

## Electronic Supplementary Information

### Co(II)-Induced Giant Vibrational CD Provides a New Design of Methods for Rapid and Sensitive Chirality Recognition

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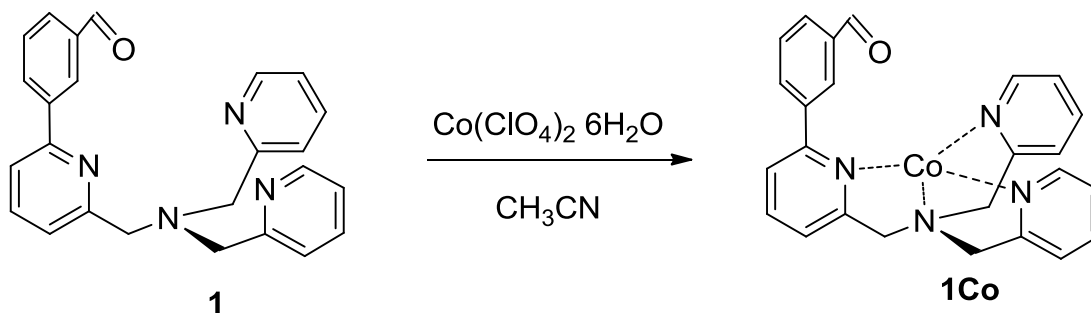
### 1. Experimental Section

**General remarks.** Chemicals were purchased from Aldrich and TCI chemicals and used without further purification. <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded at 301 K on a Bruker AC-400, AC-300 and AC-200 MHz instruments. The <sup>1</sup>H NMR spectra were referenced to the solvent residual peak of CD<sub>3</sub>CN-d<sub>3</sub> (1.94 ppm); the <sup>13</sup>C NMR spectra (50 MHz) were referenced to CD<sub>3</sub>CN peaks (1.32±0.02 and 118.26±0.02 ppm). ESI-MS experiments were carried out in positive mode with an Agilent Technologies LC/MSD Trap SL AGILENT instrument (mobile phase methanol or acetonitrile). MS peaks are reported as monoisotopic mass. Microanalyses were performed with a Flash 2000 Thermo Scientific Analyser. Crystal structure was determined by using a Bruker D8 Quest Kappa diffractometer equipped with monochromatic Mo K $\alpha$  ( $\lambda = 0.71073 \text{ \AA}$ ) radiation. The structure of the crystals was solved by direct methods and refined by full-matrix least squares method with SHELXTL software. VCD spectra were recorded with a JASCO FVS-6000 spectrometer. ECD spectra were recorded with a JASCO J-715 spectrometer

### Synthesis of **1** and **1Zn**

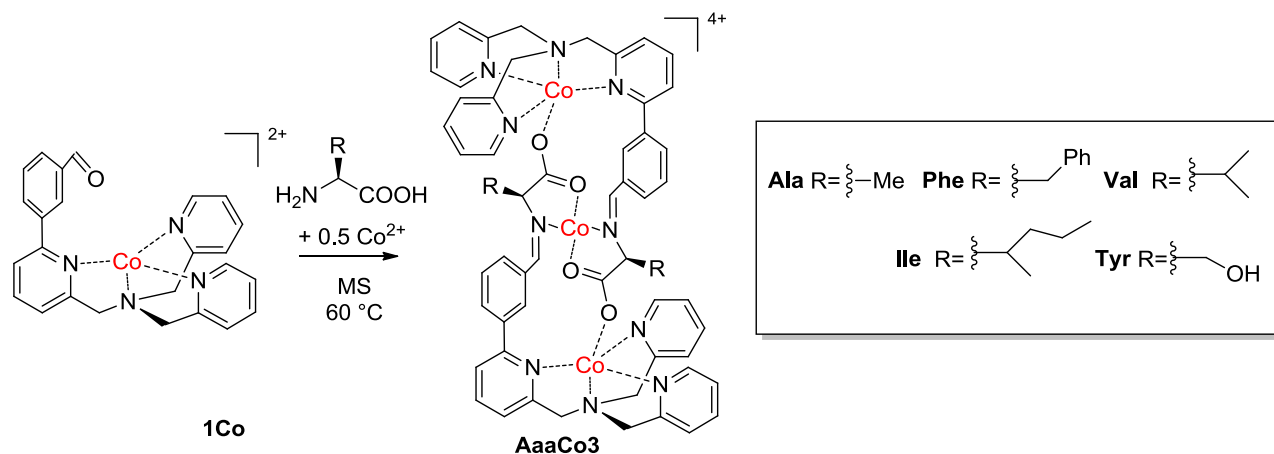
Compounds **1** and **1Zn** has been synthesized accordingly to: F.A. Scaramuzzo, G. Licini, C. Zonta. *Chem. Eur. J.* **2013**; 19, 16809-16813.

