Syntheses of 3-Arm and 4-Arm Star-Branched Polystyrene Ru(II) Complexes by the Click-to-Chelate Approach

CHUNHONG ZHANG,[1] XIANDE SHEN,[1] RYOSUKE SAKAI,[2] MICHAEL GOTTSCHALDT,[3] ULRICH S. SCHUBERT,[3] SHIHO HIROHARA,[4] MASAO TANIHARA,[4] SHIGENOBU YANO,[4] MAKOTO OBATA,[5] NAO XIAO,[6] TOSHIFUMI SATOH,[6] TOYOJI KAKUCHI[6]

[1]College of Materials Science and Chemical Engineering, Harbin Engineering University, Harbin 150001, China

[2]Department of Materials Chemistry, Asahikawa National College of Technology, Asahikawa 071-8142, Japan

[3]Laboratory for Organic and Macromolecular Chemistry, Friedrich-Schiller-University Jena, Jena 07743, Germany

[4]Graduate School of Materials Science, Nara Institute of Science and Technology, Nara 630-0101, Japan

[5]Interdisciplinary Graduate School of Medicine and Engineering, University of Yamanashi, 4-4-37 Takeda, Kofu 400-8510, Japan

[6]Division of Biotechnology and Macromolecular Chemistry, Graduate School of Engineering, Hokkaido University, Sapporo 060-8628, Japan

Received 9 September 2010; accepted 29 October 2010
DOI: 10.1002/pola.24487
Published online 3 December 2010 in Wiley Online Library (wileyonlinelibrary.com).

ABSTRACT: Metal template synthesis is a useful methodology to make sophisticated macromolecular architectures because of the variety of metal ion coordination. To use metal template methodology, chelating functionalities should be introduced to macromolecules before complexation. In this article, we demonstrate the click-to-chelate approach to install chelating functionality to polystyrene (PS) and complexation with Ru(II) ions to form 3-arm and 4-arm star-branched PS Ru(II) complexes. Azide-terminated PS (PS-N_3) was readily prepared by atom transfer radical polymerization using 1-bromoethylbenzene as an initiator followed by substitution of bromine by an azide group. The Cu(I)-catalyzed 1,3-dipolar cycloaddition of PS-N_3 with 2-ethynylpyridine or 2,6-diethynylpyridine affords 2-(1*H*-1,2,3-triazol-4-yl)pyridine (PS-tapy) or 2,6-bis(1*H*-1,2,3-triazol-4-yl)pyridine (PS-bitapy) ligands bearing one or two PS chains at the first-position of the triazole rings. Ru(II) complexes of PS-tapy and PS-bitapy were prepared by conventional procedure. The number-averaged molecular weights (M_ns) of these complexes were determined to be 6740 and 10,400, respectively, by size exclusion chromatography using PS standards. These M_n values indicated the formation of 3-arm and 4-arm star-branched PS Ru(II) complexes $[Ru(PS\text{-}tapy)_3](PF_6)_2$ and $[Ru(PS\text{-}bitapy)_2](PF_6)_2$ on the basis of the M_n values of PS-tapy (2090) and PS-bitapy (4970). The structures of these complexes were also confirmed by UV–vis spectroscopy and X-ray crystallography of the Ru(II) complexes $[Ru(Bn\text{-}tapy)_3](PF_6)_2$ and $[Ru(Bn\text{-}bitapy)_2](PF_6)_2$, which bear a benzyl group instead of a PS chain. © 2010 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 49: 746–753, 2011

KEYWORDS: atom transfer radical polymerization (ATRP); click chemistry; Ru(II) complex; star-branched polystyrene; star polymer

INTRODUCTION Metal template synthesis is a powerful methodology to prepare macromolecules with sophisticated architectures due to the large coordination numbers, variety of coordination geometries, and liability and redox activity of metal ions.[1–3] To use metal ions to form certain architectures, chelating functionalities, for example, polypyridyl groups, polyamines, and diketones, must be incorporated into macromolecules at a suitable position. Macromolecular ligands are then subjected to complexation with certain metal ions to form the certain architecture spontaneously.

Oligopyridine functionalities including heteropolycyclic compounds such as phenanthroline are the most widely used chelating motif for this purpose.[4] There are two methods to install a chelating functionality on a macromolecule: one is the use of an initiator bearing chelating moieties, and the other is the postfunctionalization of macromolecules with chelating molecules. Fraser and coworkers[5–7] extensively used the first approach to form (mikto-arm) star polymers. They used an atom transfer radical polymerization (ATRP) initiator (e.g., halomethyl group and 2-bromopropionate) covalently bonded with bipyridine at 4,4′-positions and then polymerized styrene, methyl methacrylate, and so forth, before or after complexation with Ru(II) and Fe(II). In contrast, Schubert and coworkers[8–10] used the second approach to prepare block copolymers. They used 4′-chloro-2,2′:6′,2"-terpyridine as a chelating moieties and installed them by Williamson-type reaction with hydroxy groups at the chain end of polyethylene glycol and end-functionalized polystyrene (PS) prepared by anion polymerization.

Correspondence to: M. Obata (E-mail: mobata@yamanashi.ac.jp) or T. Kakuchi (E-mail: kakuchi@poly-bm.eng.hokudai.ac.jp)

Recently, Schibli's group[11] proposed a new approach to install chelating moieties on biologically relevant molecules. They used a 1,2,3-triazole ring as a coordinating functionality; this is easily synthesized by Cu(I)-catalyzed 1,3-dipolar cycloaddition of azide to acetylene derivatives, so-called click chemistry.[12] They synthesized a metal chelating peptide by click chemistry of azide-terminated peptide (bombesin) with L-propargyl glycine, in which amino acid bearing 1,2,3-triazole acted as a tridentate chelating functionality, and they prepared Re(I) and ^{99m}Tc complexes for nuclear medicine application. They called this approach click-to-chelate.[11,13,14] Other research groups demonstrated the versatility of this approach for synthesizing metal chelating fluorophores,[15] Zn(II) ion probes,[16] ligands of Cu(I) complexes for click reaction,[17] sugar-containing metal chelaters,[18] and Ag(I) coordination polymers.[19] We demonstrated the synthesis of 2-(1-benzyl-1,2,3-triazol-4-yl)pyridine (Bn-tapy) by click chemistry of benzyl azide with 2-ethynylpyridine and preparation of the Re(I) complex.[18] X-ray-crystallography of the Re(I) complex showed clear evidence that the tapy moiety acts as a bipyridine-like chelator. This approach affords a promising method to introduce bipyridine-like functionality to macromolecules because of the excellent feasibility of azide substitution and click chemistry.

