Up-conversion luminescent switch based on photochromic diarylethene and rare-earth nanophosphors†

Zhiguo Zhou, He Hu, Hong Yang, Tao Yi,* Kewei Huang, Mengxiao Yu, Fuyou Li* and Chunhui Huang

Received (in Cambridge, UK) 28th May 2008, Accepted 7th July 2008
First published as an Advance Article on the web 12th August 2008
DOI: 10.1039/b809021a

We have demonstrated a novel and unique route to a highly efficient luminescent switch with nondestructive readout capability by utilizing photochromic diarylethene and up-conversion LaF_3:Yb,Ho nanophosphors.

Photochromic materials such as spiropyrans, fulgides and azobenzenes have recently attracted significant attention from both the fundamental and practical points of view for their potential applications as optical memory devices and switches.[1] Diarylethene derivatives (DTEs) are the most promising candidates because of their notable irreversible thermal photochromic behaviour, high photoisomerization quantum yields and outstanding fatigue resistance.[2] For practical applications in high density data storage systems, nondestructive readout capability is indispensable. So far, several attempts have been made to achieve this. In general, the objective is the synthesis of photochromic materials with a gated photochromic system in which two different kinds of stimuli such as thermal–optical, magneto–optical or electrical–optical can read the memory non-destructively.[3] Another approach is to use the readout light which should not induce any photochromic reactions.[4] Among various types of signal outputs such as fluorescence, infrared, refractive index, electric conductance and so on, fluorescent emission is one of the most promising signal modes owing to its high sensitivity, high resolution and high contrast. Many different classes of fluorescent DTEs have been obtained in which fluorescent chromophores are covalently attached to DTEs[5] or doped in the polymer films of DTEs.[6] It is a requirement that DTEs (in both the open and closed states) should have zero absorbance at the fluorescence excitation wavelength, so generating no photochromic reactions during the fluorescence readout process. Despite this simple strategic principle for the nondestructive readout process, few suitable material systems have been found so far due to the inherent limitation of the Stokes' shift in conventional fluorescent fluorophores.

Up-conversion rare-earth nanophosphors (UCNPs) consisting of certain lanthanide dopants embedded in a crystalline host lattice can convert low energy near-infrared excitation light into emission at visible wavelengths *via* the sequential absorption of two or more low energy photons.[7] Different colours of visible light can be obtained from different up-conversion nanophosphors when excited by the same IR laser.[8] Compared with the conventional down-conversion luminescent materials, UCNPs show very low background fluorescence, minimal photo damage, deep penetration and so on. In addition, UCNPs generate large anti-Stokes shifts of up to 500 nm, which results in well-separated emission and excitation bands. For this reason they have already recently received significant attention for possible uses in bioassay and bioimaging.[9] Recently, our group reported a versatile synthetic strategy for carboxylic acid-functionalized UCNPs and applied it as a highly sensitive DNA sensor.[10] In the present paper, we have employed a DTE derivative (compound **1**,[11] Scheme 1) in LaF_3:Yb,Ho loaded poly(methyl methacrylate) (PMMA) film, and demonstrated an up-conversion luminescent switch by an intermolecular energy transfer process[12] from UCNPs to the closed state of **1**.

The LaF_3:Yb,Ho was synthesized by a modified hydrothermal process.[13] These nanophosphors have been characterized by transmission electron microscopy (TEM) and powder X-ray diffraction (XRD) analyses. The representative TEM image of the as-prepared LaF_3:Yb,Ho clearly showed very uniform nanocrystals, with an average diameter of about 30 nm (Fig. 1). From the powder X-ray diffraction pattern (Fig. S1 in ESI†), we can see that the as-prepared Yb/Ho co-doped LaF_3 nanocrystals displayed the pure hexagonal LaF_3 phase (JCPDS card 72-1435). LaF_3:Yb,Ho also has high crystallinity, contributing to the strong luminescence.

