## Fluorophoric [2]Rotaxanes: Post-Synthetic

## Functionalization, Conformational Fluxionality and Metal

## **Ion Chelation**

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Chart 1S. Chemical diagram of the previously reported [2] rotaxane





*Figure 2S.* <sup>1</sup>*H-NMR spectrum of II in CDCl*<sub>3</sub> *at 400 MHz (298K)* 



Figure 3S. <sup>13</sup>C-NMR spectrum of **II** in CDCl<sub>3</sub> at 100 MHz (298K)



Figure 4S. ESI-MS (+ve mode) of MC



Figure 5S. FTIR spectrum of MC



Figure 6S. <sup>1</sup>H-NMR spectrum of MC in CDCl<sub>3</sub> at 300 MHz (298K)





Figure 8S. MALDI-TOF MS of MCa



Figure 9S. FTIR spectra of MCa



Figure 10S. <sup>1</sup>H-NMR of MCa in CDCl<sub>3</sub> (300 MHz, 298 K)



Figure 11S. <sup>1</sup>H-NMR of MCa in DMSO-d<sub>6</sub> (300 MHz, 298 K)





Figure 13S. ESI-MS (+ve mode) of MCb



Figure 14S. FTIR spectrum of MCb



Figure 15S. <sup>1</sup>H-NMR of MCb in CDCl<sub>3</sub> (300 MHz, 298 K)



Figure 16S. <sup>1</sup>H-NMR of MCb in DMSO-d<sub>6</sub> (300 MHz, 298K)





Figure 18S. ESI-MS (+ve mode) of MCc



Figure 19S. FTIR spectrum of MCc





Figure 22S. <sup>13</sup>C-NMR of MCc in CDCl<sub>3</sub> (300 MHz, 298K)



**Figure 23S.** Absorption spectra of wheels: (a) **MCa** in  $(1.14 \times 10^{-5} \text{ M})$ , (b) **MCb**  $(1.82 \times 10^{-5} \text{ M})$  and (c) **MCc**  $(1.15 \times 10^{-5} \text{ M})$  in 9:1 (v/v) CH<sub>3</sub>CN and CHCl<sub>3</sub> binary solvent mixture. Photoluminescence spectra of wheels: (d) **MCa**; (e) **MCb**; (f) **MC** having same concentration in 9:1 (v/v) CH<sub>3</sub>CN and CHCl<sub>3</sub> solvent systems. Excitation wavelength was fixed at 285 nm in each case. Emissions are observed at around 340 nm in each case.



**Figure 24S.** ESI-MS (+ve) of  $Ni^{II}$  complex of **MC**, Peak at m/z = 684.2 attributed for  $[MC.Ni^{II}.ClO_4^-]^+$  and m/z = 292.2 corresponds to  $[MC.Ni^{II}]^{+2}$  species. This complex is not isolated. Solution was taken from the crude reaction mixture and mass spectrometric analysis has been carried out.



**Figure 25S.** Absorption spectrum of  $MC.Ni^{II}$  complex in  $CH_3CN$ . This complex is not isolated. Solution was taken from the crude reaction mixture and spectrum was taken with an arbitrary concentration.



*Figure 26S.* (a) *ESI-MS* (+ve) of *PROT.* (b) *Isotopic distribution pattern (Black Dotted)* shows well agreement with the experimentally observed pattern (Blue Bold)



**Figure 27S.** (a) Absorption spectroscopic titration profile between AXL as host and MC-Ni<sup>II</sup> complex as guest and (b) Equivalent plot (right) indicate the1:1 stoichiometric binding between host and guest. Concentration of AXL is 1 X 10<sup>-5</sup> M and for MC-Ni<sup>II</sup> is 1 X 10<sup>-4</sup> M. Titration was carried out by adding the MC-Ni<sup>II</sup> solution to the solution of AXL in 9:1 (v/v) Acetonitrile and DMF binary solvent mixture.



Figure 28S. FTIR of spectrum of PROT



*Figure 29S.* Chemical diagram of *MROT*, pink circle indicate the metal ion and the overall species is positively charged depending upon the charge on metal ions.



