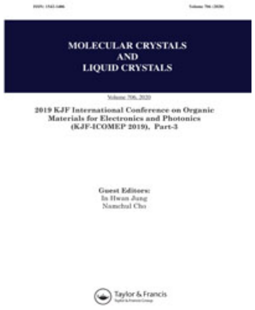

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An "electron lock" toward the photochromic activity of phenylacetylene appended bisthienylethene

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ABSTRACT

Photochromic core structure of BTEs was configured in the design of **BT** (2,3-Bis(2,5-dimethylthiophen)−5-phenylethynylthiophene) and **NT** (2,3-Bis(2,5-dimethylthiophen)−5-(4-methoxyphenyl)−1,3-butadiene-1,1,4,4-tetracarbonitrile). **BT** exhibits regular photochromic behavior in hexane when excited with UV (254 nm) and visible light (>400 nm). The solution can be cycled between pink colors and colorless. Correspondingly, **NT**, with a more electron-withdrawing group attached, the photochromic reactivity was totally quenched. It is the lowered electron density on reactive carbon atoms in LUMO that influence the photochromism, which is one of the key elements to photochromism. Apart from the distance between reactive atoms, electron distribution on reactive atoms is another important key to the configuration of photochromic dyes.

KEYWORDS
Electron distribution; LUMO; photochromism; photochromic reactivity; tetracarbonitrile

1. Introduction

Switching function in a molecule scale is of great importance in the next generation of information storage and corresponding smart logic application based on processing big data. Therefore, establishing a reversible switch in chemistry became the new task of chemists and physicists. Switching molecules can be defined as a transformer that can reversibly change between two distinct configurations when exerting external stimuli, such as photo, electricity, magnetism, heat, etc. This transformation associated with a series of physical properties changes, which can be developed in material science and structural biological technologies [1–8]. Basically, this switching character is based on the reversible change in their electronic and topological characteristics. The computer disk currently used is established inorganic/organic switching elements with dynamic components in optoelectronic devices [3,9]. It is obvious that photos are the appealing one among various stimuli ways due to fast response time and nondestructive

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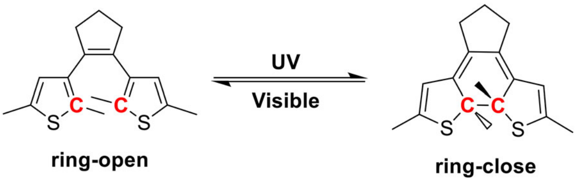


Scheme 1. Open and closed forms of typical bisthienylethene structure. The reactive carbon atoms are in red.

processing. Photochromism is of photo-controllable switching molecule science, referring to as interconverting molecule between two isomers. When stimulated, there exist unique absorption spectra. Hidden behind this toggle is luminescence, reactivity, chirality, etc. [10–20]. Photochromic elements, together with other functions, have been integrated to achieve photo-controlled multi-color modulation [21–23]. One stimulus induced multi-response is indispensable for the development of smart-logic systems.

It has been established several switching building blocks and the most promising one is bisthienylethenes (BTE) [24]. The most fascinating property is a highly bistable state [3]. The skeleton of BTE possesses the hexatriene framework, with which a reversible conrotatory 6π-cyclization reaction could have occurred upon photo stimuli (Scheme 1) [25–27]. Based on the hexatriene framework, variation of multi-functionalized BTEs were configured and documented. The bridge ring of BTE has been engineered as perfluorocyclopentene, maleic anhydride, maleic imide, etc. However, higher degree of aromaticity of the central unit could lead to unstable of photo-cyclization isomer [28]. In this contribution, introduction of electron withdrawing group to the central unit of BTE significantly change the electron distribution and suppression of the photochromism.

