Electronic Supporting Information Available

ESIPT-capable Eu^{3+}-metallopolymer with colour-tunable emission for selective visual sensing of Zn^{2+} ion

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Contents Page

Materials and Methods

High performance liquid chromatography (HPLC)-grade tetrahydrofuran (THF) or acetonitrile (MeCN) was purchased from Fisher Scientific and purified over solvent columns. Other solvents were used as received from Sigma Aldrich and stored over 3 Å activated molecule sieves. Azobis(isobutyronitrile) (AIBN) was purified by recrystallization twice from absolute MeOH prior to use. Other chemicals were commercial products of reagent grade and were used without further purification. (1,3-bis(4,4,4-trifluoro-1,3-dioxobutyl)phenyl) (H_2BTP), the series of bis(β-diketonate) tetrahydrate Ln^{3+}-complex precursors [$Ln_2(BTP)_3(H_2O)_4$] (Ln = La, Eu or Gd), 2-(pyridin-2-yl)-5-(4-vinylphenyl)pyridine (4-VP-BPY) were synthesized according to well-established procedures from the literatures,[1,2] respectively. All manipulations of air and water sensitive compounds were carried out under dry N_2 using the standard Schlenk line techniques.

Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer. Infrared spectra were recorded on a Nicolet Nagna-IR 550 spectrophotometer in the region 4000-600 cm^{-1} using KBr pellets. ^{1}H NMR spectra were recorded on a Bruker Plus 400 spectrometer with $SiMe_4$ as the internal standard in $CDCl_3$ and/or DMSO-δ_6 at room temperature. Electronic absorption spectra in the UV/Visible region were recorded with a Shimadzu UV-3159 UV-Vis-NIR spectrophotometer. Emission and excitation spectra were collected by a combined fluorescence lifetime and steady-state spectrometer (FLS-980, Edinburgh) with a 450 W Xe lamp. X-ray photoelectron spectroscopy (XPS) was measured using a Thermo ESCALAB250i X-ray photoelectron spectrometer. Excited-state decay times were obtained by the same spectrometer but with a μF900 Xe lamp. Thermogravimetric (TG) analyses were carried out on a NETZSCH TG 209 instrument under flowing nitrogen by heating the samples from 25 to 800 ^{o}C. MS study was

performed on a Waters ZQ2000 mass spectrometer using MeOH as solvent. The luminescent absolute overall quantum yield in solid state was determined by the same spectrometer using a 450 W Xe lamp and an integrating sphere. Gel permeation chromatography (GPC) analyses of the polymers were performed using a Waters 1525 binary pump coupled to a Waters 2414 refractive index detector with HPLC THF as the eluant on American Polymer Standard 10 μm particle size, linear mixed bed packing columns. The GPC was calibrated using polystyrene standards. The Commission International de I'Eclairage (CIE) coordinate of each sample were calculated on the basis of the international CIE standards.

Electronic structure calculations

The ground state (S_0) properties of the small-molecule organic probe **4-VP-PHI** and its different metal ion (Cd^{2+}/ Zn^{2+}) complexes were calculated by DFT (density function theory) and TD-DFT (time-dependent DFT) of Gaussian 09 package in gas phase using the Becke's three parameterized Lee-Yang-Parr (B3LYP)[3] exchange functional with the 6-31G (d,p)[4] basis set for nonmetallic elements and LANL2DZ[5] basis set for metallic elements. The electronic density diagrams of molecular orbits were obtained with the GaussianView 6.0 software. Orbital composition was analyzed through Multiwfn[6] software.

Absorbance and fluorescence of 4-VP-PHI or Eu^{3+}-metallopolymer with different cationic metal ions

The organic small-molecule dye **4-VP-PHI** or Eu^{3+}-metallopolymer **Poly[(4-VP-PHI)-*co*-Eu-*co*-MMA]** was dissolved in MeCN-H_2O mixed (9:1, v/v) solvent to afford the stock solution with a concentration of 1×10^{-3} M or 5 mg/ml. The solutions containing different inorganic chloride salts (Na^+, K^+, Li^+, Ni^{2+}, Mg^{2+}, Sn^{2+}, Ca^{2+}, Hg^{2+}, Mn^{2+}, Cd^{2+}, Cr^{2+}, Al^{3+}, Zn^{2+}) with a stipulated

