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Strapped-Porphyrin-Based Molecular Turnstiles

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Abstract: The synthesis of a series of molecular turnstiles that contained both H-bond-donor and -acceptor sites was achieved. Their structures were based on tetra-aryl X_2Sn^{IV} porphyrins (X = Cl or OH) as H-bond-acceptor sites that were equipped with a rotor that contained a pyridyldiamide moiety as a H-bond donor. In the solution phase, 1D and 2D NMR spectroscopic analysis showed that switching between the closed state, which resulted from the formation of intramolecular H-bonds, and the open state of the turnstile was achieved by using external H-bond-acceptor molecules, such as DMSO. The solid-state structure of the closed state of the turnstile was established by single-crystal X-ray diffraction.

Keywords: hydrogen bonds · molecular turnstiles · NMR spectroscopy · porphyrins · X-ray diffraction

Introduction

Controlling movement in molecular systems is a matter of much current interest.[1–8] Among several approaches that have been reported, the two that were based on rotaxanes[9] and on catenanes[10] are particularly inspiring. Elegant examples of molecular motors that were based on thermal[11] or photochemical[12] processes have been reported, whilst the design of molecular cars,[13] wheelbarrows,[14] and turnstiles[15] have also been published. We have previously reported the synthesis of molecular gates[16] and turnstiles,[17] which were based on Sn-porphyrin, derivatives that were composed of a stator, a hinge, and a rotor.

Herein, we report the design and synthesis of strapped-porphyrin-based molecular turnstiles in their closed (Figure 1b) and open states (Figure 1c) and the study of their dynamics by using NMR spectroscopy.

A molecular turnstile may be defined as a two-component system that is composed of a stator and a rotor as static and mobile parts, respectively, that display intramolecular rotational movement. Such movement is relative and thus one may exchange the values of the two parts. For this type of dynamic systems, the control of 1) movement and 2) direction are important considerations. For this first feature, imposing open and closed states with the possibility of switching between the two is of interest. The second aspect, that is, control of the direction of the rotary movement, is rather challenging and will not be discussed herein. To afford a system that contains two distinct open and closed states, it is compulsory to introduce specific reversible interactions, such as H bonds or coordinate bonds between the stator and the rotor.

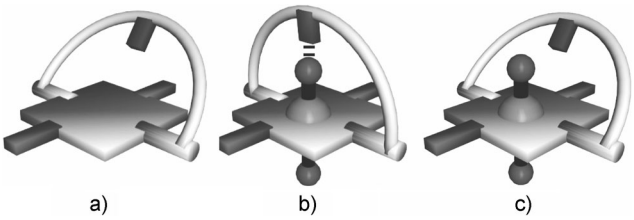

Figure 1. A strapped porphyrin (a) and a turnstile that contains both H-bond-donor and -acceptor sites in its closed (b) and open states (c).

Results and Discussion

Design of the system: For the design of molecular turnstiles, the porphyrin backbone was a particularly interesting stator for the following reasons: 1) by using two opposite *meso* positions, one may connect the rotor through robust covalent bonds, thereby generating a strapped porphyrin[18] (Figure 1a); 2) by using the tetra-aza core, one may introduce metal cations or metal complexes (Figure 1b) and thus set up interactions between the stator and the rotor; 3) by using the remaining two *meso* positions, one may equip the stator with other interaction sites; 4) one may introduce a variety of substituents onto the β-pyrrolic positions.

Turnstiles **2** and **3** (Figure 2) were based on a *meso*-tetraarylporphyrin backbone that contained two benzonitrile units on opposite *meso* positions and a rotor that was con-

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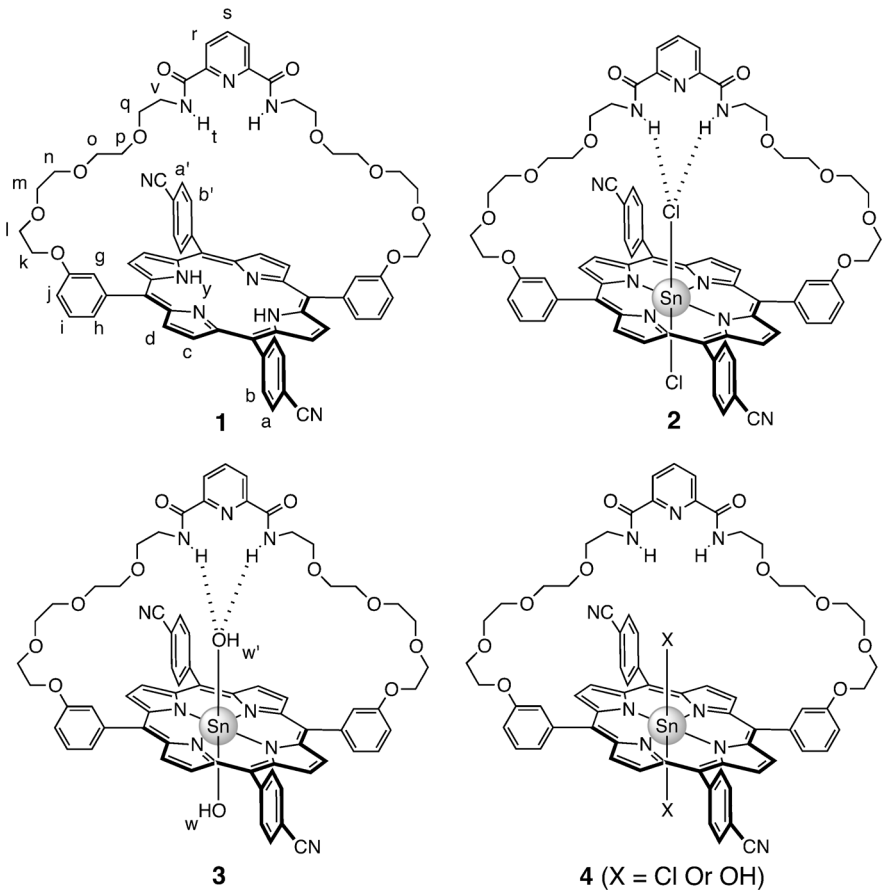
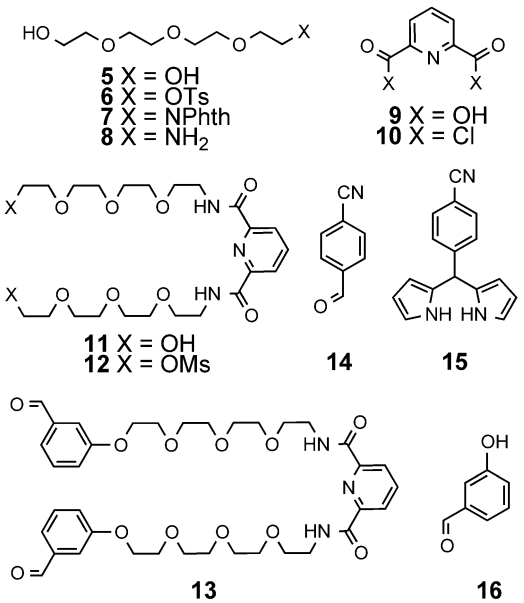


