

Imidazole Diarylethene Switches: An Alternative to Acid-Gated Photochromism

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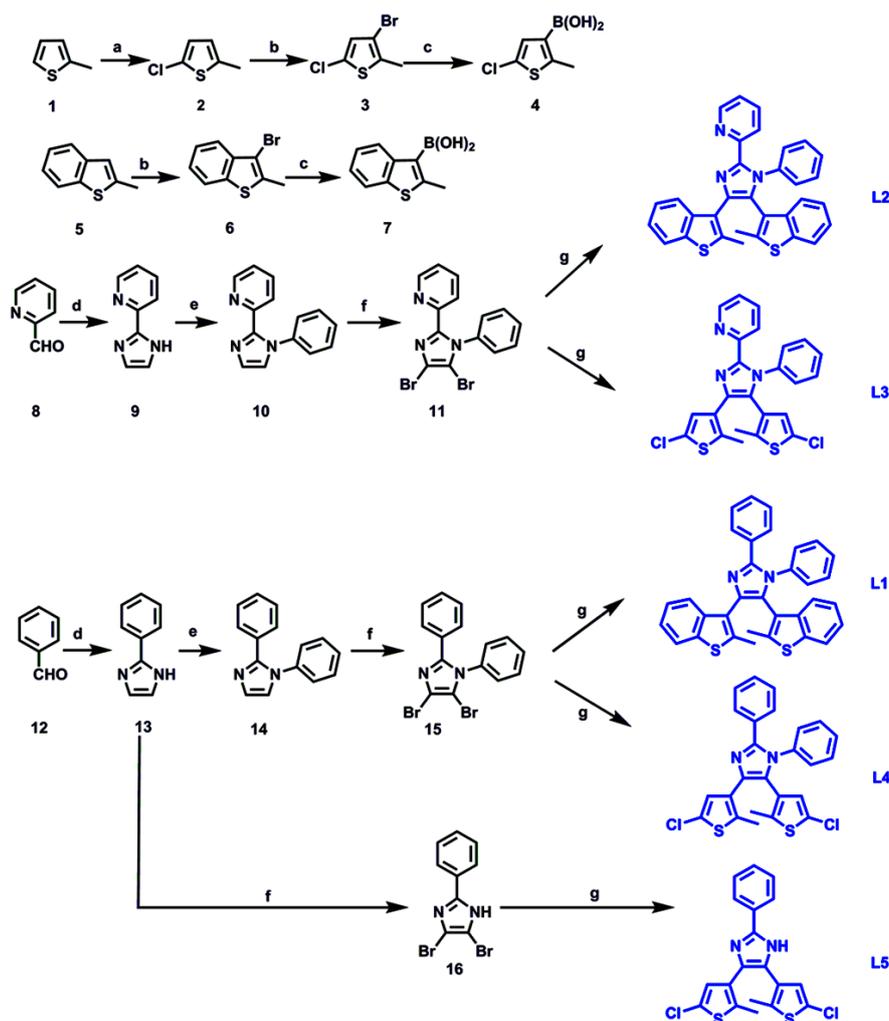
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1. EXPERIMENTAL SECTION

General Procedures. Commercially available reagents and solvents for syntheses were of reagent grade and used without further purification. Solvents for spectral measurements were of spectroscopic grade. ^1H and ^{13}C NMR spectra were measured with an NMR spectrometer (Bruker, Avance 400). Tetramethylsilane was used as an internal standard. Electrospray ion mass spectra (ESI-MS) were performed on a Thermo Exactive Plus mass spectrometer using methanol as mobile phases (Shimadzu, GCMS-QP2010Plus). The closed-ring isomers were isolated from the photostationary solutions using HPLC (Hitachi L-2130 pump system, L-2420 detector, Wakosil 5SIL). UV-vis absorption spectra were measured on an Agilent Cary6000i UV-VIS-NIR spectrophotometer.



Scheme S1. Structure relationships of 2-(2-pyridine)imidazole diarylethene derivatives.