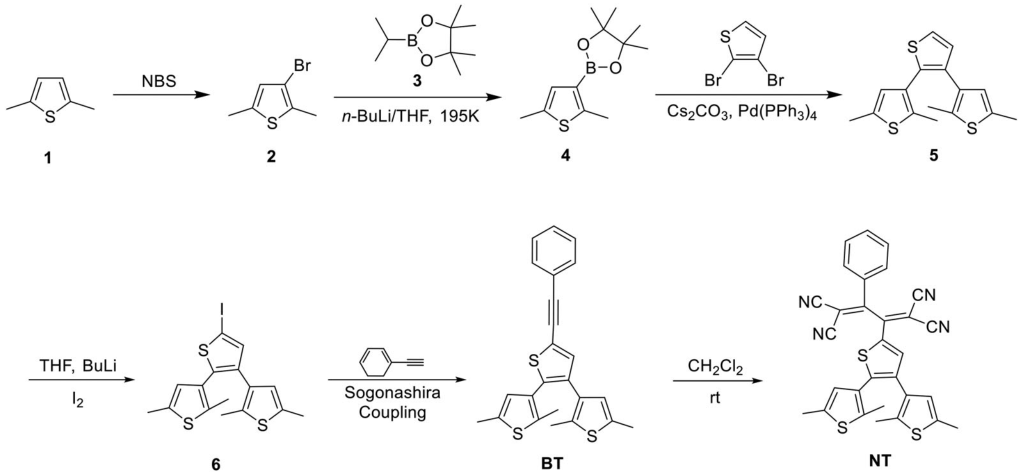
2. Experiment

2.1. General procedures and materials

The solvents used in the reaction were carefully dried according to the standard procedure and stored over 4 Å molecular sieve. All the reagent-grade chemicals were purchased from Sigma-Aldrich CO. LLC. (South Korea) and used without further purification. All synthesized compounds were routinely characterized by TLC and NMR. TLC was performed on aluminum-backed silica gel plates (Merck DC. Alufolien Kieselgel 60 F254).

2.2. NMR spectroscopy and high resolution mass spectra (HRMS)

Nuclear magnetic resonance (NMR) spectra were recorded on a Brucker AM-400 spectrometer operating at frequencies of 400 MHz for proton in $CDCl_3$. Proton chemical shifts (δ) are relative to tetramethylsilane (TMS, $\delta = 0$) as internal standard and expressed in parts per million. Spin multiplicities are given as *s* (singlet), *d* (doublet), *t* (triplet), and *m* (multiplet) as well as *b* (broad). Coupling constants (*J*) are given in Hertz. The mass spectra measured on a LC-MS (Waters UPLC-TQD) mass spectrometer. High resolution mass spectra (HRMS) were measured on a Brucker micrOTOF II Focus instrument.



Scheme 2. The synthesis of **BT** and **NT**.

2.3. UV-Vis

The absorption spectra were measured with a PERSEE TU-1900 spectrophotometer. The solvents used in photochemical measurement were spectroscopic grade and were purified by distillation. The stock solution of compounds (2×10^{-3} M) was prepared and a fixed amount of these concentrated solutions were added to each experimental solution. All the experiments were done repeatedly, and reproducible results were obtained. Prior to the spectroscopic measurements, solutions were deoxygenated by bubbling nitrogen through them.

3. Synthesis

Scheme 2 shows the synthesis of 2,3-Bis(2,5-dimethylthiophen)−5-(4-phenyl)−1,3-butadiene-1,1,4,4-tetra-carbonitrile (**NT**). 2,5-dimethylthiophene, a commercially available reagent, was first brominated by NBS (*N*-bromosuccinimide). Then, it was treated with *n*-BuLi and 2-isopropyl- 4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**3**), yielding 2-(2,5-dimethylthiophen-3-yl)−4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**4**). Photochromic skeleton, 2,3-bis(2,5-dimethyl-thiophen-3- yl)thiophene (**5**), was obtained by Suzuki coupling method between **4** and 2,3-dibromothiophene [29]. Subsequently, **five** was iodinated and coupled with phenylacetylene under Sogonashira condition, yielding **BT**. Finally, **BT** mixes with tetracyanoethylene at room temperature yielding **NT**. Overall, the configuration of the core structure of BTE is constituted by three thiophene ring, which is different from the conventional BTE unit with electron withdrawing bridging unit, such as perfluorocyclopentene, maleic anhydride, maleic imide [24]. The coupling between dibromo heterocycle and corresponding thiophene derivatives by Suzuki other coupling strategies can be used to configure the core structure unit for desired photochromism [30–33].

