View Article Online View Journal

NJC Accepted Manuscript

This article can be cited before page numbers have been issued, to do this please use: B. Godde, D. Ritaine, A. Jouaiti, M. Mauro and M. W. Hosseini, *New J. Chem.*, 2018, DOI: 10.1039/C8NJ00890F.



This is an Accepted Manuscript, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this Accepted Manuscript with the edited and formatted Advance Article as soon as it is available.

You can find more information about Accepted Manuscripts in the **author guidelines**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard <u>Terms & Conditions</u> and the ethical guidelines, outlined in our <u>author and reviewer resource centre</u>, still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this Accepted Manuscript or any consequences arising from the use of any information it contains.



rsc.li/njc

Published on 06 April 2018. Downloaded by Freie Universitaet Berlin on 07/04/2018 06:37:12.

COPAL SOCIETY

Journal Name

ARTICLE

xsReceived 00th January 20xx,

A pyridyl-benzimidazole based molecular luminescent turnstile

Accepted 00th January 20xx DOI: 10.1039/x0xx00000x

www.rsc.org/

Bérangère Godde, Dialia Ritaine, Abdelaziz Jouaiti,*, Matteo Mauro, and Mir Wais Hosseini*

A molecular turnstile T1 based on a luminescent pyridylbenzimidazole stator and a rotor containing a pyridyl coordinating site is designed and its multi-step synthesis described. The turnstile T1 undergoes free rotation of the rotor around the stator. In the presence of Ag^+ cation as an effector, the rotational movement is locked through simultaneous binding of the cation by both pyridyl coordinating sites. The dynamic reversible behaviour of the turnstile in solution was investigated by 1- and 2D-NMR spectroscopy and by absorption and emission spectroscopies.

Introduction

The design and synthesis of dynamic of molecular architectures and the control of their intramolecular movement is a topic of current interest. Since the pioneering investigations by Sauvage *et al*,¹ Stoddart et al,² Feringa *et al*³ and Balzani *et al*,⁴ a variety of molecular motors, rotors and machines subject to rotational or translational movement has been reported.⁵⁻¹³ Molecular turnstiles¹⁴⁻²¹ constitute a particular class of dynamic systems undergoing rotational movement. These molecules are based on two interconnected parts, *i.e.* a stator and a rotor. The designation of the two parts, *i.e.* rotor and stator, is relative since they both undergo a rotational movement (Fig. 1).



Figure 1. Schematic representations of a turnstile in its open and closed states. In the absence of the effector (yellow sphere) the rotor spins freely around the stator whereas in the presence of the effector the rotational movement is blocked.

For turnstiles not equipped with specific interactions sites, the rotor

Molecular Tectonics Laboratory, UMR UdS-CNRS 7140, University of Strasbourg, Institut Le Bel, 4, rue Blaise Pascal, F-67000 Strasbourg, France.

Electronic Supplementary Information (ESI) available: full synthetic procedures and characterizations together with 1D and 2D NMR, and photophysical data. See DOI: 10.1039/x0xx00000x

This journal is © The Royal Society of Chemistry 20xx

freely rotate around the stator. However, for those bearing simultaneously interactions units on both rotor and stator, the rotational movement may be blocked using an external (Fig. 1).

Here we report on the design and synthesis of a novel turnstile composed of a rotor bearing a pyridyl moiety and a stator based on a benzimidazole unit bearing also a pyridyl group as coordinating sites. In solution, the switching between the open **T1** and closed **T1**-Ag⁺ states of the turnstile was monitored by NMR (1- and 2D) and by absorption and emission spectroscopies.

Experimental

Experimental details dealing with synthetic procedures, characterization, NMR and photophysical investigations are reported in the Electronic Supplementary Information (ESI).

Results and discussion

Design of turnstiles

The design of the turnstile **T1** (Scheme **1**) is based on a stator and a rotor connected to the stator by covalent bonds. As for the latter, a benzimidazole hydroquinone unit has been chosen owing to its photophysical properties. The benzimidazole based stator is equipped with a pyridyl unit as a coordinating site. The rotor is composed of a pyridyl moiety as the coordinating site, symmetrically substituted at positions 2 and 6 by two tetraethyleneglycol spacers linking the rotor to the stator. The junction between the rotor and the stator is ensured by two other groups using positions 1 and 4 of the substituted benzimidazole moiety.