concentration of 1×10^{-3} M in a MeCN-H_2O mixed (9:1, v/v) solvent were also prepared, respectively. During the experiments, the 40 μL stock solution (1×10^{-3} M) and each of the 40 μL cationic metal ion solutions (1×10^{-3} M) and 3 mL MeCN-H_2O mixed (9:1, v/v) solvent were placed in a quartz cell (10.0 mm wide), and then MeCN-H_2O mixed (9:1, v/v) solvent was further supplemented to a constant volume of 4 mL. Spectral data were recorded after 10 min at room temperature for equilibrating each addition. The UV-visible absorption spectrum was recorded in the wavelength range of 200-600 nm, and the fluorescence spectrum was recorded from 350 nm to 650 nm with excitation at 320 nm.

Absorbance and fluorescence titrations of 4-VP-PHI or Eu^{3+}-metallopolymer with Zn^{2+} ion

A series of solutions having the 40 μL stock solution of **4-VP-PHI** or Eu^{3+}-metallopolymer **Poly[(4-VP-PHI)-*co*- Eu-*co*-MMA]** in MeCN-H_2O (9:1, v/v) (1×10^{-3} M or 5 mg/ml) and $ZnCl_2$ (1×10^{-3} M) in MeCN-H_2O (9:1, v/v) were obtained in such a manner that the volume (4 mL) supplemented with MeCN-H_2O (9:1, v/v) was kept constant. The amount of the $ZnCl_2$ (1×10^{-3} M) in MeCN-H_2O (9:1, v/v) was taken through adjusting the final concentrations of the Zn^{2+} ion in the range of 0-1.79×10^{-8} M or 0-1.45×10^{-8} for **4-VP-PHI** and **Poly[(4-VP-PHI)-*co*-Eu-*co*-MMA]** respectively. The mixed solutions were blended for 10 min at room temperature, and both the UV-visible absorption and the fluorescence spectra were well recorded as the above-mentioned.

Competition experiments

Eu^{3+}-metallopolymer **Poly[(4-VP-PHI)-*co*- Eu-*co*-MMA]** was dissolved in MeCN-H_2O (9:1, v/v) to afford the stock solution with a concentration of 5 mg/ml. The solutions containing Zn^{2+} ion and one of the other different inorganic chloride salts (Na^+, K^+, Li^+, Ni^{2+}, Mg^{2+}, Sn^{2+}, Ca^{2+}, Hg^{2+}, Mn^{2+}, Cd^{2+}, Cr^{2+}, Al^{3+}, Zn^{2+}) with the similarly stipulated concentration of 1×10^{-3} M in a MeCN-

H_2O-mixed (9:1, v/v) solvent were prepared, respectively. During the experiments, the 40 μL stock solution (1×10^{-3} M) and each of the 40 μL containing Zn^{2+} and metal ion solutions (1×10^{-3} M) were placed in a quartz cell (10.0 mm wide), and then MeCN-H_2O (9:1, v/v) was further supplemented to a constant volume of 4 mL. The mixed solutions were blended for 10 min at room temperature, and the fluorescence spectra were well recorded as the above-mentioned.

Calculation of the Stern–Volmer constant (K_{SV}) and limit of detection (LOD).

The extent of fluorescence quenching was calculated using the Stern–Volmer equation below[7]:

$$\frac{I_0}{I} = 1 + K_{sv} \times \left[z^{2}{}_{n}^{+} \right] \quad (1)$$

where K_{SV} represents the Stern–Volmer quenching constant, and I_0 and I respectively indicate the fluorescence intensities in the absence and presence of Zn^{2+} ions at various concentrations.

The limit of detection (LOD) was calculated using equation below[8]:

$$LOD = \frac{3\sigma}{K_{sv}} \quad (2)$$

where σ represent the standard deviation (for ten measurements, n = 10).

Synthesis of 1,3-bis(4,4,4-trifluoro-1,3-dioxobutyl)phenyl (H_2BTP)

