ORGANIC LETTERS

2005
Vol. 7, No. 22
4835−4838

Energy Transfer Switching in a Bistable Molecular Machine

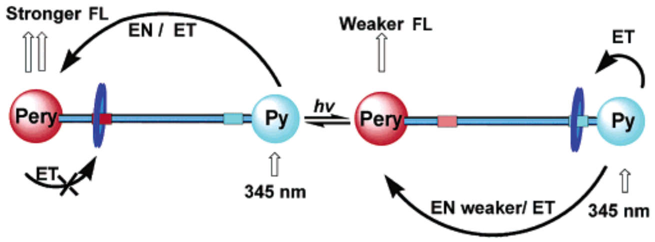
Yongjun Li, Hao Li, Yuliang Li,* Huibiao Liu, Shu Wang, Xiaorong He, Ning Wang, and Daoben Zhu*

CAS Key Laboratory of Organic Solids, Institute of Chemistry, Chinese Academy of Sciences, and Graduate School of the Chinese Academy of Sciences, Chinese Academy of Sciences, Beijing 100080, P. R. China

ylli@iccas.ac.cn

Received July 5, 2005

ABSTRACT



A novel [2]rotaxane, containing pyrene and perylene bisimide as both stoppers and photoactive units, has been prepared. The shuttling of the protonated macrocycle switched the energy transfer (EN) from a pyrene moiety to a perylene moiety, which resulted in changes of fluorescence of the perylene moiety.

Molecular machines that are controllable, reversible, and readable at a molecular level are of great interest because of their potential applications in the creation of nanometer-scale molecular devices.[1] Mechanically interlocked molecules, such as catenanes and rotaxanes, have received a great deal of attention in the design of molecular machines because of their ability to switch between two or more states as a result of induced relative movement of their noncovalently interacting components on application of external stimuli.[2] This shuttling motion can be driven chemically,[3] electrochemically,[4] or photochemically.[5] The use of photons as input (light-driven shuttling) is now under prominent consideration because excitation with lasers can lead to a fast response

---

(1) (a) Balzani, V.; Credi, A.; Raymo, F. M.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2000**, *39*, 3348. (b) Molecular machines special issue: *Acc. Chem. Res.* **2001**, *34*, 409. Electronic devices based on molecular machines have been reported, see: (c) Collier, C. P.; Wong, E. W.; Belohradsky, M.; Raymo, F. M.; Stoddart, J. F.; Kuekes, P. J.; Williams, R. S.; Heath, J. R. *Science* **1999**, *285*, 391. (d) Collier, C. P.; Mattersteig, G.; Wong, E. W.; Luo, Y.; Beverly, K.; Sampaio, J.; Raymo, F. M.; Stoddart, J. F.; Heath, J. R. *Science* **2000**, *289*, 1172.

