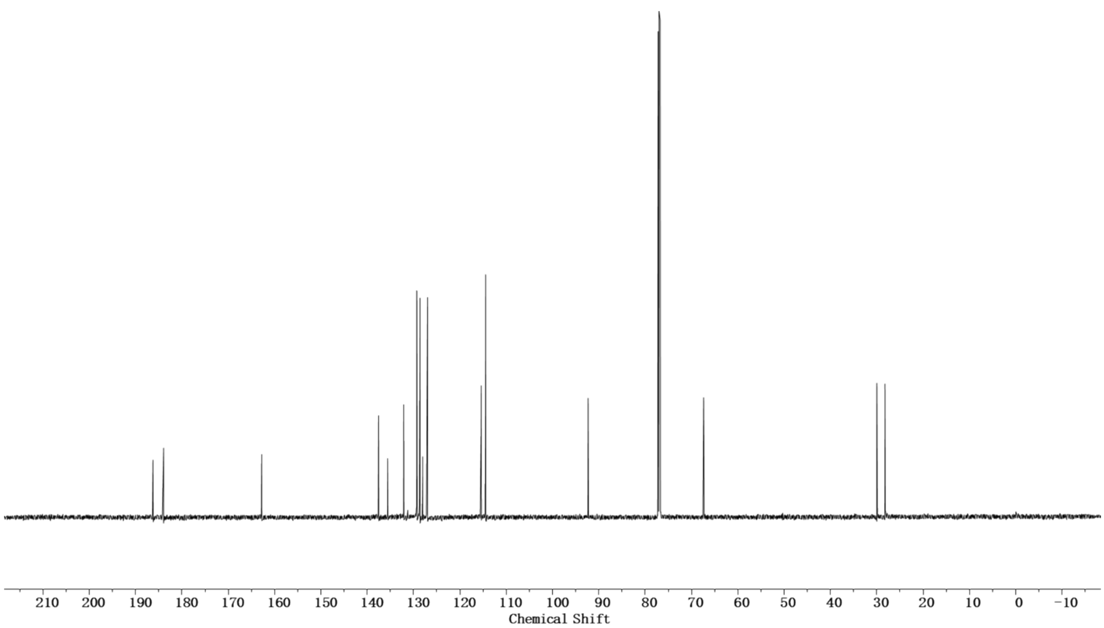


Figure S7. ^{13}C NMR (600 MHz, Chloroform-*d*, 298 K) spectrum of compound 2.