In this study, we synthesized star-branched PS Ru(II) complexes by the click-to-chelate approach. The coordination structures of macromolecular complexes were established on the basis of model Ru(II) complexes bearing benzyl groups instead of PS, whose structures were confirmed by conventional analytical techniques and X-ray crystallography.

EXPERIMENTAL

Materials and Analytical Techniques

All chemicals were analytical grade. 2-Ethynylpyridine was purchased from Sigma-Aldrich. 2,6-Diethynylpyridine and Bn-tapy were prepared according to methods in the literature.[18,20] ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded using JNM-A400II (400 MHz; JEOL, Tokyo, Japan), AVANCE 400 (400 MHz; Bruker Biospin K. K., Yokohama, Japan), and JNM-EC600 (600 MHz; JEOL) instruments. Infrared (IR) spectra were recorded on a PerkinElmer Paragon 1000 FTIR instrument. UV–vis spectra were recorded on a Jasco V-550 spectrophotometer. Electron spray ionization (ESI) and fast atom bombardment (FAB) mass spectrometry (MS) were performed using a JEOL JMS-SX102A instrument. Elemental analysis was carried out using a YANACO CHN corder MT-6 instrument. Preparative size exclusion chromatography (SEC) was performed on a JAI LC-9201 HPLC system equipped with a JAI RI-50s refractive index detector and a JAI JAIGEL-3H column (20 mmϕ × 600 mm; exclusion limit, 7 × 10^4) using tetrahydrofuran (THF) or $CHCl_3$ (flow rate, 3.5 mL min^{-1}) at 23 °C. SEC measurements in THF were performed on a Jasco GPC-900 system equipped with a Waters Ultrastyragel column (linear; 7.8 mmϕ × 300 mm; exclusion limit, 1 × 10^7) and two Shodex KF-804L columns (linear; 8 mmϕ × 300 mm; exclusion limit, 4 × 10^5) with a flow rate of 1.0 mL min^{-1} at 40 °C. SEC measurements in $CHCl_3$ were performed on a Jasco GPC-900 system equipped with two Shodex K-805L columns (linear; 8 mmϕ × 300 mm; exclusion limit, 4 × 10^6) with a flow rate of 0.8 mL min^{-1} at 40 °C. The number-average molecular weight (M_n) and polydispersity (M_w/M_n) were calculated based on a PS calibration. The matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF MS) measurements were performed using an Applied Biosystems Voyager-DE STR-H mass spectrometer with a 25-kV acceleration voltage. The positive ions were detected in the reflector mode (25 kV). A nitrogen laser (337 nm, 3 ns pulse width, 106–107 W cm^{-2}) operating at 3 Hz was used to produce the laser desorption, and 100 shots were summed. The spectrum was externally calibrated using PS standard with a linear calibration. Samples for the MALDI-TOF MS were prepared by mixing the polymer (10 mg mL^{-1}, 2 μL), the matrix (dithranol, 20 mg mL^{-1}, 100 μL), and the cationizing agent (sodium trifluoroacetate, 10 mg mL^{-1}, 4 μL) in THF.

2,6-Bis(1-benzyl-1,2,3-triazol-4-yl)pyridine

2,6-Diethynylpyridine (254.1 mg, 2.00 mmol) and benzyl azide (591.2 mg, 4.44 mmol) were dissolved in a mixture of THF and H_2O (1/1, v/v; 80 mL). Aqueous $CuSO_4$ solution (7.5 wt %, 1.27 mL) and 1 M sodium ascorbate (aq.; 0.76 mL) were added to the solution. The reaction mixture was stirred at 55 °C for 4 h. THF was removed under reduced pressure, and water (200 mL) was added to the residue. The insoluble powder was collected and dried *in vacuo*. The crude product was purified by column chromatography (silica gel, acetone) followed by recrystallization from acetone and hexane to give 2,6-bis(1-benzyl-1,2,3-triazol-4-yl)pyridine (Bn-bitapy) as colorless needle-like crystals (381.3 mg, 48%).

Anal. calcd. for $C_{23}H_{19}N_7$: C, 70.21; H, 4.87; N, 24.92. Found: C, 70.73; H, 4.99; N, 25.04. ^{1}H NMR (600 MHz, $CDCl_3$, $Si(CH_3)_4$ = 0 ppm): δ (ppm) = 8.08 (d, ^3J = 7.8 Hz, 2H, 3,5-pyridine*H*), 8.03 (s, 2H, 5-triazole*H*), 7.85 (t, ^3J = 7.8 Hz, 1H, 4-pyridine*H*), 7.39–7.35 (m, 6H, Ph*H*), 7.30–7.28 (m, 4H, Ph*H*), 5.57 (s, 4H, —CH_2—). ^{13}C{^{1}H} NMR (150 MHz, $CDCl_3$, $CDCl_3$ = 77 ppm): δ (ppm) = 149.9, 148.7, 137.7, 134.6, 129.1, 128.8, 128.1, 122.0, 119.4, 54.3.

[Ru(Bn-tapy)$_3$](PF$_6$)$_2$

$RuCl_3 \cdot nH_2O$ (67.4 mg, 0.33 mmol for n = 0), Bn-tapy (235.3 mg, 1.0 mmol), and *N*,*N*-dimethylformamide (DMF; 4 mL) were placed in a 10-mL flask. The mixture was heated at 145 °C for 3 h. The mixture was concentrated under reduced pressure, and saturated aqueous solution of $NaPF_6$ was added to the residue. The resulting orange powder was collected by filtration. The powder was dissolved in CH_3CN, and the insoluble part was removed by filtration. The filtrate was concentrated under reduced pressure. The residue was purified by Sephadex LH-20 using a mixture of $CHCl_3$ and CH_3OH (1/1, v/v) as an eluent to give a yellow powder (88.5 mg, 0.0805 mmol, 24%).

Anal. calcd. for $C_{42}H_{36}N_{12}F_{12}P_2Ru \cdot H_2O$: C, 45.13; H, 3.43; N, 15.04. Found: C, 45.14; H, 3.35; N, 15.17. ESI-MS: m/z for $C_{42}H_{36}N_{12}F_6PRu$ ([M − PF_6]$^+$) calcd. 954.8, found 955.1. ^{1}H

NMR (600 MHz, CD_3CN, CHD_2CN = 1.93 ppm): δ (ppm) = 8.66–8.62 (3H), 8.09–7.70 (9H), 7.40–7.14 (18H), 5.57–5.54 (6H, —CH_2—). $^{13}C\{^1H\}$ NMR (150 MHz, CD_3CN, CD_3CN = 1.3 ppm): δ (ppm) = 153.6, 153.3, 153.2, 152.5, 152.4, 152.2, 149.5, 149.4, 149.2, 149.1, 139.2, 139.1, 139.02, 138.98, 135.1, 135.1, 134.7, 134.7, 130.17, 130.15, 130.12, 130.1, 129.9, 129.4, 129.3, 128.9, 126.9, 126.8, 126.7, 126.4, 126.15, 126.12, 126.10, 125.8, 123.7, 123.4, 123.0, 122.9, 56.62 (—CH_2—), 56.59 (—CH_2—), 56.38 (—CH_2—), 56.34 (—CH_2—). UV–vis (c = 45.5 μM, DMF, path length = 1 cm): λ nm^{-1} (ε M^{-1} cm^{-1}) = 383 (15.9×10^3).

