Electronic Supporting Information Available

Bipolar single-component Sm^{3+}-containing metallopolymer capable of multi-stimuli responses

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Supporting information

Materials and methods

High performance liquid chromatography (HPLC) grade MeCN or THF was purchased from Fisher Scientific and purified over solvent columns prior to use. Other solvents were used as received from Sigma Aldrich and stored over 3 Å activated molecular sieves. N-vinyl-carbazole (**NVK**) was a commercial product of reagent grade and was used without further purification. 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. Elemental analyses (EA) were performed on a Perkin-Elmer 240C elemental analyzer. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet Nagna-IR 550 spectrophotometer in the region 4000-400 cm^{-1} using KBr pellets. ^1H NMR spectra were recorded on a Bruker Plus 400 spectrometer with $SiMe_4$ as internal standard in DMSO-d_6 at room temperature. Electronic absorption spectra in the UV/Vis region were recorded with a Cary 300 UV spectrophotometer, and steady-state visible fluorescence, PL excitation spectra on a Photon Technology International (PTI)

Alphascan spectrofluorometer and visible decay spectra on a pico-N_2 laser system (PTI Time Master). The luminescent absolute overall quantum yield (Φ_{PL}) was determined by the same spectrometer using a 450 W Xe lamp and an integrating sphere. X-ray photoelectron spectroscopy (XPS) was measured using a Thermo ESCALAB250i X-ray photoelectron spectrometer. 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 *m*m particle size, linear mixed bed packing columns. The GPC was calibrated using polystyrene standards. The powder X-ray diffraction (PXRD) patterns were recorded on a D/Max-IIIA diffractometer with graphite-monochromatized Cu Ka radiation (λ = 1.5418 Å). Thermogravimetric (TG) analyses were carried out on a NETZSCH TG 209 instrument under flowing nitrogen by heating the samples from 25 to 800 °C.

Synthesis of the benzimidazole-based precursor HPBI (HPBI = 2-(pyridin-2-yl)-1*H*-benzo[*d*]imidazole)

The benzimidazole-based precursor **HPBI** was synthesized from the reaction of 1,2-diaminobenzene (2.2 g, 20 mmol) and picolinaldehyde (1.9 ml, 20 mmol) in the presence of 4-methylbenzenesulfonic acid (0.3 g, 1.8 mmol) according to a well-established procedure from the literature.[1] Yield: 3.3 g (84%). Anal. Calcd for $C_{12}H_9N_3$: C, 73.83; H, 4.65; N, 21.52%. Found: C, 73.80; H, 4.70; N, 21.48%. FT-IR (KBr, cm^{-1}): 3196 (b), 3054 (w), 2769 (w), 2219 (w), 1593 (m), 1570 (m), 1511 (w), 1439 (s), 1391 (s), 1317 (m), 1280 (m), 1228 (w), 1151 (w), 1098 (w), 994 (w), 902 (w), 799 (w), 749 (vs), 699 (s), 649 (w), 616 (w), 590 (w), 571 (w), 534 (w), 489 (w). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 13.13 (s, 1H, -NH-), 8.75 (d, 1H, -Py), 8.33 (t, 1H, -Py), 8.01 (t, 1H, -Py), 7.71 (d, 1H, -Py), 7.54 (t, 2H, -Ph), 7.24 (t, 2H, -Ph).

Synthesis of the vinyl-functional ancillary ligand 4-VB-PBI (1-(4-vinylbenzyl)-2-(pyridin-2-yl)-1H-benzo[*d*]imidazole)

The vinyl-functional ancillary ligand **4-VB-PBI** was prepared from an improved synthetic procedure from the literature.[2] To the solution of the precursor **HPBI** (**HPBI** = 2-(pyridine-2-yl)-1*H*-benzo[*d*]imidazole; 2.0 g, 10 mmol) in absolute DMSO (20 ml), tetraethylammonium bromide ($(C_2H_5)_4NBr$; 0.2 g, 10 mmol) was added, and the mixture was reacted under a N_2 atmosphere at room temperature. After 2 h, an aqueous solution (5 mL) of KOH (0.67 g, 12 mmol) was added dropwise, and the resulting mixture was stirred under a N_2 atmosphere at room temperature for another 2 h. 1-(Chloromethyl)-4-vinylbenzene (1.8 g, 12 mmol) was added and the resultant mixture was continuously stirred under a N_2 atmosphere at room temperature overnight. And then, the resulting mixture was poured into deionized water (200 ml) to give a white precipitate. The crude product was filtrated and further dissolved into absolute EtOH (30 ml) to give the white polycrystalline solid by evaporation at room temperature. Yield: 2.4 g (76%). Anal. Calcd for $C_{21}H_{17}N_3$: C, 81.00; H, 5.50; N, 13.49%. Found: C, 79.46; H, 5.58; N, 13.42%. FT-IR (KBr, cm^{-1}): 3083 (w), 3048 (w), 3000 (w), 2987 (w), 2951 (w), 2901 (w), 1744 (w), 1716 (w), 1628 (w), 1610 (w), 1589 (m), 1568 (m), 1510 (m), 1463 (m), 1440 (s), 1407 (w), 1390 (s), 1350 (w), 1331 (m), 1275 (m), 1267 (m), 1259 (m), 1210 (w), 1165 (m), 1148 (w), 1111 (m), 1097 (m), 1083 (w), 1046 (m), 1017 (w), 992 (m), 979 (m), 910 (m), 824 (s), 791 (m), 774 (m), 764 (m), 738 (vs), 700 (m), 626 (m), 612 (m), 578 (w), 562 (w), 543 (w). ^{1}H NMR (400 MHz, DMSO-d_6): δ(ppm) 8.70 (d, 1H, -Py), 8.37 (d, 1H, -Py), 8.01 (t, 1H, -Py), 7.67 (m, 1H, -Py), 7.58 (t, 1H, -Ph), 7.52 (t, 1H, -Ph), 7.34 (d, 2H, -Ph), 7.28 (m , 2H, -Ph), 7.10 (d, 2H, -Ph), 6.63 (m, 1H, -CH), 6.21 (s, 2H, -CH_2-), 5.73 (d, 1H, =CH_2), 5.19 (d, 1H, =CH_2).