Scheme 1. Chemical structures of molecular turnstiles in its open T1 and closed T1-Ag states and assignment of H-atoms.

DOI: 10.1039/C8NJ00890F

The turnstile is designed to undergo a switching process between its open **T1** and closed **T1**-Ag⁺ states (Fig. 1) using Ag(I) cation as the external effector (Scheme 1). The locking of the rotational movement of the turnstile **T1** in the presence of Ag⁺ as effector results from simultaneous binding of the metal cation by both coordinating sites located on the stator and on the rotor. The choice of Ag⁺ cation was based on its affinity to interact with pyridyl units in a reversible manner and its propensity to adopt a linear coordination geometry. Furthermore, taking advantage of the poor solubility of silver halide salts, the locking process may be reversed leading to the open state of the turnstile upon addition of a salt such as Et₄NBr for example.

Synthesis of turnstiles

Published on 06 April 2018. Downloaded by Freie Universitaet Berlin on 07/04/2018 06:37:12.

The strategy adopted for the synthesis of **T1** is based on the functionalization of 1,4-dimethoxybenzene as the precursor of the stator and a cyclization step using 2,6-difluoropyridine **8** (Scheme 2).



Scheme 2. Schematic general synthetic strategy for the preparation of the turnstile **T1**. Reaction conditions: i) HNO₃, O °C during 1 hour, room temperature, 1 hour then 100 °C, 1 hour; ii) H₂, Pd/C, dry THF, room temperature, 24 hours; iii) H₂, Pd/C, dry THF, room temperature, 24 hours; iv) pyridine-4-carboxaldehyde, Na₂S₂O₅, Ethanol, 70 °C, 15 hours; v) CH₃I, Cul, Cs₂CO₃, 1,10-phenantroline, DMF, 90 °C, 20 hours; vi) BBr₃, dry CH₂Cl₂, -78°C \rightarrow room temperature, 20 hours, vii) tetraethyleneglycol, NaH, THF, resflux, 4 days; viii) mesityl chloride, Et₃N, THF, room temperature, 12 hours; ix) 7, Cs₂CO₃, DMF, 90°C, 48 hours.

The synthesis of the stator **7** is achieved in six steps. Starting with 1,4-dimethoxybenzene **1**, compound **2** was prepared as a mixture of ortho/para dinitro isomers using a reported procedure.²² Reduction of the mixture by H₂ (3 bars) in dry THF afforded the compound **3**²² after purification by column chromatography. The latter was further quantitatively hydrogenated into the desired compound **4**.²³ The condensation in ethanol of **4** with the commercially available 4-pyridinecarboxaldehyde in the presence of Na₂S₂O₅²⁴ afforded the corpound **5** in 70%. To prevent the deprotonation of **5** during the cyclisation step, the –NH group of the benzimidazole moiety was methylated by iodomethane affording the compound **6**. This step was achieved using copper iodide, 1,10-phenantroline and cesium carbonate. Finally, the compound **7** was obtained in 82% yield by deprotection in dry dichloromethane of compound **6** using BBr₃. On the other hand, the commercially available tetraethyleneglycol was

first mono deprotonated using NaH in dry THF and then condensed with 2,6-difluropyridine **8**. The reaction afforded the compound **9** in 87% yield. The latter was activated as its dimesylate derivative **10** upon treatment with mesyl chloride (MsCl) in presence of Et₃N in anhydrous THF. Finally, the cyclization, leading to the turnstile **T1** in 33% yield, was achieved upon condensation of the compound **10** with the hydroquinone derivative **7** in DMF using Cs₂CO₃ as base.