[Ru(Bn-bitapy)$_2$](PF$_6$)$_2$

$RuCl_3 \cdot nH_2O$ (42.4 mg, 0.20 mmol for n = 0), Bn-bitapy (160.0 mg, 0.41 mmol), and DMF (4 mL) were placed in a 10-mL flask. The mixture was heated at 145 °C for 3 h. The mixture was concentrated under reduced pressure, and saturated aqueous solution of $NaPF_6$ was added to the residue. The resulting orange powder was collected by filtration. The powder was dissolved in CH_3CN, and the insoluble part was removed by filtration. The solvent was removed under reduced pressure. The residue was purified by Sephadex LH-20 using a mixture of $CHCl_3$ and CH_3OH (1/1, v/v) as an eluent and followed by recrystallization from CH_3CN and CH_3OH to give orange needle-like crystals (32.6 mg, 14%).

Anal. calcd. for $C_{46}H_{38}N_{14}F_{12}P_2Ru \cdot CH_3OH$: C, 46.66; H, 3.50; N, 16.21. Found: C, 46.35; H, 3.25; N, 16.45. FAB-MS: m/z for $C_{46}H_{38}N_{14}F_6PRu$ ($[M - PF_6]^+$) calcd. 1032.9, found 1033.2. ^1H NMR (600 MHz, CD_3CN, CHD_2CN = 1.93 ppm): δ (ppm) = 8.59 (s, 4H, 5-triazole*H*), 8.23 (t, ^3J = 7.8 Hz, 2H 4-pyridine*H*), 8.18 (d, ^3J = 7.2 Hz, 4H, 3,5-pyridine*H*), 7.36 (t, ^3J = 7.2 Hz, 4H, 4-Ph*H*), 7.31 (t, ^3J = 7.5 Hz, 8H, 3,5-Ph*H*), 7.12 (d, ^3J = 7.2 Hz, 8H, 2,6-Ph*H*), 5.38 (s, 8H, —CH_2—). $^{13}C\{^1H\}$ NMR (150 MHz, CD_3CN, CD_3CN = 1.3 ppm): δ (ppm) = 151.5, 150.7, 138.8, 134.4, 130.11, 130.07, 129.3, 126.5, 121.2, 56.5. UV–vis (c = 42.4 μM, DMF, path length = 1 cm): λ nm^{-1} (ε M^{-1} cm^{-1}) = 394 (16.7×10^3).

Bromine-Terminated PS

CuBr (0.55 g, 3.84 mmol) was placed in a Schlenk tube, and the tube was evacuated and backfilled with argon three times. A degassed mixture of styrene (13.25 mL, 115.2 mmol), 1-bromoethylbenzene (0.52 mL, 3.84 mmol), and *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDETA; 0.80 mL, 3.84 mmol) was added to the tube. The tube was heated at 90 °C for 30 min. The resulting mixture was diluted with CH_2Cl_2 and washed with distilled water three times. The organic layer was dried over Na_2SO_4 and evaporated to remove the solvent. The crude product was purified by reprecipitation from THF and CH_3OH to give white solids (5.14 g, 43%). $M_{n,THF}$ = 2100, M_w/M_n = 1.13.

Azide-Terminated PS

Bromine-terminated PS (PS-Br; $M_{n,THF}$ = 2100, 5.0 g, 2.4 mmol), NaN_3 (0.78 g, 12 mmol), and distilled DMF (40 mL) were added to a flask. The mixture was stirred at room temperature for 8 h. The resulting mixture was evaporated to remove DMF. The crude product was purified by reprecipitation from THF and CH_3OH to give white solids (4.4 g, 88%). $M_{n,THF}$ = 1940, M_w/M_n = 1.13.

2-(1*H*-1,2,3-Triazol-4-yl)pyridine

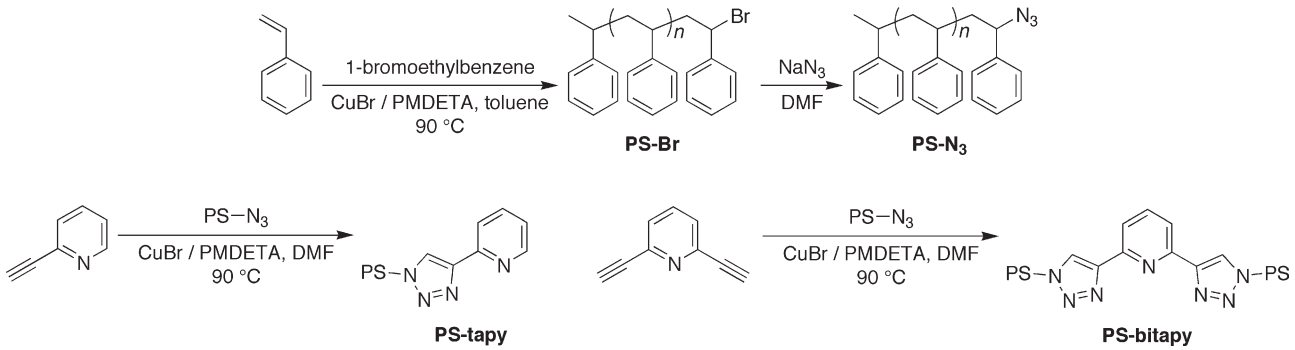
Azide-terminated PS (PS-N_3; $M_{n,THF}$ = 1940, 3.1 g, 1.6 mmol) and CuBr (22.9 mg, 1.6 mmol) were placed in a Schlenk tube. The tube was evacuated and backfilled with argon three times. The following was added to another flask: PMDETA (0.333 mL, 1.6 mmol), 2-ethynylpyridine (0.323 mL, 3.2 mmol), and distilled DMF (15.32 mL). The mixture was degassed by argon bubbling for 30 min and transferred to the Schlenk tube. The reaction mixture was stirred at 90 °C for 24 h. After removal of the solvent under reduced pressure, the residue was diluted with CH_2Cl_2 (100 mL), and washed with distilled water (100 mL × 2). After drying over Na_2SO_4, the solvent was removed under reduced pressure. The crude polymer was purified by reprecipitation from THF and CH_3OH four times and dried *in vacuo* to give a white solid (2.49 g, 80%). $M_{n,THF}$ = 2090 and M_w/M_n = 1.11. $M_{n,CHCl3}$ = 2910 and M_w/M_n = 1.18.

