

SUPPORTING INFORMATION

Metallo-supramolecular diblock copolymers based on heteroleptic cobalt(III) and nickel(II) *bis*-terpyridine complexes

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Materials and instrumentation

The chemicals used for this work were either purchased from Aldrich, Fluka, or Acros. As reported in the literature, the terpyridine ligand was introduced to the poly(ethylene-oxide) end chain by polymer end group modification reaction,¹ while polystyrene block was prepared by nitroxide mediated controlled radical polymerization of styrene using a terpyridine functional initiator.² The latter one has been synthesized according to well-known procedures.² ¹H-NMR were recorded on a 500 MHz Bruker spectrometer at 25°C. Chemical shifts are given in ppm downfield from TMS. Gel permeation chromatography (GPC) was carried out a system composed of two PSS Gram columns, 100 Å and 1000 Å, connected to a Waters 410 differential refractometer. DMF with 5 mM NH₄PF₆ was used as the carrier solvent. UV-vis absorption spectra were recorded on a Varian Cary 50 spectrometer.

Synthesis

a. Synthesis of the metallo-supramolecular block copolymer PS₂₄₀-[Co^{III}]-PEO₂₃₀

The precursor complex of CoCl₂.6DMF was prepared by dissolution of cobalt(II) chloride salt (0.5 mg, 3.84 μmol) in 1 mL of DMF, and were allowed to stir for 30 min at room temperature. The *mono*-complex was synthesized by a direct addition of PS₂₄₀-[(1 eq; 84 mg; 3.66 μmol)block dissolved in 1 mL of DMF to the precursor complex. After one minute, the PEO₂₃₀-[block (37 mg; 3.66 μmol) dissolved in 1 mL of DMF was added, leading to the *bis*-complex of cobalt(II). The latter complex was oxidized into cobalt(III) with an excess of silver nitrate (5.00 mg; 36.60 μmol.) and was stirred overnight. The chloride counter ions were exchanged by hexafluorophosphate ones by addition of an excess of NH₄PF₆ (5.80 mg; 36.60 μmol) to the reaction mixture and was allowed to stir for one hour. Silver particles (Ag and AgCl) resulting from the oxidation process of cobalt(II) were readily removed by filtration, while, DMF was removed under reduced pressure. Afterward, the crude reaction mixture was washed with diethyl ether (48 hours) and water (48 hours) containing 20% v/v of H₂O₂. The reaction yield was estimated at 60%. ¹H-NMR (CDCl₃, 500 MHz): δ = 8.52-8.22 (m, 8H; H_a; H_b PEO&PS), 8.20-8.00 (m, 4H; H_c PEO&PS), 7.60-7.40 (m, 8H; H_d; H_e PEO&PS), 7.20-6.28 (m, 1100H; H_{PS} backbone aromatics), 3.90-3.40 (m, 960H, H_{PEO} backbone), 2.20-1.20 (m, 690H_{PS} backbone aliphatics).

b. Synthesis of the metallo-supramolecular block copolymer $PS_{240}-[Ni^{II}]-PEO_{230}$

The precursor complex of $NiCl_2 \cdot 6DMF$ was prepared by dissolution of nickel(II) chloride salt (0.5 mg, 2.08 μmol) in 1 mL of DMF, and was allowed to stir for 30 min at room temperature. The *mono*-complex was synthesized by a direct addition of $PS_{240}-[$ (46 mg; 1.98 μmol) block dissolved in 1 mL of DMF to the precursor complex. After one minute, the $PEO_{230}-[$ block (22 mg; 1.98 μmol) dissolved in 1 mL of DMF was added, leading to the *bis*-complex of nickel(II). The solution was allowed to stir for 3 hours. The chloride counter ions were exchanged by hexafluorophosphate ones by addition of an excess of NH_4PF_6 (3.22 mg; 19.80 μmol) to the reaction mixture and was allowed to stir for one hour. Afterward, DMF was removed under reduced pressure, the crude reaction mixture was washed with diethyl ether (48 hours) and water (48 hours). The reaction yield was estimated at 40%. $^1\text{H-NMR}$ ($CDCl_3$, 500 MHz): δ 7.20-6.28 (m, 1100H; H_{PS} backbone aromatics), 3.90-3.40 (m, 960H, H_{PEO} backbone), 2.20-1.20 (m, 690H; H_{PS} backbone aliphatics).