(2) For rotaxanes, see: (a) Bissell, R. A.; Cordova, E.; Kaifer, A. E.; Stoddart, J. F. *Nature* **1994**, *369*, 133. (b) Collin, J.-P.; Gaviña, P.; Sauvage, J.-P. *New J. Chem.* **1997**, *21*, 525. (c) Murakami, H.; Kawabuchi, A.; Kotoo, K.; Kunitake, M.; Nakashima, N. *J. Am. Chem. Soc.* **1997**, *119*, 7605. (d) Armaroli, N.; Balzani, V.; Collin, J.-P.; Gaviña, P.; Sauvage, J.-P.; Ventura, B. *J. Am. Chem. Soc.* **1999**, *121*, 4397. (e) Leigh, D. A.; Troisi, A.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2000**, *39*, 350. (f) Kawaguchi, Y.; Harada, A. *Org. Lett.* **2000**, *2*, 1353. (g) Brouwer, A. M.; Frochot, C.; Gatti, F. G.; Leigh, D. A.; Mottier, L.; Paolucci, F.; Roffia, S.; Wurpel, G. W. H. *Science* **2001**, *291*, 2124. (h) Kihara, N.; Hashimoto, M.; Takata, T. *Org. Lett.* **2004**, *6*, 1693. (i) Hernández, J. V.; Kay, E. R.; Leigh, D. A. *Science* **2004**, *306*, 1532. For pseudorotaxanes, see: (a) Ballardini, R.; Balzani, V.; Gandolfi, M. T.; Prodi, L.; Venturi, M.; Philp, D.; Ricketts, H. G.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1301. (b) Ishow, E.; Credi, A.; Balzani, V.; Spadola, F.; Mandolini, L. *Chem. Eur. J.* **1999**, *5*, 984. (c) Jeon, W. S.; Ziganshina, A. Y.; Lee, J. W.; Ko, Y. H.; Kang, J.-K.; Lee, C.; Kim, K. *Angew. Chem., Int. Ed.* **2003**, *42*, 4097. For catenanes see: (a) Ashton, P. R.; Goodnow, T. T.; Kaifer, A. E.; Reddington, M. V.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Vincent, C.; Williams, D. J. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1396. (b) Cardenas, D. J.; Livoreil, A.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1996**, *118*, 11980. (c) Andrievsky, A.; Ahuis, F.; Sessler, J. L.; Vogtle, F.; Gudat, D.; Moini, M. *J. Am. Chem. Soc.* **1998**, *120*, 9712. (d) Jeppesen, J. O.; Perkins, J.; Becher, J.; Stoddart, J. F. *Angew. Chem., Int. Ed.* **2001**, *40*, 1216. (e) Leigh, D. A.; Wong, J. K. Y.; Dehez, F.; Zerbetto, F. *Nature* **2003**, *424*, 174.

(3) Ashton, P. R.; Ballardini, R.; Balzani, V.; Baxter, I.; Credi, A.; Fyfe, M. C. T.; Gandolfi, M. T.; Gómez-López, M.; Martínez-Díaz, M.-V.; Piersanti, A.; Spencer, N.; Stoddart, J. F.; Venturi, M.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1998**, *120*, 11932.

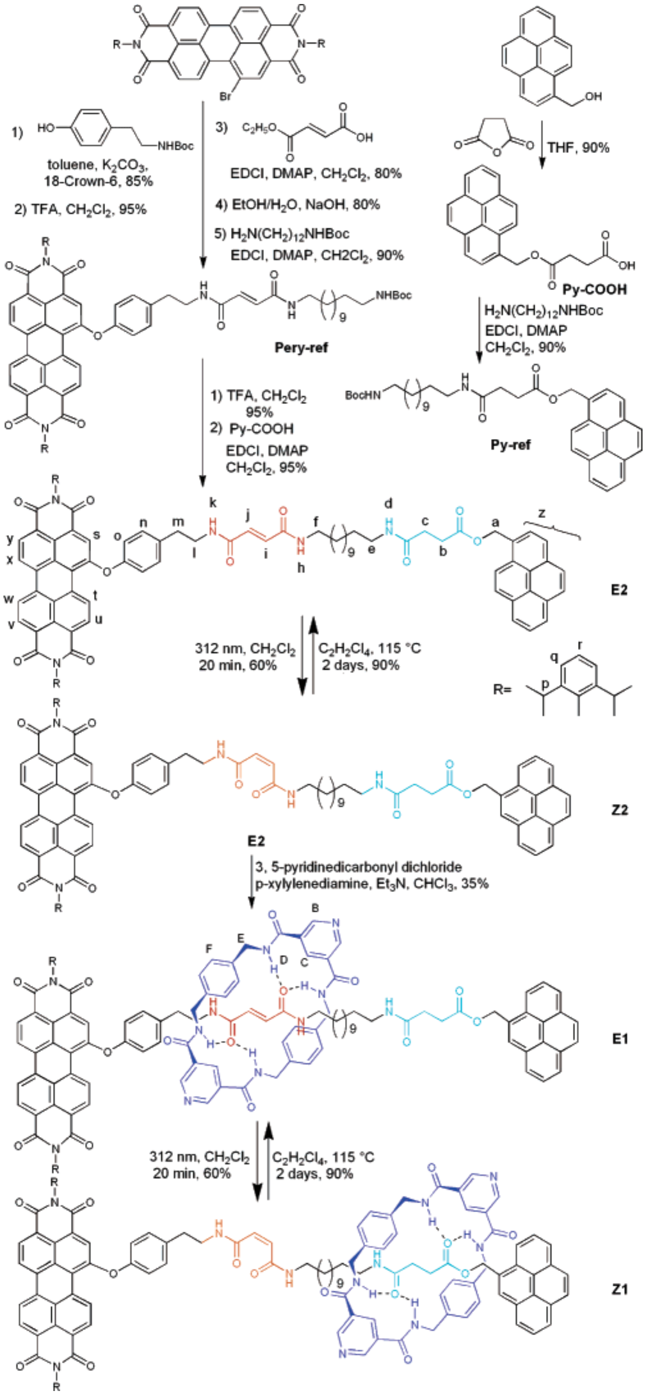
(4) (a) Collier, C. P.; Jeppesen, J. O.; Luo, Y.; Perkins, J.; Wong, E. W.; Heath, J. R.; Stoddart, J. F. *J. Am. Chem. Soc.* **2001**, *123*, 12632. (b) Altieri, A.; Gatti, F. G.; Kay, E. R.; Leigh, D. A.; Martel, D.; Paolucci, F.; Slawin, A. M. Z.; Wong, J. K. Y. *J. Am. Chem. Soc.* **2003**, *125*, 8644.

