

两个基于二噻吩乙烯结构单元双核钉乙烯配合物的合成,表征和性质

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摘要: 合成了 2 个含二噻吩乙烯结构单元双核钉乙烯配合物 $[\text{RuCl}(\text{CO})(\text{PMe}_3)_3]_2(\mu\text{-}2,2'\text{-(CH=CH)}_2\text{-DTE})(\mathbf{1a})$ 和 $[\text{RuCl}(\text{CO})(\text{PMe}_3)_3]_2(\mu\text{-}2,5\text{-(CH=CH)}_2\text{-DTE})(\mathbf{1b})$, 利用元素分析、红外、核磁共振谱和电化学对它们的结构进行了表征, X-射线单晶衍射分析表明, 配合物 **1a** 晶体属单斜晶系, $C2/c$ 空间群, 晶胞参数为: $a=3.445\ 75(6)\ \text{nm}$, $b=1.459\ 45(2)\ \text{nm}$, $c=2.321\ 91(5)\ \text{nm}$, $\beta=110.977\ 0(10)^\circ$, $V=10.902\ 8(3)\ \text{nm}^3$, $Z=8$, $D_c=1.467\ \text{g}\cdot\text{cm}^{-3}$, $\lambda=0.071\ 073\ \text{nm}$, $\mu(\text{Mo K}\alpha)=0.956\ \text{mm}^{-1}$, $F(000)=4\ 912$ 。测定了它们光照前后的紫外-可见吸收光谱变化图, 并对其光致变色性质进行了讨论。

关键词: 钉乙烯配合物; 二噻吩乙烯; 合成; 晶体结构; 性质

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Synthesis, Characterization and Properties of Two Binuclear Ruthenium Vinyl Complexes Based on Dithienylethene Unit

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Abstract: Two binuclear ruthenium vinyl complexes with dithienylethene unit $[\text{RuCl}(\text{CO})(\text{PMe}_3)_3]_2(\mu\text{-}2,2'\text{-(CH=CH)}_2\text{-DTE})$ (**1a**) and $[\text{RuCl}(\text{CO})(\text{PMe}_3)_3]_2(\mu\text{-}2,5\text{-(CH=CH)}_2\text{-DTE})$ (**1b**) have been synthesized and characterized by elemental analysis, IR spectra, NMR spectra and electrochemical property. Single crystal X-ray diffraction analysis showed that complex **1a** crystallized in Monoclinic, space group $C2/c$ with $a=3.445\ 75(6)\ \text{nm}$, $b=1.459\ 45(2)\ \text{nm}$, $c=2.321\ 91(5)\ \text{nm}$, $\beta=110.977\ 0(10)^\circ$, $V=10.902\ 8(3)\ \text{nm}^3$, $Z=8$, $D_c=1.467\ \text{g}\cdot\text{cm}^{-3}$, $\lambda=0.071\ 073\ \text{nm}$, $\mu(\text{Mo K}\alpha)=0.956\ \text{mm}^{-1}$ and $F(000)=4\ 912$. The UV-Vis absorption spectral changes of the two complexes were measured upon UV and visible light, and their photochromic properties were also discussed. CCDC: 1003551, **1a**.

Key words: ruthenium vinyl complex; dithienylethene; synthesis; crystal structure; property

0 Introduction

Photochromic compounds have attracted remark-

able attention because of their potential ability for optical memory media and optical switching devices^[1]. Among them dithienylethenes (DTE) are the most

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promising candidates for the applications because of their fatigue resistant and thermally irreversible photochromic properties^[2-4]. A highly active area of current research into dithienylethenes is to develop novel structures with unique properties. Because metal-coordination complexes provide their own diverse assortment of photophysical and electrochemical characteristics, the combination of a DTE system with a metal ion should facilitate such application of switching devices^[5-7]. Much research into these metal-coordination complexes with DTE unit has been focused on the metalation of the 5, 5' site on the thiophene moiety. Whereas there are few reports concerning the metal attached to the 2,2' or 2,5 site of thiophene.

