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Photochromic alkynylplatinum(II) diimine complexes containing a versatile dithienylethene-functionalized 2-(2′-pyridyl)imidazole ligand

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The synthesis and incorporation of a versatile photochromic dithienylethene-containing diimine ligand, 2-(2′-pyridyl)imidazole, into platinum(II) bis-alkynyl system have been described. All the platinum(II) complexes have been successfully characterized by ^{1}H NMR spectroscopy, ESI mass spectrometry as well as elemental analysis. One of the complexes has been characterized by X-ray crystallography. Their photochromic, photophysical and electrochemical properties have been studied. Upon photo-excitation, all the platinum(II) complexes exhibited reversible photochromism. Their photophysical and electrochemical behaviors were found to be tunable by various substituents on the ligands.

1. Introduction

The research on photochromic molecular functional materials is currently one of the most active areas of topical interest owing to their potential applications as molecular devices, such as multifunctional switches and optical memory storage [1–6]. In particular, diarylethene-based photochromic system has attracted enormous attention due to its good stability, fatigue resistance and fast response time [1–3]. Nevertheless, design and synthesis of molecular materials with desirable photochromic and photophysical properties often involve tedious modification of the diarylethene frameworks. Thus, researchers have started developing versatile diarylethene-containing building blocks to facilitate the tuning of the photochromic behaviors for various purposes [1–3]. One important approach employed by our group is to utilize transition metal complex systems and to connect functional moieties with the photochromic ligands so as to obtain photoswitchable functional materials [3]. Recently, metal complexes with photochromic groups, such as azobenzenes [4], stilbenes [5], diarylethenes [1–3] and spirooxazines [6], have received much attention. More importantly, participation of transition metal centers would enrich the resulting photophysical and photochromic properties and enable the use of the relatively non-destructive, lower-energy metal-to-ligand charge transfer (MLCT) absorption bands to sensitize the photocyclization reaction in order to improve the robustness of the materials. We anticipate that incorporation of diarylethene moieties into the ligand framework could introduce a more dramatic change after the photocyclization reaction. This idea has been realized in a variety of metal complex systems [3].

Platinum(II) diimine bis(alkynyl) complexes, with a general formula of $[\mathrm{Pt}(\widehat{\mathrm{NN}})(\mathrm{C{\equiv}CR})_2]$, have aroused enormous attention due to their ease of design and synthesis, good solubility as well as the ease of probing of the excited states [7]. Rich photophysical properties with strong phosphorescence in the fluid state at room temperature have been observed [7]. With our previous experience on the photophysical studies of platinum(II) alkynyl systems and photochromic transition metal complexes [3,8], it is envisaged that the combining of the platinum(II) diimine bis(alkynyl) system, which possess highly tunable MLCT/LLCT excited state, with the diarylethene-containing 2-(2′-pyridyl)imidazole ligand could give rise to photochromic materials with interesting photophysical and sensitized photochromic properties. Herein, we describe the synthesis, characterization, crystal structure, photophysical, photochromic and electrochemical studies of this new class of complexes.

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2. Experimental

2.1. Materials and reagents

1-Ethynylnaphthalene, 4-ethynylbenzonitrile and copper(I) iodide were obtained from Aldrich Chemical Company. Phenylacetylene, 1-ethynyl-4-methylbenzene and *N*,*N*-diethylamine were purchased from Lancaster Synthesis Ltd. Potassium tetrachloroplatinate(II) was purchased from Strem Chemicals, Inc. The diarylethene-containing diimine ligands, 1-(4-methylphenyl)-4,5-bis-(2,5-dimethyl-3-thienyl)-2-(2′-pyridyl)imidazole (**L1**) [3d], 1-(4-methoxyphenyl)-4,5-bis-(2,5-dimethyl-3-thienyl)-2-(2′-pyridyl)-imidazole (**L2**) [3d], and 1-(4-trifluoromethylphenyl)-4,5-bis-(2,5-dimethyl-3-thienyl)-2-(2′-pyridyl)-imidazole (**L3**) [3d], together with their respective dichloroplatinum(II) complexes, $[Pt(\mathbf{L1})Cl_2]$ [9], $[Pt(\mathbf{L2})Cl_2]$ [9] and $[Pt(\mathbf{L3})Cl_2]$ [9], were prepared according to literature procedures with modifications. Diethylamine was distilled over potassium hydroxide and stored over potassium hydroxide prior to use. Tetra-*n*-butylammonium hexafluorophosphate was purified by at least three times of recrystallization in absolute ethanol and was dried prior to use. Benzene was distilled over sodium before use. Dichloromethane was purified using Innovative Technology, Inc. model PureSolv MD 5 Solvent Purification System before use. Acetonitrile was distilled over calcium hydride before use. All other solvents and reagents were of analytical grade and were used as received.

2.2. Synthesis

2.2.1. $[Pt(L1)Cl_2]$

The titled compound was synthesized by modification of a literature procedure [9]. To a mixture of $[Pt(DMSO)_2Cl_2]$ (93 mg, 0.220 mmol) and **L1** (100 mg, 0.220 mmol) was added degassed acetonitrile (20 mL). The reaction mixture was heated under reflux for overnight under argon. The resulting yellow solution was evaporated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel (70–230 mesh) using dichloromethane as eluent. Further purification was done by slow diffusion of pentane vapor into its concentrated dichloromethane solution. Yield: 105 mg, 0.146 mmol; 66%. ^{1}H NMR (400 MHz, DMSO-d_6, 353 K): δ 1.97 (s, 3H, $-CH_3$), 2.19 (s, 3H, $-CH_3$), 2.29 (s, 6H, $-CH_3$), 2.40 (s, 3H, $-C_6H_4CH_3$), 6.43 (m, 3H, thienyl protons, pyridyl proton at 5-position), 7.37 (d, $J = 7.3$ Hz, 2H, tolyl protons at 3-position), 7.49 (m, 3H, tolyl protons at 2-position, pyridyl proton at 4-position), 7.98 (m, 1H, pyridyl proton at 3-position), 9.55 (d, $J = 4.3$ Hz, 1H, pyridyl proton at 6-position). Positive FAB mass spectrum: *m*/*z* 722 $\{M\}^+$.

2.2.2. $[Pt(L2)Cl_2]$

The target compound was prepared according to a procedure similar to that of $[Pt(\mathbf{L1})Cl_2]$ except **L2** (100 mg, 0.212 mmol) was used instead of **L1**. Yield: 112 mg, 0.152 mmol; 72%. ^{1}H NMR (400 MHz, DMSO-d_6, 353 K): δ 1.98 (s, 3H, $-CH_3$), 2.20 (s, 3H, $-CH_3$), 2.27 (s, 6H, $-CH_3$), 3.84 (s, 3H, $-C_6H_4OCH_3$), 6.39 (s, 1H, thienyl), 6.43 (s, 1H, thienyl), 6.51 (d, $J = 8.2$ Hz, 1H, pyridyl proton at 5-position), 7.09 (d, $J = 8.1$ Hz, 2H, *p*-methoxyphenyl protons at 3-position), 7.52 (m, 3H, *p*-methoxyphenyl protons at 2-position, pyridyl proton at 4-position), 8.00 (m, 1H, pyridyl proton at 3-position), 9.55 (d, $J = 5.7$ Hz, 1H, pyridyl proton at 6-position). Positive FAB mass spectrum: *m*/*z* 738 $\{M\}^+$