3.1. 2,3-Bis(2,5-dimethylthiophen)-5-phenylethynylthiophene (BT))

In a flamed dried Schlenk flask, 2,3-Bis(2,5-dimethylthiophen)−5-henylethynylthiophene (200 mg, 0.48 mmol), iodide copper (9 mg), $Pd(PPh_3)_4$ (28 mg) were mixed with triethylamine (5 mL) under nitrogen atmosphere. After stirring for 30 min, phenylacetylene (48 mg, 0.48 mmol) was added and stirred for another 12 h. Then the mixture was poured into water (30 mL) and extracted with dichloromethane (3 × 20 mL). The organic phase was combined and dried over anhydrous $MgSO_4$. After the solvent was evaporated in vacuum, the residue was loaded to the column. Column separation (silica gel 200–300 mesh, hexane) produced 150 mg deep red solid (77%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.55 (m, 2H), 7.37 (m, 3H), 7.22 (s, 1H), 6.49 (s, 1H), 6.42 (s, 1H), 2.38 (s, 6H), 2.07 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 135.5, 135.7, 135.4, 134.9, 134.5, 134.4, 133.2, 132.5, 131.4, 129.9, 128.4, 127.4, 127.0, 123.0, 121.1, 93.6, 82.7, 15.2, 14.0. EI$^+$/MS m/z 427 $[M]^+$. HRMS calcd for $C_{24}H_{20}S_3$ 404.0727, found 427.0692 $[M+Na]^+$.

3.2. 2,3-Bis(2,5-dimethylthiophen)-5-(4-phenyl)-1,3-butadiene- 1,1,4,4-tetracarbonitrile (NT)

In a Schlenk tube with inner gas, tetracarbonitrile (32 mg, 0.25 mmol) and **BT** (100 mg, 0.25 mmol) dissolve in dichloromethane 20 mL. The mixture is stirred at room temperature for 48 h. And then it is poured into water (30 mL). After the organic phase is separated and dried over $MgSO_4$, it is condensed and loaded on the column. Purification is on silica gel (200–300 mesh) with dichloromethane:hexane (2:1) as the eluent, yielding 53 mg deep red solid (40%).

^{1}H NMR (400 MHz, $CDCl_3$) δ 7.8 (s, 3H), 7.69 (s, 1H), 7.58 (s, 2H), 6.49 (s, 1H), 6.35 (s, 1H), 2.37 (s, 6H), 2.07 (s, 6H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 207.1, 166.6, 156.7, 149.1, 139.8, 138.2, 137.4, 137.3, 136.8, 134.8, 131.5, 131.1, 130.3, 130.1, 129.4, 128.2, 126.7, 126.2, 112.9, 112.0, 111.6, 111.0, 87.7, 77.8, 31.0, 29.7, 15.1, 14.4, 13.8. EI+/MS m/z 555 $[M]^+$. HRMS calcd for $C_{30}H_{20}N_4S_3$ 532.0850, found 555.0804 $[M+Na]^+$.

4. Result and discussion

The molecular structure of **BT** possesses the hexatriene skeleton, which is the typical photochromic structure character of BTEs. With phenylacetylene appended at the 5-position of **BT**, the π-conjugate system is expanded. Both the bridging thiophene group and the triple bond are electron-rich units. This is a benefit to gather the electron density to the photochromic hexatriene part, which is significant to the photochromic reactivity. Partial NMR spectra of **BT** and **NT** are shown in Fig. 1. With or without the addition of tetracarbonitrile to the triple bond, the core structural unit was identical to each other. However, the typical proton signal in NMR is the proton at the β-position of two sides thiophen rings, which does not overlap with the proton of the aromatic benzene ring in the downfield. For **BT**, two single peaks can be found at 6.49 and 6.42 ppm, which can be assigned to the β-photos of side thiophene ring. The two peaks were separated by 0.07 ppm When tetracarbonitrile added, the electron-withdrawing character of carbonitrile significantly shifted the electron distribution of molecular skeleton, then the magnetic field. Therefore, in **NT**, the β-proton signals of two side thiophene rings (6.49 and 6.35 ppm) were still single peaks, and the separation between the two photons was enlarged to 0.14 ppm. Simultaneously, the proton signals of benzene rings turned to be more complex due to the polarized magnetic field.

