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Article

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All-Visible-Light Activated Dithienylethenes Induced by Intramolecular Proton Transfer

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KEYWORDS Photochromism, Dithienylethene, All-visible-light photoswitching, Intramolecular proton transfer

ABSTRACT: The fast light-responsive dithienylethenes (DTEs) are one of the most attractive photochromic families due to their excellent thermal irreversibility and fatigue resistance. However, all-visible-light induced DTE system still remains challenging since most of them require the harmful high-energy ultraviolet light to trigger their photocyclization reaction. Here, we have for the first time borrowed a specific intramolecular proton transfer (IPT) process, and rationally designed a series of all-visible-light driven DTEs. Incorporating the IPT-functional group to DTE unit gives rise to an extra absorption band with a distinct redshift, which enables the photocyclization of DTEs under stimuli of visible light at 450 nm, as well as ensuring the desirable photoswitching efficiency. The isomerization from OH-form to NH-form induced by IPT can decrease the energy gap for excitation and photocyclization, thereby affording the all-visible-light triggered photochromic performance, which can not only work well in polar solvent system, but also show its effectiveness in polymeric gel systems. In this regard, we can provide a general and reliable platform to construct all-visible-light driven DTEs with excellent reversible photoswitching and broad applicability, especially with avoiding the use of harmful ultraviolet light to induce their photocyclization.

INTRODUCTION

Molecular photoswitches[1-3] have drawn much attention due to their excellent reversible photoresponse performance in optic-electronic devices,[4,5] liquid crystal,[6] molecular motor[7,8] and other light-regulated functional materials.[9-15] Among them, dithienylethene (DTE) derivatives have been widely investigated for their excellent thermal stability, rapid photoresponse and robust fatigue resistance.[16-21] In general, ultraviolet (UV) light is necessary to switch DTEs from open form to close form, while the reverse process relies on the visible light.[16] However, high-energy UV light irradiation may generate undesired by-products in photoreactions[18] and would be detrimental to biological tissues, severely restricting to burgeoning bio-applications, such as super-resolution bioimaging,[22,23] bioactivity controls[24] and photopharmacology[25,26]. Therefore, all-visible-light driven photoswitchable systems[27-31] are urgently demanded.

For DTE derivatives, much efforts have been devoted to induce absorption in visible region,[32-35] including the uncommon inverse type of DTE with 2-position of heterorings connected to the ethene bridge.[36,37] For the normal type DTE, in which 3-position of thiophene is tethered with the ethene backbone, extending π-conjugation through the side thiophene rings was broadly utilized to shift the excitation wavelength to visible region.[38-41] However, most of these systems displayed extremely low photo reaction quantum yields ($\Phi_{\text{o-c}} < 1\%$) because the additional π-systems could decrease the contribution of the excited singlet state to the photo-responsive central hexatriene unit.[37] As an alternative approach, Yam and coworkers put forward the visible light excitation via modification of the central ethene bridge (Figure 1a, right).[42,43] Nevertheless, the photochromic behavior of these systems was hampered by the interaction between the additional π-conjugation and the photoswitchable backbone. Recent work has clearly demonstrated that the mismatched combination would lead to complete loss of photochromic activity,[44] thus making it rather difficult to predict the photo-responsive performance of the resulting DTE via ethene bridge modification. As a consequence, it is still challenging to obtain a general all-visible-light DTE platform, and sometimes calculations is necessary to find out a suitable structure.[32] Therefore, efficient and reliable strategies for building up all-visible-light activated DTEs still remain to be unexplored.

Intramolecular proton transfer (IPT) is an important feature of hydrogen bonded systems,[45,46] which is crucial for the thermo- and solvatochromism of salicylidene Schiff base and derivatives.[47,48] The IPT process in these systems has been well investigated as follows: the equilibrium exists between two tautomers, the one with hydrogen bond proton covalently bonded to the oxygen (OH-form) and the other with the proton bonded to the nitrogen (NH-form, Figure 1b).[49] It is of great concern that the two tautomers possess different electronic absorption properties, the NH-form absorbs at longer wavelength.[49-51] Herein we have for the first time exploited the IPT characteristic, and designed a series of novel DTEs by

