

Syntheses of Monosubstituted Rhodocenium Derivatives, Monomers and Polymers

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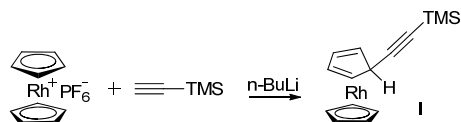
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Supporting Information

I. Synthesis

Synthesis of 2-Azidoethanol:

Sodium azide (4.5 g, 69 mmol) and 2-bromoethanol (5.4 g, 43 mmol) were dissolved in a mixture of acetone (25 mL) and water (15 mL) and heated at 65 °C under N₂ for 3 days. After evaporating acetone under vacuum, the product was extracted with ethyl acetate 50 mL×5. The organic phase was dried using anhydrous Na₂SO₄ and followed by solvent removal, yielding 2.8 g (74%) of 2-azidoethanol as light yellow oil. ¹H NMR (CDCl₃, 300 MHz, δ , ppm): 3.77 (t, J = 6.0 Hz, 2H, CH₂OH), 3.43 (t, J = 6.0 Hz, 2H, CH₂N₃). **Safety Warning: It is extremely important not to run this reaction as a large scale!!**



Synthesis of

(η^5 -Cyclopentadienyl)[η^4 -(exo-5-trimethylsilylethynyl)-1,3-cyclopentadiene]

Rhodium (compound I):

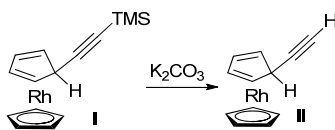
To a 100 mL flask, a solution of trimethylsilylacetylene (0.83 g, 8.46 mmol) in 40 mL of anhydrous THF was cooled to $-30\text{ }^{\circ}\text{C}$ by acetone-dry ice bath. Then, 2.5 mL 2.5 M *n*-butyl lithium solution (6.35 mmol) was added dropwise. The mixture was stirred for 45 minutes, then rhodocenium hexafluorophosphate (2.0 g, 4.23 mmol) was added quickly. The resulting suspension was allowed to warm to room temperature and stirred under N_2 for another 1.5 h, after which almost all the rhodocenium was dissolved to give a clear red-orange solution. The solvent was removed in vacuum, and the residue taken up in hexane and chromatographed on basic alumina (activity III) with hexane to give 1.18 g (86%) product as yellow solid. ^1H NMR (CDCl_3 , 400 MHz, δ , ppm): 5.19 (s, 5H, *Cp*), 5.16 (s, 2H), 3.56 (s, 1H), 3.45 (s, 2H), 0.07 (s, 9H, *TMS*). ^{13}C NMR (CDCl_3 , 100 MHz, δ , ppm): 111.67, 82.59, 82.54, 74.16, 74.07, 45.24, 45.19, 44.33, 44.03, 0.29. MS (EI), m/z calcd for $\text{C}_{15}\text{H}_{19}\text{SiRh}$ 330; found 329 (M-H). Elemental analysis (%) calcd for $\text{C}_{15}\text{H}_{19}\text{SiRh}$: C 54.54, H 5.80; found C 55.19, H 5.54.

Synthesis of (η^5 -Cyclopentadienyl)[η^4 -(exo-5-ethynyl)-1,3-cyclopentadiene]

Rhodium (compound II):

To a solution of (η^5 -Cyclopentadienyl)[η^4 -(exo-5-trimethylsilylethynyl)-1,3-cyclopentadiene] rhodium (1.0 g, 3.03 mmol) in 50 mL of methanol, K_2CO_3 (1.67 g, 12 mmol) was added. The reaction mixture was stirred at room temperature for 4 h. The solution was filtered, evaporated, and re-dissolved in dichloromethane, washed with water, dried over anhydrous Na_2SO_4 and evaporated to give a product 0.78 g (98%) as light yellow powder. ^1H NMR (CDCl_3 , 400 MHz, δ , ppm): 5.20 (m, 7H), 3.54 (m, 1H), 3.47 (m,

2H), 1.94 (d, $J = 0.6$ Hz, 1H). ^{13}C NMR (CDCl_3 , 100 MHz, δ , ppm): 82.65, 82.60, 74.07, 73.98, 64.51, 43.92, 43.79. MS (EI), m/z calcd for $\text{C}_{12}\text{H}_{10}\text{Rh}$ 257; found 257 (M^+). Elemental analysis (%) calcd for $\text{C}_{12}\text{H}_{10}\text{Rh}$: C 56.06, H 3.92; found C 55.45, H 3.55.

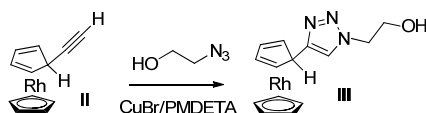


Synthesis of Hydroxyl-terminated

(η^5 -Cyclopentadienyl)[η^4 -(exo-5-ethynyl)-1,3-cyclopentadiene] Rhodium

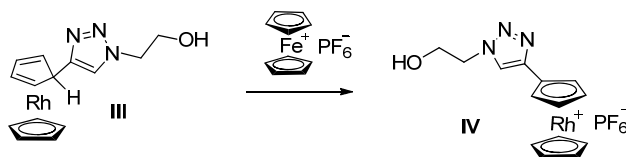
(compound III):

2-Azidoethanol (0.3 g, 3.45 mmol), (η^5 -Cyclopentadienyl)[η^4 -(exo-5-ethynyl)-1,3-cyclopentadiene] rhodium (0.89 g, 3.45 mmol) and PMDETA (0.24 g, 1.40 mmol) were dissolved in 60 mL anhydrous THF, and degassed with N_2 for 30 min. In another flask, CuBr (0.10 g, 0.69 mmol) was charged and degas with N_2 for 30 min. Transfer the above THF solution to the CuBr flask, and stirred at room temperature under N_2 overnight. After reaction, 100 mL water was added and stirred for 1 h. Extract with DCM, and the organic phase was dried over anhydrous Na_2SO_4 , and concentrated under vacuum. The crude product was purified by flash chromatography on aluminum oxide with dichloromethane: methanol = 10:1 (v:v) as an eluent, gave 0.95 g of product as a light yellow solid (80% yield). ^1H NMR (CDCl_3 , 400 MHz, δ , ppm): 7.13 (s, 1H, *triazole H*), 5.25 (s, 5H), 5.16 (s, 2H), 4.33 (m, 2H, $\text{CH}_2\text{CH}_2\text{OH}$), 4.18 (t, $J = 0.6$ Hz, 1H), 4.01 (t, $J = 0.6$ Hz, 2H), 3.62 (m, 2H, $\text{CH}_2\text{CH}_2\text{OH}$), 2.53 (br, 1H, $\text{CH}_2\text{CH}_2\text{OH}$). MS (EI), m/z calcd for $\text{C}_{14}\text{H}_{16}\text{RhN}_3\text{O}$ 345; found 344 (M^+). Elemental analysis (%) calcd for $\text{C}_{14}\text{H}_{16}\text{RhN}_3\text{O}$: C 48.71, H 4.67, N 12.17; found C 48.45, H 4.55, N 12.89.



