Supporting Informtion

Surface Plasmon Resonance Assisted Circularly Polarized Luminescent Hybrid Assemblies of Eu-Containing Polyoxometalates

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Experimental Section

Materials

Diblock copolymers PEO_{114}-*b*-PLL_{109} and PEO_{114}-*b*-PLL_{85} were prepared through ring-opening polymerization[S1]. The degree of polymerization of the PLL block was determined by ^1H NMR measurement. EuW_{10} was prepared according literature[S2]. Silver nitrate (98%) and sodium citrate (AR) were purchased from J & k Chemical and used as received. Sodium borohydride was obtained from Tokyo Chemical Industry Co. without further purification. Ultrapure water from a Millipore Milli-Q system was used to synthesize Ag Nanoparticles and prepare aqueous solutions of polyoxometalates and polymers. Without otherwise noted, the other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd and used as received.

Measurements

The number average molecular weight (M_n) and the polydispersity indices (PDI) of polymers were determined by a gel permeation chromatography (GPC) apparatus, equipped with a Waters 2414 refractive-index detector, a Waters 1525 binary HPLC pump, and three Waters Styragel columns (HR1, HR2, and HR3), at 45 °C with DMF (containing 0.02 M LiBr) as eluent (1.0 ml/min). ^1H NMR were recorded on a Bruker Avance III spectrometer operating at 400.23 MHz at room temperature in D_2O solution. TEM images were obtained from a JEM-2100 (JEOL, Japan) transmission electron microscopy operated at 200 KV. The samples were prepared by dripping a drop of solution onto the copper grids coated with amorphous membranes and then drying in air. Dynamic light scatter (DLS) measurements were performed on a commercialized spectrometer from Brookhaven Instrument Corporation (BI-200SM Goniometer, Holtsville, NY), using a vertically polarized 100 mW solid-state laser (GXC-III, CNI, Changchun, China) operated at 633 nm as the light source and a BI-TurboCo digital correlator (Brookhaven Instruments Corp.) to collect data. The samples were filtered through 220 nm filters and the scattering angle was 90°. A Lambda 35 UV-Vis spectrometer was used to measure the absorption of the spectra. Circular dichroism spectra were acquired from a J-810 circular dichroism spectrometer (Jasco Corporation, Japan). The HT potential was controlled under 600 V by using the cells with different widths according to the absorption of the samples at various bands. The photoluminescence and lifetimes of the solutions were performed on an FLS920 Steady State & Time-resolved Fluorescence Spectrometer (Edinburgh Instruments Ltd.). The luminescent dissymmetry factor, g_{CPL}, were attained from a commercial instrument DSM 17 Spectrometer (Olis Co.) equipped with the Olis DM 245 fluorescence spectrometer, the Olis DSM 17 CD spectropolarimeter, and the Olis Polarization Toolbox together. The inductively coupled plasma atomic emission (ICP) was achieved from an Inductively Coupled Plasma-Atomic Emission Spectrometer (Leeman Co.)

Synthesis of AgNPs

Ag nanoparticles were prepared through a stepwise seeded growth method[S3]. 1.7 ml of $AgNO_3$ solution (0.1 M) was mixed with 95 ml of ultrapure water containing 0.17 mmol sodium citrate at 70 °C in a 250 ml round bottom flask. 10 min later, 2.0 ml of fresh sodium borohydride solution (0.031 M) was quickly added into the solution. The yellow solution of Ag seeds was obtained after 1 h at 70 °C.

To a 47 ml aqueous solution containing 0.078 mol sodium citrate, 5.0 ml of Ag seeds solution and 1.7 ml of $AgNO_3$ (0.1 M) were successively added to obtain golden solution. After three times of centrifugation and sonification, the final AgNPs solution was achieved. The concentration of Ag was 8.38×10^{-2} g/L determined by ICP.

Supplementary Figures and Tables

The degree of polymerization (DP) of poly(L-lysine) was calculated from the ratios of the integral values of the peak at 2.92 ppm (peak c in Fig.S1, CH_2 connected to amino group of lysine unit) to the peak at 3.61 ppm (peak b in Fig.S1, -CH_2-CH_2O- of PEO).

