Research article

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# Design, syntheses and photochromic properties of dithienylcyclopentene optical molecular switches

Chuanming Yu[a], Bingcheng Hu[a]*, Cheng Liu[a] and Jiting Li[a]

**A kind of basal diarylethene through an easy synthetic procedure was synthesized and characterized, and a Suzuki coupling reaction was frequently operated to obtain the diarylethenes derivatives with some vivid functional groups like bromo, amido and pyridine. Two methods for derivatives of these switches contain porphyrins were described. All of their spectroscopic and photochromic properties were studied and intercompared. It is indicated that the difference in electron densities of the π-conjugated system of the closed forms has effects upon the absorption maxima in visible region of UV–Vis spectra. Dithienylcyclopentenes linked to porphyrins could emit luminescence substantially that display potentials to be used in the applications of nondestructive readout upon binary data storage and smart materials.**

**Keywords:** photochromism; diarylethene; UV–Vis spectroscopy; photo-conversion

## INTRODUCTION

Organic photochromic molecules are playing an increasing vital role in optical electronic devices,[1,2] such as molecular switches,[3] molecular probes[4] and optical information storage[5] because of their photochromic reversibility.[6] Nondestructive readout is one of the most attractive aims[7] in optical materials for their applications in photo memory area.[8] The fluorescent tuning with fast response times and high sensitivity is a convenient mean of modulating the variable properties.[9]

Photochromism is defined as reversible transformation of a molecule between two isomers having different absorption spectra under the appropriate light.[10] Several kinds of photochromic compounds have been reported in the past decades, including diarylethenes,[11] spiropyrans,[12] fulguides[13] stilbenes,[14] azobenzenes,[15] nitrones,[16] naphthopyrans,[17] spirooxazines,[18] quinines[19] and viologens[20] etc. These compounds characteristically exhibit two different chemical forms (open-ring form and closed-ring form) which would transformed from one to the other upon irradiation with light of corresponding wavelength. Among many known photochromic systems, diarylethenes exhibited the most favorable thermal and optical stability.

Recently we synthesized a series of diarylethenes through a rather easy synthetic procedure[21] wherein than perfluorocyclopentene derivatives are prepared. In this paper we present the full details on the synthesis and derivatization of these dithienylcyclopentene through a Suzuki coupling reaction. We also report methods for derivatization of these switches with porphyrins, and conclude with preliminary data on the photochromic properties of these compounds.

## RESULTS AND DISCUSSION

### Synthesis

The synthetic approach to functionalized dithienylcyclopentenes is shown in **Scheme** 1. In this route, the central cycloalkene ring is formed from the halogenated cycloalkene (always contain 4, 5 or 6 carbons) by a Suzuki–Miyaura reaction. Another useful method to form this ring in the last procedure is the ring closure reaction of a diketone by a McMurry reaction which is exhibited in **Scheme** 2. Thus, the generation of substituted cycloalkene can be achieved either through a ring-closure by a McMurry reaction or directly get from a cycloalkene by the Suzuki coupled reaction. The McMurry reaction was preferred, because the previous materials were not obtained so conveniently in the Suzuki coupled reaction, and the McMurry reaction can be carried out in two successful steps in a one-pot procedure.

The key intermediates of the McMurry reaction shown in **Scheme** 2 are 1,5-dithienyl-1,5-diketones **3**, **7** and **9**. The most direct method for the preparation of thienyl diketones is a Friedel–Crafts acylation reaction of the corresponding aryl compounds with a glutaryl chloride. The 2- and 5-positions of thiophene should be substituted in view of that the most active positions in the thiophene molecule are the 2- and 5-positions, but in the synthetic route shown in **Scheme** 2 the acylation must occur at the 3-position. Thus, the chlorination reaction of **1** with N-chlorosuccinimide was operated in THF superseding traditional benzene because of its better solubleness and hypotoxicity. The Friedel–Crafts acylation of **3** and **6** with glutaryl dichloride in $CH_2Cl_2$ using $AlCl_3$ as a Lewis acid gave the oily reaction products, from which the desired 1,5-diketone **3** and **7** could be separated by column chromatography with petroleum-ether (PE) in both about 40% yield. Ring closure of **3**, **7** and **9** by a McMurry reaction with Zn and $TiCl_4$ in THF at 65 °C gave the desired 1,5-dithienylcyclopentenes **4**, **8** and **10** in 56%, 12% and 32% yield after purification using column chromatography with PE.