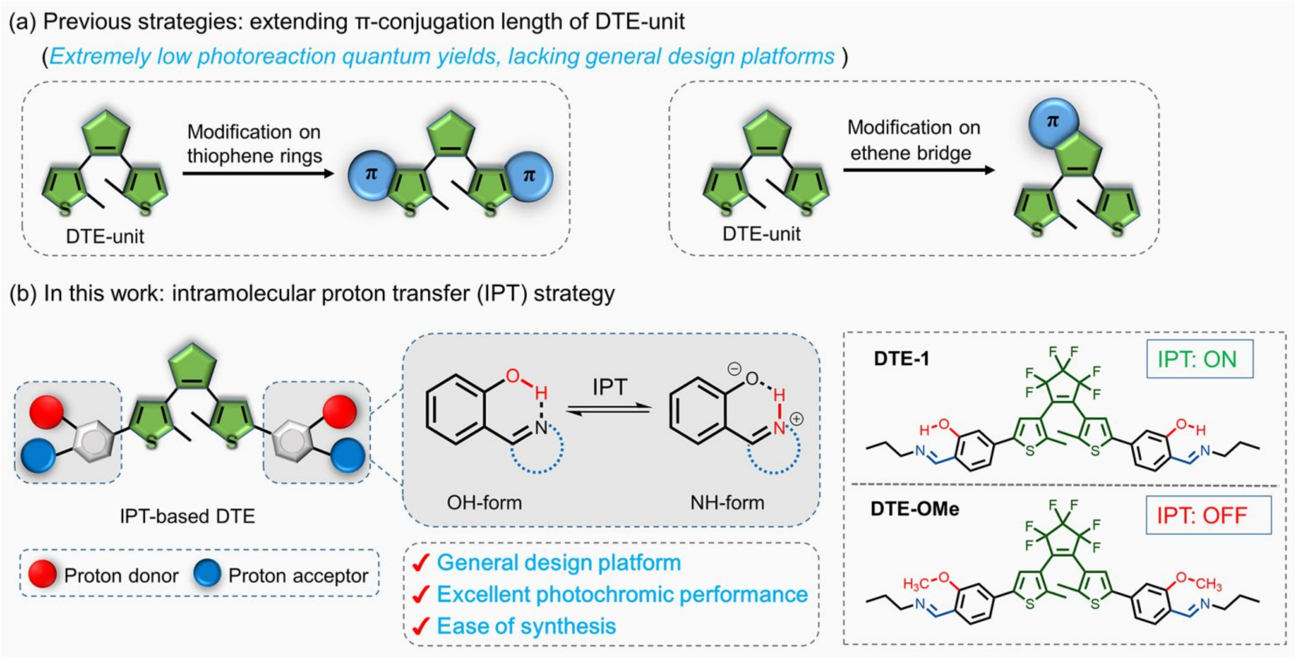

Figure 1. Strategies for designing all-visible-light activated DTEs. (a) Extending π-conjugation on the thiophene ring or the ethene bridge of DTE unit. (b) General platform exploiting IPT process to induce all-visible-light response: schematic illustration of IPT-based DTE, target system DTE-1 as well as reference system DTE-OMe.

incorporating IPT-functional groups into DTE unit (Figure 1b). With the typical IPT process in targeted DTEs, all-visible-light photochromic performance has successfully realized with the following extraordinary features: i) exhibiting an additional red-shifted absorption band induced by the specific IPT process, ii) achieving an unprecedented photocyclization of DTE with a visible light of 450 nm, iii) providing a reliable platform to build up all-visible-light activated DTEs, and iv) being widely applicable in polar/protic solvents and polymeric gel systems.

RESULTS AND DISCUSSION

Rational Design of Introducing IPT Characteristic into DTE. To borrow the IPT process in salicylidene Schiff base, we designed a specific system DTE-1 bearing two functional units: the photoswitching DTE core and the salicylidene-propylamine moiety attached to the thiophene rings. The target DTE-1 was readily synthesized by condensation of propylamine with the aldehyde intermediate which was obtained through Suzuki-Miyaura reaction of a dibromo-substituted DTE and salicylaldehyde borate. DTE-OMe was also prepared as reference compound via the similar synthetic procedures (Figure 1b and Scheme S1 in the Supporting Information), the introduction of methoxy group into the phenol functionality would inhibit IPT characteristic. All target products and intermediates have been characterized by ^{1}H and ^{13}C NMR spectra as well as HRMS spectra.

Endowing a Visible Absorption Band with Tuning IPT Equilibrium. With DTE-1 and DTE-OMe in hand, we firstly compared the absorption spectra of their open form in acetonitrile solution. As depicted in Figure 2a, both DTE-1 and DTE-OMe exhibited an obvious absorption band in UV region with the λ_{max} located at 325 and 337 nm, respectively, while an extra absorption band in 400-475 nm visible region was found for DTE-1. To test their essential photochromic behavior, DTE-1 and DTE-OMe in solution were irradiated with 365 nm UV light, a new low-energy absorption band in 500-700 nm appeared along with the decreasing absorbance at UV region. These features are consistent with typical photochromic performance of DTEs switching from open form to close form.[16,19] The preliminary test reveals that the DTE-1 and DTE-OMe possess similar electronic absorption spectra and photochromic peformance due to their similar chemical structures. Thus we infer the additional absorption band in visible light region of 400-475 nm for open form DTE-1 may be associated with the IPT process.

