The isolation and photochemistry of individual atropisomers of photochromic diarylethenes†

Martin Walko and Ben L. Feringa*

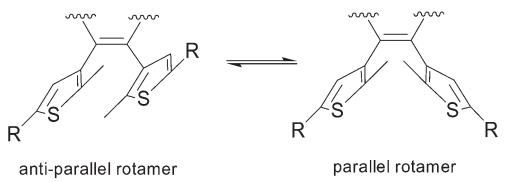
Received (in Cambridge, UK) 13th February 2007, Accepted 13th March 2007
First published as an Advance Article on the web 3rd April 2007
DOI: 10.1039/b702264f

All three atropisomers of photochromic diarylethenes were isolated for the first time and the stereospecific photochemical switching process studied by UV–vis and CD spectroscopy.

Atropisomers can be interconverted by rotation around single bonds but the barriers of rotation are large enough to prevent ready interconversion at ambient temperature and allow isolation of individual stereoisomers.[1] This chiral phenomenon has found numerous applications in the field of asymmetric catalysis where a variety of privileged chiral ligands featuring a chiral axis are shown to provide high enantioselectivities.[2] Atropisomerism has also become a key element of some molecular devices in which the single bond is an ideal shaft connecting two parts of a molecule that rotate with respect to each other.[3] To control the movement, the rotation should be restricted, under specific conditions.[4] This principle has been used in chiroptical molecular switches, ratchets and motors.[5]

Chiral photochromic switches have potential applications in data storage with non-destructive read-out.[6] The remarkable influence of chiral photochromic compounds on the organization of supramolecular systems such as liquid crystals[7] and gels[8] has been reported. A number of systems based on diarylethenes have been described, in which the photochemical reaction proceeds in a stereoselective fashion, *e.g.* helicenes,[9] chiral aggregates,[8] or due to chirality induced by 1,3-allylic strain[10] or by complexation.[11]

Photochromic dithienylethenes exist in two conformations (rotamers); the parallel (*meso*) and the anti-parallel (racemic) forms[12] (Scheme 1). These conformations can be distinguished by NMR spectroscopy for dithienylperfluorocyclopentenes but were not observed for dithienylperhydrocyclopentenes due to the presence of extremely low energy barriers of isomerization.



Scheme 1 Conformational isomers of dithienylethenes.

Organic and Molecular Inorganic Chemistry, Stratingh Institute for Chemistry, and Zernicke Institute for Advanced Materials, University of Groningen, Nijenborgh 4, 9747 AG Groningen, The Netherlands. E-mail: B.L.Feringa@rug.nl; Fax: +31 50 3634296; Tel: +31 50 3634235

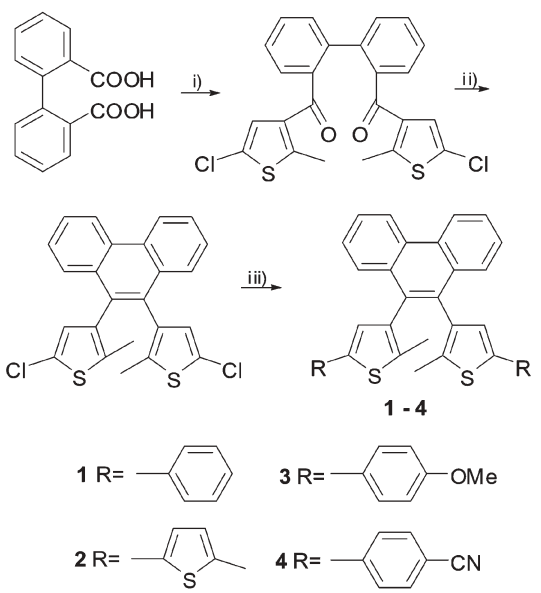
† Electronic supplementary information (ESI) available: Synthetic procedures and full characterization of new compounds, as well as additional spectroscopic data. See DOI: 10.1039/b702264f

Because the parallel rotamer cannot undergo photochemical ring closure (*vide infra*), its presence lowers the quantum yield of the switching process. This was addressed by several studies trying to increase the amount of the anti-parallel isomer by structural variations,[13] confinement of the diarylethene into a restricted environment[14] or isolation of isomers.[15] However all three possible conformational isomers of a single diarylethene have never been isolated.

