An electrochemically driven molecular shuttle controlled and monitored by C_{60}†

Aurelio Mateo-Alonso,*[a] Giulia Fioravanti,[b] Massimo Marcaccio,[b] Francesco Paolucci,*[b] G. M. Aminur Rahman,[c] Christian Ehli,[c] Dirk M. Guldi*[c] and Maurizio Prato*[a]

Received (in Cambridge, UK) 19th December 2006, Accepted 26th January 2007
First published as an Advance Article on the web 16th February 2007
DOI: 10.1039/b618504e

Herein we describe a fullerene rotaxane, in which shuttling between two well-defined and distant co-conformations is both induced and monitored by the C_{60} stopper.

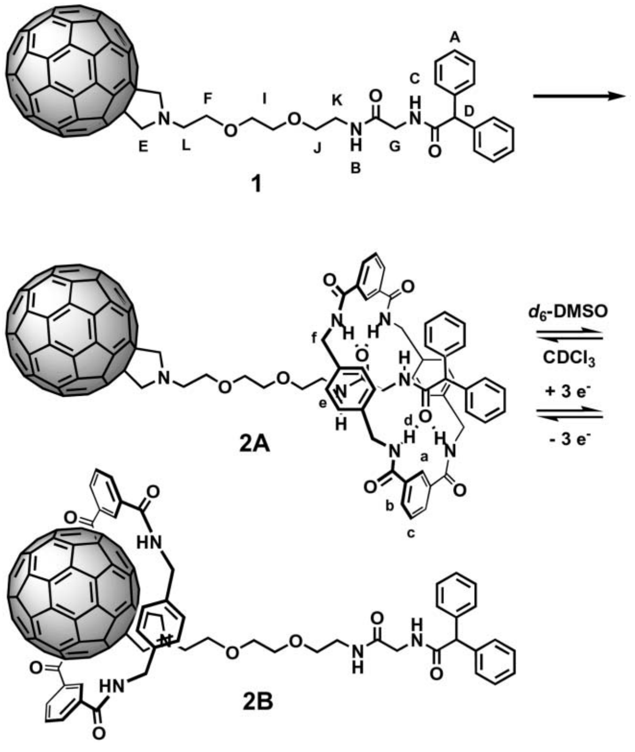
The potential applicability of rotaxanes in technology relies directly on the control of the basic motions that they can be subjected to. Full and efficient control of such motions will contribute to the design of novel devices at the molecular level, leading to miniaturization.[1] Lately, a wide variety of switches have been developed to shuttle the macrocycle reversibly between two different parts of the thread. Electrochemical[2–8] and light[9–15] controlled shuttles have emerged to be among the best candidates for the development of novel nanodevices for practical reasons. Additionally, shuttling can be coupled with a change in the physical properties of the molecule, providing a way to monitor the position of the macrocycle, avoiding the use of spectroscopic techniques that require specialized equipment (*i.e.* NMR spectrometers). In this light, several rotaxanes have been designed to produce detectable responses, including conductivity,[2,16] circular dichroism[12] and fluorescence.[14,17,18]

Fullerenes have well-established photophysical[19] and electrochemical properties.[20] The different excited and charged species of fullerenes are typically generated either photophysically or electrochemically and their characteristics have shown to be affected in some cases by the presence or the motion of the macrocycle.[21–24]

In this article we describe a fullerene rotaxane in which shuttling is induced by π–π interactions between the C_{60} stopper and the macrocycle, which in some cases are strong enough to overpower four hydrogen bonds. This is remarkable, since π–π interactions are usually considered weaker than hydrogen bonds.[25] Simultaneously, some selected physical properties of fullerenes are used to monitor the position of the macrocycle along the thread. Therefore, the fullerene stopper is used both to induce and to monitor shuttling.

