Metallo-Supramolecular Cyclic Polymers

Ke Zhang,[a,b] *Yongping Zha,*[a] *Bo Peng,*[b] *Yongming Chen,*[b] *Gregory N. Tew**[a]

[a] Department of Polymer Science and Engineering, University of Massachusetts, Amherst, MA 01003, USA

[b] State Key Laboratory of Polymer Physics and Chemistry, Institute of Chemistry, The Chinese Academy of Sciences, Beijing 100190, China

* Corresponding author: Fax: +1-413-545-0082; e-mail: tew@mail.pse.umass.edu

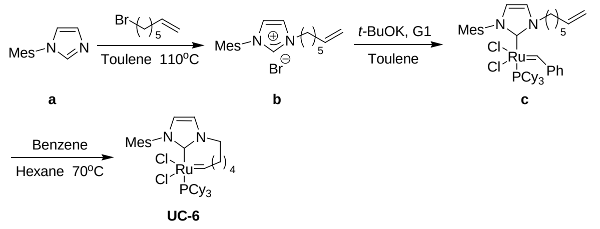
Supporting Information

Experimental

Materials

First generation Grubbs' catalyst (G1), paraformaldehyde, glyoxal aqueous solution (40%), mesitylamine, 7-bromo-1-heptene, *cis*-5-norbornene-*exo*-2,3-dicarboxylic anhydride, 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene, 5-amino-1-pentanol, triethylamine, 3-aminopropionic acid, pentafluorophenol, *N,N'*-dicyclohexylcarbodiimide (DCC), 4-(dimethylamino)pyridine (DMAP), 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide (EDC), 1-hydroxybenzotriazole (HOBt) 2,2':6',2"-terpyridine, 4'-chloro-2,2':6',2"-terpyridine, *N*-ethylmorpholine, 1-propanethiol, 2-bromo-2-methylpropionic acid, carbon disulfide (CS_2), styrene, 2,2'-azobis(2-methylpropionitrile) (AIBN), poly(ethylene glycol) monomethylether, 750 (PEG750), ammonium chloride, phosphoric acid, hydrochloric acid (HCl), sodium hydroxide (NaOH), anhydrous sodium sulfate, potassium tert-butoxide (*t*-BuOK), potassium hydroxide (KOH), potassium phosphate (K_3PO_4), ruthenium chloride hydrate ($RuCl_3.3H_2O$), iron(II) chloride tetrahydrate, nickel(II) chloride hexahydrate, ammonium hexafluorophosphate, 1,4-dioxane, hexane, ethyl acetate, diethyl ether, pentane, toluene, benzene, methanol, ethanol, chloroform, acetone, dichloromethane (DCM), tetrahydrofuran (THF), and *N,N*-dimethylformamide (DMF) were purchased as regent grade from Aldrich, Acros, Alfa Aesar, or Fisher and used as received unless otherwise noted. AIBN was recrystallized twice from methanol and stored in the dark at -18°C. For making dry solvents: DCM was refluxed over calcium hydride; THF, hexane, toluene, and benzene were distilled from sodium/benzophenone. Spectra/Por® 7 dialysis membranes with the molecular weight cut off (MWCO) of 10000 and 2000 Da were purchased from Spectrum Medical Industries.

Preparation of Cyclic Ruthenium-Alkylidene Catalyst (UC-6)[1-3]



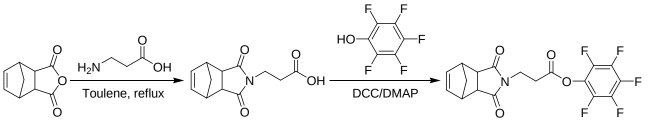
Compound **a**[1]: ammonium chloride (5.35 g, 0.10 mol) in 20 mL H_2O was added drop-wise to a rapidly stirring mixture of H_2O (100 mL), 1,4-dioxane (100 mL), paraformaldehyde (3.00 g, 0.10 mol), glyoxal aqueous solution (40%) (11.5 mL, 0.10 mol), and mesitylammonium salt (prepared from the addition of phosphoric acid to mesitylamine (13.5 g, 0.10 mol) in 50 mL H_2O until a pH of ca. 2 was reached). After the addition, the reaction was maintained at 100 ºC for 3 h and then chilled in an ice bath. NaOH aqueous solution (1 M) was added at 0 ºC until a pH > 12 was reached and the mixture was extracted with hexane (3 × 500 mL). The combined hexane extracts were dried over $MgSO_4$ and evaporated to yield the product as a light brown solid, which was recrystallized from ethyl acetate as a colorless crystalline solid (5.50 g, 30% yield). ^1H-NMR ($CDCl_3$) δ (ppm): 7.43 (s, 1H), 7.23 (s, 1H), 6.97 (s, 2H), 6.89 (s, 1H), 2.34 (s, 3H), 1.98 (s, 6H).

