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New terpyridine macroligands as potential synthons for supramolecular assemblies

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ABSTRACT

A Williamson type etherification approach was applied for the reaction of 4′-chloro-2,2′:6′,2″-terpyridine with a number of well-defined *mono*- and *bis*-hydroxy functionalized polymers, namely poly(tetrahydrofuran), poly(2-ethyl-2-oxazoline) and Pluronics®. The resulting terpyridine functionalized polymers were characterized by ^{1}H NMR spectroscopy and SEC, as well as MALDI-TOF-MS demonstrating the successful functionalization. This type of end-functionalized chelating macromolecules could be considered as key candidates for the preparation of metallo-supramolecular polymers *via* metallo-terpyridine complexation; the principle feasibility was demonstrated by UV–vis titration of iron(II) chloride to *bis*-terpyridine functionalized poly(tetrahydrofuran).

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1. Introduction

Polymers containing *N*-heterocyclic chelating ligands have become important macromolecular candidates in the field of metallo-supramolecular chemistry. The availability of various types of chelating ligands and transition metal ions gives countless possibilities for the preparation of metal-coordinating motifs characterized by different stabilities, geometries and properties. The architecture of such systems is strongly determined by the nature of the chelating ligand but also by the characteristics of the utilized metal ion. Therefore, the combination of macromolecules and metal–ligand coordination interactions could be seen as an appealing concept towards the preparation of new materials that embrace the characteristics of the starting materials but also reveal novel properties as a result of the newly created metal-coordinating connections among the reaction components [1–4]. In case of polymers containing terpyridine ligands, the literature provides a large variety of metallo-supramolecular systems that aim for different applications in various fields [5]. Due to its specific structure, *e.g.* lack of isomers and diastereoisomers as well as the strong affinity for a wide range of metal ions, 4′-functionalized-2,2′:6′,2″-terpyridines offer great opportunities for the construction of supramolecular assemblies [5,6]. In addition, if the substituent in the 4′-position of the terpyridine is a polymer, supramolecular polymers or block copolymers can be synthesized by the complexation of the terpyridine moieties with suitable transition metal ions [7,8].

In this contribution, we present the preparation of new well-defined macromolecular polymeric ligands containing one or two 2,2′:6′,2″-terpyridine end groups bearing different polymeric spacers with different properties, *e.g.* poly(tetrahydrofuran) as a soft material and Pluronics® as well as poly(2-ethyl-2-oxazoline) as thermoresponsive materials [9]. The successful preparation of the terpyridine functionalized polymers is confirmed by ^{1}H NMR spectroscopy, size exclusion chromatography (SEC) and Matrix-Assisted Laser Desorption/Ionization Time-of-Flight mass spectrometry (MALDI-TOF-MS). The resulting

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macromolecular ligands could be considered as promising candidates for the construction of metallo-terpyridine polymers and block copolymers as demonstrated by a UV–vis titration experiment. Even though the synthesis of a *mono*-terpyridine end-functionalized poly(tetrahydrofuran) was previously reported *via* an elaborative multistep procedure using isocyanato-terpyridine [10], the here reported direct etherification procedure provides a much simpler and direct access to such polymers.

2. Experimental

2.1. Materials and general experimental details

Solvents were purchased from Biosolve and all other compounds were obtained from Aldrich, Acros or Fluka. All chemicals were of reagent grade and used as received unless otherwise specified. Purified solvents were used where required. Tetrahydrofuran was distilled from molecular sieves and DMSO was dried over molecular sieves. Reactions were performed under an atmosphere of argon. Preparative size exclusion chromatography was carried out on a BioBeads S-X1 column in tetrahydrofuran. Visualization of the collected fractions was done by spotting onto TLC plates followed by evaluation under UV irradiation or by subjecting the TLC plates to an aqueous solution of $FeCl_2{\cdot}4H_2O$ to visualize the terpyridine moiety.

2.1.1. Instrumentation

Size exclusion chromatography (SEC) was performed on a Shimadzu system with a RID-6A refractive index detector and a PL gel 5 mm Mixed-D column. A solution of 49.5 mmol/L of lithium chloride in *N,N*-dimethylacetamide (DMA) was used as the eluent at a flow rate of 1 mL/min; polystyrene or polyethylene glycol calibrations were utilized. The column temperature was set to 50 °C. Size exclusion chromatograms were also measured on a Waters SEC system consisting of an isocratic pump, a solvent degasser, a column oven, a 2996 photodiode array (PDA) detector, a 2414 refractive index detector, a 717 plus autosampler and a Styragel HT 4 GPC column with a precolumn installed. The eluent was *N,N*-dimethylformamide (DMF) with 5 mM NH_4PF_6 at a flow rate of 0.5 mL/min; a linear PEG calibration was used. The column temperature was set to 50 °C. Proton nuclear magnetic resonance (^{1}H NMR) spectra were recorded on a Varian Gemini 400 MHz spectrometer at 298 K. Chemical shifts are reported in parts per million (ppm) downfield from an internal standard, tetramethylsilane (TMS) in $CDCl_3$ and CD_2Cl_2. Coupling constants (*J* values) are reported in Hertz (Hz). MALDI-TOF-MS was performed on a Voyager-DE(tm) PRO Biospectrometry(tm) Workstation (Applied Biosystems) time-of-flight mass spectrometer reflector, using dithranol as matrix.

2.2. General methods

2.2.1. Synthesis of methoxy-PTHF$_{60}$ (**2**)

THF was polymerized in a dry flask by the addition of methyl triflate (100 mL, 0.88 mmol) to dry THF (50 mL) at room temperature under argon. After 15 min of rigorous stirring, the polymerization was quenched by the addition of 50 mL H_2O followed by the extraction of the reaction mixture in $CHCl_3$ (200 mL). The organic solvent was dried with Na_2SO_4 and removed under reduced pressure. The *mono*-hydroxy-PTHF **2** was obtained as a white wax (3.31 g, 60%). ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$, 25 °C): δ (ppm) = 3.62 (m, 2H, CH_2), 3.48–3.39 (m, 240H, PTHF backbone), 3.35 (s, 3H, OCH_3), 1.72–1.55 (m, 240H, PTHF backbone), 2.83 (1H, OH). SEC ($CHCl_3$ system; PEG calibration): M_n = 4350 g/mol, M_w = 5100 g/mol, PDI = 1.17. MALDI-TOF-MS: M_n = 3900 g/mol, M_w = 4000 g/mol, PDI = 1.02.

