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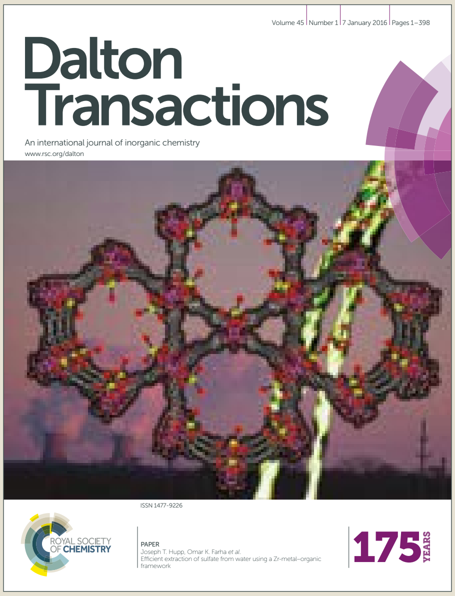

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Threading of various ‘U’ shaped bidentate axles into a heteroditopic macrocyclic wheel *via* Ni^{II}/ Cu^{II} templation

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Abstract

Threading of ‘U’ shaped bent axles having diverse functionalities (**Axle1-Axle10**) is investigated by using a heteroditopic amido-amine macrocyclic (**MC**) wheel *via* Ni^{II} or Cu^{II} metal ion templation. These bent shaped axles are the derivatives of 4, 4' substituted 2, 2' bipyridine, which are composed of various terminal groups like alkene, alkyne, bromide, hydroxyl and azide. Such metallo [2]pseudorotaxanes are well characterised by ESI-MS, EPR and FT-IR spectroscopic studies, UV-Vis absorption studies, elemental analysis and Single-crystal X-ray diffraction studies wherever possible. Experimental evidences support 1:1:1 ternary complexation between **MC**, metal ion and axle. The single crystal X-ray structures of three Cu^{II} templated ternary complexes (**PR1'**, **PR3'** and **PR7'**) show the penta-coordination arrangement around the templating metal ion. Interestingly, judicious selection of chemical functionalities in the complementary wheel and axle components enables to show the existence of various covalent and non covalent interactions.

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Introduction

In the field of supramolecular chemistry, pseudorotaxanes are considered as a primary building block to construct mechanically interlocked molecules (MIM's)[1] such as rotaxanes,[2] and catenanes[3] which attract enormous research interest owing to their potential applications in the various fields.[4] These building blocks are constructed *via* different templation strategies such as cation/ anion,[5] hydrogen bonding,[6] π-π stacking,[7] and halogen bonding[8] interactions. However, use of metal ion as a template is one of the popular approaches to synthesize multi-functional pseudorotaxanes through the involvement of [2+2], [3+1], [3+2] or [3+3] orthogonal sets of ligands.[4b, 9] In this context over the last few years, Sauvage and co-workers have extensively utilised Cu^{I} as templating agent to develop multifunctional mononuclear/ multinuclear pseudorotaxanes by using bidentate chelating unit containing wheel and axle components ([2+2] donor sets).[10] On the other hand, Leigh *et al.* has explored Pd^{II} metal ion templated threaded architectures[11] based on pyridine and bis-amide functionalised macrocylic wheel ([3+1] donor sets). Moreover, Cu^{II},[12] Ni^{II},[12] Zn^{II},[12-13] Fe^{II},[14] Ru^{II},[15] Rh^{II},[16] Co^{III},[11b, 16] Au^{I} [5f] have also been explored as templates to construct threaded assemblies upon judicious choice of complimentary wheel and axle units. Generally, pseudorotaxanes having linear axles are preferred to synthesise rotaxanes,[17] whereas bent shaped threaded axles are utilised as a potential candidate towards the development of catenanes *via* threading followed by clipping method.[18] Recently, our group has reported multi-functional [2]pseudorotaxanes and [2]rotaxanes by using heteroditopic macrocyclic wheels and various linear rod shaped axles derived from 5, 5' dimethyl 2, 2' bipyridine precursor.[17c, 19] In this regard, our interest is to develop bent shaped axles based threaded assemblies that can be used as a precursor to construct interlocked systems like catenane with multiple functionalities. Thus, it would be advantageous to explore the derivatives

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of 4, 4' substituted 2, 2' bipyridine with various chemical functionalities in the axle backbone to introduce versatilities within the threaded assemblies. Herein, we report Ni^{II} and Cu^{II} templated threading of a series of relatively uncommon 'U' shaped axles based on the derivatives of 4, 4' dimethyl 2, 2' bipyridine in the amido-amine macrocyclic wheel to develop two new generation of [2]pseudorotaxanes through [3+2] metal ion chelation assisted by other non-covalent interactions .

Result and discussion

Axle designing aspects

4, 4' dimethyl 2, 2' bipyridine (**Axle1**) and its derivatives (Fig. 1) are chosen as the 'U' shaped axles to coordinate with the metallo-macrocycle complexes of **MC** *via* [3+2] orthogonal mode of orientation where tris and bis chelation are satisfied by the wheel and axle components respectively. Threaded axles having alkene,[10c, 18b] alkyne,[18c] hydroxyl,[18c, 20] halide,[21] or azide[3a, 18c] terminal groups are well known to act as a precursor for the clipping reactions to develop

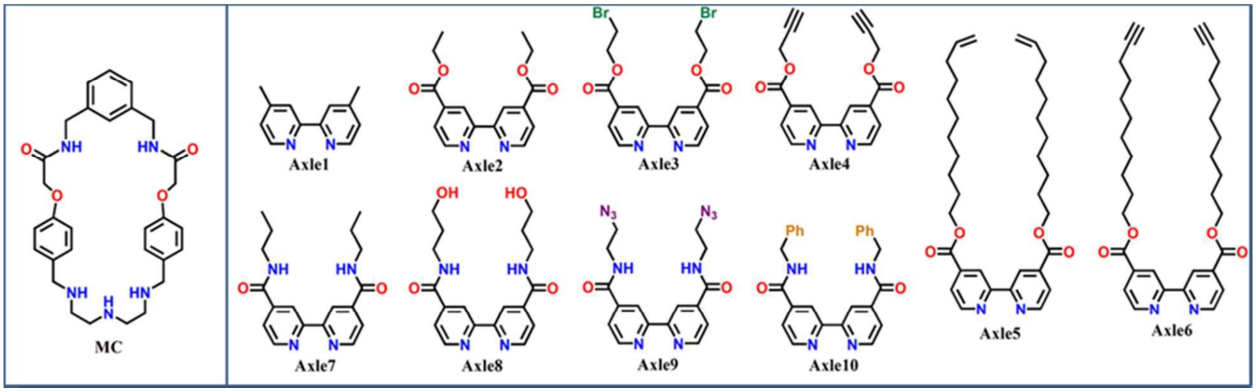

Fig. 1 *Chemical structure of* ***MC*** *and 'U' shaped bidentate axles (****Axle1*** *-* ***Axle10****)*

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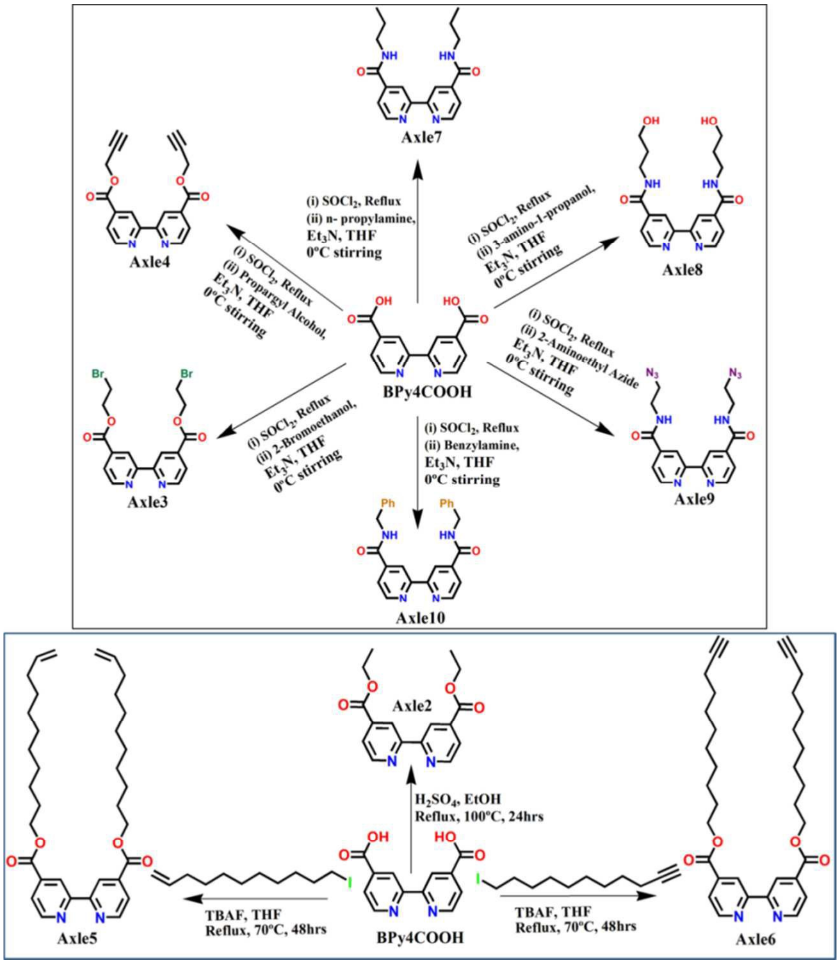
catenated structures hence, we have designed a series of amide/ester functionalised bipyridine axles by incorporating (i) bromide (**Axle3**), (ii) alkyne (**Axle4**, **Axle6**), (iii) alkene (**Axle5**) (iv) hydroxyl (**Axle8**), (v) azide (**Axle9**), and (vi) aromatic (**Axle10**) unit termini.