A mixture of sodium ethylate (1.36 g, 20 mmol) and ethyl trifluoroacetate (2.84 g, 20 mmol) in 40 mL dry THF (tetrahydrofuran) was stirred for 10 min under nitrogen atmosphere, followed by the addition of 1,3-Diacetylbenzene (1.36 g, 8.4 mmol), the solution was further stirred at room temperature for 24 h. Finally, the resulting mixture was poured into 100 mL ice water and acidified to pH 2−3 using hydrochloric acid (2 M), the

resulting white precipitate was filtered, dried in vacuum, and was purified from recrystallization in isopropanol. Yield 2.08 g (70%). Anal. Calcd for $C_{14}H_8F_6O_4$: C, 47.47; H, 2.28. Found: C, 47.42; H, 2.33. IR (KBr, cm^{-1}): 3434 (w), 3125 (w), 1593 (s), 1265 (s), 1202 (s), 1156 (s), 1081 (s), 929 (m), 786 (m), 721 (w), 708 (w), 677 (w), 627 (m), 579 (m). ^{1}HNMR ($CDCl_3$, 400 MHz): δ (ppm) 8.50 (s, 1H, -Ph), 8.17 (d, 2H, -Ph), 7.70 (t, 1H, -Ph), 6.64 (s, 2H, -CH).

Synthesis of 2-(pyridin-2-yl)-5-(4-vinylphenyl)pyridine (4-VP-BPY)

To a stirred solution of 5-Br-2,2'-bpy (1.40 g, 6 mmol), 4-vinylphenylboronic acid (0.89 g, 6 mmol), and $Pd(PPh_3)_4$ (0.69 g of 6 mmol) in 20 ml toluene in three-necked round-bottom flask equipped with a condenser, an addition funnel, and a magnetic stirrer. degassed aqueous solution of Na_2CO_3 (2 M, 6 mL) was added. The resulting mixture was further refluxed at 90℃ for 48 h. After cooling down to room temperature, the mixture was extracted using CH_2Cl_2 (3 × 30 mL) and dried over $MgSO_4$. Then, the organic layer was poured into n-hexane (50 mL). The precipitate was further purified through silica column chromatography by using ethyl acetate and n-hexane (v/v, 1/3) as the eluent to give a white powder product. Yield 1.33 g (86%). Anal. Calcd for $C_{18}H_{14}N_2$: C, 83.69; H, 5.46. Found: C, 83.56; H, 5.55. FT-IR (KBr, cm^{-1}): 3461 (w), 3152 (w), 1961 (w), 1912 (w), 1810 (w), 1631 (s), 1591 (s), 1513 (m), 1461 (s), 1441 (vs), 1410 (m), 1372 (m), 1273 (w), 1241 (w), 1171 (s), 1122 (s), 1091 (w), 1072 (w), 1041 (w), 1031 (w), 988 (s), 931 (w), 902 (m), 836 (s), 795 (s), 751 (s), 722 (s), 695 (s), 647 (w), 634 (w), 618 (w), 587 (w), 541 (s), 516 (w), 446 (w). ^{1}HNMR (400MHz, $CDCl_3$): δ (ppm) 8.96 (d, 1H, -Py), 8.73 (d, 1H, -Py), 8.48 (q, 2H, -Py), 8.06 (q, 1H, -Py), 7.87 (t, 1H, -Py), 7.67 (d, 2H, -Ph), 7.57 (d, 2H, -Ph), 7.36 (m, 1H, -Py), 6.81 (q, 1H, -CH=),

5.86 (d, 1H, =CH_2), 5.35 (d, 1H, =CH_2).

Synthesis of divinyl-functionalized complex monomers [$Ln_2(BTP)_3$(4-VP-BPY)$_2$] (Ln = La, 1; Eu, 2 or Gd, 3)

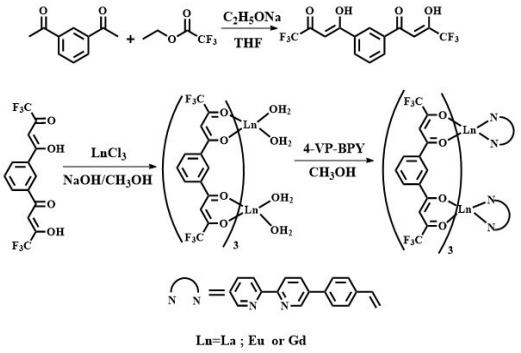
To a stirred suspension of **[$Ln_2(BTP)_3(H_2O)_4$]** (0.3 mmol; Ln = La, 0.422 g; Ln = Eu, 0.430 g; Ln = Gd, 0.433 g) in absolute MeOH (10 mL), another solution of **4-VP-BPY** (0.155 g, 0.6 mmol) in absolute EtOH (10 mL) was added, and the reaction mixture was refluxed for 4 h under an N_2 atmosphere. After cooling to room temperature, each of the resultant clear solution was filtered and left to stand at room temperature for several days to give pale-yellow polycrystalline products, respectively.

