Functionalized Oligomers and Copolymers with Metal Complexing Segments: A Simple and High Yield Entry towards 2,2':6',2''-Terpyridine Monofunctionalized Telechelics

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SUMMARY: 4'-Chloro-2,2':6',2''-terpyridine was reacted in a high yield Williamson type reaction with α-hydroxy-ω-carboxy-functionalized poly(ethylenoxide) to obtain monoterpyridine terminated telechelics. The completeness of the functionalization was proven by NMR, GPC and MALDI-TOF-MS investigations. Addition of transition metal ions resulted in the formation of the corresponding octahedral terpyridine metal complexes and resulted in the formation of metallo-supramolecular dimers.

Introduction

The blending of supramolecular with macromolecular systems is a major aim in today's research (see, e.g.[1,2]). In particular, metallo-supramolecular polymer composites could provide novel organic-inorganic hybrid materials with a wide range of interesting potential properties, e.g. concerning smart materials, intelligent glues or electro- and photoactive compounds. There are several different entries into this field. Besides the final complexation of special block copolymers and micelles with metal binding sites or compartments[3], the construction of composites utilizing non-covalent interactions is of special interest[4]. For practical applications, supramolecular segments with an availability in usable quantities and with recognition-directed self-assembly features are necessary. This requires a careful selection of suitable building blocks. Very promising systems come from the area of *N*-heterocyclic ligands, which have been known for nearly a century as very effective and stable complexation agents for transition metal ions[5]. In particular 2,2':6',2''-terpyridine compounds,

which spontaneously form stable octahedral metal complexes with a wide range of transition metal ions (such as cobalt(II), copper(II), manganese(II), iron(II), iron(III), chromium(III), nickel(II) or ruthenium(II)) have been studied extensively[6], due to their interesting electronic and redox properties[7]. However, the difficulty in obtaining a straightforward and high yield preparation of terpyridine-containing oligomers and polymers has always been a major drawback in this direction. Usually, special terpyridine ligands were functionalized with hydroxy, amino or carboxy end groups and then reacted in a polycondensation type reaction with suitable monomers, oligomers or polymers (see e.g.[8]). Recently we developed a different approach in this direction utilizing very simple and meanwhile commercially available 4'-functionalized terpyridine ligands as new starting materials (for first preliminary results, see[9]). As first example we used α-hydroxy-ω-carboxy-functionalized poly(ethylen-oxide) oligomers to prepare monofunctionalized terpyridine-containing systems (Fig. 1). Addition of suitable transition metal ions to these oligomers resulted in mono-complexes or in a dimerisation and thus in a doubling of the molecular weight. In addition, the carboxyl end group allows the attachment onto surfaces, e.g. via silane chemistry, onto glass or Si_3N_4 substrates. Extension of this strategy leads towards oligomers and polymers with two or more terpyridine end groups.
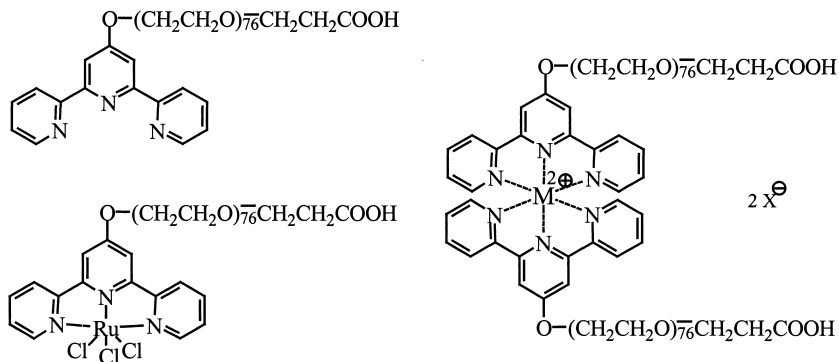

Fig. 1: Schematic representation of the synthesized monofunctionalized oligomers and the corresponding metal-containing systems (M = Co, Ru, Zn).