It has been well recognized that solvent effect is very crucial to the IPT equilibrium.[52-54] Thus we further investigated the absorption spectra of DTE-OMe and DTE-1 in different aprotic and protic solvents (Figure 2b-2d). Interestingly, when increasing the solvent polarity, a new absorption band at 420 nm became emerged and gradually enhanced for DTE-1. Moreover, this absorption band became quite noticeable in protic solvents such as methanol. In contrast, no additional absorption band can be observed for methyl-protected DTE-OMe upon solvent change. The absorption spectra of DTE-1 are closely related with the combined interaction of solvent polarization and protonation. Given the fact that the NH-form in IPT equilibrium system exhibits longer wavelength absorption than OH-form,[49-51] the emerged absorption band in visible region was attributed to the NH-form of DTE-1 generated by the IPT process: the acidic proton shift from oxygen to nitrogen (from OH-form to NH-form, Figure 2e). The NH-form can be stabilized with increase of the solvent polarity

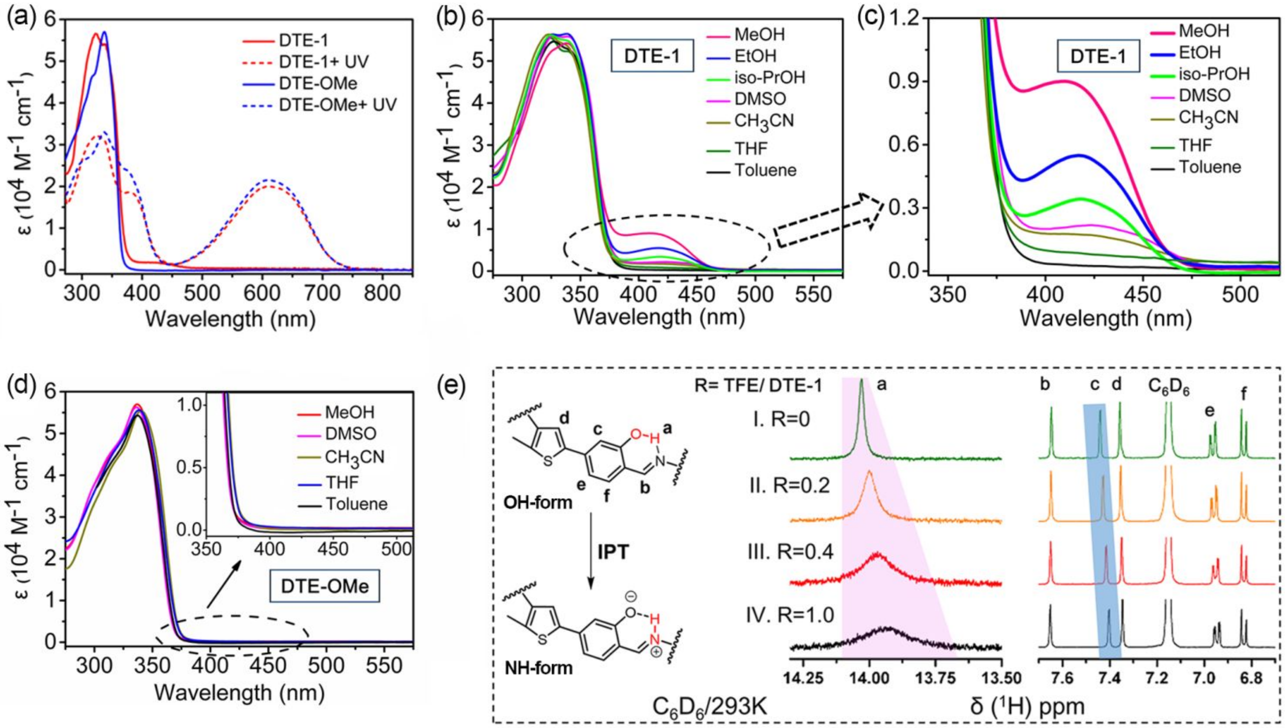

Figure 2. Effect of IPT unit on absorption and ^{1}H NMR spectra. (a) Absorption spectra of open-form DTE-1 and DTE-OMe as well as their photostationary state spectra irradiated with 365 nm light in acetonitrile solution; (b, c and d) Absorption spectra of open-form DTE-1 and DTE-OMe in different solvents (10 μM, 293 K); (e) Partial ^{1}H NMR (400 MHz) spectra of DTE-1 in benzene-d_6 at 293 K in the presence of trifluoroethanol (TFE): R stands for the molar ratio of TFE to DTE-1. The chemical structure shows the attribution of hydrogen atoms during the IPT process in DTE-1.

or proton donating ability,[49] thereby increasing its contribution to the IPT equilibrium (Table S1 in Supporting information).