2.2.2. General synthesis and purification of mono-terpyridine PTHF$_{60}$ (**4**)

Powdered ^{t}BuOK (3 eq.) and *mono*-hydroxy-PTHF (1 eq.) were stirred under argon in dry THF at 65 °C. After 30 min, a 2-fold excess of 4′-chloro-2,2′:6′,2″-terpyridine **3** was added *via* a dropping funnel to the solution. The mixture was refluxed for 24 h, then poured into cold water and extracted with CH_2Cl_2. The reaction product was purified by preparative size exclusion chromatography (BioBeads SX1, THF). Yield: 440 mg (83%). ^{1}H NMR spectroscopy (400 MHz, CD_2Cl_2, 25 °C): δ (ppm) = 8.68 (m, 2H; H^6, $H^{6''}$), 8.62 (m, 2H; H^3, $H^{3''}$), 8.00 (s, 2H, $H^{3'}$, $H^{5'}$), 7.86 (m, 2H; H^4, $H^{4''}$), 7.34 (m, 2H; H^5, $H^{5''}$), 4.25 (m, 2H, tpyOCH_2), 3.62 (m, 2H, tpyOCH_2CH_2), 3.49–3.34 (m, 280H, PTHF backbone), 1.69–1.50 (m, 280H, PTHF backbone). 3.32 (s, 3H, OCH_3). SEC ($CHCl_3$ system; PEG calibration): M_n = 4500 g/mol, M_w = 6500 g/mol, PDI = 1.44. MALDI-TOF-MS: M_n = 3800 g/mol, M_w = 3870 g/mol, PDI = 1.01.

2.2.3. Synthesis of telechelic-PTHF$_{90}$ (**5**)

THF was polymerized in a dry flask by the addition of triflic anhydride (200 mL, 1.18 mmol) to dry THF (50 mL) at room temperature under argon. After 15 min of rigorous stirring, the polymerization was quenched by the addition of 50 mL H_2O followed by the extraction of the reaction mixture in $CHCl_3$ (200 mL). The organic solvent was dried with Na_2SO_4 and removed under reduced pressure. The *bis*-hydroxy-PTHF **5** was obtained as a white wax (12.56 g, 65%). ^{1}H NMR spectroscopy (400 MHz, $CDCl_3$, 25 °C): δ (ppm) = 3.63 (m, 2H, CH_2), 3.53–3.35 (m, 360H, PTHF backbone), 1.73–1.48 (m, 360H, PTHF backbone), 2.53 (2H, OH). SEC ($CHCl_3$ system; PEG calibration): M_n = 5800 g/mol, M_w = 7000 g/mol, PDI = 1.20. MALDI-TOF-MS: M_n = 5330 g/mol, M_w = 5400 g/mol, PDI = 1.01.

2.2.4. General synthesis and purification of bis-terpyridine PTHF$_{90}$ (**6**)

Powdered ^{t}BuOK (4 eq.) and telechelic-PTHF **5** (1 eq.) were stirred under argon in dry THF at 65 °C. After 30 min, a 4-fold excess of 4′-chloro-2,2′:6′,2″-terpyridine **3** was added *via* a dropping funnel to the solution. The mixture was refluxed for 48 h, subsequently poured into cold water and extracted with CH_2Cl_2. No precipitation was performed for the pure fractions of **6** collected from the BioBeads SX1-THF. Yield: 2.2 g (73%). ^{1}H NMR spectroscopy (400 MHz, CD_2Cl_2, 25 °C): δ (ppm) = 8.69 (m, 2H; H^6, $H^{6''}$), 8.61 (m, 2H; H^3, $H^{3''}$), 8.00 (s, 2H, $H^{3'}$, $H^{5'}$), 7.84 (m, 2H; H^4, $H^{4''}$), 7.33 (m, 2H; H^5, $H^{5''}$), 4.25 (m, 2H, tpyOCH_2), 3.64 (m, 2H, tpyOCH_2CH_2), 3.50–3.29 (m, 380H, PTHF

backbone), 1.67–1.55(m, 380H, PTHF backbone). SEC ($CHCl_3$ system; PEG calibration): M_n = 7300 g/mol, M_w = 8100 g/mol, PDI = 1.11. MALDI-TOF-MS: M_n = 6500 g/mol, M_w = 6600 g/mol, PDI = 1.01.

*2.2.5. Synthesis of PEtOx$_{50}$ (**8**)*

Compound **8** was prepared and fully characterized as described in the literature [11].

*2.2.6. Synthesis of mono-terpyridine PEtOx$_{50}$ (**9**)*

The synthesis of the *mono*-terpyridine PEtOx$_{50}$ **9** was performed *via* the ^{t}BuOK/THF route (see the preparation of **4**). Reflux temperature 60 °C. Yield of **9**: 3.2 g (90%). ^{1}H NMR spectroscopy (400 MHz, CD_3Cl, 25 °C): δ (ppm) = 8.61 (m, 4H; H^6, $H^{6''}$, H^3, $H^{3''}$), 7.95 (s, 2H, $H^{3'}$, $H^{5'}$), 7.80 (m, 2H; H^4, $H^{4''}$), 7.29 (m, 2H; H^5, $H^{5''}$), 4.39 (m, 2H, tpyOCH_2), 3.68 (s, 3H, CH_3), 3.43–3.31 (m, 240H, PEtOx backbone), 2.38–2.15 (m, 120H, PEtOx backbone), 1.06 (s, 180 H, CH_3). SEC (DMF system; PEG calibration): M_n = 5400 g/mol, M_w = 4500 g/mol, PDI = 1.20. MALDI-TOF-MS: M_n = 4600 g/mol, M_w = 4800 g/mol, PDI = 1.04.

2.2.7. General synthesis of bis-terpyridine Pluronics®

Powdered KOH (4 eq.) and telechelic Pluronic® (3.00 g, 1 eq.) were stirred under argon in dry DMSO at 60 °C. After 30 min, a 4-fold excess of 4′-chloro-2,2′:6′,2″-terpyridine **3** was added *via* a dropping funnel to the solution. The reaction mixture was refluxed for 48 h, then poured into cold water and extracted with CH_2Cl_2. The purification was done using the same steps as in the case of **6**.

*2.2.8. Bis-terpyridine PEG$_{10}$-PPG$_{30}$-PEG$_{10}$ (**10**)*

*Yield of **10**:* 1.2 g (83%). ^{1}H NMR spectroscopy (400 MHz, CD_2Cl_2, 25 °C): δ (ppm) = 8.68 (m, 2H; H^6, $H^{6''}$), 8.62 (m, 2H; H^3, $H^{3''}$), 8.06 (s, 2H, $H^{3'}$, $H^{5'}$), 7.86 (m, 2H; H^4, $H^{4''}$), 7.34 (m, 2H; H^5, $H^{5''}$), 4.39 (m, 2H, tpyOCH_2), 3.92 (m, 2H, tpyOCH_2CH_2), 3.75–3.29 (m, 110H, PEG backbone and –CH backbone), 1.22–1.07 (m, 30H, CH_3 backbone). SEC (DMA system; PS calibration): M_n = 3600 g/mol, M_w = 4400 g/mol, PDI = 1.23.