2.2.3. $[Pt(L3)Cl_2]$

The target compound was prepared according to a procedure similar to that of $[Pt(\mathbf{L3})Cl_2]$ except **L3** (100 mg, 0.196 mmol) was used instead of **L1**. Yield: 103 mg, 0.133 mmol; 68%. ^{1}H NMR (400 MHz, CD_2Cl_2, 298 K): δ 1.95, 1.97 (s, 3H, $-CH_3$) [10], 2.15, 2.54 (s, 3H, $-CH_3$) [10], 2.24 (s, 3H, $-CH_3$), 2.36, 2.4 (s, 3H, $-CH_3$) [10], 6.16 (s, 1H, thienyl), 6.32, 6.69 (s, 1H, thienyl) [10], 6.49 (m, 1H, pyridyl proton at 5-position), 7.40 (m, 2H, 4-(trifluoromethyl) phenyl protons at 3-position), 7.76 (m, 2H, 4-(trifluoromethyl) phenyl protons at 2-position), 7.81 (m, 1H, pyridyl proton at 4-position), 7.90 (m, 1H, pyridyl proton at 3-position), 9.76 (d, $J = 5.5$ Hz, 1H, pyridyl proton at 6-position). Positive FAB mass spectrum: *m*/*z* 776 $\{M\}^+$

2.2.4. $[Pt(L1)(C{\equiv}C{-}C_6H_5)_2]$ (**1**)

The titled compound was prepared by modification of a literature method for the related bis-alkynylplatinum(II) bipyridine complexes [3c]. To a mixture of $[Pt(\mathbf{L1})Cl_2]$ (100 mg, 0.138 mmol) and catalytic amount of copper(I) iodide were added degassed dichloromethane (20 mL) and dry diethylamine (2 mL). The mixture was stirred under argon for 10 min, followed by addition of an excess of phenylacetylene (141 mg, 0.152 mL, 1.38 mmol). The resulting suspension was stirred for 24 h. The solution was evaporated to dryness, dissolved in dichloromethane, and purified by column chromatography on neutral aluminum oxide using *n*-hexane-dichloromethane (4:1 v/v) as eluent. Further purification was achieved by slow diffusion of pentane vapor into a concentrated dichloromethane solution of the complex or by layering of methanol over a concentrated dichloromethane or chloroform solution of the complex. Yield: 30 mg, 0.035 mmol; 26%. ^{1}H NMR (400 MHz, DMSO-d_6, 353 K): δ 1.93 (s, 3H, $-CH_3$), 2.06 (s, 3H, $-CH_3$), 2.20 (s, 3H, $-CH_3$), 2.36 (s, 3H, $-CH_3$), 2.42 (s, 3H, $-C_6H_4CH_3$), 6.40 (s, 1H, thienyl), 6.50 (s, 1H, thienyl), 6.58 (d, $J = 8.2$ Hz, 1H, pyridyl proton at 5-position), 6.99 (m, 3H, phenyl protons at 2,4-positions), 7.11 (m, 3H, phenyl protons at 2,4-positions), 7.23 (m, 2H, phenyl protons at 3-position), 7.31 (d, $J = 7.5$ Hz, 2H, tolyl protons at 3-position), 7.40 (d, $J = 7.5$ Hz, 2H, tolyl protons at 2-position), 7.50 (m, 2H, phenyl protons at 3-position), 7.64 (m, 1H, pyridyl proton at 4-position), 7.99 (m, 1H, pyridyl proton at 3-position), 9.66 (d, $J = 5.4$ Hz, 1H, pyridyl proton at 6-position). ESI mass spectrum: *m*/*z* 852 $\{M\}^+$. Elemental analyses, Found (%): C 54.54, H 3.62, N 4.13; Calcd (%) for $C_{43}H_{35}N_3PtS_2{\cdot}CHCl_3$: C 54.35, H 3.73, N 4.32.

2.2.5. $[Pt(L1)(C{\equiv}C{-}C_6H_4CH_3\text{-}p)_2]$ (**2**)

The target compound was prepared according to a procedure similar to that of $[Pt(\mathbf{L1})(C{\equiv}C{-}C_6H_5)_2]$ except 4-tolylacetylene (160 mg, 1.38 mmol) was used instead of phenylacetylene. Yield: 52 mg, 0.059 mmol; 43%. ^{1}H NMR (400 MHz, DMSO-d_6, 353 K): δ 1.93 (s, 3H, $-CH_3$), 2.08 (s, 3H, $-CH_3$), 2.20 (s, 3H, $-CH_3$), 2.24 (s, 3H, $-CH_3$), 2.27 (s, 3H, $-C_6H_4CH_3$), 2.35 (s, 3H, $-C_6H_4CH_3$), 2.40 (s, 3H, $-C_6H_4CH_3$), 6.39 (s, 1H, thienyl), 6.50 (s, 1H, thienyl), 6.57 (d, $J = 8.2$ Hz, 1H, pyridyl proton at 5-position), 6.87 (d, $J = 8.1$ Hz, 2H, *N*-tolyl protons at 3-position), 6.92 (d, $J = 8.1$ Hz, 2H, *N*-tolyl protons at 2-position), 7.05 (d, $J = 8.0$ Hz, 2H, tolyl protons at 3-position), 7.20 (d, $J = 8.0$ Hz, 2H, tolyl protons at 2-position), 7.39 (d, $J = 8.2$ Hz, 2H, tolyl protons at 3-position), 7.50 (d, $J = 8.2$ Hz, 2H, tolyl protons at 2-position), 7.62 (m, 1H, pyridyl proton at 4-position), 7.97 (m, 1H, pyridyl proton at 3-position), 9.65 (d, $J = 5.4$ Hz, 1H, pyridyl proton at 6-position). ESI mass spectrum: *m*/*z* 880 $\{M\}^+$. Elemental analyses, Found (%): C 60.72, H 4.47, N 4.84; Calcd (%) for $C_{45}H_{39}N_3PtS_2{\cdot}0.5CH_3OH$: C 60.92, H 4.61, N 4.68.

2.2.6. $[Pt(L1)(C{\equiv}C{-}C_6H_4CN\text{-}p)_2]$ (**3**)

The target compound was prepared according to a procedure similar to that of $[Pt(\mathbf{L1})(C{\equiv}C{-}C_6H_5)_2]$ except 4-ethynylb enzonitrile (175 mg, 1.38 mmol) was used instead of phenylacetylene. Yield: 82 mg, 0.091 mmol; 66%. ^{1}H NMR (400 MHz, DMSO-d_6, 353 K): δ 1.94 (s, 3H, $-CH_3$), 2.05 (s, 3H, $-CH_3$), 2.20 (s, 3H, $-CH_3$), 2.34 (s, 3H, $-CH_3$), 2.42 (s, 3H, $-C_6H_4CH_3$), 6.39 (s, 1H, thienyl), 6.48 (s, 1H, thienyl), 6.60 (d, *J* = 8.2 Hz, 1H, pyridyl proton at 5-position), 7.10 (d, *J* = 8.3 Hz, 2H, tolyl protons at 3-position), 7.39 (d, *J* = 8.2 Hz, 2H, *p*-cyanophenyl protons at 3-position), 7.44 (d, *J* = 8.3 Hz, 2H, tolyl protons at 2-positions), 7.51 (m, 4H, *p*-cyanophenyl protons at 2,4-positions), 7.64 (m, 3H, *p*-cyanophenyl protons at 2-position, pyridyl proton at 4-position), 8.00 (m, 1H, pyridyl proton at 3-position), 9.52 (d, *J* = 4.9 Hz, 1H, pyridyl proton at 6-position). ESI mass spectrum: *m*/*z* 902 {M}$^+$. Elemental analyses, Found (%): C 59.71, H 3.69, N 7.59; Calcd (%) for $C_{45}H_{33}N_5PtS_2$: C 59.85, H 3.68, N 7.76.