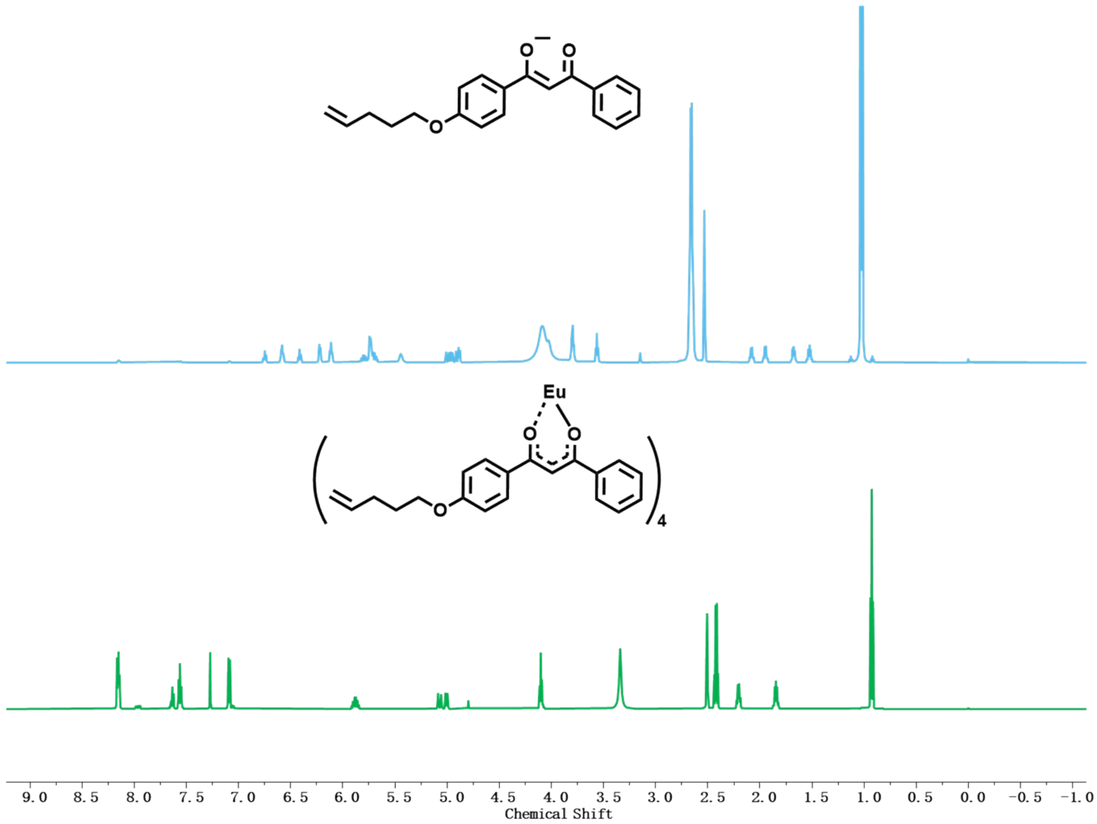


Figure S8. ^{1}H NMR (600 MHz, CD_3OD/DMSO-d_6 = 1:10, v/v, 298 K) spectrum of L^- and Na[EuL_4].

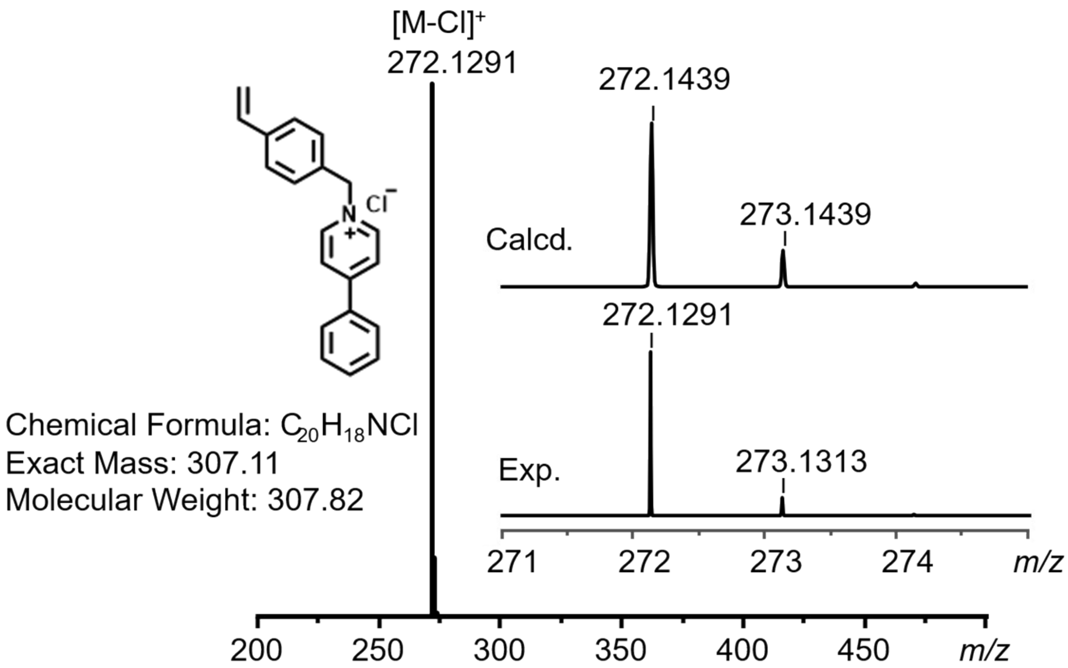


Figure S9. ESI-MS mass spectrometry of $[M-Cl]^+$. Illustration: theoretical and experimental diagram of ions.