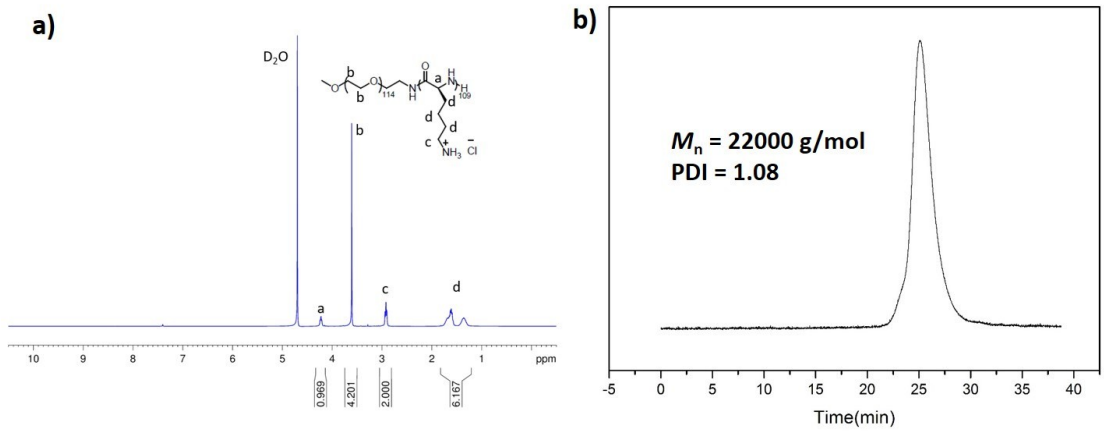

Fig.S1 a) ^{1}H NMR (400 MHz) spectra and b) GPC results of PEO_{114}-*b*-PLL_{109}.

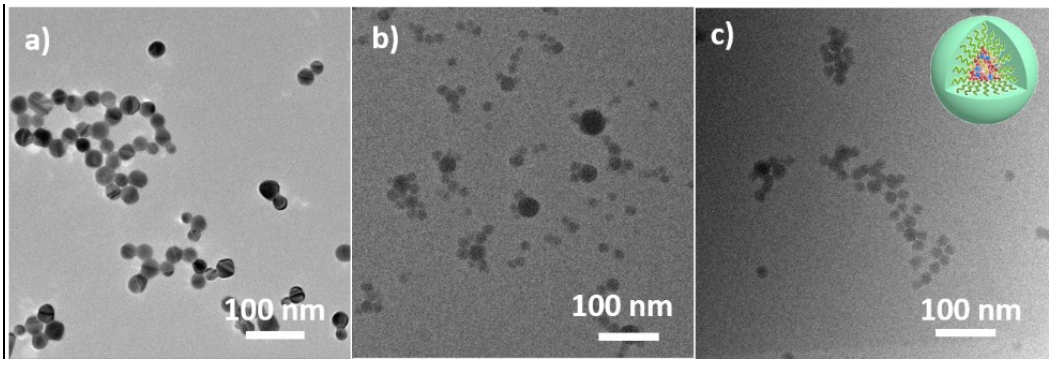

Fig.S2 TEM images of a) AgNPs, b) AgNPs/EuW_{10}/PEO_{114}-*b*-PLL_{85} at EuW_{10} = 1.00 mg/ml, f_+ = 0.63, and Ag = 1.40×10^{-2} mg/ml, and c) PEO_{114}-*b*-PLL_{85}/EuW_{10} at EuW_{10} = 1.00 mg/ml and f_+ = 0.63. Inset in c) is the schematic illustrations of the assembly.