*2.2.9. Bis-terpyridine PPG$_{14}$-PEG$_{24}$-PPG$_{14}$ (**11**)*

*Yield of **11**:* 1.1 g (80%). ^{1}H NMR spectroscopy (400 MHz, CD_2Cl_2, 25 °C): δ (ppm) = 8.68 (m, 2H; H^6, $H^{6''}$), 8.62 (m, 2H; H^3, $H^{3''}$), 8.06 (s, 2H, $H^{3'}$, $H^{5'}$), 7.87 (m, 2H; H^4, $H^{4''}$), 7.35 (m, 2H; H^5, $H^{5''}$), 4.92 (m, 2H, tpyOCH_2), 3.83–3.37 (m, 130H, PEG backbone and –CH backbone), 1.17–1.07 (m, 28H, CH_3 backbone). SEC (DMA system; PS calibration): M_n = 3300 g/mol, M_w = 4100 g/mol, PDI = 1.24.

3. Results and discussions

Mono- and *bis*-hydroxy polymers offer straightforward and convenient opportunities to introduce 2,2′:6′,2″-terpyridine moieties at the terminal hydroxy groups of the polymer backbone *via* nucleophilic substitution reactions, *e.g.* Williamson type etherification using 4′-chloro-2,2′:6′,2″-terpyridine. For this type of functionalization, two similar synthetic approaches can be followed: either using a suspension of KOH in DMSO at 60–80 °C or using ^{t}BuOK in dry THF at 60–70 °C [12]. Previous studies performed in our group devoted a special attention to the conversion of the 4′-chloro-2,2′:6′,2″-terpyridine reactant by varying the reaction temperature [13,14]. Generally, in this type of substitution reaction 4′-chloro-2,2′:6′,2″-terpyridine can be utilized in excess in order to avoid the possibility of having non-functionalized starting materials in the final product. This aspect is in particular important for polymers since the separation of functionalized and non-functionalized polymer chains is very complicated while removal of unreacted 4′-chloro-2,2′:6′,2″-terpyridine is relatively easy. Thus, the molar ratio between 4′-chloro-2,2′:6′,2″-terpyridine and the utilized functional polymer is 2:1 for the case of *mono*-hydroxy-polymer and 4:1 when a telechelic polymer is utilized. The presence of the strong base in the system initiates the nucleophilic attack by abstracting the proton from the hydroxy-end group. Subsequently, the generated anion attacks the 4′-chloro-2,2′:6′,2″-terpyridine in 4′-position perturbing the electronic system of the middle ring. This intermediate could be easily noticed during the addition of 4′-chloro-2,2′:6′,2″-terpyridine to the reaction mixture by the formation of a red-brownish color, which disappeared as soon as all the intermediate was consumed. By the elimination of the chloride anion, the aromaticity of the ring was re-established and the desired terpyridine moiety was attached to the polymer. The reaction could be performed in 24–48 h. The purification of the crude terpyridine functionalized polymers could easily be achieved by performing preparative size exclusion chromatography (BioBeads®) where the excess of 4′-chloro-2,2′:6′,2″-terpyridine could be removed. Further precipitation of the purified fractions yielded the desired *mono*- or *bis*-terpyridine functionalized polymers.

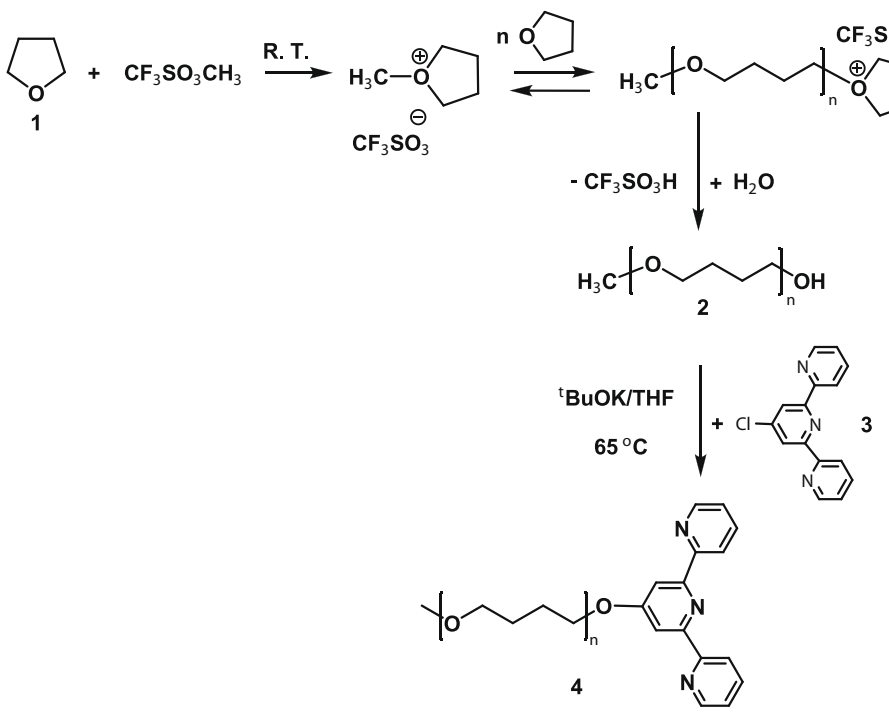
3.1. Polytetrahydrofuran functionalized terpyridines

Polytetrahydrofuran (PTHF) exhibits a very low glass transition temperature (T_g) as well as melting temperature (T_m), and it is frequently used as a soft segment for thermoplastic and crosslinked elastomers [15]. By attaching terpyridine moieties to *mono*-hydroxy-PTHF or telechelic-PTHF, new chelating macro-monomers with high flexibility in the self-assembly process could be made available for further metallo-complexation.

It is known that THF reacts with electrophilic initiators in order to form PTHF. Such types of polymerizations have been intensively studied by, *e.g.* Goethals et al. [16,17] Polymerization of THF proceeds *via* a cationic mechanism, in which the propagating species is an oxonium ion that is ring-opened by the attack of an additional THF monomer. A counter anion of relatively low basicity, such as $–BF_4$, $–PF_6$, $–CF_3SO_3$ or $–FSO_3$, is required to achieve a living polymerization. In the following, the formation of *mono*-hydroxy-PTHF **2** and telechelic-PTHF **5** followed by the post-functionalization with 4′-chloro-2,2′:6′,2″-terpyridine **3** is discussed.

3.1.1. Methoxy-polytetrahydrofuran functionalized terpyridine

In order to synthesize *mono*-hydroxy-PTHF **2**, a bulk polymerization of THF **1** was performed at room temperature using trifluoromethanesulphonate (methyl triflate) as



Scheme 1. Schematic representation of the polymerization of THF **1** with methyl triflate resulting in *mono*-hydroxy-PTHF **2** and the subsequent synthesis of *mono*-terpyridine methoxy-PTHF **4**.

initiator. The general living cationic polymerization mechanism is presented in Scheme 1 [18].

