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Photochromic Alkynes as Versatile Building Blocks for Metal Alkynyl Systems: Design, Synthesis, and Photochromic Studies of Diarylethene-Containing Platinum(II) Phosphine Alkynyl Complexes

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The synthesis of newly designed photochromic dithienylethene-containing ethynylthiophene and ethynylthieno[3,2-*b*]-thiophene has been described, and their incorporation as versatile ligands into the platinum(II) phosphine system was demonstrated. All platinum(II) complexes have been successfully characterized by ^{1}H and ^{31}P NMR spectroscopies, positive fast atom bombardment (FAB) mass spectrometry, as well as elemental analysis. One of the complexes has been characterized by X-ray crystallography. Their photophysical, photochromic, and electrochemical properties have been studied. Upon photoexcitation, all the photochromic diarylethene-containing alkynes and platinum(II) complexes exhibited reversible photochromism. The thermal bleaching kinetic of complex **6** was studied in toluene at 298 and 313 K. Complexes **1**, **3**, and **4**, which contained the labile chloro- ligand, represent a new class of versatile building blocks for photoswitchable functional materials.

Introduction

The research on molecular functional materials is undoubtedly one of the most active areas of topical interest owing to their potential capability for applications as useful devices from the bottom-up approach. Scientists have started developing and searching for versatile building blocks for the construction of materials with desired properties to facilitate various applications. Among them, the platinum(II) phosphine bis-alkynyl system, with its simple square planar geometry, has been quite widely explored[1] as the connecting unit because of its well developed synthetic procedures and ease of synthesis of unsymmetrical complexes.[2,3,4a−4c] Recently, utilization of the platinum(II) phosphine bis-alkynyl building block for the construction of polymeric light-harvesting materials,[5] optical power limiting materials,[3] dendrimers,[4] polymers,[1p,3a,5a,5b,6] and others[7] has been achieved.

On the other hand, researches have shown that through the incorporation of metal centers into the photochromic moieties, such as azo,[8] stilbene,[9] diarylethene,[10−12] and spirooxazine,[13] various attractive photochromic and photophysical behaviors might result. In addition, the presence of the photochromic moiety introduces an additional photocontrolled switching functionality which could be utilized to modulate the luminescence,[11,12b,12c] magnetic,[10c] and non-linear optical properties.[14] Moreover, upon photoinduced isomerization from open form to closed form, the relatively lower-lying excited state of the closed form may alter the direction of energy transfer between various chromophores, resulting in interesting photophysical properties.[15] With our recent interest in the design and synthesis of various photochromic diarylethene-containing ligands and their metal complexes[12a,d,16] as well as various luminescence switchable materials,[12c,e] we herein describe the design and synthesis of a new class of photochromic diarylethene-containing alkynes and the photophysical and photochromic studies of their platinum(II) phosphine complexes.

Experimental Section

Materials. *n*-Butyllithium in hexanes (1.6 M, 2.5 M), thiophene, cesium carbonate, copper powder, quinoline, *trans*-[Pt(PEt$_3$)$_2$Cl$_2$], copper(I) iodide and 1-formylpiperidine were obtained from Aldrich Chemical Co. Phenylacetylene, *N*,*N*-diisopropylamine, and *N*,*N*-diethylamine were purchased from Lancaster Synthesis Ltd. 2,5-Dimethylthiophene, 2,3-dibromothiophene, and *N*-iodosuccinimide were obtained from Fluorochem, Inc. (Trimethylsilyl)-acetylene was obtained from GFS Chemical, Inc. Potassium tetrachloroplatinate(II) and palladium(II) chloride were purchased from Strem Chemicals, Inc. Tri-*n*-butyl borate and triphenylphosphine were obtained from Acros Organics, Inc. Tetrakis(triphenylphosphine)palladium(0)[17] as catalyst for Suzuki cross-coupling, dichlorobis(triphenylphosphine)palladium(II)[18] as catalyst for Sonogashira coupling, *trans*-[Pt(PPh$_3$)$_2$Cl$_2$],[19] and 2,3,4,5-tetrabromothiophene[20] were prepared according to literature procedures with slight modifications. All amines were distilled over

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potassium hydroxide and stored over potassium hydroxide prior to use. Tetra-*n*-butylammonium hexafluorophosphate was purified by recrystallization from ethanol for at least three times and dried prior to use. Benzene (Lab Scan, AR), tetrahydrofuran (THF, Lab Scan, AR) and diethyl ether (Scharlau, anhydrous) were distilled over sodium before use. Acetonitrile was distilled over calcium hydride before use. All other solvents and reagents were of analytical grade and were used as received.

