

## Supporting information

### Supramolecular Architectures Self-Assembled Using Long Chain Alkylated Spin Crossover Cobalt(II) Compounds

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#### Experimental

##### *Dialkyl-L-glutamate hydrochloride*

L-glutamic acid (5.00 g, 0.0378 mol), distilled 1-dodecyl alcohol (17.6 g, 0.0100 mol), *p*-toluene sulfonic acid (8.07 g, 0.0421 mol) and toluene (100 mL) were added to a 300 mL round bottom flask and the reaction mixture was refluxed at 120 °C for 5 h then allowed to cool to room temperature. After removing the toluene *in vacuo*, chloroform (40 mL) was added to the residue and the solution was washed with aqueous Na<sub>2</sub>CO<sub>3</sub> solution (100 mL, pH = 9) then with distilled water (100 mL × 2). The organic phase was separated and dried over Na<sub>2</sub>SO<sub>4</sub>. After removing the chloroform under reduced pressure, the product was dissolved in acetone (600 mL). To this solution, conc. HCl solution was slowly added (6.7 mL, 0.12 mol). A colourless precipitate formed on standing the solution in a refrigerator for 3 h, The crude product was separated by filtration and recrystallized from acetone to afford a colorless powder.

##### *4-(1,3-Bis-dodecyloxycarbonyl-propylcarbamoyl)-benzenesulfonic (C12-Glu)*

Sulfoacetic acid (3.60 g, 15.0 mmol) and pyridine (2.40 g, 30.0 mmol) were added to a 300 mL bottle and the mixture was sonicated for 10 min. Separately, dialkyl-L-glutamate hydrochloride, triethylamine (7.80 g, 15.0 mmol) and dried DMF (150 mL) were added to a 100 mL round bottom flask. EDC [= 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride] (2.90 g, 15.0 mmol; as coupling agent) and triethylamine (2.55 g, 25.0 mmol) were added to the DMF solution. The mixture was stirred for 20 min under cooling. Sulfoacetic acid pyridinium salt was added and the solution was stirred for 4 h with ice-cooling; it was then stirred at room temperature for an additional day. The reaction mixture was transferred to a separating funnel and the organic layer was washed with distilled water (50 mL × 2) and aqueous 1.9% NaHCO<sub>3</sub> solution (1 g, 50 mL × 2). The organic phase was separated and dried over Na<sub>2</sub>SO<sub>4</sub>. After removing dichloromethane under reduced pressure, the *C12-Glu* product was washed with acetone then recrystallized from acetyl acetate.

C<sub>n</sub>-terpy (4'-alkoxy-2,2':6'2''-terpyridine with n = 15, 16, 17, 18, 19 or 20) was prepared as previously described<sup>1</sup> using a three step procedure:

##### *1,5-Bis(2'-pyridyl)pentane-1,3,5-trione*

A mixture of acetone (1.48 g, 27 mmol) and ethyl 2-pyridinecarboxylate (7.56 g, 50 mmol), in 1,2-dimethoxyethane (30 mL) was maintained under an atmosphere of dry argon. The mixture was stirred at room temperature then heated at reflux for 6h. The solvent was removed and the orange paste that remained was treated with water. The resulting orange solution was filtered and the filtrate was adjusted to pH 7 by addition of dilute hydrochloric acid. The yellow solid that formed was collected and washed with water. The solid retains water tenaciously, and was dried by dissolution in diethyl ether and drying the obtained solution over anhydrous magnesium sulphate. Evaporation of diethyl ether gave 1,5-bis(2'-pyridyl)pentane-1,3,5-trione as yellow solid. (3.35 g, yield: 60.5 %) The product was used for the next reaction without further purification.

##### *6-Bis(2'-pyridyl)-4(1H)-pyridone (= OH-terpy)*

1,5-Bis(2'-pyridyl)pentane-1,3,5-trione (3.35 g, 12.5 mmol,) and ammonium acetate (9.64 g, 125 mmol,) in ethanol (80 mL) was refluxed for 12 h after which the dark solution was concentrated to half volume. The solution was cooled, and the white precipitate that formed was collected by filtration

and washed with diethyl ether and water.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ ):  $\delta = 7.08$  (s 2H), 7.42 (td 2H), 7.87 (td 2H), 7.90 (d 2H), 8.78 (d 2H), 12.10 (br) ppm.

#### ***4'-Alkyl-2,2':6'2''-terpyridine ( $C_n$ -terpy)***

1-Bromoalkane (2 mmol,) was added to a mixture of 2,6-bis(2-pyridyl)-4(1H)-pyridone (0.33 g, 1.33 mmol,) and  $\text{K}_2\text{CO}_3$  (excess, 2 g) in DMF. The mixture was stirred at 80 °C for 12 h. After cooling to room temperature, the reaction solution was poured into ice/water. The white precipitate that formed was removed by filtration and dissolved in  $\text{CHCl}_3$ . The solution was washed with 10% aqueous  $\text{K}_2\text{CO}_3$ . The organic layer was dried with  $\text{MgSO}_4$  and filtered and the filtrate was evaporated to give the product as a white powder. These manipulations were carried out under a purified Ar atmosphere.

