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# Synthesis and properties of dithienylethene-based binuclear gold complexes and a palladium chlorine-bridged macrocycle

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ABSTRACT

Two dithienylethene-based binuclear gold complexes and a palladium chlorine-bridged macrocycle bearing bis(phosphine) ligands have been synthesized. Their structures have been thoroughly characterized by NMR spectrometry, single-crystal X-ray diffraction, and elemental analyses. The two binuclear gold complexes display excellent photoisomerization properties upon irradiation with UV/Vis light in $CH_2Cl_2$. Moreover, we found that the introduction of metal atoms can stabilize the dithienylethene-based bis(phosphine) ligands, and that the absorption spectra of gold complexes **3** and **4** showed 6–12 nm red-shifts upon irradiation with UV light compared with those of the ligands **1** and **2**. However, no such isomerization was observed when the palladium chlorine-bridged macrocycle **5** in $CH_2Cl_2$ was irradiated with UV light, but it showed excellent catalytic activity for the Suzuki coupling reaction. Moreover, we found that the non-photochromic macrocycle **5** can perform the photochromic reaction when the solution of $CH_3CN$ was irradiated by UV light.

## 1. Introduction

Photochromism is a reversible transformation between two isomers with different absorption spectra caused by alternating irradiation with UV and visible light. Dithienylethenes have excellent thermal stability, remarkable fatigue resistance, and high sensitivity, and have attracted much attention in recent years due to their potential application in optical memory media and switching devices [1,2].

Research on such systems has been largely concerned with optimizing the substituents on the core unit, such as those at the sites labeled R in Scheme 1 [1–5]. For practical applications, several attempts to modulate the photochromic properties of dithienylethenes have recently been reported. In particular, after the introduction of ligands, dithienylethene-based metal complexes may provide some new advanced molecular functions and show some novel behaviors, such as photophysical and electrochemical characteristics that are not observed for organic dithienylethenes. For example, some research groups have attached pyridine [6–16], bipyridine [17–21], and tripyridine [22] ligands to the dithienylethene system, whereupon it was found that the addition of metal ions led to an obvious change in the photochromism. Furthermore, carbon–metal $\sigma$ bonds and cyclopentadiene metal complexes have been shown to offer good strategies for the introduction of metal atoms by ourselves and others [23–32]. In addition, there have also been a few reports on the use of complexes with N-heterocyclic [33], Schiff base [34], and porphyrin [7,35] ligands to adjust the photochromism of dithienylethenes. In our previous work, a series of binuclear alkynyl gold complexes with dithienylethene units was synthesized. It was found that the efficiencies of the photochromic processes and conversions from the open- to the closed-ring isomers in the photostationary state (PSS) were greatly improved compared with those of the corresponding processes in the ligands [23]. Phosphine ligands are widely applied in coordination chemistry. Branda and co-workers [36] were the first to synthesize a 1,2-dithienylethene gold complex bearing bis(phosphine) groups. Recently, we also reported some bis(phosphine) ligands and derivatives [37]. However, we believe that knowledge remains incomplete concerning the effects of different ligands on photochromic properties and coordinative chemistry. Hence, we have been inspired to develop new photochromic materials. Furthermore, such dithienylethene phosphine ligand is different from previous reported phosphine ligands such as dppf, dppe and BINAP et al in the structure and the distance between two phosphine atoms, so the dithienylethene phosphine ligand can give us some novel structure when it is treated with the metal.