Figure 2. Strapped porphyrins in their open (compounds **1** and **4**) and closed states (compounds **2** and **3**), together with the assignment of the H atoms.

nected to the porphyrin through ether junctions by using the remaining two *meso* positions. The two benzonitrile groups were introduced for other purposes and their presence didn't interfere with the process described herein. The rotor was symmetrical and was based on a 2,6-pyridyldiamide moiety as a double-H-bond-donor site that was connected to two tetraethyleneglycol spacers (Figure 2). To set up a hydrogen-bond-acceptor site, an X_2Sn^{IV} moiety was introduced within the tetra-aza core of the porphyrin, thereby affording turnstiles **2** (X = Cl) and **3** (X = OH). For both compounds, the closed and open states (**4**, X = Cl or X = OH) were studied in solution by using 1D and 2D NMR spectroscopy.

Synthesis of strapped porphyrins: Our synthetic strategy for the preparation of strapped porphyrin **1** was based on the condensation of dialdehyde **13** with functionalized dipyrromethane **15**[19] (Scheme 1). The starting material for the synthesis of compound **13** was tetraethyleneglycol **5**, which was transformed into its monotosylate derivative (**6**)[20] in 43% yield upon treatment with TsCl in CH_3CN in the presence of triethylamine. The condensation of compound **6** with potassium phthalimide at 110°C in DMF afforded compound **7** in 73% yield, which was subsequently transformed into amino-derivative **8**[21] in 90% yield by hydrazinolysis in the presence of hydrazine. Moreover, a pyridine diacid derivative (**9**) was converted into its acyl chloride derivative (**10**)[22] upon treatment with $SOCl_2$ in 96% yield. Condensation of compound **10** with compound **8** in the presence of triethylamine afforded α,ω-diol **11**[23] in 96% yield. The activation of the diol into its dimesylate derivative (**12**) was achieved in 92% yield upon treatment with MsCl. The desired compound (**13**) was obtained in 62% yield upon condensation of dimesylate **12** with 3-hydroxybenzaldehyde (**16**) in the presence of potassium carbonate in refluxing CH_3CN. Dipyrromethane derivative **15** was obtained from the reaction of aldehyde **14** with pyrrole in the presence of trifluoroacetic acid (TFA) in 63% yield. Finally, condensation of dialdehyde **13** with dipyrromethane derivative **15** in the presence of TFA in CH_2Cl_2/EtOH, followed by oxidation with DDQ[24] in THF, afforded the desired strapped porphyrin (**1**) in 9% yield. The formation of dichlorotin(IV) complex **2** was achieved in 57% yield by treatment of compound **1** with $SnCl_2{\cdot}2H_2O$ in pyridine.[25] Compound **1** was also converted into its dihy-



Scheme 1. Intermediates used in the synthesis of compound **1**.

droxy derivative (**3**) in 37% yield upon treatment with potassium carbonate in CH_2Cl_2/MeOH followed by hydrolysis on alumina.[26]

Structure and behavior of the strapped porphyrins: The structure of compounds **1–3** was investigated in solution in CD_2Cl_2, CD_2Cl_2/[D_6]DMSO (9:1), and in pure [D_6]DMSO by using NMR spectroscopy. All hydrogen atoms were assigned by using 1D and 2D NMR techniques, such as COSY and ROESY, at 20°C (Figure 2).

At 25°C, the ^{1}H NMR spectrum of strapped porphyrin **1** in CD_2Cl_2 (Figure 3a) showed the presence of four doublets, Ha, Ha′ and Hb, Hb′ (Figure 2), owing to the splitting

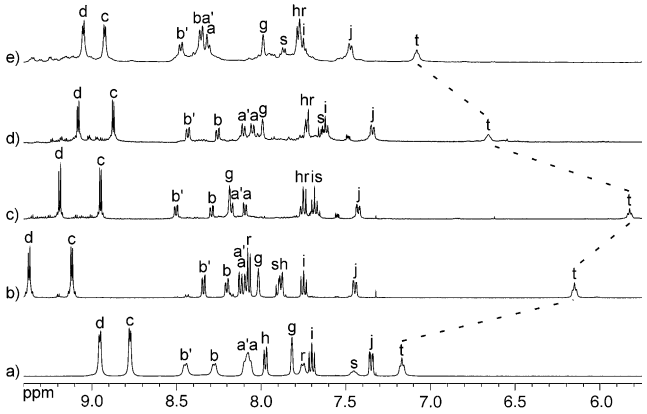


Figure 3. ^{1}H NMR spectra (500 MHz, 25°C) of compounds **1** (a), **2** (b), and **3** (c) in CD_2Cl_2 in the range $\delta = 5.75$–9.45 ppm. ^{1}H NMR spectra of compound **3** in CD_2Cl_2/[D_6]DMSO (9:1) (d) and pure [D_6]DMSO (e). For assignment of the H atoms, see Figure 2. The upfield shift of the NH signal (t) was due to the shielding effect of the porphyrin ring.

of the H atoms on the benzonitrile moiety. Furthermore, these signals appeared to be rather broad, thereby implying a dynamic process. To investigate this process, we performed a variable-temperature study in [D_6]DMSO in the range 25–100°C (Figure 4).

