Electronic Supplementary Material (ESI) for Photochemical & Photobiological Sciences

Supporting information

Facile synthesis and characterization of new photochromic *trans*-dithienylethenes functionalized with pyridines and fluorenes

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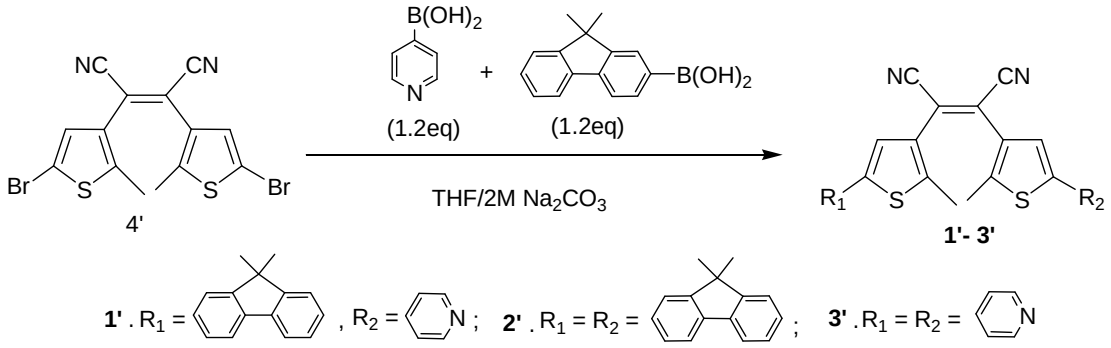
CONTENTS

1.0 The synthesis of *cis*-diarylethenes (1′- 3′)

The synthetic procedure was analogous to the synthesis of **1-3**: Dibromo-dithienylethene **(4′**) (0.8 mmol), pyridyl boronic acid (1.0 mmol), fluorenyl boronic acid (1.0 mmol), $Pd(PPh_3)_4$(0.2 mmol) and Na_2CO_3 (3.18g) were placed in a reaction flask under inert atmosphere. THF (20 ml, degassed) and water (10ml, degassed) were subsequently added, and the solution was stirred under reflux under argon. After 48h, completeness of the reaction was proved by TLC. The mixture was quenched with 10 ml water. The organic layer was separated, and the water phase was extracted further 3 times with ether. The combined organic phases were dried

(Na_2SO_4), filtered, and the solvent was evaporated in vacuum. Three yellow solids were obtained after purification by column chromatography on silica gel.



Scheme 1. The synthetic routes of the compound **1′**, **2′** and **3′.**

2.0 The ^{1}H NMR data of compounds 1′, 2′ and 3′

2.1 Compound 1′:

Cis-Open-ring form, orange solid, δ_H (500MHz, $CDCl_3$, ppm) 1.508 (s, 6H, $-CH_3$), 2.351 (s, 3H, thienyl-CH_3), 2.473 (s, 3H, thienyl-CH_3), 6.942 (s, 1H, thienyl-H), 7.322 (s, 1H, thienyl-H), 7.362-7.344 (m, 2H, Ar-H), 7.381 (s, 1H, Ar-H), 7.431-7.419 (d, 2H, pyridine-H), 7.451-7.460 (d, 2H, Ar-H), 7.773-7.751 (m, 2H, Ar-H), 8.614-8.604 (d, 2H, pyridine-H); TOF-MS(EI70eV) m/z: 539.1.

Cis-Closed-ring form, blue solid, δ_H (500MHz, $CDCl_3$, ppm) 1.427 (s, 6H, $-CH_3$), 2.340 (s, 3H, thienyl-CH_3), 2.370 (s, 3H, thienyl-CH_3), 6.908 (s, 1H, thienyl-H), 7.168 (s, 1H, thienyl-H), 7.308-7.296 (d, 2H, pyridine-H), 7.376-7.366 (m, 2H, Ar-H), 7.434-7.420 (d, 1H, Ar-H) , 7.566-7.550 (d, 1H, Ar-H), 7.644 (s, 1H, Ar-H), 7.784-7.748 (d, 2H, Ar-H), 8.584-8.574 (d, 2H, pyridine-H); TOF-MS(EI70eV) m/z: 539.1.

