Photochromism

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Separation of Photoactive Conformers Based on Hindered Diarylethenes: Efficient Modulation in Photocyclization Quantum Yields**

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Abstract: *Endowing both solvent independency and excellent thermal bistability, the benzobis(thiadiazole)-bridged diarylethene system provides an efficient approach to realize extremely high photocyclization quantum yields ($\Phi_{\text{o-c}}$, up to 90.6%) by both separating completely pure anti-parallel conformer and suppressing intramolecular charge transfer (ICT).*

Photochromic diarylethenes (DAEs)[1] have attracted much attention because chemical and physical properties are well-controlled by photo-irradiation, along with specific explorations in molecular switches,[2] logic gates,[3] and information storage.[4] Generally, DAEs bestow two conformers with two aryl rings in mirror symmetry (parallel conformation, p-) and C_2 symmetry (anti-parallel conformation, ap-). As the conrotatory reaction can only result from the antiparallel conformation,[5] the photocyclization quantum yield ($\Phi_{\text{o-c}}$) in conventional DAEs is usually limited to 50%. With critical concerns on the photo-switching efficiency and thermal irreversibility especially for practicable device application, it is pivotal to tailor the equilibrium between p- and ap-conformations for an increase in the photocyclization quantum yield.

DAEs with extraordinary high photocyclization $\Phi_{\text{o-c}}$ have been realized by employing hydrogen bond or other intramolecular weak interactions to fix the ap-conformation as geometrically desirable conformation.[6] However, as a main drawback, their quantum yields behave intrinsic solvent dependency. Alternatively, confining DAEs into a restricted environment with covalently bonding reactive units[7] or steric hindrance[8] can drive molecules to adopt sterically favorable ap-conformation. Hecht et al. have exploited sterically crowded ethene bridges for enhancing photo-switching performance in $\Phi_{\text{o-c}}$, along with no distinct solvent effect.[8i] However, there still leaves much room to enhance $\Phi_{\text{o-c}}$ owing to the residual of p-conformation. Moreover, their specific perhydrocyclopentene bridging motifs with extra intramolecular strain usually bring forth undesirable thermal reversibility in the corresponding closed forms.

Our group has recently reported a benzobis(thiadiazole)-bridged DAE system with unprecedented thermal stability.[9] Typically, the six-membered benzobis(thiadiazole) bridge exhibits an extremely low aromaticity as a result of its essentially high polarity and electron-withdrawing tendency. In contrast to the common perfluorocyclopentene- or cyclopentene-bridged counterparts, the benzobis(thiadiazole)-based ethene bridge contains two extending thiadiazole units. Herein, we conjugate a benzene ring to the thiophene unit as a larger bulky terminal benzothiophene for further development of the thermally irreversible DAE system (DAEs **1**–**4**, Figure 1A). Unexpectedly, the additional benzene unit brings forth very high steric strain to the rotation of benzothiophene unit, and even completely blocking the interconversion between p- and ap-conformations. As demonstrated, benzobis(thiadiazole)-bridged diarylethenes system opens up a breakthrough to realize extremely high photocyclization quantum yield (up to 90.6%) by both separating completely pure ap-conformer and suppressing intramolecular charge transfer (ICT). For the first time, we provide an attractive and efficient approach to step-by-step modulate photocyclization quantum yield, especially bestowing both solvent independency and excellent thermal bistability.

Compound **1** was conveniently synthesized (Supporting Information, Scheme S1) by the Suzuki coupling reaction. In contrast to the reference compound BTTE (Figure 1B),[9a] the steric interaction between the bulky terminal benzothiophene and the benzobis(thiadiazole) bridge is so large that the rotation of benzothiophene is extremely hindered (Figure 1C). That is, the common interconversion between the p- and ap-conformers was not observed, and we successfully separated **1a** and **1p** as ap- and p-conformers (Figure 1A) with silica gel chromatography and recrystallization. More efficiently, the employing preparative HPLC with common C18 column can directly separate the two isomers. The ratio of **1a** and **1p** was close to 1:1 (Experimental Section in the

