Electronic Supplementary Material (ESI) for Polymer Chemistry

Supporting Information

Amphiphilic supramolecular A(B)$_2$A quasi-triblock copolymers

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Experimental Details

Methods and Instrumentation. All chemicals were received from Aldrich, Fluka and Acros; solvents were purchased from Biosolve. Unless otherwise stated, the chemicals and solvents were used without further purifications. DMF was dried over molsieves (pore size of 4 Å). THF and toluene were dried using a PureSolv-EN^{TM} solvent purification system. Styrene was freshly purified prior to use by filtration over neutral aluminium oxide 90 (Merck). 1D (^{1}H, ^{13}C) nuclear magnetic resonance (NMR) spectra were recorded on a Varian Mercury 400 MHz spectrometer at 298 K, 348 K or 368 K. Chemical shifts are reported in parts per million (ppm) downfield from tetramethylsilane (TMS) and were calibrated to the residual solvent peaks. Deuterated solvents for NMR spectroscopy were obtained from Cambridge Isotope Laboratories as well as Eurisotop. Two different set-ups for size-exclusion chromatography (SEC) were used: A Shimadzu system equipped with a SCL-10A system controller, a LC-10AD pump, a RID-10A refractive index (RI) detector, an UV-vis absorption detector (250 and 290 nm) and a PSS SDV column utilizing chloroform/*iso*propanol/triethylamine [94/2/4] as eluent. The column temperature was 40 °C at a flow rate of 1 mL min^{-1}. Linear polystyrene was used as the calibration standard. Additionally, SECs were measured on a Waters SEC system consisting of an isocratic pump (HPLC 1515), a solvent degasser (DG-980-50), a column oven (Column Heater 1500), a photodiode array detector (Detector 2996), a RI detector (2414) and a Phenomenex Phenogel column with a precolumn installed. The eluent was DMAc containing 0.08 % NH_4PF_6 at a flow rate of 1 mL min^{-1}. The column temperature was 50 °C. AFM measurements were performed on a Nanoscope IIIa Multimode.

Synthesis

tpy-MPEG$_{44}$ was synthesized as described elsewhere.[1]
SEC (RI, eluent: $CHCl_3$): M_n = 2 050 g mol^{-1}, PDI = 1.13. UV-vis ($CHCl_3$): λ_{max} = 277 nm.

General styrene polymerization procedure[2]

Styrene monomers were freshly purified by filtration over Al_2O_3 prior to use in order to remove the inhibitor. The freshly purified styrene was added to a clear anisole solution of the TIPNO-based initiator in a polymerization vessel. After applying three freeze-pump-thaw-cycles to remove the oxygen, the vessel was purged with argon and immersed in an oilbath at 123 °C for a certain period of time. To remove residual monomer the reaction mixture was precipitated from $CHCl_3$ into cold methanol. The monomer conversion was determined by GC measurements (before precipitation), the molar masses (*i.e.* M_n and M_w) and the polydispersity index (PDI) values were determined by SEC, whereas ^{1}H NMR spectroscopy was applied for the determination of the endgroup functionality (by integration and comparison of the corresponding endgroup signals) and M_n values (by integration of the polymer backbone to the terpyridine signals).

tpy-PS-UPy, **1a**

The heterotelechelic macroligand **1a** (tpy-PS-UPy) was synthesized by using the initiator tpy-TIPNO-UPy that was synthesized according to literature.[2]

m(tpy-TIPNO-UPy) = 15 mg; m(Styrene) = 350 mg; V(anisole) = 800 µL; monomer to initiator ratio: M/I = 200; concentration: c = 3 mol L^{-1}; polymerization time: t = 300 min.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.06–2.63 (set of multiplets), 3.05–3.37 (m, 4H), 3.39–3.66 (m, 1H), 3.99–4.24 (m, 1H), 4.95–5.35 (m, 5H), 5.83 (s, 1H), 6.30–7.50 (m, 560H), 7.81 (m, 2H), 8.12–8.22 (m, 2H), 8.61–8.74 (m, 4H), 10.13 (s, 1H), 11.83 (s, 1H), 13.09 (s, 1H) ppm. SEC ($CHCl_3$, RI): M_n = 9,300 g·mol^{-1}, PDI = 1.17.