Rotaxane **2** was assembled from thread **1** through hydrogen bond recognition between the peptidic residue and the precursors of the macrocycle, using Leigh's protocol.[26] In the neutral state, rotaxane **2** exists in two co-conformations in different solvents (Scheme 1 and Fig. 1), as shown by NMR spectroscopy. In CD_2Cl_2, $CDCl_3$ and THF-d_8, protons G, C and D (the assignments correspond to the lettering shown in Scheme 1) are shielded because of the anisotropic effect of the benzylic rings of the macrocycle over the thread, which confirms that the macrocycle stays preferentially on the peptidic station (co-conformer **2A**). In DMSO-d_6 and DMF-d_7 the hydrogen bonds are weakened favoring π–π interactions between the macrocycle and the fullerene. Thus, the macrocycle shuttles to the opposite end of the thread, assuming the stacked co-conformation **2B**, which is reflected by the shielding of protons E, L and F.

The existence of such π-stacking interactions is well supported by photophysical experiments carried out on thread **1** and



Scheme 1 Synthesis and behaviour of molecular shuttle **2**.

---

[a] *Italian Interuniversity Consortium on Materials Science and Technology (INSTM), Unit of Trieste. Dipartimento di Scienze Farmaceutiche, Università degli Studi di Trieste, Piazzale Europa 1, 34127, Trieste, Italy. E-mail: amateo@units.it; prato@units.it; Fax: +39 040 52572; Tel: +39 040 5587883*
[b] *Dipartimento di Chimica "G. Ciamician", Università di Bologna, v. Selmi 2, 40126, Bologna, Italy. E-mail: francesco.paolucci@unibo.it; Fax: +39 051 2099456; Tel: +39 051 2099460*
[c] *Lehrstuhl für Physikalische Chemie I, Universität Erlangen-Nürnberg, Egerlandstraße 3, D-91058, Erlangen, Germany. E-mail: guldi@chemie.uni-erlangen.de; Fax: +49 (0)91 318528307; Tel: +49 (0)91 318527341*

† Electronic supplementary information (ESI) available: Full experimental procedures. Molecular, photophysical and electrochemical characterisation. See DOI: 10.1039/b618504e

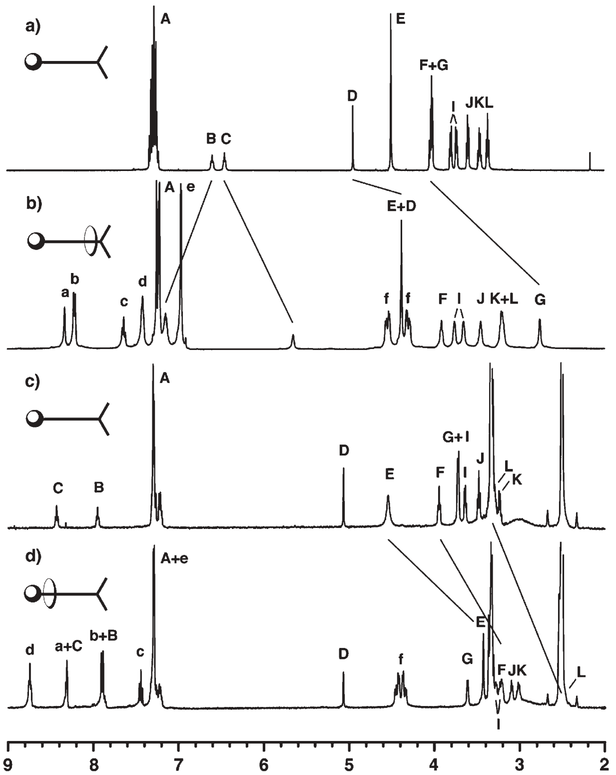


Fig. 1 400 MHz ^{1}H NMR spectra of (a) thread **1** in $CDCl_3$ (b) rotaxane **2** in $CDCl_3$ (c) thread **1** in DMSO-d_6 (d) rotaxane **2** in DMSO-d_6.