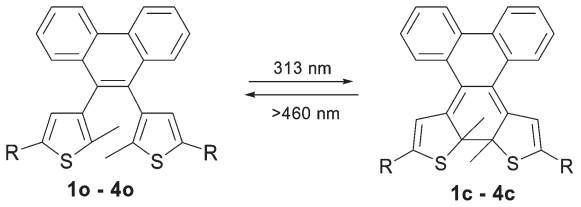
Here we report a group of photochromic diarylethene derivatives with restricted rotation of the reactive thienyl moieties that allows, for the first time, separation of individual atropisomers and study of their photochemistry.

The synthesis of the new photochromic switches is outlined in Scheme 2. It starts with the Friedel–Crafts acylation of 2-chloro-5-methylthiophene with the diacid chloride of diphenic acid. The resulting diketone is then cyclized under McMurry coupling conditions to yield the dichloride, a general precursor that can be easily substituted with various aryl groups using Suzuki coupling reactions.

All the synthesized compounds **1o–4o**† undergo reversible photocyclization reaction upon irradiation with UV light (313 nm) (Scheme 3). The formation of the closed form **1c–4c** is indicated by the colour change and the appearance of a new



Scheme 2 *Reagents and conditions*: i) 1) $SOCl_2$, pyridine (cat.), 2) $AlCl_3$, CH_2Cl_2, 2-chloro-5-methylthiophene; ii) $TiCl_4$, Zn, THF, reflux; iii) 1) n-BuLi, THF, 2) $B(OBu)_3$, 3) RI or RBr, $Pd(PPh_3)_4$, aq. Na_2CO_3, reflux.



Scheme 3 Reversible switching upon irradiation.

absorption band in the visible region of the UV–vis spectra (Table 1 and Fig. 1b). Irradiation with visible light (>460 nm) results in a photochemical ring-opening process and the original spectrum of **1o–4o** is restored. The presence of an isosbestic point and reversible ring-opening and ring-closing over several cycles indicate that the transformations do not involve any side reactions.

The ^{1}H NMR spectra of **1o–4o** show two signals for the methyl groups located at the C_2 carbon, as well as two signals for the protons located on the central thiophene rings. These are assigned to the parallel (*meso*) and anti-parallel (racemic) isomers, respectively. Irradiation with UV light leads to the appearance of a third signal belonging to the closed form but surprisingly only one of the original methyl signals decreased upon irradiation.

This can be explained assuming that the interconversion between the parallel and anti-parallel forms is slow enough not only at the NMR timescale as observed previously for dithienylethenes,[12] but also on the timescale of the whole irradiation process which generally takes about 30 min. Indeed the isomers can also be separated by chiral HPLC (Fig. 1a) and the compounds **3o** and **4o** can be resolved into the parallel and anti-parallel isomers even by normal column chromatography.[16]

The open form of the switches contains three isomers: a pair of enantiomers, the R_a,R_a[17] and the S_a,S_a isomers which adopt the anti-parallel conformation and the *meso* isomer, the R_aS_a isomer, which has the parallel orientation of the thienyl groups (Scheme 4). All three isomers were separated by chiral HPLC (Fig. 1a) and their photochemical properties were studied individually.

For both **3o** and **4o**, the isomer with the longest retention time (14.25 min) is the parallel *meso* form as judged by the lack of sensitivity to UV irradiation. The compounds corresponding to the two peaks with shorter retention times (7.00 and 11.70 min) are the chiral anti-parallel forms. The area of those peaks is equal, indicating the enantiomeric relationship of the compounds. Although all three isomers have identical UV–vis spectra (Fig. 1b), only the two anti-parallel forms can be observed by CD spectroscopy whereas the parallel (*meso*) isomer is CD silent. As expected, their CD spectra are mirror images in the open as well as in the closed form (Fig. 1c). As can be seen from Scheme 4, the ring closing reaction of one of the anti-parallel isomers gives rise to a single stereoisomer with two stereogenic centres as well as a helical arrangement of the thiophene rings relative to the phenanthrene moiety. Thus the (R_a,R_a)[17] atropisomer in the open form leads upon irradiation exclusively to the closed form having the (R,R)[17] configuration at the stereogenic carbons and the overall (P,P)[17] helicity of the molecule. The axial chirality of the open form is in this manner translated to the central chirality of the closed form. However, we have not yet succeeded in isolating enantiomerically pure single crystals to determine the absolute configuration of the isomers.