3,4,5-Tribromothiophene-2-carbaldehyde. The reaction was performed under anhydrous condition using standard Schlenk techniques. To a well stirred solution of 2,3,4,5-tetrabromothiophene (5 g, 12.5 mmol) in anhydrous diethyl ether (50 mL) at -10 °C was added *n*-butyllithium (2.5 M, 5.5 mL, 13.8 mmol)

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in a dropwise manner. The reaction mixture was then stirred at −10 °C for 2 h, after which 1-formylpiperidine (1.56 g, 1.53 mL, 13.8 mmol) was slowly added. The resulting mixture was gradually raised to room temperature and stirred for another further 18 h. The reaction was quenched with deionized water and poured into a separating funnel. The organic layer was washed with deionized water, dried over anhydrous magnesium sulfate, filtered, and evaporated to dryness under reduced pressure. The crude product was then purified by column chromatography on silica gel (70−230 mesh) using hexane as eluent to give after solvent removal the product as a pale yellow solid. Yield: 2.62 g, 7.5 mmol; 60%. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 9.85 (s, 1H, −CHO). Positive-ion EI mass spectrum: *m*/*z* 348 $\{M\}^+$.

Ethyl 5,6-Dibromothieno[3,2-*b*]thiophene-2-carboxylate. To a stirred solution of 3,4,5-tribromothiophene-2-carbaldehyde (5.65 g, 16.2 mmol) and anhydrous potassium carbonate (2.95 g, 21.3 mmol) in dimethylformamide (DMF, 60 mL) was added ethyl thioglycolate (1.91 g, 1.74 mL, 15.9 mmol). The resulting mixture was stirred for 3 days, after which deionized water (300 mL) was added slowly to commence precipitation. The solid was collected by filtration and was dissolved in chloroform. The organic layer was washed with water and then dried over anhydrous magnesium sulfate, filtered, and evaporated to dryness under reduced pressure to give a brown oil. The crude product was purified by column chromatography on silica gel (70−230 mesh) using hexane-dichloromethane (4:1 v/v) as eluent to give the product as a white solid. Yield: 2.52 g, 6.84 mmol; 43%. ^{1}H NMR (300 MHz, $CDCl_3$, 298K): δ 1.40 (t, J = 7.1 Hz, 3H, $-CH_3$), 4.39 (q, J = 7.1 Hz, 2H, $-CH_2-$), 7.93 (s, 1H, 3-thienothienyl). Positive-ion EI mass spectrum: *m*/*z* 369 $\{M\}^+$, 324 $\{M-OEt\}^+$.

Ethyl 5,6-Bis(2,5-dimethylthiophen-3-yl)thieno[3,2-*b*]thiophene-2-carboxylate. The target compound was synthesized according to standard Suzuki coupling reaction under a heterogeneous mixture of water and THF. To a solution mixture of ethyl 5,6-dibromothieno[3,2-*b*]thiophene-2-carboxylate (2 g, 5.42 mmol), 2,5-dimethylthien-3-yl boronic acid[12e] (2.54 g, 16.3 mmol) and tetrakis(triphenylphosphine)palladium(0) (484 mg, 0.419 mmol) in THF (80 mL) was added aqueous cesium carbonate solution (2 M, 10.6 g, 16.3 mL, 32.6 mmol). The reaction mixture was vigorously stirred and refluxed in the dark, and the progress was monitored by thin layer chromatography (TLC). This was then extracted with diethyl ether. The combined extracts were washed with brine and water, and finally dried over anhydrous magnesium sulfate. After filtration and removal of the solvent, the crude product was purified by column chromatography on silica gel (70−230 mesh) using hexane-dichloromethane (4:1 v/v) as the eluent to give the product as a white solid. Yield: 1.9 g, 4.39 mmol; 81%. ^{1}H NMR (300 MHz, $CDCl_3$, 298K): δ 1.39 (t, J = 7.1 Hz, 3H, $-CH_3$ in carboxylate group), 1.96 (s, 3H, $-CH_3$), 2.06 (s, 3H, $-CH_3$), 2.38 (s, 3H, $-CH_3$), 2.43 (s, 3H, $-CH_3$), 4.37 (q, J = 7.1 Hz, 2H, $-CH_2-$), 6.53 (s, 1H, dimethylthienyl), 6.66 (s, 1H, dimethylthienyl), 7.97 (s, 1H, 3-thienothienyl). Positive-ion EI mass spectrum: *m*/*z* 432 $\{M\}^+$.

2,3-Bis(2,5-dimethylthiophen-3-yl)thiophene. The target compound was prepared according to a procedure similar to that of ethyl 5,6-bis(2,5-dimethylthiophen-3-yl)thieno[3,2-*b*]thiophene-2-carboxylate except 2,3-dibromothiophene (2 g, 0.936 mL, 8.27 mmol) was used instead of ethyl 5,6-dibromothieno[3,2-*b*]thiophene-2-carboxylate. The crude product was purified by column chromatography on silica gel (70−230 mesh) using hexane as the eluent. Further purification was achieved by recrystallization from a minimal amount of hexane and stored at −18 °C to afford a white crystalline solid. Yield: 1.8 g, 5.91 mmol; 72%. ^{1}H NMR (300 MHz, $CDCl_3$, 298K): δ 2.01 (s, 3H, $-CH_3$), 2.03 (s, 3H, $-CH_3$), 2.38 (s, 6H, $-CH_3$), 6.43 (s, 1H, dimethylthienyl), 6.48 (s, 1H, dimethylthienyl), 7.03 (d, J = 5.2 Hz, 1H, 4-thienyl), 7.28 (d, J = 5.2 Hz, 1H, 5-thienyl). Positive-ion EI mass spectrum: *m*/*z* 304 $\{M\}^+$.

