A molecular gate based on a porphyrin and a silver lock

Aurélie Guenet,[a] Ernest Graf,[a] Nathalie Kyritsakas,[a] Lionel Allouche[b] and Mir Wais Hosseini*[a]

Received (in Cambridge, UK) 1st May 2007, Accepted 4th June 2007
First published as an Advance Article on the web 20th June 2007
DOI: 10.1039/b706527b

A Sn(IV) metallaporphyrin bearing a 4-pyridyl group on one *meso* position and a handle equipped also with a pyridyl unit functions in solution as a molecular gate in the presence of silver cation: the complexation–decomplexation of Ag(I) corresponds to the opening and closing motions of the gate.

The design of molecular machines is a challenging task that has attracted considerable attention over the last fifteen years.[1–17] The primary objective is a strict control, both in terms of speed and amplitude, of the relative movements of different parts of a molecule. Thus, the design of molecules in which intramolecular motions may be controlled by external stimuli is a crucial step towards the elaboration of molecular rotors, motors and machines. With this in mind, we have undertaken the synthesis of a controllable molecular gate. Here, we report on our progress in this area.

The design of the molecular gate is based on a hinge bearing a coordination site oriented divergently from its centre and a rotatable handle equipped with a coordination site oriented towards the hinge (Fig. 1). In the absence of a metal ion to "lock" the coordination sites together, the handle should rotate freely about the hinge. Thus, without the metal ion, the gate would be "open" but in its presence, "closed". In such a system, the energy required for the closing of the gate is furnished by the favourable binding of the metal cation.

Realisation of the above mentioned design requires specification of the hinge and handle, the junction between the two parts, and the coordination sites. As a hinge with locking sites, the porphyrin backbone is particularly well suited. Up to 12 lock sites may be introduced through functionalisation with coordinating units at the *meso* and/or the β-pyrrolic positions. The axial binding sites of a metalloporphyrin may be used as the termini of an hinge to which a handle is connected. Our initial choice was the *meso* monopyridine porphyrin **2** (Scheme 1) bearing a single peripheral monodentate coordination site.[18] To impose a divergent orientation of the coordination site, a 4-pyridyl group was connected to the porphyrin. Sn(IV) was chosen as the central metal, since its high charge favours strong axial binding in its porphyrin complex.[19] Fragment **15** was designed as a handle, based on a central pyridine moiety connected to two triethylene glycol units each bearing a resorcinol terminus. To orient the nitrogen atom of the pyridine towards the porphyrin core, the two polyether arms were attached to positions 2,6. The choice of triethylene glycol connectors between the pyridine and resorcinol units was based on inspection of CPK models, which showed that binding, under basic conditions, of the free resorcinol phenoxo donors to the axial sites of the Sn(IV) porphyrin would allow rotation of the handle about the hinge. The 1,3 positioning of the resorcinol substituents is also dimensionally important. It is worth noting that Sn(IV) retains a strong Lewis acidity even when bound to a porphyrin dianion, and the coordination of two anionic donors to the axial sites of course leads to the neutral complex **1** (Fig. 2).

The synthesis of the compound **1** was achieved in 13 steps (Scheme 1). The detailed experimental procedures will be reported elsewhere. The starting material for the synthesis of the hinge part of **1** was 5,10,15-triphenyl-20-(4-pyridyl)porphyrin **2**. This was obtained in 5% yield following the described procedure.[18] Upon refluxing a mixture of the free porphyrin **2** and $SnCl_2{\cdot}2H_2O$ in pyridine, the dichloro complex **3** was obtained in 81% yield.[20] This was converted in 81% yield into the dihydroxo species **4** by treatment with K_2CO_3 in refluxing 4 : 1 THF–H_2O mixture.[20] For the synthesis of the handle, one of the starting materials was the monoprotected resorcinol **5**. Reaction under acidic conditions (trifluoroacetic acid) with dihydropyran in dry EtOAc gave **6** in 74% yield. Hydrolysis of **6** with NaOH in THF–H_2O gave **7** in 97% yield. Another starting material was triethylene glycol, which was transformed in 50% yield into its monoprotected derivative **8**

