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A novel gated photochromic reactivity controlled by complexation/dissociation with BF_3†

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A photochemically active dithiazolethene BN was designed and synthesized, exhibiting a specific gated photochromism. That is, the photochromic reactivity of BN is prevented to a great extent by BF_3, showing a "Lock" gate.

Diarylethenes are the most promising candidates for photoelectronic applications due to their fatigue resistant and thermally irreversible properties.[1] Their potential applications could be in molecular level devices, such as photoresponsive self-assemblies, molecular switches, logic gates and information storage.[2] Although much progress has been made in diarylethene systems, a property that is strongly desirable, but is still inadequate is gated photochromic reactivity, which has rarely been reported in recent years. Gated reactivity is the property that the ON/OFF photoactivity of molecules is dependent on the external stimuli, such as reaction,[3] heat[4] and coordination.[5] The threshold reactivity is, in particular, moving forward data processing on the molecular level, with potential applications in sensing and labeling, as well as data manipulation. Moreover, the photocyclization quantum yield is also very critical to the photochromic system. Recently, a number of dithiazolethenes have been studied,[6] exhibiting a very high photocyclization quantum yield.[7] With this in mind, we designed and synthesized a photochromic molecule **BN** (Fig. 1a) with gated reactivity and high quantum yield.

The dithiazolethene **BN** was synthesized from 2,3-dibromobenzo[*b*]thiophene-1,1-dioxide[8] and the corresponding borate of 4-bromo-5-methyl-2-phenylthiazole through a Suzuki reaction with 45% yield. The structure was confirmed with ^{1}H NMR and ^{13}C NMR, HRMS spectra and X-ray crystallography (ESI†).

Photochromic properties of **BN** was studied in CH_3CN solution. Upon light irradiation at 365 nm, the colorless open-ring form **BN** promptly turned red (λ_{max} = 526 nm, Figs 1a and 2a), which can be ascribed to the transformation from its open form **BN** to the closed form ***c*-BN**. A well-defined isosbestic point appeared at 374 nm, suggesting a two component mixture. The photostationary state (PSS) was reached after irradiation at 365 nm (0.5 mW) for nearly 40 s. **BN** can be photochemically regenerated from ***c*-BN** by irradiation with visible light (546 nm), meanwhile, the characteristic red color of the closed form returns to its originally colorless open form. Impressively, upon the alternating irradiation with UV (365 nm) and visible light (546 nm), compound **BN** can be toggled repeatedly between the open-form and closed-form, remaining intact without any obvious degradation (Fig. 2b).

As is well-known, diarylethenes possess two conformations in solution, with the two rings in a parallel conformation or anti-parallel conformation. Since the photocyclization reaction proceeds only from the anti-parallel conformation, the quantum yield is about 50% at most. The $\Phi_{o\rightarrow c}$ of dithiazolethene **BN** and the reference dithienylethene **BT** (Fig. 1b) in THF was 41.2 and 21.4%, respectively (Table 1).[9] Apparently, dithiazolethene **BN** displays a higher cyclization quantum yield than **BT**,

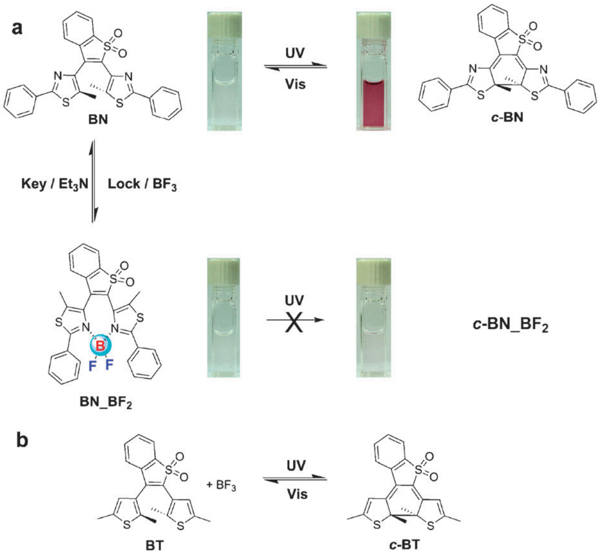

Fig. 1 (a) The proposed mechanism and photographic images of the "Lock and Key" gated process of **BN**. (b) The structural changes of the reference compound **BT** under the alternative irradiation of UV and visible light after the addition of $BF_3 \cdot Et_2O$.