5,6-Bis(2,5-dimethylthiophen-3-yl)thieno[3,2-*b*]thiophene-2-carboxylic Acid. To a stirred solution of ethyl 5,6-bis(2,5-dimethylthiophen-3- yl)thieno[3,2-*b*]thiophene-2-carboxylate (1 g, 2.31 mmol) in ethanol−water (40 mL, 1:1 v/v) was added potassium hydroxide (389 mg, 6.93 mmol). The resulting mixture was heated under reflux for 1.5 h, after which it was allowed to cool to room temperature and was acidified with hydrochloric acid (2 M). This was followed by extraction using ethyl acetate (3 × 30 mL). The combined organic layers were washed with water and then dried over anhydrous magnesium sulfate, filtered, and evaporated to dryness under reduced pressure to give a white solid. Yield: 890 mg, 2.2 mmol; 95%. ^{1}H NMR (300 MHz, $CDCl_3$, 298K): δ 1.99 (s, 3H, $-CH_3$), 2.09 (s, 3H, $-CH_3$), 2.41 (s, 3H, $-CH_3$), 2.45 (s, 3H, $-CH_3$), 6.56 (s, 1H, dimethylthienyl), 6.69 (s, 1H, dimethylthienyl), 8.08 (s, 1H, 3-thienothienyl). Positive-ion EI mass spectrum: *m*/*z* 404 $\{M\}^+$.

2,3-Bis(2,5-dimethylthiophen-3-yl)thieno[3,2-*b*]thiophene. To a stirred solution of 5,6-bis(2,5-dimethylthiophen-3-yl)thieno[3,2-*b*]thiophene-2-carboxylic acid (1 g, 2.47 mmol) in quinoline (15 mL) was added copper powder (188 mg, 2.97 mmol). The resulting mixture was heated to reflux for at least 2 h, and the progress was monitored by TLC. After that, it was cooled to room temperature, followed by the slow addition of hydrochloric acid (2 M, 50 mL) and extraction with diethyl ether (3 × 30 mL). The combined etheral layers were washed with hydrochloric acid (2 M), water and then dried over anhydrous magnesium sulfate, filtered, and evaporated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel (70−230 mesh) using hexane as the eluent. Further purification was achieved by recrystallization from a minimal amount of hexane and stored at −18 °C to afford a white crystalline solid. Yield: 653 mg, 1.81 mmol; 73%. ^{1}H NMR (300 MHz, $CDCl_3$, 298K): δ 2.01 (s, 3H, $-CH_3$), 2.10 (s, 3H, $-CH_3$), 2.43 (s, 3H, $-CH_3$), 2.47 (s, 3H, $-CH_3$), 6.58 (s, 1H, dimethylthienyl), 6.73 (s, 1H, dimethylthienyl), 7.30 (d, J = 5.2 Hz, 1H, 4-thienothienyl), 7.40 (d, J = 5.2 Hz, 1H, 5-thienothienyl). Positive-ion EI mass spectrum: *m*/*z* 360 $\{M\}^+$.

2,3-Bis(2,5-dimethylthiophen-3-yl)-5-iodothieno[3,2-*b*]thiophene. To a stirred solution of 2,3-bis(2,5-dimethylthiophen-3-yl)thieno[3,2-*b*]thiophene (1 g, 2.77 mmol) in chloroform-acetic acid (40 mL, 1:1 v/v) was added *N*-iodosuccinimide (686 mg, 3.05 mmol). The reaction mixture was stirred overnight. Water (70 mL) was added to the mixture. The resulting solution was extracted with chloroform (3 × 50 mL). The combined extracts were neutralized with aqueous sodium carbonate solution, followed by washing with deionized water. The organic layer was then dried over anhydrous magnesium sulfate, filtered, and evaporated to dryness under reduced pressure. The crude product was purified by column chromatography on silica gel (70−230 mesh) using hexane as the eluent. Yield: 1.1 g, 2.26 mmol; 82%. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 1.96 (s, 3H, $-CH_3$), 2.05 (s, 3H, $-CH_3$), 2.39 (s, 3H, $-CH_3$), 2.42 (s, 3H, $-CH_3$), 6.52 (s, 1H, dimethylthienyl), 6.64 (s, 1H, dimethylthienyl), 7.40 (s, 1H, 4-thienothienyl). Positive-ion EI mass spectrum: *m*/*z* 486 $\{M\}^+$.