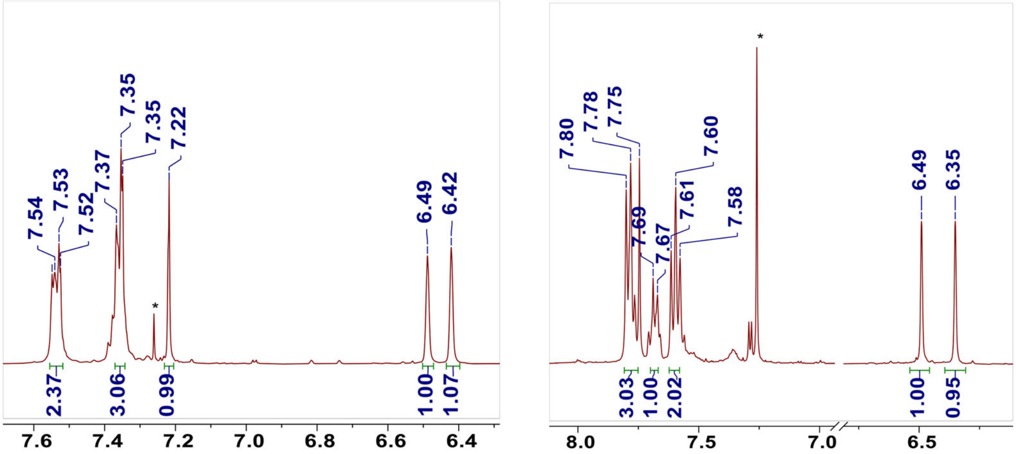


Figure 1. Partial NMR spectra of **BT** (left) and **NT** (right) in the downfield.

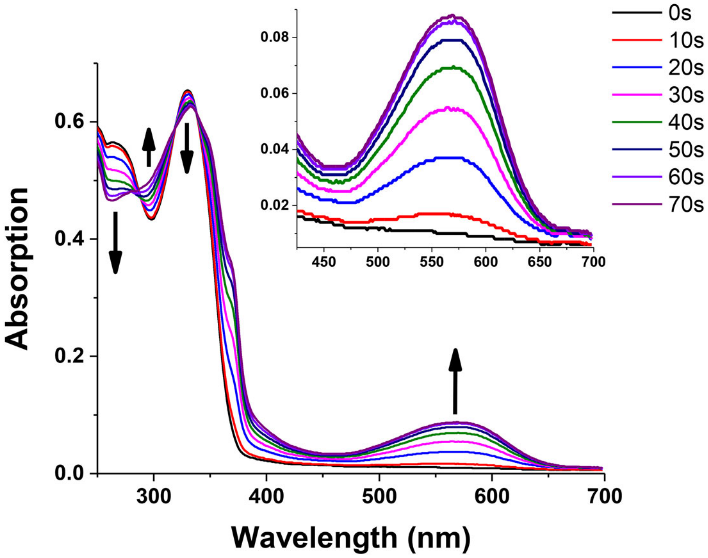


Figure 2. Absorption changes of **BT** in hexane (1×10^{-5} M).

The photochromic behavior of **BT** is investigated in a different organic medium, including hexane, dichloromethane, tetrahydrofuran (THF), and acetonitrile, under irradiation of 254 nm light. Different polarity environment must lead to different absorption profiles. However, the photochromic wavelength at a longer wavelength side is same as each other with the peak value around 570 nm. With thiophene and phenyl rings constituting the whole molecular skeleton, there must be evenly electron density distribution. Therefore, hexane, the non-polar solvent, would be the best choice for photochromic behavior investigation. Fig. 2 shows the spectral change in hexane when excited with UV light. In hexane, there exists strong absorption before 325 nm. Therefore, hand held 254 nm UV lamp is well-matched to the excitation requirement of **BT**. Upon 254 nm irradiation UV light irradiation, a gradual absorption band increase can be found with the band center around 570 nm in hexane, corresponding to the π-π^*