*Figure 30S. ESI-MS* (+ve) of *ROT*'. *This compound was used without further purification to synthesized ROTa-c* 



Figure 31S. <sup>1</sup>H-NMR spectrum of **ROT'** in CDCl<sub>3</sub> at 500 MHz (298 K). This compound was used without further purification to synthesized **ROTa-c** 



Figure 32S. ESI-MS (+ve) of ROTa



Figure 33S. FTIR spectrum of ROTa



Figure 34S. <sup>1</sup>H-NMR spectrum of ROTa in CDCl<sub>3</sub> at 500 MHz (298 K)



Figure 35S. <sup>1</sup>H-NMR spectrum of ROTa in DMSO-d<sub>6</sub> at 300 MHz (298 K)



Figure 36S. <sup>13</sup>C-NMR spectrum of ROTa in CDCl<sub>3</sub> at 298K (75.47 MHz)



Figure 37S. NOESY-NMR spectrum of ROTa in DMSO-d<sub>6</sub> at 400 MHz



Figure 38S. ROESY-NMR spectrum of ROTa in CDCl<sub>3</sub> at 400MHz



Figure 39S. DOSY-NMR spectrum of ROTa in CDCl<sub>3</sub> at 500 MHz



Figure 40S. ESI-MS (+ve mode) of ROTb



Figure 41S. FTIR spectrum of ROTb



Figure 42S. <sup>1</sup>H-NMR spectrum of ROTb in CDCl<sub>3</sub> at 500 MHz (298 K)



Figure 43S. <sup>1</sup>H-NMR spectrum of ROTb in DMSO-d<sub>6</sub> at 500 MHz (298 K)



Figure 44S. <sup>13</sup>C-NMR spectrum of ROTb in DMSO-d<sub>6</sub> at 75.47 MHz (298 K)



Figure 45S. COSY-NMR spectrum of ROTb in DMSO-d<sub>6</sub> at 300 MHz (298 K)



Figure 46S. NOESY-NMR spectrum of ROTb in DMSO-d<sub>6</sub> at 300 MHz (298 K)



Figure 47S. ROESY-NMR spectrum of ROTb in DMSO-d<sub>6</sub> at 300 MHz



**Figure 48S.** DOSY-NMR spectrum of **ROTb** in CDCl<sub>3</sub> at 500 MHz (Diffusion co-efficient value:  $4.30 \times 10^{-10} \text{ m}^2/\text{s}$ )



Figure 49S. MALDI-TOF-MS of ROTc



Figure 50S. ESI-MS of ROTc (+ve mode)



Figure 51S. FTIR Spectrum of ROTc



Figure 52S. <sup>1</sup>H-NMR spectrum of ROTc in CDCl<sub>3</sub> at 500 MHz



Figure 53S. <sup>1</sup>H-NMR spectrum of ROTc in DMSO-d<sub>6</sub> at 300 MHz (298 K)



Figure 54S.<sup>13</sup>C-NMR spectrum of ROTC in DMSO-d<sub>6</sub> at 298K



Figure 55S. COSY-NMR spectrum of ROTc in DMSO-d<sub>6</sub> at 500 MHz



Figure 56S. NOESY-NMR spectrum of ROTc in DMSO-d<sub>6</sub> at 500 MHz



Figure 57S. ROESY-NMR spectrum of ROTc in DMSO-d<sub>6</sub> at 500 MHz



**Figure 58S.** DOSY-NMR spectrum of **ROTc** in CDCl<sub>3</sub> at 500 MHz (Diffusion co-efficient value:  $3.9 \times 10^{-10} \text{ m}^2/\text{s}$ )



Figure 59S. Absorption spectrum of (a) ROTa (1.12 X 10<sup>-5</sup> M), (b) ROTb (1.03 X 10<sup>-5</sup> M), (c) ROTc (1.03 X 10<sup>-5</sup> M) in CH<sub>3</sub>CN at RT. Photoluminescence spectrum of (a) ROTa, (b) ROTb, (c) ROTc in CH<sub>3</sub>CN at RT (Excitation at 285 nm)