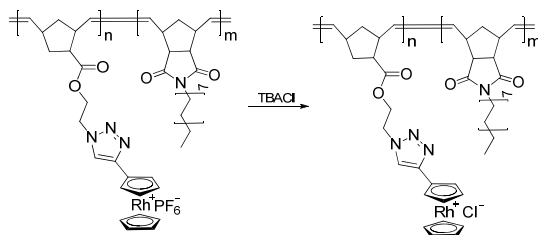
Synthesis of Hydroxyl-terminated Rhodocenium (Compound IV):

Compound **III** (0.2 g, 0.58 mmol) was dissolved in 20 mL dry THF, then, ferrocenium hexafluorophosphate (0.192 g, 0.58 mmol) was added. The mixture was stirred in the dark for 5 h. After removing solvent, the mixture was purified on basic Al₂O₃ column (activity III) with hexane, then dichloromethane to dichloromethane:methanol = 10:1 to give product compound **IV** 0.24 g (85%) as yellow powder. ¹H NMR (CD₃OD, 300 MHz, δ , ppm): 8.39 (s, 1H, *triazole H*), 6.58 (t, J = 1.8 Hz, 2H, *Cp*), 6.10 (t, J = 0.6 Hz, 2H, *Cp*), 5.93 (s, 5H, *Cp*), 4.61 (br, 1H, CH₂CH₂OH), 4.54 (t, J = 5.4 Hz, 2H, CH₂CH₂OH), 3.97 (t, J = 5.4 Hz, 2H, CH₂CH₂OH). ¹³C NMR (CD₃CN, 75 MHz, δ , ppm): 124.82, 88.28, 87.02, 84.12, 78.36, 68.22, 60.57, 53.26. ¹⁹F NMR (CD₃CN, δ , ppm): -71.59, -74.10. MS (EI), m/z calcd for C₁₄H₁₅RhN₃OPF₆ 489.1582; found 344.0270 (M⁺). Elemental analysis (%) calcd for C₁₄H₁₅RhN₃OPF₆: C 34.38, H 3.09, N 8.59; found C 34.17, H 3.58, N 8.42.



II. Counterion Exchange

Counterion Exchange of Rhodocenium-containing Copolymers to Amphiphilic Copolymers:



A general procedure is as follows: a block copolymer was dissolved in a mixture of acetonitrile and DMF (4:1 (v/v)), then added dropwise to TBACl acetonitrile solution under strong stir. The exchanged block copolymer precipitated from the solution, washed with acetonitrile several times and dried under vacuum.

III. Characterization of Rh(I)-/Rhodocenium-containing Monomers and Polymers

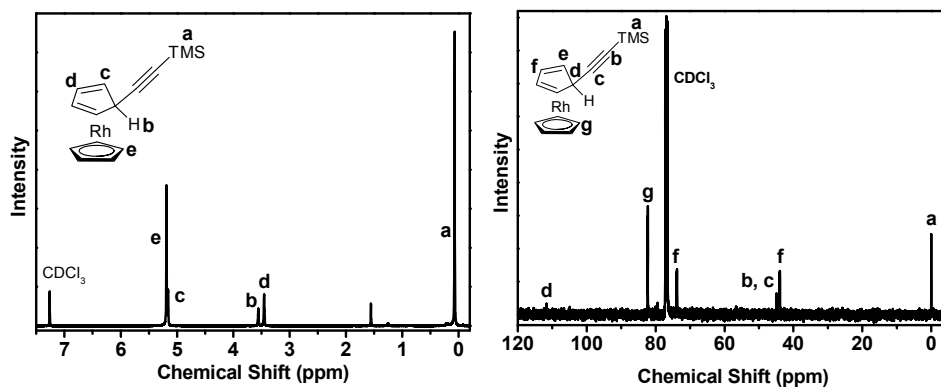


Figure S1. ^1H and ^{13}C NMR spectra of $(\eta^5\text{-Cyclopentadienyl})[\eta^4\text{-(exo-5-trimethylsilylethynyl)-1,3-cyclopentadiene}]$ rhodium (I).

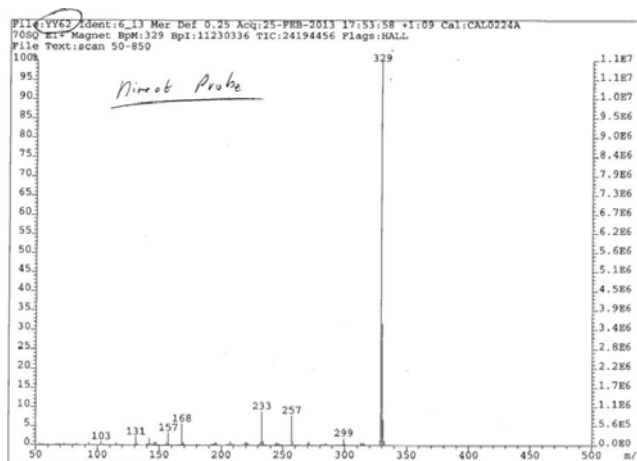


Figure S2. Mass spectrum of $(\eta^5\text{-Cyclopentadienyl})[\eta^4\text{-(exo-5-trimethylsilylethynyl)-1,3-cyclopentadiene}]$ rhodium (I).

