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Synthesis of 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10-, 11-, and 12-Armed Star-shaped Poly(styrene oxide) Ru(II) Complexes by Click-to-Chelate Approach

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This study describes the first convenient preparation of 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10-, 11-, and 12-armed star-shaped poly(styrene oxide) (PSO) Ru(II) complexes by a click-to-chelate approach. This approach involves the combination of the click reaction and stepwise chelating reactions of $Ru(II)(DMSO)_4Cl_2$ with macroligands, 2-(1-PSO_n-1,2,3-triazol-4-yl)pyridine (PSO_n-tapy) or 2-(1-PSO_m-1,2,3-triazol-4-yl)-6-(1-PSO_n-1,2,3-triazol-4-yl)pyridine (PSO_m-bitapy-PSO_n) (m, n = 1, 2, or 3). Click chemistry was used to prepare the PSO_n-tapy and PSO_m-bitapy-PSO_n macroligands. More specifically, the PSO_n-tapy was prepared by reacting the azido-functionalized PSO_n (PSO_n-N_3) with excess 2-ethynylpridine. On the other hand, the PSO_m-bitapy-PSO_n was obtained by the click reaction of excess PSO_n-N_3 with 2,6-diethynylpridine to afford $(PSO_n)_2$-bitapy when m equals n, and by the stepwise click reactions of PSO_m-N_3 and PSO_n-N_3 with 2,6-diethynylpridine to produce PSO_m-bitapy-PSO_n when m is not equal to n. In order to obtain these polymer-substituted macroligands, PSO_n-N_3 was initially synthesized by the living ring-opening polymerization (ROP) of styrene oxide (SO) using *t*-Bu-P_4 as a catalyst and the azido-functionalized mono- or multi-hydroxyl compounds, *e.g.*, 6-azido-1-hexanol, 2-((6-azidohexyloxy)methyl)-2-methylpropane-1,3-diol (**1**) and 2-((6-azidohexyloxy)methyl)-2-(hydroxymethyl)propane-1,3-diol (**2**), as the initiators.

Introduction

Non-covalent interactions, such as hydrogen bonding, guest-host inclusion, and electrostatic interaction, have been recognized to play an incredibly significant role in many natural phenomena and life processes. The most famous event in such fields can date back to the first discovery of the double-helix DNA, in which its two strands arrange in an anti-parallel way through strong hydrogen bonds between nucleotides. In general, such non-covalent interactions normally exhibit an interacting directionality and liability, and thus produce a very high accuracy in constructing molecular geometries. Among these non-covalent interactions, metal-ligand coordination undoubtedly plays a critical role and is a particularly attractive non-covalent interaction because of its diversity, specification, and directionality. For instance, metalloproteins and metalloenzymes have been found to serve as specific transporters of oxygen and other nutrients in living bodies. In the field of polymer chemistry, the metal-ligand coordination has been widely used to build macromolecular architectures, and the resulting metal-containing polymers, also referred to as polymer metal complexes or metallopolymers, are anticipated to have promising applications in catalysis,[1-3] luminescent devices, [4-5] and biological systems including sensing, imaging, surface modification, and drug delivery systems.[6-10] A variety of metals, *e.g.*, Zn(II), Fe(II), Cu(II), Ni(II), and Ru(II), can be used for building various molecular structures, and their chelating bonding strength significantly varies from labile to inert. This nature makes the structures of polymer metal complexes tunable and offers fascinating reversible or irreversible properties. For example, polymer metal complexes with labile metals, such as Zn(II) and Fe(II), are highly sensitive to external stimuli like heat and pH, for which they can be possibly utilized to design sensors. In comparison, those with inert metals, such as Ru(II) and Ir(II), are as stable as covalently bonded materials, which can be conveniently characterized. To date, a vast number of polymer metal complexes with various topologies, such as linear, star, dendric, and even two-dimensional motifs,[11-13] have been synthesized by either a metalloinitiation (divergent) or a macroligand chelation (convergent) approach.[14]

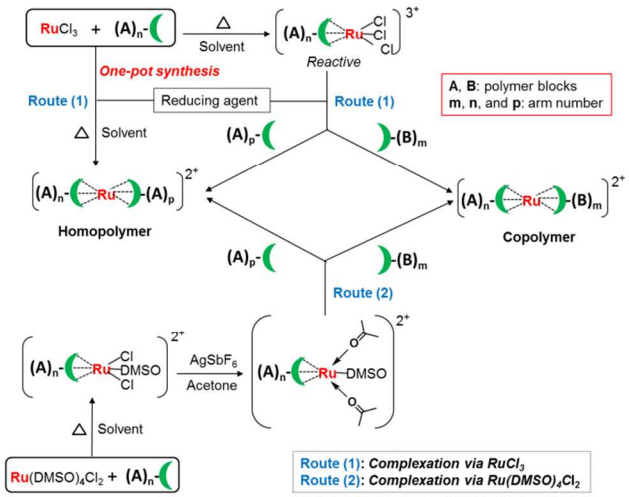
In this study, the Ru(II)/ligand coordination as an extremely strong non-covalent interaction is used to prepare stable multi-arm star poly(styrene oxide)s (PSOs) whose arms are held together by a luminescent Ru(II) core. In most cases, the synthesis of star polymers has been dominantly performed based on either an arm-first or a core-first procedure (covalent approach) so far, in which their arms are covalently bonded together by a core linker unit. The recent progress in the living/controlled polymerizations and click reactions has, in particular, afforded great versatility in preparing such star (co)polymers. However, this approach sometimes

encounters serious difficulty in precisely controlling the arm length and/or number due to various issues such as steric hindrance, side reactions between the living polymers, solubility problems, etc. In addition, the covalent approach also shows shortages in synthesizing mikto-arm copolymers due to the difficulty in controlling the stepwise introduction of different types of polymer arms. In contrast, for some cases, the non-covalent approach for star polymer synthesis is of great advantage. For instance, the synthesis of the star PSO with an arm number greater than four can be hardly achieved by the direct core-first ring-opening polymerization of styrene oxide (SO) due to the slight solubility of the multi-hydroxyl initiators in the solvents used for polymerization, *eg.*, D-mannitol bearing six hydroxyl moieties only has a low solubility of 0.3 g in 100 g THF. In comparison, its synthesis can be readily realized by the non-covalent method as reported in this study.