Compound **b**[2,3]: Compound **a** (1.2 g, 6.44 mmol) and 7-bromo-1-heptene (1.37 g, 7.73 mmol) were dissolved in 20 mL toluene. After refluxing the mixture for 24 h, the crude material was precipitated from diethyl ether 3 times. The final white solid (1.75 g) was obtained with a yield of 75%. ^1H-NMR ($CDCl_3$) δ (ppm): 10.50 (s, 1H), 7.62 (s, 1H), 7.14 (s, 1H), 6.99 (s, 2H), 5.78-5.68 (m, 1H), 4.99-4.90 (t, 2H), 4.77-4.72 (t, 2H), 2.33 (s, 3H), 2.06-1.97 (m, 10H), 1.45-1.38 (m, 4H).

Compound **c**[2,3]: Compound **b** (264.9 mg, 0.73 mmol), *t*-BuOK (81.8 mg, 0.73 mmol), and G1 (300 mg, 0.36 mmol) in 6 mL toluene were stirred for 1 h under N_2 at room temperature. The suspension was purified by a silica gel column with diethyl ether : pentane (1 : 4, v/v) as the eluent under N_2 pressure. The red powder product was obtained in a yield of ca. 60%. ^1H-NMR (C_6D_6) is shown in Figure S1.

UC-6[2,3]: Compound **c** (150 mg, 0.18 mmol) was dissolved in a trace amount of benzene and then diluted with 180 mL dry hexane in a Schlenk tube under N_2. The solution was placed in an oil bath at 70 ºC and stirred for 1 h. Upon completion, the solution was cooled to room temperature and concentrated under vacuum without heating. The crude was purified by recrystallization from DCM/pentane as a red crystalline solid (89.9 mg, 60% yield). ^1H-NMR (C_6D_6) is shown in Figure S2.

Preparation of Monomer 1

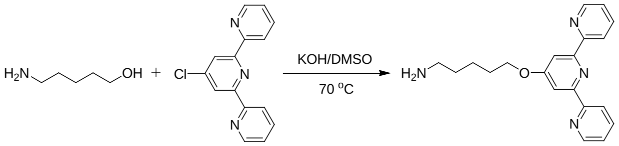


d **1**

Compound **d**: cis-5-Norbornene-exo-2,3-dicarboxylic anhydride (5 g, 30.46 mmol), 3-aminopropionic acid (3.39 g, 38.06 mmol), and triethylamine (385.1 mg, 3.81 mmol) were mixed with 20 mL toluene in a 50 mL round-bottom flask fitted with a Dean-Stark apparatus. After refluxing the reaction for around 12 h, the reaction solution was cooled and concentrated. The resulting crude solid was then dissolved in chloroform (150 mL) and extracted by acidic water (pH = 1) (3 × 150 mL). After drying the chloroform phase by anhydrous Na_2SO_4, the chloroform was evaporated to produce the white solid product with a yield of 80%. ^{1}H-NMR ($CDCl_3$) δ (ppm): 9.24 (s, 1H), 6.29 (s, 2H), 3.79 (t, 2H), 3.28 (s, 2H), 2.70-2.65 (m, 4H), 1.54-1.50 (d, 1H), 1.27-1.23 (d, 1H).

Monomer **1**: compound **d** (3 g, 12.75 mmol) and pentafluorophenol (2.93 g, 15.94 mmol) were dissolved in anhydrous DCM (20 mL). The mixture was cooled to 0 ºC and DCC (3.29 g, 15.94 mmol) was added. DMAP (194.8 mg, 1.59 mmol) in anhydrous DCM (2 mL) was added drop-wise by a syringe. After 1 h, the reaction mixture was warmed to room temperature and stirred for approximately 24 h further. Purification was by recrystallization from ethyl acetate to provide the white solid product with a yield of ca. 75%. ^{1}H-NMR ($CDCl_3$) δ (ppm): 6.30 (s, 2H), 3.92 (t, 2H), 3.31 (s, 2H), 3.03 (t, 2H), 2.73 (t, 2H), 1.56-1.52 (d, 1H), 1.25-1.22 (d, 1H).