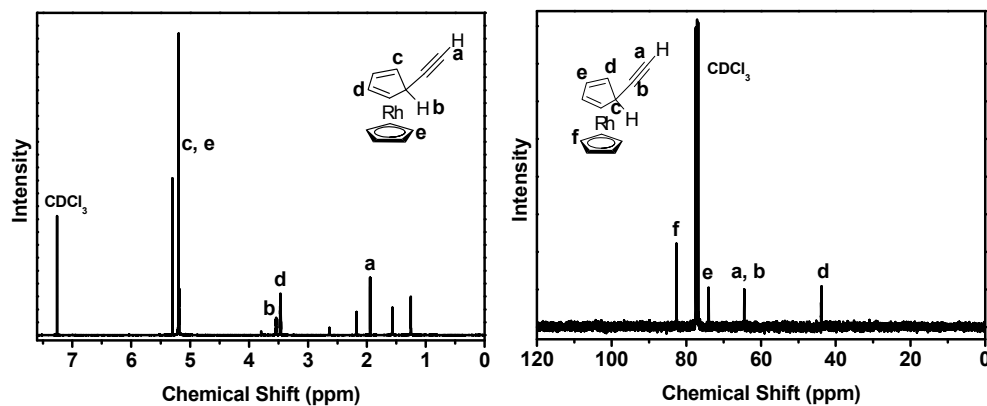


Figure S3. ^1H and ^{13}C NMR of spectra
 $(\eta^5\text{-Cyclopentadienyl})[\eta^4\text{-(exo-5-ethynyl)-1,3-cyclopentadiene}]$ rhodium (II).

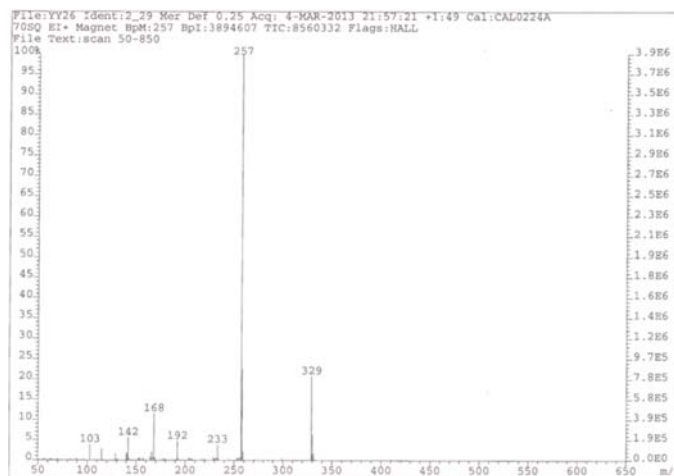


Figure S4. Mass spectrum of
 $(\eta^5\text{-Cyclopentadienyl})[\eta^4\text{-(exo-5-ethynyl)-1,3-cyclopentadiene}]$ rhodium (II).

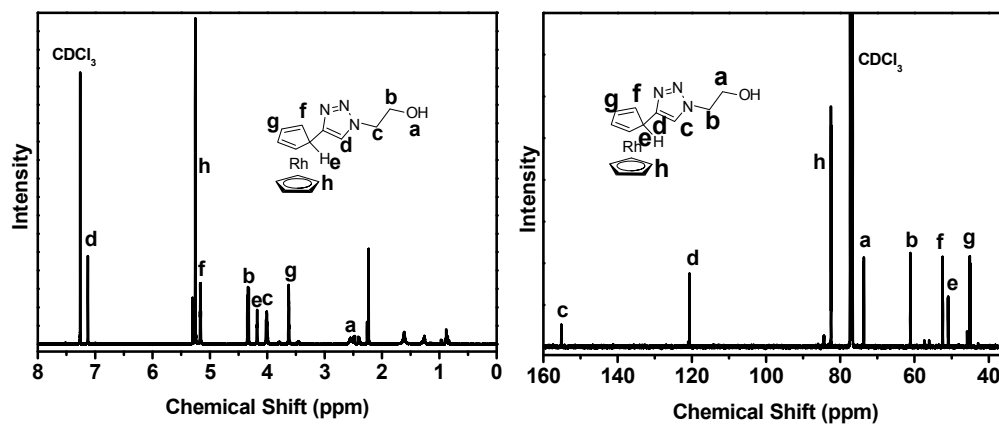


Figure S5. ^1H and ^{13}C NMR spectra of hydroxyl-terminated $\eta^4/\eta^5\text{-Rh(I)}$ (III) in CDCl_3 .

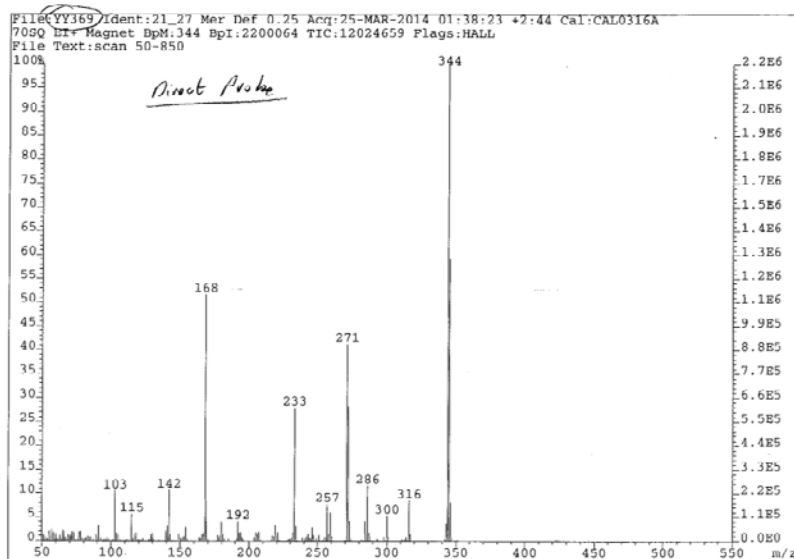


Figure S6. Mass spectrum of hydroxyl-terminated η^4/η^5 -Rh(I) (**III**).

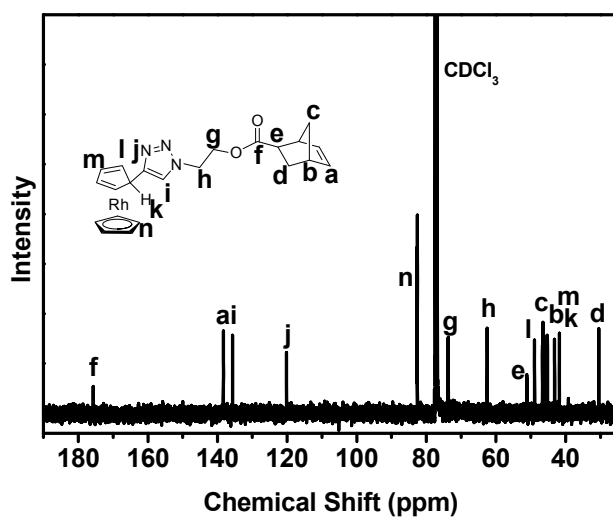


Figure S7. ^{13}C NMR spectrum of η^4/η^5 -Rh(I)-containing monomer **M1** in CDCl_3 .