For complex monomer **[$La_2(BTP)_3$(4-VP-BPY)$_2$]**: Yield: 0.339 g, 61%. Anal. Calcd for $C_{78}H_{46}F_{18}O_{12}N_4La_2$: C, 50.61; H, 2.50; N, 3.03%. Found: C, 50.65; H, 2.41; N, 3.09%. FT-IR (KBr, cm^{-1}): 2383 (w), 1688 (w), 1619 (s), 1536 (m), 1463 (m), 1298 (s), 1188 (m), 1140 (vs), 1078 (m), 956 (w), 839 (w), 780 (s), 738 (w), 694 (m), 635 (s). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 9.06 (d, 2H, -Py), 8.73 (d, 2H,-Py), 8.47 (m, 6H, -Py), 8.29 (q, 2H,-Py), 7.98 (m, 2H, -Py), 7.83 (d, 4H,-Ph), 7.54 (m, 14H, -Ph), 7.21 (t, 2H,-Ph), 6.82 (q, 2H, -CH=C), 6.14 (s, 3H, =CH-), 5.98 (d, 2H, =CH_2), 5.76 (s, 3H, =CH-), 5.35 (d, 2H, =CH_2). MS (MeOH, *m/z*): 1873.64, $[M+Na]^+$.

For complex monomer **[$Eu_2(BTP)_3$(4-VP-BPY)$_2$]**: Yield: 0.332 g, 59%. Anal. Calcd for $C_{78}H_{46}F_{18}O_{12}N_4Eu_2$: C, 49.91; H, 2.47; N, 2.98%. Found: C, 49.83; H, 2.51; N, 3.03%. FT-IR (KBr, cm^{-1}): 2383 (w), 1689 (w), 1619 (s), 1536 (m), 1464 (m), 1299 (s), 1188 (m), 1140 (vs), 1079 (m), 956 (w), 837 (w), 780 (s), 738 (w), 694 (m), 635 (s). MS (MeOH, *m/z*): 1899.56, $[M+Na]^+$.

For complex monomer **[$Gd_2(BTP)_3$(4-VP-BPY)$_2$]**: Yield: 0.362 g, 64%. Anal. Calcd for $C_{78}H_{46}F_{18}O_{12}N_4Gd_2$: C, 49.63; H, 2.46; N, 2.97%. Found: C, 49.56; H, 2.51; N, 2.91%. FT-IR (KBr,

cm^{-1}): 2383 (w), 1689 (w), 1618 (s), 1532 (m), 1471 (m), 1290 (s), 1185 (m), 1350 (vs), 1072 (m), 950 (w), 835 (w), 779 (s), 738 (w), 694 (m), 638 (s). MS (MeOH, *m/z*): 1913.48, [M+Na]$^+$.



Scheme S1. Synthesis procedure for **[Ln$_2$(BTP)$_3$(4-VP-BPY)$_2$]** (Ln = La, Eu or Gd)

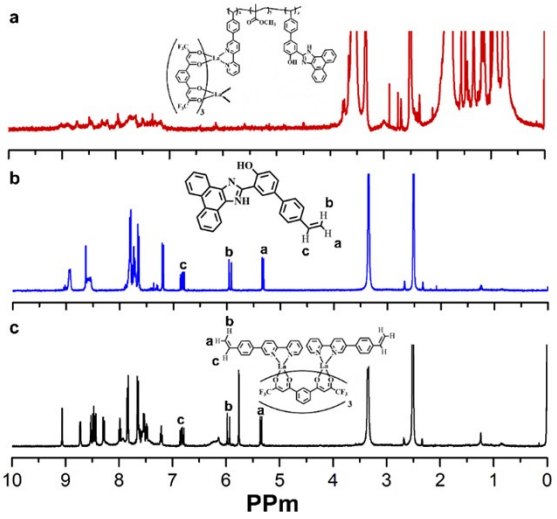


Fig. S1. The ^{1}H NMR spectra of **4-VP-PHI**, **La(BTP)$_3$(4-VP-BPY)$_2$** and **Poly[(4-VP-PHI)-*co*-La-*co*-MMA]** in DMSO-d_6 at room temperature.