2.2.7. [Pt(L2)(C≡C–C_6H_5)$_2$] (**4**)

The target compound was prepared according to a procedure similar to that of [Pt(**L1**)(C≡C–C_6H_5)$_2$] except [Pt(**L2**)Cl_2] (100 mg, 0.136 mmol) was used instead of [Pt(**L1**)Cl_2]. Yield: 58 mg, 0.067 mmol; 49%. ^{1}H NMR (400 MHz, DMSO-*d*$_6$, 353 K): δ 1.94 (s, 3H, –CH_3), 2.06 (s, 3H, –CH_3), 2.21 (s, 3H, –CH_3), 2.32 (s, 3H, –CH_3), 3.85 (s, 3H, –OCH_3), 6.40 (s, 1H, thienyl), 6.51 (s, 1H, thienyl), 6.62 (d, *J* = 8.2 Hz, 1H, pyridyl proton at 5-position), 6.98 (m, 3H, phenyl protons at 2,4-positions), 7.11 (m, 5H, *p*-methoxyphenyl protons at 3-position, phenyl protons at 2,4-positions), 7.22 (m, 2H, phenyl protons at 3-position), 7.30 (m, 2H, phenyl protons at 3-position), 7.54 (d, *J* = 7.7 Hz, 2H, *p*-methoxyphenyl protons at 2-position), 7.64 (m, 1H, pyridyl proton at 4-position), 8.01 (m, 1H, pyridyl proton at 3-position), 9.66 (d, *J* = 5.6 Hz, 1H, pyridyl proton at 6-position). ESI mass spectrum: *m*/*z* 868 {M}$^+$. Elemental analyses, Found (%): C 58.60, H 4.11, N 4.76; Calcd (%) for $C_{43}H_{35}N_3OPtS_2 \cdot CH_3OH$: C 58.65, H 4.36, N 4.66.

2.2.8. [Pt(L2)(C≡C-1-Np)$_2$] (**5**)

The target compound was prepared according to a procedure similar to that of [Pt(**L1**)(C≡C–C_6H_5)$_2$] except [Pt(**L2**)Cl_2] (200 mg, 0.272 mmol) and 1-ethynylnaphthalene (414 mg, 2.72 mmol) were used instead of [Pt(**L1**)Cl_2] and phenylacetylene, respectively. Yield: 56 mg, 0.058 mmol; 21%. ^{1}H NMR (400 MHz, DMSO, 353 K): δ 1.86 (s, 3H, –CH_3), 1.95 (s, 3H, –CH_3), 2.21 (s, 3H, –CH_3), 2.37 (s, 3H, –CH_3), 3.86 (s, 3H, –OCH_3), 6.43 (s, 1H, thienyl), 6.54 (s, 1H, thienyl), 6.68 (d, *J* = 8.2 Hz, 1H, pyridyl proton at 5-position), 7.11 (m, 3H, *p*-methoxyphenyl protons at 3-position, naphthyl), 7.20 (m, 2H, naphthyl), 7.35 (m, 4H, naphthyl), 7.57 (m, 4H, naphthyl, *p*-methoxyphenyl protons at 3-position, pyridyl proton at 4-position), 7.66 (d, 2H, *J* = 7.8 Hz, *p*-methoxyphenyl protons at 2-position), 7.75 (d, *J* = 8.1 Hz, 1H, naphthyl), 7.80 (d, *J* = 8.1 Hz, 1H, naphthyl), 8.04 (m, 1H, pyridyl proton at 3-position), 8.55 (d, *J* = 8.4 Hz, 1H, naphthyl), 8.66 (d, *J* = 8.4 Hz, 1H, naphthyl), 9.79 (d, *J* = 5.6 Hz, 1H, pyridyl proton at 6-position). ESI mass spectrum: *m*/*z* 968 {M}$^+$. Elemental analyses, Found (%): C 63.16, H 4.21, N 4.31; Calcd (%) for $C_{51}H_{39}N_3OPtS_2$: C 63.21, H 4.06, N 4.34.

2.2.9. [Pt(L3)(C≡C–C_6H_5)$_2$] (**6**)

The target compound was prepared according to a procedure similar to that of [Pt(**L1**)(C≡C–C_6H_5)$_2$] except [Pt(**L3**)Cl_2] (100 mg, 0.129 mmol) was used instead of [Pt(**L1**)Cl_2]. Yield: 55 mg, 0.061 mmol; 47%. ^{1}H NMR (400 MHz, DMSO-*d*$_6$, 353 K): δ 1.94 (s, 3H, –CH_3), 2.06 (s, 3H, –CH_3), 2.18 (s, 3H, –CH_3), 2.37 (s, 3H, –CH_3), 6.36 (s, 1H, thienyl), 6.52 (s, 1H, thienyl), 6.62 (d, *J* = 8.2 Hz, 1H, pyridyl proton at 5-position), 6.96 (m, 3H, 4-(trifluoromethyl)phenyl protons at 3-position, phenyl proton at 4-position), 7.11 (m, 3H, phenyl protons at 2,4-positions), 7.23 (m, 2H, phenyl protons at 2-position), 7.31 (d, *J* = 7.3 Hz, 2H, 4-(trifluoromethyl)phenyl protons at 2-position), 7.68 (m, 1H, pyridyl proton at 4-position), 7.93 (m, 5H, pyridyl proton at 3-position, phenyl protons at 3-position), 9.67 (d, *J* = 5.4 Hz, 1H, pyridyl proton at 6-position). ESI mass spectrum: *m*/*z* 906 {M}$^+$. Elemental analyses, Found (%): C 53.21, H 3.44, N 4.05; Calcd (%) for $C_{43}H_{32}F_3N_3PtS_2 \cdot CH_2Cl_2$: C 53.28, H 3.46, N 4.24.

2.3. Physical measurements and instrumentation

^{1}H NMR spectra were recorded either on a Bruker DPX-300 (300 MHz) or a Bruker AV400 (400 MHz) at 353 K. Chemical shifts (δ, ppm) for ^{1}H NMR and ^{31}P NMR were recorded relative to tetramethylsilane (Me_4Si) and 85% phosphoric acid respectively. Positive-ion electrospray ionization (ESI) mass spectra were recorded on a Finnigan LCQ 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 Oriel Corporation Model 66011 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-2 Modal F111 spectrofluorometer. For solution emission and excitation spectra, samples were degassed on a high-vacuum line in a degassing cell with a 10 cm [3] Pyrex round-bottomed 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. Excited state lifetimes of solution, solid and glass samples were measured using a conventional laser system. The excitation source was the 355 nm output (third harmonic, 8 ns) of a Spectra-Physics Quanta-Ray Q-switched GCR-150 pulsed Nd-YAG laser (10 Hz). Luminescence decay traces at a selected wavelength were detected by a Hamamatsu R928 photomultiplier tube connected to a 50 Ω load resistor and the voltage signal recorded on a Tekronix Modal TDS 620A digital oscilloscope (500 MHz, 2 GS/s). The lifetime (τ) determination was achieved by the single exponential fittings of the luminescence decay traces with the model equation, $I(t) = I_o \exp(-t/\tau)$, where $I(t)$ and I_o refer to the luminescence intensity at the time = *t* and time = 0, respectively. Luminescence quantum yield was measured by the optical dilute method developed by Demas and Crosby [11]. A degassed aqueous solution of $[Ru(bpy)_3]Cl_2$ was used as the standard [12] at 298 K.

