Supporting Information

Intercalation of Alkynylplatinum(II) Terpyridine Complexes into a Helical poly(Phenylene Ethynylene) Sulfonate. Application to Protein Sensing

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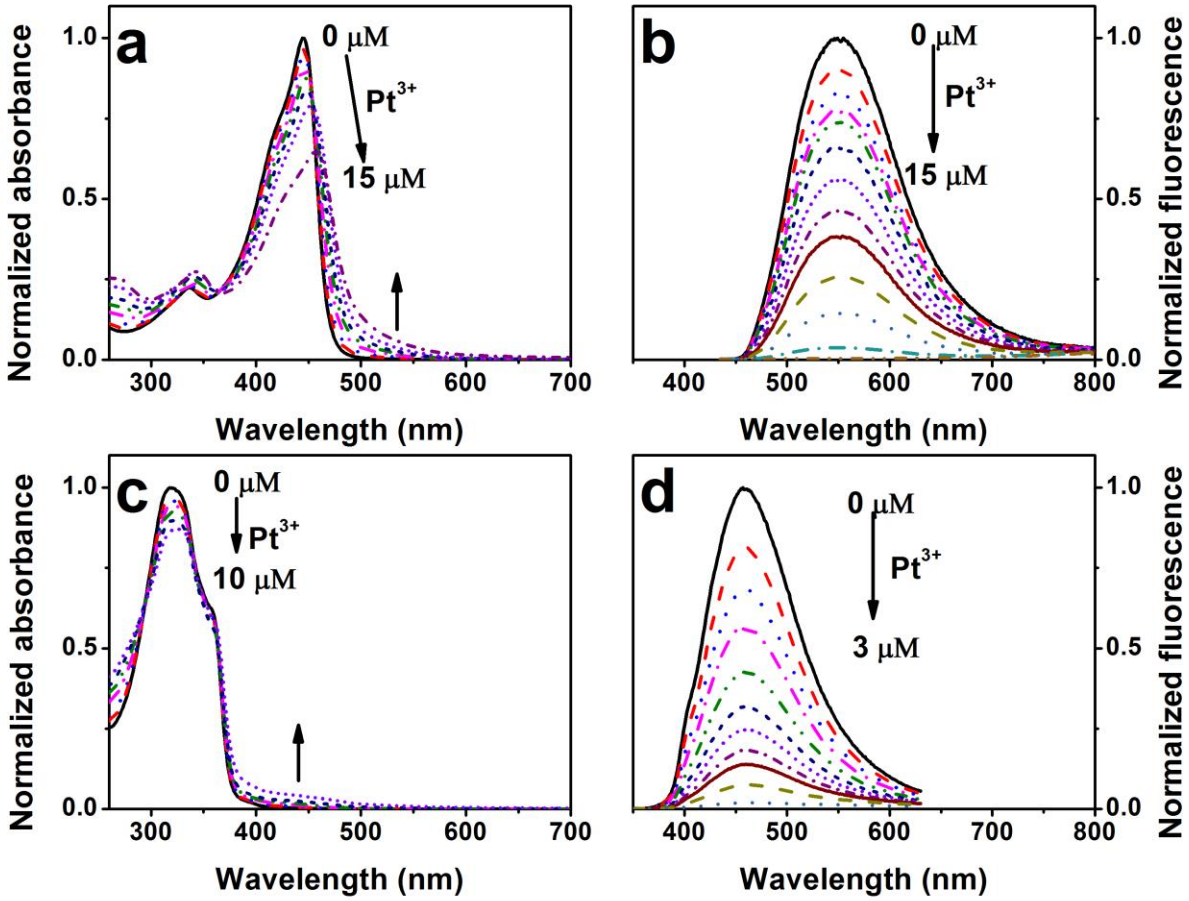


Figure S1. (a) Normalized UV-visible absorbance and (b) Fluorescence change of *p*PPESO$_3^-$ titrated with Pt^{3+}; (c) Normalized UV-visible absorbance and (d) Fluorescence change of *m*PPESO$_3^-$ titrated with Pt^{3+}. Titrations are in 30 mM Tris-HCl, 30 mM NaCl, pH 7.5 buffer, the concentrations of both *p*PPESO$_3^-$ and *m*PPESO$_3^-$ are 45 μM; excitation wavelengths for (b) and (d) are 430 nm and 322 nm respectively.

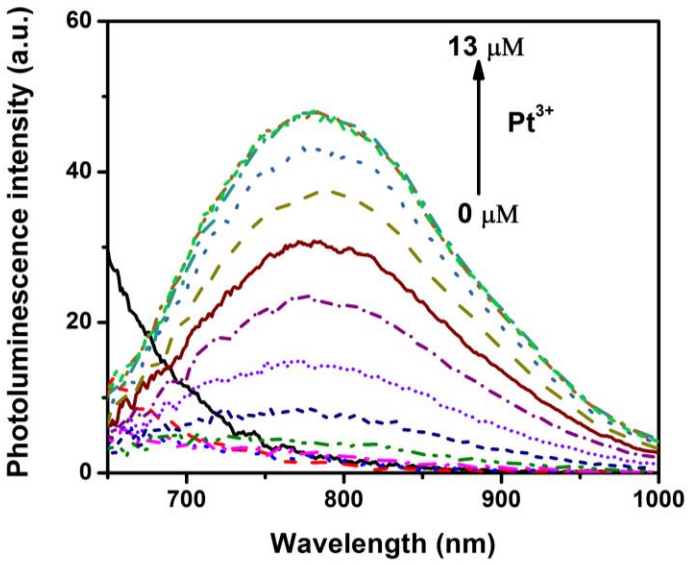


Figure S2. Photoluminescence spectrum of Pt^{3+} in the titration of *m*PPESO_3^- in 30 mM Tris-HCl, 30 mM NaCl, pH 7.5 buffer.