Thus, the polymerization is initiated by methyl triflate (electrophilic initiator) that leads to the formation of the cationic oxonium ring. Subsequently, the newly formed species undergoes a nucleophilic attack from the monomer (THF), and propagation occurs in equilibrium with depolymerization. By addition of a nucleophilic terminating agent to the system, such as water, the polymerization is stopped by end capping the polymer chain with a new functionality, in this case –OH.

Following the mechanism depicted in Scheme 1, the living polymerization of THF **1** was performed in bulk for 15 min at ambient temperature followed by end capping with water yielding *mono*-hydroxy-PTHF **2**. Characterization of the resulting waxy PTHF **2** was performed by ^{1}H NMR spectroscopy, SEC and MALDI-TOF-MS. The ^{1}H NMR spectrum of **2** revealed the presence of the polymer backbone at 3.5–3.3 and 1.7–1.5 ppm as it can be seen in Fig. 1. SEC investigations (RI detector) showed a monomodal molar mass distribution of the synthesized *mono*-hydroxy-PTHF **2** with a M_n of 4400 g/mol and a PDI of 1.17 when a PEG calibration was used (Fig. 2).

In a first attempt, the postfunctionalization of the synthesized *mono*-hydroxy-PTHF **2** with 4′-chloro-2,2′:6′,2″-terpyridine was performed in DMSO with KOH as base. However, these harsh conditions led to substantial depolymerization of the PTHF resulting in ill-defined polymers. Therefore, the postfunctionalization reaction of PTHF **2** was performed using ^{t}BuOK in dry THF where the deprotonation of the hydroxy group of the polymer took place; subsequent addition of an excess of 4′-chloro-2,2′:6′,2″-terpyridine **3** led to the formation of the desired *mono*-terpyridine methoxy-PTHF **4** (Scheme 1). The nucleophilic substitution reaction was performed for 24 h at 65 °C. The purification of the reaction product was achieved by size exclusion chromatography (BioBeads S-X1 in THF).

^{1}H NMR spectroscopy, SEC and MALDI-TOF-MS were used to prove the purity of *mono*-terpyridine-PTHF **4**. The change of functionality in **4** was clearly observed by ^{1}H NMR spectroscopy (Fig. 1), where a shift for the methylene protons next to the terpyridine end-group of the PTHF towards lower magnetic field was noticed compared to the methylene protons in the unfunctionalized methoxy-PTHF **2**.

In addition, a typical upfield shift of the 3′,5′ singlet protons from the terpyridine moiety was observed when the 4′-chloro-2,2′:6′,2″-terpyridine **3** was converted into the *mono*-terpyridine PTHF **4** (Fig. 1).

SEC (RI detector with $CHCl_3$ eluent) of *mono*-terpyridine-PTHF **4** demonstrated an increased molar mass in comparison to the starting material **2** (Fig. 2). Moreover, SEC with a UV detector revealed that compound **4** is UV–vis active due to the attachment of the terpyridine moiety at the end of the polymer in contrast to the non-absorbing unfunctionalized methoxy-PTHF **2** (Fig. 2). It should be noted that the SEC (RI and UV) curves of *mono*-terpyridine-PTHF **4** revealed some tailing at higher elution volumes that might be caused by smaller molar mass species, which can be the result of a depolymerisation process as a side (or competitive) reaction during the terpyridine functionalization reaction.

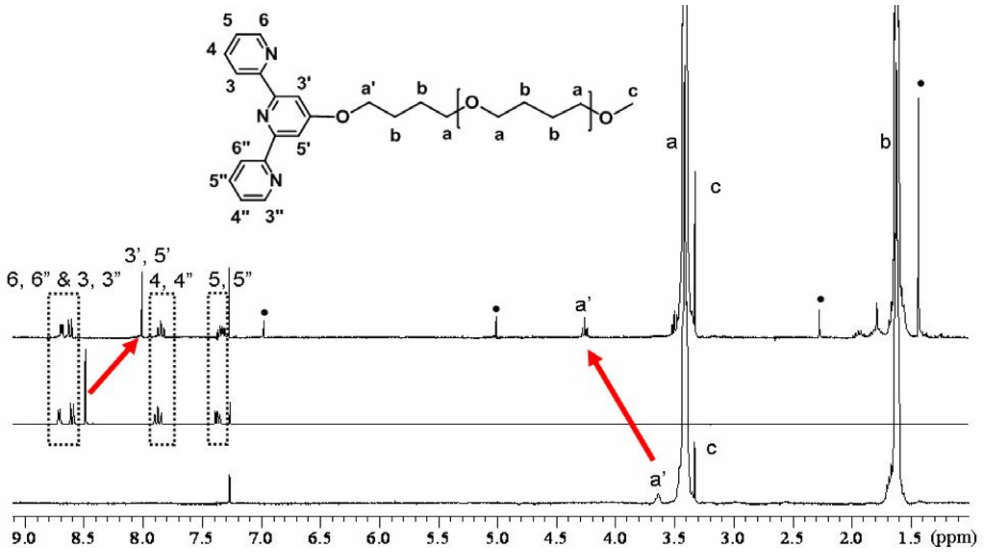


Fig. 1. ^{1}H NMR spectra (in $CDCl_3$) for *mono*-hydroxy-PTHF **2** (bottom), 4′-chloro-2,2′:6′,2″-terpyridine **3** (middle) and *mono*-terpyridine PTHF **4** (top). The dots represent BHT (butylated hydroxytoluene: stabilizer in diethyl ether and THF).

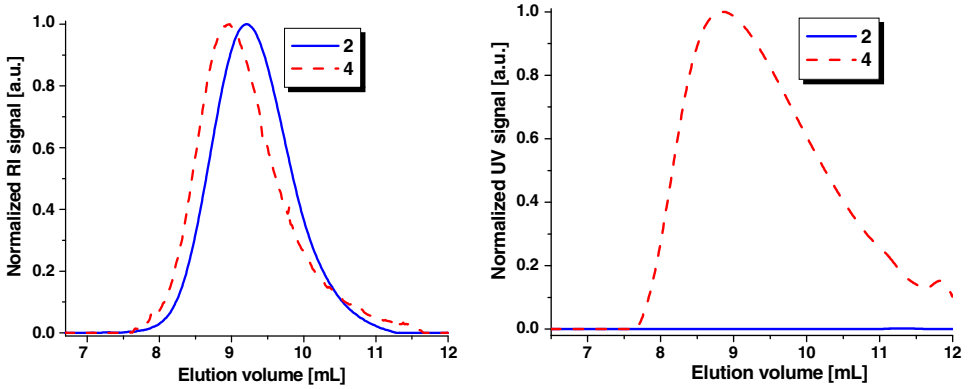


Fig. 2. SEC elution distribution (left: RI detector; right: UV-detector) for the *mono*-terpyridine PTHF **4** (dashed line) and *mono*-hydroxy-PTHF **2** (solid line). Eluent: $CHCl_3$:NEt_3:2-PrOH (94:4:2).

