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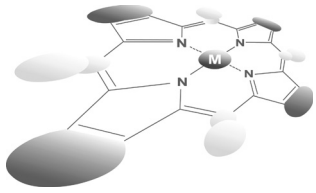

Synthesis and spectroscopic properties of photochromic dithienylethene-functionalized subphthalocyanine conjugate

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Dedicated to Professor Tomás Torres on the occasion of his 65th birthday

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ABSTRACT: A subphthalocyanine-dithienylethene dyad has been synthesized and characterized by ^{1}H-, ^{13}C-NMR, HR-MS, UV-visible and emission spectroscopy. The results show that photoinduced isomerization of dithienylethene moiety from close-form to opened form can be achieved under visible light using subphthalocyanine as a light-harvesting unit and the fluorescence properties of subphthalocyanine could be modulated by the isomerization state of the dithienylethene moiety.

KEYWORDS: subphthalocyanine, dithienylethene, dyad, photochromic, fluorescence.

INTRODUCTION

Dithienylethene (DTE) derivatives [1] are well-known photochromic compounds, in which diarylethenes with heterocyclic aryl groups can be interconverted between colorless open and colored closed form under UV and visible light irradiation, respectively. The spectrum of ring opened isomer is similar to a substituted thiophene, since π-conjugation is localized in each thiophene ring. While the spectrum of ring closed isomer shifts to a longer wavelength, because the π-conjugation delocalizes throughout the molecule. The structural differences between the two states result in a large difference such as luminescence [2–6], color [7], refractive index [8] and conformational flexibility [9]. Based on the light harvesting ability of conjugated macrocycle molecules (such as porphyrins, phthalocyanines and subphthalocyanines) in visible region, the light energy could be delivered to covalent attached DTE unit. Therefore it is possible to modulate the switching properties of DTE molecule depending on the covalently linked moieties. Porphyrin-DTE [6] complex showed that from closed-form to open form was accomplished by irradiation Q-band of porphyrin moiety, but the change was very weak in the UV-vis absorption spectrum. And phthalocyanine-DTE [10–14] complexes displayed solvent-dependent and ultraviolet photocontrolable J-aggregation behavior. Subphthalocyaninatoboron (SubPc) complexes [15] are ring contracted congener of phthalocyanines consisting of three *N*-fused diiminoisoindoline units arranged around a central four-coordinate boron atom. Due to the 14 π-electron aromatic system, it shows intense absorption (550–600 nm) and fluorescence in the visible region and makes it possible to be an excellent light-harvesting unit [16, 17]. Due to easily axial ligand exchange [18], multi-functional subphthalocyanines not only apply to organic photodetectors [19, 20], molecular cages [21, 22], organic solar cells [23–28] and organic light-emitting diodes [29, 30], but also photodynamic therapy (PDT) [31, 32] and probes [19, 20]. The previous research of subphthalocyanine-DTE [33] complex only illustrated that closed form was obtained with UV light. In this work close-form and opened form isomerization of a novel subphthalocyanine-DTE complex was studied in detail. Importantly, close-form to opened form can be achieved under visible light using subphthalocyanine as a light-harvesting unit.

◊ SPP full member in good standing

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EXPERIMENTAL

Synthesis

Preparation of 1,5-bis(5-chloro-2-methylthiene-3-yl)pentane-1,5-dione (2). 1,5-Bis(5-chloro-2-methylthiene-3-yl)pentane-1,5-dione was prepared in a manner somewhat similar to the method reported previously [34]. Anhydrous $AlCl_3$ (8 g, 60 mmol) was added to dichloroethane (50 mL) at 0 °C with vigorous stirring. Glutaryl dichloride (4.23 g, 25 mmol) in dichloroethane (5 mL) and 2-chloro-5-methylthiophene **1** (5.97 g, 45 mmol) in dichloroethane (5 mL) were added dropwise to the solution successively, and the color of the solution was observed to turn aubergine. The resulting mixture was stirred for 3 h at room temperature. Then the crude product was poured into the mixture solution of ice-cold concentrated hydrochloric acid, and the water layer was extracted with dichloromethane. The combined organic phase was neutralized using the saturated aqueous $NaHCO_3$, then subsequently washed with water and saturated brine, dried over Na_2SO_4, and the solvent was removed under reduced pressure. The crude residue was purified by silica gel chromatography (1:9 (v/v) ethyl acetate/petroleum ether) and crystallized from dichloromethane/methanol to give **2** as a white solid. Yield 4.06 g (50%). ^{1}H NMR (400 MHz; $CDCl_3$-d_1, Me_4Si): δ_H, ppm 7.18 (2H, s, thienyl-*H*), 2.86 (4H, t, ^3J = 7 Hz, CH_2), 2.66 (6H, s, CH_3), 2.03–2.10 (2H, m, CH_2). MS (ESI): *m*/*z* 361.17, 383.25 (calcd. for $[M + H]^+$ 360.99, $[M + Na]^+$ 382.97).

