NJC

Cite this: *New J. Chem.*, 2012, **36**, 2223–2227

www.rsc.org/njc

PAPER

Selective photoconversion of photochromic diarylethenes and their properties

Huan-huan Liu and Yi Chen*

Received (in Montpellier, France) 10th May 2012, Accepted 2nd August 2012
DOI: 10.1039/c2nj40377c

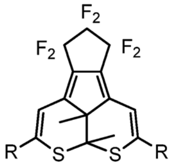
Selective photoconversions of photochromic diarylethene derivatives has been described using diarylethene derivative **1a** as a model compound. Upon irradiation with 254 nm light, **1a** undergoes photocyclization to yield the ring-closed isomer **1b** in the absence of oxygen, or is transformed to the thiolactone derivative **1c** in the presence of oxygen (in the air), respectively. It was found that **1b** can be reversed back to **1a** with visible light irradiation, the ring-opening and ring-closing photoswitch can be performed in the absence of oxygen. **1c** is, however, photo-inactive and cannot be reversed back to **1a** with UV or visible light irradiation. It was also found that **1c** shows fluorescence whereas both **1a** and **1b** show no fluorescence.

Introduction

Selective reaction plays a key role not only in biological processes, such as the inhibition of enzymes,[1] detection of metal ions,[2] functionalization of peptides,[3] and activation of proteins,[4] but also in chemical processes, such as asymmetric synthesis,[5] specific recognition,[6] and catalytic reactions.[7] Currently, controllable and selective reactions have attracted considerable attention in material science from both fundamental and practical points of view.[8]

Photo-active molecules have generated considerable interest due to wide potentials in chemistry,[9] biochemistry,[10] environmental science[11] and material science.[12] Light is a particularly effective stimulus to spatially and temporally trigger changes in the structure and function of molecules and materials.[13] Diarylethenes, notably the bis(thien-3-yl) system,[14] are photo-active molecules and have been widely used as promising photoswitches to control various chemical and physical properties, including absorption and fluorescence,[15] electrochemical response,[16] magnetic interactions,[17] electronic conduction,[18] chemical reactivity,[19] and self-assembling behavior,[20] because of their fatigue resistant and thermally irreversible properties.[21]

Diarylethenes undergo not only ring-opening and ring-closing photoisomerization but also photo-rearrangement upon irradiation with UV light. It has been reported that thiopyranothiopyran derivatives[22] (Scheme 1) as the main by-product was obtained during the photochromic interconversion of diarylethenes under UV light irradiation. The mechanism study demonstrated that the ring-closed isomers of diarylethenes are photo-unstable and are photo-rearranged to thiopyranothiopyran derivatives with UV light irradiation. Although thiopyranothiopyran derivatives as the main by-product was reported,[22] the known diarylethene systems show good fatigue resistance, and only a little by-product was obtained after the photochromic interconversion reaction. In this paper, we report a new finding, that photochromic diarylethenes with a bis (5-chloro-2-methylthiophen-3-yl) system are selectively converted to the ring-closed isomers and thiolactone derivatives (not thiopyranothiopyran derivatives) in the absence and in the presence of oxygen, respectively. Property studies show that the formation of the thiolactone derivatives undergoes two steps: first photocyclization, and then photooxidation (not photo-rearrangement). The selective photo-conversion of diarylethene **1a** to the ring-closed isomer **1b** and thiolactone derivative **1c** is outlined in Scheme 2.



Scheme 1 Structure of thiopyranothiopyran derivatives.

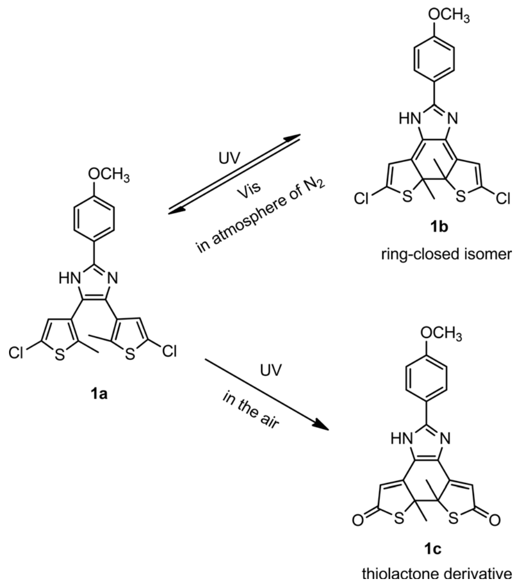
Experimental

General

^{1}H NMR spectrum was recorded at 400 MHz with TMS as an internal reference and DMSO-d$_6$ as solvent. ^{13}C NMR spectra were recorded at 100 MHz with TMS as an internal reference and DMSO-d$_6$ as solvent. MS spectra were recorded with a Trio-2000 GC-MS spectrometer. HRMS spectra were recorded