conversion [%] (GC)	M_n [g/mol] theoret.	M_n [g/mol] (SEC)	PDI (SEC)	M_n [g/mol] (^{1}H NMR)
41	9 400	9 300	1.17	12 300

tpy-PS-OH, **1b**

The heterotelechelic macroligand **1b** (tpy-PS-OH) was synthesized using the initiator tpy-TIPNO-OH that was prepared according to literature.[2]

m(tpy-TIPNO-OH) = 10 mg; m(Styrene) = 350 mg; V(anisole) = 800 µL; monomer to initiator ratio: M/I = 200; concentration: c = 3 mol L^{-1}; polymerization time: t = 300 min.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.06–2.60 (set of multiplets), 3.07–3.35 (m, 1H), 4.00–4.22 (m, 1H), 4.50–4.72 (m, 2H), 5.20–5.38 (m, 2H), 6.26–7.50 (m, 530H), 7.38-7.94 (m, 2H), 8.10–8.22 (m, 2H), 8.62–8.75 (m, 4H) ppm. SEC ($CHCl_3$, RI): M_n = 9,000 g·mol^{-1}, PDI = 1.14.

conversion [%] (GC)	M_n [g/mol] theoret.	M_n [g/mol] (SEC)	PDI (SEC)	M_n [g/mol] (^{1}H NMR)
38	8 900	9 000	1.14	11 400

$\{[(MPEG_{44})Ni(\mathbf{1a})]_2\}(PF_6)_4$

The precursor complex of $NiCl_2$ 6DMF was prepared by stirring of $NiCl_2 \times 6H_2O$ (0.83 mg, 3.5 µmol) in 1.7 mL of dry DMF for 1 h at room temperature under argon. The polymeric mono-complex was synthesized by addition of tpy-PS_{110}-UPy (31 mg, 3.3 µmol) in 1.7 mL of DMF. After stirring the solution for 10 min the macroligand tpy-PEG_{44} (7.4 mg, 3.3 µmol) in 1.7 mL of DMF was added and the solution was stirred under argon overnight at room temperature. An exchange of the counterion was made by addition of an excess of NH_4PF_6 (10 mg) to the reaction mixture and stirring for 3 h. Subsequently the reaction mixture was concentrated under vacuum and the residue was washed under stirring with diethyl ether (2 days) and with water (1 day). The reaction yield was estimated at 50%.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.06–2.65 (set of multiplets), 3.09–3.29 (m, 4H), 3.45–3.89 (m, 140H), 4.02–4.21 (m), 4.52–4.72 (m), 4.95–5.21 (m, 3H), 5.74–5.92 (m), 6.30–7.45 (m, 570H), 7.72–7.97 (m), 10.13 (s, 1H), 11.83 (s, 1H), 12.73–13.42 (m) ppm.

{[(MPEG$_{44}$)Ni(**1b**)]}$(PF_6)_2$

The precursor complex of $NiCl_2$ 6DMF was prepared *in situ* by stirring of $NiCl_2 \times 6\ H_2O$ (0.83 mg, 3.5 µmol) in 1.7 mL of dry DMF for 1 h at room temperature under argon. The polymeric mono-complex was synthesized by addition of tpy-PS$_{100}$-OH (30 mg, 3.3 µmol) in 1.7 mL of DMF. After stirring the solution for 10 min, the macroligand tpy-PEG$_{44}$ (7.4 mg, 3.3 µmol) in 1.7 mL of DMF was added and the solution was stirred under argon overnight at room temperature. An exchange of the counterion was made by addition of an excess of NH_4PF_6 (10 mg) to the reaction mixture and stirring for 3 h. Subsequently the reaction mixture was concentrated under vacuum and the residue was washed under stirring with diethyl ether (2 days) and with water (1 day). The reaction yield was estimated at 35%.