Table 1 Major absorptions in the UV–vis spectra of **1–4** before and after irradiation

Compound	Open form[a]	Photostationary state[a]
1	256 (60.3); 297 (41.1)	386 (15.0); 565 (5.8); 586 (5.8)
2	257 (61.5); 314 (37.1)	396 (15.2); 581 (8.2); 606 (7.8)
3	255 (64.3); 302 (48.9)	386 (33.4); 567 (13.8); 595 (13.6)
4	256 (55.1); 323 (50.7)	420 (29.3); 589 (13.4); 626 (13.8)

[a] The values correspond to λ_{max} (nm) and values in parentheses to $\varepsilon \times 10^{-3}$ (dm^3 mol^{-1} cm^{-1}) measured in CH_3CN.

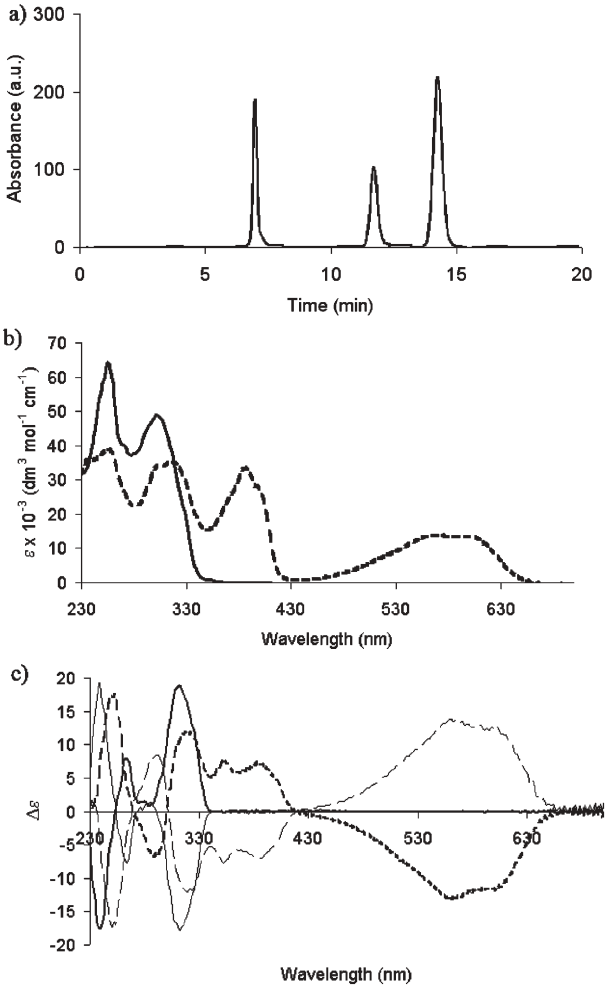
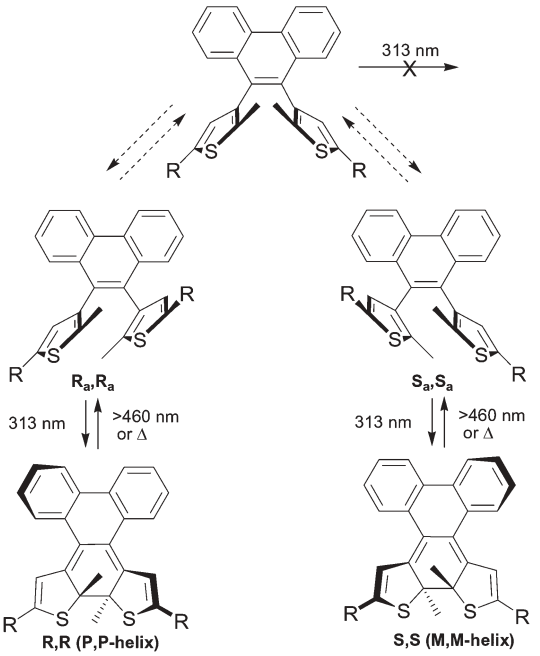


Fig. 1 a) The HPLC chromatogram (Chiracel AD column, heptane–isopropanol: 97 : 3) of **3o**. The first two peaks (with retention times 7.00 min and 11.70 min) have equal intensity and these compounds are photochromic while the isomer corresponding to the third peak (with the retention time 14.25 min) is inactive. b) UV–vis spectrum (in CH_3CN) of the anti-parallel form and c) CD spectra of the isolated first (thick line) and second (thin line) isomer (in heptane). The solid line represents the open form and the broken line the photostationary state.