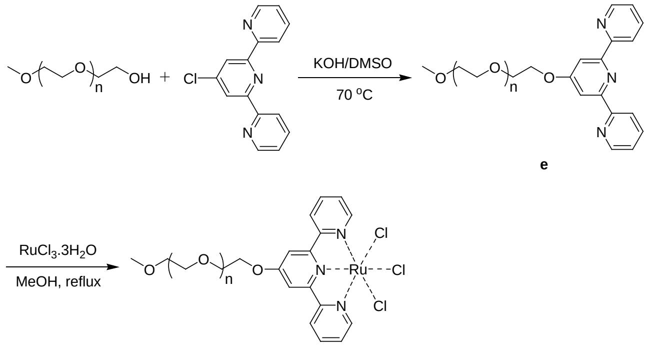
Preparation of Compound 2



2

5-Amino-1-pentanol (963.3 mg, 9.33 mmol) and KOH (2.09 g, 37.35 mmol) were stirred in dry DMSO (20 mL) at 70 ºC. After 30 min, 4’-chloro-2,2’:6’,2”-terpyridine (2 g, 7.47 mmol) was added. After stirring for another 48 h, the mixture was poured into cold water (500 mL). The white solid product was then collected by filtration with a yield of 85%. ^{1}H-NMR ($CDCl_3$) δ (ppm): 8.69 (m, 2H), 8.62 (m, 2H), 8.02 (s, 2H), 7.85 (m, 2H), 7.33 (m, 2H), 4.23 (t, 2H), 2.74 (t, 2H), 1.84 (m, 2H), 1.55 (m, 4H), 1.22 (s, 2H).

Preparation of PEG Terpyridine-$RuCl_3$ Mono-Complex



e

f

Terpyridine terminated PEG **e**: PEG750 (2 g, 2.67 mmol) and KOH (1.02 g, 13.33 mmol) were stirred in dry DMSO (15 mL) at 70 ºC. After 30 min, 4’-chloro-2,2’:6’,2”-terpyridine (1 g, 3.73 mmol) was added. After stirring for another 48 h, DMSO was removed by vacuum evaporation. The crude product was re-dissolved in water (50 mL) and filtered. The filtrate was extracted with DCM (3 × 50 mL). The combined DCM solution was dried over anhydrous Na_2SO_4. The pure product **e** was obtained by evaporating DCM with a yield of 67%. ^{1}H-NMR ($CDCl_3$) δ (ppm): 8.67 (m, 2H), 8.61 (m, 2H), 8.02 (s, 2H), 7.85 (m, 2H), 7.33 (m, 2H), 4.39 (t, 2H), 3.92 (t, 2H), 3.76-3.52 (m, 70H), 3.36 (s, 3H).

PEG terpyridine-$RuCl_3$ mono-complex **f**: Terpyridine terminated poly(ethylene glycol) (**e**) (2 g, 2.04 mmol) and $RuCl_3 \cdot 3H_2O$ (0.64 g, 2.44 mmol) were dissolved in 30 mL methanol. The mixture solution was then refluxed for 12 h. After evaporating the methanol, the crude product was re-dissolved in water (50 mL) and extracted by DCM (3 × 50 mL). The combined DCM solution was dried by anhydrous Na_2SO_4. The pure product **f** was obtained by evaporating DCM with a yield of 70%. ^{1}H-NMR ($CDCl_3$) δ (ppm): 16.87 (s, 2H), 5.84 (s, 2H), 3.94-3.33 (m, 77H), -8.75 (s, 2H), -11.66 (s, 2H).

Preparation of Carboxylic Trithiocarbonate RAFT Agent 3

1-Propanethiol (2.74 g, 35.94 mmol) was added into a stirred suspension of K_3PO_4 (7.63 g, 35.94 mmol) in acetone (50 mL). 10 min later, CS_2 (8.21 g, 107.78 mmol) was added. After another 10 min, 2-bromo-2-methylpropionic acid (5 g, 29.94 mmol) was added. The reaction mixture was kept to stir for overnight. After that, the solvent was removed and the residue was extracted into CH_2Cl_2 (2 x 100 mL) from 1M HCl aqueous solution (100 mL). After the organic phase was washed with water (2 x 100 mL) and dried by anhydrous Na_2SO_4, the DCM was removed by rotary evaporation. The pure product was obtained by recrystallization from ethyl acetate and hexane with a yield of 70%. ^{1}H-NMR (CDCl3) δ (ppm): 9.49 (b, 1H), 3.27 (t, 2H), 1.75-1.68 (m, 8H), 1.00 (t, 3H).