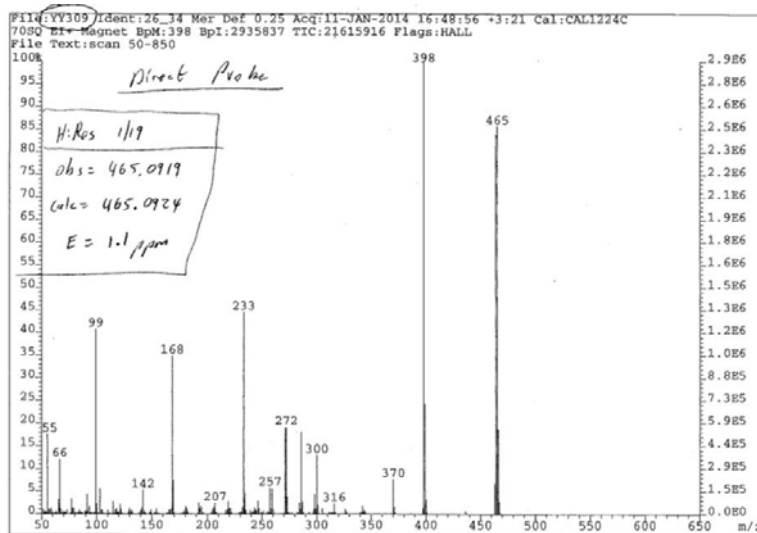


Figure S8. Mass spectrum of η^4/η^5 -Rh(I)-containing monomer **M1**.

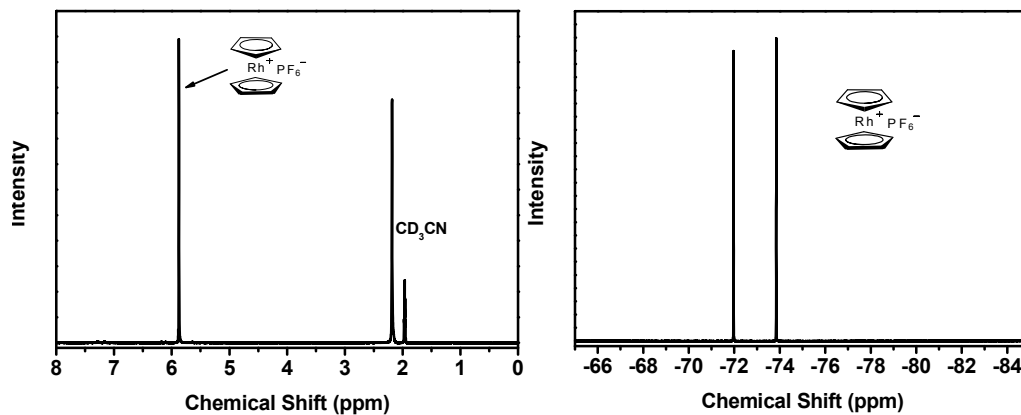


Figure S9. ^1H and ^{19}F NMR spectra in CD_3CN after treating compound **I** with tritylium hexafluorophosphate.

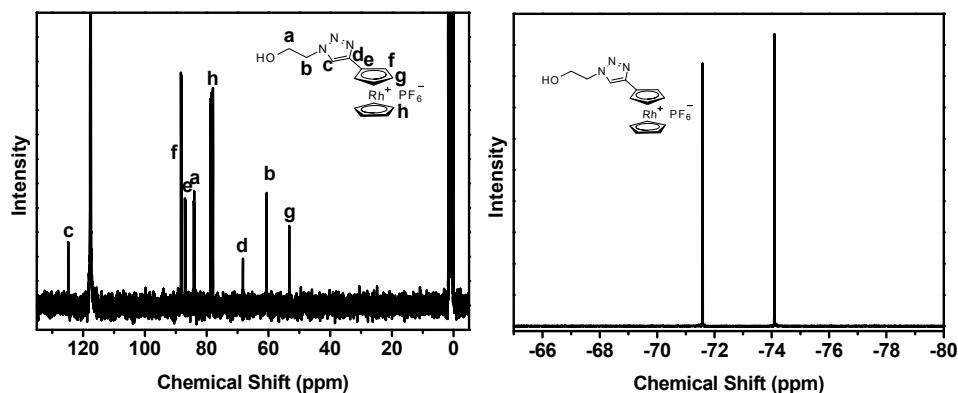


Figure S10. ^{13}C and ^{19}F NMR spectra of hydroxyl-terminated rhodocenium (**IV**) in CD_3OD .

