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Optical reading of the open and closed states of a molecular turnstile†‡

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A molecular turnstile composed of a hydroquinone based rotor and a stator bearing a tridentate coordinating site can be reversibly switched between open and closed states. The locking and unlocking processes may be read optically.

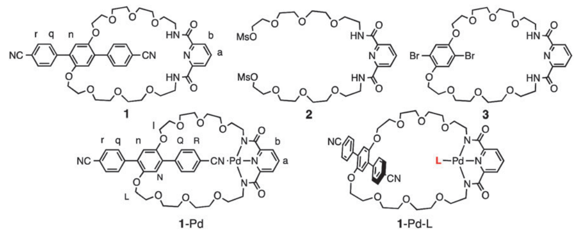
The control of intramolecular movements has attracted considerable efforts over the last two decades and is still of current interest.[1–3] Among many dynamic systems such as motors, rotors and machines, molecular turnstiles form an interesting ensemble.[4] Over the last few years, we have investigated a series of porphyrins[5] or Pt(II) organometallic[6] based turnstiles.

Herein, we report on a new system for which the open and closed states display different luminescence properties.

The turnstile **1** (Scheme 1) is composed of a rotor based on a hydroquinone moiety equipped with two divergently oriented benzonitrile units as monodentate coordinating sites and a stator bearing a tridentate chelating unit. The terphenyl group was chosen as the hinge due to its luminescence properties. As the external effector leading to the closed state of the turnstile **1**-Pd, Pd(II) was used.

The rational behind the choice of the latter was its square planar coordination geometry allowing thus its simultaneous binding by the rotor and stator and its propensity to behave as a heavy atom and thus to quench the emission of the terphenyl moiety.

For the open state of the turnstile **1** (Fig. 1O1), the rotor should freely rotate around the stator, whereas in the presence of Pd(II), the turnstile would be locked in its closed state (Fig. 1C).



Scheme 1 Structures of compounds **1–3** (L = DMAP or CN^-).

The synthesis of **1** (see ESI‡) was achieved in 8 steps. The precursor macrocyclic compound **3** was obtained in 90% yield upon condensation of the handle **2**, prepared in 6 steps,[5g] with 2,5-dibromohydroquinone in DMF in the presence of Cs_2CO_3. The turnstile **1** was obtained in 68% yield by coupling 4-benzonitrile boronic acid with the dibromo compound **3** in the presence of $Pd(PPh_3)_4$. The closed state of the turnstile (**1**-Pd) was generated quantitatively upon metallation of compound **1** by $Pd(OAc)_2$.

In addition to solution characterization, the solid-state structure of **1**-Pd was studied by X-ray diffraction (Fig. 2, see ESI‡). Single crystals of **1**-Pd were obtained at 25 °C upon slow diffusion of Et_2O into a $CHCl_3$ solution of **1**-Pd. The latter crystallizes (monoclinic $P2_1/n$) without any solvent. The Pd(II) cation, adopting a strongly distorted square planar geometry ($NPdN_{cis}$ angle in the 80.7°–99.8° range and $NPdN_{trans}$ angles of 161.6° and 175.9°), is coordinated to the tridentate chelating moiety of the stator (Pd–N distance in the 1.92–2.02 Å range) and to the N atom of the benzonitrile unit of the rotor (d_{PdN} = 2.01 Å).

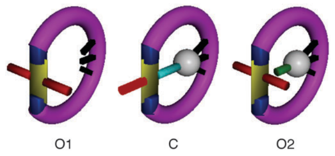


Fig. 1 Schematic representation of the turnstile in its open (O1 and O2) and closed (C) states.

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† This contribution is dedicated to J.-P. Sauvage on the occasion of his 70th birthday.

‡ Electronic supplementary information (ESI) available: Experimental details, characterisation of new compounds, additional 2D-NMR and UV/luminescence spectra. CCDC 985992. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4cc01071j

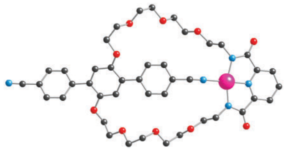

Fig. 2 X-Ray structure of **1**-Pd. H atoms are omitted for clarity. For bond angles and distances see the text.

