

Sterically Hindered Diaryl Benzobis(thiadiazole)s as Effective Photochromic Switches**

Juyoung Yoon* and A. Prasanna de Silva*

chiroptical switches · data processing ·
enantiospecificity · photochromism · steric hindrance

The dream of storing (reading and writing) and processing data at the molecular scale^[1] has been with us since the late 1950s when Hirshberg outlined such a possibility with photochromic compounds.^[2] Since then, diarylethenes with thermal bistability have replaced the spiropyrans that were initially used as the most practical way forward in the area of photochromism. Over the past three decades, Irie and co-workers^[3] have delineated most of the basic principles of these compounds as well as their applications in memory devices, switches, and actuators. However, in practice, when these photochromic devices are employed, a severe problem, namely destructive readout, is always encountered. Common readout methods by UV/Vis absorption partially erase the encoded information (even at low light intensities) as the writing and reading light cannot be fully separated. A while ago, Würthner et al. achieved inspiring improvements on photoinduced electron transfer (PET) based fluorescence modulation.^[4] Meanwhile, several other readout methods that are based on infrared (IR) absorption and optical rotation^[5] at wavelengths far from the UV/Vis absorption bands have also proven to be promising routes to non-destructive readout. The Zhu and Tian groups^[6] have now achieved significant further improvements towards the realization of practical photomemory devices.

Previously, the Feringa, Takeshita, and Andréasson groups had developed diastereo- and enantioselective photochromic reactions of several well-designed diarylethenes as well as an enantioselective cyclization of dithienylethenes bound to DNA.^[7] However, thermally bistable diarylethenes with an enantiospecific photoresponse for non-destructive readout are still rare as they present great challenges. In

2011,^[8] however, Zhu, Tian, and co-workers exploited the benzobis(thiadiazole) unit, with the six-membered ring acting as an ethene bridge, to develop new diarylethene derivatives: The colored ring-closed isomer is of excellent thermal stability, benefiting from the low aromaticity and strongly electron-withdrawing nature of the unique bridge. A couple of years later, a sterically more hindered version, which is based on the same conjugated bridge, was constructed. In this system (**BBTE**, Figure 1a), the anti-parallel and parallel open-ring conformers, which are commonly in equilibrium (in solution), are disturbed to such an extreme that they become thermally stable with a lifetime of over 1000 years at room temperature, which is long enough for their isolation, crystallization, and practical application.^[6a] Recently, the enantiomers could even be separated by chromatography on a chiral stationary phase.^[6b] Therefore, the parallel and the two antiparallel conformers of the colorless ring-open states and the two colored ring-closed isomers could be analyzed by X-ray crystallography. Indeed, the ground-breaking full isolation of five sterically hindered and thermally bistable diarylethene derivatives was achieved, and the absolute configurations were obtained from the enantiomerically pure single crystals (Figure 1b).

For **BBTE**, each of the photochromic interconversions [*P*-*ap*-**BBTE** → (*R,R*)-*c*-**BBTE** and *M*-*ap*-**BBTE** → (*S,S*)-*c*-**BBTE**] was found to proceed with high conversion (91 %) and to be enantiospecific, which is due to the hindered rotation of the aryl groups resulting from the intramolecular steric hindrance exerted by the benzobis(thiadiazole) bridge. High photocyclization quantum yields of up to 90 % were observed when intramolecular charge transfer (ICT) from the benzothiophene unit to the electron-poor benzobis(thiadiazole) ethene bridge was suppressed by the addition of electron-withdrawing substituents (such as a nitro group) to the benzothiophene moieties.^[6a] However, the difficulties associated with ring rotation in these highly sterically hindered systems were found to inhibit photochromism in the crystalline state in spite of favorable topochemical parameters (distance between the reactive C atoms in *ap*-**BBTE** ca. 3.4 Å).^[2]

In summary, the problems associated with the racemization of common diarylethenes have been solved by the development of new, thermally stable derivatives. These bistable chiroptical switches undergo unimolecular, reversible, and enantiospecific transformations. The stage should

[*] Prof. Dr. J. Y. Yoon
Department of Chemistry and Nano Science BK21
Ewha Womans University
Seoul 120-750 (Republic of Korea)
E-mail: jyoony@ewha.ac.kr

Prof. Dr. A. P. de Silva
School of Chemistry and Chemical Engineering
Queen's University
Belfast BT9 5AG (UK)
E-mail: a.desilva@qub.ac.uk

[**] This research was supported by the National Creative Research Initiative programs of the National Research Foundation of Korea (NRF) funded by the Korean government (MSIP; 2012R1A3A2048814).

