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Facile synthesis and photochromic properties of diarylethene-containing terpyridine and its transition metal ($Zn^{2+}/Co^{2+}/Ru^{2+}$) complexes

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Several transition metal complexes based on 2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride (DTE) bearing terpyridine (TPY) have been designed and synthesized. Furthermore, the photochromism of the free ligand and the influence of transition metal moieties on the photochemical properties have been thoroughly characterized by monitoring the changes in their UVvis spectra. Compounds 3–6 all display excellent response to UV irradiation, especially Co complex 5 with optimum sensitivity that took only 5 s to reach photostationary state. The photochromic properties of DTE unit have been found to be strongly influenced by the bridging transition metals, as complexes 4 (L–Zn–L) and 6 (L–Ru–L) exhibit much better photochromic properties in tetrahydrofuran solution than complex 5 (L–Co–L) and the free ligand 3 (L). It is worth noting that the optical/chemical thermal stabilities of photochromic compounds 3–6 are all greatly improved after the precursor functionalized with TPY and further coordinated with metal ions. Copyright © 2012 John Wiley & Sons, Ltd.

Keywords: diarylethene; metal complex; photochromism; thermal stability

INTRODUCTION

Photochromic molecules, which refer to the reversible color change with light irradiation, have been studied extensively because of their capability to modulate physical and chemical properties for photoresponsive functional materials, such as molecular optical switches,[1–4] rewritable data memories,[5,6] and chemical sensing.[7] Among these materials, the photochromic dithienylethene derivatives have received much attention for their excellent photochromic properties with good fatigue resistance, thermal irreversibility, and short response time, not only in solution but also in the single-crystalline phase.[8–10] In recent years, transition metal complexes with ligands containing different photochromic families have been developed. In view of the photoswitching capability of the metal complex, organometallic photochromic complex is an interesting alternative to pure organic photochromes. They can provide new properties deriving from the combination of redox, optical, and magnetic properties of the metal complexes. Through combining a photochromic moiety with an organometallic compound, the photochromic properties could be simply modulated by different coordinating metal centers.[1,3,11–13] In addition, the metal terpyridine (TPY) complexes have excellent stability and remarkably high binding affinity towards transition metal ions, showing photophysical/photochemical properties,[14] which have led to the development of various luminescent metal compounds and sensitizers for photovoltaic devices.[15] Therefore, we focus our attention on coupling different metal ions with the functionalized photochromic TPY–2,3-bis(2,4,5-trimethyl-3-thienyl)maleic anhydride (DTE) ligand in a linear structure with L–M–L arrangement in order either to modulate the photochromic properties or to photoregulate the optical properties of the organometallic moieties.

Herein, the synthesis of 1-(4-([2,2′:6′,2″-terpyridin]-4′-yl)phenyl)-3,4-bis(2,4,5-trimethylthiophen-3-yl)-1*H*-pyrrole-2,5-dione and its transition metal ($Zn^{2+}/Co^{2+}/Ru^{2+}$) complexes is firstly reported. The synthetic strategies are outlined in Scheme 1. The photochromic properties, thermal irreversibility, and chemical thermal stability of these compounds are also described.

EXPERIMENTAL

Materials and measurements

Acetyl pyridine, 4-nitrobenzaldehyde, potassium hydroxide, tin (II) chloride dehydrate, ammonium hexafluorophosphate, and DTE were purchased from Sigma-Aldrich (Shanghai, China) or TCI (Tokyo, Japan) chemical company. Toluene was dried over 0.4 nm molecular sieves prior to use. All other solvents were bought from commercial sources and used without further purification. Thin-layer chromatography was carried out using commercially prepared 100–400 mesh silica gel plates (GF_{254}) that were visualized by irradiation (254 nm), and column chromatography was carried out using silica gel (200–300 mesh). Melting points (m.p.) were determined with a YUHUA X4 melting point

