

Syntheses, Luminescence Switching, and Electrochemical Studies of Photochromic Dithienyl-1,10-phenanthroline Zinc(II) Bis(thiolate) Complexes

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A series of zinc(II) diimine bis(thiolate) complexes with photochromic diarylethene-containing phenanthroline ligands was synthesized, and their photophysical and photochromic properties were studied. The X-ray crystal structures of two of these complexes have been characterized. All complexes exhibit strong ³LLCT phosphorescence at 510–620 nm in the solid state at 77 and 298 K and in EtOH–MeOH glass at 77 K. Detailed studies revealed that the absorption, emission, and electrochemical properties of the complexes could be readily switched via the photochromic ring-closing and ring-opening reactions.

Introduction

Photochromism refers to the reversible transformation of a chemical species by absorption of electromagnetic radiation between two forms having distinguishable absorption spectra.¹ Many families of photochromic compounds have been discovered, as they are promising candidates for the manufacture of advanced materials.² In addition to these applications, they are also ideal candidates for use in photofunctional molecular switches, such as photoswitchable liquid crystals, molecular receptors, luminescence materials, and biomaterials.³ One strategy employed in the design of photoswitches is to incorporate these photochromic units as a part of the

metal complex systems. The amalgamation of the photochromic moieties, such as azo, stilbene,⁴ diarylethene,⁵

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spiropyran, and spirooxazine,⁶ with the metal complexes has also been shown to afford materials that possess novel and perturbed photochromic properties. We recently reported the synthesis of the first diarylethene-containing phenanthroline ligand and the photosensitization of its photochromism through the incorporation into the rhenium(I) tricarbonyl diimine complex system.^{5b-p} Extension of the work to other metal complex systems may represent an interesting approach to tune the photochromic properties. We believe that through the coordination to different metal complex systems, the photochromic behavior of the ligands could be utilized as a photoswitch for the tuning of the photophysical properties of the metal complex systems; conversely, the excited-state properties of the metal complex systems could be used to fine-tune or control the photochromic behavior of the ligands. In view of the well-known ligand-to-ligand charge transfer (LLCT) excited-state properties and the associated intense luminescence in the zinc(II) diimine bis(thiolate) system,⁷ the incorporation of photochromic phenanthroline ligands into this metal complex system has been pursued. Herein, we report the syntheses, crystal structures, photophysical, and photochromic properties of a series of zinc(II) bis(thiolate) complexes with the photochromic phenanthroline ligands.

Experimental Section

Materials. 1,10-Phenanthroline, fuming sulfuric acid, and *n*-butyllithium (1.6 M) in hexane were purchased from Aldrich Chemical Co. and were used as received. 2,5-Dimethylthiophene, 2-methylthiophene, tri-*n*-butylborate, bromine, glacial acetic acid, zinc dust, *p*-thiocresol, thiophenol, and *p*-chlorothiophenol were obtained from Lancaster Synthesis Limited and were used as received. Zinc acetate dihydrate was purchased from Merck Chemicals and recrystallized from water prior to use. 3-Bromo-2-methylthiophene was prepared according to a literature procedure.⁸ Tetrakis(triphenylphosphine)palladium(0) as a catalyst for Suzuki coupling was synthesized according to a literature procedure.⁹ Tetrahydrofuran was distilled over sodium benzophenone ketyl before use. 2-Methylthien-3-yl boronic acid was synthesized according to modification of a previously reported procedure^{5p} for 2,5-dimethylthien-3-yl boronic acid except 3-bromo-2-methylthiophene was used in place of 3-bromo-2,5-dimethylthiophene. 5,6-Bis(2,5-dimethyl-3-thienyl)-1,10-phenanthroline (**L1**) was synthe-

sized according to a procedure previously reported by us.^{5p} 5,6-Bis(2-methyl-3-thienyl)-1,10-phenanthroline (**L2**) was synthesized according to a procedure similar to that of **L1** except 2-methylthien-3-yl boronic acid was used in place of 2,5-dimethylthien-3-yl boronic acid.^{5p} Acetonitrile and benzene for physical measurements were distilled over calcium hydride and sodium, respectively, before use. Tetra-*n*-butylammonium hexafluorophosphate (^tBu₄NPF₆) (Aldrich, 98%) was purified by recrystallization from hot ethanol for 3 times and vacuum-dried for several days before use. All other reagents were of analytical grade and were used as received.

Zn(L1)(SC₆H₄-CH₃-*p*)₂ (1**).** This was prepared by modification of a literature method for the synthesis of the related Zn(II) diimine bis(thiolate) complexes.⁷ To a stirred solution of zinc acetate dihydrate (29.6 mg, 0.135 mmol) and *p*-thiocresol (33.5 mg, 0.270 mmol) in methanol (4 mL) was added **L1** (54.3 mg, 0.135 mmol) in methanol (20 mL) in a dropwise manner. The reaction mixture was stirred overnight at room temperature to give a yellow solution. The yellow solution was reduced in volume under reduced pressure, during which time the crude product was precipitated out. This was filtered and washed successively with cold methanol and hexane. Subsequent recrystallization by vapor diffusion of *n*-hexane into a concentrated chloroform solution of the complex gave **1**, isolated as yellow microcrystals. Yield: 56.1 mg, 0.079 mmol, 58%. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 8.92 (dd, 2H, *J* = 4.7, 1.4 Hz, phenanthroline proton at 2,9-position), 8.20 (dd, 2H, *J* = 8.4, 1.4 Hz, phenanthroline proton at 4,7-position), 7.76 (dd, 2H, *J* = 8.4, 4.7 Hz, phenanthroline proton at 3,8-position), 7.12 (d, 4H, *J* = 7.2 Hz, phenyl H ortho to S), 6.60 (d, 4H, *J* = 7.2 Hz, phenyl H meta to S), 6.32 (s, 1H, thienyl proton at 4-position), 6.30 (s, 1H, thienyl proton at 4-position), 2.42 (s, 3H, 5-Me on thiophene ring), 2.34 (s, 3H, 5-Me on thiophene ring), 2.09 (s, 6H, Me on phenyl ring), 1.98 (s, 3H, 2-Me on thiophene ring), 1.94 (s, 3H, 2-Me on thiophene ring). Positive-ion FAB (fast atom bombardment) mass spectrum: *m/z* 587 [M - SC₆H₄-CH₃-*p*]⁺. Anal. Calcd for C₃₈H₃₄N₂S₄Zn·1/2H₂O: C 63.27, H 4.89, N 3.88. Found: 63.39, H 4.80, N 3.76.