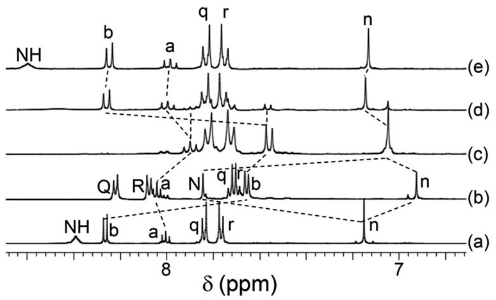

Fig. 3 Portions of ^{1}H-NMR (CD_2Cl_2, X00 MHz, *X* = 5 for (a) and (b) and *X* = 3 for (c–e), 298 K): (a) turnstile **1**, (b) **1**-Pd, (c) **1**-Pd + 1 eq. of TBACN, (d) **1**-Pd + 3 eq. of TBACN, (e) **1**-Pd + excess of TBACN. For signal assignment see Scheme 1.

The solution dynamic behaviour of **1** was studied at 25 °C by 1- and 2-D NMR. In the aromatic region of the ^{1}H-NMR spectrum (Fig. 3a), the signal at 7.15 ppm corresponding to H_n appears as a unique singlet whereas signals corresponding to H_q and H_r at 7.84 and 7.77 ppm, respectively, appear as two doublets (see Scheme 1 for assignment). These observations imply a free rotation of the rotor around the stator defining thus the open state of the turnstile (Fig. 1O1).

The closed state of the turnstile (**1**-Pd) was obtained upon binding of Pd(II) behaving as the external effector. Indeed the latter, in a square planar geometry, is bound simultaneously to the tridentate moiety of the handle and one of the two monodentate sites of the rotor freezing thus the rotational movement (Fig. 1C). This is evidenced by the disappearance of the NH signal and by the shift of signals corresponding to H_a and H_b hydrogen atoms of the central pyridyl moiety of the handle by 0.04 and −0.60 ppm respectively (Fig. 3b). Furthermore, the insertion of Pd(II) caused the splitting of the H_n signal into two singlets H_n at 6.93 and H_N at 7.84 ppm corresponding to the unbound and bound benzonitrile moieties (Fig. 3b). As expected, the two doublets corresponding to H_q and H_r were also split into four doublets assigned (Scheme 1) to H_q (7.73 ppm), H_r (7.69 ppm), H_N (9.22 ppm) and H_R (8.08 ppm).

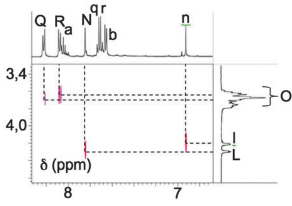

Fig. 4 A portion of the NOESY spectrum of **1**-Pd (CD_2Cl_2, 298 K, 500 MHz). For signal assignment see Scheme 1.

These observations have been further substantiated by ^{1}H–^{1}H NOESY experiments (Fig. 4). Indeed, in addition to the expected H_n/H_l and H_N/H_L correlations, only through space correlations between the H_Q and H_R atoms of the benzonitrile moiety bound to the Pd(II) centre and hydrogen atoms of the oligoethylenglycol chains (OCH_2) are observed.

The return to the open state was achieved using a CN^- anion as an external ligand competing with the benzonitrile moiety. The addition of 1 eq. of CN^- (Fig. 3c) leads to the opening of the turnstile (Fig. 1O2) leading to **1**–Pd–CN^- (Scheme 1). This was evidenced by ^{1}H-NMR, which revealed a unique singlet for H_n and two doublets for H_q and H_r indicating the equivalence of the two benzonitrile moieties and thus the unlocking of the turnstile. The fact that H_a and H_b are only slightly shifted and no NH signal is observed indicate that the Pd(II) remains bound to the handle and its coordination sphere is completed by a CN^- ligand. Further addition of 3 eq. of CN^- (Fig. 3d) leads to the coexistence of the two open states O1 (**1**) and O2 (**1**-Pd-CN^-) resulting from the strong affinity of the cyanide anion for Pd(II). Finally, the complete return to the turnstile **1** is achieved by addition of 8 eq. of CN^- anion (Fig. 3e).

Interestingly, owing to the rather weak binding propensity of benzonitrile towards transition metals, the open state O2 was reached in the presence of *p*-dimethylaminopyridine (DMAP), a stronger ligand replacing the bound benzonitrile within the coordination sphere of Pd(II). The process was again monitored by ^{1}H-NMR at 25 °C in CD_2Cl_2 (Fig. 5). Upon addition of 1 eq. of DMAP, the two singlets corresponding to H_n and H_N (Fig. 5a) were transformed into a unique singlet (Fig. 5b). The same behaviour was observed for the four doublets corresponding to H_q, H_r, H_Q and H_R, which appeared as two doublets (Fig. 5b). These observations imply the equivalence of the two benzonitrile units resulting from the free rotation of the handle (Fig. 1O2). Taking advantage of the strong basicity of DMAP, the return to the closed state of the turnstile was achieved upon addition of methanesulfonic acid (MsOH) causing the protonation of DMAP and its replacement by one of the two benzonitrile groups (Fig. 5c). This, as expected, leads to the splitting of signals corresponding to H_n, H_r, and H_q. Finally, the open state O2 was regenerated upon deprotonation of DMAP-H^+ by addition of 1.5 eq. of NEt_3 (Fig. 5d).

