
Peer reviewed version

Link to published version (if available):
10.1021/jacs.8b03112

Link to publication record in Explore Bristol Research
PDF-document

University of Bristol - Explore Bristol Research
General rights

This document is made available in accordance with publisher policies. Please cite only the published version using the reference above. Full terms of use are available: http://www.bristol.ac.uk/pure/about/ebr-terms
Supporting Information

Chiral Transcription to Cationic Polycobaltocenes over Multiple Length Scales using Anionic Surfactants

Rebecca A. Musgrave,¹ Paul Choi,¹ Robert L. Harniman,¹ Robert M. Richardson,² Chengshuo Shen,³ George R. Whittell,¹ Jeanne Crassous,⁴ Huibin Qiu³,*, and Ian Manners¹,*

¹School of Chemistry and ²School of Physics, University of Bristol, Bristol, BS8 1TS, United Kingdom.
³School of Chemistry and Chemical Engineering, Shanghai Jiao Tong University, Shanghai 200240, China.
⁴Institut des Sciences Chimiques de Rennes UMR 6226, CNRS Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France.

*To whom correspondence should be addressed,
E-mail: ian.manners@bristol.ac.uk, hbqiu@sjtu.edu.cn.
Figure S1. Representative photographs of the \([\text{PCE}]^{[\text{A*}]}_{\text{n}}\) complexes during dialysis against water and ethanol: a) the \([\text{PCE}]^{[\text{A*}]}_{\text{n}}\) complexes are insoluble in water and formed a precipitate during dialysis against water b) on further dialysis against ethanol, the precipitate gradually dissolves, and a clear yellow solution eventually formed.
Figure S2. $^1$H NMR (500 MHz, CD$_3$OD) spectrum of [PCE][C$_{16}$-L-Ala]$_n$ complex.
Figure S3. CD and UV-vis spectra of aqueous solutions of a) [Na][C_{16}-L-Ala] and [Na][C_{16}-D-Ala], and b) [Na][C_{16}-L-Phe] and [Na][C_{16}-D-Phe], all at 0.5 mg mL\(^{-1}\) in EtOH.

Figure S4. CD spectra of [PCE][C_{16}-L-Ala]\(_n\) at 0.5 mg mL\(^{-1}\) in EtOH taken at 5 °C and 55 °C.
Figure S5. CD response of [PCE][C_{16}-L-Ala]_{n} at 0.5 mg mL$^{-1}$ in EtOH at 266 nm over a range of temperatures (5 °C to 55 °C).
Figure S6. CD spectra of complexes formed by (a) bis(ethylcyclopentadienyl) cobalt(III), (b) dicarba[2]cobaltocenophanium and (c) tricarba[3]cobaltocenophanium with $[C_{16}\text{-L-Ala}]^-$ (red lines) and $[C_{16}\text{-D-Ala}]^-$ (blue line), all at 0.5 mg mL$^{-1}$ in EtOH.
**Figure S7.** $^1$H NMR (300 MHz, CD$_3$OD) spectrum of [OCE$_5$][OTf]$_5$ complex.

**Figure S8.** CD and UV-vis spectra of solutions of a) [OCE$_5$][C$_{16}$-L-Ala]$_5$ and [OCE$_5$][C$_{16}$-D-Ala]$_5$ complexes and b) [OCE$_5$][C$_{16}$-L-Phe]$_5$ and [OCE$_5$][C$_{16}$-D-Phe]$_5$ complexes, all at 0.5 mg mL$^{-1}$ in EtOH.
Figure S9. EDX analyses of spots A, B, C, D, E, F, G and H of [PCE][C_{16}-L-Ala]_n solution in ethanol, drop cast onto a carbon-coated copper TEM grid. The detection of Cu in all cases is due to the use of copper TEM grids.
Figure S10. DLS size distribution by volume of [PCE][C_{16}-L-Ala]_n complex (EtOH, 25 °C, 12 mg mL^{-1}). \( R_h = 1.2 \text{ nm} \).

Figure S11. Raw DLS correlation data of [PCE][C_{16}-L-Ala]_n complex (EtOH, 25 °C, 12 mg mL^{-1}).
**Figure S12.** DLS size distribution by intensity of [PCE][C_{16}-L-Ala]_n complex (EtOH, 25 °C, 12 mg mL$^{-1}$). $R_h = 1.6$ nm, 12.2 nm, 147.5 nm.

**Figure S13.** DLS size distribution by volume of [PCE][Cl]_n complex (H$_2$O, 25 °C, 2 mg mL$^{-1}$). $R_h = 18.2$ nm.
**Figure S14.** Raw DLS correlation data of [PCE][Cl]$_n$ complex (H$_2$O, 25 °C, 2 mg mL$^{-1}$).