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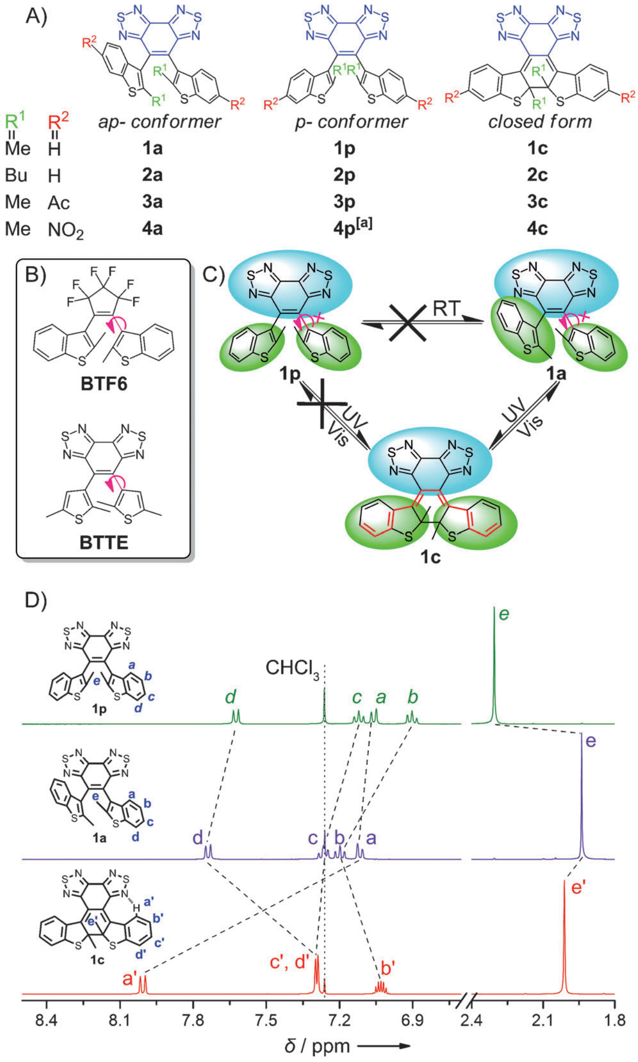

Figure 1. Chemical structures of A) DAEs **1**–**4** with complete separation of p- and ap-conformers, and corresponding closed forms, and B) reference compounds BTF6 and BTTE with freely rotatable aryl groups. C) The conversion relationship of **1a**, **1p**, and **1c** with a hindered aryl group. D) Comparison of ^{1}H NMR spectra of **1p**, **1a**, and **1c** in CDCl$_3$. [a] **4p** was not obtained owing to the direct nitration of **1a**, resulting in only **4a**.

Supporting Information), indicating that the two conformers were formed with almost equal possibility. Similarly, we also synthesized butyl-, acetyl-, and nitro-substituted derivatives **2**, **3**, and **4**. Their corresponding closed forms (**1c**–**4c**, Figure 1A) were also successfully isolated owing to their high thermal irreversibility. The chemical structures were fully confirmed with ^{1}H and ^{13}C NMR spectroscopy, HRMS, and X-ray single-crystal analysis.

Firstly, we compared the optical properties of **1a** and **1p**. Both have a very small absorption band in visible range, and are colorless in THF. Their absorption spectra are almost the same, except a little difference in the shoulder peak around 340–400 nm, where **1p** is slightly stronger than **1a** (Figure 2A). They also show medium fluorescence, resulting from the ICT owing to their typical donor–π-acceptor (D–π-A) characteristics. Compared with **1p**, the emission wavelength

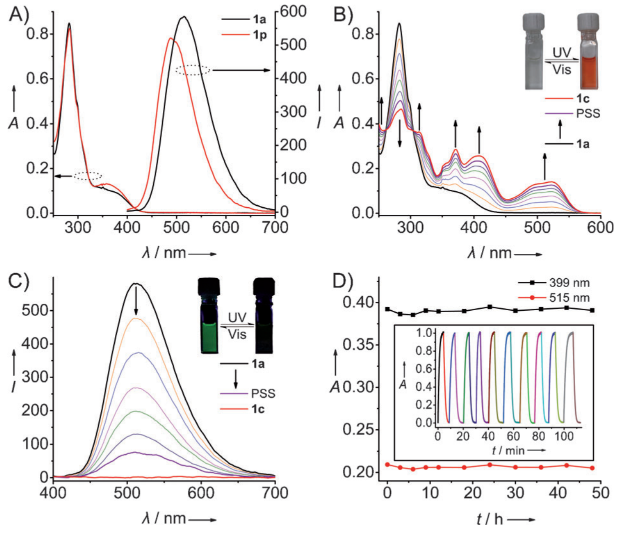

Figure 2. A) Comparison of absorption and fluorescence spectra of **1a** and **1p** (2.09×10^{-5} M) in THF. B) Absorption and C) fluorescence of **1a** (2.09×10^{-5} M) in THF upon irradiation at 313 nm. Excitation for fluorescence at isosbestic point (304 nm). D) Decay curves of absorption peaks of **1a** at PSS upon irradiation of 313 nm at 343 K in CH$_3$CN (3.10×10^{-5} M). Insets in (B) and (C): photographic images of the color and emission changes of **1a**, respectively. Inset in (D): fatigue resistance of **1a** upon alternation irradiation of 313 nm UV light and broadband visible light ($\lambda > 450$ nm) monitored at 515 nm in CH$_3$CN (1.65×10^{-4} M).