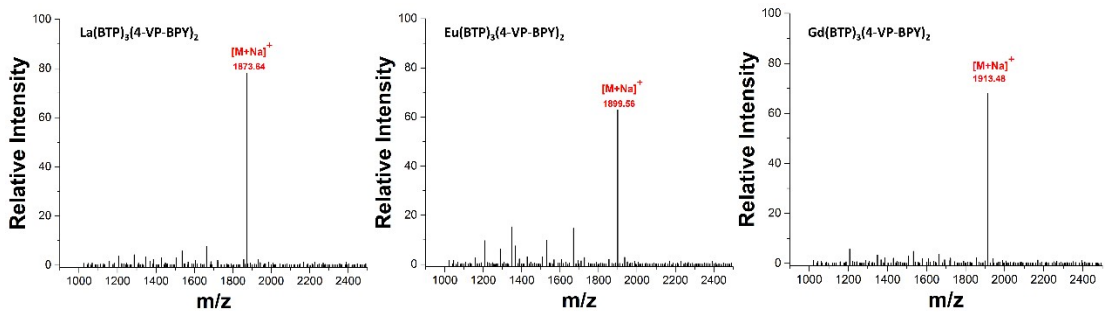


Fig. S2. Mass spectrum of **Ln(BTP)$_3$(4-VP-BPY)$_2$ (Ln = La, Eu or Gd).**

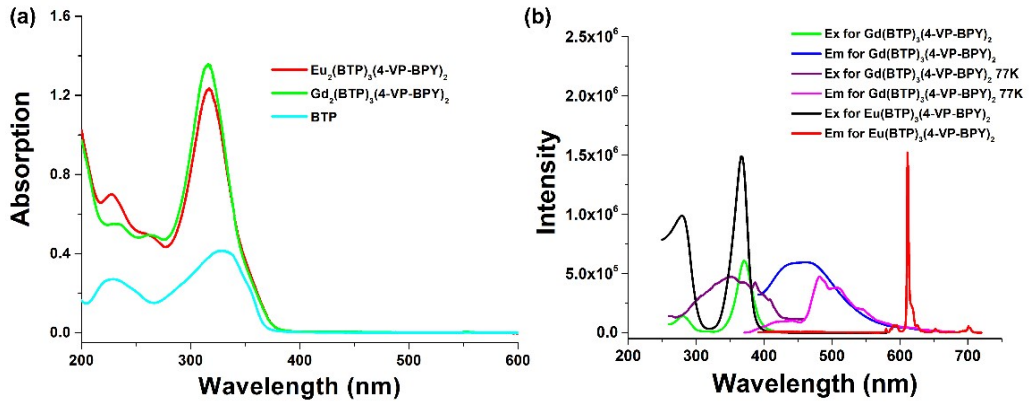


Fig. S3. (a) UV-visible absorption spectra of **Ln(BTP)$_3$(4-VP-BPY)$_2$** (**Ln = La, Eu, Gd**) and **BTP** at room temperature; (b) Emission and Excitation spectra of **Gd(BTP)$_3$(4-VP-BPY)$_2$** at room temperature and 77 K.

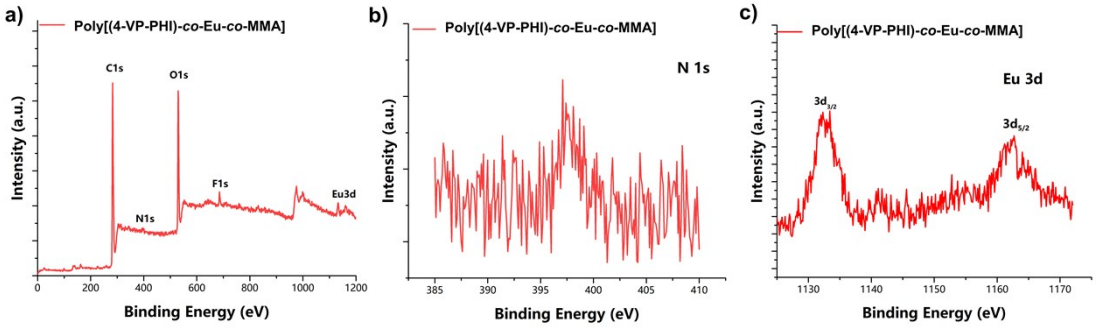


Fig. S4. High resolution XPS patterns of **Poly[(4-VP-PHI)-*co*-Eu-*co*-MMA]**.

