Electronic Supporting Information

for

An efficient long fluorescence lifetime polymer-based sensor based on europium complex as chromophore for the specific detection of F^-, CH_3COO^-, and $H_2PO_4^-$

[a]Guangzhou institute of Chemistry, Chinese Academy of Sciences, Guangzhou 510650, PR China

[b]Graduate School of the Chinese Academy of Sciences, Beijing100039, PR China

[c]School of Chemistry and Engineering, Sun Yat-sen University, Guangzhou 510275, PR China

Corresponding author. Tel/ Fax: +86 20 85232978 Email address: mglu@gic.ac.cn

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1. Materials and Methods

All reagents used were of analytical grade. DMSO was dried with CaH_2 for about 24 h and distilled at reduced pressure. FT-IR spectra were carried out using a Tensor 27 (Bruker) Fourier Transform Infrared Spectrometer. Elemental analysis data were obtained from Vario EL elemental analyzer. NMR spectra were taken on a DRX-400 MHz (Bruker) superconducting-magnet NMR spectrometer with TMS as an internal standard. UV-vis absorption spectrum was determined on a Shimadz spectrophotometer (UV 2550). Cyclic voltammetry (CV) measurement was performed on a computer-controlled CHI600D electrochemical analyzer with a Pt working electrode, a Pt plate counter electrode, and an SCE reference electrode immersed in 0.1 M Bu_4NClO_4 in dry acetonitrile purged with dried Argon. The scanning rate was 50 mV/s, and all electrochemical potentials were calibrated with the ferrocene/ferrocenium (Fc/Fc+) standard. The photoluminescence (PL) measurements in solid state and THF solution were conducted in a Hitachi F-4600 florescence spectrophotometer. Luminescence lifetimes were obtained with the FLS920 steady state spectrometer with a pulsed xenon lamp.

Fluorescence titration procedure.

The 1×10^{-4} mol/L solution of $Eu(TTA)_2$vinyl and Eu-polymer in DMSO was prepared and stored under dark conditions. A 1×10^{-2} mol/L solution of tetrabutylammonium salts was prepared in pre-dried and dry DMSO and was stored under an inert gas. All titration experiments were carried out with 3 ml of the europium complexes solution as host in a quartz cell at 25 ± 0.5°C, and fluorescence spectra were recorded upon the addition of aliquots of the stock anions solution as guest. The 30 μL CH_3COO^- solution equals to 1 eq host solution. After each addition of the anion guest to the quartz cell, the PL spectra were recorded after 3 min equilibration.

2. Synthetic procedures and characterization.

4-(4-vinylbenzyloxy)benzaldehyde: Solid KOH (2.25 g, 40 mmol) was added to a solution of 4-hydroxybenzaldehyde (4.89 g, 40 mmol) and 4-vinylbenzyl chloride (7.16 g, 40 mmol) in DMF (100 mL), and the mixture was stirred for 12 h at room temperature. Water (800 mL) was added to precipitate the product, which was isolated, washed with water (3×50 mL), and dried in a vacuum at 60°C. Excess 4-vinylbenzyl chloride was removed by triturating the product in hexane (50 mL). The product was then washed with additional hexane (3×20 mL) and dried under a positive air flow. Yield: 8.11 g (85%). ^{1}H NMR (400 MHz $CDCl_3$): 5.14 (s, 2 H); 5.27-5.29 (d, 1 H, J_{HH} = 11); 5.75-5.80 (d, 1 H, J_{HH} =18); 6.69-6.76 (dd, 1 H, J_{HH} = 18, J_{HH} = 12); 7.06-7.09 (d, 2 H, J_{HH} = 9); 7.38-7.46 (dd, 4 H, J_{HH} = 8, J_{HH} = 8); 7.83-7.85 (d, 2 H, J_{HH} = 8); 9.89 (s, 1 H). ESI-MS: m/z 242.4 $(M + H)^+$. FTIR (KBr pellet, cm^{-1}): 2935, 1706 (C=O stretching), 1601, 1512, 1380, 1261, 1160, 1008, 832.

2-(4-(4-vinylbenzyloxy)phenyl)imidazo[4,5-f][1,10]phenanthroline (vinyl-phen)
1,10-phenanthroline-5,6-diketone (2.1 g, 10 mmol) and ammonium acetate (11.4 g, 148 mmol) were dissolved in 60 ml of glacial acetic acid with stirring. A solution of hot 4-(4-vinylbenzyloxy)benzaldehyde (2.36 g, 10 mmol) in 60 ml glacial acetic acid was added dropwise to the mixture. The mixture was heated to 115 °C and kept at the temperature for 5 h. After the reaction was finished, the solution was poured into 600 ml distilled water, carefully neutralized to pH = 7 with ammonium hydroxide and was then cooled to room temperature. The precipitate was filtered off and washed with large portions distilled water. The product was dried overnight in vacuo at 60 °C. Yield: 8.11 g (85%). ^{1}H NMR (400 MHz DMSO-d_6): 5.19 (s, 2 H); 5.26-5.28 (d, 1 H, J_{HH} = 11); 5.83-5.85 (d, 1 H, J_{HH} =10); 6.71-6.78 (dd, 1 H, J_{HH} = 11, J_{HH} = 11); 7.22-7.24 (d, 2 H, J_{HH} = 8); 7.46-7.52 (q, 4 H); 7.79-7.82 (q, 2 H); 8.21-8.23(d, 2 H, J_{HH} = 8); 8.89-8.91 (t, 2 H); 8.99-9.01 (q, 4H); 13.63 (s, 1H). ^{13}C NMR (300 MHz, $CDCl_3$): δ = 173.57, 159.3, 150.91, 147.36, 143.18, 136.7, 136.4, 136.26, 129.75, 128.06, 126.20, 123.16, 121.63, 115.08, 114.48, 69.08, 22.99. ESI-MS: m/z 429.3 $(M + H)^+$. FTIR (KBr pellet, cm^{-1}): 3412, 3166, 1681, 1606, 1565, 1524, 1477, 1407,

1242, 1178, 1008, 826, 745.

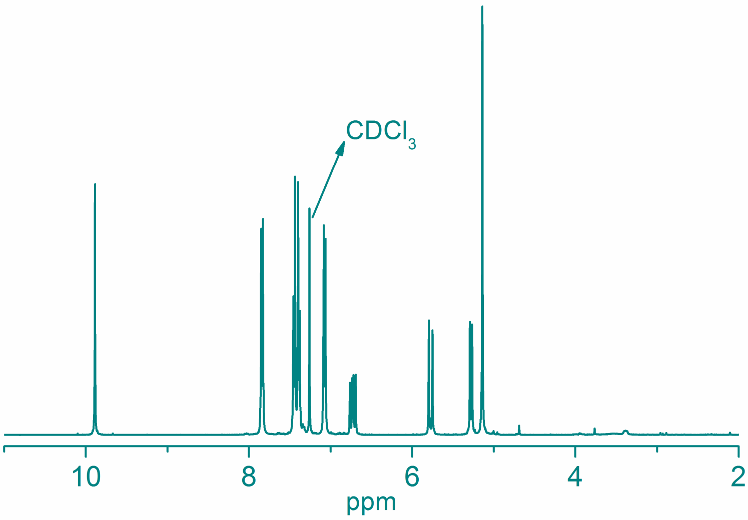
Preparation of the Europium monomer Eu(TTA)$_2$vinyl-phen

Vinyl-phen (0.43 g, 1 mmol) was dissolved in THF (50 ml), to which Eu(TTA)$_2$ .4H$_2$O (0.67 g, 1 mmol) was added. The whole mixture was refluxed for 3 h and cooled to room temperature. The resulting precipitate was collected and washed twice with water to give the titled complex (0.87 g, 83%) as pale yellow powder. (Found: C, 49.76; H, 3.13; N, 5.32. $C_{44}H_{32}EuF_6N_4O_7S_2$ [Eu(TTA)$_2$vinyl-phen] requires C, 49.91; H, 3.05; N, 5.29%). ^{1} H NMR (400 MHz DMSO-*d*$_6$): 3.67 (s, 2 H, -COHCO-); 5.21 (s, 2 H, -CH$_2$-); 5.24-5.29(t, 1 H, CH$_2$=CH-); 5.83-5.88 (t, 1 H, CH$_2$=CH-); 6.29 (s, 2 H, Th-H); 6.48 (s, 2 H, Th-H); 6.72-6.79 (t, 1 H, -CH=CH$_2$); 7.18-7.20 (d, 2 H, J_{HH} = 8, Th-H); 7.24-7.26 (t, 8 H, phen-H and Ph-H); 7.81 (s, 2H, Ph-H), 7.87 (s, 1 H, Ph-H); 7.94 (s, 1 H, phen-H); 8.22 (s, 1 H, phen-H); 9.01(s, 1 H, phen-H); 13.61 (s, 1 H, -NH). ESI-MS: m/z 1022.9 (M + H)$^+$. FTIR (KBr pellet, cm^{-1}): 3097, 1612, 1543, 1531 (C=C stretching in TTA), 1489, 1464, 1415, 1355, 1307, 1191, 1149, 1058, 943, 791, 725, 634, 580.