Preparation of 1,2-bis(5-chloro-2-methylthien-3-yl)cyclopentene (3). 1,2-Bis(5-chloro-2-methylthien-3-yl)cyclopentene was prepared in a manner somewhat similar to the method reported previously [34]. A mixture $TiCl_4$ $(THF)_2$ (4 g, 11.6 mmol) and activated Zn dust (1.14 g, 17.4 mmol) in dry THF (50 mL) was stirred and heated to reflux for 3 h under argon. After cooling to room temperature, **2** (2.09 g, 5.8 mmol) in THF (5 mL) was added to the solution and heated to reflux for 4 h. The reaction mixture was cooled to room temperature and a 20% aqueous solution of $NaHCO_3$ was added. The mixture was filtered. The filter cake was extracted with ethyl ether and the organic layer was dried over Na_2SO_4. The solvent was removed under reduced pressure. The crude residue was purified by silica gel chromatography (petroleum ether) and crystallized from dichloromethane/methanol to give **3** as a white solid. Yield 917 mg (48%). ^{1}H NMR (400 MHz; $CDCl_3$-d_1, Me_4Si): δ_H, ppm 6.57 (2H, s, thienyl-*H*), 2.71 (4H, t, ^3J = 7.4 Hz, CH_2), 2.66 (6H, s, CH_3), 1.98–2.05 (2H, m, CH_2). MS (ESI): *m*/*z* 330.42 (calcd. for $[M + H]^+$ 329.00).

Preparation of 1,2-bis[5-(dibutoxybory)-2-methylthien-3-yl]cyclopentene (4). 1,2-Bis[5-(dibutoxybory)-2-methylthien-3-yl]cyclopentene was prepared in a manner somewhat similar to the method reported previously [34]. To a solution of 3 (800 mg, 2.43 mmol) in anhydrous THF (20 mL) was added *n*-BuLi (1.6 M, 4 mL) dropwise at -78 °C for 30 min. Then $B(OBu)_3$ (1.12 g, 1.32 mL, 4.86 mmol) was added and stirred for 1 h at -78 °C, then for 2 h at room temperature and used for further reaction without any workup.

Preparation of 2-(4-iodo-phenoxy)tetrahydropyran (5). 2-(4-Iodo-phenoxy)tetrahydropyran was prepared in a manner somewhat similar to the method reported previously [34]. 4-Iodophenol (2.20 g, 10 mmol) was stirred for 30 min in dry CH_2Cl_2 (50 mL) and then pyridinium *p*-toluenesulfonate (PPTS) (251 mg, 1 mmol) was added into the solution and stirred for 10 min. 3,4-Dihydro-2H-pyran (1.37 mL, 15 mmol) in dichloroethane (5 mL) was added dropwise to the solution and stirred for 2.5 h at room temperature. The reaction mixture was diluted with diethyl ether and washed once with saturated brine. The organic layer was dried over anhydrous Na_2SO_4 and the solvent was removed under reduced pressure. The crude residue was purified by silica gel chromatography (1:9 (v/v) ethyl acetate/petroleum ether) to afford **5** as a white solid. Yield 2.9 g (95%). ^{1}H NMR (500 MHz; $CDCl_3$-d, Me_4Si): δ_H, ppm 7.55 (d, ^3J = 8.8 Hz, 2H, Ar), 6.83 (d, ^3J = 8.8 Hz, 2H, Ar), 5.38–5.37 (t, ^3J = 3.2 Hz, 1H, C*H*), 3.88–3.83 (m, 1H, CH_2), 3.61–3.57 (m, 1H, CH_2), 2.00–1.95 (m, 1H, CH_2), 1.85–1.84 (m, 1H, CH_2), 1.71–1.56 (m, 4H, CH_2). MS (ESI): *m*/*z* 305.33 (calcd. for $[M + H]^+$ 305.00).