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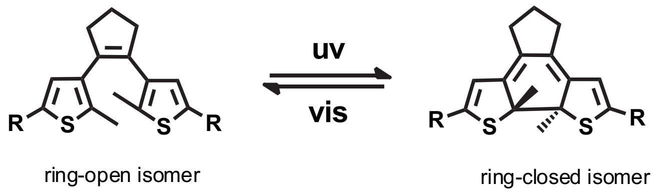


**Scheme 1.** Reversible photocyclization reactions of diarylethene.

In view of the above, we have synthesized two binuclear gold complexes with different phosphine ligands and a palladium chlorine-bridged macrocycle based on dithienylethene phosphine ligand. Moreover, the single crystal of macrocycle **5** was obtained. We have investigated their photochromic properties, which indicated that the metal centers of gold complexes can affect the photochromic properties of the free ligands and enhance their stability while the macrocycle **5** do not perform the photochromic reaction in $CH_2Cl_2$. However, we found that the non-photochromic macrocycle **5** can perform the photochromic reaction when the solution of $CH_3CN$ was irradiated by UV light and proved to be effective in catalyzing the Suzuki coupling reaction.

## 2. Materials and methods

### 2.1. Experimental

### 2.1.1. General

All manipulations were carried out under an argon atmosphere by using standard Schlenk techniques, unless otherwise stated. Bis(phosphine) ligand **1** and **2** were prepared by literature methods [37]. All other starting materials were obtained commercially as analytical-grade and used without further purification. $^1H$ NMR (400 MHz), $^{13}C$ NMR (100.6 MHz) and $^{31}P$ NMR (121.5 MHz) spectra were collected on a Varian MERCURY Plus 400 spectrometer (400 MHz). $^1H$ and $^{13}C$ NMR chemical shifts are relative to TMS, and $^{31}P$ NMR chemical shifts are relative to 85% $H_3PO_4$. Elemental analyses (C, H, N) were performed by the Microanalytical Services, College of Chemistry, CCNU. UV–Vis spectra were obtained on U-3310 UV Spectrophotometer. Photoisomerization measurements were carried out under a PHK 125-W mercury lamp as an irradiation source. The ring-opening reactions were carried out using the light of a 200-W tungsten source that was passed through the appropriate cutoff filter to eliminate higher energy light. The distance between the sample and the lamp is 10 cm.

**Table 1**
Crystal data and structure refinement parameters for **5**.

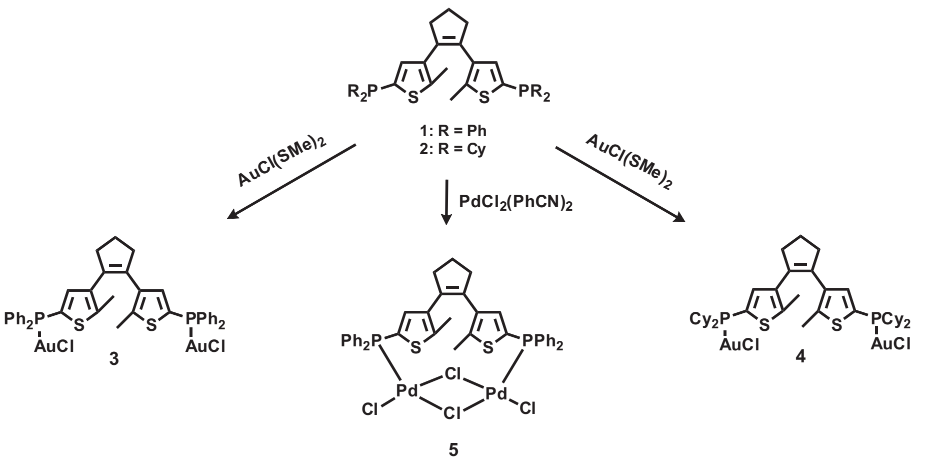
| Compound | **5** |
|---|---|
| Empirical formula | $C_{39}H_{34}Cl_4P_2Pd_2S_2 \cdot 1.5CH_2Cl_2$ |
| Molecular weight | 1110.71 |
| Wavelength (Å) | 0.71073 |
| Temperature (K) | 292(2) |
| Crystal system | Triclinic |
| Space group | P-1 |
| $a$ (Å) | 9.4139(5) |
| $b$ (Å) | 11.8320(7) |
| $c$ (Å) | 21.5333(12) |
| $\beta$ (o) | 89.3330(10) |
| $V$ (Å$^3$) | 2226.5(2) |
| $Z$ | 2 |
| $D_{cala}$ (Mg m$^{-3}$) | 1.657 |
| $\mu$ (mm$^{-1}$) | 1.423 |
| $F$(000) | 1106 |
| $\theta$ (min-max) (°) | 0.95–27.00 |
| Reflections collected | 18785 |
| Independent reflection | 9545 |
| $R_{int}$ | 0.0272 |
| Crystal size (mm) | 0.24 × 0.20 × 0.12 |
| $R$ indices [$I > 2\sigma$] | $R_1 = 0.0496$, $\omega R_2 = 0.1399$ |
| $R$ indices (all date) | $R_1 = 0.0705$, $\omega R_2 = 0.1503$ |
| Goodness-of-fit on $F^2$ | 1.047 |