Preparation of Terpyridine Functionalized RAFT Agent 4

Compound **2** (1.50 g, 4.49 mmol) and carboxylic RAFT agent **3** (1.60 g, 6.71 mmol) were dissolved in anhydrous DMF (18 mL). The mixture was cooled to 0 ºC and EDC (1.07 g, 5.58 mmol) was added. HOBt (0.76 g, 5.58 mmol) in anhydrous DMF (2 mL) was added drop-wise by a syringe. After 1 h, the reaction mixture was warmed to room temperature and stirred for approximately 24 h further. The reaction mixture was dissolved in DCM (200 mL) and washed by water (2 x 100 mL). After the organic phase was dried by anhydrous Na_2SO_4, the DCM was removed. The pure product was obtained by recrystallization from ethyl acetate with a yield of ca. 70%. ^{1}H-NMR ($CDCl_3$) δ (ppm): 8.68 (d, 2H), 8.60 (d, 2H), 8.00 (s, 2H), 7.85 (t, 2H), 7.32 (t, 2H), 6.54 (t, 1H), 4.21 (t, 2H), 3.29-3.23 (m, 4H), 1.88-1.82 (m, 2H), 1.70-1.48 (m, 12H), 0.96 (t, 3H).

Preparation of End-Functionalized Polystyrene 5

Styrene (2.60 g, 24.96 mmol), RAFT agent **4** (276.6 mg, 0.50 mmol), and AIBN (8.19 mg, 5.00×10^{-2} mmol) were dissolved in 2 mL DMF. After degassing through four freeze-evacuate-thaw cycles, the polymerization was carried out in an oil bath at 90 °C under N_2 for 24 h. The polystyrene **5** was purified by precipitating from THF into methanol three times.

Preparation of Polystyrene Terpyridine-$RuCl_3$ Mono-Complex 6

Terpyridine terminated polystyrene **5** (1.65 g, 0.50 mmol) and $RuCl_3 \cdot 3H_2O$ (0.65 g, 2.49 mmol) were dissolved in 15 mL THF/ethanol (v/v = 10/1). The solution was then refluxed for 12 h. Polystyrene **6** was purified by precipitating from THF into methanol four times.

Preparation of Cyclic Poly-1

Monomer **1** (400 mg, 1 mmol) and **UC-6** (3.60 mg, 4.98×10^{-3} mmol) were each dissolved in 5 mL DMF. After degassing through four freeze-evacuate-thaw cycles, the catalyst solution was added all at once to the monomer solution at room temperature under N_2 while stirring vigorously. The polymerization was carried out in an oil bath at 55 °C for 12 h.

Preparation of Cyclic Poly-2

Compound **2** (500 mg, 1.50 mmol) was added to 5 mL of the **Poly-1** in-situ polymerization solution, where the theoretical weight of **Poly-1** was 200 mg (0.5 mmol). The reaction mixture was stirred at room temperature for 24 h. The resultant cyclic **Poly-2** was purified by dialysis from $CHCl_3$. The MWCO of dialysis membrane was 2000 g/mol.

Preparation of Hybrid Cyclic Brush Polymer with PEG Side Chains

Cyclic **Poly-2** (55 mg), PEG terpyridine-$RuCl_3$ mono-complex **f** (237.2 mg), and 0.1 mL *N*-ethylmorpholine were dissolved in the mixed solvents of $CHCl_3$ (5 mL) and ethanol (1 mL). The reaction mixture was then stirred at 70 ºC for 12 h. The resultant cyclic brush polymer with PEG side chains was purified by dialysis from H_2O, methanol and $CHCl_3$. The MWCO of dialysis membrane was 10000 g/mol.

Preparation of Hybrid Cyclic Brush Polymer with PS Side Chains

Cyclic **Poly-2** (55 mg), polystyrene terpyridine-$RuCl_3$ mono-complex **6** (800 mg), and 0.1 mL *N*-ethylmorpholine were dissolved in the mixed solvents of DMF (5 mL) and ethanol (1 mL). The reaction mixture was then stirred at 70 ºC for 12 h. The resultant cyclic brush polymer with polystyrene side chains was purified by precipitating from DFM into THF three times.

Characterization

^{1}H-NMR spectra were recorded on a Bruker DPX400 spectrometer at room temperature.

UV/Vis spectra were recorded using a PerkinElmer Lambda 25 UV/Vis spectrometer.