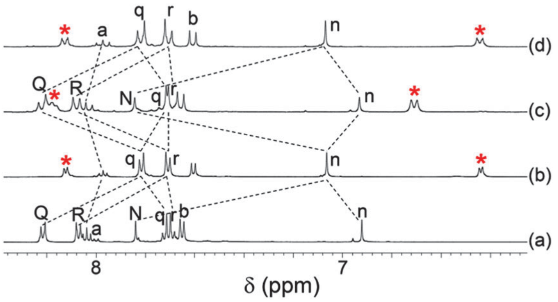

Fig. 5 Portions of ^{1}H-NMR (CD_2Cl_2, X00 MHz, *X* = 5 for (a) and (b) and *X* = 3 for (c) and (d), 298 K): (a) **1**-Pd, (b) **1**-Pd + 1 eq. of DMAP, (c) addition of 1 eq. MsOH to **1**-Pd-DMAP, (d) addition of 1.5 eq. Et_3N. For signal assignment see Scheme 1. * correspond to signals of DMAP.

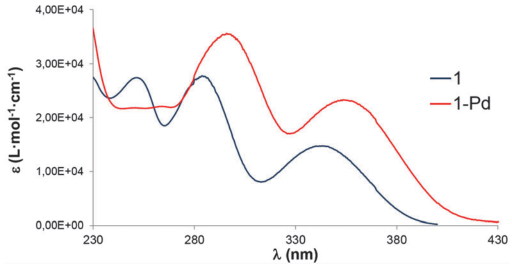

Fig. 6 UV-visible spectra (CH_2Cl_2, 298 K) of **1** (black) and **1**-Pd (red).

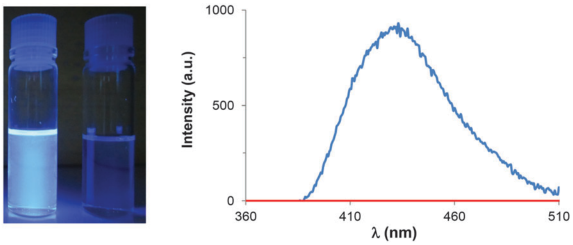

Fig. 7 Picture of **1** (left) and **1**-Pd (right) in CH_2Cl_2 (298 K, aerated, λ_{exc} = 365 nm) and emission spectra for iso-absorbing solutions of the open **1** (blue) and closed **1**-Pd (red) states of the turnstiles (CH_2Cl_2, 298 K, aerated, λ_{exc} = 350 nm).

For the open state of the turnstile **1**, the UV-visible spectrum (CH_2Cl_2, 298 K, ε in L·mol^{-1}·cm^{-1}) displays three major bands at *ca.* 251 ($\varepsilon = 26.9 \times 10^3$), 284 ($\varepsilon = 27.5\ 1\times\ 0^3$) and 347 nm ($\varepsilon = 14.8 \times 10^3$) (Fig. 6). For the closed state **1**-Pd, the peak at 251 nm vanishes and the other two bands are red shifted to 296 ($\varepsilon = 35.5 \times 10^3$) and 354 nm ($\varepsilon = 23.4 \times 10^3$) with a hyperchromic effect. Interestingly, whereas for the turnstile **1** in its open state, excitation at 350 nm, assigned to π–π* transitions, leads to strong emission in the blue domain of the visible spectrum (λ_{em} = 434 nm, Φ_F = 0.96), the closed state **1**-Pd (λ_{em} = 436 nm, Φ_F = 0.03) is far less emissive (Fig. 7). For the determination of the quantum yields, quinine sulphate was used as a reference. Lifetimes of the excited state of 3.2 and 3.1 ns for **1** and **1**-Pd, respectively, have been determined. A plausible hypothesis for the observed decrease of luminescence resulting from the binding of Pd(II) could be that, upon excitation of the π–π* transition of the rotor, an S_1 excited state with a lifetime of *ca.* 3 ns is generated. For the closed state of the turnstile, the heavy atom effect of Pd(II) promotes the transition to a T_1 excited state which is efficiently quenched by the solvent or O_2 under aerated conditions.