### Synthesis of **1Co**



0.300 g (0.761 mmol) of [6-(3-formylphenyl)-2-pyridylmethyl]bis(2-pyridylmethyl)-amine **1** were dissolved in the minimum amount of anhydrous acetonitrile and 0.365 g (0.761 mmol) of  $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  were added. The solution was left at room temperature for 15 minutes and diethyl ether was added giving a light purple precipitate (0.364 g, 0.560 mmol, yield = 73.6%) that was filtered and the residual solvent removed under reduced pressure. Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. They should be handled in small quantity and with caution. **IR (KBr,  $\text{cm}^{-1}$ ):** 3447, 1697, 1610, 1571, 1441, 1092. **ESI+ MS(m/z):** Calc.  $\text{C}_{25}\text{H}_{22}\text{N}_4\text{OCo}$  453.4, Found 226.5 ( $\text{M}^{2+}/2$ ). **Anal. Calcd.** ( $\text{C}_{25}\text{H}_{22}\text{Cl}_2\text{N}_4\text{O}_9\text{Co}$ ): C, 46.03; H, 3.40; N, 8.59. **Found:** C, 45.88; H, 3.21; N, 8.46.

## Synthesis of 3Co



The desired amino acid (0.033 mmol) was mixed with the desired chlorate salt of the metal (0.017 mmol) in 1 mL of methanol. The mixture was heated and stirred at 60 °C for 10 minutes. To the resulting solution the desired tris-pyridine metal complex (0.031 mmol) was added and the mixture stirred at 60 °C for 10 minutes and activated molecular sieves (3Å) added. Leaving the resulting mixture 12 hours at room temperature results in the formation of a precipitate that is filtered, washed with diethyl ether.

### L-Phe-CoCoCo(R = CH<sub>2</sub>Ph, M<sub>1</sub>=M<sub>2</sub>= Co)

Light green (Yield 46 %). ESI-MS(m/z): Calc. C<sub>68</sub>H<sub>60</sub> N<sub>10</sub>O<sub>4</sub>Co<sub>3</sub> · 3 ClO<sub>4</sub> 1556.4, Found 1556.2 (M<sup>+</sup>).  
 Elemental analysis: Calc. C<sub>68</sub>H<sub>60</sub>N<sub>10</sub>O<sub>16</sub>Co<sub>3</sub> · 4 ClO<sub>4</sub> · 5 H<sub>2</sub>O: 46.78%, H = 4.04%, N = 8.02%, Found: C = 46.20%, H = 3.91%, N = 7.69%

### D-Phe-CoCoCo(R = CH<sub>2</sub>Ph, M<sub>1</sub>=M<sub>2</sub>= Co)

Light green (Yield 46 %). ESI-MS(m/z): Calc. C<sub>68</sub>H<sub>60</sub> N<sub>10</sub>O<sub>4</sub>Co<sub>3</sub> · 3 ClO<sub>4</sub> 1556.4, Found 1556.2 (M<sup>+</sup>).  
 Elemental analysis: Calc. C<sub>68</sub>H<sub>60</sub>N<sub>10</sub>O<sub>16</sub>Co<sub>3</sub> · 4 ClO<sub>4</sub> · 5 H<sub>2</sub>O: 46.78%, H = 4.04%, N = 8.02%, Found: C = 46.20%, H = 3.91%, N = 7.69%

