DOI: 10.1002/ange.201105136

Photochromism

Unprecedented Stability of a Photochromic Bisthienylethene Based on Benzobisthiadiazole as an Ethene Bridge**

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Photochromic systems are of increasing interest as a result of their applications in ophthalmic lenses[1] and as smart molecular materials that act as photoresponsive self-assembling systems, molecular switches, logic gates, and information storage media.[2] In particular, bisthienylethenes (BTEs)[3] have become one of the most promising families because of their thermal irreversibility and outstanding fatigue resistance since the 1,3,5-hexatriene section can adopt an appropriate conformation to undergo a conrotatory 6π-electron photocyclization. To date, the rational design of symmetric or asymmetric BTEs has mainly been carried out by modifying the thiophene rings.[4] In contrast, the central ethene bridges necessary for the versatility of the BTE architectures reported so far have been mostly limited to a cyclopentene unit or its strong electron-withdrawing analogues, such as perfluorocyclopentene, maleic anhydride, or maleic imide. As alternatives to this, several research groups have investigated the use of six-membered rings containing a C=C bond, such as 1,10-phenanthroline[5] and cyclohexene obtained by a [4+2] cycloaddition of butadiene with a dienophile, as the central ethene bridge of BTEs.[6] Recently, we incorporated highly polar and electron-withdrawing chromophores of 2,1,3-benzothiadiazole and naphthalimide units as a novel family of six-membered rings that act as ethene bridges and result in good photochromic performance with moderate fatigue resistance in solution or in organogel systems.[7] Moreover, their fluorescence can be modulated by solvato- and photochromism, eventually leading to a combined NOR and INHIBIT logic operation system. However, the two building blocks have a degree of aromaticity, which can facilitate the undesirable thermal back reaction in the dark as a result of the large loss of aromatic stabilization energy upon photocyclization from the open to the closed form.

Accordingly, a lower aromaticity of the central ethene moiety in BTEs is expected to lead to a higher thermal stability of the closed form. Since the ethene bridge within a six-membered ring has its own advantages, such as a higher quantum yield in its closed-ring form and longer absorption wavelength, we envisioned that the use of a non-aromatic six-membered ring with a C=C bond as the central ethene bridge might widely extend the diversity of the thermally irreversible photochromic systems. With this in mind, we report herein an original BTE photochromic system (BTTE, Figure 1) based on the benzo[1,2-*c*:3,4-*c*′]bis[1,2,5]thiadiazole (abbreviated as benzobisthiadiazole) chromophore as a novel six-membered ring containing a central bridging ethene unit, which is expected to have a low aromaticity, and yield a thermally stable closed form (*c*-BTTE).

As depicted in Figure 1A, BTTE was easily prepared by conventional Suzuki cross-coupling with the corresponding boronic acid. The key intermediate of 4,5-dibromobenzo[1,2-*c*:3,4-*c*′]bis[1,2,5]thiadiazole (BBT) was conveniently synthesized from benzothiadiazole according to the reported procedure.[8] The Suzuki coupling of BBT and 2,5-dimethylthien-3-yl boronic acid in the presence of a $[Pd(PPh_3)_4]$ catalyst in a mixture of aqueous Na_2CO_3 (2 M) and 1,4-dioxane under reflux gave the target molecule BTTE, which was fully characterized by ^{1}H NMR and ^{13}C NMR spectroscopy as well as HRMS (see the Supporting Information).

Interestingly, the ^{1}H NMR spectrum of BTTE shows two well-resolved sets of signals for the methyl protons which correspond to the parallel ($\delta = 2.09$ and 2.42 ppm) and antiparallel ($\delta = 1.96$ and 2.46 ppm) conformations commonly found in BTE systems (Figure 1D).[9] In general, the two conformations, parallel (photochromic inactive) and antiparallel (photochromic active) conformations, undergo very fast single-bond rotation in most BTEs, thereby resulting in only one set of time-averaged signals in the ^{1}H NMR spectrum. Only in the cases of diarylethenes bearing substituents can the rotation of the aryl groups be slowed down sufficiently to give two sets of signals. As found by integration of the ^{1}H NMR spectrum, the ratio between the parallel and antiparallel conformations of BTTE in $CDCl_3$ is 55:45.