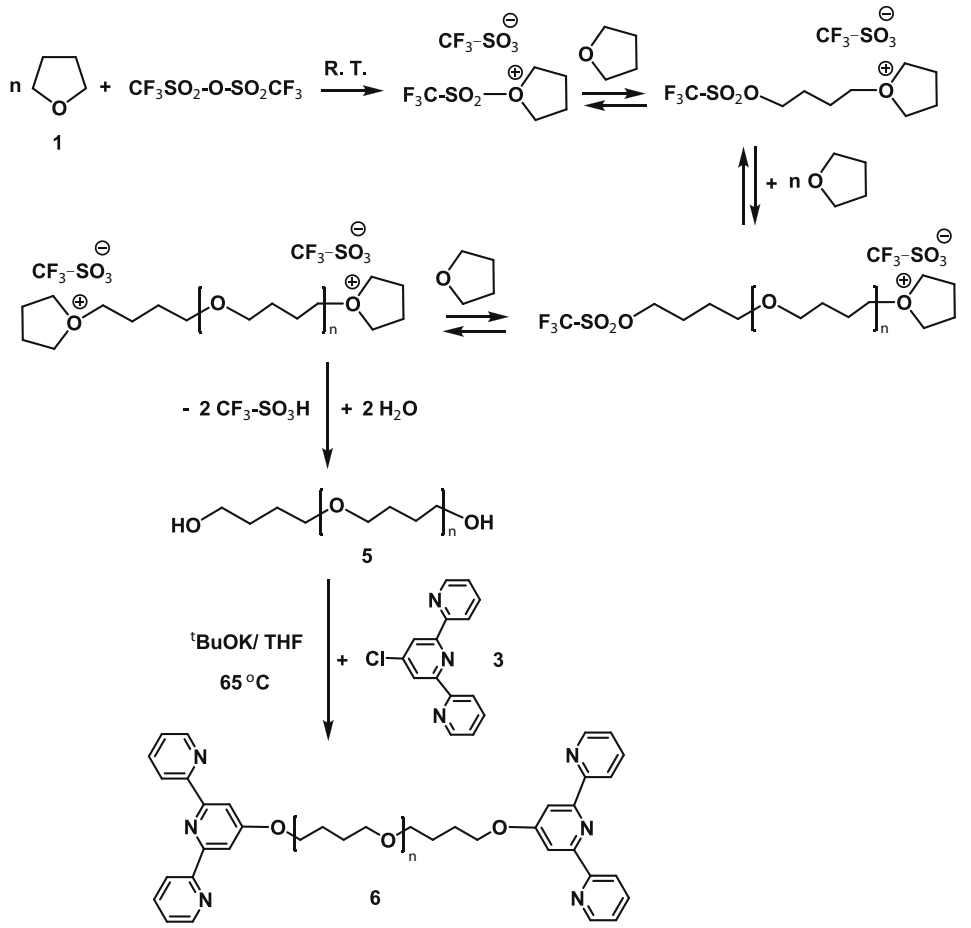
In addition, MALDI-TOF-MS indicated the derivatization of the hydroxyl group with the terpyridine moiety and the expected signal spacing for the utilized monomer of $m/z = 72$ could be observed.

3.1.2. Telechelic-polytetrahydrofuran functionalized terpyridine

To obtain telechelic-PTHF, a bulk polymerization of THF **1** using triflic anhydride as initiator was performed at room temperature. The reaction followed a living cationic polymerization mechanism as depicted in Scheme 2 [18]. In this case, the polymerization is initiated at room temperature by triflic anhydride (electrophilic initiator) that leads to the formation of the cationic tetrahydrofuranic ring. Subsequently, the newly formed species undergoes nucleophilic attack from the monomer (THF), and propagation occurs in competition with depolymerization. By the addition of water as nucleophile (terminating agent) to the system, the polymerization was stopped by end capping the polymer chain with an –OH functionality.

The bulk polymerization of **1** was performed for 15 min at room temperature followed by the addition of the nucleophilic terminating agent (water) yielding telechelic hydroxy-PTHF **5**. Characterization of the waxy PTHF **5** was performed by means of ^{1}H NMR spectroscopy and SEC. The ^{1}H NMR spectrum of **5** revealed the presence of the characteristic polymer backbone at 3.5–3.4 and 1.7–1.5 ppm. Moreover, SEC investigations showed a monomodal molar mass distribution of the synthesized telechelic-PTHF **5** with a M_n of 5800 g/mol and a PDI of 1.20 when a PEG calibration was used (Fig. 3).

The postfunctionalization of the synthesized telechelic-PTHF **5** with 4′-chloro-2,2′:6′,2″-terpyridine (Scheme 2) was achieved by following the same approach utilized for the derivatization of *mono*-hydroxy-PTHF **2** (^{t}BuOK in dry THF at 65 °C).



Scheme 2. Schematic representation of the mechanism for the polymerization of THF **1** with triflic anhydride resulting in *bis*-hydroxy-PTHF **5** and the subsequent synthesis of telechelic-PTHF **5** and *bis*-terpyridine PTHF **6**.

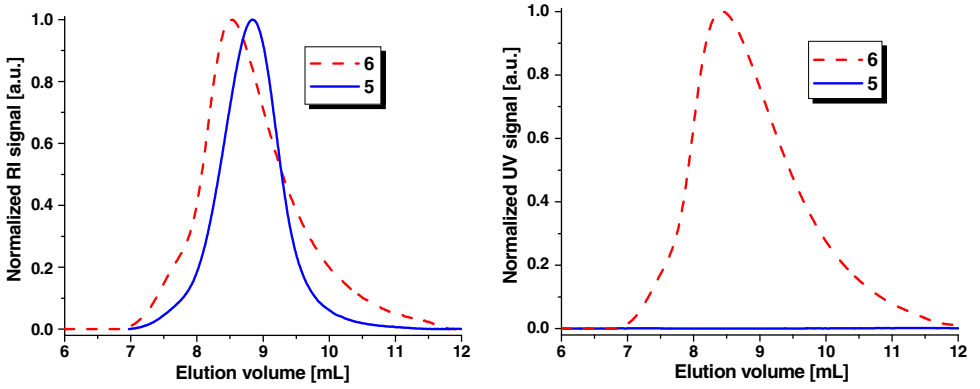


Fig. 3. SEC elution distribution (left: RI detector; right: UV-detector) for the *bis*-terpyridine PTHF **6** (dashed line) and the telechelic-PTHF **5** (solid line). Eluent: $CHCl_3$:NEt_3:2-PrOH (94:4:2).