### L-Ile-CoCoCo(R = CH(CH<sub>3</sub>)CH<sub>2</sub>CH<sub>3</sub>, M<sub>1</sub>=M<sub>2</sub>= Co)

Light green (Yield 28 %). ESI+ MS(m/z) Calc. C<sub>62</sub>H<sub>61</sub>N<sub>10</sub>O<sub>4</sub>Co<sub>3</sub> · 3 ClO<sub>4</sub> 1488.4, Found 1488.2 (M<sup>+</sup>).  
 Elemental analysis: Calc. C<sub>62</sub>H<sub>61</sub>N<sub>10</sub>O<sub>4</sub>Co<sub>3</sub> · 4 ClO<sub>4</sub> · 6 H<sub>2</sub>O: 43.91%, H = 4.52%, N = 8.26%, Found: = 43.49%, H = 4.24%, N = 8.02%

### L-Val-CoCoCo(R = CH(CH<sub>3</sub>)<sub>2</sub>, M<sub>1</sub>=M<sub>2</sub>= Co)

Light green (Yield 82 %). ESI+ MS(m/z) Calc. C<sub>60</sub>H<sub>60</sub>N<sub>10</sub>O<sub>4</sub>Co<sub>3</sub> · 3 ClO<sub>4</sub> 1460.3, Found 1460.1 (M<sup>+</sup>).  
 Elemental analysis Calc. C<sub>60</sub>H<sub>60</sub> N<sub>10</sub>O<sub>4</sub>Co<sub>3</sub> · 4 ClO<sub>4</sub> · 6 H<sub>2</sub>O: 43.21%, H = 4.35%, N = 8.40%, Found: C = 42.47%, H = 4.20%, N = 8.16%

### L-Ala-CoCoCo(R = CH<sub>3</sub>, M<sub>1</sub>=M<sub>2</sub>= Co)

Light green (Yield 23 %). ESI+ MS(m/z) Calc. C<sub>56</sub>H<sub>52</sub>N<sub>10</sub>O<sub>4</sub>Co<sub>3</sub> · 3 ClO<sub>4</sub> 1404.2, Found 1404.1 (M<sup>+</sup>).  
 Elemental analysis Calc. C<sub>56</sub>H<sub>52</sub>N<sub>10</sub>O<sub>4</sub>Co<sub>3</sub> · 4 ClO<sub>4</sub> · 6 H<sub>2</sub>O C: 41.73%, H = 4.00%, N = 8.86%, Found: C = 41.83%, H = 3.78%, N = 8.58%

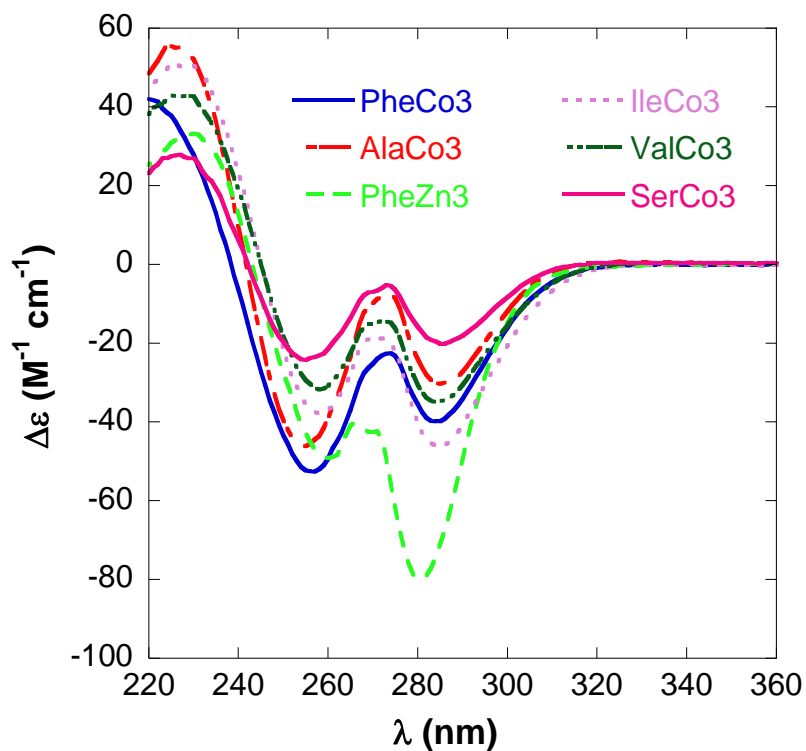
**L-Ser-CoCoCo**(R= CH<sub>2</sub>OH, M<sub>1</sub>=M<sub>2</sub>= Co)