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} $^nBu_4NPF_6$ as supporting electrolyte at room temperature. The reference electrode was a Ag/$AgNO_3$ (0.1 M in acetonitrile) electrode, and the working electrode was a glassy carbon (CH Instrument) electrode with a platinum wire as a counter electrode in a compartment separated from the working electrode by a sintered-glass frit. The ferrocenium/ferrocene couple ($FeCp_2^{+/0}$) was used as the internal reference [13]. All solutions for electrochemical studies were deaerated with prepurified argon gas before measurement.

2.4. Crystal structure determination

All the experimental details are given in Table 1. Single crystals of complex **1** suitable for X-ray studies were obtained by vapor diffusion

Table 1
Crystal and structure determination data for complex **1**.

Empirical formula	$C_{44}H_{36}Cl_3N_3PtS_2$	
Formula weight	972.32	
Temperature	301 (2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	$P\overline{1}$(No. 2)	
Unit cell dimensions	$a = 12.948$ (1) Å	$\alpha = 109.74$ (2)°
	$b = 15.968$ (1) Å	$\beta = 96.05$ (2)°
	$c = 22.538$ (2) Å	$\gamma = 95.13$ (2)°
Volume	4322.4 (6) $Å^3$	
Z	4	
Density (calculated)	1.494 g cm^{-3}	
Absorption coefficient	3.561 mm^{-1}	
F (000)	1928	
Crystal size	0.35 mm × 0.15 mm × 0.1 mm	
Theta range for data collection	1.93–25.68°	
Index ranges	$-15 \leqq h \leqq 15$, $-18 \leqq k \leqq 19$, $-27 \leqq l \leqq 25$	
Reflections collected	25,582	
Independent reflections	16,029 [R(int) = 0.0176]	
Completeness to theta = 25.68°	97.60%	
Absorption correction	None	
Refinement method	Full-matrix least-squares on F^2	
Data/restraints/parameters	16,029/0/955	
Goodness-of-fit on F^2	1.066	
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0400$, $wR_2 = 0.1109$	
R indices (all data)	$R_1 = 0.0553$, $wR_2 = 0.1173$	
Largest diff. peak and hole	2.409 and −0.893 e $Å^{-3}$	

of pentane vapor into a concentrated chloroform solution of complex **1**. A crystal of dimensions 0.35 mm × 0.15 mm × 0.10 mm mounted in a glass capillary was used for data collection at 28 °C on a Bruker Smart CCD 1000 using graphite monochromatized Mo-K_α radiation (λ = 0.71073 Å). The structure was solved by direct methods employing SHELXS-97 [14] program on PC. Pt, S and many non-H atoms were located according to the direct methods. The positions of the other non-hydrogen atoms were found after successful refinement by full-matrix least-squares using program SHELXL-97 [14] on PC. Detailed experimental procedures and other results including atomic coordinates, equivalent isotropic displacement parameters, bond lengths, bond angles, anisotropic displacement parameters, hydrogen coordinates and isotropic displacement parameters for complex **1** were included in Supplementary material and were tabulated in Tables S1–S4.

3. Results and discussion

3.1. Synthesis and characterization

The diarylethene-functionalized 2-(2′-pyridyl)imidazole ligands have been designed and reported by Yam and co-workers previously [3d]. The incorporation of diimine ligands into the platinum(II) center followed a general synthetic procedure, which was achieved by the reaction of the diimine ligand with $[Pt(DMSO)_2Cl_2]$ in acetonitrile [9]. The resulting $[Pt(diimine)Cl_2]$ complex was readily functionalized with various terminal alkynes in dichloromethane in the presence of diethylamine and a catalytic amount of copper(I) iodide. The target complexes were purified by column chromatography on aluminum oxide and several times of recrystallization by slow diffusion of pentane vapor into their chloroform solutions. The synthetic pathway for this type of platinum(II) diimine complexes is outlined in Scheme 1.

All the complexes gave broad signals in the ^1H NMR spectra at room temperature, suggestive of isomer interconversion at a timescale similar to that of NMR. This is most likely due to the conversion between the antiparallel and the parallel forms of the complexes. At 353 K in DMSO-d_6, the signals were sharpened and became well-resolved. The presence of a signal at δ 9.52–9.79 ppm in the ^1H NMR spectra, which was downfield shifted from that observed in the free ligand and characteristic of the proton at the 5-position of pyridine, was indicative of the successful coordination of the ligand to the platinum(II) center. The identities of the compounds have also been established by ESI-MS and satisfactory elemental analysis.