FT-IR spectra were recorded on a PerkinElmer FT-IR spectrometer at room temperature.

Gel permeation chromatography (GPC) was performed using a Polymer Laboratories PL-GPC50 instrument with two 5 µm mixed-D columns, a 5 µm guard column, and a Knauer RI detector. DMF with 0.01 M LiCl was used as the eluent at a flow rate of 1.0 mL/min. Poly(methyl methacrylate) standards were used for the calibration.

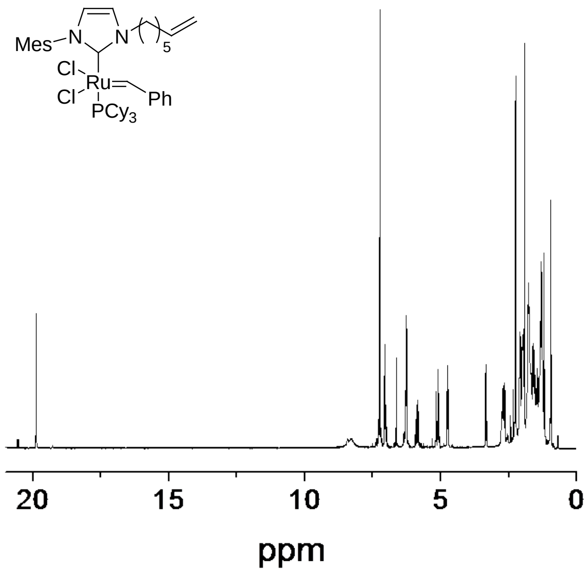


Figure S1. ^{1}H-NMR spectrum of compound **3** in C_6D_6.

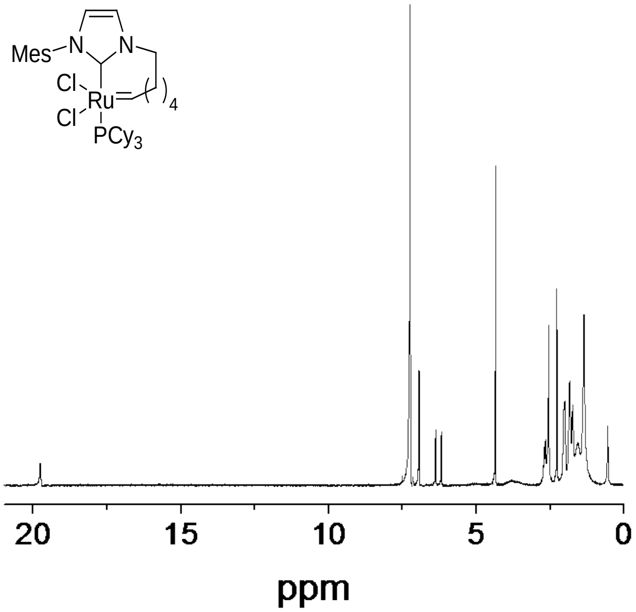


Figure S2. ^{1}H-NMR spectrum of **UC-6** in C_6D_6.

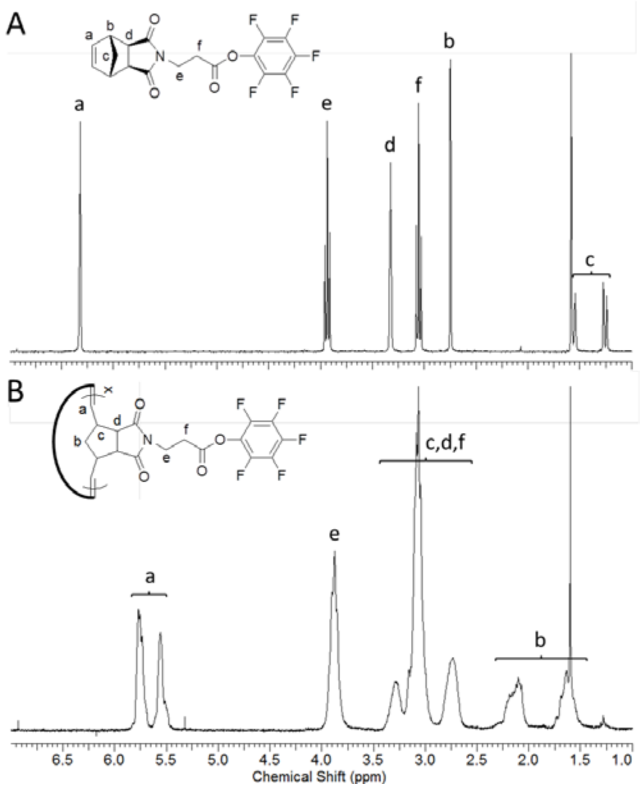


Figure S3. ^{1}H-NMR spectra of (A) monomer **1** (in CDCl$_3$) and (B) the resultant cyclic **Poly-1** (in CDCl$_3$)