Zn(L1)(SC₆H₅)₂ (2**).** This was synthesized according to a procedure similar to that of **1** except thiophenol (29.7 mg, 0.270 mmol) was used in place of *p*-thiocresol. Yield: 58.0 mg, 0.085 mmol, 63%. ¹H NMR (300 MHz, CD₃CN, 298 K): δ 9.01 (dd, 2H, *J* = 4.7, 1.4 Hz, phenanthroline proton at 2,9-position), 8.13 (dd, 2H, *J* = 8.4, 1.4 Hz, phenanthroline proton at 4,7-position), 7.90 (dd, 2H, *J* = 8.4, 4.7 Hz, phenanthroline proton at 3,8-position), 6.94 (dd, 4H, *J* = 7.5, 1.4 Hz, phenyl H ortho to S), 6.60 (m, 6H, phenyl H meta and para to S), 6.46 (s, 1H, thienyl proton at 4-position), 6.44 (s, 1H, thienyl proton at 4-position), 2.39 (s, 3H, 5-Me), 2.37 (s, 3H, 5-Me), 1.98 (s, 3H, 2-Me), 1.95 (s, 3H, 2-Me). Positive-ion FAB mass spectrum: *m/z* 573 [M - SC₆H₅]⁺. Anal. Calcd for C₃₆H₃₀N₂S₄Zn·1/2H₂O: C 62.37, H 4.51, N 4.04. Found: C 62.31, H 4.51, N 3.91.

Zn(L1)(SC₆H₄-Cl-*p*)₂ (3**).** This was synthesized according to a procedure similar to that of **1** except *p*-chlorothiophenol (39.0 mg, 0.270 mmol) was used in place of *p*-thiocresol. Yield: 57.1 mg, 0.076 mmol, 56%. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 8.97 (dd, 2H, *J* = 4.7, 1.4 Hz, phenanthroline proton at 2,9-position), 8.24 (dd, 2H, *J* = 8.4, 1.4 Hz, phenanthroline proton at 4,7-position), 7.83 (dd, 2H, *J* = 8.4, 4.7 Hz, phenanthroline proton at 3,8-position), 7.09 (d, 4H, *J* = 8.2 Hz, phenyl H ortho to S), 6.69 (d, 4H, *J* = 8.2 Hz, phenyl H meta to S), 6.38 (s, 1H, thienyl proton at 4-position), 6.36 (s, 1H, thienyl proton at 4-position), 2.42 (s, 3H, 5-Me), 2.41 (s, 3H, 5-Me), 2.01 (s, 3H, 2-Me), 1.96 (s, 3H, 2-Me). Positive-ion FAB mass spectrum: *m/z* 609 [M - SC₆H₄-

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$\text{Cl-}p\text{]}^+$. Anal. Calcd for $\text{C}_{36}\text{H}_{28}\text{Cl}_2\text{N}_2\text{S}_4\text{Zn}\cdot\frac{1}{2}\text{H}_2\text{O}$: C 56.73 H 3.84, N 3.68. Found: C 56.86, H 3.74, N 3.55.

Zn(L2)(SC₆H₄-CH₃-p)₂ (4). This was synthesized according to a procedure similar to that of **1** except **L2** (50.5 mg, 0.135 mmol) was used in place of **L1**. Yield: 0.054 g, 0.079 mmol, 59%. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 8.95 (dd, 2H, $J = 4.7, 1.4$ Hz, phenanthrolyl proton at 2,9-position), 8.12 (dd, 2H, $J = 8.5, 1.4$ Hz, phenanthrolyl proton at 4,7-position), 7.78 (dd, 2H, $J = 8.5, 4.7$ Hz, phenanthrolyl proton at 3,8-position), 7.12 (m, 6H, phenyl H ortho to S and thienyl proton at 5-position), 6.69 (d, 2H, $J = 5.2$ Hz, thienyl proton at 4-position), 6.60 (d, 4H, $J = 7.2$ Hz, phenyl H meta to S), 2.17 (s, 3H, 2-Me on thiophene ring), 2.11 (s, 3H, 2-Me on thiophene ring), 2.03 (s, 6H, Me on phenyl ring). Positive-ion FAB mass spectrum: m/z 559 [M - SC₆H₄-CH₃-p]⁺. Anal. Calcd for $\text{C}_{36}\text{H}_{30}\text{N}_2\text{S}_4\text{Zn}\cdot\frac{1}{2}\text{H}_2\text{O}$: C 61.79, H 4.47, N 3.95. Found: C 61.93, H 4.40, N 4.06.

Zn(L2)(SC₆H₅)₂ (5). This was synthesized according to a procedure similar to that of **1** except **L2** (50.5 mg, 0.135 mmol) and thiophenol (29.7 mg, 0.270 mmol) were used in place of **L1** and *p*-thiocresol, respectively. Yield: 0.056 g, 0.085 mmol, 63%. ¹H NMR (400 MHz, CDCl₃, 298 K): δ 8.94 (dd, 2H, $J = 4.7, 1.4$ Hz, phenanthrolyl proton at 2,9-position), 8.18 (dd, 2H, $J = 8.5, 1.4$ Hz, phenanthrolyl proton at 4,7-position), 7.84 (dd, 2H, $J = 8.5, 4.7$ Hz, phenanthrolyl proton at 3,8-position), 7.21 (dd, 4H, $J = 7.5, 1.4$ Hz, phenyl H ortho to S), 7.12 (d, 2H, $J = 5.2$ Hz, thienyl proton at 5-position), 6.76 (m, 6H, phenyl H meta and para to S), 6.68 (d, 2H, $J = 5.2$ Hz, thienyl proton at 4-position), 2.09 (s, 3H, 2-Me), 2.06 (s, 3H, 2-Me). Positive-ion FAB mass spectrum: m/z 545 [M - SC₆H₅]⁺. Anal. Calcd for $\text{C}_{34}\text{H}_{26}\text{N}_2\text{S}_4\text{Zn}\cdot\frac{1}{2}\text{H}_2\text{O}$: C 61.13 H 4.13, N 3.96. Found: 61.37, H 3.98, N 4.14.