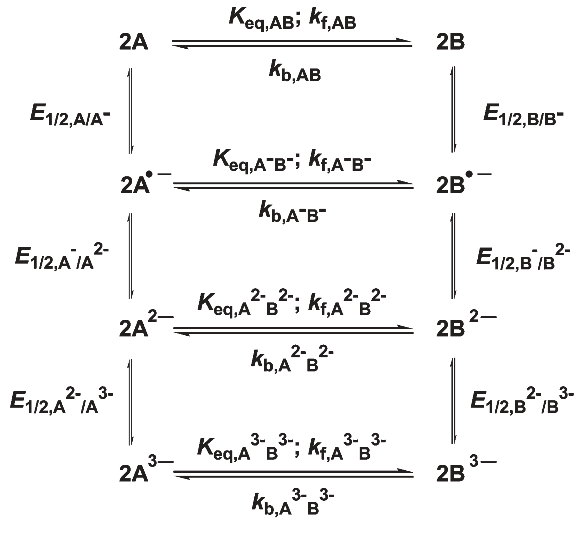
rotaxane **2** (see ESI†) in CH_2Cl_2, CH_2Cl_2–HFIP (1 : 1) (HFIP = hexafluoroisopropanol), DMF and DMSO (*i.e.*, increasing hydrogen bonding basicity). The ground state absorption spectra obtained in DMF and DMSO, in which co-conformer **2B** is mainly present, show broadening, red-shifts and reduced oscillator strengths in the transition around 330 nm. In the excited state absorption measurements, the fluorescence of the fullerene is quenched by the proximity of the macrocycle with 28 ± 7% and 44 ± 6% respectively in DMF and DMSO. When photoexciting at 325 nm, the residual fullerene fluorescence in DMSO is 51% of that in CH_2Cl_2.[27,28]

The translocation of the macrocycle is also achieved by the reduction of the fullerene to its trianion in THF, which is both effected and observed by cyclic voltammetry. In DMSO, where the rotaxane adopts co-conformation **2B**, anodic half-wave potential shifts ($\Delta E_{1/2}$) on reduction waves II and III are observed in rotaxane **2** when compared with those of thread **1** (see Table 1). This indicates that the macrocycle stabilizes the charge by the close proximity to the fullerene through π–π interactions. Such stabilization increases with the anionic charge of the fullerene. In THF, smaller $\Delta E_{1/2}$ values are expected since the macrocycle is bound to the peptidic residue and far from the fullerene. Surprisingly, the $\Delta E_{1/2}$ value in reduction process III is comparable with that of DMSO, which is contradictory with the NMR spectrum in THF-d_8 that shows preferentially **2A** and with previous electrochemical studies on fullerene rotaxanes reported by us.[23,24] Although contradictory, these results can be easily rationalized in terms of electrochemically-induced shuttling. The high $\Delta E_{1/2}$ values in THF provide evidence for the existence of π–π interactions between the macrocycle and the electrogenerated trianion. Therefore, a co-conformational change takes place, transforming **2A** into **2B**, in the benefit of the stabilization of the negative charge present on the fullerene. The fact that this phenomenon is solely observed in this particular system, in comparison with previous fullerene rotaxanes,[23,24] is explained as a consequence of the less efficient binding between the peptidic template and the macrocycle, which is in agreement with the relative binding strengths of the different templates (fumaramide ≫ succinamide > glycylglycine).[3,24,29]

Table 1 Second and third half-wave reduction values ($E_{1/2}/V$ *vs* Fc^+/Fc) of thread **1** and rotaxane **2** in different solvents

Wave	**1**[a]	**2**[a]	$\Delta E_{1/2}$[a]	**1**[b]	**2**[b]	$\Delta E_{1/2}$[b]
I	−0.381	−0.381	0	−0.621	−0.621	0
II	−0.816	−0.790	0.026	−1.180	−1.170	0.010
III	−1.436	−1.390	0.046	−1.790	−1.750	0.040

[a] 0.5 mM in a 0.05 M solution of $TBAPF_6$ in DMSO, [b] THF. 5 V s^{-1}



Scheme 2 Square scheme mechanism for molecular shuttle **2**.

