



Multi-responsive diarylethene-phenolphthalein hybrids by multiple stimuli



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ABSTRACT

Photochromic diarylethene derivatives cherishing phenolphthalein moieties were designed and constructed. We present efforts to investigate their versatile performances in multi-responsive properties with multiple stimuli of light, acid/base and temperature/heat. Results show their fluorescence could be on–off switched not only by different lights but also by acid/base. Besides lights and acid/base controllable colour change and fluorescence-changing, altering phase states could also tune their colours via different temperature, which is rare performance for diarylethene derivatives. Especially, the photocyclization ratio is as high as 100% for compound **2o** bearing two phenolphthalein groups. These versatile properties are helpful to the design of pH sensitive photoswitches, fluorescent sensors, and molecular logical gates.

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1. Introduction

Phenolphthalein is one of the most representative acid/base indicators¹ and widely employed in pH indicators,² colour-change humidity indicators,³ visual recognition of chemicals⁴ and so on. It exists as the colourless lactone form at pH=8 and lower, but as red quinonoid isomer at pH values from 8 to 12.⁵ Addition of acid/base to modulate the pH value can conveniently make the structure of phenolphthalein interconvert between lactone form and quinonoid form. As a result, the colour of phenolphthalein will interconvert between colourless and pink.⁶ This performance of colour-changing stimulated by acid/base is complementary to photochromic compounds triggered by light. Because most of the multi-functional groups reported in photochromic system are colourable under acidic conditions. It is well known that organic photochromic compounds have been applied in many fields such as photonic switch device, optical memory media and logical gates.^{7–9} As a vigorous member of photochromic materials, diarylethene derivatives attract increasing attention in recent years owing to their excellent fatigue resistance and thermal stability at different isomers.^{10–13} Many photochromic diarylethene systems which respond to a given combination of multiple stimuli have been developed recently.^{14–17} The diarylethene structures connected

various functional moieties usually exhibit interesting behaviours under external stimuli besides lights, such as chemicals,^{18,19} heat,²⁰ electricity²¹ and so forth. These diarylethene systems with multiple states can increase the capacity of data storage, full colour display and logical gates, etc.

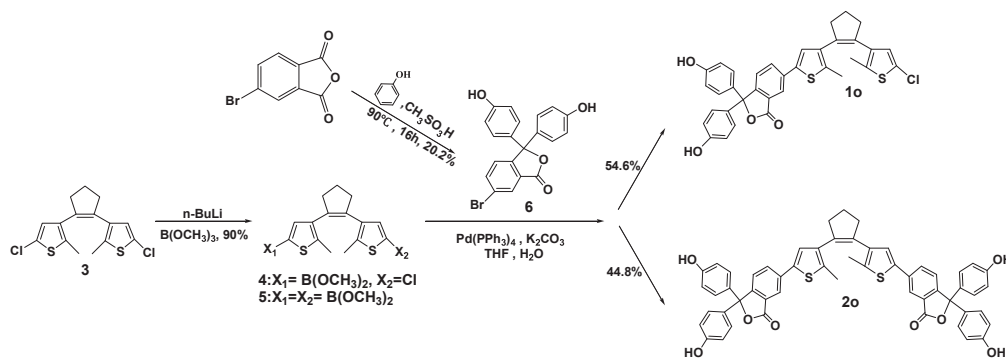
In view of these advantages, we present efforts to introduce different phenolphthalein groups into diarylethene system, which could be expected to undergo new complementary characteristics. New compounds **1o** and **2o** were designed and synthesized (Scheme 1). Results showed they exhibited photochromism, bischromism and phase state chromism by external stimuli, which are rare performance for diarylethene derivatives reported. Meanwhile, we also found hybrid **1o** and **2o** performed significant fluorescence, while their precursors, diarylethene and phenolphthalein moiety, were nearly non-fluorescent. Moreover, their on-off fluorescence changes could be reversibly modulated not only by UV/vis light, but also by acid/base stimulus. Although they have similar structures, the photocyclization ratio of compound **1o** was detected to be 62%, while the compound **2o** could reach 100%.