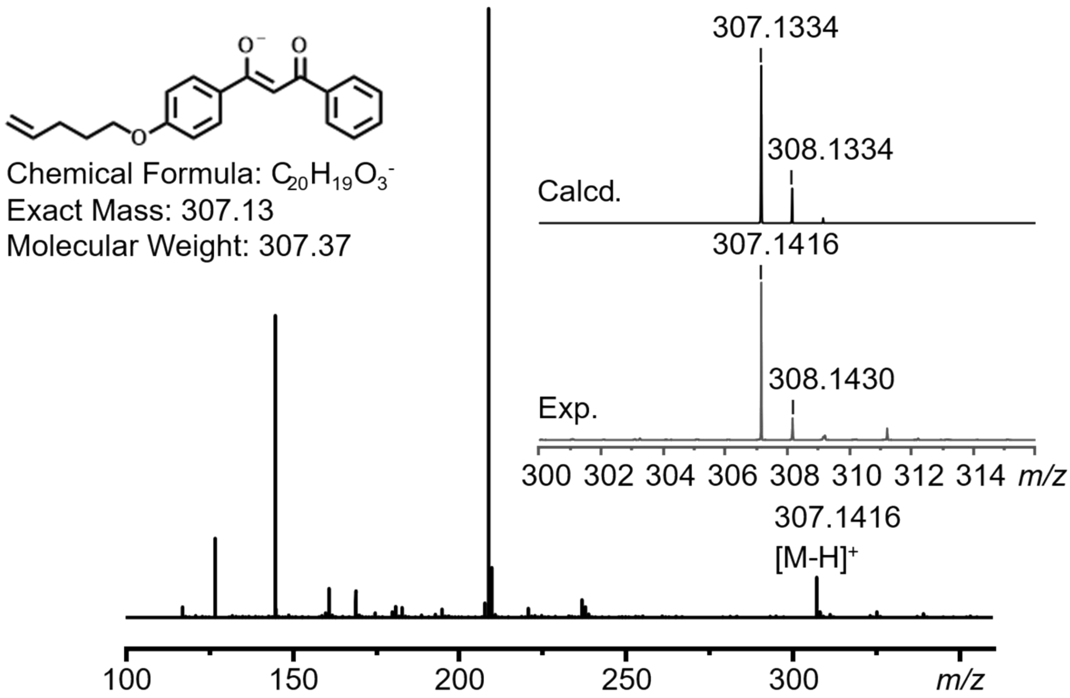


Figure S10. ESI-MS mass spectrometry of $[M\text{-}H]^-$. Illustration: theoretical and experimental diagram of ions.