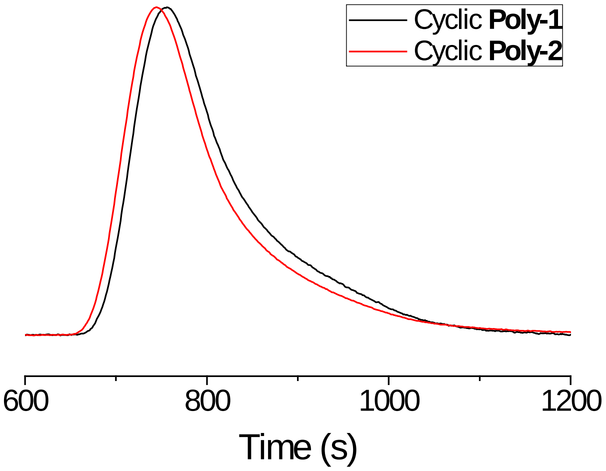


Figure S4. GPC traces for cyclic **Poly-1** and the resultant cyclic **Poly-2**, where DMF with 0.01M LiCl was used as the eluent and poly(methyl methacrylate) standards were used for the calibration.

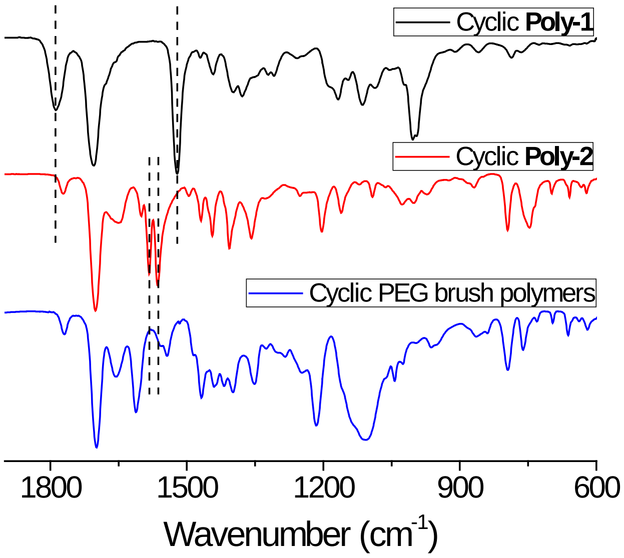


Figure S5. FT-IR spectra for cyclic **Poly-1**, cyclic **Poly-2**, and the corresponding metallo-supramolecular hybrid cyclic brush polymers with PEG side chains.

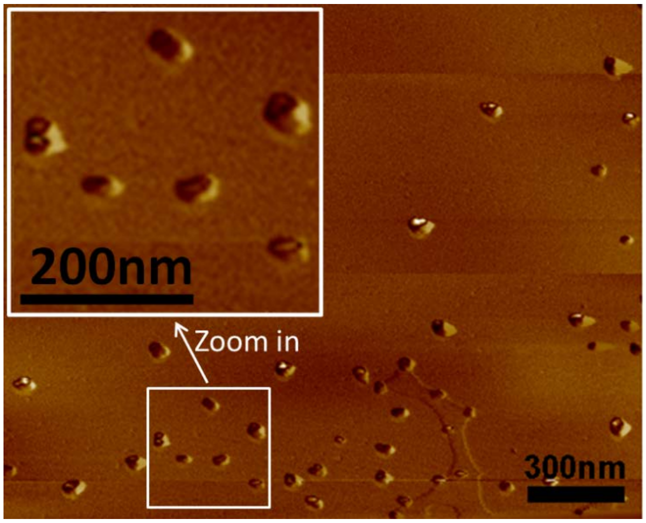


Figure S6. AFM phase image of the metallo-supramolecular hybrid cyclic brush polymers with PEG side chains.