Preparation of 1,2-bis[2-methyl-5-[(*p*-((tetrahydropyran-2-yl)oxy)phenyl]-3-thienyl]cyclopentene (6). 1,2-Bis[2-methyl-5-[(*p*-((tetrahydropyran-2-yl)oxy)phenyl]-3-thienyl]cyclopentene was prepared in a manner somewhat similar to the method reported previously [34]. A mixture of 2-(4-iodo-phenoxy)tetrahydropyran (1.48 g, 4.86 mmol) and $Pd(PPh_3)_4$ (57.7 mg, 0.05 mmol) in THF (20 mL) was added to **4**, and the resulting solution was stirred for 15 min at room temperature. Then, 2 M aqueous Na_2CO_3 (10 mL) was added and the reaction mixture was refluxed for 30 min. 1,2-Bis[5-(dibutoxybory)-2-methylthien-3-yl]cyclopentene was added and refluxed for 12 h. The mixture was cooled to room temperature and extracted with ether, washed with water, dried over anhydrous Na_2SO_4. The solvent was removed under reduced pressure. The crude residue was purified by silica gel chromatography [1:9 (v/v) ethyl acetate/petroleum ether] to afford **5** as a brownish solid. Yield 745 mg (69%). ^{1}H NMR (400 MHz; $CDCl_3$-d_1, Me_4Si): δ_H, ppm 7.41–7.35 (m, 4H, Ar), 7.02 (d, ^3J = 8.8 Hz, 2H, Ar), 6.90 (d, ^3J = 7.8 Hz, 2H, Ar), 6.79 (d, ^3J = 8.6 Hz, 2H, thienyl-*H*), 5.43–5.41 (t, ^3J = 3.0 Hz, 1H, CH_2), 4.93–4.86 (m, 1H, CH_2), 4.00–3.81 (m, 2H, CH_2), 3.63–3.63 (m, 2H, CH_2), 2.84 (t, J = 7.4 Hz, 4H, CH_2), 2.14–1.93 (m, 10H, CH_2), 1.93–1.80 (m, 4H, CH_2), 1.75–1.58 (m, 6H, CH_3).

Preparation of 1,2-bis[2-methyl-5-(4-hydroxyphenyl)-3-thienyl]cyclopentene (7). 1,2-Bis[2-methyl-5-(4-hydroxyphenyl)-3-thienyl]cyclopentene was prepared in a manner somewhat similar to the method reported previously [34]. A solution of **6** (612 mg, 1 mmol)

and pyridinium *p*-toluenesulfonate (PPTS) (20 mg, 0.08 mmol) in MeOH–CH_2Cl_2 (20 mL) was stirred at room temperature over night. The solvent was removed under reduced pressure. The crude residue was purified by silica gel chromatography (1:1 (v/v) ethyl acetate/petroleum ether) to afford **7** as a brownish solid. Yield 222 mg, (50%). ^{1}H NMR (400 MHz; $CDCl_3$-d_1, Me_4Si): δ_H, ppm 7.37 (d, ^3J = 8.6 Hz, 4H, Ar), 6.90 (s, 2 H, thienyl-*H*), 6.80 (d, ^3J = 8.6 Hz, 4H, Ar), 2.82 (t, ^3J = 7.4 Hz, 4H, CH_2), 2.06 (q, ^3J = 7.4 Hz, 2H, CH_2), 1.98 (s, 6H, CH_3). MS (ESI): *m*/*z* 443.25 (calcd. for $[M - H]^-$ 443.11).

Preparation of boron subphthalocyanine chloride (8). Boron subphthalocyanine chloride was prepared in a manner somewhat similar to the method reported previously [35]. In a 50 mL two-neck round bottom flask, 2 mL of 1.0 M solution of BCl_3 (234 mg, 2 mmol) in dichloromethane was added to a solution of phthalonitrile (256 mg, 2 mmol) in *p*-xylene (15 mL). The mixture was heated to remove the dichloromethane through distillation using a Dean–Stark condenser. After distillation the flask was heated to reflux for 3 h under argon. The mixture was then cooled and the solvent was removed under reduced pressure. The resultant solid was thoroughly washed with methanol until the filtrate became colorless to afford **8** as a golden solid. Yield 158 mg (55%). ^{1}H NMR (400 MHz, $CDCl_3$-d_1, Me_4Si): δ_H, ppm 8.90–8.93 (m, 6H, Ar), 7.95–7.97 (m, 6H, Ar). MS (MALDI-TOF): *m*/*z* 430.931, 395.067 (calcd. for $[M + H]^+$ 430.091, $[M - Cl]^+$ 395.122).

Preparation of subphthalocyanine-dithienylethene dyad (9). Subphthalocyanine-dithienylethene dyad was prepared in a manner somewhat similar to the method reported previously [33]. In a 15 mL pressure vessel, compound **7** (66.7 mg, 0.15 mmol) was added to a solution of compound **8** (21.5 mg, 0.05 mmol) in dry toluene and heated at 130 °C for 16 h. The solvent was evaporated under reduced pressure. The resultant solid was thoroughly washed with methanol until the filtrate became colorless. The crude residue was purified by neutral alumina column chromatography (THF) to afford **9** as a cardinal red solid. Yield 42 mg (60%). ^{1}H NMR (400 MHz, $CDCl_3$-d_1, Me_4Si): δ_H, ppm 8.56 (s, 1H, Ar-O*H*), 8.87–8.84 (m, 6H, Ar), 8.03–8.01 (m, 6H, Ar), 7.30 (d, ^3J = 8.6 Hz, 2H, Ar), 7.00–6.97 (m, 2H, thienyl-*H*), 6.93 (d, ^3J = 8.6 Hz, 2H, Ar), 6.74 (d, ^3J = 8.6 Hz, 2H, Ar), 5.31 (d, ^3J = 8.4 Hz, 2H, Ar), 2.80–2.71 (m, 4H, CH_2), 2.00–1.95 (m, 2H, CH_2), 1.81 (d, ^3J = 5.6 Hz, 6H, CH_3). ^{13}C NMR (125 MHz, $(CD_3)_2SO$-d_6, Me_4Si): δ_C, ppm 157.37, 151.66, 138.88, 136.95, 134.54, 130.82, 130.61, 126.70, 125.97, 122.80, 122.50, 119.92, 116.20, 38.52, 22.70, 14.38. HR-MS (ESI) *m*/*z* 861.2253 (calcd. for $[M + Na]^+$ 861.2254).

