

Electronic Supporting Information Available

Efficient and high color-purity green-light polymer light-emitting diode (PLED) based on Tb³⁺-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. Other chemicals including NVK (N-vinylcarbazole) 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 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 ($\Phi_{\text{Tb}}^{\text{L}}$) was determined by the same spectrometer using a 450 W Xe lamp and an integrating sphere. The overall quantum yield ($\Phi_{\text{Tb}}^{\text{L}}$) is calculated by the equation: $\Phi_{\text{Tb}}^{\text{L}} = \frac{S(\text{Em})}{S(\text{Abs})} = \frac{\int \frac{\lambda}{hc} [I_{\text{sample (em)}}(\lambda) - I_{\text{reference (em)}}(\lambda)] d\lambda}{\int \frac{\lambda}{hc} [I_{\text{reference (ex)}}(\lambda) - I_{\text{sample (ex)}}(\lambda)] d\lambda}$, where $S(\text{Abs})$ is the number of photons absorbed by the sample and $S(\text{Em})$ is the number of photons emitted from the sample, λ is the wavelength, h is Planck's constant, c is the velocity of light, $I_{\text{sample (ex)}}$ and $I_{\text{reference (ex)}}$ are the integrated intensities of the excitation light with and without a sample, and $I_{\text{sample (em)}}$ and $I_{\text{reference (em)}}$ are the photo-luminescent intensities with and without a sample, respectively. 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 powder X-ray diffraction (PXRD) patterns were recorded on a D/Max-III A diffractometer with graphite-monochromatized Cu K α radiation ($\lambda = 1.5418 \text{ \AA}$). 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 $^{\circ}\text{C}/\text{min}$.

Synthesis of the pyrazolone ligand Heb-PMP

(4-(2-ethylbutanoyl)-1-phenyl-3-methyl-1*H*-pyrazol-5(4*H*)-one)

The pyrazolone ligand Heb-PMP was synthesized according to an improved procedure from the literature.¹ To a stirred solution of 1,4-dioxane (40 mL), solid 1-phenyl-3-methyl-pyrazolone-5 (PMP; 0.014 mol, 2.44 g) was added and the mixture was heated to 70 °C for 10 min. Then calcium hydroxide (0.0525 mol, 3.89 g) and barium hydroxide (0.0087 mol, 1.50 g) in small portions were added, respectively. After another 10 min, the resulting pink mixture was cooled to room temperature, and 2-ethylbutyryl chloride (0.014 mol, 2 mL) was added dropwise. Whereupon the mixture became light white and substantially more viscous, heated the resulting mixture at reflux temperature for 10 h. Cooled the cloudy pinkish mixture to room temperature and then poured into a stirred solution of ice-cold hydrochloric acid (350 mL of a 3 mol·L⁻¹ solution). The pink oil precipitated was extracted by chloroform and washed extensively by using deionized water and dried with anhydrous sodium sulfate. Then the oil product was purified by chromatograph on a silica gel column with CHCl₃-oil ether (15:1, v/v) obtain pale yellow oil. Yield: 1.64 g, 43%. Calc. for C₁₆H₂₀N₂O₂: C, 70.56; H, 7.40; N, 10.29%. Found: C, 70.43; H, 7.35; N, 10.18%. ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 13.61 (s, 1H, -OH), 7.90 (d, 2H, -Ph), 7.43 (t, 2H, -Ph), 7.25 (t, 1H, -Ph), 2.85 (m, 1H, -CH), 1.81 (m, 2H, -CH₂), 1.61 (m, 2H, -CH₂), 1.28 (s, 3H, -CH₃), 0.95 (t, 6H, -CH₃).