Light green (Yield 46.03 %). ESI+ MS(m/z) Calc. C<sub>56</sub>H<sub>52</sub>N<sub>10</sub>O<sub>6</sub>Co<sub>3</sub> · 3 ClO<sub>4</sub> 1436.2, Found 1436.0 (M<sup>+</sup>).

Elemental analysis Calc. C<sub>56</sub>H<sub>52</sub>N<sub>10</sub>O<sub>4</sub>Co<sub>3</sub> · 4 ClO<sub>4</sub> · 6 H<sub>2</sub>O: C= 40.92%, H = 3.92%, N = 8.52%, Found: C = 40.80 %, H = 3.80%, N = 8.48 %

## 2. ECD measurements

All the ECD spectra were collected with a Jasco J-715 spectrophotometer in 0.02 cm cylindrical cells with the following acquisition parameters: 100 nm/min (scan speed); 1 nm (data pitch); 1 s (response time); 2 nm (band width)



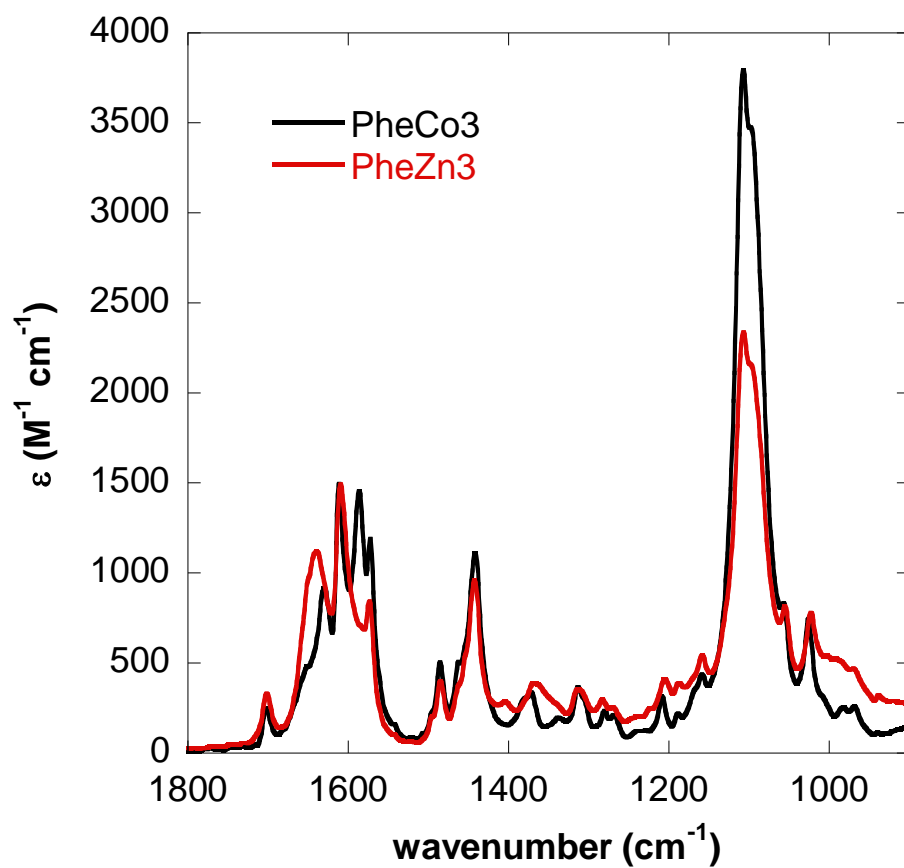
**Figure S1** ECD spectra of five trinuclear complexes.: PheZn3 incorporates three Zn atoms, while in the other cases Co ions are present.

