

**Reversible pH- and Solvent-Responsive Micelle-Mediated Self-Assembly
of Platinum(II) Terpyridyl-Based Metallo-Supramolecular Diblock
Copolymers**

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Supporting Information

Experimental Section:

Instrumentation: ^1H NMR spectra were recorded with a Bruker AVANCE 400 (400 MHz) Fourier transform NMR spectrometer at ambient temperature with tetramethylsilane (Me_4Si) as an internal reference. Measurements of molecular mass and molecular weight distribution of the polymers were performed at 35 °C on a Waters 150C gel permeation chromatograph (GPC) equipped with an ISCO 2350 pump, a Viscotek 250/refractive index dual detector and micro-Styrigel columns (500 Å, 1000, and 10000 Å). Polystyrenes with narrow molecular weight distribution were used as calibration standards. *N*-Methylpyrrolidone (NMP) was used as an eluent at a flow rate of 1.0 mL/min. Dynamic light scattering (DLS) measurements were performed at 25 °C using Zetasizer 3000HSA with internal HeNe laser ($\lambda_0 = 632.8$ nm) from Malvern (UK). UV-Vis absorption spectra were recorded on a Cary 50 (Varian) spectrophotometer equipped with a Xenon flash lamp. Steady state emission spectra were recorded using a Spex Fluorolog-3 Model FL3-211 fluorescence spectrofluorometer equipped with a R2658P PMT detector. Unless specified otherwise, the emission spectra were obtained with an excitation wavelength of > 400 nm and were corrected for PMT response.

4-(Trimethylsilylethynyl)benzyl benzodithioate (**TMSEBDB**): The synthesis of **TMSEBDB** was carried out according to modified literature procedure.¹ Yield: 1.09 g (80 %). ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 0.25 (s, 9H, $\text{Si}(\text{CH}_3)_3$), 4.58 (s, 2H, $(\text{S}=\text{C})\text{SCH}_2\text{Ar}$), 7.32 (d, $J = 8.1$ Hz, 2H, ArH meta to the ethynyl group), 7.41 (d, $J = 8.1$ Hz, 2H, ArH ortho to the ethynyl group), 7.38 (dt, $J = 7.8, 7.8$ Hz, 2H, ArH meta to the thiocarbonyl group), 7.53 (t, $J = 7.4$ Hz, 1H, ArH para to the thiocarbonyl group), 7.98 (d, $J = 7.4$ Hz, 2H, ArH ortho to the thiocarbonyl group).

$(\text{CH}_3)_3\text{Si}-\text{C}\equiv\text{C}-\text{C}_6\text{H}_4-\text{CH}_2-\{\text{CH}_2\text{CH}(\text{C}_5\text{H}_4\text{N})\}_{44}-\text{SC}=\text{S}(\text{C}_6\text{H}_5)$ (**Me₃Si-C≡C-P2VP₄₄**): **Me₃Si-C≡C-P2VP₄₄** was prepared according to modification of the RAFT polymerization procedure.² Yield: 510 mg. ^1H NMR (400 MHz, CDCl_3 , 298 K): δ 0.23 (s, $(\text{CH}_3)_3\text{Si}$), 1.83 (br, $-\text{CH}_2-$ from P2VP backbone), 2.33 (br, HC-Ar from P2VP backbone), 6.20–7.32 (br, 2-vinylpyridine protons), 7.84 (m, phenyl protons of benzodithioate), 8.08–8.50 (br, 2-vinylpyridine protons). (Monomer conversion: 35.3 %, $M_{n, \text{theory}} = 4,100$, $M_{n, \text{NMR}} = 5,000$, $M_{n, \text{GPC}} = 8,900$, $M_w/M_n = 1.06$).

$\text{HC}\equiv\text{C}-\text{C}_6\text{H}_4-\text{CH}_2-\{\text{CH}_2\text{CH}(\text{C}_5\text{H}_4\text{N})\}_{44}-\text{SC}=\text{S}(\text{C}_6\text{H}_5)$ (**HC≡C-P2VP₄₄**): The **Me₃Si-C≡C-P2VP₄₄** (150 mg, 0.03 mmol) was dissolved in THF-methanol mixture (3:1 v/v), and potassium carbonate (83 mg, 0.6 mmol) in minimum amount of water was added. The reaction mixture was stirred overnight at room temperature, and then

passed through a short neutral Al₂O₃ column by THF. The product was precipitated by pouring the polymer solution into a large amount of *n*-hexane-diethyl ether (1:1 v/v) and dried under reduced pressure to give **HC≡C-P2VP₄₄** as a pink powder. Yield: 120 mg. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 1.83 (br, -CH₂- from P2VP backbone), 2.31 (br, HC-Ar from P2VP backbone), 3.01 (s, C≡CH), 6.33–7.40 (br, 2-vinylpyridine protons), 7.82 (m, phenyl protons of benzodithiophate), 8.07–8.40 (br, 2-vinylpyridine protons).