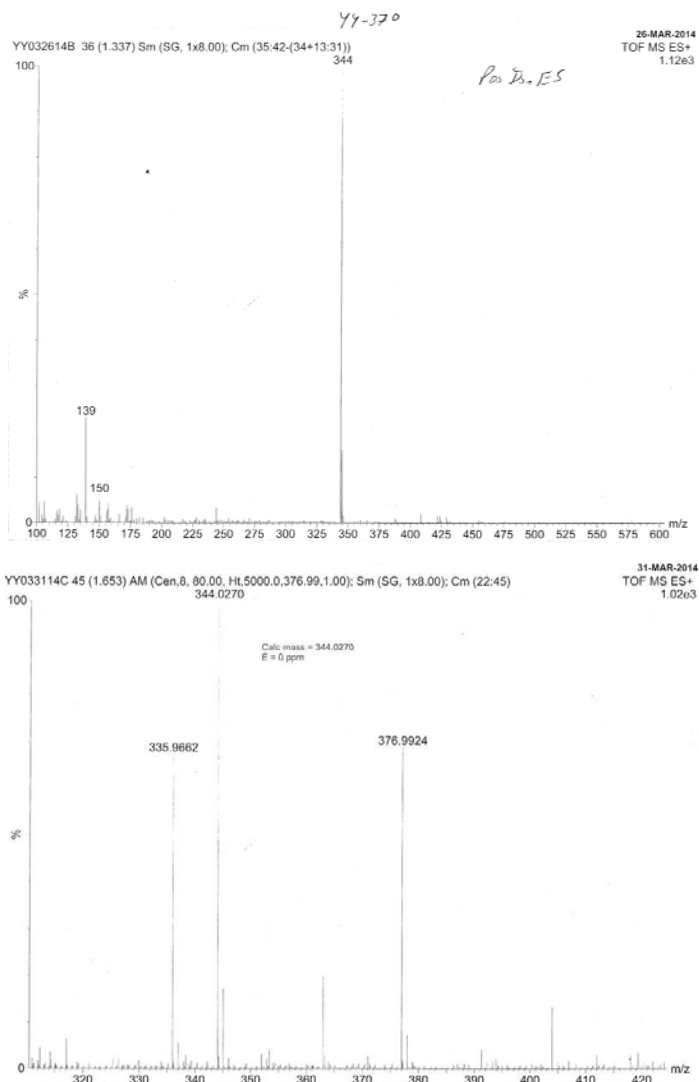


Figure S11. Low and high resolution mass spectra of hydroxyl-terminated rhodocenium (**IV**).

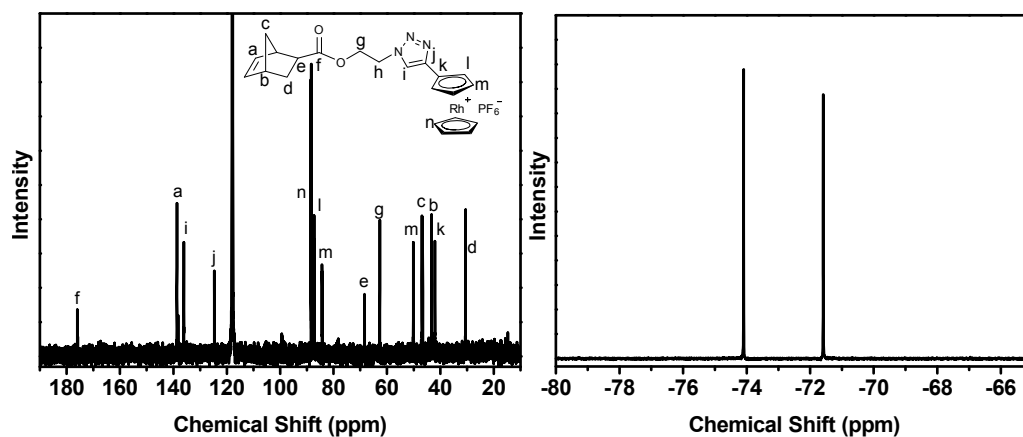


Figure S12. ^{13}C and ^{19}F spectra of rhodocenium-containing monomer **M2** in CDCl_3 .

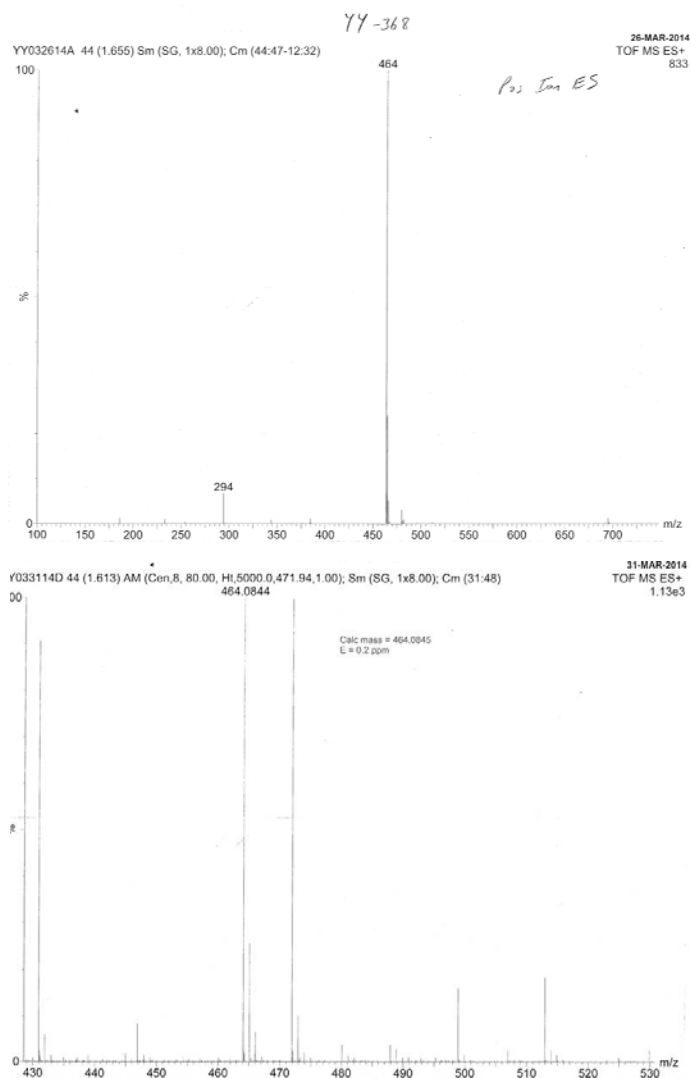


Figure S13. Low and high resolution mass spectra of rhodocenium-containing monomer **M2**.

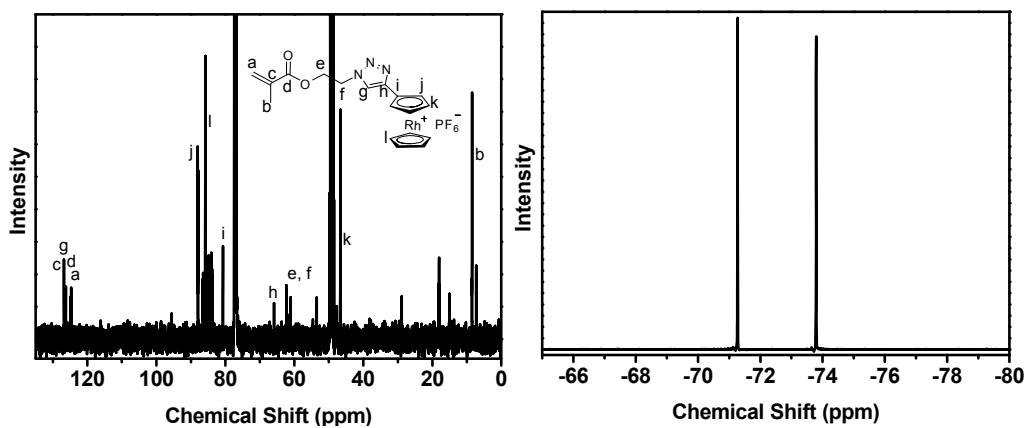


Figure S14. ^{13}C and ^{19}F NMR spectra of rhodocenium-containing monomer **M3** in mixture solvent (CDCl_3 and CD_3OD).

