

Influence of Protonation on the Photochromic Behavior, Phase Transfer and Thermal Stability of Phenylamine-Substituted Diarylethenes

S. Mahvidi^{1,2,3}, Ch. G. Elles², B. Shirkavand Hadavand⁴, Y. Yokoyama³, F. Nourmohammadian^{1, 5*}

¹ Department of Organic Colorants, Institute for Color Science and Technology, P. O. Box: 16765-654, Tehran, Iran

² Department of Chemistry, University of Kansas, Lawrence, KS 66045, United States

³ Department of Advanced Materials Chemistry, Graduate School of Engineering, Yokohama National University, Yokohama, Japan

⁴ Department of Resin and Additives, Institute for Color Science and Technology, P. O. Box: 16765-654, Tehran, Iran

⁵ Center of Excellence for Color Science and Technology, Institute for Color Science and Technology, P.O. Box: 16765-654, Tehran, Iran

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ABSTRACT

This paper examines the role of protonation on the photochromic reactions of multi-responsive phenyl amine diarylethene derivatives (PA-DAEs). Reversible protonation and deprotonation provide a secondary stimulus for controlling the properties of light-responsive PA-DAEs, including solubility and thermal stability. For this reason, the phenylamine substituted DAEs were synthesized using a novel and efficient microwave-assisted synthetic route. Steady-state spectroscopy results indicated that the photocyclization and photocycloreversion reactions were reversible at different pH values. Even though, the acidic condition caused red-shift of the visible light absorption bands and generated a new absorption band at near-IR to IR region in the closed-ring structure but made blue-shift in the absorption spectra of the open-ring isomers. Also, it was showed that the excess amount of proton locked back the photochromic reaction. Results also indicated that the protonated closed-ring isomers of PA-DAEs are hydrophilic, whereas the deprotonated forms and protonated open-ring forms are hydrophobic. In addition to photoswitching and solubility of PA-DAEs under irradiation at different light wavelengths, the thermal stability of P-type PA-DAEs was also monitored in the presence of trifluoroacetic acid at different temperatures as external stimuli. Prog. Color Colorants Coat. 13 (2020), 105-119© Institute for Color Science and Technology.

1. Introduction

Multi-responsive photochromic molecules allow the development of novel optoelectronic devices based on different responses in the presence of disparate stimulus. Photochromic molecules present an ability to remotely regulate and control the physiochemical properties of a compound with external stimuli which is highly appealing not only for modern materials science applications such as optoelectronic devices and

information storage media [1-4], molecular machines [5-7], various optical memories and devices [4, 8], but also at the boundary between life and material sciences [9, 10]. Among thermally reversible (T-type) and thermally stable (P-type) photochromic compounds, diarylethenes have been well recognized as the most promising P-type photochromic molecules owing to their thermal stability, superb fatigue resistance, ultrafast response and high reactivity in the solid state [2, 4, 11, 12].

*Corresponding author: nour@icrc.ac.ir

Recently, synthesis of new diarylethene-based molecular switches with specific functional moieties, introduced new capability to remotely control properties not only with UV, visible and IR light but also using other external stimuli such as pH [13-15], charged species, redox [16], photon [17], heat [18, 19] or biomolecules [20, 21] resulting in multi-responsive switching systems. In this context, the developments of diarylethenes that integrate several switchable functions into a single molecule are of considerable interest [22-28].

Protonation and de-protonation process of diarylethenes by control of pH and charged species stimulus [29-31] affect their photochromic activities like as absorption spectra and quantum yields [32-34]. Comparing to the neutral diarylethene, protonated species generally show different photo-ability and wide physico-chemical properties such as locked photochromism of ring-opened isomers [31], switching between P-type and T-type photochromism [29], and water-solubility control [30].

Moreover, controlling the phase transfer and solubility of photochromic compounds in aqueous phase for biological application is promising. There has been different research area on developing water soluble diarylethenes using methods such as modifying the structure, binding with water soluble species and using nanocavity and species [35-37]. Also, Y. Chen et al. [30] demonstrated the effect of acid on solubility of diarylethene photoswitch and they showed that the protonated ring-closed isomer was hydrophilic whereas the protonated ring-opened isomer was hydrophobic. However, controlling the water solubility of diarylethenes with tuning pH and reversible phase transfer of photoswitches between two immiscible phases is still challenging.

In this research, mono- and di-phenylamino-diarylethenes (MPA-DAE (compound 1) and DPA-DAE (compound 2)) were synthesized and employed to study the effect of protonation with CF_3COOH (Trifluoroacetic acid/TFA) on the photochromic properties. Based on the above mentioned facts, we designed and developed pH- and light-dependent multi-addressable molecular switches using photochromic diarylethenes with functional amine groups. The photophysical responses also specific properties of the synthesized PA-DAEs by protonation and switching between aqueous and organic phases by controlling light, pH and temperature were investigated.

2. Materials and Methods

2.1. Materials

All reactions were run under dry nitrogen atmosphere using spectroscopic grade anhydrous tetrahydrofuran (THF) solvent. All reagents were obtained from Sigma-Aldrich or Wako and used as received. Products were purified using flash column chromatography on 230-400 mesh silica gel with ethyl acetate and hexane as diluents. Analytical thin-layer chromatography was performed on a pre-coated 0.25 mm thick silica gel TLC plates.

Protonated forms of 1 and 2 were prepared by adding tetrafluoroacetic acid (TFA) to the solution of open-ring form of each compound (2.0×10^{-5} M in toluene) in the dark and stirring at room temperature for 10 min. We labeled the protonated forms as 1- H^+ , 2-1 H^+ , and 2-2 H^+ . The neutral forms were recovered by adding triethylamine (TEA) and stirring at room temperature for 10 min to neutralize the acid.

2.2. Methods

Photoreactions were carried out in quartz cells with 1 and 10 mm optical path length using a 300 nm UV LED (Thorlabs, M300L4) for cyclization or a white-light LED lamp for cycloreversion. Absorption spectra were recorded with JASCO V-550 and Thermo Scientific Evolution 300 UV/Vis spectrophotometers.

^1H NMR Spectra were recorded on Bruker DRX500 (500 MHz) NMR spectrometer using deuteriochloroform (CDCl_3) as solvent and tetramethylsilane (TMS) as an internal standard. J values are expressed in Hz and the chemical shifts are in ppm. Splitting patterns are indicated as s, singlet; d, doublet; t, triplet; q, quartet, m, multiple. IR spectra were recorded on a JASCO FT/IR-4100 spectrometer. Mass spectra were measured by the electron impact mass spectrometry using a JEOL JMS-AX-600 mass spectrometer. Melting points were measured using Digimelt MPA160 (MSRS).

Quantum chemical calculations were performed using Spartan'14 (Wavefunction) with B3LYP/6-31G* for DFT geometry optimization for the open- and closed-ring isomers of 1, 2, 1- H^+ , 2-1 H^+ and 2-2 H^+ .

2.3. Synthesis and Characterization

2.3.1. Synthesis of (1,2-bis(5-chloro-2-methyl-3-thienyl) cyclopentene) (3)

This compound was synthesized according to the

procedure mentioned in the literature and the spectroscopic data are in good agreement with those from the literature [38].