---

Key Laboratory of Photochemical Conversion and Optoelectronic Materials, Technical Institute of Physics and Chemistry, The Chinese Academy of Science, Beijing, 100190, China. E-mail: yichencas@yahoo.com.cn; Fax: +86 10 6487 9375; Tel: +86 10 8254 3595

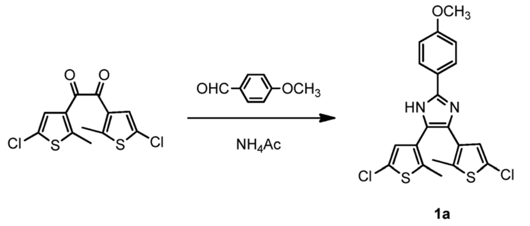


Scheme 2 Selective photoconversion of diarylethene **1a** to ring-closed isomer **1b** and thiolactone derivative **1c** with 254 nm light irradiation.

with a GC-TOF MS spectrometer. Absorption and fluorescence spectra were measured with an absorption spectrophotometer (Hitachi U-3010) and a fluorescence spectrophotometer (Hitachi F-2500), respectively. All chemicals for synthesis were purchased from commercial suppliers, and solvents were purified according to standard procedures. Reactions were monitored by TLC silica gel plates (60F-254). Column chromatography was performed on silica gel (Merck, 70–230 mesh) and neutral Al_2O_3 (100–200 mesh), respectively. A 360 nm lamp (36 W) and a Xenon light (500 W), with different wavelength filters, were used as light sources for photocoloration and photobleaching, respectively.

Material

Diarylethene **1a** was prepared according to the synthetic route shown in Scheme 3. Diketone was obtained starting from commercially available 2-methlthiophene, which was chlorinated at the 5-position with NCS in AcOH,[23] followed by acylation with oxalyl chloride in DCM.[24] Treatment of the diketone with 4-methoxybenzaldehyde in the presence of NH_4Ac afforded the target compound **1a**. The detailed procedures and spectra data were as follows: To a solution of diketone (100 mg, 0.31 mmol) in acetic acid (10 ml) was added 4-methoxybenzaldehyde (0.37 mmol) and NH_4Ac (143 mg, 1.86 mmol). The resulting solution was stirred at reflux until all the starting material had reacted (TLC detection). The resulting solution was then slowly poured into $NaHCO_3$ solution (10%, 50 ml), and the product was extracted with $CHCl_3$ (3 × 20 ml). The combined organic phases were washed with H_2O (30 ml) and dried over $MgSO_4$. After evaporation of the solvent, the crude product was purified by flash column chromatography (petroleum ether (60–90 °C)–ethyl acetate = 10 : 1, v/v) to give diarylethene **1a** in 75% yield. ^1H NMR (400 MHz, DMSO-d_6): 12.54 (s, 1H), 7.95 (d, 2H, J = 8.6 Hz), 7.10 (s, 1H), 7.05 (d, 2H, J = 8.7 Hz), 6.81 (s, 1H), 3.81 (s, 3H), 2.19 (s, 3H), 2.01 (s, 3H). HRMS (GC-TOF) (m/z) calcd for $C_{20}H_{16}Cl_2N_2OS_2$: 435.9602, found: 435.9602 (100%).



Scheme 3 Synthesis of diarylethene **1a**.

Thiolactone derivative **1c** was prepared as follows: **1a** (50 mg, 0.15 mmol) was dissolved in CH_3CN (50 ml). The resulting solution was then irradiated for 30 min under a high pressure Hg lamp (500 W). After the conversion was complete (detection by TLC), the solvent was evaporated under reduce pressure, the crude product was purified by flash column chromatography (neutral Al_2O_3, 100–200 mesh, elute: petroleum ether/acetone = 1 : 3, v/v) to afford **1c** in 63% yield. IR (KBr) ν: 3318 (NH), 3251 (arom, CH), 2879 (alipha, CH), 1687, 1786 (C=O), 1615 (arom, CH). ^1H NMR (400 MHz, DMSO-d_6): 13.69 (s, 1H), 8.10 (d, 2H, J = 8.8 Hz), 7.14 (d, 2H, J = 8.9 Hz), 6.74 (s, 2H), 3.84 (s, 3H), 1.58 (s, 6H). ^{13}C NMR (100 MHz, DMSO-d_6: 194.3, 161.2, 152.8, 148.1, 130.2, 128.3, 121.1, 120.7, 114.6, 67.4, 55.4, 26.9. HRMS (GC-TOF) (m/z) calcd. for $C_{20}H_{16}N_2O_3S_2$: 396.0602, found: 396.0608 (100%). Anal. calcd. for $C_{20}H_{16}N_2O_3S_2$: C, 60.59, H, 4.07; N, 7.07. Found: C, 60.71; H, 3.98; N, 6.96.