The purity of **6** was proven by ^{1}H NMR spectroscopy, SEC and MALDI-TOF-MS. The change of functionality for the telechelic-PTHF **5** could be followed by ^{1}H NMR spectroscopy. A clear shift was observed for the methylene protons next to the terpyridine moiety towards lower magnetic field compared to the methylene protons next to the hydroxyl groups of the unfunctionalized PTHF **5**. A characteristic moderate upfield shift of the 3′,5′ singlet protons ($\Delta\delta \approx 0.5$ ppm) from the terpyridine moiety was observed, when the 4′-chloro-2,2′:6′,2″-terpyridine **3** was converted into its corresponding *bis*-terpyridine PTHF **6**.

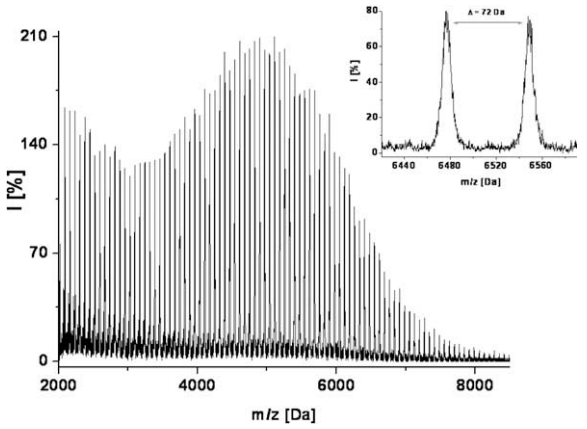


Fig. 4. MALDI-TOF-MS for the *bis*-terpyridine PTHF **6** (dithranol as matrix and sodium iodide as salt).

SEC (RI detector) of *bis*-terpyridine-PTHF **6** demonstrated a slightly increased molar mass in comparison to the unfunctionalized PTHF **5**. In addition, SEC coupled with a UV detector revealed that compound **6** is UV–vis active due to the attachment of the terpyridine moiety at the end of the polymer backbone in comparison to **5** that does not give an UV–vis signal since no conjugated units are present in the polymer chain (Fig. 3). As it can be observed in Fig. 3, SEC (RI and UV) curves of *bis*-terpyridine PTHF **6** revealed some tailing at higher elution volume as was already addressed for the *mono*-terpyridine-PTHF **4** before. The presence of some fractions with lower molar mass species in the final compound **6** could be explained by possible depolymerization reactions called retro-scission (as side process), since the functionalization reaction is performed at 65 °C, which is close to the ceiling temperature for PTHF (T_c = 83 °C) [19].

Furthermore, MALDI-TOF-MS revealed an m/z = 72 difference between peaks, which correspond to one THF repeat unit (Fig. 4). Moreover, the end-group analysis confirmed the presence of the terpyridine moieties at the end of the polymer chain of **6**.

*3.1.2.1. UV–vis titration of bis-terpyridine polytetrahydrofuran **6** with iron(II) chloride.*

In order to demonstrate the complete functionalization of the telechelic-PTHF **5** with terpyridine ligands, an UV–vis titration experiment was performed. It is known that in the presence of Fe(II) ions terpyridines give a characteristic purple color due to the formation of Fe(II) *bis*-terpyridine complexes which is characterized by a strong metal-to-ligand (MLCT) absorption band around 560 nm. The experiment consists in the stepwise addition of Fe(II) chloride (dissolved in methanol) to a solution of *bis*-terpyridine polytetrahydrofuran **6** dissolved in chloroform. The maximum absorption was obtained close to the calculated equivalence point (using the M_n from ^{1}H NMR spectroscopy) indicating full complexation of all terpyridine units, which clearly shows the potential of such 2,2′:6′,2″-terpyridine functionalized polymers to act as building blocks for supramolecular chemistry. Overtitration of the analyzed chelating macroligand **6** did not result in any further increase or decrease of the MLCT band demonstrating that the formed iron(II) terpyridine complexes are stable and do not exchange at ambient temperature (Fig. 5).

3.2. Poly(2-ethyl-2-oxazoline) terpyridine functionalization

The living cationic ring-opening polymerization of 2-oxazolines is a well-known technique for the synthesis of well-defined polymers [20–22]. The living cationic polymerization of 2-ethyl-2-oxazoline (EtOx) initiated by methyl tosylate and terminated with water is outlined in Scheme 3. Following the mechanism shown in Scheme 3, $PEtOx_{50}$ **8** with M_n = 5000 g/mol was synthesized [11].

In the next step, the synthesized $PEtOx_{50}$ was postfunctionalized with 4′-chloro terpyridine **3** *via* the ^{t}BuOK/THF route at 60 °C (Scheme 4). Further purification of the reaction product **9** was performed by BioBeads S-X1 in THF, where the excess of the 4′-chloro terpyridine **3** could be removed.

The resulting *mono*-terpyridine PEtOx **9** was characterized by means of ^{1}H NMR and UV–vis spectroscopy as well as SEC. The ^{1}H NMR spectrum is dominated by the characteristic peaks of the terpyridine moiety in the aromatic region (specific shift for 3′,5′ singlet from 8.5 to 8.0 ppm in **9**) and by the polymeric chain of $PEtOx_{50}$ in the aliphatic region. Molar mass characterization was performed using SEC with a refractive index (RI) as well as an in-line diode array detector (PDA) (Fig. 6). The overlay of the SEC traces (RI detector) displayed a typical slightly increased molar