2.2 Compound 2′:

Cis-Open-ring form, orange solid, δ_H (500MHz, $CDCl_3$, ppm) 1.406 (s, 12H, $-CH_3$), 2.364 (s, 6H, thienyl-CH_3), 6.980 (s, 2H, thienyl-H), 7.346-7.294 (m, 4H, Ar-H), 7.394 (s, 2H, Ar-H), 7.416-7.412 (d, 4H, Ar-H), 7.698-7.662 (d, 4H, Ar-H); TOF-MS (EI70eV) m/z: 654.2 .

Cis-Closed-ring form, blue solid, δ_H (500MHz, $CDCl_3$, ppm) 1.544 (s, 12H,

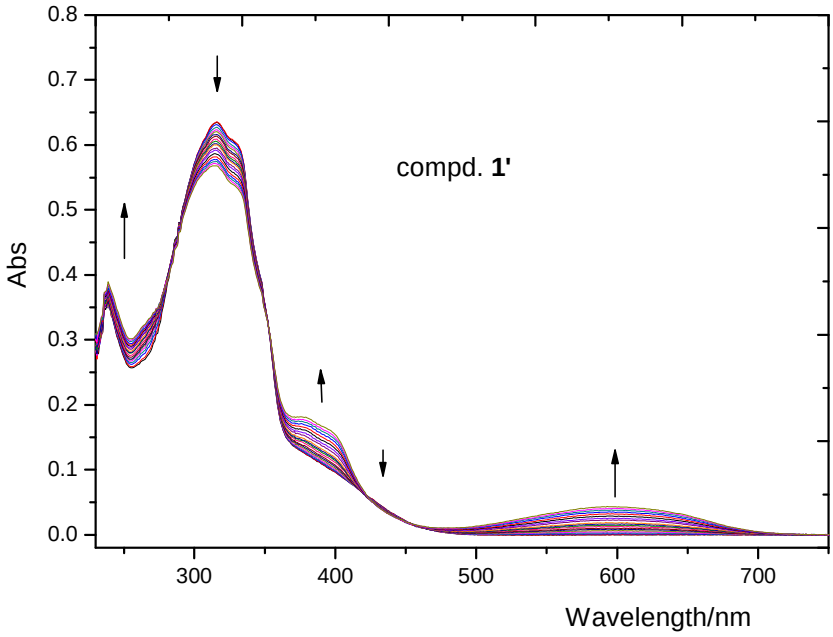
-CH_3), 2.202 (s, 6H, thienyl-CH_3), 6.816 (s, 2H, thienyl-H), 7.416-7.388 (m, 4H, Ar-H), 7.490-7.474 (m, 2H, Ar-H), 7.578-7.560 (d, 2H, Ar-H), 7.652 (s, 2H, Ar-H), 7.784-7.768 (d, 4H, Ar-H); TOF-MS(EI70eV) m/z: 654.2 .