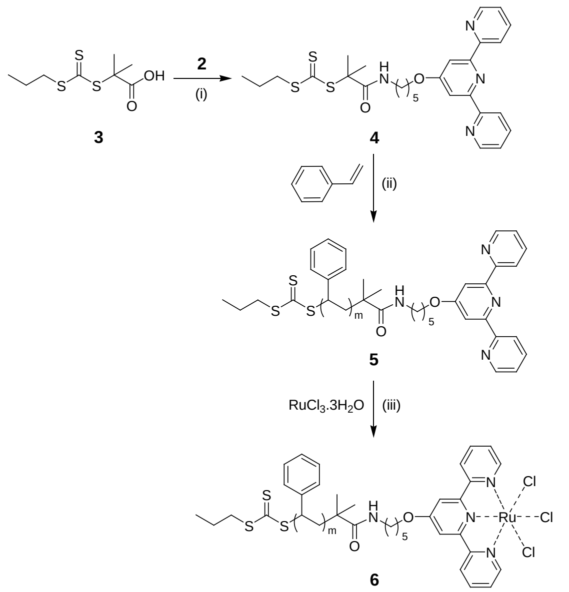


Figure S7. Synthetic scheme for the polystyrene terpyridine-RuCl$_3$ mono-complex. (i) EDC/HOBt, DMF, room temperature, 24h; (ii) AIBN, DMF, 90 ^{o}C, 24h; (iii) THF/ethanol = 10/1 (v/v), reflux, 12h. As shown in Figure 5(i), **4** was prepared by EDC coupling of the carboxylic trithiocarbonate RAFT agent **3** and the terpyridine-functionalized amine **2**. When the terpyridine-functionalized RAFT agent **4** was used to polymerize styrene (Figure 5(ii)), well-defined terpyridine end-functionalized polystyrene **5** was obtained. As shown in Figure S9, the corresponding GPC curve (black) was symmetric and monomodal, and the M_n and PDI were measured as 2700 g/mol and 1.15, respectively. Characterization of **5** by both FT-IR (Figure S8, black curve) and ^{1}H NMR (Figure S10) confirmed the successful introduction of the terpyridine end groups to the polystyrene chains, with the peak at 1562 cm^{-1} from the *C=C* stretching vibration of the free pyridine rings and the appearance of the characteristic peaks for the terpyridine protons in the range of 7.20-8.80 ppm, respectively. In addition, from the area ratio between peak *d* (*5H* from the benzene ring) and peaks *p* and *s* (*4H* from the terpyridine end group) in the ^{1}H NMR spectrum, the degree of polymerization of polystyrene **5** was calculated to be 34.

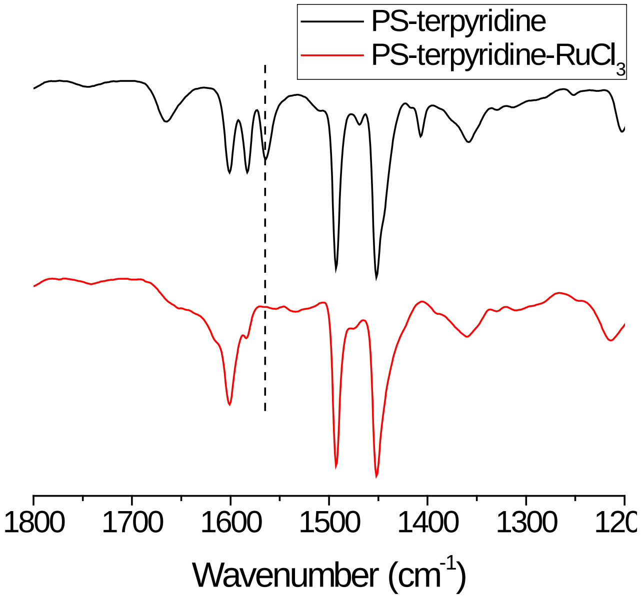


Figure S8. FT-IR spectra for terpyridine end-functionalized polystyrene (**5**) and the resultant polystyrene terpyridine-RuCl$_3$ mono-complex (**6**).