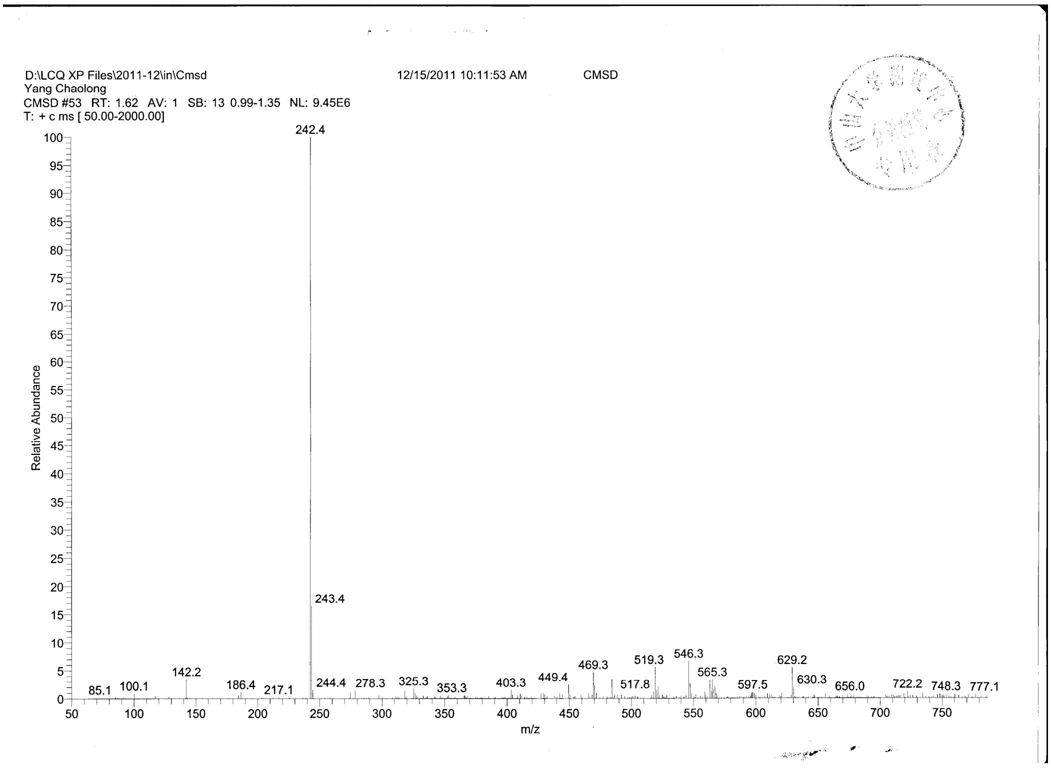
Preparation of the Eu^{3+} Chelate Copolymers (Eu-polymer). A mixture of *N*-vinyl carbarzole (0.51 g, 2.6 mmol), Eu(TTA)$_2$vinyl-phen (61.2 mg, 0.058 mmol), and AIBN initiator (8 mg, 0.8 wt% of the total monomers) was dissolved in dry DMF (3 mL) in a glass polymerization tube. The homogeneous solution was purged with argon for 5 min and sealed under a reduced argon atmosphere. The mixture was heated to 60^{o}C with continuous stirring for 72 h. The reaction mixture remained clear throughout the copolymerization process. The viscous mixture was diluted with DMF (3 mL) and precipitated into methanol (50 mL) under vigorous stirring. The reprecipitation procedure was repeated for three times. The resulting solid material was collected by filtration. The copolymer was further purified by Soxhlet extraction with boiling acetone for 48 h and finally dried in a vacuum oven at 60^{o}C for 24 h. Yield 0.46 g (81%). ^{1}H NMR (400 MHz, CDCl$_3$): δ = 8.01, 7.68, 6.89, 6.35, 4.86, 3.47, 3.18, 2.51, 0.97 ppm. FTIR (KBr pellet, cm^{-1}): 3058, 2931, 1676, 1628, 1598, 1531 (C=C stretching in TTA), 1482, 1453, 1332, 1227, 1167, 1157, 1124, 743, 713. Elemental analysis calcd (%): C 77.97, H 6.37, N 6.07. Found: C 79.63, H 6.14, N 6.31. Molecular weight: *M*n = 7714, *M*w = 13607, PDI = 1.76. The content of Eu^{3+} = 1.96 wt %. Polymer composition: x:y = 1:50, which is determined according to the results of elemental analysis and Eu^{3+} titration.

3. The NMR and ESI-MS data of compounds.

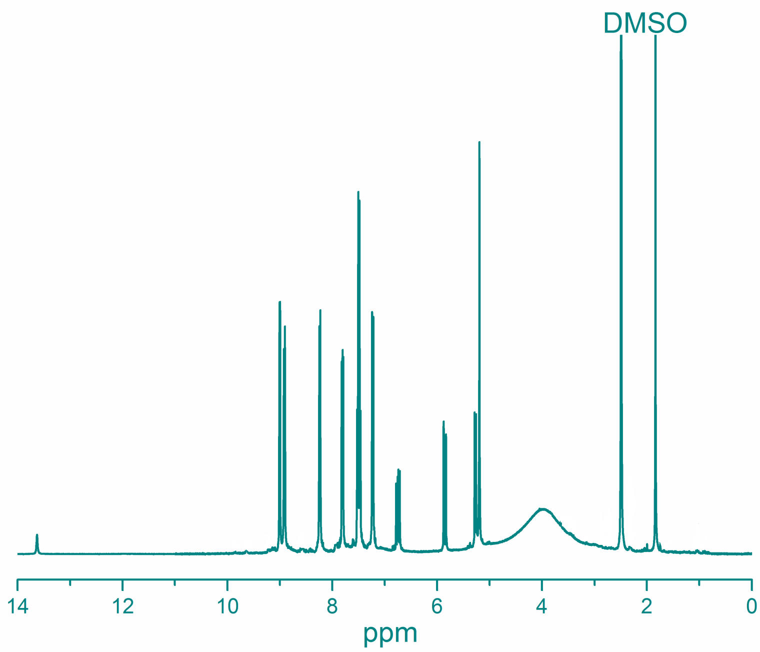
^{1}H NMR of 4-(4-vinylbenzyloxy)benzaldehyde