Synthesis and characterization

Compounds **1–9** were prepared according to the literature procedures.^{1, 2, 3,4}

Synthesis of 1-Phenyl-2-(2-pyridyl)imidazole (**10**)

2-(2-pyridyl)imidazole (30 mmol), halogenobenzene (50 mmol), CuI (10 mmol), 1,10-phenanthroline (20 mmol) and Cs₂CO₃ (45 mmol) were dissolved in anhydrous DMF (120 mL) under reflux in an inert atmosphere of argon for 30 h. Then the solvent was removed in vacuum, and the crude product was purified by silica gel column chromatography to give the corresponding product (White solid, 6.3 g, 94%, mp 65–66 °C).

Synthesis of 1-Phenyl-4,5-dibromo-2-(2-pyridyl)imidazole (**11**)

To a solution of 1-aryl-2-(2-pyridyl)imidazole (20 mmol) in CHCl₃ (350 mL), Br₂ (50 mmol) in CHCl₃ (15 mL) was added dropwise with stirring at room temperature. After reaction for 2 h under reflux, the resulting solid was filtered and washed with aqueous NaHSO₃ solution. The residue was purified by column chromatography on silica gel to afford the corresponding product. (White solid, 5.5 g, 72%, mp 115–116 °C; ¹H NMR (400 MHz, *d*₆-DMSO): δ 8.18–8.19 (*m*, 1H), 7.82–7.91 (*m*, 2H), 7.48–7.50 (*m*, 3H), 7.32–7.37 (*m*, 2H), 7.26–7.30 (*m*, 1H); ¹³C NMR (150 MHz, *d*₆-DMSO): δ 148.4, 147.6, 146.1, 144.6, 137.1, 136.9, 136.0, 129.1, 129.0, 128.9, 128.0, 127.8, 123.6, 122.8, 119.6, 117.0, 113.2, 108.9; anal. calcd for C₁₄H₉Br₂N₃: C, 44.36; H, 2.39; N, 11.09. Found: C, 44.21; H, 2.33; N, 11.15).

Synthesis of 2-phenyl-1H-imidazole (**13**)

Benzaldehyde (21 mL, 207 mmol) was dissolved with anhydrous ethanol (20 mL) in the single round bottom flask of 250 mL. Then the round bottom flask was cooled to 0 °C in a cryogenic reactor, adding the mixture of Glyoxal (32 mL, 39% aqueous solution) and anhydrous ethanol (20 mL) while stirred, next the cooled concentrated ammonia water (70 mL) was added to the round bottom, after half an hour of reaction at 0 °C, let the mixture react overnight at room temperature, and then spin the solvent in vacuum. The crude product was purified by silica gel column chromatography (hexane:ethyl acetate = 10:1 f 8:1) to give **13** (11.3 g, 38% yield) as a white solid. mp: ¹H NMR (400 MHz, *d*₆-DMSO): δ 12.56 (*br s*, 1H), 7.97 (*d*, *J* = 4.8 Hz, 2H), 7.43 (*t*, *J* = 5.2 Hz, 2H), 7.32 (*t*, *J* = 4.8 Hz, 1H), 7.15 (*s*, 2H); ¹³C NMR (100 MHz, *d*₆-DMSO): δ 145.6, 130.9, 128.7, 127.9, 124.8.

Synthesis of 1,2-diphenyl-1H-imidazole (14)

13 (5.8 g, 40.3 mmol), bromobenzene (8 mL, 60 mmol), cuprous iodide (2.5 g, 13.1 mmol), 1,10-phenanthroline (5 g, 27.7 mmol) and caesium carbonate (19 g, 58.3 mmol) were added to 250 mL double neck bottom flask, under argon protection, inject dried DMF (100 mL) to the system, then the reaction were heat up overnight at 150 °C. After reaction, naturally cooling to room temperature, vacuum distillation to remove most of the DMF solvent, cooling the residue and adding distilled water (100 mL) to it, and extracted with chloroform, dried with magnesium sulphate and filtered, the organic layer was evaporated in vacuo. The crude product was purified by silica gel column chromatography to give **14** (8.1 g, 92% yield) as a white solid. ¹H NMR (400 MHz, CDCl₃): δ 7.33-7.38 (*m*, 5H), 7.17-7.23 (*m*, 6H), 7.12 (*br s*, 1H); ¹³C NMR (100 MHz, CDCl₃): δ 146.5, 138.4, 130.2, 129.3, 128.9, 128.4, 128.1, 128.0, 127.9, 125.7, 122.7.

