Photoswitching and sensor applications of a spiropyran–polythiophene conjugate†

In Sung Park,[a] Young-Sik Jung,*[b] Kee-Jung Lee[a] and Jong-Man Kim*[a]

Received (in Cambridge, UK) 11th December 2009, Accepted 3rd February 2010
First published as an Advance Article on the web 4th March 2010
DOI: 10.1039/b926211c

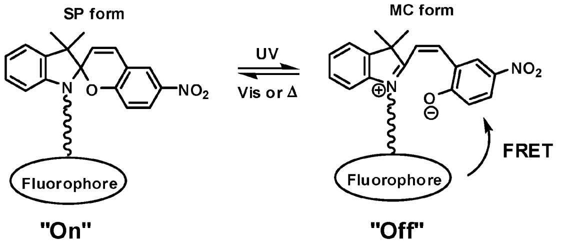
A new FRET-based, photoswitchable fluorescent dyad derived from a spiropyran–polythiophene conjugate was developed and applied to the detection of cyanide anion.

Upon irradiation at specific wavelengths, photochromic materials undergo photochemically reversible structural changes that result in the interconversion of two distinct isomeric forms.[1–3] Owing to this intriguing light-driven molecular switching phenomenon, photochromic compounds have been extensively investigated as key materials in optical memory, switching and sensor fields.[4–13] Recently, fluorescence-coupled photochromism has been a central focus among many potential applications of photochromic compounds.[14–24] In these systems, fluorescent chromophores are either covalently incorporated into or physically mixed with photochromic dyes. Fluorophore-coupled spiropyran derivatives also have gained substantial attention owing to the unique optical properties associated with the spiropyran units.[25–29] The spirocyclic (SP) and ring opened merocyanine (MC) forms of these fluorophore-coupled photochromic compounds participate as "Switch On" and "Switch Off" functions (Scheme 1). Specifically, fluorescence emission from the fluorophore is observed when the photochromic compound is in the SP form. In contrast, emission is severely quenched when the photochromic compound is in the MC form as a result of fluorescence resonance energy transfer (FRET) from the excited state of the fluorophore to the MC form of the photochromic compound. Irradiation with visible light results in transformation of the MC to the SP form of the compound and recovery of the fluorescence. By using this strategy, a variety of spiropyran-derived, fluorophore-coupled (covalently bonded or physically mixed) photochromic compounds have been designed and probed in molecular switching applications.[25–29]

For effective functioning of a fluorescence-coupled spiropyran photoswitch, it must incorporate a FRET system in which emission from the fluorophore is absorbed efficiently by the MC form of the photochromic molecule. In this regard, polythiophenes (PTs) are very attractive substances. Fig. 1 shows the emission spectrum of poly-3-hexylthiophene (P3HT) and the absorption spectrum of the MC form of 1′,3′-dihydro-1′,3′,3′-trimethyl-6-nitrospiro[2*H*-1-benzopyran-2,2′-(2*H*)-indole] (SPP) in THF. Inspection of these spectra clearly shows that the MC form of the photochromic compound is able to absorb the emission from P3HT efficiently as a result of large overlap of the emission and absorbance spectra. As a consequence, the spiropyran–P3HT system is ideally suited for incorporation into a FRET based photoreversible switching system.

Encouraged by the photophysical properties related to the donor emission and acceptor absorption described above, we designed the photoswitchable spiropyran–polythiophene conjugate P(TSP/3HT) shown in Scheme 2. The thienyl group containing spiropyran monomer TSP was readily prepared in 76% yield by use of a EDC coupling reaction between commercially available 1′-(2-hydroxyethyl)-3′,3′-dimethyl-6-nitrospiro[1(2*H*)-benzopyran-2,2′-indoline] (SP-OH) and 4-(3-thieyl)butanoic acid (TBA) (see ESI† for experimental details). Copolymerization of the monomer TSP with 3-hexylthiophene (3-HT) was carried out with a respective 1 : 5 molar feed ratio in the presence of $FeCl_3$ in chloroform. The copolymer, P(TSP/3HT), obtained as a dark brown powder in 55% yield after precipitation from and thorough washing with MeOH, was determined to have an average molecular weight (M_w) of 120 000, compared to a polystyrene standard, by using gel permeation chromatography (GPC) (polydispersity (PD) = 5.28). Interestingly, ^1H NMR analysis showed that the composition of P(TSP/3HT) was almost the same as the molar ratio of the monomer feed employed in its preparation. Finally, the copolymer is soluble in common organic solvents, such as chloroform, THF, methylene chloride and toluene but insoluble in acetonitrile and methanol.