2,6-Bis(1*H*-1,2,3-triazol-4-yl)pyridine

PS-N_3 ($M_{n,THF}$ = 1940, 0.4 g, 0.154 mmol) and CuBr (2.21 mg, 0.154 mmol) were placed in a Schlenk tube. The tube was evacuated and back-filled with argon three times. The following was added to another flask: PMDETA (32.1 μL, 0.154 mmol), 2,6-diethynylpyridine (9.7 mg, 0.0762 mmol), and distilled DMF (1.5 mL). The mixture was degassed by argon bubbling for 30 min and transferred to the Schlenk tube. The reaction mixture was stirred at 90 °C for 24 h. After removal of the solvent under reduced pressure, the residue was diluted with CH_2Cl_2 (50 mL), and washed with distilled water (50 mL × 2). After drying over Na_2SO_4, the solvent was removed under reduced pressure. The residue was purified by preparative SEC using THF as an eluent followed by reprecipitation from THF and CH_3OH and dried *in vacuo* to give white solid (0.1855 g, 62%). $M_{n,THF}$ = 4970 and M_w/M_n = 1.09. $M_{n,CHCl3}$ = 5310 and M_w/M_n = 1.06.

[Ru(PS-tapy)$_3$](PF$_6$)$_2$

2-(1*H*-1,2,3-Triazol-4-yl)pyridine (PS-tapy; $M_{n,THF}$ = 2090, 160 mg, 0.0765 mmol) and $RuCl_3$ (5.2 mg, 0.025 mmol) were placed in a Schlenk tube. The tube was evacuated and back-filled with argon three times. Degassed dry DMF (0.75 mL) was added to the tube under an argon atmosphere. The reaction mixture was stirred at 100 °C for 48 h. After cooling to room temperature, a 10-fold excess of NH_4PF_6 (122.3 mg, 0.72 mmol) was added. The mixture was stirred for 10 min at room temperature. The reaction mixture was diluted with $CHCl_3$, and the insoluble part was removed by filtration. The filtrate was evaporated under vacuum, and the residue was dissolved in $CHCl_3$ (15 mL) and washed with water (20 mL × 2). After drying over Na_2SO_4, the solvent was removed under reduced pressure. The crude product was purified by preparative SEC using $CHCl_3$ as an eluent to give [Ru(PSt-tapy)$_3$](PF$_6$)$_2$ as yellow solids (89.5 mg, 56%). $M_{n,CHCl3}$ = 6740 and M_w/M_n = 1.07.



SCHEME 1 Synthesis of triazolylpyridine ligand-bearing PS.

$[Ru(PS\text{-}bitapy)_2](PF_6)_2$

2,6-Bis(1*H*-1,2,3-triazol-4-yl)pyridine (PS-bitapy; $M_{n,THF}$ = 4970, 150 mg, 0.030 mmol) and $RuCl_3$ (2.70 mg, 0.013mmol) were placed in a Schlenk tube. The tube was evacuated and back-filled with argon three times. Degassed dry DMF (0.3 mL) was added to the tube under an argon atmosphere. The reaction mixture was stirred at 130 °C for 48 h. After cooling to room temperature, a 10-fold excess of NH_4PF_6 (122.3 mg, 0.72 mmol) was added. The mixture was stirred for 10 min at room temperature. The reaction mixture was diluted with $CHCl_3$, and the insoluble part was removed by filtration. The filtrate was evaporated under vacuum, and the residue was dissolved in $CHCl_3$ (15 mL) and washed with water (20 mL × 2). After drying over Na_2SO_4, the solvent was removed under reduced pressure. The crude product was purified by preparative SEC using $CHCl_3$ as an eluent to give $[Ru(PS\text{-}bitapy)_2](PF_6)_2$ as yellow solids (40.3 mg, 27%). $M_{n,CHCl3}$ = 10,400 and M_w/M_n = 1.09.

X-Ray Structural Determination

Single crystal X-ray diffraction data were recorded on a Rigaku RAXIS RAPID imaging plate area detector using filtered Mo *Kα* radiation. All data sets were corrected for Lorentzian polarization effects and for absorption. All structures were solved by the direct method (SIR92[21]). Hydrogen atoms were placed into calculated positions and refined with isotropic thermal parameters riding on those of the parent atoms. Refinement of the nonhydrogen atoms was carried out with the full-matrix least-squares technique.

RESULTS AND DISCUSSION

PS-Br was prepared by ATRP using 1-bromoethylbenzene as an initiator and CuBr and PMDETA as a catalyst at 90 °C (Scheme 1). The M_n and M_w/M_n values of the resulting polymer PS-Br were estimated to be 2100 and 1.13 by SEC using PS standards. The resulting polymer PS-Br was treated with sodium azide in dry DMF to give the PS-N_3. The introduction of the azide group was confirmed by its characteristic stretching band at 2094 cm^{-1} (Fig. 1). PS-N_3 afforded a unimodal SEC trace with the same M_w/M_n value (1.13) as that of PS-Br. Cu(I)-catalyzed 1,3-dipolar cycloadditions between PS-N_3 and 2-ethynylpyridine or 2,6-diethynylpyridine were conducted in degassed DMF using CuBr/PMDETA as a catalyst at 90 °C to give PS-tapy and PS-bitapy ligands bearing one or two PS chain(s) at the first-position of the triazole ring(s). After purification of PS-tapy by reprecipitation from THF and methanol and of PS-bitapy by preparative SEC, the stretching band due to the azide group completely disappeared from the IR spectra. The M_n values of PS-tapy and PS-bitapy were estimated to be 2090 and 4970, respectively. The M_w/M_n values of PS-tapy and PS-bitapy remained comparable with that of the starting PS-N_3. The IR spectra and SEC traces suggested the formation of (1,2,3-triazol-4-yl)pyridine type ligand bearing PS chain(s) as shown in Scheme 1. To provide further insight into the polymer structure, a MALDI-TOF MS measurement of PS-tapy was carried out. As shown in Figure 2, only one series of peaks was observed in the MS spectrum. The peak interval is 104.1, which is identical with the molecular weight of styrene. Additionally, the peak at 1835.3 (m/z) is in a good agreement with the theoretical isotopic molecular weight of sodium-cationized PS (n = 15) with the tapy chain end