Zn(L2)(SC₆H₄-Cl-*p*)₂ (6). This was synthesized according to a procedure similar to that of **1** except **L2** (50.5 mg, 0.135 mmol) and *p*-chlorothiophenol (39.0 mg, 0.270 mmol) were used in place of **L1** and *p*-thiocresol, respectively. Yield: 0.054 g, 0.075 mmol, 55%. ¹H NMR (300 MHz, CDCl₃, 298 K): δ 9.00 (dd, 2H, $J = 4.7, 1.4$ Hz, phenanthrolyl proton at 2,9-position), 8.18 (dd, 2H, $J = 8.5, 1.4$ Hz, phenanthrolyl proton at 4,7-position), 7.84 (dd, 2H, $J = 8.5, 4.7$ Hz, phenanthrolyl proton at 3,8-position), 7.14 (d, 2H, $J = 5.2$ Hz, thienyl proton at 5-position), 7.07 (d, 4H, $J = 8.2$ Hz, phenyl H ortho to S), 6.75 (d, 2H, $J = 5.2$ Hz, thienyl proton at 4-position), 6.68 (d, 4H, $J = 8.2$ Hz, phenyl H meta to S), 2.12 (s, 3H, 2-Me), 2.04 (s, 3H, 2-Me). Positive-ion FAB mass spectrum: m/z 581 [M - SC₆H₄-Cl-*p*]⁺. Anal. Calcd for $\text{C}_{34}\text{H}_{24}\text{Cl}_2\text{N}_2\text{S}_4\text{Zn}\cdot\text{H}_2\text{O}$: C 54.95, H 3.53, N 3.77. Found: C 54.92, H 3.37, N 3.70.

Physical Measurements and Instrumentation. ¹H NMR spectra were recorded either on a Bruker DPX-300 (300 MHz) or a Bruker AV400 (400 MHz) at 298 K. Chemical shifts (δ , ppm) were recorded relative to tetramethylsilane (Me₄Si). Positive-ion fast atom bombardment (FAB) and electron impact (EI) mass spectra were recorded on a Finnigan MAT95 mass spectrometer. Elemental analyses of the new compounds were performed on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences, Beijing.

UV-vis absorption spectra were recorded on a Hewlett-Packard 8452A diode array spectrophotometer. Photoirradiation was carried out using a 300 W Xe (ozone-free) lamp, and monochromic light was obtained by passing the light through an Applied Photophysics F 3.4 monochromator. All measurements were conducted at room temperature.

Steady-state emission and excitation spectra at room temperature and 77 K were recorded on a Spex Fluorolog 111 spectrofluorom-

eter. For solution emission and excitation spectra, samples were degassed on a high-vacuum line in a degassing cell with a 10 cm³ Pyrex round-bottom flask connected by a sidearm to a 1-cm quartz fluorescence cuvette and were sealed from the atmosphere by a Rotaflo HP6/6 quick-release Teflon stopper. Solutions were rigorously degassed with no fewer than four freeze-pump-thaw cycles prior to the measurements. Solid-state emission and excitation spectra at room temperature were recorded with solid samples loaded in a quartz tube inside a quartz-walled Dewar flask. Solid samples at low temperature (77 K) and in EtOH-MeOH (4:1, v/v) glass at 77 K were recorded similarly, with liquid nitrogen inside the optical Dewar flask. Closed forms in 77 K glasses were prepared by irradiation at 365 nm at 298 K to reach the photostationary state, at which time the amount of the closed form, monitored by the UV-vis absorption spectroscopy, remained unchanged on continuous irradiation before immersion of the samples into the liquid nitrogen bath for emission measurements. Emission lifetimes of the solution samples were determined by the time-correlated single-photon counting (TCSPC) technique using an IBH Fluorocube system with a NanoLED-11 excitation source, which has its excitation peak wavelength at 371 nm and a pulse width shorter than 200 ps.

Chemical actinometry was employed for the photochemical quantum yield determination.¹⁰ Incident light intensities were taken from the average values measured just before and after each photolysis experiment using ferrioxalate actinometry.¹⁰ In the determination of the photochemical quantum yield, the sample solutions were prepared at concentrations with absorbance slightly greater than 2.0 at the excitation wavelength. The quantum yield was determined at a small percentage of conversion by monitoring the initial rate of change of absorbance ($\Delta A/\Delta t$) in the absorption maximum of the closed forms in the visible region.

Cyclic voltammetric measurements were performed by using a CH Instruments, Inc., model CHI 620 electrochemical analyzer interfaced to a personal computer. The electrolytic cell used was a conventional two-compartment cell. The salt bridge of the reference electrode was separated from the working electrode compartment by a vycor glass. Electrochemical measurements were performed in acetonitrile solutions with 0.1 mol dm⁻³ Bu₄NPF₆ as supporting electrolyte at room temperature. The reference electrode was a Ag/AgNO₃ (0.1 M in acetonitrile) electrode, and the working electrode was a glassy carbon (CH Instrument) electrode with a piece of platinum gauze as a counter electrode in a compartment separated from the working electrode by a sintered-glass frit. The ferrocenium/ferrocene couple (FeCp₂⁺⁰) was used as the internal reference.¹¹ All solutions for electrochemical studies were deaerated with prepurified argon gas before measurement. The UV-vis spectral changes for the photocyclization process of **3** were monitored using an Ocean Optics USB2000 with DT-1000CE deuterium-tungsten halogen light source and transmission T400-RT dip probe during the electrochemical measurements.

Crystal Structure Determination. All the experimental details are given in Table 1. Single crystals of **4** suitable for X-ray studies were obtained by vapor diffusion of *n*-hexane into a concentrated dichloromethane solution of **4**. A yellow crystal of dimensions 0.7 mm × 0.2 mm × 0.1 mm mounted in a glass capillary was used

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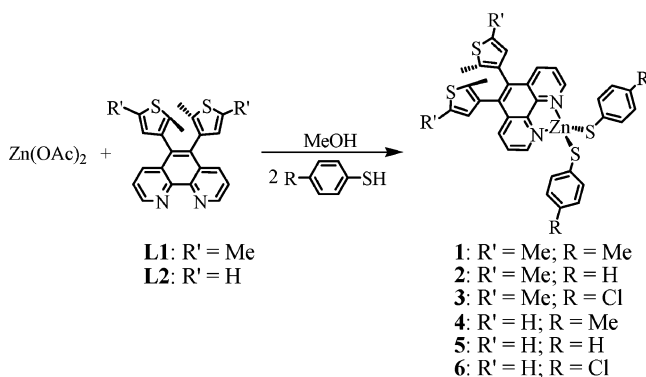
Table 1. Crystal and Structure Determination Data for Complexes **4** and **5**