^{1}H NMR (400 MHz, CD_2Cl_2): δ = 0.06–2.36 (set of multiplets), 3.07–3.65 (m, 1H), 3.33–4.01 (m, 160), 4.04–4.20 (m), 4.50–4.80 (m), 5.20–5.38 (m, 2H), 6.23–7.41 (m, 530H), 7.70-7.94 (m), 12.81–13.44 (m) ppm.

AFM investigations of the polymer films

100 µL of a solution of {[(MPEG$_{44}$)Ni(**1b**)]}$(PF_6)_2$ in toluene (2 wt%) was spin-coated on a silicon wafer (500 rpm, 30 s) and the resulting polymeric films were allowed to dry for 24 h and were subsequently investigated by AFM without further temperature annealing. The samples were investigated by light and hard tapping mode.

Theoretical aspects on the selective formation of heteroleptic nickel(II) *bis*-terpyridine complexes in a one-pot reaction.

Considering only the thermodynamic stability of the Ni(II) complex the selectivity for the heteroleptic complex formation cannot be explained for the present one-pot strategy:

Both the *mono*- as well as the *bis*-terpyridine complex of Ni(II) have high stability constants compared to other transition metal ions: lgK_1 =10.7 and lgK_2 = 11.1 (in water at 25 °C) as determined by Wilkins and coworkers.[3] In contrast to iron(II), the stability of the *mono*-complex is only slightly lower compared to the stability of the *bis*-complex: This results in the formation of comparable equilibrium concentrations of both complexes at the metal-to-ligand ratio of 1:1 that is visualized in Figure S1. But as this ratio has to be ensured for the stoichiometric formation of the *mono*-complex within the stepwise one-pot complexation, kinetic considerations have to be taken into account to understand the A-B selectivity: The *mono*-terpyridine complex of Ni(II) is of unique inertness indicated by a high stability against

disproportionation[4] and due to the fact that the *bis*-complex formation is not enhanced as it was observed for other transition metals.[5] Furthermore, by using DMF as solvent the kinetic stability of the *mono*-complex is tentatively enhanced as the formation rates of the *bis*- as well as the *mono*-complex are significantly decreased changing the solvent from water[3] to DMSO[6] due to the higher coordination rate of the solvent.

The addition of the second ligand after a short period of time guarantees the kinetic control for the first step with non-equilibrium concentrations pronouncing the formation of the *mono*-complex as precursor at a metal-to-ligand ratio of 1:1 before the addition. The metal-to-ligand ratio of 1:2 after addition of the second ligand ensures the formation of the heteroleptic *bis*-complex under thermodynamic control with equilibrium concentrations (visualized in Figure S1) as the reaction mixture was allowed to stir overnight. The inert character of the *bis*-terpyridine Ni(II) complex maintains the heteroleptic complex and thus allows the integrity of the A-B formation.[4,7]

$$M + L \rightleftharpoons ML \quad \text{with} \quad K_1 = \frac{[ML]}{[M][L]}$$

$$ML + L \rightleftharpoons ML_2 \quad \text{with} \quad K_2 = \frac{[ML_2]}{[ML][L]}$$