Experimental

Materials and Characterization

Materials were obtained from commercial suppliers and used without further purification. Anhydrous dimethylformamide (DMF) was purchased from Aldrich Chemical Company. ^{1}H and ^{13}C NMR spectra were recorded at 300 and 75 MHz, respectively, on a Bruker AC 300 spectrometer. The chemical shifts were calibrated to the residual solvent peak or TMS. Gel permeation chromatography (GPC) analysis was performed on a Waters Liquid Chromatograph system using Shodex GPC K-802S columns, Waters Differential Refractometer 410 and Waters UV Absorption Detector 486 with chloroform as eluent. Calibration was conducted with polystyrene standards. UV/VIS measurements were recorded using a Varian Cary 3 UV/VIS spectrometer. MALDI-TOF-mass spectra were measured with Bruker Biflex 3 mass spectrometer (matrix dithranol, solvent acetone).

Synthesis:

Preparation of the 4'-chloro-2,2':6',2''-terpyridine 1: Synthesized according to[10]. Mp. 152°C; ^{1}H-NMR (CHCl$_3$, 300 MHz): 7.35 (dd), 7.87 (dd), 8.49 (s), 8.60 (d), 8.71 (d).

Preparation of the α-carboxyl-ω-(2,2':6',2''-terpyrid-4'-yl)-poly(ethylenoxide) 2: To a suspension of KOH (0.900 g, 16.07 mmol) in DMSO (10 ml) α-carboxy-ω-hydroxy-poly-(ethylenoxide) (0.100 g, 27 µmol) was added. After stirring 1 h at 60°C 4'-chloroterpyridine (0.015 g, 54 µmol) was added. The mixture was stirred at 60°C for 24 h. The heater was removed and the mixture was poured into cold water (50 ml). The solution was extracted with chloroform (3 × 100 ml). The combined organic phases were dried over Na$_2$SO$_4$ and the solvent removed *in vacuo*. The residue was solved in THF and dropwise added to diethyl ether. α-Carboxyl-ω-(2,2':6',2''-terpyrid-4'-yl)-poly(ethylenoxide) precipitates as a white solid yielding 95 mg (26 µmol, 96%). ^{1}H-NMR (CDCl$_3$, 300 MHz): δ (ppm) 2.60 (t, J = 6.1 Hz, 4 H, H$_{PEG}$), 3.40 (t, J = 4.8 Hz, 4 H, H$_{PEG}$), 3.64 (m, 410 H, H$_{PEG}$), 4.42 (m, 3 H, H$_{PEG}$), 7.35 (m, 2 H, H-5,5''), 7.87 (m, 2 H, H-3',5'), 8.07 (m, 2 H, H-3,3''), 8.66 (m, 4 H, H-6,6''). MALDI-TOF-MS: $\overline{M}_n$: 3635; $\overline{M}_w$: 3659, PDI: 1.01. GPC (CHCl$_3$, PS-standard): $\overline{M}_n$: 6202; $\overline{M}_w$: 6808, PDI: 1.09. UV/VIS (acetonitrile): λ(ε) = 239 nm (26100), 276 nm (23900). Anal. Calc. for C$_{170}$H$_{319}$N$_3$O$_{79}$: calcd.: C, 55.65; H, 8.76; N, 1.15; found: C, 55.71; H, 8.27; N, 1.05.

Preparation of the α-carboxyl-ω-(2,2:6',2''-terpyrid-4'-yl-ruthenium(III)chlorid)-poly-(ethylenoxide) 3: To a solution of $RuCl_3 \times 3\ H_2O$ (4.0 mg, 15 μmol) in ethanol (4 ml) α-carboxyl-ω-(2,2':6,2''-terpyrid-4'-yl)-poly(ethylenoxide) was added. After stirring 4h at 60°C the heater was removed. The mixture was cooled to ambient temperature when brown precipitate was formed. After 4 h at −78°C the precipitat was separated and washed with cold ethanol yielding 35 mg (9.03 μmol, 66%) α-carboxyl-ω-(2,2':6,2''-terpyrid-4'-yl-ruthenium(III)chlorid)-poly(ethylenoxide). ^{1}H-NMR (300MHz, CDCl$_3$): δ (ppm) 3.64 - 3.77 (m, H$_{PEG}$); MALDI-TOF-MS: $\overline{M}_n$: 3361; $\overline{M}_w$: 3420, PDI: 1.02; GPC (CHCl$_3$, PS-standard): $\overline{M}_n$: 4706; $\overline{M}_w$: 6956, PDI: 1.48. UV/VIS (methanol): $\lambda(\varepsilon)$ = 275 nm (26118), 303 nm (15304), 391 nm (5532).