^{1}H NMR study was performed to confirm the IPT-induced transformation from OH-form to NH-form. The increasing of the proton donating ability of the NMR solvent was achieved through gradual addition of trifluoroethanol (TFE), which is a polar solvent with strong proton donating ability, into the benzene-d_6 solution of DTE-1. As shown in Figure 2e, upon increasing the molar ratio of TFE/DTE-1 from 0 to 1, the signal of hydroxyl proton showed upfield along with the peak shape turning from sharp to broad, and the signal of hydrogen adjacent to the hydroxyl exhibited upfield shift synchronously. These changes can be attributed to IPT process and formation of the NH-form of DTE-1, along with the proton transferring from oxygen to nitrogen, which strengthens the interaction with nitrogen atom and changes the chemical environment. The results were in exact accordance with the typical feature of IPT process,[47,54,55] indicative of the possible IPT channel in DTE-1.

All-Visible-Light Driven Photochromic Behavior of IPT-Based DTE. The IPT induced absorption band emerged in visible region inspired us to explore the visible light photochromic behavior of DTE-1. In dark condition, we irradiated the open form of DTE-1 in acetonitrile solution with 450 nm blue light, and recorded its absorption spectra at every 30 s until the spectra did not changed. After the irradiation, the color turned from pale yellow to blue, a broad absorption band at 500-700 nm became grown, and the absorption peak at 325 nm became decreased, along with a clear isosbestic point at 360 nm (Figure 3a). Interestingly, this photochromic behavior is similar to that of 365 nm UV light driven as shown above. To exclude the possibility that this absorption spectra change was caused by the *trans-cis* isomerization of imine bond,[56] the pure close form DTE-1c was synthesized (Scheme S2). As shown in Figure 3a, the absorption spectra of DTE-1 at photostationary state (PSS) was in accordance with its pure close form, demonstraing the formation of DTE-1c via the visible light activated photocyclization. ^{1}H NMR studies were also performed and confirmed this result (Figure S22-S23). The absorption spectra of pure DTE-1c in different solvents were depicted in Figure S8, showing identical IPT characteristic as open form DTE-1 that the absorption band at around 420 nm increases upon solvent polarity or proton donating ability increasing. Irradiating with 600 nm light can induce the photocycloreversion of DTE-1c (Figure S9). These results turn out an unprecedented pathway for switching IPT-based DTE-1 with all visible light (Figure 3b): with the IPT progress generated in open form DTE-1, the proton-transferred NH-form absorbs the visible light and undergo photocyclization, then photocycloreversion of closed form can be induced by longer-wavelength visible light. Thus UV light can be replaced by visible light in this IPT-based DTE system. We further investigated this visible light photochromic behavior in more solvents. As summarized in Figure S6 and Table S3, DTE-1 can achieve photochromic behavior upon irradiation with 450 nm light in various solvents including less polar toluene. In contrast, the reference system DTE-OMe shows no visible light

