Electronic Supporting Information Available

Efficient and weak efficiency-roll-off near-infrared (NIR) polymer lightemitting diode (PLED) based on PVK-supported Zn²⁺-Yb³⁺-containing metallopolymer

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Supporting information

Materials and methods

High performance liquid chromatography (HPLC)-grade THF or 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. The Salentype Schiff-base ligand H₂L¹ (N,N'-bis(salicylidene)cyclohexane-1,2-diamine) was synthesized from the condensation of an equimolar mixture (30 mmol) of *cis*- and *trans*-1,2diaminocyclohexane and salicylaldehyde (60 mmol) according to a well-established procedure from the literature.¹ The pyrazolone ligand HL² (*(Z)*-3-methyl-1-phenyl-4-(2,2,2trifluoro-1-hydroxyethylidene)-1*H*-pyrazol-5(4*H*)-one) was synthesized from the reaction of 1-methyl-3-phenyl-1*H*-pyrazol-4(5*H*)-one and trifluoroacetic anhydride in the presence of excess pyridine (Py) from the literature.² Other chemicals including NVK (N-vinylcarbazole) and Poly(*N*-vinylcarbazole) ($M_w \approx 90000$) were commercial products of reagent grade and were used without further purification. All manipulations of air and water sensitive compounds were carried out under dry N₂ using the standard Schlenk line techniques.

Elemental analyses 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 JEOL EX 400 spectrometer with SiMe₄ as internal standard in DMSO- d_6 at room temperature. ESI-MS was performed on a Finnigan LCQ^{DECA} XP HPLC-MS_n mass spectrometer with a mass to charge (m/z) range of 4000 using a standard electro-spray ion source and MeCN as the solvent. Electronic absorption spectra in the UV/Visible region and diffuse reflection (DR) spectra were recorded with a Cary 300 UV spectrophotometer. Visible or NIR emission and excitation spectra were collected by a combined fluorescence lifetime and steady-state spectrometer (FLS-980, Edinburgh) with a 450 W Xe lamp. Excited-state decay times were obtained by the same spectrometer but with a μ F900 Xe lamp. The luminescent absolute overall quantum yield (\mathcal{P}_{Ln}^L) 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 μ m particle size, linear mixed bed packing columns. The GPC was calibrated using polystyrene standards. X-ray photoelectron spectroscopy (XPS) was carried out on a PHI 5700 XPS system equipped with a dual Mg X-ray source and monochromatic Al X-ray source with the complete depth profile and angle-resolved

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capabilities. Powder X-ray diffraction (PXRD) patterns were recorded on a D/Max-IIIA diffractometer with graphite-monochromatized Cu K α radiation (λ = 1.5418 Å). Thermal properties were characterized using Thermogravimetric (TG) and differential scanning calorimetry (DSC) analyses on a NETZSCH TG 209 instrument under flowing nitrogen at a heating rate of 10 °C/min.

Synthesis of the precursor [Zn(L¹)(4-vinyl-Py)]