Results and discussion

(1) Photoconversion of 1a to 1b and its photoswitching properties

The ring-opening and ring-closing photoisomerization of **1a** is described in Scheme 1. Upon irradiation with UV light, the absorption band (λ_{max} = 300 nm, $\varepsilon = 2.5 \times 10^4$ L mol^{-1} cm^{-1}), in CH_3CN solution in the atmosphere of N_2, which is attributed to the ring-open isomer **1a**, decreased in intensity, and two new bands (λ_{max} = 520 nm and 330 nm, respectively), which correspond to the ring-closed isomer **1b** (whose structure was identified by ^1H NMR spectroscopy), appeared at the same time (Fig. 1). The band at 520 nm increased in intensity with the increase of irradiation time until the photostationary state (**PSS**) was reached (quantum yield: $\phi_{1a\rightarrow 1b}$ = 0.364, conversion yield: 90%). This process was accompanied by a colour change of the solution from colourless to red. The red solution could be bleached back to colourless with visible light ($\geq$ 400 nm) irradiation, and the coloration and decoloration could be recycled. As presented in Fig. 1, the figure shows the typical absorption spectra changes of the photochromic diarylethene derivatives in solution, and the clear isosbestic point (λ = 318 nm) indicates that only two isomers (**1a** and **1b**) exist when **1a** undergoes photo-conversion to **1b**.

(2) Photoconversion of 1a to 1c and its formation mechanism

The photoconversion of **1a** to **1c** was performed in the presence of oxygen with 254 nm light irradiation, and the spectral changes of **1a** were examined in acetonitrile solution in air. As presented in Fig. 2, it was found that the absorption spectral changes of **1a**, that are a function of irradiating time, involved two stages: before 45 s (irradiation time), the absorption

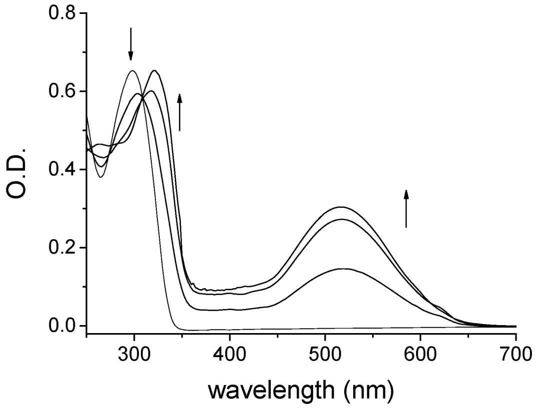


Fig. 1 Absorption changes of diarylethene **1a** (25 μM, CH_3CN) in a N_2 atmosphere with 254 nm light irradiation until the photostationary state (periods: 0, 15, 30, 45 s).

of 520 nm increased in intensity with the increase of irradiation time, but after 45 s, the absorption of 520 nm, however, decreased in intensity with the increase of irradiation time, and the absorption at 520 nm almost disappeared when the solution was irradiated for 105 s. It was also found that accompanying the decrease of 520 nm, another absorption at 380 nm appeared. Careful examination of Fig. 2 reveals that there are two clear isosbestic points that have appeared at 318 nm and 420 nm, respectively. The first isosbestic point appears at 318 nm, which was produced before 45 s, and the second one at 420 nm was formed after 45 s. Besides, the experiments also revealed that the colour of the solution was changed from colourless to red when the irradiating time is not more than 45 s, and with continuous irradiating of the solution, the colour of solution changed from red to yellow. All results suggested that a new chemical species (**1c**), rather than **1b**, was formed when the solution of **1a** was irradiated in the air.