Switching of turnstiles

As schematically shown in figure 1, the turnstile **T1** is designed to undergo a switching between its open **T1** state subject to a free rotational movement and its closed **T1**-Ag⁺ state for which the movement is blocked by simultaneous binding of Ag⁺ cation by both pyridyl coordinating sites located on the stator and on the rotor (Scheme 1). The close state of the turnstile **T1**-Ag⁺ was quantitatively prepared as a yellow solid upon treatment at room temperature and in the dark of **T1** with AgCF₃SO₃ in CH₃CN.

Solution dynamic behaviour of the turnstiles T1

The dynamic behaviour of **T1** and **T1**-Ag⁺ was investigated in solution by both 1D and 2D NMR spectroscopies. For the open (**T1**) and closed states (**T1**-Ag⁺) of the turnstile, all H-atoms signals were assigned (Scheme 1) by means of ¹H- and ¹³C-NMR spectroscopy (see ESI).

For **T1**, the 1D ¹H-NMR (Fig.2, trace 1) spectrum recorded at room temperature in CD₃CN displays highly symmetric resonance patterns. In the aromatic region, two doublets at 8.71 ppm and 7.73 ppm are assigned to H*m* and H*n* of the pyridyl unit. Signals corresponding to H*k* and H*l*, two doublets characterized by a roof effect appear at 6.57 and 6.67 ppm. Signals corresponding to H atoms of the pyridyl moiety appear as a doublet (H*b* and H*b*') and a triplet (H*a*) at 6.20 ppm and 7.45 ppm respectively.

For the closed state **T1**-Ag⁺, signals corresponding to the pyridyl moiety of the stator (Hm and Hn) and Hk and Hl are downfield shifted by 0.05 ppm and 0.18 ppm respectively (Fig2, trace 2). For the pyridyl unit of the rotor, Ha, Hb and Hb' are upfield shifted by 0.07, 0.04 ppm respectively (Fig2, trace 2).



Figure 2. A portion of the aromatic region of the 1 H-NMR (CD₃CN, 400 MHz, 298K) spectrum of T1 (trace 1), T1-Ag⁺ (trace 2) and T1 after the addition of 1 eq. of Et₄NBr (trace 3).

The reversibility of the locking/unlocking process was also studied by 1D-1H NMR spectroscopy. The addition of one equivalent of Published on 06 April 2018. Downloaded by Freie Universitaet Berlin on 07/04/2018 06:37:12.

Journal Name

 Et_4NBr in CH_3CN to a CH_3CN solution of $T1-Ag^+$ caused the precipitation of AgBr. After evaporation of the solvent and dissolution of the reaction product in CD_3CN , the ¹H-NMR spectrum confirmed that the open states of **T1** is restored (Fig. 2, trace 3).

The locking of the turnstile **T1** was investigated by 2D ¹H-¹H NOESY techniques Correlation maps are displayed on Fig. 3 for **T1** and **T1**-Ag⁺ complex. For the turnstile **T1** (open state), the bidimensional ¹H-¹H correlation map (Fig. 3 *top*) shows only the expected short range cross-correlations between H*m* and H*o*, H*I* and H*j*' as well as between H*k* and H*j* of the imidazole moiety. For the rotor part, as expected, H*b* and H*b*' atoms correlate with H*c* and H*c*'.

Owing to the fast rotation of the rotor around the stator at room temperature with respect to the NMR time scale, no through-space correlations between Hm and Hn and hydrogen atoms of the tetraethyleneglycol spacers are observed.



Figure 3. Portion of the 2D ROESY correlations $({}^{1}H^{-1}H$ NMR, 400 MHz) for T1 in CD₃CN (*top*) and for T1-Ag⁺ in CD₃CN (*bottom*) at 298 K.

The locking of the rotational movement leading to the closed state of the turnstile **T1**-Ag+ upon addition of Ag⁺ was also studied by 2D NMR experiments at room temperature (Fig. 3 *bottom*). Upon binding of Ag⁺ cation by both pyridyl units belonging to the rotor and to the stator, a novel set of correlations was observed. Indeed, through-space correlations between H*n*, H*m* and the hydrogen atoms of the polyethylene glycol chains demonstrated the proximity of the pyridyl unit of the stator with the hydrogen of the rotor and the location of the stator within the cavity of the macrocycle. Furthermore, a strong correlation between H*o* (methyl unit on the imidazole) and the hydrogen atoms of the polyethyleneglycol spacers is observed. The observation of other through spaces correlations between H*m* and H*c* and H*c*' further confirms the above mentioned observations.