In our previous work, we constructed a photoswitchable organometallic molecular wire by combining a DTE unit with a redox-active ruthenium metal center, which exhibited switching behavior triggered by either photochemical or electrochemical stimuli^[8]. Inspired by the successful construction of new multifunctional switchable molecules, we considered it an attractive goal to synthesis new ruthenium vinyl complexes with photoswitchable dithienylethene linkers. Herein, we report the first example of binuclear ruthenium vinyl complexes with metal center linked to the 2,2' or 2,5 site of thiophene rings (Scheme 1). To the best of our knowledge, the

crystal structure of DTE unit with ruthenium vinyl groups in the photo reaction active center has never been reported so far.

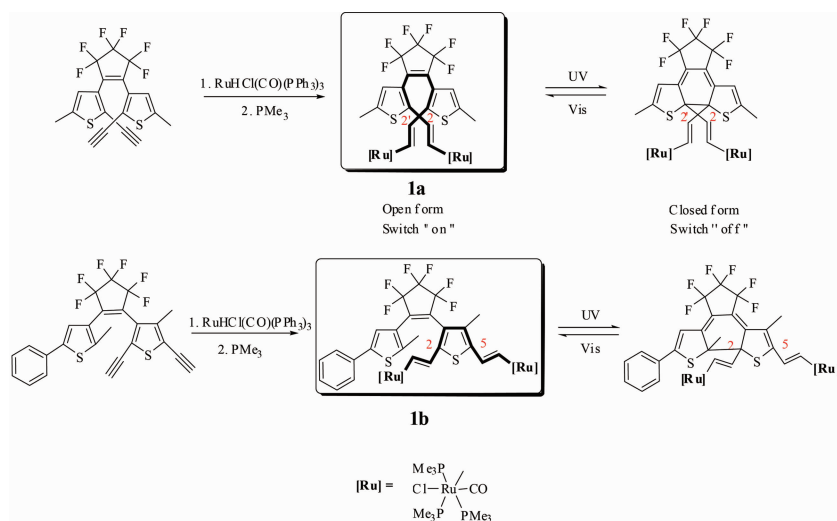
1 Experimental

1.1 Materials and measurements

The key intermediate terminal bisacetylide compounds were conveniently synthesized as the procedures described by our previous report^[9]. All reactions were carried out under nitrogen with anhydrous solvents unless otherwise stated. Dichloromethane and hexane were freshly distilled over calcium hydride. Elemental analysis was performed on a Vario El III Chnso instrument. IR spectrum was recorded on a Nicolet Avatar 380 FTIR instrument with KBr pellets in the range of 400~4 000 cm^{-1} . UV-Vis spectra were obtained on U-3310 UV spectrophotometer. ^1H , ^{13}C , and ^{31}P NMR spectra were collected on American 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 . Cyclic voltammetry was performed in a three-electrode cell using a CHI-660C electro-chemistry station.

1.2 Synthesis of complexes 1

To a suspension of $\text{RuHCl}(\text{CO})(\text{PPh}_3)_3$ (0.152 g, 0.16 mmol) in CH_2Cl_2 (10 mL) was slowly added a solution of bisacetylide compounds (0.10 mmol) in



Scheme 1

CH_2Cl_2 (10 mL). The reaction mixture was stirred for 30 min to give a red solution. Then a $1 \text{ mol} \cdot \text{L}^{-1}$ THF solution of PMe_3 (2.0 mL, 2.0 mmol) was added to above solution. The reaction mixture was stirred for 15 h. The solution was filtered through a column of Celite. The volume of the filtrate was reduced to ca. 2 mL under vacuum. Addition of hexane (30 mL) to the residue produced a light yellow solid, which was collected by filtration, washed with hexane, and dried under vacuum. The appropriate crystals for X-ray data collection were obtained by slow evaporation of dichloromethane to n-hexane solution at room temperature.

1a: Yield: 92 mg, 93%. Anal. Calcd. for $\text{C}_{41}\text{H}_{80}\text{Cl}_2\text{F}_6\text{O}_2\text{P}_6\text{Ru}_2\text{S}_2$ (%): C, 39.65; H, 6.49. Found (%): C, 39.43; H, 6.23. ^1H NMR (400 MHz, CDCl_3): δ 1.29 (t, $J=3.4$ Hz, 36H, PMe_3), 1.44 (d, $J=7.2$ Hz, 18H, PMe_3), 2.30 (s, 6H, CH_3), 6.67 (s, 2H, thiophene-H), 6.33~6.39 (m, 2H, thiophene-CH=), 7.91 (m, 2H, RuCH=). ^{13}C NMR (100 MHz, CDCl_3): δ 15.56 (s, CH_3), 16.54 (t, $J=16.5$ Hz, PMe_3), 19.90 (d, $J=24.2$ Hz, PMe_3), 116.19, 125.81, 127.27, 134.42, 148.16, 174.46, 201.50 (CO). ^{31}P NMR (160 MHz, CDCl_3): δ -20.28 (t, $J=22.6$ Hz), -8.84 (d, $J=22.6$ Hz).