### 3 VCD Measurements

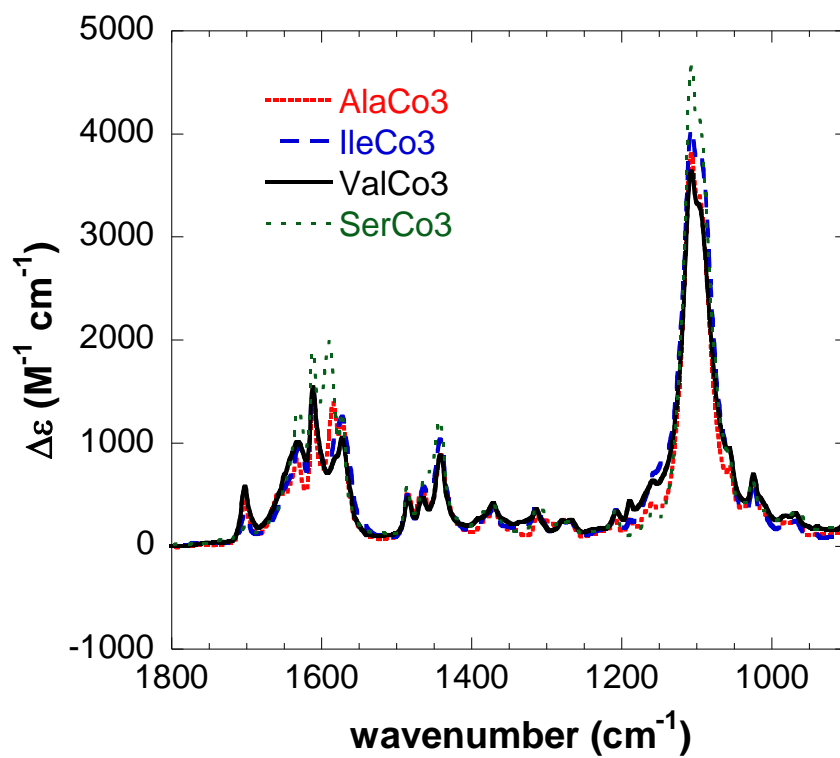
All samples were prepared in deuterated acetonitrile (dry CD<sub>3</sub>CN, Armar) and inserted in sealed infrared cells with 3 mm thick CaF<sub>2</sub> windows and 50 or 100 μm pathlength. The concentrations were as reported in the following table. Fourier-transform infrared (FTIR) and VCD spectra (with spectral resolution of 2 and 4 cm<sup>-1</sup>, respectively) were obtained with a JASCO FVS-6000 spectrometer. All spectra were baseline subtracted using the spectra of dry CD<sub>3</sub>CN in the same cell.

**Table S1** Concentrations of different Aaa-metal systems measured. The number of scans was 2000 in all the experiments.