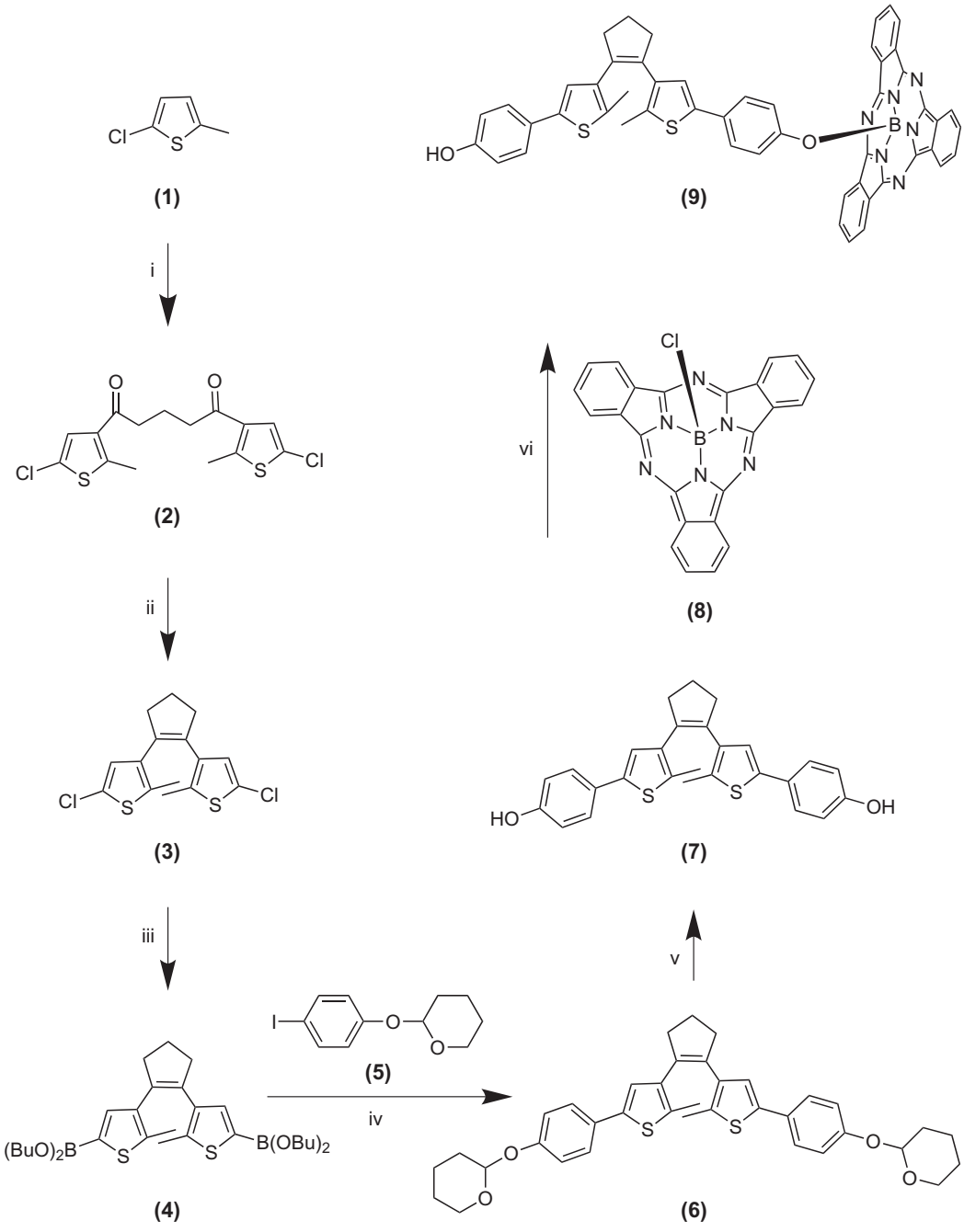
Materials and equipment

All reagents were obtained from commercial suppliers and used without further purification, unless otherwise indicated. The NMR spectra were measured on a Bruker 600 or 500 or 400 MHz spectrometer. UV-visible absorption spectra were measured on a Shimadzu UV-2550 double beam spectrophotometer. Fluorescence emission spectra were measured on a Hitachi F-4600 fluorescence spectrophotometer with a 150 W-xenon arc lamp used as the light source with a working voltage of 700 V. The emission slit was set at 5 nm. Fluorescence quantum yield (Φ_F) was determined by the comparative method and the absorbance values of the solutions were between 0.04 and 0.05 at the excitation wavelength. Fluorescence lifetime was measured using a time correlated single photon counting (TCSPC) setup (Single Photon Avalanche Diodes, PDM series, PicoQuant GmbH). The excitation source was a diode laser (LDH-P-C-405 with 10 MHz repetition rate, 70 ps pulse width). MALDI-TOF mass spectra (MS) were collected using Bruker Daltonics autoflex^{II} MALDI-TOF MS spectrometer. The MS analysis was carried out on a Thermo scientific LCQ Fleet mass spectrometer (Thermo, USA) with ESI and the X calibur 2.1 software work station. ESI-Q-TOF-MS was collected using Model 6540 Agilent high definition quadrupole time-of-flight mass spectrometer.

RESULTS AND DISCUSSION

Synthesis and characterization

The synthetic procedure for 1,2-bis[2-methyl-5-(4-hydroxyphenyl)-3-thienyl]cyclopentene **7** and the novel subphthalocyanine-dithienylethene dyad **9** was outlined in Scheme 1. **7** was prepared starting from 2-chloro-5-methylthiophene **1**, which was reacted with glutaryl dichloride in dichloroethane to give 1,5-bis(5-chloro-2-methylthiene-3-yl)pentane-1,5-dione **2**. **2** was treated with $TiCl_4(THF)_2$ and Zn in THF to get dithienylcyclopentene **3** which was reacted with $B(OBu)_3$ and *n*-BuLi to give bis-(boronic) ester **4** followed by the Suzuki coupling reaction with protected *p*-iodophenol **5** and $Pd(PPh_3)_4$ to obtain