^1H NMR (500 MHz, chloroform-*d*) δ ppm 1.87-1.91 (6 H, s), 1.98-2.05 (2 H, m), 2.71 (4 H, t, $J = 7.4$ Hz), 6.57 (2 H, s); $\text{C}_{15}\text{H}_{14}\text{Cl}_2\text{S}_2$ ESI-MS= 328 m/z; Mp = 75.5-79.0 °C.

2.3.2. Synthesis of mono and di-phenyl amino diarylethenes 1, 2 (General Procedure A)

In a microwave vial (10-20 mL) with a magnetic stir bar containing degassed THF-H₂O mixture (18 mL, 3:1) was added a mixture of 3 (1 equiv.), 4-aminophenylboronic acid pinacol ester (1.2/2.4 equiv. for compounds 1/2 respectively), Pd(PPh₃)₄ (0.05 equiv.), and Na₂CO₃ (10 equiv.). The vial was purged with nitrogen, sealed and heated (110 °C, 3bar, 24 W) under microwave irradiation (Biotage Initiator) for 10 min. After cooling down to room temperature, the reaction was quenched with water (20 mL) and ether (40 mL). The aqueous layer was extracted with ethyl acetate (2×20 mL). The combined organic layers were dried over Na₂SO₄, filtered, and evaporated under reduced pressure. The crude products were subjected to flash column chromatography on silica gel (eluent: ethyl acetate/Hexane, 1/1).

2.3.3. Synthesis of mono and di-phenyl amino diarylethenes 1, 2 (General Procedure B)

Compounds 1 and 2 were also prepared using a slightly modified procedure described in the literature [39]. 4-aminophenylboronic acid pinacol ester (1.2/2.4 equiv. for compounds 1/2, respectively), 3 (1 equiv.), Na₂CO₃ (10 equiv.), and Pd(PPh₃)₄ (0.05/0.1 equiv. for compounds 1/2, respectively) were placed in a reaction flask under inert atmosphere. DME (degassed) and water (degassed) were subsequently added, and the solution was refluxed under argon. After 24 h, completion of the reaction was proved by TLC. After cooling down to room temperature, the reaction was quenched with water (20 mL) and ether (40 mL). The aqueous layer was extracted with ethyl acetate (2×20 mL). The combined organic layers were dried over Na₂SO₄, filtered and evaporated under reduced pressure. The crude products were subjected to flash column chromatography on silica gel (eluent: ethyl acetate/Hexane, 1/1).

2.3.4. Synthesis of 1-[2-methyl-5-(4-aminophenyl)-3-thienyl]-2-[2-methyl-5-chloro-3-thienyl] (1)

This compound was prepared according to the general procedure A and B, from compound 3 (280 mg, 0.85 mmol), 4-aminophenylboronic acid pinacol ester (224 mg, 1.02 mmol), Pd(PPh₃)₄ (57 mg, 0.05 mmol), and Na₂CO₃ (869 mg, 8.2 mmol) to yield 281 mg (86%) following general procedure A and according to general procedure B, 258 mg (79%).

^1H NMR (500 MHz, chloroform-*d*) δ ppm 1.88 (3 H, s), 1.96 (3 H, s), 2.04 (2 H, m), 2.73 (2 H, t, $J = 7.2$ Hz), 2.79 (2 H, t, $J = 7.4$ Hz), 3.69 (2 H, br. s.), 6.62 (1 H, s), 6.66 (2 H, d, $J = 8.5$ Hz), 6.82 (1 H, s), 7.29 (2 H, d, $J = 8.2$ Hz); $\text{C}_{21}\text{H}_{20}\text{ClNS}_2$ ESI-MS=385.2; Mp = 109-110 °C.

2.3.5. Synthesis of (1,2-bis-[2-methyl-5-(4-aminophenyl)-3-thienyl] cyclopentene) (2)

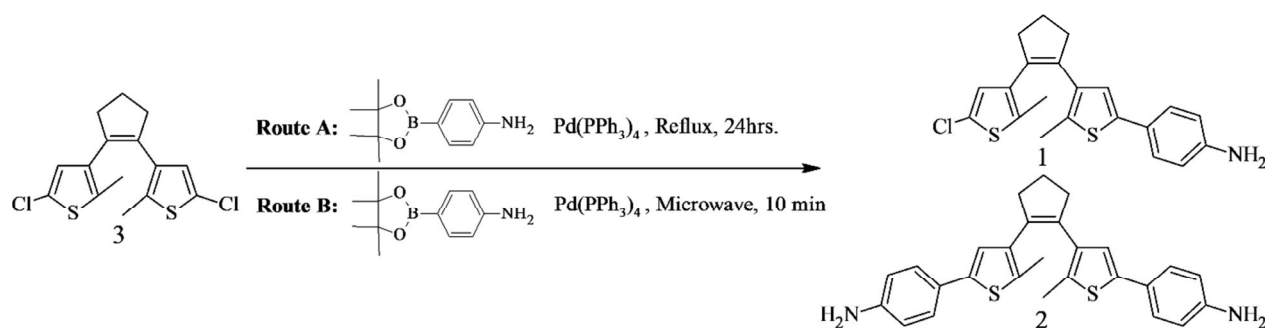
This compound was prepared according to the general procedure A and B, from compound 3 (250 mg, 0.76 mmol), 4-aminophenylboronic acid pinacol ester (399 mg, 1.82 mmol), Pd(PPh₃)₄ (92 mg, 0.08 mmol), and Na₂CO₃ (769 mg, 8.2 mmol) to yield 279 mg (83%) following general procedure A and according general procedure B, 252 mg (79%).

^1H NMR (500 MHz, chloroform-*d*) δ ppm 1.96 (6 H, s), 2.06 (2 H, m), 2.82 (4 H, t, $J = 7.4$ Hz), 3.68 (4 H, br. s.), 6.65 (4 H, d, $J = 8.5$ Hz), 6.87 (2 H, s), 7.30 (4 H, d, $J = 8.2$ Hz); $\text{C}_{27}\text{H}_{26}\text{N}_2\text{S}_2$ ESI-MS= 442.2 m/z; Mp = 121-122 °C.

3. Results and Discussion

3.1. Synthesis of mono and di-phenyl amino diarylethenes (1 and 2)

1-[2-methyl-5-(4-aminophenyl)-3-thienyl]-2-[2-methyl-5-chloro-3-thienyl] (1) and (1,2-bis-[2-methyl-5-(4-aminophenyl)-3-thienyl] cyclopentene) (2) were prepared from compound 3 (1,2-bis(5-chloro-2-methyl-3-thienyl) cyclopentene) via a Suzuki-coupling reaction using two different synthetic approaches (Scheme 1). The first approach followed a previously reported procedure with more than 24 h reflux [39]. The second approach used a novel route based on microwave irradiation to achieve the same results in higher yield in shorter time (10 min). Synthetic and product characterization are provided in experimental section.



Scheme 1: Synthesis of compounds 1 and 2.