	4	5
formula	C ₃₇ H ₃₂ Cl ₂ N ₂ S ₄ Zn	C ₃₄ H ₂₆ N ₂ S ₄ Zn
fw	769.16	656.18
T, K	253	301
a, Å	15.205(3)	25.168(5)
b, Å	8.952(2)	14.457(3)
c, Å	26.552(5)	17.048(3)
α, deg	90	90
β, deg	91.49(3)	91.28(3)
γ, deg	90	90
V, Å ³	3612.9(12)	6201(2)
cryst color	pale yellow	pale yellow
cryst syst	monoclinic	monoclinic
space group	P2 ₁ /c	P2 ₁ /c
Z	4	8
F(000)	1 584	2 704
D _c , g cm ⁻³	1.414	1.406
cryst dimens, mm	0.7 × 0.2 × 0.1	0.6 × 0.3 × 0.2
λ, Å (graphite, monochromated, Mo Kα)	0.71073	0.71073
collection range, deg	2θ _{max} = 50.34	2θ _{max} = 50.68
h	-15 to 15	-29 to 29
k	-10 to 9	-17 to 16
l	-31 to 31	-18 to 17
oscillation, deg	2	2
no. of images collected	100	100
distance, mm	120	120
exposure time, s	600	600
no. of data collected	13 484	29 036
no. of unique data	4 319	8 288
no. of data used in refinement, m	2 489	4 646
no. of parameters refined, p	419	743
R ^a	0.0376	0.0422
wR ^a	0.0765	0.0956
GOF, S	0.847	0.883
maximum shift, (Δ/σ) _{max}	0.001	0.001
residual extrema in final difference map, e Å ⁻³	0.435, -0.236	0.334, -0.293

$$^a w = 1/[\sigma^2(F_0^2) + (aP)^2 + bP], \text{ where } P = [2F_c^2 + \max(F_0^2, 0)]/3$$

for data collection at -20 °C on a MAR diffractometer with a 300 mm image plate detector using graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). Data collection was made with 2° oscillation step of φ , 600 s exposure time, and scanner distance at 120 mm. The images were collected and interpreted, and intensities were integrated using the program DENZO.¹² The structure was solved by direct methods employing the SHELXS-97 program¹³ on a PC. The Zn, S, and most non-hydrogen atoms were located according to the direct methods. The positions of the other non-hydrogen atoms were found after successful refinement by the full-matrix least-squares method using the program SHELXL-97¹³ on a PC. One dichloromethane solvent molecule was also located. One crystallographic asymmetric unit consists of one formula unit, including one dichloromethane molecule. In the final stage of least-squares refinement, all non-hydrogen atoms were anisotropically refined. Hydrogen atoms were generated by the program SHELXL-97.¹³ The positions of hydrogen atoms were calculated on the basis of the riding mode with thermal parameters equal to 1.2 times those of the associated carbon atoms and participated in

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- (13) Sheldrick, G. M.; SHELX-97: Programs for Crystal Structure Analysis, Release 97-2; University of Gottingen: Gottingen, Germany, 1997.

Scheme 1


calculation of final R-indices. The final difference Fourier map showed maximum rest peaks and holes of 0.435 and -0.236 e Å⁻³, respectively.

Single crystals of **5** suitable for X-ray studies were obtained by vapor diffusion of *n*-hexane into a concentrated dichloromethane solution of **5**. A yellow crystal of dimensions 0.6 mm × 0.3 mm × 0.2 mm mounted in a glass capillary was used for data collection at 28 °C on a MAR diffractometer with a 300 mm image plate detector using graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). Data collection was made with 2° oscillation step of φ , 600 s exposure time, and scanner distance at 120 mm. The images were collected and interpreted, and intensities were integrated using the program DENZO.¹² The structure was solved by direct methods employing the SHELXS-97 program¹³ on a PC. The Zn, S, and most non-hydrogen atoms were located according to direct methods. The positions of the other non-hydrogen atoms were found after successful refinement by the full-matrix least-squares method using the program SHELXL-97¹³ on a PC. One crystallographic asymmetric unit consists of two formula units. In the final stage of least-squares refinement, all non-hydrogen atoms were anisotropically refined. Hydrogen atoms were generated by the program SHELXL-97.¹³ The positions of hydrogen atoms were calculated on the basis of the riding mode with thermal parameters equal to 1.2 times those of the associated carbon atoms and participated in the calculation of final R-indices. The final difference Fourier map showed maximum rest peaks and holes of 0.334 and -0.293 e Å⁻³, respectively.

Results and Discussion

Phenanthroline-based photochromic ligands **L1** and **L2** were synthesized by Suzuki cross-coupling reactions¹⁴ of 5,6-dibromo-1,10-phenanthroline and the substituted 3-thienyl boronic acid using a previously reported procedure.^{5p} Through the functionalization of thienyl boronic acid, functionalized photochromic dithienyl-1,10-phenanthroline ligand could be readily synthesized. Reaction of these ligands with Zn(OAc)₂·2H₂O in the presence of various substituted thiophenols in methanol in a mole ratio of 1:1:2 afforded a series of photochromic zinc(II) bis(thiolate) dithienylphenanthroline complexes (Scheme 1). All of them gave satisfactory elemental analyses and were characterized by ¹H NMR spectroscopy and positive-ion FAB mass spectrometry. Due

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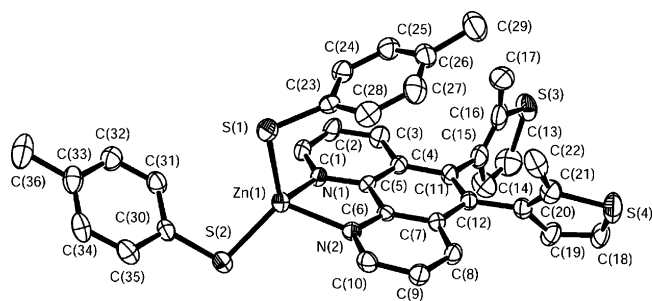


Figure 1. Perspective drawing of **4** with the atomic numbering scheme. Hydrogen atoms have been omitted for clarity; thermal ellipsoids are drawn at the 30% probability level.