Synthesis of 4,5-dibromo-1,2-diphenyl-1H-imidazole (15)

14 (1.3 g, 5.9 mmol), dissolved in chloroform (50 mL) at the single neck round bottom flask of 100 mL. The mixture of Br₂ (0.8 mL, 15.6 mmol) and chloroform (10 mL) was slowly dripped into the round bottom flask through a constant pressure funnel, then the system was heated and refluxed for two hours, and the system was naturally cooled to room temperature. The solution was washed with 10% sodium bisulfite aqueous solution (100 mL), the organic layer was washed with saturated salt water (2×100 mL), and dried with anhydrous magnesium sulphate. The product was obtained by silica gel column chromatography as a white solid. (2 g, 90% yield). ¹H NMR (400 MHz, *d*₆-DMSO): δ 7.52-7.55 (*m*, 3H), 7.40-7.42 (*m*, 2H), 7.25-7.32 (*m*, 5H); ¹³C NMR (100 MHz, *d*₆-DMSO): δ 147.4, 136.2, 129.9, 129.7, 129.0, 128.3, 128.2, 127.8, 117.0, 107.2.

Synthesis of 4,5-dibromo-2-phenyl-1H-imidazole (16)

15 (1.2 g, 8.3 mmol) dissolved in chloroform (50 mL) were sequentially added to a 100 mL single-neck round-bottom flask, a mixture of Br₂ (1 mL, 19.5 mmol) and chloroform (10 mL) was slowly added dropwise to a round bottom flask through a constant-pressure funnel and dropwise over about 30 minutes while stirring, the system was then heat to reflux for two hours. Naturally cooled to room temperature, and 10% aqueous sodium bisulfite solution (100 mL) was added to the solution, and the organic layer was washed and separated with saturated brine (2 × 100 mL), dried with anhydrous magnesium sulphate and filtered, the solvent was removed under vacuum, and the purified product was then isolated by column chromatography on silica gel, and finally 1.7

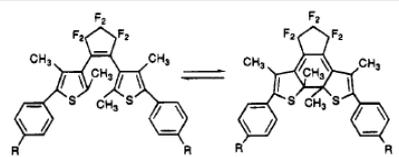
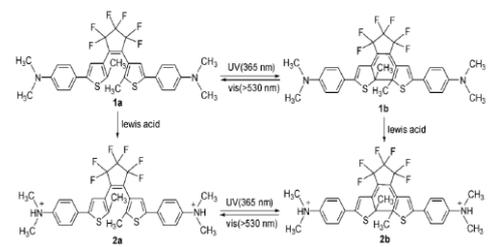
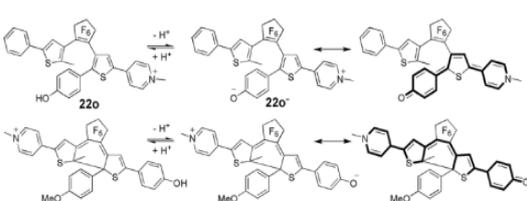
g of a white compound **16** was obtained, with a yield of 68%. ^1H NMR (400 MHz, d_6 -DMSO): δ 13.61 (*br s*, 1H), 7.89 (*d*, $J = 4.8$ Hz, 2H), 7.46 (*t*, $J = 4.8$ Hz, 2H), 7.38 (*t*, $J = 4.8$ Hz, 1H); ^{13}C NMR (100 MHz, d_6 -DMSO): δ 146.9, 129.0, 128.8, 124.7.

References:

- [1] Y.-B. Lee, H.-K. Shim and S.-W. Ko, *Macromol. Rapid Commun.*, 2003, **24**, 522.
 [2] C.-C. Ko, W.-M. Kwok, V. W.-W. Yam and D. L. Phillips, *Chem. Eur. J.*, 2006, **12**, 5840.
 [3] L. N. Lucas, J. J. D. D. Jong, J. H. Esch, R. M. Kellogg and B. L. Feringa, *Eur. J. Org. Chem.*, 2003, 155.
 [4] A. El Yahyaoui, G. F'elix, A. Heynderickx, C. Moustrou and A. Samat, *Tetrahedron*, 2007, **63**, 9482.