In order to gain quantitative information from the shifts in the reduction potentials, simulations of the cyclic voltammograms (DigiSim®) were carried out using the well-established square scheme mechanism[30] set out in Scheme 2 (see also ESI†). The equilibrium constants (K_{eq}) calculated for each of the redox states (Table 2) corroborate the electrochemically-induced shuttling. In the neutral state, the K_{eq} values for DMSO (Table 2) shows preferential formation of **2B**, which is in agreement with the NMR experiments. The K_{eq} values tend to increase by increasing the anionic charge on the fullerene, due to stronger π–π interactions with the more cathodic species. On the other hand, the K_{eq} value for THF in the neutral state speaks for **2A**, which is consistent with

Table 2 Calculated equilibrium constants of rotaxane **2** by simulation of the experimental voltammograms using DigiSim®

Equilibrium	K_{eq} (k_f/k_b) (DMSO)	K_{eq} (k_f/k_b) (THF)
$\mathbf{2A} \rightleftharpoons \mathbf{2B}$	9.5×10^2	1×10^{-2}
$\mathbf{2A}^- \rightleftharpoons \mathbf{2B}^-$	1×10^3	1×10^{-1}
$\mathbf{2A}^{2-} \rightleftharpoons \mathbf{2B}^{2-}$	2.8×10^3	1
$\mathbf{2A}^{3-} \rightleftharpoons \mathbf{2B}^{3-}$	1.5×10^4	8

the NMR spectrum. Consecutive increase of the negative charge shifts the equilibrium towards **2B**. The interaction between the fullerene dianion and the macrocycle is sufficiently strong to compete with the hydrogen bonding station, which is expressed in a 1 : 1 ratio of **2A** and **2B** in the equilibrium. Finally, the even stronger π–π interactions between the trianion and the macrocycle overwhelm the hydrogen bonds favoring the formation of **2B** over **2A** in an 8 : 1 ratio.

In conclusion, we have demonstrated that C_{60} induces shuttling in benzylic amide rotaxanes. Remarkably, π–π interactions between the macrocycle and the trianion of the fullerene are strong enough to overcome the hydrogen bonds between the macrocycle and the peptidic template. Alternatively, shuttling in the neutral state is achieved by a solvent change. It is noteworthy that the position of the macrocycle in the different stations is identified through measurable changes in electrochemical, absorption and fluorescence measurements centered on the fullerene. Fullerene-based switches provide new perspectives not only for the design of novel molecular shuttles but also for extending their applicability in research fields where fullerenes have proven to play an active role such as photovoltaics, non-linear optics and self-organization.[31–33]

We thank Prof. David A. Leigh for helpful discussions and for introducing us to this field. European Union (Networks EMMMA and WONDERFULL), Università di Trieste and MIUR (PRIN 2006, prot. 2006034372, FIRB prot. RBNE033KMA) are gratefully acknowledged for funding.