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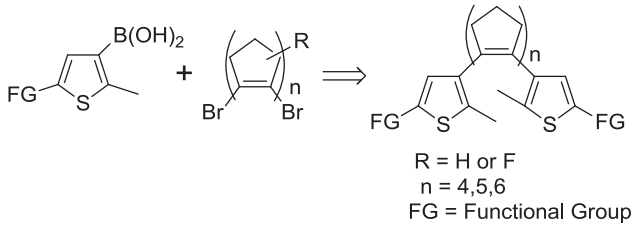
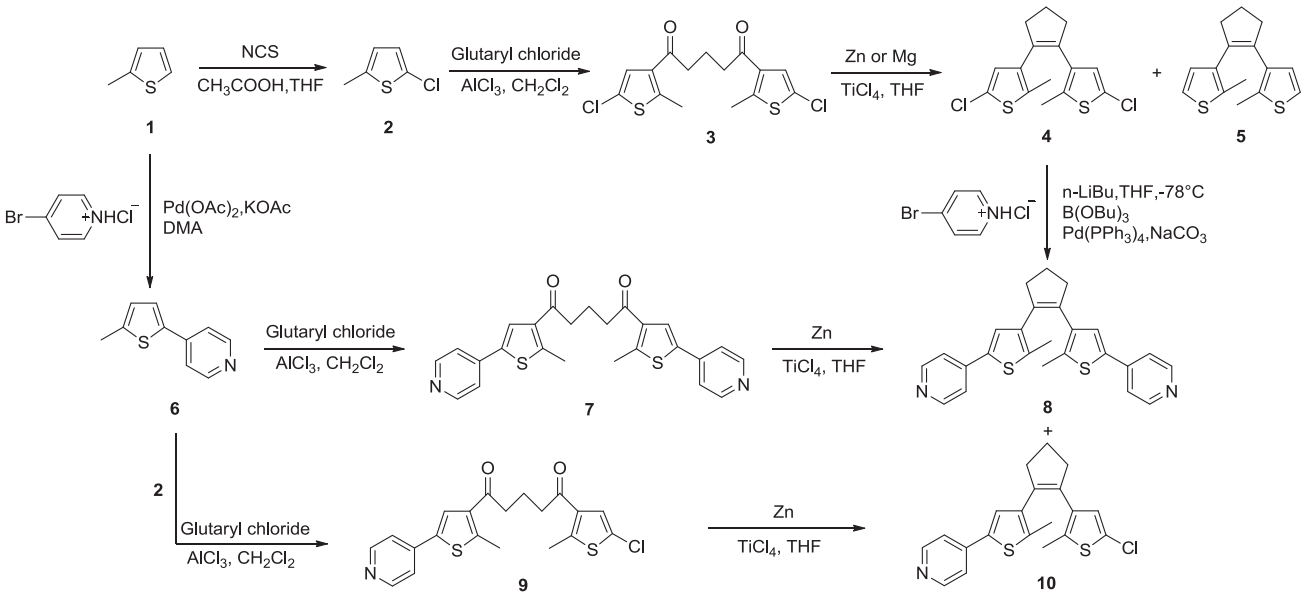



**Scheme 1**. Synthesis of dithienylethenes

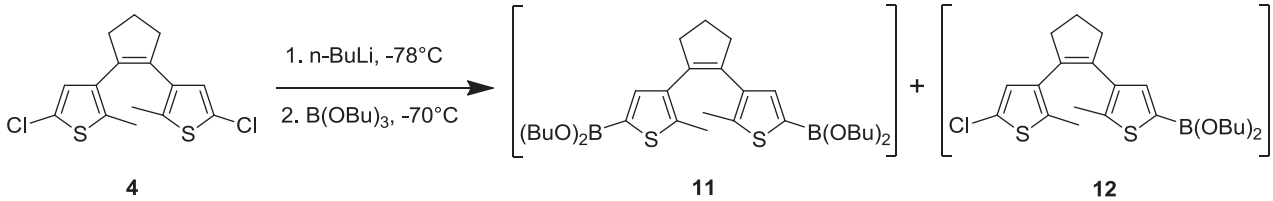
The second approach of 1,5-dithienylcyclopentenes **8** and **10** shown in **Scheme** 2 starting from compound **4** can be more readily functionalized by a Suzuki coupled reaction, because the synthesis of compound **4** can be performed on a large scale and in a satisfactory yield. The Suzuki coupled reaction was carried out with *n*-BuLi in anhydrous THF at −78 °C under nitrogen atmosphere, and the chlorine was substituted by lithium which can be further replaced by $-B(OBu)_2$ with tributyl borate at −70 °C to afford the intermediates **11** or **12** according to the proportion of feeding materials. The intermediates **11** and **12** can be used directly in the next Suzuki coupled reaction with 4-bromopyridinium chloride as feeding materials, and $Pd(PPh_3)_4$, $Na_2CO_3$ were added as catalysts to gave the desire product 1,5-bis(2-methyl-5-pyridylthiophene)-cyclopentene **8** and 1-(2-methyl-5-pyridylthiophene)-5-(2-methyl-5-chlothiophene)-cyclopentene **10**.

Halogens are very versatile functional groups, and bromine always exhibit better react activity than chlorine in the Suzuki coupled reaction. So we attempted to synthesize the 1,5-bis(2-methyl-5-bromothiophene)-cyclopentene **17** followed the synthetic routes in **Scheme** 3 starting from 2-bromo-5-methylthiophene **13** which is brominated from 2-methylthiophene **1** with NBS. The next Friedel–Crafts acylation of **13** with glutaryl chloride and $AlCl_3$ was carried out in $CH_2Cl_2$ to afford an oleosus bar, in which the desired product **16** was unfortunately not been detected, however the 1,5-diketone **14** and **15** were isolated by column chromatography with PE in 28% and 21% yield. Because of the lack of 1,5-diketone **16**, another approach was performed in accordance with **Scheme** 4. Before the addition of bromine, the 1,5-diketone **4** was lithiated with *n*-BuLi in THF at −78 °C to gave the product **17**.