1b: Yield: 129 mg, 63%. Anal. Calcd. for $\text{C}_{45}\text{H}_{72}\text{Cl}_2\text{F}_6\text{O}_2\text{P}_6\text{Ru}_2\text{S}_2$ (%): C, 42.16; H, 5.66. Found

(%): C, 42.56; H, 5.23. ^1H NMR (400 MHz, CDCl_3): δ 1.42 (t, $J=3.4$ Hz, 36H, PMe_3), 1.45 (d, $J=6.8$ Hz, 18H, PMe_3), 1.91 (s, 6H, CH_3), 2.25 (s, 6H, CH_3), 6.36~6.42 (m, 1H, thiophene-CH=), 6.58~6.66 (m, 1H, thiophene-CH=), 7.17 (s, 1H, thiophene-H), 7.23~7.42 (m, 5H, ph-H), 7.69 (m, 1H, RuCH=), 7.87 (m, 1H, RuCH=). ^{13}C NMR (100 MHz, CDCl_3): δ 14.69, 15.69 (s, CH_3), 16.98 (t, $J=17.8$ Hz, PMe_3), 18.96 (d, $J=23.4$ Hz, PMe_3), 118.19, 119.89, 124.16, 125.17, 125.81, 125.96, 126.78, 127.01, 127.27, 129.79, 134.42, 148.16, 174.46, 202.09 (CO). ^{31}P NMR (160 MHz, CDCl_3): δ -20.51 (t, $J=22.6$ Hz), -9.15 (d, $J=22.6$ Hz).

1.3 Crystal Structure determination

A yellow block crystal of the complex **1a** (0.13 mm×0.10 mm×0.10 mm) was pasted on a quartz fiber with protection oil. Cell dimensions and intensities were measured at 150(2) K on a Bruker SMART APEX CCD area detector diffractometer equipped with a graphite-monochromatic Mo $K\alpha$ radiation ($\lambda=0.071\ 073$ nm). A total of 66 452 reflections were collected in the range of $1.85^\circ \leq \theta \leq 28.30^\circ$, of which 13 524 were independent ($R_{\text{int}}=0.061\ 4$), and 10 249 observed reflections ($I>2\sigma(I)$) were used in the succeeding refinements. The structure was solved by direct methods using the SHELXS-97^[10], and refined on F^2 by the

Table 1 Crystallographic data for complex 1a

Formula	$\text{C}_{39}\text{H}_{66}\text{Cl}_2\text{F}_6\text{O}_2\text{P}_6\text{Ru}_2\text{S}_2$	Radiation	Mo $K\alpha$
Formula weight	1 203.90	Abs coeff / mm^{-1}	0.956
T / K	150(2)	θ range / ($^\circ$)	1.85~28.30
Crystal system	Monoclinic	hkl range	-45 to 45, -19 to 19, -30 to 30
Space group	$C2/c$	Total no. of rflns	66 452
a / nm	3.445 75(6)	No. of unique rflns	13 524
b / nm	1.459 45(2)	No. of obsd rflns ($I>2\sigma(I)$)	10 249
c / nm	2.321 91(5)	No. of restraints/params	18/552
$\beta / (^\circ)$	110.977 0(10)	a, b for W^a	0.072 3, 4.060 3
V / nm^3	10.902 8(3)	Final R	0.050 3
Z	8	wR	0.126 8
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.476	R (all data)	0.069 7
Crystal size / mm	$0.13 \times 0.10 \times 0.10$	wR (all data)	0.135 3
$F(000)$	4 912	Goodness of fit on F^2	1.019
Diffractometer	KappaCCD	Largest diff. peak and hole / ($\text{e} \cdot \text{nm}^{-3}$)	1 774 and -913