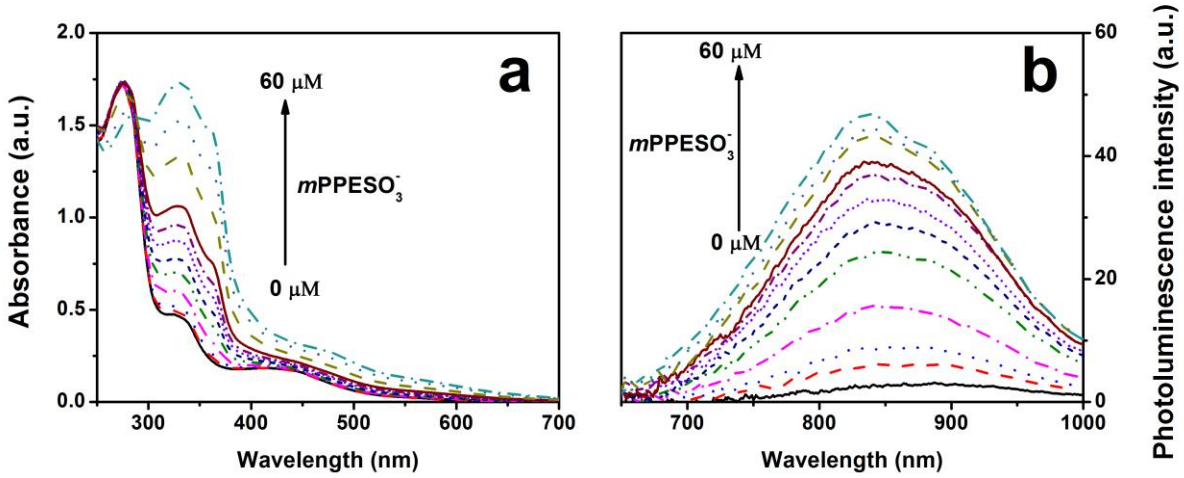


Figure S3. (a) UV-visible absorbance and (b) photoluminescence intensity change of 45 μM Pt^{2+} titrated with *m*PPESO_3^-. All measurements are in 30 mM Tris-HCl, 30 mM NaCl, pH 7.5 buffer. Excitation wavelength for (b) is 322 nm.

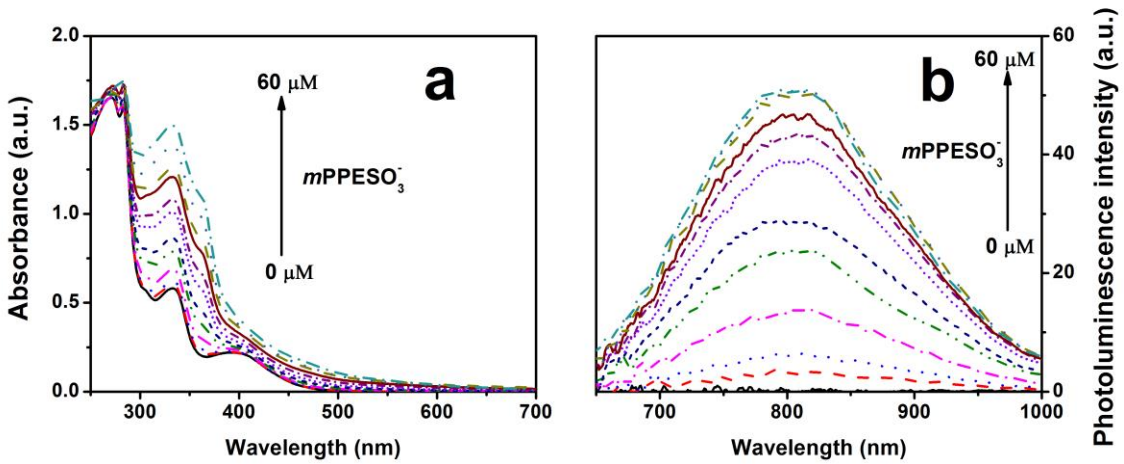


Figure S4. (a) UV-visible absorbance and (b) photoluminescence intensity change of 45 μM Pt^{3+} titrated with *m*$PPESO_3^-$. All measurements are in 30 mM Tris-HCl, 30 mM NaCl, pH 7.5 buffer. Excitation wavelength for (b) is 322 nm.