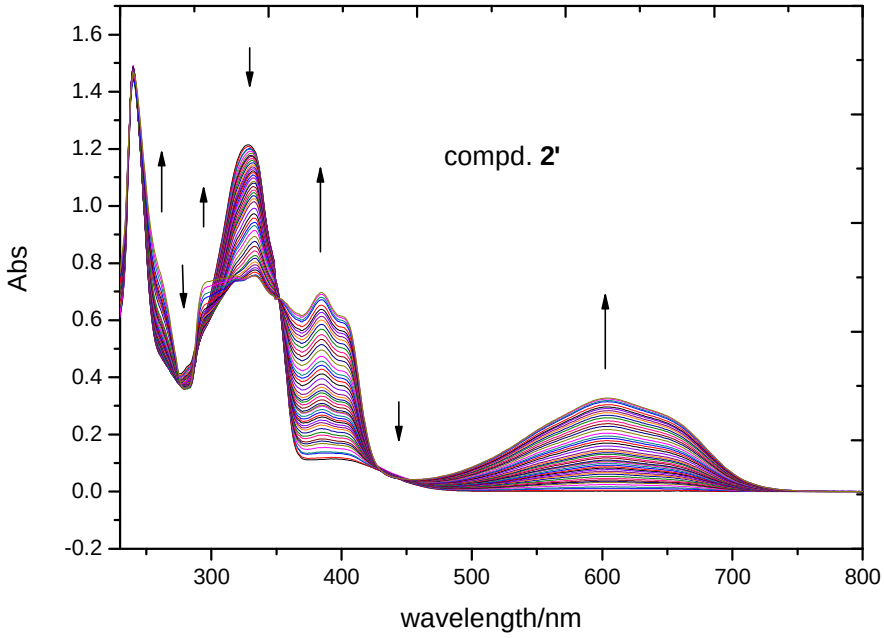
2.3 Compound 3′:

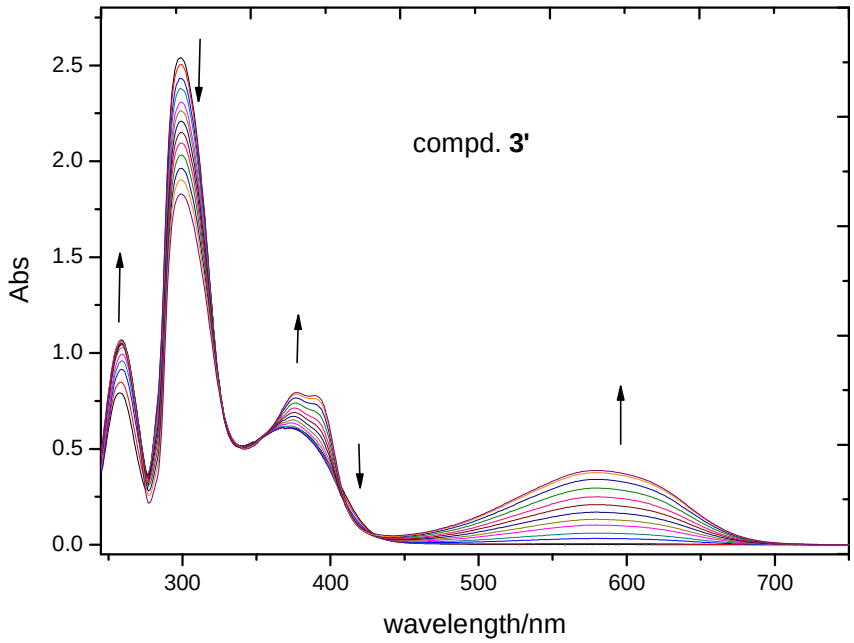
Cis-Open-ring form, yellow solid, δ_H (500MHz, $CDCl_3$, ppm) 2.701 (s, 6H, thienyl-CH_3), 7.457-7.443 (d, 4H, pyridine-H), 7.621 (s, 2H, thienyl-H), 8.647-8.633 (d, 4H, pyridine-H); TOF-MS (EI70eV) m/z: 424.1.

Cis-Closed-ring form, blue solid, δ_H (500MHz, $CDCl_3$, ppm) 2.366 (s, 6H, thienyl-CH_3), 7.085 (s, 2H, thienyl-H), 7.445-7.440 (d, 4H, pyridine-H), 8.589-8.575 (d, 4H, pyridine-H); TOF-MS (EI70eV) m/z: 424.1.