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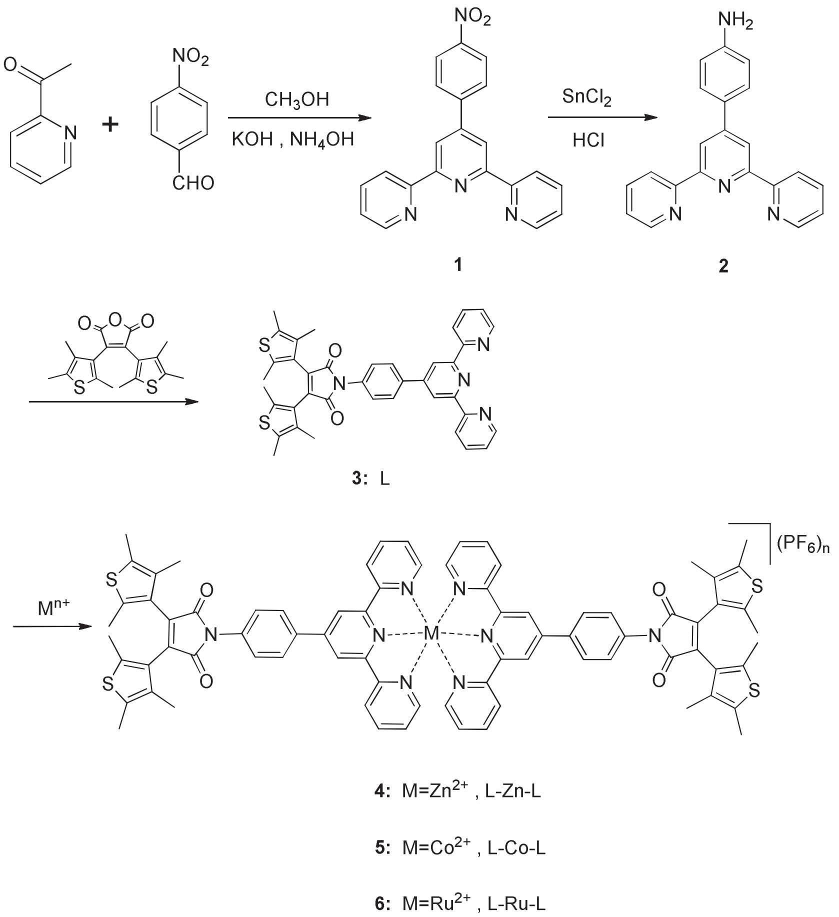

Scheme 1. Synthetic route to the diarylethene-containing terpyridine and its transition metal complexes

apparatus (Gongyi, China) and were uncorrected. ^1H nuclear magnetic resonance (^1H NMR) spectra and ^{13}C NMR were recorded on a Bruker DRX-400 MHz spectrometer (Stuttgart, Germany) with tetramethylsilane as internal standard and dimethyl sulfoxide (DMSO)-d_6/$CDCl_3$ as solvent. Electrospray ionization/atmospheric pressure chemical ionization (ESI/APCI) mass spectra were recorded on a Brucker Esquire HCT plus (Stuttgart, Germany) with methanol or tetrahydrofuran (THF) as solvent. UV–visible absorption spectra were recorded on a HITACHI U3010 spectrophotometer (Tokyo, Japan). Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere with a TGA/DSC Q600 SDT TA Instruments apparatus (New Castle, DE, USA) at an elevation temperature of 10 °C/min.

Synthesis

Compounds **1**, **2**, and **3** were prepared according to the corresponding procedure in the literatures.[16–18]

4′-(4-nitrophenyl)-2,2′:6′,2″-terpyridine (1)

A mixture of 2-acetylpyridine (5 g, 41.5 mmol) and 4-nitrobenzaldehyde (3.17 g, 21 mmol) in CH_3OH (170 mL) was stirred vigorously with 15% aq. KOH (15 mL) and conc. NH_4OH (160 mL) for 3 days at room temperature. The precipitate was collected by vacuum filtration, washed with water then with cold methanol, and dissolved in ethyl acetate. The organic fraction was washed with 1% $NaHCO_3$ and dried with $MgSO_4$. After removal of the solvent under reduced pressure, the crude brown product was purified by recrystallization twice with C_2H_5OH to give the pure product (Yield: 34%). m.p. 210–211 °C; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.74 (m, 4H), 8.69 (d, *J* = 7.95 Hz, 2H), 8.37 (d, *J* = 8.57 Hz, 2H), 8.05 (d, *J* = 8.54 Hz, 2H), 7.91 (t, *J* = 7.73 Hz, 2H), 7.38 (m, 2H).