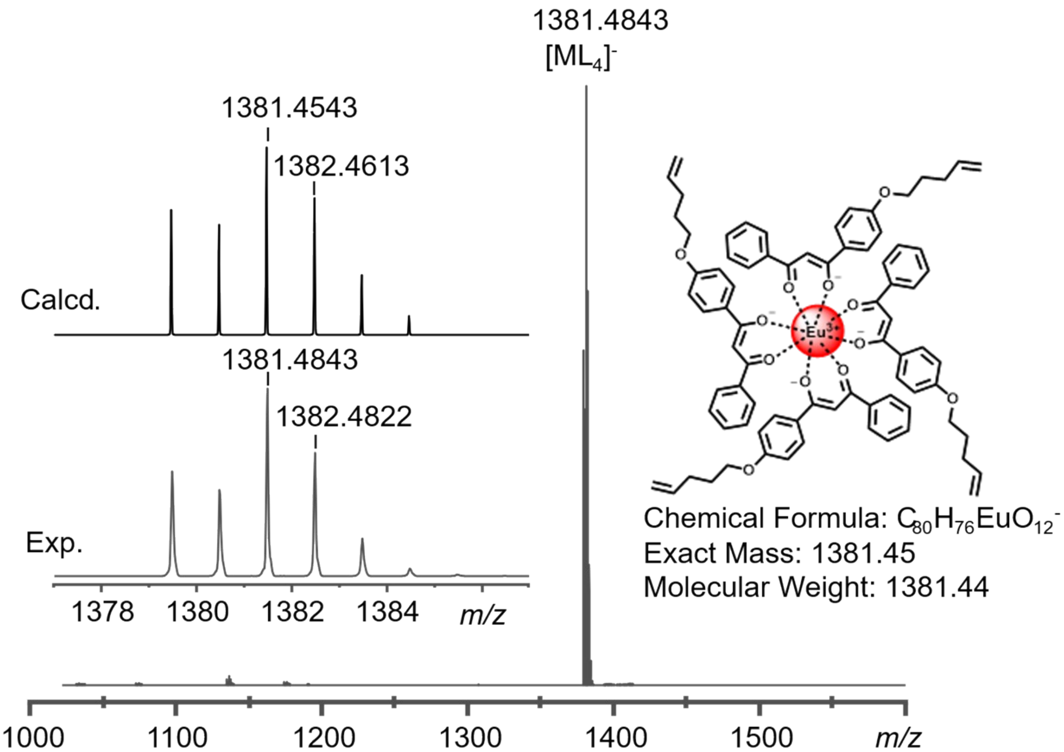


Figure S11. ESI-MS mass spectrometry of $[ML_4]^-$. Illustration: theoretical and experimental diagram of ions.

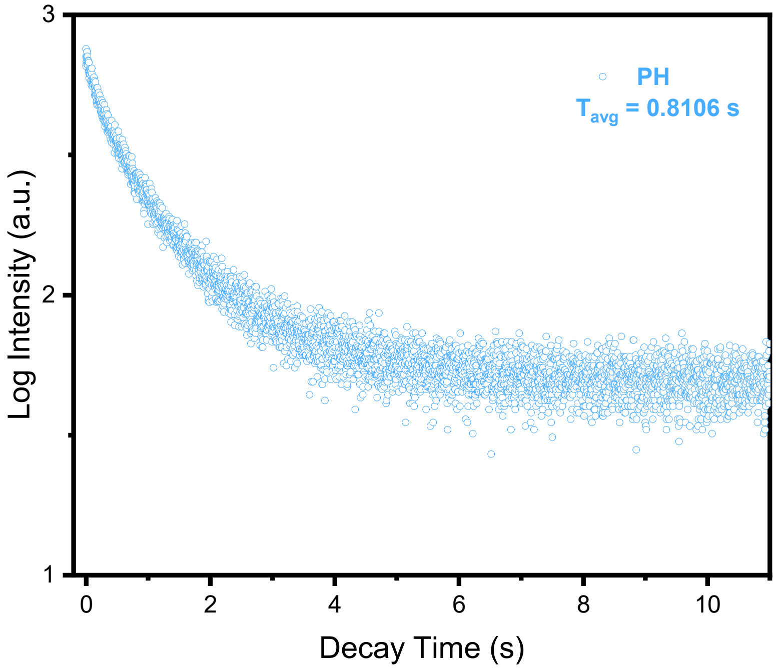


Figure S12. Phosphorescence-decay profiles of PH powder.

