Supporting information

Cu(II) templated formation of \([n]\)Pseudorotaxanes (\(n= 2,3,4\)) using a tris-amino ether macrocyclic wheel and multidentate axles

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X-ray crystallographic data details:

All the X-ray crystallographic details of \([\text{[CuPR]}_2]^{2+}\) were given in Table 1S. Single green block-shaped crystals of \([\text{[pseudorotaxane][CuPR]}]^{2+}\) were obtained upon slow evaporation of a solution of \([\text{[CuPR(CINO}_4)]_2\) and excess NaOTf in CH$_3$CN. A suitable crystal 0.06×0.03×0.02 mm$^3$ was selected and mounted on a suitable support on a Bruker APEX-II CCD diffractometer using the SAINT/ SMART APEX II software.\textsuperscript{1, 2} The crystal was kept at a steady $T = 127$ K during data collection. The structure was solved with the ShelXT 2014/5\textsuperscript{3} structure solution program using suitable methods and by using Olex2\textsuperscript{4} as the graphical interface. The model was refined with version 2018/3 of ShelXL\textsuperscript{5} using Least Squares minimisation. SADABS\textsuperscript{6} was applied for empirical absorption corrections. PLATON\textsuperscript{7} and MERCURY 3.7\textsuperscript{8} were used to generate graphical pictures of \([\text{[CuPR]}_2]^{2+}\).

**Calculation of Association Constants:**

The association constants were calculated from UV/Vis titration experiments by plotting the absorbance changes ($\Delta A$) at a fixed $\lambda$ value against the guest concentration by using nonlinear fitting of the curves. Equation 1 is used for 1:1 (host: guest) binding model:\textsuperscript{9}

$$\Delta A = \left( \frac{A}{2+H} \right) \times \left\{ \left( G_0 + H_0 + \frac{1}{K} \right) - \sqrt{\left( G_0 + H_0 + \frac{1}{K} \right)^2 + 4G_0H_0} \right\} \ldots (1)$$

Where, $A =$ absorbance intensity value upon each addition of the guest, change in absorption intensity $\Delta A = (A - A_0)$, $[H]_0 =$ initial concentration of the host, $[G]_0 =$ initial concentration of the guest and $K$ is the association constants.

Similarly, equations 2 is used for non-linear curve fitting of 1:2 (host: guest) binding model.\textsuperscript{10}

$$\Delta A = \frac{A_{\Delta HG1}K_1[H]_0[G] + A_{\Delta HG2}K_1K_2[H]_0[G]^2}{1 + K_1[G] + K_1K_2[G]^2} \ldots \ldots \ldots \ldots \ldots \ldots . (2)$$

Where, $K_1$ and $K_2$ are the stepwise association constants.
Scheme 1S. Synthesis route of NaphMC\textsuperscript{11}; (i) 1,2-dibromoethane, K\textsubscript{2}CO\textsubscript{3}, CH\textsubscript{3}CN, reflux; (ii) 1,2-dihydroxybenzene, K\textsubscript{2}CO\textsubscript{3}, CH\textsubscript{3}CN, reflux; (iii) diethylenetriamine, CH\textsubscript{2}Cl\textsubscript{2}-CH\textsubscript{3}OH, RT, 15h, NaBH\textsubscript{4}.

Scheme 2S. Synthetic route of Phen-Acid\textsuperscript{12} : (i) SeO\textsubscript{2}, dioxane, reflux; (ii) Conc. HNO\textsubscript{3}, reflux.
Figure 1S. $^1$H-NMR spectrum of compound A in CDCl$_3$ in 400 MHz at 298K.

Figure 2S. $^{13}$C-NMR spectrum of compound A in CDCl$_3$ in 100 MHz at 298K.
Figure 3S. ESI-MS(+) spectrum of compound A at 298K.

Figure 4S. $^1$H-NMR spectrum of L2 in CDCl$_3$ in 500 MHz at 298K.
Figure 5S. $^{13}$C-NMR spectrum of L2 in CDCl$_3$ in 100 MHz at 298K.

Figure 6S. ESI-MS(+ve) spectrum of L2 at 298K.
Figure 7S. $^1$H-NMR spectrum of compound B in CDCl$_3$ in 400 MHz at 298K.

Figure 8S. $^{13}$C-NMR spectrum of B in CDCl$_3$ in 100 MHz at 298K.
Figure 9S. ESI-MS(+) spectrum of compound B at 298K.

Figure 10S. $^1$H-NMR spectrum of L3 in CDCl$_3$ in 400 MHz at 298K.
Figure 11S. $^{13}$C-NMR spectrum of L3 in CDCl$_3$ in 100 MHz at 298K.

Figure 12S. ESI-MS(+ve) spectrum of L3 at 298K.
Scheme 3S. Synthetic route of NaphMC-Cu(II) complex

Figure 13S. ESI-MS(+ve) spectrum of [2]CuPR(ClO$_4$)$_2$ at 298K.
Figure 14S. ESI-MS(+ve) spectrum of [3]CuPR(ClO$_4$)$_4$ at 298K.

Figure 15S. ESI-MS(+ve) spectrum of [4]CuPR(ClO$_4$)$_6$ at 298K.
**Figure 16S.** Equivalence plot from UV/Vis titration experiment between L1 and NaphMC-Cu(II) complex.

**Figure 17S.** Equivalence plot from UV/Vis titration experiment between L2 and NaphMC-Cu(II) complex.
Figure 18S. Equivalence plot from UV/Vis titration experiment between L3 and NaphMC-Cu(II) complex.