4′-(4-aminophenyl)-2,2′:6′,2″-terpyridine (2)

A mixture of compound **1** (0.46 g, 1.3 mmol) and $SnCl_2$ (1.536 g, 6.8 mmol) in concentrated hydrochloric acid (12 mL) was heated at 80 °C for 8 h. After cooling to room temperature, the residue collected by vacuum filtration was poured into cool water and adjusted to pH 12–13 with $NaHCO_3$ solution. The solid was filtered and purified by column chromatography (basic alumina, eluting with petroleum ether/ethyl acetate = 1:1) to give the pure product (Yield: 62%). m.p. 253–254 °C; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.73 (d, *J* = 4.16 Hz, 2H), 8.69 (s, 2H), 8.66 (d, *J* = 7.98 Hz, 2H), 7.87 (m, 2H), 7.79 (d, *J* = 8.50 Hz, 2H), 7.34 (m, 2H), 6.80 (d, *J* = 8.51 Hz, 2H).

1-(4-([2,2′:6′,2″-terpyridin]-4′-yl)phenyl)-3,4-bis(2,4,5-trimethylthiophen-3-yl)-1*H*-pyrrole-2,5-dione (3)

A mixture of DTE (0.2 g, 0.578 mmol), compound **2** (0.272 g, 0.84 mmol), and dry Et_3N (0.3 mL) in dry toluene (25 mL) was refluxed for 2 days under nitrogen atmosphere. After removal of the solvent under reduced pressure, the crude product was purified by column chromatography (basic alumina, eluting with petroleum ether/ethyl acetate) to give the pure product (Yield: 87%). m.p. 130–131 °C; ^1H NMR (400 MHz, $CDCl_3$) δ (ppm): 8.78 (s, 2H), 8.75 (d, *J* = 4.00 Hz, 2H), 8.69 (d, *J* = 7.95 Hz, 2H), 8.05 (d, *J* = 8.58 Hz, 2H), 7.90 (m, 2H), 7.69 (d, *J* = 8.54 Hz, 2H), 7.37 (m, 2H), 2.28 (d, *J* = 9.75 Hz, 6H), 2.14 (s, 3H), 1.98 (s, 6H), 1.82 (s, 3H); ^{13}C NMR (101 MHz, $CDCl_3$) δ (ppm): 168.95, 168.85, 156.12, 156.02, 149.35, 149.13, 137.45, 137.14, 136.96, 136.93, 136.75, 136.48, 132.82, 132.80, 131.97, 131.65, 130.70, 127.95, 127.40, 127.26, 125.98, 123.91, 121.43, 118.86, 14.58, 14.31, 14.21, 13.49, 13.17, 13.16; APCI-mass spectrometry (MS) (*m/z*): 652.6 [$(M+H)^+$]; Anal. Calcd. for $C_{39}H_{32}N_4O_2S_2$: C, 71.75; H, 4.94; N, 8.58; S, 9.82. Found: C, 71.48; H, 5.11; N, 8.65; S, 9.97.

Complex L–Zn–L (4)

$Zn(CH_3COO)_2$ $2H_2O$ (4.8 mg, 0.022 mmol) was dissolved in C_2H_5OH (10 mL) and then added drop-wise to the solution of ligand **3** (32.6 mg, 0.05 mmol) in C_2H_5OH (10 mL) and $CHCl_3$ (1.5 mL). The mixture was stirred at room temperature for 30 min. Then, an excess of KPF_6 (160 mg) was added. After 1 h, the solid was centrifuged, washed with ethanol, water, and Et_2O, and dried in vacuum to give a yellow product (Yield: 84%). m.p. > 300 °C; ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 9.46 (s, 4H), 9.16 (d, $J=7.59$ Hz, 4H), 8.58 (d, $J=7.49$ Hz, 4H), 8.32 (s, 4H), 8.00 (s, 4H), 7.91 (d, $J=7.25$ Hz, 4H), 7.53 (s, 4H), 2.28 (d, $J=8.86$ Hz, 12H), 2.16 (s, 6H), 2.01 (s, 12H), 1.85 (s, 6H); ESI-MS (*m/z*): 684.5 $[M-2PF_6]^{2+}$; Anal. Calcd. for $C_{78}H_{64}F_{12}N_8O_4P_2S_4Zn$: C, 56.40; H, 3.88; N, 6.75; S, 7.72. Found: C, 56.15; H, 3.99; N, 6.91; S, 7.53.