Preparation of the cobalt(II) polymer ion complex 4: To a solution of α-carboxyl-ω-(4'-terpyridyl)-poly(ethylenoxide) (0.478 mg,) **2** in methanol (5 ml) a solution of Co(CH$_3$COO)$_2$ × 4 H$_2$O (1.118 mg in 10 ml methanol) was added dropwise. The formation of the polymer ion complex was monitored by UV/VIS-spectroscopy. UV/VIS (methanol): $\lambda(\varepsilon)$ = 308 (14573). MALDI-TOF-MS: $\overline{M}_n$: 7525; $\overline{M}_w$: 7568, PDI: 1.01.

Preparation of the zink(II) polymer ion complex 5: To a solution of ZnCl$_2$ (10 mg, 73 μmol) a solution of α-carboxyl-ω-(4'-terpyridyl)-poly(ethylenoxide) **2** (20 mg, 5.45 μmol) in methanol was added dropwise. The successful formation of the single sided polymer ion complex was detected by MALDI-TOF mass spectrometry. MALDI-TOF-MS: $\overline{M}_n$: 3738; $\overline{M}_w$: 3792, PDI: 1.01.

Preparation of the model complex *bis*[4'-oxytetramethylenoxy^{t}butyl-(2,2':6',2''-terpyridine)]cobalt(II) hexafluorophosphat 6:** Synthesized according to[11]. UV/VIS (methanol): $\lambda(\varepsilon)$ = 307 (27500). MALDI-TOF-MS: 814 (M$^+$ - 2 PF$_6^-$).

Results and Discussion

The combination of *N*-heterocyclic ligands and other metal complexing segments with oligomers and polymers has attracted much interest during the last decade. Such materials could offer a new entrance to organic-inorganic hybrid composites. Besides the applications in bulk material the use in thin films and on surfaces is of particular interest. Systems with one metal complexing unit could be e.g. tethered to substrates or used for the formation of supramolecular dimers (Fig. 2).
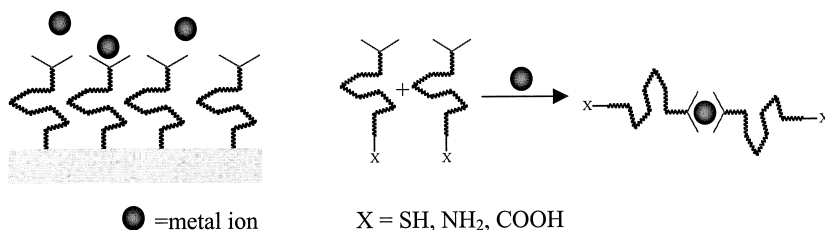
● =metal ion   X = SH, NH₂, COOH

Fig. 2: Schematic representation of polymers with one metal complexing unit: Bound to surfaces (left) or utilized for the formation of dimers (right).

In most cases bipyridine or terpyridine ligands have been used, due to the outstanding complexing abilities of these units. Recently, we have demonstrated the incorporation of 5,5"-*bis*(hydroxymethyl)terpyridine segments into the backbone of a block copolymer and the successful crosslinking in presence of transition metal ions like cobalt(II). However, all these approaches suffer from the complicated and time consuming synthetic accessibility of the utilized functionalized *N*-heterocyclic segments. Therefore we developed a new synthetic strategy towards terpyridine containing systems based on a different starting material: 4'-chloro-2,2':6',2"-terpyridine **1** (Fig. 3).
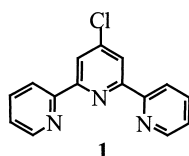

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Fig. 3: Schematic representation of the central terpyridine building block **1**.