10.1021/ol051567t CCC: $30.25

and can function in a small space without producing any byproducts.[5,6] Light-driven translational motion has been achieved in rotaxanes with use of photoinduced electron transfer (ET),[4,5] excited-state changes in hydrogen bonding,[5c] and E/Z photoisomerization of azobenzene dumbbells.[2c,5c,5d] Recording the changes of ^{1}H NMR, absorption, and circular dichroism spectroscopies[5e] are the usual methods used to monitor the co-conformational changes of rotaxanes. The use of changes in fluorescence as an output signal is preferable because it is easy to transform these changes into the easily detectable output signals and is inexpensive. But reports based on rotaxanes that can be induced to switch between different fluorescent states (output) in response to clean inputs are rare.[7]

Here we describe a fluorescence switch in which light-induced shuttling of the macrocycle along the thread produces the changes of the interaction between two chromophores in the thread. The molecular shuttle **Z1/E1** consists of a benzylic amide macrocycle mechanically locked onto a thread, **Z2/E2**, featuring two potential H bonding stations—a fumaramide group and a succinic amide ester unit—separated by a C_{12} alkyl spacer, and highly fluorescent perylene bisimide and pyrene (which were sufficiently bulky to also act as "stoppers") attached to the fumaramide group and a succinic amide ester (Scheme 1). The macrocycle contains two pyridine units, which are good fluorescence quenchers of perylene bisimide and pyrene upon protonation. It is well-known that there exist both photoinduced electron and energy transfer processes in the pyrene−perylene dyads.[8] The relative orientation of the donor and acceptor transition dipoles, and the distance between the donor and acceptor molecules have great influence on the energy transfer and electron-transfer process. [9] So with proper spacers to control the distance between fluorescence units and H bonding stations, we can design a molecular machine with a macrocycle to control the energy and/or electron transfer between the perylene and pyrene moieties. This molecular machine can be a switch, and features the convenient use of optical input and easy reading of the optical output.