We found that, upon heating the solution in [D_6]DMSO, only two sharp doublets were observed, which corresponded to protons Ha and Hb. The coalescence temperature for proton Hb was about 55°C, which corresponded to a rotation rate of about 153 Hz, and an activation energy of about 67 kJ.

At room temperature, the 2D ROESY sequence only revealed correlations between H atoms that were in close spatial proximity to one another owing to the connectivity pattern of the molecule (Figure 5a).

As expected from the design of dichloro-tin-strapped-porphyrin **2**, the simultaneous presence of the pyridyldiamide moiety on the handle, as a double-H-bond donor, and chloride anions, which were coordinated onto the Sn^{IV} cation that was located in the center of the porphyrin backbone, as H-bond acceptors led to the formation of CONH···Cl-type H bonds, thereby affording the closed state of the turnstile.

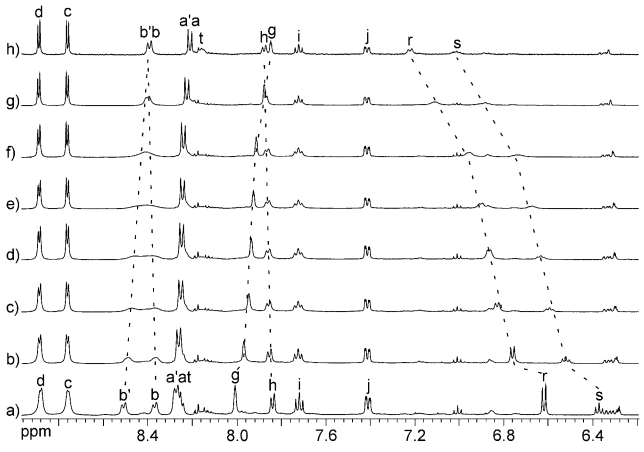


Figure 4. Region of the ^{1}H NMR spectra (500 MHz, [D_6]DMSO) of compound **1** at 25 (a), 40 (b), 45 (c), 50 (d), 55 (e), 60 (f), 80 (g), and 100°C (h).

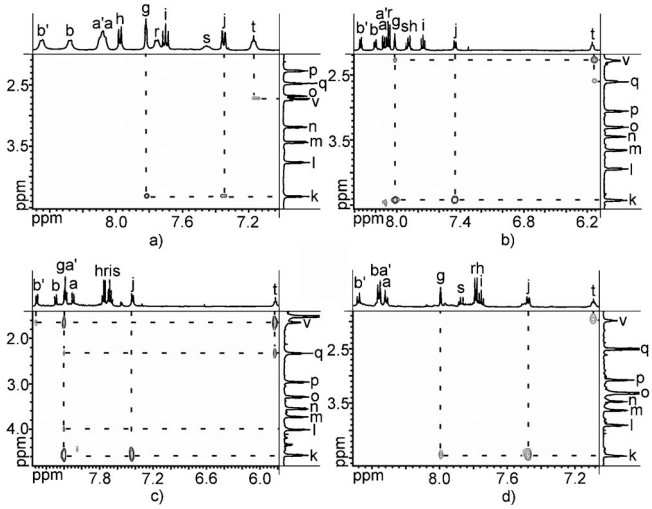


Figure 5. Region of the 2D ROESY correlations for compounds **1** (a), **2** (b), and **3** (c) in CD_2Cl_2. d) Region of the 2D ROESY correlations for compound **3** in [D_6]DMSO. For the assignment of the H atoms, see Figure 2.

The establishment of the H-bonds, which conserved the C_{2v} symmetry of the molecule, led to several characteristic features. As expected, the ^{1}H NMR spectrum (Figure 3b) showed that the locking process led to a narrowing of the signals that corresponded to the Ha, Ha′, Hb, and Hb′ protons. Furthermore, with respect to parent compound **1**, a significant upfield shift of about $\delta = 1.03$ ppm was observed for the NH (Ht) protons, as well as the reorganization of protons Hp, Hq, and Hv on the ethyleneglycol spacer. In addition, 2D ROESY measurements (CD_2Cl_2, 25°C) revealed new correlations (Figure 5b) between the Hg protons of the *meso*-phenyl groups and the Hv atoms that were located on the handle at the α position of the amide groups (for atom labeling, see Figure 2).

The unlocking process that afforded the open state of turnstile **2** (compound **4**, X = Cl; Figure 2) was achieved by

using DMSO[27] as a H-bond-acceptor competitor. The process was monitored by ^{1}H NMR spectroscopy (Figure 6).

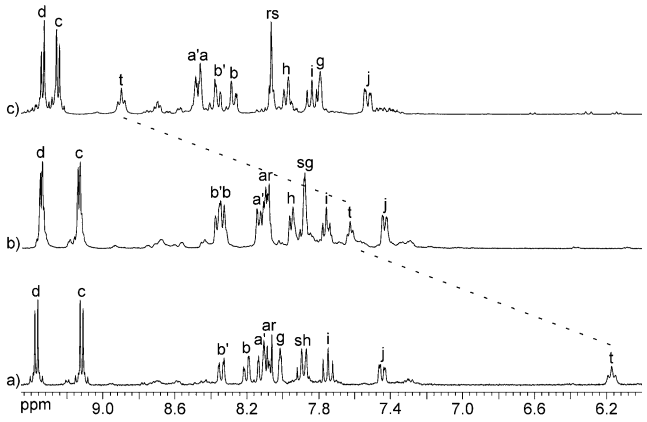


Figure 6. ^{1}H NMR spectra (500 MHz, 25 °C) of compound **2** in CD_2Cl_2 (a), CD_2Cl_2/[D_6]DMSO (9:1) (b), and [D_6]DMSO (c).

Indeed, by taking the ^{1}H NMR spectrum of turnstile **2** in CD_2Cl_2 as a reference (Figure 6a), the addition of 10% [D_6]DMSO caused a significant downfield shift of about $\delta =$ 1.46 ppm of the Ht protons of the CONH group (Figure 6b). In pure [D_6]DMSO (Figure 6c), a downfield shift of about $\delta = 2.73$ ppm was observed for the same protons.