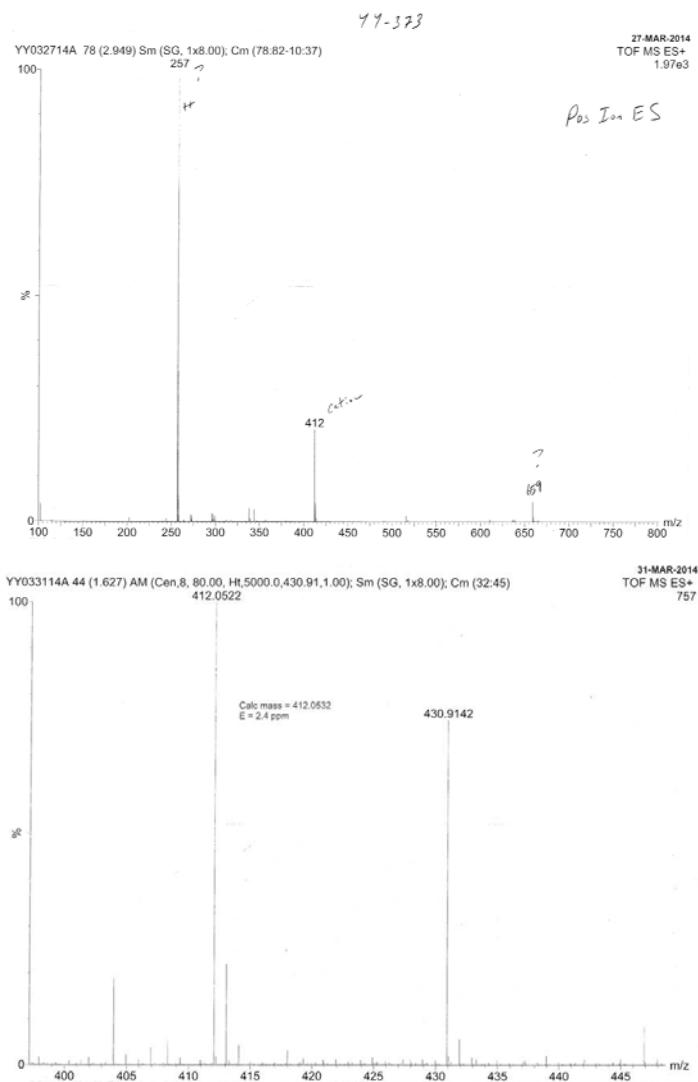


Figure S15. Low and high resolution mass spectrum of rhodocenium-containing monomer **M3**.

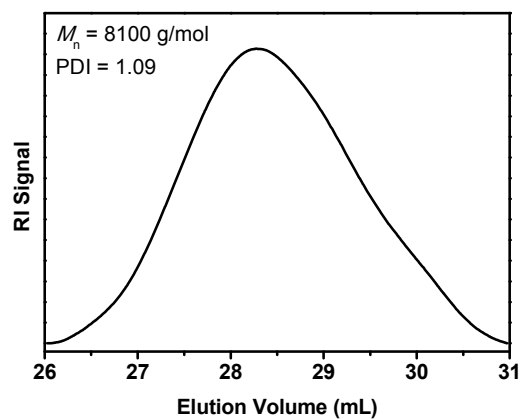


Figure S16. Representative GPC trace for η^4/η^5 -Rh(I)-containing polymer **P1**.

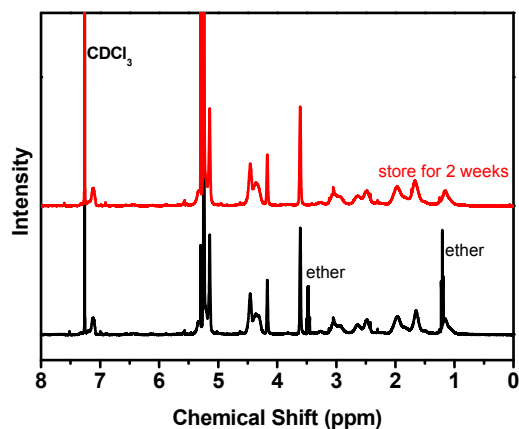


Figure S17. ^1H NMR spectra for polymer **P1** before and after being stored at room temperature under N_2 for 2 weeks.

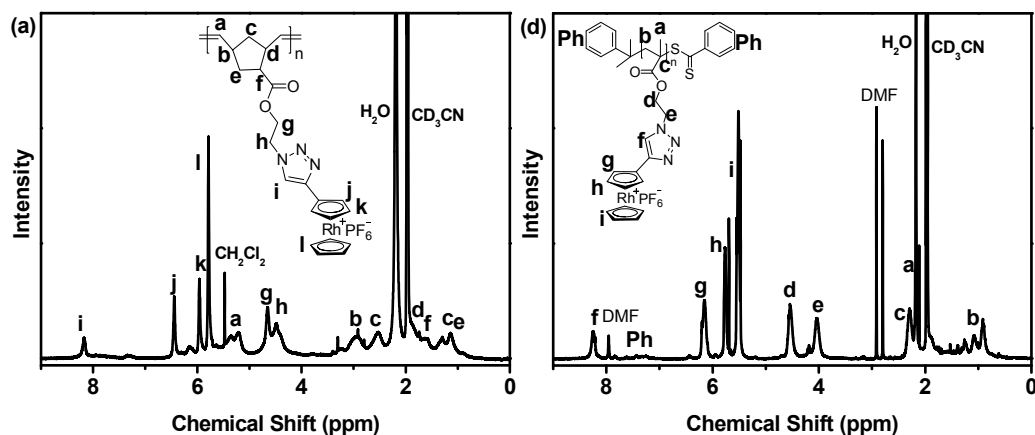


Figure S18. ^1H NMR spectra of rhodocenium-containing polymers: (a) **P2**, (b) **P3**.