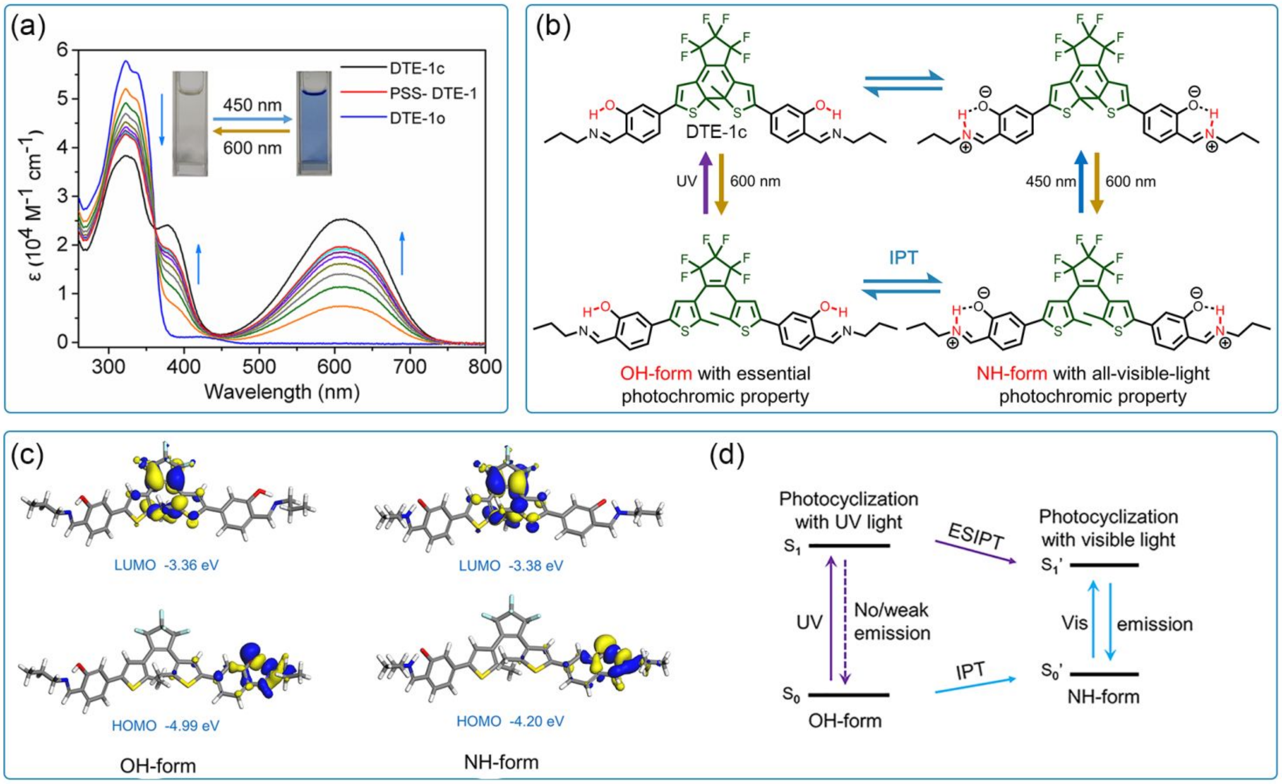

Figure 3. Visible light photochromic performance based on IPT strategy and related mechanism study. (a) Absorption spectra of DTE-1 upon irradiation with 450 nm blue light (10 μM in acetonitrile, 293 K, inset shows the color changes); (b) Related reactions of this all-visible-light photochromic DTE system conferred by IPT process; (c) Spatial plots of HOMOs and LUMOs as well as corresponding energy level of OH- and NH-form of open-form DTE-1; (d) Schematic description of the IPT strategy for visible-light-actived DTE (blue arrow) and the ESIPT pathway for fluorescence emission (violet arrow).

photochromic behavior at all (Figure S10). These results turn the IPT-based DTE-1 to be a novel all-visible-light induced photoswitch. There is also an interesting phenomenon that DTE-1 exhibits obvious fluorescence emission while DTE-OMe has no emission at all (Figure S15), which may result from the IPT process in DTE-1.

To delineate the nature of the ground and excited states in OH- and NH-forms of the open form DTE-1, the calculations with quantum density functional theory (DFT) were performed. The HOMO and LUMO profiles for OH- and NH-forms of DTE-1 were shown in Figure 3c. The HOMOs of OH-form mainly localize at the peripheral pendant while the LUMOs localize at the thiophene and perfluorocyclopentene bridge group. For IPT generated NH-form, the profiles of HOMOs and LUMOs closely resemble those of OH-form. Both the OH- and NH- form are suitable for the photocyclization reaction since the LUMOs distribute throughout the photo responsive central hexatriene part of DTE-1.[19,37] It is worth noting that the HOMO energy level increases by 0.79 eV upon transformation from OH-form to NH-form, which results in a narrower energy gap between LUMO and HOMO by 0.81 eV. Herein the decreased energy gap is exactly corresponding to the 95 nm red-shifted absorption band for the NH-form of DTE-1 (from 325 to 420 nm). And the energy difference between the HOMO of OH-form and NH-form is only 0.02 eV.

The DFT calculation results unambiguously support the IPT mechanism as depicted in Figure 3d: (i) the isomerization from OH-form to NH-form induced by IPT in ground state can decrease the energy gap for excitation and photocyclization, thereby affording the unusual all-visible-light triggered photochromic performance; and (ii) the fluorescence property of DTE-1 can also be attributed to IPT process (Figure S16-S17), including the OH-form excitation at 360 nm via the excited-state intramolecular proton-transfer (ESIPT, [57,58] violet arrow) and the IPT-induced NH-form excitation at 450 nm (blue arrow).

Exploring IPT-Based Structure as a General and Reliable Platform to Design All-Visible-Light Activated DTEs. In general, a molecular system can exhibit IPT characteristic when incorporating an intramolecular hydrogen bonding interaction between proton donor and proton acceptor. [59] We expect that the IPT-based structure in model DTE-1 could serve as a flexible platform to build up more all-visible-light activated DTEs. Therefore, we further developed DTE-2, DTE-3 and DTE-4, containing phenolic hydroxyl group as proton donor and various nitrogen-containing group as proton acceptor (Figure 4 and Scheme S3). It was found that, all DTE-2, DTE-3 and DTE-4 exhibit analogical absorption behaviors as DTE-1, showing an extra absorption band in visible region under the combined polarization and protonation effect of the solvent (Figure S11), indicating the formation of corresponding NH-forms. Their photochromic performance is very similarly as investigated with 450 nm visible light. As shown in Figure 4, a broad absorption band in the range of 500-800 nm grows gradually,