Scheme 1



Rotaxane **E1** was prepared in 35% yield from thread **E2** and converted into **Z1** by photoisomerization (Scheme 1). Since the xylylene rings of the macrocycle shielded encapsulated regions of the thread, the position of the macrocycle in CDCl$_3$ could be determined for each pair of rotaxane diastereomers by comparing the chemical shift of the protons in the rotaxane with those of the corresponding thread.[6] The ^{1}H NMR spectra of **E1/Z1** and **E2/Z2** in CDCl$_3$ (400 MHz, 298 K) are shown in Figure 1. The Hi and Hj protons of the fumaramide group were shielded in the rotaxane **E1**, compared with the thread **E2**, by δ 1.08 ppm, whereas the chemical shifts of the Hb and Hc protons of the succinic amide ester group were similar in both compounds. In the

---

(5) (a) Ashton, P. R.; Ballardini, R.; Balzani, V.; Credi, A.; Dress, K. R.; Ishow, E.; Kleverlaan, C. J.; Kocian, O.; Preece, J. A.; Spencer, N.; Stoddart, J. F.; Venturi, M.; Wenger, S. *Chem. Eur. J.* **2000**, *6*, 3558. (b) Wurpel, G. W. H.; Brouwer, A. M.; van Stokkum, I. H. M.; Farran, A.; Leigh, D. A. *J. Am. Chem. Soc.* **2001**, *123*, 11327. (c) Asakawa, M.; Ashton, P. R.; Balzani, V.; Brown, C. L.; Credi, A.; Matthews, O. A.; Newton, S. P.; Raymo, F. M.; Shipway, A. N.; Spencer, N.; Quick, A.; Stoddart, J. F.; White, A. J. P.; Williams, D. J. *Chem. Eur. J.* **1999**, *5*, 860. (d) Stanier, C. A.; Alderman, S. J.; Claridge, T. D. W.; Anderson, H. L. *Angew. Chem., Int. Ed.* **2002**, *41*, 1769. (e) Bottari, G.; Leigh, D. A.; Pérez, E. M. *J. Am. Chem. Soc.* **2003**, *125*, 13360.

(6) Altieri, A.; Bottari, G.; Dehez, F.; Leigh, D. A.; Wong, J. K. Y.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2003**, *42*, 2296.

(7) (a) Leigh, D. A.; Morales, M. Á. F.; Pérez, E. M.; Wong, J. K. Y.; Saiz, C. G.; Slawin, A. M. Z.; Carmichael, A. J.; Haddleton, D. M.; Brouwer, A. M.; Buma, W. J.; Wurpel, G. W. H.; León, S.; Zerbetto, F. *Angew. Chem., Int. Ed.* **2005**, *44*, 3062. (b) Wang, Q.-C.; Qu, D.-H.; Ren, J.; Chen, K.-C.; Tian, H. *Angew. Chem., Int. Ed.* **2004**, *43*, 2661. (c) Pérez, E. M.; Dryden, D. T. F.; Leigh, D. A.; Teobaldi, G.; Zerbetto F. *J. Am. Chem. Soc.* **2004**, *126*, 12210.

(8) Kaletaş, B. K.; Dobrawa, R.; Sautter, A.; Würthner, F.; Zimine, M.; De Cola, L.; Williams, R. M. *J. Phys. Chem. A* **2004**, *108*, 1900.

(9) Förster, T. *Ann. Phys.* **1948**, 55.