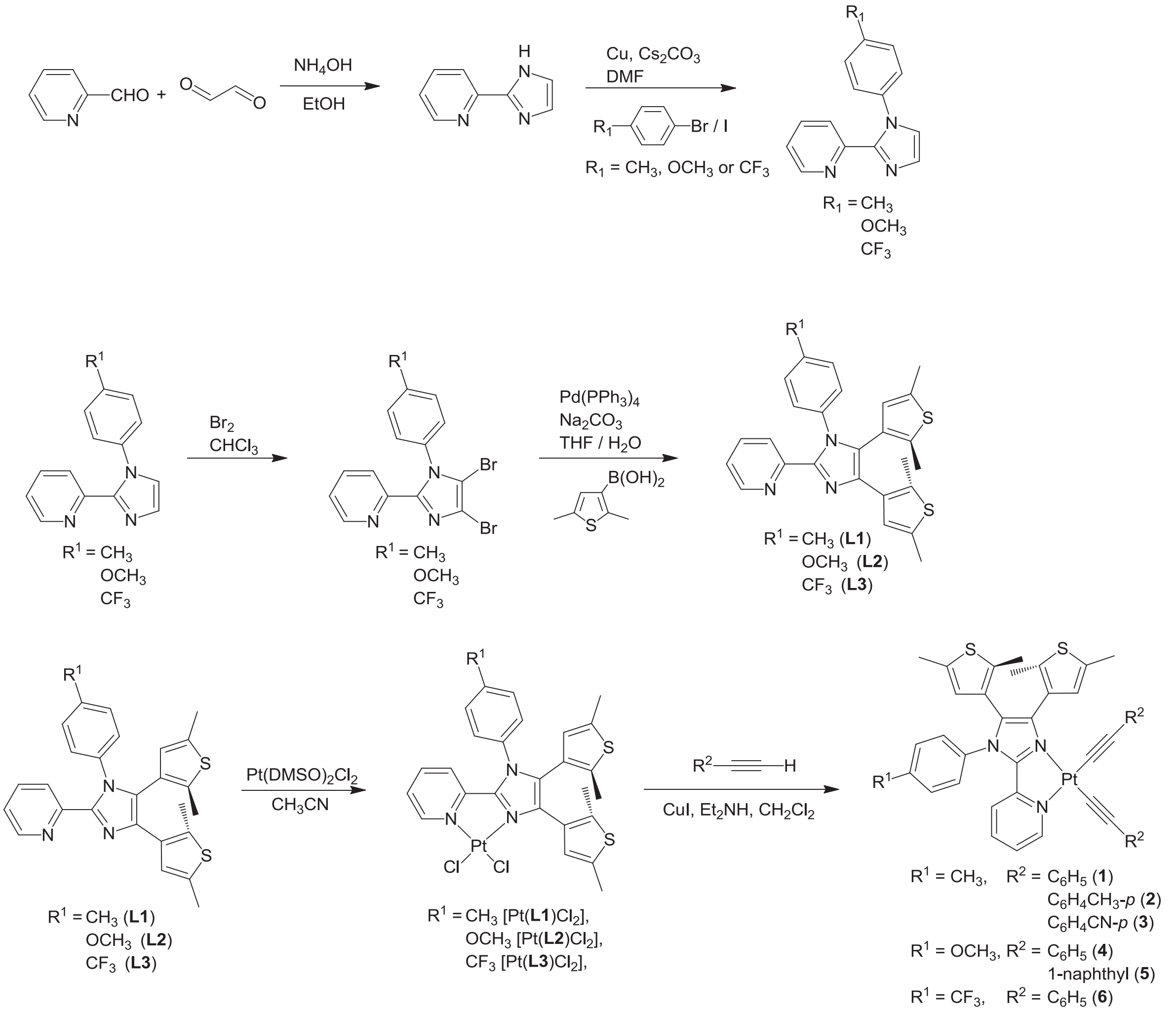
3.2. X-ray crystal structure

The perspective drawing and selected bond distances (Å) and angles (°) of complex **1** are depicted and tabulated in Fig. 1 and Table 2 respectively. The crystal structure showed the antiparallel conformation. The interplanar angles between the dimethylthiophene rings and the imidazole ring were both *ca.* 54°. The interplanar angle between the *N*-aryl ring and the imidazole ring was 74°, indicating a deviation from coplanarity. The d [8] platinum(II) metal center adopted a distorted square planar geometry, which has been commonly observed in other platinum(II) diimine systems [7c]. This could probably be due to the steric demand required for the *N*,*N*-chelating diimine ligand. In addition, the Pt—N bond distances were found to be around 2.08 Å, slightly longer than those of $[Pt(5,5'\text{-dmbpy})Cl_2]$ [15] and $[Pt(phen)Cl_2]$ [16]. This could be ascribed to the *trans* effect imposed by the σ-bonded alkynyl groups, whose bond distances with the platinum center were *ca.* 1.95 Å. In addition, the shortest Pt···Pt distance between two adjacent molecules was found to be 3.8162(7) Å, indicating the absence of any significant Pt···Pt interaction.

3.3. Electronic absorption and emission properties

All complexes were dissolved in benzene to give yellow to orange solutions. The electronic absorption spectra showed high-energy absorption bands at *ca.* 310 and 360 nm, with molar extinction coefficients in the order of 10^4 dm^3 mol^{-1} cm^{-1} and a long absorption tail at *ca.* 420 nm with molar extinction coefficient in the order of 10^3 dm^3 mol^{-1} cm^{-1}. The high-energy absorption bands are ascribed to the intraligand (IL) $\pi \rightarrow \pi^*$ transitions of the diimine and alkynyl ligands. The low-energy absorption tails at *ca.* 400–500 nm were found to be shifted to the lower energy when the platinum center was coordinated to the more electron-rich alkynyl ligand with the absorption energies in the order of **3** (405 nm) > **1** (421 nm) > **2** (423 nm) or to the more π-accepting diimine ligand with the absorption energies in the order of **1** (421 nm) ~ **4** (422 nm) > **6** (429 nm). Thus, the low-energy absorption tails were assigned as the metal-to-ligand charge transfer MLCT [dπ(Pt) → π^*(diimine)] transitions, probably with some mixing of ligand-to-ligand charge transfer LLCT [π(alkynyl) → π^*(diimine)] character. This assignment is consistent with those reported in other related platinum(II) diimine bis-alkynyl systems [3c,7a,c,o]. The electronic absorption data are summarized in Table 3.

Upon excitation into either the IL or MLCT/LLCT bands of the complexes in degassed benzene solution at 298 K, luminescence at *ca.* 540–580 nm was observed, with lifetimes in the range of microseconds. These, together with the large Stokes shift, are suggestive of a triplet emission origin. As shown in Fig. 2, the emission was found to be slightly blue-shifted in energy (**4** > **1** > **6**) upon increasing the electron-richness of the diimine ligand, while a red shift in energy (**3** > **1** > **2**) was observed upon increasing the electron-richness of the alkynyl ligand. This was suggestive of an emission origin of ^{3}MLCT [dπ(Pt) → π^*(diimine)]/LLCT [π(alkynyl) → π^*(diimine)] character. Similar assignments have also been reported for other platinum(II) diimine bis-alkynyl systems [3c,7a,c,o]. The rather small effect observed on the emission maxima upon a variation of the electron-richness of the diimine



Scheme 1. Synthetic pathway of complexes **1**–**6**.

ligand could be ascribed to the long distance between the substituent and the central diimine core. In addition, the aryl ring was not coplanar to the imidazole ring (74°), which minimized communication between them.

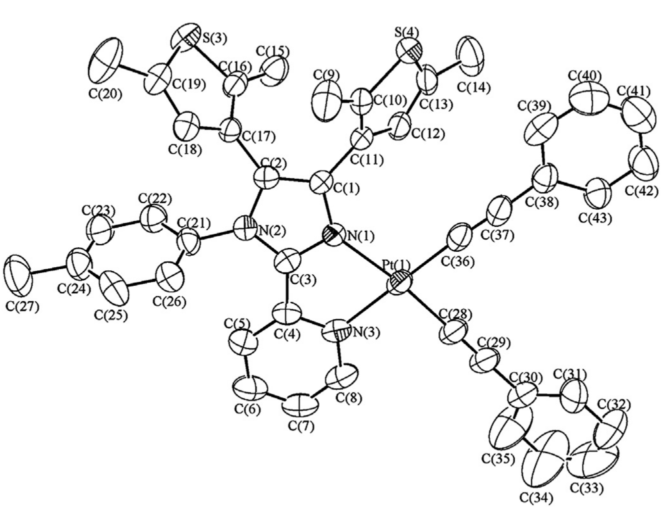


Fig. 1. Perspective view of complex **1** with atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids were shown at the 30% probability level.

Most complexes showed photoluminescence in the solid state at 77 K, 298 K and in glass at 77 K, with a blue shift in the emission maxima relative to the solution state with well-resolved vibrational progressional spacings, indicative of substantial involvement of ligand orbitals in the emissive state. Representative spectra have been shown in Figs. S1,S2. Thus, for complexes **1**–**6**, the emissions were assigned as derived from an ^{3}IL [$\pi \rightarrow \pi^*$ (diimine)] origin. The emission data for all the complexes are summarized in Table 4.

3.4. Photochromic properties

Upon photo-excitation into either the intraligand or the metal-to-ligand charge transfer transitions, the degassed benzene solutions of complexes **1**–**6** turned green, suggesting the formation of a new absorption band in the visible region, commonly observed in the formation of the closed forms [1–3]. The newly emerged bands were located at *ca.* 720 nm, with slight variations between different complexes and were comparable to that observed in the rhenium(I) analogs [3d]. The large bathochromic shift with respect to the open form could be attributed to the increase in the extent of π-conjugation in the two dimethylthiophene rings (8a,8b-dimethyl-1,8-thia-*as*-indacene) upon ring-closing, suggesting its origin as a predominantly π–π^* intraligand transition. When compared to the free ligands [3d], the lowest new energy absorption band of the closed form showed a red shift from *ca.* 580 nm to *ca.* 720 nm. This could

Table 2
Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s.) in parentheses for complex **1**.