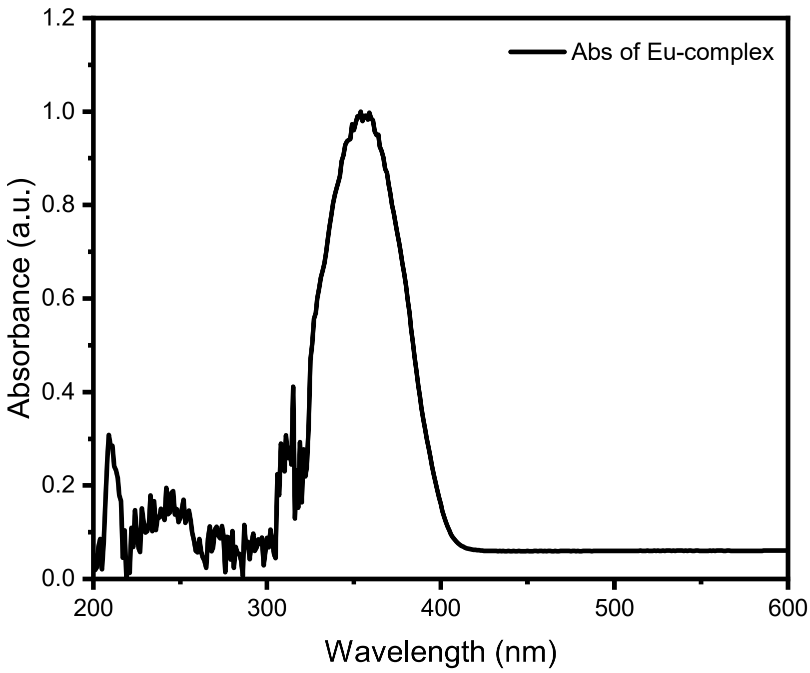


Figure S13. UV–vis absorption spectra of $Na[EuL_4]$.

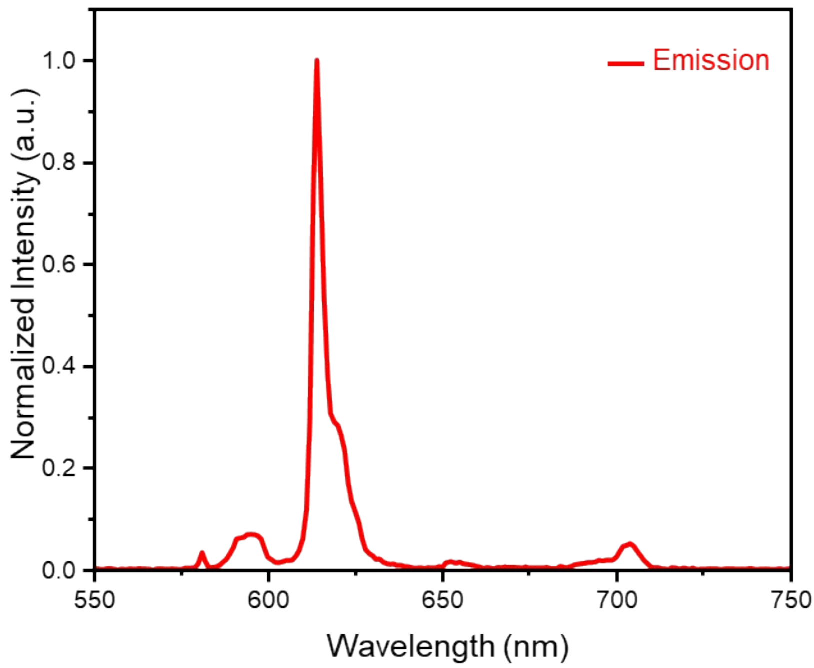


Figure S14. Photoluminescence spectra of Na[EuL$_4$].