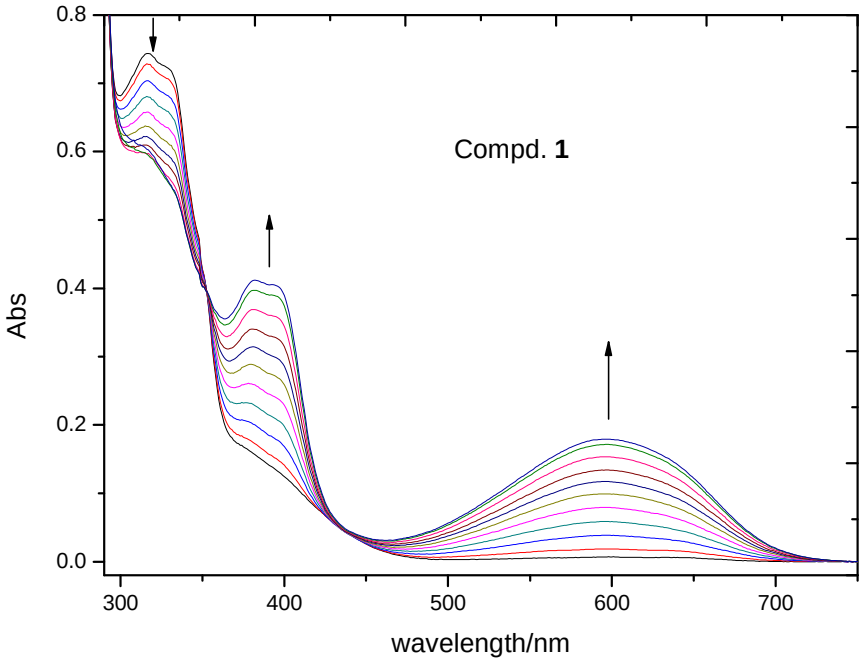
3.0 UV/vis absorption spectra of compounds **1′, 2′** and **3′** in THF solutions and their absorption spectral changes under different irradiation time by light of 254 nm.

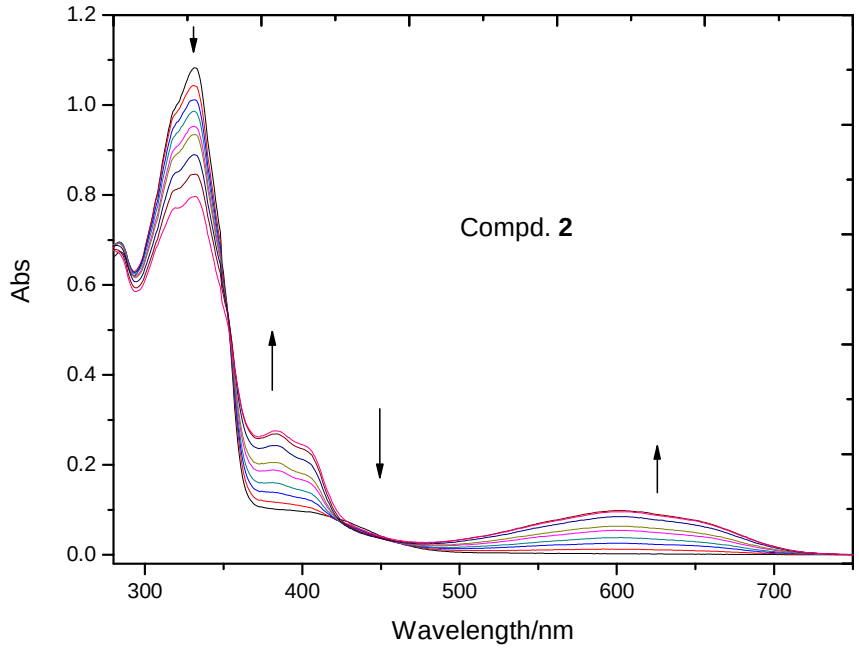






4.0 UV/vis absorption spectra of compounds **1, 2** and **3** and their spectral changes under different irradiation time by light of 254 nm.