Several switching cycles of compound **3** observed by CD spectroscopy show that no isomerization is taking place during the photochemical process and the closed form gives after the ring opening always the original isomer (Fig. 2).

To determine the energy barrier for isomerization, the change in CD absorption upon heating the samples containing enantiomerically pure anti-parallel open forms was followed. For both the



Scheme 4 Stereoisomers, and thermal and photochemical processes of atropisomeric dithienylethenes.

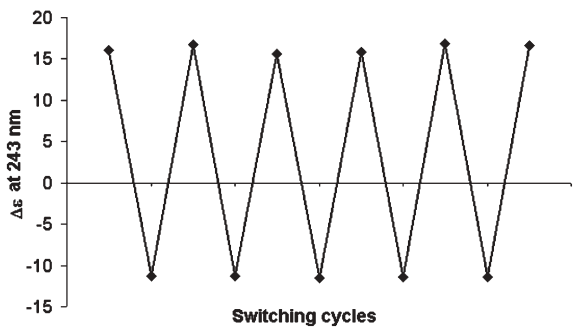


Fig. 2 Switching cycles observed upon alternated irradiation with UV light (λ = 313 nm) and visible light (λ > 460 nm) as detected by CD at 243 nm.

donor- and acceptor-substituted diarylethenes **3o** and **4o** the activation energy for the rotation about the single bond connecting the thiophene with the phenanthrene unit is similar, 109.6 kJ mol^{-1} and 111.5 kJ mol^{-1}, respectively.[18] This indicates that the barrier to rotation is determined by steric interactions, and that the difference in the electronic properties plays only a minor role. This high activation energy allows isolation of individual isomers, and provides these compounds with a half-life of several thousand hours at room temperature.

In conclusion, all three individual atropisomers of a photochromic diarylethene were isolated for the first time. While the parallel *meso* form is photochemically inactive, the two anti-parallel enantiomers are photochemically active and undergo reversible ring-closure in a stereospecific process. The inherent chirality that can be modulated in a fully reversible and stereospecific manner provides a useful basis for chiroptical molecular switches and molecular memory elements.

This work was supported by the Zernike Institute for Advanced Materials. Dr M. M. Pollard is gratefully acknowledged for valuable discussions.