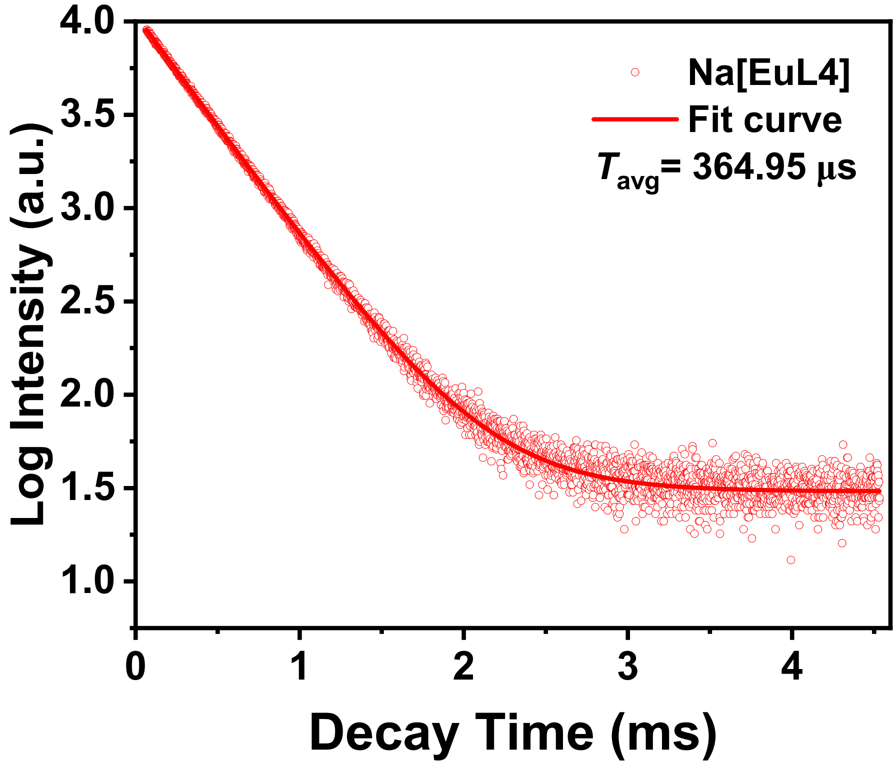


Figure S15. Decay curves at 616 nm for Na[EuL$_4$].

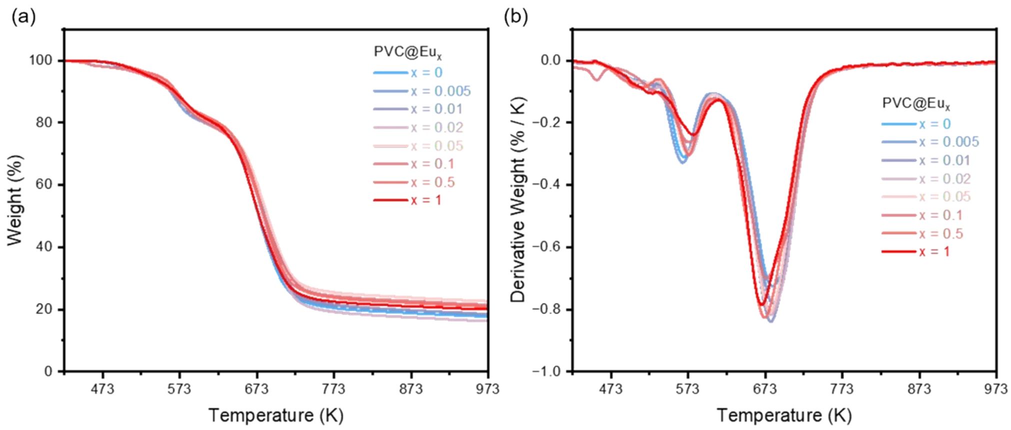


Figure S16. (a)TGA curves of PH (x=0) and PVC@Eu$_x$ (x = 0.005, 0.01, 0.1, 0.5, 1.0) under N_2 flow (50 mL·min^{-1}) with a heating rate of 10 °C·min^{-1}.(b) DTG curves corresponding to the TGA data