The synthesis of the precursor [Zn(L¹)(4-vinyl-Py)] was in a same way to the precursor $[Zn(L^1)(Py)]$ as the literature¹ except 4-vinyl-Py was used instead of Py. To a stirred solution of the Salen-type Schiff-base ligand H₂L¹ (0.645 g, 2.0 mmol) in absolute MeOH (20 mL), solid $Zn(OAc)_2 \cdot 2H_2O$ (0.440 g, 2.0 mmol) and 215 μ L (2.0 mmol) 4-vinyl-pyridine (4-vinyl-Py) were added separately, and the resulting mixture was refluxed under the protection of N₂ atmosphere for 5 h. After cooling to room temperature, the insoluble yellow precipitate was filtered out, washed with MeOH and CH₂Cl₂, and dried at 45 °C under vacuum to constant weight. Yield: 0.795 g (81%). Calc. for C₂₇H₂₇N₃O₂Zn: C, 66.06; H, 5.54; N, 8.56%. Found: C, 66.15; H, 5.61; N, 8.49%. FT-IR (KBr, cm⁻¹): 3436 (w), 2928 (w), 2858 (w), 2079 (w), 1632 (vs), 1597 (s), 1531 (s), 1468 (s), 1445 (s), 1416 (w), 1396 (w), 1342 (m), 1321 (w), 1242 (w), 1184 (w), 1146 (s), 1123 (s), 1051 (w), 1016 (w), 937 (w), 907 (w), 843 (w), 802 (w), 758 (m), 741 (w), 667 (w), 633 (w), 617 (w), 563 (w), 538 (w), 474 (w), 409 (w). ¹H NMR (400 MHz, DMSO d_6): δ (ppm) 8.53 (d, 2H, -Py), 8.44 (s, 1H, -CH=N), 8.34 (s, 1H, -CH=N), 7.47 (d, 2H, -Py), 7.22 (t, 2H, -Ph), 7.13 (t, 2H, -Ph), 6.75 (m, 1H, -CH=C), 6.61 (m, 2H, -Ph), 6.42 (t, 2H, -Ph), 6.15 (d, 1H, -C=CH₂), 5.54 (d, 1H, -C=CH₂), 3.73 (s, 1H, -Ch), 3.19 (s, 1H, -Ch), 2.45 (d, 1H, -Ch), 1.97 (m, 2H, -Ch), 1.56 (d, 1H, -Ch), 1.41 (m, 4H, -Ch).

The characterization of complex monomers 2-5

For complex monomer **2**: Yield: 0.237 g (82%). Calc. for C₆₃H₅₁F₉N₉O₈ZnNd: C, 52.45; H, 3.56; N, 8.74%. Found: C, 52.40; H, 3.66; N, 8.68%. FT-IR (KBr, cm⁻¹): 3431 (w), 2937 (w), 2860 (w), 1641 (vs), 1601 (s), 1555 (w), 1524 (m), 1446 (m), 1380 (m), 1357 (m), 1255 (m), 1200 (s), 1138 (s), 1071 (w), 1058 (w), 1021 (w), 956 (s), 903 (m), 840 (m), 786 (m), 752 (s), 692 (m), 621 (m), 580 (m), 512 (m), 448 (w), 409 (w). ESI-MS (in MeCN) *m/z*: 1443.77 (%), [M-H]⁺.

For complex monomer **3**: Yield: 0.230 g (78%). Calc. for C₆₃H₅₁F₉N₉O₈ZnYb: C, 51.42; H, 3.49; N, 8.57%. Found: C, 51.40; H, 3.58; N, 8.49%. FT-IR (KBr, cm⁻¹): 3428 (w), 2939 (w), 2860 (w), 1642 (vs), 1599 (s), 1555 (w), 1526 (m), 1447 (m), 1380 (m), 1357 (m), 1259 (m), 1202 (s), 1139 (s), 1072 (w), 1058 (w), 1020 (w), 955 (s), 903 (m), 839 (m), 786 (m), 754 (s), 692 (m), 622 (m), 580 (m), 512 (m), 447 (w), 409 (w). ESI-MS (in MeCN) *m/z*: 1472.57 (%), [M-H]⁺.

For complex monomer **4**: Yield: 0.226 g (77%). Calc. for C₆₃H₅₁F₉N₉O₈ZnEr: C, 51.62; H, 3.51; N, 8.60%. Found: C, 51.65; H, 3.63; N, 8.54%. FT-IR (KBr, cm⁻¹): 3430 (w), 2935 (w), 2860 (w), 1642 (vs), 1604 (s), 1555 (w), 1526 (m), 1448 (m), 1382 (m), 1357 (m), 1260 (m), 1201 (s), 1139 (s), 1072 (w), 1058 (w), 1021 (w), 957 (s), 901 (m), 839 (m), 786 (m), 755 (s), 692 (m), 624 (m), 579 (m), 512 (m), 447 (w), 410 (w). ESI-MS (in MeCN) *m/z*: 1466.79 (%), [M-H]⁺.