(a) General procedure for the synthesis of ‘U’ shaped bidentate axles

Axle3, **Axle4**, **Axle8**, **Axle9**, **Axle10** are synthesised in moderate yields by following Scheme 1A whereas **Axle5** and **Axle6** are synthesised according to Scheme 1B by using 4, 4' dimethyl 2, 2' bipyridine (**Axle1**) as a starting material. 4, 4' dimethyl 2, 2' bipyridine is reacted with $K_2Cr_2O_7$



Scheme 1A** and **1B**. Synthetic route for the synthesis of **Axle1 - Axle10

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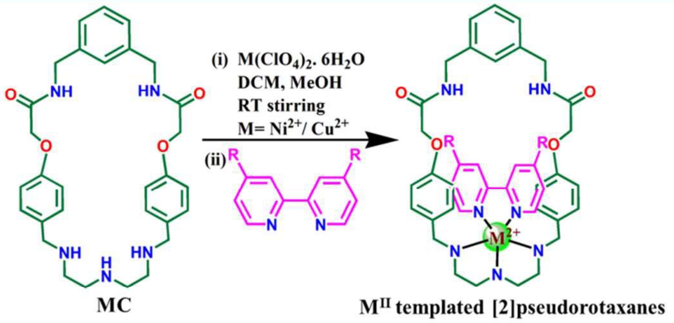
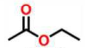
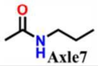
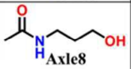
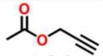
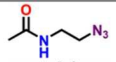
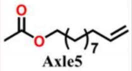
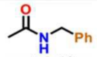
H_2SO_4 to synthesise 4, 4' diacid 2, 2' bipyridine (BPy4COOH) followed by reaction with $SOCl_2$, Et_3N and respective chemical precursors to afford different bidentate axles. BPy4COOH, **Axle2** and **Axle7** are synthesised by following the literature procedure.[22] All the axles are characterized by usual spectroscopic methods such as ESI-MS, ^{1}H NMR, ^{13}C NMR and FT-IR (Fig. 1S - 28S, ESI†) studies. The details of synthetic procedures and characterization are presented in the experimental section and in the supporting information.

(b) General procedure for the synthesis of [2]pseudorotaxanes (PR1 - PR10, PR1'- PR10')

Scheme 2 shows the ternary complex formations upon treatment of respective axles (**Axle1-Axle10**) in the stirring solution of corresponding metallo - macrocycle complexes (**MC**-Ni^{II},



R=	Ni^{II} templated [2]pseudorotaxanes	Cu^{II} templated [2]pseudorotaxanes	R=	Ni^{II} templated [2]pseudorotaxanes	Cu^{II} templated [2]pseudorotaxanes
—CH_3 Axle1	PR1	PR1'	 Axle6	PR6	PR6'
 Axle2	PR2	PR2'	 Axle7	PR7	PR7'
 Axle3	PR3	PR3'	 Axle8	PR8	PR8'
 Axle4	PR4	PR4'	 Axle9	PR9	PR9'
 Axle5	PR5	PR5'	 Axle10	PR10	PR10'

Scheme 2. *Synthesis of Ni^{II} and Cu^{II} templated [2]pseudorotaxanes with their corresponding abbreviations.*

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MC-Cu^{II}) in a DCM-MeOH binary solvent mixture. Ni^{II} templated and Cu^{II} templated [2]pseudorotaxanes are isolated as greenish-yellow and blue colour solid upon evaporating the solvent and successive washing with DCM. Threaded ternary complexes are characterized by ESI-MS, EPR, FT-IR and UV-Vis spectroscopic studies, elemental analysis and single crystal X-Ray diffraction studies (wherever possible). The details of synthetic procedures and characterization are described in the experimental section and supporting information.

ESI-MS studies

Electrospray ionisation (ESI-MS) analysis is carried out to characterise [2]pseudorotaxanes (**PR1 - PR10** and **PR1' - PR10'**). ESI-MS spectra of **PR1**, **PR5**, **PR7**, **PR2'**, **PR6'** and **PR8'** are

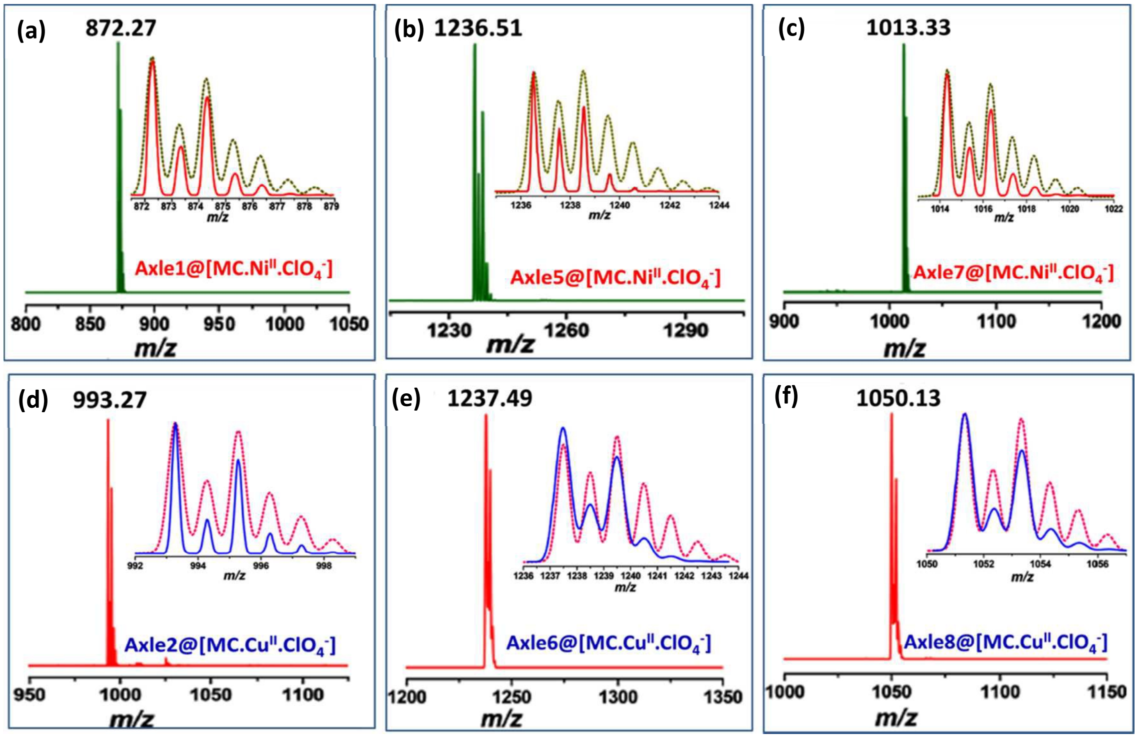

Fig. 2 *ESI-MS spectra of (a)* ***Axle1*** *vs* ***MC****-Ni^{II}* ***(PR1)****, (b)* ***Axle5*** *vs* ***MC****-Ni^{II}* ***(PR5)****, (c)* ***Axle7*** *vs* ***MC****-Ni^{II}* ***(PR7)****, (d)* ***Axle2*** *vs* ***MC****-Cu^{II}* ***(PR2')****, (e)* ***Axle6*** *vs* ***MC****-Cu^{II}* ***(PR6')****, (f)* ***Axle8*** *vs* ***MC****-Cu^{II}* ***(PR8')*** *templated [2]pseudorotaxanes.*

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shown in Fig. 2 and rest of the ESI - MS spectra are presented in the supporting information (Fig. 29S-48S, ESI†**)**. The inset pictures show merging of isotopic pattern with the experimental pattern (Fig. 2, 29S-48S, ESI†). In each of the Ni^{II} templated ESI-MS, **Axle1** - **Axle10** threaded ternary complexes show molecular ion peak at *m/z* 872.3, 988.3, 1148.1, 1008.2, 1236.5, 1231.4, 1013.3, 1047.3, 1069.3, 1110.3 respectively that correspond to single charged ([**MC**-Ni-AxleX-$ClO_4]^+$) (X = **1 - 10)** species. Similarly, Cu^{II} templated heteroleptic complexes **(PR1' - PR10')** show respective signature peaks at *m/z* 877.3, 993.3, 1151.1, 1013.2, 1242.4, 1237.5, 1018.3, 1050.3, 1072.3, 1115.3 which also reveal the existence of single charged species ([**MC**-Cu-X-$ClO_4]^+$) (X = **1 - 10)**. In each case isotopic distribution pattern shows good agreement with the experimental pattern, which supports the involvement of 1:1:1 **MC**, metal and corresponding bidentate axles.