In order to explore the feasibility of fluorescence switching, a THF (0.1 mM) solution of P(TSP/3HT) was irradiated with 365 nm light (1 mW cm^{-2}). Inspection of the UV-visible absorption and emission spectra monitored before and after UV irradiation (Fig. 2) shows that UV-irradiation for 2 min results in the formation of a new absorption band at 585 nm, corresponding to the MC form of the spiropyran (Fig. 2A). In addition, UV irradiation results in a substantial decrease in fluorescence intensity, dropping to 12% of the initial value



Scheme 1 Fluorescence switching of a fluorophore-coupled spiropyran system.

---

[a] *Department of Chemical Engineering, Hanyang University, Seoul 133-791, Korea. E-mail: jmk@hanyang.ac.kr; Fax: +82-2-2298-4101; Tel: +82-2-2220-0522*

[b] *Bioorganic Science Division, Korea Research Institute of Chemical Technology, Daejeon 305-606. E-mail: ysjung@krict.re.kr*

† Electronic supplementary information (ESI) available: Experimental details and NMR spectra of the monomer and the polymer. See DOI: 10.1039/b926211c

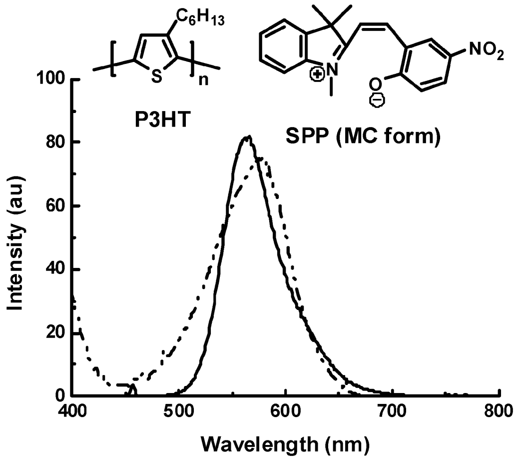
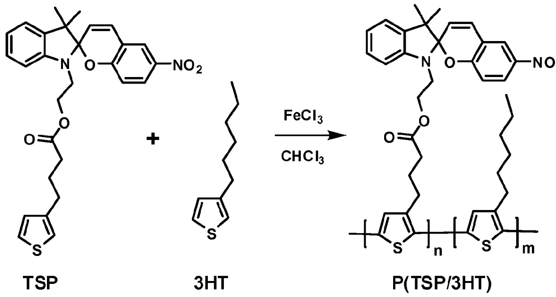


Fig. 1 Emission spectrum of P3HT (—) and absorption spectrum of the MC form of spiropyran (---) in THF (0.1 mM). P3HT is excited at 448 nm.



Scheme 2 Preparation of the spiropyran–polythiophene conjugate, P(TSP/3HT).

(Fig. 2B). The UV-induced fluorescence quenching is caused by effective energy transfer from polythiophene moieties to the MC form of the spiropyran. In addition, the degree of fluorescence quenching increases as the concentration of the polymer increases (Fig. 2B, inset). This phenomenon is likely a consequence of increased interchain energy transfer when the concentration of the polymer is high. It should be noted that UV irradiation of a THF solution of the polymer results in the appearance of a new emission band around 614 nm. This result indicates that part of the energy transferred from excited state polythiophene moieties is used to promote excitation of the MC form of the spiropyran molecule, since the MC form displays a weak fluorescence band near 614 nm when excited at 435 nm.

