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 ($1'$-$3'$)
2.0 The $^1$H NMR data of compounds $1'$, $2'$ and $3'$
3.0 UV/vis absorption spectra of compound $1'$, $2'$ and $3'$ in THF and their absorption spectral changes under different irradiation time by light of 254 nm.
4.0 UV/vis absorption spectra of compound $1$, $2$ and $3$ and their spectral changes under different irradiation time by light of 254 nm.
5.0 The optimized conformations of the trans-isomers (1-3) and their corresponding cis-isomers ($1'$-$3'$)

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$_2$CO$_3$ (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$_2$SO$_4$), filtered, and the solvent was evaporated in vacuum. Three yellow solids were obtained after purification by column chromatography on silica gel.

\[
\text{NC} = \text{CN} \quad \text{B(OH)$_2$} \quad \text{THF/2M Na$_2$CO$_3$}
\]

![Scheme 1. The synthetic routes of the compound 1', 2' and 3'.](image)

### 2.0 The $^1$H NMR data of compounds 1', 2' and 3'

#### 2.1 Compound 1':

**Cis-Open-ring form**, orange solid, $\delta_H$ (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, $\delta_H$ (500MHz, CDCl$_3$, ppm) 1.427 (s, 6H, -CH$_3$), 2.340 (s, 3H, thienyl-CH$_3$), 2.370 (s, 3H, thienyl-CH$_3$), 6.848 (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), 7.566-7.500 (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, $\delta_H$ (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, $\delta_H$ (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, $\delta_H$ (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, $\delta_H$ (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.
**Compd. 1**

**Compd. 2**
Figure 2. UV/vis absorption spectra of compounds 1, 2 and 3 in THF (2.0×10⁻⁵M) 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)

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<th>1’ (cis)</th>
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