A solution of BTTE in THF is colorless, with an intense absorption band at 288 nm and a moderate one at 361 nm (Table 1). As expected, irradiation of the solution of BTTE with light at a wavelength of 365 nm results in the solution

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[**] This work was supported by NSFC/China, National 973 Program (2011CB808400), the Oriental Scholarship, SRFDP 200802510011, and the Fundamental Research Funds for the Central Universities (WK1013002). The China Scholarship Council and PHENICS international network (CNRS GDRI93) supported this collaboration.

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201105136.

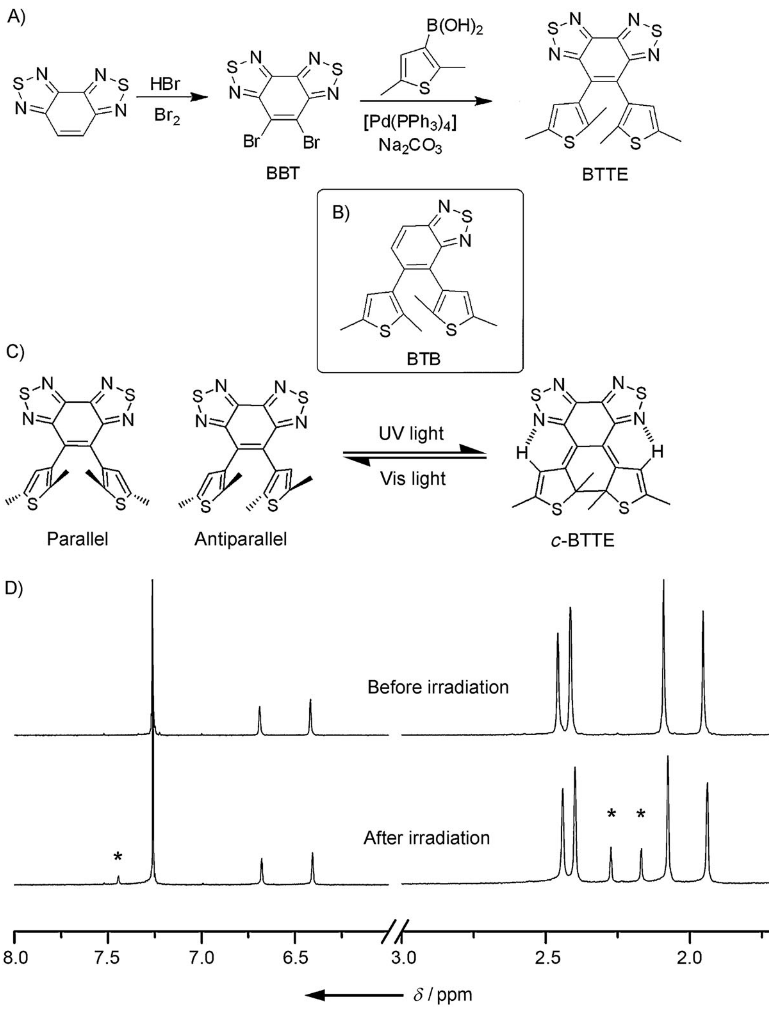

Figure 1. A) Synthetic route to BTTE, B) chemical structure of reference compound BTB, C) structural changes of BTTE under alternate irradiation with UV and visible light in THF (2.09×10^{-4} mol L^{-1}), and D) changes in the ^{1}H NMR signals of BTTE upon UV irradiation in CDCl$_3$.

quickly turning brown, with formation of an intense absorption band at 382 nm and two moderate low-lying bands at 455 and 585 nm (Figure 2A; see also Figures S1 and S2 in the Supporting Information), which are indicative of the appearance of the closed form (*c*-BTTE) produced by the photocyclization (Figure 1C). The existence of *c*-BTTE is evident in the ^{1}H NMR spectrum (Figure 1D). The two sets of well-resolved signals were converted into one set of signals for the methyl protons on the thiophene rings (moved to $\delta = 2.29$ and 2.18 ppm). This finding indicates that a slow interconversion between the parallel and antiparallel conformations takes place in the system, and that the chemical environment of the two sets of methyl groups becomes identical after the cyclization reaction. Interestingly, only one downfield-shifted signal for the thiophene protons is present ($\delta = 7.45$ ppm) in the closed form, in contrast to the two signals ($\delta = 6.42$ and 6.69 ppm) in the open form. This shift can be attributed to the possible formation of intramolecular hydrogen bonds between these protons and the nitrogen atoms in the benzobisthiadiazole unit upon photocyclization (Figure 1C).