[(PEO₁₁₂tpy)Pt(C≡C-C₆H₄-P2VP₄₄)]OTf (**PEO₁₁₂-[Pt]-P2VP₄₄**): This was synthesized by modification of the Cu(I)-catalyzed reaction for platinum(II) alkynyl complexes.³ The chloroplatinum(II) precursor complex, [Pt(PEO₁₁₂tpy)Cl]OTf (159 mg, 0.028 mmol), was dissolved in degassed dichloromethane (15 mL) containing triethylamine (1 mL), followed by addition of **HC≡C-P2VP₄₄** (214 mg, 0.0428 mmol) and a catalytic amount of copper(I) iodide. The reaction mixture was stirred for 48 hours at room temperature; after which *n*-hexane (200 mL) was added and stirred for 10 minutes. The product precipitates were isolated by filtration, washed with *n*-hexane, and dried. The crude diblock copolymers were purified by dissolving into deionized water, and then saturated sodium chloride solution was added to precipitate out the diblock copolymers. The product was collected and was purified by repeating the procedure in order to eliminate the unreacted PEO₁₁₂ homopolymers. The obtained product was dissolved in 2-propanol and precipitated in an ice-bath for two times. The purified platinum(II) diblock copolymer was dried under reduced pressure for 24 hours. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 1.35–2.00 (br, -CH₂- from P2VP backbone), 2.30 (br, HC-Ar from P2VP backbone), 3.38 (s, -OCH₃ from PEG terminal), 3.45–3.81 (m, -OCH₂CH₂O- from PEG backbone), 5.01 (m, -OCH₂-ethylene oxide unit attached to terpyridine), 6.10–7.30 (br, 2-vinylpyridine protons), 7.80 (m, phenyl protons of benzodithiophate), 8.05–8.50 (br, 2-vinylpyridine protons), 8.67 (m, terpyridyl protons), 9.04 (m, terpyridyl protons), 9.25 (m, terpyridyl protons). $M_{n, \text{NMR}}=10,100$, $M_{w, \text{GPC}}=14,065$, $M_{n, \text{GPC}}=12,477$, $M_w/M_n = 1.13$

UV-Vis Absorption and Emission Spectra:

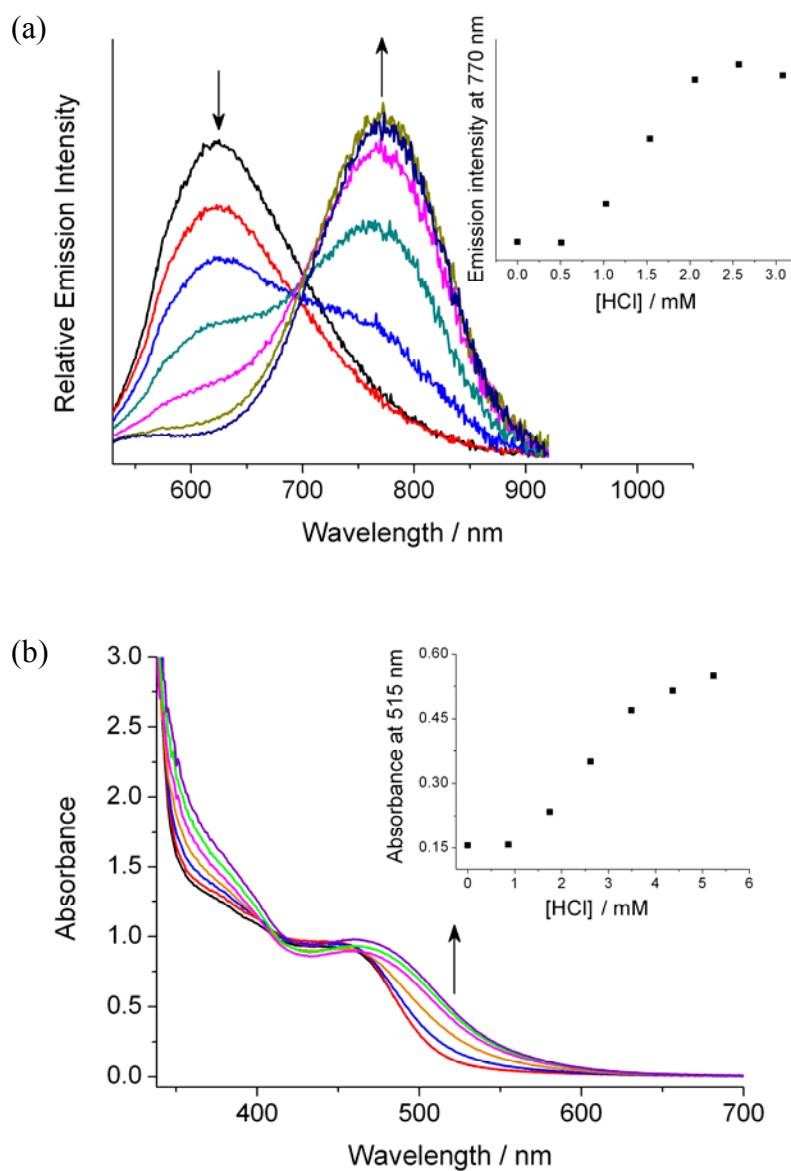


Figure S1 Electronic absorption (a) and emission (b) spectral changes of **PEO-[Pt]-P2VP** (2 mg/mL) in acetone-water mixture (20:1 v/v) upon addition of various amount of 1 M hydrochloric acid. Inset: Plot of the absorbance at 515 nm and emission intensity at 770 nm against concentration of HCl

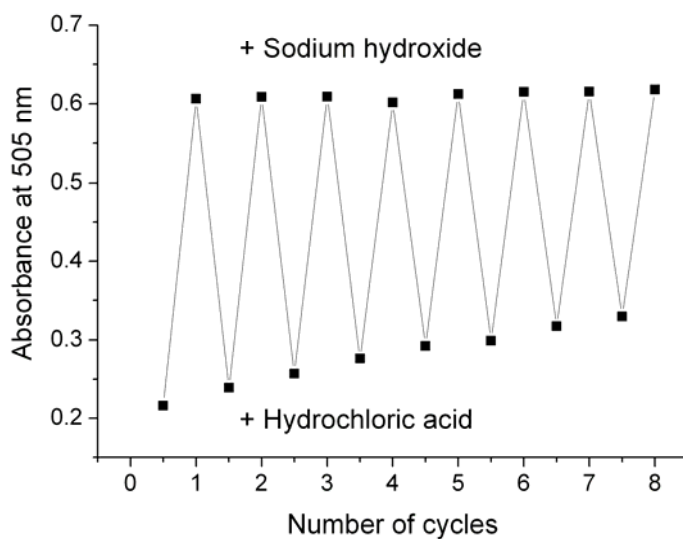


Figure S2 UV-Vis absorption changes of **PEO-[Pt]-P2VP** in water with alternate addition of hydrochloric acid and potassium hydroxide for eight repeating cycles

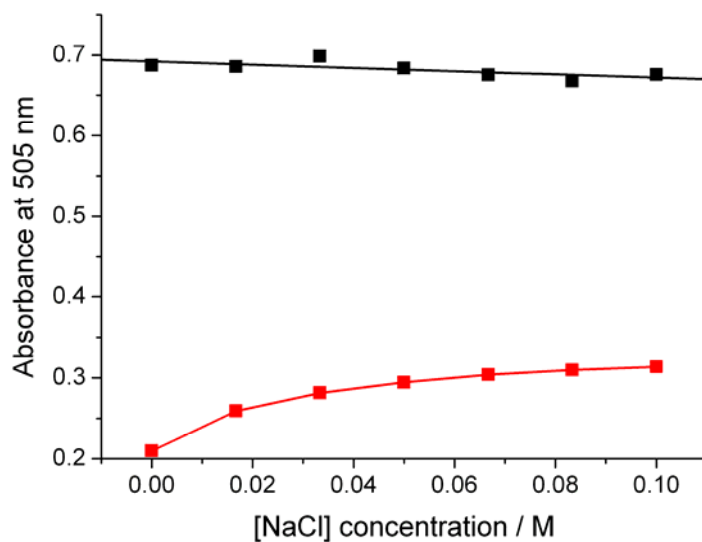


Figure S3 UV-Vis absorption changes of **PEO-[Pt]-P2VP** in water with various concentration of NaCl at pH 9.5 (■) and pH 2.6 (■)