In general, the preparation of star polymer Ru(II) complexes can be implemented through two strategies (Scheme 1): (1) one-pot complexation using $Ru(III)Cl_3$, and (2) stepwise complexation using $Ru(II)(DMSO)_4Cl_2$ with ligands. It is notable that the utilization of $Ru(III)Cl_3$ initially involves the formation of a sensitive polymer Ru(III) *mono*-complex, which was then reduced to the Ru(II) *mono*-complex and further chelated with macroligands to form the polymer Ru(II) complex. Therefore, strategy (1) is very suitable for the one-pot synthesis of homopolymers. In contrast, the employment of $Ru(II)(DMSO)_4Cl_2$ can offer the opportunity to directly introduce Ru(II) species without any more reduction steps because $Ru(II)(DMSO)_4Cl_2$ can complex with a macroligand (macroligand A) at the ratio of 1:1 to form a stable Ru(II) *mono*-complex that can be easily isolated under common conditions. After isolation, the Ru(II) *mono*-complex can further chelate with another macroligand (macroligand B) to produce a polymer Ru(II) complex, which can be a homopolymer when A = B or a copolymer when A ≠ B. Strategy (2) is thus rather suitable for the stepwise synthesis of copolymers. The pioneering work involving the synthesis of star homoleptic and heteroleptic polystyrene Ru(II) complexes with arm numbers exactly controlled in the range from three to six was reported by Fraser et al.[15-18] Harruna and coworkers then succeeded in the synthesis of thermoresponsive miktoarm Ru(II) complexes composed of a Ru(II) core and polystyrene and poly(*N-iso*propylacrylamide) arms.[19-20] Thereafter, Schubert et al. reported the synthesis of homoleptic 3- and 4-arm star-shaped poly(ethylene oxide) (PEO) Ru(II) complexes.[21] We also previously reported the one-pot synthesis of 3- and 4-arm star-branched polystyrene Ru(II) complexes and stepwise chelating synthesis of mikto-arm copolymers by the click-to-chelate approach.[22-23] Based on the previously mentioned background, the click-to-chelate approach is now creatively utilized to synthesize 3- to 12-arm star PSOs, $[Ru(PSO_n\text{-tapy})_3](SbF_6)_2$, $[Ru((PSO_n)_2\text{-bitapy})(DMSO)](SbF_6)_2$, $[Ru((PSO_n)_2\text{-bitapy})(PSO_3\text{-tapy})(DMSO)](SbF_6)_2$, and $[Ru(PSO_2\text{-bitapy-}PSO_n)((PSO_3)_2\text{-tapy})(DMSO)](SbF_6)_2$ (n =1, 2 or 3).

Experimental

Scheme 1. Synthetic routes of polymer Ru(II) complexes by complexation using (1) $Ru(III)Cl_3$ and (2) $Ru(II)(DMSO)_4Cl_2$.



Materials. Toluene (> 99.5%; water content, < 0.001%) was purchased from Kanto Chemical Co., Inc., and distilled over sodium benzophenone ketyl before use. Styrene oxide (SO; > 98.0%, Tokyo Chemical Industry Co., Ltd., (TCI) was distilled over NaH prior to use. *N,N*-Dimethylformamide (DMF; > 99.5%) and *N,N,N′,N″,N″*-pentamethyldiethylenetriamine (PMDETA; > 99.0%) from TCI, were used after distillation over CaH_2 under reduced pressure. Copper(I) bromide (Cu(I)Br; 99.999%), 1-*tert*-butyl-4,4,4-tris(dimethylamino)-2,2-bis[tris(dimethylamino)phosphoranylidenamino]-2Λ^5,4Λ^5-catenadi(phosphazene) (*t*-Bu-P_4, 1.0 M solution in *n*-hexane), 2-ethynylpyridine (98%), and silver hexafluoroantimonate ($AgSbF_6$; 98%) were commercially available from the Sigma-Aldrich Chemicals Co. and used as received. Sodium azide (NaN_3, > 97.0%) and benzoic acid (> 99.5%) were purchased from Kanto Chemical Co., Inc., and used as received. 6-Azido-1-hexanol, 2-((6-azidohexyloxy)methyl)-2-methylpropane-1,3-diol (**1**), 2-((6-azidohexyloxy)methyl)-2-(hydroxymethyl)propane-1,3-diol (**2**), 2,6-diethynylpyridine, and $Ru(II)(DMSO)_4Cl_2$ were prepared according to methods in the literatures.[24-26]

Measurements. The ^{1}H NMR spectra was recorded using a JEOL JNM-A400II instrument in $CDCl_3$ as the solvent. The infrared (IR) spectra were recorded using a Perkin-Elmer Paragon 1000 FTIR instrument. The ring-opening polymerizations of styrene oxide (SO) using 6-azido-1-hexanol, **1**, and **2** as initiators were carried out in an MBRAUN stainless steel glove-box equipped with a gas purification system (molecular sieves and copper catalyst) under a dry argon atmosphere (H_2O, O_2 < 1 ppm). The moisture and oxygen contents in the glove-box were monitored by an MB-MO-SE 1 and an MB-OX-SE 1, respectively. Preparative size exclusion chromatography (SEC) was performed using a JAI LC-9201 HPLC system equipped with a JAI RI-50s refractive index detector and a JAI JAIGEL-3H column (20 mm × 600 mm; exclusion limit, 7 × 10^4) using $CHCl_3$. The SEC measurements in THF were performed using a Jasco GPC-900 system equipped with a Waters Ultrastyragel column (linear; 7.8 mm × 300 mm; exclusion limit, 1 × 10^7) and two Shodex KF-804L columns (linear; 8 mm × 300 mm;

exclusion limit, 4×10^5) at the flow rate of 1.0 mL min^{-1} and 40 °C. The SEC measurements in $CHCl_3$ were performed using a Jasco GPC-900 system equipped with two Shodex K-805L columns (linear; 8 mm × 300 mm; exclusion limit, 4×10^6) with the flow rate of 0.8 mL min^{-1} at 40 °C. The number-average molecular weight ($M_{n(SEC)}$) and polydispersity (M_w/M_n) of the polymers were calculated on the basis of a polystyrene calibration. Matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF MS) of the obtained polymers was performed using an Applied Biosystems Voyager-DE STR-H equipped with a 337-nm nitrogen laser (3-nm pulse width). Two hundred shots were accumulated for the spectra at a 25 kV acceleration voltage in the reflector mode and calibrated using the PS standard as a linear calibration. For the MADLI-TOF MS measurement, the polymer (10 mg mL^{-1}) in THF, a matrix (dithranol, 20 mg mL^{-1}) in THF, and a cationizing agent (sodium trifluoroacetate, 10 mg mL^{-1}) in methanol were mixed in the ratio of the polymer/matrix/cationizing agent of 5 μL/25 μL/5 μL, and 1 μL, respectively, and the mixed solution was deposited on the sample holder.

Synthesis of azido-functionalized poly(styrene oxide) (PSO-N_3). *t*-Bu-P_4 (221 μL, 1.0 M solution in *n*-hexane, 221 μmol) was added to a solution of 6-azido-1-hexanol (183.1 mg, 1.7 mmol) in toluene (1.5 mL). SO (2.52 mL, 2.66 g, 22.1 mmol) was then added to the solution. After stirring for 24 h, the polymerization was quenched by the addition of a small amount of benzoic acid (50 mg). The monomer conversion (Conv.) was directly determined by the ^{1}H NMR measurement. Conv. = 93%. The polymerization mixture was purified by dialysis in methanol and dried *in vacuo* to give PSO-N_3 as a colorless glassy liquid (2.60 g, 90%). PSO-N_3: $M_{n(NMR)}$, 2,200 g mol^{-1}; $M_{n(SEC)}$, 2,200 g mol^{-1}; M_w/M_n, 1.06. Using the same polymerization procedure, the preparation of PSO_2-N_3 and PSO_3-N_3 was also achieved using **2** and **3** as initiators to give glassy solid products with yields of 90% (1.85 g) and 86% (1.72 g), respectively. PSO_2-N_3: Conv., 99%; $M_{n(NMR)}$, 4,200 g mol^{-1}; $M_{n(SEC)}$, 3,500 g mol^{-1}; M_w/M_n, 1.04. PSO_3-N_3: Conv., > 99%; $M_{n(NMR)}$, 6,400 g mol^{-1}; $M_{n(SEC)}$, 4,800 g mol^{-1}; M_w/M_n, 1.03.