Photophysical investigations

The absorption and emission properties of the turnstile in its open **T1** and closed **T1**-Ag⁺ were studied in dilute CH₃CN solution at room temperature (Table **1**).

Table 1.	Photophysical	data	recorded	for	Τ1,	T1-Ag ⁺	in	CH_3CN	at
1.0×10 ⁻⁵	M concentratio	n at r	oom temp	berat	ture				

	Absorbance (ε) [nm, (10 ³ M ⁻¹ cm ⁻¹)]	$\lambda_{\text{em}}[\text{nm}]$	τ[ns]	PLQY (%)
T1	257(22.5), 283 (15.5),	521	8.3	10
	303 <i>sh</i> (10.3)			
T1- Ag ⁺	257 (21.4), 283(14.8),	521	8.5	8.5(air)
	303sh (9.6)			

sh denotes a shoulder; $^{a} \lambda_{exc} = 350 \text{ nm}$

For the turnstile **T1**, the UV visible absorption spectrum is composed of three bands (Fig. 4). At shorter wavelength, a narrow ($\lambda_{abs,max} = 257 \text{ nm}$) and intense ($\epsilon = 2.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$) absorption band which can be ascribed to a transition with spin-allowed singlet-manifold ligand centred (¹LC) character is observed. At longer wavelengths, two others absorption bands at 283 and 303 nm with lower intensity ($\epsilon = 1.5 \times 10^4 \text{ and } 1 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ respectively) are observed. These bands can also be ascribed to a ¹LC on the basis of the lack of neat solvatochromic effect upon changing the solvent polarity while using identical concentrations (Fig. S5).

However, at lower energy, the presence of an overlapping band with partial intraligand charge transfer (¹ILCT) character involving the π -conjugated pyridyl-benzimidazole chromophore, cannot be completely ruled out at the present stage owing to the very small bathochromic shift observed at lower energy going from toluene to CH₂CH₂, CH₃CN and finally DMF.



Figure 4. UV-visible absorption spectra of turnstiles T1 (red trace) and T1-Ag⁺ (blue trace) in CH₃CN (1.0×10^{5} M) at room temperature.

Surprisingly, the presence of Ag⁺ cation leading to the closed-state **T1**-Ag⁺, did not induce spectral changes in the electronic absorption profile (Fig. 4). This is most likely due to the concentration (10^{-5} M) used for the investigation. In order to study this hypothesis, absorption and emission measurements of **T1**-Ag⁺ were carried out at of 1.0×10^{-4} and 1.0×10^{-3} M concentration. It can be noticed that the absorption band at *ca*. 300 nm undergoes a hypochromic shift upon increase of the concentration of the **T1**-Ag⁺ complex (Fig 5 *top*). Concomitantly, for the two bands at *ca* 260 nm and 280 nm, a

Journal Name

Published on 06 April 2018. Downloaded by Freie Universitaet Berlin on 07/04/2018 06:37:12.

decrease of the molar extinction coefficient is observed (Fig. 5 *top*). The expanded portion of the spectra between 340 and 370 nm (Fig. 5 *bottom*) shows a slight increase of the lowest-lying absorption band that can be attributed to a charge transfer transition of the **T1**-Ag⁺ species. This observation suggests a lower affinity of **T1** for Ag(I) cation when compared to previously reported turnstiles.^{18,19}



Figure 5. UV-visible absorption spectra of turnstiles **T1** (1.0×10^{-5} M) (red trace), **T1**-Ag⁺ (1.0×10^{-5} M) (blue trace), 1.0×10^{-4} M (green trace, 1.0×10^{-3} M (black trace) in CH₃CN at room temperature (*top*) and zoom of the UV-visible spectra of the turnstile **T1** at (1.0×10^{-5} M) between 340 and 370 nm (*bottom*)

In order to investigate this assumption, a titration experiment in the 0–25 eq. range of **T1** by Ag⁺ was carried out using ¹H-NMR spectroscopy by observing the shifts of signals corresponding to H*n* and H*i*/H*i*' H atoms (see Fig. S1–S3).