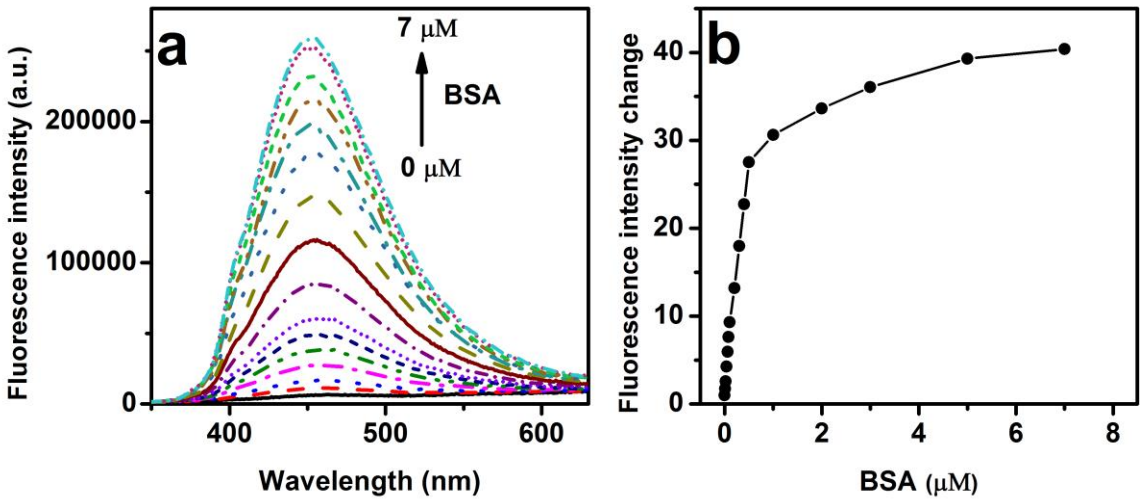


Figure S5. (a) Fluorescence spectra of 45 μM **mPPESO$_3^-$** and 7 μM **Pt^{3+}** mixture with addition of BSA in 30 mM Tris-HCl, 30 mM NaCl, pH 7.5 buffer. (b) Relative fluorescence intensity change at 455 nm as a function of BSA concentration (intensity is normalized to 1 in the absence of BSA).

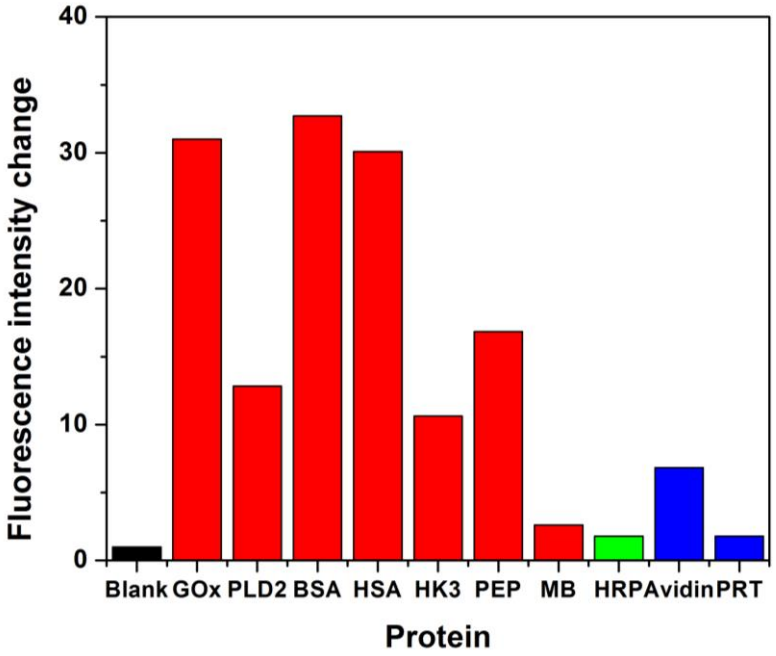


Figure S6. Fluorescence intensity change at 455 nm of 45 uM **mPPESO$_3^-$** and 7 uM **Pt^{3+}** in 30 mM Tris-HCl, 30 mM NaCl, pH 7.5 buffer upon addition of different proteins. Proteins include 1 μM GOx (glucose oxidase), PLD2 (phospholipase D), BSA (bovine serum albumin), HSA (human serum albumin), HX3 (hexokinase), PEP (peptidase), MB (myoglobin), HRP (peroxidase), Avidin, and PRT (protease). Proteins with PI value smaller than 7.5 are labeled red, proteins with PI value higher than 7.5 are labeled blue and with unknown PI value are labeled green.