2,3-Bis(2,5-dimethylthiophen-3-yl)-5-iodothiophene. The target compound was prepared according to a procedure similar to that of 2,3-bis(2,5-dimethylthiophen-3-yl)-5-iodothieno[3,2-*b*]thiophene except 2,3-bis(2,5-dimethylthiophen-3-yl)thiophene (1 g, 3.28 mmol) was used instead of 2,3-bis(2,5-dimethylthiophen-3-yl)thieno[3,2-*b*]thiophene. Yield: 1.07 g, 2.49 mmol; 76%. ^{1}H NMR (300 MHz, $CDCl_3$, 298K): δ 2.00 (s, 6H, $-CH_3$), 2.36 (s, 6H, $-CH_3$), 6.38 (s, 1H, dimethylthienyl), 6.45 (s, 1H, dimethylthienyl), 7.15 (s, 1H, 4-thienyl). Positive-ion EI mass spectrum: *m*/*z* 430 $\{M\}^+$.

((5,6-Bis(2,5-dimethylthiophen-3-yl)thieno[3,2-*b*]thiophen-2-yl)-ethynyl)trimethylsilane (TMS—C≡C—TTh-DTE). To a solution of 2,3-bis(2,5-dimethylthiophen-3-yl)-5-iodothieno[3,2-*b*]thiophene (1 g, 2.06 mmol), dichlorobis(triphenylphosphine)palladium(II) (144 mg, 0.205 mmol), copper(I) iodide (39 mg, 0.205 mmol), and triphenylphosphine (161 mg, 0.616 mmol) in degassed *N*,*N*-diisopropylamine (60 mL) was added trimethylsilylacetylene (302 mg, 0.431 mL, 3.08 mmol) under an inert atmosphere of

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argon. The reaction mixture was maintained at 60 °C overnight. After cooling to room temperature, the mixture was acidified with hydrochloric acid (2 M) and followed by extraction with diethyl ether (3 × 40 mL). The combined organic layers were washed with deionized water and dried over anhydrous magnesium sulfate. After filtration and evaporation under reduced pressure, the crude product was purified by column chromatography on silica gel (70−230 mesh) using hexane as eluent to give the product as a pale yellow solid. Yield: 645 mg, 1.41 mmol; 69%. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 0.26 (s, 9H, $-SiMe_3$), 1.95 (s, 3H, $-CH_3$), 2.03 (s, 3H, $-CH_3$), 2.37 (s, 3H, $-CH_3$), 2.40 (s, 3H, $-CH_3$), 6.51 (s, 1H, dimethylthienyl), 6.63 (s, 1H, dimethylthienyl), 7.35 (s, 1H, 3-thienothienyl). Positive-ion EI mass spectrum: *m*/*z* 456 $\{M\}^+$.

((5,6-Bis(2,5-dimethylthiophen-3-yl)thiophen-2-yl)ethynyl)trimethylsilane (TMS—C≡C—Th-DTE). The target compound was prepared according to a procedure similar to that of **TMS—C≡C—TTh-DTE** except 2,3-bis(2,5-dimethylthiophen-3-yl)-5-iodothiophene (1 g, 2.33 mmol) was used instead of 2,3-bis(2,5-dimethylthiophen-3-yl)-5-iodothieno[3,2-*b*]thiophene. Yield: 670 mg, 1.67 mmol; 72%. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 0.25 (s, 9H, $-SiMe_3$), 2.02 (s, 6H, $-CH_3$), 2.36 (s, 6H, $-CH_3$), 6.36 (s, 1H, dimethylthienyl), 6.42 (s, 1H, dimethylthienyl), 7.16 (s, 1H, 3-thienyl). Positive-ion EI mass spectrum: *m*/*z* 400 $\{M\}^+$.

2,3-Bis(2,5-dimethylthiophen-3-yl)-5-ethynylthieno[3,2-*b*]thiophene (HC≡C—TTh-DTE). To a solution of **TMS—C≡C—TTh-DTE** (500 mg, 1.30 mmol) in THF-methanol (40 mL, 3:1 v/v) was added an excess of anhydrous potassium carbonate. The mixture was stirred overnight, after which the volume was reduced and water was added. It was followed by extraction with diethyl ether (3 × 30 mL). The combined organic layers were washed with deionized water and dried over anhydrous magnesium sulfate. After filtration and evaporation under reduced pressure, the crude product was purified by column chromatography on silica gel (70−230 mesh) using hexane as eluent to give the product as a pale yellow solid. Yield: 461 mg, 1.20 mmol; 92%. ^{1}H NMR (300 MHz, $CDCl_3$, 298K): δ 2.05 (s, 3H, $-CH_3$), 2.13 (s, 3H, $-CH_3$), 2.45 (s, 3H, $-CH_3$), 2.49 (s, 3H, $-CH_3$), 3.48 (s, 1H, $-C{\equiv}CH$), 6.61 (s, 1H, dimethylthienyl), 6.73 (s, 1H, dimethylthienyl), 7.48 (s, 1H, 4-thienothienyl). Positive-ion EI mass spectrum: *m*/*z* 384 $\{M\}^+$.