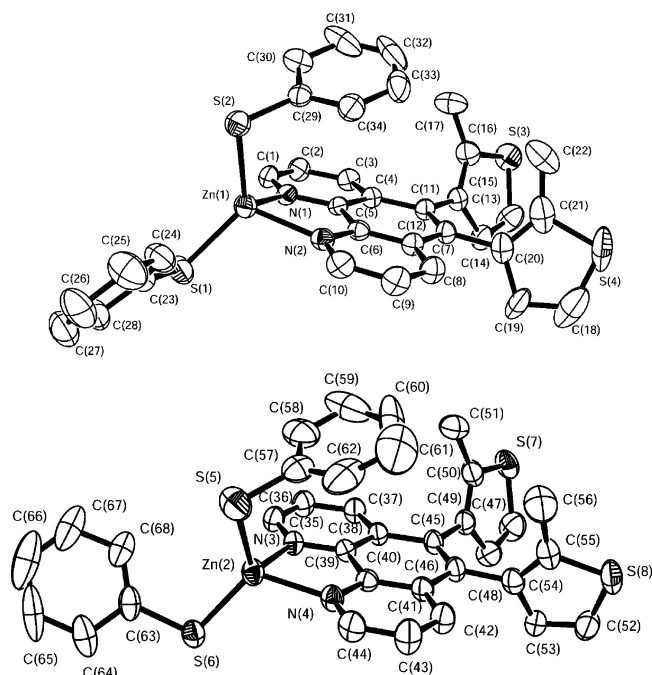


Figure 2. Perspective drawings of the two conformations of **5** with their atomic numbering. Hydrogen atoms have been omitted for clarity; thermal ellipsoids are drawn at the 30% probability level.

to the sterically demanding nature of the 1,10-phenanthroline ring, with the protons at the 4- and 7-positions hindering the rotation of the thiophene moieties, two sets of ^1H NMR signals, corresponding to the resonances of the parallel (photochromic inactive) and the antiparallel (photochromic active) conformers, were observed. Similar observations have also been reported in the related systems.^{3d,5p} Complexes **4** and **5** were also structurally characterized by X-ray crystallography.

X-ray Crystal Structures. Figures 1 and 2 depict the perspective drawings of the complexes **4** and **5** with their atomic numbering. The crystal and structure determination data are collected in Table 1 and selected bond distances and angles are summarized in Table 2. For complex **5**, two conformations with the thiolate ligands in different orientations were also determined. Except for the orientations in the thiolate ligands, both conformations show very similar bond lengths, bond angles, and geometries for the metal center and the dithienylphenanthroline ligand. The Zn(II) center in both crystal structures adopted a distorted tetrahedral geometry with an average S–Zn–S angle of 124.0° and an

Table 2. Selected Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations (esds) in Parentheses for **4** and Both Conformations of **5**

4	Zn(1)–N(2)	2.082(3)	Zn(1)–N(1)	2.086(3)
	Zn(1)–S(1)	2.272(13)	Zn(1)–S(2)	2.246(14)
	S(1)–C(23)	1.772(4)	S(2)–C(30)	1.760(4)
	S(1)–Zn(1)–S(2)	121.42(5)	N(1)–Zn(1)–N(2)	79.18(13)
	C(23)–S(1)–Zn(1)	98.97(13)	C(30)–S(2)–Zn(1)	102.78(15)
5a	Zn(1)–N(2)	2.096(3)	Zn(1)–N(1)	2.010(3)
	Zn(1)–S(1)	2.248(13)	Zn(1)–S(2)	2.266(13)
	S(1)–C(23)	1.751(4)	S(2)–C(29)	1.751(4)
	S(1)–Zn(1)–S(2)	126.69(5)	N(1)–Zn(1)–N(2)	78.49(12)
	C(23)–S(1)–Zn(1)	107.85(17)	C(29)–S(2)–Zn(1)	97.29(13)
5b	Zn(2)–N(3)	2.105(3)	Zn(2)–N(4)	2.105(3)
	Zn(2)–S(5)	2.262(16)	Zn(2)–S(6)	2.238(13)
	S(5)–C(57)	1.757(6)	S(6)–C(63)	1.770(5)
	S(5)–Zn(2)–S(6)	124.17(5)	N(3)–Zn(2)–N(4)	78.42(13)
	C(57)–S(5)–Zn(2)	96.98(17)	C(63)–S(6)–Zn(2)	105.78(19)

average N–Zn–N angle of 78.8° . The deviation of both the N–Zn–N and S–Zn–S bond angles from the ideal angle of 109.5° for tetrahedral geometry is ascribed to the steric requirement of the chelating diimine ligands. The average bond distances of Zn–S and Zn–N were 2.26 Å for **4** and 2.25 Å for **5** and 2.08 Å for **4** and 2.10 Å for **5**, respectively. These observations are typical of the related Zn(II) diimine bis(thiolate) systems.^{7,15} The distances between the phenanthroline and the phenyl ring of one of the thiolate ligands were in the range of 3.4–4.2 Å for both complexes, indicative of the possible presence of π – π interactions between the phenanthroline and the phenyl rings. Such intramolecular π -stacking of aromatic rings has also been observed in other related systems.^{7c,15d} For the **L2** moiety, both crystal structures adopted a parallel conformation with the two methyl groups pointing in the same direction. Due to the steric hindrance exhibited by the two thiophene moieties, they tend to orient themselves perpendicular to the plane of the phenanthroline moiety. The interplanar angles between the thiophene rings and 1,10-phenanthroline in the crystal structures were determined to be 84.5° and 63.0° for **4** and 83.0° and 70.3° and 69.7° and 63.9° for the two conformations of **5**, all of which are essentially orthogonal and typical for the dithienylphenanthroline unit.^{5h} As a result, the π -conjugation between the thiophene rings and the phenanthroline moiety can be assumed to be almost negligible in the open form.

Electronic Absorption and Emission Properties. All the complexes dissolve in benzene to give clear yellow solutions. Their electronic absorption spectra showed an intense absorption at ca. 320 nm, which is ascribed to the intraligand $\pi \rightarrow \pi^*$ transitions of the phenanthroline, probably with some mixing of $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the thiophene rings and the benzenethiolate ligands, as ligands **L1**, **L2**, and the benzenethiolate ligands were found to absorb in a similar

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Table 3. Photophysical Data for the Open and Closed Forms of the Ligands and Their Zinc(II) Bis(thiolate) Complexes