### 2.2. Synthesis of dithienylethene-based complexes 3–5

### 2.2.1. Compound 3

$AuCl(SMe_2)_2$ (178 mg, 0.50 mmol) were added at room temperature to a stirred solution of bis(phosphine) ligand **1** (157 mg, 0.25 mmol) in $CH_2Cl_2$ (30 mL). The resulting solution was heated to reflux for 14 h, and the reaction mixture was slowly cooled to room temperature. After removal of the solvent in vacuo, the desired product was purified by column chromatography (silica gel, eluent: petrol ether/$CH_2Cl_2$, 1:1) to give a white solid (243 mg) in a yield of 89%. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 2.06 (s, 6 H, $CH_3$), 2.04–2.09 (m, 2H, $CH_2$), 2.75 (t, $J$ = 7.2 Hz, 4H, $CH_2$), 7.12 (d, $J$ = 9.2 Hz, 2H, thienyl-H), 7.41–7.56 (m, 20H, Ph). $^{13}C$ NMR (100.6 MHz, $CDCl_3$): $\delta$ 14.67 (s, $CH_3$), 22.90 (s, $CH_2$), 38.13 (s, $CH_2$), 124.50, 129.21, 129.84, 132.09, 133.25, 135.16, 137.82, 139.96, 145.33 (s, thiophene, ethane, Ph). $^{31}P$ NMR ($CDCl_3$, 121.5 MHz), $\delta$ 18.46 (s, $PPh_2$). Anal. calcd for $C_{39}H_{34}Au_2Cl_2P_2S_2$: C, 42.83; H, 3.13; S, 5.86. Found: C, 43.04; H, 2.96; S, 6.02.

The synthesis is similar to **3**, with bis(phosphine) ligand **1** being replaced by bis(phosphine) ligand **2**