For complex monomer **5**: Yield: 0.230 g (79%). Calc. for C₆₃H₅₁F₉N₉O₈ZnGd: C, 51.98; H, 3.53; N, 8.66%. Found: C, 52.02; H, 3.59; N, 8.62%. FT-IR (KBr, cm⁻¹): 3432 (w), 2935 (w),

2860 (w), 1640 (vs), 1599 (s), 1555 (w), 1525 (m), 1447 (m), 1381 (m), 1358 (m), 1259 (m), 1203 (s), 1141 (s), 1072 (w), 1058 (w), 1020 (w), 958 (s), 903 (m), 841 (m), 786 (m), 754 (s), 690 (m), 623 (m), 580 (m), 511 (m), 447 (w), 409 (w). ESI-MS (in MeCN) *m/z*: 1456.78 (100%, [M-H]⁺.

X-ray crystallography

X-ray quality crystals of $[Zn(L^1)(4-vinyl-Py)Yb(L^2)_3]$ (**3**) were mounted onto thin glass fibers. Intensity data were collected on a Bruker SMART CCD diffractometer ((Mo-K α radiation and $\lambda = 0.71073$ Å) in Φ and ω scan modes. Structures were solved by Direct methods followed by difference Fourier syntheses, and refined by full-matrix least-squares techniques against F² using SHELXTL.³ All other non-hydrogen atoms were refined with anisotropic thermal parameters. Absorption corrections were applied using SADABS.⁴ All hydrogen atoms were placed in calculated positions and refined isotropically using a riding model. Crystallographic data and selected bond lengths and angles are presented in Tables 1S and 2S, respectively. CCDC reference number 1041172 for **3**.

The characterization of Poly(NVK-*co*-2) (75:1), Poly(NVK-*co*-3) (50:1, 75:1, 100:1, 150:1 or 200:1) and Poly(NVK-*co*-4) (75:1)

For **Poly(NVK-co-2)** (75:1): Yield: 81%. Found: C, 83.11; H, 5.50; N, 7.40%. FT-IR (KBr, cm-1): 3060 (w), 2940 (w), 1625 (w), 1598 (m), 1531 (w), 1483 (s), 1451 (s), 1410 (w), 1332 (s), 1258 (w), 1232 (m), 1224 (s), 1156 (m), 1124 (w), 1026 (w), 1001 (w), 958 (w), 926 (w), 840 (w), 744 (s), 720 (s), 616 (w), 594 (w), 526 (w).

For **Poly(NVK-co-3)** (50:1, 75:1, 100:1, 150:1 or 200:1): Yield: 75% (50:1); Found: C, 81.78; H, 4.53; N, 7.52%. 80% (75:1); Found: C, 83.00; H, 5.45; N, 7.42%. 83% (100:1); Found: C, 84.90; H, 4.64; N, 7.36%. 87% (150:1); Found: C, 86.16; H, 4.58; N, 7.18%. 89% (200:1); Found: C, 86.39; H, 4.69; N, 7.34%. FT-IR (KBr, cm-1): 3064 (w), 2943 (w), 1627 (w), 1599 (m), 1532 (w), 1484 (s), 1450 (s), 1412 (w), 1333 (s), 1259 (w), 1230 (m), 1226 (s), 1158 (m), 1124 (w), 1026 (w), 1000 (w), 958 (w), 926 (w), 840 (w), 743 (s), 721 (s), 618 (w), 597 (w), 531 (w).

For **Poly(NVK-co-4)** (75:1): Yield: 79%. Found: C, 83.13; H, 5.50; N, 7.37%. FT-IR (KBr, cm-1): 3060 (w), 2944 (w), 1628 (w), 1598 (m), 1530 (w), 1482 (s), 1451 (s), 1410 (w), 1336 (s), 1260 (w), 1232 (m), 1229 (s), 1158 (m), 1120 (w), 1029 (w), 1007 (w), 960 (w), 924 (w), 840 (w), 741 (s), 722 (s), 617 (w), 599 (w), 536 (w).