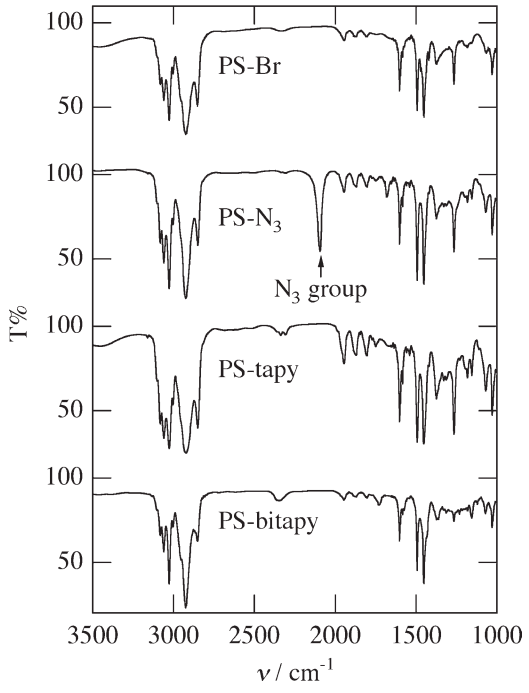


FIGURE 1 IR spectra of PS-Br, PS-N_3, PS-tapy, and PS-bitapy.

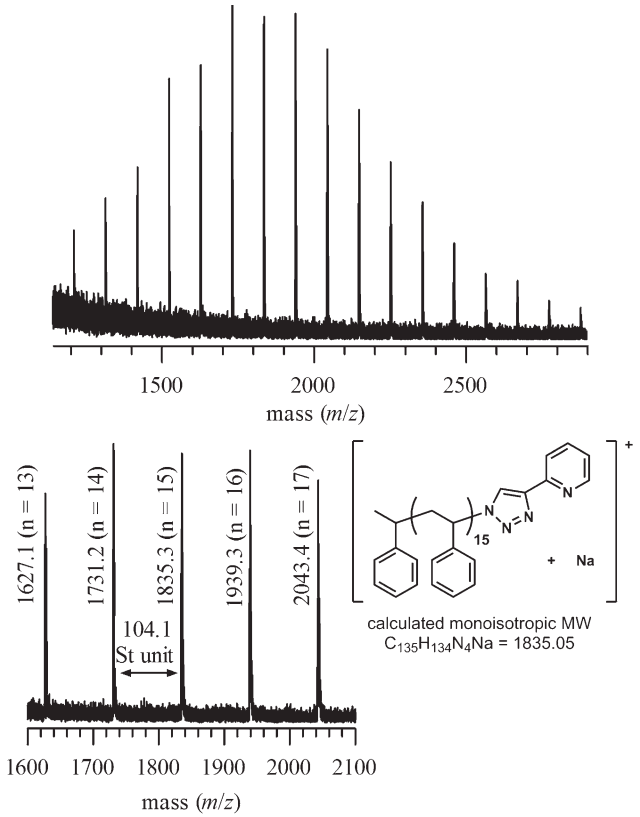
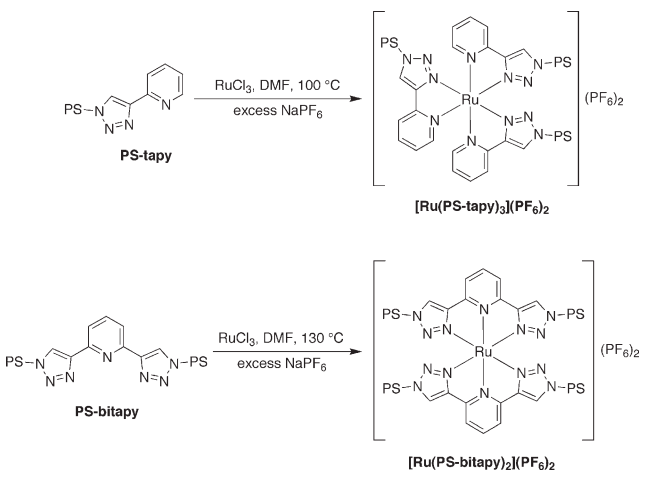


FIGURE 2 MALDI-TOF MS spectra of PS-tapy in reflector mode.

(C135H134N4Na: 1835.05). These results clearly indicated that the tapy functionality was quantitatively introduced into the PS chain. Therefore, the click reaction between PS-N_3 and ethynylpyridine derivatives was demonstrated to be useful and straightforward strategy to produce a polymer with a desired chelating functionality.

Ru(II) complexes of PS-tapy and PS-bitapy were prepared by heating with $RuCl_3$ as a metal source in DMF followed by the addition of $NaPF_6$ (Scheme 2). After the removal of unreacted PS-tapy and PS-bitapy by preparative SEC, Ru(II) complexes of PS-tapy and PS-bitapy were obtained as yellow solids. The M_n values of these solids were determined to be 6740 and 10,400, respectively.[22] These M_n values suggest the formation of a 3-arm complex $[Ru(PS\text{-}tapy)_3](PF_6)_2$ and a 4-arm complex $[Ru(PS\text{-}bitapy)_2](PF_6)_2$, even though the M_n values determined by SEC are on a relative scale calibrated by linear PS standards (Figure 3).

To explore the detailed structure of the Ru(II) complexes of PS-tapy and PS-bitapy, we synthesized Ru(II) complexes bearing benzyl groups instead of PS chains (Chart 1). The ligands Bn-tapy and Bn-bitapy were synthesized by the same method as previously reported.[18] The Ru(II) complexes $[Ru(Bn\text{-}tapy)_3](PF_6)_2$ and $[Ru(Bn\text{-}bitapy)_2](PF_6)_2$ were prepared by the reaction of $RuCl_3$ with Bn-tapy or Bn-bitapy in DMF for 3 h at 145 °C and were obtained as yellow powders in 24 and 14% yields, respectively. Elemental analysis and mass spectrometry clearly indicated the formations of Ru(II) complexes formulated as $[Ru(Bn\text{-}tapy)_3](PF_6)_2$ and $[Ru(Bn\text{-}bitapy)_2](PF_6)_2$. $[Ru(Bn\text{-}tapy)_3](PF_6)_2$ has a complex ^1H NMR spectrum plausibly because of a mixture of *fac*-isomers and *mer*-isomers. Four peaks due to methylene carbon were found at 56.62, 56.59, 56.38 and 56.34 ppm in $^{13}C\{^1H\}$ NMR spectrum of $[Ru(Bn\text{-}tapy)_3](PF_6)_2$ corresponding to one peak from the C_3 symmetric *fac*-isomer and three peaks from the asymmetric *mer*-isomer. In contrast, $[Ru(Bn\text{-}bitapy)_2](PF_6)_2$ has a very simple ^1H NMR spectrum and ^{13}C NMR spectrum, showing only 10 peaks, clearly indicating an S_4 symmetric structure in acetonitrile solution. Recrystalization from a mixture of acetonitrile and methanol affords yellow crystals suitable for X-ray crystallography. Figure 4 shows an ORTEP drawing of $[Ru(Bn\text{-}bitapy)_2]^{2+}$, and Table 1 lists the selected bond lengths and angles. Although the $[Ru(Bn\text{-}bitapy)_2]^{2+}$ structure is distorted in the crystal packing, the space group *P*-1 and the *Z* value of two means that two $[Ru(Bn\text{-}bitapy)_2]^{2+}$ molecules, which distorted each other enantiomerically, are packed in an asymmetric unit. Chart 2 shows



SCHEME 2 Synthesis of 3-arm and 4-arm star-branched PS Ru(II) complexes.