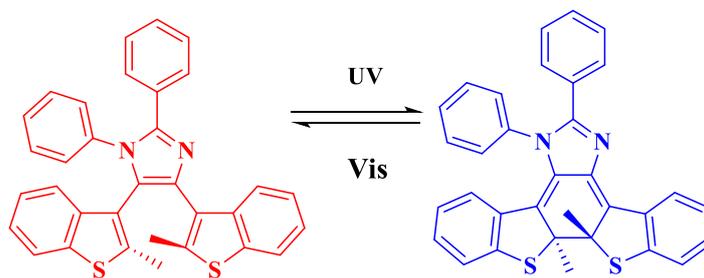
2. RESULTS AND DISCUSSION

Table S1. List of acid-gated diarylethene switches with their response sites in the lower part of the ethene bridge.

Structure	Title	Reference
 <p>2a: R = H 3a: R = OCH₃ 4a: R = N (C₂H₅)₂ 5a: R = CN</p> <p>2b: R = H 3b: R = OCH₃ 4b: R = N (C₂H₅)₂ 5b: R = CN</p>	Photochromism of Dithienylethenes with Electron-Donating Substituents	<i>J. Org. Chem.</i> 1995 , <i>60</i> , 8305-8309
	Lewis Acid Modulation in an Amido-functional Diarylethene and Its Hypsochromism Effect	<i>Chin. J. Chem.</i> , 2006 , <i>24</i> , 1462-1464
	pKa Switching Induced by the Change in the π -Conjugated System Based on Photochromism	<i>Chem. Eur. J.</i> 2006 , <i>12</i> , 4283-4288

<p> $5c-6c$ (P-type) $\xrightarrow{\text{acid}}$ $5c-H^+-6c-H^+$ (T-type) $\xrightarrow{\text{base}}$ $5c-6c$ $t_{5c, 1/2, 25^\circ\text{C}} = 2.7 \text{ yr}$, $t_{6c, 1/2, 25^\circ\text{C}} = 7.9 \text{ yr}$ $t_{5c-H^+, 1/2, 160^\circ\text{C}} = 0.48 \text{ s}$, $t_{6c-H^+, 1/2, 160^\circ\text{C}} = 11 \text{ s}$ </p>	<p>Acid-induced photochromic system switching of diarylethene derivatives between P- and T-types</p>	<p><i>Chem. Commun.</i>, 2007, 1698–1700.</p>
<p> $24o$ (Photoactive) $\xrightarrow{\text{OH}^-}$ $24o^*$ (H-bonding "lock" Photoinactive) $\xrightarrow{\text{H}^+}$ $24o$ </p>	<p>Gated Photochromism and Acidity Photomodulation of a Diacid Dithienylethene Dye</p>	<p><i>Chem. Eur. J.</i> 2012, <i>18</i>, 6568–6575</p>
<p> $10-R$, $20-R$, $30-R$ $\xrightarrow{\text{UV/Vis}}$ $1c-R$, $2c-R$, $3c-R$ 10^+-R, 20^+-R, 30^+-R $\xrightarrow{\text{UV/Vis}}$ $1c^+-R$, $2c^+-R$, $3c^+-R$ </p>	<p>Synthesis and photochromic properties of novel pyridine-containing diarylethenes</p>	<p><i>Dye Pigment</i>, 2012, <i>95</i>, 553–562</p>
<p> IO $\xrightleftharpoons[\text{Vis}]{\text{UV}}$ IC </p>	<p>A new multi-addressable molecular switch based on a photochromic diarylethene with a thieno-imidazole unit</p>	<p><i>Tetrahedron Lett.</i>, 2016, <i>57</i>, 1877–1881</p>
<p> Active photochromism $\xrightarrow{\text{Toluene EXM}}$ Inactive photochromism Active photochromism $\xrightarrow{\text{CH}_3\text{CN}}$ Inactive photochromism </p>	<p>Multi-modulated photochromic behavior of a D-A type dithienylethene</p>	<p><i>Dye Pigment</i>, 2019, <i>162</i>, 712–720</p>
<p> $L1$, $L4$ \rightarrow $L2$, $L5$ $L4$ \rightarrow $L3$ </p>	<p>Our work</p>	