To investigate the chemical structure of **1c** and to explore its formation mechanism, the following control experiments were carried out. First, the photo-product **1c** (Scheme 1) was obtained by the photoconversion of **1a** in solution. After purification, the chemical structure of **1c** was confirmed by NMR, HRMS, IR, and elemental analysis (see experimental). The different structure of **1c** from the fused 6-membered rings is probably due to chlorination of the thiophene ring. The control experiment showed that no thiolactone derivative was formed when the chloro-substitutent was replaced by methyl-substituents. Secondly, after careful irradiation of the solution of **1a** with a controlled irradiation time of within 30 s, we found that the colourless solution was changed to the red solution, and the red solution was completely bleached back to colourless solution with visible light (≥ 400 nm) irradiation, both coloration and decoloration could be repeated with UV/Vis light irradiation, which indicated that **1a** underwent a photochromic reaction to yield the ring-closed isomer **1b** within 30 s of irradiation. Thirdly, no **1c**, but only **1b**, was detected when the solution of **1a** was irradiated in a N_2atmosphere (O_2-free). Finally, **1b** was converted to **1c** upon irradiation with UV light in air. The colour change experiments demonstrated that the colour of the solution changed from colourless to yellow *via* two steps: colourless → red → yellow during the photoconversion of **1a** to **1c**. All results indicated that the photoconversion of **1a** to **1c** underwent two steps: first **1a** was photo-cyclized to **1b**, and then **1b** was photo-oxidised to **1c** (Scheme 4). Further investigation found that **1c** could not be reversed back to **1a** or **1b** with UV light or visible light irradiation. Moreover, **1c** was found to be photo-inactive and no significant change was detected (colour and absorption spectral) after irradiation for more than 10 min with UV light.

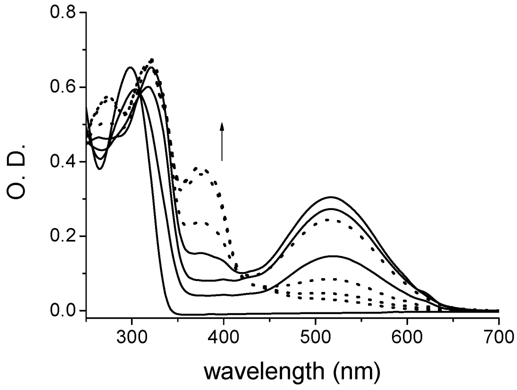
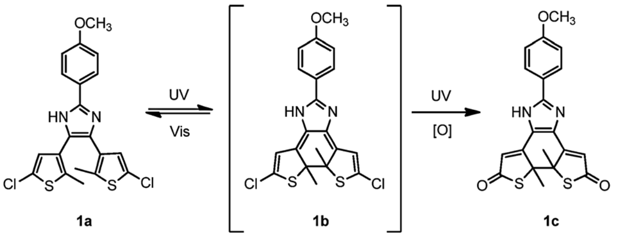


Fig. 2 Absorption changes of diarylethene **1a** (25 μM, CH_3CN) in air with 254 nm light irradiation (periods: 0, 15, 30, 45, 60, 75, 90, 105 s) (λ_{max} = 520 nm, 0 → 45 s, solid, increase with irradiation time; λ_{max} = 520 nm, 60 → 105 s, dot, decrease with irradiation time).

(3) Absorption and fluorescence of 1c

The absorption and fluorescence of **1c** were studied in acetonitrile solution using pure **1c** as the target. Fig. 3 and 4 represent the absorption and fluorescence of **1c**, respectively. There are three absorption bands at 274 nm (ε = 2.5×10^4 L mol^{-1} cm^{-1}), 300 nm (ε = 4.9×10^4 L mol^{-1} cm^{-1}) with a shoulder at 335 nm, and 388 nm (ε = 2.1×10^4 L mol^{-1} cm^{-1}), respectively, which corresponded to the n → π* and π → π* transition, respectively. With 365 nm light as excitation wavelength, the fluorescence at λ_{em} = 490 nm was observed (Fig. 4), and a moderate fluorescence quantum yield (Π_f = 0.17) was obtained by using quinine sulfate (Π_f=0.577, in H_2SO_4) as a reference.

The fluorescence changes of the photoconversion of **1a** to **1c** in acetonitrile solution with UV light irradiation was investigated. A very weak fluorescence emission of **1a** (λ_{em} = 375 nm, Π_f = 0.002) was detected when the solution of **1a** was excited with an excitation wavelength of 300 nm before irradiation. Upon irradiation with 254 nm light, a new fluorescence at 490 nm was detected with a 365 nm excitation wavelength, which was



Scheme 4 Photoconversion of diarylethene **1a** to the thiolactone derivative **1c** *via* the ring-closed isomer **1b**.