3.2. Photochromic response

Diarylethene derivatives 1 and 2 reversibly switch between open- and closed-ring isomers under UV and visible irradiation. Solutions of the open-ring isomers absorb only in the UV region ($\lambda_{\text{max}1} = 317 \text{ nm}$ and $\lambda_{\text{max}2} = 352 \text{ nm}$). Irradiation of 1 and 2 derivatives at 300 nm leads to the appearance of visible absorption bands centered near 506 and 525 nm, respectively, due to the formation of the closed-ring isomers. Closed-ring isomers reversibly convert back to the open-ring isomer under visible light exposure. The amino substituents on the phenyl rings present an opportunity to modify the photochromic behavior of 1 and 2 by selectively changing the protonation state. In this way, Figure 1 and 2 show the spectral changes of the two

compounds under UV and visible irradiation after adding 1 or 2 eq. of TFA in order to protonate the phenylamine groups. Addition of 1 eq. of TFA to the solution of compound 1 gives nearly complete conversion to the protonated form of compound, 1-H^+ , due to the efficient acid-base reaction. In contrast, addition of single eq. of acid to the solution of compound 2 probably gives a distribution of protonation states, including unprotonated, single protonated, and double protonated compounds (2 , 2-H^+ , and 2-2H^+ , respectively), which makes it difficult to separate out the results for the single protonated species. However, the addition of 2 eq. of acid gives essentially complete conversion to the fully protonated state, 2-2H^+ .

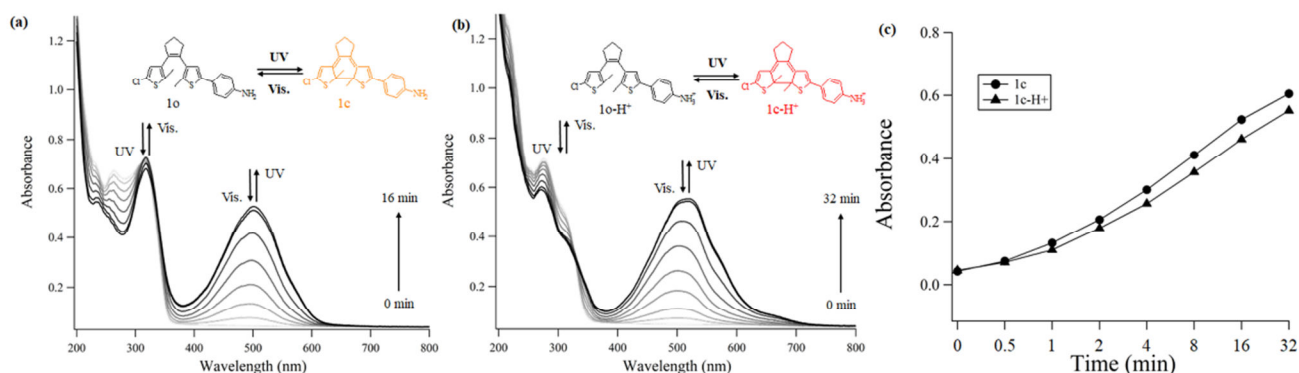


Figure 1: Spectral changes associated with the photochromic conversion of 1 (a) 1-H^+ (b) in acetonitrile ($2 \times 10^{-5} \text{ M}$) and (c) the rate of conversion.

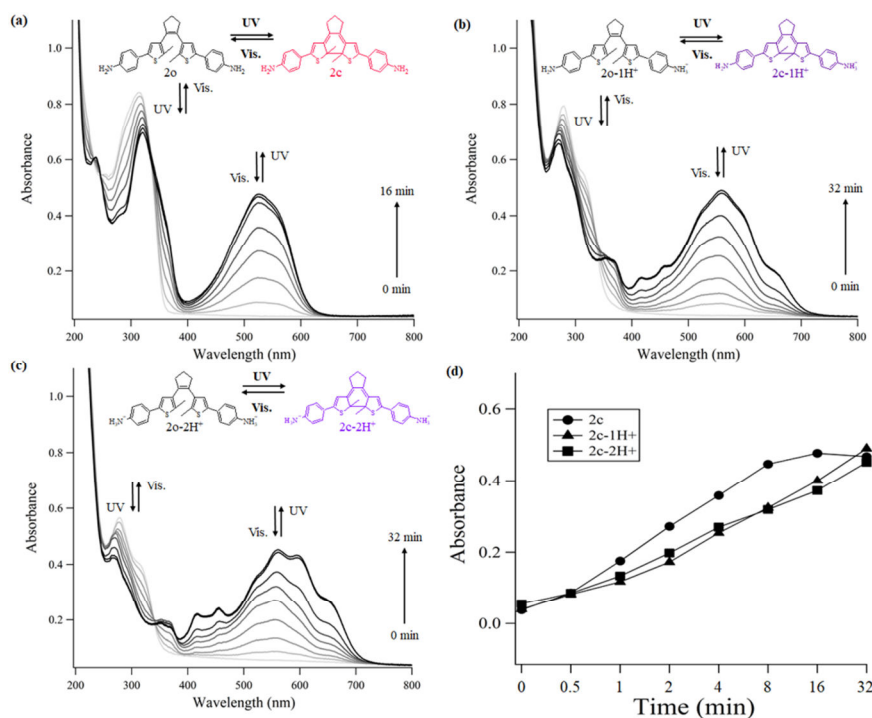


Figure 2: Spectral changes associated with the photochromic conversion of 2 (a), 2-1H⁺, (b) and 2-2H⁺, (c) in acetonitrile (2 × 10⁻⁵ M) and (d) the rate of conversion.

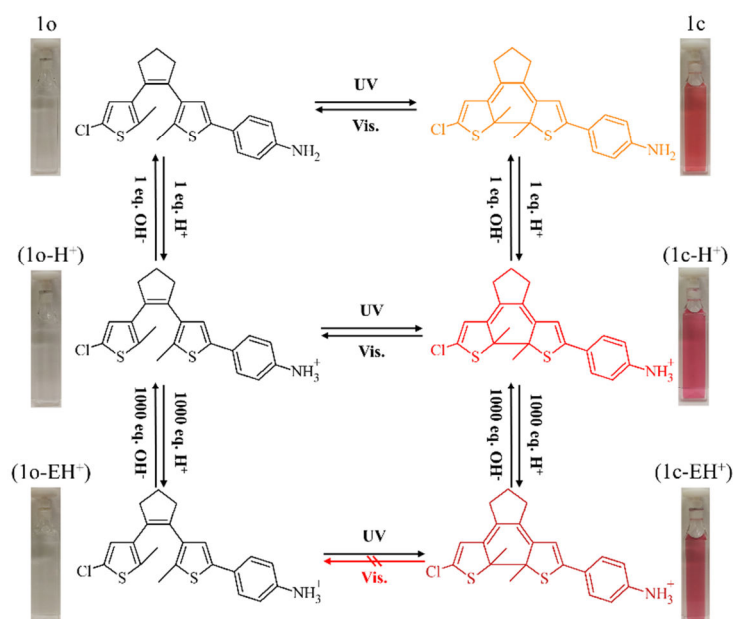
Except for some changes in the absorption spectra, the photochromic behavior for the protonated compounds 1-H⁺, 2-1H⁺ and 2-2H⁺ is similar to that of the neutral compounds. Protonation shifts the UV absorption bands to shorter wavelength by about 40 nm, but the compounds still undergo photocyclization under irradiation with UV light to produce visible-absorbing closed-ring isomers. The absorption bands of the closed-ring isomers shift to longer wavelength and become more structured in the protonated compounds. There is only a slight shift for compound 1 from 506 to 513 nm upon protonation, but a more substantial shift for compound 2, increasing from 525 to 557 nm after addition of 1 eq. of acid, and 562 nm in the doubly protonated state (Figure 3). The additional vibronic structure of the protonated compounds, especially 2-2H⁺, indicates a more rigid molecule in the protonated state due to the shift from an electron-rich amine to an electron-withdrawing ammonium group interacting with the conjugated backbone of the molecule.