Synthesis of the complex monomers [Ln(tta)$_3$(4-VB-PBI)] (Ln = La, 1; Sm, 2; Gd, 3)

To a solution in MeOH (20 ml) of **Htta** (2-thenoyltrifluoroactone; 133 mg, 0.6 mmol), solid NaOH (24 mg, 0.6 mmol) was added, and the mixture was stirred at room temperature. After 20 min, another solution in MeOH (5 ml) containing $LnCl_3 \cdot 6H_2O$ (0.2 mmol; Ln = La, 71 mg; Ln = Sm, 73 mg, Ln = Gd, 75 mg) was added dropwise within 10 min to at room temperature. And then, the **4-VB-PBI** (0.2 mmol, 62 mg) was added, and the resultant mixture was refluxed under a N_2 atmosphere for 6 h. After cooling to room temperature, each of the yellow solution was filtered. Diethyl ether was allowed to diffuse slowly into the filtrate at room temperature, and the pale-yellow microcrystalline products of complex monomers **1**-**3** were afforded in a few weeks, respectively. For [La(tta)$_3$(4-VB-PBI)] (**1**): Yield: 0.162 g (75%). Anal. Calcd for $C_{45}H_{29}F_9LaN_3O_6S_3$: C, 48.52; H, 2.62; N, 3.77%. Found: C, 48.54; H, 2.64; N, 3.75. FT-IR (KBr, cm^{-1}): 2989 (w), 2901 (w), 1596 (s), 1535 (s), 1507 (m), 1476 (m), 1457 (m), 1411 (s), 1355 (m), 1298 (s), 1288 (m), 1246 (m), 1229 (m), 1182 (s), 1134 (vs), 1083 (w), 1060 (m), 1034 (w), 1010 (w), 989 (w), 932 (m), 913 (w), 859 (m), 836 (w), 785 (s), 746 (s), 717 (s), 692 (w), 680 (s), 640 (s), 605 (w), 578 (w), 542 (w), 532 (w). ^{1}H NMR (400 MHz, DMSO-d_6): δ(ppm) 8.70 (d, 1H, -Py), 8.37 (d, 1H, -Py), 8.01 (t, 1H, -Ph), 7.62 (s, 7H, -Py and -β-diketonate), 7.58 (t, 1H, -Ph), 7.52 (t, 1H, -Ph), 7.34 (d, 2H, -Ph), 7.28 (m, 2H, -Ph), 7.10 (d, 5H, -Ph and -β-diketonate), 6.64 (d, 1H, =CH), 6.21 (d, 5H, -β-diketonate), 5.73 (d, 1H,

$=CH_2$), 5.19 (d, 1H, $=CH_2$).

For [Sm(tta)$_3$(4-VB-PBI)] (**2**): Yield: 0.190 g (85%). Anal. Calcd for $C_{45}H_{29}F_9SmN_3O_6S_3$: C, 48.03; H, 2.60; N, 3.73%. Found: C, 48.03; H, 2.64; N, 3.75%. FT-IR (KBr, cm^{-1}): 2988 (w), 2973 (w), 2901 (w), 1626 (m), 1599 (s), 1538 (s), 1506 (m), 1477 (m), 1460 (m), 1412 (s), 1356 (m), 1304 (s), 1248 (m), 1230 (m), 1186 (s), 1138 (vs), 1082 (w), 1062 (m), 1038 (w), 1015 (w), 991 (w), 934 (m), 913 (w), 859 (m), 835 (w), 787 (s), 768 (w), 747 (s), 715 (s), 693 (w), 681 (s), 664 (w), 658 (w), 653 (w), 641 (s), 605 (w).

For [Gd(tta)$_3$(4-VB-PBI)] (**3**): Yield: 0.180 g (80%). Anal. Calcd for $C_{45}H_{29}F_9GdN_3O_6S_3$: C, 47.74; H, 2.58; N, 3.71%. Found: C, 47.74; H, 2.57; N, 3.73%. FT-IR (KBr, cm^{-1}): 2988 (w), 2901 (w), 1628 (m), 1598 (s), 1505 (m), 1477 (m), 1459 (m), 1428 (w), 1411 (s), 1354 (m), 1303 (s), 1291 (sh), 1246 (m), 1230 (m), 1184 (s), 1133 (vs), 1083 (w), 1061 (m), 1035 (w), 1014 (w), 1010 (sh), 989 (w), 934 (m), 914 (w), 859 (m), 835 (w), 785 (s), 768 (m), 746 (s), 717 (s), 693 (w), 681 (s), 641 (s), 605 (w), 580 (m), 562 (w), 543 (w).

Synthesis of the precursor PI-DMBA (4-(1*H*-phenanthro[9,10-*d*]imidazol-2-yl)-N ,N-dimethyl-benzenamine)

The organic monomer **PI-DMBA** was synthesized from an improved procedure as the literature.[3] A mixture of 9,10-phenanthrenequinone (2.5 mmol, 0.52 g), ammonium acetate (NH_4OAc; 5.0 mmol, 0.60 g), 4-(dimethylamino)benzaldehyde (2.5 mmol, 0.37 g) and sodium dihydrogen phosphate (NaH_2PO_4; 0.06 g, 0.75 mmol) was added into 10 ml anhydrous EtOH. The resulting suspension was refluxed under a N_2 atmosphere for 6 h. After cooling to room temperature, the mixture was filtered and the filtrate was left at room temperature to give yellow green polycrystalline product. Yield: 0.801 g (95%). Anal. Calcd for $C_{23}H_{19}N_3$: C, 81.87; H, 5.68; N, 12.45%. Found: C, 81.90; H, 5.81; N, 12.49%. FT-IR (KBr, cm^{-1}): 3068 (w), 2972 (w), 2909 (w), 2816 (w), 1657 (w), 1611 (vs), 1581 (w), 1531 (s), 1490 (s), 1461 (m), 1453 (m), 1408 (m), 1375 (s), 1339 (w), 1235 (m), 1205 (s), 1153 (s), 1125 (w), 1063 (w), 1047 (w), 947 (m), 868 (w), 850 (w), 814 (s), 757 (s), 740 (s), 724 (s), 691 (w), 673 (w), 660 (w), 645 (w). ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 13.09 (s, 1H, -NH-), 8.81 (d, 2H, -Ph), 8.54 (d, 2H, -Ph), 8.13 (d, 2H, -Ph), 7.70 (t, 2H, -Ph), 7.58 (t, 2H, -Ph), 6.87 (d, 2H, -Ph), 2.99 (s, 6H, $-CH_3$).

Synthesis of the organic monomer 4-VB-PI-DMBA (4-(1-(4-vinylbenzyl)-1*H*-phenanthro[9,10-*d*]imidazol-2-yl)-N ,N-dimethyl-benzenamine)

The organic monomer **4-VB-PI-DMBA** was prepared in ca. 80% yield from our reported synthetic procedure.[4] Anal. Cacld for $C_{32}H_{27}N_3$: C, 84.74; H, 6.00; N, 9.26%. Found: C, 84.66; H, 6.08; N, 9.22%. ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 8.90 (s, 1H, -Ph), 8.84 (d, 1H, -Ph), 8.65 (d, 1H, -Ph), 8.05 (d, 1H, -Ph), 7.74 (t, 1H, -Ph), 7.66 (t, 1H, -Ph), 7.55 (t, 1H, -Ph), 7.48 (m, 3H, -Ph), 7.12 (d, 2H, -Ph), 6.83 (d, 2H, -Ph), 6.68 (m, 1H, =CH), 5.92 (d, 2H, $-CH_2$), 5.78 (d, 1H, $=CH_2$), 5.23 (d, 1H, $=CH_2$), 2.97 (s, 6H, $-CH_3$).