of **1a** is red-shifted by 24 nm, along with a decrease in fluorescence lifetime (Figure 2A; Supporting Information, Table S1). Moreover, their fluorescence can be conveniently modulated with solvatochromism from blue to yellow. The observed solvatochromism is due to the ICT from the donor benzothiophene unit to the electron-withdrawing benzobis(-thiadiazole) ethene bridge. The positive linearity of Lippert–Mataga plot illustrates that the dipole moment in the excited state is higher than in the ground state (Supporting Information, Figure S4 and Table S1).

We then checked the photochromic behaviors of **1a** and **1p**. Upon UV irradiation at 313 nm, the THF solution of **1a** turned reddish orange, along with an increase in a series of peaks located at 371, 408, and 522 nm in the absorption spectra (Figure 2B). The behavior is identical to its closed form **1c**, resulting in a photocyclization conversion yield of 89.5% at the photostationary state (PSS). Moreover, its fluorescence located at 514 nm was quenched by 88.1% upon excitation at the isosbestic point of 304 nm (Figure 2C).

Owing to the extremely weak fluorescence of **1c**, the quenching is mainly caused by the disappearance of **1a** upon photocyclization. Obviously, the fluorescence can also be easily modulated by photochromism. The color of **1c** can be completely bleached as a result of photocycloreversion upon visible light irradiation, showing the excellent fatigue resistance without any apparent degradation. Meanwhile, **1c** endows excellent thermal stability, showing no obvious decays at 343 K (Figure 2D). However, for the p-conformer, **1p** appears neither color nor fluorescence change under the same condition (Supporting Information, Figures S1–S3).

Similar photochromic properties can also be found in its derivatives **2**, **3**, and **4** (Supporting Information, Figures S5–S7).

The photochromism was further traced by NMR spectroscopy for the separated conformers (Figure 1D; Supporting Information, Figures S8–S11). ^{1}H NMR spectra of **1a** and **1p** show only one signal at $\delta = 1.94$ and 2.30 ppm, respectively, corresponding to the methyl protons adjacent to the reactive carbon atoms. It is quite different from the reference compounds BTTE and BTF6 (Figure 1B), which have two well-resolved signals representing the coexistence of ap- and p-conformers.[9a] During UV irradiation, while all the signals of **1p** stay constant, the signal of the methyl protons of **1a** moves to $\delta = 2.01$ ppm, along with signals of H_a shifting from 7.12 to 8.00 ppm attributed to the formation of intramolecular hydrogen bonds between H_a and N of the thiadiazole upon photocyclization. HPLC was also employed to confirm the conversion relationships of **1a**, **1p**, and **1c** (Supporting Information, Figures S16 and S17). All of these results indicate that **1p** is photoinactive, and the photocyclization and cycloreversion can only take place between **1a** and **1c**.

To gain insight into the rotation limitation for the separation of conformers **1a** and **1p**, some theory simulations were performed (see the Supporting Information), especially for the rotational barriers of single bond connecting aryl group to the ethene bridge (Figure 3A). The barrier of BTF6 is 65.7 kJ mol^{-1}, which is high enough to make ap- and p-conformations distinguishable in NMR spectroscopy, while that of BTTE is even higher (72.0 kJ mol^{-1}). In contrast, owing to the high steric crowding between the ethene bridge of benzobis(thiadiazole) and the side benzothiophene units, the rotational barrier of **1** is much higher than 93.5 kJ mol^{-1} (the minimum energy value required to their rotation at 300 K),[10] and increases to 139.3 and 139.8 kJ mol^{-1} at a dihedral angle of ±10°, respectively. Further rotating the dihedral angle towards 0° (co-planar) causes the overlap of ethene and aryl groups, and thus the barrier cannot be computed any further. Accordingly, the ap- and p-conformers of **1a** and **1p** do not show any interconversion at ambient temperature, which can be further confirmed from the excellently thermal stability of **1a** and **1p** at 343 K (Supporting Information, Figure S18). Consequently, we have successfully separated them as thermally stable conformers.