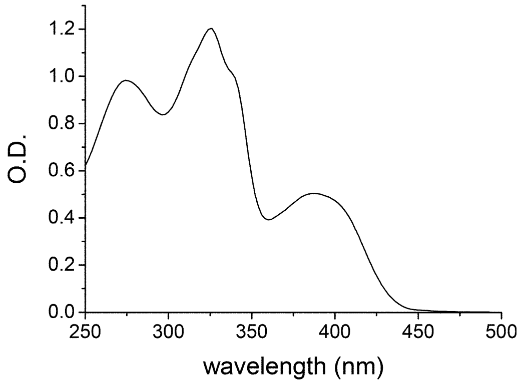


Fig. 3 Absorption spectrum of thiolactone derivative **1c** (25 μM, CH_3CN).

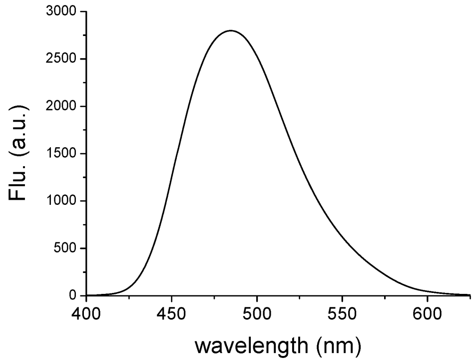


Fig. 4 Fluorescence spectrum of thiolactone derivative **1c** (25 μM, CH_3CN, $\lambda_{ex} = 300$ nm).

attributed to the emission of **1c**. As presented in Fig. 5, the fluorescence increased in intensity with increasing irradiation time, and the largest fluorescence intensity was obtained when the solution of **1a** was irradiated for 120 s, at that time, the photoconversion of **1a** to **1c** was completed. The difference in fluorescence properties (strength and wavelength) between **1a** and **1c**, and the turn-on fluorescence during the photoconversion of **1a** to **1c**, are probably beneficial for applications such as fluorescence probes, fabrication images and information storage.

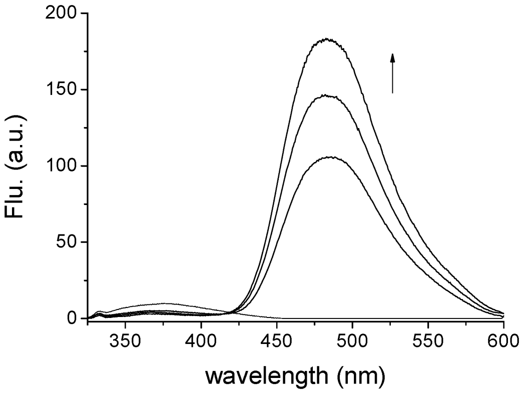


Fig. 5 Fluorescence changes during 254 nm irradiation of **1a** (25 μM, CH_3CN, $\lambda_{ex} = 365$ nm) (periods: 0, 40, 80, 120 s).

Conclusions

In summary, a photochromic diarylethene derivative, which shows selective photoconversion, has been developed. It has been demonstrated that the diarylethene derivative photoconverts to the ring-closed isomer in the absence of oxygen, and both the ring-open and ring-closed isomers show photoswitching properties with UV/Vis light irradiation. It has also been demonstrated that, in the presence of oxygen (in the air), the diarylethene derivative photoconverts to the thiolactone derivative *via* two-step photo-cyclization and photo-oxidation reaction. The thiolactone derivative exhibits fluorescence, and the turn-on fluorescence is also observed during the photoconversion of the diarylethene derivative to the thiolactone derivative.

Acknowledgements

This work was supported by the National Basic Research Program of China (2010CB934103) and the National Nature Science Foundation of China (91123032 and 21073214).

Notes and references

1 (*a*) C. Baskakis, V. Magrioti, N. Cotton, D. Stephens, V. Constantinou-Kokotou, E. A. Dennis and G. Kokotos, *J. Med. Chem.*, 2008, **51**, 8027; (*b*) D. C. Endringer, K. G. Guimaraes, T. P. Kondratyuk, J. M. Pezzuto and F. C. Braga, *J. Nat. Prod.*, 2008, **71**, 1082; (*c*) C. N. Monty, N. J. Londono and R. I. Masel, *Anal. Chem.*, 2009, **81**, 6416; (*d*) E. Bellavance, V. Luu-The and D. Poirier, *J. Med. Chem.*, 2009, **52**, 7488; (*e*) H. Wang, Z. Yan, S. Yang, J. Cai, H. Robinson and H. Ke, *Biochemistry*, 2008, **47**, 12760; (*f*) E. A. Sabens, A. M. Distler and J. J. Mieyal, *Biochemistry*, 2010, **49**, 2715.

