Porphyrin based molecular turnstiles†

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Received (in Cambridge, UK) 23rd December 2009, Accepted 26th February 2010
First published as an Advance Article on the web 18th March 2010
DOI: 10.1039/b927112k

Molecular turnstiles, based on a hinge composed of a Sn–porphyrin bearing coordinating sites at the *meso* positions and a handle, equipped with a tridentate coordinating pole or its Pd(II) complex, connected to the porphyrin through Sn–O bonds, offering open (free rotation of the handle around the hinge) and close states (blockage of rotation through binding of Pd(II)) were designed, prepared and studied both in solution and in the solid state.

Controlling movements in molecular systems is a topic of current interest. Molecular machines for which the amplitude as well as the direction of motion are imposed by external stimuli have been attracting considerable interest over the past years.[1–7] Among many systems reported, molecular turnstiles,[8–11] by essence subject to rotational movement, are interesting objects as rather primitive prototypes for the design of molecular motors and rotors. We have previously reported a molecular gate which may also be regarded as a molecular turnstile.[12]

Here, we report on the design, synthesis and structural characterisation of molecular turnstiles composed of a porphyrin based hinge bearing a monodentate coordinating site and a handle equipped with a tridentate coordinating pole or its Pd complex.

The design of turnstiles reported here is based on a stator and a handle (Fig. 1). More precisely, the stator is composed of a Sn(IV)–porphyrin bearing two anisole and two benzonitrile groups in *trans* disposition (Fig. 2). The presence of two benzonitriles as monodentate sites instead of one is for synthetic reasons. The introduction of Sn(IV), a strong Lewis acid and an oxophilic centre adopting octahedral coordination geometry, within the porphyrin core is essential since it allows the porphyrin based stator to behave as a hinge. Indeed, the Sn(IV) centre coordinated by the tetraaza core of the porphyrin offers two apical positions to be used as connecting points to attach the handle through Sn–O bonds (compound **1**). The handle, a symmetrical fragment, is based on a central tridentate coordinating pole or its Pd(II) complex connected to two $-CH_2CH_2OCH_2CH_2OCH_2CH_2-$ units each bearing a resorcinate type terminus (Fig. 2).

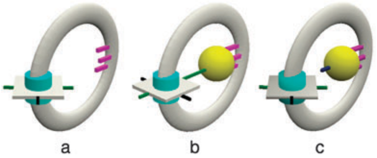

Fig. 1 Schematic representation of the open (a) and close (b) states of a molecular turnstile composed of a hinge bearing a monodentate coordination site (green) and a handle equipped with a tridentate coordination pole (purple). The yellow sphere represents a metal adopting the square planar coordination geometry. (c) represents the opening of **2** upon addition of a competing ligand.

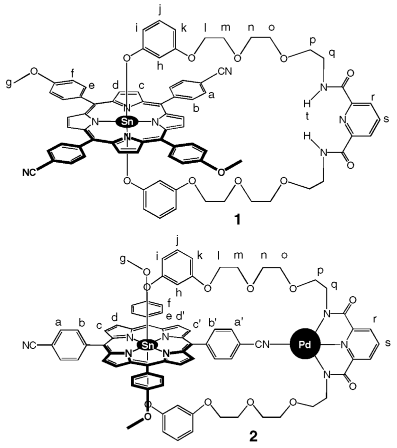

Fig. 2 Representation of the molecular turnstile in the open (compound **1**) and close (compound **2**) states and the assignment of H atoms based on 2-D NMR studies.

Compound **1** may be qualified as a turnstile because, in the absence of metal, the handle, owing to its length and curvature, freely rotates around the hinge (open state, Fig. 1a). The turnstile **1** may be considered as a dynamic ligand offering a monodentate site on the hinge and a tridentate pole on the handle. In the presence of a metal centre such as Pd(II) adopting square planar coordination geometry, the two types of coordinating sites should simultaneously bind the metal leading to compound **2**. Thus, the binding event stops the rotational movement (close state, Fig. 1b).