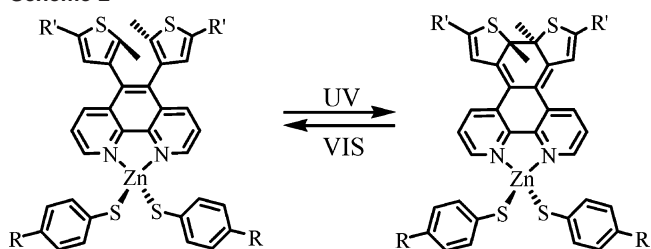
compound	medium (T/K)	emission $\lambda_{em}/$ nm (τ_e/ns)	absorption ^a $\lambda_{abs}/$ nm ($\epsilon/dm^3 mol^{-1} cm^{-1}$)
L1 (open form) ^b	benzene (298)	383	304 (8670)
	solid (298)	-- ^d	
	solid (77)	-- ^d	
	glass (77) ^c	-- ^d	
L1 (closed form) ^b	glass (77) ^c	577	366 (31730), 510 (3950), 540 (3730)
L2 (open form)	benzene (298)	391	298 (9730)
	solid (298)	-- ^d	
	solid (77)	-- ^d	
	glass (77) ^c	-- ^d	
L2 (closed form)	glass (77) ^c	584	368 (21830), 510 (3610), 540 (3400)
1 (open form)	benzene (298)	390 (3.4)	320 (6540), 382 (1470)
	solid (298)	610	
	solid (77)	619	
	glass (77) ^c	513	
1 (closed form)	glass (77) ^c	604	382 (31780), 534 (4700), 566 (4270)
2 (open form)	benzene (298)	389 (2.7)	320 (6480), 380 (1720)
	solid (298)	567	
	solid (77)	551	
	glass (77) ^c	513	
2 (closed form)	glass (77) ^c	607	382 (31800), 538 (4600), 566 (4070)
3 (open form)	benzene (298)	398 (2.2)	328 (6070), 382 (1680)
	solid (298)	538	
	solid (77)	524	
	glass (77) ^c	513	
3 (closed form)	glass (77) ^c	605	386 (30680), 540 (4540), 572 (3960)
4 (open form)	benzene (298)	383 (5.6)	322 (7000), 382 (1300)
	solid (298)	618	
	solid (77)	624	
	glass (77) ^c	508	
4 (closed form)	glass (77) ^c	-- ^e	380, 512, 558 ^e
5 (open form)	benzene (298)	383 (5.5)	320 (7500), 380 (1620)
	solid (298)	580	
	solid (77)	584	
	glass (77) ^c	508	
5 (closed form)	glass (77) ^c	-- ^e	382, 514, 560 ^e
6 (open form)	benzene (298)	392 (6.0)	322 (6400), 374 (1770)
	solid (298)	543	
	solid (77)	558	
	glass (77) ^c	507	
6 (closed form)	glass (77) ^c	-- ^e	383, 510, 558 ^e

^a In benzene solution, at 298 K. ^b From ref 5p.h. ^c EtOH/MeOH = 4:1 (v/v). ^d Emission not detected (indicated by --). ^e Due to low percentage of conversion, the λ_{em} or ϵ values could not be obtained with certainty (indicated by --).

region.⁷ In addition to this intense absorption, all complexes show a moderately intense absorption shoulder at ca. 380 nm, which is assigned as the ligand-to-ligand charge transfer [LLCT, $p\pi(SR^-) \rightarrow \pi^*(phen)$] transition, typical of the zinc(II) diimine bis(thiolate) system.^{7,15} The photophysical data for the ligands and complexes **1–6** are summarized in Table 3.

On excitation at $\lambda \geq 310$ nm, complexes **1–6** in their open forms in benzene solution displayed luminescence at ca. 390 nm. These emissions are tentatively assigned as fluorescence and of metal-perturbed intraligand (IL) $\pi \rightarrow \pi^*$ origin, probably from the phenanthroline moiety, since the emission bands are found to be very similar in energy, band shape, and lifetime to those of the corresponding free ligands **L1** and **L2**, which exhibit fluorescence at ca. 383 and 391 nm, respectively, upon excitation at $\lambda \geq 310$ nm.^{5h,p}

On the other hand, the open forms of complexes **1–6** in the solid state at 298 and 77 K exhibited strong luminescence

Scheme 2


at ca. 520–620 nm upon excitation at $\lambda \geq 310$ nm. The energies of these emissions are found to be sensitive to the nature of the thiolate ligand. With the same diimine ligand, the emission energies are in the order of **3** > **2** > **1** and **6** > **5** > **4**, which is in the reverse order as the electron-donating ability of their thiolate ligands, $p\text{-Cl-C}_6\text{H}_4\text{S}^- < \text{C}_6\text{H}_5\text{S}^- < p\text{-Me-C}_6\text{H}_4\text{S}^-$. With reference to previous spectroscopic works on the related monomeric $[\text{Zn}(\text{phen})(\text{SR})_2]$ system⁷ and the observed emission energy dependence on the thiolate ligands, these broad low-energy emission bands are ascribed to be derived from the LLCT [$p\pi(\text{SR}^-) \rightarrow \pi^*(\text{phen})$] origin. In general, the presence of electron-donating substituents on the thiolate ligands would raise the π -orbital energies of the ligands, leading to a lower LLCT [$p\pi(\text{SR}^-) \rightarrow \pi^*(\text{phen})$] energy, whereas with electron-withdrawing substituents on the thiolate ligands, the converse is true. The 77 K EtOH–MeOH glass emissions showed well-resolved vibronic structures, which are suggestive of the emission origin derived from admixtures of ³LLCT and ³IL states, similar to those observed in related systems.^{7b,g}

Photochromic Properties. On excitation at $\lambda = 313$ nm, complexes **1–3** undergo photocyclization reactions (Scheme 2), leading to the formation of an intense absorption band at ca. 382 nm with molar extinction coefficients on the order of $10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ and two moderately intense absorptions at ca. 534 and 566 nm with molar extinction coefficients on the order of $10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$. The significant bathochromic shift in absorption maxima of the closed forms compared with their open forms is mainly due to the increase in the extended π -conjugation across the condensed thiophene rings, resulting in a reduced HOMO–LUMO energy gap for $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions. The close resemblance of these new absorption bands in different complexes to the closed form absorptions of the free ligands is suggestive of an assignment as metal-perturbed $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ intraligand transitions of the condensed thiophene rings. The slight red shift of the absorption bands of the closed form in the complexes (382, 534, and 566 nm) relative to those in the closed form of free ligands (366, 510, and 540 nm) is attributed to perturbation of the transition by the metal center in the metal complexes. On the other hand, excitation into the absorption bands of the closed form results in photocycloreversion as reflected by the decrease in the intensity of the absorption bands of the closed form. A slight amount of precipitate was observed after one cycle in aerated solution, indicative of photodecomposition, whereas under anaerobic conditions, these photoprocesses could be recycled a number of times without significant decomposition (Figure 3). Representative UV–vis absorption spectral changes of

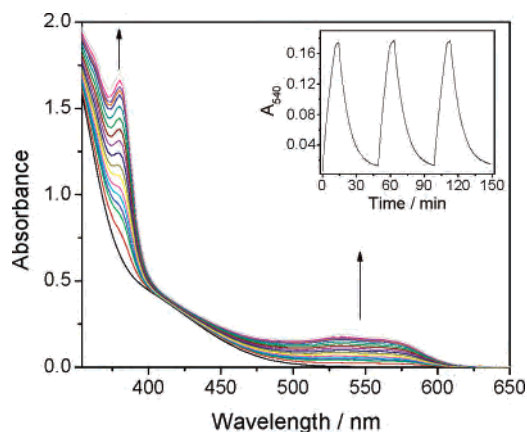


Figure 3. UV-vis absorption spectral changes of **1** (3.4×10^{-4} M) upon photoirradiation at 313 nm in benzene solution. The inset show absorbance changes at 540 nm on alternating excitation at 313 and 540 nm over three cycles.

complex **1** upon irradiation at 313 nm in benzene solution are shown in Figure 3.