Transmission Electron Microscopy (TEM):

An aqueous micellar solution of the polymer with concentration of 2 mg/mL was prepared and examined by transmission electron microscopy (TEM). Spherical micelles with diameter of around 14 nm were observed (Figure S4a). In addition, larger structures which seem to be resulting from the merging of individual micelles were also formed. Then in a subsequent experiment, an aqueous 0.25 M HCl solution and NaOH solution were utilized on the polymer solution, respectively, to induce dissociation and reformation of micelles. The result is shown in Figure S4b, in which the merging of individual micelles did not exist with the characteristic size of the micelles at around 37 nm, which is much larger than that of the micelles found in pure aqueous solution. The merging of individual micelles formed by direct dissolving of sample in distilled water may be attributed to the difficulty of complete dispersing of metallo-supramolecular sample in water and/or the resulting smaller micellar size with greater aggregation tendency; while micelles formed after one pH variation cycle experienced a process during which the polymer chains can molecularly dissolve in the presence of acid, then with the progressive increasing of pH, the polymer chains in aqueous solution can fully self-assemble into micelles with larger aggregation number, resulting in larger micellar size.

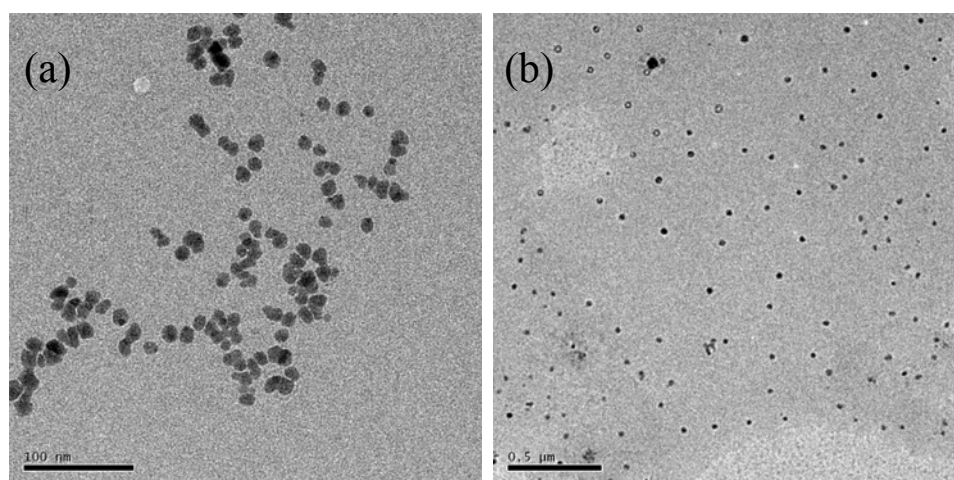
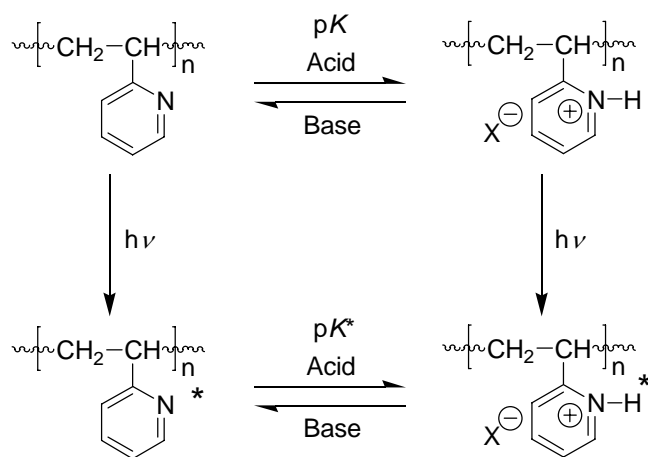


Figure S4 TEM images of **PEO-[Pt]-P2VP** micelles formed by directly dissolving the sample in (a) de-ionized water and (b) after one pH variation cycle



Scheme S1. Ground- and excited-state equilibria for the poly(2-vinylpyridine) acid-base system

References:

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