2,3-Bis(2,5-dimethylthiophen-3-yl)-5-ethynylthiophene (HC≡C−Th-DTE). The target compound was prepared according to a procedure similar to that of **HC≡C—TTh-DTE** except **TMS—C≡C—Th-DTE** (500 mg, 1.52 mmol) was used instead of **TMS—C≡C—TTh-DTE**. Yield: 450 mg, 90%. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 2.01 (s, 3H, $-CH_3$), 2.03 (s, 3H, $-CH_3$), 2.36 (s, 6H, $-CH_3$), 3.38 (s, 1H, $-C{\equiv}CH$), 6.38 (s, 1H, dimethylthienyl), 6.45 (s, 1H, dimethylthienyl), 7.20 (s, 1H, 3-thienyl). Positive-ion EI mass spectrum: *m*/*z* 328 $\{M\}^+$.

[Pt(PPh$_3$)$_2$(C≡C—TTh-DTE)Cl] (1). The reaction was performed under argon. To a solution of **HC≡C—TTh-DTE** (100 mg, 0.260 mmol) and *trans*-[Pt(PPh_3)$_2$$Cl_2$] (205 mg, 0.260 mmol) in chloroform (15 mL) was added diethylamine (0.5 mL). The resulting mixture was heated under reflux for 3 h, after which it was filtered and the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane, washed with water, and dried over anhydrous magnesium sulfate. After filtration and evaporation under reduced pressure, the crude product was purified by column chromatography on silica gel (70−230 mesh) using hexane-dichloromethane (4:1 v/v) as eluent. Further purification was achieved by slow diffusion of pentane vapor into its concentrated dichloromethane solution to yield **1** as a yellow solid. Yield: 145 mg, 0.127 mmol; 49%. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 1.89 (s, 3H, $-CH_3$), 1.95 (s, 3H, $-CH_3$), 2.34 (s, 3H, $-CH_3$), 2.40 (s, 3H, $-CH_3$), 5.97 (s, 1H, 3-thienothienyl), 6.42 (s, 1H, dimethylthienyl), 6.48 (s, 1H, dimethylthienyl), 7.38 (m, 18H, $-PPh_3$), 7.75 (m, 12H, $-PPh_3$); ^{31}P NMR (162 MHz, $CDCl_3$): δ 21.54 (s, $J(^{31}P-^{195}Pt)$ = 2634 Hz). Positive fast atom bombardment (FAB) mass spectrum: *m*/*z* 1138 $\{M\}^+$, 1103 $\{M-Cl\}^+$, 840 $\{M-Cl-PPh_3\}^+$. Elemental analyses, Found (%): C 55.64 H 3.84; Calcd (%) for $C_{56}H_{45}ClP_2PtS_4\cdot CH_2Cl_2$: C 55.94, H 3.87.

[Pt(PPh$_3$)$_2$(C≡C—TTh-DTE)(C≡C-Ph)] (2). The reaction was performed under argon. To a solution of **[Pt(PPh$_3$)$_2$(C≡C—TTh-DTE)Cl]** (150 mg, 0.132 mmol) and phenylacetylene (14.8 mg, 0.145 mmol) in chloroform (15 mL) was added diethylamine (0.5 mL) and a catalytic amount of copper(I) iodide. The resulting mixture was heated under reflux for 3 h, after which it was filtered and the solvent was removed under reduced pressure. The residue was dissolved in dichloromethane, washed with water, and dried over anhydrous magnesium sulfate. After filtration and evaporation under reduced pressure, the crude product was purified by column chromatography on silica gel (70−230 mesh) using hexane-dichloromethane (4:1 v/v) as eluent. Further purification was achieved by slow diffusion of pentane vapor into its concentrated dichloromethane solution. Yield: 64 mg, 0.0532 mmol; 40%. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 1.92 (s, 3H, $-CH_3$), 1.97 (s, 3H, $-CH_3$), 2.35 (s, 3H, $-CH_3$), 2.41 (s, 3H, $-CH_3$), 6.10 (s, 1H, 3-thienothienyl), 6.26 (m, 2H, $-C{\equiv}CPh$), 6.44 (s, 1H, dimethylthienyl), 6.51 (s, 1H, dimethylthienyl), 6.89 (m, 3H, $-C{\equiv}CPh$), 7.39 (m, 18H, $-PPh_3$), 7.80 (m, 12H, $-PPh_3$); ^{31}P NMR (162 MHz, $CDCl_3$, 298K): δ 18.39 (s, $J(^{31}P-^{195}Pt)$ = 2630 Hz). Positive FAB mass spectrum: *m*/*z* 1203 $\{M\}^+$, 941 $\{M-PPh_3\}^+$. Elemental analyses, Found (%): C 64.09, H 4.34; Calcd (%) for $C_{64}H_{50}P_2PtS_4$: C 63.82, H 4.18.