2. Experimental section

2.1. General methods

All chemicals were purchased from commercial sources and used as received unless otherwise mentioned. ¹H NMR and ¹³C NMR spectra were recorded on a Bruker AV400 spectrometer

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Scheme 1. The synthetic routes of diarylethene **1o** and **2o**.

working at 400 MHz for ^1H NMR and 100 MHz for ^{13}C NMR. All the spectra used DMSO and CD_3OD as the solvent and tetramethylsilane (TMS) as an internal standard. HRMS were recorded on a Waters ESI-TOF mass spectrometer. Absorption and fluorescence spectra were recorded on an Agilent Technologies Cary 60 and a Varian Cary Eclipse using quartz cuvette at room temperature, respectively. Photo-irradiation was carried out using SHG-200 UV hand lamp. HPLC was measured using Agilent 1100 Series.

For convenience, the following abbreviations are used: **1o**, **2o**: open-ring isomers of the two titled compounds; **1c**, **2c**: closed-ring isomers; **1o-q**, **2o-q**: open-ring isomer of quinoid forms; **1c-q**, **2c-q**: closed-ring isomer of quinoid forms.

2.2. Synthesis

The synthetic routes of diarylethene **1o** and **2o** are shown in Scheme 1. Dithienylcyclopentene precursor **3** was achieved following previously published protocol.²² The coupling partner **4** and **5**, which are boronoaryl compounds of the dithienylethene unit, are prepared in one pot from **3**. The intermediate material **6** were obtained according to the literature methods reported.²³ With them in hand, the target molecules were conveniently synthesized by Suzuki cross-coupling reaction of compounds **4**, **5** and **6**. Their chemical structures were confirmed by ^1H NMR, ^{13}C NMR and HRMS.

2.2.1. Synthesis of bromo-phenolphthalein (6). Phenol (0.02 mol, 1.88 g) and 4-bromophthalic anhydride (0.01 mol, 2.27 g) were dissolved in a mixture of methanesulfonic acid (0.09 mol, 8.65 g), then the reaction mixture was stirred and heated to 90 °C for 16 h. After cooled to room temperature, the reaction mixture was slowly added to ice-water while stirring. The aqueous layer was extracted with ethyl acetate (3×15 mL), and washed with water (3×10 mL). The combined organic phases were dried over anhydrous sodium sulfate and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether and ethyl acetate ($v:v=2:1$) and recrystallized from petroleum ether and ethyl acetate to obtain 0.8 g compound as a white solid in 20.2% yield. Mp 248.7–251.5 °C; ^1H NMR (400 MHz, DMSO- d_6 , ppm): $\delta=6.73$ – 6.77 (m, 4H), 7.06–7.10 (m, 4H), 7.84 (m, 2H), 8.05 (s, 1H), 9.69 (s, 2H); ^{13}C NMR (100 MHz, DMSO- d_6 , ppm): $\delta=91.22$, 115.38, 123.73, 127.33, 127.37, 128.30, 128.33, 129.23, 130.62, 130.65, 133.16, 154.55, 157.73, 168.30; HRMS (ESI $^+$): m/z calcd for $\text{C}_{20}\text{H}_{13}\text{O}_4\text{Br}[\text{M}-\text{H}]^+$: 394.9919; found: 394.9921.

2.2.2. Synthesis of 1-(2-methyl-5-chloro-3-thienyl)-2-(2-methyl-5-phenolphthalein-3-thienyl)cyclopentene (1o). In an argon atmosphere, compound **6** (0.3 mmol, 0.12 g) and tetrakis(triphenyl-