Cyclic voltammetry (CV) measurement

Cyclic voltammetry (CV) measurement was performed on a computer-controlled EG&G Potentiostat/Galvanostat model 283 at room temperature with a conventional threeelectrode cell using using a an Ag/AgNO₃ (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 Bu₄NPF₆ as supporting electrolyte. The cyclic voltammogram was measured at a scan rate of 100 mV·s⁻¹. The highest occupied molecular orbit (HOMO) and the lowest unoccupied molecular orbit (LUMO) energy levels of **Poly(NVK-co-3)** (50:1, 75:1 or 100:1) are calculated according to the following equations,⁵ $E_{HOMO} = -(E_{OXD} - E_{OXD, ferrocene}) - 4.8 \text{ eV}$, $E_{LUMO} = E_{HOMO} + E_{g} \text{ eV}$, and where E_{g} is the energy band gap estimated from the low-energy edge of the absorption spectra from the samples. The HOMO and LUMO energy levels for the other used materials were obtained from the literatures.⁶

PLEDs' fabrication and testing

Each of the two types of PLEDs 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 (poly(3,4ethylenedioxythiophene):poly(styrenesulfonate)) 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 30 nm thickness. The toluene solution (5 mg/mL) of Poly(NVK-co-3) (50:1, 75:1 or 100:1) as the emitting layer was prepared under an N₂ atmosphere and spin-coated (at 3000 rpm) on the PEDOT:PSS layer with a thickness of 40 nm. Subsequently, the BCP (2,9dimethyl-4,7-diphenyl-1,10-phenanthroline) layer (20 nm) and/or the TPBI (1,3,5-tris(2-Nphenylbenzimidazolyl)benzene) layer (20 nm) were thermally deposited onto the emitting layer for PLEDs I-II, respectively. Finally, a thin layer (1 nm) followed by 100 nm thickness Al capping layer was deposited onto the substrate under vacuum of 5 \times 10⁻⁶ Pa. Current density-voltage (J-V) characteristics were collected using a Keithley 2400 source meter equipped with a calibrated silicon photodiode. The NIR EL irradiance was measured through a calibrated UDT Model 280 Germanium Detector. The eternal quantum efficiencies (EQEs) of the NIR emission were obtained by measuring the irradiance in the forward direction and assuming the eternal emission profile to Lambertian.

References

- 1 C. Yu, Z. Zhang, L. Liu, H. Y. Li, Y. N. He, X. Q. Lü, W. K. Wong and R. A. Jones, *New J. Chem.*, 2015, 39, 3698-3707.
- 2 C. H. Huang, S. W. Zhang, A. P. Deng, H. T. Tang and G. X. Xu, Chin. J. Chem., 1990, 8, 29-36.
- 3 G. M. Sheldrick, *SHELXL-97*, Program for Crystal Structure Refinement, University of Göttingen, Göttingen, Germany, 1997.
- 4 G. M. Sheldrick, SADABS, University of Göttingen, Göttingen, Germany, 1996.
- 5 H. Y. Chen, C. T. Chen and C. T. Chen, *Macromolecules*, 2010, 43, 3613-3623.
- E. Zysman-Colman, S. S. Ghosh, G. Xie, S. Varghese, M. Chowdhury, N. Sharma, D. B.
 Cordes, A. M. Z. Slawin and I. D. W. Samuel, ACS Appl. Mater. & Interfaces, 2016, 8, 9247-9253.

Compound	3
Empirical formula	C ₆₃ H ₅₁ F ₉ N ₉ O ₈ ZnYb
, Formula weight	1471.54
Crystal system	Monoclinic
Space group	C2/c
a/Å	23.4453(16)
b/Å	13.4882(9)
c/Å	41.770(6)
α/°	90
<i>в</i> /°	102.3530(10)
γ/°	90
V/Å ³	12903.4(15)
Ζ	8
ρ/g·cm⁻³	1.515
Crystal size/mm	$0.31 \times 0.29 \times 0.25$
μ(Mo-Kα)/mm⁻¹	1.898
Data/restraints/parameters	13735/1280/821
Quality-of-fit indicator	1.194
No. unique reflections	13735
No. observed reflections	36130
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0663$
	$wR_2 = 0.1624$
R indices (all data)	$R_1 = 0.1022$
	$wR_2 = 0.1751$

 Table 1S. Crystallographic data and structure refinement for complex monomer 3.