^a $W=1/[\sigma^2(F_o)^2+(aP)^2+bP]$, where $P=(F_o^2+F_c^2)/3$

full-matrix least-squares methods using the SHELXL-97 program package^[11]. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were added according to theoretical models. Intensity data were corrected for empirical absorption. The final refinement converged at $R = 0.050\ 3$, $wR = 0.126\ 8$ ($w = 1/[\sigma^2(F_o)^2 + (0.072\ 3P)^2 + 4.060\ 3P]$), where $P = (F_o^2 + F_c^2)/3$, $S = 1.019$, $(\Delta\rho)_{\max} = 1\ 774\ \text{e} \cdot \text{nm}^{-3}$ and $(\Delta\rho)_{\min} = -913\ \text{e} \cdot \text{nm}^{-3}$. Crystallographic data of complex **1a** are shown in Table 1.

CCDC: 1003551, **1a**.

2 Results and discussion

2.1 Synthesis and characterization

The general synthetic route for the preparation of binuclear ruthenium vinyl complexes is outlined in Scheme 1. Bisacetylides were reacted with the ruthenium hydride complex $[\text{RuHCl}(\text{CO})(\text{PPh}_3)_3]$ to give the insertion products $[\text{RuCl}(\text{CO})(\text{PPh}_3)_2]_2(\mu\text{-(CH=CH)}_2\text{-DTE})$, which were not isolated because they are air-sensitive, especially in solution. PMe_3 was then added to give the corresponding six-coordinated complexes $[\text{RuCl}(\text{CO})(\text{PMe}_3)_3]_2(\mu\text{-(CH=CH)}_2\text{-DTE})$ (**1**).

The target complexes **1** were confirmed by NMR spectroscopy (^1H , ^{31}P , and ^{13}C) and elemental analysis. The PMe_3 ligands in **1** are meridionally coordinated to ruthenium, as indicated by an AM_2 pattern in the ^{31}P $\{^1\text{H}\}$ NMR spectrum. The ^1H NMR spectrum (in CDCl_3) of **1a** features the two Ru-CH proton signals at $\delta = 7.91$. However, two different Ru-CH proton signals are

observed in **1b**. The ^1H NMR spectrum of **1b** displays the Ru-CH signals at $\delta = 7.69$ and 7.87 , respectively, which may be attributed to the asymmetrical structure of this complex. The ^{31}P NMR spectra of complex **1a** showed a doublet at -8.2 for the mutually *trans* PMe_3 and a triplet at -20.28 for the unique PMe_3 , as well as -9.15 and -20.51 for complex **1b**. These chemical shifts being similar to that found in $[\text{RuCl}(\text{CO})(\text{PMe}_3)_3]_2(\mu\text{-(CH=CH)}_n)$ ^[8,12-13]. The presence of the thiophene rings is indicated by the ^1H NMR spectrum, which features characteristic singlet signals at $\delta = 6.67$ for **1a** and 7.17 for **1b**.