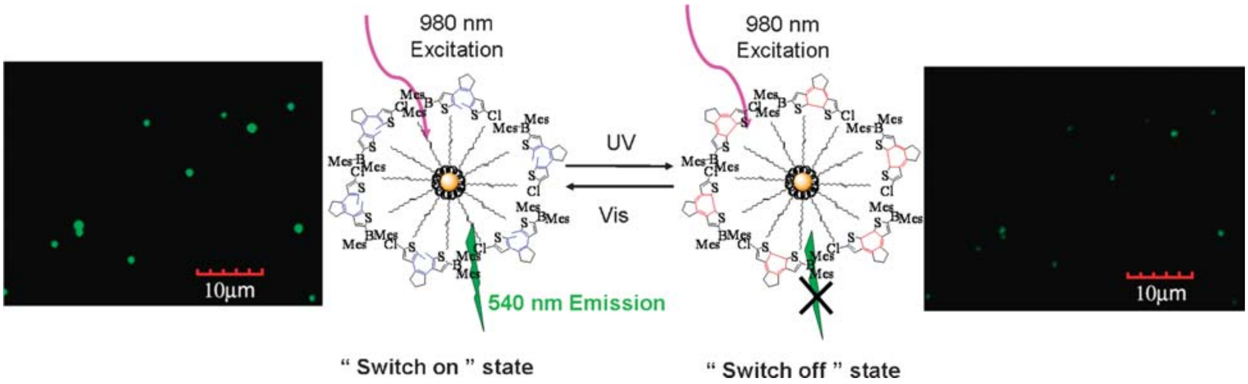
1 underwent a reversible photocyclization reaction under alternating illumination by ultraviolet and visible light, displaying a new absorption band centred at 560 nm in THF solution.[11] The hybrid system **1**/LaF_3:Yb,Ho loaded into PMMA film performed a reversible photochromic reaction similar to that of the isolated species **1**. The open form of **1** on the film showed an absorption located at 340 nm. Upon irradiation by UV light (365 nm), a new absorption band centred at 560 nm appeared in a photostationary state (PSS, Fig. 2). On the other hand, the PSS converted to the open-ring form upon irradiation with visible light of wavelength greater than 450 nm.

The up-conversion luminescence of **1**/LaF_3:Yb,Ho-loaded PMMA film pumped with 980 nm diode lasers shows a green colour (Fig. 2 inset), with the emission peaks mainly located at 540 and 645 nm, corresponding to energy transfer from the

---

Department of Chemistry & Laboratory of Advanced Materials, Fudan University, Shanghai, 200433, PR China.
E-mail: yitao@fudan.edu.cn. E-mail: fyli@fudan.edu.cn;
Fax: +86-21-55664621; Tel: +86-21-55664185

† Electronic supplementary information (ESI) available: Experimental details and XRD profiles. See DOI: 10.1039/b809021a



Scheme 1 Principle and confocal luminescence images of the up-conversion luminescent switch consisting of **1**/LaF_3:Yb,Ho-loaded PMMA film. Before (left), and after (right) irradiation with 365 nm light for 30 min, λ_{ex} = 980 nm.

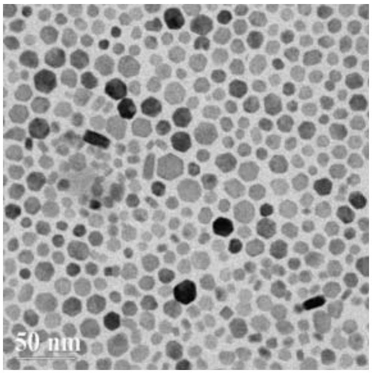


Fig. 1 TEM image of LaF_3:Yb,Ho.

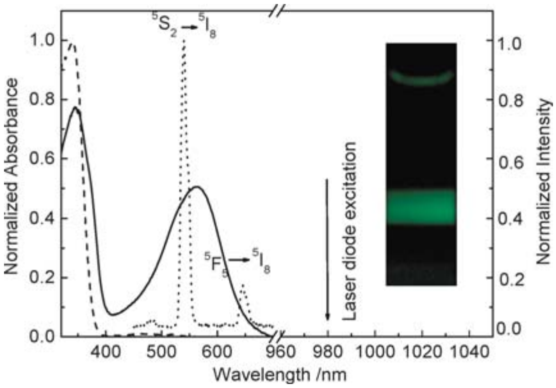


Fig. 2 UV-visible absorption spectra of **1**/LaF_3:Yb,Ho-loaded PMMA film before (dashed line) and after (solid line) irradiation with 365 nm light for 30 min, and the normalized up-conversion luminescence spectra of the prepared film (dotted line, λ_{ex} = 980 nm). Inset shows the image of the up-conversion emission of the film.