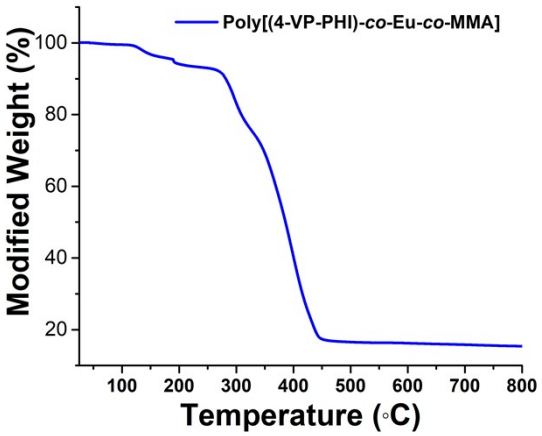


Fig S5. TGA curve of **Poly[(4-VP-PHI-*co*-Eu-*co*-MMA)]**.

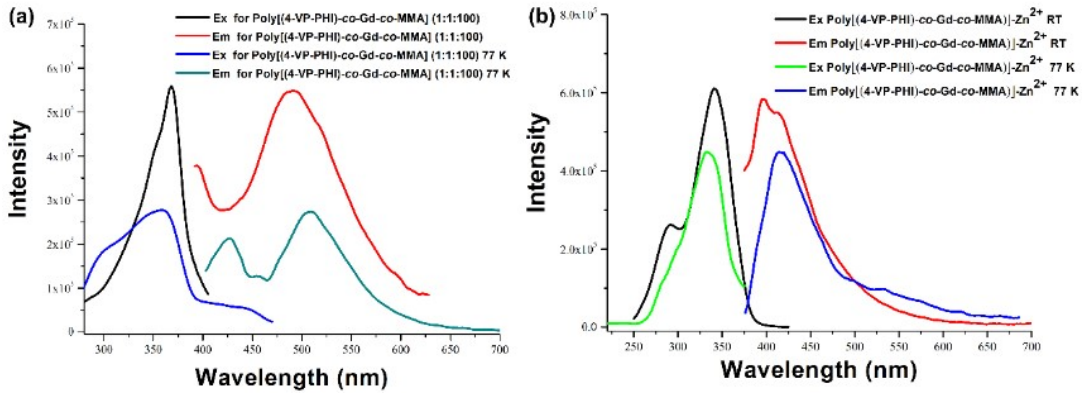


Fig S6. Emission and Excitation spectra of **Poly[(4-VP-PHI)-*co*-Gd-*co*-MMA]** with or without Zn^{2+} at room temperature and 77 K.

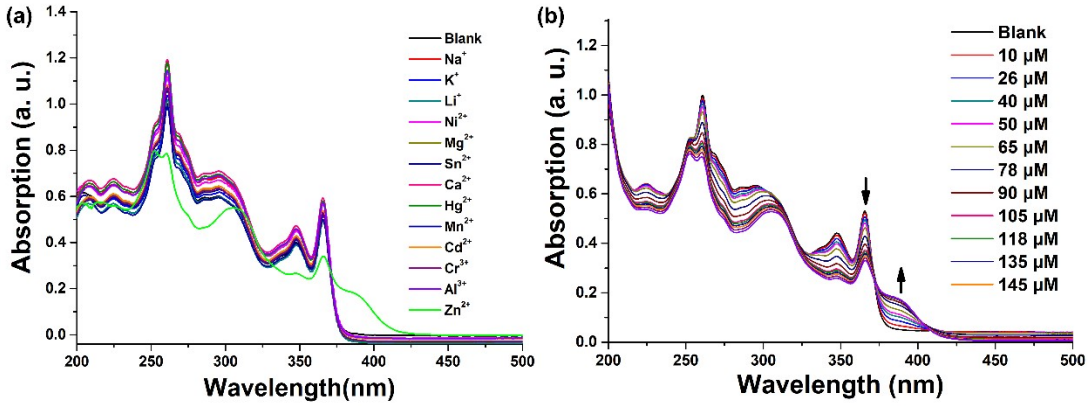


Fig. S7. (a) UV-vis spectra of **4-VP-PHI** with different metal ions and (b) Zn^{2+} titration.