Upon fitting the complete titration curves, stability constants $K_{1:1} = 4.0 \times 10^3 \text{ M}^{-1}$ and $K_{2:1} = 1.6 \times 10^6 \text{ M}^{-1}$ were calculated. These two binding constants correspond to the 1:1 and 2:1 Ag⁺/ **T1** complexes respectively. The $K_{1:1}$ is in agreement with stability constants described in the literature for silver complexes by ligands bearing two pyridines units.¹⁸ The formation of the 1:1 and 2:1 Ag⁺/**T1** complexes were further confirmed by electron spray ionization mass spectrometry (ESI-MS) using a sample of **T1** and 25 equivalents of CF₃SO₃Ag. The mass spectra, represented in Fig. S6, display peaks at 777.21 and 1033.05 which correspond to the 1:1 and 2:1 Ag⁺/**T1** complexes respectively. For the 2:1 species, it can be tentatively assigned to the binding of one Ag⁺ cation by the two pyridine moieties and a second one by the benzimidazole unit.

Upon photo-excitation with λ_{exc} = 350 nm, **T1** and **T1**-Ag⁺ in CH₃CN display broad and featureless yellow emission at room temperature with maxima centred at 521 nm with photoluminescence quantum yield (PLQY) of 10% and 8.5%, respectively (table 1). As shown in Fig. 6, the emission spectra profile is unaffected by the presence of 1 eq. of Ag⁺, while PLQY seems to be only slightly affected.



Figure 6. Normalized emission spectra (λ_{exc} = 350 nm) of T1 (red trace) and T1-Ag⁺ (blue trace) in dilute CH₃CN (1.0×10⁻⁵ M) at room.

Excited state lifetime measurements showed a mono-exponential decay kinetics with $\tau = 8.3$ and 8.5 ns for **T1** and **T1**-Ag⁺, respectively indicating that, under the concentration used $(1.0 \times 10^{-5} \text{ M})$, the turnstile is in its open state **T1**. This is substantiated by the stability constants $K_{1:1} = 4.0 \times 10^{3} \text{ M}^{-1}$ determined by NMR spectroscopy. Indeed, considering 1.0×10^{-3} M concentration of the turnstile **T1**, 43%, 50% and 7% distribution for the free turnstile **T1**, **T1**-Ag⁺ (1:1 [**T1**-Ag₂]²⁺ species respectively may be calculated (Fig. S4). At 1.0×10^{-5} M concentration, for an equimolar mixture of **T1** and CF₃SO₃Ag, the simulated speciation profile (Fig. S4) shows the presence of 96.3%, and 3.7% of **T1** and **T1**-Ag⁺, respectively.

Furthermore, for **T1**-Ag⁺ complex in CH₃CN, emission spectra were recorded at different concentrations (Fig. 7). By increasing the concentration of **T1**-Ag⁺ from 1.0×10^{-4} to 1.0×10^{-3} M, a small bathochromic effect with maxima shifting from 525 to 527 nm is observed. Such minor variation is in agreement with the weak binding propensity of **T1** for silver cation.



Figure 7. Normalized emission (λ_{exc} = 350 nm) spectra of T1 (red trace) and T1-Ag⁺ at different concentrations: 1.0×10⁻⁵ M (blue trace), 1.0×10⁻⁴ M (green trace), 1.0×10⁻³ (dark trace) in dilute CH₃CN and at room.

Finally, in order to assess the nature of the emitting excited state, a solvent effect study was carried out for **T1** (Fig. 8) using toluene ($\lambda_{em} = 478 \text{ nm}$), CH₂Cl₂ ($\lambda_{em} = 508 \text{ nm}$) CH₃CN ($\lambda_{em} = 521 \text{ nm}$) and DMF ($\lambda_{em} = 522 \text{ nm}$) with $\lambda_{exc} = 350 \text{ nm}$. The investigation highlighted the partial charge transfer nature of the radiative transition. Indeed, the emission spectra recorded at identical

dilution $(1.0 \times 10^{-5} \text{ M})$ show a bathochromic shift of its maximum upon increasing solvent polarity.