EPR Studies

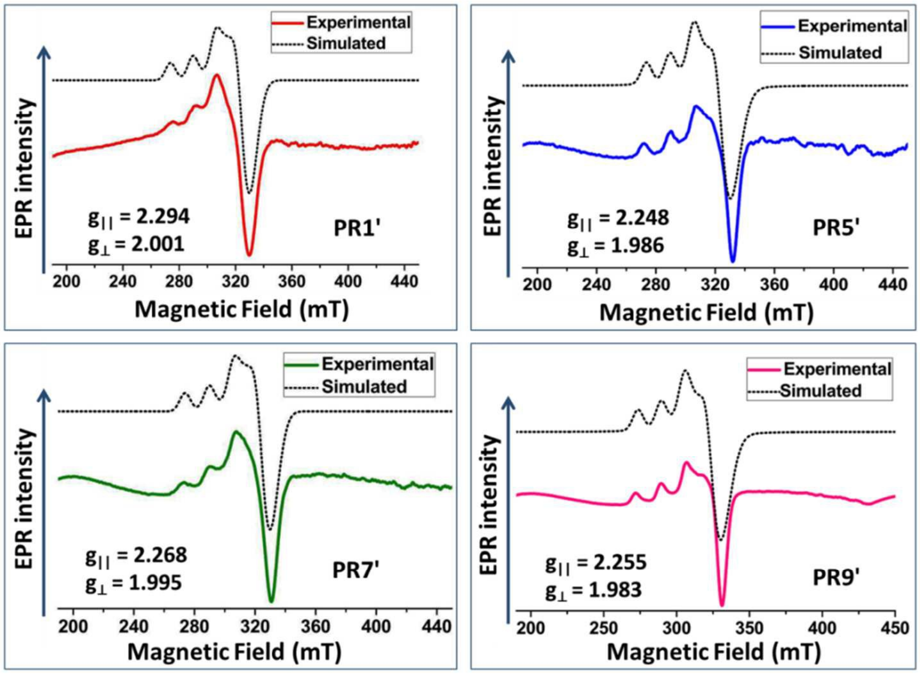

Fig. 3 *Simulated X-band EPR spectra of **PR1'**, **PR5'**, **PR7'** and **PR9'** at 80K.*

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Cu^{II} templated [2]pseudorotaxanes (**PR1'** - **PR10'**) show well resolved X band EPR spectrum at 80K. X band EPR spectra of **PR1'**, **PR5'**, **PR7'**, **PR9'** are presented in Fig. 3 and other spectra are given in supporting information (Fig. 49S, ESI†**)**. The EPR spectra of the Cu^{II} templated pseudorotaxanes are found to be anisotropic in nature as depicted by comparing with the simulated EPR spectra (dotted line), as given in Figure 3. However, all of the X band EPR spectra data show the pattern with $\mathbf{g_{||}} > \mathbf{g_{\perp}}$ invariably in all cases, which indicates a penta-coordinated distorted square pyramidal geometrical arrangement around Cu^{II} metal centre upon coordination of **MC** and axles in threaded complexes.[19b, c]

Absorption spectroscopic Studies

Absorption spectroscopic studies are carried out to investigate the binding efficiency of ‘U’ shaped axles (**Axle1** - **Axle10**) with the metallo-macrocycle complexes in heteroleptic fashion. Binding stoichiometry of the ternary complexes and the association constant values are evaluated *via* titration experiments. A similar spectral feature is observed in all of the titration experiments. Titrations are performed in binary solvent mixtures (CH_3CN - DMF/ DMSO) (9:1 v/v) by using bidentate axles as host and **MC**-Ni^{II} complex as guest. However, UV-Vis spectra of the bidentate ligands (host) in CH_3CN show absorption peak maxima (initial λ_{max}) in the range of 280 nm - 300 nm that corresponds to n - π^* transition. With the gradual addition of the guest (**MC**-Ni^{II}) into the solution of bidentate axles, absorption peak is red shifted and a new absorption peak (final λ_{max}) is generated upon complex formation between axles and **MC**-Ni^{II} (Table 1). However, it is shown from the Table 1 that initial λ_{max} values in cases of PR2 - PR10 are quite similar as well as the final λ_{max} values also remain in close proximity. But, only in case of PR1 the initial and also the final λ_{max} values differ from those above mentioned λ_{max} values. Such difference could be attributed to the nature of substituents on bipyridyl moiety, i.e. in PR1 only

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methyl substitution is present in the axle, whereas in PR2-PR10 ester or amide functionalities along with different substituents are involved. During titration, a single isosbestic point is

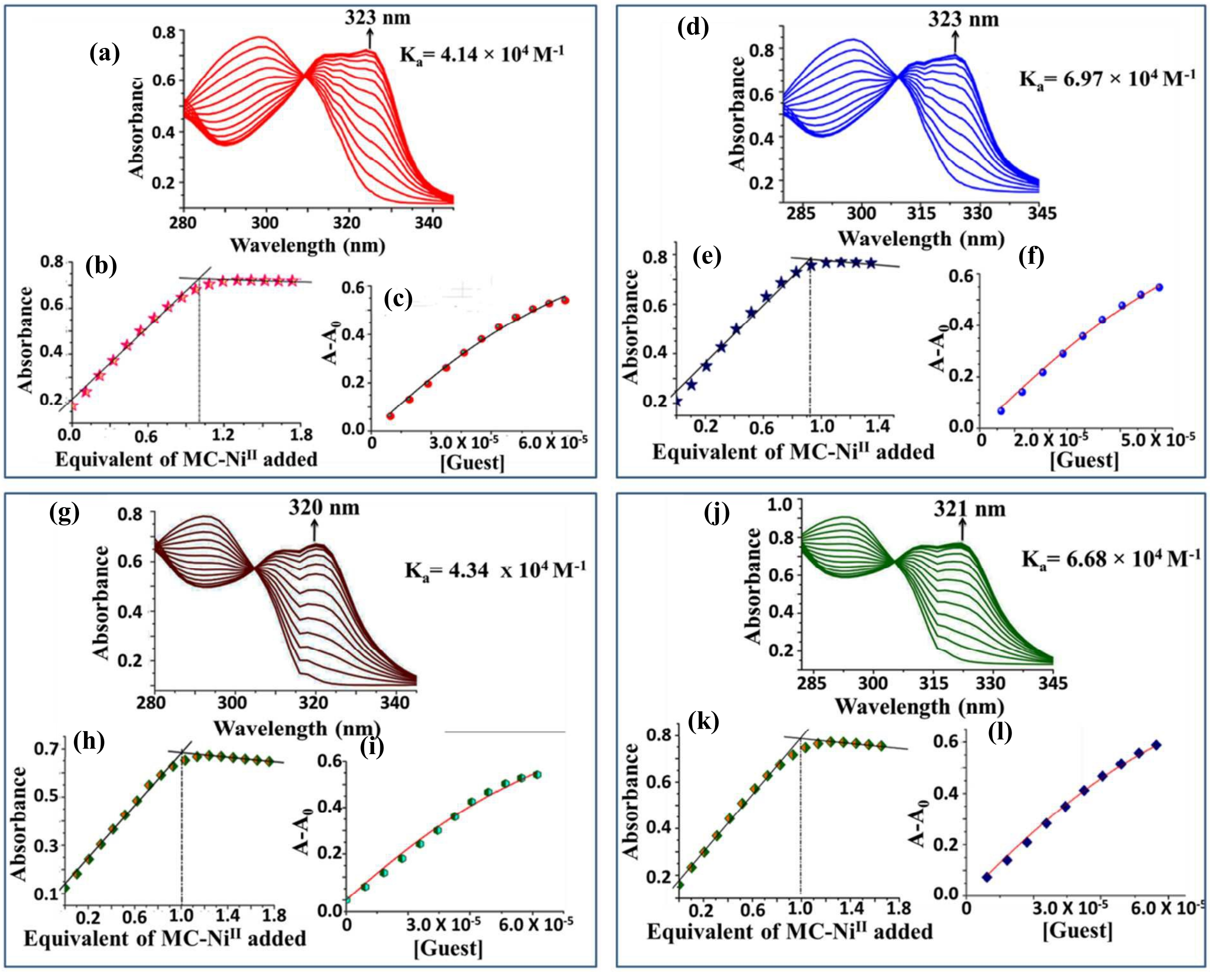

Fig. 4 *(i) UV-Vis titration profile of (a)* ***Axle3*** *(6 x 10^{-5}) vs.* ***MC****-Ni^{II} complex (6.5 x 10^{-4}) (d)* ***Axle6*** *(6.0 x 10^{-5}) vs.* ***MC****-Ni^{II} complex (6.2 x 10^{-4}), (g)* ***Axle8*** *(6.0 x 10^{-5}) vs.* ***MC****-Ni^{II} complex (6.2 x 10^{-4}), (j)* ***Axle10*** *(6.0 x 10^{-5}) vs.* ***MC****-Ni^{II} complex (6.2 x 10^{-4}); (ii) corresponding* ***1:1*** *equivalence plot (b, e, h and k); (iii) non-linear 1:1 curve fitting of (c, f, i and l) absorption titration data.*

observed in n-π* region in all cases, that reveals the existence of single equilibrium for every Ni^{II} templated ternary complexation (Fig. 4, 50S, ESI†). Further, the equivalence plot analysis (Fig.

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4, 50S, ESI†) clearly indicates the formation of 1:1:1 ternary complexes in solution state. Non-linear 1:1 curve fitting method (Fig. 4 and Fig. 51S, ESI†) is utilised to evaluate the association constant values (**K$_a$**) for each of the ternary complex formation, which are within the range of 2.37 X 10^4 - 8.70 X 10^4 M^{-1}. For each of the PR1 - PR10 ternary complexes λ_{max}, association constant (K_a), molar extinction coefficient (***ε***) and free energy of complexation (**ΔG°**) values are tabulated in Table 1.

Table 1. *λ_{max} values, isosbestic point, molar extinction coefficient (ε), association constant (K_a) and free energy change values (ΔG^0) obtained from absorption spectroscopic data for PR1-PR10 at 298K.*

Ternary complexes[a]	Initial λ_{max} (nm)	Final λ_{max} (nm)	Isosbestic point (nm)	Molar extinction coefficient, ε (L mol^{-1} cm^{-1})[c]	K_a (M^{-1})[b]	ΔG° (Kcal.M^{-1}) at 298K
PR1	280	304	293	9.29×10^3	2.37×10^4	-6.00
PR2	297	323	309	1.29×10^4	4.26×10^4	-6.35
PR3	298	323	309	1.21×10^4	4.14×10^4	-6.34
PR4	298	324	309	9.97×10^3	3.76×10^4	-6.28
PR5	297	323	309	1.50×10^4	8.70×10^4	-6.78
PR6	297	323	309	1.29×10^4	6.97×10^4	-6.65
PR7	292	323	307	1.17×10^4	4.08×10^4	-6.33
PR8	292	320	304	1.12×10^4	4.34×10^4	-6.36
PR9	292	319	304	1.19×10^4	6.70×10^4	-6.62
PR10	292	321	305	1.29×10^4	6.68×10^4	-6.62

[a] For **PR1 - PR8** threaded complexes absorption titration are performed in CH_3CN - DMF mixture and PR9 - PR10 complexes titrations are obtained in CH_3CN - DMSO mixture.