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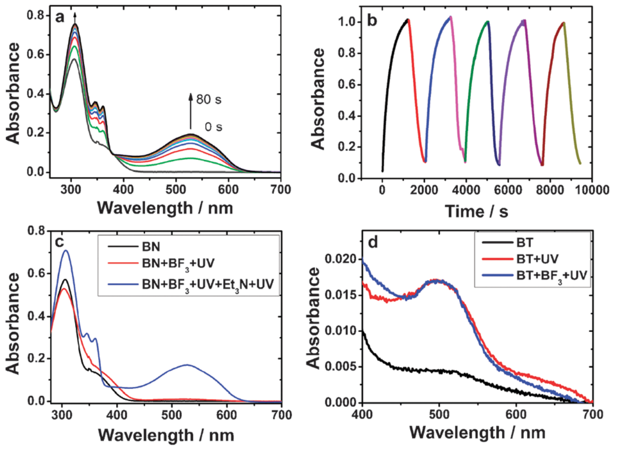

Fig. 2 (a) UV/Vis absorption changes of **BN** (2.0×10^{-5} M) in CH_3CN upon irradiation with 365 nm light every 5 s until 80 s. (b) Fatigue resistance of **BN** upon prolonged irradiation with alternation of 365 and 546 nm for forward and backward reactions in toluene, respectively. (c) Absorption changes of **BN** in CH_3CN before irradiation with 365 nm light (black line) and upon addition of $BF_3{\cdot}Et_2O$ (6.0×10^{-2} M) with 365 nm light irradiation (red line), finally irradiation with 365 nm light (blue line) after adding Et_3N (6.0×10^{-2} M). (d) Absorption changes of reference compound **BT** in CH_3CN solution before (black line) and after irradiation with 365 nm light (red line), or irradiation with 365 nm light after adding $BF_3{\cdot}Et_2O$ (blue line). Note: the absorption band resulting from the photocyclized closed form is much lower than that of **BN** due to the low photocyclization conversion yield (8.1%) in the system of **BT** (Table 1), which might be a result of the forming of methylthiophene CH···O hydrogen bonds in BT.[3e]

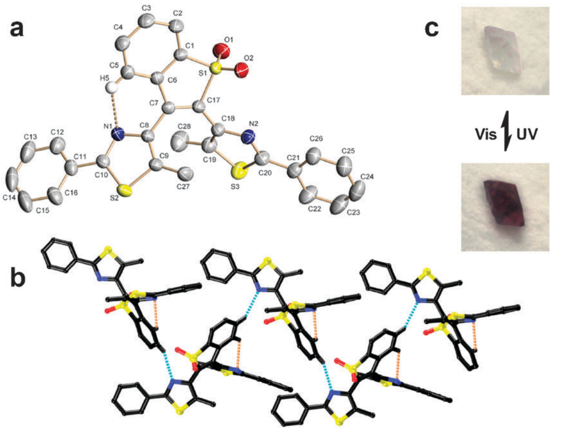

Fig. 3 (a) The single-crystal structure of **BN** with displacement ellipsoids shown at the 50% probability level. Non-hydrogen bonded hydrogen atoms are omitted for clarity. Selected bond lengths (Å): C9···C19, 3.700(3); N1···H5, 2.680; N2···O2, 3.223; N2···O1, 3.828; C6–C7, 1.483(3); C17-S1, 1.787(3); C7–C17, 1.341(3). (b) A view of the one-dimensional structure of **BN** formed by hydrogen bonding (light blue line), with non-hydrogen bonded hydrogens omitted for clarity. Selected bond lengths: N···H, 2.53 Å. (c) Color changes of **BN** in the crystal state.