[Pt(PEt$_3$)$_2$(C≡C—TTh-DTE)Cl] (3). The target compound was prepared according to a procedure similar to that of **[Pt(PPh$_3$)$_2$(C≡C—TTh-DTE)Cl]** except *trans*-[Pt(PEt_3)$_2$$Cl_2$] (131 mg, 0.26 mmol) was used instead of *trans*-[Pt(PPh_3)$_2$$Cl_2$]. Yield: 95 mg, 0.112 mmol; 43%. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 1.22 (m, 18H, $P(CH_2CH_3)_3$), 1.96 (s, 3H, $-CH_3$), 2.03 (s, 3H, $-CH_3$), 2.15 (m, 12H, $P(CH_2CH_3)_3$), 2.37 (s, 3H, $-CH_3$), 2.42 (s, 3H, $-CH_3$), 6.50 (s, 1H, dimethylthienyl), 6.64 (s, 1H, dimethylthienyl), 7.01 (s, 1H, 3-thienothienyl); ^{31}P NMR (162 MHz, $CDCl_3$, 298K): δ 11.52 (s, $J(^{31}P-^{195}Pt)$ = 2342 Hz). Positive FAB mass spectrum: *m*/*z* 850 $\{M\}^+$. Elemental analyses, Found (%): C 45.49, H 5.22; Calcd (%) for $C_{32}H_{45}ClP_2PtS_4$: C 45.19, H 5.33.

[Pt(PPh$_3$)$_2$(C≡C−Th-DTE)Cl] (4). The target compound was prepared according to a procedure similar to that of **[Pt(PPh$_3$)$_2$(C≡C—TTh-DTE)Cl]** except **HC≡C−Th-DTE** (100 mg, 0.304 mmol) was used instead of **HC≡C—TTh-DTE**. Yield: 175 mg, 0.162 mmol; 53%. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 1.89 (s, 3H, $-CH_3$), 1.90 (s, 3H, $-CH_3$), 2.31 (s, 3H, $-CH_3$), 2.32 (s, 3H, $-CH_3$), 5.78 (s, 1H, 3-thienyl), 6.17 (s, 1H, dimethylthienyl), 6.26 (s, 1H, dimethylthienyl), 7.40 (m, 18H, $-PPh_3$), 7.76 (m, 12H, $-PPh_3$); ^{31}P NMR (162 MHz, $CDCl_3$, 298K): δ 21.20 (t, $J(^{31}P-^{195}Pt)$ = 2640 Hz). Positive FAB mass spectrum: *m*/*z* 1083 $\{M\}^+$, 1046 $\{M-Cl\}^+$. Elemental analyses, Found (%): C 53.96, H 3.74; Calcd (%) for $C_{54}H_{45}ClP_2PtS_3\cdot 2CH_2Cl_2$: C 53.70, H 3.94.

[Pt(PPh$_3$)$_2$(C≡C−Th-DTE)(C≡C-Ph)] (5). The target compound was prepared according to a procedure similar to that of **[Pt(PPh$_3$)$_2$(C≡C—TTh-DTE)(C≡C-Ph)]** except **[Pt(PPh$_3$)$_2$(C≡C−Th-DTE)Cl]** (150 mg, 0.139 mmol) was used instead of **[Pt(PPh$_3$)$_2$(C≡C—TTh-DTE)Cl]**. Yield: 77 mg, 0.0671 mmol; 48%. ^{1}H NMR (300 MHz, $CDCl_3$, 298K): δ 1.94 (s, 6H, $-CH_3$), 2.34 (s, 6H, $-CH_3$), 5.93 (s, 1H, 3-thienyl), 6.22 (s, 1H, dimethylthienyl), 6.30 (m, 3H, dimethylthienyl, $-C{\equiv}CPh$), 6.91 (m, 3H, $-C{\equiv}CPh$), 7.40 (m, 18H, $-PPh_3$), 7.81 (m, 12H, $-PPh_3$); ^{31}P NMR (162 MHz, $CDCl_3$, 298K): δ 18.29 (s, $J(^{31}P-^{195}Pt)$ = 2636 Hz). Positive FAB mass spectrum: *m*/*z* 1147 $\{M\}^+$. Elemental analyses, Found (%): C 63.21, H 4.39; Calcd (%) for $C_{62}H_{50}P_2PtS_3\cdot 0.5\,CH_2Cl_2$: C 63.04, H 4.32.

[Pt(PEt$_3$)$_2$(C≡C−Th-DTE)$_2$] (6). The target compound was prepared according to a procedure similar to that of **[Pt(PPh$_3$)$_2$(C≡C—TTh-DTE)(C≡C-Ph)]** except *trans*-[Pt(PEt_3)$_2$$Cl_2$] (150 mg, 0.299 mmol) was used instead of **[Pt(PPh$_3$)$_2$(C≡C—TTh-DTE)Cl]**, together with the use of **HC≡C−Th-DTE** (215 mg, 0.657 mmol) instead of phenylacetylene. Yield: 173 mg, 0.159 mmol; 53%. ^{1}H NMR (400 MHz, $CDCl_3$, 298K): δ 1.22 (m, 18H, $P(CH_2CH_3)_3$), 1.99 (s, 12H, $-CH_3$), 2.17 (m, 12H, $P(CH_2CH_3)_3$), 2.35 (s, 6H, $-CH_3$), 2.36 (s, 6H, $-CH_3$), 6.42 (s, 2H, dimethylthienyl), 6.45 (s, 2H, dimethylthienyl), 6.79 (s, 2H, 3-thienyl); ^{31}P NMR (162 MHz, $CDCl_3$, 298K): δ 11.39 (s, $J(^{31}P-^{195}Pt) = 2350$ Hz). Positive FAB mass spectrum: m/z 1086 $\{M\}^+$. Elemental analyses, Found (%): C 50.67, H 5.39; Calcd (%) for $C_{48}H_{60}P_2PtS_6 \cdot 0.5\ CHCl_3$: C 50.83, H 5.32.