[b] Errors are estimated to be approximately less than 10% for association constant values calculated from non-linear 1:1 curve fitting.

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[c] Molar extinction coefficient values are evaluated in n - π* transition region.

On the other hand, our previous report has shown that, the absorption peak maxima of **MC** - Cu^{II} complex appeared at 600 nm in CH_3CN, which corresponds to the d-d transition. At present studies, each of the UV-Vis spectra of the isolated 1:1 (MC-Cu^{II} : axle) Cu^{II} templated ternary complexes (1 x 10^{-3}) show absorption peak maxima (λ_{max}) in the range of 630 nm to 660 nm (Fig. 5, 52S, ESI†), which indicates the red shifting of the previous absorption peak from 600 nm upon 1:1 ternary complexes formation (**PR1' - PR10'**). However, in case of only **Axle1** threaded ternary complex (**PR1'**), the binding stoichiometry is monitored upon titration of 1.06 x 10^{-2} M solution of corresponding axle (guest) with the MC-Cu^{II} (host) complex (1 x 10^{-3} M), in which 1:1 equivalence plot shows complete 1:1:1 ternary complexation (**MC** : Cu^{II} : **Axle1)** with λ_{max} and isosbestic point values at 668 nm and 649 nm (Fig. 53S, ESI†) respectively. But, our repeated attempts to carry out the UV-Vis absorption titration between **MC**-Cu^{II} and other axles (**Axle2** - **Axle10**) remain unsuccessful due to appearance of precipitate in higher order of concentration under experimental condition. For each of the Cu^{II} threaded ternary complexes λ_{max} values and molar extinction coefficient values (*ε*) are tabulated in Table 2. Thus, absorption spectroscopic studies in solution state for both Ni^{II} and Cu^{II} templated [2]pseudorotaxanes

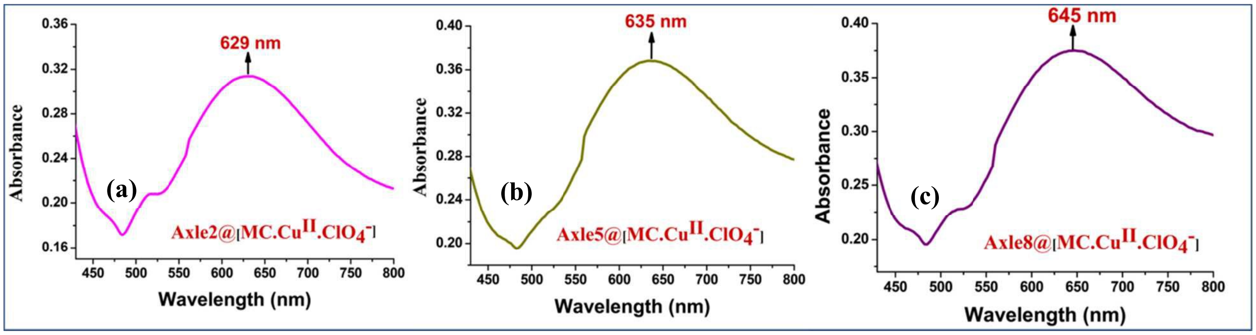

Fig. 5 *UV-Vis spectra of* ***PR2'*** *(*1 x 10^{-3} M)*,* ***PR5'*** *(*1 x 10^{-3} M) *and* ***PR8'*** *(*1 x 10^{-3} M) *in* CH_3CN.

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supports the formation of 1:1 ternary heteroleptic single complexation between the bidentate axles and metallo-macrocycle complexes.

Table 2. *λ_{max} values and molar extinction coefficient (ε) (L mol^{-1} cm^{-1}) values for* ***PR1' - PR10'*** *at 298K.*

Ternary complexes[a]	λ_{max} (nm)	Molar extinction coefficient *ε* (L mol^{-1} cm^{-1})^{b}		Ternary complexes[a]	λ_{max} (nm)	Molar extinction coefficient Ɛ (L mol^{-1} cm^{-1})^{b}
PR1'	668	2.24×10^2		**PR6'**	629	3.31×10^2
PR2'	629	3.14×10^2		**PR7'**	641	3.53×10^2
PR3'	631	3.57×10^2		**PR8'**	645	3.75×10^2
PR4'	631	3.14×10^2		**PR9'**	643	3.50×10^2
PR5'	635	3.69×10^2		**PR10'**	648	3.32×10^2

[a] absorption spectroscopic studies are performed in CH_3CN

[c] Molar extinction coefficient values are evaluated in d-d transition region.

Single Crystal X- Ray analysis

Single crystals suitable for X-Ray crystallographic analysis, are isolated for Cu^{II} templated **PR1'**, **PR3'** and **PR7'** threaded complexes. Block size greenish **PR1'** and **PR3'** crystals are obtained by slow evaporation of CH_3CN by using ClO_4^- as the counter anion whereas crystal of **PR7'** is found by slow evaporation of DMF - CH_3CN mixture by exchanging ClO_4^- anion with PF_6^- counter anion. All the crystals are generated after several weeks of crystallization from the multiple data sets of crystals. Thermal ellipsoid model of all the crystal structures (Fig. 6) indicate the complete threading of 'U' shaped axles into the **MC** *via* 1:1:1 (**MC**: metal ion: axle) complex formation followed by [3+2] orthogonal orientation. Due to the poor crystal quality and

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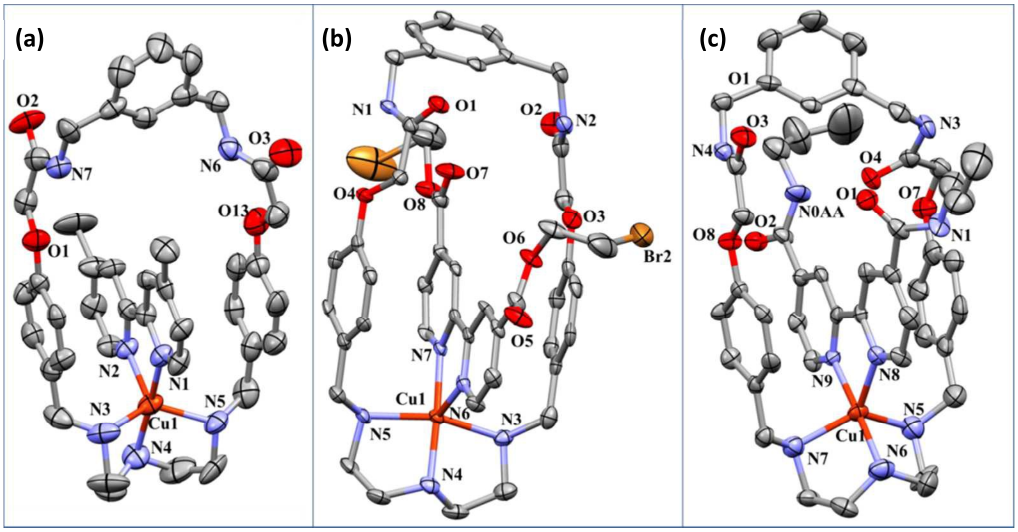

Fig. 6 *Thermal ellipsoids model of the (a)* ***PR1',*** *(b)* ***PR3'*** *and (c)* ***PR7'*** *single X- Ray crystal structures at the 50% probability level. Hydrogen atoms, solvent molecules and anions have been removed for clarity.*

low resolution these values should be discussed with the greatest care, and we abstain from a more detailed discussion of structural parameters. Detailed crystallographic details of all the crystal structures are given in supporting information (Fig. 74S-75S, Table S1-S6, ESI†).

Conclusions

In conclusion, we have successfully demonstrated the threading of ‘U’ shaped axles having diverse chemical functionalities, into a bis (amido) tris (amine) wheel (**MC**) assisted by $\mathrm{Ni^{II}}$ or $\mathrm{Cu^{II}}$ as templating metal ion. Consequently, the characterization studies confirm the suitability of heteroditopic **MC** towards the bent ‘U’ shaped bidentate axles to construct [2]pseudorotaxanes *via* [3+2] ternary complex formation. We envisage that these [2]pseudorotaxanes would act as precursors towards the development of catenated structures with multiple functionalities which can be easily be derivatised in different direction for the generation of new smart materials. Presently, we are focusing on the development of interlocked systems having complex functionalities by suitably choosing ‘U’ shaped axle and complementary heteroditopic wheel.