At 25 °C, as for the parent strapped porphyrin (**1**), the observation of four doublets Ha, Ha′ and Hb, Hb′ in [D_6]DMSO (Figure 2) for the H atoms of the benzonitrile moiety of compound **2** indicated a dynamic rotational process. Again, this process was investigated by variable-temperature ^{1}H NMR spectroscopy in the range 25–100 °C (Figure 7). We found that, upon heating the solution, only two doublets, which corresponded to protons Ha and Hb, were observed. The coalescence temperature for proton Hb was about 85 °C, which corresponded to a rotation rate of about 96 Hz and an activation energy of about 75 kJ.

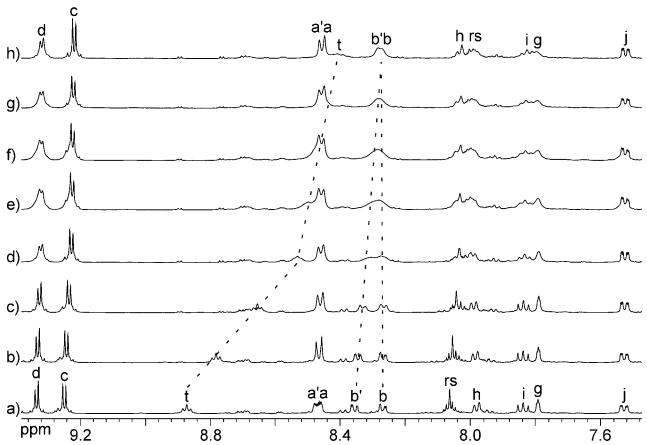


Figure 7. Region of the ^{1}H NMR spectra (500 MHz, [D_6]DMSO) of compound **2** at 25 (a), 40 (b), 60 (c), 80 (d), 85 (e), 90 (f), 95 (g), and 100 °C (h).

For turnstile **2**, the locking process through the formation of H bonds between the stator and the handle that had been observed in CD_2Cl_2 was further confirmed in the crystalline phase by using X-ray diffraction on a single crystal that was obtained by slow diffusion of pentane into a solution of compound **2** in CH_2Cl_2. Owing to the presence of disordered solvent molecules, the structure (Figure 8) was solved by using the SQUEEZE command.[28]

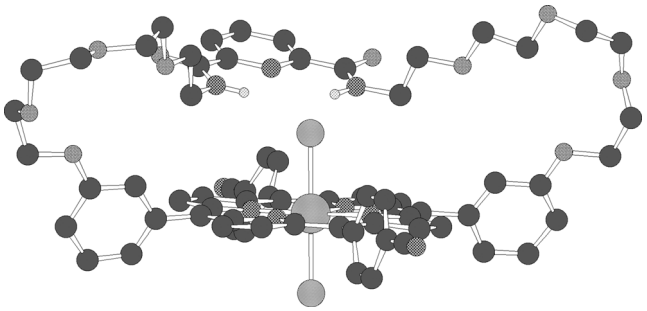


Figure 8. Solid-state structure of turnstile **2**; hydrogen atoms are omitted for clarity except for the two NH atoms that were involved in H-bonding interactions.

This single crystal (monoclinic; space group: *C2/c*) was composed of compound **2** and disordered solvent molecules. The Sn^{IV} atom was hexacoordinated and almost located at the center of the porphyrin core, with Sn–N distances of $\delta =$ 2.067–2.124 Å with no distortion of the planarity of the porphyrin backbone. The remaining two apical positions on the Sn^{IV} center were occupied by two chloride atoms with Sn–Cl distances of $\delta = 2.480$ and 2.452 Å. The coordination geometry around the metal center was almost octahedral, with N-Sn-N, N-Sn-Cl, and Cl-Sn-Cl angles of 177.9–178.9° (N-Sn-N_{trans}), 89.5–90.5° (N-Sn-N_{cis}), 89.1–91.2°, and 178.9° respectively. The *meso* aryl substituents were tilted with respect to the porphyrin plane, with CCCC dihedral angles of −70.2° and 68.7° for the two phenyl moieties and −75.6° and 66.9° for the benzonitrile groups. One of the two chloride anions that were oriented towards the handle formed weak hydrogen bonds with CONH groups with a NH···Cl distance in the range 2.68–2.65 Å and N-H-Cl angles in the range 147.6–149.4°.

Upon replacement of the two Cl atoms by OH groups to afford turnstile **3** with *C2v* symmetry, as was the case for compound **2**, the closed state that resulted from the formation of CONH···OH H bonds in CD_2Cl_2 was again confirmed by both 1D and 2D NMR spectroscopy. Indeed, a significant upfield shift of about $\delta = 1.29$ ppm was observed for the Ht signal (Figure 3c), along with reorganization of the ethyleneglycol spacer (changes in the Hp, Hq and Hv signals when compared to compounds **1** and **2**).

As expected and, as observed for turnstile **2**, the 2D ROESY investigation (Figure 5c) in CD_2Cl_2 at room temperature revealed new correlations between the Hg protons of the *meso*-phenyl groups and the Hv atoms of the handle

(for atom labeling, see Figure 2). Furthermore, the two OH groups that occupied the apical positions on the Sn^{IV} center afforded two distinct signals at about $\delta = -7.51$ and -6.49 ppm, which corresponded to the hydroxy groups that pointed away from (Hw) and towards the handle (Hw′), respectively (Figure 9a). The 2D ROESY study showed a correlation between the Hw′ and Ht atoms (Figure 9a), thereby further confirming the presence of the H bond between the OH and CONH groups.

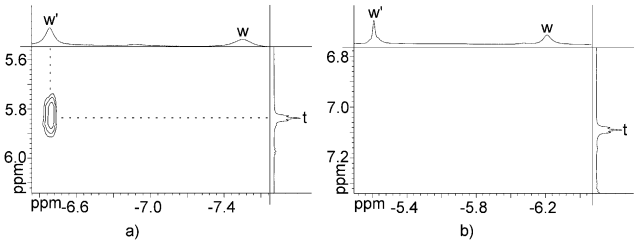


Figure 9. 2D ROESY correlations in the region of OH groups H_w and $H_{w'}$ for compound **3** in CD_2Cl_2 (a), and for compound **4** (OH) in [D_6]DMSO (b). For the assignment of the H atoms, see Figure 2.