3			
Zn(1)-N(1)	2.058(8)	Zn(1)-N(2)	2.075(7)
Zn(1)-N(3)	2.045(6)	Zn(1)-O(1)	2.012(5)
Zn(1)-O(2)	2.019(5)		
Yb(1)-O(1)	2.363(5)	Yb(1)-O(2)	2.349(5)
Yb(1)-O(3)	2.369(5)	Yb(1)-O(4)	2.261(5)
Yb(1)-O(5)	2.379(5)	Yb(1)-O(6)	2.281(5)
Yb(1)-O(7)	2.395(5)	Yb(1)-O(8)	2.260(5)
Zn(1)…Yb(1)	3.3707(9)	C(26)-C(27)	1.292(14)
N(1)-Zn(1)-N(2) 79.1(3)	N(1)-Zn(1)-N	(3) 106.8(3)
N(1)-Zn(1)-O(1) 91.3(2)	N(1)-Zn(1)-O	(2) 152.7(3)
O(1)-Yb(1)-O	(2) 69.99(16)	O(3)-Yb(1)-O	(4) 72.56(17)
O(5)-Yb(1)-O	(6) 71.95(17)	O(7)-Yb(1)-O	(8) 72.8(2)

Table 2S. Relevant atomic distances (Å) and bond angles (°) for complex monomer 3.

Table 3S. Photophysical properties of the ligands H_2L^1 and HL^2 , the precursor [Zn(L¹)(4-vinyl-Py)] and complex monomers 2-5 in dilute MeCN solution (2 × 10⁻⁵ M) and the series of metallopolymers Poly(NVK-*co*-[Zn(L¹)(4-vinyl-Py)Ln(L²)₃] (Ln = Nd, Yb or Er) with different feed molar ratios (50:1, 75:1, 100:1, 150:1 or 200:1) in solid state at RT or 77 K.

	Absorption	Excitatio	Emission
Compound		n	
	$\lambda_{ab}/nm [log(\epsilon/dm^3mol^{-1}cm^{-1})]$	λ_{ex}/nm	$\lambda_{em}/{ m nm}~(au,~{\cal O} imes 10^3)$
H ₂ L ¹	214(0.92), 252(0.56), 314(0.23)	369	468(s, 25.6 ns, 18)
HL ²	229(0.29), 280(0.34)	379	432(s, 28.2 ns, 34)
[Zn(L ¹)(4-vinyl-Py)]	230(0.89), 266(0.38), 354(0.22)	319, 394	453(39.4 ns, 384)
2	236(1.72), 276(1.10), 348(0.22)	384	467(w, <1 ns, <10 ⁻²), 892, 1062(3.11 μs), 1336
3	234(1.56), 274(1.08), 346(0.18)	382	467(w, <1 ns, <10 ⁻²), 981(28.41µs)
4	234(1.60), 272(1.12), 345(0.21)	385	467(w, <1 ns, <10 ⁻²), 1519(21.75 μs)
5	236(1.79), 276(1.15), 350(0.22)	383	467(m, 1.92 ns)
		387	532(s, 1.16ms, 77 K)
Poly(NVK- <i>co</i> -2) (75;1)	221, 292, 332, 585, 746, 804, 872	364	890, 1062(3.46 µs), 1334
Poly(NVK- <i>co</i> -3) (50:1)	-	-	980(27.82 µs)
Poly(NVK- <i>co</i> -3) (75:1)	220, 294, 335, 978	362	980(32.24 µs)
Poly(NVK- <i>co</i> -3) (100:1)	-	-	425(w), 980(31.89 <i>µ</i> s)
Poly(NVK- <i>co</i> -3) (150:1)	-		425, 980(31.78 µs)
Poly(NVK- <i>co</i> -3) (200:1)	-		425, 980(31.57 µs)
Poly(NVK- <i>co</i> -4) (75:1)	220, 294, 334, 524, 654, 992	362	1528(32.46 μs)

Table 4S. The Cartesian coordinates and the summary of excitation energies and oscillator strengths for complex monomer $[Zn(L^1)(4-vinyl-Py)Y(L^2)_3]$ from TD-DFT (TD-B3LYP/6-31G*) calculations.