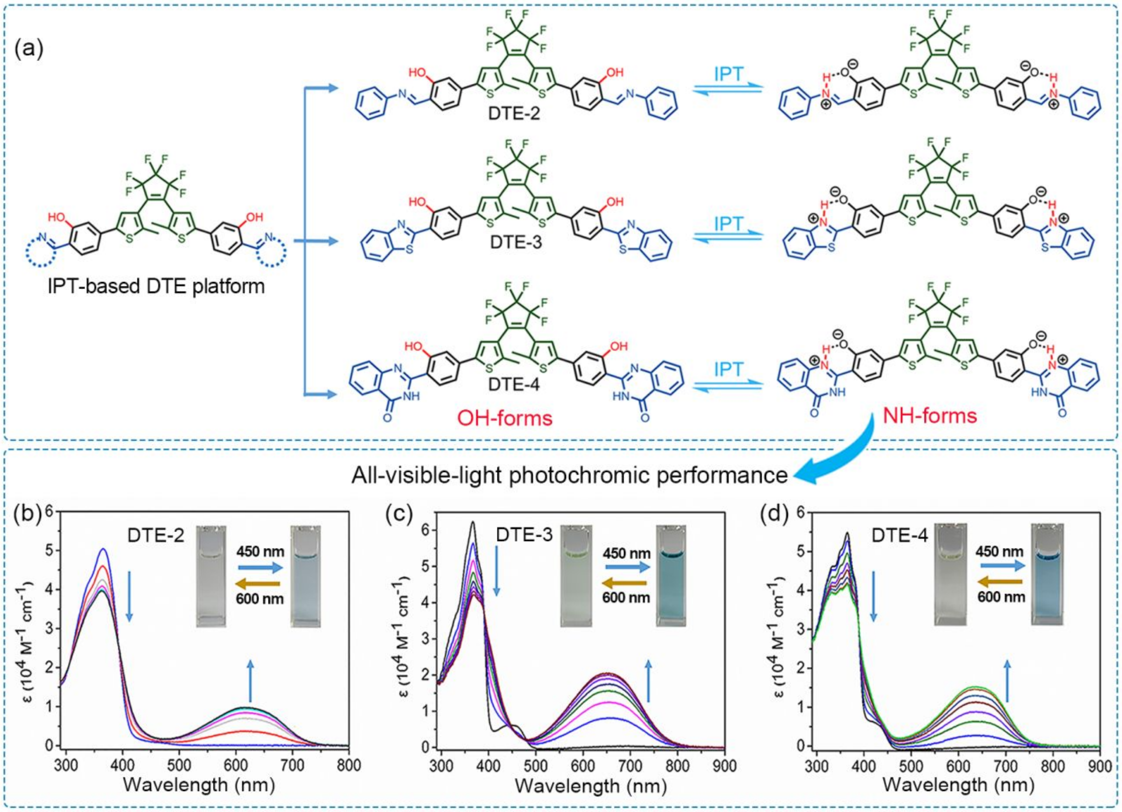

Figure 4. Platform for constructing all-visible-light activated DTEs based on IPT strategy. (a) Modified derivatives of DTE-2, DTE-3, DTE-4 and IPT process in target systems; (b, c and d) Absorption spectra changes of DTE-2, DTE-3 and DTE-4 with visible light excitation at 450 nm (solvent for DTE-2: MeOH, for DTE-3 and DTE-4: DMSO, 10 μM, 293 K).

accompanied by the absorption decreasing in UV region. There observed a clear isosbestic point, indicating the generation of the closed form of DTEs via photocyclization. Identically, photocycloreversion of these close forms can be triggered by irradiating with longer wavelength light (Figure S13). These IPT-based DTEs also show fluorescence emission property due to ESIPT mechanism, and the emission intensity can also be switched by 450 nm visible light irradiation (Figure S18-S20). DFT calculations for DTE-2, DTE-3 and DTE-4 manifest the same all-visible-light induced photochromism as the model compound DTE-1 (Figure S28-S30, and Table S6): the corresponding NH-form show a narrower HOMO-LUMO energy gap with respect to OH-form, and the LUMOs distributions also keep suitable for the photocyclization reaction. It is notable that the pH value has effect on the performance of photo-switching. In strong base condition, the phenol group (-OH) in salicylidene Schiff base turns to phenoate anion (-O$^-$), which terminates the IPT process. Also in acidic condition, the possible protonation of nitrogen can inhibit the IPT process to some extent, and thus resulting in the lower conversion than that in neutral condition (Supporting Information, Figure S14). Hence, we choose neutral condition during the whole investigation. These results demonstrate the all-visible-light photochromic performances induced by IPT is not an individual phenomenon, but provides a reliable strategy to activate photochromic DTEs, especially without requiring the harmful high-energy UV light to trigger their photocyclization.