$$c_M = [M] + [ML] + [ML_2]$$

$$c_L = [L] + [ML] + 2 \bullet [ML_2]$$

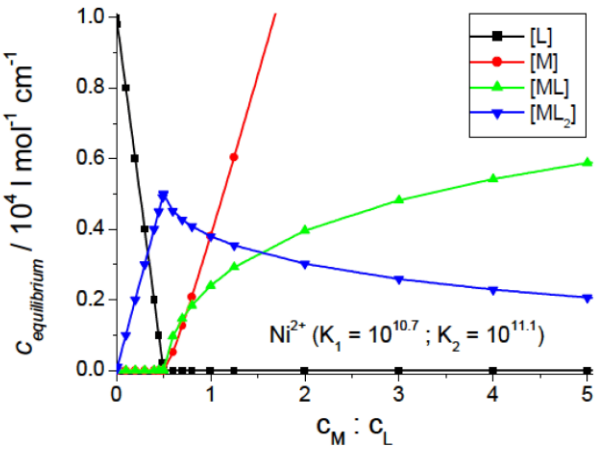

Figure S1. Modeling of the equilibrium concentrations of ligand [L], metal ion [M], mono-complex [ML] and *bis*-complex [ML2] as a function of the initial ratio of metal to ligand c_M:c_L using the equilibrium constants $\lg K_1$ =10.7 and $\lg K_2$ = 11.1 for Ni^{II} in water at 25 °C as determined by Wilkins and coworkers[3] (image was reprinted from literature[8]).

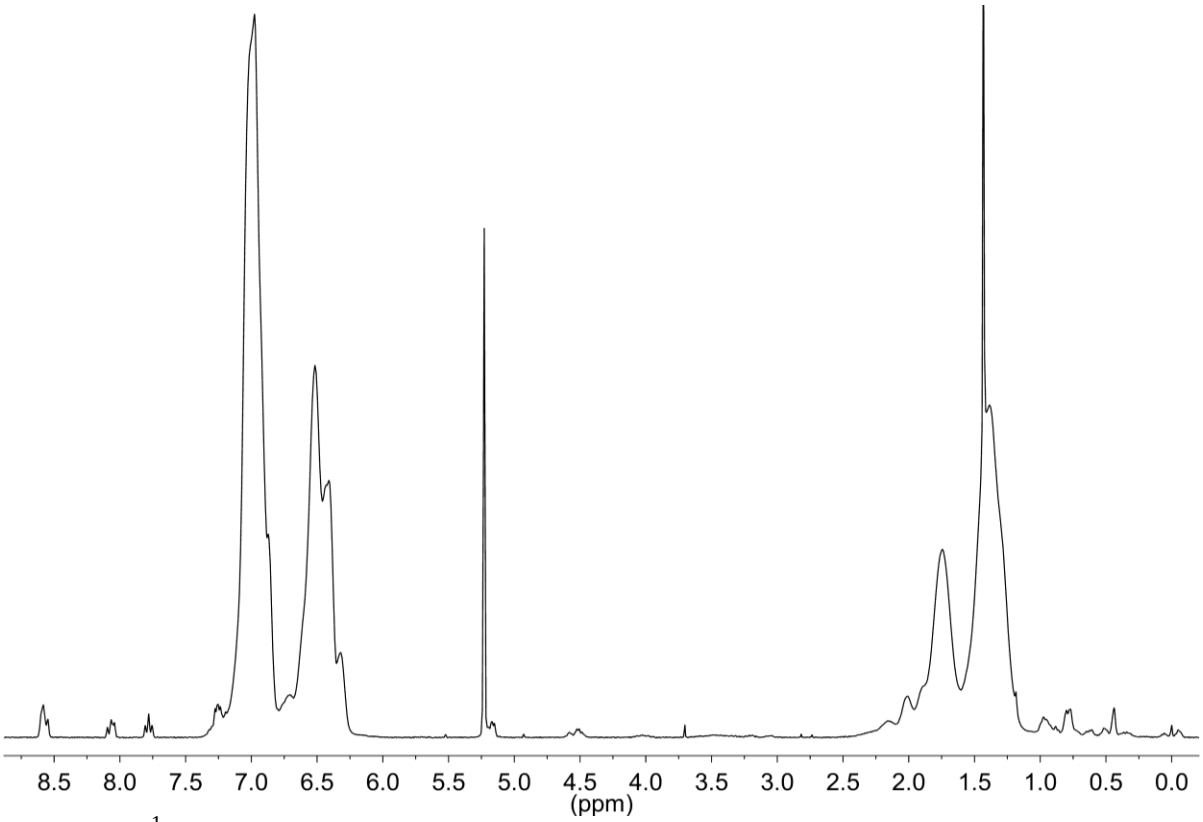

Figure S2. ^{1}H NMR spectrum of tpy-PS-OH, **1b** (400 MHz, CD_2Cl_2, 298 K).