Similar to the neutral compounds, the closed-ring isomers of the protonated diarylethenes changed back to open-ring forms (colorless) upon irradiation with visible light (>520 nm) which the original absorption spectrum was recovered. The results also confirmed

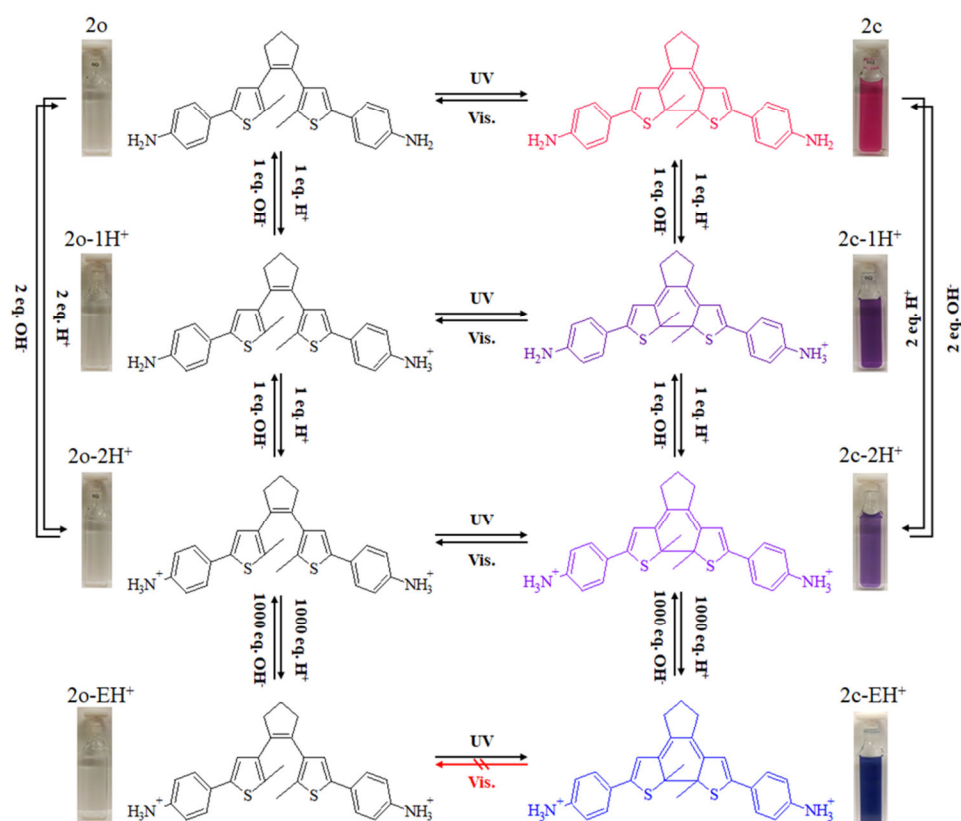
that the effects of protonation are completely reversible by adding the base triethylamine (TEA) to the initial spectrum is fully restored for both the open- and closed-ring structures. Additional experiments revealed that the recovered deprotonated form converts back to open-ring form under irradiation with visible light.

The red shifted absorption wavelength in 2 is due to more extensive π -conjugation after replacing the chlorine atom with a second phenyl-amine moiety. Schemes 2, 3 and Figure 3 summarize the multi-responsive photochromic properties of 1 and 2, including the color change upon protonation, as well as the different states due to protonation and ring-opening/closing reactions.

To study the effect of protonation, the molar absorption coefficients of molecules 1 and 2 in the presence of different amounts of proton are measured and presented in Table 1. The results showed that molar extinction coefficient of 2-1H⁺ in closed-ring form, when the color of solutions reached the steady state, is more than neutral and 2-2H⁺. As shown in Table 1, molar absorption coefficient of both molecules in neutral forms are calculated based on the maximum wavelength of absorption in the UV and visible areas.



Scheme 2: Photochromism and color change of 1 in different pH with stimulation of light.



Scheme 3: Photochromism and multicolor switching of 2 with light and acid/base stimuli.

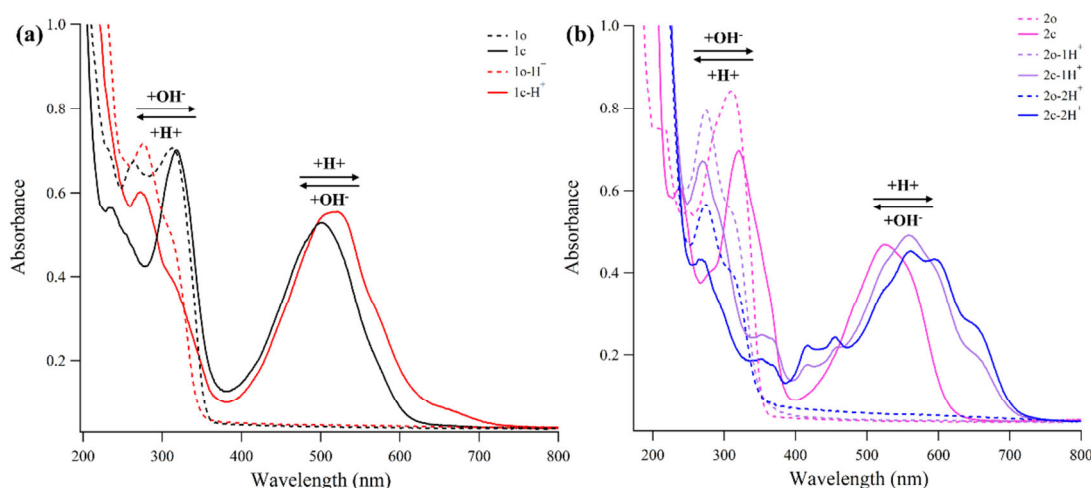


Figure 3: Absorption spectra shift and comparison between neutral and protonated forms in open and closed forms of a: 1 and b: 2 in both open-ring and closed-forms (2×10^{-5} M, CH_3CN).

Table 1: Maximum absorbance wavelength of molecules 1 and 2 in acetonitrile with concentration of 2×10^{-5} M.

Compounds	eq. of acid	$\lambda_{\text{max}} (\text{nm})/\epsilon \times 10^{-4} (\text{M}^{-1}\text{cm}^{-1})$			
		Open-ring form		Closed-ring form	
1	0	318	2.63	506	1.08
1- H^+	1	275	2.58	513	0.97
2	0	315	4.21	525	1.39
2-1 H^+	1	279	3.97	557	1.55
2-2 H^+	2	279	2.84	562	1.16

Addition of TFA to the solution of 1 and 2 caused changing of amino groups and formation of ammonium salts. This change from electron donor to electron acceptor group affect UV-Vis absorption peaks due to the electron transition from the conjugate π to excited state π^* . As mentioned before, the intermediate molecule of 2c-1H^+ in scheme 3 possesses a long electronic conjugated push-pull system (D- π -A) which has been produced by addition of maximum 1 equimolar acid and protonation of one of the amines and changed from an electron donating to an electron-withdrawing group (Figure 4.).