Notes and references

1 M. Oki, *Top. Stereochem.*, 1983, **14**, 1; M. Oki, *The Chemistry of Rotational Isomers*, Springer-Verlag, Berlin, 1993; E. L. Eliel and S. H. Wilen, *Stereochemistry of Carbon Compounds*, John Wiley & Sons, New York, 1994, p. 1142.
2 M. McCarthy and P. J. Guiry, *Tetrahedron*, 2001, **57**, 3809; T. T.-L. Au-Yeung and A. S. C. Chan, *Coord. Chem. Rev.*, 2004, **248**, 2151; *Comprehensive Asymmetric Catalysis*, ed. E. N. Jacobsen, A. Pfaltz and H Yamamoto, Springer, New York, 1999.
3 G. S. Kottas, L. I. Clarke, D. Horinek and J. Michl, *Chem. Rev.*, 2005, **105**, 1281; W. R. Browne and B. L. Feringa, *Nat. Nanotechnol.*, 2006, **1**, 25.
4 H. Iwamura and K. Mislow, *Acc. Chem. Res.*, 1988, **21**, 175; Z. Rappoport and S. E. Biali, *Acc. Chem. Res.*, 1997, **30**, 307.
5 T. R. Kelly, J. P. Sestelo and I. Tellitu, *J. Org. Chem.*, 1998, **63**, 3655; T. R. Kelly, M. C. Bowyer, K. V. Bhaskar, D. Bebbington, A. Garcia, F. Lang, M. H. Kim and M. P. Jette, *J. Am. Chem. Soc.*, 1994, **116**, 3657; T. R. Kelly, H. De Silva and R. A. Silva, *Nature*, 1999, **401**, 150; S. P. Fletcher, F. Dumur, M. Pollard and B. L. Feringa, *Science*, 2005, **310**, 80.
6 Y. Yokoyama and M. Saito, in *Chiral Photochemistry*, ed. Y. Inoue and V. Ramamurthy, Marcel Dekker, New York, 2004, p. 235; B. L. Feringa, R. A. van Delden and M. K. J. ter Wiel, in *Molecular Switches*, ed. B. L. Feringa, Wiley-VCH, Weinheim, 2001, p. 123.
7 N. P. Huck, W. F. Jager, B. De Lange and B. L. Feringa, *Science*, 1996, **237**, 1686; C. Denekamp and B. L. Feringa, *Adv. Mater.*, 1988, **10**, 1080; T. Yamaguchi, T. Inagawa, H. Nakazumi, S. Irie and M. Irie, *Chem. Mater.*, 2000, **12**, 869; K. Uchida, Y. Kawai, Y. Shimizu, V. Vill and M. Irie, *Chem. Lett.*, 2000, 654; T. Yamaguchi, T. Inagawa, H. Nakazumi, S. Irie and M. Irie, *J. Mater. Chem.*, 2001, **11**, 2453; R. Eelkema, M. M. Pollard, J. Vicario, N. Katsonis, B. S. Ramon, C. W. M. Bastiaansen, D. J. Broer and B. L. Feringa, *Nature*, 2006, **440**, 163.
8 J. J. D. de Jong, L. N. Lucas, R. M. Kellogg, J. H. Van Esch and B. L. Feringa, *Science*, 2004, **304**, 278; J. J. D. de Jong, Th. D. Tiemersma-Wegman, J. H. van Esch and B. L. Feringa, *J. Am. Chem. Soc.*, 2005, **127**, 13804.
9 T. J. Wigglesworth, D. Sud, T. B. Norsten, V. S. Lekhi and N. R. Branda, *J. Am. Chem. Soc.*, 2005, **127**, 7272; T. B. Norsten, A. Peters, R. McDonald, M. Wang and N. R. Branda, *J. Am. Chem. Soc.*, 2001, **123**, 7447.
10 Y. Yokoyama, *Chem.–Eur. J.*, 2004, **10**, 4388; Y. Yokoyama, H. Shiraishi, Y. Tani, Y. Yokoyama and Y. Yamaguchi, *J. Am. Chem. Soc.*, 2003, **125**, 7194.
11 E. Murguly, T. B. Norsten and N. R. Branda, *Angew. Chem., Int. Ed.*, 2001, **40**, 1752.
12 K. Uchida, Y. Nakayama and M. Irie, *Bull. Chem. Soc. Jpn.*, 1990, **63**, 1311.
13 K. Uchida, E. Tsuchida, Y. Aoi, S. Nakamura and M. Irie, *Chem. Lett.*, 1999, 63; L. Dinescu and Z. Y. Wang, *Chem. Commun.*, 1999, 2497.
14 M. Takeshita, M. Yamada, N. Kato and M. Irie, *J. Chem. Soc., Perkin Trans. 2*, 2000, 619; M. Takeshita, N. Kato, S. Kawauchi, T. Imase, J. Watanabe and M. Irie, *J. Org. Chem.*, 1988, **63**, 9306; M. Takeshita, C. N. Choi and M. Irie, *Chem. Commun.*, 1997, 2265.
15 M. Takeshita and T. Yamato, *Angew. Chem., Int. Ed.*, 2002, **41**, 2156.
16 The compounds **1o** and **2o** suffer from very low solubility in heptane which makes their resolution difficult.
17 R_a and S_a indicate atropisomers of the open anti-parallel form, *P*,*P* and *M*,*M* indicate helicities in the closed form, *R* and *S* indicate the configuration of the stereogenic centres in the closed form.
18 For an analysis of the kinetic process, see supplementary material.