The photochromic switch **4** can easily be functionalized in many different ways. Compound **4** can successfully achieve a lithium exchange at a low temperature (**Scheme** 4) thus providing an available bridge for the introduction of functionality. The Suzuki coupled reaction provides a productive way to obtain many functional photochromic switches. The synthetic routes shown in **Scheme** 5 exhibited the practicability of Suzuki coupled reaction on 1,5-dithienylcyclopentenes ulteriorly. The photochromic switches **18** and **19** were easily obtained in 68% and 71% yield by employing Suzuki coupled reaction with the intermediates **11**, **12** and paradibromobenzene (**PDBB**) in THF; the $Pd(PPh_3)_4$ and $Na_2CO_3$ were added as the catalysts. The synthesis of target product **18** and **19** can be severally achieved by controlling the different molar ratios when feeding materials. So we attempted to synthesize the photochromic switch **20** as the same method, but no desired diarylethene could be achieved.




**Scheme 2**. Synthesis of dithienycyclopentenes




**Scheme 3**. Boron esterification for dichlorothienycyclopentene

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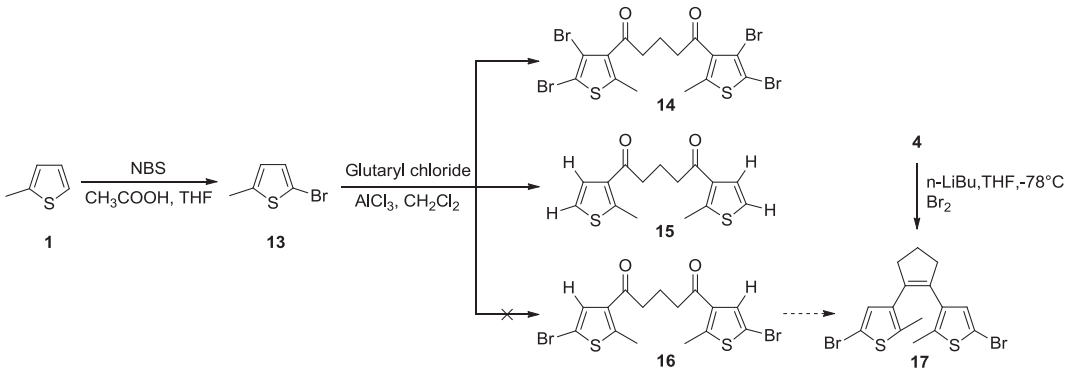
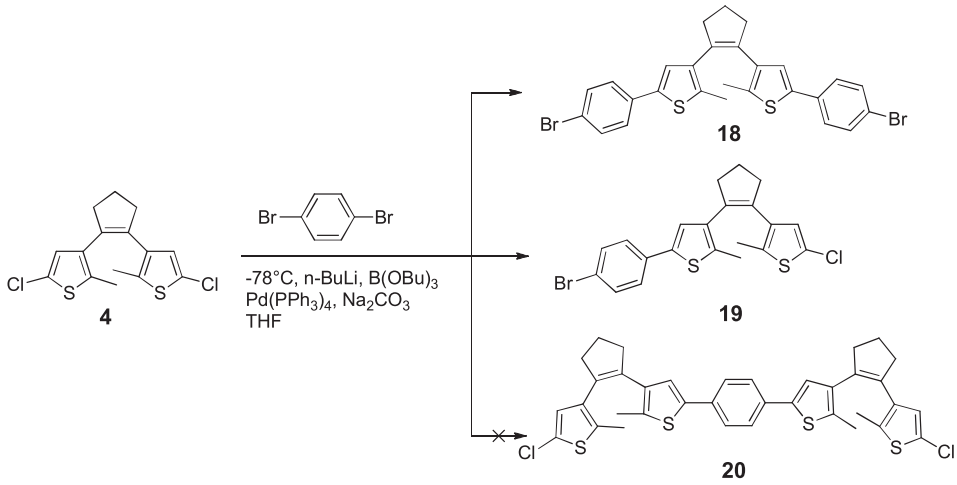
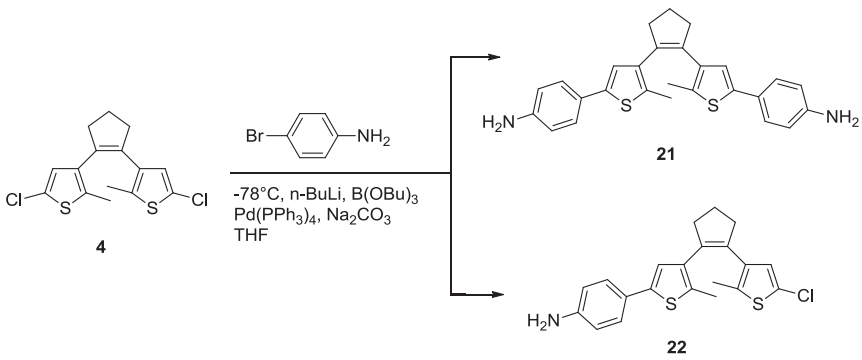