intermediate **6**. After removal of tetrahydropyran-protected group in MeOH–CH_2Cl_2, diphenol **7** was reacted with boron subphthalocyanine chloride **8** in dry toluene (closed ampoule) to afford the target compound **9**. **7** and **9** were characterized by ^{1}H NMR and UV-visible absorption. In the ^{1}H NMR spectra, the benzene ring protons of **7** were located at 7.37 and 6.80 ppm as typical double peaks, and the protons on the thiophene moiety were at 6.90 ppm as a singlet peak. While the benzene ring protons of **9** on the dithienylethene (DTE) moiety were located at 7.30, 6.93, 6.74 and 5.31 ppm as typical double peaks, the protons on the thiophene moiety were at 7.00–6.97 ppm. Molecular ion peaks were observed by MS at *m*/*z* 443.25 $[M - H]^-$ for **7** and 861.2253 $[M + Na]^+$ for **9**.



Scheme 1. Synthetic route for the subphthalocyanine-dithienylcyclopentene dyad (**9**). (i) Glutaryl dichloride, $AlCl_3$, dichloroethane, argon atmosphere; (ii) $TiCl_4(THF)_2$, Zn, THF; (iii) *n*-BuLi, $B(OBu)_3$, THF; (iv) $Pd(PPh_3)_4$, aqueous Na_2CO_3, THF; (v) pyridinium *p*-toluenesulfonate(PPTS), CH_3OH–CH_2Cl_2; (vi) toluene, reflux, 16 h

Fluorescence spectroscopy, quantum yield and lifetime

Fluorescence quantum yields (Φ_F) are determined by the comparative method, using Equation 1 [36, 37]:

$$\Phi_F = \Phi_F^{Std} \frac{F \cdot A^{Std} \cdot n^2}{F^{Std} \cdot A \cdot (n^{Std})^2} \quad (1)$$

where F and F_{Std} are the integrated areas under the emission curves for the sample and standard, respectively, A and A_{Std} are the absorbance values, and *n* and n_{Std} are the refractive indices of the solvents used. Cresyl violet perchlorate (in methanol) ($\Phi_F = 0.54$) [31, 38] was used as the standard, exciting at 530 nm. The fluorescence quantum yield of compound **9** is approximately 0.086 in DMSO. The absorption and fluorescence spectra of **9** in DMSO are shown in Fig. 1. Figure 2 contains the TCSPC trace for **9** in toluene. A double-exponential luminescence decay curve with an average τ_F value of 0.77 ns was observed.