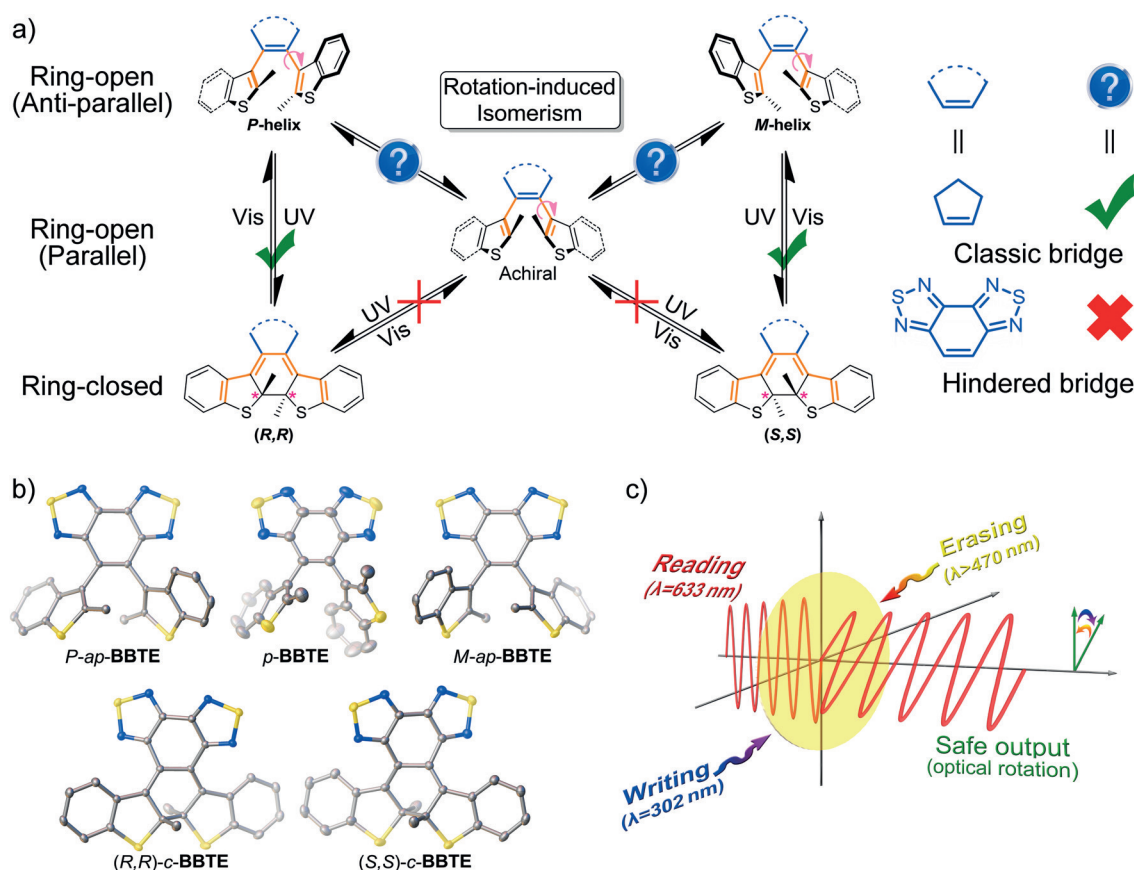


Figure 1. a) Illustration of the photochromic reaction of diarylethenes. b) ORTEP representations of the X-ray single-crystal structures of all thermally stable isomers of **BBTE**; ellipsoids set at 50% probability. c) Enantiospecific photoresponse for all-photonic chiroptical switches and photomemory devices with non-destructive readout: writing with ultraviolet light ($\lambda = 302$ nm), erasing with visible light ($\lambda > 470$ nm), and reading by determining the optical rotation with long-wavelength light ($\lambda = 633$ nm) without fear of erasure.

now be set for the design of all-photonic switches that are suitable for logic gates and information processing, with clean control, easy re-setting, and remote-access abilities.^[9] Further studies in a polymer matrix, such as poly(D/L-lactic acid) (PDLLA, $M_w = 2.5 \times 10^5$),^[6b] should provide a method for reading photo-written data by determining the optical rotation at long wavelengths ($\lambda = 633$ nm), again without fear of erasure (Figure 1c). Writing with ultraviolet light ($\lambda = 302$ nm) and erasure with visible light ($\lambda > 470$ nm) completes the set of colors required to unleash the information-handling capability in this novel photochromic system. Although the wavelengths of the writing and reading light are currently a little too long for building practical high-density storage devices, these problems should be easily overcome in the future with the help of multi-component, three-dimensional, and near-field optical recording technologies.^[10] At that time, writing and reading with light based on the power of enantiomer separation would not be just a dream.