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) for ^1H NMR and ^{31}P NMR were recorded relative to tetramethylsilane (Me_4Si) and 85% phosphoric acid, respectively. Positive-ion 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 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 side arm 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 butyronitrile 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.[21a] A degassed aqueous solution of $[Ru(bpy)_3]Cl_2$ was used as standard[21b,c] at 298 K.

Chemical actinometry was employed for the photochemical quantum yield determination.[22] Incident light intensities were taken from the average values measured just before and after each photolysis experiment using ferrioxalate actinometry.[22] 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} $^nBu_4NPF_6$ 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.[23] All solutions for electrochemical studies were deaerated with prepurified argon gas before measurement.

Table 1. Crystal and Structure Determination Data for Complex **2**

empirical formula	$C_{64}H_{50}P_2PtS_4 \cdot (CHCl_3)_{2.5}$
formula weight	1502.73
temperature	301(2) K
wavelength	0.71073 Å
crystal system	triclinic
space group	$P\bar{1}$ (No. 2)
unit cell dimensions	$a = 8.196(1)$ Å
	$b = 11.971(1)$ Å
	$c = 36.875(5)$ Å
	$\alpha = 97.64(2)°$
	$\beta = 95.55(2)°$
	$\gamma = 97.61(2)°$
volume	3530.1(7) $Å^3$
Z	2
density (calculated)	1.414 g cm^{-3}
absorption coefficient	2.472 mm^{-1}
$F(000)$	1502
crystal size	0.6 mm × 0.25 mm × 0.15 mm
θ range for data collection	1.68 to 25.68°
index ranges	$-9 \leq h \leq 9$
	$-14 \leq k \leq 14$
	$-44 \leq l \leq 41$
reflections collected	20702
independent reflections	13071 [R(int) = 0.0182]
completeness to $\theta = 25.68°$	97.60%
absorption correction	empirical
refinement method	1.000000 and 0.330019
refinement method	full-matrix least-squares on F^2
data/restraints/parameters	13071/43/744
goodness-of-fit on F^2	1.179
final R indices [$I > 2\sigma(I)$]	$R^1 = 0.0424$, $wR^2 = 0.1058$
R indices (all data)	$R^1 = 0.0463$, $wR^2 = 0.1074$
largest diff. peak and hole	1.307 and −2.848 e $Å^{-3}$

Crystal Structure Determination. All the experimental details are given in Table 1. Single crystals of complex **2** suitable for X-ray studies were obtained by vapor diffusion of pentane into a concentrated chloroform solution of complex **2**. A crystal of dimensions 0.6 mm × 0.25 mm × 0.15 mm mounted in a glass capillary was used for data collection at 28 °C on a Bruker Smart CCD 1000 using graphite monochromatized $Mo-K_\alpha$ radiation ($\lambda = 0.71073$ Å). Raw frame data were integrated with the SAINT[24] program. Semiempirical absorption correction with SADABS[25] was applied. The structure was solved by direct methods employing the SHELXS-97 program[26] on a PC. Pt, S,

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(21) (a) Demas, J. N.; Crosby, G. A. *J. Phys. Chem.* **1971**, *75*, 991–1024. (b) Van Houten, J.; Watts, R. J. *J. Am. Chem. Soc.* **1976**, *98*, 4853–4858. (c) Caspar, J. V.; Meyer, T. J. *J. Am. Chem. Soc.* **1983**, *105*, 5583–5590.

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(24) *SAINT+; SAX area detector integration program*, version 7.34A; Bruker AXS, Inc.: Madison, WI.