Preparation of 2-[1-poly(styrene oxide)-1*H*-1,2,3-triazol-4-yl]pyridine (PSO-tapy). PSO-N_3 ($M_{n(NMR)}$, 2,200; 0.44 g, 0.2 mmol) and CuBr (22.9 mg, 1.6 mmol) were placed in a Schlenk tube. The tube was evacuated and backfilled with argon three times. A degassed mixture of 2-ethynylpyridine (60.6 μL, 0.6 mmol), PMDETA (41.8 μL, 0.2 mmol), and THF (10.0 mL) was then added. The reaction mixture was stirred at 90 °C for 24 h. After the removal of the solvent under reduced pressure, the residue was diluted in CH_2Cl_2, and washed with distilled water. The organic layer was dried over Na_2SO_4. CH_2Cl_2 was then evaporated under reduced pressure to give PSO-tapy as a light yellow viscous liquid (0.43 g, 93%). PSO-tapy: $M_{n(NMR)}$, 2,300 g mol^{-1}; $M_{n(SEC)}$, 2,000 g mol^{-1}; M_w/M_n, 1.06. Similarly, 2-[1-PSO_2-1*H*-1,2,3-triazol-4-yl]pyridine (PSO_2-tapy) and 2-[1-PSO_3-1*H*-1,2,3-triazol-4-yl]pyridine (PSO_3-tapy) were prepared by click reactions with excess 2-ethynylpyridine to afford PSO_2-tapy (192.4 mg) and PSO_3-tapy (293.2 mg) with high yields of 90% and 90%, respectively. PSO_2-tapy: $M_{n(NMR)}$, 4,500 g mol^{-1}; $M_{n(SEC)}$, 3,600 g mol^{-1}; M_w/M_n, 1.04. PSO_3-tapy: $M_{n(NMR)}$, 6,600 g mol^{-1}; $M_{n(SEC)}$, 4,900 g mol^{-1}; M_w/M_n, 1.03.

Preparation of 2,6-bis[1-poly(styrene oxide)-1*H*-1,2,3-triazol-4-yl]pyridine ($(PSO)_2$-bitapy). PSO-N_3 ($M_{n(NMR)}$, 2,200; 1.1 g, 0.5 mmol) and Cu(I)Br (71.7 mg, 0.5 mmol) were placed in a Schlenk tube. The tube was evacuated and backfilled with argon three times. A degassed mixture of 2,6-diethynylpyridine (31.8 mg, 0.25 mmol), PMDETA (104.4 μL, 0.5 mmol), and THF (10.0 mL) was then added. The reaction mixture was stirred at 90 °C for 24 h. After the removal of the solvent under reduced pressure, the residue was diluted in CH_2Cl_2, and washed with distilled water. The organic layer was dried over Na_2SO_4. CH_2Cl_2 was then evaporated under reduced pressure to give $(PSO)_2$-bitapy as a light yellow solid (0.93 g, 82%). PSO_2-bitapy: $M_{n(NMR)}$, 4,900 g mol^{-1}; $M_{n(SEC)}$, 4,400 g mol^{-1}; M_w/M_n, 1.03. Similarly, 2,6-bis[1-PSO_2-1*H*-1,2,3-triazol-4-yl]pyridine ($(PSO_2)_2$-bitapy) and 2,6-bis[1-PSO_3-1*H*-1,2,3-triazol-4-yl]pyridine ($(PSO_3)_2$-bitapy) were prepared by click reactions with stoichiometric 2-ethynylpyridine to afford $(PSO_2)_2$-bitapy (307.4 mg) and $(PSO_3)_2$-bitapy (493.8 mg) with moderate yields of 72% and 76%, respectively. $(PSO_2)_2$-bitapy: $M_{n(NMR)}$, 9,000 g mol^{-1}; $M_{n(SEC)}$, 6,600 g mol^{-1}; M_w/M_n, 1.03. $(PSO_3)_2$-bitapy: $M_{n(NMR)}$, 13,700 g mol^{-1}; $M_{n(SEC)}$, 8,900 g mol^{-1}; M_w/M_n, 1.03.

Preparation of 2-ethynyl-6-(1-PSO_2-1*H*-1,2,3-triazol-4-yl)pyridine (PSO_2-etapy). Cu(I)Br (7.2 mg, 0.05 mmol) was added to a single-neck 100-mL flask capped with a rubber plug under an argon atmosphere. A degassed mixture of PSO_2-N_3 ($M_{n(NMR)}$, 4,200; 210 mg, 0.05 mmol), 2,6-diethynylpyridine (12.7 mg, 0.1 mmol), PMDETA (10.4 μL, 0.05 mmol), and THF (10.0 mL) was added to the 100-mL flask. After the reaction mixture was stirred at room temperature for 48 h, the reaction mixture was diluted with THF, then passed through a short SiO_2 column. The solvent was removed under reduced pressure. The residue was purified by dialysis in methanol and dried *in vacuo* to give PSO_2-etapy as a light yellow solid (197.5 mg, 91%). PSO_2-etapy: $M_{n(NMR)}$, 4,600 g mol^{-1}; $M_{n(SEC)}$, 3,600 g mol^{-1}; M_w/M_n, 1.04.

Preparation of 2-(1-PSO_2-1*H*-1,2,3-triazol-4-yl)-6-[1-PSO_3-1*H*-1,2,3-triazol-4-yl]pyridine (PSO_2-bitapy-PSO_3). Cu(I)Br (3.6 mg, 25 μmol) was added to a single-neck 100-mL flask capped with a rubber plug under an argon atmosphere. A degassed mixture of PSO_2-etapy ($M_{n(NMR)}$, 4,600; 115 mg, 25 μmol), PSO_3-N_3 ($M_{n(NMR)}$, 6,400; 160 mg, 25 μmol), PMDETA (5.2 μL, 25 μmol), and THF (10.0 mL) was added to the 100-mL flask. After stirring at room temperature for 48 h, the reaction mixture was diluted with THF and passed through a short SiO_2 column. The residue was purified by preparative SEC using $CHCl_3$ as the eluent followed by dialysis in methanol to obtain PSO_2-bitapy-PSO_3 as a light yellow solid (193.9 mg, 71%). PSO_2-bitapy-PSO_3: $M_{n(NMR)}$, 11,300 g mol^{-1}; $M_{n(SEC)}$, 8,100 g mol^{-1}; M_w/M_n, 1.04.

Preparation of Ru(PSO-tapy)$(DMSO)_2Cl_2$. To a 10-mL needle flask containing $CHCl_3$ (1.0 mL), $Ru(DMSO)_4Cl_2$ (24.2 mg, 50 μmol) and PSO-tapy ($M_{n(NMR)}$, 2,300 g mol^{-1}; 57.5 mg, 25 μmol) were added. The mixture was degassed by three freeze-pump-thaw cycles. The yellow-green mixture was then heated at 65 °C for 24 h.