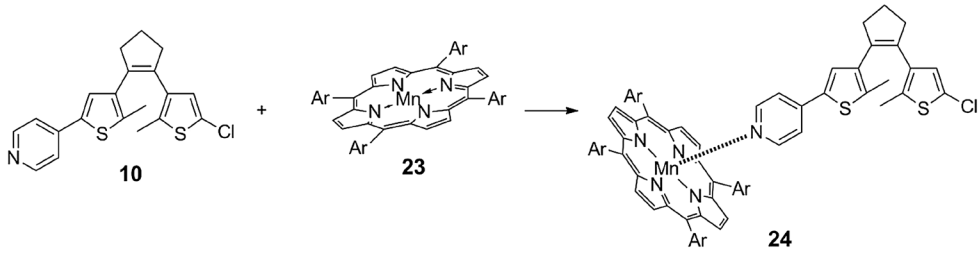

**Scheme 4**. Tentative synthetic routes for dibromothienycyclopentene




**Scheme 5**. Synthesis of dibromothienycyclopentenes




**Scheme 6**. Synthesis of dianilinothienycyclopentenes




**Scheme 7**. Synthesis of dithienycyclopentenes contain pyridine complexing with tetraphenylporphyrin

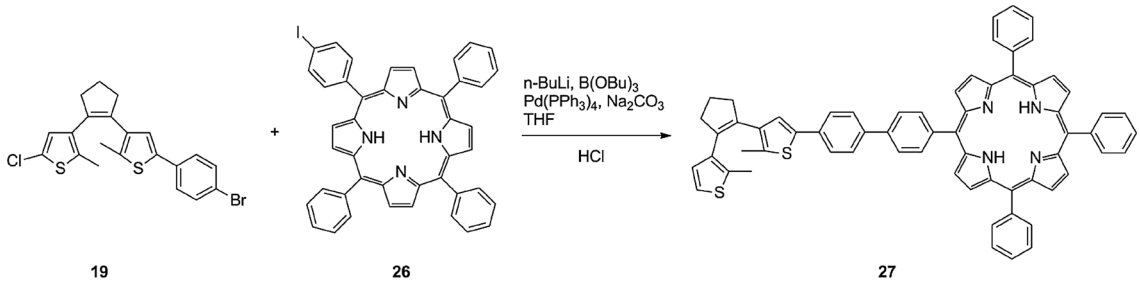
The photochromic switches **18** and **19** were predicted to provide a versatile handle for more functional groups than diarylethene **4**.

The amino is an active chemical group, on which many reactions occur with many common chemicals such as inorganic acids, carboxylic acid, acyl halide, ketone, nitrite, etc., so we attempt to join an amino to the molecular switch. The photochromic switches **21** and **22** were obtained as the above mentioned method (**Scheme** 6). This switch is expected to react with many functional groups to generate desirable compounds.

In order to investigate the availability of these photochromic switches as bridges that can link to functional compounds. The chemicals **24** was obtained through the treatment of **10** with equal molar equivalent of **23** in $CH_2Cl_2$ followed by precipitation with hexane in **Scheme** 7 and detected in the mass spectroscopy. The photoswitch **27** was synthesized through the Suzuki reaction of **19** and iodicporphyrin (**Scheme** 8).

## Photochromic behavior

The photochromic behavior of compounds induced by photoirradiation in dichloromethane was measured at room temperature. The diarylethene underwent photoisomerization between ring-open isomer and ring-closed isomer upon alternating irradiation with UV light and visible light (**Fig**. 1). The presence of isosbestic points in all cases indicates clean photochemical transformations occur. **Figures** 2–6 respectively show the changes of UV–Vis absorption of **10**, **19**, **24** and **27** of solution in $CH_2Cl_2$ upon the appropriate UV light. Table 1 shows the absorption maxima for the




19 26 27

**Scheme 8**. Synthesis of 1-[2-methyl-5-(4-tetraphenylporphyrinphenyl)-3-thienyl)-2-[2-methyl-3-thienyl]cyclopentene

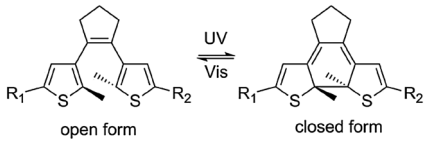



**Figure 1**. Photochemical reactions of dithienylcyclopentene with irradiation of UV and visible light

open and closed forms of a number of the synthesized derivatives

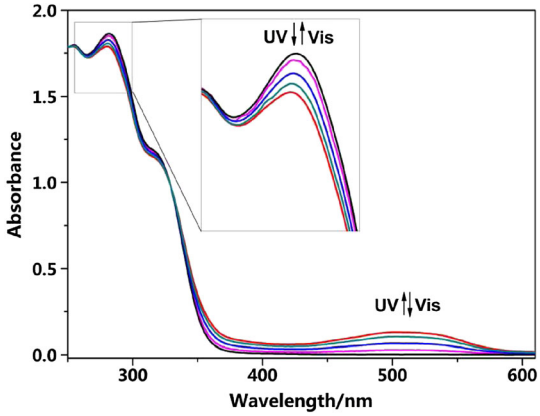



**Figure 2**. Changes in UV–Vis absorption spectra of a $CH_2Cl_2$ solution of **10** upon irradiation with 254-nm light. Irradiation periods are 0, 30, 60, 100 and 150 s