Notes and references

1 V. Balzani, A. Credi and M. Venturi, *Molecular Devices and Machines*, Wiley-VCH, Weinheim, 2003.
2 A. H. Flood, J. F. Stoddart, D. W. Steuerman and J. R. Heath, *Science*, 2004, **306**, 2055.
3 A. Alteri, F. G. Gatti, E. R. Kay, D. A. Leigh, D. Martel, F. Paolucci, A. M. Z. Slawin and J. K. Y. Wong, *J. Am. Chem. Soc.*, 2003, **125**, 8644.
4 N. Kihara, M. Hashimoto and T. Takata, *Org. Lett.*, 2004, **6**, 1693.
5 J. P. Collin, V. Heitz and J. P. Sauvage, *Top. Curr. Chem.*, 2005, **262**, 29.
6 J. P. Sauvage, *Chem. Commun.*, 2005, 1507.
7 M. C. Jimenez-Molero, C. Dietrich-Buchecker and J. P. Sauvage, *Chem. Commun.*, 2003, 1613.
8 R. A. Bissell, E. Cordova, A. E. Kaifer and J. F. Stoddart, *Nature*, 1994, **369**, 133.
9 A. Altieri, G. Bottari, F. Dehez, D. A. Leigh, J. K. Y. Wong and F. Zerbetto, *Angew. Chem., Int. Ed.*, 2003, **42**, 2296.
10 V. Balzani, M. Clemente-Leon, A. Credi, B. Ferrer, M. Venturi, A. H. Flood and J. F. Stoddart, *Proc. Natl. Acad. Sci. U. S. A.*, 2006, **103**, 1178.
11 G. Bottari, F. Dehez, D. A. Leigh, P. J. Nash, E. M. Perez, J. K. Y. Wong and F. Zerbetto, *Angew. Chem., Int. Ed.*, 2003, **42**, 5886.
12 G. Bottari, D. A. Leigh and E. M. Perez, *J. Am. Chem. Soc.*, 2003, **125**, 13360.
13 D. A. Leigh, J. K. Y. Wong, F. Dehez and F. Zerbetto, *Nature*, 2003, **424**, 174.
14 E. M. Perez, D. T. F. Dryden, D. A. Leigh, G. Teobaldi and F. Zerbetto, *J. Am. Chem. Soc.*, 2004, **126**, 12210.
15 A. M. Brouwer, C. Frochot, F. G. Gatti, D. A. Leigh, L. Mottier, F. Paolucci, S. Roffia and G. W. H. Wurpel, *Science*, 2001, **291**, 2124.
16 A. H. Flood, R. J. A. Ramirez, W. Q. Deng, R. P. Muller, W. A. Goddard and J. F. Stoddart, *Aust. J. Chem.*, 2004, **57**, 301.
17 D. H. Qu, G. C. Wang, J. Ren and H. Tian, *Org. Lett.*, 2004, **6**, 2085.
18 Q. C. Wang, D. H. Qu, J. Ren, K. C. Chen and H. Tian, *Angew. Chem., Int. Ed.*, 2004, **43**, 2661.
19 D. M. Guldi and M. Prato, *Acc. Chem. Res.*, 2000, **33**, 695.
20 L. Echegoyen and L. E. Echegoyen, *Acc. Chem. Res.*, 1998, **31**, 593.
21 T. Da Ros, D. M. Guldi, A. F. Morales, D. A. Leigh, M. Prato and R. Turco, *Org. Lett.*, 2003, **5**, 689.
22 A. Mateo-Alonso and A. M. Prato, *Tetrahedron*, 2006, **62**, 2003.
23 A. Mateo-Alonso, G. Fioravanti, M. Marcaccio, F. Paolucci, D. C. Jagesar, A. M. Brouwer and M. Prato, *Org. Lett.*, 2006, **8**, 5173.
24 A. Mateo-Alonso, G. M. A. Rahman, C. Ehli, D. M. Guldi, G. Fioravanti, M. Marcaccio, F. Paolucci and M. Prato, *Photochem. Photobiol. Sci.*, 2006, **5**, 1173.
25 C. A. Hunter, K. R. Lawson, J. Perkins and C. J. Urch, *J. Chem. Soc., Perkin Trans. 2*, 2001, 651.
26 D. A. Leigh, A. Murphy, J. P. Smart and A. M. Z. Slawin, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 728.
27 Quantitative similar results were gathered when photoexciting at 300, 325, 350, 375, 425 and 450 nm.
28 The proposed π–π-interactions have no impact on the inherent fluorescence, singlet and triplet deactivation dynamics.
29 F. G. Gatti, D. A. Leigh, S. A. Nepogodiev, A. M. Z. Slawin, S. J. Teat and J. K. Y. Wong, *J. Am. Chem. Soc.*, 2001, **123**, 5983.
30 S. A. Lerke, D. H. Evans and S. W. Feldberg, *J. Electroanal. Chem.*, 1990, **296**, 299.
31 M. Prato, *Top. Curr. Chem.*, 1999, **199**, 173.
32 D. M. Guldi, F. Zerbetto, V. Georgakilas and M. Prato, *Acc. Chem. Res.*, 2005, **38**, 38.
33 A. Mateo-Alonso, C. Sooambar and M. Prato, *Org. Biomol. Chem.*, 2006, **4**, 1629.