**Scheme 2.** Synthesis of dithienylethene-based metal complexes **3**–**5**.

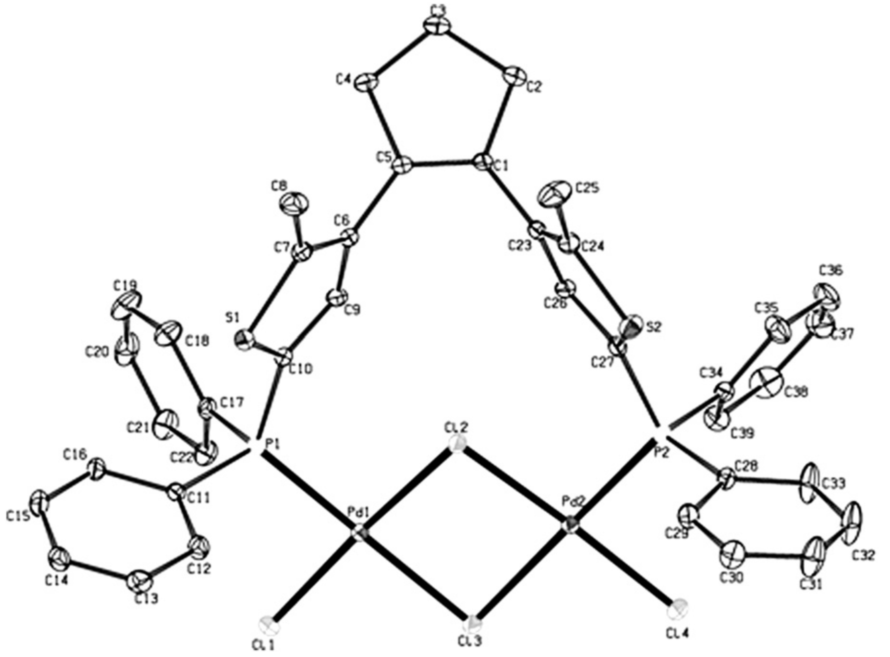


**Fig. 1.** Molecular structures of **5**. The H atoms have been omitted for clarity.

### 2.2.2. *Compound **4***

The bis(phosphine) ligand **2** (163 mg, 0.25 mmol) with $AuCl(SMe_2)_2$ (178 mg, 0.50 mmol) is similar to **3**. White solid, yield: 310 mg, 83%. $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 1.16–1.87 (m, 44H, Cy), 2.08 (s, 6H, $CH_3$), 2.02–2.10 (m, 2H, $CH_2$), 2.79 (t, $J$ = 7.2 Hz, 4H, $CH_2$), 7.14 (d, $J$ = 8.4 Hz, 2H, thienyl-H). $^{13}C$ NMR (100.6 MHz, $CDCl_3$): $\delta$ 14.33 (s, $CH_3$), 22.94 (s, $CH_2$), 25.64, 26.24, 26.37, 28.25 (s, Cy), 38.14 (s, $CH_2$), 125.34, 126.70, 134.68, 141.18, 144.05 (s, thiophene, ethene). $^{31}P$ NMR ($CDCl_3$, 121.5 MHz), $\delta$ 37.15 (s, $PCy_2$). Anal. calcd for $C_{39}H_{58}Au_2Cl_2P_2S_2$: C, 41.91; H, 5.23; S, 5.74. Found: C, 42.15; H, 5.18; S, 5.87.

### 2.2.3. *Compound **5***

The self-assembly of bis(phosphine) ligand **1** (79 mg, 0.125 mmol) with $[PdCl_2(PhCN)_2]$ (96 mg, mmol) is similar to **3**. Yellow solid, yield: 104 mg (85%). $^1H$ NMR (400 MHz, $CDCl_3$): $\delta$ 2.01–2.04 (m, 2H, $CH_2$), 2.19 (s, 6 H, $CH_3$), 2.65 (t, $J$ = 7.2 Hz, 4H, $CH_2$), 6.76 (d, $J$ = 5.2 Hz, 2H, thienyl-H), 7.47–8.06 (m, 20H, Ph). $^{31}P$