Synthesis of the vinyl-functionalized ancillary ligand 4-VB-PBI

(1-(4-vinylbenzyl)-(pyridin-2-yl)-1*H*-benzo[*d*]imidazole)

The vinyl-functionalized ancillary ligand 4-VB-PBI was synthesized from the reaction² of 1-(chloromethyl)-4-vinylbenzene and the precursor 2-(pyridine-2-yl)-1*H*-benzo[*d*]imidazole (HPBI), which was obtained from the condensation reaction of 2-pyridinecarboxaldehyde and 1,2-diaminobenzene, giving a white solid in a good yield of 76%. Calc. for C₂₁H₁₇N₃: C, 81.00; H, 5.50; N, 13.49%. Found: C, 79.46; H, 5.58%; N, 13.42%. ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 8.70 (d, 1H, -Py), 8.37 (d, 1H, -Py), 8.01 (t, 1H, -Py), 7.77 (m, 1H, -Py), 7.59 (m, 1H, -Ph), 7.52 (m, 1H, -Ph), 7.34 (d, 2H, -Ph), 7.28 (m, 2H, -Ph), 7.10 (d, 2H, -Ph), 6.63 (m, 1H, -CH=C), 6.22 (s, 2H, -CH₂), 5.73 (d, 1H, =CH₂), 5.19 (d, 1H, =CH₂).

Synthesis of PVK through AIBN-initiated free-radical polymerization of NVK

The homogeneous polymerization of NVK in activation with AIBN for comparison was carried out in a Fisher-Porter glass reactor and protected by a N₂ atmosphere according to the typical procedure.³ For PVK: yield: 86%. FT-IR (KBr, cm⁻¹): 3045 (w), 3022 (w), 1624 (w), 1598 (m), 1483 (m), 1452 (s), 1402 (w), 1322 (s), 1220 (m), 1155 (m), 1126 (w), 1092 (w), 1031 (w), 1000 (w), 926 (w), 840 (w), 744 (vs), 719 (s), 660 (w), 614 (w), 572 (w), 529 (w), 472 (w), 424 (w). ¹H NMR (400 MHz, DMSO-*d*₆): δ (ppm) 8.25-3.95 (b, 8H), 3.95-2.15 (b, 1H), 2.15-0.50 (b, 2H).

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 three-electrode 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-2)** (50:1) are calculated according to the following equations,⁴ $E_{\text{HOMO}} = -(E_{\text{OXD}} - E_{\text{OXD, ferrocene}}) - 4.8 \text{ eV}$, $E_{\text{LUMO}} = E_{\text{HOMO}} + E_g \text{ eV}$, 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.⁵

PLEDs' fabrication and determination

The two PLEDs I-II were fabricated on ITO coated glass substrates with a sheet resistance of 20 Ω per square. Patterned ITO coated glass substrates were washed with acetone, detergent, distilled 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 30 nm thickness. The CH₂Cl₂ solution (at a concentration of 10 mg/mL) of **Poly(NVK-co-2)** (50:1) as the emitting layer was prepared under N₂ atmosphere and spin-coated on the PEDOT:PSS layer with a thickness of 40 nm. Subsequently, the BCP layer (10 or 20 nm) and the following TPBI layer (30 nm) were thermally deposited onto the emitting layer. Finally, a thin layer of LiF (1 nm) 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 two devices is 9

mm². Current density(*J*)-voltage(*V*)-luminance (*L*) was collected using a Keithley 2400 source meter equipped with a calibrated silicon photodiode. The electroluminescent (EL) spectra were measured by a PR655 spectrometer. The external quantum efficiencies (EQE) values were determined by a Si photodiode with calibration in an integration sphere (IS080, Labsphere).

References

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Table 1S. GPC data of the samples of **Poly(NVK-co-1)** and **Poly(NVK-co-2)**.

Sample	Monomer	NVK/monomer	$M_n^a/\text{g}\cdot\text{mol}^{-1}$	$\text{PDI}^b = M_w/M_n$
Poly(NVK-co-1)	NVK and 1	100:1	11168	1.21
Poly(NVK-co-2)	NVK and 2	50:1	8264	1.17
Poly(NVK-co-2)	NVK and 2	75:1	9478	1.23
Poly(NVK-co-2)	NVK and 2	100:1	11279	1.20
Poly(NVK-co-2)	NVK and 2	200:1	19646	1.26
Poly(NVK-co-2)	NVK and 2	400:1	37795	1.31

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

Figure 1S. ^1H NMR spectra for Heb-PMP, 4-VB-PBI, PVK, complex monomer **1** and **Poly(NVK-co-1)** (100:1) in $\text{DMSO}-d_6$ at room temperature.