excited states $^5S_2$ and $^5F_5$ to the ground state $^5I_8$, respectively (Fig. 2).[14] It is obvious that the up-conversion luminescence of LaF_3:Yb,Ho significantly overlaps the absorption band of the PSS of **1** (Fig. 2) and therefore can be effectively quenched by the PSS of **1** through an intermolecular energy transfer process[12] from UCNPs (energy donor) to the closed state of **1** (energy acceptor) upon irradiation with UV light. Scheme 1 shows the fundamental principle of the up-conversion luminescent switch. What is more important is that **1** has zero absorbance in the near-infrared region, so this nondestructive up-conversion luminescent switch process, excited by near-infrared light (980 nm), is performed perfectly. This is confirmed by the confocal luminescence images of **1**/LaF_3:Yb,Ho-loaded PMMA film before and after UV light irradiation (Scheme 1).

To make the intermolecular energy transfer process in PMMA film more effective, the ratio of **1** to LaF_3:Yb,Ho was optimized. The up-conversion luminescence spectra of **1**/LaF_3:Yb,Ho-loaded PMMA films were measured after the photochromic reaction, with the weight of LaF_3:Yb,Ho fixed and that of **1** was varied. As shown in Fig. 3(a), upon irradiation with UV light, the up-conversion luminescent intensity at

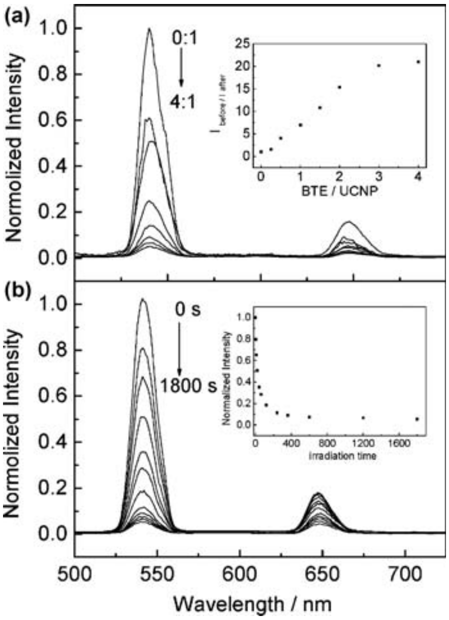


Fig. 3 (a) Up-conversion luminescence spectra of **1**/LaF_3:Yb,Ho loaded PMMA films in the PSS with different weight ratio of **1** to LaF_3:Yb,Ho (**1** : UCNP = 0 : 1, 1 : 4, 1 : 2, 1 : 1, 1.5 : 1, 2 : 1, 3 : 1 and 4 : 1, respectively). Inset graph shows the change of up-conversion luminescence at 540 nm as a function of weight ratio of **1** to LaF_3:Yb,Ho; (b) Up-conversion luminescence spectra of **1**/LaF_3:Yb,Ho (4 : 1) loaded PMMA film after different irradiation times with 365 nm light (time interval: 0, 5, 10, 20, 40, 60, 120, 240, 360, 600, 1200, 1800 s, λ_{ex} = 980 nm).

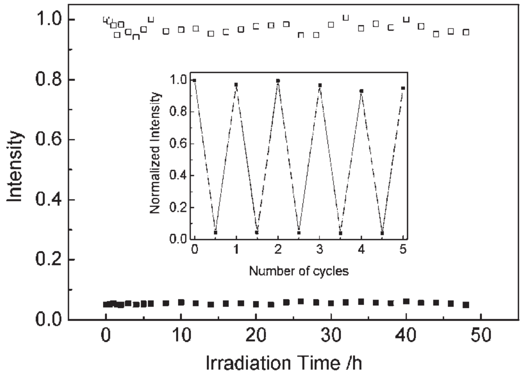


Fig. 4 Nondestructive readout capability of **1**/LaF_3:Yb,Ho-loaded PMMA film in the open state (□) and in the PSS state (■), λ_{ex} = 980 nm. Inset graph shows the modulated up-conversion luminescence intensity at 540 nm of the PMMA film during alternating UV and visible light irradiation.

540 nm decreased as the proportion of **1** increased. The up-conversion luminescent intensity levelled off when the ratio was above 3 : 1. The maximum difference of up-conversion luminescent intensity before and after UV irradiation was up to a factor 20, which is a sufficiently high contrast for information storage with luminescence mode. In addition, the change of up-conversion luminescent intensity at 540 nm with variation of irradiation time by UV light was also investigated on a film of **1**/LaF_3:Yb,Ho (4 : 1). After irradiation for 30 min, the up-conversion luminescent spectra remained stable.