Synthesis of the AIBN-initiated PVK (poly(*N*-vinyl-carbazole)

The homogeneous polymerization of in activation with AIBN for comparison was carried out in a Fisher-Porter glass reactor and protected by nitrogen according to the typical procedure. To a solution of N-vinyl-carbazole (NVK, 3.67 g, 19 mmol) in dry 1,2-dichlorobenzene (15 mL), AIBN initiator (46.8 mg, 1.5 mol% of NVK) was added, and the resultant homogeneous solution was purged with N_2 for 10 min and sealed under a reduced N_2 atmosphere. The mixture was heated to 80 °C with continuous stirring for 48 h. The viscous mixture was diluted with dry 1,2-dichlorobenzene (15 mL) and precipitated with absolute diethyl ether (50 mL) three times. The resulting solid **PVK** was collected by filtration and dried at 45 °C under vacuum to constant weight. For **PVK**: Yield: 90%. FT-IR (KBr, cm^{-1}): 3074 (w), 3022 (w), 2969 (w), 2927 (w), 1623 (w), 1481 (m), 1450 (vs), 1406 (w), 1321 (s), 1220 (m), 1154 (m), 1124 (w), 1092 (w), 1031 (w), 1001 (w), 924 (w), 744 (s), 719 (s), 656 (w), 614 (w), 572 (w), 476 (w). ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 8.25-3.95 (b, 8H), 2.15-3.95 (b, 1H), 2.15-0.5 (b, 2H).

Synthesis of the series of Ln^{3+}-containing metallopolymers Poly(NVK-*co*-2-*co*-[4VB-PI-DMBA]) (200:1[2/4V-PI-DMA] = 5:1 or 7:1) and Poly(NVK-*co*-1-*co*-[4VB-PI-DMBA]) (200:1[1/4V-PI-DMA] = 7:1)

To a dry 1,2-dichlorobenzene (30 mL) solution containing NVK, the complex monomer [Sm(tta)$_3$(4-VB-PBI)] (**2**) or [La(tta)$_3$(4-VB-PBI)] (**1**) together with the organic monomer 4-VB-PI-DMBA in a stipulated feed molar ratio of 200:1[**2/4V-PI-DMA**] = 5:1 or 7:1) or 200:1[**1/4V-PI-DMA**] = 7:1) in the presence of AIBN (1,5 mol%) were added, and the resultant homogeneous solution was purged with N_2 for 10 min and sealed under a reduced N_2 atmosphere. The mixture was heated to 80 °C with continuous stirring for 48 h. The viscous mixture was diluted with dry 1,2-dichlorobenzene (15 mL) and precipitated with absolute diethylether (50 mL) three times. The resulting solid products were collected by filtration and dried at 45 °C under vacuum to constant weight, respectively. For the representative **Poly(NVK-*co*-1-*co*-[4VB-PI-DMBA])** (200:1[**1**/**4V-PI-DMA**] = 7:1): Yield: 96%. FT-IR (KBr, cm^{-1}): 3420 (w), 3062 (w), 2962 (w), 2882 (w), 1675 (s), 1599 (s), 1543 (w), 1510 (w), 1483 (m), 1453 (s), 1412 (m), 1326 (m), 1307 (m), 1200 (s), 1142 (s), 1094 (m), 1064 (m), 929 (w), 841 (w), 798 (w), 751 (vs), 724 (s), 697 (w), 680 (w), 653 (w), 642 (w), 592 (w), 522 (w), 480 (w), 436 (w). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 8.52-5.93 (b, 880H), 5.80-3.90 (b, 204H), 2.90 (s, 6H), 2.31 (s, 8H), 2.16-0.50 (b, 496H+16H (1.45 ppm)).

X-ray crystallography

Single crystals of the complex monomer [Sm(tta)$_3$(4-VB-PBI)] (**2**) of suitable dimensions were mounted onto thin glass fibers. All the intensity data were collected on a Bruker APEX-II CCD diffractometer (Cu radiation and λ = 1.54184 Å) at 293(2) K in Φ and ω scan modes. Structures were solved by Direct methods followed by difference Fourier syntheses, and then refined by full-matrix least-squares techniques against F^2 using SHELXTL.[5] All other non-hydrogen atoms were refined with anisotropic thermal parameters. Absorption corrections were applied using SADABS.[6] All hydrogen atoms were placed in calculated positions and refined isotropically using a riding model. Crystallographic data and selected atomic distances and bond angles are presented in **Tables S1-2**, respectively. CCDC reference number 2176563 is for the complex monomer [Sm(tta)$_3$(4-VB-PBI)] (**2**).

Absorption and fluorescence titrations of the bipolar single-component Sm^{3+}-containing metallopolymer Poly(NVK-*co*-2-*co*-[4-VB-PI-DMBA]) (200:1[2/4-VB-PI-DMBA = 7:1]) with

different cationic metal ions

Poly(NVK-*co*-2-*co*-[4-VB-PI-DMBA]) (200:1[**2**/**4-VB-PI-DMBA** = 7:1]) was dissolved in the DMF-H_2O mixed (9:1, v/v) solvents to afford the stock solution with a concentration of 2.0 × 10^{-3} M. The solutions containing different inorganic nitrate salts (Cu^{2+}, Al^{3+}, Ca^{2+}, Cr^{3+}, Fe^{3+}, Mg^{2+}, Ni^{2+}, Zn^{2+}, Ag^{+}, Ba^{2+}, Co^{2+}, K^{+}, Na^{+}) with a stipulated concentration of 2.0 ×10^{-3} M in the DMF-H_2O mixed (9:1, v/v) solvents also were prepared, respectively. During the titrations, the 30 μL stock solution (2.0 ×10^{-3} M) and each of the 30 μL cationic metal ion solutions (2.0 × 10^{-3} M) and 3 mL DMF-H_2O were placed in a quartz cell (1 cm wide and 5 mL capacity), and then DMF-H_2O mixed (9:1, v/v) solvent was further supplemented to a constant volume of 3 mL, ensuing the regulated concentrations of both the blank solution and the every cationic solution at 2.0 × 10^{-5} M. Spectral data were recorded after 30 min at room temperature for equilibrating each addition. The UV-visible absorption spectra were recorded in the wavelength range of 200-600 nm, and the fluorescence spectra were recorded from 340 nm to 750 nm with excitation at 365 nm.