2.1 Effect of Acid on Absorption and Fluorescence Spectra



Scheme S2. Photochromism of **L1** in methanol under different irradiation wavelengths

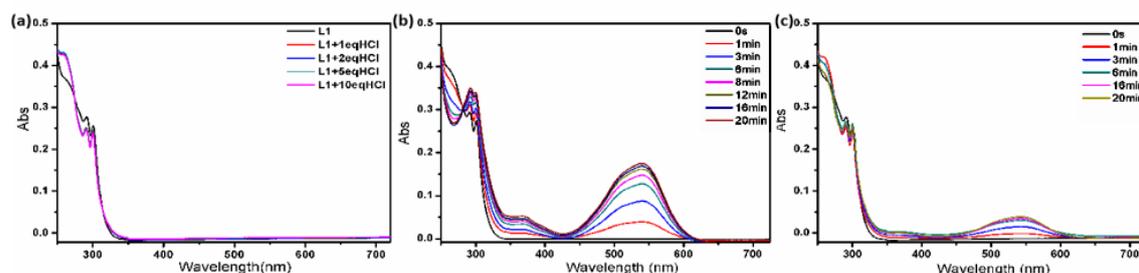
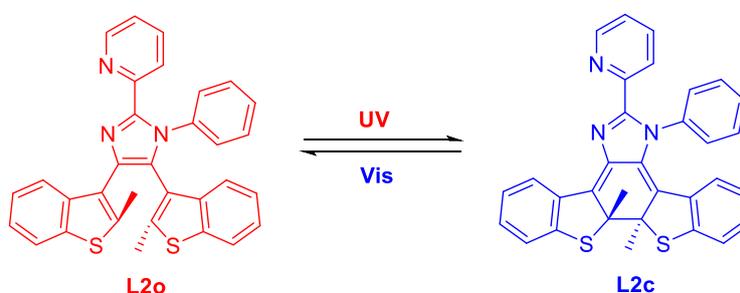


Figure S1. Absorption spectra of **L1** under introduction of 1→2→5→10eq. HCl (a), and the one of **L1** (5.0×10^{-5} M) before (b) and after (c) acidified with 10 eq. HCl in methanol under irradiation with 302 nm light



Scheme S3. Photochromism of **L2** in methanol under different irradiation wavelengths.

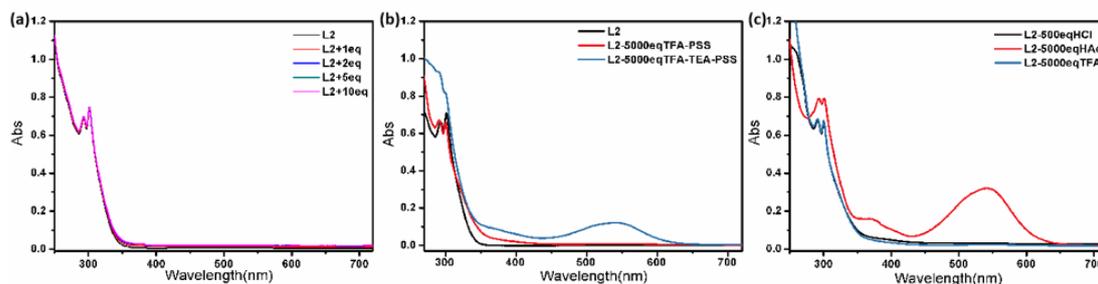
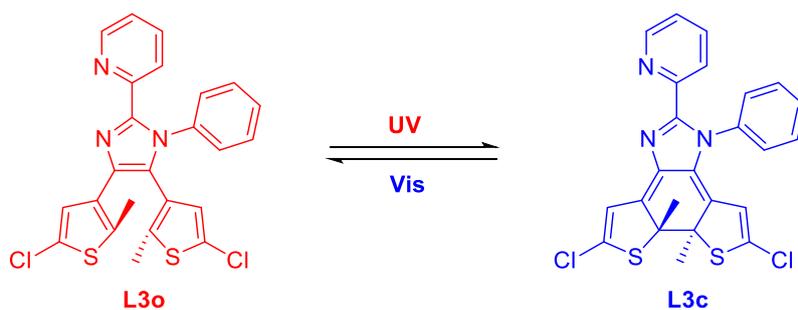