Therefore, in the presence of one equimolar amount of acid (0.01:1 Eq. TFA/Eq. 2), 2c-1H^+ exhibits a more intramolecular charge transition (ICT) than other molecules which is consistent with a bathochromic shift with new broad absorption bands at the near-infrared area with two maxima appeared in this region. This new peak with a shoulder around 820 and 913 nm

that increased gradually proportional of equivalent of acid is because of appearance of donor-acceptor system and is related to a new transition because of charge transfer from donor to acceptor groups through π -conjugation in closed ring form of 2c-1H^+ ($\text{NH}_2 \rightarrow \text{NH}_3^+$) (Figures 5 and 6). By adding more acid, this peak has increment to its maximum, gradually decreased and finally disappeared due to the protonation of both amine groups (Figure 5-d) and consuming of molecule 2. The variation in absorbance at near-infrared (NIR) with maxima around 820 nm is shown in Figure 6.

As expected, this bathochromic shift was not seen in closed form of mono-functional molecular switch 1 in Figures 5a and 5b because of not being donor-acceptor system neither in both open-ring forms because of absence of long π conjugation (Figures 5a and 5c).

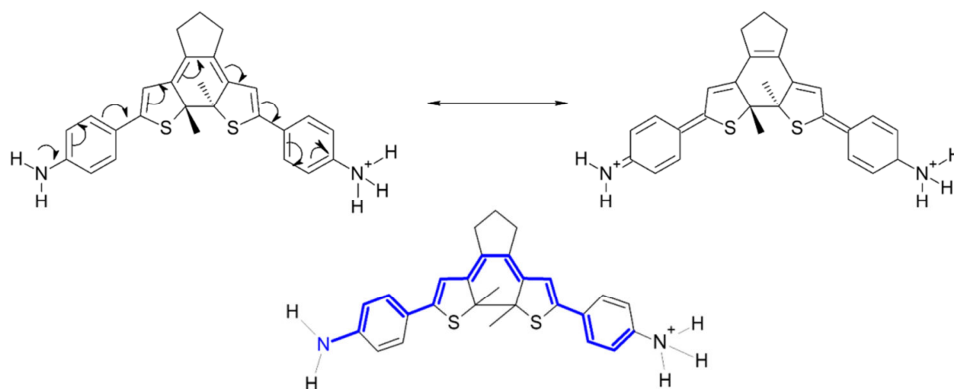


Figure 4: Schematic structure of the extent of conjugation in the closed-ring isomer of molecule 2c-1H⁺.

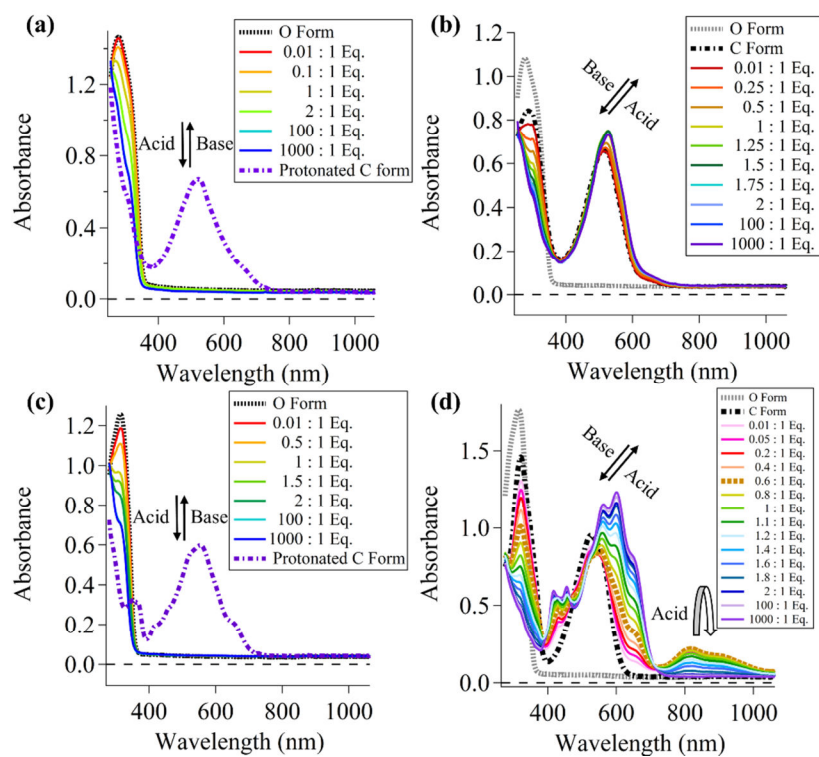


Figure 5: Absorption spectra changes of a:10, b:1c, c:2o and d:2c (2×10^{-5} M, CH₃CN) upon gradually addition of Acid/Base.

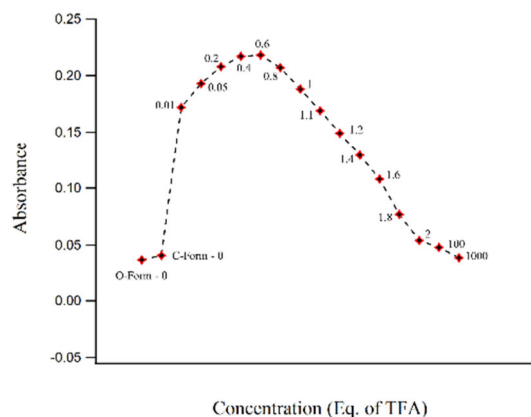


Figure 6: Absorption intensity changes of molecule 2 (2×10^{-5} M, CH₃CN) at 820 nm peak upon gradually addition of TFAEq. (0.01, 0.05, 0.2, 0.4, 0.6, 0.8, 1, 1.1, 1.2, 1.4, 1.6, 1.8, 2, 100, 1000eq.TFA).

Consequently, controllable NIR photoswitch based on diarylethene with modulating the equimolar of acid (pH) and charge delocalization, by taking advantage of two known parameters push-pull system and extended π -conjugation was shown. It is worthy to mention that no thermal or other type of cycloreversion was observed during acid-base titration at room temperature.

3.3. TD-DFT calculation results

To explain the difference in the absorption spectra and also to shed light on the bathochromic effect resulted from pH modulated push-pull system, theoretical calculations were carried out using TD-DFT with B3LYP/3-21G* basis set. As expected, the TD-DFT calculations demonstrated that the lowest-energy transitions in the visible wavelength region correspond to HOMO–LUMO transitions. As shown in Figures 7, 8 and Table 2 and according to the optimized molecular energy for molecules 1 and 2, the HOMO and LUMO of protonated ring-closed forms have lower energy than neutral closed ring- forms. Specifically, both HOMO and LUMO levels of 1c-protonated decrease, although there is also slight decrement in the HOMO–LUMO gap that make red shifted spectrum.

