

Electronic Supporting Information Available

Red to white polymer light-emitting diode (PLED) based on Eu³⁺-Zn²⁺-Gd³⁺-containing metallpolymer

Lin Liu, Hongyan Li, Peiyang Su, Zhao Zhang, Guorui Fu, Baoning Li,
Xingqiang Lü*

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. Methyl methacrylate (MMA) was dried over CaH₂, distilled and stored under dried N₂ prior to use. 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. 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 Magna-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 CDCl₃ and/or

DMSO- d_6 at RT. 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 (Φ_{em} or Φ_{Eu}^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 complete with depth profile and angle-resolved capabilities. 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 °C/min. Cyclic voltammetry (CV) measurements 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 all compounds 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(2-co-MMA-co-8)** (120:1[**2/8** = 2:1 or 1:2]) are calculated according to the following equations,¹ $E_{\text{HOMO}} = -(E_{\text{OXD}} - E_{\text{OXD, ferrocene}}) - 4.8 \text{ eV}$, $E_{\text{LUMO}} = E_{\text{HOMO}} + E_{\text{g}}$ 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.²

X-ray Crystallography

Single crystals of [Zn(L)(4-vinyl-Py)Eu(NO₃)₃] (**6**) of suitable dimensions were mounted onto thin glass fibers. All the intensity data were collected on a Bruker SMART CCD diffractometer (Mo-K α radiation and $\lambda = 0.71073 \text{ \AA}$) 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.³ All other non-hydrogen atoms were refined with anisotropic thermal parameters. Absorption corrections were applied using SADABS.⁴ Hydrogen atoms were placed in calculated positions and refined isotropically using a riding model. Crystallographic data and refinement parameters for complex monomer **6** are presented in Table S1, and relevant atomic distances and bond angles are collected in Table S2. CCDC reference number 1535076 for complex monomer **6**.

Synthesis of PMMA activated with AIBN

The homogeneous polymerization of MMA in activation with AIBN for comparison was carried out in a Fisher-Porter glass reactor and protected by N₂ according to the typical procedure.⁵ Yield: 91%. FT-IR (KBr, cm⁻¹): 3000 (w), 2952 (m), 2843 (w), 1730 (s), 1631 (m), 1602 (m), 1486 (w), 1454 (w), 1433 (w), 1398 (m), 1384 (m), 1336 (w), 1269 (w), 1238 (w), 1138 (vs), 993 (m), 914 (w), 840 (m), 806 (w), 750 (m), 618 (w), 544 (w), 513 (w), 482 (w). ¹H NMR (400 MHz, DMSO-*d*₆-CDCl₃ (v/v = 10:1)): δ (ppm) 3.57 (s, 3H, -COOMe), 1.85 (b, 2H, -CH₂), 0.91 (m, 3H, -CH₃).

Fabrication and testing of PLEDs

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 15 minutes, 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 35 nm thickness. For Device I, PVK ($M_w = 1 \times 10^6$ g/mol) as the hole-transporting material, was spin-coated from chlorobenzene solution onto the PEDOT:PSS layer. A mixture of CBP, PBD and **Poly(2-co-MMA-co-8)** (120:1[**2/8** = 2:1]) as the emitting layer in CH₂Cl₂ solution (at a concentration of 10 mg/mL) was prepared under N₂ atmosphere and spin-coated on the PVK layer. Subsequently, the TPBI layer (60 nm) was then thermally deposited onto the emitting layer. Finally, a thin layer of LiF (1 nm) followed by 100 nm thick Al capping layer was deposited onto the substrate under vacuum of 10⁻⁶ Pa.

As to device II, a mixture of PVK:PBD:**Poly(2-co-MMA-co-8)** (120:1[2/8 = 1:2]) as the emitting layer in CH₂Cl₂ solution (at a concentration of 10 mg/mL) was prepared under N₂ atmosphere and directly spin-coated on the PEDOT:PSS layer. The typical active area of the two devices is 0.15 cm². 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 (ISO80, Labsphere).

References

- 1 H. Y. Chen, C. T. Chen and C. T. Chen, *Macromolecules*, 2010, **43**, 3613-3623.
- 2 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.
- 3 G. M. Sheldrick, *SHELXL-97: Program for crystal structure refinement*, Göttingen, Germany, 1997.
- 4 G. M. Sheldrick, *SADABS*, University of Göttingen, 1996.
- 5 W. A. Braunecker and K. Matyjaszewski, *Prog. Polym. Sci.*, 2007, **32**, 93-146.