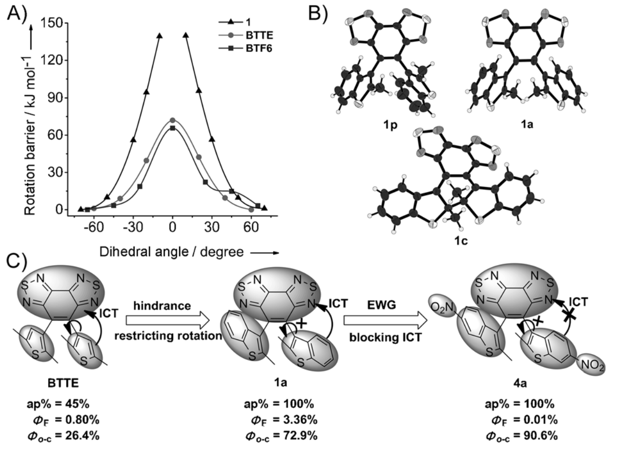

Figure 3. (A) Calculated rotational barriers of **1**, BTTE, and BTF6. A negative dihedral angle corresponds to the ap-conformation, while positive dihedral angle corresponds to p-conformation. (B) ORTEP representations (ellipsoids set at 50% probability) of the crystals **1p**, **1a**, and **1c**. Note the solvent molecule (dioxane) in **1p** is omitted for clarity. (C) Efficient modulation of $\Phi_{o\text{-}c}$ through separating completely pure ap-conformer and suppressing ICT.

Moreover, the theoretical calculation can be very useful to see the possible geometry at different rotation angles for each p- or ap-conformer in solution.[11] In the case of compound **1**, the ap-conformer contains two different geometries (**1a** and **1a**′), and the parallel conformer actually has a pair of equivalent mirrored geometries (Supporting Information, Figure S20, and Tables S6 and S7). As calculated, the non-photochromic **1a**′ at ambient temperature can readily convert to the photochromic **1a** at the converting rate constant of 1.69×10^{12} s^{-1} (exactly in the range of picoseconds), which hence facilitates photoisomerization under light irradiation (see the Supporting Information).

Fortunately, we obtained the single crystals of **1p**, **1a**, and **1c** (Figure 3B; Supporting Information, Figure S25). Indeed, **1a** exhibits the C_2 symmetry as ap-conformation, while **1p** bears the mirror symmetry as p-conformation (Supporting Information, Table S10). Generally, to show photochromism in the single crystal, DAEs should meet two basic requirements: packing into ap-conformation and the distance between the photoactive carbon atoms being less than 4.2 Å.[12] As expected, the parallel conformer crystal (**1p**) does not exhibit any color change upon UV irradiation. Strangely, the ap-conformer crystal (**1a**), in which the distance between reactive carbon atoms is evaluated as 3.480 Å, which is only slightly longer than that of BTTE (3.451 Å), also does not show any obvious color change upon UV irradiation. It is in distinct contrast with BTTE bearing the same ethene bridge, which can turn red quickly with the characteristic photochromic behavior.[9a] Such exceptions are really rare,[13] especially when the distance between photoactive carbons is among the shortest known. For BTTE, the rotation of small terminal thiophene unit is free enough to proceed photocyclization both in solution and crystal state. While introducing the benzene ring into thiophene unit as larger bulky terminal group, the strong intramolecular hindrance of **1a** might freeze the rotation of benzothiophene group seriously, thus suppressing the photochromism in well-ordered crystal state. This can be further supported by the non-photochromic feature for ap-crystals of **2a**, **3a**, and **4a** (Supporting Information, Figure S26), despite particularly short distances between the reacting carbon atoms, which are 3.773, 3.380 (the shortest distance to date) and 3.944 nm, respectively. As a consequence, in photochromic DAE systems, the appropriate rotation of aryl groups in the single crystal state should be taken into account, and the empirical distance of 4.2 Å is only suitable to common freely rotatable DAEs, rather than these hindered DAEs **1a**–**4a**.