Complex L–Co–L (5)

$CoCl_2{\cdot}6H_2O$ (5.2 mg, 0.022 mmol) was dissolved in C_2H_5OH (10 mL) and then added drop-wise to the solution of ligand **3** (32.6 mg, 0.05 mmol) in C_2H_5OH (10 mL)/$CHCl_3$ (1.5 mL). The mixture was refluxed for 3 h under nitrogen atmosphere. After filtration, an excess of KPF_6 (160 mg) was added, and the yielding solid was centrifuged, washed with ethanol, water, and Et_2O, and dried in vacuum to give a brown product (Yield: 86%). m.p. > 300 °C; ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 85.69 (br, 4H), 50.29 (s, 4H), 35.82 (s, 4H), 31.04 (s, 4H), 13.55 (s, 4H), 10.09 (s, 4H), 8.96 (s, 4H). The C–H peaks of the thienyl rings in the ^1H NMR spectrum were overlapped with the solvent residual peak of DMSO; ESI-MS (*m/z*): 681.3 $[M-2PF_6]^{2+}$; Anal. Calcd. for $C_{78}H_{64}F_{12}N_8O_4P_2S_4Co$: C, 56.62; H, 3.90; N, 6.77; S, 7.75. Found: C, 56.34; H, 4.08; N, 6.92; S, 7.96.

Complex L–Ru–L (6)

$RuCl_3$ (4.6 mg, 0.022 mmol) was dissolved in C_2H_5OH (10 mL) and then added drop-wise to the solution of ligand **3** (32.6 mg, 0.05 mmol) in C_2H_5OH (10 mL)/$CHCl_3$ (1.5 mL). The mixture was refluxed for 4 h under nitrogen atmosphere. After filtration, an excess of KPF_6 (160 mg) was added, and the yielding solid was centrifuged, washed with ethanol, water, and Et_2O, and dried in vacuum to give a brown product (Yield: 82%). m.p. > 300 °C; ^1H NMR (400 MHz, DMSO-d_6) δ (ppm): 9.54 (s, 4H), 9.11 (d, $J=8.17$ Hz, 4H), 8.57 (d, $J=8.27$ Hz, 4H), 8.10 (t, $J=7.60$ Hz, 4H), 7.91 (d, $J=7.90$ Hz, 4H), 7.59 (d, $J=5.33$ Hz, 4H), 7.31 (d, $J=6.58$ Hz, 4H), 2.28 (d, $J=9.02$ Hz, 12H), 2.16 (s, 6H), 2.01 (d, $J=4.33$ Hz, 12H), 1.85 (s, 6H); ESI-MS (m/z): 702.6 $[M-2PF_6]^{2+}$; Anal. Calcd. for $C_{78}H_{64}F_{12}N_8O_4P_2S_4Ru$: C, 55.22; H, 3.80; N, 6.60; S, 7.56. Found: C, 55.49; H, 3.57; N, 6.51; S, 7.80.

RESULTS AND DISCUSSION

Synthesis and characterization

The particular type of diarylethene unit was chosen to be incorporated into our molecule for its good photochromic property and ease of functionalization at the maleic anhydride oxygen. Scheme 1 outlines the synthetic route for the chemically modified dithienylethene maleic anhydride, allowing a fine tune of its photochromic and thermal properties. 4′-(4-nitrophenyl)-2,2′:6′,2″-terpyridine was synthesized following a facile one-pot reaction by the previously reported procedure.[16] The nitro group was reduced to amino compound by using $SnCl_2$/HCl. Ligand **3** was prepared from DTE by a conventional thermal imidization with the amino TPY compound **2** in toluene and then coordinated with different metal ions to give L–M–L complexes **4–6**. All the synthesized complexes were fully characterized by ESI-MS, ^1H NMR, UV–vis spectra, and elemental analysis. In ^1H NMR spectra of the complexes, signals of the protons attached to the TPY moieties appeared at lower magnetic fields than those of the free ligand because of the strong electron-withdrawing effects of the metal centers.

Electronic absorption and photochromic behaviors

The absorption spectra of ligand **3** in *n*-hexane and complexes **4–6** in dilute (10^{-4} mmol/L) THF solution were recorded. Their photochromic behaviors were investigated by monitoring the changes in the absorption spectra upon irradiation at a specific wavelength capable of triggering the open/closed isomerization in the DTE units. The results are summarized in Table 1.

The photocyclization of ligand **3** was studied in different-polarity solvents including CH_3CN, THF, and *n*-hexane by irradiation at 254 nm (Fig. 1). Remarkable solvent dependence of the photochromic reaction was observed. The conversion of ligand **3** from an open-ring to a closed-ring isomer in the photostationary state (PSS) under irradiation with UV light decreased with increasing solvent polarity, in good agreement with the previous report, which presumed that it was due to the contribution of twisted intramolecular charge transfer.[19] In acetonitrile, no appreciable color change was observed upon irradiation with UV light, as shown in Fig. 1(c).