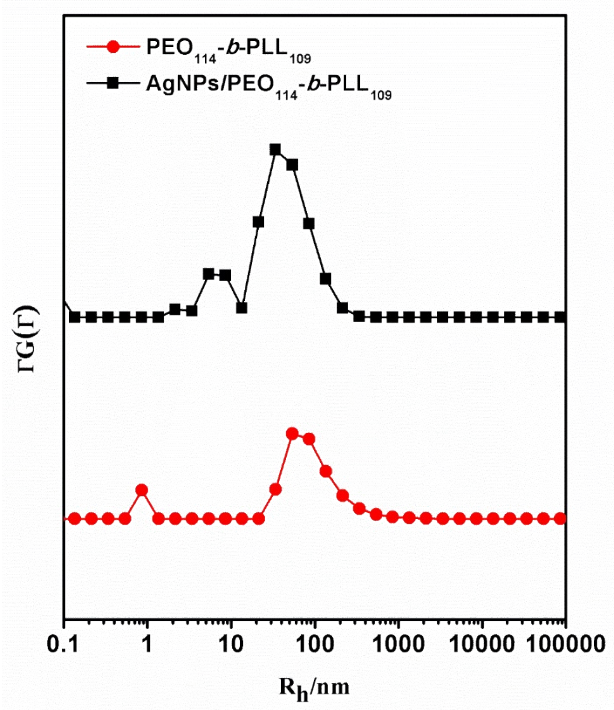

Fig.S3 DLS results of PEO_{114}-*b*-PLL_{109} and AgNPs/PEO_{114}-*b*-PLL_{109} = 1/5.

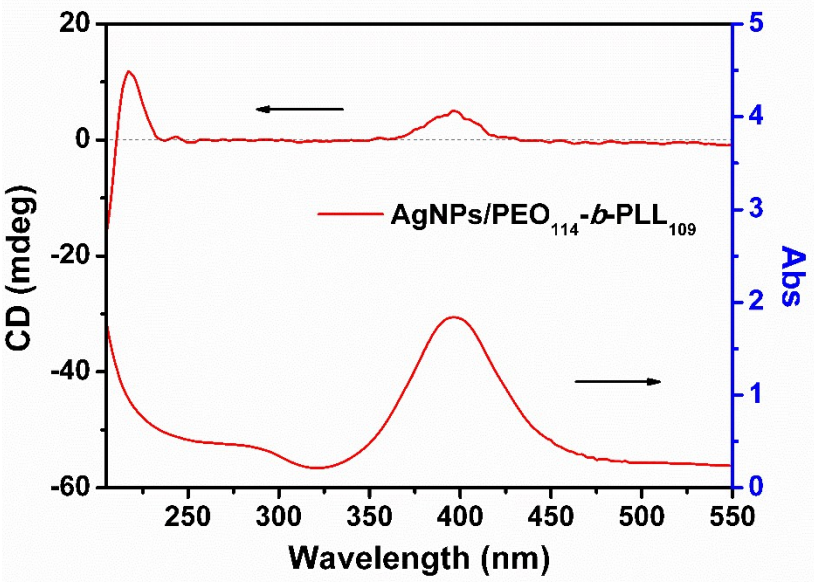

Fig.S4 CD and absorption spectra of AgNPs/PEO114-b-PLL109 (Ag = 1.40×10^{-2} mg/ml) at molar ratios of 1/5.