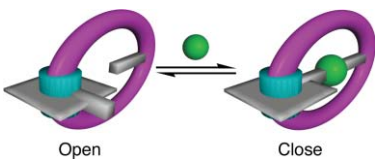
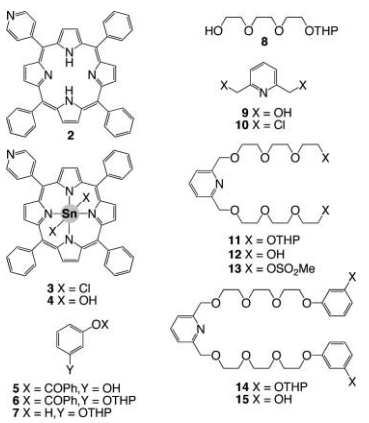


Fig. 1 Schematic representation of a molecular gate based on an hinge (square) and a handle each one bearing a coordination site. Whereas in the absence of the metallic effector (sphere) the gate is open (left), in its presence the closing of the gate takes place through the binding of the metal centre by both donor atoms.



Scheme 1

[a]*Laboratoire de Chimie de Coordination Organique, UMR CNRS 7140, 4, rue Blaise Pascal, F-67000, Strasbourg, France*
[b]*Service commun de RMN, Fédération de Recherche Chimie FR CNRS 2351, Université Louis Pasteur, Institut Le Bel, 4, rue Blaise Pascal, F-67000, Strasbourg, France. E-mail: hosseini@chimie.u-strasbg.fr*

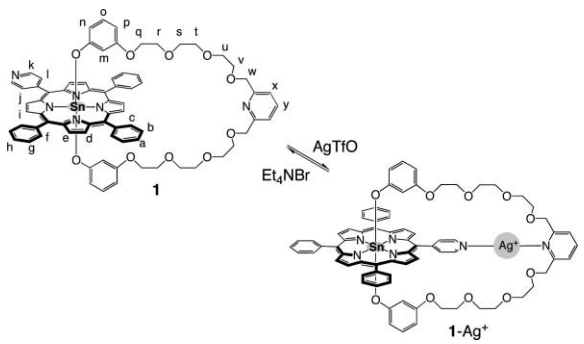


Fig. 2 A representation (top) of **1** showing the numbering of inequivalent H-atoms and (bottom) of the **1**–Ag^+ complex. The coordination of silver cation by the two pyridine units of **1** leads to the closing of the gate (**1**–Ag^+). The gate may be opened by addition of Et_4NBr.

by treatment at room temperature with dihydropyran in dry chloroform in the presence of pyridinium tosylate.[21] The third reactant was 2,6-bis(hydroxymethyl)pyridine **9**. Its chlorination to the dichloro derivative **10** was achieved in 88% yield upon treatment with thionyl chloride in dry THF.[22] Upon refluxing for 5 days a mixture of **10**, monoprotected triethylene glycol **8** and sodium hydride in dry THF the functionalised pyridine derivative **11** was obtained in 65% yield. Deprotection of **11** using methanol/aqueous HCl at room temperature gave **12** in 94% yield. **12** was transformed into the dimesylate derivative **13** by treatment at room temperature with methanesulfonyl chloride in dry THF and the reaction of **13** with the monoprotected resorcinol derivative **7** under reflux for 3 days in dry THF and in the presence of NaH gave **14** in 83% yield. The deprotected derivative **15** was obtained in 99% yield upon treatment of **14** at room temperature with methanol/aqueous HCl. Finally, the condensation at room temperature of the metallaporphyrin **4** with **15** in chloroform afforded **1** in 97% yield.

The solid state structure of **1** was determined by single-crystal X-ray diffraction. The lattice of the triclinic crystals contains only unsolvated molecules of **1** (Fig. 3). The porphyrin core is almost perfectly planar and the Sn atom is located almost at the centre of the four pyrrolic units (Sn–N *ca* 2.10 Å; NSnN *ca* 89.6° to 90.6° (*cis*), 179.0°–179.7° (*trans*)). The Sn(IV) cation is six-coordinated by four N atoms of the porphyrin and two O atoms of the two resorcinol groups (Sn–O *ca* 2.05 Å). The coordination geometry is essentially octahedral with an OSnO angle of 176.9° and OSnN angles in the range 87.2 to 92.2°. The four aromatic *meso* substituents are tilted with respect to the porphyrin plane (CCCC dihedral angles 53.5°, −60.6°, −65.0 and −72.9°). The pyridine group is disordered over four positions. One of the two triethylene glycol units is also disordered.