Figure 61S. <sup>1</sup>H-NMR spectrum of ROTa at 370K in DMSO-d<sub>6</sub> at 300MHz <sup>1</sup>H-NMR spectral evidences from Figure 57S shows that aromatic protons of the bipyridine part of the centre piece,  $H_{Ar}^{1}$ ,  $H_{Ar}^{2}$  and  $H_{Ar}^{3}$  which resonates at  $\delta = 8.62$  to 8.74 and 8.15 to 8.30 ppm as multiplets, start to accumulate with increasing temperature and finally coalesce at 370K. With increasing temperature, amide  $-NH^4$  protons show gradual upfield shift due to the clevage of intermolecular H-bond with the polar solvent (DMSO-d<sub>6</sub>) (Figure 57S). It is clear from the Figure 58S. that at 370K,  $-NH^4$  merged with the proton signals appeared for  $H_{Ar}^2$  and  $H_{Ar}^3$  with proper integral value (Figure 58S). Similarly, triazole ( $H_{Ar}^7$ ), aliphatic  $-H^8$ protons show two different set of multiplets and resonates at  $\delta = 7.98$  to 7.99 ppm and 5.20 to 5.23 ppm respectively at room temperature. At higher temperature they accumulate to two singlet peaks at 7.85 and 5.21 ppm respectively. Proton signals associated with the wheel component of **ROTa** shows peaks multiplicity at  $\delta = 6.25$  to 6.73 ppm and  $\delta = 5.70$  to 6.09 ppm for  $H_{Ar}^{f}$  and  $H_{Ar}^{e}$  respectively due to tertiary amide bond rotations, they started to accumulate with increasing temperature and finally coalesce into two different set of peaks at 6.03 and 6.48 ppm with proper integration ratio at high temperurature (Figure. 58S). Methyl protons of the tertiary acetamido groups which split in the ranges of  $\delta = 1.95$ -2.25 ppm at room temperarute, show two broad peaks with expected integral values at high temperature. Except  $H^{k}$ ,  $H^{k'}$  and  $H^{k}$  protons, **ROTa** consist seven other aliphatic protons, which includes five from wheel  $(H^c, H^d, H^g, H^h, H^i)$  and two from centre piece  $(H^5, H^6)$  that resonate between  $\delta = 3.25$  to 4.50 ppm as multiplets at room temperature. But upon heating, the multiplicity of all those seven proton signals convert to seven distinguishable peaks with proper integration ratio in the range of  $\delta = 3.42$  to 4.57 ppm at 393K (Figure 57S, Figure 58S).



**Figure 62S.** Variable temperature <sup>1</sup>H-NMR data of **ROTc** in DMSO-d<sub>6</sub> (300 MHz) As stated in the main text that due to restricted rotation of the tris-tertiary butyl group appended rotaxane **ROTc**, the numbers of conformers and co-conformers are less compared to the **ROTa** and **ROTb**. However, we have undertaken the variable temperature <sup>1</sup>H-NMR experiment of **ROTC** in DMSO-d<sub>6</sub> solvent system and the data analysis reveals that there is practically no significant changes has been observed at higher temperature NMR data except the amide peak of the centre piece component which is resonate around  $\delta = 8.75$  ppm at 298K and shifted to upfield with raising temperature.



Figure 63S. Low temperature <sup>1</sup>H-NMR data of **ROTb** in CDCl<sub>3</sub>, 500 MHz



**Figure 64S**. Low temperature <sup>1</sup>H-NMR data of **ROTC** in CDCl<sub>3</sub>, 500 MHz indicate that no significant changes in the peak multiplicities are observed compared to <sup>1</sup>H-NMR data at  $25^{\circ}C$ .