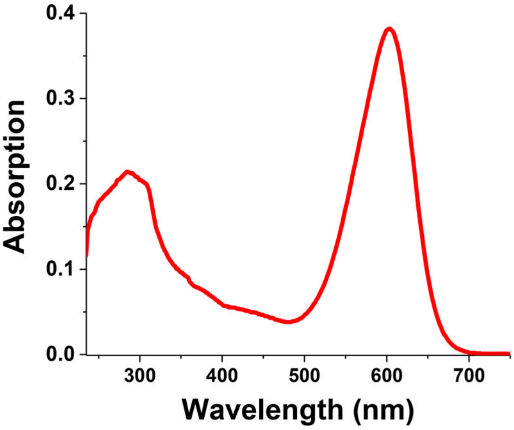
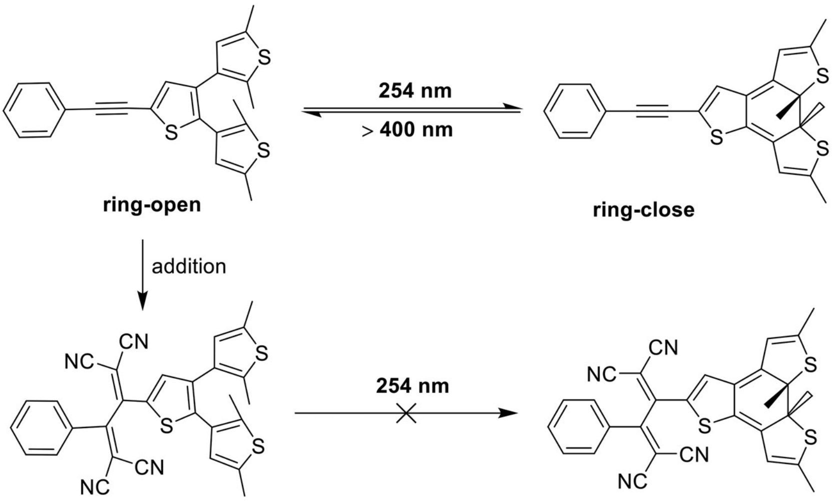


Figure 3. Absorption of **NT** in chloroform. (1×10^{-5} M).

transition. Meanwhile, a decrease at 265, 330 nm is concomitant with the increase at 570 nm. When excited with 254 nm, the absorption spectra were recorded every 10 s. Generally, the absorption band contributed by ring-open form is at UV region and extended to visible region once the ring-closed form generated due to the delocalization of π-electrons to cyclizing thiophene rings. 570 nm' absorption turns **BT**'s hexane solution to a pink color. Well-defined isosbestic points can be determined to be 285 ($\varepsilon = 4.8 \times 104$ M^{-1}cm^{-1}), 318 ($\varepsilon = 5.9 \times 104$ M^{-1}cm^{-1}), and 338 nm ($\varepsilon = 6.1 \times 104$ M^{-1}cm^{-1}). It indicates that the photochromic transformation only occurs between two components in the photochromic reaction. Contrary to the above photochromic process, the pink solution can be decolorized by irradiation with visible light ($\geq$400 nm, LED lamp) and the band around 570 nm decreases gradually until its disappearance totally. Simultaneously, the pink solution was decolored to totally transparent. And this coloration/decoloration can be cycled by UV/Vis excitation cycle. The conversion efficiency (α_{ps}) between ring-open and ring-closed forms at the photo-stationary state, induced by UV light irradiation, is estimated to be 0.37, which can be calculated following the equation based on the absorbance of the two forms [29]. According to the already established molecular configuration of BTEs, the attaching of phenylacetylene does not quench the photochromic reactivity or shift the photochromic wavelength. At least, the electron distribution around the reactive carbon of the two side thiophene ring was not lowered, which is a key requirement for photochromic activity [34].

It is well-known that a carbon–carbon triple bond can be added with tetracarbonitrile efficiently, which can introduce an electron-withdrawing group and significant change of the electron distribution. **BT** mixed with tetracarbonitrile at room temperature and yielded **NT** efficiently. Simply structural analysis shows that the addition of tetracarbonitrile does not alter the photochromic core. However, the photochromic reactivity of **NT** was totally quenched. Fig. 3 shows the absorption of **NT** in chloroform. A new strong absorption peak was observed at 603 nm ($\varepsilon = 3.8 \times 104$ M^{-1}cm^{-1}) and a shorter wavelength band 230–400 nm. No matter how to irradiate the **NT** solution or alter the solvent polarity, there is no absorption change that happened as that of **BT** in hexane. Based on the analysis of the absorption of **BT** and **NT**, we found that there is a significant overlap of the photochromic wavelength of **BT** (475–650 nm) and the strong



Scheme 3. Photochromic reaction of **BT** and **NT**.

absorption band (500–700 nm) of **NT**. When **NT** was excited with UV light, there would be an efficient energy transfer to the lower energy band (603 nm), which quenched the photochromic activity of **NT**. We initially believed that the switch core would be independent of the substitution to it. However, whether the molecules exhibit a positive photochromic response to UV irradiation is closely related to the electronic structure of the whole molecules. In **NT**, the tetracarbonitrile is a newly introduced fluorophore. The two photo-responsive regions will effectively compete for the lowest energy transitions. The absorption around 603 nm outweighs the photochromic wavelength of the switching unit around 570 nm. In fact, the photochromic activity of **NT** is suppressed completely. By comparison of the structural variation of **BT** and **NT**, the addition of tetracarbonitrile induce a significant change to the photochromic activity. The photochromic activity of the switching unit was suppressed by an "electron lock."