Figure S2. Absorption spectra of **L2** (5.0×10^{-5} M) under introduction of 1→2→5→10eq HCl (a) and the one of **L2** before and after being acidified with 5000eq TFA and neutralized with an equal amount of Et_3N (b), and the one for **L2** acidified by equivalent HCl, TFA and HAC in methanol (c) under irradiation with 302 nm light



Scheme S4. Photochromism of **L3** in methanol under different irradiation wavelengths

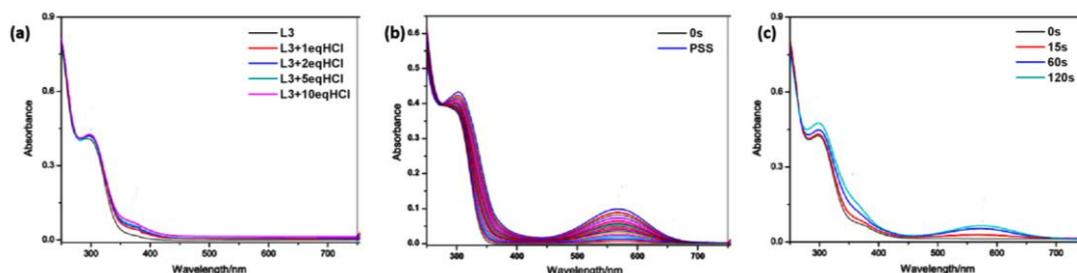
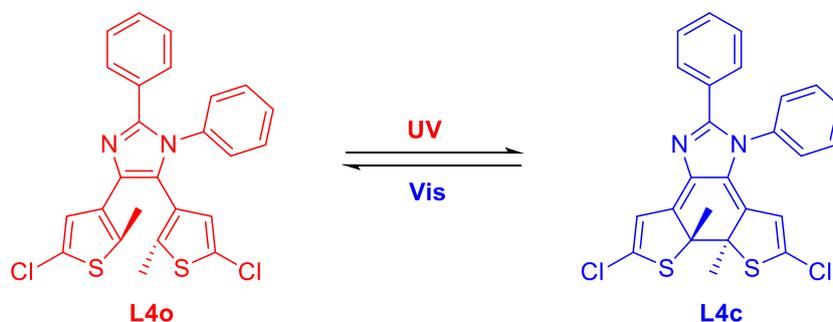


Figure S3. Absorption spectra of **L3** under introduction of 1→2→5→10eq. HCl (a), and the one of **L3** (5.0×10^{-5} M) before (b) and after (c) acidified with 10eq. HCl in methanol under irradiation with 302 nm light



Scheme S5. Photochromism of **L4** in methanol under different irradiation wavelengths

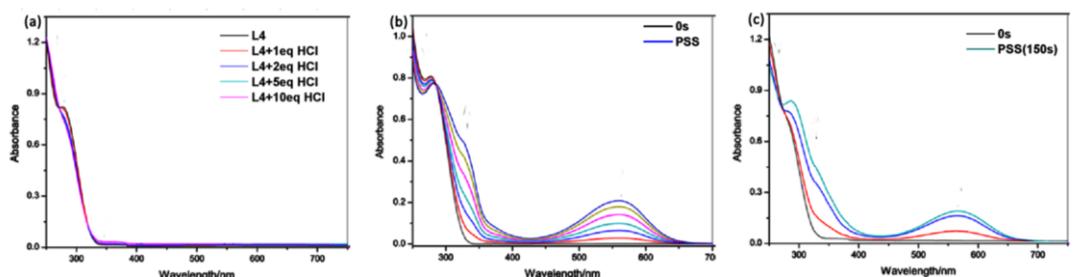
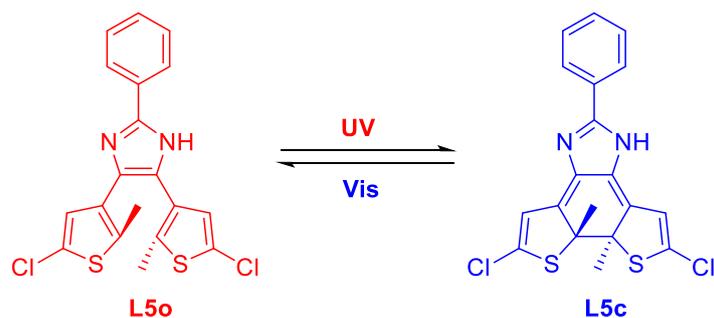