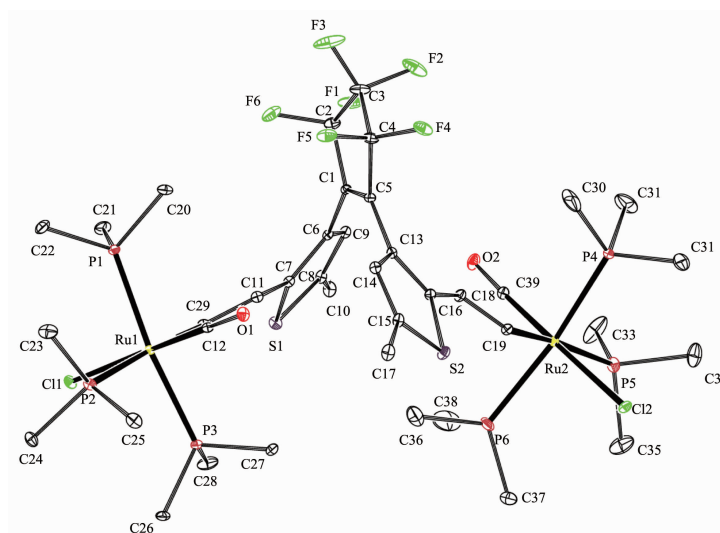
2.2 Crystal structure analysis

The crystal structure of **1a** is revealed in Fig.1. Selected bond lengths and bond angles are shown in Table 2. As shown in Fig.1, the complex **1a** introduced two ruthenium vinyl groups in the photo reaction active center on carbon position connected with the thiophene ring. It is evident that the thiophene moieties of the complex are packed in an antiparallel conformation in the crystalline phase, a conformation that is crucial for the compound to exhibit photochromic and photoinduced properties^[14]. The two planar thiophene ring systems have similar geometries, with dihedral angles between the cyclopentene ring and the adjacent thiophene rings of 51.99° (S1/C6-C7-C8-C9) and 50.12° (S2/C13-C14-C15-C16). The intramolecular distance between the two reactive carbons C(7)-C(15) is $0.376\ \text{nm}$, which is short enough for the cyclization reaction to take place,

Table 2 Selected bond lengths (nm) and bond angles ($^\circ$)

C(1)-C(5)	0.134 7(5)	C(2)-F(1)	0.135 2(5)	C(8)-C(10)	0.149 8(5)
C(11)-C(12)	0.133 6(5)	Ru(1)-P(1)	0.235 58(10)	Ru(1)-P(3)	0.235 47(10)
C(5)-C(1)-C(6)	129.4(3)	C(7)-C(6)-C(1)	123.1(3)	C(6)-C(7)-C(11)	130.4(3)
C(12)-C(11)-C(7)	125.2(3)	C(12)-Ru(1)-P(2)	177.14(10)	C(12)-Ru(1)-Cl(1)	89.43(11)
C(1)-C(6)	0.146 8(5)	C(2)-F(6)	0.136 9(5)	C(7)-C(11)	0.145 9(5)
Ru(1)-C(12)	0.208 7(4)	Ru(1)-P(2)	0.240 02(10)		
C(9)-C(6)-C(1)	123.6(3)	C(9)-C(8)-C(10)	129.3(4)	C(11)-C(7)-S(1)	119.9(3)
C(12)-Ru(1)-P(1)	82.00(10)	C(12)-Ru(1)-P(3)	81.94(10)	C(29)-Ru(1)-C(12)	92.04(16)

Symmetry code: A: $-x, y, -z+1/2$; B: $x+1/2, y+1/2, z$; C: $-x+1/2, y+1/2, -z+1/2$



H atoms are omitted for clarity; Symmetry code: A: $-x, y, -z+1/2$; B: $x+1/2, y+1/2, z$; C: $-x+1/2, y+1/2, -z+1/2$

Fig.1 Crystal structure of **1a** shown with 10% probability displacement ellipsoids

as photochromic reactivity usually appears when the distance between the reactive carbon atoms is less than 0.42 nm^[15]. The geometry around ruthenium can be described as a distorted octahedron with three meridionally bound PMe₃ ligands. The vinyl group is *trans* to the unique PMe₃ ligand, as well as the chloride is *trans* to the CO. The two olefinic double bonds are also in a *trans* configuration. The overall geometry about the two ruthenium centers in **1a** closely resembles that in bimetallic ruthenium complexes of the type [RuCl(CO)(PMe₃)₃]₂(μ -(CH=CH)_n)^[8,12].

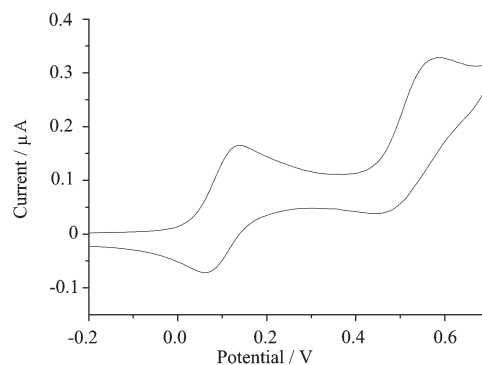
2.3 IR spectra

IR spectra of the complexes **1a** and **1b** reflect the binding patterns of [RuCl(CO)(PMe₃)₃] and diarylethene units. In the IR spectra of the complex **1a** (or **1b**), A strong band at about 1 910 cm⁻¹ is attributed to the C=O stretching vibration of the carbonyl groups. The C-H stretching mode for the thiophene ring is relatively weak and observed at about 2 982 cm⁻¹. The typical bands of the asymmetrical and symmetrical vibrations of C-H of CH₃ are at about 2 942 and 2 869 cm⁻¹. The strong absorption band at about 954 cm⁻¹ is the characteristic of *trans* C-H in the vinyl groups. These spectral information of complex **1a** is consistent with the results of X-ray analysis.