Bond distances/Å			
Pt(1)–N(1)	2.076 (4)	C(28)–C(29)	1.190 (8)
Pt(1)–N(3)	2.083 (5)	C(29)–C(30)	1.442 (8)
Pt(1)–C(28)	1.949 (6)	C(36)–C(37)	1.207 (9)
Pt(1)–C(36)	1.959 (7)	C(37)–C(38)	1.419 (9)
C(3)–C(4)	1.451 (7)		
Bond angles/°			
N(1)–Pt(1)–N(3)	78.07 (17)	C(28)–C(29)–C(30)	178.4 (8)
N(1)–Pt(1)–C(36)	101.5 (2)	C(36)–C(37)–C(38)	177.0 (7)
C(36)–Pt(1)–C(28)	86.1 (3)	Pt(1)–N(1)–C(3)	112.8 (3)
C(28)–Pt(1)–N(3)	94.5 (2)	Pt(1)–N(1)–C(1)	140.8 (3)
Pt(1)–C(28)–C(29)	175.9 (6)	Pt(1)–N(3)–C(4)	117.0 (4)
Pt(1)–C(36)–C(37)	175.4 (6)	Pt(1)–N(3)–C(8)	124.9 (5)

most likely be attributed to the difference in conjugation, either due to the extended conjugation through the central metal center or the effect of planarization triggered by metal coordination. The insignificant difference in absorption wavelengths between the present platinum(II) system and a previously reported rhenium(I) system [3d] suggested that the participation of the metal center in the conjugation might not be the predominant factor. This could also be supported by the smaller amount of red shift observed in the platinum(II) complexes containing photochromic 1,10-phenanthroline ligand where planarization was not possible [3d]. Therefore, the large red shift observed would best be ascribed to the metal coordination-assisted planarization of the diimine ligand (Fig. 3), leading to good conjugation between the pyridine ring and the imidazole ring. Some representative spectral changes were illustrated in Fig. 4 and Fig. S3. In addition, the emission spectral changes upon photo-irradiation have been studied for complex **3**. Upon excitation at the isosbestic point at *ca.* 363 nm, reduction in luminescence intensity was observed (Fig. S4), indicative of emission quenching upon photocyclization, which is commonly found in photochromic diarylethene systems [3].

Table 3
Electronic absorption data for **L1**, **L2**, **L3** and complexes **1**–**6** in the open form and closed form.

Compound	Configuration	Absorption[a] λ_{abs}/nm (ε/dm^3 mol^{-1} cm^{-1})
L1	Open	320 (9080)
	Closed	342 (16,550), 406 sh (4100), 566 (4930)
L2	Open	320 (9540)
	Closed	344 (19,840), 422 sh (3810), 568 (5790)
L3	Open	324 (13,110)
	Closed	304 (21,580), 354 (25,760), 418 sh (6400), 582 (9240)
1	Open	361 (11,410), 421 sh (6060)
	Closed	719[b]
2	Open	360 (14,720), 423 sh (7350)
	Closed	717[b]
3	Open	318 (41,930), 372 (12,900), 405 sh (9270)
	Closed	730[b]
4	Open	302 sh (18,230), 364 (10,120), 422 sh (5320)
	Closed	717[b]
5	Open	326 (38,990), 344 (42,800), 384 sh (15,130)
	Closed	714[b]
6	Open	301 sh (24,150), 366 (12,030), 429 sh (6060)
	Closed	715[b]

[a] Data obtained in benzene at 298 K.

[b] Only the lowest energy absorption band was shown. Extinction coefficients could not be measured with certainty due to small conversion.

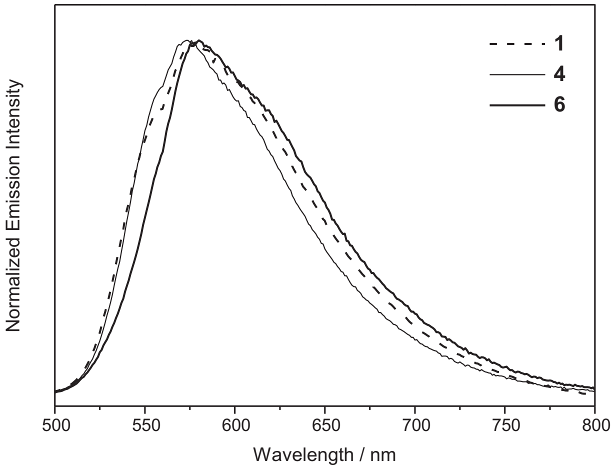


Fig. 2. Normalized corrected emission spectra of the open forms of complexes **1**, **4** and **6** in degassed benzene solutions at 298 K.

3.5. Electrochemical studies

The electrochemical behavior of the compounds in acetonitrile was studied and representative cyclic voltammograms of complex **3** are shown in Fig. S5. Complexes **1**–**6** showed an irreversible oxidation wave at *ca.* +1.05 to +1.32 V vs. SCE, which is commonly observed in platinum(II) diimine complexes [17] and platinum(II)

Table 4
Emission data for complexes **1**–**6** in various media.

Compound	Medium (*T*/K)	Emission λ_{em}[a]/nm (τ_o/μs)	ϕ_{lum}[b]
1	Benzene (298)	577 (0.2)	0.04
	Solid (298)	573 (1.2)	
	Solid (77)	547, 587 (8.3)	
	Glass[c] (77)	522, 568 (19.3)	
2	Benzene (298)	581 (1.5)	0.02
	Solid (298)	537, 574 (1.2)	
	Solid (77)	538, 578 (11.8)	
	Glass[c] (77)	520, 556, 571 (15.7)	
3	Benzene (298)	574 (0.3)	0.02
	Solid (298)	541, 572, 659 (1.4)	
	Solid (77)	533, 573 (16.8)	
	Glass[c] (77)	520, 555 (27.3)	
4	Benzene (298)	573 (3.1)	0.04
	Solid (298)	573 (1.3)	
	Solid (77)	570 (11.5)	
	Glass[c] (77)	520, 555 (21.2)	
5	Benzene (298)	581 (0.1)	0.05
	Solid (298)	626 (0.2)	
	Solid (77)	579, 625 (3.1)	
	Glass[c] (77)	549, 597 (167.8)	
6	Benzene (298)	579 (0.2)	0.03
	Solid (298)	571 (1.5)	
	Solid (77)	573 (6.06)	
	Glass[c] (77)	526, 568(20.5)	

[a] Emission maxima are corrected values.

[b] Luminescence quantum yields were reported relative to a degassed aqueous solution of [Ru(bpy)$_3$]Cl$_2$ as standard at 298 K.

[c] EtOH–MeOH (4:1 v/v).

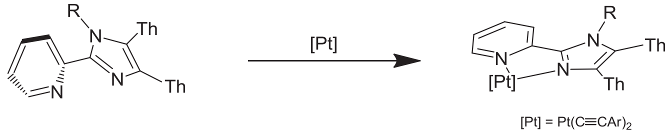


Fig. 3. Planarization of pyridine and imidazole rings by incorporation into platinum(II) center.

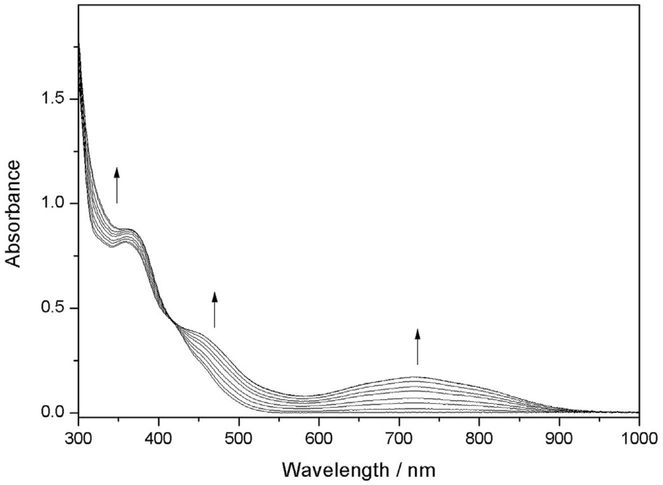


Fig. 4. Electronic absorption spectral changes of complex **1** in benzene upon irradiation at 395 nm at 298 K.