Table 1. Photochromic Data of IPT-Based DTEs[a]

compound[b]	photocyclization		photocycloreversion		conversion at PSS
	λ_{irr}[nm]	$\Phi_{o\text{-}c}$[%][c]	λ_{irr}[nm]	$\Phi_{c\text{-}o}$[%][d]	$CR_{o\text{-}c}$[%]
DTE-1	365	46.5	600	7.3	95.6
	450	31.9			94.9
DTE-2	365	38.1	600	6.2	85.1
	450	25.0			61.6
DTE-3	365	37.5	600	7.5	89.8
	450	26.7			76.7
DTE-4	365	44.4	600	8.4	89.3
	450	28.4			68.9

[a]data collected at 293 K; [b]solvent for DTE 1-2: MeOH, for DTE 3-4: DMSO; [c]ferrioxalate was used as chemical actinometer; [d]aberchrome 670 was used as chemical actinometer.

Excellent Photoreaction Yields and Preferable Fatigue Resistance Achieved by IPT Strategy. In addition, the typical criteria for photochromic compounds, such as photoconversion ratios, quantum yields, fatigue resistance as well as the thermostability of ring-closed isomers[32] were also determinated to evaluate this IPT-based DTE platform. The photocyclization quantum yields ($\Phi_{o\text{-}c}$) at 450 nm was measured to be 31.9% for

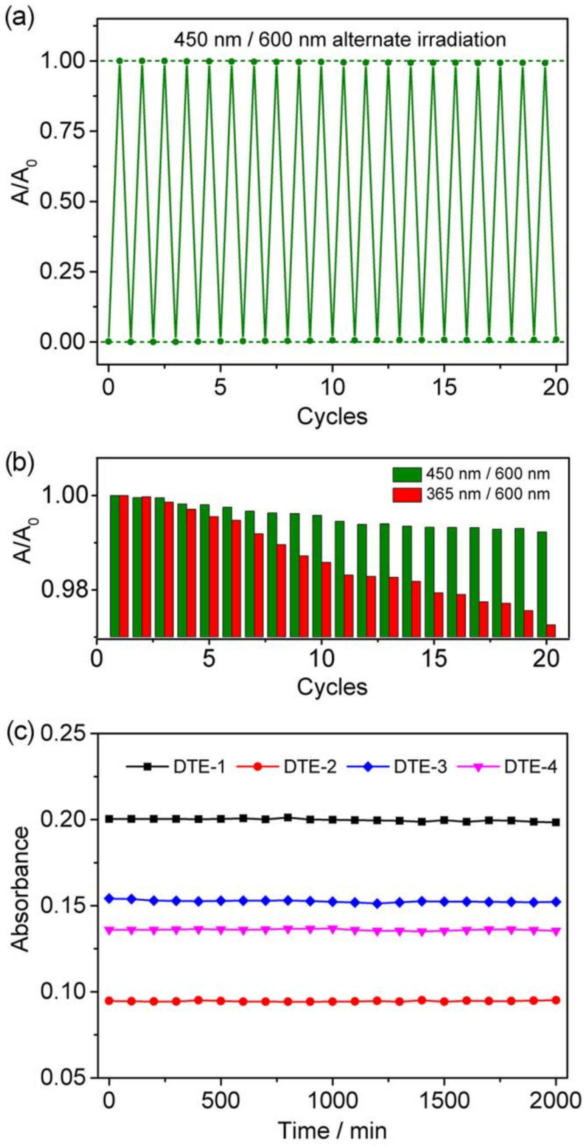

Figure 5. Preferable fatigue resistance realized by IPT strategy. (a) Absorption changes of DTE-3 at 635 nm upon alternate irradiation with 450 and 600 nm for 20 cycles; (b) Comparison of the fatigue resistance of DTE-3 under UV light excitation or visible light excitation (one cycle equal to irradiating with shorter-wavelength light for 10 s and then longer-wavelength light for 120 s); (c) Thermal decay plot of absorbance versus time for IPT-based DTEs monitored at λ_{max} at 293 K.

DTE-1, along with an execellent open-to-close conversion ratio (CR_{o-c}) as high as 94.9% (Table 1). For DTE-2, DTE-3 and DTE-4, desirable photoswitching efficiencies ($\Phi_{o-c} > 25\%$ and $CR_{o-c} > 60\%$) were also achieved upon irradiation with visible light at 450 nm. These photocyclization quantum yields measured at 450 nm are one third less than those at 365 nm UV light, and the photocycloreversion quantum yields are 6.2-8.4%. Moreover, the photocyclization quantum yield is independent with solvent although the photoconversion ratio shows a dependency on solvent (Table S3 and S4). These solid data prove the high efficiency of such IPT-based DTE platform.