Table S1 Crystallographic data and refinement parameters for complex monomer 6

Compound	6
Empirical formula	C ₂₉ H ₂₅ N ₆ O ₁₃ ZnEu
Formula weight	882.88
Crystal system	Monoclinic
Space group	<i>P2(1)/c</i>
T/K	296 (2)
<i>a</i> /Å	9.421 (8)
<i>b</i> /Å	15.789 (12)
<i>c</i> /Å	22.299 (18)
α /°	90
β /°	102.2
γ /°	90
<i>V</i> /Å ³	3242 (4)
<i>Z</i>	4
ρ /g·cm ⁻³	1.809
Crystal size/mm	0.25 × 0.24 × 0.21
μ (Mo-K α)/mm ⁻¹	2.733
Data/restraints/parameters	5775/99/451
Quality-of-fit indicator	0.797
No. Unique reflections	5775
No. Observed reflections	14468
Final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0647 <i>wR</i> ₂ = 0.1472
Final <i>R</i> indices (all data)	<i>R</i> ₁ = 0.1512 <i>wR</i> ₂ = 0.1856

Table S2 Relevant atomic distances and bond angles for complex monomer **6**

Complex monomer 6			
Zn(1)-N(1)	2.055(9)	Zn(1)-N(2)	2.070(9)
Zn(1)-N(6)	2.044(10)	Zn(1)-O(2)	2.036(7)
Zn(1)-O(3)	2.013(8)	Eu(1)-O(1)	2.75(9)
Eu(1)-O(2)	2.373(8)	Eu(1)-O(3)	2.372(9)
Eu(1)-O(4)	2.694(10)	Eu(1)-O(5)	2.610(2)
Eu(1)-O(6)	2.44(2)	Eu(1)-O(8)	2.454(13)
Eu(1)-O(9)	2.492(12)	Eu(1)-O(11)	2.428(11)
Eu(1)-O(12)	2.508(12)	C(28)-C(29)	1.284(19)
N(1)-Zn(1)-N(2)	80.5(4)	N(1)-Zn(1)-N(6)	80.5(4)
N(1)-Zn(1)-O(2)	91.9(3)	N(1)-Zn(1)-O(3)	151.5(3)
O(1)-Eu(1)-O(4)	171.8(3)	O(2)-Eu(1)-O(3)	67.1(3)
O(5)-Eu(1)-O(6)	46.7(7)	O(8)-Eu(1)-O(9)	48.7(5)
O(11)-Eu(1)-O(12)	47.0(5)		

Table S3 The photophysical property of complex monomers **2-4** and **6-8** in dilute MeCN solution (1×10^{-5} M) and metallopolymers **Poly(MMA-co-2)**, **Poly(MMA-co-8)**, **Poly(2-co-MMA-co-8)** and **Poly(4-co-MMA-co-8)** in solid state at RT or 77 K

Compound	Absorption	Excitation	Emission
	λ_{ab}/nm	λ_{ex}/nm	λ_{em}/nm (τ , Φ (%))
2	212, 274, 296, 334, 352	380	594, 612 (251 μ s, 42.0), 651, 701
3	212, 272, 298, 332, 354	380	445, 480 (sh)
4	214, 272, 298, 334, 356	388	442 (2.5 ns)
	-	343	494 (11 μ s), 528
6	234, 304, 336	366	500 (w)
7	236, 302, 338	365	495 (w)
8	236, 302, 337	365	500 (4.7 ns, 7.8)
		350	502 (6.4 ns)
Poly(MMA-co-2) (60:1)	224, 266, 300, 368, 394	376	594, 612 (359 μ s), 651, 701
Poly(MMA-co-2) (120:1)	224, 265, 300, 366, 392	378	594, 612 (472 μ s), 651, 701
Poly(MMA-co-2) (240:1)	222, 268, 298, 368, 394	378	594, 612 (418 μ s), 651, 701
Poly(MMA-co-4) (120:1)		361	496 (35 μ s)
Poly(MMA-co-8) (60:1)	212, 312, 348	336, 398	493 (46.4 ns)
Poly(MMA-co-8) (120:1)	212, 316, 352	335, 404	493 (39.2 ns)
Poly(MMA-co-8) (240:1)	216, 312, 350	335, 398	492 (34.1 ns)
		341	502 (88.1 ns)
Poly(2-co-MMA-co-8) (120:1[2/8 = 2:1])	224, 306, 348	365	590, 612 (608 μ s, 64.3), 652, 701
Poly(2-co-MMA-co-8) (120:1[2/8 = 1:2])	212, 404	380	498 (29.7 ns, 590, 612 (532 μ s, 17.1), 652, 701
Poly(4-co-MMA-co-8) (120:1[4/8 = 2:1])	212, 404	355, 376	501 (9 μ s, 77 K)