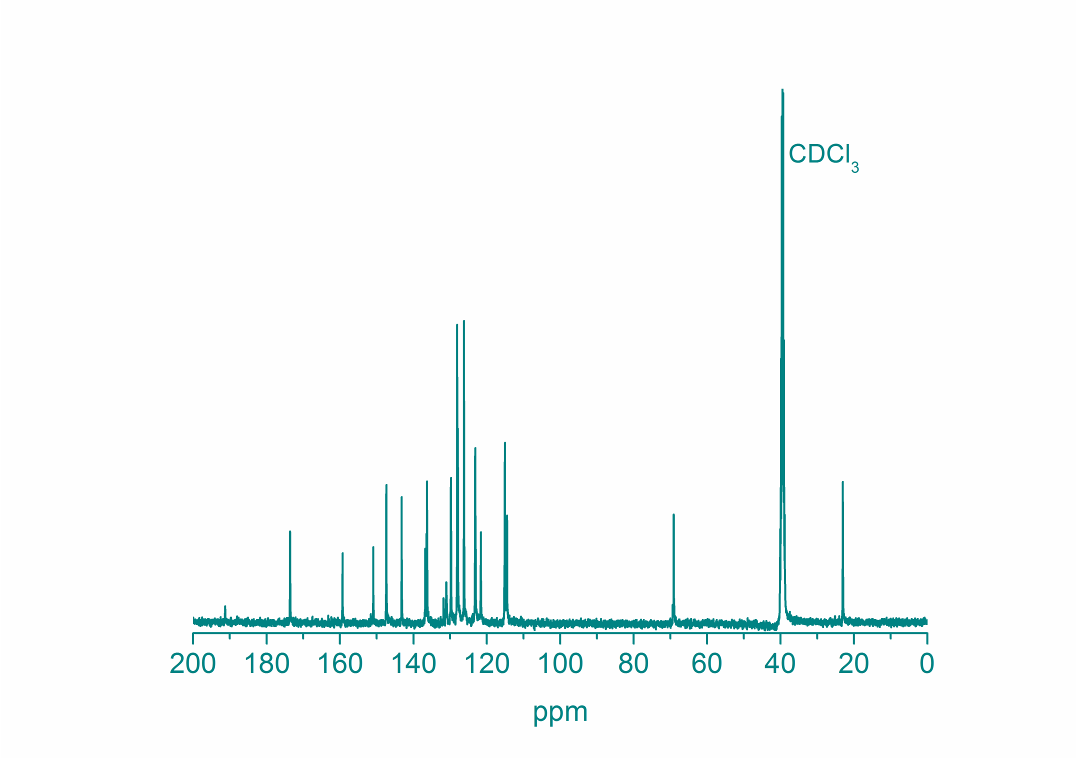
ESI-MS of 4-(4-vinylbenzyloxy)benzaldehyde