Moreover, the absorption bands in the visible region are gradually bleached as a result of the photochromic back-reaction upon irradiation at 575 nm. The typical photochromic properties of BTTE and *c*-BTTE are summarized in Table 1. Specifically, BTTE exhibits comparatively larger quantum yields for ring closure in polar solvents than in more nonpolar solvents (from 14.5 % in toluene to 42.1 % in acetonitrile), a result that is rarely observed in photochromic diarylethene systems.[10] The quantum yields for ring opening are almost the same in cyclohexane and acetonitrile (see Table S1 in the Supporting Information). In contrast to the quantum yield for ring closure, the quantum yield for ring opening is not solvent-dependent, and is hardly affected by the polarity.

As shown in Table 1, the absorption maxima of the open form BTTE remains in the wavelength range 357–375 nm, and the closed form *c*-BTTE in the range 575–587 nm, thus indicating that the solvent dependence of the absorption band is rather small. BTTE shows some noticeable fluorescence, which can conveniently be modulated with photochromism and solvatochromism (see Figures S2–S4 in the Supporting Information). Indeed, no significant fluorescence signal could be recorded from pure *c*-BTTE (see Figure S3 in the Supporting

Table 1: Spectrascopic data of the open form and closed form of BTTE in various solvents.

Solvents	BTTE (λ_{max}, nm)	*c*-BTTE[a] (λ_{max}, nm)	$\Phi_{O\text{-}C}$ [%][b]
cyclohexane	287, 375	284, 387, 453, 485, 575	15.0
toluene	293, 366	284, 380, 455, 581	14.5
THF	288, 361	289, 382, 455, 585	26.4
ethanol	285, 364	284, 382, 458, 587	27.5
acetonitrile	285, 357	284, 379, 454, 576	42.1

[a] The pure closed form was separated on silica gel by eluting with petroleum ether/dichloromethane (130:80). [b] The cyclization quantum yield was measured by irradiation with UV light at a wavelength of 365 nm in various solvents.

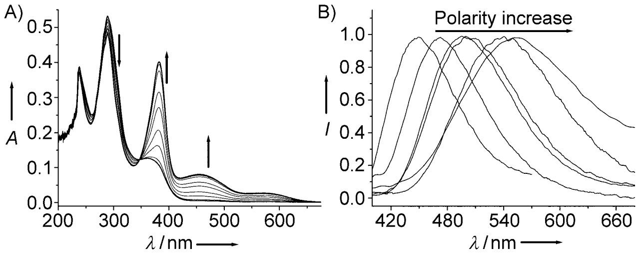

Figure 2. Spectra of BTTE: A) changes in the absorption spectrum upon irradiation at 365 nm in THF (2.09×10^{-5} mol L^{-1}) over 360 s, B) normalized fluorescence spectra in various solvents (from left to right: cyclohexane, chloroform, THF, acetonitrile, DMF, and ethanol).

Information). The photostationary state (PSS) reached from the open form BTTE in THF shows a fluorescence quenching of 48% (excitation at the isosbestic point, 347 nm), which is consistent with the conversion yield of 53% (see Table S1 in the Supporting Information). The quenching of the fluorescence of BTTE is simply due to the disappearance of the open form upon photocyclization. Moreover, the solvent polarity is decisive for the wavelength of the fluorescence emission, in that BTTE is a typical donor-π-acceptor (D-π-A) system. The maximum of the emission band of BTTE appears at 449, 497, 504, 542, 549, and 553 nm in cyclohexane, chloroform, THF, acetonitrile, DMF, ethanol, respectively (Figure 2B, and see Table S2 in the Supporting Information). The solvatochromism of BTTE is due to a photoinduced charge transfer from the donor thiophene group to the electronegative benzobisthiadiazole ring. The positive linearity of the Lippert–Mataga plot of BTTE illustrates that there is a higher dipole moment in the excited state than in the ground state (see Figure S5 in the Supporting Information).