In solution, the structure of **1** was investigated in CD_3CN at 25 °C by 2-D NMR experiments which allowed assignment of all hydrogen (COSY and ROESY) and carbon atom (HSQC and HMBC) signals (Fig. 2). These studies also revealed free rotation of the handle around the O–Sn–O axis at room temperature.

The binding of Ag^+ cation by the ligand **1** was investigated in CD_3CN by ^{1}H-NMR. To aliquots of a solution of **1** in CH_2Cl_2, different amounts of silver triflate (AgOTf) in CH_3CN were added and the mixtures stirred at room temperature for 2 h. The solvents were evaporated, the residual purple solids dissolved in CD_3CN

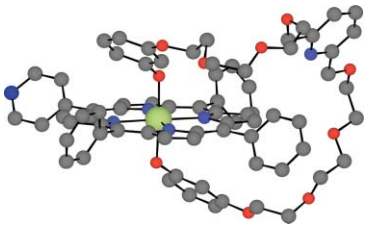


Fig. 3 The molecular unit found in the lattice of **1**. The 4-pyridyl *meso* substituent is disordered over all four possible positions and the location shown is arbitrarily chosen. A fragment of one of the two triethylene glycol units was also found to be disordered. H atoms are omitted for the sake of clarity. For bond distances and angles, see text.†

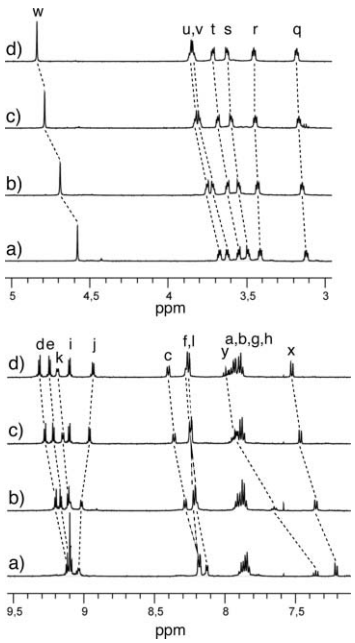


Fig. 4 Portions of the ^{1}H-NMR spectra (500 MHz, CD_3CN, 25 °C) and assignment of signals between 3–5 (top) and 7.1–9.5 ppm (bottom) in the presence of 0 (a), 0.5 (b), 1.0 (c) and 3.0 (d) equivalents of silver triflate. For attribution of H-atoms see Fig. 2.

and their ^{1}H-NMR (500 MHz, 25 °C, mM concentration) spectra recorded. The results are presented in Fig. 4.

The complexation of **1** by Ag^+ caused substantial downfield shifts of proton signals belonging to both pyridine units (H_k, H_l, H_x and H_y) and those located in their proximity (H_u, H_v and H_w). Furthermore, the signals corresponding to the β-pyrrolic protons (H_e, H_d, H_i, H_j) were also shifted. The spectrum obtained in the presence of 0.5 equivalent of AgOTf clearly demonstrated that the binding process was rapid on the NMR time scale, with only a single set of signals being observed, implying fast exchange. A gradual shift of the signals occurred for the Ag^+ : **1** ratio in the range of 0–1. Further addition of Ag^+ cation (2–3 equivalents) had almost no effect (Fig. 4). The plot of the observed shift ($\Delta\delta$) *versus* equivalents of Ag^+ cation added (Fig. 5) clearly demonstrated a 1 : 1 stoichiometry for the complex. This was further confirmed by mass spectrometry (ESI-MS peak at 1425.4). From these data, a stability constant K_s of *ca* 5700 mol L^{-1}, corresponding to a ΔG of *ca* −21.4 kJ mol^{-1}, was estimated.

In order to prove that the two pyridine units of the hinge and the handle simultaneously bind to Ag(I), ROESY experiments

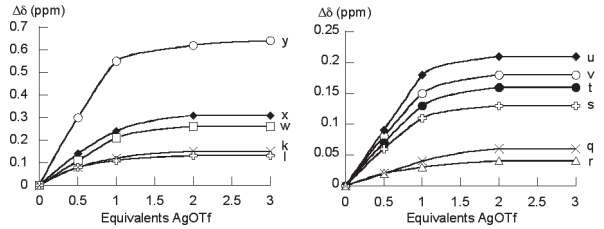


Fig. 5 Plots of $\Delta\delta$(ppm) of selected ^{1}H-NMR signals (500 MHz, CD_3CN, 25 °C) *versus* equivalents of silver triflate added (signals between 3–5 (top) and 7.1–9.5 ppm (bottom)) For attribution of H-atoms see Fig. 2.