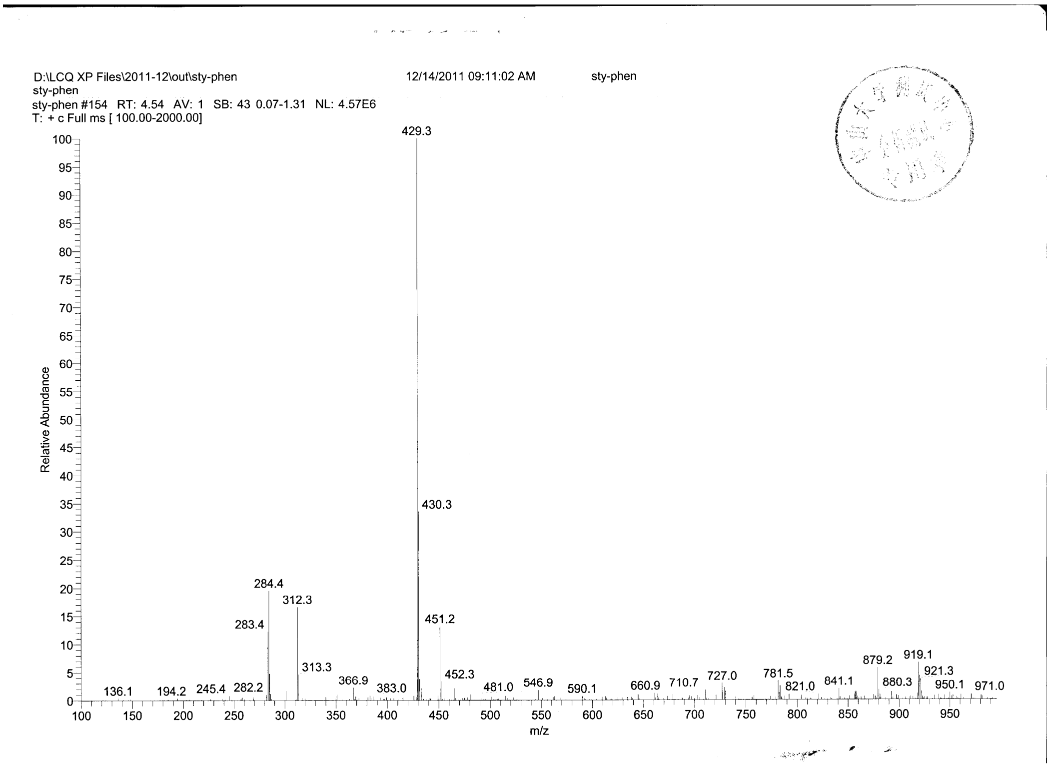
^{1}H NMR of vinyl-phen



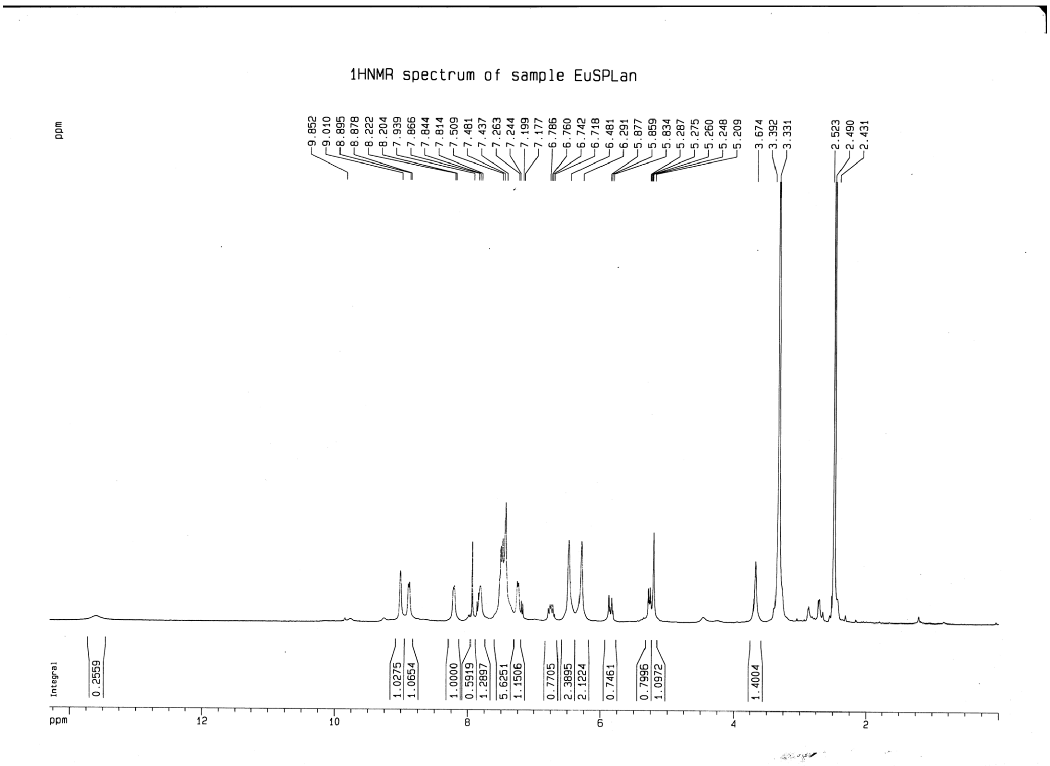
^{13}C NMR of vinyl-phen



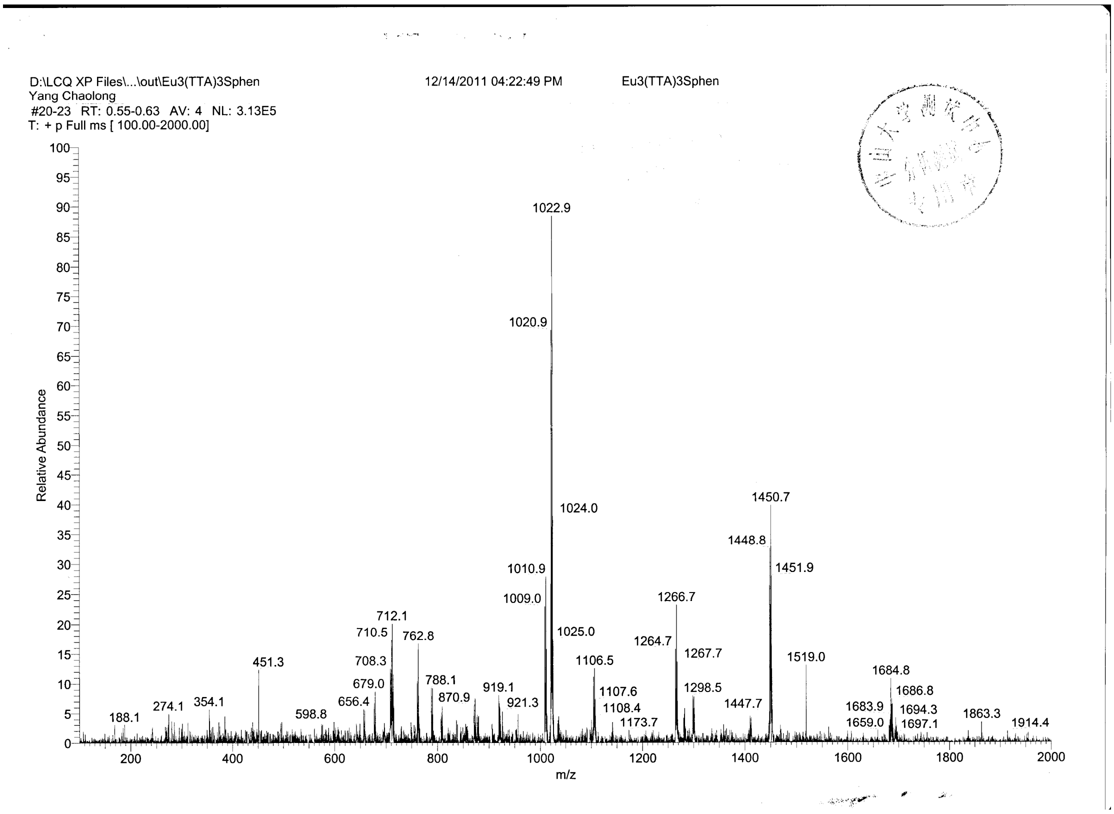
ESI-MS of vinyl-phen



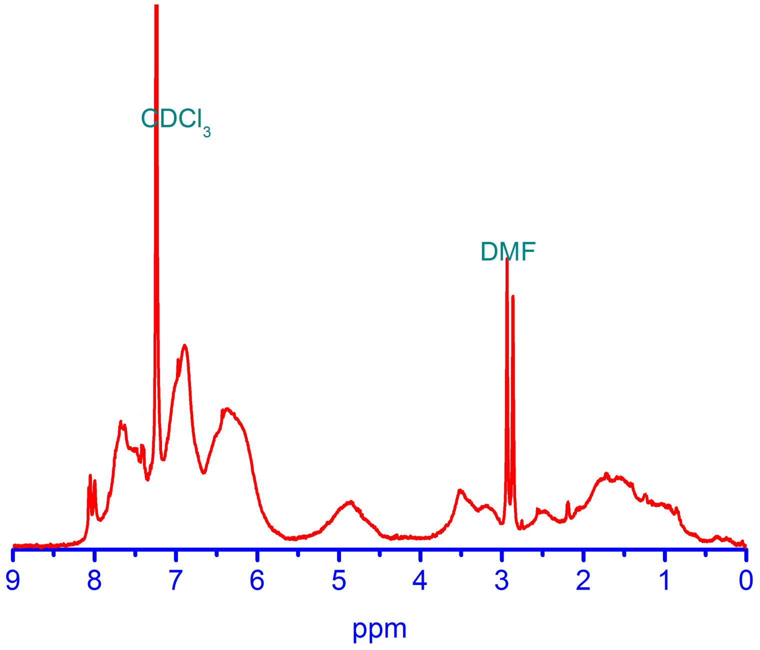
^{1}H NMR of Eu(TTA)$_2$vinyl-phen



ESI-MS of Eu(TTA)$_2$vinyl-phen



^{1}H NMR of Eu-polymer



4. Electrochemical properties of Eu(TTA)$_2$vinyl-phen and Eu-polymer.

Table S1 Electrochemical properties of Eu(TTA)$_2$vinyl-phen and Eu-polymer

Complexes	E_{ox}[a](V)	E_{red}[b](V)	E_{HOMO}[c](eV)	E_{LUMO}[d](eV)	E_g[e](eV)
Eu(TTA)$_2$vinyl-phen	1.91	-1.28	-6.29	-3.1	3.19
Eu-polymer	1.94	-1.51	-6.32	-2.87	3.45

[a] Estimated according to the reduction potential and the UV-vis absorption spectra

[b] Measured in acetonitrile solution at 298 K

[c] $E_{HOMO} = -(E_{ox}+4.38)$ eV

[d] $E_{\mathrm{LUMO}} = -(E_{\mathrm{red}}+4.38)$ eV

[e] Estimated according to the UV-vis absorption spectra

5. **Additional Fig.s (Fig. S1-S12).**

Fig. S1 The FTIR spectra of vinyl-phen, monomer Eu(TTA)$_2$vinyl-phen and Eu-polymer.

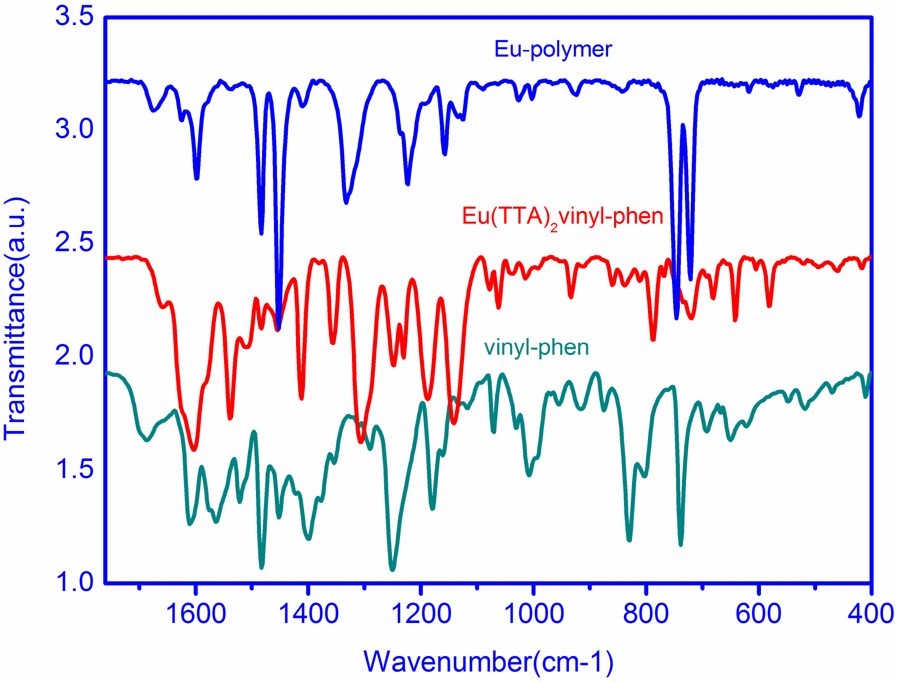


Fig. S2 The ground state geometry of monomer Eu(TTA)$_2$vinyl-phen calculated using the Sparkle/PM3 model.