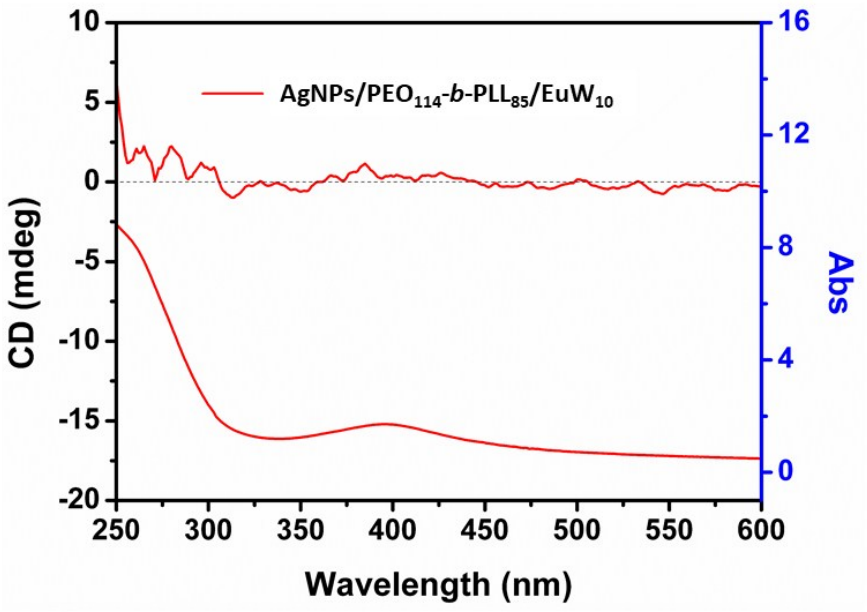

Fig.S5 The CD and absorption spectra of AgNPs/PEO_{114}-*b*-PLL_{85}/EuW_{10} at EuW_{10} = 1.00 mg/ml, Ag = 1.40×10^{-2} mg/ml and f_+ = 0.63.

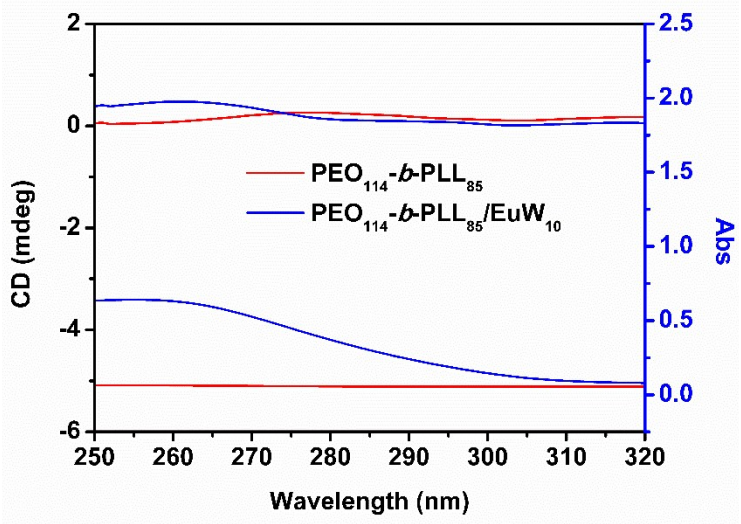

Fig. S6 CD and absorption spectra of polymer PEO_{114}-*b*-PLL_{85} (2.46×10^{-5} M) and the PEO_{114}-*b*-PLL_{85}/EuW_{10} assembly (EuW_{10} = 1.00 mg/ml) at f_+ = 0.63.

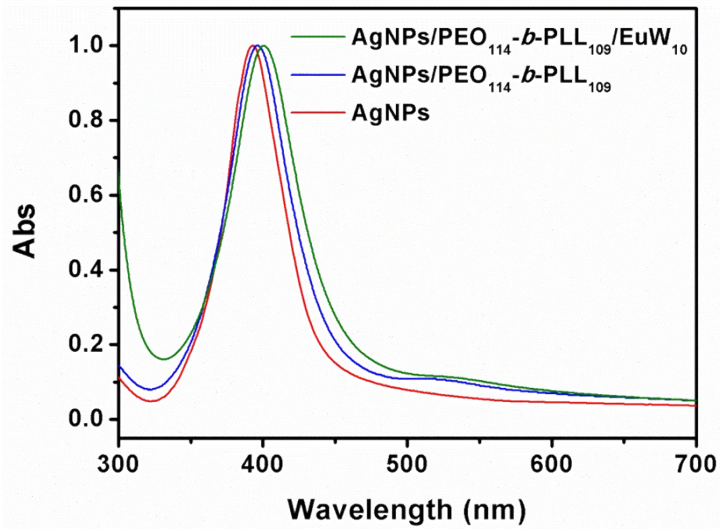

Fig. S7 Normalized absorption spectra of AgNPs, AgNPs/PEO_{114}-*b*-PLL_{109} binary mixture, and AgNPs/PEO_{114}-*b*-PLL_{109}/EuW_{10} ternary assembly.