Sample	Concentration
AlaCo3	39.96 mM
IleCo3	35.44 mM
ValCo3	38.76 mM
SerCo3	24.85 mM
GlyCo3	26.66 mM
D-PheCo3	13.16 mM

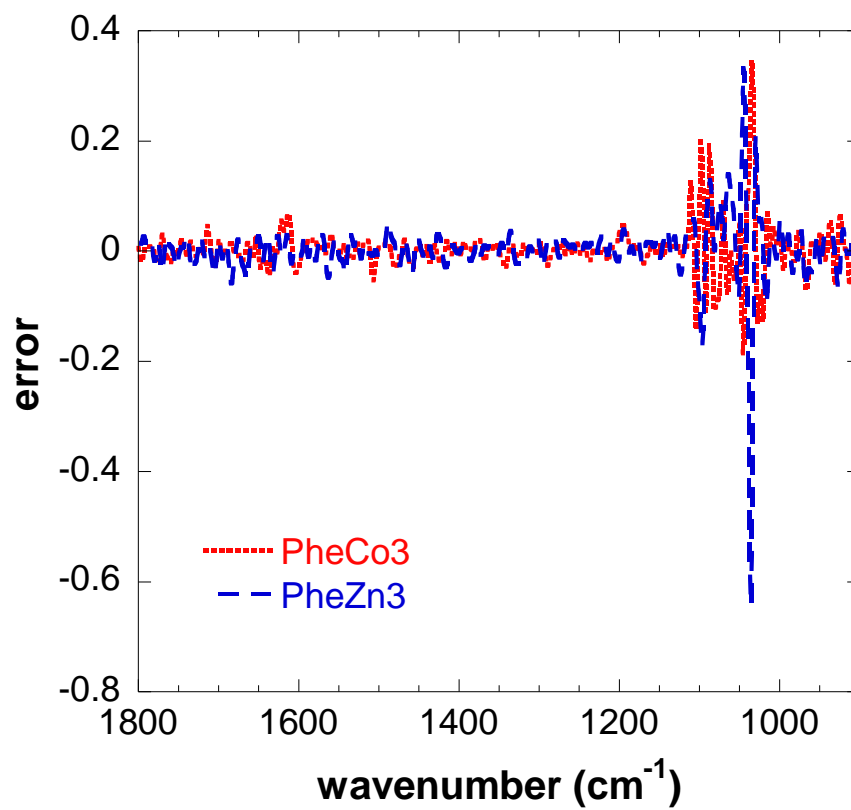


**Figure S2** IR spectra of PheCo3 (solid black line) and the analogue PheZn3 (solid red line).

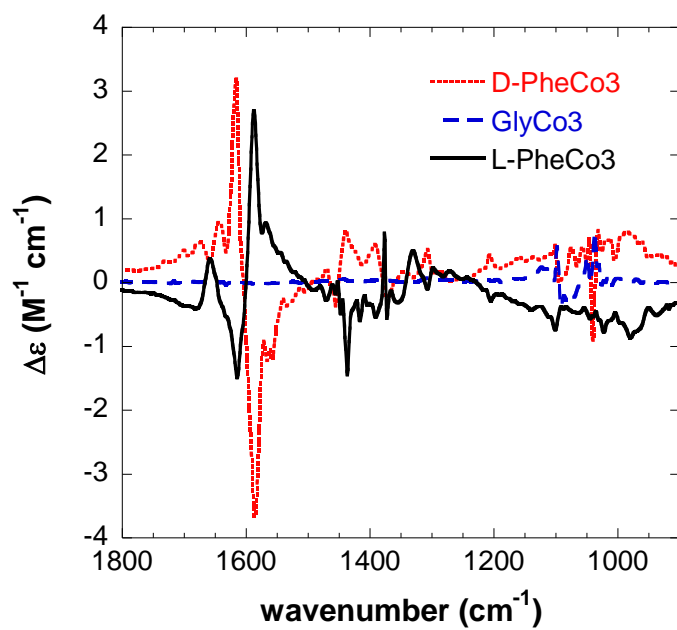


**Figure S3** IR spectra of AlaCo3, ValCo3, IleCo3 and SerCo3.





**Figure S4** The so-called Jasco error channel of PheCo3 (point red line) and PheZn3 (dashed blue line).



**Figure S5** VCD spectra of L-PheCo3 (solid black line), its enantiomer D-PheCo3 (dotted red line) and the achiral GlyCo3 (dashed blue line).