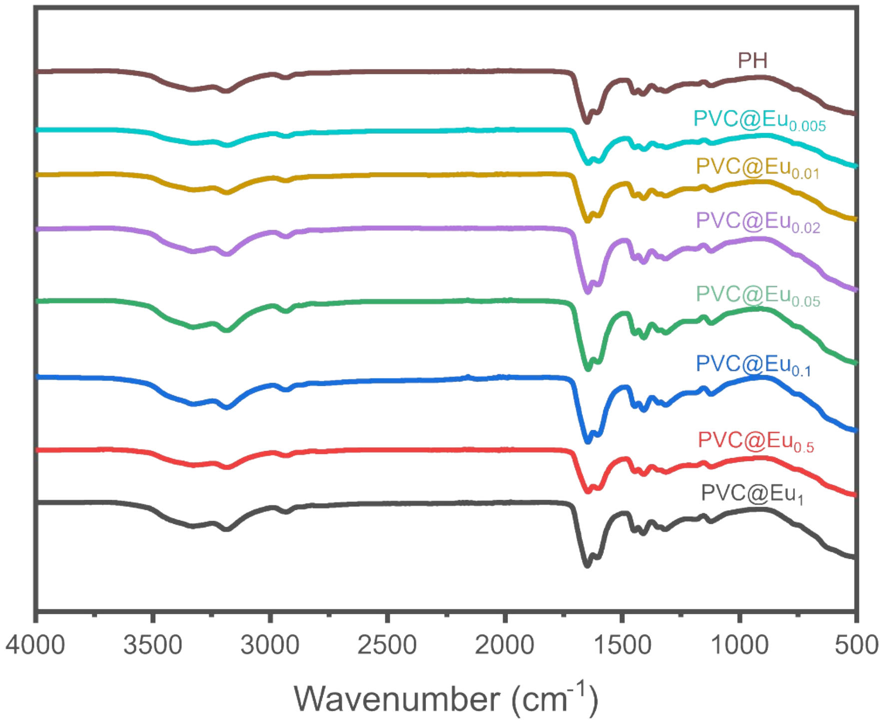


Figure S17. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra of PVC@Eu$_x$ powers at different doping ratios of Eu^{3+} complex.

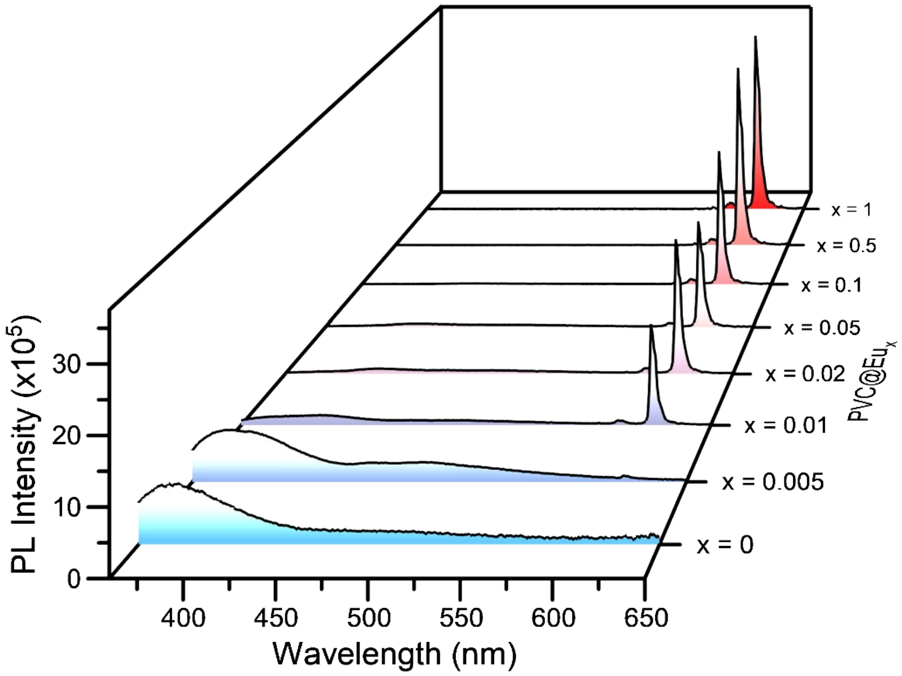


Figure S18. Photoluminescence emission spectra of PVC@Eu_x powders.