Table S4 GPC data of the samples of PMMA and metallopolymers **Poly(MMA-co-2)**, **Poly(MMA-co-8)**, **Poly(1-co-MMA-co-5)**, **Poly(2-co-MMA-co-8)** and **Poly(4-co-MMA-co-8)**

Sample	Monomers	MMA/monomer	M_n^a /g mol ⁻¹	PDI ^b
PMMA	MMA	-	40324	1.08
Poly(MMA-co-1)	MMA and 1	120:1	10981	1.13
Poly(MMA-co-2)	MMA and 2	60:1	5881	1.09
Poly(MMA-co-2)	MMA and 2	120:1	10734	1.12
Poly(MMA-co-2)	MMA and 2	240:1	17842	1.19
Poly(MMA-co-4)	MMA and 4	120:1	10115	1.15
Poly(MMA-co-5)	MMA and 5	120:1	10081	1.10
Poly(MMA-co-8)	MMA and 8	60:1	5487	1.07
Poly(MMA-co-8)	MMA and 8	120:1	10212	1.14
Poly(MMA-co-8)	MMA and 8	240:1	16910	1.21
Poly(1-co-MMA-co-5)	MMA, 1 and 5	120:1[1/5 = 1:1]	10103	1.18
Poly(2-co-MMA-co-8)	MMA, 2 and 8	120:1[2/8 = 2:1]	10876	1.17
Poly(2-co-MMA-co-8)	MMA, 2 and 8	120:1[2/8 = 1:2]	10142	1.23
Poly(4-co-MMA-co-8)	MMA, 4 and 8	120:1[4/8 = 2:1]	10745	1.19

^a M_n is the number-average molecular weight. ^bPDI = M_w/M_n , where M_w is the weight-average molecular weight.

Table S5 Electroluminescent performance of the red-light PLED I and the white-light PLED II

PLED	V_{on}^a (V)	CE_{max}^b (cd/A)	PE_{max}^c (lm/W)	L_{max}^d (cd m ⁻²)	EQE_{max} (%)	CIE_{EL}^e
I	20	0.25	0.037	5.9	0.20	(0.664, 0.329)
II	/	0.005	0.001	0.28	0.003	(0.339, 0.288)

^a The turn-on voltage at which luminance reaches 1 cd/m². ^bMaximum current efficiency at 21 V. ^cMaximum power efficiency at 21 V. ^dMaximum brightness at 21 V. ^eCIE coordinates from EL at 21 V.

Figure S1. UV-visible absorption spectra of complex monomers **2-4** and **6-8** in dilute MeCN (1×10^{-5} M) at RT.

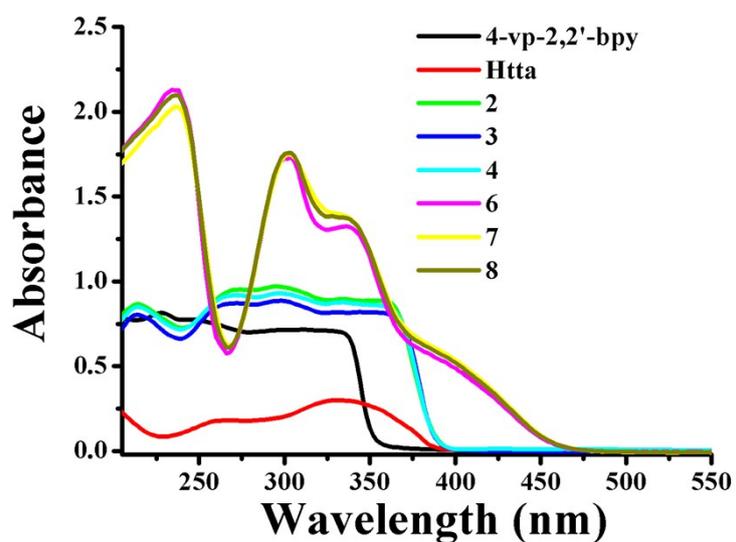


Figure S2. Energy level diagram and energy transfer process for the complex monomers and metallopolymer.