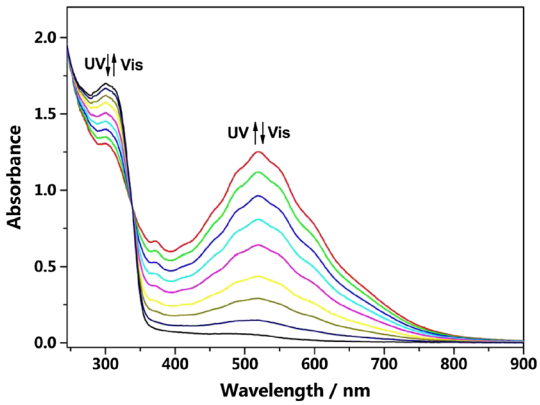



**Figure 3**. Changes in UV–Vis absorption spectra of a $CH_2Cl_2$ solution of **19** upon irradiation with 254-nm light. Irradiation periods are 0, 10, 20, 30, 50, 70, 100, 130 and 160 s

described in this article and their corresponding color. The absorption maxima of the open forms of **10** and **19** both appear at wavelengths < 305 nm, but new absorption of the switches with

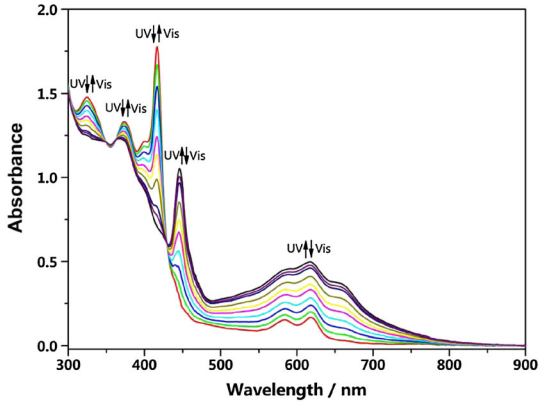



**Figure 4**. Changes in UV–Vis absorption spectra of a $CH_2Cl_2$ solution of **24** upon irradiation with 365-nm light. Irradiation periods are 0, 10, 20, 40, 60, 80, 100, 120, 150 and 180 s

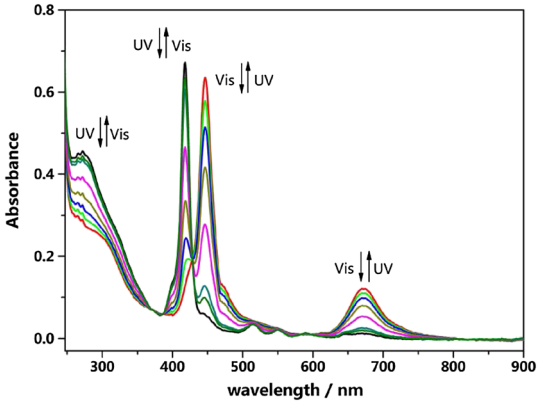



**Figure 5**. Changes in UV–Vis absorption spectra of a $CH_2Cl_2$ solution of **27** upon irradiation with 282-nm light. Irradiation periods are 0, 10, 20, 40, 60, 80, 100 and 150 s

functional groups which possess π-conjugation electron arise at ~417 nm. The new absorption is the Soret band of porphyrin and always occurs nearby. Upon irradiation at wavelength of their absorption maxima, the solutions of compounds **10** and **19** turned to purple, and new absorption bands appear in the visible region at 500–520 nm.

As shown in **Fig**. 4, the absorption maximum of the open form of compound **24** in dichloromethane was observed at 325 nm and 373 nm. Within the first 10 s of irradiation with the UV light, absorption band centered between 500 and 700 nm appears as the photochromic compound is converted from the light-colored ring-open form to the linearly π-conjugated dark-colored ring-closed form. The absorption maxima of compound **24** occurs at a longer wavelength and the band is

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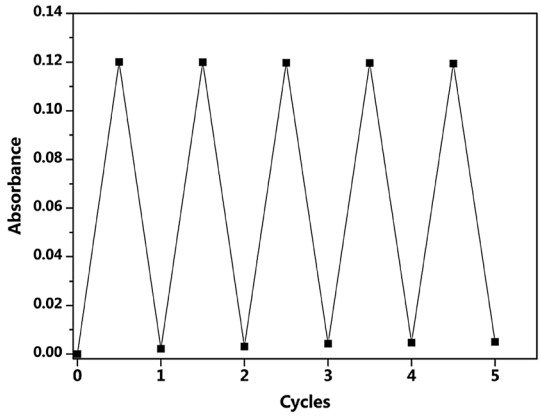


**Figure 6**. Cycling between the open and closed forms of the **27** by repetitive irradiation at $\lambda = 282$ nm and visible light at 20 °C in $CH_2Cl_2$. The ordinate shows the formation of the closed form as monitored by the absorbance at 674 nm