Again, unlocking turnstile **3** by the addition of [D_6]DMSO led to its open state (**4**, X = OH; Figure 2). First, the behavior of turnstile **3** was studied by ^{1}H NMR spectroscopy at 25 °C in CD_2Cl_2/[D_6]DMSO (9:1; Figure 3d). As observed for compound **2**, sharp signals were observed in the ^{1}H NMR spectrum. When compared to compound **3**, a downfield shift of the Ht signal of about $\delta = 0.79$ ppm was observed, thereby implying the rupture of the H bond between the NH and OH groups (Figure 3d); the same trend was also observed in pure [D_6]DMSO (Figure 3e). The Ht signal at $\delta = 7.09$ ppm, which corresponded to the CONH amide group, was even more downfield shifted. 2D ROESY analysis (Figure 5d) showed the disappearance of the correlation between the Hg and Hv atoms that was observed for turnstile **3** in its closed state. Interestingly, the 2D ROESY investigation also revealed that the correlation between the Hw′ and Ht atoms (Figure 9a) for compound **3** disappeared in [D_6]DMSO (Figure 9b), thus indicating the unlocking of the movement.

Interestingly, at 25 °C, the splitting of the Ha and Hb atoms into four doublets (Ha, Ha′ and Hb, Hb′) for the open state of turnstile **2** and its closed state (**4**, X = Cl) in CD_2Cl_2 and in [D_6]DMSO, respectively, was also observed for compounds **3** and **4** (X = OH). Furthermore, in [D_6]DMSO, the two OH groups also remained differentiated owing to the slow rotational movement of the handle on the NMR timescale. To investigate the dynamics of this process, variable-temperature ^{1}H NMR spectroscopy in the range 25–105 °C was performed on compound **3** in [D_6]DMSO (Figure 10).

The increase in temperature led to coalescence of the signals that corresponded to benzonitrile protons Ha and Ha′ and Hb and Hb′ (Figure 10 left), as well as of hydroxy protons Hw and Hw′ (Figure 10 right).

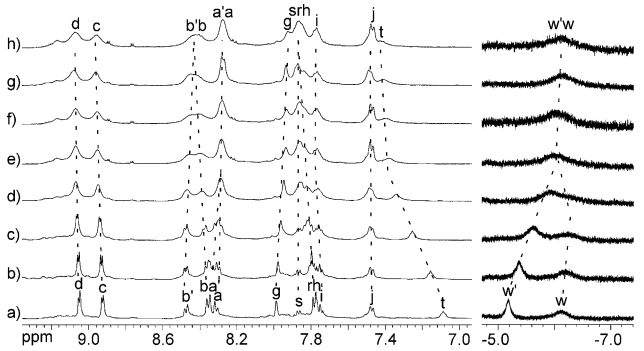


Figure 10. Region of the ^{1}H NMR spectra ([D_6]DMSO, 500 MHz) of compound **3** at 25 (a), 40 (b), 60 (c), 80 (d), 90 (e), 95 (f), 100 (g), and 105 °C (h). For assignment of the H atoms, see Figure 2.

From the coalescence temperature of about 100 °C, a rotation rate of about 133 Hz and an activation energy of about 76 kJ were calculated.

Conclusion

We have synthesized a series of molecular turnstiles that contained both H-bond-donor and -acceptor sites. The design was based on tetra-aryl X_2Sn^{IV} porphyrins (X = Cl or OH) as H-bond acceptor sites that were equipped with a rotor that contained a pyridyldiamide moiety as a H-bond donor. The linkage of these two parts was achieved through covalent bonds on the two opposite *meso* positions on the porphyrin backbone. By using 1D and 2D NMR techniques, we showed that switching between the closed state, which was due to the formation of intramolecular H-bonds, and the open state of the turnstile could be achieved by using external H-bond-acceptor molecules, such as DMSO. The formation of turnstiles by using metal cations to lock the rotation of the rotor around the stator, based on the same design principles, is currently under investigation.

Experimental Section

General: CH_3CN and DMF were dried over molecular sieves; THF and triethylamine were distilled over sodium and KOH, respectively. Analytical grade CH_2Cl_2, EtOH, MeOH, and pyridine were used without further purification. ^{1}H- and ^{13}C NMR spectra were acquired at 25 °C on either Bruker AV 300, Brucker AV 400, Brucker AV 500, or Brucker AV 600 spectrometers with deuterated solvent to lock the spectra and residual solvent as the internal reference. Absorption spectra were recorded on an Uvikon XL spectrophotometer. IR spectra were recorded on a FTIR-8400S ATR, Pike miracle germanium. MS was performed by the Service de Spectrometrie de Masse, University of Strasbourg.

X-ray crystal-structure analysis: Data were collected on a Bruker APEX8 CCD Diffractometer that was equipped with an Oxford Cryosystem liquid-N_2 device at 173(2) K by using a molybdenum microfocus sealed-tube generator with mirror-monochromated $Mo_{K\alpha}$ radiation (λ = 0.71073 Å) operated at 50 kV/600 mA. The structure was solved by using SHELXS-97 and refined by full-matrix least-squares on F^2 by using SHELXL-97 with anisotropic thermal parameters for all non-hydrogen atoms.[29] The hydrogen atoms were introduced at calculated positions

and not refined (riding model). Owing to the presence of disordered solvent molecules, the SQUEEZE[28] command was used.

Crystallographic data for strapped porphyrin 2: $C_{69}H_{61}Cl_2N_9O_{10}Sn$; $M_w = 1365.86$; monoclinic; space group: $C2/c$; $a = 63.9066(17)$, $b = 10.1342(3)$, $c = 25.7502(8)$ Å; $\beta = 105.579(2)°$; $U = 16064.2(8)$ Å^3; $Z = 8$; $\mu = 0.438$ mm^{-1}; total reflns: 72794; unique reflns: 19772 [R(int) = 0.0648]; final R indices [$I > 2\sigma(I)$]: $R_1 = 0.1138$; $wR_2 = 0.3093$; R indices (all data): $R_1 = 0.1737$; $wR_2 = 0.3159$; GOF on F^2: 1.319. CCDC-867898 (**2**) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis: Compounds **6**,[20b] **10**,[22] and **15**[19] were prepared according to literature procedures.