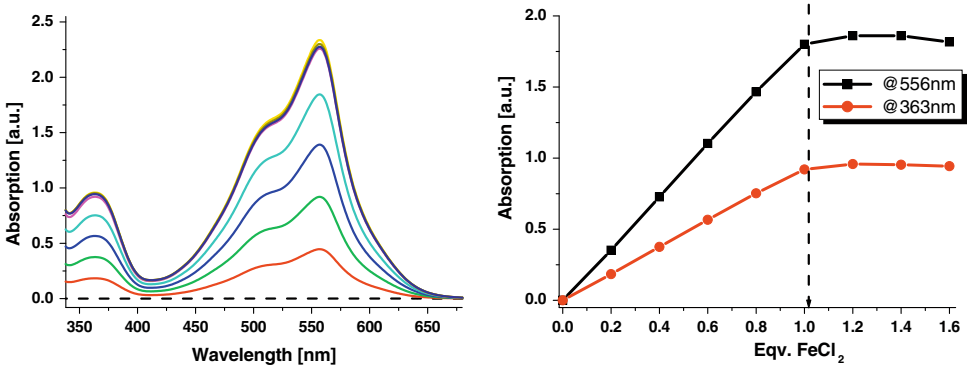
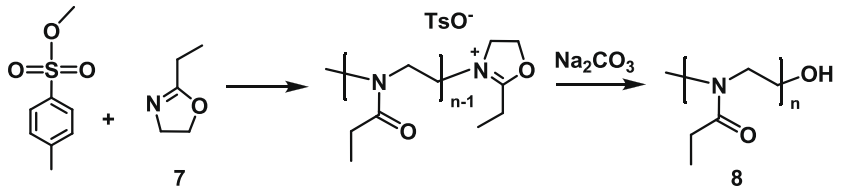
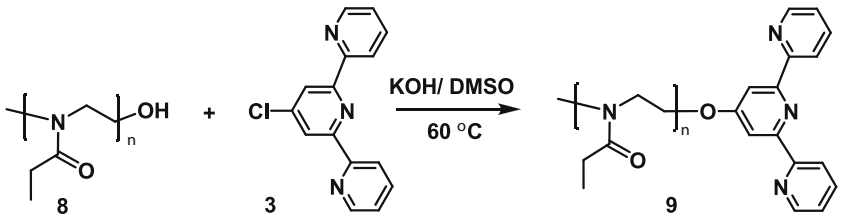


Fig. 5. UV/Vis titration of **6** with iron(II) chloride in $CHCl_3$/MeOH (1:1 v/v) (left); rise of the MLCT band at 556 nm and the ligand absorption at 363 nm in relation to the equivalents iron(II) titrated (right).



Scheme 3. Schematic representation of the mechanism for the cationic ring-opening polymerization of EtOx **7** with methyl tosylate.



Scheme 4. Schematic representation of the synthesis of *mono*-terpyridine PEtOx **9** *via* the ^{t}BuOK/THF route.

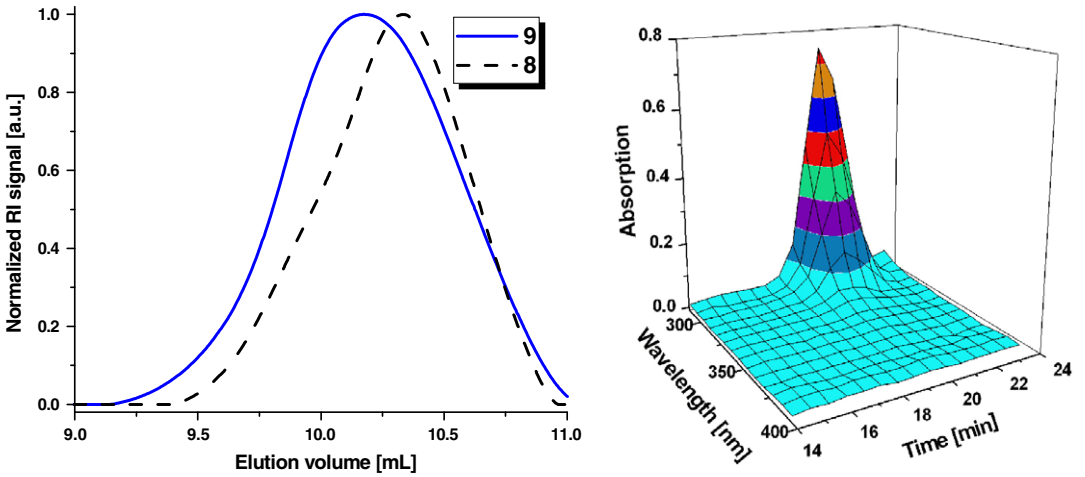


Fig. 6. Left: SEC elution distribution (RI detector) for *mono*-terpyridine $PEtOx_{50}$ **9** in comparison to the $PEtOx_{50}$ **8**. Right: SEC elution distribution (PDA detector) for the *mono*-terpyridine $PEtOx_{50}$ **9**. Eluent containing DMF with 5 mM NH_4PF_6.

mass of the *mono*-terpyridine PEtOx **9** in comparison to the unfunctionalized PEtOx **8**. In addition, SEC with PDA detector revealed the existence of the terpyridine moiety in the complete polymer distribution as indicated by the strong absorption at 290 nm demonstrating full functionalization of the polymer (Fig. 6).

The IR spectra also showed that indeed the functionalization of **9** with the terpyridine moiety was successful as indicated by the presence of the typical IR bands such as, *e.g.* 1650 cm^{-1} (C=O), 2971 cm^{-1} (CH aliphatic) and 1430 (C–N) of the polymer backbone as well as the terpyridine moiety in the final product **9**.

3.3. Pluronic terpyridine functionalization

Block copolymers are another important targeted class for the 4′-terpyridine postfunctionalization. From the multitude of available triblock copolymers our attention was attracted by the polymers/copolymers that are able to undergo reverseble phase transitions upon increasing the temperature, such as *e.g.* poly(ethylene oxide) (PEG)-poly(propylene oxide) (PPG) copolymers and poly(*N*-isopropylacrylamide) (PNIPAM). We recently demonstrated that the phase transition temperature of PNIPAM can be tuned by metal complexation using various metals and counterions resulting in multiresponsive polymers [23].

Triblock copolymers of poly(ethylene oxide) (PEG) and poly(propylene oxide) (PPG) with the block sequence $(PEG)_m$-*b*-$(PPG)_n$-*b*-$(PEG)_m$ consisting of hydrophilic (PEG) segments and hydrophobic (PPG) segments are an important class of temperature-responsive copolymers known as Pluronics® (BASF) or Polaxomers® (ICI) [24]. They are non-ionic amphiphilic molecules which are both surface active and capable of forming micelles or vesicles in aqueous solutions induced by a temperature change; the block copolymers self-assemble upon rising the temperature due to collapse of the PPG segments. The mentioned triblock copolymers represent an industrially important class of

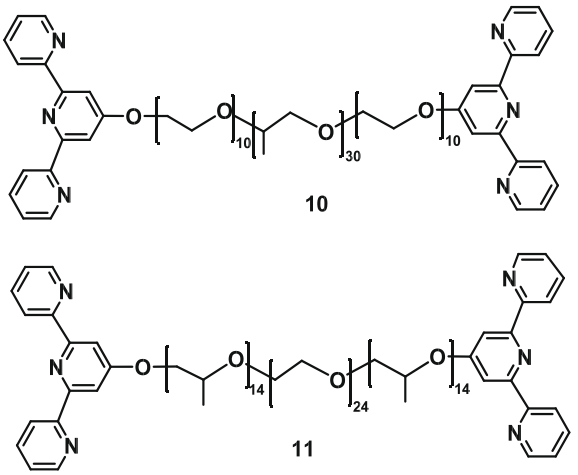


Fig. 7. Schematic representation of the synthesized *bis*-terpyridine Pluronics® **10**, **11**.

surfactants and are intensively used in different fields with a special interest in pharmaceutics and personal care [25].