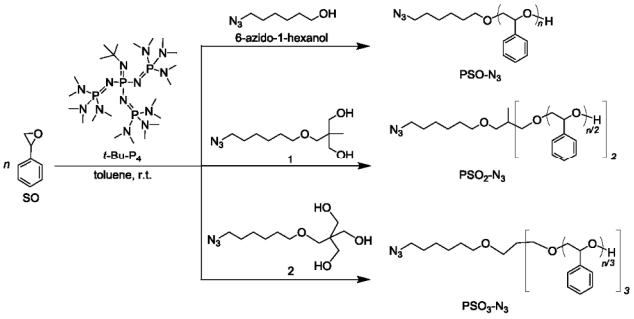
After cooling to room temperature, the solvent was removed. The crude product was further purified by preparative SEC using $CHCl_3$ as the eluent, followed by dialysis in methanol to give Ru(PSO-tapy)$(DMSO)_2Cl_2$ as a yellow solid (53.7 mg, 83%). Using the same method, the Ru(II) *mono*-complexes, Ru(PSO_2-tapy)$(DMSO)_2Cl_2$ (96.4 mg, 80%), Ru(PSO_3-tapy)$(DMSO)_2Cl_2$ (136.6 mg, 79%), Ru(PSO_2-bitapy)$(DMSO)Cl_2$ (213.5 mg, 82%), Ru($(PSO_2)_2$-bitapy)$(DMSO)Cl_2$ (175.3 mg, 75%), and Ru($(PSO_3)_2$-bitapy)$(DMSO)Cl_2$ (268.8 mg, 77%) were also prepared in moderate to high yields.

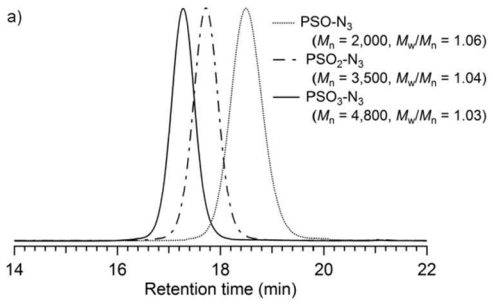
Preparation of [Ru(PSO-tapy)$_3$](SbF$_6$)$_2$. A mixture of Ru(PSO-tapy)$(DMSO)_2Cl_2$ (52 mg, 0.02 mmol) and $AgSbF_6$ (34.4 mg, 0.1 mmol) in acetone (2.0 mL) was heated in a 10-mL needle flask at 65 °C for 12 h. Followed by filtration of the precipitated AgCl, the solvent was removed to give [Ru(PS-tapy)$(DMSO)_2(COMe_2)_2](SbF_6)_2$ as a yellow solid. The intermediate [Ru(PS-tapy)$(DMSO)_2(COMe_2)_2](SbF_6)_2$ was then dissolved in acetone (2.0 mL) and added to a 10-mL needle flask containing a two molar ratio of PSO-tapy ($M_{n(NMR)}$, 2,300 g mol^{-1}; 92.0 mg, 0.04 mmol). The reaction mixture was heated at 65 °C for 24 h. After cooling to room temperature, the reaction mixture was filtered, then purified by preparative SEC using $CHCl_3$ as the eluent to give the 3-arm star-shaped PSO [Ru(PSO-tapy)$_3$]$(SbF_6)_2$ as a yellow solid (109.5 mg, 78%). [Ru(PSO-tapy)$_3$]$(SbF_6)_2$: $M_{n(SEC)}$, 5,300 g mol^{-1}; M_w/M_n, 1.12. The preparations of 4- to 12-armed star-shaped PSO Ru(II) complexes were also achieved using the same method; [Ru($(PSO)_2$-bitapy)$_2](SbF_6)_2$ (159.4 mg, 81%; $M_{n(SEC)}$, 7,700 g mol^{-1}; M_w/M_n, 1.14), [Ru($(PSO)_2$-bitapy)(PSO_3-tapy)(DMSO)]$(SbF_6)_2$ (177.0 mg, 76%; $M_{n(SEC)}$, 8,000 g mol^{-1}; M_w/M_n, 1.12), [Ru(PSO_2-tapy)$_3](SbF_6)_2$ (220.6 mg, 81%; $M_{n(SEC)}$, 10,000 g mol^{-1}; M_w/M_n, 1.19), [Ru($(PSO_2)_2$-bitapy)(PSO_3-tapy)(DMSO)]$(SbF_6)_2$ (243.0 mg, 77%; $M_{n(SEC)}$, 12,000 g mol^{-1}; M_w/M_n, 1.14), [Ru($(PSO_2)_2$-bitapy)$_2](SbF_6)_2$ (129.8 mg, 72%; $M_{n(SEC)}$, 12,000 g mol^{-1}; M_w/M_n, 1.14), [Ru(PSO_3-tapy)$_3](SbF_6)_2$ (235.6 mg, 59%; $M_{n(SEC)}$, 13,400 g mol^{-1}; M_w/M_n, 1.18), [Ru($(PSO_2)_2$-bitapy)($(PSO_3)_2$-bitapy)]$(SbF_6)_2$ (97.1 mg, 43%; $M_{n(SEC)}$, 14,500 g mol^{-1}; M_w/M_n, 1.16), [Ru($(PSO_3)_2$-bitapy)(PSO_2-bitapy-PSO_3)]$(SbF_6)_2$ (96.4 mg, 38%; $M_{n(SEC)}$, 15,600 g mol^{-1}; M_w/M_n, 1.12), and [Ru($(PSO_3)_2$-bitapy)$_2](SbF_6)_2$ (85.8 mg, 31%; $M_{n(SEC)}$, 16,100 g mol^{-1}; M_w/M_n, 1.19).

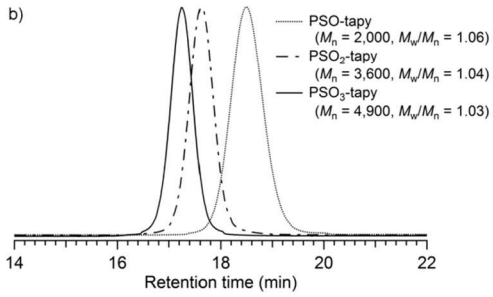
Results and discussion

Synthesis of azido-functionalized PSO$_n$-N$_3$ (n = 1, 2, or 3). Azido-functionalized poly(styrene oxide)s (PSO-N_3, PSO_2-N_3, and PSO_3-N_3) were synthesized by the ring-opening polymerizations of styrene oxide (SO) in toluene using the phosphazene base of *t*-Bu-P_4 as the catalyst and 6-azido-1-hexanol, **1**, and **2** as the initiators (Scheme 2), as described in our previous report.[27] Table 1 summarizes the synthetic results of the PSO$_n$-N$_3$s (n = 1, 2, or 3). The yields of the PSO$_n$-N$_3$s were reasonable in the range of 86 - 90%. The number-average molecular weights ($M_{n(SEC)}$) of PSO-N_3, PSO_2-N_3, and PSO_3-N_3 estimated by the SEC measurements in $CHCl_3$ were 1,900, 3,800, and 5,800 g mol^{-1}, and were 2,000, 3,500, and 4,800 g mol^{-1} in THF, respectively (Figure 1 (a)). The SEC traces measured in either $CHCl_3$ or THF showed uinmodal and narrow molecular weight distributions ($M_w/M_n \leq 1.16$). In order to maintain a uniform arm length in the homoleptic star PSO Ru(II) complexes, the degree of polymerization (DP) of each arm in PSO$_n$-N$_3$s was well controlled. The calculated values of the repeating SO unit were 17.5 (nearly 17 × 1) for PSO-N_3, 33.3 (nearly 17 × 2) for PSO_2-N_3, and 51.5 (nearly 17 × 3) for PSO_3-N_3, which indicated that each arm in the PSO$_n$-N$_3$s had the same average length.