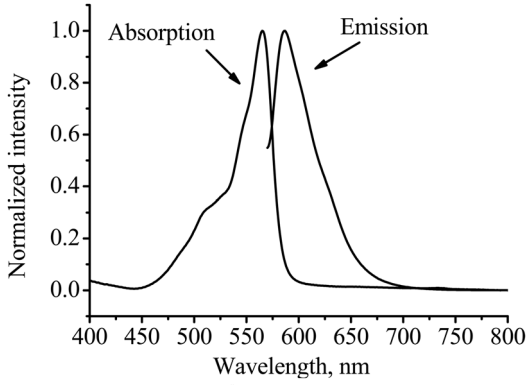


Fig. 1. Normalized absorption and emission spectral of **9** in DMSO (λ_{ex} = 530 nm)

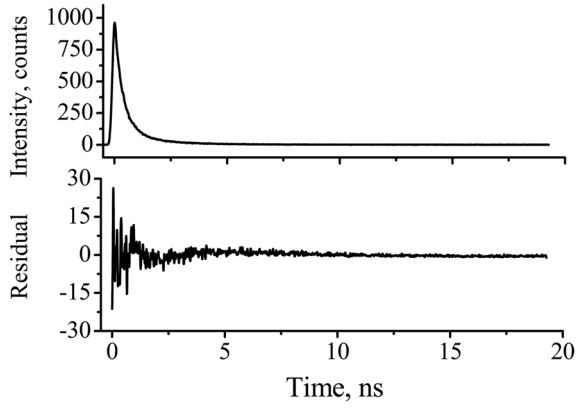


Fig. 2. Fluorescence decay curve of **9** in toluene (top) and the residual of the fit (bottom)

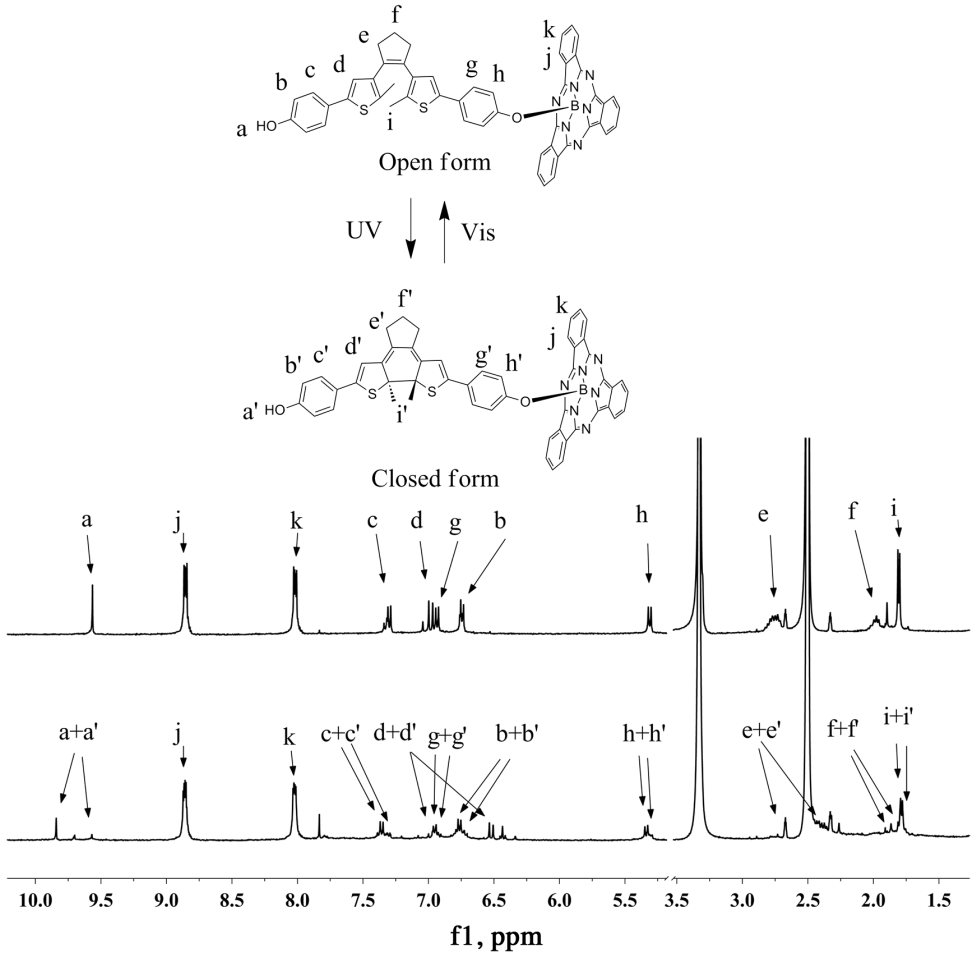


Fig. 3. ^{1}H NMR changes of **9** before (top) and after (bottom) UV irradiation (312 nm, 800 μW.cm^{-2}) for 2 h in DMSO-d_6