In molecule 2, with protonation of one amino group and change to push-pull system, the same effect was observed and the 2-1H⁺ HOMO and LUMO have lower energy levels and also decrease in HOMO–LUMO gap.

Due to push pull systems and intramolecular charge transfer (ICT) phenomenon molecules exhibit a red shifted absorption band. Addition of more acid and change to 2-2H⁺ still make decrease in HOMO and LUMO energy levels than 2-1H⁺ and also lower HOMO–LUMO gap than neutral 2 and slightly increase in comparison to 2-1H⁺. This increase is related to the diminishing the push pull structure. Still, gap between HOMO and LUMO in 2-1H⁺ is the lowest among the three derivatives of molecule 2. According to the results, protonation of amino groups and formation of ammonium salts significantly lowers the energy level of the HOMO and LUMO and also less energy of molecules than neutral forms. These findings are consistent with the experimental results (Figures 1 and 2) which showed that the protonation of amino groups affect the absorption maximum of the closed-ring isomer and induces the bathochromic shift. So, these results showed new photoresponsive system with external stimulus can control HOMO-LUMO band gap similar to other different methods [40] i.e. conjugation length [41, 42], donor-acceptor charge-transfer [43], intramolecular interactions [44].

The optimized conformation (HOMO-1, HOMO, LUMO and LUMO+1) of diarylethene 1 and 2 in neutral and protonated state at the ground state obtained by TD-DFT calculations in vacuum is shown in Figures 7 and 8.

Table 2: Calculated optimized conformation energies of open- and closed-ring forms of molecules 1 and 2 in neutral and protonated forms by TD-DFT calculations (B3LYP/6-31G*).

Energy (KJ/mol)			
Molecules	Open-ring form	Closed-ring form	ΔE_{c-o}
1	943.94	982.19	38.25
1-H ⁺	0	41.34	41.34
2	1783.31	1822.74	39.43
2-1H ⁺	828.19	860.28	32.09
2-2H ⁺	0	52.5	52.5

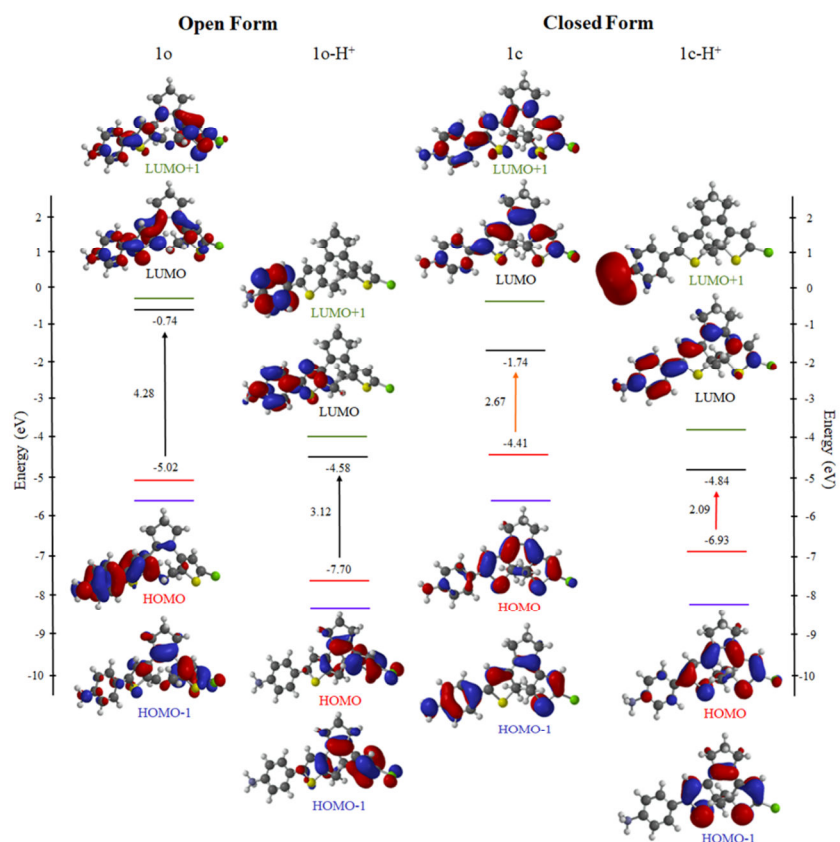


Figure 7: HOMO, HOMO-1 and LUMO, LUMO+1 of open- and closed-ring form of **1** and **1-H⁺** in protonated and neutral state obtained by TD-DFT calculation.

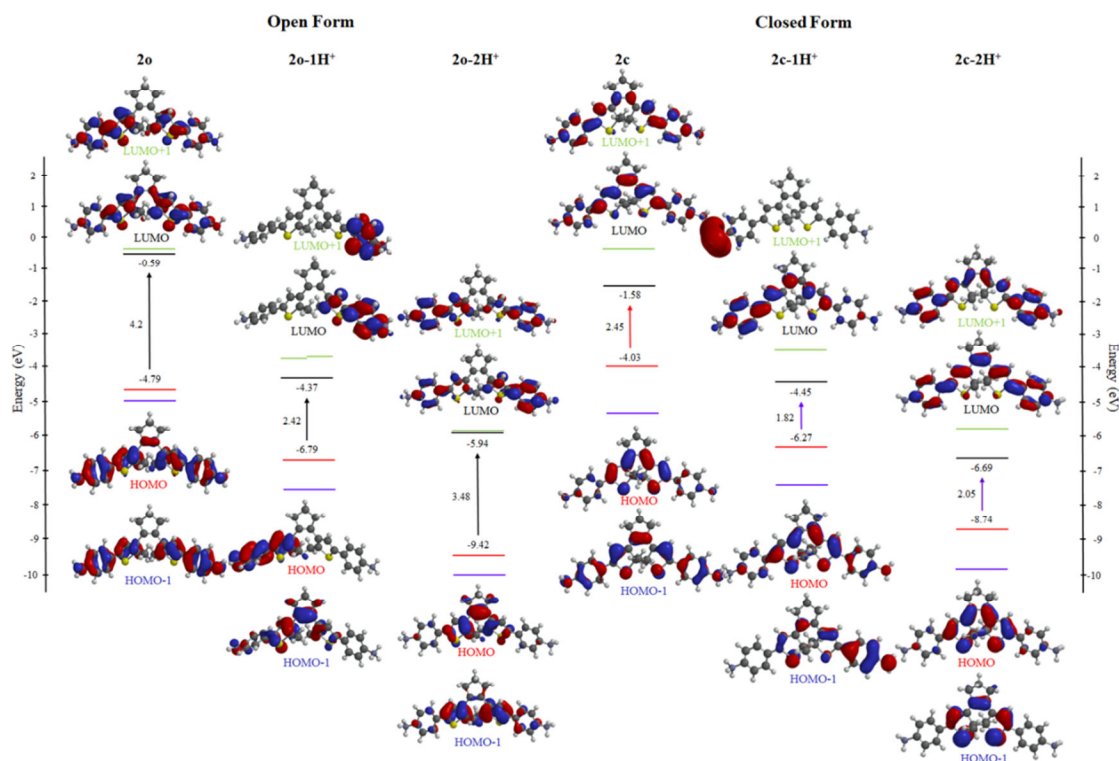


Figure 8: HOMO, HOMO-1 and LUMO, LUMO+1 of open- and closed- ring form of **2**, **2-1H⁺** and **2-2H⁺** obtained by TD-DFT calculation.