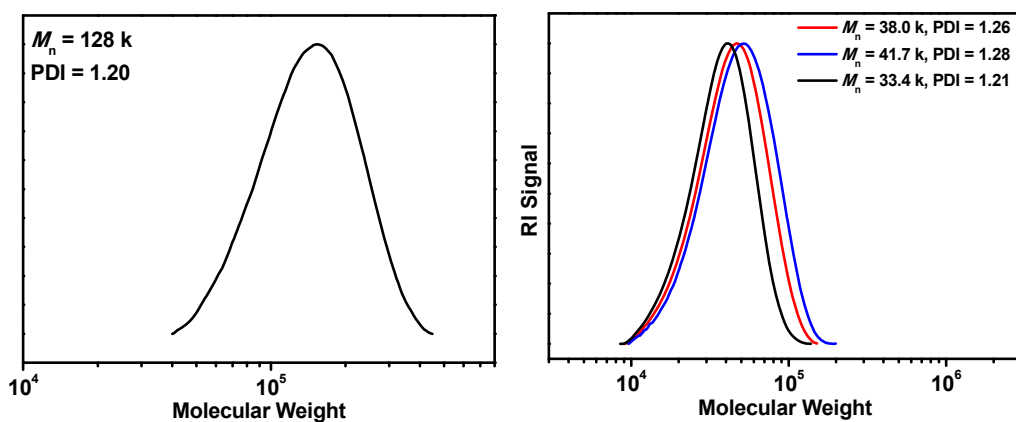


Figure S19. (Left) GPC trace for rhodocenium-containing polymers **P2**, (Right) GPC traces for rhodocenium-containing polymers with similar structure to polymer **P2** but with different DP (black and blue line), and polymer **P3** (red line).

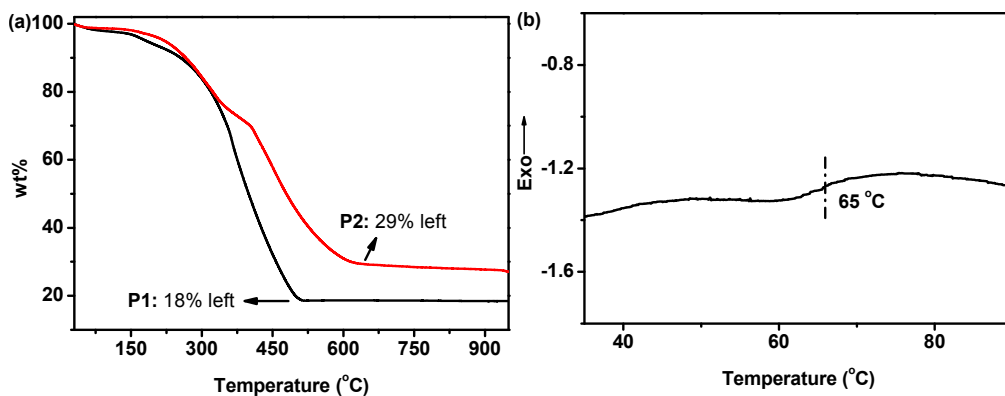


Figure S20. (a): TGA curves of η^4/η^5 -Rh(I)-containing polymer **P1** and rhodocenium-containing polymer **P2**; (b) DSC curve of polymer **P2**. Scanning rate is 10 °C/min.

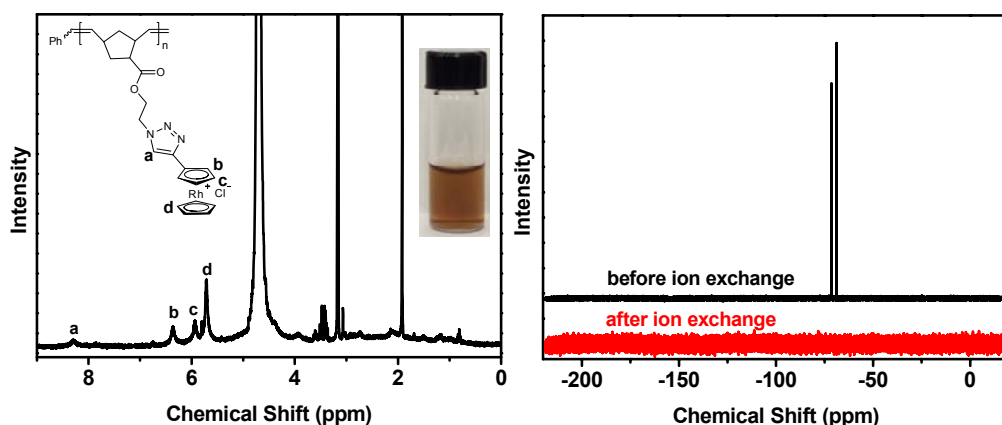


Figure S21. ¹H (left) and ¹⁹F (right) NMR spectra of rhodocenium-containing polymer **P2** after counterion exchange with tetrabutylammonium chloride, inset is the image of aqueous solution of polymer **P2** paired with Cl⁻.

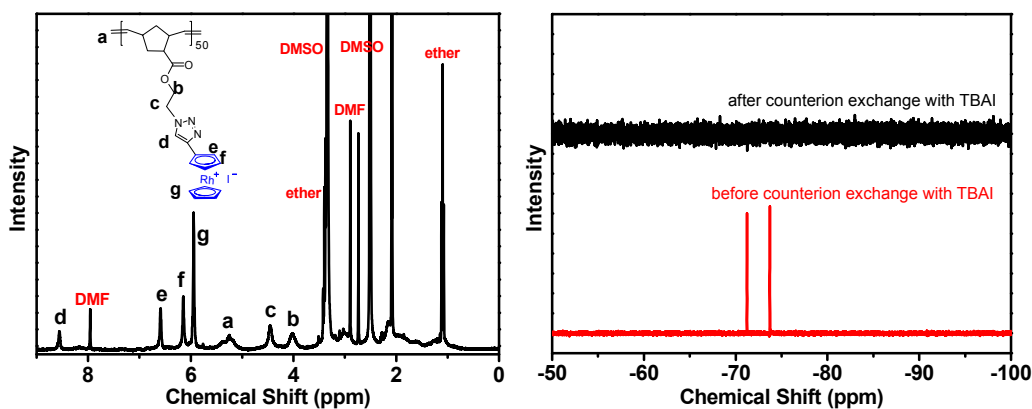


Figure S22. ¹H (left) and ¹⁹F (right) NMR spectra of rhodocenium-containing polymer **P2** after counterion exchange with tetrabutylammonium iodide.