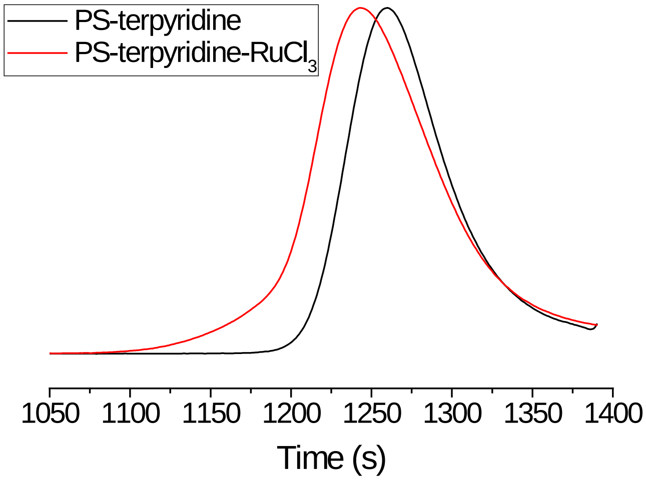


Figure S9. GPC traces for terpyridine end-functionalized polystyrene (**5**) and the resultant polystyrene terpyridine-RuCl$_3$ mono-complex (**6**), where DMF with 0.01M LiCl was used as the eluent and poly(methyl methacrylate) standards were used for the calibration.

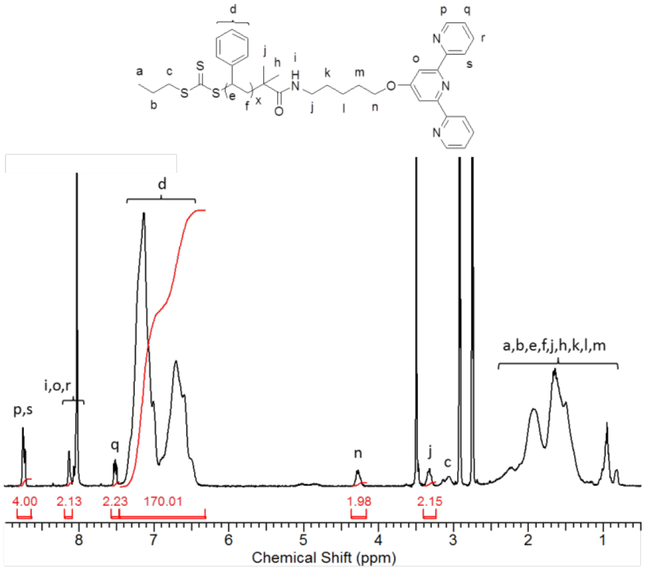


Figure S10. ^{1}H-NMR spectrum of the terpyridine end-functionalized polystyrene (**5**) (in DMF-d$_7$).

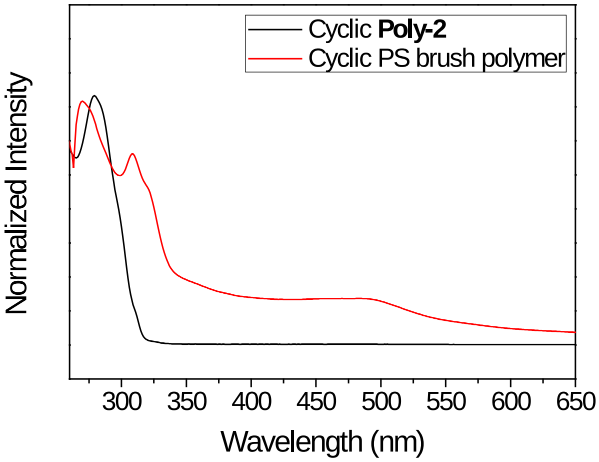


Figure S11. UV-Vis spectra for cyclic **Poly-2** and the resultant hybrid cyclic brush polymers with polystyrene side chains (in DMF).

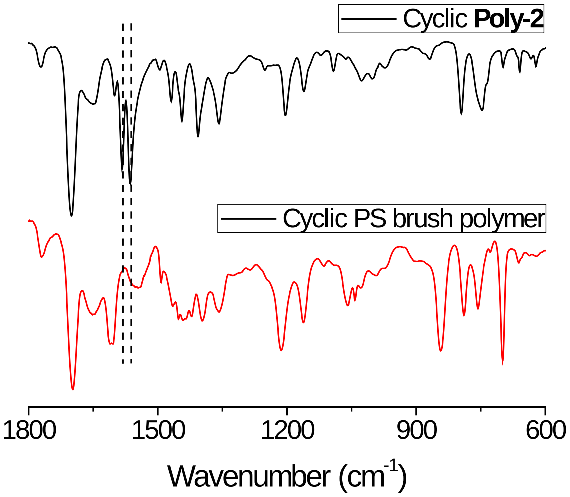


Figure S12. FT-IR spectra for cyclic **Poly-2** and the resultant metallo-supramolecular cyclic brush polymers with polystyrene side chains.

Figure S13. Picture of the metallo-supramolecular cyclic gel after reacting with a large excess of free 2,2';6',2"-terpyridine.

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