(1) Cartesian coordinates

С	2.1101	14.7646	4.3311
С	1.2057	15.2535	3.3949
н	0.7129	14.6454	2.8942
С	1.0033	16.6051	3.1832
н	0.4067	16.8935	2.5319
С	1.6863	17.5016	3.9322
Н	1.5499	18.4131	3.8019
С	2.5679	17.0818	4.8644
Н	3.0158	17.7156	5.3773
С	2.8284	15.7343	5.0923
С	3.8095	15.4174	6.0693
Н	4.0742	16.108	6.6351
С	5.2495	14.0373	7.4126
Н	4.6547	13.7719	8.1412
С	6.0284	15.2101	7.9458
Н	5.4141	15.9117	8.2145
Н	6.6024	15.5636	7.2497
С	6.868	14.7998	9.1303
Н	7.447	15.5419	9.3705
Н	6.28	14.6346	9.8834
С	7.6602	13.6662	8.9268
Н	8.0486	13.4116	9.7776
Н	8.3921	13.9087	8.3366
С	6.9489	12.4298	8.3284
Н	7.6032	11.7932	8.0028
Н	6.4113	11.9923	9.0082
С	6.0578	12.9187	7.1765
Н	6.6922	13.2234	6.4967
С	5.4296	10.6258	6.749
н	6.0158	10.3902	7.4288
С	4.7524	9.5586	6.053
С	5.2788	8.2694	6.285

Н	5.9583	8.1637	6.9119
С	4.8146	7.1656	5.6093
н	5.1892	6.3273	5.7517
С	3.7867	7.3322	4.7341
н	3.458	6.5941	4.2741
С	3.2248	8.5714	4.5143
н	2.5254	8.6526	3.9037
С	3.6718	9.6873	5.1701
С	4.6231	13.3046	2.2307
н	3.862	13.8301	2.3162
С	5.1838	13.2694	1.0095
Н	4.8652	13.8288	0.3379
С	6.1528	12.4704	0.7612
С	6.7436	11.926	1.8928
н	7.5345	11.4425	1.8114
С	6.1332	12.1074	3.1954
н	6.5658	11.7932	3.9566
С	7.0007	12.4772	-0.4559
н	7.8148	12.9146	-0.5699
С	6.392	11.7621	-1.3026
н	5.5799	11.368	-1.0828
Н	6.7559	11.6321	-2.1493
С	-1.5361	15.4824	6.513
С	-0.5201	14.338	6.6473
С	0.2644	14.1931	7.7667
С	0.4675	14.9366	9.0164
С	1.1231	13.0961	7.897
С	2.614	12.3214	9.7776
С	2.8954	11.0822	9.2891
Н	2.482	10.7992	8.5035
С	3.7951	10.2277	9.9363
Н	3.9648	9.3812	9.5903
С	4.4305	10.6407	11.0924
н	5.0332	10.0909	11.5401
С	4.1376	11.8704	11.5442
н	4.5788	12.1548	12.3095
С	3.2544	12.7399	10.9784
н	3.0772	13.5701	11.361
С	-0.1819	16.2137	9.4804
н	0.1535	16.4466	10.3474
н	-1.133	16.0904	9.5252
н	0.0175	16.9193	8.8617
С	0.5536	7.3755	7.0666
С	-0.007	8.5632	6.25