Absorption and fluorescence titrations of the bipolar single-component Sm^{3+}-containing metallopolymer Poly(NVK-*co*-2-*co*-[4-VB-PI-DMBA]) (200:1[2/4-VB-PI-DMBA = 7:1]) with different concentrations of Cu^{2+} ion

For the absorption and fluorescence titration experiments, the blank just have the bipolar single component Sm^{3+}-containing metallopolymer **Poly(NVK-*co*-2-*co*-[4-VB-PI-DMBA])** (200:1[**2**/**4-VB-PI-DMBA** = 7:1]) was obtained as above. As the Cu^{2+} solutions (DMF-H_2O; v/v 9:1), $Cu(NO_3)_2{\cdot}6H_2O$ was used, where different concentrations of Cu^{2+} ion in the range of 0.0-

2.0×10^{-5} M were adopted, respectively. Both the UV-visible absorption 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]

$$\frac{I_0}{I} = 1 + K_{sv} \times \left[Cu^{2+}\right] \qquad (1)$$

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 Cu^{2+} ions at various concentrations. The limit of detection (LOD) was calculated using equation below,[8]

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

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

Cyclic voltammetry (CV) measurement

CV measurement was performed on a computer-controlled EG&G Potentiostat/Galvanostat model 283 at room temperature with a conventional three-electrode cell using an $Ag/AgNO_3$ (0.1 M) reference electrode, Pt carbon working electrode of 2 mm in diameter, and a platinum wire counter electrode. CV of the sample was performed in nitrogen-saturated dichloromethane containing 0.1 M Bu_4NPF_6 as supporting electrolyte. The CV was measured at a scan rate of 100 $mV \cdot s^{-1}$. The HOMO and the LUMO energy levels of each complex are calculated according to the following equations,[9] $E_{HOMO} = -(E_{OX}^{on} + 4.8)$ eV, $E_{LUMO} = -(E_{red}^{on} + 4.8)$

eV, and where E_{OX}^{on} is the recorded onset oxidation potential of the complex, and E_{red}^{on} is the recorded onset reduction potential of the complex. The HOMO and LUMO energy levels for the other used materials were obtained from the literatures.[10]

WPLED fabrication and testing

The WPLED was fabricated on ITO (Indium tin oxide) coated glass substrates with a sheet resistance of 20 Ω per square. Patterned ITO coated glass substrates were washed with acetone, detergent, D. I. water and isopropanol in an ultrasonic bath. After being exposed under oxygen plasma for 20 min, PEDOT:PSS from water solution was spin-coated (at 2000 rpm) on the substrate and followed by drying in a vacuum oven at 140 °C for 20 min, giving a film of 40 nm thickness. The chlorobenzene solution (20 mg/mL) of the mixture of CBP and **Poly(NVK-*co*-2-*co*-[4VB-PI-DMBA])** (200:1[**2**/**4V-PI-DMA**] = 7:1) in 50:50 wt% ratio as the emitting layer (EML) was prepared under an N_2 atmosphere and spin-coated (at 4000 rpm) on the PEDOT:PSS layer with a thickness of 90 nm. The TPBi layer (30 nm) and the following BCP layer (10 nm) were thermally deposited onto the EML, respectively. Finally, a thin layer (1 nm) of LiF followed by 100 nm thickness Al capping layer was deposited onto the substrate under vacuum of 5×10^{-6} Pa. The typical active area of the four devices is 9 mm^2. Current density (*J*)-voltage (*V*)-luminance (*L*) was collected using a Keithley 2400 source meter equipped with a calibrated silicon photodiode. The electroluminescent spectra were measured by a PR655 spectrometer. The eternal quantum efficiency (η_{EQE}) values were determined by a Si photodiode with calibration in an integration sphere (IS080, Labsphere).

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Table S1 Crystallographic data and structure refinement for the complex monomer [Sm(tta)$_3$(4-VB-PBI)] (**2**)

Compound	[Sm(tta)$_3$(4-VB-PBI)] (**2**)
Empirical formula	$C_{45}H_{29}N_3O_6S_3F_9Sm$
Formula weight	1125/24
Crystal system	triclinic
Space group	*P-1*
a/Å	9.5896(4)
b/Å	10.3341(4)
c/Å	23.0846(9)
α/°	82.591(3)
β/°	82.151(3)
γ/°	83.326(3)
V/Å^3	2235.98(15)
Z	2
ρ/g·cm^{-3}	1.671
Crystal size/mm	0.26× 0.21× 0.18
μ(Cu-Kα)/mm^{-1}	11.968
Data/restraints/parameters	8797/0/ 633
Quality-of-fit indicator	1.051
No. unique reflections	16246
No. observed reflections	7688
Final R indices [$I > 2\sigma(I)$]	R_1 = 0.0566
	wR_2 = 0.1555
R indices (all data)	R_1 = 0.0655
	wR_2 = 0.1475

Table S2 Relevant atomic distances (Å) and bond angles (°) for for the complex monomer [Sm(tta)$_3$(4-VB-PBI)] (**2**)

Compound	[Sm(tta)$_3$(4-VB-PBI)] (**2**)		
Sm(1)-O(1)	2.398(4)	Sm(1)-O(2)	2.369(4)
Sm(1)-O(3)	2.390(4)	Sm(1)-O(4)	2.388(4)
Sm(1)-O(5)	2.348(4)	Sm(1)-O(6)	2.371(4)
Sm(1)-N(1)	2.561(5)	Sm(1)-N(3)	2.615(5)
C(44)-C(45)	1.292(17)		
O(1)-Sm(1)-O(2)	71.51(15)	O(3)-Sm(1)-O(4)	70.83(15)
O(5)-Sm(1)-O(6)	71.59(15)	N(1)-Sm(1)-N(3)	62.18(17)

Table S3 XPS data of all the atoms in the representative bipolar Sm^{3+}-containing metallopolymer **Poly(NVK-*co*-2-*co*-[4-VB-PI-DMBA])** (200:1[**2**/**4-VB-PI-DMBA** = 7:1])

Type	Binding Energy	FWHM (eV)	Atomic (%)
C1s	285.31	1.39	82.97
F1s	688.72	2.15	0.63
N1s	400.65	1.24	15.70
O1s	532.89	1.61	0.42
S2p	164.47	0.65	0.21
Sm3d	1084.21	0.18	0.07

Table S4 GPC data of the bipolar single-component Ln^{3+}-containing metallopolymers **Poly(NVK-*co*-2-*co*-[4VB-PI-DMBA])** (200:1[**2**/**4V-PI-DMA**] = 5:1 or 7:1) and **Poly(NVK-*co*-1-*co*-[4VB-PI-DMBA])** (200:1[**1**/**4V-PI-DMA**] = 7:1)

Sample	Feeding	$M_n{}^a$/g mol^{-1}	PDI^b
PVK	-	26316	1.20
Poly(NVK-*co*-2-*co*-[4VB-PI-DMBA])	5:1	30496	1.33
	7:1	32156	1.39
Poly(NVK-*co*-1-*co*-[4VB-PI-DMBA])	7:1	33498	1.43

$^a M_n$ is the number-average molecular weight. ^{b}PDI = M_w/M_n, where M_w is the weight-average molecular weight.