Figure 65 (a). Comparative <sup>1</sup>H-NMR Spectra of (a) DMBL, (b) ROTb and (c) MCb in DMSO-d<sub>6</sub>, 500MHz



Figure 65 (b). Comparative <sup>1</sup>H-NMR Spectra of (a) DMBL, (b) ROTc and (c) MCc in DMSO-d<sub>6</sub>, 500MHz



Figure 66S. Absorption spectrum of center piece DMBL (7.5 X 10<sup>-6</sup> M) of DMBL



**Figure 67S.** Absorption spectrum of (a) 1:1 MCb: DMBL (8.5 X  $10^{-6}$  M) and of DMBL and MCc (6.3.0 X  $10^{-6}$  M)



*Figure 68S.* Absorption spectrum of (a) centre piece *DMBL* (red) and *MCa* (black), separately, (b) extended version of "(a)" at higher wavelength, (c) *ROTa* 



Figure 69S. Absorption spectrum of (a) center piece DMBL and MCb, separately, (b) extended version at higher wavelength, (c) ROTb



Figure 70S. Absorption spectrum of (a) center piece DMBL and MCc, separately, (b) extended version of (a) at higher wavelength, (c) ROTc for the purpose of comparing with Figure 63S (c)



*Figure 71S.* Photoluminescence spectrum of centre piece 1:1 mixture of (a) **DMBL** and **MCa**, (b) **DMBL** and **MCb**, (c) **DMBL** and **MCc** (excitation at 285 nm) in 9:1 (v/v) CH<sub>3</sub>CN and CHCl<sub>3</sub> In all the cases concentration are 3.0 X 10<sup>-5</sup> M.



**Figure 72S.** Solvochromatic studies of **ROTa** (2.9 X  $10^{-5}$  M) via PL experiment in (excitation at 285 nm) in 9:1 (v/v) CH<sub>3</sub>CN and CHCl<sub>3</sub>.



**Figure 73S**. Upon gradual addition of methanol to the solution of **ROTa** in CH<sub>3</sub>CN, the fluorescence intensity of the exciplex of is decreased. Upon 10% addition of methanol ( $\nu/\nu$ ) to the CH<sub>3</sub>CN solution of **ROTa**, exciplex intensity is completely quenched. [Excitation at 285 nm, in 9:1 ( $\nu/\nu$ ) CH<sub>3</sub>CN and CHCl<sub>3</sub> binary solvent mixture, concentration = 2.9 X 10<sup>-5</sup> M.]



**Figure 74S.** Upon gradual addition of methanol to the solution of **ROTb** in acetonitrile, the fluorescence intensity of the exciplex of is decreasing. Upon 10% addition of methanol (v/v) to the acetonitrile solution of **ROTb**, exciplex intensity is completely quenched. [Excitation at 285 nm, in 9:1 (v/v) CH<sub>3</sub>CN and CHCl<sub>3</sub> binary solvent mixture, concentration = 2.75 X 10<sup>-5</sup> M.]



**Figure 75S.** Solvent dependent PL intensity vs. concentration plot of **ROTa**, [Excitation at 285 nm, in 9:1 (v/v) CH<sub>3</sub>CN and CHCl<sub>3</sub> binary solvent mixture, concentration = 1.2 X 10<sup>-5</sup> M.]



**Figure 76S**. Solvent dependent PL intensity vs. concentration plot of **ROTb** [Excitation at 285 nm, in 9:1 (v/v) CH<sub>3</sub>CN and CHCl<sub>3</sub> binary solvent mixture, concentration = 1.4 X 10<sup>-5</sup> M]



**Figure 77S.** Solvent dependent PL intensity vs. concentration plot of **ROTc**, [Excitation at 285 nm, in 9:1 (v/v) CH<sub>3</sub>CN and CHCl<sub>3</sub> binary solvent mixture, concentration = 1.41 X 10<sup>-5</sup> M.]



*Figure 78S:* Thermal Stability of exciplex generated by **ROTa** revealed via variable temperature PL experiments. [Excitation at 285 nm, in 9:1 (v/v) CH<sub>3</sub>CN and CHCl<sub>3</sub> binary solvent mixture, concentration = 2.75 X 10<sup>-5</sup> M.]

Recording Temperatures are: 298 K, 303 K, 313 K, 323K, 333 K, 343 K, 353 K.