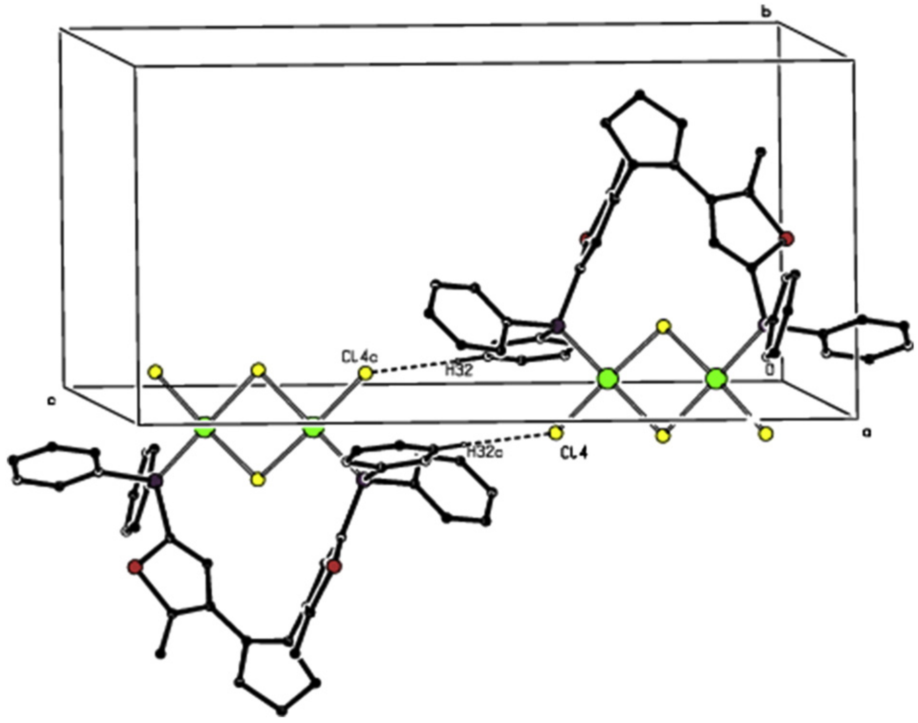


**Fig. 2.** Crystal packing of **5** showing C–H···Cl intermolecular interactions.

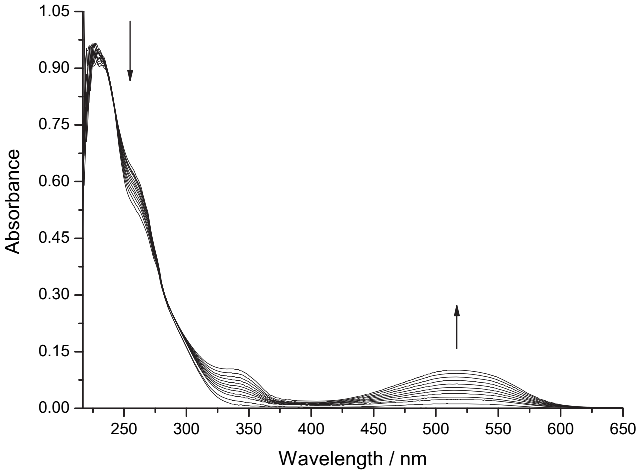


**Fig. 3.** UV/Vis absorption spectra of compound **3** ($2.0 \times 10^{-5}$ mol/L) in $CH_2Cl_2$ upon irradiation with UV light at 0, 2, 4, 6, 8s….

NMR ($CDCl_3$, 121.5 MHz), $\delta$ 20.78 (s, $PPh_2$). Anal. calcd for $C_{39}H_{34}Cl_4P_2Pd_2S_2$: C, 47.63; H, 3.48; S, 6.52. Found: C, 47.85; H, 3.39; S, 6.67.

## 3. Results and discussion

### 3.1. Discussion of the synthetic strategy

The dithienylethene bis(phosphine) ligands **1**, **2** and derivatives **3**–**5** were synthesized in good yields according to Scheme 2. The bis(phosphine) ligands **1** and **2** were synthesized as described in our previous report [37]. The intermediates **1** and **2** were reacted with $[AuCl(SMe)_2]$ to afford the binuclear gold complexes **3** and **4** in yields of 89% and 83%, respectively. The palladium chlorine-bridged macrocycle complex **5** was obtained by the coordination of bis(phosphine) ligand **1** with $[PdCl_2(PhCN)_2]$.