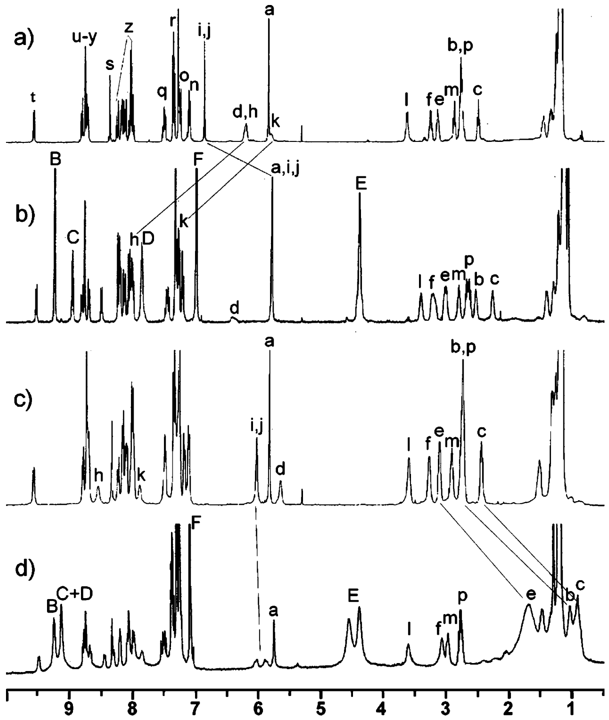


Figure 1. ^{1}H NMR spectra of (a) thread **E2**, (b) [2]rotaxane **E1**, (c) thread **Z2**, and (d) [2]rotaxane **Z1**. The assignments correspond to the lettering shown in Scheme 1.

maleamide isomer, the situation was completely reversed. The Z olefin protons (Hi′ and Hj′) resonated at almost identical chemical shifts in the rotaxane and thread, whereas the succinic amide ester methylene groups (Hb and Hc) were each shielded by >1.5 ppm in the rotaxane.

The absorption spectra of **E2**, **Z2**, **E1**, and **Z1** showed superposition features of the pyrene and perylene moieties, only **Z1** showed red-shifted pyrene absorption. The absorption patterns allow the virtually selective excitation of pyrene and perylene moieties in these compounds (Figure S1).

As shown in Figure 2a, upon excitation of pyrene moiety in **E2** and **Z2**, both compounds had strongly quenched pyrene emission (λ_{max} = 377 nm) and enhanced perylene emission (λ_{max} = 556 nm) compared with pyrene and perylene reference, which indicate the present of a photoinduced energy transfer process.[8] In the case of excitation of **E2** and **Z2** at 500 nm, where only the perylene moiety absorbs, energy transfer could not be observed; however, the emission intensity of the perylene unit of **E2** and **Z2** was quenched (~30%) as compared with the reference compound **Pery-ref**. It is well-known that pyrene and perylene are good donor and acceptor groups, respectively; therefore it is not surprising that an electron transfer occurs from the excited perylene.[9] All these indicated the presence of both photoinduced electron and energy transfer processes in these pyrene−perylene dyads as reported by the Würthner group.[8]

The fluorescence intensity of perylene in **Z2** was quenched stronger than that in **E2**, which may be due to the shorter distance between pyrene and perylene bisimide in **Z2** because