phosphine)-palladium(0) (0.016 mmol, 18 mg) were dissolved in a mixture of THF (6 mL) and 2 M aqueous potassium carbonate solution (4 mL). When the reaction mixture was stirred and heated to 60 °C, compound **4** (0.3 mmol, 0.11 g) was added drop wise. The mixed solution was stirred and refluxed at 100 °C for 24 h and monitored by TLC. Then the mixture was cooled to room temperature, followed by adding 20 mL of water and extracted with ethyl acetate (3×15 mL). The combined organic phases were dried over anhydrous sodium sulfate and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether and ethyl acetate ($v:v=3:1$) to obtain 0.1 g of compound as a brown solid in 54.6% yield. Mp 124.1–128.5 °C; ^1H NMR (400 MHz, DMSO- d_6 , ppm): $\delta=1.85$ (s, 3H), 1.93 (s, 3H), 1.99–2.02 (m, 2H), 2.75 (t, $J=7.2$ Hz, 2H), 2.82 (t, $J=7.2$ Hz, 2H), 6.75–6.77 (m, 4H), 6.85 (s, 1H), 7.10–7.12 (m, 4H), 7.61 (s, 1H), 7.75 (dd, $J=1.6$ Hz, $J=8.0$ Hz, 1H), 7.82 (s, 1H), 7.86 (d, $J=8.0$ Hz, 1H), 9.67 (s, 2H); ^{13}C NMR (100 MHz, CH_3OD , ppm): $\delta=14.17$, 14.64, 23.96, 30.75, 39.03, 39.11, 93.67, 116.24, 120.85, 124.48, 126.24, 127.23, 127.44, 128.13, 129.68, 132.92, 134.72, 135.82, 136.50, 136.65, 138.49, 138.54, 138.97, 141.84, 155.66, 158.98, 171.63; HRMS (ESI $^+$): m/z calcd for $\text{C}_{35}\text{H}_{27}\text{O}_4\text{S}_2\text{Cl}[\text{M}+\text{H}]^+$: 611.1118; found: 611.1113.

2.2.3. Synthesis of 1,2-bis(2-methyl-5-phenolphthalein-3-thienyl)cyclopentene (2o, 2c). In an argon atmosphere, compound **6** (1 mmol, 0.40 g) and tetrakis(triphenyl-phosphine)-palladium(0) (58 mg, 0.05 mmol) were dissolved in a mixture of THF (10 mL) and 2 M aqueous potassium carbonate solution (5 mL). When the reaction mixture was stirred and heated to 60 °C, compound **5** (0.5 mmol, 0.20 g) was added drop wise. The mixed solution was stirred and refluxed at 100 °C for 24 h and monitored by TLC. Then the mixture was cooled to room temperature, followed by adding to 20 mL of water and extracted with ethyl acetate (3×15 mL). The combined organic phases were dried over anhydrous sodium sulfate and the solvent was evaporated under reduced pressure. The residue was purified by column chromatography on silica gel using petroleum ether and ethyl acetate ($v:v=1:1$) to obtain 0.2 g of compound as a brown solid in 44.8% yield. Mp 290.3–293.5 °C; **2o**: ^1H NMR (400 MHz, DMSO- d_6 , ppm): $\delta=1.89$ (s, 6H), 2.02–2.06 (m, 2H), 2.86 (t, $J=7.2$ Hz, 4H), 6.72–6.75 (m, 8H), 7.08–7.11 (m, 8H), 7.66 (s, 2H), 7.72 (dd, $J=1.2$ Hz, $J=8.0$ Hz, 2H), 7.82–7.86 (m, 4H), 9.66 (s, 4H); **2c**: ^{13}C NMR (100 MHz, CH_3OD , ppm): $\delta=14.72$, 24.02, 38.96, 93.65, 116.24, 120.80, 124.40, 127.26, 127.34, 128.18, 129.68, 132.85, 136.08, 138.54, 138.60, 138.84, 141.70, 155.55, 158.86, 171.62; HRMS (ESI $^+$): m/z calcd for $\text{C}_{55}\text{H}_{40}\text{O}_8\text{S}_2[\text{M}+\text{H}]^+$: 893.2243; found: 893.2248.

2c was obtained in NMR tube monitored with ^1H NMR. Firstly, compound **2o** was dissolved in deuterium DMSO (3.7×10^{-3} mol/L). Then irradiation the solution with 254 nm UV light, after 60 min **2o** totally converted to its closed-ring isomer **2c** detected by ^1H NMR.

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