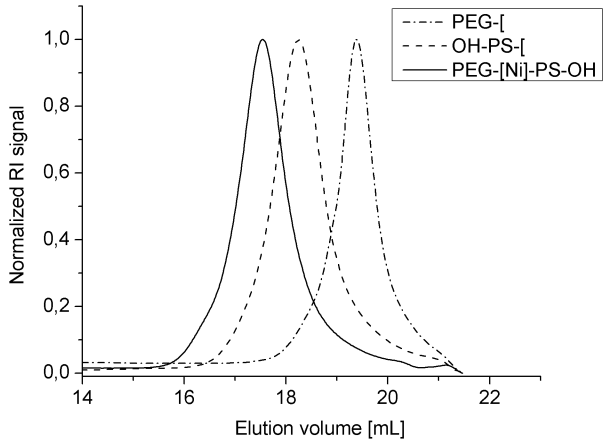

Figure S3. SEC traces (RI detector) of the diblock copolymer [(MPEG-tpy)Ni(**1b**)]$^{2+}$ (solid line) in comparison to those of the building blocks MPEG-tpy (dotted line) and **1b** (dashed line). For all measurements: DMAc containing 0.005 M NH_4PF_6 as eluent.

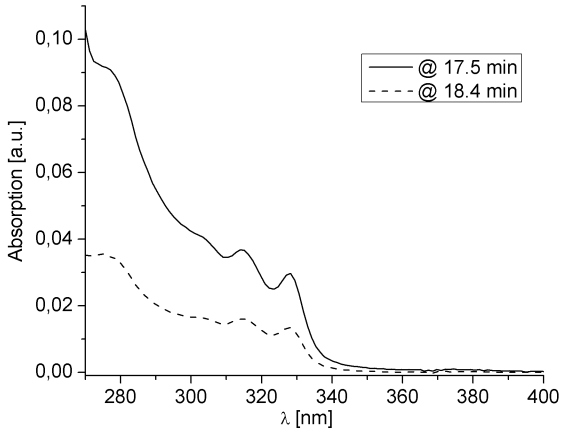

Figure S4. UV-vis absorption spectra of [(MPEG-tpy)Ni(**1a**)]$^{2+}$ as recorded with a PDA detector at 17.5 min and 18.4 min (solvent: DMAc containing 0.005 M NH_4PF_6).

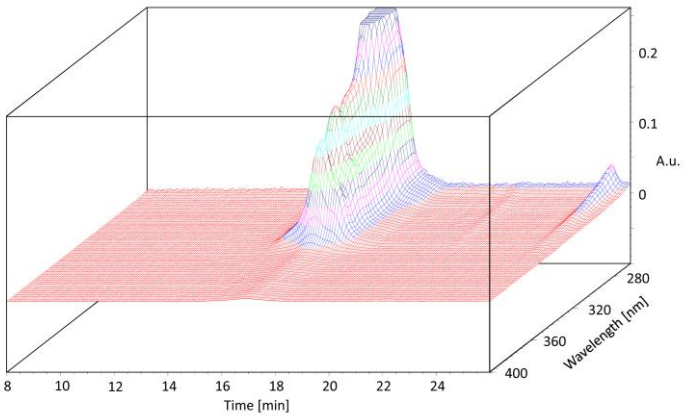

Figure S5. 3D-SEC trace of [(MPEG)Ni(**1b**)]$^{2+}$ as recorded with a PDA detector showing the formation of the Ni(II) *bis*-terpyridine complex with the characteristic ligand-centered bands at 329 nm and 315 nm. A small shoulder at low molar masses represents the formation of $[(MPEG)_2Ni]^{2+}$ (eluent: DMAc containing 0.005 M NH_4PF_6).