2.4 Electrochemical properties

The redox behavior of the complexes **1** was investigated by cyclic voltammetry in CH₂Cl₂ (1.0×10⁻³

mol·dm⁻³) using 0.1 mol·dm⁻³ *n*-Bu₄NPF₆ as the supporting electrolyte. Fig.2 displays the cyclic voltammogram for the complex **1b** during scanning from -0.20 to 0.70 V in 0.1 V·s⁻¹. Both of the Complexes **1** undergo two consecutive, chemically and electrochemically one-electron oxidation processes, corresponding to oxidation of Ru₂^{II,III} to Ru₂^{III,III} and then of Ru₂^{III,III} to Ru₂^{IV,IV}. For complex **1b**, the first redox process of is quasi-reversible, with i_{pc}/i_{pa} being 0.77, the second redox process is irreversible. However, both of the redox processes of complex **1a** are irreversible.



Potentials are given relative to the Ag/Ag⁺ standard. $v=0.1$ V·s⁻¹

Fig.2 Cyclic voltammograms (CV) of complex **1b** in CH₂Cl₂/Bu₄NPF₆

2.5 Photochromic properties

The photochromic properties of the binuclear ruthenium vinyl complexes **1** were examined by means

of UV-Vis spectrophotometry. Therefore, UV-Vis absorption spectral changes of the complexes **1** were measured in dichloromethane upon irradiation with UV light (302 nm) and visible light ($\lambda > 420$ nm) using cut-off filters at 298 K. As shown in Fig.3, for complex **1b**, the original absorption maximum of which appeared at 371 nm. Upon irradiation with light of wavelength 302 nm for 40 s, the system reached a photostationary state and the colorless solution of the open-ring isomer turned blue, showing a new band in the visible region at 629 nm due to the formation of the closed isomer. This blue color was bleached by subsequent irradiation with visible light, owing to the

complex reverting to its original open-ring state. This suggested that complex **1b** undergo reversible photochromic reactions. The complex **1a** was also studied in a similar fashion. There are two main peaks located at 307 and 390 nm. Upon illumination at a wavelength of 302 nm, the two peaks in UV region decreased. However, there are no new bands in the visible region increased. Whereas the solution of complex **1a** did not turned dark as other photochromic diarylethene compounds. The absorption spectrum characteristics indicated that the photocyclization of **1a** in dichloromethane was failed. We induced that may be ascribing for decomposition of the complex **1a**.

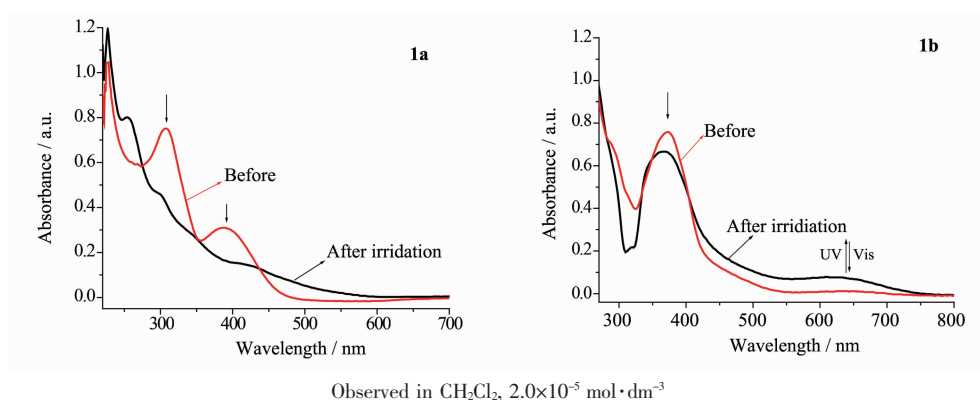


Fig.3 UV-Vis spectral changes of complexes **1a** and **1b** upon 302 nm light irradiation

3 Conclusions

The crystal structure of the complex **1a** with ruthenium vinyl groups in the photo reaction active center has been reported for the first time. The photochromic behavior of the two complexes has been examined by means of UV-Vis spectrophotometry. It was revealed that metalation in different sites of diarylethene unit led to significant impact on the photochromic properties.

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