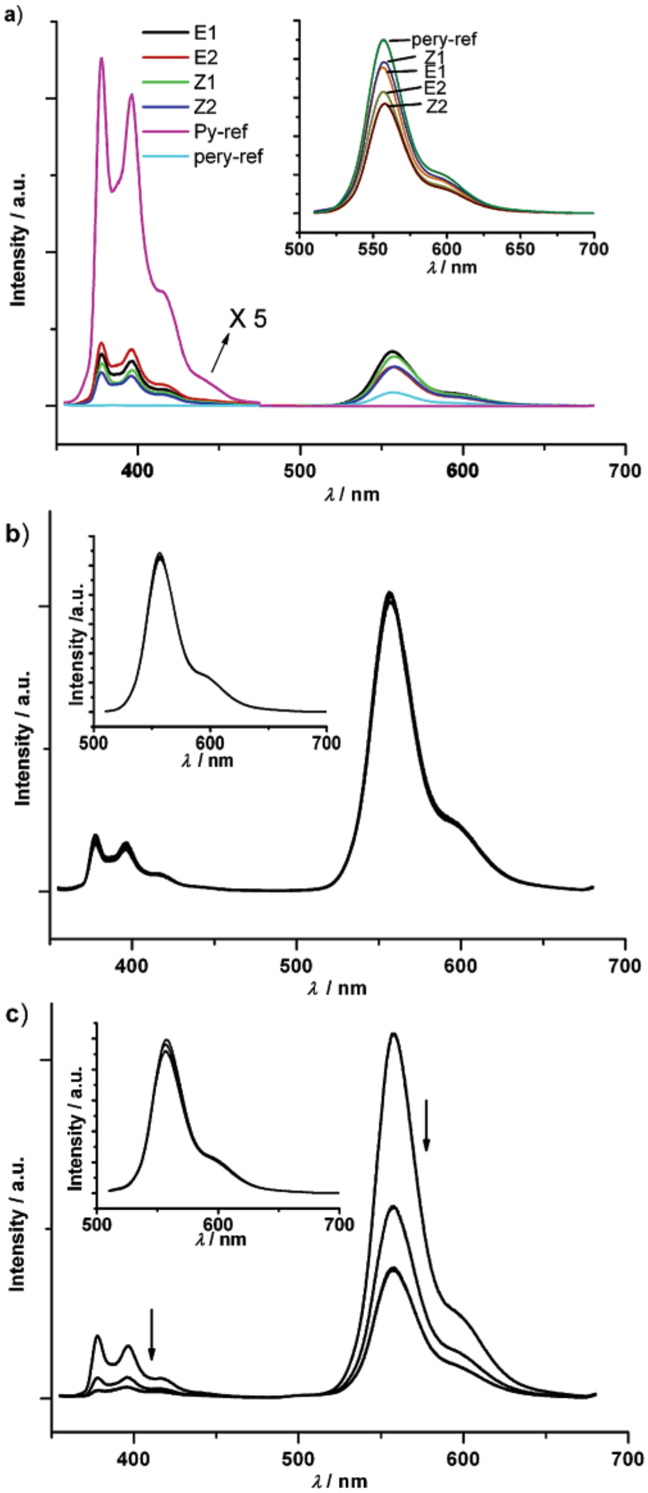


Figure 2. (a) Fluorescence emission spectra (λ_{exc} = 345 nm, 2 × 10^{-6} M, 298 K) of **E1/E2**, **Z1/Z2**, **py-ref**, and **pery-ref** in $CHCl_3$. Inset: λ_{exc} at 500 nm. All spectra are corrected according to absorptions at 345 or 500 nm, and below 475 nm a multiplying factor of 5 is used. (b) Fluorescence emission spectra changes (λ_{exc} = 345 nm) of **E1** upon the addition of CF_3COOH (TFA). Inset: λ_{exc} at 500 nm. (c) Fluorescence emission spectra changes (λ_{exc} = 345 nm) of **Z1** upon the addition of CF_3COOH (TFA). Inset: λ_{exc} at 500 nm.

of the easier intramolecular folding. For rotaxane **E1** and **Z1**, the macrocycle prevented the intramolecular folding of the thread, so the photoinduced electron transfer was slowed and the emission of the perylene moiety was enhanced compared with that of the thread **E2** and **Z2** (Figure 2a and Figure 4a).

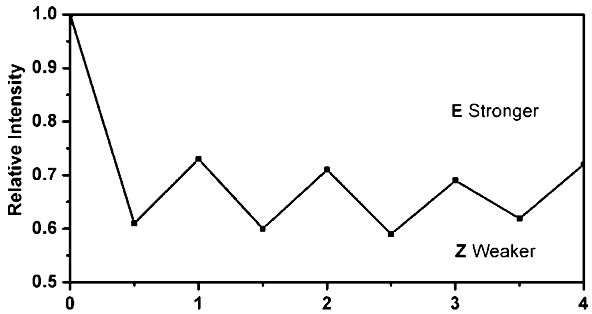


Figure 3. Changes in fluorescence intensity at 556 nm (excited at 345 nm) for CH_2Cl_2 solution of pronated **E1** on alternating irradiation at 254 and 365 nm for four complete cycles.