As shown in Fig. 1(a), the starting open form of ligand **3** in *n*-hexane solution showed two peaks at 282 and 375 nm. The former peak was assigned to the TPY-based transition, and the peak at 375 nm was responsible for the $S_0 \rightarrow S_1$ (^{1}IL) transition of the DTE unit. Upon irradiation with 254 nm light, the yellowish solution turned reddish, the peak at 282 nm gradually decreased, and new absorption bands appeared at 378 and 532 nm, which were assigned to $S_0 \rightarrow S_2$ and $S_0 \rightarrow S_1$ transitions, respectively. Such behavior was characteristic of the formation of the closed form of DTE derivatives, because

Table 1. UVvis absorption maxima of all compounds studied

	λ_{max}/nm ($c=2\times10^{-4}$ mmol/L)			
Compound	TPY-based	$S_0 \rightarrow S_2$[b]	$S_0 \rightarrow S_1$[b]	MLCT
3(O)	282	—	375	—
3(PSS)	280	378	532	—
4(O)	344	—	410	—
4(PSS)	344	380	532	—
5(O)	285	—	320	—
5(PSS)	286	378	522	—
6(O)	285,310	—	380	491
6(PSS)	286,309	378	567	491

TPY, terpyridine; MLCT, metal-to-ligand charge transfer; PSS, photostationary state.

[a] All spectra were recorded in a conventional 1.0 cm quartz cell at a concentration of 2×10^{-4} M in tetrahydrofuran except **L** in *n*-hexane.

[b] Dithienylethene-based transitions.

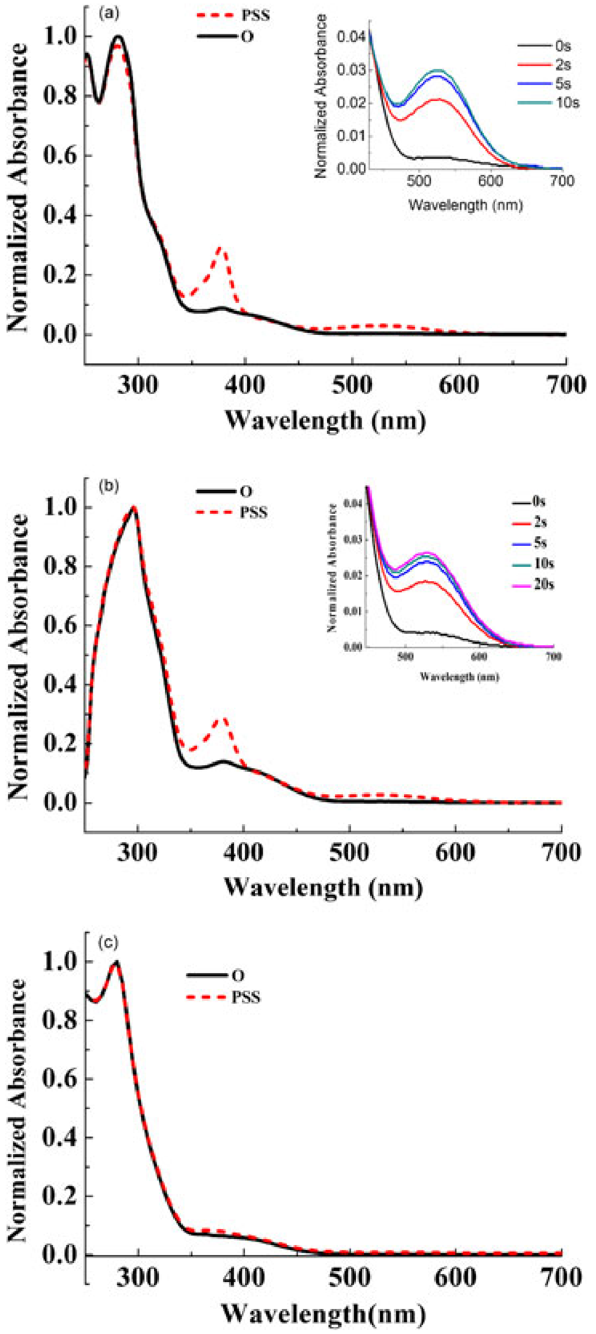

Figure 1. UVvis absorption spectra of the ligand **3** at a concentration of 2×10^{-4} M (a) in *n*-hexane, (b) in tetrahydrofuran, and (c) in CH_3CN before (solid line) and after (dashed line) irradiation at 254 nm to the photostationary state (PSS). The inset in Fig. 1 shows the absorption change between 450 and 700 nm

the closed form was more conjugated than the open form with greater electron delocalization resulting in a redshift of the $S_0 \rightarrow S_1$ transition. Upon irradiation with visible light ($\lambda = 550$ nm), the peaks at 378 and 532 nm gradually decreased and finally disappeared (the reddish solution returned to a yellowish solution).