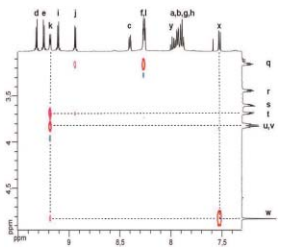


Fig. 6 A portion of the 2-D ROESY correlation.

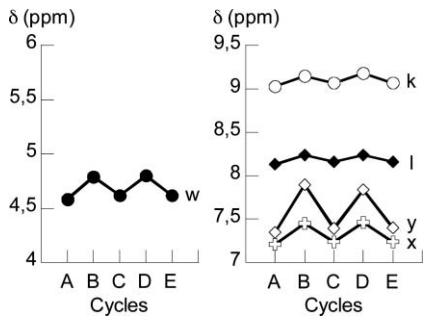


Fig. 7 Chemical shifts (500 MHz, CD_3CN, 25 °C) of selected H atoms (for attribution of H-atoms see Fig. 2) in the absence (A) and in the presence of added silver triflate (B, D) and Et_4NBr (C, E). For description of the experiment see text.

were performed on both free ligand **1** and its silver complex, **1**–Ag^+. Whereas for **1** no correlation could be observed between H_k and H_w protons because of the fast rotation of the handle around the O–Sn–O axis, for **1**–Ag^+, such a correlation was indeed observed, implying the spatial proximity of the two sites (Fig. 6).

Finally, the reversibility of the closing and opening of the gate was demonstrated using ^{1}H-NMR by adding Et_4NBr to the **1**–Ag^+ complex (Fig. 7). As stated above, upon addition of 1 equivalent of Ag^+ cation, considerable shifts of some of the signals were observed. The addition of 1 equivalent of Et_4NBr, resulting in precipitation of AgBr, leads to the spectrum corresponding to that of the free ligand **1**. This process, *i.e.* addition of AgOTf causing the closing of the gate and addition of Et_4NBr responsible for its opening, was repeated several times and produced the same results. This experiment is significant since it demonstrates that the gate may be opened and closed in a reversible manner by external chemical stimuli.

In conclusion, the Sn metallaporphyrin **1** bearing two pyridine units, one on the hinge and the other on the handle behaves as a molecular gate controlled by the locking action of Ag(I). The opening and closing of the gate is based on complexation/decomplexation processes and can be determined by external chemical stimuli (addition of Ag^+ and Br^- respectively). The system presented here, which may also be considered as a molecular switch, is rather primitive since it is based on only two coordination sites. However, it is one first step towards the design of molecular machines and motors. By increasing the number of divergent binding sites attached to the hinge, systems for which the handle would travel from station to station, producing a system more akin to an electric motor, can be envisaged. Related systems based on the presence and absence of protons are also possible. Work along these lines is currently in progress.

Université Louis Pasteur, Institut Universitaire de France, the CNRS and the Ministry of Education and Research are acknowledged for financial support and for a scholarship to A. G.

Notes and references

† Data were collected at 173(2) K on a Bruker SMART CCD Diffractometer equipped with an Oxford Cryosystem liquid N_2 device, using graphite-monochromated Mo-Kα (λ = 0.71073) radiation. For the structure, diffraction data were corrected for absorption and structural determination was achieved using SHELEXL-97. All hydrogen atoms have been calculated except those connected to disordered atoms. *Crystallographic data for* **1** (purple) $C_{74}H_{66}N_6O_{10}Sn$, M = 1318.02, triclinic, a = 10.6530(6), b = 14.5219(9), c = 22.1502(13) Å, α = 74.790(9)°, β = 80.042(8)°, γ = 70.823(9)°, U = 3109.0(4) Å^3, D_{calc} = 1.408 g cm^{-3}, space group $P\bar{1}$, Z = 2, refls measured: 36623, independent refls: 14084, Final R indices [$I > 2\sigma(I)$]: R_1 = 0.080, wR_2 = 0.1998, GOF = 1.034. CCDC 631306. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b706527b

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