This very simple and now commercially available unit (Aldrich) can be synthesized in multihundred gram quantities utilizing a modified Kröhnke synthesis[10]. The ligand can be used directly for the functionalization of hydroxy terminated oligomers and polymers. As a first example we reacted a commercially available α-carboxy-ω-hydroxy functionalized prepolymer **2** with 4'-chloro-2,2':6',2"-terpyridine **1** in a Williamson type ether synthesis in the presence of potassium hydroxide in anhydrous DMSO. The desired α-carboxyl-ω-(4'-terpyridyl)-poly(ethylenoxide) **3** with both a complexing and a carboxyl end group could be isolated by precipitation in 88% yield (Fig. 4).
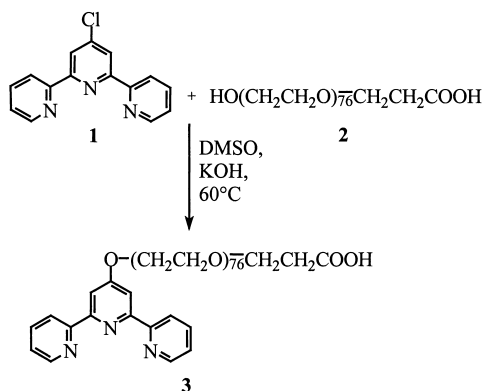
Fig. 4: Synthesis of α,ω-functionalized metal complexing polymers **3**.

The complete monofunctionalization of the poly(ethylenoxide) with the terpyridine moiety could be proven by various techniques. Fig. 5 compares the ^{1}H-NMR-spectra of the basic telechele and the terpyridine containing product. The left inset in the product spectrum (b) shows the signals of the terpyridine with the characteristic shift of the protons 3 and 5 after exchange of the chloro by an oxygen group in position 4 (see also[12]).
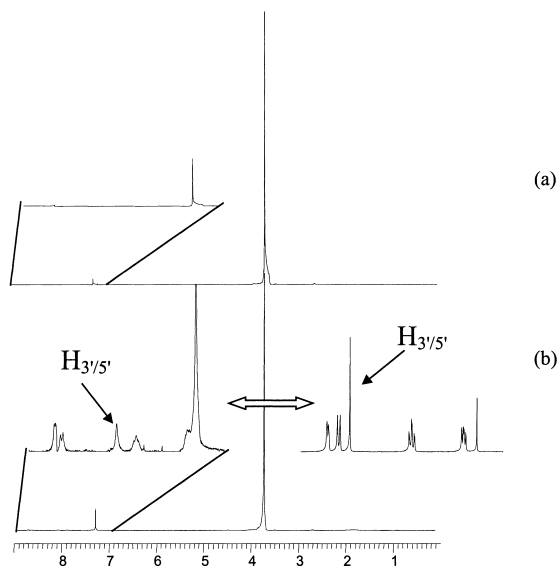
Fig. 5: ^{1}H-NMR spectra: (a) α-carboxyl-ω-hydroxy-poly(ethylenoxide) **2**; (b) α-carboxyl-ω-(4'-terpyridyl)-poly(ethylenoxide) **3**; the right inset shows the aromatic region of the 4'-chloro-terpyridine **1** spectrum.

Utilizing GPC the incorporation of the terpyridine moiety can be easily seen by applying a UV/VIS detector (254 nm) due to the different absorption properties of the poly(ethylenoxide) and the terpyridine unit (Fig. 6).
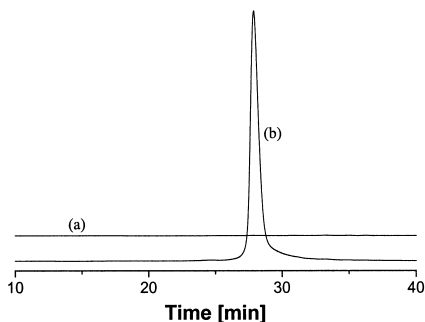

Fig. 6: GPC results of (a) α-carboxyl-ω-hydroxy-poly(ethylenoxide) **2** and (b) α-carboxyl-ω-(4'-terpyridyl)-poly(ethylenoxide) **3** utilizing a UV/VIS detector (254 nm).