**Figure S15.** $^1$H DOSY NMR (500 MHz, CD$_3$OD) spectrum of [PCE][C$_{16}$-L-Ala]$_n$ complex.
Figure S16. WAXS data for [PCE][C\textsubscript{16}-L-Ala\textsubscript{n}] drop cast from an ethanolic solution (12 mg mL\textsuperscript{-1}).

Figure S17. Small angle X-ray scattering data: plot of the scattered intensity ($I$) versus the magnitude of the scattering vector ($Q$) for [PCE][C\textsubscript{16}-L-Ala\textsubscript{n}] at various concentrations in ethanol.
Figure S18. Small angle X-ray scattering data: log-log plot of the scattered intensity ($I$) versus the magnitude of the scattering vector ($Q$) for [PCE][C$_{16}$-L-Ala]$_n$ at various concentrations in ethanol.

Figure S19. Small angle X-ray scattering data: plot of the product of the scattering factor $S(Q)$ versus the magnitude of the scattering vector ($Q$) for [PCE][C$_{16}$-L-Ala]$_n$ at various concentrations in ethanol.
Figure S20. Small angle X-ray scattering data: plot of the product of the scattered intensity and the scattering vector ($I^*Q$) versus the magnitude of the scattering vector ($Q$) for [PCE][C$_{16}$-L-Ala]$_n$ at various concentrations in ethanol.

Figure S21. TGA thermogram for [PCE][C$_{16}$-L-Ala]$_n$ drop cast from an ethanolic solution (12 mg mL$^{-1}$).
Figure S22. DSC thermogram for [PCE][C_{16}-L-Ala]_n drop cast from an ethanolic solution (12 mg mL\(^{-1}\)) obtained at a scan rate of 10 °C min\(^{-1}\).

Figure S23. DSC thermogram for [PCE][Cl]_n solid obtained at a scan rate of 10 °C min\(^{-1}\).
Figure S24. WAXS data for [PCE][Cl]₆ solid.

Figure S25. DSC thermogram for [Na][C₁₆-L-Ala] (drop cast from a concentrated ethanol solution) obtained at a scan rate of 10 °C min⁻¹.
Figure S26. WAXS data for [Na][C_{16}-L-Ala] (drop cast from a concentrated ethanol solution)

Figure S27. Additional representative TEM images of assemblies of [PCE][C_{16}-L-Ala]_n in water on a carbon-coated copper grid, showing a) tightly twisted helices, and b) a larger twisted coil.
**Figure S28.** EDX analyses of spots A, B, C and D of [PCE][C_{16}-L-Ala]_{n} suspension in water, drop cast onto a carbon-coated copper TEM grid. The detection of Cu in all cases is due to the use of copper TEM grids.
Figure S29. TEM images obtained by drop-casting an aliquot of solutions of (a) [PCE][NO₃]ₙ in water and (b) [Na][C₁₆-L-Ala] in a mixture of water and ethanol (1:1 in volume ratio) drop cast onto carbon-coated copper grids.

Figure S30. a) Molecular structure of [PCE][SDS]ₙ and b) TEM image obtained by drop-casting an aliquot of solution of [PCE][SDS]ₙ complex in ethanol on a carbon-coated copper grid.

Figure S31. a) Molecular structure of PFS-C₁₂ and TEM images obtained by drop-casting an aliquot of solutions of PFS-C₁₂ in b) hexane and c) isopropanol on a carbon-coated copper grid.
Figure S32. Photograph of yellow [PCE][C_{16}-L-Ala]_n precipitate of helical assemblies (isolated after dialysis with water) pressed between two quartz plates during sample preparation for solid-state CD measurements.

Figure S33. WAXS data for helical assemblies of [PCE][C_{16}-L-Ala]_n from water.
Figure S34. Additional representative SEM images of helical assemblies of [PCE][C\text{16}-\text{L-Ala}]_n in water onto a carbon-coated copper grid which has been sputter-coated with Pt/Pd alloy.
**Figure S35.** Additional representative field emission SEM (FE-SEM) images of assemblies of [PCE][C_{16}-L-Ala]_n in water on a carbon-coated copper grid with subsequent sputter-coating with Pt/Pd alloy.
Figure S36. Additional AFM images obtained by drop-casting an aliquot of suspensions of [PCE][C_{16}-L-Ala]_{n} in water onto a carbon-coated copper TEM grid
**Figure S37.** Additional AFM images obtained by drop-casting an aliquot of suspensions of [PCE][C\textsubscript{16}-L-Ala]\textsubscript{n} in water onto a freshly cleaved mica surface.