С	-1.2716	8.4739	5.6325
С	-2.2088	7.4256	5.3545
С	-1.8803	9.6521	5.1212
С	-4.0854	9.9988	3.9648
С	-4.0595	11.3626	3.8956
Н	-3.3835	11.8312	4.3311
С	-5.0239	12.0506	3.1954
Н	-4.9858	12.9796	3.1588
С	-6.0134	11.4086	2.5604
Н	-6.6425	11.884	2.0679
С	-6.0852	10.0706	2.6459
н	-6.7987	9.6182	2.2551
С	-5.0726	9.3406	3.3297
н	-5.0931	8.4116	3.3379
С	-2.0711	5.9224	5.536
н	-2.8834	5.4917	5.2592
н	-1.9031	5.726	6.46
Н	-1.3406	5.6027	4.9987
С	-0.1643	8.0743	1.905
С	-0.226	9.5261	2.3581
С	-1.0671	10.4593	1.7593
С	-2.0235	10.4159	0.6961
C	-0.9224	11.819	2.0801
С	-1.942	13.8965	1.095
С	-2.1514	14.6508	2.2144
Н	-2.1682	14.2472	3.0489
С	-2.3351	16.0281	2.0964
Н	-2.4894	16.559	2.8413
С	-2.2812	16.5848	0.8019
н	-2.3745	17.5043	0.692
С	-2.0861	15.7871	-0.3053
н	-2.0952	16.1703	-1.152
С	-1.8804	14.4382	-0.1791
Н	-1.7081	13.906	-0.92
С	-2.6743	9.2702	-0.0488
н	-3.2994	9.6196	-0.6879
н	-3.1389	8.7068	0.574
н	-2.0014	8.7596	-0.5007
Ν	4.3502	14.3014	6.2541
Ν	5.2891	11.8474	6.5003
Ν	5.0263	12.6871	3.298
Ν	1.7181	13.1922	9.1352
Ν	1.2876	14.3298	9.8105
Ν	-3.0944	9.2377	4.6498

Ν	-3.2779	7.8549	4.7744
Ν	-1.7385	12.4948	1.22
Ν	-2.4338	11.6104	0.3696
0	2.2557	13.4536	4.5098
0	3.0475	10.8723	4.938
0	-0.5658	13.5552	5.6679
0	1.3539	12.1427	7.113
0	0.7206	9.5586	6.23
0	-1.4744	10.8385	5.1005
0	0.5739	9.7848	3.2862
0	-0.1829	12.423	2.9109
F	-0.8945	16.6674	6.5618
F	-2.4179	15.5474	7.4793
F	-2.2148	15.458	5.4188
F	-0.3354	6.9178	7.9181
F	1.6332	7.729	7.7341
F	0.9101	6.3666	6.2675
F	0.1918	7.9714	0.657
F	0.633	7.3349	2.6027
F	-1.3486	7.4581	1.9706
Zn	4.0112	12.6414	5.0932
Υ	0.7432	11.6116	4.9189

(2) Summary of excitation energies and oscillator strengths

Excited State	1:	Singlet-A	3.0434 eV	407.39 nm	f=0.0003
329 -> 331		-0.11894			
330 -> 331		0.68486			
330 -> 332		0.11784			
Excited State	2:	Singlet-A	3.1395 eV	394.91 nm	f=0.0006
329 -> 331		0.28102			
330 -> 332		0.63528			
Excited State	3:	Singlet-A	3.1532 eV	393.21 nm	f=0.0003
329 -> 331		0.63493			
330 -> 331		0.15526			
330 -> 332		-0.25716			
Excited State	۷۰	Singlet-A	3 2646 eV	379 78 nm	f=0 0014
378 -> 332	т.	-0 10391	5.2040 CV	575.70 mm	1-0.0014
320 -> 332		0.68655			
JZJ -> JJZ		0.00000			

Excited State	5:	Singlet-A	3.3329 eV	372.00 nm	f=0.0063
327 -> 331		0.13148			
327 -> 332		0.17225			
328 -> 331		0.45767			
328 -> 332		0.46228			
329 -> 332		0.11327			
Excited State	1:	Triplet-A	2.3653 eV	524.25 nm	f=0.0000
323 -> 336		-0.27886			
329 -> 336		0.60992			
330 -> 336		-0.14461			
Excited State	2:	Triplet-A	2.4556 eV	504.96 nm	f=0.0000
325 -> 331		-0.13584			
325 -> 332		-0.33816			
325 -> 333		0.20985			
326 -> 331		0.16736			
326 -> 332		0.39737			
326 -> 333		-0.14478			
327 -> 332		0.14749			
328 -> 332		0.10492			
Excited State	3:	Triplet-A	2.4938 eV	497.23 nm	f=0.0000
322 -> 335		-0.10110			
327 -> 337		-0.32634			
328 -> 335		-0.14323			
328 -> 337		0.17388			
330 -> 336		-0.11892			
330 -> 337		-0.51994			
Excited State	4:	Triplet-A	2.5077 eV	494.47 nm	f=0.0000
322 -> 335		-0.38469			
327 -> 335		-0.19194			
328 -> 335		-0.48019			
330 -> 335		0.14033			
330 -> 337		0.15325			
Excited State	5:	Triplet-A	2.5603 eV	494.31 nm	f=0.0000
319 -> 333		0.11546			
325 -> 331		-0.11230			
325 -> 332		-0.23409			
325 -> 333		-0.21485			
326 -> 331		-0.14140			
326 -> 332		-0.27042			