Scheme 2. Synthesis of tapy- and bitapy-functionalized polymer ligands by click reactions of PSO$_n$-N$_3$ (n = 1, 2, or 3) with 2-ethynylpridine or 2,6-diethynylpridine.







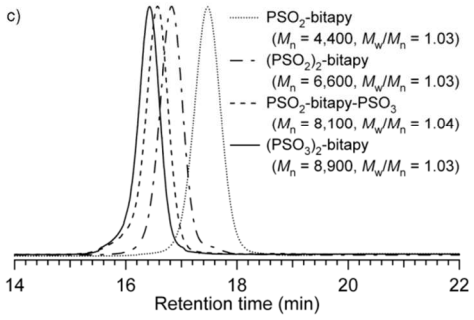


Figure 1. SEC traces of a) PSO_n-N_3s, b) PSO_n-tapys, and c) $(PSO_n)_2$-bitapys and PSO_2-bitapy-PSO_3, determined in THF at the flow rate of 1.0 mL min^{-1}, n = 1, 2, or 3.

Table 1. Synthesis of azido-functionalized PSO_n-N_3 (n = 1, 2, or 3).

run	Polymers	Conv. (%) [a]	Yield (%)	$M_{n(NMR)}$ (DP) [a]	$M_{n(SEC)}$ [b]	M_w/M_n [b]	$M_{n(SEC)}$ [c]	M_w/M_n [c]
1	PSO-N_3	93	90	2,200 (17.5)	1,900	1.14	2,000	1.06
2	PSO_2-N_3	99	90	4,200 (33.3)	3,800	1.16	3,500	1.04 [c]
3	PSO_3-N_3	> 99	86	6,400 (51.5)	5,800	1.12	4,800	1.03 [c]

[a] Determined by ^{1}H NMR in $CDCl_3$. [b] Determined by SEC in $CHCl_3$ using PS standards. [c] Determined by SEC in THF using PS standards.

The structural information of PSO_n-N_3s was investigated by ^{1}H NMR measurements. As a typical analysis for PSO-N_3 (Figure 2 (a)), the proton signals of "a" neighboring the azido group and of "b-e" due to the initiator residue were clearly observed around 3.21 ppm and in the range of 1.19-1.62 ppm, respectively. Similarly, the proton signals of "b-e" due to the residues of initiators **1** and **2** were also clearly observed in the range of 1.20-1.60 ppm for PSO_2-N_3 and 1.15-1.60 ppm for PSO_3-N_3 in Figures S1 (a) and S2 (a), respectively. In addition, the successful introduction of the azido group to PSO_n-N_3s was verified by the FT-IR measurements. For instance, the characteristic stretching of azido group around 2100 cm^{-1} in PSO-N_3 was clearly observed in Figure 3 (a). The same findings were also correspondingly observed for PSO_2-N_3 and PSO_3-N_3, as shown in Figures S4 (a) and S5 (a), respectively. These results, to an extent, suggested that the azido groups were introduced into PSO, PSO_2, and PSO_3 using the azido-functionalized initiators.

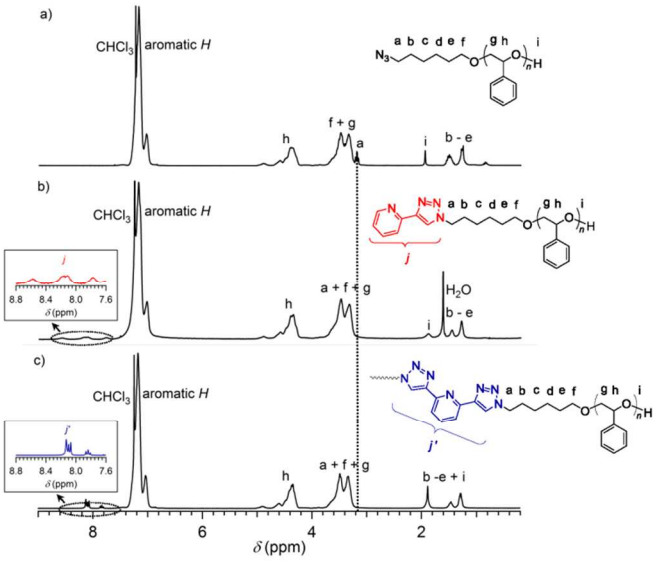


Figure 2. ^{1}H NMR spectra of a) PSO-N_3, b) PSO-tapy, and c) $(PSO)_2$-bitapy determined in $CDCl_3$.

In order to provide a much deeper insight into the polymer structures of PSO_n-N_3s, MALDI-TOF MS measurements were further carried out. As a typical example, the MALDI-TOF MS spectrum of PSO-N_3 showed a sub (●) and main series (○) of peaks in Figure 4 (a). The peak interval between the main/sub series was 120.1, which is identical to the molecular weight (M.W.) of SO. Additionally, a certain peak value of 1968.2 (m/z) agrees well with the theoretical isotopic M.W. of the sodium-cationized PSO (DP = 15) bearing an azido end group ($C_{126}H_{133}O_{16}N_3Na$: 1967.96). The main series with a stronger intensity were due to those of the denitrogenized products, which were generated during the ionization process. No other impurities were observed in the MALDI-TOF MS spectrum. These results lead to the conclusion that the azido group was quantitatively introduced to the PSO chain end. The same results were also obtained for PSO_2-N_3 and PSO_3-N_3, as supported by their MALDI-TOF MS measurements in Figures S6 (a) and S7 (a).

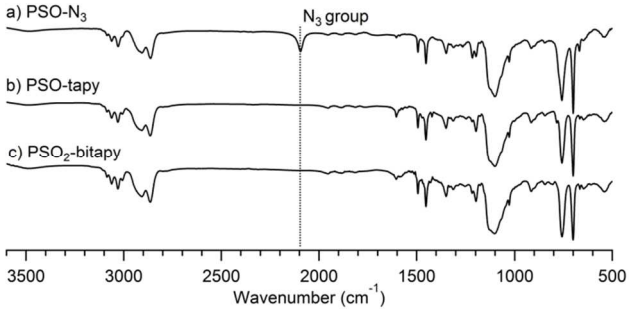


Figure 3. IR spectra of a) PSO-N_3, b) PSO-tapy, and c) $(PSO)_2$-bitapy.

