

COMMUNICATION

Electronic Supplementary Information (ESI)

Supramolecular control of reverse spin transitions in cobalt(II) terpyridine complexes with diblock copolypeptide amphiphiles

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Materials and instrumentation

Tetrahydrofuran (THF) and hexane were dried by purging with nitrogen. Co(PMe₃)₄ was prepared according to procedures previously published in the literature.¹ All chemicals were purchased from commercial suppliers (Tokyo Kasei, Wako Co., Ltd., Kanto Chemical Co., Ltd., and Sigma-Aldrich Chemical Co.) and used without further purification unless otherwise noted. Fourier Transform Infrared Spectroscopy (FTIR) measurements were obtained on a Spectrum 65 FT-IR (PerkinElmer, Inc.). ¹H NMR spectra were acquired using an ESC 400 (JEOL Ltd.). Gel permeation chromatography/light scattering (GPC/LS) was performed at 333 K using a Shimadzu LC solution GPC system incorporating a RID-10A differential refractometer detector and a CBM-20A pump/controller. Separations were achieved using 10⁵, 10³ Å, and 500 Å Phenomenex Phenogel 5 µm columns with 0.1 M LiBr in DMF as the eluent and sample concentrations of 5 mg/mL. Pyrogen-free deionized water (DI) was obtained from Advantec RFD240NA and RFU655DA purification units. Transmission electron microscopy was performed using a Tecnai G2 F20 (FEI Co.) operating at 200 kV. Transmission electron microscope samples were prepared by transferring the surface layers of dispersions to carbon-coated Cu TEM grids.

General polypeptide synthesis

All diblock copolypeptide amphiphiles were synthesized using Co(PMe₃)₄ as the initiator, according to the literature procedures^{1,2}. Protected diblock copolypeptide amphiphiles were synthesized, purified, and then characterized using GPC/LS and FTIR. The protecting groups on the α -benzyl-L-glutamate moieties were removed to produce residual L-glutamate. Poly(α -benzyl-L-glutamate)-*block*-poly(L-Leusine) was dissolved in methylene chloride (~100 mL) in dry box. Iodotrimethyl silane (TMSI) (5 equivalents per benzyl group) was added, and heated to 313 K. The solution was left to stir for 1 day after cooling. Dry hexanes (~100 mL) were then added to reaction mixture and deionized water was sprayed into solution until all polymer appeared to have precipitated from solution. The precipitated polymer was washed with hexanes and acetone until white. It was then extracted and suspended in 100 mM NaOH solution (~30 mM). The solution were dialyzed in deionized water using dialysis bag (regenerated cellulose, Spectrapor, MWCO 6-8 kDa). Lyophilisation of these solutions gave the copolymers and the polymer as white powders. Chain lengths of Glu_m segments were determined using GPC, with measured polydispersities (M_w/M_n) ranging from 1.19 to 1.27. ¹H NMR in deuterium oxide (D₂O) indicated over 99.9 % removal of the benzyl groups from the glutamate residues.

Table S1 Properties of DCH samples.

Predicted composition	M_n^a	$M_w/M_n^{a,b}$	Glu _m length ^c	Found composition ^d
(Glu) ₂₅₄ - <i>block</i> -(Leu) ₇	3.85X10 ⁴	1.25	(Glu) ₂₅₄	(Glu) ₂₅₄ - <i>block</i> -(Leu) ₇
(Glu) ₁₁₉ - <i>block</i> -(Leu) ₄	2.34X10 ⁴	1.27	(Glu) ₁₁₉	(Glu) ₁₁₉ - <i>block</i> -(Leu) ₄
(Glu) ₉₂₂	10.99X10 ⁴	1.19	(Glu) ₉₂₂	(Glu) ₉₂₂

^a Determined using gel permeation chromatography of Glu_m.

^b M_w/M_n = Polydispersity index.

^c Determined from M_n measurements.

^d Determined by M_n measurements and ¹H NMR analysis of deprotected samples.

General preparation of copolypeptide/cobalt(II) composites

Ternary composites were prepared by mixing DI water solutions of $[\text{Co}^{\text{II}}(\text{MeOterpy})_2](\text{BF}_4)_2$ (10 mM, 1 mL) with DI water solutions of **1** to **3** (10 mM per Glu unit, 1 mL) at room temperature. The precipitated composite was filtered and freeze-dried to pale-brown powders. All composites were stable in air over a period of one month, and all composite dispersions were stable in oxygen-free DI water for a period of one month. The observed stabilization induced on adding the amphiphiles indicates that aggregation of the composites subsequent to the copolypeptides addition prevents cobalt complexes from reacting with oxygen.