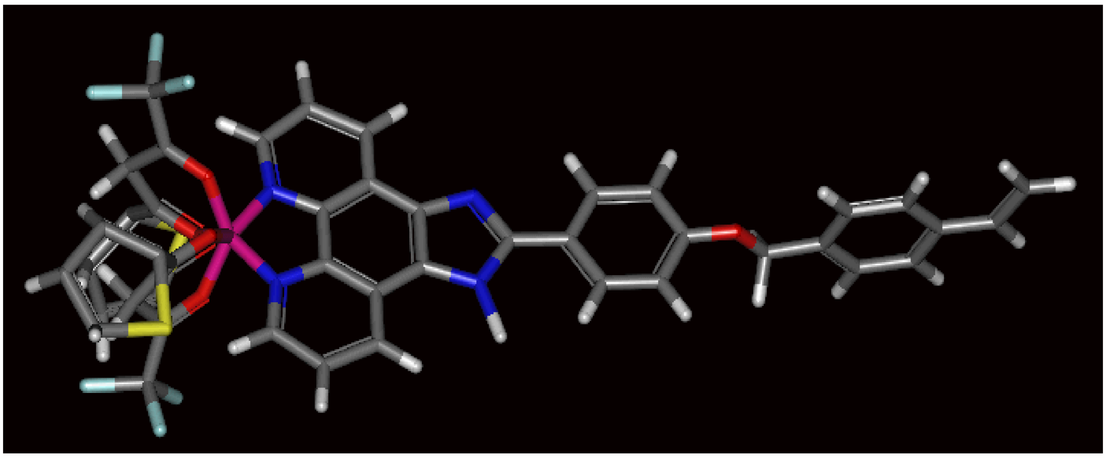


Fig. S3 Cyclic voltammogram of monomer Eu(TTA)$_2$vinyl-phen and Eu-polymer measured in acetonitrile solution, containing 0.1 M Bu$_4$NClO$_4$ at 298 K. Scans rates 50 mv/s.

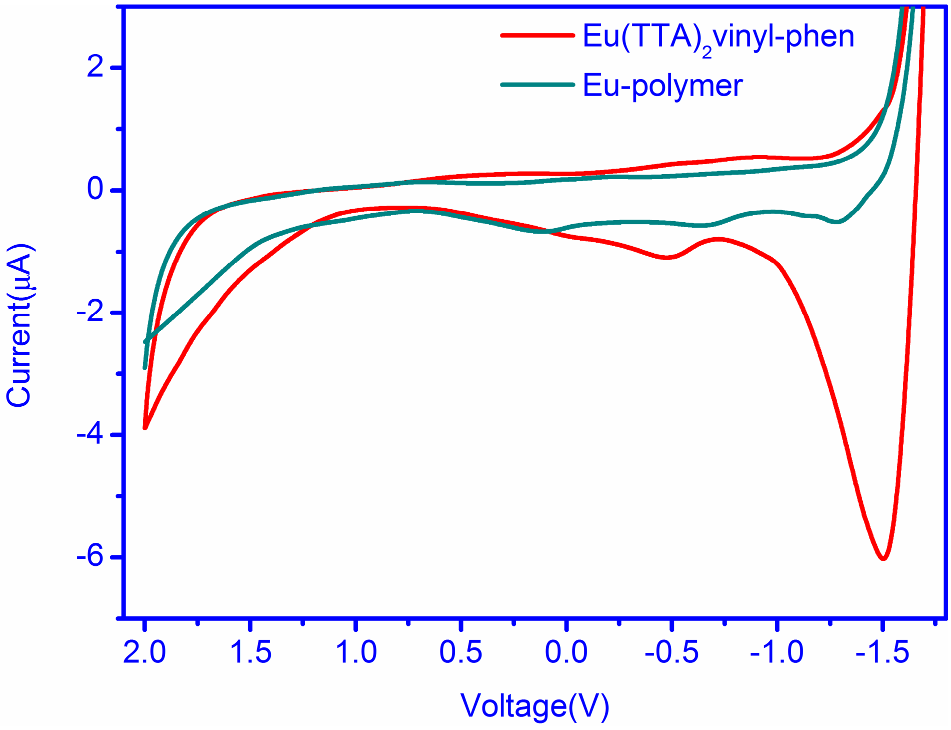


Fig. S4 Thermogravimetric analysis of Eu-polymer.

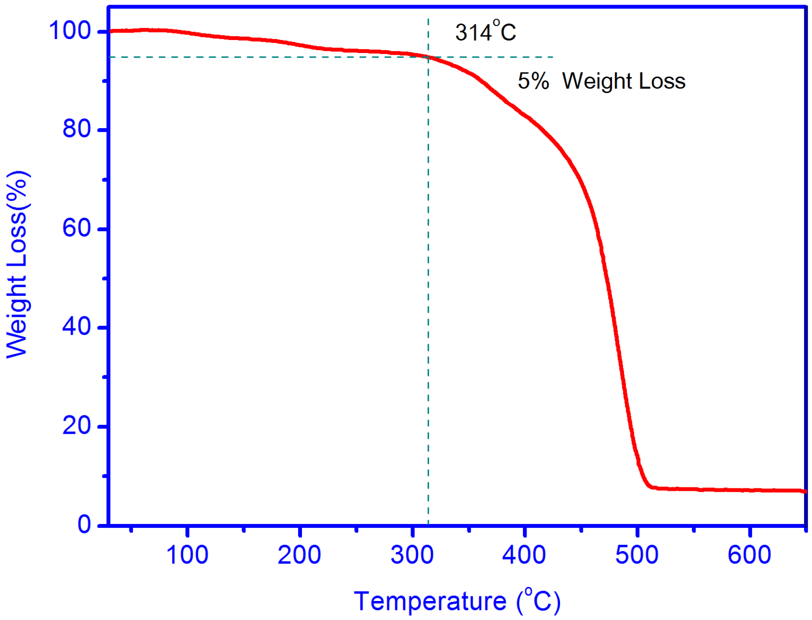


Fig. S5 The decay curves of Eu(TTA)$_2$vinyl-phen and Eu-polymer in solid state and in THF solutions (λ_{em} = 616 nm, λ_{ex} = 360 nm).

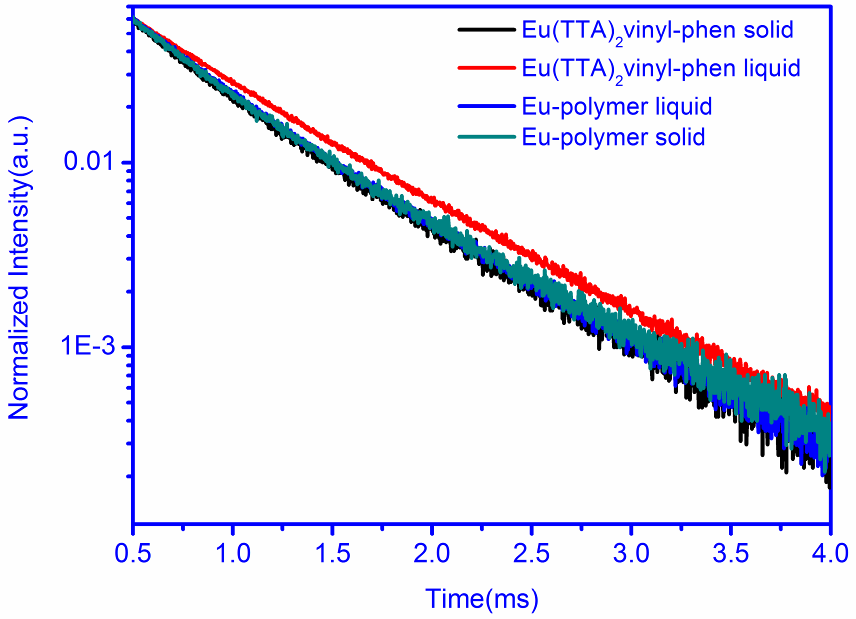


Fig. S6 Emission intensity change at 616 nm as a function of F$^-$ concentration.

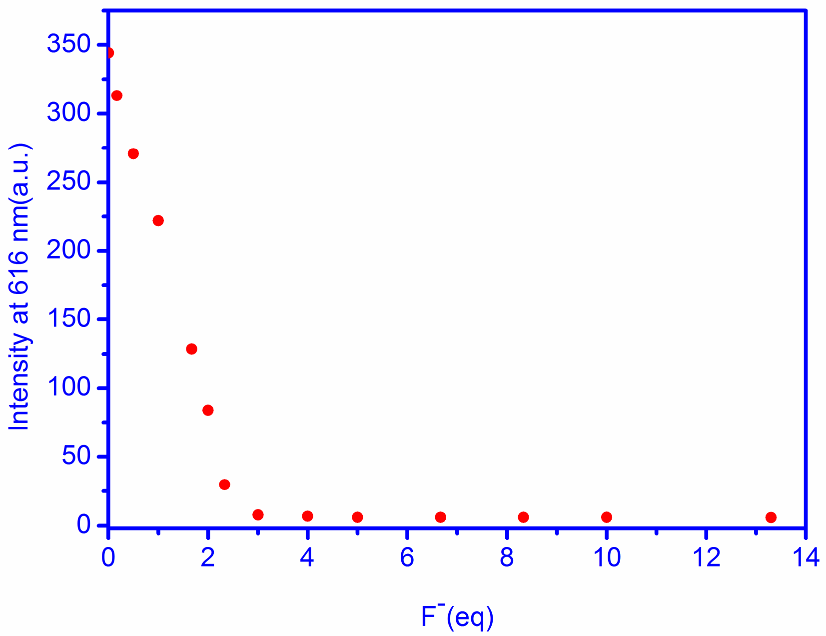


Fig. S7 Emission intensity change at 616 nm as a function of CH_3COO^- concentration.