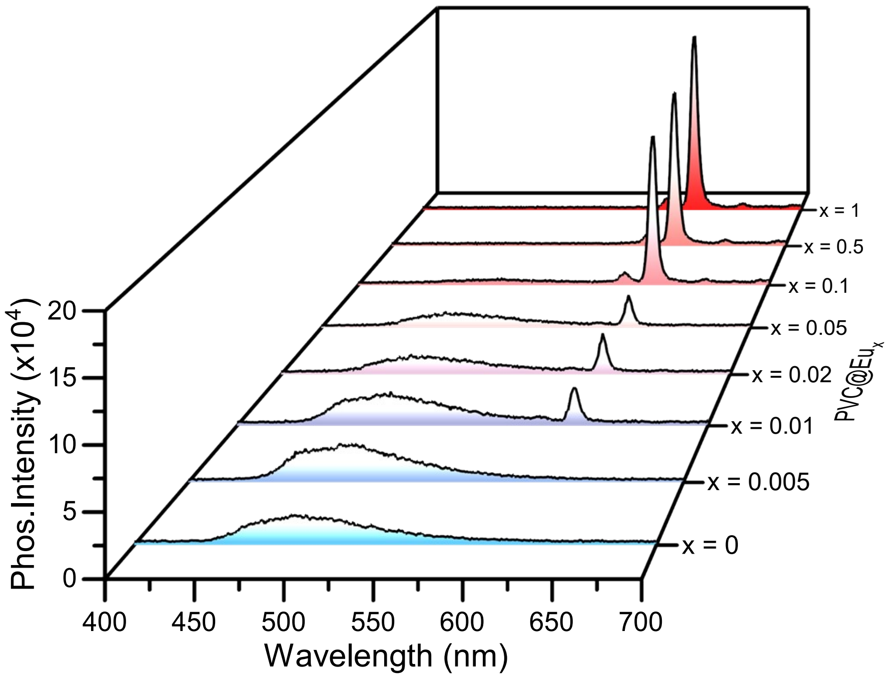


Figure S19. Phosphorescence emission spectra of PVC@Eu_x powders (delay time 1 ms).

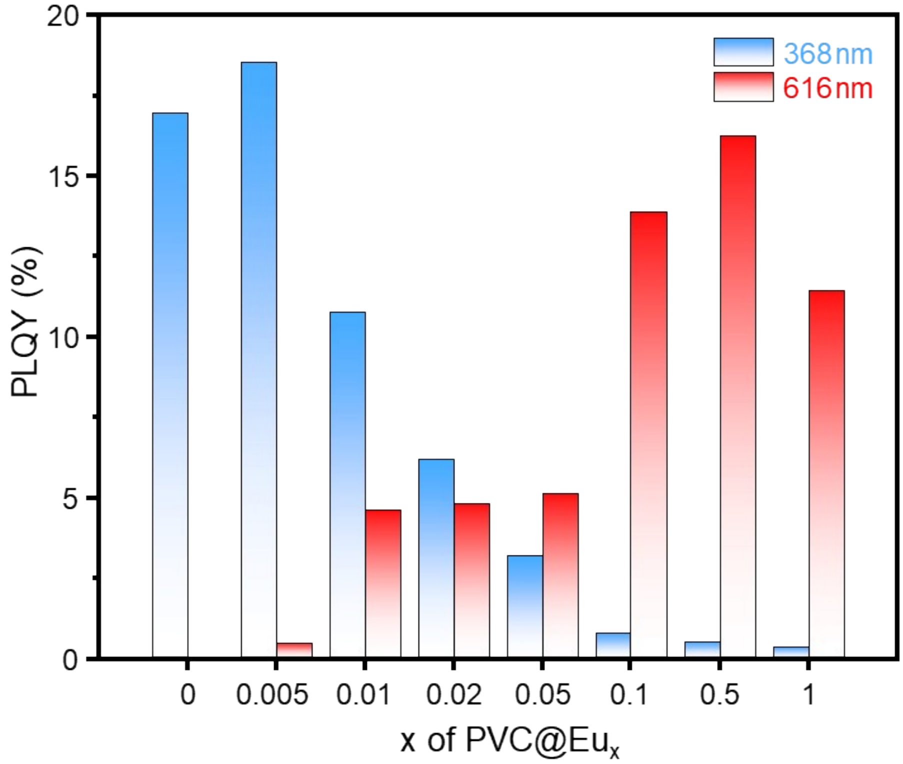


Figure S20. Attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectra of PVC@Eu_x powers at different doping ratios of Eu^{3+} complex.

Table S1. Characterizations of polymers by aqueous GPC(a: PH; b-h: PVC@Eu_x

x=0.001-1).

a

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	11357	6577	13014	21541	31002	20245	1.978714

b

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	9056	6803	13113	22212	31694	20839	1.927532

c

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	9179	6295	11459	18148	25201	17149	1.820334

d

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	14423	7834	13986	21923	30584	20722	1.785295

e

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	13716	7027	14242	24026	34672	22548	2.026754

f

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	15360	7684	14655	23159	32137	21901	1.90721

g

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	11574	6926	13460	22551	32752	21154	1.943402

h

Peak	Mp (g/mol)	Mn (g/mol)	Mw (g/mol)	Mz (g/mol)	Mz+1 (g/mol)	Mv (g/mol)	PD
Peak 1	11647	6816	13491	22879	33677	21422	1.979313