How to cite: *Angew. Chem. Int. Ed.* **2015**, *54*, 9754–9756
Angew. Chem. **2015**, *127*, 9890–9892

[1] a) A. P. de Silva, *Nature* **2008**, *454*, 417–418; b) S. Z. Kou, H. N. Lee, D. K. Noort, M. K. Swamy, S. H. Kim, J. H. Soh, K.-M. Lee, S.-W. Nam, J. Y. Yoon, S. S. Park, *Angew. Chem. Int. Ed.* **2008**,

- 47, 872–876; *Angew. Chem.* **2008**, *120*, 886–890; c) H. Tian, *Angew. Chem. Int. Ed.* **2010**, *49*, 4710–4712; *Angew. Chem.* **2010**, *122*, 4818–4820.
- [2] a) Y. Hirshberg, *J. Am. Chem. Soc.* **1956**, *78*, 2304–2312; b) H. Bach, J. G. Calvert, *J. Am. Chem. Soc.* **1970**, *92*, 2608–2614; c) Y. Iseki, E. Watanabe, A. Mori, S. Inoue, *J. Am. Chem. Soc.* **1993**, *115*, 7313–7317.
- [3] a) M. Irie, T. Fukaminato, K. Matsuda, S. Kobatake, *Chem. Rev.* **2014**, *114*, 12174–12277; b) M. Irie, *Chem. Rev.* **2000**, *100*, 1685–1716.
- [4] a) M. Berberich, A.-M. Krause, M. Orlandi, F. Scandola, F. Würthner, *Angew. Chem. Int. Ed.* **2008**, *47*, 6616–6619; *Angew. Chem.* **2008**, *120*, 6718–6721; b) T. Fukaminato, T. Doi, N. Tamaoki, K. Okuno, Y. Ishibashi, H. Miyasaka, M. Irie, *J. Am. Chem. Soc.* **2011**, *133*, 4984–4990.
- [5] a) K. Uchida, M. Saito, A. Murakami, S. Nakamura, M. Irie, *Adv. Mater.* **2003**, *15*, 121–125; b) M. Takeshita, T. Yamato, *Chem. Lett.* **2004**, *33*, 844–845; c) M. Fukagawa, I. Kawamura, T. Ubukata, Y. Yokoyama, *Chem. Eur. J.* **2013**, *19*, 9434–9437; d) T. Nakashima, K. Yamamoto, Y. Kimura, T. Kawai, *Chem. Eur. J.* **2013**, *19*, 16972–16980; e) T. J. Wigglesworth, D. Sud, T. B. Norsten, V. S. Lekhi, N. R. Branda, *J. Am. Chem. Soc.* **2005**, *127*, 7272–7273.
- [6] a) W. L. Li, C. H. Jiao, X. Li, Y. S. Xie, K. Nakatani, H. Tian, W. H. Zhu, *Angew. Chem. Int. Ed.* **2014**, *53*, 4603–4607; *Angew. Chem.* **2014**, *126*, 4691–4695; b) W. L. Li, X. Li, Y. S. Xie, Y. Wu, M. Q. Li, X. Y. Wu, W. H. Zhu, H. Tian, *Sci. Rep.* **2015**, *5*, 9186.
- [7] a) J. J. D. de Jong, L. N. Lucas, R. M. Kellogg, J. H. van Esch, B. L. Feringa, *Science* **2004**, *304*, 278–281; b) M. Walko, B. L.

- Feringa, *Chem. Commun.* **2007**, 1745–1747; c) D. J. van Dijken, J. M. Beierle, M. C. A. Stuart, W. Szymański, W. R. Browne, B. L. Feringa, *Angew. Chem. Int. Ed.* **2014**, *53*, 5073–5077; *Angew. Chem.* **2014**, *126*, 5173–5177; d) M. Takeshita, T. Yamato, *Angew. Chem. Int. Ed.* **2002**, *41*, 2156–2157; *Angew. Chem.* **2002**, *114*, 2260–2261; e) H. Jin-nouchi, M. Takeshita, *Chem. Eur. J.* **2012**, *18*, 9638–9644; f) T. C. S. Pace, V. Müller, S. Li, P. Lincoln, J. Andréasson, *Angew. Chem. Int. Ed.* **2013**, *52*, 4393–4396; *Angew. Chem.* **2013**, *125*, 4489–4492.
- [8] W. H. Zhu, Y. H. Yang, R. Métivier, Q. Zhang, R. Guillot, Y. S. Xie, H. Tian, K. Nakatani, *Angew. Chem. Int. Ed.* **2011**, *50*, 10986–10990; *Angew. Chem.* **2011**, *123*, 11178–11182.
- [9] a) J. Andréasson, U. Pischel, *Isr. J. Chem.* **2013**, *53*, 236–246; b) J. Andréasson, U. Pischel, S. D. Straight, T. A. Moore, A. L. Moore, D. Gust, *J. Am. Chem. Soc.* **2011**, *133*, 11641–11648.
- [10] a) K. Uchida, M. Saito, A. Murakami, T. Kobayashi, S. Nakamura, M. Irie, *Chem. Eur. J.* **2005**, *11*, 534–542; b) C. C. Corredor, Z. L. Huang, K. D. Belfield, *Adv. Mater.* **2006**, *18*, 2910–2914; c) K. Mori, Y. Ishibashi, H. Matsuda, S. Ito, Y. Nagasawa, H. Nakagawa, K. Uchida, S. Yokojima, S. Nakamura, M. Irie, H. Miyasaka, *J. Am. Chem. Soc.* **2011**, *133*, 2621–2625.

Received: April 8, 2015

Revised: May 21, 2015

Published online: July 15, 2015