Figure 2 shows the absorption spectral change along with photochromic reaction of complexes **4–6** in THF solution. Upon irradiation with 254 nm light, solutions of complexes **4–6** in the PSS exhibited reddish, reddish, and red colors, respectively, which were attributed to the photocyclization reaction from the open-ring isomer to the closed-ring isomer. The $S_0 \rightarrow S_1$ transitions of the DTE units were centered at 532, 522, and 567 nm respectively, and peaks at 380, 378, and 378 nm were assigned to their $S_0 \rightarrow S_2$ transitions. Upon excitation into the absorption bands of the closed form ($\lambda = 550$ nm), absorptions decreased in intensities, indicative of the regeneration of the open form as a result of the photochromic backward reaction. After comparing the absorption spectra of complexes **4–6** in the closed form with that of free ligand **3** (Fig. 3), we can find a considerable redshift of the S_0 S_1 transition of the DTE units after complexation with Ru^{2+} (532–567 nm) and a slight blueshift after complexation with Co^{2+} (532–522 nm), which were attributed to perturbation of

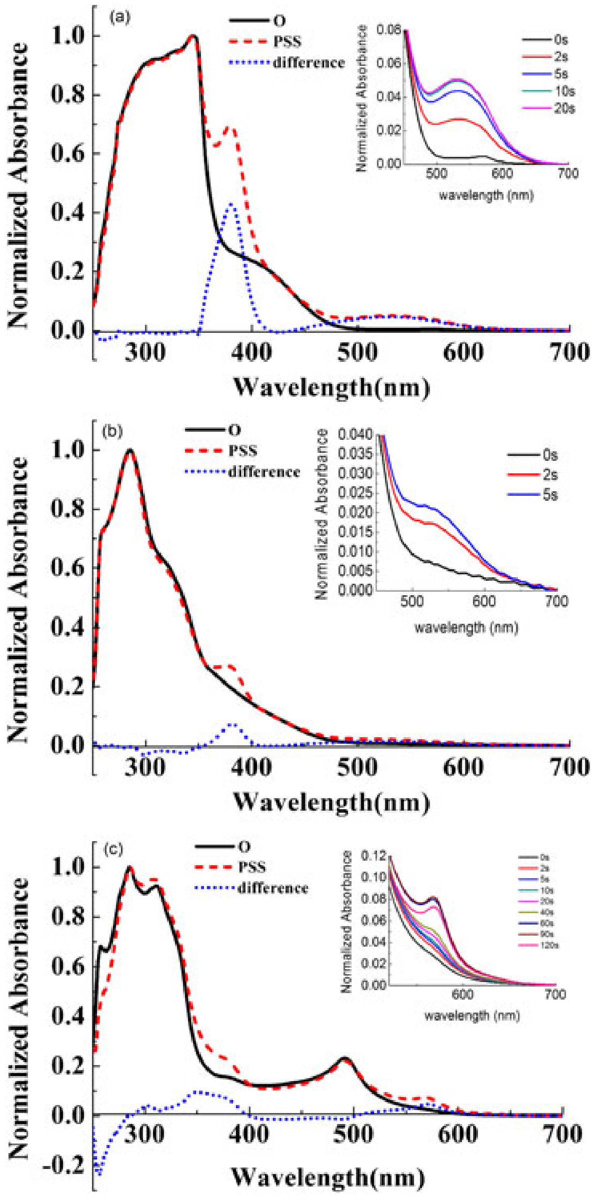

Figure 2. UVvis absorption spectra of complexes **4–6** (a) L–Zn–L, (b) L–Co–L, and (c) L–Ru–L at a concentration of 2×10^{-4} M in tetrahydrofuran before (solid line) and after (dashed line) irradiation at 254 nm to the photostationary state (PSS). The inset in Fig. 2 shows the absorption change between 450 and 700 nm