As **1a** can be successfully separated and definitely confirmed as ap-conformer, what attracts us most is its photochromic quantum yield. Indeed, $\Phi_{o\text{-}c}$ of **1a** was determined to be as high as 72.9% in THF, more than twice as high as that of BTF6 (35% in hexane)[6b,14] and BTTE (26.4% in

THF).[9a] Meanwhile, unlike BTTE with solvent polarity dependent behavior (from 15% in cyclohexane to 42.1% in acetonitrile), **1a** exhibits almost the same $\Phi_{\text{o-c}}$ in polar or low polar solvents (Supporting Information, Table S2). But although **1a** is a pure ap-conformer, its $\Phi_{\text{o-c}}$ is still a little far from the theory value (100%). According to Irie's early work on maleic anhydride based DAEs,[15] the presence of ICT is deleterious to the photocyclization owing to the existence of the competing deactivating channel in excited states. As **1a** is a typical D–π-A system with emitting fluorescence resulted from ICT, for further improving the quantum yield, the ICT effect is expected to be blocked by introducing strong electron-withdrawing acetyl or nitro groups on the benzothiophenes (**3a** and **4a**, Figure 1A). As listed in Table 1, the fluorescence quantum yield (Φ_F) and emission wavelength (λ_{em}) are changed from 3.36% and 514 nm (**1a**), 0.66% and 492 nm (**3a**), to 0.01% and 458 nm (**4a**). Moreover, the low-lying excited states of **1a** consist mainly of HOMO→LUMO, HOMO−1→LUMO, and HOMO→LUMO+1 transitions (Supporting Information, Figure S21), which correspond to ICT from the donor benzothiophene unit to the electron-withdrawing benzobis(thiadiazole) ethene bridge. When introducing nitro group, the ICT channel of **4a** was efficiently blocked (Supporting Information, Figure S22 and Table S8) with a serious quenching in fluorescence. In this way, we successfully increased $\Phi_{\text{o-c}}$ step by step (Figure 3C), from BTTE (26.4%, coexistence of ap- and p-conformers with ICT), **1a** (72.9%, pure ap-conformer with ICT), **3a** (84.3%, pure ap-conformer with partly blocked ICT) to **4a** (90.6%, pure ap-conformer with efficiently blocked ICT). However, upon incorporation of larger butyl group at reactive carbon, $\Phi_{\text{o-c}}$ of **2a** is decreased by 6.1% with respect to **1a**. It is indicative that besides the effect of ICT, its large hindrance also involves the decrease in $\Phi_{\text{o-c}}$. Consequently, the benzobis(thiadiazole)-bridged DAE system can efficiently modulate $\Phi_{\text{o-c}}$ through both separating pure ap-conformer and suppressing ICT (Figure 3C).

Table 1: Spectroscopic data of **1a**–**4a** in THF.

	λ_{max}/nm	λ_{em}/nm	Φ_F[a]/%	α_{PSS}[b]/%	$\Phi_{\text{o-c}}$[c]/%
1a	282	514	3.36	89.5	72.9
2a	282	514	5.75	88.0	66.8
3a	285	492	0.66	93.1	84.3
4a	284	458	0.01	95.8	90.6
BTTE[d]	289	504	0.80	53.0	26.4
BTF6[e]	258	–	–	45.0	35.0

[a] Fluorescence quantum yield (Φ_F). [b] Conversion yield at PSS (α_{PSS}). [c] Quantum yields of cyclization ($\Phi_{\text{o-c}}$) were calculated upon irradiation at 313 nm, using BTF6 as the reference. [d] BTTE (365 nm) in THF was taken from reference [9a]. [e] BTF6 (313 nm) in hexane was taken from reference [6b] and [14].

In conclusion, a novel photochromic DAE system based on benzobis(thiadiazole) ethene bridge has been established and well-studied. Specifically, the system can bring forth very high steric strain barrier to the rotation of benzothiophene unit, even completely blocking the interconversion between p- and ap-conformations, thus possessing several merits: 1) being able to completely separate ap- and p-conformers with high thermal stability; 2) realizing impressively high $\Phi_{\text{o-c}}$ (up to 90.6%) through pure ap-conformer with intrinsic solvent independency; 3) tailoring the fluorescence of ap-conformer with photochromism and solvatochromism; and 4) exhibiting high thermal bistability for the open and closed forms based on the low aromaticity ethene bridge. Regardless of meeting the empirical distance of 4.2 Å and the ap-conformation, the separated pure ap-conformers **1a**–**4a** cannot proceed towards the photochromic cyclization in well-ordered single-crystal states. The exceptional case well-illustrates that the limited rotation of benzothiophene groups in crystal state should be taken into account. This work provides deep insight into how hindered conformation affects the photochromism of DAEs in solution and solid state, opening up a breakthrough to high $\Phi_{\text{o-c}}$ through both separating completely pure ap-conformer and suppressing intramolecular charge transfer.

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