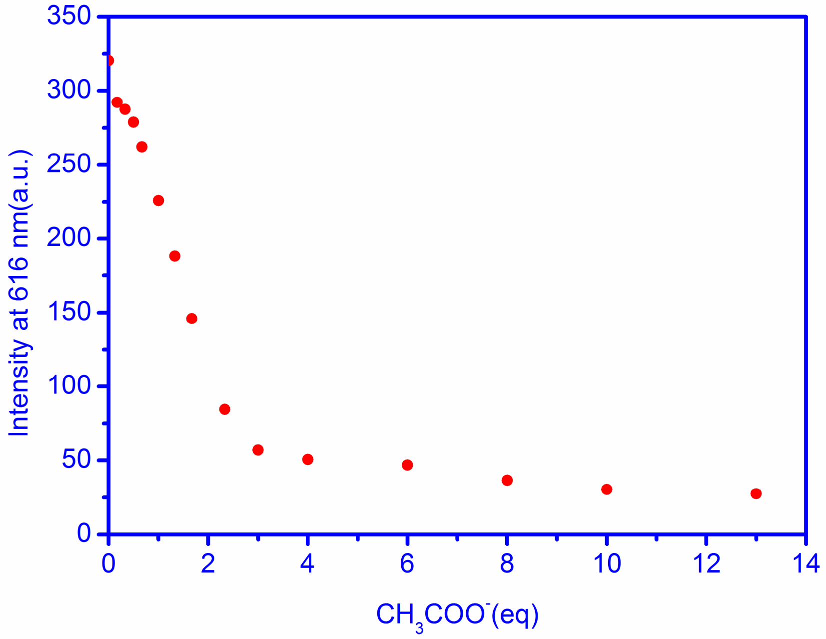


Fig. S8 Emission intensity change at 616 nm as a function of $H_2PO_4^-$ concentration.

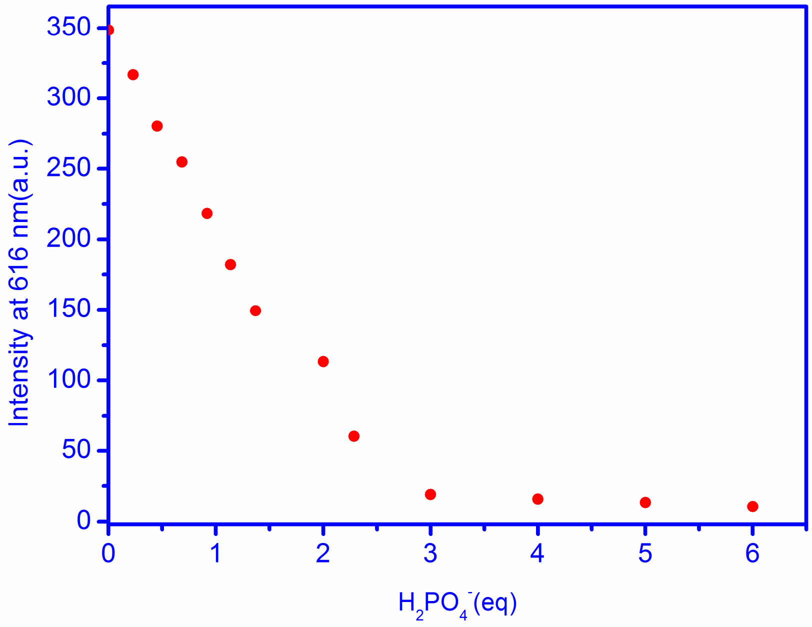


Fig. S9 Fluorescence quenching of monomer Eu(TTA)$_2$vinyl-phen by various concentration of F$^-$, in which F_0 and F denote the intensity of the fluorescence signal of the sensing materials in the absence and presence of the anions, respectively. K_{SV} = $(F_0/F-1)/[\text{anions}]$.

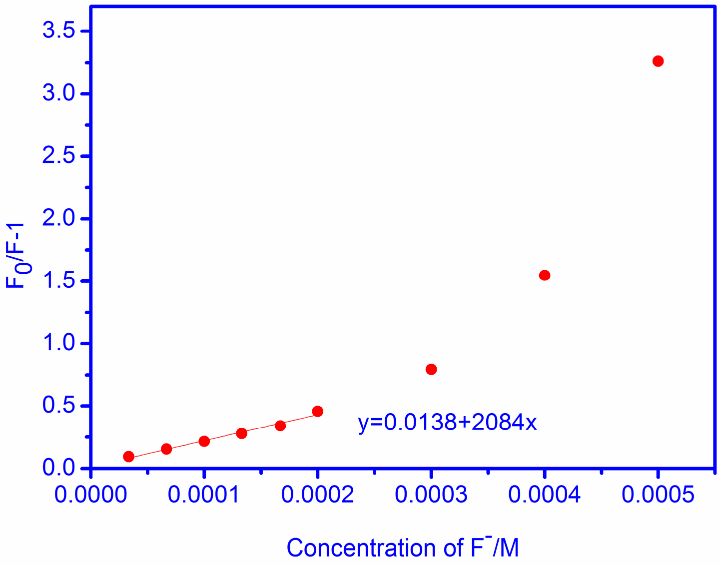


Fig. S10 Fluorescence quenching of monomer Eu(TTA)$_2$vinyl-phen by various concentration of CH$_3$COO$^-$, in which F_0 and F denote the intensity of the fluorescence signal of the sensing materials in the absence and presence of the anions, respectively. $K_{SV} = (F_0/F\text{-}1)/[\text{anions}]$.

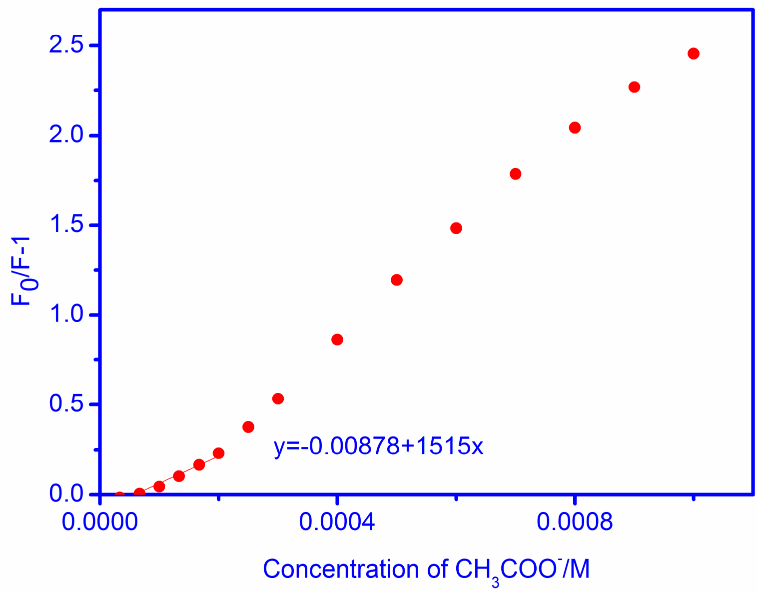


Fig. S11 Fluorescence quenching of monomer Eu(TTA)$_2$vinyl-phen by various concentration of $H_2PO_4^-$, in which F_0 and F denote the intensity of the fluorescence signal of the sensing materials in the absence and presence of the anions, respectively. $K_{SV} = (F_0/F\text{-}1)/[\text{anions}]$.