Compound 1: Compound **13** (650 mg, 896 μmol, 1 equiv) and compound **15** (443 mg, 1.8 mmol, 2 equiv) were dissolved under an argon atmosphere in CH_2Cl_2/EtOH (95:5, 100 mL) in a 250 mL dry two-necked round-bottomed flask. In the dark, TFA (200 μL, 2.7 mmol, 3 equiv) was added and the reaction mixture was stirred at RT for 2 days. First, triethylamine was added to neutralize any excess TFA; then, a solution of DDQ (610 mg, 2.7 mmol, 3 equiv) in THF (20 mL) was added and the mixture was stirred overnight. After evaporation under reduced pressure, the crude product was purified by column chromatography on silica gel (CH_2Cl_2 to CH_2Cl_2/MeOH, 95:5) to yield compound **1** (100 mg, 9%) as a purple powder.

^{1}H NMR (CD_2Cl_2, 400 MHz): $\delta = -2.92$ (br s, 2H; NH), 2.29 (m, 4H; OCH_{2p}), 2.48 (t, 4H, $^3J = 6.0$ Hz; OCH_{2q}), 2.69 (m, 4H; OCH_{2o}), 2.73 (q, 4H, $^3J = 6.0$ Hz; NCH_{2v}), 3.18 (m, 4H; OCH_{2n}), 3.44 (m; OCH_{2m}), 3.76 (m, 4H; OCH_{2l}), 4.31 (m, 4H; OCH_{2k}), 7.16 (m, 2H; NH_t), 7.35 (dd, 2H, $^3J = 8.5$ Hz, $^4J = 2.0$ Hz; Ar_j), 7.45 (m, 1H; Py_s), 7.70 (t, 2H, $^3J = 8.0$ Hz; Ar_i), 7.75 (d, 2H, $^3J = 8.0$ Hz; Py_r), 7.81 (br s, 2H; Ar_g), 7.98 (d, 2H, $^3J = 7.5$ Hz; Ar_h), 8.08 (m, 4H; $Ar_{aa'}$), 8.28 (m, 2H; Ar_b), 8.45 (m, 2H; $Ar_{b'}$), 8.78 (d, 4H, $^3J = 5.0$ Hz; β-pyr_c), 8.95 ppm (d, 4H, $^3J = 5.0$ Hz; β-pyr_d); ^{13}C NMR (CD_2Cl_2, 100 MHz): $\delta = 38.5$, 68.4, 68.7, 69.2, 69.9, 70.2, 70.3, 70.9, 115.3, 122.6, 124.2, 127.3, 128.0, 131.1, 132.3, 135.4, 138.4, 148.5, 157.9, 163.2; IR (ATR): 2228 (CN), 1674 cm^{-1} (CO amide); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 418 (5.6), 516 (4.3), 550 (3.9), 589 (3.8), 646 nm (3.6 mol^{-1} dm^3 cm^{-1}); MS (MALDI-TOF): m/z calcd for $C_{69}H_{63}N_9O_{10}$: 1178.478 [M+H]$^+$; found: 1178.481.

Compound 2: In a 50 mL round-bottom flask, compound **1** (30 mg, 25 μmol, 1 equiv) and $SnCl_2{\cdot}2H_2O$ (23 mg, 100 μmol, 4 equiv) were dissolved in pyridine (15 mL) and the solution was refluxed overnight. The solvent was removed under vacuum and the residue was filtered over celite and the latter was washed with CH_2Cl_2. Removal of the solvent afforded the compound **2** (20 mg, 57%) as a purple solid.

^{1}H NMR (CD_2Cl_2, 400 MHz): $\delta = 2.28$ (br s, 4H; NCH_{2v}), 2.60 (br s, 4H; OCH_{2q}), 3.05 (br s, 4H; OCH_{2p}), 3.31 (br s, 4H; OCH_{2o}), 3.45 (br s, 4H; OCH_{2n}), 3.65 (br s; OCH_{2m}), 3.94 (br s, 4H; OCH_{2l}), 4.42 (br s, 4H; OCH_{2k}), 6.13 (br s, 2H; NH_t), 7.45 (d, 2H, $^3J = 8.0$ Hz; Ar_j), 7.75 (t, 2H, $^3J = 8.0$ Hz; Ar_i), 7.89 (m, 3H; Ar_h, Py_s), 8.02 (br s, 2H; Ar_g), 8.06 (d, 2H, $^3J = 7.5$ Hz; Py_r), 8.12 (d, 4H, $^3J = 7.5$ Hz; $Ar_{aa'}$), 8.21 (m, 2H; Ar_b), 8.34 (m, 2H; $Ar_{b'}$), 9.12 (d, 4H, $^3J = 5.0$ Hz; β-pyr_c), 9.37 ppm (d, 4H, $^3J = 5.0$ Hz; β-pyr_d); ^{13}C NMR (CD_2Cl_2, 100 MHz): $\delta = 38.1$, 68.4, 68.8, 69.9, 70.1, 70.5, 71.3, 113.2, 115.3, 118.7, 122.9, 124.7, 128.5, 131.4, 132.4, 133.9, 135.3, 135.9, 138.8, 141.3, 144.8, 145.8, 146.8, 148.5, 158.0, 162.8 ppm; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 431 (5.6), 562 (4.3), 602 nm (4.0 mol^{-1} dm^3 cm^{-1}); MS (ESI): m/z calcd for $C_{69}H_{61}Cl_2N_9O_{10}Sn$: 1388.284 [$M$+Na]$^+$; found: 1388.256.

Compound 3: Compound **2** (20 mg, 15 μmol, 1 equiv) and potassium carbonate (87 mg, 660 μmol, 44 equiv) were dissolved in CH_2Cl_2/MeOH (4:1, 20 mL) in a 50 mL round-bottomed flask and heated to reflux for 5 h. The organic layer was washed with distilled water and dried over $MgSO_4$. After removal of the solvent under vacuum, the residue was purified by column chromatography on alumina ($CHCl_3$ to $CHCl_3$/MeOH, 98:2) to yield the desired compound **3** (7 mg, 37%) as a purple solid.