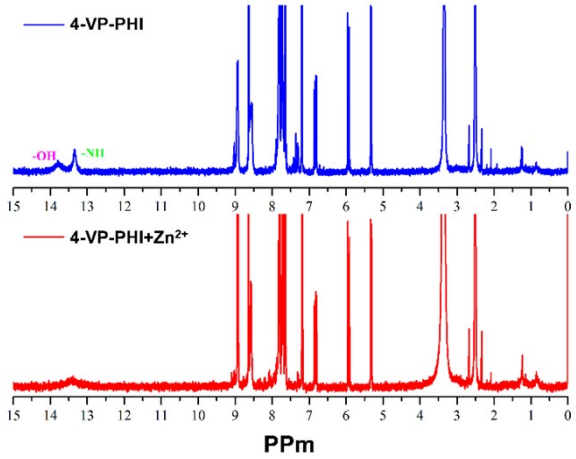


Fig. S8. The ^{1}H NMR spectra of pure **4-VP-PHI** (up) and in the presence of Zn^{2+} (down) in DMSO-d_6 at room temperature.

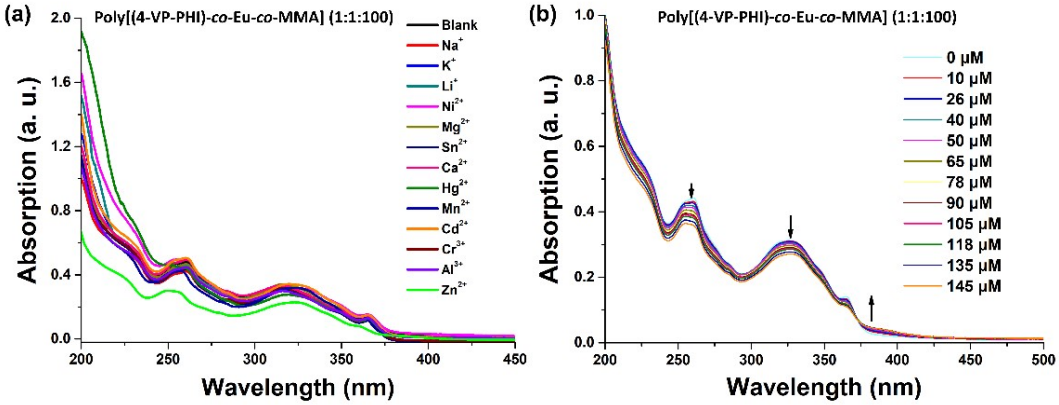


Fig. S9. (a) UV-vis spectra of **Poly[(4-VP-PHI)-co-Eu-co-MMA]** with different metal ions and (b) Zn^{2+} titration.

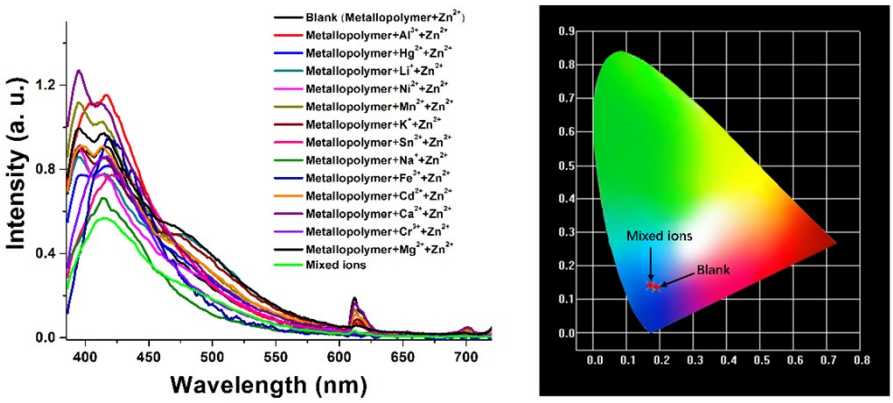


Fig S10. Changes in the fluorescence of Eu^{3+}-metallopolymer induced by mixing with Zn^{2+} ion and/or other different cationic metal ions at λ_{ex} = 365 nm.

Table S1. Photophysical properties of complex monomers in absolute MeCN solution at room temperature or 77K.

Compound	Absorption λ_{ab}(nm)	Excitation λ_{ex}(nm)	Emission λ_{em}(nm) (τ, *Φ*)
$[Eu_2(BTP)_3(4\text{-vp-bpy})_2]$	228, 318	280, 366	580, 591, 611 (474.24 μs), 652, 701 (*Φ:* 38.4%)
$[Gd_2(BTP)_3(4\text{-vp-bpy})_2]$	238, 264, 317	282 ,370 353 (77K)	462 439, 482 (4.71 μs, 77K), 507
4-VP-PHI	224, 260, 298, 347, 364	303, 362	493 (*Φ:* 9.4%)

Table S2. GPC data for **Poly[(4-VP-PHI)-*co*-Eu-*co*-MMA]**.