In the rotaxane **Z1**, the protonation of the pyridines in the macrocycle by CF_3COOH (TFA) resulted in the quenching of the emission of pyrene through electron transfer (Figure 2c).[10] The energy transfer from pyrene to perylene moiety was then switched off, and the fluorescence of the perylene moiety became weaker. In the case of **E1**, the photoinduced electron transfer from the perylene moiety to pyridinium was less efficient, which may due to the larger distance between the perylene moiety and the fumaramide group, and the fluorescence of perylene and pyrene moieties could not be quenched by pyridinium, that is, TFA had no effect on the emission spectra of **E1** as shown in Figure 2b.

There existed different photostationary states of **E1/Z1** at different wavelengths (relative percentage of **E1/Z1** was not tested),[5e,7c] and evident fluorescent change could be achived by irradiating with light of different wavelengths. Because of the reversibility of the photoisomerization process, the photoinduced shuttling motion of the macrocycle could be repeated with reversible fluorescent output signals (Figure 3). Thus, the photinduced shuttling motion could be easily detected by means of a fluorescent output signal at 556 nm. This molecular shuttle worked remarkably well.

Thus this molecular shuttle could be made a fluorescence switch as depicted in Figure 4. The macrocycle in the thread

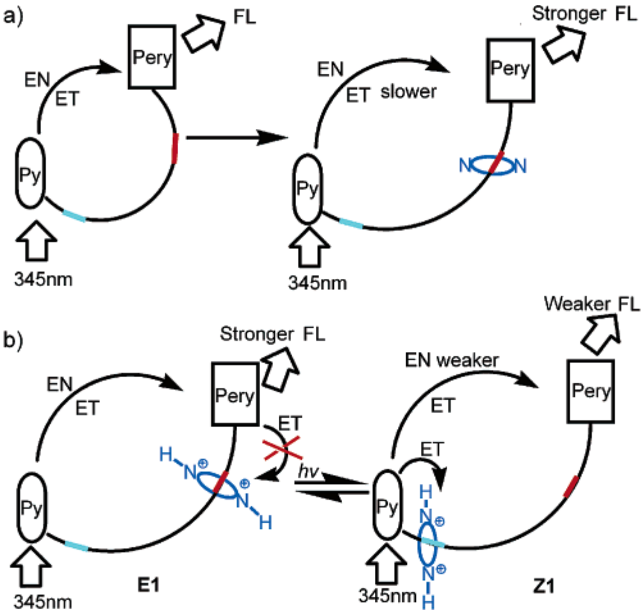


Figure 4. Schematic presentation describing the intertranslation of different states: (a) the macrocycle influence of the intramolecular folding and (b) the protonated macrocycle acting as a switcher for the energy transfer from pyrene to perylene moiety.

weakened the electron transfer from the pyrene to the perylene moiety, and the protonated macrocycle could act as a switcher for the energy transfer from the pyrene to the perylene moiety, which resulted in changes of fluorescence of the perylene moiety.

In conclusion, we have synthesized a novel pyrene, perylene bisimide containing [2]rotaxane in which the macrocycle can be shuttled between co-conformations that position it close to either pyrene or perylene bisimide. The protonated macrocycle can act as a switcher for the energy transfer from the pyrene to the perylene moiety, which elicits a fluorescence response.

Acknowledgment. This work was supported by the Major State Basic Research development Program and the National Natural Science Foundation of China (20131040, 50372070, 20418001, 20473102, and 20421101).

Supporting Information Available: Full experimental details pertaining to the preparation of **E1**/**Z1**. This material is available free of charge via the Internet at http://pubs.acs.org.

OL051567T

---

[10] Palit, D. K.; Sapre, A. V.; Mittal, J. P. *Chem. Phys. Lett.* **1997**, *269*, 286.