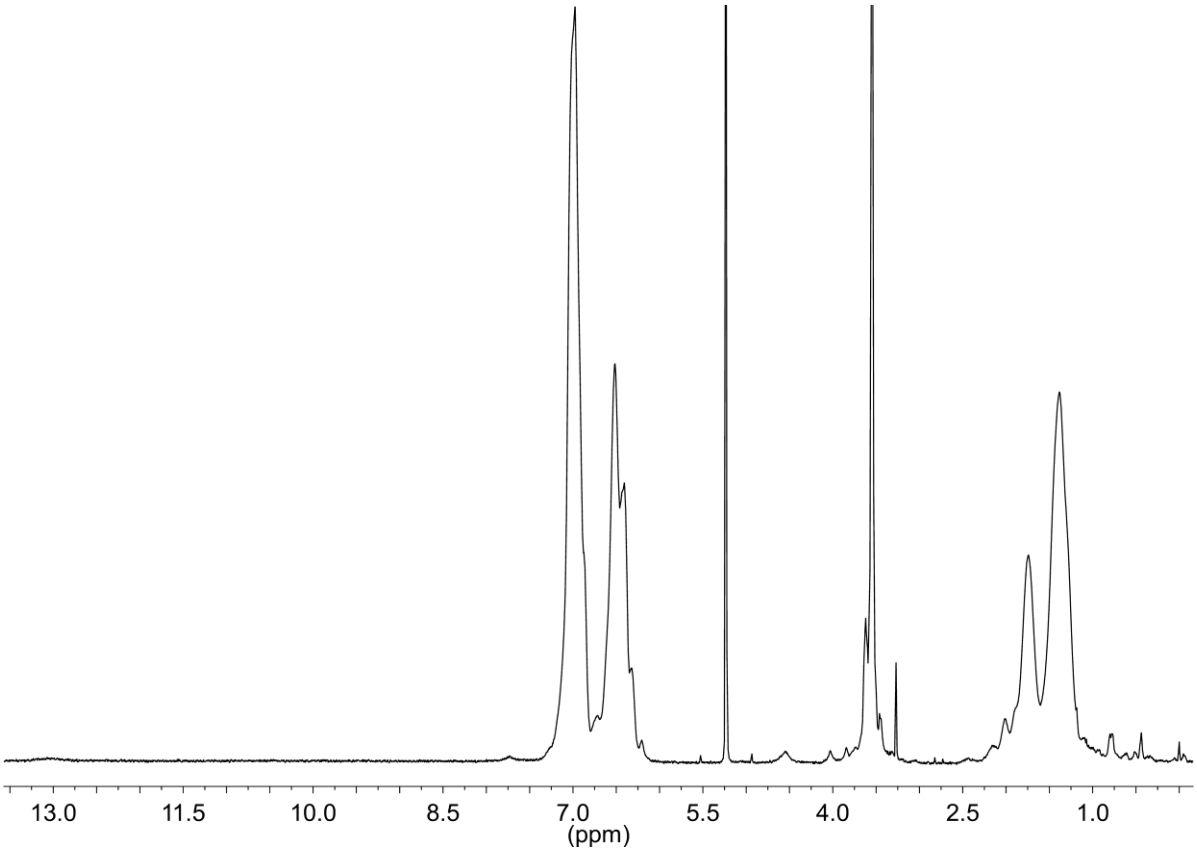

Figure S6. ^{1}H NMR spectrum of {(MPEG)Ni(**1b**)}$(PF_6)_2$ (400 MHz, CD_2Cl_2, 298 K).

References

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