The synthetic strategy (see ESI†) adopted for the preparation of **1** and **2** was based on the coupling reaction between handles **14** or **15** and the dihydroxo Sn–porphyrin **21** respectively (Scheme 1). The starting materials for the synthesis of the handle were monochloro triethyleneglycol **3**, pyridine dicarboxylic acid **6** and the monoester derivative of resorcinol **8**. Compound **3** was first converted in 80% yield into the phthalimido derivative **4** upon treatment by potassium phthalimidate in DMF at 120 °C. The ethanolysis in the presence of hydrazine of **4** afforded the monoamino derivative **5** in 64% yield. On the other hand, the diacid compound **6** was converted to its acyl chloride derivative **7** in 96% yield upon treatment with $SOCl_2$. The monoester derivative of resorcinol **8** was first protected in 74% yield (compound **9**) upon reaction

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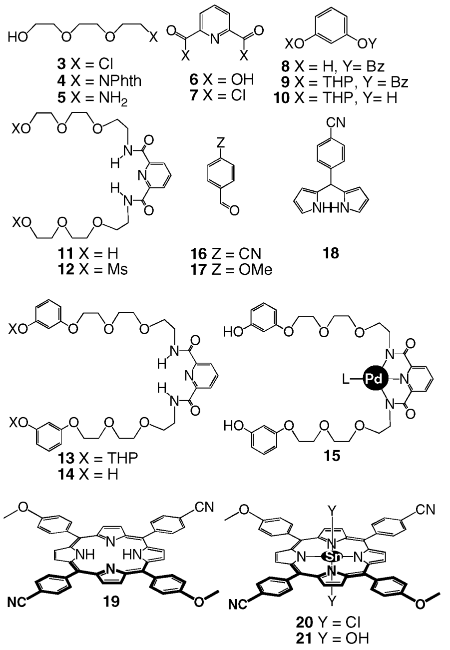
† Electronic supplementary information (ESI) available: Synthetic procedures. CCDC 759474. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b927112k



Scheme 1

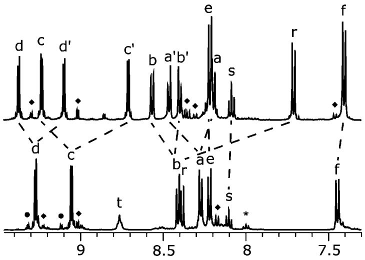


Fig. 3 Portions of the ^{1}H-NMR spectra (500 MHz, CD_2Cl_2, 25 °C) and assignment of signals between 7.3–9.5 ppm for **1** (bottom) and **2** (top). For assignment of H atoms see Fig. 2. ★, ● and ◆ correspond, respectively, to **14** and **20** resulting from the hydrolysis of **1** or **2** and to the unreacted **21**.

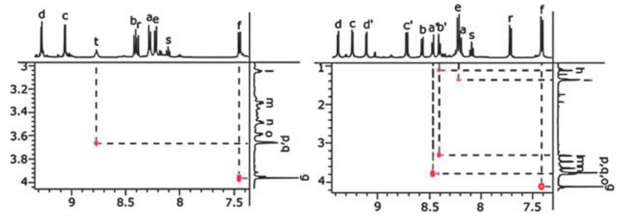


Fig. 4 Portions of the 2-D ROESY correlations for **1** (left) and **2** (right). For attribution of H-atoms see Fig. 2.