Figure 19S. Molar ratio plot from UV/Vis titration experiment between L1 with NaphMC-Cu(II) solution.
Figure 20S. Molar ratio plot from UV/Vis titration experiment between L2 with NaphMC-Cu(II) solution.

Figure 21S. Molar ratio plot from UV/Vis titration experiment between L3 with NaphMC-Cu(II) solution.
Figure 22S. Characteristic (A) UV/Vis and (B) emission spectra of pseudorotaxanes: [2]CuPR(ClO$_4$)$_2$, [3]CuPR(ClO$_4$)$_4$ and [4]CuPR(ClO$_4$)$_6$ in CH$_3$CN at 298K.

Figure 23S. Nonlinear 1:1 curve fitting to determine binding constant from UV/Vis titration experiment between L1 with NaphMC-Cu(II) solution.

K = 3.08 x 10$^6$ M$^{-1}$
R$^2$ > 99%
Figure 24S. Nonlinear 1:1 curve fitting to determine binding constant from UV/Vis titration experiment between L2 with NaphMC-Cu(II) solution.

Crystallographic details of ([2]CuPR)$_2^{2+}$

Figure 25S. Geometry around the Cu(II) center of ([2]CuPR)$_2^{2+}$ ($\tau = 0.638$).
Table 1S. Crystallographic data of ([2]CuPR)\(^{2+}\)

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<th><strong>[2]pseudorotaxane</strong></th>
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Figure 26S. Single Crystal X-ray structure of ([2]CuPR)²⁺ (Ball and stick model). Hydrogen atoms are omitted for clarity.

Figure 27S. Single Crystal X-ray structure of ([2]CuPR)²⁺ (ellipsoid model using platon version).
Figure 28S: EPR spectrum of $[2]\text{CuPR(ClO}_4\text{)}_2$ in CH$_3$CN at 80K.

Figure 29S. EPR spectrum of $[3]\text{CuPR(ClO}_4\text{)}_4$ in CH$_3$CN at 80K.

Figure 30S. EPR spectrum of $[4]\text{CuPR(ClO}_4\text{)}_6$ in CH$_3$CN at 80K.
Scheme 4S: Synthetic route of axle L4; (i) 1,2-dibromoethane, K₂CO₃, DMF, RT, 20h, 86%, (ii) Phen-Acid, TBAF, THF, RT, 80%.

Figure 31S. ¹H-NMR spectrum of compound C in CDCl₃ in 400 MHz at 298K.
Figure 32S. $^{13}$C-NMR spectrum of compound C in CDCl$_3$ in 100 MHz at 298K.

Figure 33S. $^1$H-NMR spectrum of L4 in CDCl$_3$ in 500 MHz at 298K.
Figure 34S. $^{13}$C-NMR spectrum of L4 in CDCl$_3$ in 125 MHz at 298K.

Figure 35S. ESI-MS(+ve) spectrum of L4 at 298K.
Figure 36S. ESI-MS(+ve) spectrum of L4 axle based threaded molecule at 298K.


1699.4115

Figure 37S. UV/Vis titration profile between L4 (1x10^{-5} M) with NaphMC-Cu(II) (1x10^{-4} M) in CH$_3$CN at 298 K.
Figure 38S. Molar ratio plot from UV/Vis titration experiment between L4 with NaphMC-Cu(II) solution.

Figure 39S. FT-IR spectrum of [2]CuPR(ClO₄)₂.
Figure 40S. FT-IR spectrum of [3]CuPR(ClO₄)₄.

Figure 41S. FT-IR spectrum of [4]CuPR(ClO₄)₆.
Scheme 5S. Synthetic route of NaphMC-Ni(II) complex

Figure 42S. ESI-MS(+ve) spectrum of NaphMC-Ni(II) complex at 298K.

Figure 43S. ESI-MS(+ve) spectrum of [2]NiPR(ClO\(_4\)_2 at 298K.
Figure 44S. ESI-MS(+ve) spectrum of [3]$\text{NiPR(ClO}_4\text{)}_4$ at 298K.

Figure 45S. ESI-MS(+ve) spectrum of [4]$\text{NiPR(ClO}_4\text{)}_6$ at 298K.
Figure 46S. UV/Vis titration profile between L1 (1x10^{-5} M) with NaphMC-Ni(II) (1x10^{-4} M) in CH_3CN at 298 K.

Figure 47S. UV/Vis titration profile between L2 (1x10^{-5} M) with NaphMC-Ni(II) (2.2x10^{-4} M) in CH_3CN at 298 K.
Figure 48S. UV/Vis titration profile between L3 (1x10^{-5} M) with NaphMC-Ni(II) (3.8x10^{-4} M) in CH$_3$CN at 298 K.

Figure 49S. Molar ratio plot from UV/Vis titration experiment between L1 with NaphMC-Ni(II) solution.
Figure 50S. Molar ratio plot from UV/Vis titration experiment between L2 with NaphMC-Ni(II) solution.

Figure 51S. Molar ratio plot from UV/Vis titration experiment between L3 with NaphMC-Ni(II) solution.
Figure 52S. Characteristic UV/Vis spectra of pseudorotaxanes: [2]NiPR(ClO$_4$)$_2$, [3]NiPR(ClO$_4$)$_4$ and [4]NiPR(ClO$_4$)$_6$ at 298K.
References

1. APEX2 suite for crystallographic software, Bruker axs, Madison, WI (2009).