As shown in Fig. 4 inset, the up-conversion luminescent switch had good reversibility with alternating UV (365 nm) and visible light (>450 nm) irradiation for many cycles. The reversible changes can be used in a repeated ''write-erase'' process. To investigate its nondestructive readout capability, **1**/LaF_3:Yb,Ho-loaded PMMA film was continuously irradiated by the 980 nm diode laser. The strong irradiation of 980 nm (800 mw) induced no discernible changes of up-conversion luminescence both in the ''switch on'' and ''switch off'' state. After irradiation with the 980 nm laser for 48 h, the increase of up-conversion luminescence was less than 2% when **1** was in the open form, and the decrease was less than 1% when **1** was in the photostationary state. This is attributed to the negligible absorbance of **1** at 980 nm in both the open and PSS states. Thus, the present system affords a good example of nondestructive readout capability.

In summary, by combination of the organic photochromic DTE and upconversion LaF_3:Yb,Ho nanophosphors, a hybrid switchable system has been obtained. Because DTE has negligible absorbance at 980 nm in both the open form and the PSS, whereas LaF_3:Yb,Ho nanophosphors can emit visible luminescence by excitation at 980 nm due to the large anti-Stokes' shift, a novel and unique route to a highly efficient nondestructive optical memory can be developed in this DTE/LaF_3:Yb,Ho hybrid nanosystem *via* an intermolecular energy transfer process.

This work was supported by the National Science Foundation of China (20571016, 20501006, 20775017 and 20771027), Shanghai Sci. Tech. Comm. (06J14016, 06QH14002), National High Technology Program of China (2006AA03Z318), and Shanghai Leading Academic Discipline Project (B108).

Notes and references

1 (*a*) B. L. Feringa, *Molecular Switches*, Wiley-VCH, 2001; M. Irie, *Chem. Rev.*, 2000, **100**, 1685–1716; (*b*) Y. Yokoyama, *Chem. Rev.*, 2000, **100**, 1741–1754; (*c*) F. M. Raymo and M. Tomasulo, *Chem. Soc. Rev.*, 2005, **34**, 327–336; (*d*) W. F. Yuan, L. Sun, H. H. Tang, Y. Q. Wen, G. Y. Jiang, W. H. Huang, L. Jiang, Y. L. Song, H. Tian and D. B. Zhu, *Adv. Mater.*, 2005, **17**, 156–160.

2 (*a*) H. Tian and S. G. Yang, *Chem. Soc. Rev.*, 2004, **33**, 85–97; (*b*) S. Kawata and Y. Kawata, *Chem. Rev.*, 2000, **100**, 1777–1788; (*c*) M. Irie, S. Kobatake and M. Horichi, *Science*, 2001, **291**, 1769–1772; (*d*) M. Irie, T. Fukaminato, T. Sasaki, N. Tamai and T. Kawai, *Nature*, 2002, **420**, 759–760; (*e*) K. Uchida, M. Saito, A. Murakami, T. Kobayashi, S. Nakamura and M. Irie, *Chem.–Eur. J.*, 2005, **11**, 534–542.

3 (*a*) T. Tsujioka, Y. Hamada, K. Shibata, A. Taniguchi and T. Fuyuki, *Appl. Phys. Lett.*, 2001, **78**, 2282–2284; (*b*) K. Uchida, M. Saito, A. Murakami, S. Nakamura and M. Irie, *Adv. Mater.*, 2003, **15**, 121–125; (*c*) J. Areephong, W. R. Browne, N. Katsonis and B. L. Feringa, *Chem. Commun.*, 2006, 3930–3932.

4 (*a*) S. J. Lim, J. W. Seo and S. J. Park, *J. Am. Chem. Soc.*, 2006, **128**, 14542–14547; (*b*) G. Y. Liang, S. Wang, W. F. Yuan, L. Jiang, Y. L. Song, H. Tian and D. B. Zhu, *Chem. Mater.*, 2006, **18**, 235–237; (*c*) C. C. Corredor, Z. L. Huang and K. D. Belfield, *Adv. Mater.*, 2006, **18**, 2910–2914; (*d*) S. Z. Xiao, Y. Zhou, M. X. Yu, T. Yi, Y. F. Zhou, F. Y. Li and C. H. Huang, *Chem. Commun.*, 2007, 4758–4760; (*e*) S. L. Lim, B. K. An and S. Y. Park, *Macromolecules*, 2005, **38**, 6236–6239; (*f*) T. Nakagawa, K. Atsumi, T. Nakashima, Y. Hasegawa and T. Kawai, *Chem. Lett.*, 2007, **36**, 372–373.