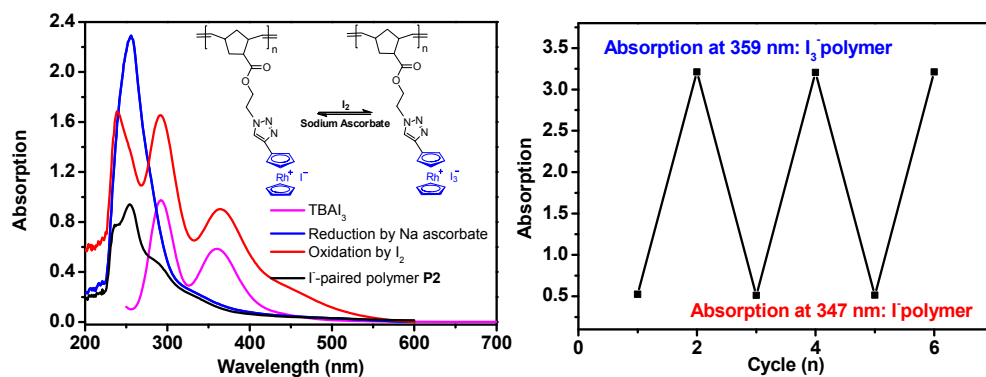


Figure S23. Left: UV-vis spectra of I⁻-paired polymer **P2**, sequential oxidation by I₂, reduction by sodium ascorbate and tetrabutylammonium triiodide (TBAI₃), inset shows the redox chemistry between I⁻ and I₃⁻; right: corresponding plot for the absorption at 347 nm (characteristic peak for I⁻-paired polymer) and 359 nm (characteristic peak for I₃⁻-paired polymer).

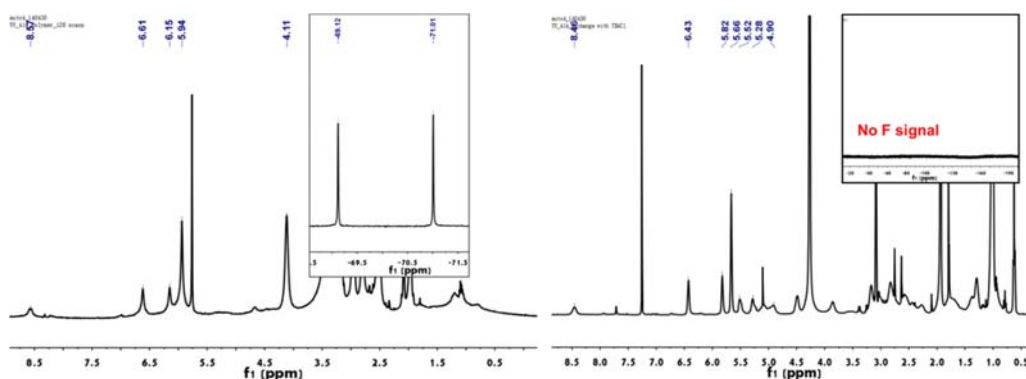


Figure S24. Representative ¹H and ¹⁹F NMR spectra (inset) of diblock copolymer before (left) and after (right) counterion exchange.

IV. Self-assembly of Side-chain Rhodocenium-containing Block Copolymer

A general preparation procedure: Amphiphilic diblock copolymer was dissolved in THF, and then added dropwise with deionized water. The solution was sealed and stirred at room temperature for 24 h. THF was removed by opening the solution to air and the solution was stirred for another 24 h at room temperature. The concentration of the obtained solution was calculated to be ~ 1 mg/mL without consideration of water evaporation. TEM samples were prepared by adding one drop of the above

aqueous solution on a carbon-coated copper mesh grid and removing the excess solution by filtration paper. DLS was carried out using the above as-prepared solution.

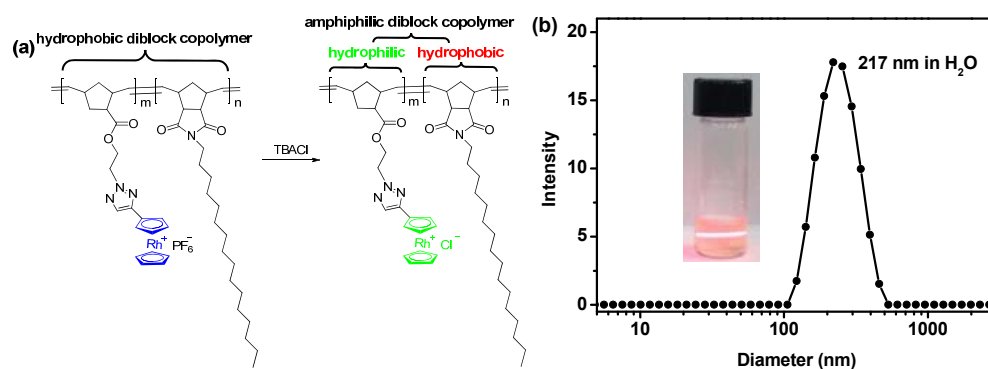


Figure S25. (a) Preparation of amphiphilic rhodocenium-containing block copolymer via phase-transfer ion-exchange; (b) DLS result for the Cl^- -paired block copolymers in water, inset shows corresponding Tyndall scattering effect.

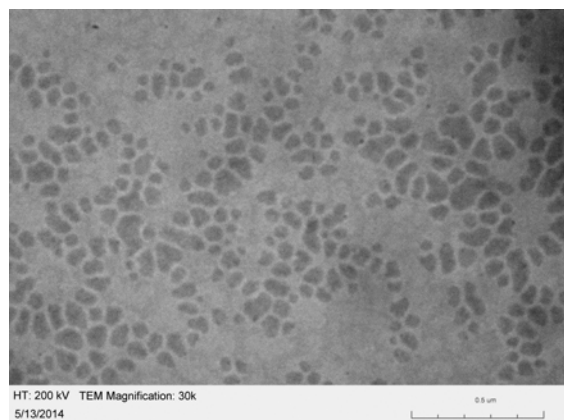


Figure S26. Representative TEM image for the self-assembled micelles in water formed by rhodocenium-containing diblock copolymer after counterion exchange with tetrabutylammonium chloride.