2 (*a*) A. G. Komarov, K. M. Linn, J. J. Devereaux and F. I. Valiyaveetil, *ACS Chem. Biol.*, 2009, **4**, 1029; (*b*) Z. Ma, F. E. Jacobsen and D. P. Giedroc, *Chem. Rev.*, 2009, **109**, 4644.

3 (*a*) Y. M. Song, Y. Park, S. S. Lim, S.-T. Yang, E.-R. Woo, I.-S. Park, J. S. Lee, J. I. Kim, K.-S. Hahm, Y. Kim and S. Y. Shin, *Biochemistry*, 2005, **44**, 12094; (*b*) H. G. Franquelim, L. M. S. Loura, N. C. Santos and M. A. R. B. Castanho, *J. Am. Chem. Soc.*, 2008, **130**, 6215; (*c*) C. C. G. Scully, J. S. Blakeney, R. Singh, H. N. Hoang, G. Abbenante, R. C. Reid and D. P. Fairlie, *J. Med. Chem.*, 2010, **53**, 4938; (*d*) Y. Cui, A. Pattabiraman, B. Lisko, S. C. Collins and M. C. McAlpine, *J. Am. Chem. Soc.*, 2010, **132**, 1204.

4 (*a*) M. Renedo, J. Gayarre, C. A. Garcia-Dominguez, A. Perez-Rodriguez, A. Prieto, F. Javier Canada, J. M. Rojas and D. Perez-Sala, *Biochemistry*, 2007, **46**, 6607; (*b*) J. Schmitz, M. Mullick Chowdhury, P. Hanzelmann, N. Nimtz, E.-Y. Lee, H. Schindelin and S. Leimkuhler, *Biochemistry*, 2008, **47**, 6479; (*c*) Y. Xia, H. Han and S. A. McLuckey, *Anal. Chem.*, 2008, **80**, 1111.

5 (*a*) S.-F. Pi, X.-H. Yang, X.-C. Huang, Y. Liang, G.-N. Yang, X.-H. Zhang and J.-H. Li, *J. Org. Chem.*, 2010, **75**, 3484; (*b*) H. Fujioka, S. Matsuda, M. Horai, E. Fujii, M. Morishita, N. Nishiguchi, K. Hata and Y. Kita, *Chem.–Eur. J.*, 2007, **13**, 5238; (*c*) P. Krumlinde, K. Bogar and J.-E. Backvall, *Chem.–Eur. J.*, 2010, **16**, 4031; (*d*) A. Lennartson, S. Olsson, J. Sundberg and M. Hakansson, *Angew. Chem., Int. Ed.*, 2009, **48**, 3137; (*e*) A. Yamaguchi, S. Matsunaga and M. Shibasaki, *J. Am. Chem. Soc.*, 2009, **131**, 10842.

6 (*a*) I.-I. S. Lim, D. Mott, M. H. Engelhard, Y. Pan, S. Kamodia, J. Luo, P. N. Njoki, S. Zhou, L. Wang and C. J. Zhong, *Anal. Chem.*, 2009, **81**, 689; (*b*) H. Bergguist, A. Nikravesh, R. D. Fernandez, V. Larsson, C.-H. Nguyen, L. Good and R. Zain, *ChemBioChem*, 2009, **10**, 2629; (*c*) L. Hernandez-Folgado, D. Baretic, I. Piantanida, M. Marjanovic, M. Kralj, T. Rehm and C. Schmuck, *Chem.–Eur. J.*, 2010, **16**, 3036; (*d*) H. Fan, R. Xing, X. Wang, Y. Xu, Q. Wang, P. He and Y. Fang, *Electroanalysis*, 2010, **22**, 1781.

7 (*a*) M. Fujita, T. Nagano, U. Schneider, T. Hamada, C. Ogawa and S. Kobyashi, *J. Am. Chem. Soc*., 2008, **130**, 2914; (*b*) S. Kobayashi and R. Matsubara, *Chem.–Eur. J*., 2009, **15**, 10694; (*c*) S.-F. Zhu, C. Chen, Y. Cai and Q.-L. Zhou, *Angew. Chem., Int. Ed*., 2008, **47**, 932; (*d*) N. E. Shepherd, H. Tanabe, Y. Xu, S. Matsunaga and M. Shibasaki, *J. Am. Chem. Soc*., 2010, **132**, 3666.