^{1}H NMR (CD_2Cl_2, 600 MHz): $\delta = -7.51$ (br s, 1H; OH_w), −6.49 (br s, 1H; OH_w), 1.67 (q, 4H, $^3J = 6.5$ Hz; NCH_{2v}), 2.34 (t, 4H, $^3J = 7.0$ Hz; OCH_{2q}), 2.96 (m, 4H; OCH_{2p}), 3.28 (m, 4H; OCH_{2o}), 3.54 (m, 4H; OCH_{2n}), 3.72 (m; OCH_{2m}), 4.00 (m, 4H; OCH_{2l}), 4.56 (m, 4H; OCH_{2k}), 5.87 (t, 2H, NH_t; $^3J = 6.0$ Hz), 7.43 (dd, 2H, $^3J = 8.5$ Hz, $^4J = 2.5$ Hz; Ar_j), 7.67 (t, 1H, $^3J = 7.5$ Hz; Py_s), 7.69 (t, 2H, $^3J = 8.0$ Hz; Ar_i), 7.75 (d, 2H, $^3J = 7.5$ Hz; Py_r), 7.77 (d, 2H, $^3J = 7.5$ Hz; Ar_h), 8.10 (dd, 2H, $^3J = 8.0$ Hz, $^4J = 1.5$ Hz; Ar_a), 8.18 (dd, 2H, $^3J = 8.0$ Hz, $^4J = 1.5$ Hz; $Ar_{a'}$), 8.19 (br s, 2H; Ar_g), 8.30 (dd, 2H, $^3J = 8.0$ Hz, $^4J = 1.5$ Hz; Ar_b), 8.51 (dd, 2H, $^3J = 8.0$ Hz, $^4J = 1.5$ Hz; $Ar_{b'}$), 8.96 (d, 4H, $^3J = 4.5$ Hz, J(Sn,H) = 15.0 Hz; β-pyr_c), 9.20 ppm (d, 4H, $^3J = 5.0$ Hz, J(Sn,H) = 15.0 Hz; β-pyr_d); ^{13}C NMR (CD_2Cl_2, 150 MHz): $\delta = 37.4$, 68.4, 68.8, 69.8, 70.0, 70.7, 70.8, 71.4, 112.8, 115.8, 119.2, 119.7, 122.5, 122.9, 123.8, 128.3, 128.8, 131.2, 131.4, 132.3, 133.9, 135.7, 136.3, 138.2, 142.1, 146.0, 146.5, 147.0, 148.2, 158.3, 163.3 ppm; IR (ATR): 2229 (CN), 1673 cm^{-1} (CO amide); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 430 (5.6), 560 (4.2), 600 nm (3.9 mol^{-1} dm^3 cm^{-1}).

^{1}H NMR ([D_6]DMSO, 600 MHz): $\delta = -6.21$ (br s, 1H; OH), −5.21 (br s, 1H; OH), 1.98 (q, 4H, $^3J = 6.5$ Hz; NCH_{2v}), OCH_{2q} overlapped with DMSO signal, 3.07 (m, 4H; OCH_{2p}), OCH_{2o} overlapped with water signal, 3.46 (m, 4H; OCH_{2n}), 3.63 (m; OCH_{2m}), 3.90 (m, 4H; OCH_{2l}), 4.46 (m, 4H; OCH_{2k}), 7.09 (t, 2H, $^3J = 6.0$ Hz; NH_t), 7.47 (dd, 2H, $^3J = 8.0$ Hz, $^4J = 1.5$ Hz; Ar_j), 7.75 (t, 2H, $^3J = 8.0$ Hz; Ar_i), 7.78 (m, 4H; Py_r, Ar_h), 7.87 (t, 1H, $^3J = 7.5$ Hz; Py_s), 7.99 (br s, 2H; Ar_g), 8.31 (dd, 2H, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz; Ar_a), 8.36 (m, 4H; $Ar_{a'}$, Ar_b), 8.48 (dd, 2H, $^3J = 7.5$ Hz, $^4J = 1.5$ Hz; $Ar_{b'}$), 8.93 (d, 4H, $^3J = 4.5$ Hz, J(Sn,H) = 13.5 Hz; β-pyr_c), 9.05 ppm (d, 4H, $^3J = 5.0$ Hz, J(Sn,H) = 13.5 Hz; β-pyr_d). MS (ESI): m/z calcd for $C_{69}H_{63}N_9O_{12}Sn$: 1330.371 [M+H]$^+$; found: 1130.289.

Compound 7: Compound **6** (15.4 g, 44 mmol, 1 equiv) was dissolved in dry DMF (150 mL) in a 500 mL two-necked round-bottomed flask. Potassium phthalate (10 g, 54 mmol, 1.2 equiv) was added and the mixture was heated under an argon atmosphere at 120°C overnight. After removal of the solvent under vacuum, the residue was dissolved in distilled water (250 mL) and extracted with CH_2Cl_2 (3 × 150 mL). The organic layer was dried over $MgSO_4$ and the solvent was removed under vacuum to afford compound **7** (14.6 g, 73%) as an oil.

^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 3.54$–3.76 (m, 14H; OCH_2), 3.90 (t, 2H, $^3J = 6.0$ Hz; OCH_2), 7.69–7.72 (m, 2H; Ar), 7.83–7.86 ppm (m, 2H; Ar); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 37.4$, 61.9, 68.1, 70.2, 70.5, 70.6, 70.8, 72.6, 123.4, 132.3, 134.1, 168.4 ppm; elemental analysis calcd (%) for $C_{16}H_{21}NO_6$: C 59.43, H 6.55, N 4.33; found: C 59.34, H 6.54, N 4.55.

Compound 8: Compound **7** (13 g, 40 mmol, 1 equiv) was dissolved in EtOH (250 mL) in a 500 mL two-necked round-bottomed flask under an argon atmosphere. Hydrazine monohydrate (4 mL, 82 mmol, 2 equiv) was added and the solution was heated at reflux overnight. The reaction mixture was acidified with 6 M HCl (15 mL) and filtered. After removal of the solvent, the residue was dissolved in EtOH (50 mL) and filtered before distilled water (50 mL) was added and the mixture was filtered again. Evaporation of the solvent under reduced pressure afforded a residue that was dissolved in water and purified on a Dowex 50WX8 column to afford compound **8** (7.1 g, 90%) as an oil.