#### ***[Co( $C_n$ -terpy) $_2$ ]( $\text{BF}_4$ ) $_2$***

$C_n$ -terpy (0.36 mmol) was dissolved in MeOH (20 mL) and  $\text{Co}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$  (0.06 g, 0.18 mmol) in MeOH (10 mL) was added to the solution. The brown solution was concentrated to about 10 mL and the micro crystals that formed were collected by filtration and recrystallized from MeOH.

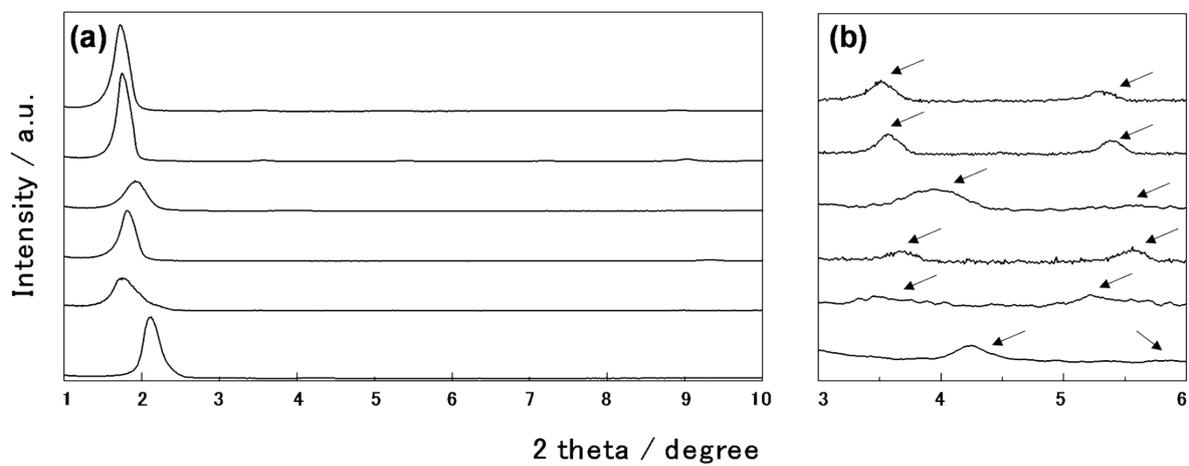
#### ***[Co( $C_n$ -terpy) $_2$ ]( $C_{12}$ -Glu) $_2$ ]***

$C_{12}$ -Glu $\cdot\text{Na}^+$  was added to distilled water and the mixture was sonicated for 15 min at 50 °C. Separately,  $[\text{Co}(C_n\text{-terpy})_2](\text{BF}_4)_2$  was dissolved in acetone.  $C_{12}$ -Glu $\cdot\text{Na}^+$  in distilled water was added and the solution was stirred for 1 day. The precipitate that formed was isolated and recrystallized from  $\text{CH}_2\text{Cl}_2$ .

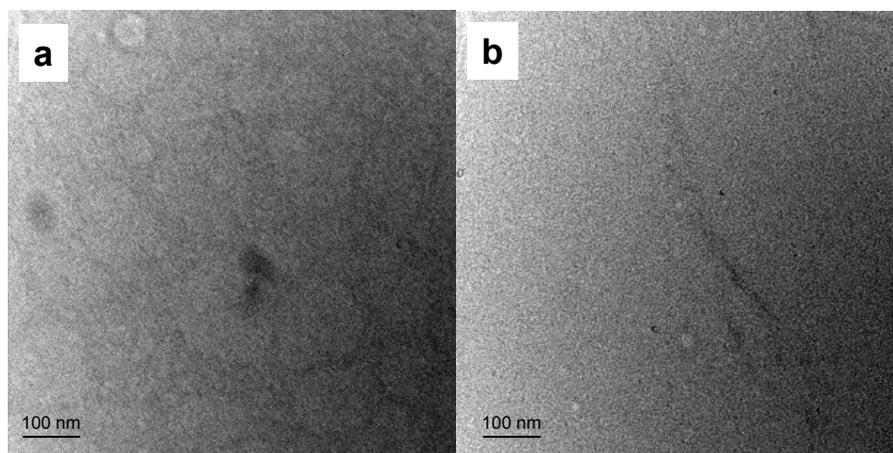
$[\text{Co}(C_{17}\text{-terpy})_2](C_{12}\text{-Glu}(\text{SO}_3)_2 \cdot 3\text{MeOH})$ : Anal.  $\text{C}_{139}\text{H}_{222}\text{CoN}_8\text{O}_2\text{S}_2$  (2462.53): calcd. C 67.75, H 9.08, N 4.55; found C 67.39, H 9.11, N 4.58.  $[\text{Co}(C_{18}\text{-terpy})_2](C_{12}\text{-Glu}(\text{SO}_3)_2 \cdot 6\text{H}_2\text{O})$ : Anal.  $\text{C}_{138}\text{H}_{226}\text{CoN}_8\text{O}_{24}\text{S}_2$  (2502.55): calcd. C 66.18, H 9.10, N 4.47; found C 66.16, H 8.99, N 4.78.  $[\text{Co}(C_{19}\text{-terpy})_2](C_{12}\text{-Glu}(\text{SO}_3)_2 \cdot 4\text{MeOH})$ : Anal.  $\text{C}_{144}\text{H}_{234}\text{CoN}_8\text{O}_{22}\text{S}_2$  (2550.62): calcd. C 67.76, H 9.24, N 4.39; found C 67.76, H 9.21, N 4.59.  $[\text{Co}(C_{20}\text{-terpy})_2](C_{12}\text{-Glu}(\text{SO}_3)_2 \cdot 6\text{MeOH})$ : Anal.  $\text{C}_{148}\text{H}_{246}\text{CoN}_8\text{O}_{24}\text{S}_2$  (2642.71): calcd. C 67.22, H 9.38, N 4.24; found C 67.28, H 9.41, N 4.46.