**Figure 79S**: Thermal Stability of exciplex generated by **ROTb** revealed via variable temperature PL experiments. [Excitation at 285 nm, in 9:1 (v/v) CH<sub>3</sub>CN and CHCl<sub>3</sub> binary solvent mixture, concentration = 2.3 X 10<sup>-5</sup> M.] **Recording Temperatures are: 298K, 308K, 328K and 348K** 



**Figure 80S.** <sup>1</sup>*H*-*NMR* spectra of (a) **ROTa**, (b) **ROTa** + 1.0 eqv of Na+, (c) **ROTa** + 1 eqv. of  $Na^+ + 1.0$  eqv. of 18-crown-6 (18-C-6) in 9:1 CDCl<sub>3</sub>/CD<sub>3</sub>CN

We are interested to exemplify the effect of  $Na^+$  on rotamer induced dynamic behaviour (originated due to tertiary amide bonds rotation), exhibit by **ROTa** via <sup>1</sup>H-NMR studies at RT. Addition of equivalent amount  $Na^+$  salt solution in CD<sub>3</sub>CN in **ROTa** in 9:1 (v/v) CDCl<sub>3</sub>:CD<sub>3</sub>CN solvent mixture executes a typical accumulation of most multiplets of **ROTa**. Comparative <sup>1</sup>H-NMR analysis of **ROTa** and (**ROTa** + Na)<sup>+</sup> clearly indicate that the peaks corresponds to the lateral aromatic rings of the wheel components i.e. H<sup>e</sup> and H<sup>f</sup> also congregate to a less number of peaks compared to **ROTa**. Na<sup>+</sup> assists to halt/retard the dynamic property upon coordinating with the metal chelating sites present in the rotaxane. When equivalent amount of 18-crown-6 is added as an input to the mixture of **ROTa** and Na<sup>+</sup>, regeneration of the multiple peaks are observed in the <sup>1</sup>H-NMR spectrum. This can be easily explained upon considering the phenomenon that crown ether removes Na<sup>+</sup> from the system and as a consequence of that the multiple conformations/ co-conformations again started to exhibit.



*Figure 81S.* Chemical diagram of amido-amine macrocyclic ring derived tri-acetylated rotaxane



**Figure 82S.** <sup>1</sup>*H*-*NMR spectra of (a)* **ROTb**, (b) **ROTb** + 1.0 eqv of Na+, (c) **ROTb** + 100 eqv. of  $Na^+$ , (d) **ROTb** + 100 eqv. of  $Na^+$  + 100.0 eqv. of 15-crown-5.



Wavelength (nm) (d) Figure 83S. Absorption spectroscopic titration profile between ROTa (1.1 X 10<sup>-5</sup> M) vs. (a)  $Co^{II} (1 X 10^{-4} M); (b) Fe^{II} (1 X 10^{-4} M); (c) Mn^{II} (1 X 10^{-4} M), (d) Cr^{II} (1 X 10^{-4} M) in 9:1 (v/v)$  $CH_3CN/CHCl_3$  binary solvent mixture



**Figure 84S.** Representative absorption spectroscopic titration profile between **ROTb** (1.0 X  $10^{-5}$  M) vs. (a)  $Cu^{II}$  (1 X  $10^{-4}$  M), (a)  $Ni^{II}$  (1 X  $10^{-4}$  M) and (a)  $Co^{II}$  (1 X  $10^{-4}$  M) as perchlorate salt in 9:1 (v/v) CH<sub>3</sub>CN/CHCl<sub>3</sub> binary solvent mixture



**Figure 85S.** Absorption spectroscopic titration profile between **ROTc**  $(1.1 \times 10^{-5} \text{ M})$  vs. (a)  $Cu^{II} (1 \times 10^{-4} \text{ M});$  (b)  $Ni^{II} (1 \times 10^{-4} \text{ M});$  (c)  $Co^{II} (1 \times 10^{-4} \text{ M});$  (d)  $Fe^{II} (1 \times 10^{-4} \text{ M});$  (e)  $Mn^{II} (1 \times 10^{-4} \text{ M});$  (f)  $Cr^{II} (1 \times 10^{-4} \text{ M})$  as perchlorate salt in 9:1 (v/v) CH<sub>3</sub>CN/ CHCl<sub>3</sub> binary solvent mixture