Using iso-absorbing solutions of **1** and **1**-Pd and under the same conditions and identical recording parameters, the excitation at 350 nm leads to a strong signal for **1**, whereas for the closed state of the turnstile **1**-Pd, the emission is below the detection limits of the spectrometer used (Fig. 7).

In conclusion, the purely organic turnstile **1**, composed of a rotor based on a hydroquinone derivative bearing two peripheral coordinating sites of the benzonitrile type connected to a stator equipped with a chelating moiety, undergoes a reversible locking–unlocking process between an open and a closed state. The closed state is generated upon binding of Pd(II) as an effector. The switch between the locked and unlocked states is achieved either by a competitive external ligand such as CN^- or DMAP or in the latter case by an acid (MsOH) and a base (Et_3N). Interestingly, owing to the emissive nature of the turnstile, whereas the open state O1 is strongly luminescent, for the closed state, the emission is quenched by the presence of Pd(II) leading thus to an optical reading of the two states.

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Notes and references

1 (*a*) J.-P. Sauvage, *Science*, 2001, **291**, 2105; (*b*) J.-P. Sauvage, *Acc. Chem. Res.*, 1998, **31**, 611; (*c*) J.-P. Sauvage, in *Molecular machines and motors, Structure and bonding*, ed. J.-P. Sauvage, Springer, Berlin, Heidelberg, 2001, vol. 99, pp. 1–282; (*d*) V. Balzani, M. Venturi and A. Credi, *Molecular devices and machines: a journey into the nanoworld*, Wiley-VCH, Weinheim, 2003, pp. 1–457; (*e*) T. R. Kelly, in *Molecular machines, Topics in Current Chemistry*, ed. T. R. Kelly, Springer, Berlin, Heidelberg, 2005, vol. 262, pp. 1–227; (*f*) Y. Shirai, J.-F. Morin, T. Sasaki, J. M. Guerrero and J. M. Tour, *Chem. Soc. Rev.*, 2006, **35**, 1043.

2 (*a*) N. Koumura, R. W. J. Zijlstra, R. A. van Delden, N. Harada and B. L. Feringa, *Nature*, 1999, **401**, 152; (*b*) V. Balzani, A. Credi, F. M. Raymo and J. F. Stoddart, *Angew. Chem., Int. Ed.*, 2000, **39**, 3348; (*c*) J. Michl and E. C. H. Sykes, *ACS Nano*, 2009, **3**, 1042; (*d*) S. Sengupta, M. E. Ibele and A. Sen, *Angew. Chem., Int. Ed.*, 2012, **51**, 8434.

3 E. R. Kay, D. A. Leigh and F. Zerbetto, *Angew. Chem., Int. Ed.*, 2007, **46**, 72.

4 (*a*) T. C. Bedard and J. S. Moore, *J. Am. Chem. Soc.*, 1995, **117**, 10662; (*b*) A. Carella, J. Jaud, G. Rapenne and J.-P. Launay, *Chem. Commun.*, 2003, 2434; (*c*) N. Weibel, A. Mishchenko, T. Wandlowski, M. Neuburger, Y. Leroux and M. Mayor, *Eur. J. Org. Chem.*, 2009, 6140; (*d*) K. Skopek, M. C. Hershberger and J. A. Gladysz, *Coord. Chem. Rev.*, 2007, **251**, 1723.

5 (*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; (*c*) T. Lang, A. Guenet, E. Graf, N. Kyritsakas and M. W. Hosseini, *Chem. Commun.*, 2010, **46**, 3508; (*d*) A. Guenet, E. Graf, N. Kyritsakas and M. W. Hosseini, *Chem. – Eur. J.*, 2011, **17**, 6443; (*e*) T. Lang, E. Graf, N. Kyritsakas and M. W. Hosseini, *Dalton Trans.*, 2011, **40**, 3517; (*f*) T. Lang, E. Graf, N. Kyritsakas and M. W. Hosseini, *Dalton Trans.*, 2011, **40**, 5244; (*g*) T. Lang, E. Graf, N. Kyritsakas and M. W. Hosseini, *Chem. – Eur. J.*, 2012, **18**, 10419; (*h*) T. Lang, E. Graf, N. Kyritsakas and M. W. Hosseini, *New J. Chem.*, 2013, **37**, 112.

6 (*a*) N. Zigon, A. Guenet, E. Graf and M. W. Hosseini, *Chem. Commun.*, 2013, **49**, 3637; (*b*) N. Zigon, A. Guenet, E. Graf, N. Kyritsakas and M. W. Hosseini, *Dalton Trans.*, 2013, **42**, 9740; (*c*) N. Zigon, N. Kyritsakas and M. W. Hosseini, *Dalton Trans.*, 2013, **43**, 152.