with DHP in EtOAc at 25 °C and then saponified upon treatment with a THF–H_2O mixture in the presence of NaOH affording thus the compound **10** in 97% yield. The condensation of the amino derivative **5** with **7** in CH_2Cl_2 afforded the compound **11** in 75% yield. The latter was activated into its dimesylate derivative **12** in 74% yield. The condensation of **10** with **12** in CH_3CN in the presence of Cs_2CO_3 afforded the protected handle **13** in 91% yield which was deprotected under acidic conditions (37% HCl in MeOH) into the diol compound **14** in 94% yield. The handle **15** was obtained in 80% yield upon treatment of the diol **14** with $Pd(OAc)_2$ in CH_3CN. For the synthesis of the porphyrin moiety, the two starting materials were the aldehydes **16** and **17**. Treatment of **16** with pyrrole in the presence of TFA afforded the dipyrromethane derivative **18** in 63% yield. The condensation of the latter with the aldehyde **17** in a mixture of CH_2Cl_2 and EtOH in the presence of TFA followed by oxidation using DDQ in THF in the presence of Et_3N afforded the desired porphyrin **19** in 12% yield. The formation of the dichloro Sn–porphyrin derivative **20** was achieved in quantitative yield upon treatment of **19** with $SnCl_2{\cdot}2H_2O$ in pyridine. The conversion of the dichloro compound **20** into the dihydroxo complex **21** was achieved in 83% yield using a solution of K_2CO_3 in CH_2Cl_2/MeOH (4 : 1). Finally, the condensation at room temperature of the metalloporphyrin **21** with either **14** or **15** in chloroform afforded compounds **1** and **2** in 91 and 90% yield respectively.

In solution, the structure and dynamics of **1** were investigated in CD_2Cl_2 at 25 °C by 2-D NMR experiments (COSY and ROESY) which allowed to assign all hydrogen atoms signals (Fig. 2). The free rotation of the handle around the O–Sn–O axis at room temperature was evidenced by the observation of a C_{2v} symmetry by ^{1}H-NMR. Indeed, a single set of signals corresponding to the H atoms of the two benzonitrile units (H_a and H_b, Fig. 3 bottom) was present. The same also holds for the anisole moiety (H_e, H_f, Fig. 3 bottom) and β-pyrrolic hydrogen atoms (H_c and H_d, Fig. 3 bottom).

Furthermore, the ROESY sequence at room temperature only showed the expected intra hinge (H_f and H_g) and intra handle (H_p, H_q and H_t) through space correlations (Fig. 4 left). This absence of correlation between the H atoms of the handle and those of the hinge is in favour of the rotation of the handle around the hinge.

The blockage of the rotational movement of the turnstile **1** through binding of Pd(II) was also investigated in solution by 2-D NMR studies. As in the case of compound **1**, for the palladium complex **2** all H atoms were assigned by COSY and ROESY sequences (Fig. 2). The ^{1}H-NMR investigation clearly demonstrated that the symmetry of compound **2** was lower (Fig. 3 top). Indeed, as expected, the number and multiplicity of signals corresponding to the anisole moiety (H_e and H_f) indicated that the two units were equivalent. In marked contrast, the number of signals corresponding to the two benzonitrile groups was doubled (H_a, $H_{a'}$, H_b and $H_{b'}$) indicating the non-equivalence of the two units. Furthermore, the number of signals corresponding to the β-pyrrolic H atoms has been also multiplied by two (H_c, $H_{c'}$, H_d and $H_{d'}$).

In order to prove that the monodentate benzonitrile group on the hinge and the tridentate site on the handle bind simultaneously Pd(II), ROESY experiments were performed on compound **2** (Fig. 4 right). As stated above, whereas for **1** no correlation could be observed between the hinge and the handle, for **2**, owing to the spatial proximity effects, several through space correlations were detected (Fig. 5). The most relevant ones are between $H_{a'}$ and H_p and H_q and between $H_{b'}$ and H_h and H_l. Finally, the result in solution by NMR was further confirmed by observation of a peak at 1558.29 by mass spectrometry (ESI-MS, M + H^+).