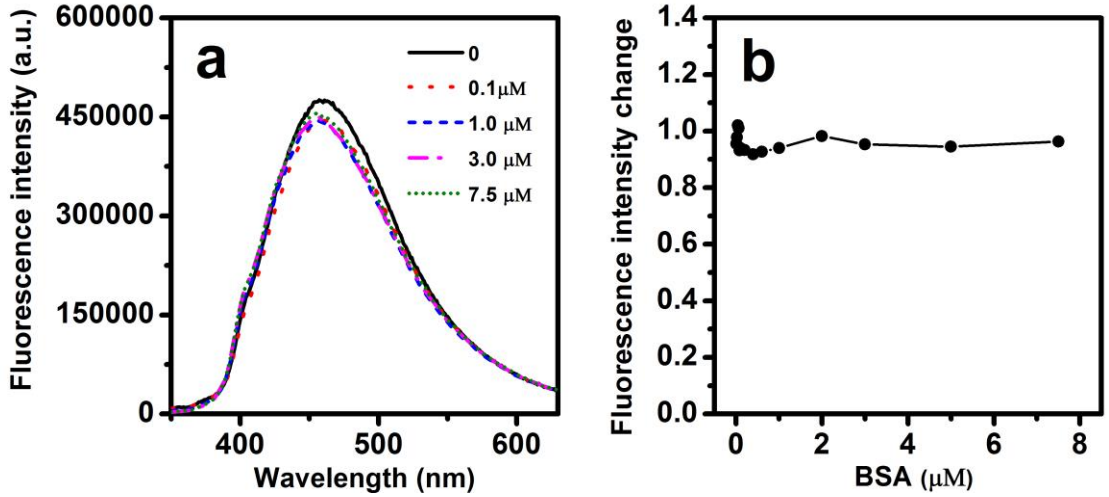
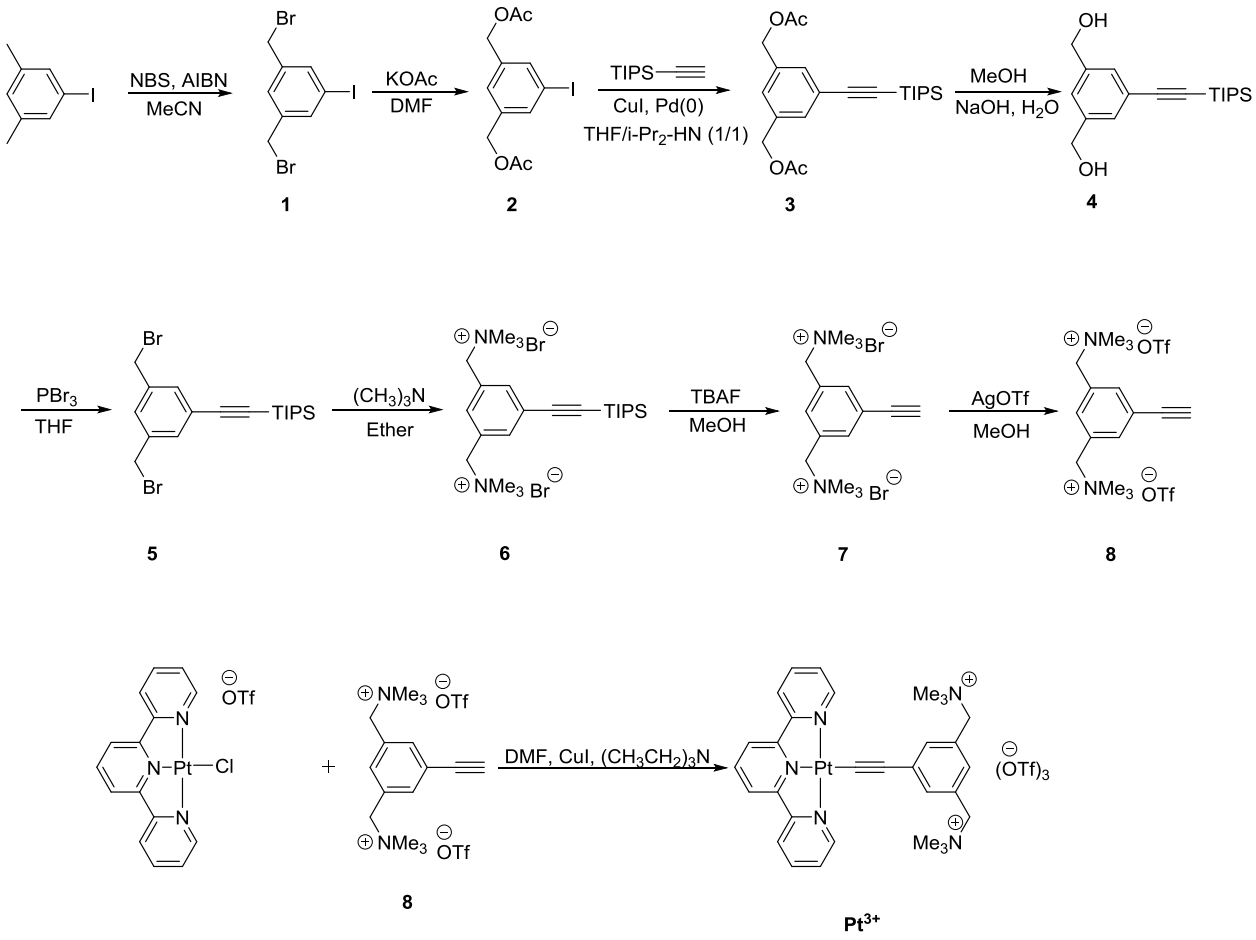


Figure S7. (a) Fluorescence spectra of 45 μM **mPPESO$_3^-$** with addition of BSA in 30 mM Tris-HCl, 30 mM NaCl, pH 7.5 buffer. (b) Fluorescence intensity change at 455 nm as a function of BSA concentration.

Synthesis of Pt^{2+} and Pt^{3+} complex:

$Pt(tpy)(C{\equiv}CC_6H_4CH_2NMe_3)[OTf]_2$ (Pt^{2+}) The complex was synthesized according to the literature.[1] ^{1}H NMR (CD_3CN, 500 MHz): δ = 8.96 (d, 2H), 8.28 (m, 3H), 8.18 (m, 4H), 7.68 (t, 2H), 7.54 (d, 2H), 7.49 (d, 2H), 4.43(s, 2H), 3.06 (s, 9H). The ^{1}H NMR spectrum of Pt^{2+} is shown in Figure S8 below.

$Pt(tpy)(C{\equiv}CC_6H_4(CH_2NMe_3)_2)[OTf]_3$ (Pt^{3+}) The complex was synthesized based on a reported method with minor modifications according to Scheme S1 shown below.[2] Characterizations of compounds were performed by ^{1}H NMR, ^{13}C NMR, mass spectra or elemental analysis. ^{1}H (500 MHz) spectra were recorded on a Varian Inova 500 spectrometer. High-resolution mass spectrometry (HRMS) was collected on an Agilent 6200 ESI-TOF in the Chemistry Department of University of Florida. Elemental analysis was provided by the Carbon, Hydrogen and Nitrogen (CHN) Services, in the Chemistry Department of University of Florida.