Table S5 Photophysical properties of the bipolar single-component Ln^{3+}-containing metallopolymers **Poly(NVK-*co*-2-*co*-[4VB-PI-DMBA])** (200:1[**2**/**4V-PI-DMA**] = 5:1 or 7:1) in solid-state at room temperature upon different λ_{ex} values

Sample	Point	λ_{ex} (nm)	CIE	CCT (K)	CRI	
5:1	A′	325	0.235, 0.229	2455	95	Greenish-blue
	B′	330	0.234, 0.229	2689	97	Greenish-blue
	C′	335	0.234, 0.229	2939	98	Greenish-blue
	D′	340	0.223, 0.230	3674	97	Greenish-blue
	E′	345	0.234, 0.231	3579	97	Greenish-blue
	F′	350	0.235, 0.230	3579	97	Greenish-blue
	G′	355	0.245, 0.235	4194	97	Greenish-blue
	H′	360	0.256, 0.242	4549	98	Greenish-blue
	I′	365	0.269, 0.258	4909	97	White-edge
	J′	370	0.281, 0.265	5302	98	White-edge
7:1	A	325	0.293, 0.285	3207	99	White
	B	330	0.289, 0.281	3243	99	White
	C	335	0.291, 0.282	3244	99	White
	D	340	0.291, 0.281	3232	98	White
	E	345	0.290, 0.279	3551	98	White
	F	350	0.297, 0.281	3872	98	White
	G	355	0.324, 0.293	3710	98	White
	H	360	0.341, 0.300	4255	98	White
	I	365	0.356, 0.308	4621	96	White
	J	370	0.263, 0.310	4929	97	White

Table S6 CIE coordinate changes (λ_{ex} = 365 nm) for the bipolar single-component Ln^{3+}-containing metallopolymers **Poly(NVK-*co*-2-*co*-[4VB-PI-DMBA])** (200:1[**2**/**4V-PI-DMA**] = 7:1) in DMF-H_2O (v/v = 9/1) solution upon titrations with different Cu^{2+} concentrations

Concentration (×10^{-5} M)	**CIE coordinate**	**Color**
0 (blank)	0.357, 0.305	white
0.1	0.356, 0.282	white
0.2	0.356, 0.282	white
0.3	0.356, 0.281	white
0.4	0.357, 0.280	white
0.5	0.361, 0.279	white
0.6	0.360, 0.278	white
0.7	0.357, 0.274	white
0.8	0.358, 0.271	white
0.9	0.361, 0.270	Purplish pink
1.0	0.362, 0.270	Purplish pink
1.1	0.363, 0.269	Purplish pink
1.2	0.365, 0.269	Purplish pink
1.3	0.366, 0.268	Purplish pink
1.4	0.366. 0.268	Purplish pink
1.5	0.367, 0.268	Purplish pink
1.6	0.368, 0.267	Purplish pink
1.7	0.369, 0.266	Purplish pink
1.8	0.371, 0.264	Purplish pink
1.9	0.371, 0.264	Purplish pink
2.0	0.371, 0.264	Purplish pink

Table S7 Electroluminescent properties **of the WPLED fabricated from** the bipolar single-component Ln^{3+}-containing metallopolymers **Poly(NVK-*co*-2-*co*-[4VB-PI-DMBA])** (200:1[**2**/**4V-PI-DMA**] = 7:1) upon different applied bias voltages

Voltage (V)	CIE	CCT (K)	CRI	Color
6 V	0.369, 0.355	4685	97	White
7 V	0.354, 0.338	4753	96	White
8 V	0.339, 0.319	4966	95	White
9 V	0.325, 0.302	5161	95	White
10 V	0.313, 0.288	5305	95	White
11 V	0.303, 0.276	5409	95	White
12 V	0.296, 0.268	5501	96	White
13 V	0.292, 0.263	5518	96	White
14 V	0.293, 0.264	5474	96	White
15 V	0.298, 0.269	5345	96	White
16 V	0.306, 0.279	5144	96	White
17 V	0.314, 0.289	4908	96	White
18 V	0.321, 0.300	4694	97	White

Scheme S1 Synthetic scheme of the precursor **4-VB-PBI**, the organic monomer **4-VB-PI-DMBA**, the complex monomers [Ln(tta)$_3$(4-VB-PBI)] (Ln = La, **1**; Sm, **2** or Gd, **3**) and the series of bipolar Ln^{3+}-containing metallopolymers Poly(NVK-*co*-[Ln(tta)$_3$(4-VB-PBI)]-*co*-[4-VB-PI-DMBA]).

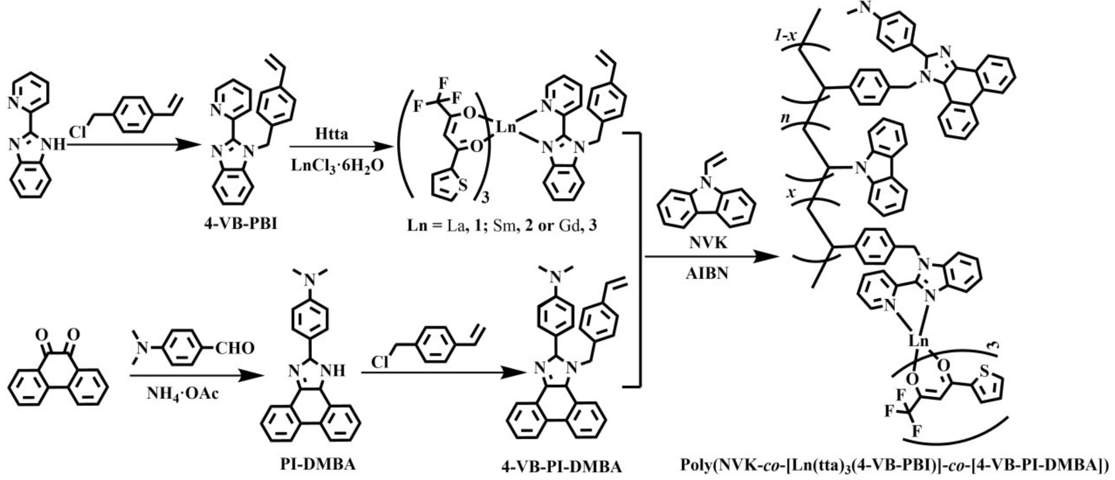

Figure S1 ^{1}H NMR spectra of the precursors **4-VB-PBI** and **PI-DMBA**, the organic monomer **4-VB-PI-DMBA**, the complex monomer [La(tta)$_3$(4-VB-PBI)] (**1**) and the representative bipolar La^{3+}-containing metallopolymer **Poly(NVK-*co*-1-*co*-[4-VB-PI-DMBA])** (200:1[**1**/**4-VB-PI-DMBA** = 7:1]) in DMSO-d_6 at room temperature, respectively.