The UV irradiation induced decrease in the fluorescence intensity of P(TSP/3HT) is substantially recovered (*ca.* 94% of the initial value) by irradiation with visible light. This is a result of the fact that the ring-closed SP form of the spiropyran moiety produced upon visible light irradiation does not quench the fluorescence of the polythiophene moieties. As shown by the plot displayed in Fig. 3, the spiropyran-polythiophene dyad is capable of undergoing a number of photoswitching cycles between high (c, e, g, i, k) and low (b, d, f, h, j) fluorescence intensity values by repetitive sequential irradiation of the solution containing P(TSP/3HT) with UV and visible light.

The final phase of the current investigation focused on demonstrating the utility of the spiropyran–polythiophene conjugate as a FRET-based chemosensor. Recently, Shiraishi

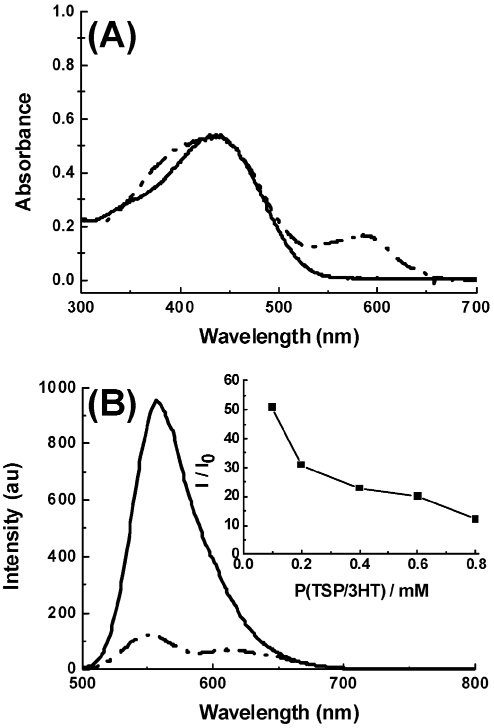


Fig. 2 Absorbtion (A) and emission (B) spectra of P(TSP/3HT) ((A): 0.1 mM, (B): 0.8 mM) in THF before (—) and after (---) UV irradiation (365 nm, 1 mW cm^{-2}) for 2 min. The emission spectra were recorded with excitation at 435 nm. Inset displays concentration dependent changes in fluorescence intensity.

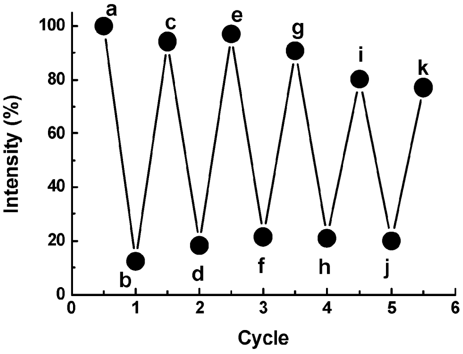
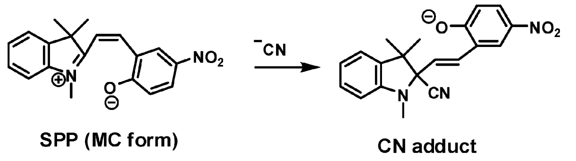


Fig. 3 Relative fluorescence intensity of a THF solution (0.8 mM) containing P(TSP/3HT) monitored at 556 nm (excitation at 435 nm) before (a) and after UV (b, d, f, h, j) and visible light (c, e, g, i, k) irradiation.

and co-workers described an interesting observation made in studies of the UV irradiation of a solution of a spiropyran containing various anions.[30] These workers showed that cyanide ion could be selectively detected (over other anions such as F^-, Cl^-, Br^-, I^-, AcO^-, $H_2PO_4^-$, HSO_4^-, NO_3^- and ClO_4^-) by monitoring the formation of an adduct, derived by nucleophilic addition of cyanide anion to the ring-opened MC form of the spiropyran (Scheme 3). Formation of the adduct results in a significant blue shift of the absorption maximum from 519 to 421 nm.