^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 3.11$ (t, 2H, $^3J = 5.0$ Hz; OCH_2), 3.60–3.71 (m, 10H; NCH_2, OCH_2), 3.75–3.79 ppm (m, 4H; OCH_2); ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 40.4$, 61.2, 68.7, 69.9, 70.1, 70.4, 70.4, 72.7 ppm; elemental analysis calcd (%) for $C_8H_{19}NO_4{\cdot}0.5\,HCl{\cdot}0.75\,H_2O$: C 42.71, H 9.41, N 6.23; found: C 42.73, H 9.37, N 6.59.

Compound 11: Compound **8** (3.1 g, 16 mmol, 1.9 equiv) and triethylamine (7 mL, 50 mmol, 6.3 equiv) were dissolved in dry CH_2Cl_2 (200 mL) in a dry 500 mL two-necked round-bottomed flask under an argon atmosphere. Compound **10** (1.7 g, 8 mmol, 1 equiv) was dissolved under an argon atmosphere in dry CH_2Cl_2 (100 mL) and added dropwise via a cannula. The reaction mixture was stirred overnight under an argon atmosphere at RT. After removal of the solvent under vacuum, the crude product was purified by column chromatography on alumina (CH_2Cl_2 to CH_2Cl_2/MeOH, 95:5) to afford compound **11** (4 g, 96%) as an oil.

^{1}H NMR ($CDCl_3$, 300 MHz): $\delta = 3.36$ (br s, 2H; OH), 3.58–3.71 (m, 32H; NCH_2, OCH_2), 7.99 (t, 1H, $^3J = 8.0$ Hz; Py), 8.32 (d, 2H, $^3J = 8.0$ Hz; Py), 8.95 ppm (br s, 2H; NH). ^{13}C NMR ($CDCl_3$, 75 MHz): $\delta = 39.8$, 61.9, 70.4, 70.4, 70.5, 70.6, 72.7, 124.9, 138.8, 149.1, 164.2 ppm; elemental analysis calcd (%) for $C_{23}H_{39}N_3O_{10}{\cdot}0.5\,H_2O$: C 52.46, H 7.66, N 7.98; found: C 52.55, H 7.90, N 7.95.

Compound 12: Compound **11** (2.9 g, 5.6 mmol, 1 equiv) and triethylamine (2.4 mL, 17 mmol, 3 equiv) were dissolved in distilled THF (100 mL) in a dry 250 mL three-necked round-bottomed flask under an argon atmosphere. Mesyl chloride (1 mL, 13 mmol, 2.3 equiv) was added and the reaction mixture was stirred at RT for 2 h. After removal of the volatile compounds, the residue was dissolved in CH_2Cl_2 (200 mL), washed with aqueous $NaHCO_3$ (5%, 3×200 mL), and dried over $MgSO_4$. The organic layer was evaporated to dryness under reduced pressure to yield compound **12** (3.5 g, 92%) as an oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.07 (s, 3H; CH_3), 3.63–3.73 (m, 28H; NCH_2, OCH_2), 4.32–4.35 (m, 4H; OCH_2), 8.01 (t, 1H, ^3J = 7.5 Hz; Py), 8.33 (d, 2H, ^3J = 7.5 Hz; Py), 8.37 ppm (br s, 2H; NH); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 37.8, 39.6, 69.1, 69.4, 70.0, 70.3, 70.5, 70.6, 70.7, 125.0, 138.9, 149.0, 154.0 ppm; elemental analysis calcd (%) for $C_{25}H_{43}N_3O_{14}S_2{\cdot}0.5\,H_2O$: C 43.98, H 6.50, N 6.15; found: C 43.88, H 6.73, N 6.64.

Compound 13: 3-Hydroxybenzaldehyde **16** (3.2 g, 26 mmol, 4 equiv) and K_2CO_3 (3.6 g, 26 mmol, 4 equiv) were dissolved in dry MeCN (200 mL) in a dry 500 mL two-necked round-bottomed flask and stirred at RT for 1 h under an argon atmosphere. Compound **12** (4.4 g, 6.5 mmol, 1 equiv) was dissolved in dry MeCN (100 mL) and added dropwise and the reaction mixture was heated at reflux overnight. After removal of the solvent under vacuum, the residue was dissolved in CH_2Cl_2 (200 mL), washed with aqueous $NaHCO_3$ (5%, 3×200 mL) and 1 M HCl (200 mL), dried over $MgSO_4$, and evaporated to dryness under reduced pressure to afford compound **13** (3 g, 62%) as an oil.

^{1}H NMR ($CDCl_3$, 300 MHz): δ = 3.65–3.71 (m, 24H; NCH_2, OCH_2), 3.81 (t, 4H, ^3J = 4.5 Hz; OCH_2), 4.13 (t, 4H, ^3J = 4.5 Hz; OCH_2), 7.13–7.18 (m, 2H; Ar), 7.34–7.36 (m, 2H; Ar), 7.41–7.44 (m, 4H; Ar), 7.98 (t, 1H, ^3J = 8.0 Hz; Py), 8.31 (d, 2H, ^3J = 8.0 Hz; Py), 8.42 (br s, 2H; NH), 9.95 ppm (s, 2H; CHO); ^{13}C NMR ($CDCl_3$, 75 MHz): δ = 39.6, 67.8, 69.7, 70.2, 70.3, 70.6, 70.6, 70.9, 113.0, 122.1, 123.8, 124.9, 130.2, 137.9, 138.8, 149.0, 159.4, 164.0, 192.2 ppm; elemental analysis calcd (%) for $C_{37}H_{47}N_3O_{12}$: C 61.23, H 6.53, N 5.79; found: C 61.92, H 6.90, N 6.03.

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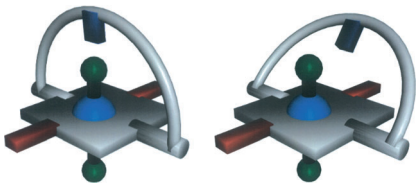
Re-turn to sender: Molecular turnstiles, which were based on strapped-type tetra-aryl X_2Sn^{IV} porphyrins (X = Cl or OH), that contained both H-bond-donor and -acceptor sites were prepared; switching between their open- and closed states was studied in solution by 1D and 2D NMR spectroscopy.



Porphyrins

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Strapped-Porphyrin-Based Molecular Turnstiles