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Experimental Section

Materials and methods

All the starting materials 4, 4'-Dimethyl-2, 2'-Bipyridine, 10- undecene -1-ol, 10-undecyn-1-ol, 3-amino-1-propanol, 2bromoethanol, benzylamine, propargyl alcohol, n-propylamine, $Ni(ClO_4)_2.6H_2O$, $Cu(ClO_4)_2.6H_2O$, and deuterated solvents were purchased from Sigma- Aldrich and used as received. Solvents like THF, acetone, DCM, $CHCl_3$, petroleum Ether, ethylacetate, DMF and DMSO were procured from Spectrochem India Limited. THF, DCM and $CHCl_3$ were distilled *via* usual procedure prior to use. All other materials Et_3N, $SOCl_2$, $K_2Cr_2O_7$, H_2SO_4, Tosyl chloride, NaI, Tetra-n-butylammonium fluoride (TBAF), NaOH were also obtained from Sigma - Aldrich. Reactions were carried out under nitrogen atmosphere and workup procedure were done at ambient conditions. In each case, column chromatography was performed by using 60-120 mesh silica gel which was purchased from Merck private limited. ^1H, ^{13}C NMR spectroscopy experiments were carried out on a FT-NMR Bruker DPX 300/400/500 MHz NMR spectrometer and the residual protons of each deuterated solvents were granted as the internal standards where the coupling constants were calculated in hertz (Hz) and chemical shifts in ppm. Electrospray ionization mass spectrometry (ESI-MS) analysis was performed with a Waters QtoF Model YA 263 spectrometer in positive ion ESI mode. Fourier transform infrared (FT-IR) spectra were recorded on a SHIMADZU FTIR-8400S IR spectrophotometer with KBr pellets. The absorption spectra were recorded in a Perkin-Elmer Lambda 900 UV/Vis/NIR spectrometer (NIR = near-infrared) (with a quartz cuvette of path length 1 cm). EPR experiment was carried out by using a JEOL JES-FA200 spectrometer with an X band micro web unit. The elemental analyses was carried out using a Perkin-Elmer 2400 Series-II CHN analyser. Crystals were solved by using a Bruker SMART APEX diffractometer, equipped with a CCD area detector at

150 K. The bis (amide) tris (amine) macrocycle (**MC**),[19a] BPy4COOH,[22a] BPy4COCl,[23] Axle2,[22b] AllI,[24] PropI,[25] Axle7[22c] and 2-aminoethyl azide[17c] were prepared by using the known procedure reported in literature. All the characterization data of the known compounds properly matched with the reported characterization details.

Synthesis of the compounds:

4, 4'-Dimethyl-2, 2'-Bipyridine was first oxidized to di-acid (BPy4COOH) by using $K_2Cr_2O_7$ in concentrated sulphuric acid (H_2SO_4) at 80˚C, which was utilised to synthesise **Axle2**, **Axle5** and **Axle6.** Afterwards, the reaction of di-acid with thionyl chloride ($SOCl_2$) affords corresponding di-acid chloride (BPy4COCl). Now the reactions of BPy4COCl with suitable respective chemical precursors produce **Axle3**, **Axle4**, **Axle7 - Axle10.**

(a) Synthesis of Axle3, Axle4, Axle7 - Axle10: BPy4COCl (1 mmol) in dry THF was added dropwise to the stirring solution of dry Et_3N (2.2 mmol) and respective chemical compounds (2.2 mmol) like 2-bromoethanol, propargyl alcohol, n-propyl amine, 3-amino-1-propanol, 2-aminoethyl azide or benzyl amine in dry THF. The solution mixture was allowed to stir at room temperature in ice cold condition for 24h under N_2 atmosphere, followed by removal of solvent in *vaccuo*. The reaction mixture was then stirred with saturated $NaHCO_3$ solution (25 ml) for 6h and appearing precipitate was collected by filtration. Finally after drying the precipitate solid **Axle3**, **Axle4**, **Axle7** – **Axle10** were obtained in moderate yields. Detail experimental procedures and characterization spectra are given in supporting information.

(b) Synthesis of Axle5, **Axle6:** To the stirring solution of BPy4COOH (1 mmol) and TBAF (3 mmol) in dry THF (20 ml), AllI or PropI (2.2 mmol) was added dropwise by dissolving it in the same solvent (25 ml). The mixture was allowed to reflux under N_2 atmosphere at 70˚C for 48h followed by removal of solvent in *vaccuo*. The reaction mixture was extracted 3 times with

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$CHCl_3$ from the aqueous layer (50 x 3). Organic extracts were combined and washed several times by using saturated $NaHCO_3$ solution (200ml) and brine solution (200 ml), dried over Na_2SO_4 and concentrated under reduced pressure. Final purification was done by silica gel column chromatography using petroleum ether/ ethylacetate as eluent to afford solid **Axle5** and **Axle6**. Detail experimental procedures and characterization spectra are given in supporting information.

Characterization Data

Axle3: M.P: 144°C-146°C. HRMS (ESI-MS): *m/z* calculated for $C_{16}H_{15}Br_2N_2O_4$ $[M + H]^+$ 458.9300, found 458.9372. IR (KBr, υ cm^{-1}): 470, 567, 690, 723, 763, 815, 860, 918, 945, 987, 1064, 1124, 1230, 1257, 1280, 1365, 1384, 1440, 1554, 1595, 1724 (ester C=0), 2854, 2923, 3028, 3072. ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 3.69 (t, 4H, J = 8 Hz, $-CH_2$), 4.71 (t, 4H, J = 8 Hz, $-CH_2$), 7.93-7.94 (m, 2H, Ar-H), 8.89 (d, 2H, J = 4 Hz, Ar-H), 8.98 (s, 2H, Ar-H). ^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) 28.3, 65.1, 120.8, 123.5, 138.3, 150.3, 156.7, 164.8. Yield: 71%.

Axle4: M.P: 140°C. HRMS (ESI- MS): *m/z* calculated for $C_{18}H_{13}N_2O_4$ $[M + H]^+$ 321.0797, found 321.0869. IR (KBr, υ cm^{-1}): 663, 690, 759, 860, 962, 999, 1064, 1095, 1124, 1164, 1247, 1286, 1369, 1442, 1460, 1554, 1591, 1662, 1720 (ester C=0), 1743, 2129 (C≡C), 2732, 2854, 2923, 3004, 3095, 3253, 3284 (H-C≡). ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.56 (t, 2H, J = 4 Hz, -CH), 5.00 (d, 4H, J = 2.4 Hz, $-CH_2$), 7.93-7.95 (m, 2H, Ar-H), 8.88 (d, 2H, J = 4 Hz, Ar-H), 8.99 (s, 2H, Ar-H). ^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) 29.8, 53.3, 75.8, 120.9, 123.5, 138.1, 150.4, 156.7, 164.6. Yield: 80%

Axle5: M.P: 55°C. HRMS (ESI-MS): *m/z* calculated for $C_{34}H_{49}N_2O_4$ $[M + H]^+$ 549.3614, found 549.3688. IR (KBr, υ cm^{-1}): 410, 667, 692, 725, 761, 862, 908, 952, 995, 1064, 1134, 1251,

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1288, 1365, 1396, 1471, 1556, 1593, 1639 (C=C), 1724 (ester C=0), 2852, 2923, 2966, 3072. ^{1}H NMR (400 MHz, $CDCl_3$): δ (ppm) 1.30-1.47 (m, 24H, $-CH_2$), 1.78-1.83 (m, 4H, $-CH_2$), 1.99-2.06 (m, 4H, $-CH_2$), 4.39 (t, 4H, J = 10 Hz, $-CH_2$), 4.89-5.02 (m, 4H, $-CH_2$), 5.73-5.85 (m, 2H, -CH), 7.89-7.91 (m, 2H, Ar-H), 8.85 (d, 2H, J = 8Hz, Ar-H), 8.94 (s, 2H, Ar-H). ^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) 26.1, 28.8 - 29.6, 33.9, 66.2, 114.3, 120.7, 123.3, 139.2, 139.3, 150.2, 156.8, 165.4. Yield: 80%

Axle6: M.P: 85°C. HRMS (ESI)): *m/z* calculated for $C_{34}H_{45}N_2O_4$ $[M + H]^+$ 545.3301, found 545.3372. IR (KBr, υ cm^{-1}): 364, 534, 644, 667, 692, 723, 767, 875, 954, 1004, 1062, 1103, 1134, 1255, 1284, 1367, 1394, 1475, 1558, 1593, 1726 (ester C=0), 2109 (C≡C), 2854, 2923, 2962, 3083, 3286 (H-C≡). ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm) 1.25-1.35(m, 24H, $-CH_2$), 1.79-1.84 (m, 4H, $-CH_2$), 1.93 (s, 2H, -CH), 2.15-2.19 (m, 4H, $-CH_2$), 4.39 (t, 4H, J = 10Hz, $-CH_2$), 7.89-7.91 (m, 2H, Ar-H), 8.86 (d, 2H, J = 10Hz, Ar-H), 8.94 (s, 2H, Ar-H). ^{13}C NMR (400 MHz, $CDCl_3$): δ (ppm) 18.5, 26.1, 28.6 - 29.5, 66.2, 68.2, 84.9, 120.7, 123.3, 139.2, 150.2, 156.7, 165.4. Yield: 73%

Axle8: M.P: 250°C. HRMS (ESI-MS): *m/z* calculated for $C_{18}H_{22}N_4NaO_4$ $[M + Na]^+$ 381.1539 found 381.1538. IR (KBr, υ cm^{-1}): 663, 692, 858, 894, 925, 995, 1072, 1099, 1332, 1352, 1407, 1446, 1467, 1537, 1591, 1637 (amide C=O), 1741, 2854, 2923, 3087, 3282 (N-H), 3577 (O-H). ^{1}H NMR (400 MHz, DMSO-d_6): δ (ppm) 3.44- 3.51 (m, 8H, $-CH_2$), 3.57 (t, 4H, J = 6 Hz, $-CH_2$), 4.59 (t, 2H, J = 6 Hz, -OH), 7.84-7.85 (m, 2H, -Ar-H), 8.78 (s, 2H, Ar-H), 8.85 (d, 2H, J = 4 Hz, Ar-H), 8.99 (t, 2H, J = 6 Hz, -NH). ^{13}C NMR (400 MHz, DMSO-d_6): δ (ppm) 60.2, 68.6, 72.1, 118.2, 121.8, 142.8, 150.0, 155.5, 164. 7. Yield: 68%