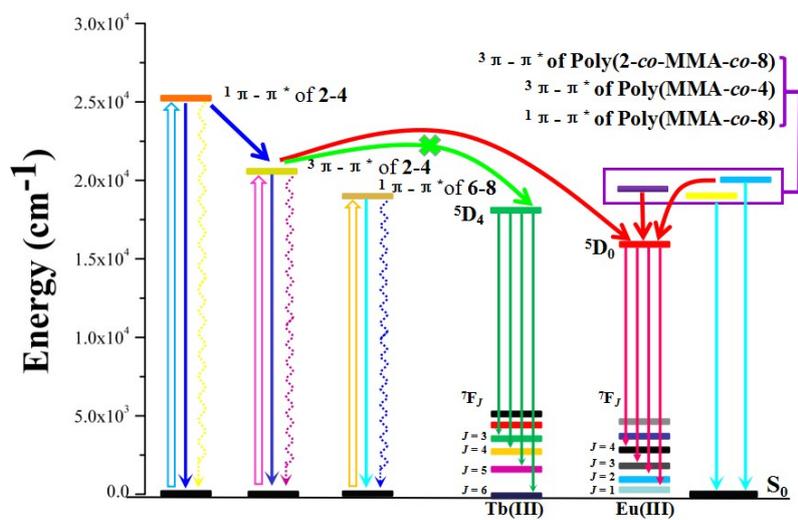


Figure S3. PXRD patterns of PMMA and metallopolymers **Poly(MMA-co-2)** (120:1), **Poly(MMA-co-8)** (120:1) and **Poly(2-co-MMA-co-8)** (120:1[2/8 = 2:1 or 1:2]) in the solid state.

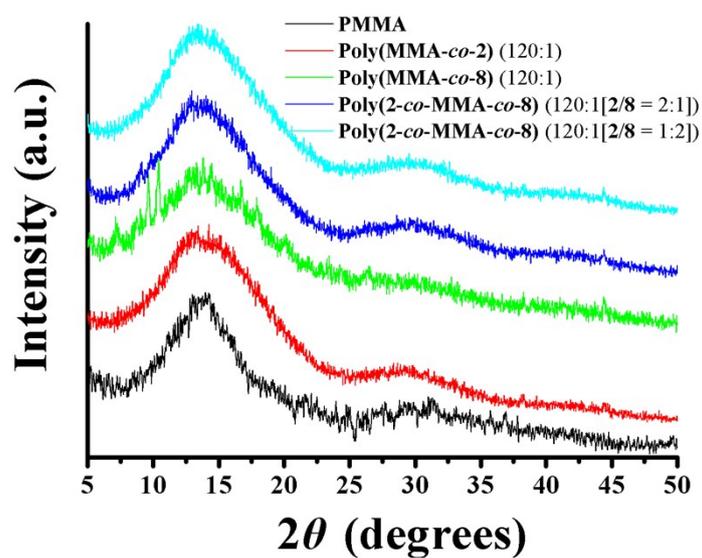


Figure S4. TG curves of complex monomers **2**, **8** and PMMA and TG and DSC (inset) curves of **Poly(2-co-MMA-co-8)** (120:1[2/8 = 1:2]) in solid state.

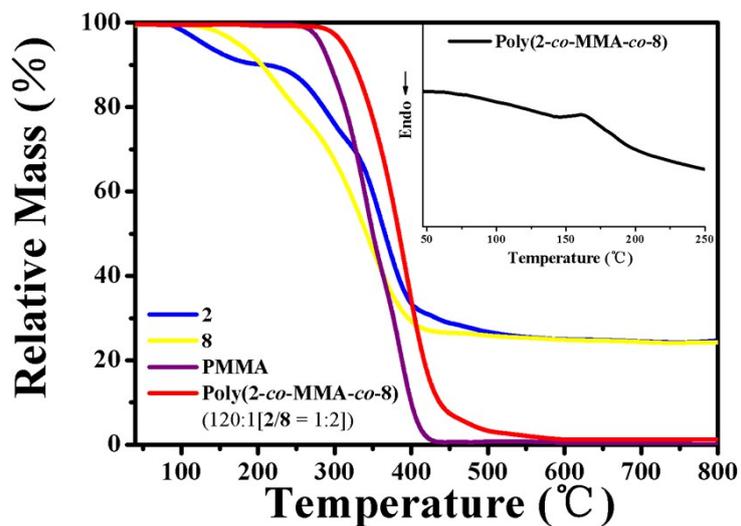


Figure S5. DR spectra of **Poly(MMA-co-2)** (120:1), **Poly(MMA-co-8)** (120:1) and **Poly(2-co-MMA-co-8)** (120:1[2/8 = 2:1 or 1:2]) in the solid state at RT.