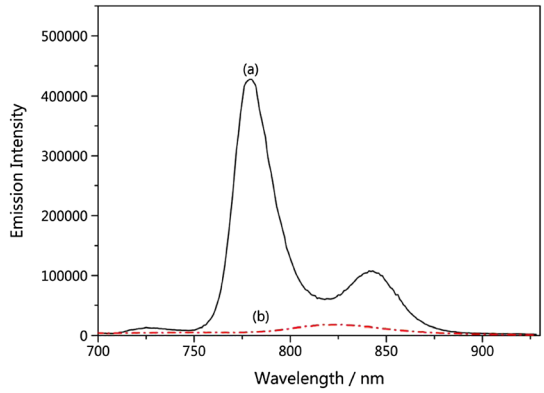


**Figure 7**. Emission spectra of photochrome **24** in solutions of $CH_2Cl_2$ (a) open form and (b) closed form. $\lambda_{ex} = 490$ nm, $\lambda_{em} = 779$, 841 nm

broader and arranges from 490 to 800 nm compared to compound **10**. Compound **27** shows a similar UV–Vis absorption as shown in **Fig**. 5. Furthermore, it has a short region arranged from 530 to 610 nm with very low absorption which could provide a potential nondestructive readout at this region in application of data storage.

Another interesting phenomenon is that the Soret band of **24** red shifts from 417 nm to 446 nm with the irradiation of the UV light. And the similar redshift occurs on **27** and turned from 418 nm to 447 nm (**Fig**. 5). The reason may be that the form of ring-closed isomer could increase the electronic density of the porphyrin and the transition energy reduces and results in redshift.

Irradiation of solutions of **10**, **19**, **24** and **27** in $CH_2Cl_2$ with visible light causes the absorption bands in the visible region to disappear and the absorption band in the UV region between 250 and 340 nm was restored. Apparently, photochemical switching between the ring-open and ring-closed form is reversible. Especially the photochromic switching of compounds **24** and **27** is excellent, and at least five photochemical switching cycles between the open and closed form can be performed without any obvious sign of degradation (**Fig**. 6). The added porphyrin group possesses obvious luminescence which could be used to read out the state of photoswitches.

Compound **24**(open) phosphoresces at 779 nm and 841 nm when induced with the light ($\lambda = 490$ nm) which has little effect on the photochemical interconversion of **24** in either direction. Accordingly, the ring-closed isomeric form luminesce quenched while excited with this light (**Fig**. 7). Hence, a nondestructive readout method would be provided refer to above. Moreover, the emission intensity could be modulated by actinic reaction between the open and closed isomers.

In summary, a practical synthetic route to diarylethene **4** has been described. The Suzuki coupling reaction can be repeatedly performed to add some functional groups to the diarylethene. A variety of dithienylcyclopentene-based compounds were obtained to be used as molecure switches. The porphyrin-based diarylethenes **24** and **27** show excellent switching behavior and little fatigue and considerable luminescence. Furthermore, it is foreseen that these favorable properties together with advanced electron devices will mightily accelerate the application in photo-information storage with high-speed and high-capacity and smart materials.

## EXPERIMENTAL SECTION

Chemicals and solvents are purchased in Aladdin or Energy-chemical. All solvents used in the reactions were distilled freshly from appropriate drying agents before use. 1H NMR spectra were recorded on a Bruker AVIII 300 or 500-MHz spectrometer with $CDCl_3$ or $d_6$-DMSO as the solvents and TMS as the internal standard. Chemical shifts are reported in $\delta$ (parts per million) values. Mass spectra (MS) were recorded using a TSQ Quantum-HPLC/MS/MS (Thermo, USA). UV–Visible spectra were measured by Shimadzu UV-1800 spectrophotometer. The irradiation intensity of UV light is 100 $\mu W/cm^2$ (365 nm) and 125 $\mu W/cm^2$ (254 nm). The UV light (282 nm) comes from a Ultraviolet High Pressure Mercury Lamps (UV LAMP, 500 $\mu W/cm^2$) with a specific filter. The Visible light comes from the sunshine with a barrier filter, and the intensity is 320 $\mu W/cm^2$.

### 2-Chloro-5-methylthiophene (2)

2-Methylthiophene (10 ml, 0.10 mol) and N-chlorosuccinimide (13.3 g, 0.1 mol) were added to a stirred solution of THF (30 ml) and acetic acid (30 ml). The suspension was stirred for 30 min

**Table 1.** UV–Vis absorption data of the open and closed forms of several compounds

| Compounds | $\lambda_{max}$/nm | | Isobestic points | Color of the | |
|---|---|---|---|---|---|
| | Ring-open form | Ring-closed form | | Ring-open form | Ring-closed form |
| **10** | 282 | 505 | 329 | Colorless | Purple |
| **19** | 301 | 519 | 338 | Colorless | Purple |
| **24** | 325, 373, 417 | 446, 617 | 429, 349, 362 | Light red | Dark magenta |
| **27** | 272, 418 | 446, 672 | 370–380, 530–600 | Light red | Dark magenta |

at room temperature, then, after 1 h of heating at reflux, the cooled mixture was poured into a 3 M NaOH solution (30 ml). The organic phase was washed with a 3 M NaOH solution (3 × 300 ml), dried ($Na_2SO_4$), filtered and the solvent evaporated in vacuo to yield a slightly yellow liquid. Purification of the product by vacuum distillation (19 Torr, 55 °C) afforded a colorless liquid(11.7 g, 88%). b.p. 55 °C(19 Torr). $^1$H NMR(300 M Hz, $CDCl_3$): δ = 2.41 (s 3H), 6.52–6.53 (d, 1H), 6.68, 6.69 (d, 1H) ppm. MS (EI): *m/z* = 131 [$M^+$].