Table 1 Quantum yields of **BN** and **BT** in THF

Compounds	$\Phi_{o\rightarrow c}$ (%)	$\Phi_{c\rightarrow o}$ (%)	Conversion at PSS (%)
BN	41.2	2.4	77.3
BT	21.4	11.6	8.1

and the PSS coversion of **BN** in THF was 77.3%, 9.6-fold higher than that of reference **BT** (8.1%).

The single crystal of dithiazolethene **BN** was obtained by the diffusion method from a mixture of ethyl acetate and octane at room temperature.‡ The structure has a typical anti-parallel conformation (Fig. 3a), with a distance of 3.700(3) Å between the photoactive carbons (C9···C19), which meets the prerequisites for a molecule to undergo the photochromic reaction[10] from colorless to a violet color in the crystalline phase (Fig. 3c). In addition, a weak CH···N hydrogen bond occurs with a N1···H5 distance of 2.68 Å, which is shorter than the sum of the van der Waals radii of H (1.2 Å) and N (1.55 Å). This is consistent with Kawai's report.[7b] Consequently, the weak CH···N hydrogen bonding in **BN** (Fig. 3a) can stabilize the anti-parallel conformation, thus resulting in an increase in the observed cyclization quantum and conversion yield. Furthermore, intermolecular CH···N hydrogen bonds (Fig. 3b) are also observed, with a H···N distance of 2.53 Å, which is even shorter than the intramolecular length.

Interestingly, no obvious UV absorption spectra changes could be observed with irradiation at 365 nm after the addition of $BF_3{\cdot}Et_2O$ (Fig. 2c). In other words, the photochromism of **BN** was prevented to a great extent by BF_3, showing a specific "Lock" gate. Moreover, the gate behavior is reversible. Upon adding Et_3N, the photochromic property could be recovered (Fig. 2c). Apparently, Et_3N is considered as a "Key" to "Lock" (BF_3). Furthermore, H^+ and metal ions, such as Zn^{2+}, Mn^{2+}, Mg^{2+}, Ca^{2+} and Ba^{2+} (Fig. S1†) had no effect on the photochromism of **BN**.

Meanwhile, dithienylethene **BT** was studied as a reference (Fig. 1b). **BT** could be changed between colorless open and colored closed forms by alternated irradiation with UV and visible light (Fig. S2†). As shown in Fig. 2d, the photochromism of **BT** is characteristically photoactive. In contrast, when adding $BF_3{\cdot}Et_2O$ and, then, upon irradiation with 365 nm, the absorption of **BT** was almost the same as that without BF_3 (Fig. 2d). With respect to **BN**, the gated reactivity of **BT** was not possible in that there is no center (like a N atom) to coordinate with BF_3. Therefore, in the system of dithiazolethene **BN**, we can rule out the interaction of the ethene bridge (benzo[*b*]thiophene-1,1-dioxide) with BF_3.

As shown in Fig. 1a, we propose the specific "Lock" gate in **BN** *via* the coordination model of **BN_BF$_3$** with $BF_3{\cdot}Et_2O$. That is, the thiazole rings rotate to coordinate with BF_3, resulting in a rigid seven-membered ring[11] and a longer distance between the two active carbon atoms. Meanwhile, the geometry becomes closer to the parallel conformer, by which the initial photochromic reaction is blocked. Consequently, the photochromism in the system of **BN** is not allowed, and the "Lock" gate is achieved by BF_3. When adding Et_3N to the system, the coordination of **BN** with BF_3 becomes interrupted, thus recovering the original characteristic photochromicity. Accordingly, Et_3N can play a role as a "Key" to the "Lock" (BF_3). The proposed mechanism was further evidenced by the ^1H NMR titration and theoretical calculation.