### 3.2. X-ray structures of 5

The molecular structure of **5** was determined by X-ray crystallography. The crystallographic details are given in Table 1. The molecular structure of **5** is depicted in Fig. 1. The two phosphorus atoms are linked by chlorine-bridged palladium atoms to form a macrocyclic compound. The two thiophene rings are each similarly distorted to facilitate adoption of this orientation. The dihedral angles between the cyclopentene ring and the two thiophene rings are 76.35(1)° and 77.76(2)°, respectively. The distance between the centers of the two thiophene rings is 4.642(1) Å, and that between the two phosphorus atoms is 6.707(1) Å. Furthermore, according to the single-crystal structure, the parallel confirmation of this molecule is not useful to take place the photo cyclization reaction [1]. In addition, the distance between the two reactive carbons (C7–C24) is 4.412 Å, which is not short enough for the cyclization reaction to take place. Photochromic reactivity usually only appears when the distance between the reactive carbon atoms is less than 4.2 Å [38]. The crystal packing view of complex **5**, depicting C(14)–H···Cl intermolecular hydrogen-bonding interactions. Subsequently, we checked the photochromism in the solution of $CH_3CN$. That the non-photochromic macrocycle **5** can perform the photochromic reaction was observed when the solution of $CH_3CN$ was irradiated by UV light possibly because the strong binding ability of $CH_3CN$ destroyed the chlorine-bridged units.

**Table 2**
Absorption characteristics of **1**–**4** in $CH_2Cl_2$ ($2.0 \times 10^{-5}$ mol/L).

| Compounds | $\lambda_{max}{}^{Abs}$/nm[a] | $\lambda_{max}{}^{Abs}$/nm[b] | $\varepsilon \times 10^{-4}$ | |
|---|---|---|---|---|
| | (Open) | (PSS) | (Open) | (PSS) |
| **1** | 228 | 505 | 10.0 | 0.8 |
| **2** | 233 | 497 | 7.8 | 0.7 |
| **3** | 229 | 517 | 4.8 | 0.5 |
| **4** | 232 | 503 | 5.5 | 0.7 |

[a] Absorption maxima of open-ring isomers.
[b] Absorption maxima of closed-ring isomers.

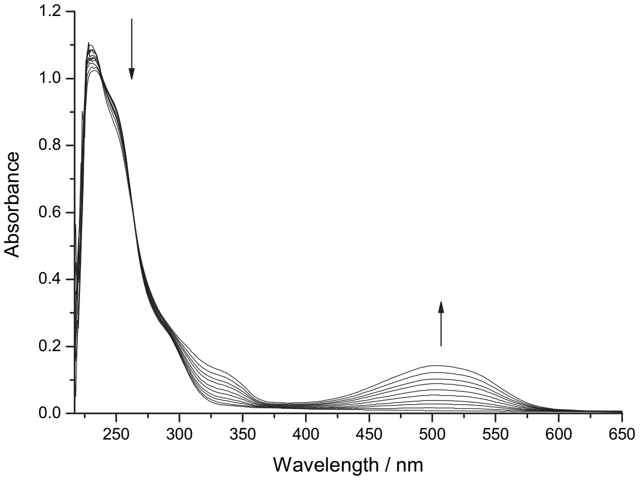


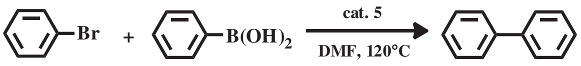
**Fig. 4.** UV/Vis absorption spectra of compound **4** ($2.0 \times 10^{-5}$ mol/L) in $CH_2Cl_2$ upon irradiation with UV light at 0, 2, 4, 6, 8s….

### 3.3. Photochromism

The synthesized dithienylethenes **3** and **4** undergo photoisomerization between **3**o/**4**o (ring-opened isomers) and **3**c/**4**c (ring-closed isomers) upon alternating irradiation with UV light ($\lambda = 302$ nm) and visible light ($\lambda > 400$ nm), as illustrated in Scheme 1. The absorption spectra of dithienylethenes **3**–**5** in dichloromethane were measured at room temperature before UV irradiation.