The photochromic fatigue resistance was also checked under alternate irradiation at 450 and 600 nm, as shown in Figure 5a, IPT-based DTE-3 displays no apparent loss of photochromic activity over 20 cycles in DMSO solution. To further reveal the superiority of this visible light photochromic behavior, a contrast test was also performed with alternate irradiation at 365 and 600 nm. When anatomizing the two set of data in the histogram depicted in Figure 5b, an obvious tendency can be observed, that the reversible photoswitching under 450 nm excitation exhibits better photostability than UV light does, demonstrating the IPT pathway for all-visible-light photochromism could reduce side reactions and enhance the fatigue resistance of DTE systerms. In addition, all these IPT-based DTEs show excellent thermostability at room temperature, their absorption at PSS showed no decrease for over 2000 min (Figure 5c). Obviously, the outstanding photochromic performance renders the IPT-based DTE platform to be an efficient and reliable protocol for constructing the bottlenecked all-visible-light activated dithienylethene systems.

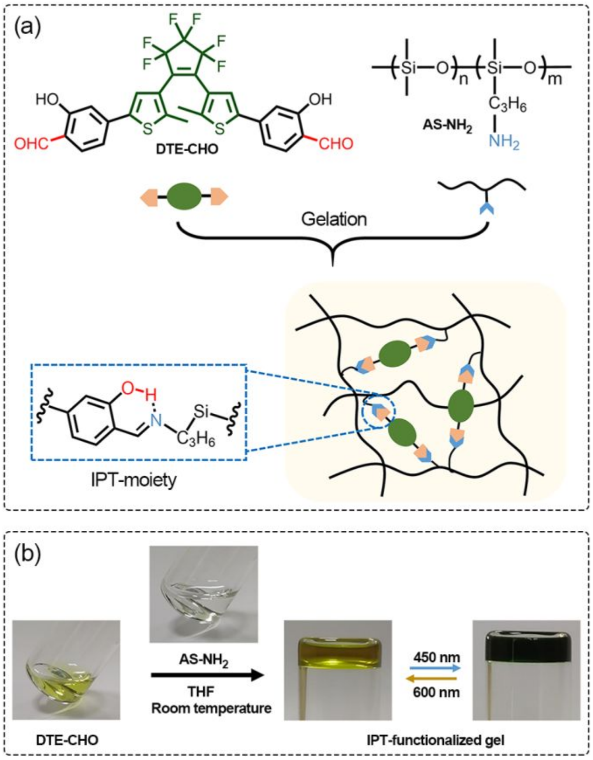

Figure 6. IPT-based DTE platform work in *in-situ* formed gel system. (a) Schematic illustration of the formation of IPT-based polymer gel system; (b) Photographs of the component and the resulting gel system, as well as its all-visible-light response.

Enabling IPT-Based DTE Platform Work in *in-situ* Formed Gel System. Given that the IPT strategy proposed here provides a new method for designing all-visible-light activated DTE systems, we anticipate that such IPT-based DTE platform could also become a reliable matrix for constructing more functional visible-light-responsive materials. By virtue of the mild reaction conditions and high reaction rates during the formation of imine bond,[60] we designed an *in-situ* formed gel system to prove the effectiveness of the IPT-based DTE platform in such soft materials.[61] By mixing the aldehyde-containing intermediate (DTE-CHO) with amino-functionalized siloxane polymer (AS-NH_2), a viscous gel was formed at room temperature immediately (Figure 6). Then irradiating it with visible light at 450 nm, a significant color change from yellow to deep blue can be observed, indicating the IPT-based DTE platform can not only work well in polar/protic solvent environment, but also is applicable in polymeric gel systems. Given that the imine bond have been widely exploited in the fields of supramolecular system, polymer networks and covalent organic framworks (COF),[62-64] we expect the further development of the IPT-based DTE platform to construct versatile all-visible-light modulated materials.

CONCLUSIONS

This work focuses on how to settle the bottleneck of the traditional photochromic DTE series that need harmful UV light to trigger the photocyclization. Given that the interplay between the π-conjugation and the photoswitchable backbone severely affects the photochromic behavior, we have well demonstrated a novel strategy with the specific IPT process to building up all-visible-light driven DTE series. The structural transformation from OH-form to NH-form in IPT-based DTEs can significantly decrease the energy gap, resulting in an extra absorption band in visible light region with a dramatic redshift up to 95 nm, thereby making a breakthrough to afford all-visible-light photochromic DTE system without requiring the harmful stimuli of UV light. This novel system can not only work well in polar solvent system, but also show its effectiveness in polymeric gel systems. The IPT-based DTE structures can provide a reliable platform to address multifunctional all-visible-light modulated materials. Based on the unprecedented IPT-based DTEs, further insights into the proton donor group and ethene bridge are now in progress.

ASSOCIATED CONTENT

More detailed experimental procedures, characterizations, supplementary optical spectra and figures can be found in Supporting Information. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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Table of contents (TOC)

All-Visible-Light Activated Dithienylethenes Induced by Intramolecular Proton Transfer

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