Elemental analysis;

1: $2(\text{Glu})_{254}\text{-block-(Leu)}_7\text{-}127[\text{Co}^{\text{II}}(\text{MeO-tpy})_2]\text{-}381\text{Na}\cdot 127\text{H}_2\text{O}$, (i.e. Glu : Co : H_2O = 4 : 1 : 1), Anal. Calcd : C, 52.56; H, 4.76; N, 11.78. Found: C, 52.81; H, 4.80; N, 12.10

2: $4(\text{Glu})_{119}\text{-block-(Leu)}_4\text{-}119[\text{Co}^{\text{II}}(\text{MeO-tpy})_2]\text{-}357\text{Na}\cdot 357\text{H}_2\text{O}$, (i.e. Glu : Co : H_2O = 4 : 1 : 3), Anal. Calcd : C, 51.02; H, 4.95; N, 11.44 Found: C, 51.57; H, 5.28; N, 11.21.;

3: $4(\text{Glu})_{922}\text{-}922[\text{Co}^{\text{II}}(\text{MeO-tpy})_2]\text{-}2766\text{Na}\cdot 3688\text{H}_2\text{O}$, (i.e. Glu : Co : H_2O = 4 : 1 : 4), Anal. Calcd : C, 50.25; H, 5.03; N, 11.27. Found: C, 50.74; H, 5.29; N, 11.01.

2d-SWAXS measurements of copolypeptide/cobalt(II) composites

The 2d-SWAXS (two-dimensional small- and wide-angle X-ray scattering simultaneous) measurements^{3,4} using the high brilliant synchrotron X-rays were carried out at BL-10C beamline with the wavelength of 0.1488 nm in Photon Factory of the High Energy Accelerator Research Organization, Tsukuba, Japan. The typical exposure time was in the range 30-100 s for SAXS and 10-30 s for WAXS, respectively. The 2d-SAXS and 2d-WAXS patterns were obtained using PILATUS-1M for SAXS and PILATUS-100K (DECTRIS) for WAXS measurements. Collagen from a chicken tendon and polyethylene were used as standard samples for SAXS and WAXS, respectively, in order to calibrate the magnitude of the scattering vector, q , as defined by $q = (4\pi/\lambda) \sin(\theta/2)$ with λ and θ being the wavelength of X-ray and the scattering angle, respectively. The 2d-SAXS and 2d-WAXS patterns were further converted to one-dimensional profiles by conducting circular average or sector average occasionally.

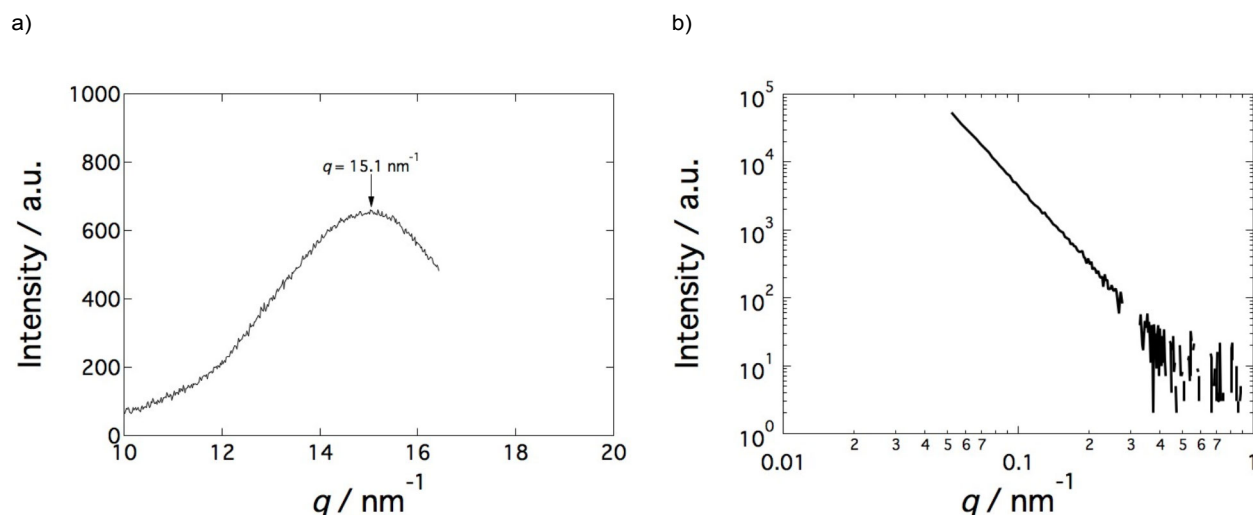


Fig. S1 WAXS (a) and SAXS (b) patterns of **1** / $[\text{Co}^{\text{II}}(\text{MeO-terpy})_2]$.

Reference

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