However, this does not provide a quantitative proof of a complete functionalization. The question can be addressed by using MALDI-TOF mass spectrometry (Fig. 7). The difference in molecular weights between prepolymer **2** and the product **3** correlates with the complete reaction of one terpyridine unit for each prepolymer.
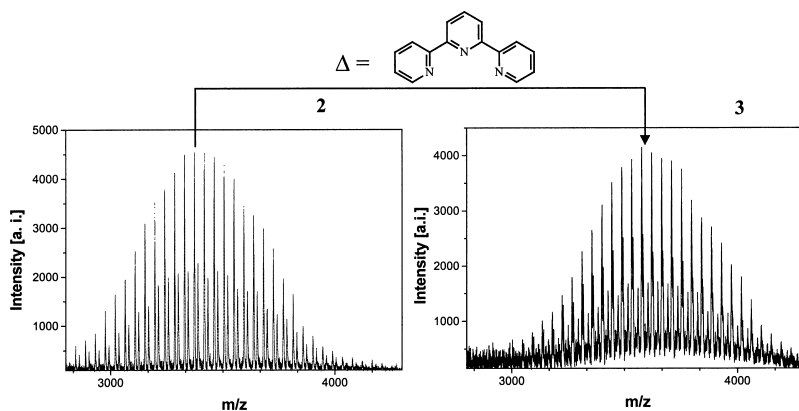

Fig. 7: MALDI-TOF-MS: Left) α-Carboxyl-ω-hydroxy-poly(ethylenoxide) **2**; right) α-carboxyl-ω-(4'-terpyridyl)-poly(ethylenoxide) **3**.

The successful functionalization can also be demonstrated by the addition of transition metal ions such as ruthenium(III), which can selectively form 1:1 complexes with terpyridine ligands[13] (Fig. 8). This allows the construction of unsymmetrical dimers.
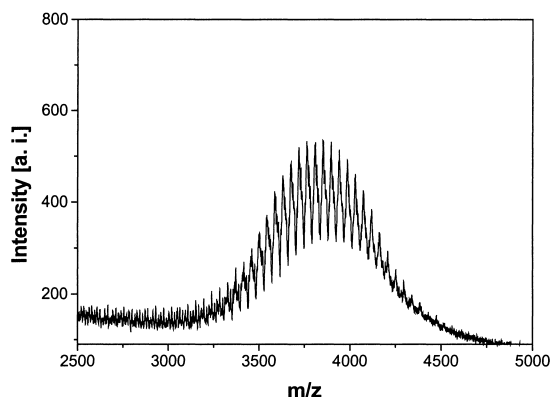

Fig. 8: MALDI-TOF-MS of the α-carboxyl-ω-(4'-terpyridyl)-poly(ethylenoxide) **4** ruthenium(III) complex.

Addition of other transition metal ions, such as cobalt(II) or zink(II) leads, to a spontaneous self-assembly of two terpyridine units and thus to a dimerisation (Fig. 9). The formation of the complexes can be reversed, e.g. by changing pH or temperature, or by applying electrochemical changes[14].
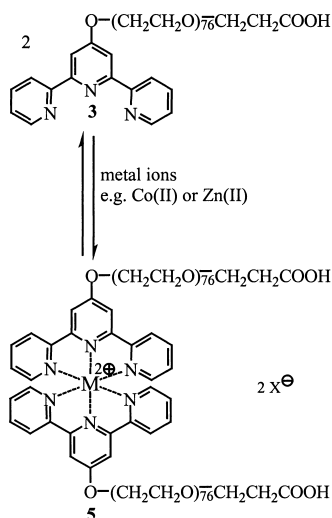

Fig. 9: Schematic representation of the dimerization of oligomer **3** by addition of transition metal ions, such as cobalt(II).