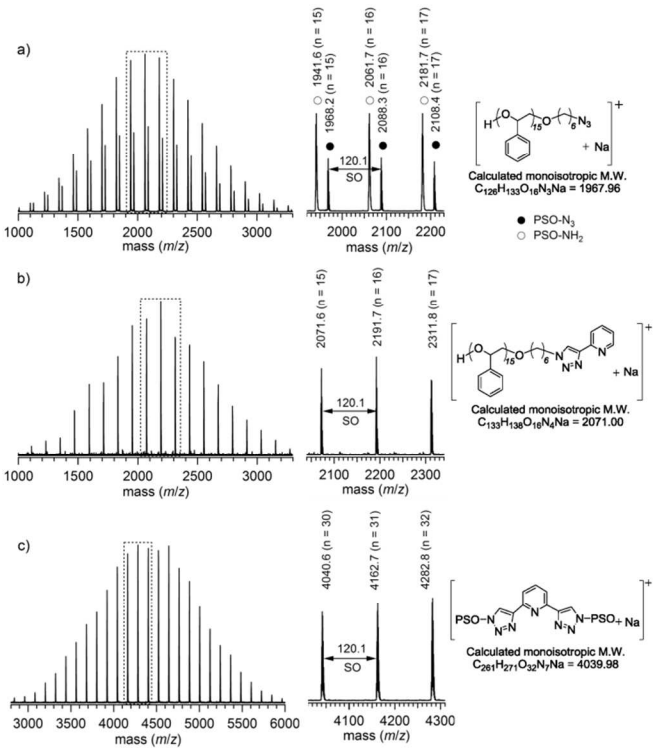


Figure 4. MALDI-TOF MS spectra (reflector mode) of a) PSO-N_3, b) PSO-tapy, and c) $(PSO)_2$-bitapy.

Scheme 3. Synthesis of tapy- and bitapy-functionalized polymer ligands by click reactions of PSO_n-N_3 (n = 1, 2, or 3) with 2-ethynylpridine or 2,6-diethynylpridine.

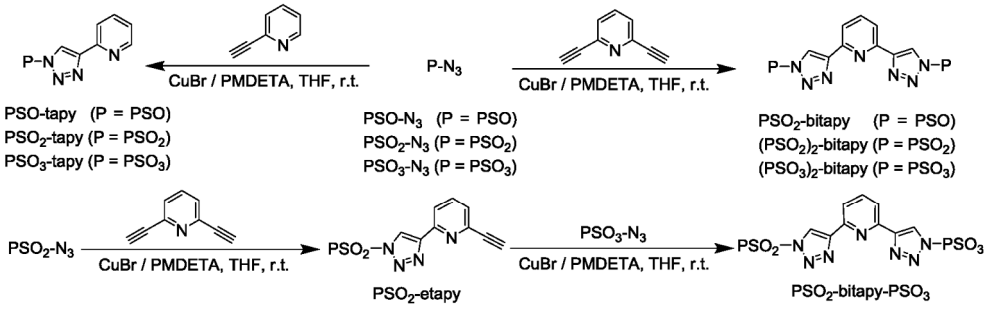


Table 2. Synthesis of polymer-substituted tapy and bitapy macroligands.

run	Polymers	Yield (%)	$M_{n(NMR)}$ (DP) [a]	$M_{n(SEC)}$ [b]	M_w/M_n [b]
4	PSO-tapy	93	2,300 (17.7)	2,000	1.06
5	PSO_2-tapy	90	4,500 (35.5)	3,600	1.04
6	PSO_2-etapy	91	4,600 (35.7)	3,600	1.04
7	PSO_2-bitapy	82	4,900 (37.4)	4,400	1.03
8	PSO_3-tapy	90	6,600 (52.8)	4,900	1.03
9	$(PSO_2)_2$-bitapy	72	9,000 (70.3)	6,600	1.03
10	PSO_2-bitapy-PSO_3	71	11,300 (88.9)	8,100	1.04
11	$(PSO_3)_2$-bitapy	76	13,700 (108.6)	8,900	1.03

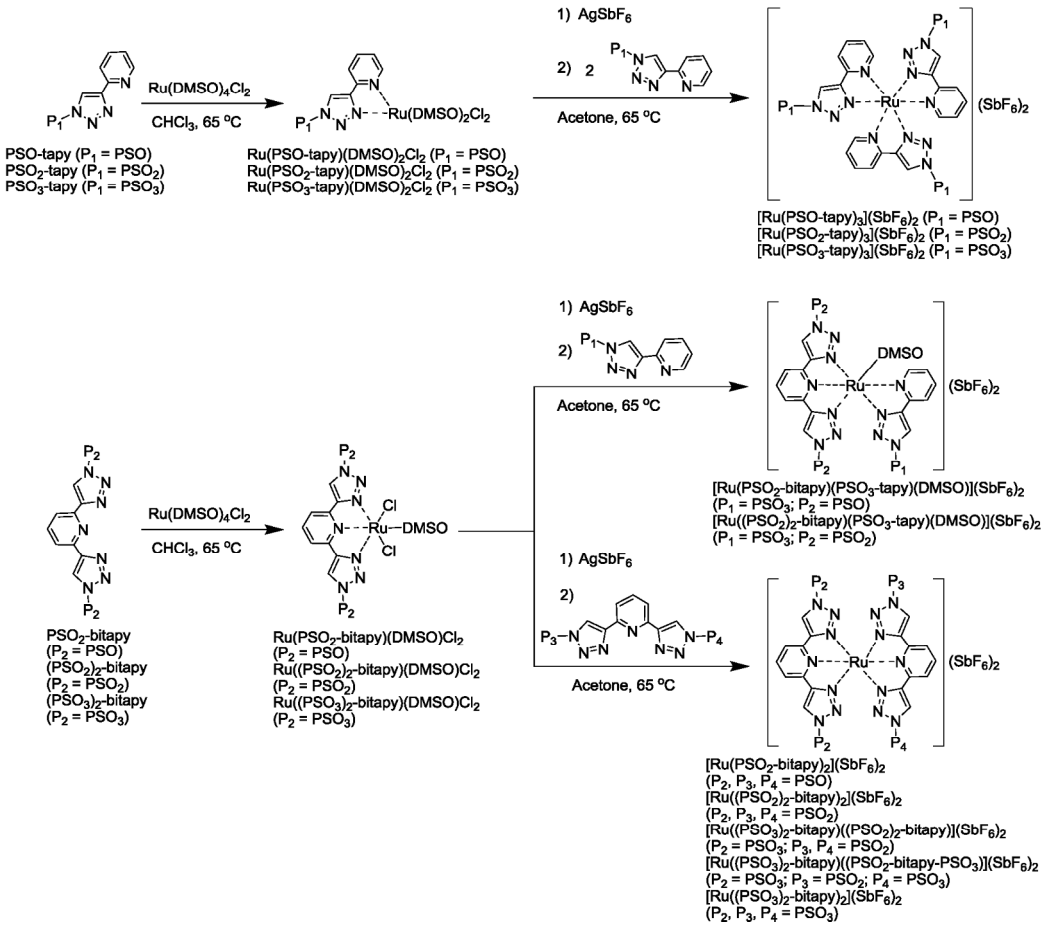
[a] Determined by ^{1}H NMR in $CDCl_3$. [b] Determined by SEC in THF using PS standards.