Scheme S1. Synthetic scheme of $\mathbf{Pt^{3+}}$.

1,3-Bis(bromomethyl)-5-iodobenzene (1). The compound was synthesized according to the method reported in the literature, with minor modifications.[3] 1-Iodo-3,5-dimethylbenzene (4 g, 17 mmole) was added to a suspension of NBS (7.6 g, 42.5 mmole) in dry MeCN (50 mL), and AIBN (0.14 g) was added as initiator. The mixture was refluxed overnight. The red reaction mixture was cooled to ambient temperature, and extracted with boiling hexane. The hexane extracts were combined and recrystallization was performed to obtain white solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.67 (d, 2H), 7.37 (t, 1H), 4.38 (s, 4H).[3]

(5-Iodo-1,3-phenylene)bis(methylene) diacetate (2). KOAc (4.3 g, 44 mmole) was added to 1,3-bis(bromomethyl)-5-iodobenzene (3.4 g, 8.7 mmole) in DMF (50 mL), and the mixture was heated at 65 ℃ overnight on an oil bath. The mixture was extracted with ethyl acetate and water. The ethyl acetate extracts were combined and solvent was removed on rotary evaporator to obtain the crude product. The crude product was used without further purification.

(5-((Triisopropylsilyl)ethynyl)-1,3-phenylene)bis(methylene) diacetate (3). (5-Iodo-1,3-phenylene)bis(methylene) diacetate (3.1 g, 8.9 mmole) was dissolved in 50 mL THF/ 50 mL isopropylamine. The mixture was degassed for 30 minutes, then CuI (0.13 g) and $Pd(PPh_3)_4$ (0.40 g) were added. After degassing for another 10 minutes, (triisopropylsilyl)acetylene (2.4 mL, 10.7 mmole) was added and the mixture was stirred for 5 hours. The solvent was removed on the rotary evaporator and the residue was extracted with CH_2Cl_2/ water. CH_2Cl_2 extracts were combined and dried with magnesium sulfonate, filtered and concentrated. The resulting mixture was purified by column chromatography (hexane/ ethyl acetate= 9/1). ^{1}H NMR ($CDCl_3$, 500 MHz): δ = 7.41 (d, 2H), 7.28 (s, 1H), 5.07 (s, 4H), 2.12 (s, 6H), 1.26 (t, 3H), 1.13 (s, 18H).

(5-((Triisopropylsilyl)ethynyl)-1,3-phenylene)dimethanol (4). (5-((Triisopropylsilyl)ethynyl)-1,3-phenylene)bis(methylene) diacetate (2.5 g, 6.2 mmole) was dissolved in 30 mL of MeOH with 2.5 g NaOH in 2.5 mL H_2O, the mixture was refluxed overnight. The resulting mixture was extracted with CH_2Cl_2/ H_2O, the CH_2Cl_2 extracts were combined and solvent was removed on rotary evaporator. The crude product was used without further purification.

((3,5-Bis(bromomethyl)phenyl)ethynyl)triisopropylsilane (5). (5-((Triisopropylsilyl)ethynyl)-1,3-phenylene)dimethanol (1.7 g crude) was dissolved in 50 mL dried THF, the flask was cooled down on an ice water bath. PBr_3 (4 mL, 42 mmole) was added drop-

wise. The ice water bath was removed at the end of the addition. The mixture was stirred overnight, then all of the solvent was removed on the rotary evaporator, the residue was extracted with CH_2Cl_2/ H_2O. The CH_2Cl_2 extracts were combined and dried with magnesium sulfonate, filtered and concentrated. The resulting mixture was purified by column chromatography (hexane/ DCM= 4/1) to obtain a white solid product.

1,1'-(5-((Triisopropylsilyl)ethynyl)-1,3-phenylene)bis(N,N,N-trimethylmethanamonium) bromide (6). A mixture of ((3,5-bis(bromomethyl)phenyl)ethynyl)triisopropylsilane (1.2 g, 2.7 mmole) and trimethylamine (20 mL, 1M in THF) was stirred in diethyl ether (50 mL) for 2 hours, during which the bromide salt precipitated. The white solid was filtered and washed with diethyl ether. The solid was used without further purification.

1,1'-(5-Ethynyl-1,3-phenylene)bis(N,N,N-trimethylmethanaminium) bromide (7). 1,1'-(5-((Triisopropylsilyl)ethynyl)-1,3-phenylene)bis(N,N,N-trimethylmethanaminium) bromide (1.08 g, 1.9 mmole) was dissolved in 50 mL MeOH and degassed for 30 minutes, then TBAF (2.8 mL 1 M THF solution) was added, the mixture was stirred for 1 hour. The solvent was removed on rotary evaporator. The residue was washed multiple times with THF. The crude product was a white solid and used without further purification.