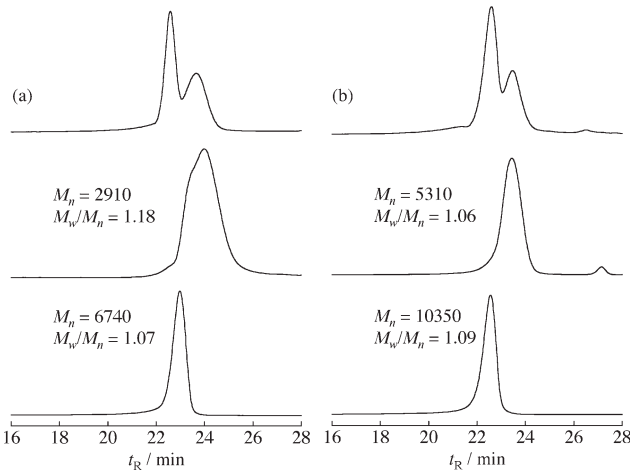
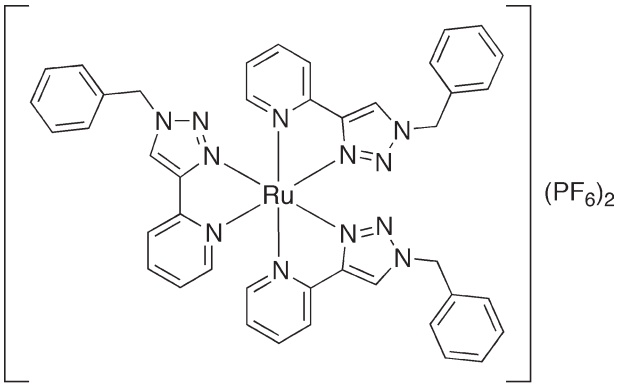
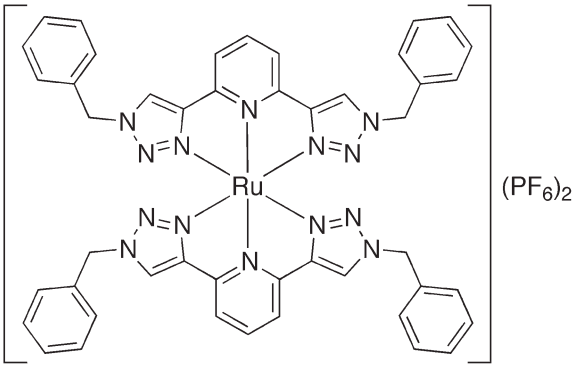


FIGURE 3 SEC traces for synthesis of Ru(II) complexes of PS-tapy (a) and PS-bitapy (b). Top: crude Ru(II) complexes; middle: PS ligands; and bottom: purified Ru(II) complexes.



[Ru(Bn-tapy)$_3$](PF$_6$)$_2$



[Ru(Bn-bitapy)$_2$](PF$_6$)$_2$

CHART 1 Ru(II) Complexes [Ru(Bn-tapy)$_3$](PF$_6$)$_2$ and [Ru(Bn-bitapy)$_2$](PF$_6$)$_2$.

schematic representation of coordination geometry for $[Ru(Bn\text{-}bitapy)_2]^{2+}$ and $[Ru(terpy)_2]^{2+}$, in which the equivalent bond lengths and angles are averaged.[23] The coordination geometry of $[Ru(Bn\text{-}bitapy)_2]^{2+}$ is quite similar to that of $[Ru(terpy)_2]^{2+}$. An interesting difference was found in the bond length between Ru and N(central pyridine): $[Ru(Bn\text{-}bitapy)_2]^{2+}$ (2.02 Å) is longer than that of $[Ru(terpy)_2]^{2+}$, plausibly because of the five-membered triazole ring. The angle between the two benzyl groups of $[Ru(Bn\text{-}bitapy)_2]^{2+}$ was calculated to be ~145°. The Ru(II) complexes [Ru(Bn-tapy)$_3$](PF$_6$)$_2$ and [Ru(Bn-bitapy)$_2$](PF$_6$)$_2$ demonstrate that tapy and bitapy, readily prepared by click reaction, act as bipyridine- and terpyridine-like chelators for Ru(II) ions.

Figure 5 shows the UV–vis spectra of [Ru(Bn-tapy)$_3$](PF$_6$)$_2$ and [Ru(Bn-bitapy)$_2$](PF$_6$)$_2$ in DMF. Characteristic absorption bands were found at 383 nm for [Ru(Bn-tapy)$_3$](PF$_6$)$_2$ and at 394 nm for [Ru(Bn-bitapy)$_2$](PF$_6$)$_2$. These absorption bands are shifted to shorter wavelength than that of $Ru(bpy)_3^{2+}$ complex (450 nm in acetonitrile) because of the poor electro-accepting property of triazole ring.[18] The Ru(II) complexes of PS-tapy and PS-bitapy afford similar UV–vis spectra to those of [Ru(Bn-tapy)$_3$](PF$_6$)$_2$ and [Ru(Bn-bitapy)$_2$](PF$_6$)$_2$, suggesting a similar coordination on Ru(II) ions. Assuming the same molar absorption coefficient in the band for Ru(II) complexes of PS-tapy and PS-bitapy, the UV–vis spectra confirm the absolute molecular weights of Ru(II) complexes of PS-tapy and PS-bitapy at 9300 and 12,000, respectively. These values are close to the calculated values of 9120 for [Ru(PS-tapy)$_3$](PF$_6$)$_2$ and 11,000 for [Ru(PS-