We envisioned that the spiropyran–polythiophene conjugate would also interact with cyanide anion after being



Scheme 3 Reaction between MC form of the spiropyran and cyanide anion.

transformed to the MC form by UV-irradiation. We also thought that the significant hypsochromic shift associated with adduct formation would render the CN adduct incapable of quenching efficiently the fluorescence emitted from polythiophene backbone. Thus, unlike the colorimetric CN sensor reported by Shiraishi, the spiropyran–polythiophene conjugate system would allow fluorescence-based detection of cyanide anion.[31]

In order to test this proposal, THF solutions (0.1 mM) of P(TSP/3HT) containing various anions were irradiated with 365 nm UV light for 2 min and their fluorescence intensities were monitored (Fig. 4). Interestingly, the degree of the fluorescence quenching promoted by irradiation of the solution containing cyanide anion is much smaller than that caused by other anions or that monitored in the absence of anions (Ctrl). In fact, no significant differences in the fluorescence quenching behavior of the polymer were seen when other ions, such as fluoride, chloride, bromide, or nitrate, were present. In addition, the color of the cyanide containing polymer solution becomes yellow after 2 min irradiation while the blue color of the solution remains unchanged or only slightly changed when other anions are present. Greater than 90% of the initial fluorescence intensity is maintained when the concentration of cyanide anion is >0.5 mM, indicating that most of the spiropyran moieties form adducts upon UV-irradiation in the presence of cyanide (Fig. 4, inset). The detection limit for cyanide anion was determined to be *ca.* 10 μM (Fig. 4, inset and Fig. S1, ESI†).

In summary, the results arising from this investigation conclusively demonstrate that it is possible to design a photoswitching system based on a spiropyran–polythiophene conjugate. Thus, UV irradiation of a solution containing the photochromic polymer results in a drastic decrease in fluorescence intensity owing to effective FRET. The fluorescence intensity is recovered by visible light irradiation of the solution. The spiropyran–polythiophene conjugate system can also be used to detect cyanide anion in a highly selective and sensitive manner.

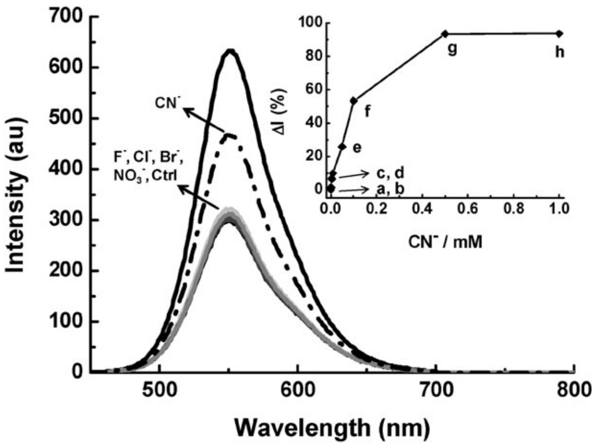


Fig. 4 Emission spectra of P(TSP/3HT) (0.1 mM in THF) monitored after 365 nm UV irradiation for 2 min in the presence of 0.1 mM of anions (counter cation: n-Bu$_4$N$^+$). The inset is a plot of fluorescence intensity as a function of CN$^-$ concentration (mM); 0 (a), 0.001 (b), 0.005 (c), 0.01 (d), 0.05 (e), 0.1 (f), 0.5 (g) and 1.0 (h).

The authors gratefully thank National Research Foundation of Korea for financial support through Basic Science Research Program (20090083161), Center for Next Generation Dye-sensitized Solar cells (2009–0063368), and International Research & Development Program (K20901000006-09E0100-00610).