Since we were interested to synthesize well-defined *bis*-terpyridine Pluronics®, our experimental efforts focused on low molar mass triblock copolymers known to be characterized by lower percentages of defect structures such as *e.g.* diblock or homopolymers. The preparation of the *bis*-terpyridine functionalized Pluronics® followed a straightforward synthetic pathway by postfunctionalization with 4′-chloro-2,2′:6′,2″-terpyridine **3** *via* nucleophilic substitution in KOH/DMSO at 60 °C. Thus, $(PEG)_{10}$-*b*-$(PPG)_{30}$-*b*-$(PEG)_{10}$ with M_n = 2800 g/mol was subjected to functionalization reactions with 4′-chloro-2,2′:6′,2″-terpyridine. Moreover, the inverse triblock copolymer $(PPG)_{14}$-*b*-$(PEG)_{24}$-*b*-$(PPG)_{14}$ with M_n = 2700 g/mol was functionalized in the same fashion. The resulting chelating triblock copolymers **10** and **11** (Fig. 7) were characterized by means of ^{1}H NMR spectroscopy and SEC.

The attachment of the terpyridine unit to the end of the block copolymers could be proven by ^{1}H NMR spectroscopy. In the purified products **10** and **11,** the characteristic moderate upfield shift of the 3′,5′ singlet protons ($\Delta\delta \approx 0.5$ ppm) from the middle ring of the terpyridine unit was observed that confirmed the ether bond formation between the 4′-chloro-2,2′:6′,2″-terpyridine **3** and the hydroxyl functionality of the Pluronics®.

Moreover, the SEC measurements with RI detector (DMA eluent) showed a slightly increased molar mass in comparison to the starting materials. In addition, SEC measurements with a UV–vis detector (performed with the same eluent) revealed a strong UV–vis absorption at 290 nm demonstrating the presence of the terpyridine moiety on the functionalized Pluronics® (Figs. 8 and 9). Similar to the PTHF functionalization, some shoulders appeared in the SEC traces of the terpyridine functionalized polymers. For the Pluronics® small high molar mass and low molar mass shoulders appeared after the reaction with 4′-chloro-2,2′:6′,2″-terpyridine **3**. These shoulders are believed to result from the occurrence of some transetherification reactions under the rather strong basic conditions. Nonetheless, these minor shoulders are believed to not interfere with the desired thermoresponsive properties of the polymers.

4. Conclusions

In this report, we described the synthesis of new 2,2′:6′,2″-terpyridine functionalized macromolecules based on poly(tetrahydrofuran), poly(2-ethyl-2-oxazoline) and Pluronics®. Due to the nature of the polymeric spacer, *e.g.* low T_g for PTHF and thermoresponsiveness for poly(2-ethyl-2-oxazoline) and Pluronics®, but also due to the presence of the terpyridine units, these polymers represent promising supramolecular building blocks for metallocomplexation. The possibility to synthesize metallo-supramolecular chain extended polymers from these building blocks is demonstrated by an iron(II) UV–vis titration experiment to *bis*-terpyridine PTHF clearly revealing metal complex formation.

The properties of the resulting metallo-supramolecular polymers can be potentially tuned by varying the metal ions as well as the counter ions [8]. Moreover, the thermosensitive properties of the Pluronics® block copolymers in combination with metal coordination are envisioned to result in multiresponsive polymer structures [23]. These aspects are under further investigation at the moment.

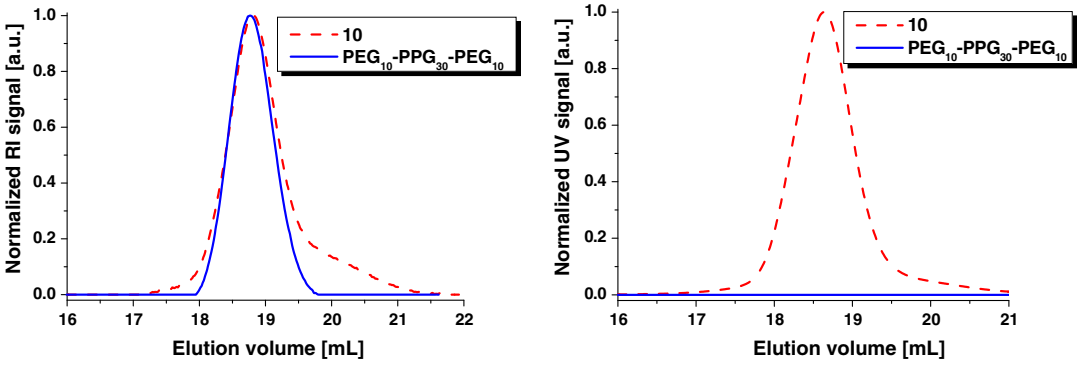


Fig. 8. Left: SEC elution distribution (left: RI detector; right: UV-detector) for the *bis*-terpyridine Pluronic® **10** in comparison to the unfunctionalized telechelic Pluronic®. Eluent: DMA with 49.5 mmol/L LiCl.

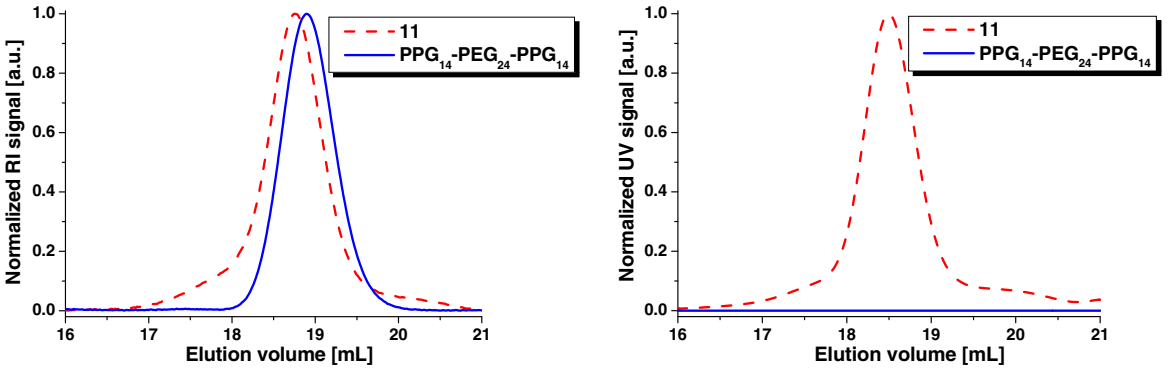


Fig. 9. Left: SEC elution distribution (left: RI detector; right: UV-detector) for the bis-terpyridine Pluronic® **11** in comparison to the unfunctionalized Pluronic®. Eluent: DMA with 49.5 mmol/L LiCl.

Acknowledgements

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