Figure 7 shows that in HOMO structure of $1o-H^+$, electron cloud is entirely located on the 5-(4-chlorophenyl)thienyl side chain while in LUMO structure, electron cloud is exclusively on 5-(4-aminophenyl)thienyl side chain. Similarly, for compound 2 (Figure), it is obvious that HOMO structure of $2o-1H^+$ is located on amino group containing side chain while LUMO is on side chain containing protonated amine group. Therefore, there is a strong donor-acceptor interaction between these side chains at the ground state of 1 and 2. By the way, very low difference between HOMO and LUMO energy levels in $2c-1H^+$ approves the full-length resonance as declared in Figure 4.

Top-side optimized conformation of 1 and 2 obtained by TD-DFT calculations (B3LYP/6-31G*) is shown in Figure 9. As expected, the closed-ring form of 1 and 2 has more planar structure than their opening forms. Addition of acid and protonation affect the planarity of compounds such that $1c$ -Protonated (c) and $2c-1H^+$ have more planar structure than other forms. This planarity accompanying long electronic conjugated push-pull system and 2 amino groups compare to the chlorine at the end of molecule structure cause pH-dependent absorption at the near-infrared area in $2c-1H^+$ whereas not in $1c-H^+$.

3.4. Effect of excess amount of H^+

At low acid concentrations, protonated closed-ring form is photo-reversible upon irradiation under visible light. By increasing the amount of acid to about 1000 equimolar ratios (Excess amount), we could lock the molecular switch $1c-EH^+$ and $2c-EH^+$ (Schemes 2 and 3) to the closed-ring forms and not reversible to open-

ring form even after long time exposure to visible light. According to Figures 7 and 8, the excess amount of proton changes the electronic density and orbital delocalization in the HOMO and LUMOs of closed forms and also probably increases the activation energy of the cycle opening process at ground state. Subsequently, cycloreversion did not happen even after longer time irradiation. That means, in this case, that there is gated photochromic reactivity by other stimulus which strongly desired but is still inadequate and could be applicable in data storage molecular systems. Meanwhile, upon changing pH, addition of TEA and deprotonation, the closed-ring forms are photo-active again (unlock) and reversible to open-ring form upon irradiation under visible light.

3.5. Effect of acid on the solubility in aqueous phase

In order to confirm the conversion of amino group to ammonium salt after addition of TFA, the influence of protonation on the solubility properties of PA-DAE's 1 and 2 were studied. To determine the effect of acid on the water solubility, samples obtained from compounds 1 and 2, (2×10^{-4} M) dissolved in toluene and prepared toluene/water (toluene: top) mixtures. As presented in Figure 10, open-ring and closed-ring forms of 1 and 2 did not dissolve in water and remained in organic phase. But after addition of acid and formation of ammonium salts, both protonated closed-ring forms of molecules 1 and 2 immigrate from organic phase to aqueous phase. Meanwhile, experiments showed that even protonated open-ring forms of 1 and 2 are hydrophobic.

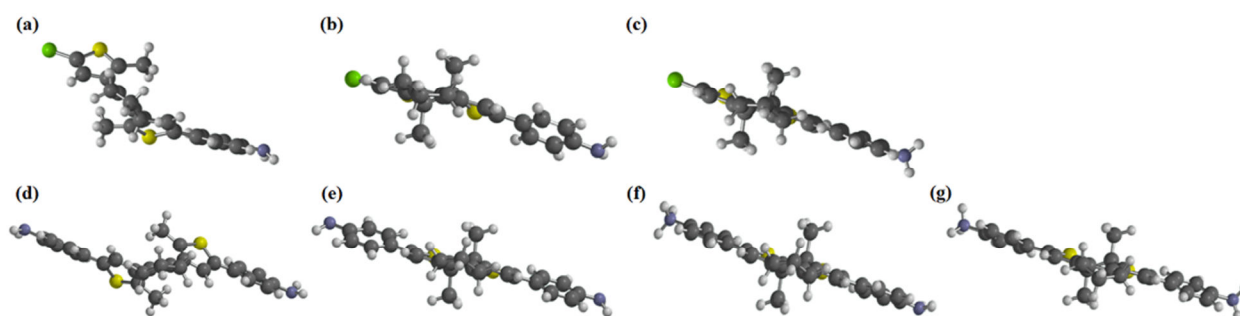


Figure 9: Optimized conformation of (a) $1o$, (b) $1c$, (c) $1c-1H^+$, (d) $2o$, (e) $2c$, (f) $2c-1H^+$ and (g) $2c-2H^+$ obtained by TD-DFT calculations (B3LYP/6-31G*).

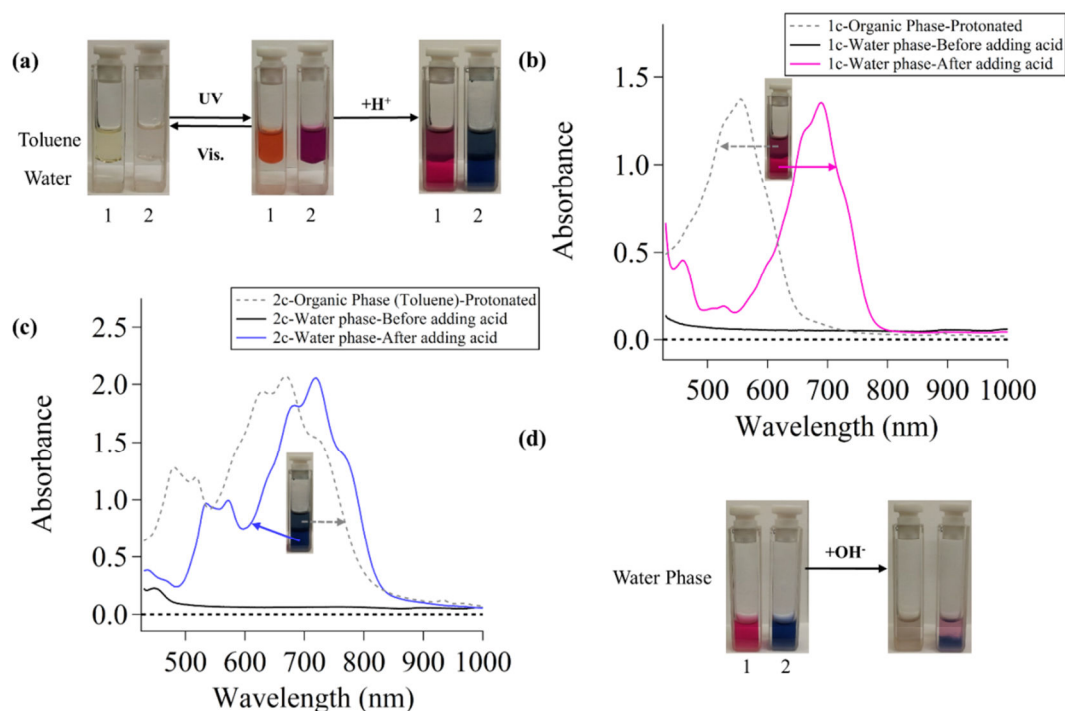


Figure 10: Acid induced a: color and solubility changes of 1 and 2 (2×10^{-4} M, toluene), absorption spectra of b: 1 and c: 2 (2×10^{-4} M, toluene) in water phase before and after addition of acid d: color change and settlement of 1 and 2 in water phase after addition of base.