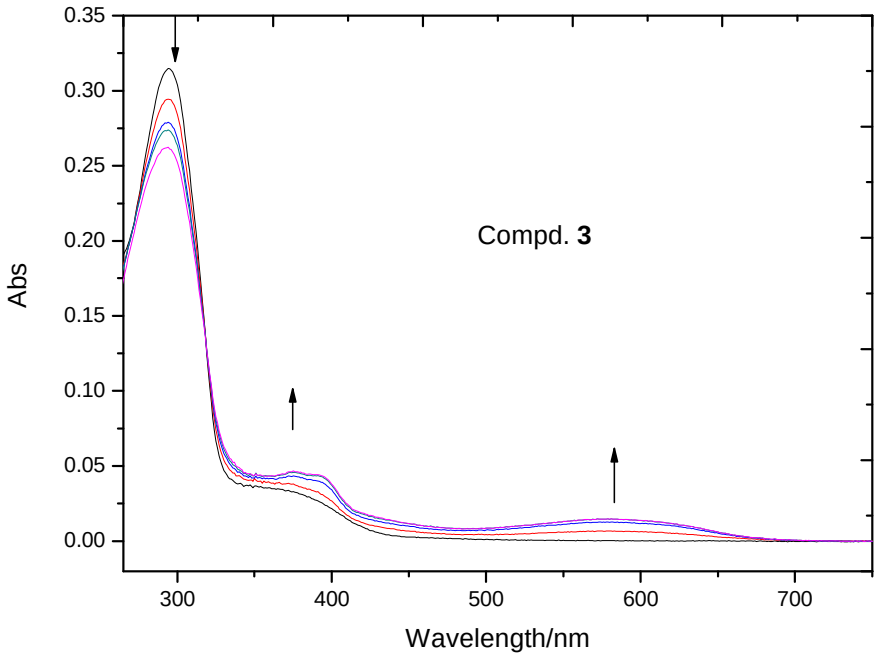
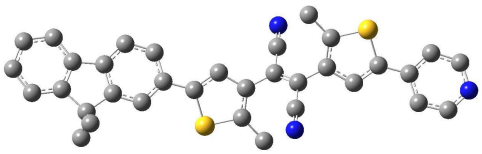
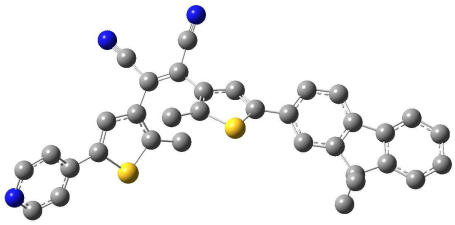
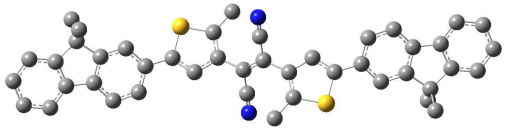
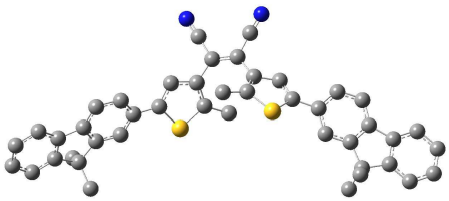


Figure 2. UV/vis absorption spectra of compounds **1**, **2** and **3** in THF (2.0×10^{-5}M) and the changes in absorption of the compounds under different irradiation time by light of 254 nm. The time they reach photostationary state was about 33, 25 and 35 minutes, respectively.

5.0 The optimized conformations of the *trans*-isomers (**1-3)** and their corresponding *cis*-isomers (**1′-3′**) (the H atoms were omitted)

1(*trans*)	**1’**(*cis*)
	
2 (*trans*)	2’ (*cis*)
	
3(*trans*)	3’(*cis*)