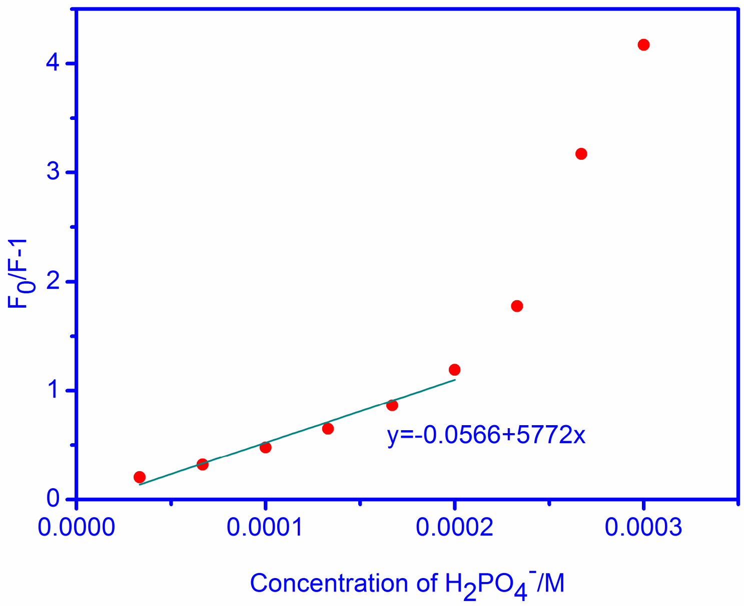


Fig. S12 Fluorescence quenching degree (*F_0/F*-1) of Eu-polymer (0.73×10^{-4} M in Eu^{3+} chelate segment) with the addition of 6.8eq CH_3COO^- in the presence of mixed anions (each 6.8eq).

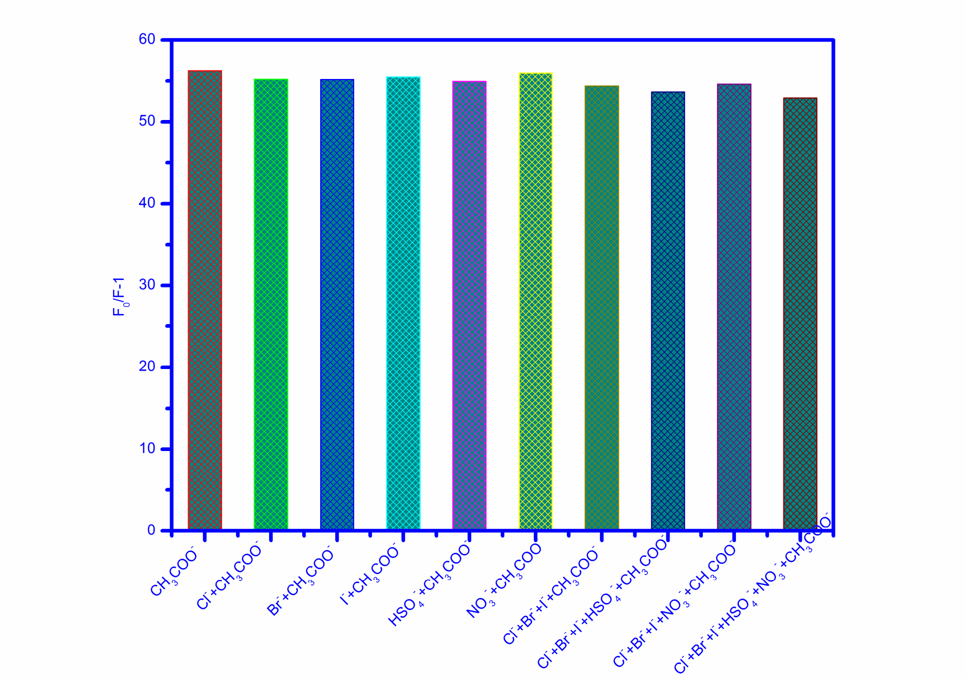


Fig. S13 Fluorescence quenching degree (*F_0/F*-1) of Eu-polymer (0.73×10^{-4} M in Eu^{3+} chelate segment) with the addition of 6.8eq $H_2PO_4^-$ in the presence of mixed anions (each 6.8eq).

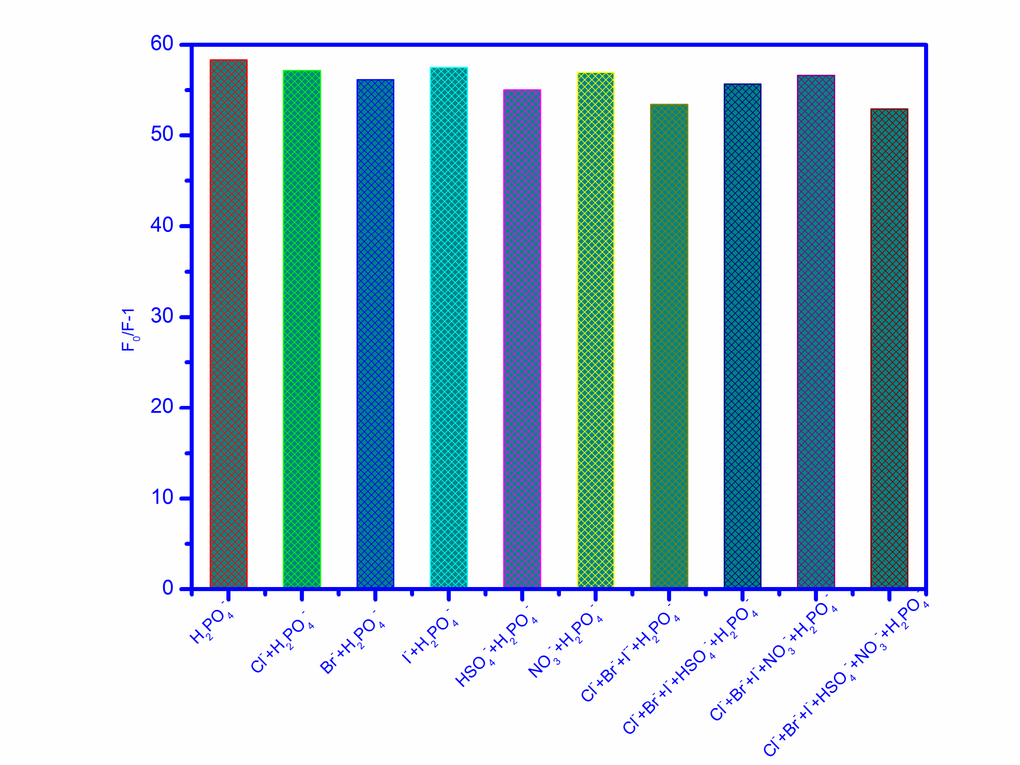


Fig. S14 Changes in the Eu-polymer sensor emission spectra showing selectivity to F^- in the presence of CH_3COO^-.