Axle9: M.P: 220-222°C. HRMS (ESI-MS): *m/z* calculated for $C_{16}H_{16}N_{10}NaO_2$ $[M + Na]^+$ 403.1355 found 403.1354. IR (KBr, υ cm^{-1}): 493, 553, 665, 713, 738, 860, 898, 989, 1095, 1217,

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1253, 1298, 1321, 1352, 1444, 1539, 1591, 1645 (amide C=O), 1728, 2100 (azide), 2854, 2929, 3066, 3272 (N-H). ^{1}H NMR (400 MHz, DMSO-d$_6$): δ (ppm) 3.53 (s, 8H, -CH$_2$), 7.87 (d, 2H, J = 2Hz, -Ar-H), 8.82 (s, 2H, Ar-H), 8.90 (d, 2H, J = 2Hz, Ar–H), 9.20 (s, 2H, -NH). ^{13}C NMR (400 MHz, DMSO-d$_6$): δ (ppm) 49.5, 118.1, 121.9, 142.6, 150.1, 155.5, 164.9. Yield: 60%

Axle10: M.P: 290°C. HRMS (ESI-MS): *m/z* calculated for $C_{26}H_{23}N_4O_2$ $[M + H]^+$ 423.1743 found 423.1816. IR (KBr, υ cm^{-1}): 480, 694, 742, 862, 892, 1074, 1238, 1317, 1361, 1452, 1535, 1591, 1639 (amide C=O), 1747, 2854, 2923, 3031, 3087, 3278 (N-H), 3413. ^{1}H NMR (400 MHz, DMSO-d$_6$): δ (ppm) 4.53 (d, 4H, J = 8 Hz, -CH$_2$), 7.27 (s, 2H, Ar-H), 7.36 (d, 8H, J = 4 Hz, Ar-H), 7.90 (d, 2H, J = 4Hz, Ar-H), 8.88 (t, 4H, J = 8Hz, Ar-H), 9.53 (t, 2H, J = 4Hz, -NH). ^{13}C NMR (400 MHz, DMSO-d$_6$): δ (ppm) 42.8, 118.2, 121.9, 126.9, 127.3, 128.3, 139.1, 142.7, 150.1, 155.5, 164.6. Yield: 80%.

Synthesis of Ni^{II} templated PR1 - PR10 complexes

To the stirring solution of **MC** (0.1 mmol) in DCM-MeOH (1:1, 5ml), the solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.1 mmol) in MeOH (5 ml) was added at room temperature and allowed to stir for 6h. To the reaction mixture, each of the axles (0.1 mmol) (**Axle1** - **Axle10**) was added separately at room temperature and stirred for 24h, followed by removal of solvent at *vaccuo*. Appearing precipitate was washed several times with DCM and finally after drying, pure product was obtained as yellowish coloured solid in high yields. Ni^{II} templated [2]pseudorotaxanes complexes were abbreviated as **PR1** [{**MC**.Ni^{II}(ClO$_4$)$_2$} @ **Axle1**], **PR2** [{**MC**.Ni^{II}(ClO$_4$)$_2$} @ **Axle2**], **PR3** [{**MC**.Ni^{II}(ClO$_4$)$_2$} @ **Axle3**], **PR4** [{**MC**.Ni^{II}(ClO$_4$)$_2$} @ **Axle4**], **PR5** [{**MC**.Ni^{II}(ClO$_4$)$_2$} @ **Axle5**], **PR6** [{**MC**.Ni^{II}(ClO$_4$)$_2$} @ **Axle6**], **PR7** [{**MC**.Ni^{II}(ClO$_4$)$_2$} @ **Axle7**], **PR8** [{**MC**.Ni^{II}(ClO$_4$)$_2$} @ **Axle8**], **PR9** [{**MC**.Ni^{II}(ClO$_4$)$_2$} @ **Axle9**], **PR10**

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[{**MC**.Ni^{II}(ClO$_4$)$_2$} @ **Axle10**]. All the complexes were well characterized by ESI-MS, IR and UV-Vis absorption titration studies.

(i) Synthesis and characterization of **PR1**: **MC**= 53 mg (0.1mmol); $Ni(ClO_4)_2{\cdot}6H_2O$ = 36 mg (0.1mmol); **Axle1**= 18 mg (0.1mmol). Yield: 77 mg (80%). Molar extinction coefficient value in CH_3CN (ε) = 9.29 x 10^3 M^{-1} cm^{-1}, λ_{max} = 304 nm. HRMS (ESI-MS): *m/z* calculated for $C_{42}H_{49}ClN_7NiO_8$ $[M]^+$ 872.2685, found 872.2683. IR (KBr, υ cm^{-1}): 393, 511, 561, 626, 676, 705, 740, 827, 1024, 1085, 1116, 1139, 1244, 1294, 1355, 1444, 1512, 1541, 1618, 1662, 2854, 2925, 3282, 3409. $C_{42}H_{49}Cl_2N_7NiO_{12}$: calcd. C, 51.82; H, 5.07; N, 10.07; found C 51.97, H 5.10, N 10.01. M.P: 179°C-180°C.

(ii) Characterization of **PR2**: **MC**= 53 mg (0.1mmol); $Ni(ClO_4)_2{\cdot}6H_2O$ = 36 mg (0.1mmol); **Axle2**= 30 mg (0.1mmol). Yield: 76 mg (70%). Molar extinction coefficient value in CH_3CN (ε) = 1.29 x 10^4 M^{-1} cm^{-1}, λ_{max} = 323 nm. HRMS (ESI-MS): *m/z* calculated for $C_{46}H_{53}ClN_7NiO_{12}$ $[M]^+$ 988.2794, found 988.2792. IR (KBr, υ cm^{-1}): 628, 651, 673, 717, 827, 1022, 1085, 1116, 1255, 1406, 1444, 1469, 1602, 1666, 1728, 2854, 2923, 3055, 3407. $C_{46}H_{53}Cl_2N_7NiO_{16}$: calcd. C, 50.71; H, 4.90; N, 9.00; found C 50.68, H 4.84, N 9.05. M.P: 194°C-196°C.

(iii) Characterization of **PR3**: **MC** = 53 mg (0.1mmol); $Ni(ClO_4)_2{\cdot}6H_2O$ = 36 mg (0.1mmol); **Axle3** = 30 mg (0.1mmol). Yield: 90 mg (73%). Molar extinction coefficient value in CH_3CN (ε) = 1.21 x 10^4 M^{-1} cm^{-1}, λ_{max} = 323 nm. HRMS (ESI-MS): *m/z* calculated for $C_{46}H_{53}Br_2ClN_7NiO_{12}$ $[M+2H]^+$ 1148.0984, found 1148.0964. IR (KBr, υ cm^{-1}): 368, 433, 514, 628, 673, 759, 853, 1085, 1116, 1253, 1323, 1404, 1442, 1512, 1604, 1664, 1730, 2952, 3269, 3384, 3454, 3533. $C_{46}H_{51}Br_2Cl_2N_7NiO_{16}$: calcd. C, 44.29; H, 4.12; N, 7.86; found C 44.42, H 4.14, N 7.81. M.P: 188°C-190°C.

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(iv) Characterization of **PR4**: **MC** = 53 mg (0.1mmol); $Ni(ClO_4)_2{\cdot}6H_2O$ = 36 mg (0.1mmol); **Axle4** = 32 mg (0.1mmol). Yield: 91 mg (83%). Molar extinction coefficient value in CH_3CN (ε) = 9.97 x 10^3 M^{-1} cm^{-1}, λ_{max} = 324 nm. HRMS (ESI-MS): *m/z* calculated for $C_{48}H_{49}ClN_7NiO_{12}$ $[M]^+$ 1008.2481, found 1008.2483. IR (KBr, υ cm^{-1}): 590, 622, 673, 756, 831, 1024, 1085, 1097, 1114, 1247, 1313, 1404, 1440, 1514, 1556, 1616, 1666, 1737, 2125, 2862, 2931, 3284, 3413. $C_{48}H_{49}Cl_2N_7NiO_{16}$: calcd. C, 51.96; H, 4.45; N, 8.84; found C 52.09, H 4.49, N 8.90. M.P: 183°C -186°C.

(v) Characterization of **PR5**: **MC** = 53 mg (0.1mmol); $Ni(ClO_4)_2{\cdot}6H_2O$ = 36 mg (0.1mmol); **Axle5** = 55 mg (0.1mmol). Yield: 113 mg (85%). Molar extinction coefficient value in CH_3CN (ε) = 1.50 x 10^4 M^{-1} cm^{-1}, λ_{max} = 323 nm. HRMS (ESI-MS): *m/z* calculated for $C_{64}H_{85}ClN_7NiO_{12}$ $[M]^+$ 1236.5298, found 1236.5052. IR (KBr, υ cm^{-1}): 516, 624, 671, 698, 763, 825, 908, 952, 993, 1085, 1116, 1182, 1251, 1319, 1400,1444, 1514, 1544, 1610, 1666, 1730, 2852, 2923, 3076, 3282, 3384. $C_{64}H_{85}Cl_2N_7NiO_{16}$ (1335.48): calcd. C, 57.45; H, 6.40; N, 7.33; found C 57.64, H 6.46, N 7.29. M.P: 99°C-101°C.