To gain further insight into the photochromic and fluorescent properties of BTTE, fluorescence decays were measured in several solvents by the time-correlated single photon counting technique. In all the investigated solvents (toluene, THF, ethanol, and acetonitrile), the fluorescence decay curves could be successfully analyzed by means of a biexponential function ($\chi^2_R < 1.2$). In these solvents, the long time constant τ_1 increases together with the solvent polarity (from 0.24 ns in toluene to 1.39 ns in acetonitrile), whereas the short time constant τ_2 remains almost unchanged, in the range 0.07–0.22 ns (see Table S1 in the Supporting Information). The corresponding fractions of intensity (f_i) show that the emission arises predominantly from the long lifetime, with an increasing contribution for the more-polar solvents. It may be concluded that the long decay time corresponds to a population of molecules in their parallel conformation, which are known to be nonphotochromic, but noticeably fluorescent. Increasing the solvent polarity results in an increase in the fluorescence quantum yield of BTTE, the fluorescence spectrum shows a red-shift (see above), and τ_1 becomes longer. These observations are consistent with a mostly fluorescent parallel conformation with perpendicular thiophene rings with respect to the benzobisthiadiazole moiety. Such an arrangement could significantly enhance the intramolecular charge-transfer (ICT) efficiency in excited states. On the other hand, τ_2 may correspond to the photochromic but weakly fluorescent antiparallel conformation. Its contribution (f_2) decreases with an increase in the solvent polarity, which is fully compatible with the increasing quantum yield for ring closure ($\Phi_{\text{o-c}}$, Table 1). Indeed, for the photochromic active conformation, it is reasonable to assert that the ring-closure reaction occurring in the excited state is in competition with the radiative pathway to the ground state.

Generally, in BTE derivatives, an aromatic character of six-membered rings containing a C=C bond favors the undesirable thermal back-reaction in the dark because of the large loss of aromatic stabilization energy upon photocyclization. In contrast, *c*-BTTE maintains its very promising thermal stability, and does not show any thermal back-reaction in various solvents, such as cyclohexane, THF, and even in ethanol in the dark at room temperature (see Figures S6 and S7 in the Supporting Information). In fact, the pure closed form was successfully separated on silica gel with a petroleum ether/dichloromethane eluent. At elevated temperature (80 °C) in toluene, BTTE shows only a 5.4% decrease in its absorbance at 457 nm after 800 min (see Figure S8 in the Supporting Information). In contrast to BTB (Figure 1B), which contains a benzothiadiazole unit as the bridge,[7b] the thermal stability of *c*-BTTE is not affected by the solvent polarity: *c*-BTB is stable at room temperature only in relatively apolar solvents such as cyclohexane and hexane, and shows first-order decay in polar solvents such as THF ($k = 3.17\times10^{-5}\,\text{min}^{-1}$) and acetonitrile ($k = 2.95\times10^{-4}\,\text{min}^{-1}$). The fatigue resistance of BTTE was also studied: BTTE can be repeatedly toggled between the open and closed forms by irradiating alternately between UV (365 nm) and visible light (575 nm) in degassed THF, and it remains intact without any apparent degradation. Thus, the introduction of the uncommon benzobisthiadiazole six-membered ring as the ethene bridge results in BTTE showing the same photochromic performance as the parent BTEs, such as the widely known five-membered hexafluorocyclopentene-based counterparts.

To gain insight into the geometry, the molecular orbitals, and eventually the role of the highly polar and remarkably electron-withdrawing benzobisthiadiazole unit on the previously mentioned properties, quantum chemical calculations (DFT) were performed with the Gaussian 09 program and compared to the reference compound BTB.[11] The geometries were optimized with the PBE0 functional[12] and 6-31G(d,p) basis set. More accurate energy determinations can be achieved with optimized structures by performing single-point calculations with the larger basis set 6-311g(d,p). The solvent effect is taken into account within the polarizable continuum model[13] in the single-point calculations (see Table S3 and Figure S9 in the Supporting Information). For example, the energy of the open-ring isomer of reference BTB is $-8.8\,\text{kcal}\,\text{mol}^{-1}$ lower than that of the closed-ring isomer in THF, while this energy difference for BTTE is only $-4.6\,\text{kcal}\,\text{mol}^{-1}$. Accordingly, the destabilization energy, which reduces the aromaticity during the course of photocyclization, is lower in BTTE than in BTB. Such a small energy difference between the open and closed forms results in *c*-BTTE having excellent thermal stability in a variety of solvents.[9]

Single crystals of BTTE were grown by slow evaporation from a THF/H_2O solution, and the X-ray crystallographic data of the open form were collected.[14] Only the antiparallel conformer exists in the single crystals (Figure 3A), although BTTE adopts both antiparallel and parallel conformations in solution, as evidenced by ^{1}H NMR spectroscopy. The resolved structure reveals that no intramolecular hydrogen bonding exists in the crystal lattice. In contrast, the benzobisthiadiazole rings are assembled into a 1D chain through π⋯π stacking interactions and intermolecular hydrogen bonds (Figure 3B). Notably, the distance between the photoactive carbon atoms (C2⋯C16) is 3.451 Å, the shortest among the reported BTE systems and meeting the prerequisites for a molecule to undergo photochromic reaction in a crystalline