Synthesis of polymer-substituted tapy and bitapy macroligands. The polymer-functionalized tapy and bitapy macroligands were respectively synthesized by the click reactions of PSO_n-N_3s with 2-ethynylpyridine or 2,6-diethynylpyridine, as illustrated in Scheme 3. Table 2 summarizes the synthetic results. For synthesizing the PSO_n-tapys, the PSO_n-N_3s were reacted with 2-ethynylpyridine to afford 2-[1-PSO-1,2,3-triazol-4-yl]pyridine (PSO-tapy), 2-[1-PSO_2-1,2,3-triazol-4-yl]pyridine (PSO_2-tapy), and 2-[1-PSO_3-1,2,3-triazol-4-yl]pyridine (PSO_3-tapy) in the good yields of 93, 90, and 90%, respectively. After the click reactions, the molecular weight measurements for PSO-tapy, PSO_2-tapy, and PSO_3-tapy were carried out by SEC measurements in THF, which, as expected, showed no obvious change when compared to those of their parent PSO_n-N_3s (Figure 1 (b)). In the ^{1}H NMR spectra of the PSO_n-tapys (Figures 2 (b), S2 (b), and S3 (b)), the novel proton signals due to the tapy group were observed in the range of 7.62-8.80 ppm along with those from the PSO chains. Additionally, the signals of the methylene protons neighboring the azido group in PSO-N_3 (3.14-3.24 ppm) completely disappeared after the click reaction. In the FT-IR measurements, it was observed that the characteristic stretching signal of the azido group around 2100 cm^{-1} in the PSO_n-N_3s completely disappeared after the click reactions with 2-ethynylpyridine (see Figures 3 (b), S4 (b), and S5 (b)), respectively). The successful syntheses of PSO_n-tapys were further proven by their MALDI-TOF MS measurements. For instance, only one series of peaks with the peak interval of 120.1 (M.W. of SO) was observed for PSO-tapy in Figure 4 (b). The peak at 2071.6 (m/z) is identical to the theoretical isotopic M.W. of the sodium-cationized tapy end-functionalized PSO when its DP is 15 ($C_{133}H_{138}O_{16}N_4Na$: 2070.00). For the PSO_2-tapy and PSO_3-tapy, the MALDI-TOF MS measurements also afforded their perfect structural consistency as depicted in Figures S6 (b) and S7 (b). These investigations indicated that the tapy moiety was quantitatively introduced into PSO_ns.

On the other hand, the synthesis of the structurally symmetrical 2,6-bis[1-PSO_n-1,2,3-triazol-4-yl]pyridines, $(PSO_n)_2$-bitapy (n = 1, 2, or 3), was achieved by reacting the PSO_n-N_3s with 2,6-diethynylpyridine. The click reaction between PSO_n-N_3 and 2,6-diethynylpyridine proceeded with the initial molar ratio of $[PSO_n\text{-}N_3]_0/[2,6\text{-diethynylpyridine}]_0 = 2.0$, after which the SEC traces of the resulting $(PSO_n)_2$-bitapys shifted substantially to the higher molecular weight region in comparison to their precursors, PSO_n-N_3s, and maintained low M_w/M_ns of 1.03 - 1.04 (Figure 1 (b)). Meanwhile, the $M_{n(NMR)}$s and DPs of the $(PSO_n)_2$-bitapys in Table 2 were almost twice those of their parent PSO_n-N_3s in Table 1. Namely, the $M_{n(NMR)}$s of $(PSO)_2$-bitapy, $(PSO_2)_2$-bitapy, and $(PSO_3)_2$-bitapy were 4,900, 9,000, and 13,700 g mol^{-1}, while those of PSO-N_3, PSO_2-N_3, and PSO_3-N_3 were 2,200, 4,200, and 6,400 g mol^{-1}, respectively. For the synthesis of the structurally asymmetrical 2-(1-PSO_2-1,2,3-triazol-4-yl)-6-[1-PSO_3-1,2,3-triazol-4-yl]pyridine (PSO_2-bitapy-PSO_3), the click reaction with 2,6-diethynylpyridine was carried out twice using two different

azido-functionalized polymers, PSO_2-N_3 and PSO_3-N_3. The click reaction between an excess amount of 2,6-diethynylpyridine and PSO_2-N_3 was first carried out to afford the 2-ethynyl-6-(1-PSO_2-1,2,3-triazol-4-yl)pyridine (PSO_2-etapy) in the yield of 91%, and

Scheme 3. Synthesis of star PSO Ru(II) complexes by stepwise chelating of polymer-substituted tapy or bitapy ligands with $Ru(DMSO)_4Cl_2$.



the PSO_2-etapy was then further reacted with PSO_3-N_3 to produce PSO_2-bitapy-PSO_3 with the yield of 71%. Similar to the PSO_n-tapys, all the characteristics concerning the structural consistency of the $(PSO_n)_2$-bitapys and PSO_2-bitapy-PSO_3 were followed by SEC, ^{1}H NMR (Figures S1-3), FT-IR (Figures S4-5), and MALDI-TOF MS (Figures S6-7) measurements.

Synthesis of multi-arm star PSO Ru(II) complexes. In this study, all the multi-arm star PSO Ru(II) complexes were synthesized by a stepwise chelating method as reported in our previous study (Scheme 4), i.e., a PSO-substituted tapy or bitapy ligand was first *mono*-chelated with excess $Ru(II)(DMSO)_4Cl_2$ to afford a stable Ru(II) *mono*-complex. Followed by purification, the Ru(II) *mono*-complex was further coordinated with another PSO-substituted tapy or bitapy ligand to produce the desired multi-arm star PSO Ru(II) complexes. After purifying by preparative SEC, the multi-arm star PSO Ru(II) complexes were obtained. During the stepwise chelating reactions, the PSO-substituted tapy/bitapy macroligands could be the same or different. When they were the same, we obtained the 3-, 4-, 6-, 8-, 9-, and 12-armed star-shaped PSO Ru(II) complexes. Otherwise, we obtained the 5-, 7-, 10-, and 11-armed star-shaped PSO Ru(II) complexes when the macroligands used in first and second chelating steps were different. In greater detail, a PSO_n-tapy/$(PSO_n)_2$-bitapy was first reacted with excess $Ru(II)(DMSO)_4Cl_2$ (first chelating step) in chloroform at 65°C to produce a stable Ru(II) *mono*-complex, Ru(PSO_n-tapy)$(DMSO)_2Cl_2$ or Ru($(PSO_n)_2$-bitapy)$(DMSO)Cl_2$, respectively. Thereafter, the isolated Ru(PSO_n-tapy)$(DMSO)_2Cl_2$ or Ru($(PSO_n)_2$-bitapy)$(DMSO)Cl_2$ was further chelated with a PSO_n-tapy or $(PSO_n)_2$-bitapy (second chelating step) to give the desired multi-arm star PSO Ru(II) complexes, i.e., 3-, 6-, and 9-arm star PSO Ru(II) complexes, $[Ru(PSO_n\text{-tapy})_3](SbF_6)_2$, which were prepared from their precursors (Ru(PSO_n-tapy)$(DMSO)_2Cl_2$) with PSO_n-tapy, respectively. The 4-, 8-, and 12-arm star-branched PSO Ru(II) complexes, $[Ru((PSO_n)_2\text{-bitapy})_2](SbF_6)_2$, were prepared from their precursors (Ru($(PSO_n)_2$-bitapy)$(DMSO)Cl_2$) with $(PSO_n)_2$-bitapy, respectively. Similarly, the 5-, 7-, 10-, and 11-arm star-branched PSO Ru(II) complexes, $[Ru((PSO)_2\text{-bitapy})(PSO_3\text{-tapy})(DMSO)](SbF_6)_2$, $[Ru((PSO_2)_2\text{-bitapy})(PSO_3\text{-tapy})(DMSO)](SbF_6)_2$, $[Ru((PSO_3)_2\text{-bitapy})((PSO_2)_2\text{-bitapy})](SbF_6)_2$, and $[Ru((PSO_3)_2\text{-bitapy})(PSO_2\text{-bitapy-}PSO_3)](SbF_6)_2$, were obtained by the chelating reactions of Ru($(PSO)_2$-bitapy)$(DMSO)Cl_2$, Ru($(PSO_2)_2$-bitapy)$(DMSO)Cl_2$, Ru($(PSO_3)_2$-bitapy)$(DMSO)Cl_2$, and Ru($(PSO_3)_2$-bitapy)$(DMSO)Cl_2$ with PSO_3-tapy, PSO_3-tapy, $(PSO_2)_2$-bitapy,