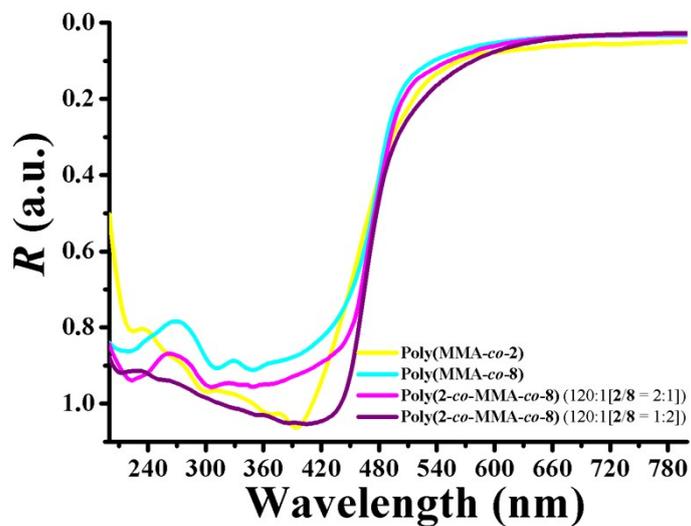


Figure S6. Emission and excitation spectra of **Poly(MMA-co-4)** (120:1), **Poly(MMA-co-8)** (120:1) and **Poly(4-co-MMA-co-8)** (120:1[2/8 = 2:1]) in the solid state at 77 K.

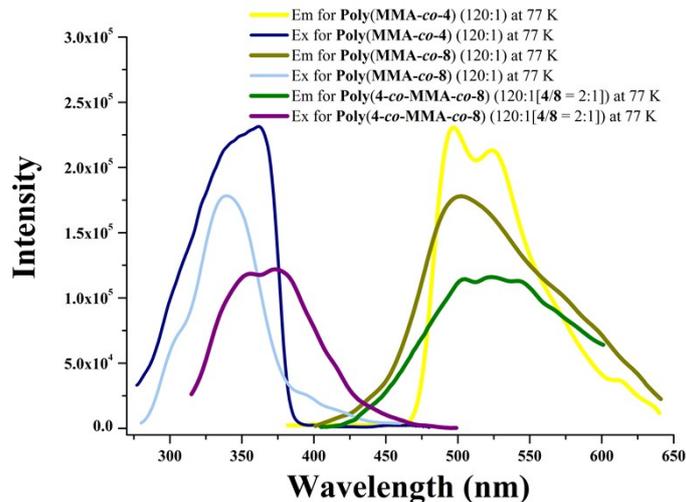


Figure S7. Normalized visible emission spectrum comparison of CBP:PBD:Poly(2-co-MMA-co-8) (120:1[2/8 = 2:1]) (65%:35%:5%) with Poly(2-co-MMA-co-8) (120:1[2/8 = 2:1]), PVK:PBD:Poly(2-co-MMA-co-8) (120:1[2/8 = 1:2]) (65%:35%:5%) with Poly(2-co-MMA-co-8) (120:1[2/8 = 1:2]) in solid state.

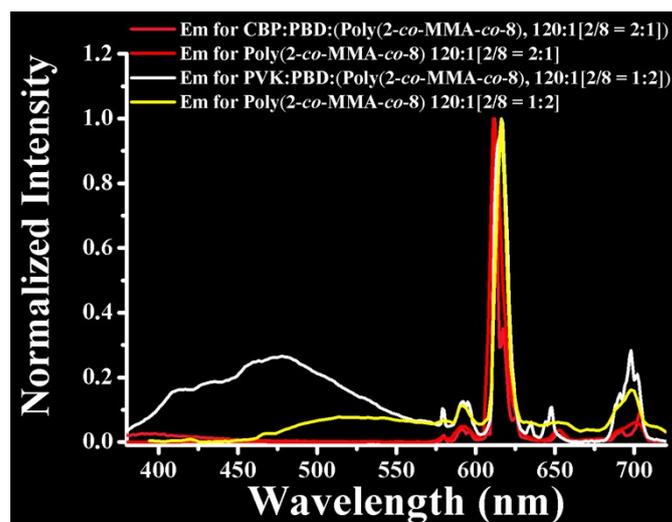


Figure S8. Normalized visible emission spectra of CBP, PBD and PVK and the UV-visible

absorption spectra of **Poly(2-co-MMA-co-8)** (120:1[2/8 = 2:1]) and **Poly(2-co-MMA-co-8)** (120:1[2/8 = 1:2]) in CH₂Cl₂ solution.