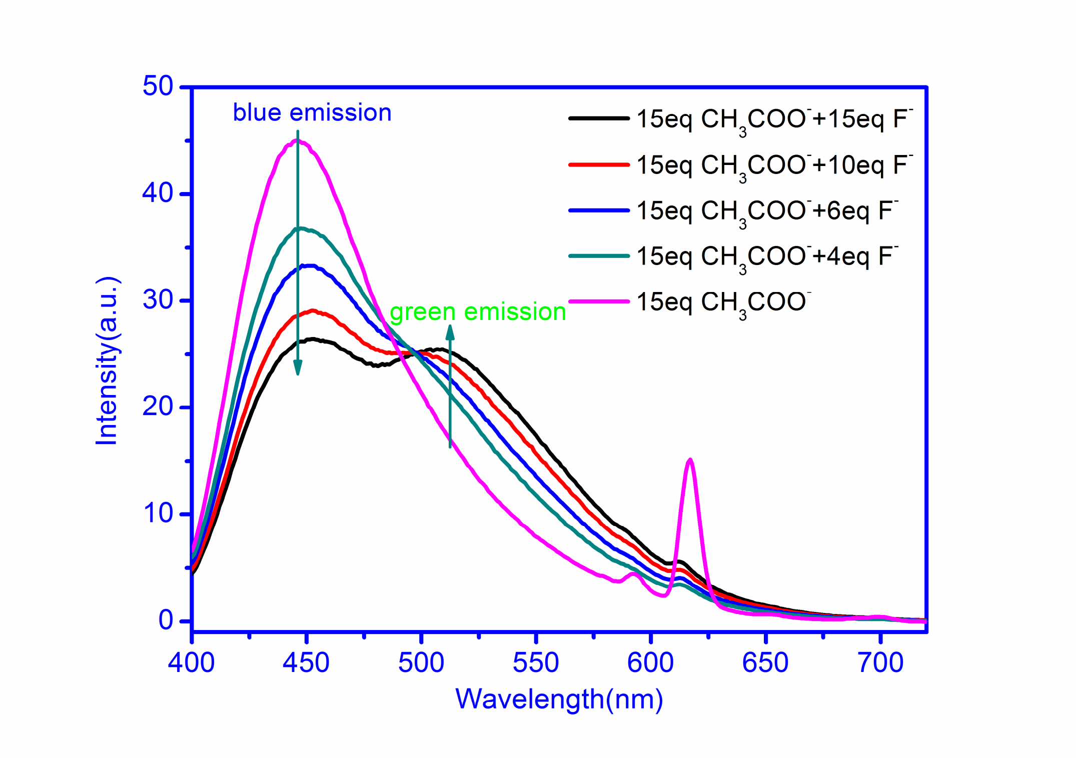


Fig. S15 Changes in the Eu-polymer sensor emission spectra showing selectivity to F^- in the presence of $H_2PO_4^-$.

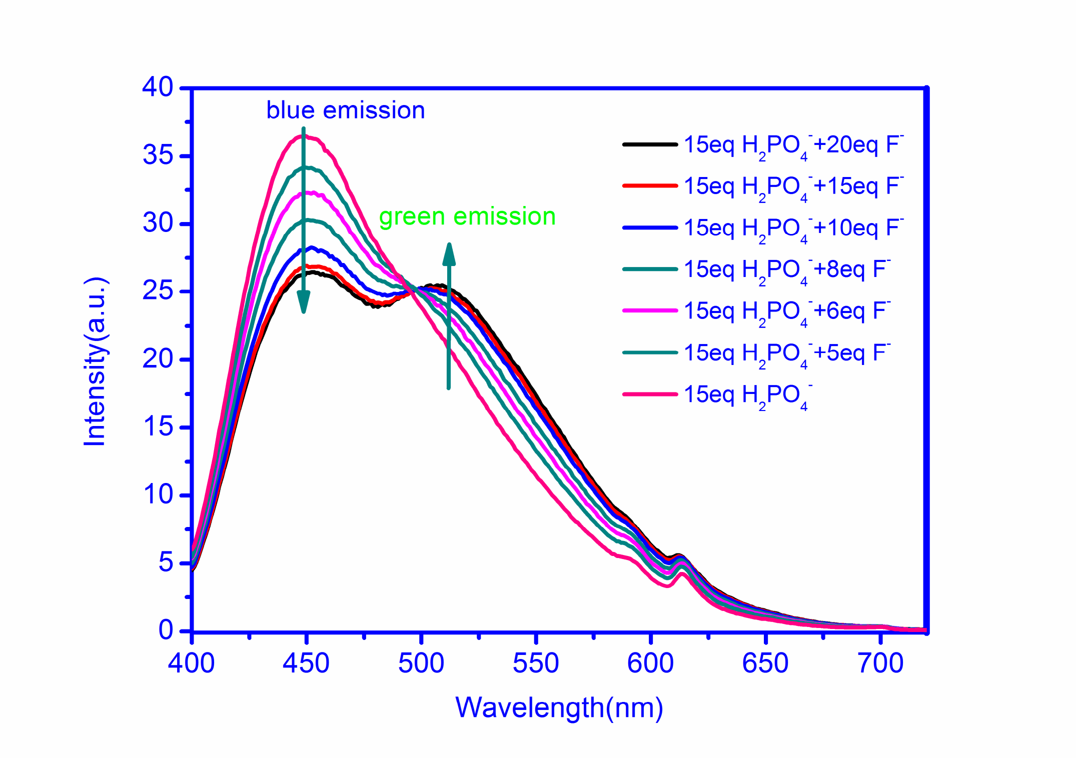


Fig. S16 The emission spectra changes of 5eq CH_3COO^- bonded Eu-polymer with the addition of 10% water.

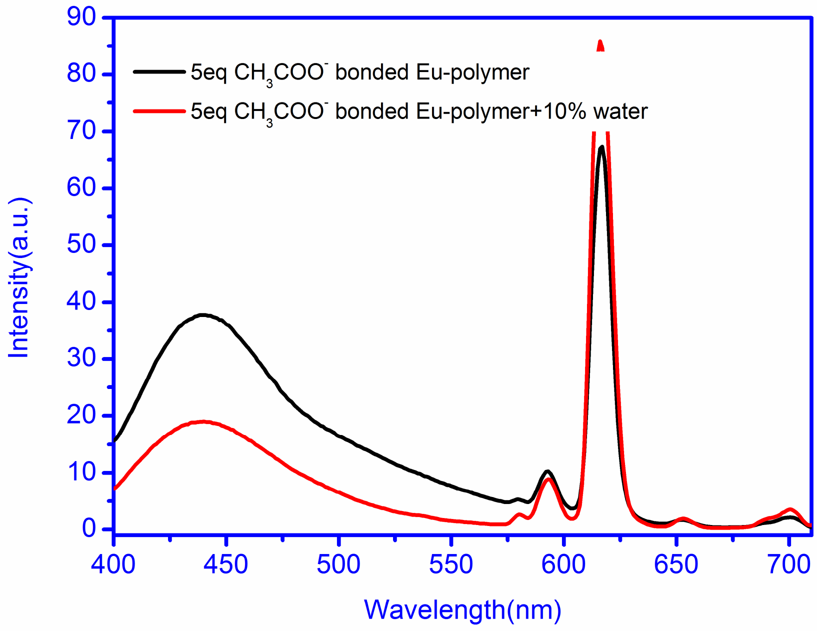


Fig. S17 The emission spectra changes of 5eq $H_2PO_4^-$ bonded Eu-polymer with the addition of 10% water.

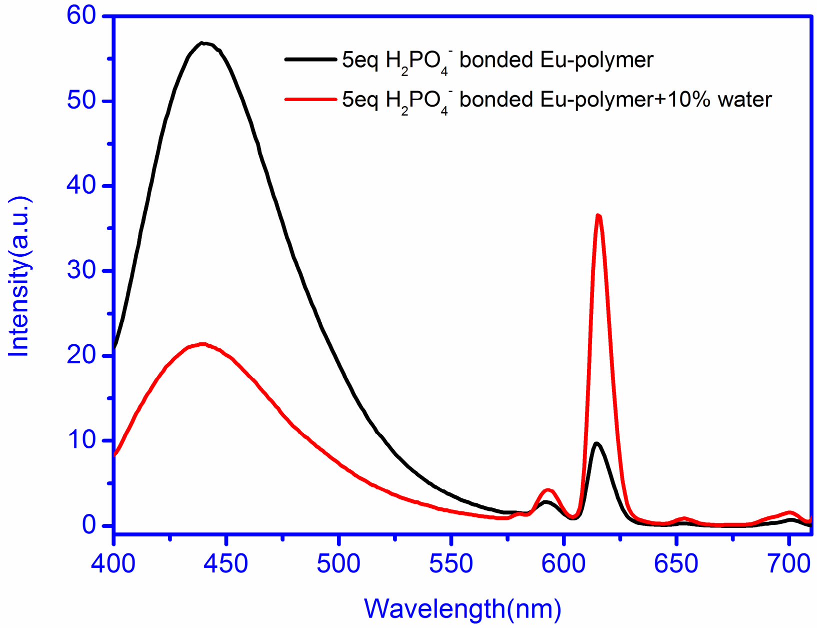


Fig. S18 The changes of ^{1}HNMR spectra for vinyl-phen upon the addition of differen concentration CH_3COO^-.