To evaluate the "Lock" mechanism with BF_3, we performed a BF_3-dependent ^1H NMR titration on **BN** in $CDCl_3$, wherein the distinct change for the characteristic methyl groups in the

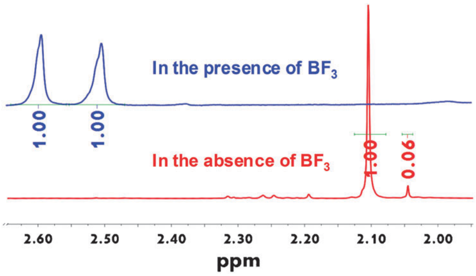

Fig. 4 Changes in the ^{1}H NMR spectra of **BN** in the absence and the presence of BF$_3$.

thiazole units were observed (Fig. 4). Before adding BF$_3$·Et$_2$O, the two signals corresponding to the photoactive methyl hydrogens appear at 2.10 and 2.04 ppm, respectively. Notably, in contrast to the reference **BT** (1 : 1, Fig. S6†), the integration ratio of the lower- and upper-field signals is 1 : 0.06 (Fig. 4), indicating that there exists a predominant anti-parallel conformation in **BN**,[7b,12] which can be further certified by hydrogen bonds of single crystals and contributes to the relative high conversion and cyclization quantum yield (Table 1). Upon adding BF$_3$, the signals of methyl hydrogens in the system of **BN** were shifted downfield to 2.60 and 2.50 ppm with an integration ratio of 1 : 1, respectively, possibly arising from the deshielding effect of the coordination of BF$_3$. This is consistent with the proposed mechanism of a "Key and Lock" process of the photochromic reaction (Fig. 1a). Obviously, the resulting conformation becomes rigid when the nitrogen in the thiazole rings are coordinated with BF$_3$.

In order to further unravel the underlying mechanism of the gated photochromism of **BN** in response to BF$_3$, the optimized geometries of all of the isomers and complexes are depicted in Table S1.† Some critical structural parameters and relative energies of the complexes are tabulated in Table S2.† Due to the unsymmetrical nature of the bridging unit of **BN**, there are four other isomers located, including the parallel isomers **BN-2-α** and **BN-2-β** and the anti-parallel isomers **BN-3-α** and **BN-3-β**. It clearly shows that all the isomers, except for **BN-2-β**, can form complexes with BF$_2$. Energy calculations have excluded the presence of **BN-1_BF2** in the formed complexes. Energies of the complexes demonstrate that **BN-3-α_BF2** and **BN-3-β_BF2** are the most stable complexes formed, which are 6.02 and 7.77 kcal mol^{-1} more favorable than **BN-1_BF2** and **BN-2-α_BF2**, respectively. Furthermore, the significantly large distances between the reactive carbons in both **BN-3-α_BF2** and **BN-3-β_BF2** are around 5.31 Å. Therefore, it can be concluded from the theoretical calculations that the gated photochromism of **BN** in response to BF$_3$ can be reasonably ascribed to the formation of the photochromically deactivated rigid boron-coordination conformation, such as **BN-3-α_BF2** and **BN-3-β_BF2**.

In summary, we designed and synthesized a triangle terarylene with gated photochromic reactivity. The dithiazolethene **BN** exhibits an obvious gated reactivity, photochromic activity of which can be manipulated by a reversible process between BF$_3$·Et$_2$O and Et$_3$N. Meanwhile, the photocyclization quantum yield of **BN** is higher than the corresponding dithienylethenes **BT** due to the existing weak CH···N hydrogen bonds, as demonstrated by X-ray crystallography.

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Notes and references

‡ Crystallographic data for **BN**: $C_{28}H_{20}N_2O_2S_3$, M = 512.64, monoclinic, space group $P2_1/n$, a = 14.2273(13) Å, b = 13.0726(12) Å, c = 14.5059(13) Å, α = 90°, β = 109.866(2)°, γ = 90°, V = 2537.4(4) Å^3, Z = 4, ρ_{calcd} = 1.342 gcm^{-3}, T = 296(2)K, 13187 reflections measured, 5638 unique (R_{int} = 0.0202) which were used in all calculations. The final w$R(F_2)$ was 0.1724 (all data). R = 0.0450, R_w = 0.1420, GOF = 1.088. CCDC 843533 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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