## Supporting Information

# Metal-Driven Ligand Assembly in the Synthesis of Cyclodextrin [2] and [3]Rotaxanes

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**Figure S1.** <sup>1</sup>H NMR (500 MHz,  $d_6$ -DMSO) of **3**<sub>2</sub>-Zn.

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**Figure S2.** (a) Spectral changes in the UV-vis spectrum of  $\mathbf{3}_2$ -Zn upon addition of  $\alpha$ -CD, and (b) fitted binding curve at 400 nm.<sup>†</sup> The titration was carried out at 298 K with a constant concentration of  $\mathbf{3}_2$ -Zn (25  $\mu$ M). Arrows indicate areas of increasing and decreasing absorbance during the titration.

#### **Pre-Complexation Equilibria Studies**



Scheme S1. Equilibria between 1, 3 and their inclusion complexes  $1 \subseteq \alpha$ -CD and  $3 \subseteq \alpha$ -CD.

<sup>&</sup>lt;sup>†</sup> Data was fitted using Specfit/32, Spectrum Software Associates, P.O. box 4494, Chapel Hill, NC 27514-4494, USA.

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**Figure S3.** <sup>1</sup>H NMR (250 MHz,  $D_2O$ , 298 K) of a mixture of 1 (46 mM) with (a) no added EDA, (b) 0.8 eq. EDA, (c) 2 eq. EDA and (d) 8 eq. EDA.



**Figure S4.** <sup>1</sup>H NMR (250 MHz, D<sub>2</sub>O, 298 K) of **1** (46 mM, red) and a mixture of **1** (46 mM) with 2 eq.  $\alpha$ -CD (blue).



**Figure S5.** <sup>1</sup>H NMR (250 MHz, D<sub>2</sub>O, 298 K) of a mixture of 1 (46 mM) with 2 eq. EDA (red) and a mixture of 1 (46 mM) with 2 eq.  $\alpha$ -CD and 2 eq. EDA (blue).

#### **NOESY Characterisation of the Rotaxanes**



Figure S6. 2D NOESY (500 MHz, D<sub>2</sub>O, 298 K, 400 ms mixing time) of 3<sub>2</sub>-Co⊂(α-CD)<sub>2</sub>-hh.



#### Figure S7. 2D NOESY (500 MHz, D<sub>2</sub>O, 298 K, 400 ms mixing time) of 3<sub>2</sub>-Co⊂(α-CD)<sub>2</sub>-ht.



Figure S8. 2D NOESY (500 MHz, D<sub>2</sub>O, 298 K, 400 ms mixing time) of 3<sub>2</sub>-Co⊂(α-CD)<sub>2</sub>-tt.

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Figure S9. 2D NOESY (500 MHz, D<sub>2</sub>O, 298 K, 400 ms mixing time) of 3-Co(EDA)(H<sub>2</sub>O)⊂α-CD-h.