Also, the aqueous layers of both **1** and **2** before and after addition of acid were extracted and absorption spectrum of both samples was taken (Figures 10b and 10c). According to the results, proportional absorption peak exists in sample containing acid, so revealed the water solubility of protonated closed-ring forms. These results illustrated that the ammonium salt of molecules was formed in TFA but it is not enough to change water solubility because protonated open-ring forms didn't show any related spectrum in aqueous phase after addition of acid. To summarize, planarity of closed-ring form structure, extension of π conjugation that exist in closed-ring forms and the presence of ammonium salts because of adding acid simultaneously cause water solubility of molecules **1** and **2**.

To certify the effect of acid addition on the solubility of compounds, sodium hydroxide was added to the solutions and drastic change was observed. Protonated ring-closed form of molecule **1** changed to dark colorless solution. Similarly, after addition of base to molecule **2**, there was settlement of compound that is shown in Figure 10d. Addition of more base to the sample decreases water solubility of molecule and changes the solution's color.

3.6. Effect of heating on the photochromic properties and thermal stability of molecules **1** and **2** in the presence of acid

In this section, the effect of thermal stability and thermal reversibility of molecules **1** and **2** in neutral and the presence of Trifluoroacetic acid (TFA) are studied. The experiments approved thermally irreversible photochromism and thermal stability of molecules **1** and **2** in both isomers in neutral acetonitrile at different temperatures for long period of time as well as toluene and other organic solvents. In other words, in both molecules related absorption spectra of each isomer didn't change after heating for long time. We measured thermal effect on the protonated form of molecules and observed color and spectral changes of protonated closed-ring forms of molecules **1** and **2** in toluene solutions. Addition of 10 Eq. of acid (TFA) to the closed-ring isomer of molecules **1** and **2** make maximum absorption bands of closed-ring isomers red shifted. Thermal or any other type of cycloreversion reactions were not observed during the acid–base titrations at room temperature. In order to study the effect of protonation on thermal stability of molecules, after irradiation under UV light and addition of TFA to the solutions of **1** and **2** and

mixing for at least 10 min, the samples were heated at 80 °C for different times. After heating the samples, absorption spectrum of molecule 1 solutions in the presence of TFA slightly red sifted, whereas spectrum of molecule 2's solution mainly changed from blue region to dark green (Figures 11 and 12). Over heating-time, simultaneously with diminishing solution's colors, brightness of molecule 1 and 2 decreased while these changes accomplished more intense for molecule 2. Meanwhile the protonated molecule 2's sample in toluene, upon adding Triethylamine (TEA) the deprotonated color were recovered with lower intensity. Subsequently, we irradiated sample 2 under visible light for 15 min and the color of sample

disappeared and changed to bleached solutions. In the case of protonated closed-ring form of 1, there is diminish of color along with the decrement of absorption spectrum and after 150 min heating the samples were locked and didn't change back to open protonated form under irradiation with visible light. Moreover, molecule 1 didn't change to colorless opening forms after addition of TEA and 10 min irradiation under visible light. These outcomes and changes in the absorption spectra and colors of molecules demonstrate that 1-H⁺ and 2-H⁺ are thermally unstable and obvious different changes after heating happened in protonated samples.

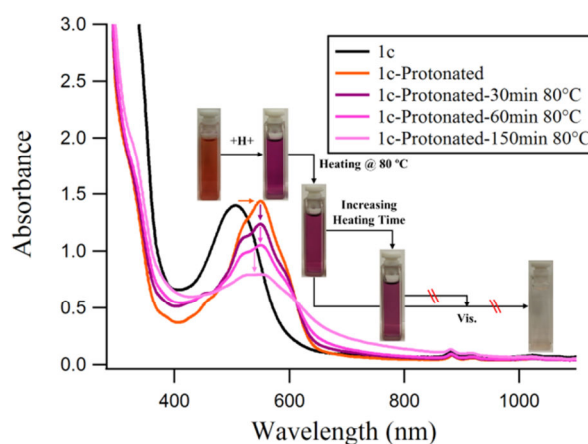


Figure 11: The thermo-stability switching of a: color change of 1 (2×10^{-5} M, Toluene) and b: absorption spectra change in the presence of 10 eq. of TFA and different heating time (30, 60 and 150 min at 80 °C).

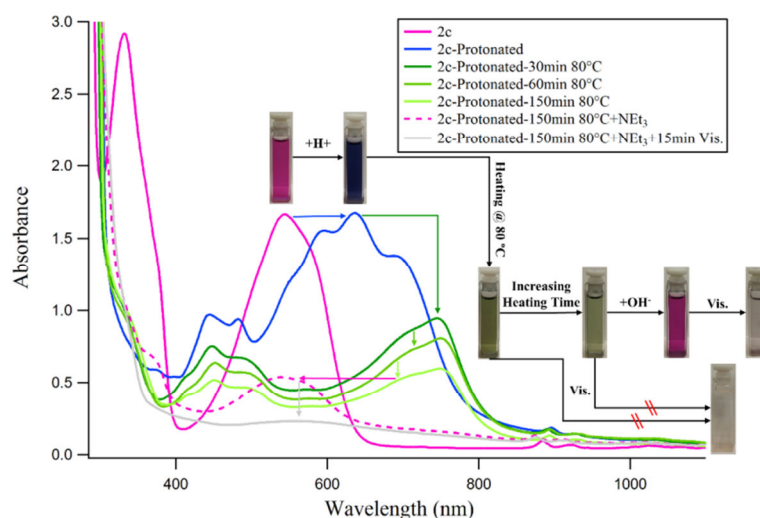


Figure 12: The thermo-stability switching of a: color change of 2 (2×10^{-5} M, Toluene) and b: absorption spectra change in the absence of 10 eq. of TFA and different heating time.

4. Conclusion

We investigated the effect of protonation as an external stimulus on the photochromic properties of phenyl amine diarylethenes. It was demonstrated that the protonated PA-DAEs are photoactive and reversible between open and closed forms upon irradiation under UV and visible lights, respectively. It was also shown that the addition of 1 eq. H^+ to 2c generates a new absorption band at near-IR to IR region and it disappeared after adding 2 equivalents of H^+ . Because of absorption at IR, these photochromic compounds are good candidate for using in heat absorbers, solar cells, biological and biomedical applications because of minimum photodamage, deeper penetration in biological tissues rather than UV and visible lights. Also, addition of excess amounts of H^+ to 1c and 2c

locked their photochromic back reaction. Reversible phase transfer of the molecular switches from organic to aqueous phase of PA-DAEs in the presence of acid along with light irradiation was illustrated. The novelty uses of this method and using photosensitive molecular switches could bring more insight to novel applications in different research areas. On the other hand, both diarylethenes isomers showed high thermal stability in neutral solutions but using elevated temperature showed different response in protonated closed ring forms of PA-DAEs.

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