Owing to the high affinity of the dianionic tridentate coordinating site on the handle and the fact that the SnO

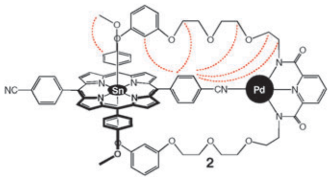


Fig. 5 Representation of the through space correlations (dotted lines) in **2** observed by ROESY experiments between the hinge and the handle.

bond is unstable in acidic media,[12b] the opening of the system was achieved using *p*-dimethylaminopyridine (DMAP) which is a much stronger ligand[13] than the benzonitrile moiety. Indeed, the addition of 1 eq. of DMAP to a CD_2Cl_2 solution of **2** was monitored by ^{1}H-NMR which revealed that: (i) h and i signals were still shifted upfield implying that the handle was coordinated to the porphyrin; (ii) r and s signals remained unchanged indicating that Pd(II) centre was still coordinated to the handle; (iii) the splitting of protons a, b, c and d was vanished implying a higher symmetry due to rotation resulting from the opening of the system; (iv) the two protons at the *ortho* positions of the pyridine moiety were downfield shifted indicating the binding of DMAP to Pd(II). Finally, ROESY studies at 25 °C revealed the disappearance of through space correlations between the handle and the porphyrin observed for **2** and the absence of new correlations. The above mentioned observations demonstrate that the addition of DMAP opens the system and restores the rotation (Fig. 1c).

The crystalline structure (Fig. 6) of **2** was determined by X-ray diffraction on single-crystal obtained upon slow diffusion of pentane into a CH_2Cl_2 solution of **2**.‡

The crystal (triclinic, $P\bar{1}$) is composed of the compound **2**, 2 CH_2Cl_2 and 4 H_2O molecules. The Sn atom is located almost at the centre of the four pyrrolic units with Sn–N distance in the range of 2.083–2.109 Å and NSnN angle in the range of 89.0°–90.8° (*cis*), 176.8°–177.2° (*trans*). The Sn(IV) cation is hexacoordinated by four N atoms of the porphyrin and two O atoms of the two resorcinol groups ($d_{\mathrm{Sn-O}}$ = 2.039 and 2.050 Å). The coordination geometry is a distorted octahedral with an OSnO angle of 175.3° and OSnN angles in the range 83.9 to 93.3°. The two differentiated benzonitrile groups (d_{CN} of 1.128 Å and 1.138 Å for the free and bound nitrile groups respectively) are tilted with respect to the porphyrin plane (CCCC dihedral angles −55.2° and 58.8° for PhCN–Pd and PhCN respectively). For the anisole groups the same trend is observed (CCCC dihedral angles of −66.6° and 73.2°). The Pd(II) is tetracoordinated and adopts a distorted square planar coordination geometry (NPdN angle in the range of 80.5°–99.9° (*cis*) and 162.0–176.7° (*trans*)). Its coordination sphere is composed of one N atom of one of the two benzonitrile groups of the hinge ($d_{\mathrm{CN-Pd}}$ = 2.003 Å) and three N atoms belonging to the tridentate coordinating pole of the handle ($d_{\mathrm{Pd-N}}$ = 2.040 Å and 2.051 Å and $d_{\mathrm{Pd-N(py)}}$ = 1.917 Å).

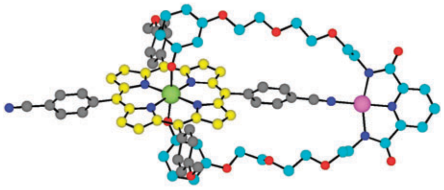


Fig. 6 X-Ray structure of the neutral turnstile (compound **2**) in the close position through the binding of Pd(II) by one of the two CN groups belonging to the hinge and the tridentate site of the handle. For sake of clarity the C atoms of the porphyrin ring and the handle are coloured in yellow and blue respectively. H atoms are omitted for clarity. For bond distances and angles see text.