NMR spectra characterization of photoisomerization process

When a DMSO-d_6 solution of **9** was irradiated by UV light (312 nm), distinct differences in ^{1}H NMR signals were observed between the open form and closed form both in the high-field and low-field regions. As shown in Fig. 3, a remarkable change occurred for the protons on the thiophene, which shifted from 7.00–6.97 ppm to 6.54–6.51 ppm. The protons benzene ring on the dithienylethene (DTE) moiety shifted slightly to the low-field, while the protons of the cyclopentene core on the DTE moiety and methyl group moved to high-field after photocyclization. These changes indicate that part of the open isomer was

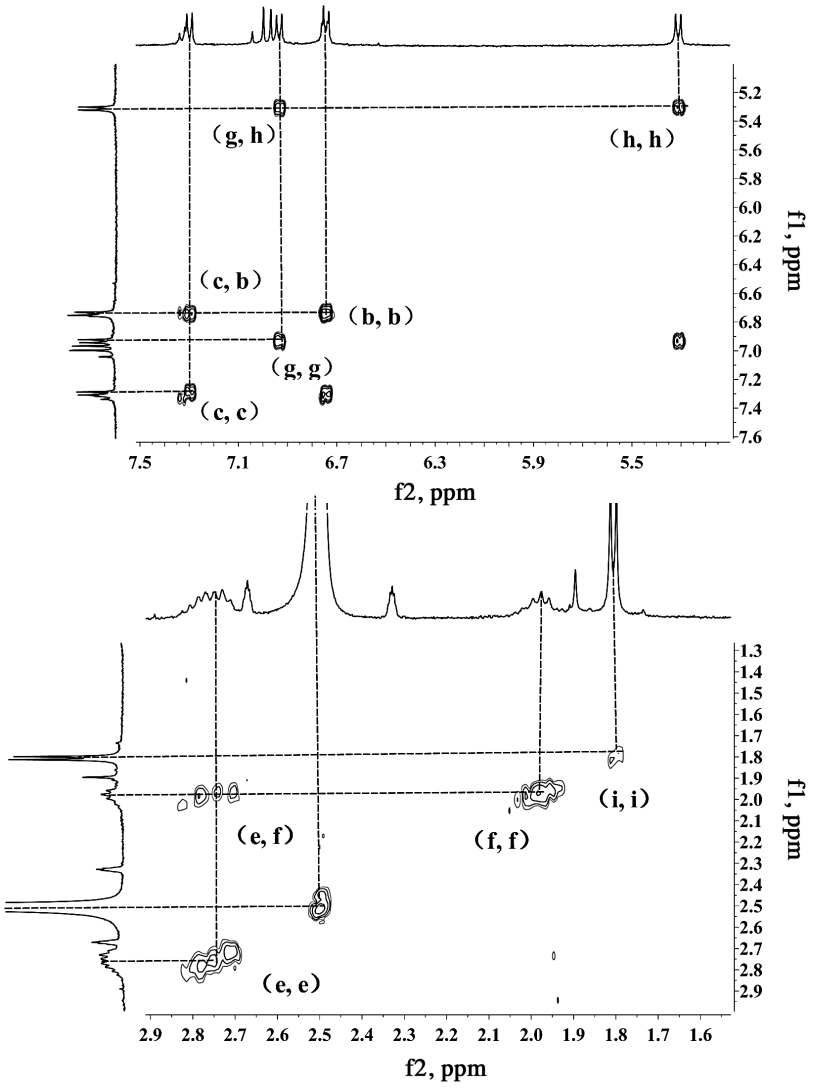


Fig. 4. ^{1}H–^{1}H COSY spectra of subphthalocyanine-dithienylethene dyad **9** in DMSO-d_6

transformed into the closed isomer upon UV irradiation. By integration in ^{1}H NMR approximately 75% of closure isomer existed in the photostationary state. ^{1}H–^{1}H COSY spectra are measured to ascertain the correlation among these protons. Two dimensional spectra protons region of **9** is depicted in Fig. 4, where the additional lines are drawn to specify the correlated peaks. The signals located at 7.30, 6.93, 6.74 and 5.31 ppm were assigned as protons from the benzene ring linked to the DTE moiety, while the signals at 2.80–2.71, 2.00–1.95 and 1.81 ppm were assigned as the protons from the cyclopentene core on the DTE moiety and methyl group, respectively.

Luminescence spectra characterization of photoisomerization process

The photoisomerization of **7** was investigated in dilute DMSO solution. Irradiation with UV light (312 nm) caused the expected spectral change due to an increasing conversion of the colorless open form to the red closed ring isomer (Fig. 5). The ring closed form exhibits a maximum absorption at λ = 524 nm whereas the absorption of the ring opened form is located in the region between *ca*. 325 and 400 nm.