1,1'-(5-Ethynyl-1,3-phenylene)bis(N,N,N-trimethylmethanaminium) trifluoromethanesulfonate (8). 1,1'-(5-Ethynyl-1,3-phenylene)bis(N,N,N-trimethylmethanaminium) bromide was dissolved in MeOH and counter ion exchanged to triflate salt with a saturated silver triflate MeOH solution. AgBr precipitate was removed and the solvent in the colorless filtrate was removed on rotary evaporator. The residue was extracted multiple

times with chloroform and removal of the solvent gave a white solid product. ^{1}H NMR (CD_3OD, 500 MHz): δ = 7.90 (s, 2H), 7.87 (s, 1H), 4.64 (s, 4H), 3.86 (s, 1H), 3.18 (s, 18H).

Pt(tpy)(C≡CC_6H_4(CH_2NMe_3)$_2$)[OTf]$_3$ (Pt^{3+}). The complex was synthesized based on a reported method with minor modifications.[2] The precursor [Pt(tpy)Cl][OTf] (153 mg, 0.25 mmole) and 1,1'-(5-ethynyl-1,3-phenylene)bis(N,N,N-trimethylmethanaminium) trifluoromethanesulfonate (340 mg, 0.62 mmole) were dissolved in DMF (10 mL) mixed with triethylamine (4 mL). The mixture was degassed for 30 minutes, CuI (2.9 mg, 0.15 mmole) was added and stirred overnight. Then diethyl ether was added and stirred for 30 minutes. The solid product was filtrated, washed multiple times with diethyl ether. Recrystallization with acetonitrile and diethyl ether gave a red solid product. ^{1}H NMR (CD_3CN, 500 MHz): δ = 8.77 (s, 2H), 8.19 (m, 3H), 8.07 (m, 4H), 7.68 (t, 4H), 7.54 (s, 1H), 4.53 (s, 4H), 3.14 (s, 18H). ^{13}C NMR (98% CD_3CN + 2% D_2O, 75 MHz): δ 158.97, 154.50, 154.45, 153.93, 142.80, 138.82, 135.96, 130.49, 130.27, 128.80, 126.04, 124.46, 123.73, 119.50, 101.05, 69.11, 53.44. HRMS (ESI): *m/z* 971.1678 $[M+(OTf)_2]^+$ (calcd: 971.1656). Elemental analysis calcd (%) for $C_{34}H_{36}N_5F_9O_6PtS_3$: C 36.43, H 3.24, N 6.25; found: C 35.35, H 2.83, N 6.13. The ^{1}H NMR and ^{13}C NMR spectra of Pt^{3+} are shown in Figure S9 and Figure S10 below.

Computational Details

Geometries of the Pt^{2+} and a trimer of *m*PPESO_3^- were optimized using density functional theory (DFT) as implemented in Gaussian 09 rev. C.01 (Gaussian, Inc.). All DFT calculations were done using the B3LYP functional along with the 6-31G(d) basis set for C, N, and H, the 6-31+G(d) basis set for S and O, and the SDD basis set for Pt. Optimizations were done in vacuum and were determined to be minima by the absence of imaginary frequencies. The partial atomic charges of the central monomeric unit of the optimized trimer were assumed to be representative

of the polymer as a whole, and these values were input into the Materials Studio software (Version 8.0) from Accelrys Inc., where the polymer was constructed in a helical conformation. Dynamics calculations were then performed using the Universal Force Field (UFF) as implemented in the Forcite module of Materials Studio for a total of 250 ps with a time step of 1 fs at 298 K with the canonical ensemble. After finding the helical conformation of *m*PPESO_3^- to be dynamically stable, Pt^{2+} with partial atomic charges from DFT were included in the simulation at a ratio of 1:2 for Pt^{2+}: *m*PPESO_3^- with the Pt^{2+} intercalated or external to the helix. Dynamics calculations were again executed for both complex positions relative to the helix to show that the helix has greater stability with intercalated Pt(II) complexes than without. Prior to all dynamics calculations, geometries were optimized and structures were annealed at the UFF level of theory with 5 heating cycles from 300 K to 700 K for 50 ps with 5 heating ramps per cycle and NVP statistics. The Nose thermostat was used for all dynamical calculations.