2-(2-pyridyl)benzimidazole bis-alkynyl complexes [9]. With different diimine ligands (**1** vs **4** vs **6**), there was insignificant effect on the potential, but with more electron-donating alkynyl ligands, the potential became less positive (**3** (+1.32 V) > **1** (+1.12 V) ~ **2** (+1.05 V)). Thus, the oxidation was assigned as metal-centered oxidation [Pt(II) → Pt(III)], probably mixed with alkynyl-centered oxidation. There was no improvement in the reversibility even upon increasing the scan rate up to 1 V s^{-1}. On the other hand, two reduction waves at *ca.* −1.54 to −1.62 V vs. SCE and −2.06 to −2.25 V vs. SCE were observed. The first quasi-reversible couple was assigned as diimine-centered reduction, commonly observed in platinum(II) bipyridine and phenanthroline systems [17] and related diimine complexes [9]. The second irreversible reduction wave, which was found to be similar to the thiophene-based reduction reported in the literature [3] and absent in the cyclic voltammograms of the related platinum(II) 2-(2-pyridyl)benzimidazole bis-alkynyl complexes [9], was assigned as the reduction of the thiophene moiety. The results are summarized in Table 5.

Table 5
Electrochemical data for complexes **1**–**6** in acetonitrile solution (0.1 mol dm^{-3} $^{n}Bu_4NPF_6$) at 298 K.[a]

Compound	Oxidation $[E_{pa}{}^{d}$/V vs. SCE]	Reduction $E_{1/2}{}^{b}$/V vs. SCE (ΔE_p/mV)[c] $[E_{pc}{}^{e}$/V vs. SCE]
1	[+1.12]	−1.61 (55), [−2.24]
2	[+1.05]	−1.62 (55), [−2.24]
3	[+1.32]	−1.55 (76), [−2.16]
4	[+1.13]	−1.61 (55), [−2.25]
5	[+1.07]	−1.54 (62), [−2.16]
6	[+1.13]	−1.55 (62), [−2.06, −2.25]

[a] Working electrode, glassy carbon; scan rate, 100 mV s^{-1}.
[b] $E_{1/2} = (E_{pa} + E_{pc})/2$; E_{pa} and E_{pc} are anodic and cathodic peak potentials respectively.
[c] $\Delta E_p = (E_{pa} - E_{pc})$.
[d] E_{pa} is reported for irreversible oxidation wave.
[e] E_{pc} is reported for irreversible reduction wave.

4. Conclusion

A new class of photochromic dithienylethene-containing platinum(II) diimine bis(alkynyl) complexes has been successfully synthesized and characterized. The photophysical, photochromic and electrochemical studies have been carried out. They show orange phosphorescence and photochromism in the red to near-infrared region. The large extent of red shift in absorption of the closed form is possibly due to the metal-co-ordination assisted planarization, which enhanced the electronic communication between the pyridine and the imidazole rings. This study demonstrates the versatility of the photochromic diarylethene-containing diimine ligand design and opens up further exploration in other transition metal complex systems.

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Appendix A. Supplementary material

CCDC 938706 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Appendix B. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.jorganchem.2013.07.048.

References

[1] (a) K. Takayama, K. Matsuda, M. Irie, Chem. Eur. J. 9 (2003) 5605;
(b) K. Matsuda, K. Takayama, M. Irie, Inorg. Chem. 43 (2004) 482;
(c) M. Morimoto, H. Miyasaka, M. Yamashita, M. Irie, J. Am. Chem. Soc. 131 (2009) 9823;
(d) K. Matsuda, K. Takayama, M. Irie, Chem. Commun. (2001) 363;
(e) M. Irie, Chem. Rev. 100 (2000) 1685.

[2] (a) E. Murguly, T.B. Norsten, N.R. Branda, Angew. Chem. Int. Ed. 40 (2001) 1752;
(b) S. Fraysse, C. Coudret, J.P. Launay, Eur. J. Inorg. Chem. (2000) 1581;
(c) A. Fernández-Acebes, J.M. Lehn, Adv. Mater. 10 (1998) 1519;
(d) A. Fernández-Acebes, J.M. Lehn, Chem. Eur. J. 5 (1999) 3285;
(e) B.Z. Chen, M.Z. Wang, Y.Q. Wu, H. Tian, Chem. Commun. (2002) 1060;
(f) H. Tian, B.Z. Chen, H. Tu, K. Mullen, Adv. Mater. 14 (2002) 918;
(g) R.T.F. Jukes, V. Adamo, F. Hartl, P. Belser, L. De Cola, Inorg. Chem. 43 (2004) 2779;
(h) H. Konaka, L.P. Wu, M. Munakata, T. Kuroda-Sowa, M. Maekawa, Y. Suenaga, Inorg. Chem. 42 (2003) 1928;
(i) B. Qin, R.X. Yao, H. Tian, Inorg. Chim. Acta 357 (2004) 3382;
(j) D. Sud, R. McDonald, N.R. Branda, Inorg. Chem. 44 (2005) 5960;
(k) I. Jung, H.B. Choi, E.Y. Kim, C.H. Lee, S.O. Kang, J.J. Ko, Tetrahedron 61 (2005) 12256;
(l) K. Uchida, A. Inagaki, M. Akita, Organometallics 26 (2007) 5030;
(m) V. Lemieux, M.D. Spantulescu, K.K. Baldridge, N.R. Branda, Angew. Chem. Int. Ed. 47 (2008) 5034;
(n) M.N. Roberts, C.-J. Carling, J.K. Nagle, N.R. Branda, M.O. Wolf, J. Am. Chem. Soc. 131 (2009) 16644;
(o) W. Tan, Q. Zhang, J. Zhang, H. Tian, Org. Lett. 11 (2009) 161;
(p) M.T. Indelli, C. Stefano, M. Ghirotti, C. Chiorboli, M. Ravaglia, M. Garavelli, F. Scandola, J. Am. Chem. Soc. 130 (2008) 7286;
(q) V. Guerchais, L. Ordronneau, H. Le Bozec, Coord. Chem. Rev. 254 (2010) 2533.

[3] (a) V.W.-W. Yam, C.-C. Ko, N. Zhu, J. Am. Chem. Soc. 126 (2004) 12734;
(b) C.-C. Ko, W.M. Kwok, V.W.-W. Yam, D.L. Phillips, Chem. Eur. J. 12 (2006) 5840;

(c) J.K.-W. Lee, C.-C. Ko, K.M.-C. Wong, N. Zhu, V.W.-W. Yam, Organometallics 27 (2007) 12;
(d) P.H.-M. Lee, C.-C. Ko, N. Zhu, V.W.-W. Yam, J. Am. Chem. Soc. 129 (2007) 6058;
(e) C.-C. Ko, W.H. Lam, V.W.-W. Yam, Chem. Commun. (2008) 5203;
(f) V.W.-W. Yam, J.K.-W. Lee, C.-C. Ko, N. Zhu, J. Am. Chem. Soc. 131 (2009) 912;
(g) C.-C. Ko, V.W.-W. Yam, J. Mater. Chem. 20 (2010) 2063;
(h) G. Duan, N. Zhu, V.W.-W. Yam, Chem. Eur. J. 16 (2010) 13199;
(i) G. Duan, V.W.-W. Yam, Chem. Eur. J. 16 (2010) 12642;
(j) J.C.-H. Chan, W.H. Lam, H.-L. Wong, N. Zhu, W.-T. Wong, V.W.-W. Yam, J. Am. Chem. Soc. 133 (2011) 12690;
(k) G. Duan, W.-T. Wong, V.W.-W. Yam, New J. Chem. 35 (2011) 2267;
(l) H.-L. Wong, C.-H. Tao, N. Zhu, V.W.-W. Yam, Inorg. Chem. 50 (2011) 471.