Notes and references

1 G. H. Brown, *Photochromism*, Wiely-Interscience, New York, 1971.
2 *Organo photochromic and Thermochromic Compounds*, ed. J. C. Crano and R. J. Guglielmetti, Kluwer Academic/Plenum Publishers, New York, 1999.
3 *Molecular Switches*, ed. B. L. Feringa, Wiley-VCH, Weinheim, 2001.
4 M. Irie, *Chem. Rev.*, 2000, **100**, 1685.
5 C. C. Corredor, Z.-L. Huang and K. D. Belfield, *Adv. Mater.*, 2006, **18**, 2910.
6 A. J. Myles and N. R. Branda, *Adv. Funct. Mater.*, 2002, **12**, 167.
7 F. M. Raymo and M. Tomasulo, *Chem. Soc. Rev.*, 2005, **34**, 327.
8 M.-Q. Zhu, L. Zhu, J. J. Han, W. Wu, J. K. Hurst and A. D. Q. Li, *J. Am. Chem. Soc.*, 2006, **128**, 4303.
9 K.-y. Tomizaki and H. Mihara, *J. Mater. Chem.*, 2005, **15**, 2732.
10 J. D. Winkler, C. M. Bowen and V. Michelet, *J. Am. Chem. Soc.*, 1998, **120**, 3237.
11 C. J. Barrett, J.-i. Mamiya, K. G. Yager and T. Ikeda, *Soft Matter*, 2007, **3**, 1249.
12 K. Fries, S. Samanta, S. Orski and J. Locklin, *Chem. Commun.*, 2008, 6288.
13 S. Kumar, D. L. Watkins and T. Fujiwara, *Chem. Commun.*, 2009, 4369.
14 M. Irie, T. Fukaminato, T. Sasaki, N. Tamai and T. Kawai, *Nature*, 2002, **420**, 759.
15 S.-J. Lim, B.-K. An and S. Y. Park, *Macromolecules*, 2005, **38**, 6236.
16 H. Cho and E. Kim, *Macromolecules*, 2002, **35**, 8684.
17 M. Bossi, V. Belov, S. Polyakova and S. W. Hell, *Angew. Chem., Int. Ed.*, 2006, **45**, 7462.
18 T. A. Golovkova, D. V. Kozlov and D. C. Neckers, *J. Org. Chem.*, 2005, **70**, 5545.
19 S. Wang, W. Shen, Y. Feng and H. Tian, *Chem. Commun.*, 2006, 1497.
20 E. J. Harbron, D. A. Vincente, D. H. Hadley and M. R. Imm, *J. Phys. Chem. A*, 2005, **109**, 10846.
21 Y. C. Liang, A. S. Dvornikov and P. M. Rentzepis, *Proc. Natl. Acad. Sci. U. S. A.*, 2003, **100**, 8109.
22 G. Jiang, S. Wang, W. Yuan, L. Jiang, Y. Song, H. Tian and D. Zhu, *Chem. Mater.*, 2006, **18**, 235.
23 Y. Chen and N. Xie, *J. Mater. Chem.*, 2005, **15**, 3229.
24 D. V. Kozlov and F. N. Castellano, *J. Phys. Chem. A*, 2004, **108**, 10619.
25 L. Zhu, m.-Q. Zhu, J. K. Hurst and A. D. Q. Li, *J. Am. Chem. Soc.*, 2005, **127**, 8968.
26 X. Guo, D. Zhang, Y. Zhou and D. Zhu, *J. Org. Chem.*, 2003, **68**, 5681.
27 F. M. Raymo and S. Giordani, *Org. Lett.*, 2001, **3**, 1833.
28 C. W. Lee, Y. H. Song, Y. Lee, K. S. Ryu and K.-W. Chi, *Chem. Commun.*, 2009, 6282.
29 W. Tan, D. Zhang, G. Wen, Y. Zho and D. Zhu, *J. Photochem. Photobiol., A*, 2008, **200**, 83.
30 Y. Shiraishi, K. Adachi, M. Itoh and T. Hirai, *Org. Lett.*, 2009, **11**, 3482.
31 A. Touceda-Varela, E. I. Stevenson, J. A. Galve-Gasión, D. T. F. Dryden and J. C. Mareque-Rivas, *Chem. Commun.*, 2008, 1998.