5 (*a*) V. W. W. Yam, C. C. Ko and N. Y. Zhu, *J. Am. Chem. Soc.*, 2004, **126**, 12734–12735; (*b*) T. A. Golovkova, D. V. Kozlov and D. C. Neckers, *J. Org. Chem.*, 2005, **70**, 5545–5549; (*c*) M. Bossi, V. Belov, S. Polyakova and S. W. Hell, *Angew. Chem., Int. Ed.*, 2006, **45**, 7462–7465; (*d*) J. Folling, S. Polyakova, V. Belov, A. Blaaderen, M. L. Bossi and S. W. Hell, *Small*, 2008, **4**, 134–142.

6 (*a*) S. Murase, M. Teramoto, H. Furukawa, Y. Miyashita and K. Horie, *Macromolecules*, 2003, **36**, 964–966; (*b*) D. V. Kozlov and F. N. Castellano, *J. Phys. Chem. A*, 2004, **108**, 10619–10622; (*c*) Y. Chen and N. Xie, *J. Mater. Chem.*, 2005, **15**, 3229–3232.

7 F. Auzel, *Chem. Rev.*, 2004, **104**, 139–173.

8 (*a*) E. Downing, L. Hesselink, J. Ralston and R. Macfarlane, *Science*, 1996, **273**, 1185–1189; (*b*) S. Heer, O. Lehmann, M. Haase and H. U. Gudel, *Angew. Chem., Int. Ed.*, 2003, **42**, 3179–3182; (*c*) S. Heer, K. Kompe, H. U. Gudel and M. Haase, *Adv. Mater.*, 2004, **16**, 2102–2104; (*d*) O. Ehlert, R. Thomann, M. Darbandi and T. Nann, *ACS Nano*, 2008, **2**, 120–124.

9 (*a*) F. V. Rijke, H. Zijlmans, S. Li, T. Vail, A. K. Raap, R. S. Niedbala and H. J. Tanke, *Nat. Biotechnol.*, 2001, **19**, 273–276; (*b*) L. Y. Wang, R. X. Yan, Z. Y. Huo, L. Wang, J. H. Zeng, J. Bao, X. Wang, Q. Peng and Y. D. Li, *Angew. Chem., Int. Ed.*, 2005, **44**, 6054–6057; (*c*) L. Y. Wang and Y. D. Li, *Chem. Commun.*, 2006, 2557–2558; (*d*) S. F. Lim, W. S. Ryu, N. Khanarian, C. K. Tung, D. Tank and R. H. Austin, *Nano Lett.*, 2006, **6**, 169–174.

10 Z. G. Chen, H. L. Chen, H. Hu, M. X. Yu, F. Y. Li, Q. Zhang, Z. G. Zhou, T. Yi and C. H. Huang, *J. Am. Chem. Soc.*, 2008, **130**, 3023–3029.

11 Z. G. Zhou, H. Yang, M. Shi, S. Z. Xiao, F. Y. Li, T. Yi and C. H. Huang, *ChemPhysChem*, 2007, **8**, 1289–1292.

12 (*a*) P. Zhang, S. Rogelj, K. Nguyen and D. Wheeler, *J. Am. Chem. Soc.*, 2006, **128**, 12410–12411; (*b*) K. Kuningas, T. Rantanen, T. Ukonaho, T. Lovgen and T. Soukka, *Anal. Chem.*, 2005, **77**, 7348–7355; (*c*) K. Kuningas, T. Ukonaho, H. Pakkila, T. Rantanen, J. Rpsenberg, T. Lovgen and T. Soukka, *Anal. Chem.*, 2006, **78**, 4690–4696.

13 X. Wang, J. Zhuang, Q. Peng and Y. D. Li, *Nature*, 2005, **437**, 121–124.

14 F. Lahoz, I. R. Martin and A. Briones, *J. Appl. Phys.*, 2004, **95**, 2957–2962.