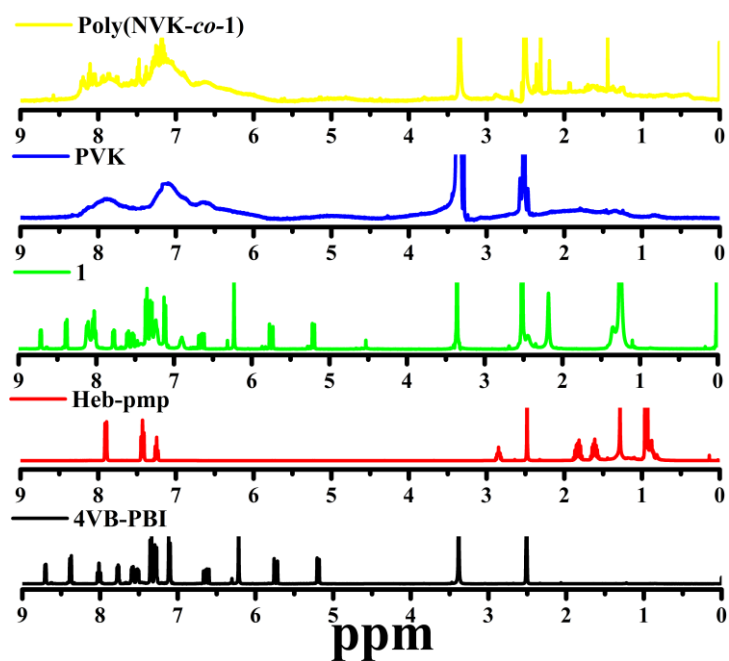


Figure 2S. UV-visible absorption spectra of Heb-PMP, 4-VB-PBI and their complex monomers **2-3** in MeCN solution (2×10^{-5} M).

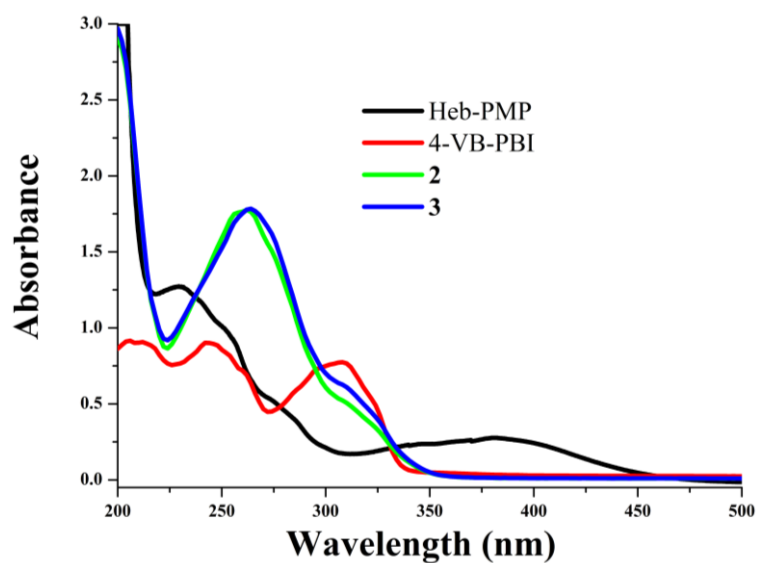


Figure 3S. PXRD patterns for PVK and the representative metallopolymer **Poly(NVK-co-1)** and **Poly(NVK-co-2)** with a stipulated feed molar ratio of 100:1.