### 1,5-Bis(5-chloro-2-methylthien-3-yl)pentane-1,5-dione (3)

Under fast stirring of an ice-cooled solution of dry $AlCl_3$ powder (4.61 g, 34.5 mmol) in dichloromethane (50 ml), glutaryl dichloride (2.05 g, 11.5 mmol) and **2** (3.06 g, 23.4 mmol) were successively dropwise added. After addition, the reaction mixture was stirred for 3 h at room temperature, and the color turned to dark red. Then ice-cold mixture solution of conc HCl (20 ml) and ice (30 g) were carefully added to the reaction mixture, and the water layer was extracted with dichloromethane (3 × 20 ml). The combined organic phases were washed with saturated aqueous solution of $NaHCO_3$, water and NaCl saturated solution, dried ($MgSO_4$), filtered and the solvent was evaporated in vacuo to yield a brown tar (3.37 g, 80%). This tar can be purified by flash chromatography (PE:ethyl acetate = 10:1) to provide a white solid (2.85 g, 68%), m.p. 82–85 °C. For further reaction, it is, however, not necessary to purify this tar. 1H NMR (500 MHz, $CDCl_3$): δ 2.03–2.09 (m, 2 H), 2.66 (s, 6 H), 2.85–2.88 (t, 2 H), 7.19 (s, 2 H) ppm. MS (EI): *m/z* = 359.99 [$M^+$].

### 1,2-Bis(2-methyl-5-chloro-3-thienyl)cyclopentene (4)

A mixture of $TiCl_4$ (0.8 ml, 5.2 mmol), Zn dust (0.44 g, 6.9 mmol) and THF (25 ml) was stirred under nitrogen at reflux temperature for 1 h. The mixture was cooled to room temperature, and **3** (1.00 g, 2.78 mmol) was added. The mixture was refluxed for 2 h, subsequently quenched with 10% aq. $K_2CO_3$ (25 ml) and extracted with dichloromethane (3× 20 ml), the combined organic layers were washed with water (50 ml), dried with anhydrous $MgSO_4$ and the solvent was removed in vacuo. The compound was purified by column chromatography (PE) to yield (0.46 g, 50%) of a white solid. m.p. 76.1–78.2. 1H NMR (500 MHz, $CDCl_3$): δ = 1.88 (s, 6 H),1.99–2.05 (m, 2 H), 2.70–2.73 (t, 4 H), 6.58 (s, 2 H) ppm. MS (EI): *m/z* = 327.77 [$M^+$].

### 1,2-Bis[2-methyl-5-(4-pyridyl)-3-thienyl]cyclopentene (8)

To a stirred solution of compound **4** (0.33 g, 1.0 mmol) in THF (20 ml) at −78 °C under dry nitrogen in the absence of light was added dropwise 1.6 M n-BuLi in hexane (0.13 g, 2 mmol), and the reaction mixture was stirred at −78 °C for a further 30 min. To the reaction mixture was quickly added tributyl borate (0.46 g, 2 mmol) by syringe, and the reaction mixture was stirred at room temperature for 1 h. The resulting reddish solution was used directly for the following addition. To another Schlenk flask filled with 30 ml of degassed THF were added bromopyridine hydrochloride (0.41 g, 2.1 mmol) and $Pd(PPh_3)_4$ (0.08 g, 0.06 mmol). After stirring for 15 min, 2.5 ml of 2 M aqueous sodium carbonate solution (5.0 mmol) and 0.30 ml of ethylene glycol were added. The solution was stirred for another 15 min under bubbling, before the temperature was raised to 40 °C. To the mixture was then added the above prepared reddish solution in one portion. The mixture was refluxed for 2 h. After cooling, 50 ml of ethyl acetate was added to dilute the mixture, followed by washing with water (20 ml × 2) and brine. Flash column chromatography on silica gel (ethyl acetate/PE = 1/5) of the concentrated residue afforded 0.29 g of **8** in a yield of 67%. 1H NMR (500 MHz, $CDCl_3$): δ = 2.03 (s, 6H), 2.09–2.15 (m, 2H), 2.84–2.87 (t, 4H), 7.23 (s, 2H), 7.36–7.37 (d, 4H), 8.53–8.54 (d, 4H) ppm. MS (ESI): *m/z* = 437.05 [M + $H^+$].

### 1-[2-Methyl-5-(4-pyridyl)-3-thienyl]-2-[2-methyl-5-chloro-3-thienyl] cyclopentene (10)

It was synthesized in the same way as described before with halving the n-BuLi and bromopyridine hydrochloride to obtain 0.28 g of **8** as a purple solid in a yield of 75%. 1H NMR (500 MHz, d-DMSO): δ = 1.85 (s, 3H), 1.94 (s, 3H), 1.99–2.05 (m, 2H), 2.75–2.78 (t, 2H), 2.80–2.83 (t, 2H), 6.86 (s, 1H), 7.52–7.53 (d, 2H), 7.60 (s, 1H), 8.52–8.54 (d, 2H) ppm. MS (ESI): *m/z* = 371.96 [M + $H^+$].