8 (*a*) S. Chidara and Y.-M. Lin, *Synlett*, 2009, **10**, 1675; (*b*) X. Li, X. Jia, L. Xu, S. H. L. Kok, C. W. Yip and A. S. C. Chan, *Adv. Synth. Catal*., 2005, **347**, 1904; (*c*) W. He, Q. Wang, Q. Wang, B. Zhang, X. Sun and S. Zhang, *Synlett*, 2009, **8**, 1311; (*d*) K. Mikami, T. Murase, L. Zhai, S. Kawauchi, Y. Itoh and S. Ito, *Tetrahedron Lett*., 2010, **51**, 1371.

9 (*a*) L. Plistil, T. Solomek, J. Wirz, D. Heger and P. Klan, *J. Org. Chem*., 2006, **71**, 8050; (*b*) H. E. Zimmerman and S. Shorunov, *J. Org. Chem*., 2009, **74**, 5411; (*c*) P. Rudolf, J. Buback and J. Aulbach, *J. Am. Chem. Soc*., 2010, **132**, 15213; (*d*) S. J. Sarma and P. B. Jones, *J. Org. Chem*., 2010, **75**, 3806; (*e*) M. Freccero and M. Fagnoni, *J. Am. Chem. Soc*., 2003, **125**, 13182.

10 (*a*) A. D. Ostrowshi, S. J. Deakin, B. Azhar, T. W. Miller, N. Franco, M. M. Cherney, A. J. Lee, J. N. Burstyn, J. M. Fukuto, I. L. Megson and P. C. Ford, *J. Med. Chem*., 2010, **53**, 715; (*b*) S. Dong, H. Hwang, X. Shi, L. Holloway and H. Yu, *Chem. Res. Toxicol*., 2000, **13**, 585; (*c*) K. H. Kim, X. J. Fan and P. E. Nielsen, *Bioconjugate Chem*., 2007, **18**, 567; (*d*) Y. A. Shieh, S. J. Yang, M. F. Wei and M. J. Shieh, *ACS Nano*, 2010, **4**, 1433; (*e*) J. Morgan, J. D. Jackson, X. Zheng, S. K. Pandey and R. K. Pandey, *Mol. Pharmaceutics*, 2010, **7**, 1789.

11 (*a*) J. Klanova, P. Klan, J. NOsek and I. Holoubek, *Environ. Sci. Technol*., 2003, **37**, 1568; (*b*) C. Lee, W. Choi and J. Yoon, *Environ. Sci. Technol*., 2005, **39**, 9702; (*c*) Y. Hou, X. Li, Q. Zhao, X. Quan and G. Chen, *Environ. Sci. Technol*., 2010, **44**, 5098; (*d*) A. C. Herath and R. M. G. Rajapakse, *Environ. Sci. Technol*., 2009, **43**, 176.

12 (*a*) D. J. Kang and B. S. Bae, *Acc. Chem. Res*., 2007, **40**, 903; (*b*) M. Faustini, L. Nicole, C. Boissire, P. Innocenzi, C. Sanchez and D. Grosso, *Chem. Mater*., 2010, **22**, 4406; (*c*) D. Kessler, F. D. Jochum, J. Choi and K. Char, *ACS Appl. Mater. Interfaces*, 2011, **3**, 124; (*d*) M. K. R. Fisher, I. Lopez-Duarte, M. M. Wienk, M. V. Martinez-Diaz, R. A. J. Janssen, P. Bauerle and T. Torres, *J. Am. Chem. Soc*., 2009, **131**, 8669.

13 (*a*) M. Kawamoto, T. Sassa and T. Wada, *J. Phys. Chem. B*, 2010, **114**, 1227; (*b*) N. Kawatsuki, T. Tsutsumi and H. Takatsuka, *Macromolecules*, 2007, **40**, 6355; (*c*) H. Yu and T. Ikeda, *J. Am. Chem. Soc*., 2006, **128**, 11010; (*d*) D. Han, X. Tong, Y. Zhao, T. Galstian and Y. Zhao, *Macromolecules*, 2010, **43**, 3664.