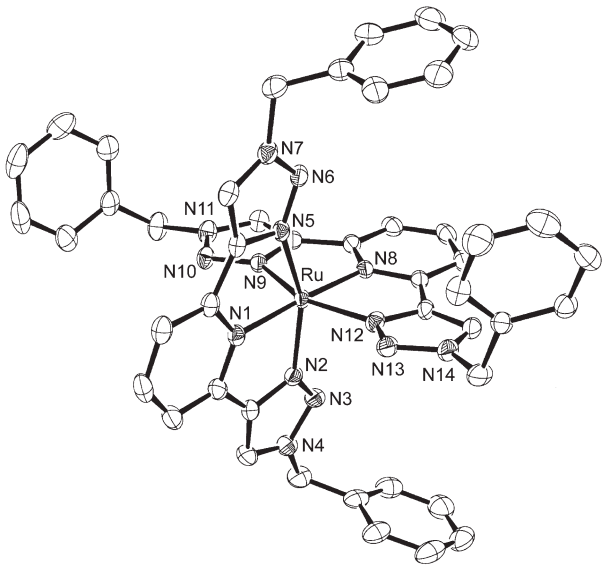


FIGURE 4 ORTEP drawing of $[Ru(Bn\text{-}bitapy)_2]^{2+}$ with thermal ellipsoids shown at the 50% probability level.

TABLE 1 Selected Bond Lengths (in Å) and Angles (in deg) for [Ru(Bn-bitapy)$_2$](PF$_6$)$_2$

Ru–N(1)	2.017(3)
Ru–N(2)	2.050(3)
Ru–N(5)	2.071(3)
Ru–N(8)	2.019(3)
Ru–N(9)	2.051(2)
Ru–N(12)	2.069(2)
N(1)–Ru–N(2)	78.45(14)
N(1)–Ru–N(5)	78.22(14)
N(1)–Ru–N(9)	102.14(10)
N(1)–Ru–N(12)	101.60(12)
N(2)–Ru–N(12)	95.11(12)
N(5)–Ru–N(9)	93.26(11)
N(1)–Ru–N(8)	175.82(14)
N(2)–Ru–N(5)	156.56(13)
N(8)–Ru–N(9)	78.19(10)
N(8)–Ru–N(12)	78.12(11)
N(8)–Ru–N(2)	97.41(14)
N(8)–Ru–N(5)	105.94(14)
N(12)–Ru–N(5)	91.76(12)
N(9)–Ru–N(2)	89.42(11)
N(9)–Ru–N(12)	156.26(13)

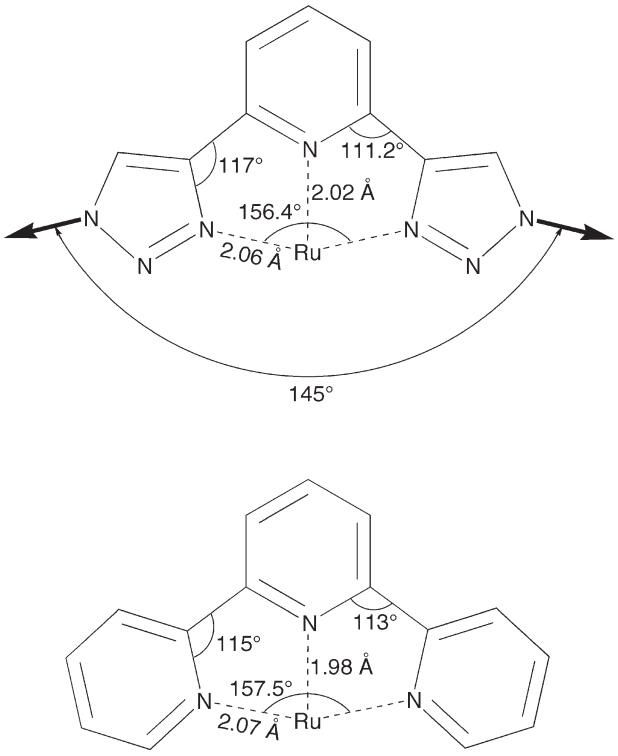


CHART 2 Schematic representation of coordination geometry for $[Ru(Bn\text{-}bitapy)_2]^{2+}$ and $[Ru(terpy)_2]^{2+}$.[23] Terpy stands for terpyridine.

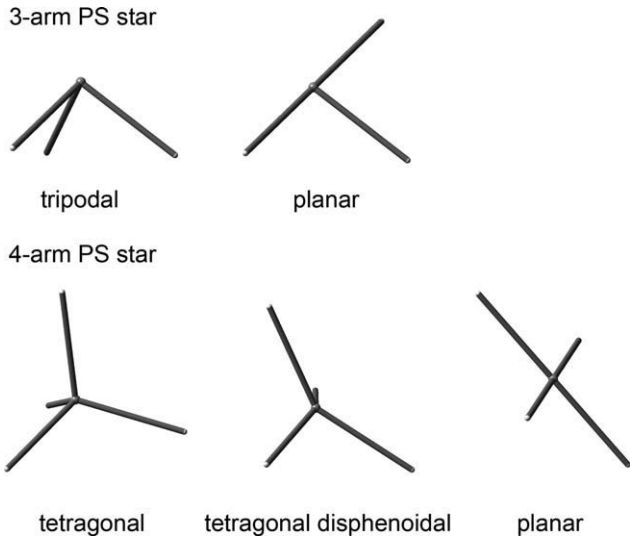


CHART 3 Schematic representation of 3-arm and 4-arm star-branched PS geometries.

bitapy)$_2$](PF$_6$)$_2$ using the M_n values of PS-tapy and PS-bitapy determined by SEC in $CHCl_3$, and are a little greater than those calculated on the basis of the M_n values determined by SEC in THF. Therefore, the SEC analyses and UV–vis spectroscopy clearly indicate that PS-tapy and PS-bitapy can be coordinated on a Ru(II) ion to form star-branched 3-arm and 4-arm PS architectures. The 3-arm PS complex is likely to be a mixture of the *fac*- (tripodally-branched 3-arm PS) and *mer*-configuration (planar-branched 3-arm PS; Chart 3). In contrast, the crystal structure of [Ru(Bn-bitapy)$_2$](PF$_6$)$_2$ affords more detailed information for 4-arm PS architecture. The 4-arm PS complex is not actually a planar structure. On the basis of the crystal structure of [Ru(Bn-bitapy)$_2$](PF$_6$)$_2$, the direction of the PS chain deviated by ~17.5° from the best plane, which is a marginal value between 35.26° for tetragonal and 0° for planar configurations.