*Figure 86S.* Nonlinear curves for determining the association constants in 9:1 (v/v) CH<sub>3</sub>CN/ CHCl<sub>3</sub> binary solvent mixture



**Figure 87S**. Photoluminescence spectrum **ROTa** in presence of (a)  $Cu^{II}$ , gradual addition of  $Cu^{II}$  salt decreases the PL intensity of the exciplex. For complete quenching, 1.0 equivalent is required; (b)  $Ni^{II}$ , Gradual addition of  $Ni^{II}$  salt decreases the PL intensity of the exciplex. For complete quenching, almost 1.0 equivalent is required. Gradual addition of other investigated metal salt decreases the PL intensity of the exciplex. For complete quenching, almost 1.0 equivalent is required. Gradual addition of other investigated metal salt decreases the PL intensity of the exciplex. For complete quenching, more than 1.0 equivalent is required. The spectra having least intensity at 470 nm indicate the presence of **ROTa** + 10.0 equivalent of respective metal ions: (c)  $Co^{II}$ , (d)  $Cr^{II}$ , (e)  $Fe^{II}$ , (f)  $Mn^{II}$ . (in all cases the solution were excited at 285 nm, in 9:1 (v/v)  $CH_3CN/ CHCl_3$  binary solvent mixture, concentration: 2.9 X  $10^{-5} M$ )



**Figure 88S**. Photoluminescence spectrum **ROTb** (**Con** in presence of (a)  $Cu^{II}$ , Gradual addition of  $Cu^{II}$  salt decreases the PL intensity of the exciplex. For complete quenching, 1.0 equivalent is required; (b) Ni<sup>II</sup>, Gradual addition of Ni<sup>II</sup> salt decreases the PL intensity of the exciplex. For complete quenching, almost 1.0 equivalent is required. Gradual addition of other investigated metal salt decreases the PL intensity of the exciplex. For complete quenching, almost 1.0 equivalent is required. Gradual addition of other investigated metal salt decreases the PL intensity of the exciplex. For complete quenching, more than 1.0 equivalent is required. The spectra having least intensity at 473 nm indicate the presence of ROTa + 10.0 equivalent of respective metal ions: (c)  $Co^{II}$ ; (d)  $Cr^{II}$ , (e)  $Fe^{II}$  (in all cases the solution were excited at 285 nm, in 9:1 (v/v) CH<sub>3</sub>CN/ CHCl<sub>3</sub> binary solvent mixture, concentration: 2.9 X  $10^{-5}$  M)



**Figure 89S**. Photoluminescence spectrum **ROTc** in presence of (a)  $Cu^{II}$ , Gradual addition of  $Cu^{II}$  salt decreases the PL intensity of the exciplex. Complete quenching is observed upon addition of 1.0 equivalent of  $Cu^{II}$  salt; (b) in presence of  $Ni^{II}$ , Gradual addition of  $Ni^{II}$  salt

decreases the PL intensity of the exciplex. Complete quenching is observed upon addition of 1.0 equivalent of Ni<sup>II</sup> salt; For complete quenching, almost 1.0 equivalent is required. Gradual addition of other investigated metal salt decreases the PL intensity of the exciplex. For complete quenching, more than 1.0 equivalent is required. The spectra having least intensity at 473 nm indicate the presence of ROTa + 10.0 equivalent of respective metal ions: (c) in presence of Co<sup>II</sup>, (d) in presence of Fe<sup>II</sup>, (e) in presence of Mn<sup>II</sup>, (f) in presence of Cr<sup>II</sup> (in all cases the solution were excited at 285 nm, in 9:1 (v/v) CH<sub>3</sub>CN/CHCl<sub>3</sub> binary solvent mixture, concentration: 1.0 X 10<sup>-5</sup> M).