Compounds **14**,**15** were obtained concurrently according to the procedure of **3**.

### 1,2-Bis(2-methyl-4,5-dibromo-3-thienyl)cyclopentene (14)

Yield 28%. 1H NMR (500 MHz, $CDCl_3$): δ = 2.15–2.21(m, 5H), 2.52 (s, 6H), 3.14–3.17(t, 4H) ppm.

### 1,2-Bis(2-methyl-3-thienyl)cyclopentene (15)

Yield 21%. 1H NMR (500 MHz, $CDCl_3$): δ = 2.13–2.19(m, 2H), 2.53 (s, 6H), 2.95–2.98(t, 4H), 6.78–6.79(d, 2H), 7.55–7.56(d, 2H) ppm.

Compounds **18**,**19**,**21**,**22**,**27** were synthesized in the same method as describe above.

### 1,2-Bis[2-methyl-5-(4-bromophenyl)-3-thienyl)cyclopentene (18)

Yield 44%. 1H NMR (400 MHz, $CDCl_3$): δ = 1.99(s, 6H), 2.08(t, 2H), 2.83(t, 4H), 7.00(s, 2H), 7.34(d, 4H), 7.44(d, 4H) ppm. 13C NMR (150 MHz, $CDCl_3$) δ = 14.60, 23.17, 38.57, 120.84, 124.55, 126.91, 132.00, 133.57, 134.86, 135.17, 136.95, 138.55 ppm.

### 1-[2-Methyl-5-(4-bromophenyl)-3-thienyl)-2-[2-methyl-5-chloro-3-thienyl]cyclopentene (19)

Yield 58%. 1H NMR (500 MHz, d-DMSO): δ = 1.84 (s,3H), 1.90 (s,3H), 1.96–2.02 (m, 2H), 2.72–2.75 (t, 2H), 2.77–2.80 (t, 2H), 6.83 (s, 1H), 7.30 (s, 1H), 7.47–7.49 (s, 2H), 7.54–7.56 (s, 2H) ppm. 13C NMR (125.7 MHz, d-DMSO): δ = 13.89, 14.06, 37.92, 38.09, 120.20, 123.67, 124.98, 126.80, 127.38, 130.50, 130.86, 131.97, 132.94, 134.35, 134.88, 135.25, 136.67, 137.81 ppm.

### 1,2-Bis[2-methyl-5-(4-amimophenyl)-3-thienyl)cyclopentene (21)

Yield, 62%. 1H NMR (400 MHz, $CDCl_3$): δ = 1.95 (s, 6H), 1.97-2.07 (m, 2H), 2.82 (t, 4H), 3.73 (s, 4H), 6.65 (d, 4H), 6.88 (s, 2H), 7.30 (d, 4H) ppm.

### 1-[2-Methyl-5-(4-4-amimophenyl)-3-thienyl)-2-[2-methyl-5-chloro-3-thienyl]cyclopentene (22)

Yield 65%. 1H NMR (500 MHz, $CDCl_3$): δ = 1.88 (s, 3H), 1.96(s, 3H), 2.0–2.05 (m, 5H), 2.72–2.75 (t, 2H), 2.78–2.81 (t, 2H), 6.59–6.60 (d, 1H), 6.62 (s, 1H), 6.74 (s, 2H), 6.83 (s, 1H), 7.23–7.25 (d, 1H), 7.31–7.32 (d, 2H) ppm.

**1-[2-Methyl-5-(4-tetraphenylporphyrinphenyl)-3-thienyl)-2-[2-methyl-3-thienyl]cyclopentene (27)**

Yield 55%. 1H NMR (500 MHz, $CDCl_3$): $\delta = 8.84$ (s, 1H), 8.56–8.60 (d, 2H), 8.22–8.23 (d, 1H), 7.99–8.00 (d, 1H), 7.75–7.76 (d, 2H), 7.47–7.50 (4H), 7.15–7.34 (13H), 6.94–7.03 (9H), 6.78–6.80 (2H), 2.72–2.76 (t, 2H), 2.65–2.68 (t, 2H), 2.03–2.09 (br, 2H), 2.00 (s, 3H), 1.92 (s, 3H), –2.76 (s, 2H) ppm. MS (ESI, m/z): 949.29 $[M + H]^+$.

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## SUPPORTING INFORMATION

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**Figure 1.** 1H NMR spectrum of 2.
**Figure 2.** MS spectrum of 2.
**Figure 3.** 1H NMR spectrum of 3.
**Figure 4.** MS spectrum of 3.
**Figure 5.** 1H NMR spectrum of 4.
**Figure 6.** MS spectrum of 4.
**Figure 7.** 1H NMR spectrum of 10.
**Figure 8.** MS spectrum of 10.
**Figure 9.** 1H NMR spectrum of 8.
**Figure 10.** MS spectrum of 8.
**Figure 10.** 1H NMR spectrum of 14.
**Figure 11.** 1H NMR spectrum of 15.
**Figure 12.** 1H NMR spectrum of 19.
**Figure 13.** 13C NMR spectrum of 19.
**Figure 14.** 1H NMR spectrum of 22.
**Figure 15.** MS spectrum of 24.
**Figure 16.** 1H NMR spectrum of 27.