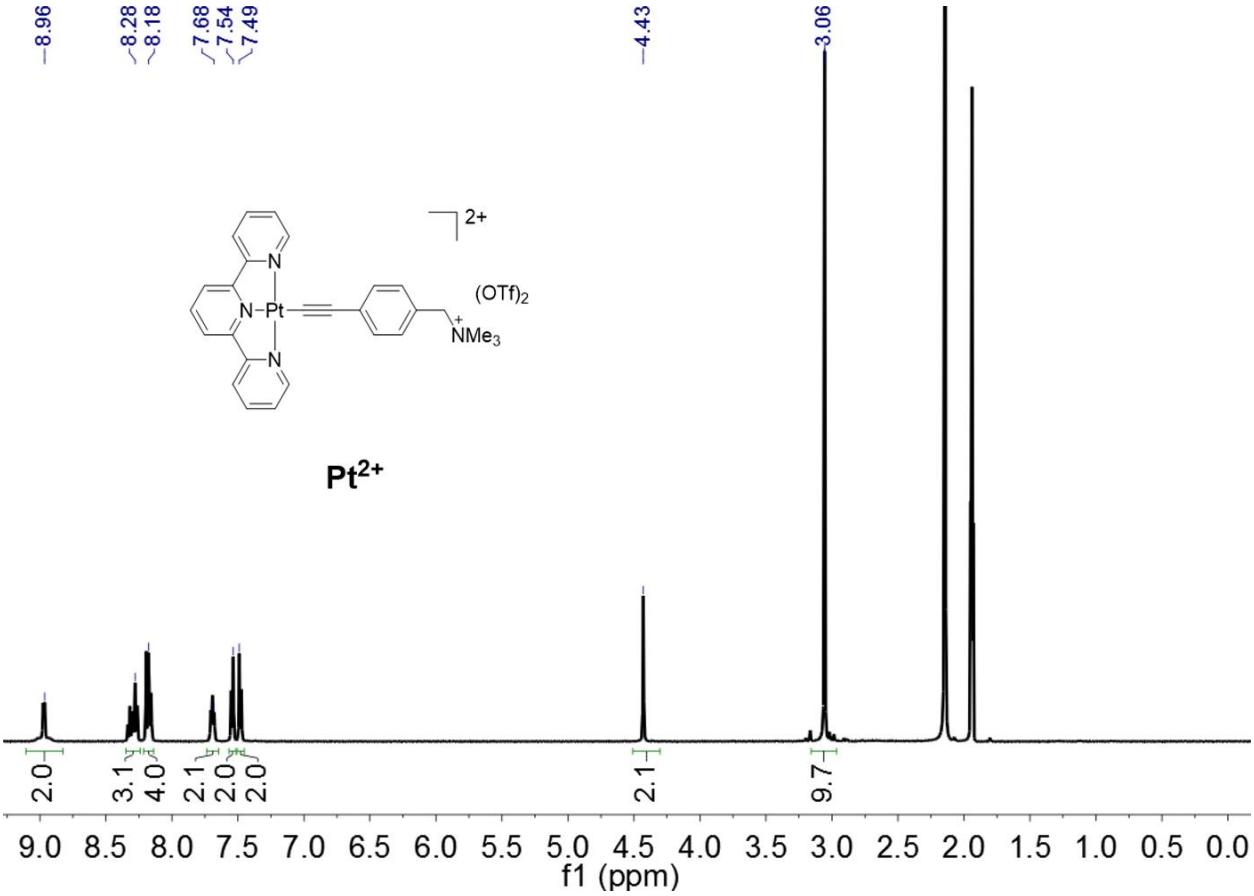


Figure S8. ^{1}H NMR spectrum of Pt^{2+} in CD_3CN solution.

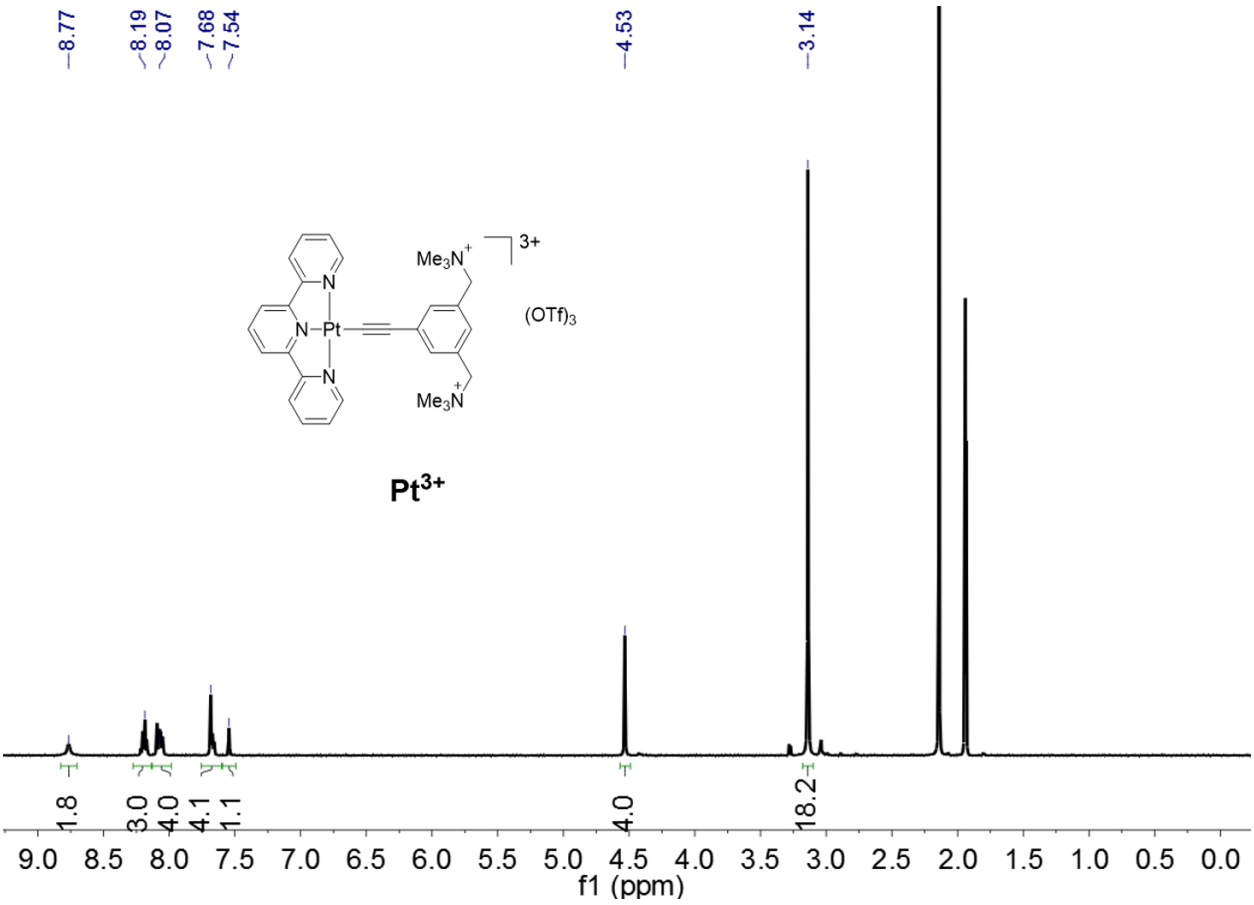


Figure S9. ^{1}H NMR spectrum of Pt^{3+} in CD_3CN solution.