Unlike in the rhenium(I) tricarbonyl diimine complex system, in which the photochromism could be sensitized by the excitation into the metal-to-ligand charge transfer absorption band,^{5h,p} excitation into the LLCT absorption band of the complexes did not produce photocyclization. This is probably attributed to the very inefficient internal conversion process from the ³LLCT to the ³IL state due to the poor coupling of these two states with an activation barrier, which is typically observed in zinc(II) diimine bis(thiolate) complex systems.^{7a,c-e} The photocyclization conversions from the open form to the closed form on 313-nm excitation corrected for the antiparallel configuration for complexes **1–3** were found to be ca. 40–50% at the photostationary state, whereas the conversion percentage for complexes **4–6** at the photostationary state was too low to be precisely measured by NMR spectroscopy (<5%). Thus the extinction coefficients for the corresponding closed form absorptions could not be determined with certainty, even though similar absorption spectral changes were also observed upon UV excitation. The exceptionally low photocyclization conversion for complexes **4–6** may be attributed to the low quantum efficiency for the photocyclization (Table 4), with comparable quantum yield for the photocycloreversion, resulting in a very low ratio of the closed form to the open form at the photostationary state. In contrast to the free ligands and most organic diarylethene systems,^{2d-f} in which the quantum yield for photocyclization is much higher than that for photocycloreversion, complexes **1–6** showed very similar quantum yields for both photocyclization and photocycloreversion. The relatively low quantum yield for the photocyclization in the complexes may be attributed to the presence of the lower-lying ¹LLCT excited state, which quenches the reactive ¹IL excited-state of the ligand. Subsequent intersystem crossing into the ³LLCT state did not efficiently populate the ³IL state due to the poor coupling between these two states. Thus the ¹LLCT state serves as a quenching state that competes with the ¹IL state that gives rise to the photocyclization reaction. A proposed qualitative energy state diagram to account for the relatively low photochromic

Table 4. A Summary of the Photochemical Quantum Yields of Complexes **1–6** in Benzene Solution at 298 K

compound	photochemical quantum yield/ ϕ		conversion ^b /%
	photocyclization, ^a ϕ_{313}	photocycloreversion, ϕ_{510}	
L1 ^c	0.33	0.012	83
L2	0.49	0.029	92
1	0.033	0.013	41
2	0.028	0.011	47
3	0.025	0.008	43
4 ^d	0.014	0.016	<5
5 ^d	0.012	0.011	<5
6 ^d	0.011	0.011	<5

^a Values reported are corrected to the ratio of the photochromic active conformation, i.e., with respect to the antiparallel configuration. ^b Conversion percentage (corrected to the active conformation) at photostationary state with 313 nm excitation. ^c From ref 5p,h. ^d Estimated using the average extinction coefficients obtained for complexes **1–3**.

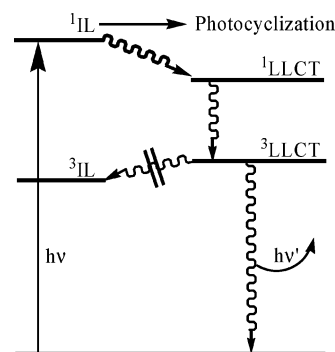


Figure 4. Proposed qualitative energy state diagram of the zinc(II) complexes.

reactivity of the zinc(II) complexes is shown in Figure 4. The relative energy ordering of the various states can be substantiated by the higher energy of the ¹IL transition than that of the ¹LLCT transition observed in the UV-vis spectrum and the lower energy of the ³IL emission of **L1** (77 K MeCN^{5p}) than that of the ³LLCT/³IL emission (508–513 nm in 77 K glass) (Table 3). The lower photocyclization quantum yields in the chlorobenzenethiolate complexes of **3** and **6** than the unsubstituted benzenethiolate complexes of **2** and **5** and the methyl substituted benzenethiolate complexes of **1** and **4**, with ϕ_{313} in the order of $3 < 2 < 1$ and $6 < 5 < 4$, though subtle, are consistent with the proposed mechanism, since this is in line with the LLCT energy trend, in which $3 > 2 > 1$ and $6 > 5 > 4$. The higher ¹LLCT energies of **3** and **6** are expected to result in a better spectral energy overlap between the ¹LLCT acceptor state and the ¹IL donor state, giving rise to a better intramolecular energy transfer efficiency, causing a more efficient quenching of the photoreactive ¹IL state.

On conversion of the open form to the closed form in the photostationary state, the emissions of all the complexes in 77 K EtOH–MeOH glass were found to shift to the red, consistent with the reduced HOMO–LUMO energy gap as a result of the extended π -conjugation in the condensed thiophene units upon occurrence of the photocyclization reaction. In view of the close resemblance of these emissions to the closed form emissions of the free ligands in the same medium as well as the insensitivity of these emissions to changes in the nature of the thiolate ligands, the emissions

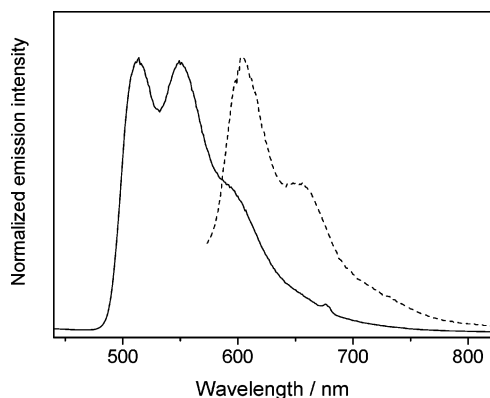


Figure 5. Overlaid emission spectra of the open (—) and closed (---) form of **1** in EtOH–MeOH (4:1 v/v) glass at 77 K.