In conclusion, compound **1** bearing two benzonitrile and two anisole groups on the hinge and a tridentate unit on the handle behaves as a molecular turnstile, *i.e.* free rotation of the handle around the hinge. The rotation may be blocked upon coordination of Pd(II) by the tridentate site on the handle and the monodentate sites on the hinge. The system may be unlocked upon addition of DMAP as competing ligand. The Pd complex **2** in its turn behaves as a turnstile bearing a stator and a rotor based on the Pd complex. Both systems may be seen as models of switch possessing two states (open and close). It seems interesting to design a turnstile offering one open and several close states. Work along these lines is currently under progress.

We thank the Université de Strasbourg, the International Centre for Frontier Research in Chemistry (FRC), Strasbourg, the Institut Universitaire de France, the Ministry of Education and Research and the CNRS for financial support.

Notes and references

‡ Crystallographic data for **2**: $C_{80}H_{75}Cl_2N_9O_{14}PdSn$, M = 1682.48, *triclinic*, $P\bar{1}$, a = 11.2051(7) Å, b = 15.7990(10) Å, c = 22.5004(15) Å, α = 99.048(2)°, β = 102.999(2)°, γ = 100.826(2)°, U = 3728.3(4) Å^3, Z = 2, μ = 0.720 mm^{-1}, reflns measured : 41 064, independent reflns: 16 696 [R(int) = 0.0811], final R indices [$I > 2\sigma(I)$]: R_1 = 0.0895, wR_2 = 0.2368, R indices (all data): R_1 = 0.1502, wR_2 = 0.2707, GOF on F^2: 1.059.

1 J. P. Sauvage, Molecular machines and motors, *Structure and Bonding*, Springer, Berlin, Heidelberg, 2001; V. Balzani, A. Credi, F. M. Raymo and J. F. Stoddart, *Angew. Chem., Int. Ed.*, 2000, **39**, 3348; V. Balzani, M. Venturi and A. Credi, *Molecular devices and machines: a journey into the nanoworld*, Wiley-VCH, Weinheim, 2003.
2 W. R. Browne and B. L. Feringa, *Nat. Nanotechnol.*, 2006, **1**, 25.
3 E. R. Kay, D. A. Leigh and F. Zerbetto, *Angew. Chem., Int. Ed.*, 2007, **46**, 72.
4 T. R. Kelly, *Molecular machines*, *Topics in Current Chemistry*, Springer, Berlin, Heidelberg, 2005, vol. 262.
5 C. A. Schalley, K. Beizai and F. Vögtle, *Acc. Chem. Res.*, 2001, **34**, 465.
6 S. Shinkai, M. Ikeda, A. Sugasaki and M. Takeuchi, *Acc. Chem. Res.*, 2001, **34**, 494.
7 G. S. Kottas, L. I. Clarke, D. Horinek and J. Michl, *Chem. Rev.*, 2005, **105**, 1281.
8 T. C. Bedard and J. S. Moore, *J. Am. Chem. Soc.*, 1995, **117**, 10662.
9 K. Skopek, M. C. Hershberger and J. A. Gladysz, *Coord. Chem. Rev.*, 2007, **251**, 1723; E. B. Bauer, F. Hampel and J. A. Gladysz, *Organometallics*, 2003, **22**, 5567.
10 A. Carella, J. Jaud, G. Rapenne and J.-P. Launay, *Chem. Commun.*, 2003, 2434; A. Carella, J.-P. Launay, R. Poteau and G. Rapenne, *Chem.–Eur. J.*, 2008, **14**, 8147.
11 N. Weibel, A. Mishchenko, T. Wandlowski, M. Neuburger, Y. Leroux and M. Mayor, *Eur. J. Org. Chem.*, 2009, 6140.
12 (*a*) A. Guenet, E. Graf, N. Kyritsakas, L. Allouche and M. W. Hosseini, *Chem. Commun.*, 2007, 2935; (*b*) A. Guenet, E. Graf, N. Kyritsakas and M. W. Hosseini, *Inorg. Chem.*, 2010, **49**, 1872.
13 R. Schneider, M. W. Hosseini, J.-M. Planeix, A. De Cian and J. Fischer, *Chem. Commun.*, 1998, 1625.