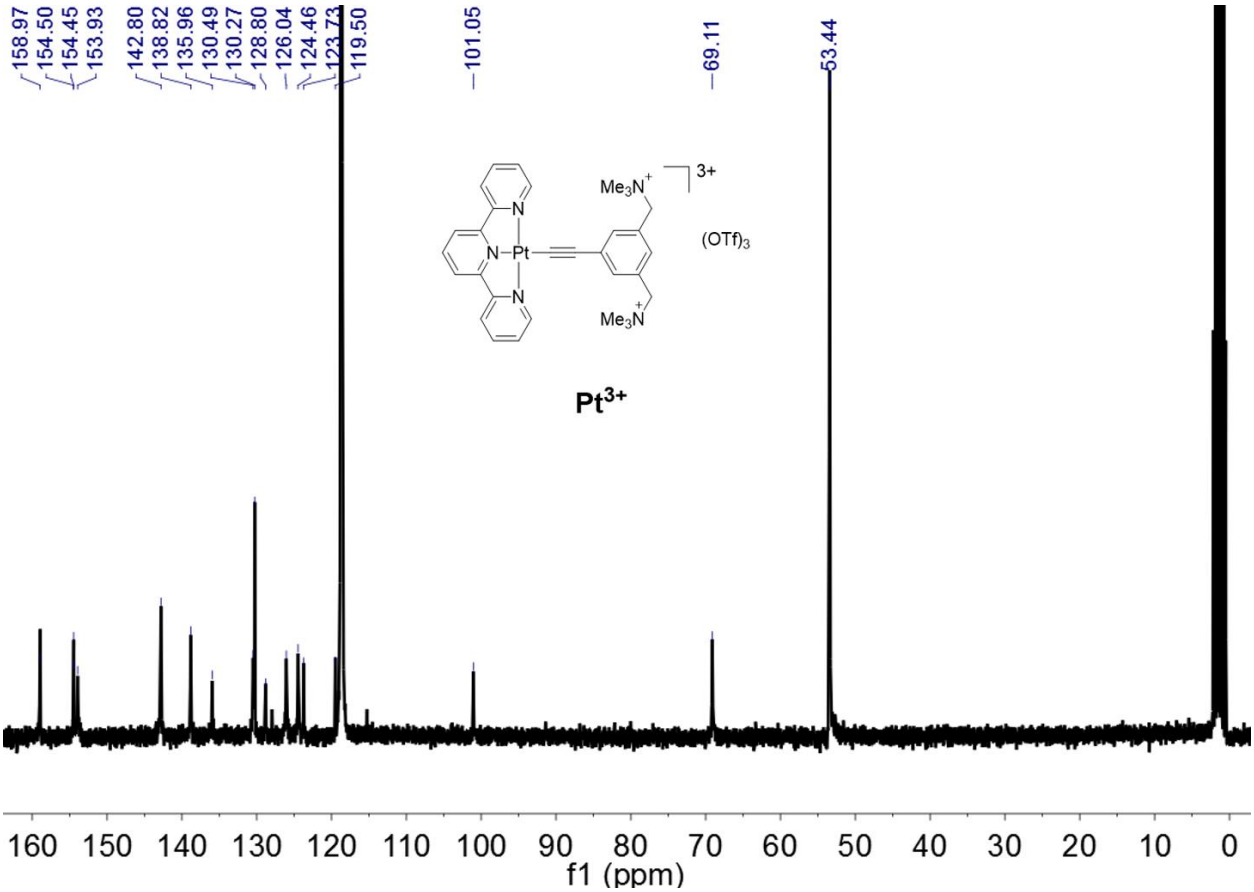


Figure S10. ^{13}C NMR spectrum of Pt^{3+} in CD_3CN solution.

References for Supporting Information

(1) Yu, C.; Chan, K. H. Y.; Wong, K. M. C.; Yam, V. W. W. Polyelectrolyte-Induced Self-Assembly of Positively Charged Alkynylplatinum(II)–Terpyridyl Complexes in Aqueous Media *Chem. Eur. J.* **2008**, *14*, 4577-4584.

(2) Chung, C. Y. S.; Yam, V. W. W. Induced Self-Assembly and Förster Resonance Energy Transfer Studies of Alkynylplatinum(II) Terpyridine Complex Through Interaction With Water-Soluble Poly(phenylene ethynylene sulfonate) and the Proof-of-Principle Demonstration of this Two-Component Ensemble for Selective Label-Free Detection of Human Serum Albumin *J. Am. Chem. Soc.* **2011**, *133*, 18775-18784.

(3) Sookcharoenpinyo, B.; Klein, E.; Ferrand, Y.; Walker, D. B.; Brotherhood, P. R.; Ke, C.; Crump, M. P.; Davis, A. P. High-Affinity Disaccharide Binding by Tricyclic Synthetic Lectins *Angew. Chem. Int. Ed.* **2012**, *51*, 4586-4590.