Figure 8. Solvent effect for T1. Normalized emission spectra of turnstiles of T1 $(1.0 \times 10^{-5} \text{ M})$ in toluene (red wine trace), in CH₂Cl₂ (black trace), CH₃CN (red trace) and DMF (olive trace).

Conclusions

In conclusion, the pyridyl-benzimidazole based molecular turnstile, **T1**, was designed and synthesised using a convergent multi-step procedure. The switching between its open state **T1** and closed state **T1**-Ag⁺ was investigated by 1- and 2D-NMR analysis and by absorption and emission spectroscopy in solution. The locking by addition of Ag⁺ cation as effector and un-locking by addition of Br⁻ anion was shown to be reversible. The turnstile shows a yellow photoluminescence in CH₃CN with PLQY value of *ca*. 10%. The bathochromic shift observed for the emission process upon increasing the solvent polarity indicated that the radiative transition arises from an excited state with partial charge transfer nature. The use of other effector such as Pd(II) is currently under investigation.

Acknowledgements

We thank the University of Strasbourg, the C.N.R.S., the International centre for Frontier Research in Chemistry (icFRC), the Labex CSC (ANR-10-LABX- 0026 CSC) within the Investissement d'Avenir program ANR-10-IDEX-0002-02, the Institut Universitaire de France and the Ministère de l'Enseignement Supérieur et de la Recherche for financial support and a scholarship to BG.

Notes and references

1 J.-P. Sauvage, Angew. Chem. Int. Ed. 2017, 56, 11080 - 11093.

2 J. F. Stoddart, *Angew. Chem. Int. Ed.* 2017, **56**, 11094 – 11125. 3 B. L. Feringa, *Angew. Chem. Int. Ed.* 2017, **56**, 11060 – 11078.

4 V. Balzani, M. Venturi, M., A. Credi, In *Molecular Devices and Machines: a Journey into the Nanoworld;* Wiley-VCH: Weinheim, 2003; pp 1–457.