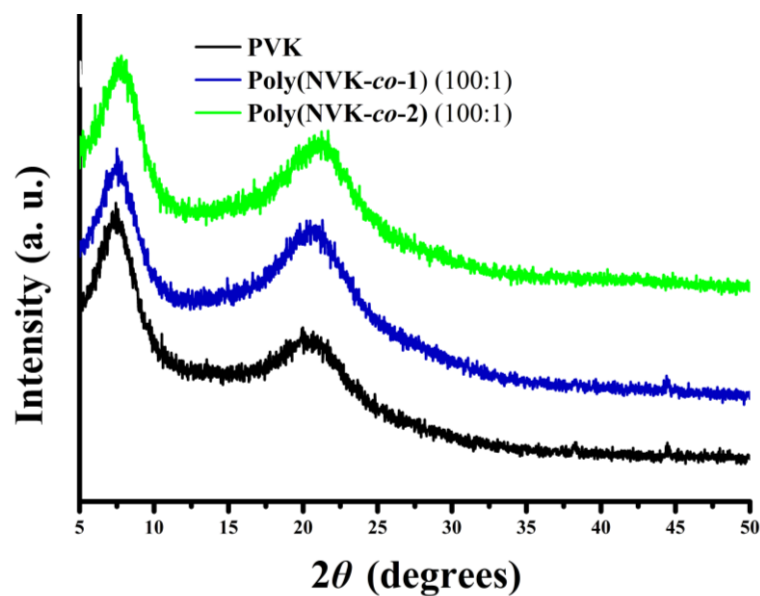


Figure 4S. TG curves of PVK and complex monomer **2** and TG and DSC (inset) curves of metallopolymer **Poly(NVK-co-2)** (50:1) in solid state.

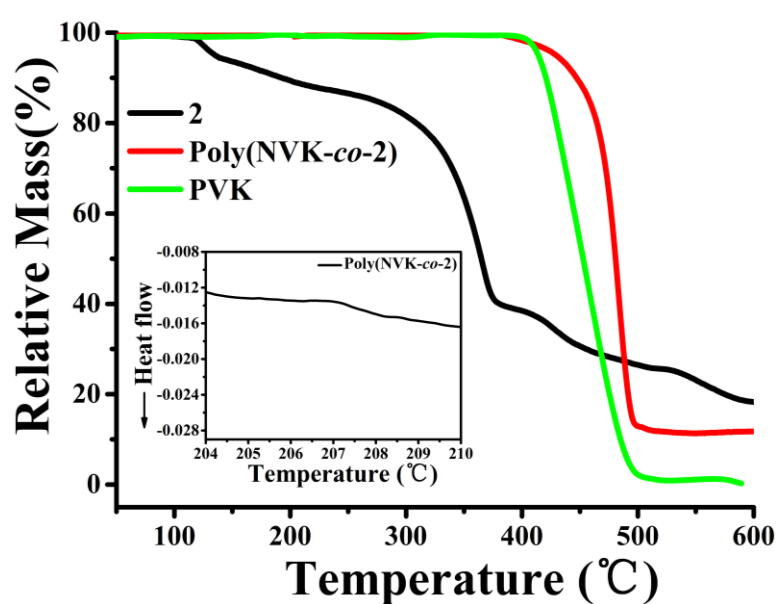


Figure 5S. DR spectra of the representative metallopolymer **Poly(NVK-co-1)** and **Poly(NVK-co-2)** with a stipulated feed molar ratio of 100:1 in solid state.

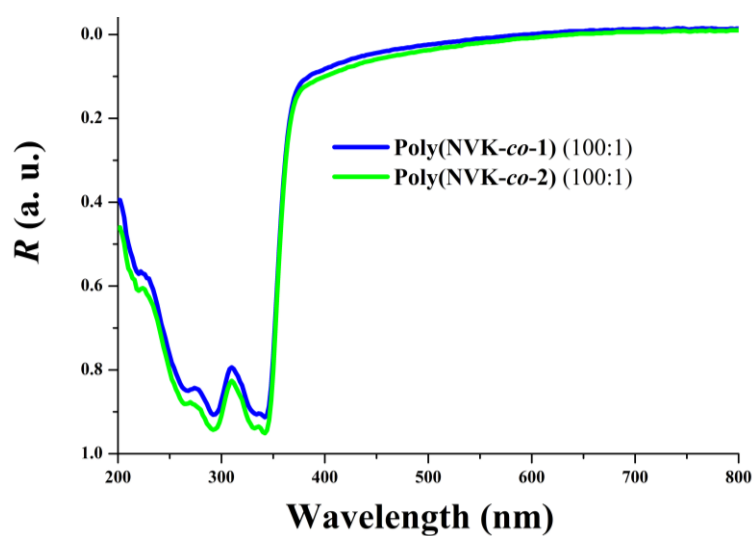


Figure 6S. The normalized spectra overlap between the visible emission of PVK and the UV-visible absorption of complex monomer **2** in CH₂Cl₂ solution.