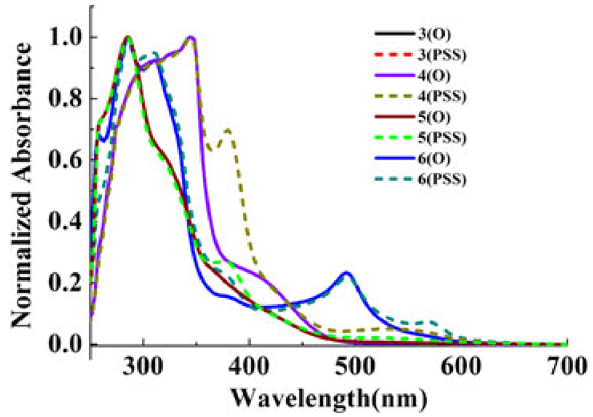

Figure 3. UVvis absorption spectra of the free ligand **3** and complexes **4–6** at a concentration of 2×10^{-4} M in tetrahydrofuran before (solid line) and after (dashed line) irradiation at 254 nm to the photostationary state (PSS)

the transitions by the metal centers in the metal complexes, indicating different electron-withdrawing properties of different conjugated metal centers.

In addition, as shown in Fig. 2(c), the starting open form of Ru complex **6** had a unique band at 491 nm, which was typically observed in Ru complex systems[11,17,20] and thus was assigned to a singlet metal-to-ligand charge-transfer (^{1}MLCT) transition. Upon UV irradiation at 254 nm, this absorption of MLCT band gradually decreased, which may be regarded as indication that the photochromic reaction of the complex not only took place in the presence of ruthenium but also influenced the MLCT transition, as shown in the difference spectra.[11] In view of the decreasing intensity of this MLCT band, we presumed that the extended conjugated system of the closed isomer could facilitate charge transfer or energy transfer from the bridging Ru^{2+} center to the closed form of the DTE unit.

It was worth mentioning that the Zn/Ru complexes showed much better photochromic properties than those of free ligand **3** and Co complex **5** (Figs. 3 and 4). As mentioned earlier, one of the drawbacks of the free ligand was that the photochromic reactions were strongly suppressed in polar solvents such as acetonitrile and THF (Fig. 1). Surprisingly, we can see from Figs. 3 and 4 that the absorption intensities in visible region of Zn/Ru complexes were stronger than those of Co complex **5** and free ligand **3**, suggesting that Zn/Ru complexes in THF solution exhibited obvious color change along with photochromic reaction, whereas the more polar solvent THF suppressed the color changes of free ligand **3** and Co complex **5**. Therefore, the color change and photocyclization of diarylethene can be easily enhanced by Zn^{2+} and Ru^{2+}.

Moreover, compounds **3–6** all displayed excellent response to UV irradiation, especially Co complex **5** with optimum sensitivity that took only 5 s to reach PSS upon irradiation with 254 nm light, which was outstanding compared with those in previous reports. Besides, Fig. 4 exhibits good linearity relationship between the absorbance and exposal time before reaching PSS, suggesting that the cyclization processes belong to the zeroth-order reaction.

Thermal stability

Optical thermal stability (thermal irreversibility)

1,4-Dioxane solutions of compounds **3–6** (2×10^{-4} M) were irradiated with 254 nm light to reach PSS. The thermal irreversibility was estimated by heating these solutions of photoproduct at 100 °C in the dark. As shown in Fig. 5, there were significant differences on their optical thermal stabilities. After heating for 72 h, only 4%, 3%, 6%, and 10% of the functionalized compounds **3–6** converted to the ring-opened form or formed the by-product from the closed-ring isomer in comparison with the 20% change for the precursor DTE. Obviously, the thermal irreversibility can be greatly improved after the precursor DTE functionalized with TPY and further coordinated with metal ions, which was critical for the practical application as data memory and readout system.

Chemical thermal stability

From Fig. 6, we can see that the thermal decomposition temperature of the precursor was 200 °C, whereas that of the