5 C. A. Schalley, K. Beizai, F. Vögtle, Acc. Chem. Res. 2001, **34**, 465–476.

6 R. Kelly, *Topics in Current Chemistry*; R. Kelly, Ed.; Springer: Berlin, Heidelberg, 2005; Vol. 262, pp 1–227.

7 G. S. Kottas, L. I. Clarke, D. Horinek, J. Michl, *Chem. Rev.* 2005, **105**, 1281–1376.

View Article Online DOI: 10.1039/C8NJ00890F

ARTICLE

8 Y. Shirai, A. J. Osgood, Y. Zhao, K. F. Kelly, J. M. Tour, *Nano Lett.* 2005, **5**, 2330–2334.

9 E. R. Kay, D. A. Leigh, F. Zerbetto, Angew. Chem. Int. Ed. 2007, 46, 72–191.

10 K. Kinbara, T. Muraoka, T. Aida, *Org. Biomol. Chem.* 2008, **6**, 1871–1876.

11 G. Vives, H.-P. J. de Rouville, A. Carella, J.-P. Launay, G. Rapenne, *Chem. Soc. Rev.* 2009, **38**, 1551–1561.

12 F. Coutrot, E. Busseron, Chem. Eur. J. 2009, 15, 5186-5190.

13 E. A. Neal, S. M. Goldup, *Chem. Sci.* 2015, **6**, 2398–2404.

14 T. C. Bedard, J. S. Moore, J. Am. Chem. Soc. 1995, **117**, 10662–10671.

15 A. Carella, J. Jaud, G. Rapenne, J.-P. Launay, *Chem. Commun.* 2003, 2434–2435.

16 N. Weibel, A. Mishchenko, T. Wandlowski, M. Neuburger, Y. Leroux, M. Mayor, *Eur. J. Org. Chem.* 2009, 6140–6150.

17 K. Skopek, M. C. Hershberger, J. A. Gladysz, *Coord. Chem. Rev.* 2007, **251**, 1723–1733.

18 a) A. Guenet, E. Graf, N. Kyritsakas, L. Allouche, M. W. Hosseini, *Chem. Commun.* 2007, 2935–2937; b) A. Guenet, E. Graf, N. Kyritsakas, M. W. Hosseini, *Inorg. Chem.* 2010, **49**, 1872–1883; c) T. Lang, A. Guenet, E. Graf, N. Kyritsakas, M. W. Hosseini, *Chem. Commun.* 2010, **46**, 3508–3510; d) A. Guenet, E. Graf, N. Kyritsakas, M. W. Hosseini, *Chem. Eur. J.* 2011, **17**, 6443–6452; e) T. Lang, E. Graf, N. Kyritsakas, M. W. Hosseini, *Dalt. Trans.* 2011, **40**, 3517–3523; f) T. Lang, E. Graf, N. Kyritsakas, M. W. Hosseini, *Dalt. Trans.* 2011, **40**, 5244–5248; g) T. Lang, E. Graf, N. Kyritsakas, M. W. Hosseini, *Chem. Eur. J.* 2012, **18**, 10419–10426; i) T. Lang, E. Graf, N. Kyritsakas, M. W. Hosseini, *New J. Chem.* 2013, **37**, 112–118.

19 a) N. Zigon, A. Guenet, E. Graf, M. W. Hosseini, *Chem. Commun.* 2013, **49**, 3637–3639 ; b) N. Zigon, A. Guenet, E. Graf, N. Kyritsakas, M. W. Hosseini, *Dalt. Trans.* 2013, **42**, 9740–9745 ; c) N. Zigon, N. Kyritsakas, M. W. Hosseini, *Dalton. Trans.* 2014, **43**, 152–157; d) N. Zigon, M. W. Hosseini, *Chem. Commun.* 2015, **51**, 12486–12489 ; e) N. Zigon, P. Larpent, A. Jouaiti, N. Kyritsakas, M. W. Hosseini, *Dalton. Trans.* 2014, **43**, 15779–15784 ; f) N. Zigon, P. Larpent, A. Jouaiti, N. Kyritsakas, M. W. Hosseini, *Chem. Commun.* 2014, **50**, 5040–5042.

20 I. N. Meshkov, V. Bulach, Y. G. Gorbunova, N. Kyritsakas-Gruber, M. S. Grigoriev, A. Y. Tsivadze, M. W. Hosseini, *Inorg. Chem*, 2016, **55**, 10774–10782.

21 B. Godde, A. Jouaiti, A. Fluck, N. Kyritsakas, M. Mauro, and M. W. Hosseini *Dalton Trans.*, 2017, **46**, 14897 14906.

22 P. Hammershøj, TK. Reenberg, M. Pittelkow, C. B. Nielsen, O. Hammerich and J. B. Christensen, *Eur. J. Org. Chem.*, 2006, **12**, 2786-2794.

23 C. Morin, T. Besset, J.-C. Moutet, M. Fayolle, M. Brückner, D. Limosin, K. Becker and E. Davioud-Charvet , *Org. & Bio. Chemistry*, 2008, **6**, 2731-2742

24 a) H. Naeimi and N. Alishahi, Research article, Organic Chemistry International, 2012; b) C.-K. Ryu, E.-H. Song, J.-Y. Shim, H.-J. You, K.-U. Choi, I.-H. Choi, E.-Y. Lee and M.-J. Chae, *Bioorg. Med. Chem. Lett.*, 2003, **13**, 17-20.

Published on 06 April 2018. Downloaded by Freie Universitaet Berlin on 07/04/2018 06:37:12.

New Journal of Chemistry Accepted Manuscript

A molecular turnstile based on a luminescent pyridyl-benzimidazole stator and a rotor containing a pyridyl coordinating site may be reversibily switched between its open and closed states upon binding/unbinding of silver cation.

New Journal of Chemistry Accepted Manuscript