The photoisomerization between open ring form and closed ring form of **9** was studied using dilute sample solutions in DMSO. As can be seen in Fig. 6(a), conversion of open form to closed form photostationary state (PSS) was accomplished by irradiating open form solution with UV light at λ = 312 nm, while the back conversion of the closed form to the open form was actively driven using visible light at λ = 570 nm. Formation of the closed form caused remarkable absorption increases in the regions between *ca*. 340 and 540 nm. In addition, the absorption band of the closed isomer overlapped with the absorption maximum of the subphthalocyanine unit was at 565 nm.

Dyad **9** exhibits emission due to the subphthalocyanine moiety and the respective luminescence maximum is located at 587 nm. As can be seen in Fig. 6(b), the

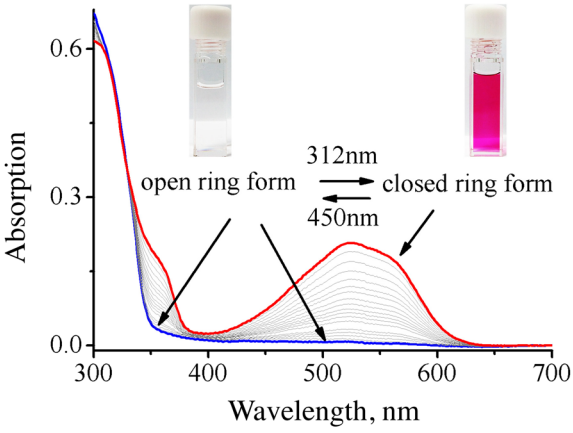


Fig. 5. The UV-vis spectral changes upon the photoisomerization of **7** in DMSO

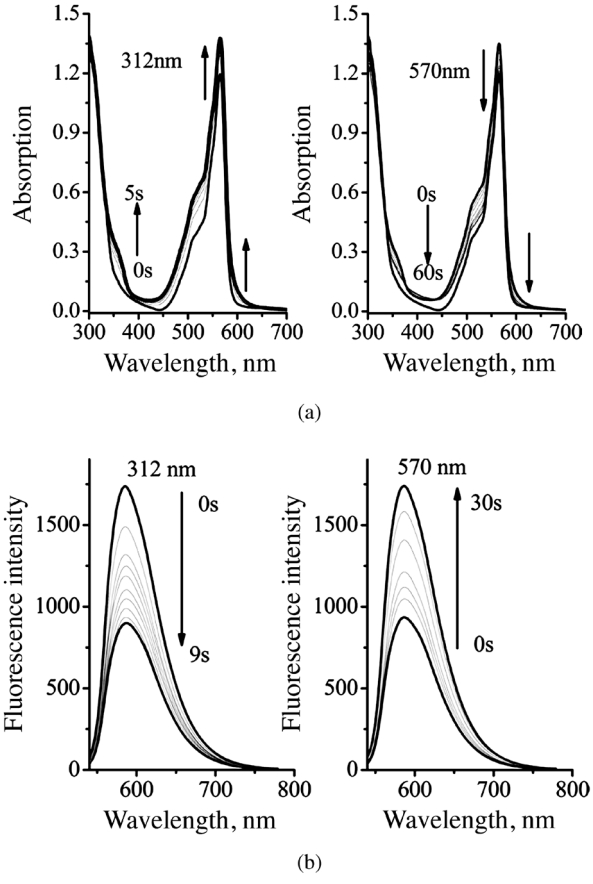


Fig. 6. (a) The UV-vis spectral changes upon the photoisomerization of **9** in DMSO. (b) Emission spectra changes upon the photoisomerization of **9** in DMSO. The left figure is that irradiation at λ = 312 nm gives closed isomer PSS and flowing the right figure irradiation at λ = 570 nm gives open isomer PSS

fluorescence emission of **9** is modulated by the open and closed state of the dithienylethene moiety. A decrease in the fluorescence intensity was observed when open form was converted into closed form by irradiation at λ = 312 nm, and recovering open form by irradiation at λ = 570 nm could bring back the fluorescence intensity. The quenching of the fluorescence of **9** by closed form could be due to the resonant energy transfer [6, 39–46] or electron transfer [47, 48].

CONCLUSION

In summary, a novel subphthalocyanine-dithienylethene complex has been synthesized by using the corresponding subphthalocyanine and 1,2-bis[2-methyl-5-(4-hydroxyphenyl)-3-thienyl]cyclopentene as the precursors in an axial exchange reaction. The dyad has been characterized by NMR, UV-visible absorption, and high resolution MS spectra. The photoisomerization process of SubPc-DTE dyad is investigated by UV-visible spectra by irradiating open form solution at λ = 312 nm and closed form solution at λ = 570 nm. Significantly, the decrease and recovery in the fluorescence intensity of the SubPc moiety were also observed during photoisomerization of SubPc-DTE dyad, which verified that the fluorescence emission of SubPc-DTE dyad could be modulated by the isomerization state of the DTE moiety.

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