Figure S4. Absorption spectra of **L4** under introduction of 1→2→5→10eq. HCl (a), and the one of **L4** (5.0×10^{-5} M) before (b) and after (c) acidified with 10eq. HCl in methanol under irradiation with 302 nm light



Scheme S6. Photochromism of **L5** in methanol under different irradiation wavelength

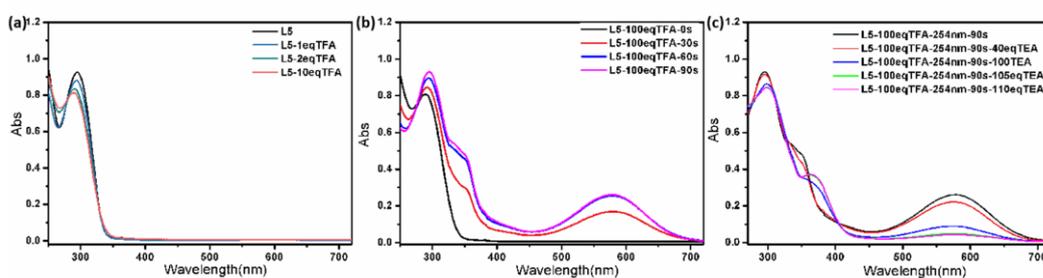


Figure S5. Absorption spectra of **L5** (5.0×10^{-5} M) under introduction of 10→20→50→100eq TFA (a), and the one of **L5** acidified with 100eq TFA before (b) and after (c) neutralization by TEA in methanol under irradiation with 302 nm light

2.2 Thermal Stability

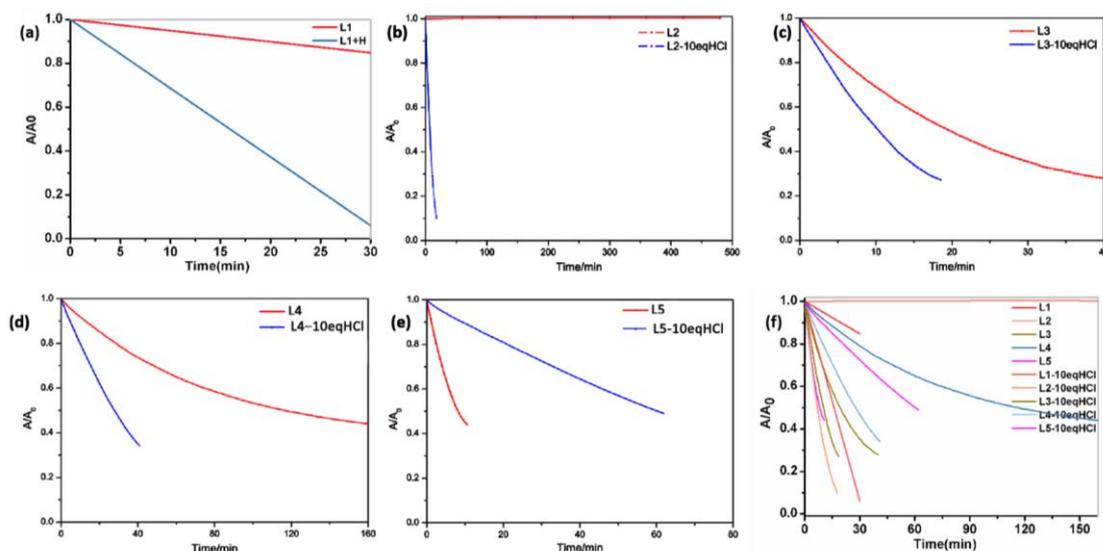


Figure S6. Thermodynamic attenuation curves of methanol solutions (5×10^{-5} mol/L) of compounds **L1-L5** and their acidified states.