326 -> 333	-0.42770
328 -> 332	0.12367
328 -> 333	0.10194

Table 5S. GPC and XPS data of the metallopolymers Poly(NVK-co-1), Poly(NVK-co-2),Poly(NVK-co-3) and Poly(NVK-co-4) with defferent feed molar ratios (50:1, 75:1, 100:1,150:1 or 200:1).

Sample	Monomer	NVK/Complex	M _n ª/g∙mol	PDI ^b	Ln ³⁺ -	[Zn ²⁺ /Ln ³⁺] ^c
					content ^c	
Poly(NVK- <i>co</i> -1)	NVK/ 1	75:1	11324	1.18	1.67	1.02
Poly(NVK- <i>co</i> -2)	NVK/ 2	75:1	11732	1.16	1.65	1.01
Poly(NVK- <i>co</i> -3)	NVK/ 3	50:1	8342	1.13	2.60	0.99
Poly(NVK- <i>co</i> -3)	NVK/ 3	75:1	11816	1.17	1.66	1.00
Poly(NVK- <i>co</i> -3)	NVK/ 3	100:1	17622	1.20	1.22	1.03
Poly(NVK- <i>co</i> -3)	NVK/ 3	150:1	20580	1.23	0.77	1.01
Poly(NVK- <i>co</i> -3)	NVK/ 3	200:1	24285	1.25	0.56	1.02
Poly(NVK- <i>co</i> -4)	NVK/ 4	75:1	11648	1.14	1.68	0.99

 $^{\rm a}$ $M_{\rm n}$ is the number average molecular weight.

^b PDI = M_w/M_n , where M_w is the weight average molecular weight.

 $^{\rm c}$ Ln^{3+-content (NVK-based actual molar ratio) and [Zn^{2+}/Ln^{3+}] molar ratio are obtained from

XPS quantitative analyses.

Figure 1S. ¹H NMR spectra of PVK, complex monomer 1 and its metallopolymer Poly(NVK-

*co***-1)** (75:1) in DMSO-*d*₆ at RT.



Figure 2S. UV-visible absorption spectra of the ligands H_2L^1 and HL^2 , the precursor [Zn(L¹)(4-vinyl-Py)], and complex monomers 2-5 in dilute MeCN solution (2 × 10⁻⁵ M) at RT.



Figure 3S. XPS data of the $[Zn(L^1)(4-vinyl-Py)Ln(L^2)_3]$ -grafted metallopolymers Poly(NVK-co-2),

Poly(NVK-co-3) and Poly(NVK-co-4) with a feed molar ratio of 75:1.



Figure 4S. PXRD patterns of PVK and the [Zn(L¹)(4-vinyl-Py)Ln(L²)₃]-grafted metallopolymers



Poly(NVK-co-2), Poly(NVK-co-3) and Poly(NVK-co-4) with a feed molar ratio of 75:1.

Figure 5S. TG and DSC (inset; for Poly(NVK-co-3) (75:1)) curves of PVK, complex monomer 3

and Poly(NVK-co-3) (75:1) in solid state.



Figure 6S. DR spectra of PVK and the $[Zn(L^1)(4-vinyl-Py)Ln(L^2)_3]$ -grafted polymers **Poly(NVK***co-2*), **Poly(NVK-***co-3*) and **Poly(NVK-***co-4*) with a feed molar ratio of 75:1.



Figure 7S. The normalized spectra overlap between the visible emission of PVK and the DR

spectrum of each of complex monomers 2-4 in solid state.



Figure 8S. The cyclic voltammetry (CV) curves of Poly(NVK-co-3) (50:1, 75:1 and 100:1) in

toluene solution at RT.