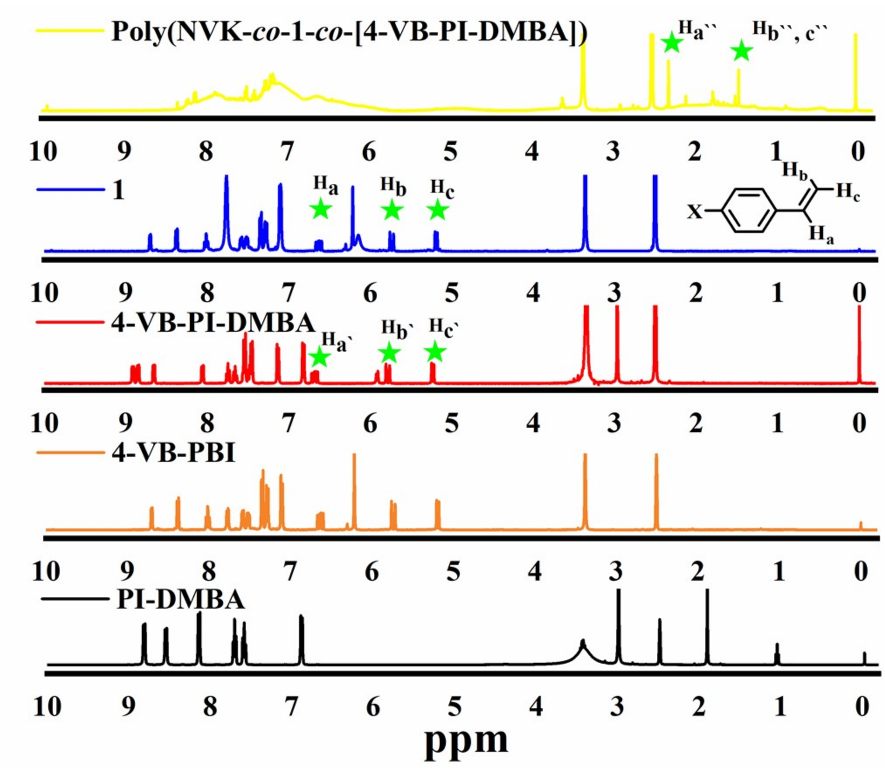

Figure S2 High resolution XPS patterns of the representative bipolar Sm^{3+}-containing metallopolymer **Poly(NVK-*co*-2-*co*-[4-VB-PI-DMBA])** (200:1[**2**/**4-VB-PI-DMBA** = 7:1])

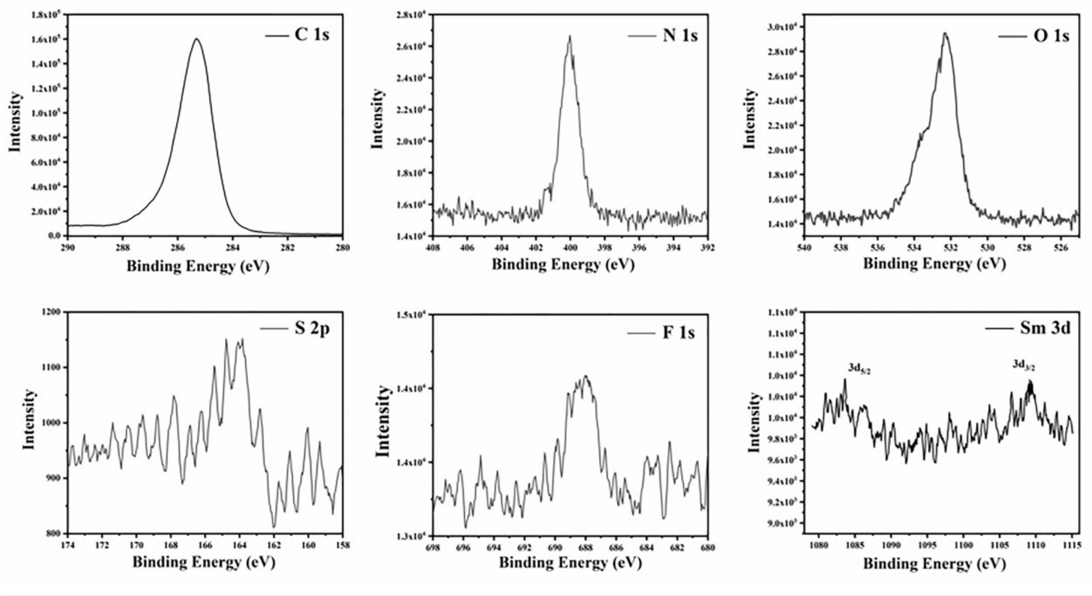

Figure S3 TG (thermogravimetic) curves of the organic monomer **4-VB-PI-DMBA**, the complex monomer [Sm(tta)$_3$(4-VB-PBI)] (**2**) and their representative bipolar Sm^{3+}-containing metallopolymer **Poly(NVK-*co*-2-*co*-[4-VB-PI-DMBA])** (200:1[**2**/**4-VB-PI-DMBA** = 7:1]) in solid-state, respectively.

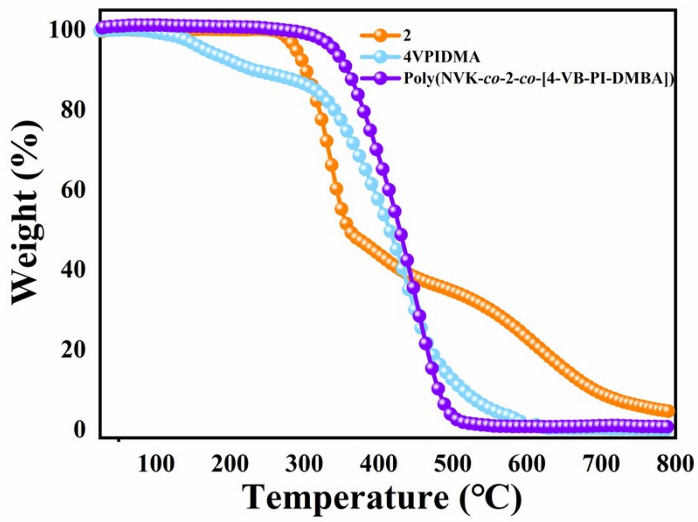

Figure S4 PXRD (powder X-ray diffraction) patterns of PVK and the representative bipolar Sm^{3+}-containing metallopolymer **Poly(NVK-*co*-2-*co*-[4-VB-PI-DMBA])** (200:1[**2**/**4-VB-PI-DMBA** = 7:1]) in solid-state, respectively.