Polymer	*M*n	*M*w	*M*z	*M*z+1	PDI
Poly[(4-VP-PHI)-*co*-Eu-*co*-MMA]	8898	14242	20978	27548	1.60

Table S3. Photoluminescent properties of the PMMA-supported **Poly[(4-VP-PHI)-*co*- Ln-*co*-MMA]** (Ln = Eu or Gd) or **Poly[(4-VP-PHI)-*co*-Eu-*co*-MMA] @Zn** at RT or 77 K.

Compound	Excitation	Emission
	λ_{ex}/nm	λ_{em}/nm (τ, Φ)
Poly[(4-VP-PHI)-*co*-Eu-*co*-MMA]	300 (sh), 351	393,489, 591, 612 (969 μs), 651 and 704 (Φ: 15.2%)
Poly[(4-VP-PHI)-*co*-Gd-*co*-MMA]	368	491
	359	508 (4.36 μs, 77 K)
Poly[(4-VP-PHI)-*co*-Gd-*co*-MMA]@Zn	341	397
	334	415 (5.19 μs, 77 K)

Table S4. Color-integration results of the metallopolymer **Poly[(4-VP-PHI)-*co*-Eu-*co*-MMA]** with different excitation in MeCN solution at room temperature.

Metallopolymer	Excitation	CIE coordinates
Poly[(4-VP-PHI)-*co*-Eu-*co*-MMA]	341	(0.489, 0.316)
	351	(0.432, 0.315)
	361	(0.385, 0.314)
	365	(0.311, 0.319)
	371	(0.293, 0.329)
	381	(0.356, 0.318)

Table S5. Color-integration results of **4-VP-PHI** at the presence of different metal ions at room temperature.

compound	Metal ion	CIE coordinates
4-VP-PHI	Blank	(0.204, 0.441)
	Na^{+}	(0.209, 0.436)
	K^{+}	(0.207, 0.440)
	Li^{+}	(0.208, 0.427)
	Ni^{2+}	(0.199, 0.448)
	Mg^{2+}	(0.202, 0.451)
	Sn^{2+}	(0.202, 0.448)
	Ca^{2+}	(0.198, 0.446)
	Hg^{2+}	(0.205, 0.451)
	Mn^{2+}	(0.203, 0.453)
	Cd^{2+}	(0.201, 0.451)
	Cr^{3+}	(0.203, 0.456)
	Al^{3+}	(0.201, 0.455)
	Zn^{2+}	(0.186, 0.330)

Table S6. The HOMO and LUMO of the **4-VP-PHI**, **4-VP-PHI@Zn^{2+}** based on optimized S_0 and S_1 Geometries.

Complex	state	Energy Level (eV)						
		E_{LUMO+2}	E_{LUMO+1}	E_{LUMO}	E_{HOMO}	E_{HOMO-1}	E_{HOMO-2}	E_g
4-VP-PHI	S_1	-0.72	-1.20	-1.59	-4.97	-5.56	-5.89	3.38
4-VP-PHI@Zn^{2+}	S_1	-1.19	-1.35	-1.58	-4.73	-5.03	-5.67	3.14

Table S7. Color-integration results of the metallopolymer **Poly[(4-VP-PHI)-*co*-Eu-*co*-MMA]** at the presence of different metal ions at room temperature.

Metallopolymer	Metal ion	CIE coordinates
Poly[(4-VP-PHI)-*co*-Eu-*co*-MMA]	Na^{+}	(0.263, 0.296)
	K^{+}	(0.269, 0.304)
	Li^{+}	(0.211, 0.297)
	Ni^{2+}	(0.243, 0.296)
	Mg^{2+}	(0.236, 0.288)
	Sn^{2+}	(0.268, 0.284)
	Ca^{2+}	(0.199, 0.274)
	Hg^{2+}	(0.177, 0.279)
	Mn^{2+}	(0.173, 0.270)
	Cd^{2+}	(0.178, 0.301)
	Cr^{3+}	(0.210, 0.308)
	Al^{3+}	(0.257, 0.309)
	Zn^{2+}	(0.181, 0.116)

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