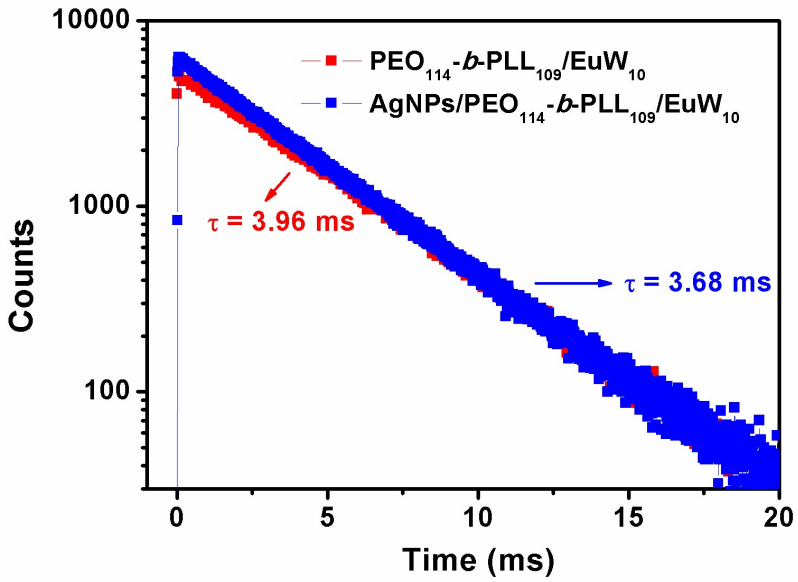

Fig. S8 Luminescence decay curves of PEO_{114}-*b*-PLL_{109}/EuW_{10} (EuW_{10} = 1.00 mg/ml, f_+ = 0.63) and AgNPs/PEO_{114}-*b*-PLL_{109}/EuW_{10} (EuW_{10} = 1.00 mg/ml, f_+ = 0.63, Ag = 1.40×10^{-2} mg/ml) assemblies excited at 280 nm and 302 nm, respectively. The monitoring wavelength was 587 nm.

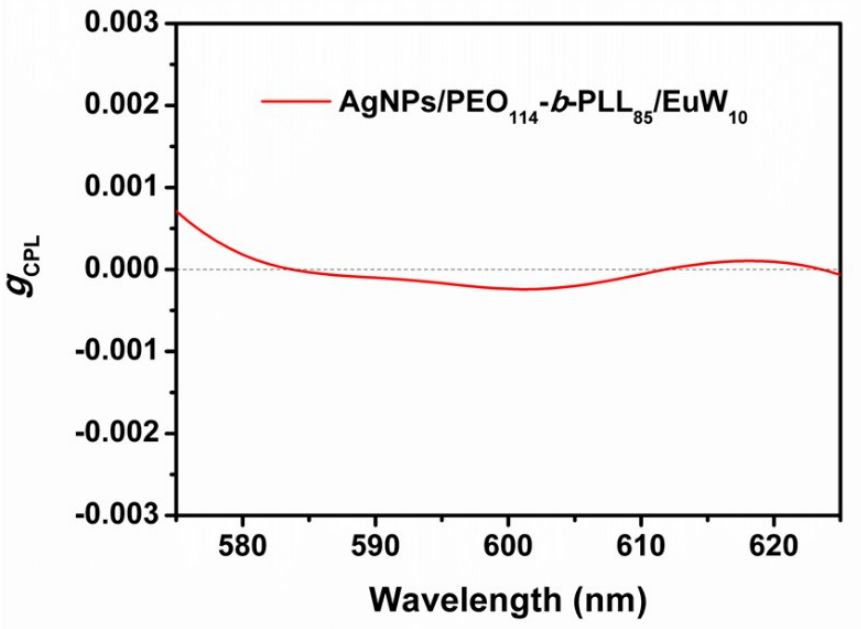

Fig. S9 CPL spectra of AgNPs/PEO_{114}-*b*-PLL_{85}/EuW_{10} (EuW_{10} = 1.00 mg/ml, Ag = 1.40×10^{-2} mg/ml and f_+ = 0.63).

References

S1. L. Shen, H. Chen, W. X. Fu and Z. B. Li, *Acta. Polym. Sin.*, 2016, **12**, 1645.

S2. M. Sugeta and T. Yamase, *Bull. Chem. Soc. Jpn.* 1993, **66**, 444.

S3. Y. Wan, Z. R. Guo, X. L. Jiang, K. Fang, X. Lu, Y. Zhang and N. Gu, *J. Colloid Interf. Sci.*, 2013, 394, 263.

S4.