14 (*a*) M. Irie, *Chem. Rev*., 2000, **100**, 1683; (*b*) H. Tian and S. Yang, *Chem. Soc. Rev*., 2004, **33**, 85; (*c*) H. Tian and S. Wang, *Chem. Commun*., 2007, 781; (*d*) B. L. Feringa, *J. Org. Chem*., 2007, **72**, 6635; (*e*) S. Kawata and Y. Kawata, *Chem. Rev*., 2000, **100**, 1777.

15 (*a*) G. M. Tsivgoulis and J.-M. Lehn, *Angew. Chem., Int. Ed. Engl*., 1995, **34**, 1119; (*b*) T. Norsten and N. R. Branda, *J. Am. Chem. Soc*., 2001, **123**, 1784; (*c*) M. Irie, T. Fukaminato, T. Sasaki, N. Tamai and T. Kawai, *Nature*, 2002, **420**, 759; (*d*) A. J. Myles, B. Gorodetsky and N. R. Branda, *Adv. Mater*., 2004, **16**, 922; (*e*) W. Tan, Q. Zhang, J. Zhang and H. Tian, *Org. Lett*., 2009, **11**, 161; (*f*) K. Morinaka, T. Ubukata and Y. Yokoyama, *Org. Lett*., 2009, **11**, 3890.

16 (*a*) S. L. Gilat, S. L. Kawai and J.-M. Lehn, *Chem.–Eur. J*., 1995, **1**, 275; (*b*) R. Baron, A. Onopriyenko, E. Katz, O. Lioubashevski, I. Willner, S. Wang and H. Tian, *Chem. Commun*., 2006, 2147; (*c*) X. Deng and L. S. Liebeskind, *J. Am. Chem. Soc*., 2001, **123**, 7703.

17 (*a*) K. Mastuda and M. Irie, *J. Am. Chem. Soc*., 2000, **122**, 7195; (*b*) N. Tanifuji, M. Irie and K. Matsuda, *J. Am. Chem. Soc*., 2005, **127**, 13344.

18 (*a*) C. Dulic, S. J. Van der Molen, T. Kudernc, H. T. Jonkman, J. J. D. De Jong, T. N. Bowden, J. Van Esch, B. L. Feringa and B. J. Van Wees, *Phys. Rev. Lett*., 2003, **91**, 207402; (*b*) A. C. Whalley, M. L. Steigerwald, X. Guo and C. Nuchkollus, *J. Am. Chem. Soc*., 2007, **129**, 12590; (*c*) T. Kawai and Y. Nakashima, *Adv. Mater*., 2005, **17**, 309.

19 (*a*) V. Lemieux, S. Gauthier and N. R. Branda, *Angew. Chem., Int. Ed*., 2006, **45**, 6820; (*b*) D. Sud, T. J. Wigglesworth and N. R. Branda, *Angew. Chem., Int. Ed*., 2007, **46**, 8017.

20 (*a*) J. J. D. de Jong, L. N. Lucas, R. M. Kellogg, J. H. van Esch and B. L. Feringa, *Science*, 2004, **304**, 278; (*b*) T. Hirose, K. Matsuda and M. Irie, *J. Org. Chem*., 2006, **71**, 7499.

21 (*a*) A. J. Myles and N. R. Branda, *Macromolecules*, 2003, **36**, 298; (*b*) K. Higashiguchi, K. Matsuda and M. Irie, *Angew. Chem., Int. Ed*., 2003, **42**, 3537; (*c*) H. Tian and Y. Feng, *J. Mater. Chem*., 2008, **18**, 1617; (*d*) H.-H. Liu and Y. Chen, *J. Mater. Chem*., 2009, **19**, 706.

22 (*a*) M. Irie, T. Lifka, K. Uchida, S. Kobatake and Y. Shindo, *Chem. Commun*., 1999, 747; (*b*) K. Higashiguchi, K. Matsuda, S. Kobatabe, T. Yamada, T. Kwai and M. Irie, *Bull. Chem. Soc. Jpn*., 2000, **73**, 2389; (*c*) H. Ikeda, A. Sakai, A. Kawabe, H. Namai and K. Mizuno, *Tetrahedron Lett*., 2008, **49**, 4972.

23 Y. Chen, D. X. Zeng and M. G. Fan, *Org. Lett*., 2003, **5**, 1435.

24 V. Z. Shirinyan, N. V. Kosterina, A. V. Kolotaev, L. I. Belenkii and M. M. Krayushkin, *Chem. Heterocycl. Compd*., 2000, **36**, 219.