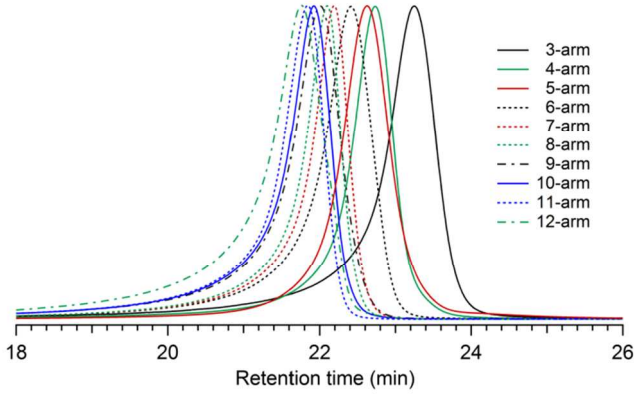
and PSO_2-bitapy-PSO_3, respectively. After removing the unreacted macroligands by preparative SEC, the pure 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10-, 11-, and 12-armed star-shaped PSO Ru(II) complexes were obtained. Table 3 summarizes the synthetic results. The $M_{n(SEC)}$s and M_w/M_ns of the 3- to 12-arm star-branched PSO Ru(II) complexes determined by SEC in $CHCl_3$ were in the range of 5,300~16,100 g mol^{-1} and 1.12~1.19, respectively. The SEC traces of the multi-arm PSO Ru(II) complexes in Figure 5 exhibited a tailing effect in the high molecular weight range. We assign the emergence of this effect to the possible aggregation of the multi-arm PSO Ru(II) complexes due to the hydrophilic interactions mostly caused by the cationic Ru(II) cores when low polarity $CHCl_3$ was used as the eluent solvent. It is rather clear that, with an increase in the arm numbers, the SEC trace obviously shifted to the higher M.W. region, which provided direct evidence that the multi-arm PSO Ru(II) complexes were successfully synthesized though we lacked the absolute molecular weight data from the SEC-MALS measurements.

Table 3. Synthesis of 3- to 12-arm star PSO Ru(II) complexes.

run	star PSO Ru(II) complexes	Yield (%)	$M_{n(theo.)}$ [a]	$M_{n(SEC)}$ [b]	M_w/M_n [b]
12	$[Ru(PSO\text{-}tapy)_3](SbF_6)_2$	78	7,500	5,300	1.12
13	$[Ru(PSO_2\text{-}bitapy)_2](SbF_6)_2$	81	10,400	7,700	1.14
14	$[Ru(PSO_2\text{-}bitapy)(PSO_3\text{-}tapy)(DMSO)](SbF_6)_2$	76	12,100	8,000	1.12
15	$[Ru(PSO_2\text{-}tapy)_3](SbF_6)_2$	81	14,100	10,000	1.19
16	$[Ru((PSO_2)_2\text{-}bitapy)(PSO_3\text{-}tapy)(DMSO)](SbF_6)_2$	77	16,200	12,000	1.14
17	$[Ru((PSO_2)_2\text{-}bitapy)_2](SbF_6)_2$	72	18,600	12,800	1.13
18	$[Ru(PSO_3\text{-}tapy)_3](SbF_6)_2$	59	20,400	13,400	1.18
19	$[Ru((PSO_2)_2\text{-}bitapy)((PSO_3)_2\text{-}bitapy)](SbF_6)_2$	43	23,300	14,500	1.16
20	$[Ru(PSO_2\text{-}bitapy\text{-}PSO_3)((PSO_3)_2\text{-}bitapy)](SbF_6)_2$	38	25,600	15,600	1.12
21	$[Ru((PSO_3)_2\text{-}bitapy)_2](SbF_6)_2$	31	28,000	16,100	1.19

[a] Calculated from (M.W. of macroligands) + (M.W. of Ru) + (2 × M.W. of SbF_6). [b] Determined by SEC in $CHCl_3$ using PS standards.

Figure 5. SEC traces of 3- to 12-arm star-shaped PSO Ru(II) complexes determined in $CHCl_3$ at the flow rate of 0.8 mL min^{-1}.



Conclusions

We succeeded in the precise synthesis of 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10-, 11-, and 12-armed star-shaped PSOs containing a chelating Ru(II) core by the click-to-chelate approach, whose synthesis can be only slightly realized by the direct living ring-opening polymerization of styrene oxide using multihydroxyl-functionalized initiators due to their slight solubility in solvent. The PSO_ns with a uniform arm length in the star-branched PSO Ru(II) complexes were non-covalently held by the central Ru(II)/tapy or Ru(II)/bitapy chelating interaction. In this study, the PSO_n-tapy and PSO_m-bitapy-PSO_n (m, n = 1, 2, or 3) macroligands can be more conveniently prepared by the simple click reactions of PSO_n-N_3 with ethynylpyridines than the previously reported polymer-substituted bipyridine and terpyridine ligands. In conclusion, the click-to-chelate approach provided a powerful tool for the preparation of the homoleptic multi-arm polymer Ru(II) complexes, which produced well-defined star polymers with precisely controlled architectures. More detailed investigations into other interesting polymer structures are now currently underway.

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Notes and references

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† Electronic Supplementary Information (ESI) available: ^{1}H NMR, IR, and MALDI-TOF MS data are available. See DOI: 10.1039/b000000x/

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Synthesis of 3-, 4-, 5-, 6-, 7-, 8-, 9-, 10-, 11-, and 12-Armed Star-shaped Poly(styrene oxide) Ru(II) Complexes by Click-to-Chelate Approach

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The convenient preparation of multi-arm star-shaped poly(styrene oxide) Ru(II) complexes was achieved by a click-to-chelate approach which combines click reactions and stepwise chelating reactions.