(vi) Characterization of **PR6**: **MC** = 53 mg (0.1mmol); $Ni(ClO_4)_2{\cdot}6H_2O$ = 36 mg (0.1mmol); **Axle6** = 54 mg (0.1mmol). Yield: 111 mg (84%). Molar extinction coefficient value in CH_3CN (ε) = 1.29 x 10^4 M^{-1} cm^{-1}, λ_{max} = 323 nm. HRMS (ESI-MS): *m/z* calculated for $C_{64}H_{80}ClN_7NiO_{12}$ $[M\text{-}H]^+$ 1231.4985, found 1231.4203. IR (KBr, υ cm^{-1}): 379, 518, 624, 669, 765, 835, 960, 1085, 1116, 1180, 1253, 1321, 1400, 1444, 1461, 1514, 1544, 1610, 1666, 1731, 2854, 2923, 3031, 3284, 3359. Despite several attempts unsatisfactory elemental analysis result has been obtained. M.P: 96°C-98°C.

(vii) Characterization of **PR7**: **MC** = 53 mg (0.1mmol); $Ni(ClO_4)_2{\cdot}6H_2O$ = 36 mg (0.1mmol); **Axle7** = 33 mg (0.1mmol). Yield: 83 mg (72%). Molar extinction coefficient value in CH_3CN (ε)

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= 1.17 x 10^4 M^{-1} cm^{-1}, λ_{max} = 323 nm. HRMS (ESI-MS): *m/z* calculated for $C_{48}H_{58}ClN_9NiO_{10}$ [M-H]$^+$ 1013.3427, found 1013.3295. IR (KBr, υ cm^{-1}): 435, 624, 675, 754, 823, 1085, 1114, 1244, 1402, 1440, 1488, 1558, 1593, 1664, 2854, 2952, 3082, 3290, 3377. $C_{48}H_{59}Cl_2N_9NiO_{14}$: calcd. C, 51.68; H, 5.33; N, 11.30; found C 51.73, H 5.29, N 11.28. M.P: 198°C-200°C.

(viii) Characterization of **PR8**: **MC** = 53 mg (0.1mmol); $Ni(ClO_4)_2 \cdot 6H_2O$ = 36 mg (0.1mmol); **Axle8** = 36 mg (0.1mmol). Yield: 79 mg (70%). Molar extinction coefficient value in CH_3CN (ε) = 1.12 x 10^4 M^{-1} cm^{-1}, λ_{max} = 320 nm. HRMS (ESI-MS): *m/z* calculated for $C_{48}H_{60}ClN_9NiO_{12}$ [M+H]$^+$ 1047.3325, found 1047.3396. IR (KBr, υ cm^{-1}): 391, 590, 630, 651, 671, 756, 827, 950, 1026, 1083, 1118, 1145, 1238, 1313, 1398, 1442, 1514, 1546, 1654, 1745, 2856, 2925, 3080, 3286, 3421. Despite several attempts unsatisfactory elemental analysis result has been obtained. M.P: 204°C-206°C

(ix) Characterization of **PR9**: **MC** = 53 mg (0.1mmol); $Ni(ClO_4)_2 \cdot 6H_2O$ = 36 mg (0.1mmol); **Axle9** = 38 mg (0.1mmol). Yield: 94 mg (81%). Molar extinction coefficient value in CH_3CN (ε) = 1.19 x 10^4 M^{-1} cm^{-1}, λ_{max}= 319 nm. HRMS (ESI-MS): *m/z* calculated for $C_{46}H_{54}ClN_{15}NiO_{10}$ [M+H]$^+$ 1069.3142, found 1069.3215. IR (KBr, υ cm^{-1}): 443, 514, 626, 694, 757, 829, 960, 1085, 1114, 1180, 1247, 1276, 1303, 1398, 1442, 1514, 1546, 1614, 1660, 2104, 2852, 2923, 3080, 3280, 3352. $C_{46}H_{53}Cl_2N_{15}NiO_{14}$: calcd. C, 47.24; H, 4.57; N, 17.96; found C 47.35, H 4.53, N 17.99. M.P: 213°C-215°C.

(x) Characterization of **PR10**: **MC** = 53 mg (0.1mmol); $Ni(ClO_4)_2 \cdot 6H_2O$ = 36 mg (0.1mmol); **Axle10** = 42 mg (0.1mmol). Yield: 91 mg (76%). Molar extinction coefficient value in CH_3CN (ε) = 1.29 x 10^4 M^{-1} cm^{-1}, λ_{max} = 321 nm. HRMS (ESI-MS): *m/z* calculated for $C_{56}H_{59}ClN_9NiO_{10}$ [M]$^+$ 1110.3427, found 1110.3428. IR (KBr, υ cm^{-1}): 626, 673, 694, 738, 825, 1027, 1085, 1114, 1242, 1286, 1355, 1402, 1442, 1544, 1606, 1621, 2856, 2927, 3093, 3290,

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3352, 3407. $C_{56}H_{59}Cl_2N_9NiO_{14}$ (1209.26): calcd. C, 55.51; H, 4.91; N, 10.40; found C 55.43, H 4.89, N 10.35. M.P: 218°C-220°C.

Synthesis of Cu^{II} templated PR1' - PR10' complexes

To the stirring solution of **MC** (0.1 mmol) in DCM - MeOH (1:1, 5ml), the solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.1 mmol) in MeOH (5 ml) was added at room temperature and allowed to stir for 6h. To the reaction mixture, each of the axles (0.1 mmol) (**Axle1** - **Axle10**) was added seperately at room temperature and stirred for 24h, followed by removal of solvent at *vaccuo*. Appearing precipitate was washed several times with DCM and finally after drying, pure solid product was obtained as blue coloured solid in high yields (90%). Cu^{II} templated [2]pseudorotaxanes complexes were abbreviated as **PR1'** [{MC.$Cu^{II}(ClO_4)_2$} @ **Axle1**], **PR2'** [{MC.$Cu^{II}(ClO_4)_2$} @ **Axle2**], **PR3'** [{MC.$Cu^{II}(ClO_4)_2$} @ **Axle3**], **PR4'** [{MC.$Cu^{II}(ClO_4)_2$}@ **Axle4**], **PR5'** [{MC.$Cu^{II}(ClO_4)_2$} @ **Axle5**], **PR6'** [{MC.$Cu^{II}(ClO_4)_2$} @ **Axle6**], **PR7'** [{MC.$Cu^{II}(ClO_4)_2$} @ **Axle7**], **PR8'** [{MC.$Cu^{II}(ClO_4)_2$} @ **Axle8**], **PR9'** [{MC.$Cu^{II}(ClO_4)_2$} @ **Axle9**], **PR10'** [{MC.$Cu^{II}(ClO_4)_2$} @ **Axle10**]. All the complexes were well characterized by ESI- MS, EPR and absorption spectra studies.

(i) Characterization of **PR1'**: **MC**= 53 mg (0.1mmol); $Cu(ClO_4)_2 \cdot 6H_2O$ = 37 mg (0.1mmol); **Axle1**= 18 mg (0.1mmol). Yield: 78 mg (81%). Molar extinction coefficient value in CH_3CN (ε) = 2.24 x 10^2 M^{-1} cm^{-1}, λ_{max} = 668 nm. HRMS (ESI-MS): *m/z* calculated for $C_{42}H_{49}ClCuN_7O_8$ $[M]^+$ 877.2627, found 877.2624. IR (KBr, υ cm^{-1}): 514, 628, 673, 744, 831, 1085, 1116, 1247, 1298, 1361, 1444, 1512, 1544, 1614, 1664, 2856, 2952, 3080, 3259, 3407. $C_{42}H_{49}Cl_2CuN_7O_{12}$: calcd. C, 51.56; H, 5.05; N, 10.02; found C 51.64, H 5.03, N 10.09. M.P: 205°C-207°C.

(ii) Characterization of **PR2'**: **MC**= 53 mg (0.1mmol); $Cu(ClO_4)_2 \cdot 6H_2O$ = 37 mg (0.1mmol); **Axle2**= 30 mg (0.1mmol). Yield: 78 mg (75%). Molar extinction coefficient value in CH_3CN (ε)

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= 3.14 x 10^2 M^{-1} cm^{-1}, λ_{max} = 629 nm. HRMS (ESI-MS): *m/z* calculated for $C_{46}H_{53}ClCuN_7O_{12}$ $[M]^+$ 993.2737, found 993.2739. IR (KBr, ʋ cm^{-1}): 514, 626, 651, 673, 717, 761, 833, 1018, 1087, 1114, 1253, 1290, 1369, 1400, 1442, 1514, 1552, 1608, 1664, 1728, 2927, 2958, 3269, 3392, 3409, 3595. $C_{46}H_{53}Cl_2CuN_7O_{16}$ (1092.22): calcd. C, 50.48; H, 4.88; N, 8.96; found C 50.60, H 4.95, 9.03. M.P: 169°C -170°C.

(iii) Characterization of **PR3'**: **MC** = 53 mg (0.1mmol); $Cu(ClO_4)_2{\cdot}6H_2O$ = 37 mg (0.1mmol); **Axle3** = 30 mg (0.1mmol). Yield: 93 mg (75%). Molar extinction coefficient value in CH_3CN (ε) = 3.57 x 10^2 M^{-1} cm^{-1}, λ_{max} = 631 nm. HRMS (ESI-MS): *m/z* calculated for $C_{46}H_{51}Br_2ClCuN_7O_{12}$ $[M]^+$ 1151.0927, found 1151.0839. IR (KBr, ʋ cm^{-1}): 439, 626, 759, 831, 1083, 1114, 1251, 1438, 1598, 1666, 1731, 2853, 2927, 3406, 3463. $C_{46}H_{51}Br_2Cl_2CuN_7O_{16}$: calcd. C, 44.12; H, 4.11; N, 7.83; found C 44.01, H 4.08, N 7.87. M.P: 174°C-176°C.