[4] (a) J. Otsuki, N. Omokawa, K. Yoshiba, T. Akasaka, T. Suenobu, T. Takido, K. Araki, S. Fukuzumi, Inorg. Chem. 42 (2003) 3057;
(b) H. Nishihara, Bull. Chem. Soc. Jpn. 77 (2004) 407;
(c) R. Sakamoto, M. Murata, S. Jume, H. Sampei, M. Sugimoto, H. Nishihara, Chem. Commun. (2005) 1215;
(d) H. Nishihara, Coord. Chem. Rev. 249 (2005) 1468;
(e) Y. Einaga, R. Mikami, T. Akitsu, G. Li, Thin Solid Films (2005) 230;
(f) P. Pratihar, T.K. Mondal, A.K. Patra, C. Sinha, Inorg. Chem. 48 (2009) 2760.

[5] (a) P.P. Zarnegar, D.G. Whitten, J. Am. Chem. Soc. 93 (1971) 3776;
(b) P.P. Zarnegar, C.R. Bock, D.G. Whitten, J. Am. Chem. Soc. 95 (1973) 4361;
(c) V.W.-W. Yam, V.C.Y. Lau, L.X. Wu, J. Chem. Soc. Dalton Trans. (1998) 1461;
(d) S.S. Sun, E. Robson, N. Dunwoody, A.S. Silva, I.M. Brinn, A. Lees, J. Chem. Commun. (2000) 201;
(e) J.D. Lewis, R.N. Perutz, J.N. Moore, Chem. Commun. (2000) 1865;
(f) V.W.-W. Yam, Y. Yang, J. Zhang, B.W.K. Chu, N. Zhu, Organometallics 20 (2001) 4911;
(g) T. Yutaka, I. Mori, M. Kurihara, J. Mizutani, N. Tamai, T. Kawai, M. Irie, H. Nishihara, Inorg. Chem. 41 (2002) 7143;
(h) O.S. Wenger, L.M. Henling, M.W. Day, J.R. Winkler, H.B. Gray, Inorg. Chem. 43 (2004) 2043;
(i) M. Busby, P. Matousek, M. Towrie, A. Vlček Jr., J. Phys. Chem. A 109 (2005) 3000.

[6] (a) C.-C. Ko, L.X. Wu, K.M.-C. Wong, N. Zhu, N.V.W.-W. Yam, Chem. Eur. J. 10 (2004) 766;
(b) M. Querol, B. Bozic, N. Salluce, P. Belser, Polyhedron 22 (2003) 655;
(c) J.L. Bahr, G. Kodis, L. Garza, S. Lin, A.L. Moore, T.A. Moore, D. Gust, J. Am. Chem. Soc. 123 (2001) 7124;
(d) V.W.-W. Yam, C.-C. Ko, L.X. Wu, K.M.-C. Wong, K.K. Cheung, Organometallics 19 (2000) 1820;
(e) R.F. Khairutdinov, K. Giertz, J.K. Hurst, E.N. Voloshina, N.A. Voloshin, V.I. Minkin, J. Am. Chem. Soc. 120 (1998) 12707.

[7] (a) C.W. Chan, L.K. Cheng, C.-M. Che, Coord. Chem. Rev. 132 (1994) 87;
(b) S.L. James, M. Younus, P.R. Raithby, J. Lewis, J. Organomet. Chem. 543 (1997) 233;
(c) M. Hissler, W.B. Connick, D.K. Geiger, J.E. McGarrah, D. Lipa, R.J. Lachicotte, R. Eisenberg, Inorg. Chem. 39 (2000) 447;
(d) M. Hissler, J.E. McGarrah, W.B. Connick, D.K. Geiger, S.D. Cummings, R. Eisenberg, Coord. Chem. Rev. 108 (2000) 115;
(e) S.-C. Chan, M.C.W. Chan, Y. Wang, C.-M. Che, K.-K. Cheung, N. Zhu, Chem. Eur. J. 7 (2001) 4180;
(f) C.E. Whittle, J.A. Weinstein, M.W. George, K.S. Schanze, Inorg. Chem. 40 (2001) 4053;
(g) J.E. McGarrah, Y.J. Kim, M. Hissler, R. Eisenberg, Inorg. Chem. 40 (2001) 4510;
(h) Y. Kang, J. Lee, D. Song, S. Wang, Dalton Trans. 18 (2003) 3493;
(i) T.J. Wadas, R.J. Lachicotte, R. Eisenberg, Inorg. Chem. 42 (2003) 3772;
(j) J.E. McGarrah, R. Eisenberg, Inorg. Chem. 42 (2003) 4344;
(k) F. Hua, S. Kinayyigit, J.R. Cable, F.N. Castellano, Inorg. Chem. 44 (2005) 471;
(l) T.J. Wadas, S. Chakraborty, R.J. Lachicotte, Q.M. Wang, R. Eisenberg, Inorg. Chem. 44 (2005) 2628;
(m) U. Siemeling, K. Bausch, H. Fink, C. Bruhn, M. Baldus, B. Angerstein, R. Plessow, A. Brockhinke, Dalton Trans. (2005) 2365;
(o) F.N. Castellano, I.E. Pomestchenko, E. Shikhova, F. Hua, M.L. Muro, N. Rajapakse, Coord. Chem. Rev. 250 (2006) 1819.

[8] (a) V.W.-W. Yam, K.M.-C. Wong, N. Zhu, J. Am. Chem. Soc. 124 (2002) 6506;
(b) V.W.-W. Yam, K.M.-C. Wong, N. Zhu, Angew. Chem. Int. Ed. 42 (2003) 1400;
(c) C.-H. Tao, N. Zhu, V.W.-W. Yam, Chem. Eur. J. 11 (2005) 1647;
(d) V.W.-W. Yam, Acc. Chem. Res. 35 (2002) 555;
(e) C.Y.-S. Chung, V.W.-W. Yam, J. Am. Chem. Soc. 133 (2011) 18775;
(f) S.Y.-L. Leung, A.Y.-Y. Tam, C.-H. Tao, H.S. Chow, V.W.-W. Yam, J. Am. Chem. Soc. 134 (2012) 1047.

[9] N.M. Shavaleev, Z.R. Bell, T.L. Easun, R. Rutkalte, L. Swanson, M.D. Ward, Dalton Trans. (2004) 3678.

[10] The signals are not well-resolved due to the presence of the isomers, possibly originated from the photochromic diarylethene moiety.

[11] J.N. Demas, G.A. Crosby, J. Phys. Chem. 75 (1971) 991.

[12] (a) J. Van Houten, R.J. Watts, J. Am. Chem. Soc. 98 (1976) 4853;
(b) J.V. Caspar, T.J. Meyer, J. Am. Chem. Soc. 105 (1983) 5583.

[13] (a) R.R. Gagne, C.A. Koval, G.C. Lisensky, Inorg. Chem. 19 (1980) 2854;
(b) N.G. Connelly, W.E. Geiger, Chem. Rev. 96 (1996) 877.

[14] SHELXS97, G.M. Sheldrick, SHELX97. Programs for Crystal Structure Analysis (Release 97-2), University of Göttingen, Germany, 1997.

[15] V.M. Miskowski, V.H. Houlding, C.-M. Che, Y. Wang, Inorg. Chem. 32 (1993) 2518.

[16] A. Hazell, A. Mukhopadhyay, Acta Crystallogr. Sect. B: Struct. Crystallogr. Cryst. Chem. 36 (1980) 1647.

[17] C.B. Blanton, Z. Murtaza, R.J. Shaver, D.P. Rillema, Inorg. Chem. 31 (1992) 3230.