The suppressed photochromic activity is considered to be the electron distribution induced by the tetracarbonitrile. It is predictable that the electron-withdrawing power of tetracarbonitrile moves the electron density away from the side thiophene rings. To get further insight into the electronic properties of **BT** and **NT**, we undertake a comprehensive computational investigation using Materials Studio. The ground-state energy-minimized structures are calculated using DFT and DND/B3LYP basis set [35,36]. The photochromic reaction upon alternated irradiation of 254/>400 nm light is shown in Scheme 3. Theoretically, there exist two conformations for the hexatriene structure with the two thiophene rings in mirror symmetry (parallel conformation) and in C_2 symmetry (unparallel conformation). Only when the two side thiophene rings in antiparallel conformations, the photochromic reaction could occur. Once the ring-closed, a new absorption band in visible region appeared. One of the key requirements to the photochromic activity is the distance between reactive carbon atoms, which has been determined to be 4.2 Å [37–39]. However, this distance is not the unique determinate factor for the photochromic reactivity. The electron distribution, topology of the molecular orbitals, must be considered. Fig. 4 shows the HOMO and LUMO distribution of **BT** and **NT**. For **BT**, the LUMO distribution gathers around one of the reactive carbon atoms. It

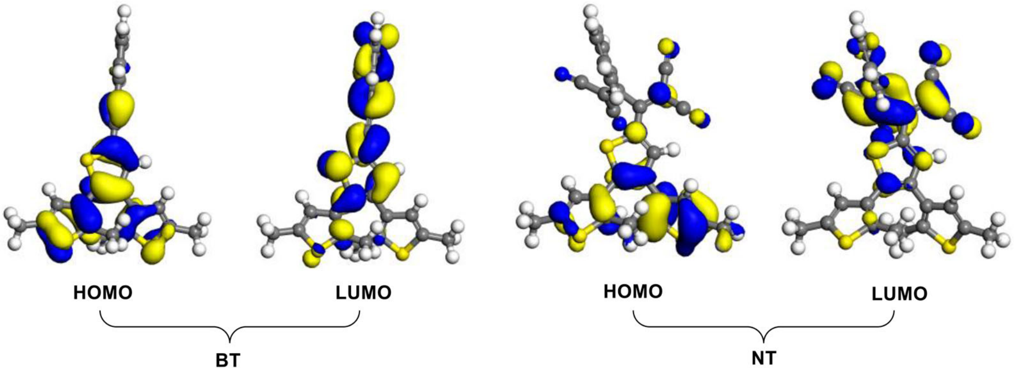


Figure 4. HOMO and LUMO distribution of **BT** and **NT** in the ring-open forms.

indicates that the electron transition from HOMO to LUMO involves the reactive carbon atoms. The photochromic photocyclization reaction must be closely related with the electron redistribution when excited with suitable light. Indeed, the photocyclization of **BT** occurs smoothly upon excitation with 254 nm light, as demonstrated above. When tetracarbonitrile was added to the triple bond, the electron density of **NT** in LUMO will move away from the reactive carbon atoms. The significantly lower level of electron density around the reactive carbon atoms leads to completely quenched photochromic reactivity. Without the strong electron-withdrawing power toward the electron around reaction atoms, **BT** maintains its photoactivity in photochromism.

5. Conclusions

In summary, photochromic core skeleton inserted molecules **BT** and **NT** are synthesized and characterized by NMR and MS techniques. The photochromic behavior for both of them is investigated. In hexane, **BT** exhibit regular photochromic properties with the photochromic wavelength extending to 570 nm and corresponding pink color upon irradiation with 254 nm light. Irradiated with visible light (>400 nm), the solution can be decolorized and reverted to the originate state. On the contrary, **NT**, with tetracarbonitrile introduction, the photochromism is quenched. HOMO/LUMO distribution analysis indicates that the lower electron density on the reactive carbon atom can completely suppress the photoactive of photochromism. It is another key factor need to be considered in the configuration of BTEs.

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