As shown in Fig. 2, the absorption maximum of compound **3** in dichloromethane was observed at 229 nm ($\varepsilon = 4.8 \times 104$ L $mol^{-1}$ $cm^{-1}$), which is in good agreement with a previous literature report [36]. Upon irradiation with 302 nm UV light, the colorless solution immediately turned red and a new absorption band was observed at 517 nm ($\varepsilon = 0.5 \times 10^4$ L $mol^{-1}$ $cm^{-1}$) as a result of formation of the ring-closed isomer **3**c. In addition, a well-defined isosbestic point was observed at 282 nm. Upon irradiation with visible light ($\lambda > 400$ nm), the colored **3**c underwent a cycloreversion reaction to the initial colorless ring-opened isomer **3**o. Similar results were obtained when a solution of complex **4** in $CH_2Cl_2$ was irradiated with UV/Vis light, as shown in Fig. 3. From these data, we found that different ancillary phosphine ligands (Ph or Py) had little effect on the efficiency of this conversion.

The absorption data for dithienylethenes **1**–**4** are summarized in Table 2. For dithienylethenes **3** and **4**, introduction of metal atoms caused 6–12 nm red shifts upon irradiation with UV light, compared with the spectra of ligands **1** and **2**. The molar absorption



**Scheme 3.** Suzuki coupling reaction catalyzed by compound **5**.

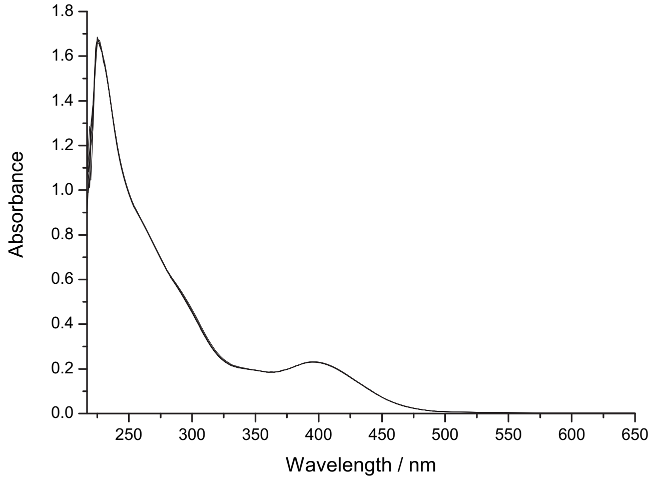


**Fig. 5.** UV/Vis absorption spectra of compound **5** ($2.0 \times 10^{-5}$ mol/L) in $CH_2Cl_2$ upon irradiation with UV light at 0, 2, 4, 6, 8s....

coefficients of **3** and **4** were seen to be decreased compared with those of the free ligands **1** and **2**.

### 3.4. Catalytic activity

Different behavior was observed when a solution of compound **5** in $CH_2Cl_2$ was irradiated with UV/Vis light (Fig. 4). As shown in Fig. 1, the dithienylethene **5** in the ring-opened form may only exist as a unique conformational isomer, that is, in a parallel conformation. Because of the rigid ring that is formed by the two phosphorus atoms and the chlorine-bridged dipalladium unit, conformational exchange from the parallel conformation to the photoactive anti-parallel conformation is precluded at room temperature. Thus, this system did not transform to the ring-closed form upon irradiation with UV light since this photocyclization can only occur from the anti-parallel conformer. Although it did not display photochromism, it was found that **5** was capable of catalyzing the Suzuki coupling reaction. As shown in Scheme 3, we found that biphenyl could be synthesized from bromobenzene and phenylboronic acid in good yield (>95%) in the presence of compound **5** (Fig. 5).

## 4. Conclusions

Three dithienylethene-based metal complexes have been synthesized, and their photochromic properties have been investigated. The absorption spectra of the two binuclear gold complexes **3** and **4** showed 6–12 nm red-shifts upon irradiation with UV light compared with the spectra of the ligands **1** and **2**. Furthermore, the introduction of metal atoms can stabilize the dithienylethene-based bis(phosphine) ligands. Although the novel palladium chlorine-bridged macrocycle **5** does not display photochromism in $CH_2Cl_2$, it can perform the photochromic reaction when the solution of $CH_3CN$ was irradiated by UV light, and that shows excellent catalytic activity for the Suzuki coupling reaction.

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