(iv) Characterization of **PR4'**: **MC** = 53 mg (0.1mmol); $Cu(ClO_4)_2{\cdot}6H_2O$ = 37 mg (0.1mmol); **Axle4** = 32 mg (0.1mmol). Yield: 91 mg (83%). Molar extinction coefficient value in CH_3CN (ε) = 3.14 x 10^2 M^{-1} cm^{-1}, λ_{max} = 631 nm. HRMS (ESI-MS): *m/z* calculated for $C_{48}H_{49}ClCuN_7O_{12}$ $[M]^+$ 1013.2424, found 1013.2422. IR (KBr, ʋ cm^{-1}): 372, 522, 576, 622, 651, 673, 761, 831, 929, 983, 1089, 1251, 1315, 1373, 1406, 1440, 1514, 1548, 1612, 1662, 1739, 2146, 2854, 2923, 3265, 3398. $C_{48}H_{49}Cl_2CuN_7O_{16}$: calcd. C, 51.73; H, 4.43; N, 8.80; found C 51.86, H 4.39, N 8.75. M.P: 210°C-212°C

(v) Characterization of **PR5'**: **MC** = 53 mg (0.1mmol); $Cu(ClO_4)_2{\cdot}6H_2O$ = 37 mg (0.1mmol); **Axle5** = 55 mg (0.1mmol). Yield: 109 mg (82%). Molar extinction coefficient value in CH_3CN (ε) = 3.69 x 10^2 M^{-1} cm^{-1}, λ_{max} = 635 nm. HRMS (ESI-MS): *m/z* calculated for $C_{64}H_{86}ClCuN_7O_{12}$ $[M+H]^+$ 1242.5241, found 1242.3867. IR (KBr, ʋ cm^{-1}): 630, 700, 761, 865, 910, 954, 995, 1089, 1128, 1186, 1253, 1296, 1357, 1396, 1467, 1514, 1554, 1593, 1612, 1647, 1668, 1718, 2852, 2921, 3076, 3444. $C_{64}H_{85}Cl_2CuN_7O_{16}$: calcd. C, 57.24; H, 6.38; N, 7.30; found C 57.32, H 6.42, N 7.32. M.P: 94°C-96°C.

(vi) Characterization of **PR6'**: **MC** = 53 mg (0.1mmol); $Cu(ClO_4)_2{\cdot}6H_2O$ = 37 mg (0.1mmol); **Axle6** = 54 mg (0.1mmol). Yield: 106 mg (80%). Molar extinction coefficient value in CH_3CN (ε) = 3.31 x 10^2 M^{-1} cm^{-1}, λ_{max} = 629 nm. HRMS (ESI-MS): *m/z* calculated for $C_{64}H_{81}ClCuN_7O_{12}$ $[M]^+$ 1237.4928, found 1237.4926. IR (KBr, υ cm^{-1}): 622, 669, 696, 721, 763, 860, 954, 1087, 1118, 1137, 1182, 1245, 1259, 1294, 1359, 1402, 1446, 1463, 1514, 1548, 1596, 1662, 1728, 2852, 2923, 3228. $C_{64}H_{81}Cl_2CuN_7O_{16}$: calcd. C, 57.42; H, 6.10; N, 7.32; found C 57.34, H 6.13, N 7.37. M.P: 98°C-100°C.

(vii) Characterization of **PR7'**: **MC** = 53 mg (0.1mmol); $Cu(ClO_4)_2{\cdot}6H_2O$ = 37 mg (0.1mmol); **Axle7** = 33 mg (0.1mmol). Yield: 80 mg (72%). Molar extinction coefficient value in CH_3CN (ε) = 3.53 x 10^2 M^{-1} cm^{-1}, λ_{max} = 641 nm. HRMS (ESI-MS): *m/z* calculated for $C_{48}H_{58}ClCuN_9O_{10}$ $[M\text{-}H]^+$ 1018.3369, found 1018.3293. IR (KBr, υ cm^{-1}): 437, 532, 557, 580, 609, 665, 1081, 1245, 1296, 1409, 1440, 1481, 1595, 1664, 1724, 1812, 2852, 2952, 3346, 3465. Despite several attempts unsatisfactory elemental analysis result has been obtained. M.P: 164°C-166°C.

(viii) Characterization of **PR8'**: **MC** = 53 mg (0.1mmol); $Cu(ClO_4)_2{\cdot}6H_2O$ = 37 mg (0.1mmol); **Axle8** = 36 mg (0.1mmol). Yield: 87 mg (76%). Molar extinction coefficient value in CH_3CN (ε) = 3.75 x 10^2 M^{-1} cm^{-1}, λ_{max} = 645 nm. HRMS (ESI-MS): *m/z* calculated for $C_{48}H_{58}ClCuN_9O_{12}$ $[M\text{-}H]^+$ 1050.3268, found 1050.3191. IR (KBr, υ cm^{-1}): 395, 426, 466, 516, 572, 595, 626, 648, 675, 752, 825, 1083, 1114, 1244, 1284, 1309, 1402, 1442, 1514, 1546, 1614, 1660, 1741, 2854, 2923, 3085, 3407, 3583, 3624. $C_{48}H_{59}Cl_2CuN_9O_{16}$: calcd. C, 50.02; H, 5.16; N, 10.94; found C 49.97, H 5.10, N 10.90. M.P: 170°C-172°C

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(ix) Characterization of **PR9'**: **MC** = 53 mg (0.1mmol); $Cu(ClO_4)_2{\cdot}6H_2O$ = 37 mg (0.1mmol); **Axle9** = 38 mg (0.1mmol). Yield: 98 mg (84%). Molar extinction coefficient value in CH_3CN (ε) = 3.50 x 10^2 M^{-1} cm^{-1}, λ_{max}= 643 nm. HRMS (ESI-MS): *m/z* calculated for $C_{46}H_{52}ClCuN_{15}O_{10}$ $[M\text{-}H]^+$ 1072.3084, found 1072.3004. IR (KBr, υ cm^{-1}): 403, 524, 624, 648, 673, 696, 748, 823, 1020, 1078, 1116, 1245, 1294, 1400, 1444, 1514, 1546, 1664, 1745, 2102, 2852, 2921, 2076, 3257, 3367. $C_{46}H_{53}Cl_2CuN_{15}O_{14}$: calcd. C, 47.04; H, 4.55; N, 17.89; found C 47.16, H 4.61, N 17.81. M.P: 175°C-177°C.

(x) Characterization of PR10': **MC** = 53 mg (0.1mmol); $Cu(ClO_4)_2{\cdot}6H_2O$ = 37 mg (0.1mmol); **Axle10** = 42 mg (0.1mmol). Yield: 96 mg (80%). Molar extinction coefficient value in CH_3CN (ε) = 3.32 x 10^2 M^{-1} cm^{-1}, λ_{max} = 648 nm. HRMS (ESI-MS): *m/z* calculated for $C_{56}H_{59}ClCuN_9O_{10}$ $[M]^+$ 1115.3369, found 1115.3202. IR (KBr, υ cm^{-1}): 621, 667, 694, 744, 823, 1085, 1114, 1244, 1309, 1359, 1406, 1444, 1514, 1546, 1604, 1660, 2854, 2952, 3082, 3269, 3350. $C_{56}H_{59}Cl_2CuN_9O_{14}$: calcd. C, 55.29; H, 4.89; N, 10.36; found C 55.35, H 4.86, N 10.32. M.P: 189°C-191°C.

Calculation of Association Constant (K_a)

Upon addition of the **MC**-Ni^{II} complex solution (guest) into the bidentate axle solution (host), absorption spectra changes gradually due to the binding of bidentate axle with the metallo-macrocycle complexes. The association constant (K_a) values of these bindings were determined by nonlinear fitting of the curves obtained by plotting the absorbance changes (ΔA) at a fixed λ value (where the absorption changes were maximal i.e λ_{max} value) against the guest concentration. All the absorption titration data were fitted to the following equation (1) for 1:1 binding:

$$\Delta A = A\cdot\ \{([H] + [X^-] + (1/K_a)) - \{([H] + [X^-] + (1/K_a))^2 - (4\cdot[H]\cdot[X^-])\}^{1/2}\} / (2\cdot[H])\ldots\ldots\ (1)$$

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A = absorbance value upon each addition of the guest, $\Delta A = (A-A_0)$, [H] = concentration of host and $[X^-]$ = concentration of guest.

X-ray Crystallographic Refinement Details

The crystallographic details of **PR1'**, **PR3'**, **PR7'** and the refinement parameters are given in **Table S1**. Crystal structures suitable for single crystal X-Ray diffraction studies were collected from either CH_3CN or DMF-CH_3CN mixture. The crystals were chosen from the mother liquor among the multiple sets of data collection, dipped in paratone oil and cemented on the tip of a glass fiber using epoxy resin. Intensity data for the complexes (PR1', PR3' and PR7') were collected using graphite-monochromatized Mo Kα radiation (0.71073 Å) at 150 K equipped with a CCD area detector at 150 K. Crystal data integration and reduction were processed on a Bruker SMART APEX II CCD diffractometer using the SAINT software[28] provided with the SMART APEX II software package. The structures were solved by using the direct method of SHELXS-97[29] and the refinements are carried out on F_2 by the full-matrix least-squares technique using the SHELXL-2014 programme package.[30] Empirical absorption corrections were applied with SADABS.[31] PLATON[32] and MERCURY 3.7[33] were used to generate graphics. For all the three complexes all non-hydrogen atoms were refined with anisotropic displacement coefficients and all hydrogen atoms were geometrically fixed at idealized positions. CCDC no. of the crystal structures (1534186- 1534188) contains the supplementary crystallographic data for this paper.

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Graphical Abstract

Ni^{II}/ Cu^{II} templated threading of various terminal groups embedded ‘U’ shaped axles into an amido amine macrocyclic wheel towards the development of new generation of [2]pseudorotaxanes *via* [3+2] coordination assisted by other non-covalent interactions.