UV-Vis characterization

The synthesis of the $PS_{240}-[Co^{III}]-PEO_{230}$ *bis*-complex has been followed by UV-Vis spectroscopy. The *bis*-complex of $PS_{240}-[Co^{II}]-PEO_{230}$ showed characteristic MLCT bands located at 450 and 510 nm. The oxidation of the latter complex into $PS_{240}-[Co^{III}]-PEO_{230}$ was confirmed by disappearance of the absorption band located at 510 nm.

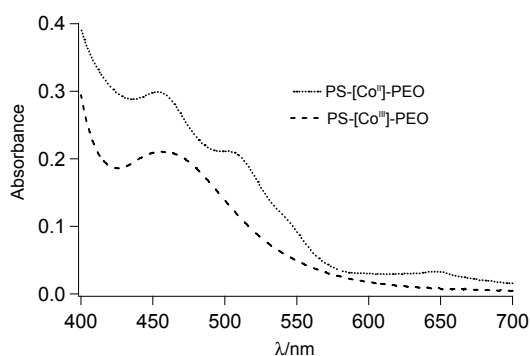


Fig. S1: UV-Vis absorption bands of the $PS_{240}-[Co^{II}]-PEO_{230}$ and $PS_{240}-[Co^{III}]-PEO_{230}$ *bis*-complexes.

Micelle preparation

The two investigated block copolymers were first dissolved in 1 mL of DMF, a non-selective solvent for both the PS and PEO block to reach a concentration of 1 g/L. A volume of water equal to half the DMF volume was then added by steps of 50 μL to induce aggregation of the PS blocks, followed by the addition of an equal volume of water in one shot to “freeze” the micelles.

Transmission Electron Microscopy characterization

Transmission electron microscopy (TEM) measurements were performed on a FEI Tecnai 20, type Sphera TEM operating at 200 kV (LaB₆ filament). Images were recorded with a bottom mounted 1k x 1k Gatan CCD camera. R2/2 Quantifoil Jena grids were purchased from SPI. A volume of 3 μ l of the micellar solution was applied to a 200 mesh carbon coated copper grid and subsequently excess liquid was quickly manually blotted away with filter paper.

Breaking of the cobalt(III) and nickel(II) *bis*-terpyridine complexes

The breaking of the *bis*-terpyridine cobalt(III) and nickel(II) complexes has been performed on micellar solutions of the PS₂₄₀-[Co^{III}]-PEO₂₃₀ and PS₂₄₀-[Ni^{II}]-PEO₂₃₀ at a concentration of 10 g/L. For the cobalt based copolymer, *N*-ethylmorpholine (1.02 mg, 8.8 μ mol) was added to the micellar solution to reduce cobalt(III) into cobalt(II). Afterward, 200 μ L of 0.01M HCl solution was added to protonate the terpyridines and open the labile cobalt(II) complex. For the nickel based copolymer, a slight excess of potassium cyanide (0.34 mg, 5.2 μ mol) were added to the PS₂₄₀-[Ni^{II}]-PEO₂₃₀ micellar solution.

In both cases, a precipitate has been observed after opening of the complexes. This precipitate has been filtered off from the solution, washed, dried, redissolved in CDCl₃ and finally analyzed by ¹H-NMR. ¹H-NMR analysis confirmed that this precipitate consists of PS₂₄₀-[chains. ¹H-NMR (CDCl₃, 500 MHz): δ = 8.69 (m, 2H; H_c PS), 8.62 (m, 2H; H_b PS), 8.20 (m, 2H; H_a PS), 7.93 (m, 2H; H_c PS), 7.57-6.32 (m, 1100H; H_{PS backbone aromatics} H_{aromatics} H_d), 2.45-0,53 (m, 690H_{PS backbone aliphatics}).

References

1. B. G. G. Lohmeijer and U. S. Schubert, *Macromol. Chem. Phys.* 2003, **204**, 1072.
2. (a) B. G. G. Lohmeijer and U. S. Schubert, *J. Polym. Sci. Part A* 2004, **42**, 4016; (b) B. G. G. Lohmeijer and U. S. Schubert, *J. Polym. Sci. Part A* 2005, **43**, 6331.