CONCLUSIONS

We successfully prepared 3-arm and 4-arm star-branched PSs with a Ru(II) complex core by the click-to-chelate approach. PS-Br was readily synthesized by ATRP and easily converted to azide groups by mixing with NaN_3 in DMF at an ambient temperature. The introduction of chelating functionalities, namely, triazolylpyridine, was carried out using click chemistry to afford triazolylpyridine (tapy) ligand bearing one PS chain (PS-tapy) and bistriazolylpyridine (bitapy) ligand bearing two polystylene chains (PS-bitapy). Ru(II) complexes of PS-tapy and PS-bitapy were prepared by a conventional procedure for the preparation of Ru(II) oligopyridine complexes. The coordination structures of the Ru(II) complexes were established to be of octahedral coordination on the basis of SEC analyses and UV–vis spectra using Ru(II) complexes with benzyl groups instead of PS. In particular,

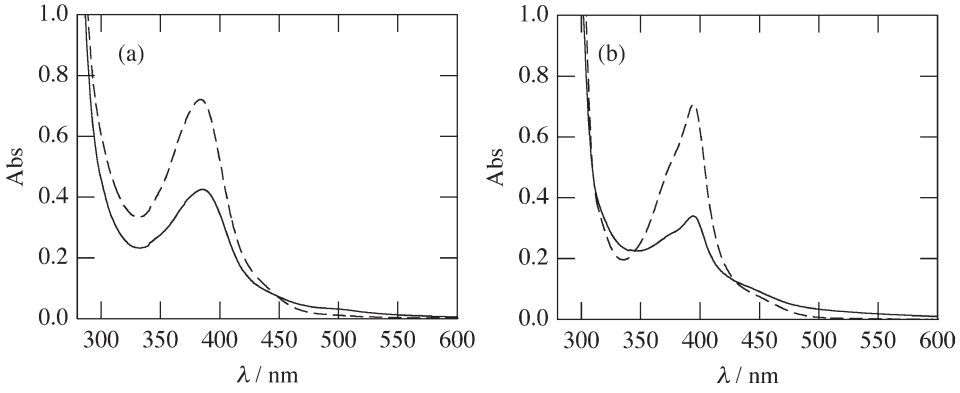


FIGURE 5 UV–vis spectra of [Ru(Bn-tapy)$_3$](PF$_6$)$_2$ (broken line) and Ru(II) complex of PS-tapy (solid line) (a) and [Ru(Bn-bitapy)$_2$](PF$_6$)$_2$ (broken line) and Ru(II) complex of PS-bitapy (solid line) (b) in DMF.

X-ray crystallography clearly indicates the coordinating fashion of the bitapy ligand that is quite similar to that of terpyridine. Because of ATRP technology, the easy conversion from bromine to azide, and click chemistry, the click-to-chelate approach was found to be a powerful tool for metal template synthesis of macromolecular with a sophisticated architecture.

The authors thank Shohei Katao at NAIST for performing the X-ray crystallography analysis. This work was supported by Grants-in-Aid for Scientific Research (no. 21550156), the Kyoto-Nanotechnology Network of the Ministry of Education, Culture, Sport, Science and Technology (MEXT), and a grant from the Japan–German exchange program supported by the Japan Society for the Promotion of Science (JSPS) of the Japanese Government. This study was also supported by Natural Science Foundation of Heilongjiang Province, China (Grant No. B201013).

REFERENCES AND NOTES

1 Raymo, F. M.; Stoddart, J. F. Chem Rev 1999, 99, 1643–1664.

2 Schubert, U. S.; Eschbaumer, C. Angew Chem Int Ed 2002, 41, 2892–2926.

3 Niu, Z.; Gibson, H. W. Chem Rev 2009, 109, 6024–6046.

4 Kaes, C.; Katz, A.; Hosseini, M. W. Chem Rev 2000, 100, 3553–3590.

5 Wu, X.;Fraser C. L. Macromolecules 2000, 33, 7776–7785.

6 Fraser, C. L.; Smith, A. P. J Polym Sci Part A: Polym Chem 2000, 38, 4704–4716.

7 Fiore, G. L.; Fraser, C. L. Macromolecules 2008, 41, 7892– 7897.

8 Schubert, U. S.; Eschbaumer, C. Macromol Symp 2001, 163, 177–187.

9 Gohy, J.-F.; Lohmeijer, B. G. G.; Varshney, S. K.; Décamps, B.; Leroy, E.; Boileau, S.; Schubert, U. S. Macromolecules 2002, 35, 9748–9755.

10 Lohmeijer, B. G. G.; Schubert, U. S. J Polym Sci Part A: Polym Chem 2003, 41, 1413–1427.

11 Mindt, T. L.; Struthers, H.; Brans, L.; Anguelov, T.; Schweinsberg, C.; Maes, V.; Tourwé, D.; Schibli, R. J Am Chem Soc 2006, 128, 15096–15097.

12 Rostovtsev, V. V.; Green, L. G.; Fokin, V. V.; Sharpless, K. B. Angew Chem Int Ed 2002, 41, 2596–2599.

13 Mindt, T. L.; Müller, C.; Melis, M.; de Jong, M.; Schibli, R. Bioconjugate Chem 2008, 19, 1689–1695.

14 Struthers, H.; Spingler, B.; Mindt, T. L.; Schibli, R. Chem Eur J 2008, 14, 6173–6183.

15 Schweinfurth, D.; Hardcastle, K. I.; Bunz, U. H. F. Chem Commun 2008, 2203–2205.

16 Huang, S.; Clark, R. J.; Zhu, L. Org Lett 2007, 9, 4999–5002.

17 Donnelly, P. S.; Zanatta, S. D.; Zammit, S. C.; White, J. M.; Williams, S. J. Chem Commun 2008, 2459–2461.

18 Obata, M.; Kitamura, A.; Mori, A.; Kameyama, C.; Czaplewska, J. A.; Tanaka, R.; Kinoshita, I.; Kusumoto, T.; Hashimoto, H.; Harada, M.; Mikata, Y.; Funabiki, T.; Yano, S. Dalton Trans 2008, 3292–3300.

19 Ohi, H.; Shimizu, M.; Obata, M.; Funabiki, T.; Yano, S. Acta Cryst 2008, E64, m1256–m1257.

20 Orita, A.; Nakano, T.; An, D. L.; Tanikawa, K.; Wakamatsu, K.; Otera, J. J Am Chem Soc 2004, 126, 10389–10396.

21 Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M.; Polidori, G.; Camalli, M. J Appl Cryst 1994, 27, 435.

22 The resulting yellow solids can be dissolved in THF and $CHCl_3$ to form a completely transparent solution. However, SEC traces obtained in THF showed significant peak tailing indicating undesired interaction between these complexes with the stationary phase (polystyrene gel). Hence, the M_n values of the resulting complexes were determined by SEC using $CHCl_3$ as an eluent.

23 Pyo, S.; Pérez-Cordero, E.; Bott, S. G.; Echegoyen, L. Inorg Chem 1999, 38, 3337–3343.