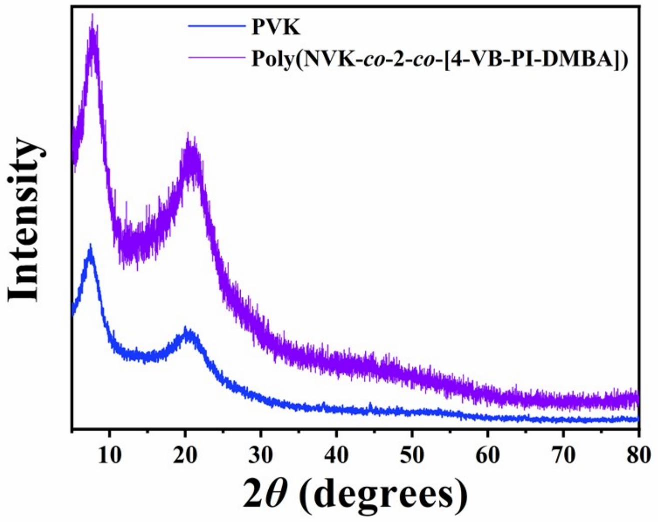

Figure S5 UV-visible absorption spectra of the ligand **Htta**, the precursor **4-VB-PBI**, the organic monomer **4-VB-PI-DMBA** and their complex monomers [Ln(tta)$_3$(4-VB-PBI)] (Ln = Sm, **2** or Gd, **3**) in MeCN solution (2.0 × 10^{-5} M) at room temperature, respectively.

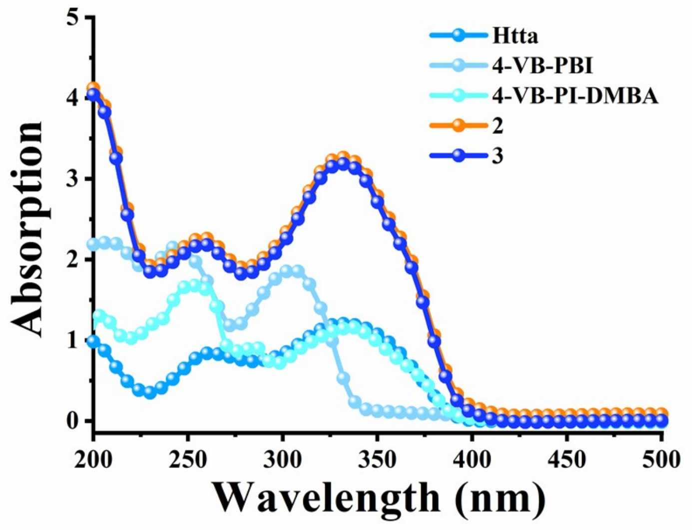

Figure S6 Emission and excitation spectra of the referenced complex monomer Gd[Ln(tta)$_3$(4-VB-PBI)] (**3**) in MeCN solution (2.0 × 10^{-5} M) at room temperature or 77 K, respectively.

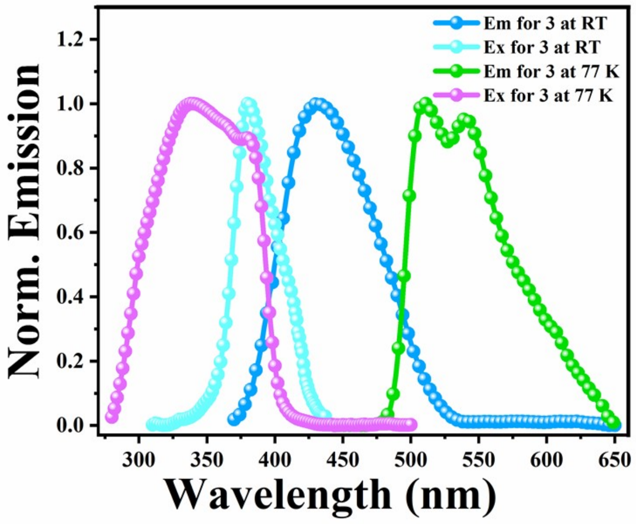

Figure S7 Schematic energy level diagram and possible energy transfer for the complex monomer [Sm(tta)$_3$(4-VB-PBI)] (**2**) and its bipolar Sm^{3+}-containing metallopolymer **Poly(NVK-*co*-2-*co*-[4-VB-PI-DMBA])** (200:1[**2**/**4-VB-PI-DMBA** = 7:1]).

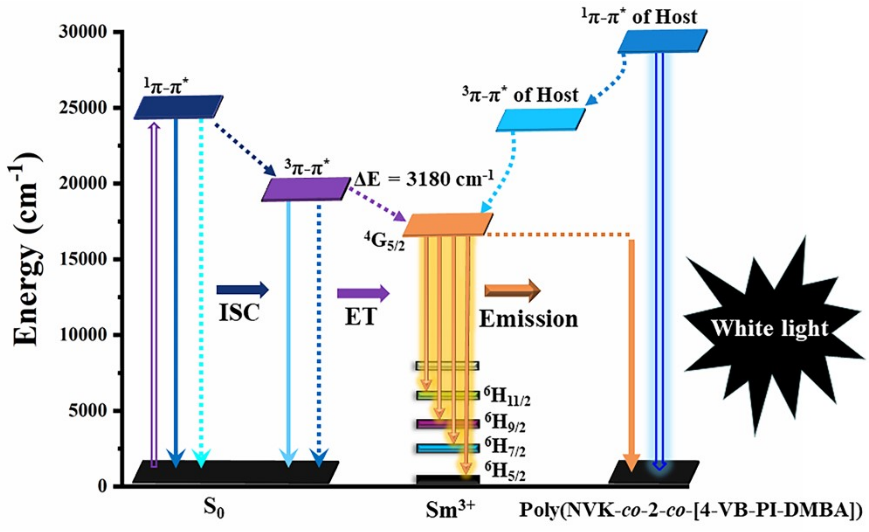

Figure S8 Emission spectrum (λ_{ex} = 273) of PVK in solid-state and UV-visible absorption spectrum of the bipolar Sm^{3+}-containing metallopolymer **Poly(NVK-*co*-2-*co*-[4-VB-PI-DMBA])** (200:1[**2**/**4-VB-PI-DMBA** = 7:1]) in DMF solution at room temperature, respectively.