#### References

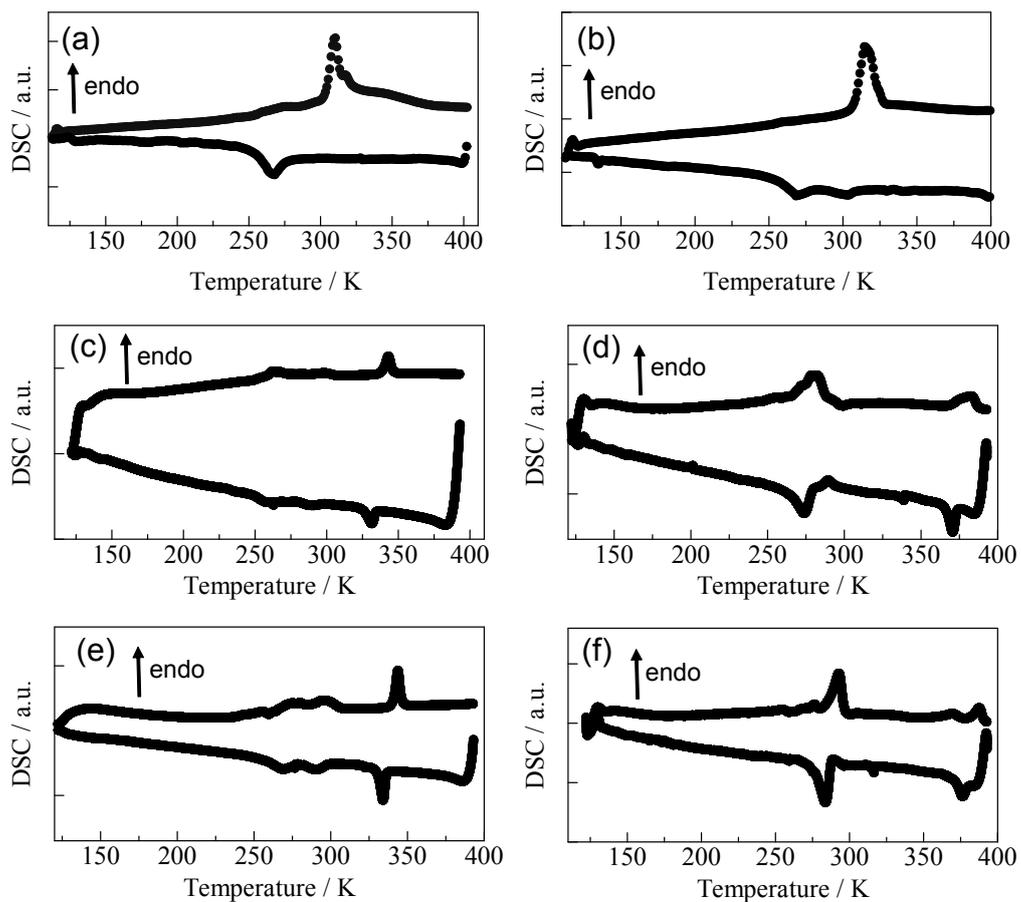
- 1 S. Hayami, Y. Shigeyoshi, M. Akita, K. Inoue, K. Kato, K. Osaka, M. Takata, R. Kawajiri, T. Mitani, Y. Maeda, *Angew. Chem. Int. Ed.*, **44**, 4899-4903 (2005).



**Fig. S1** PXRD measurement for compounds **1-6** in the range (a) from 1 to 10 degree and (b) from 3 to 6 degree.



**Fig. S2** TEM image of the compounds, (a)  $n = 0$  and (b)  $n = 14$ .



**Fig. S3** DSC measurement for compounds (a) 1, (b) 2, (c) 3, (d) 4, (e) 5, and (f) 6.