The complexation can easily be monitored by different techniques. Fig. 10 shows the change of the UV/VIS absorption behavior following addition of cobalt(II) acetate to the terpyridine-containing polymer. A redshift of the π-π*-band can be observed which is typical for the formation of terpyridine transition metal complexes.
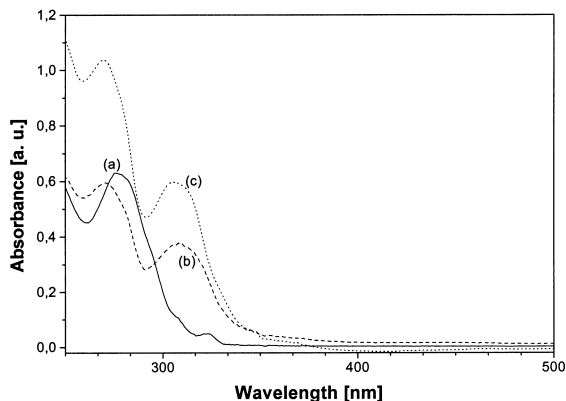
Fig. 10: UV/VIS spectra of (a) the uncomplexed polymer **3**, (b) the polymer ion complex **5** in methanol, (c = 458 µg/5ml), and (c) the terpyridine-cobalt-model complex **6**.

Again, MALDI-TOF mass spectrometry revealed to be very useful for the characterization of such metallo-supramolecular assemblies and polymers: As shown in Fig. 11, the molecular weight of the polymer has doubled after addition of metal ions.
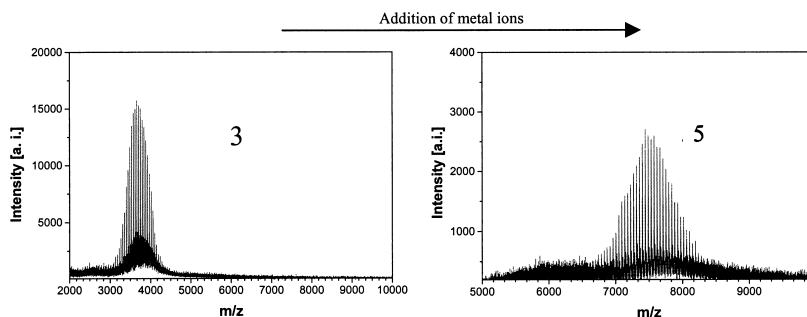
Fig. 11: MALDI-TOF MS of the terpyridine containing polymer **3** (left) and the polymer-ion complex **5** (right).

Extension of this methology can lead to systems functionalized with two or more terpyridine units and therefore to a non-covalent polymerization (in principle a polyaddition reaction) or crosslinking (Fig. 12).
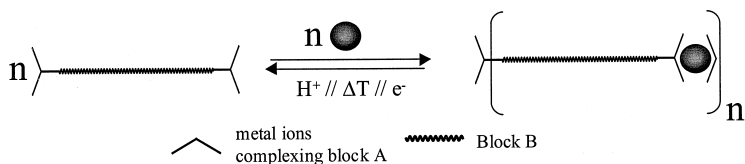
Fig. 12. Schematic representation of a potential non-covalent polymerization.

Conclusions

In this paper we showed a simple and high yield synthesis of a new class of terpyridine monofunctionalized metal complexing telechelics. The complete functionalization could be proven by various techniques, including NMR spectroscopy, MALDI-TOF mass spectrometry and GPC. The complexation of the polymer by addition of transition metal ions results in the case of ruthenium(III) ions in 1:1 complexes and in the case of metal ions such as cobalt(II) in the formation of non-covalent dimers. Further studies will concentrate on the investigation of this materials and the preparation of *bis*functional and multifunctional building blocks.

Acknowledgements

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