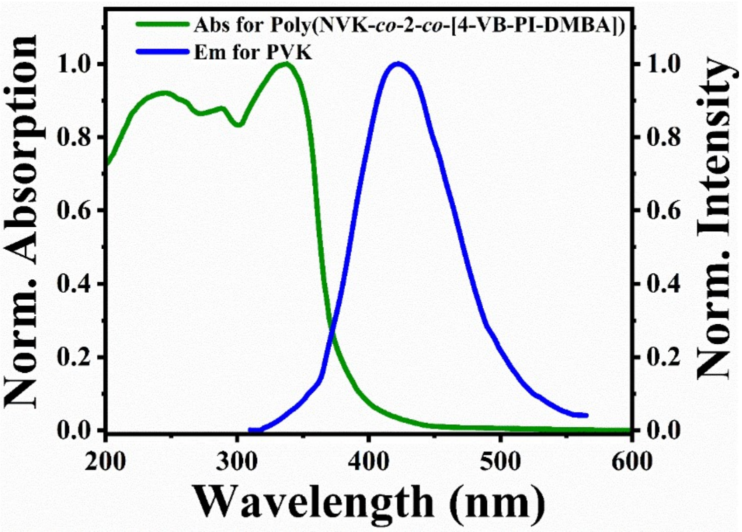

Figure S9 Emission spectra and corresponding CIE chromatic coordinates (inset) of the bipolar Sm^{3+}-containing metallopolymer **Poly(NVK-*co*-2-*co*-[4-VB-PI-DMBA])** (200:1[**2**/**4-VB-PI-DMBA** = 5:1])

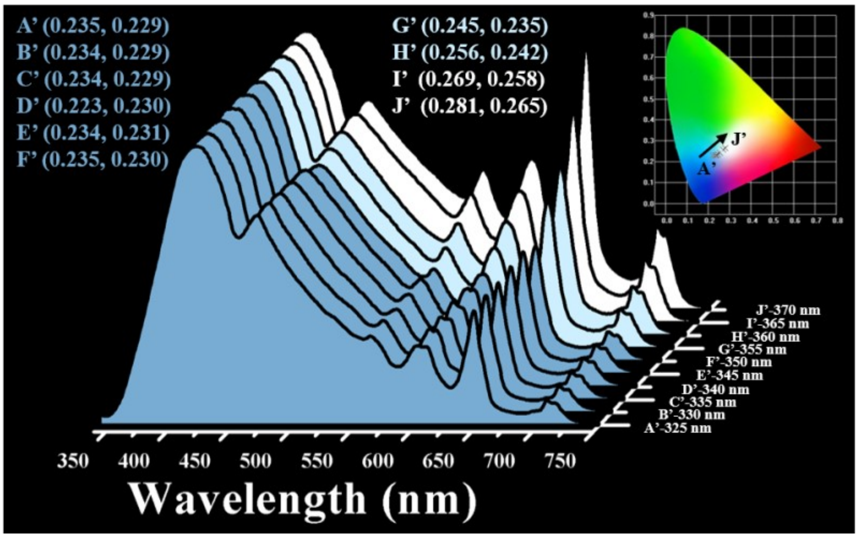

Figure S10 UV-visible absorption titrations of the bipolar Sm^{3+}-containing metallopolymer **Poly(NVK-*co*-2-*co*-[4-VB-PI-DMBA])** (200:1[**2**/**4-VB-PI-DMBA** = 7:1]) with the presence of different cationic ions (2.0×10^{-5} M; **a**) or different concentrations ($0.1\text{-}2.0 \times 10^{-5}$ M; **b**) of Cu^{2+} ion in DMF-H_2O (v/v = 9:1) solution at room temperature, respectively.

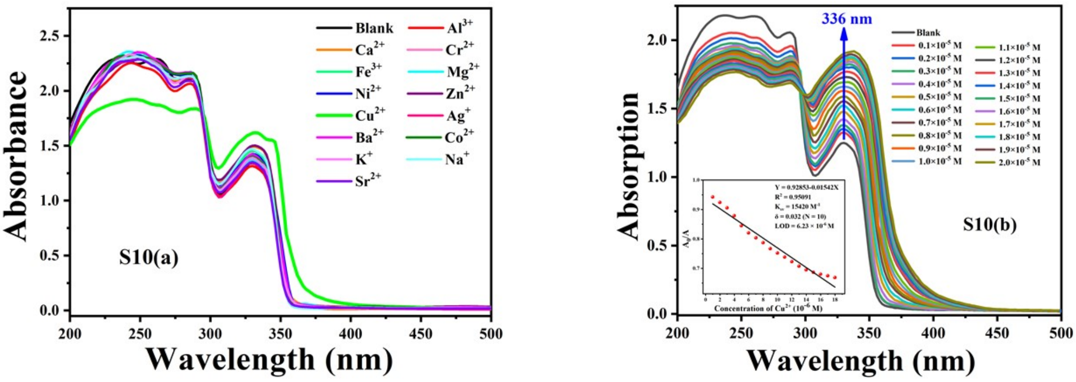

Figure S11 Fluorescence titrations (**a**) and Stern-Volmer plot (**b**) of the bipolar Sm^{3+}-containing metallopolymer **Poly(NVK-*co*-2-*co*-[4-VB-PI-DMBA])** (200:1[**2**/**4-VB-PI-DMBA** = 7:1]) with the presence of different concentrations (0.0-2.0 × 10^{-5} M) of Cu^{2+} ion in DMF-H_2O (v/v = 9:1) solution at room temperature, respectively.

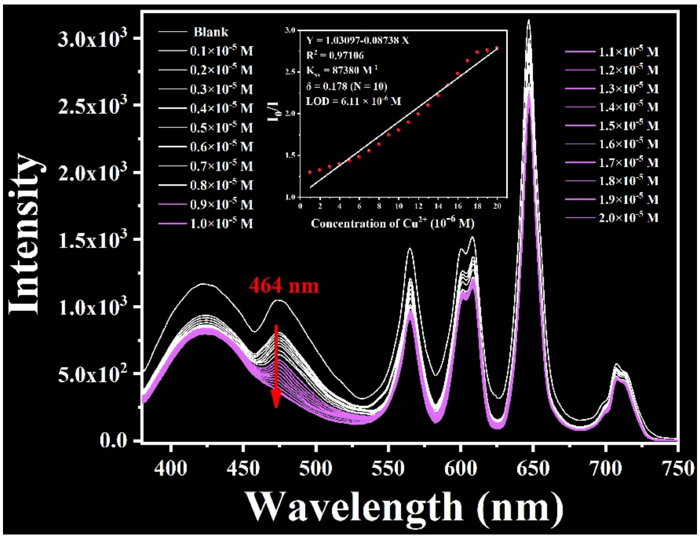

Figure S12 CV (cyclic voltammetry) curve of the bipolar Sm^{3+}-containing metallopolymer **Poly(NVK-*co*-2-*co*-[4-VB-PI-DMBA])** (200:1[**2**/**4-VB-PI-DMBA** = 7:1]) versus Fc^+/Fc in solution (scan rate = 100 mV/s).