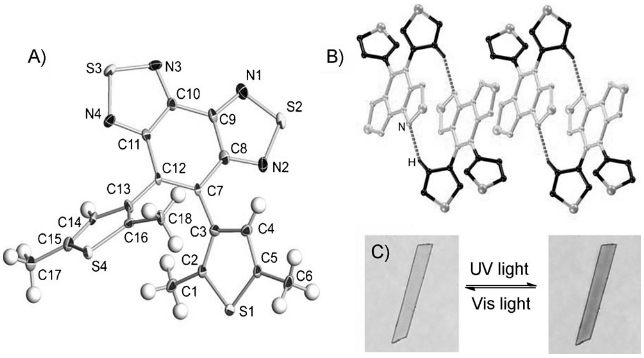

Figure 3. A) ORTEP representation of the crystal structure of BTTE with displacement ellipsoids shown at the 50% probability level. Selected bond lengths [Å]: C11-C12, 1.491(3); C7-C8, 1.483(3); C7-C12, 1.395(3); C2⋯C16, 3.451(6). B) View of the one-dimensional structure of BTTE formed by cooperative hydrogen bonding and π⋯π stacking interactions. Methyl groups and non-hydrogen-bonded hydrogen atoms are omitted for clarity. Selected bond lengths and bond angles: N⋯H, 2.65 Å; N⋯H-C, 151°; N⋯C, 3.488(6) Å. Interplane (π⋯π) angle, 0°; S⋯centroid (benzene), 3.55 Å; centroid (thiadiazole)⋯centroid (thiadiazole), 3.43 Å. C) Changes in a single crystal of BTTE with alternate irradiation at 365 and 575 nm.

phase.[15] Indeed, bulk crystals of BTTE can readily become colored through typical photochromic reactions, and the reaction is fully reversible (Figure 3C). In addition, the lengths of the C11–C12 (1.491 Å) and C7–C8 (1.483 Å) bonds are indicative of single-bond character, while the C7–C12 bond (1.395 Å) is clearly a double bond. Apparently, the benzobisthiadiazole chromophore shows almost no aromaticity and the center bridge linking the two thiophene units is typical of a double bond, thus ensuring the 1,3,5-hexatriene section adopts an appropriate conformation to undergo the conrotatory 6π-electron photocyclization. Nakamura and Irie[9] have demonstrated that a low aromaticity correlates well with the thermal stability of the closed form, and these features of BTTE explain the excellent thermal stability of the closed-ring isomer.

In conclusion, a novel photochromic bisthienylethene BTTE based on benzobisthiadiazole as a six-membered ring that incorporates an ethene bridge has been synthesized and studied. This compound possesses several merits: 1) excellent photochromic performance in both solution and single crystals; 2) an extremely low aromaticity of the central ethene bridging unit of benzobisthiadiazole as a result of the high polarity and electron-withdrawing tendency of the benzobisthiadiazole unit; 3) an unprecedented thermal stability in a variety of solvents (ranging from nonpolar cyclohexane to polar ethanol) among BTEs bearing a six-membered ring containing a $C{=}C$ bridge, correlated to the limited loss of aromatic stabilization energy upon photocyclization, and 4) a convenient modulation of the fluorescence of BTTE with photochromism and solvatochromism. This compound opens up the possibility for the molecular design of BTE-based bistable systems.

Received: July 21, 2011

Keywords: aromaticity · fluorescence · photochromism · solid-state reaction

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[14] Crystallographic data for BTTE: $C_{18}H_{14}N_4S_4$, $M_r = 414.61$, triclinic, space group $P\bar{1}$, $a = 7.679(2)$, $b = 8.799(2)$, $c = 14.555(4)$ Å, $\alpha = 99.149(7)$, $\beta = 99.196(7)$, $\gamma = 109.666(7)°$, $V = 890.0(4)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.547\ \mathrm{g\,cm^{-3}}$, $T = -173(1)\,°\mathrm{C}$, 13351 measured reflections, 4947 unique reflections ($R_{int} = 0.0727$), 3304 with $I \geq 2\sigma(I)$ used in refinement, $R = 0.0943$, $R_w = 0.2451$, GOF = 1.139. CCDC 825620 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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