Table 5. Electrochemical Data for the Ligands and Complexes in Acetonitrile Solution (0.1 mol dm⁻³ nBu₄NPF₆) at 298 K^a

compound	oxidation, ^b <i>E</i> _{pa} / V vs SCE	reduction, ^b <i>E</i> _{pc} / V vs SCE (<i>E</i> _{1/2} / V vs SCE)
1 (open form)	+1.80	(-1.47), -2.08
1 (closed form)	+1.80	-1.51, -1.78
2 (open form)	+1.79	(-1.48), -2.04
2 (closed form)	+1.80	-1.51, -1.77
3 (open form)	+1.80	(-1.45), -2.06
3 (closed form)	+1.80	-1.35, -1.72
4 (open form)	+1.76	(-1.48), -2.08
4 (closed form)	+1.76	-1.53, -1.74
5 (open form)	+1.72	(-1.51), -2.04
5 (closed form)	+1.72	-1.51, -1.72
6 (open form)	+1.74	(-1.45), -2.04
6 (closed form)	+1.74	-1.34, -1.70

^a Working electrode, glassy carbon; scan rate, 100 mV s⁻¹. ^b *E*_{1/2} is (*E*_{pa} + *E*_{pc})/2; *E*_{pa} and *E*_{pc} are peak anodic and peak cathodic potentials, respectively.

are tentatively assigned as derived from states of a metal-perturbed IL origin, probably originating from the condensed thiophene moiety. However, a mixing of the ³LLCT emission could not be completely excluded as similar red shift in emission energy for the ³LLCT state and poor coupling of the ³LLCT and ³IL are also anticipated in the closed form. It is believed that the ³LLCT state is the predominant emissive state in the open form, whereas on conversion to the closed form, the extended π -conjugation renders the ³IL excited state to an even lower lying energy level and becomes the predominant emissive state in the closed form. The representative overlaid emission spectra of the open and closed forms of complex **1** in 77 K EtOH–MeOH glass are revealed in Figure 5.

Electrochemical Studies. The electrochemical data for the complexes in acetonitrile (0.1 mol dm⁻³ nBu₄NPF₆) are tabulated in Table 5. The open form of all the complexes in acetonitrile (0.1 mol dm⁻³ nBu₄NPF₆) displayed similar cyclic voltammograms with an irreversible oxidation wave at ca. +1.72 to +1.80 V vs SCE, a reversible reduction couple at ca. -1.45 to -1.51 V vs SCE, and an irreversible reduction wave at ca. -2.04 to -2.08 V vs SCE. On the basis of previous electrochemical studies on other related zinc(II) diimine bis(thiolate) systems,¹⁶ the first irreversible oxidation,

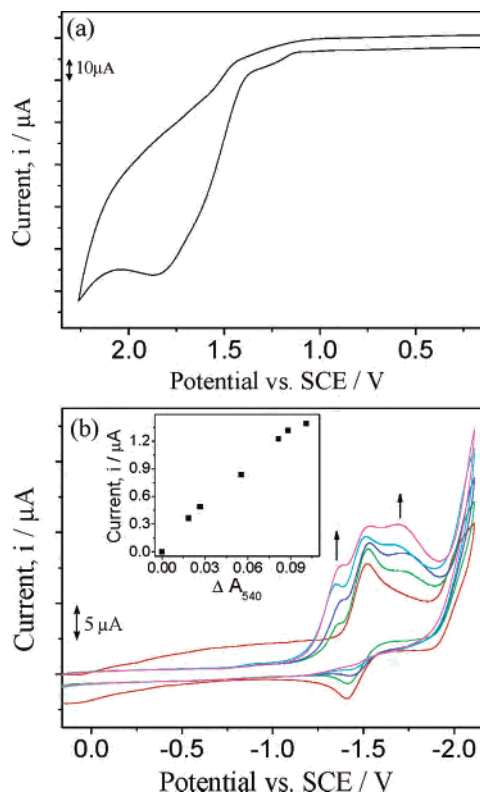


Figure 6. Cyclic voltammograms of (a) the oxidative scan of **3** and (b) the repetitive reductive scans of **3** during the course of photochromic conversion from open form to closed form in MeCN (0.1 mol dm⁻³ nBu₄NPF₆). Scan rate: 100 mV s⁻¹. The inset shows the plot of current at -1.35 V vs SCE against the change in absorbance at 540 nm.

which is typically observed in zinc(II) diimine bis(thiolate) complexes, is attributed to the thiolate ligand-centered oxidation. The reversible reduction couples at ca. -1.45 to -1.51 V are assigned to the phenanthroline ligand-centered reduction. The irreversible reduction waves at ca. -2.04 to -2.08 V, which are similar to the thiophene-based irreversible reduction of the free ligand^{5p} and absent in the related zinc(II) diimine bis(thiolate) complexes,^{7d,16} are assigned to the reduction of the thiophene moiety.

The electrochemical changes upon the conversion of the open form to the closed form have also been studied using cyclic voltammetric measurements (Figure 6) containing a mixture of the open and closed forms in their photostationary state. The lack of observable changes in the irreversible oxidation wave at +1.72 to +1.80 V is in accord with the assignment of a thiolate ligand-centered oxidation. The insignificant perturbation of the π -accepting ability of the phenanthroline moiety upon condensation of the thiophene units could be reflected by a slight potential shift (≤ 0.1 V) in the reversible phenanthroline-based reduction couple. A drop in the electrochemical signal of the irreversible reduction wave at ca. -2.04 V, with the concomitant formation of a new irreversible reduction wave at less cathodic potential (-1.72 to -1.78 V), was observed upon conversion of the open form to the closed form. This supports the assignment of a thiophene-based reduction, as photocyclization of the thiophene rings in the open form to the condensed thiophene units in the closed form would result in a better π -conjugation and hence a better π -accepting ability, causing a shift of the

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reduction wave to a less negative potential. To further confirm the assignment, a correlation of the growth of the newly formed reduction wave with the amount of the closed form generated in **3** upon irradiation was attempted. A linear relationship between the current of the new reduction wave and the absorbance of the closed form in the visible region was established, giving further support to the assignment (Figure 6). Although electrochemically induced cyclization and cycloreversion have been recently¹⁷ reported for some diarylethenes, no electrocyclization or electrocycloreversion products were observed during the course of the electrochemical measurement.

Conclusion

A series of zinc(II) diimine bis(thiolate) complexes with photochromic diarylethene-containing phenanthroline ligands was synthesized and structurally characterized, and their photophysical and photochromic properties were studied. All

complexes exhibit strong ³LLCT phosphorescence at 510–620 nm in the solid state at 77 and 298 K. The switching of absorption, emission, and electrochemical properties of the complexes via photochromic reactions has been demonstrated.

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Supporting Information Available: Crystallographic data for complexes **4** and **5**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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