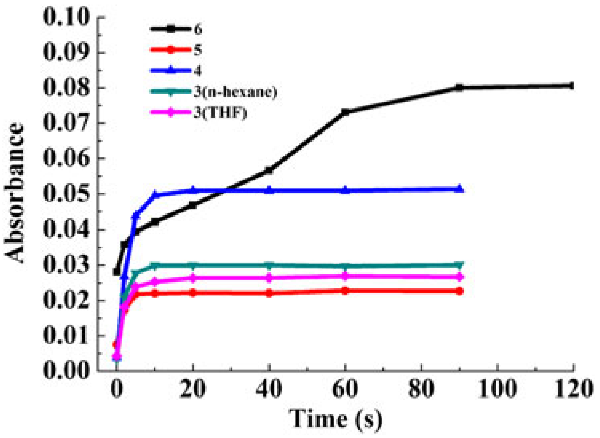

Figure 4. The absorbance changes of **3** (in *n*-hexane/tetrahydrofuran (THF)) and **4–6** (in THF) at maximum absorption wavelength in the visible region (**3**: 532 nm; **4**: 532 nm; **5**: 522 nm; **6**: 567 nm) with the irradiation time

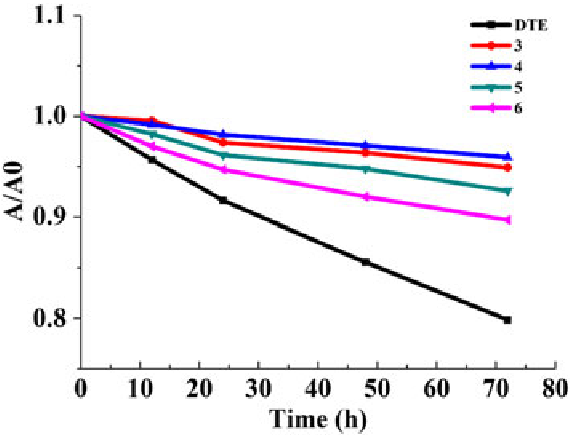

Figure 5. The absorbance changes of **3–6** (photostationary state) in 1,4-dioxane (2×10^{-4} M) at maximum absorption wavelength in the visible region (**3**: 532 nm; **4**: 532 nm; **5**: 522 nm; **6**: 567 nm) with the heating time

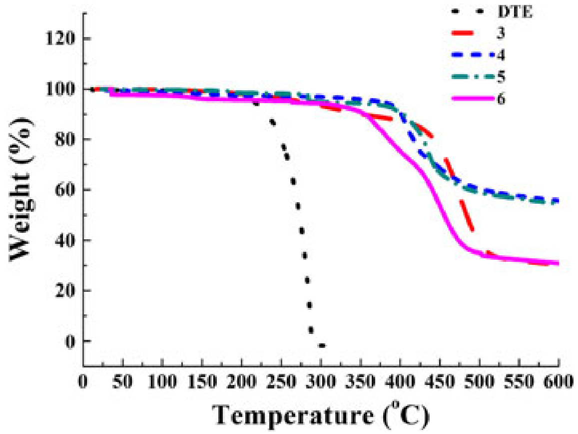

Figure 6. Thermogravimetric analysis curves of the precursor (2,3-bis (2,4,5-trimethyl-3-thienyl)maleic anhydride [DTE]) and compounds **3–6**

photochromic DTE unit functionalized at TPY 4′-position (ligand **3**) was 410 °C because of the good stability of TPY, and those of complexes **4–6** were also high (370 °C, 372 °C, and 330 °C, respectively). The results indicated that the photochromic precursor functionalized with TPY and further coordinated with different metal ions can also improve their chemical thermal stability, which was promising for some special photoresponsive materials, as protective packaging materials.

CONCLUSIONS

In summary, a series of transition metal complexes based on DTE bearing TPY were synthesized and characterized. The photochemical behavior of all photochromic compounds met our expectations regarding reversibility. They all displayed excellent response to UV irradiation, especially Co complex **5** with optimum sensitivity that took only 5 s to reach PSS. The functionalization of the photochromic precursor with TPY and metal ions provided enhanced thermal stability: (1) thermal irreversibility: after heating at 100 °C for 72 h, only 3–10% of photoproducts decomposed or converted to open-ring form compared with 20% of the precursor DTE; and (2) chemical stability: the thermal decomposition temperatures of functionalized compounds **3–6** were increased from 200 °C to 300–400 °C because of the good stability of TPY. It was also shown that the presence of different bridging metal ions had distinct influences on the photochromism: the more polar solvent THF suppressed the color change of the free ligand **3**, whereas Zn/Ru complexes in THF solution showed high photochromic reactivity, and Co^{2+} had no significant influence on the photochromism of the DTE unit. In addition, the photochromic reaction of Ru complex **6** influenced the MLCT transition,[11] indicating that the extended conjugated system of the closed isomer could facilitate charge transfer or energy transfer from the bridging Ru center to the DTE unit.

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