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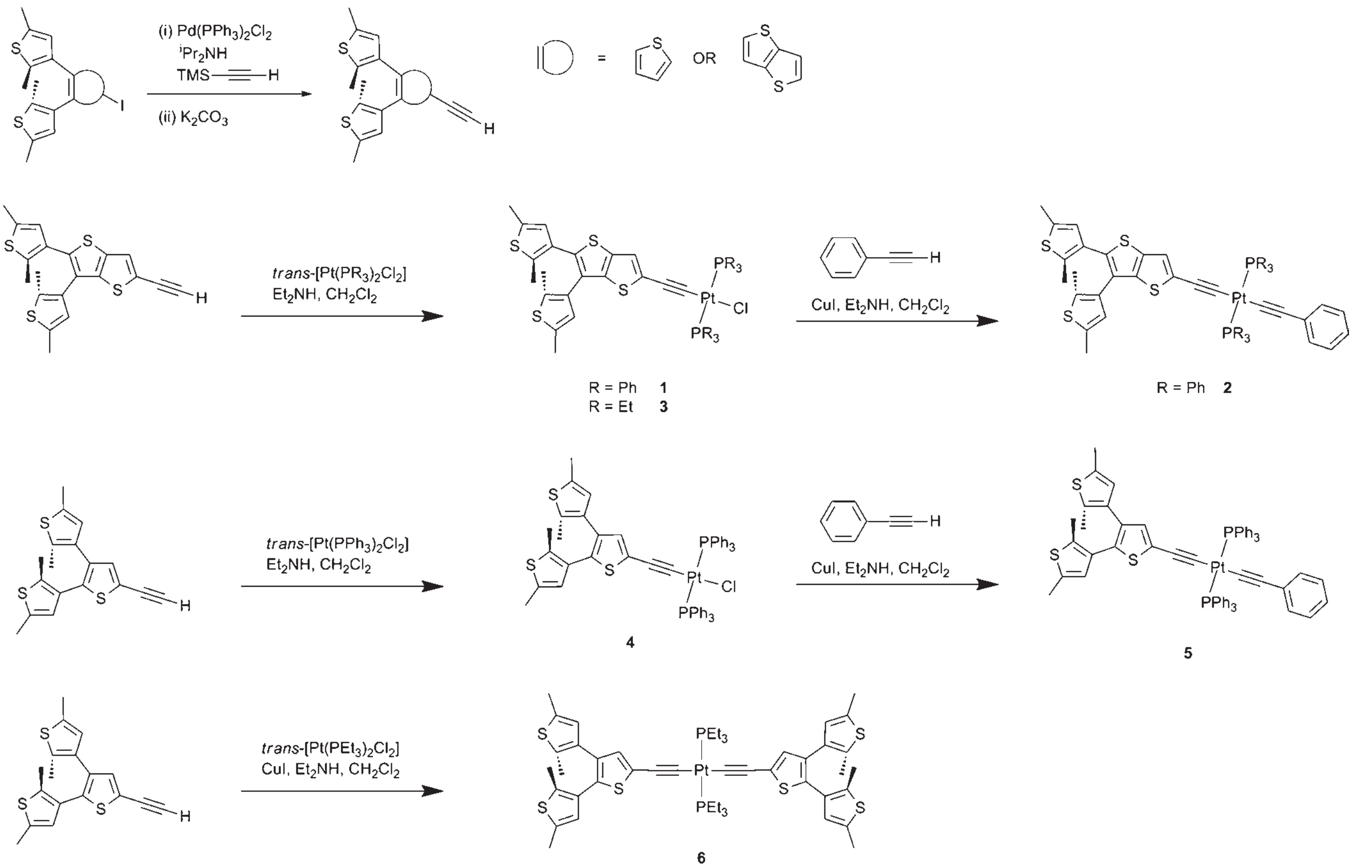
Scheme 1. Synthetic Pathway of Complexes **1**−**6**



P, 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 the program SHELXL-97[26] on a 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 **2** were included in the Supporting Information and were tabulated in Supporting Information, Tables S1−S4.

Results and Discussion

Synthesis. Complexes **1**−**6** were prepared by standard dehydrohalogenation of *trans*-[Pt(PR$_3$)$_2$Cl$_2$] with different alkynes in the presence of copper(I) iodide and diethylamine according to literature procedures.[2,3,5] The intermediate, 2,3-bis(2,5-dimethylthiophen-3-yl)-thiophene, was prepared by modification of a procedure previously reported by us[12a,c−e] through the bis-Suzuki cross-coupling reaction between 2,3-dibromothiophene and 2,5-dimethylthien-3-yl boronic acid. The resulting 2,3-bis(2,5-dimethylthiophen-3-yl)-thiophene was subjected to iodination, standard Sonogashira reaction with trimethylsilylacetylene, and finally deprotection by potassium carbonate to yield the alkyne. On the other hand, the preparation of 2,3-bis(2,5-dimethylthiophen-3-yl)-5-ethynylthieno[3,2-*b*]thiophene was accomplished by first synthesizing ethyl 5,6-dibromothieno[3,2-*b*]thiophene-2-carboxylate as the precursor for the bis-Suzuki cross-coupling reaction using a method similar to that described previously.[27] After successive cross-coupling reaction, de-esterification and decarboxylation, 2,3-bis(2,5-dimethylthiophen-3-yl)thieno[3,2-*b*]thiophene was obtained in moderate yield. The alkyne, **HC≡C—TTh-DTE**, was then synthesized using the similar synthetic pathway as **HC≡C−Th-DTE**. Complexes **1**−**6** were characterized by ^{1}H NMR, ^{31}P NMR, FAB mass spectroscopy, and elemental analysis. The *trans*- configuration of the complexes was confirmed by the sharp singlet signals at about δ 11.39−21.54 ppm in the ^{31}P NMR spectra, accompanied by a platinum satellite with J(P−Pt) values of 2342−2640 Hz, typical of the *trans*-platinum(II) bis-phosphine systems.[28] The synthetic scheme is outlined in Scheme 1.

X-ray Crystal Structure. The perspective drawing and selected bond distances (Å) and angles (deg) of complex **2** are depicted and tabulated in Figure 1 and Table 2, respectively. The crystal structure of complex **2** adopted an antiparallel conformation, in which two dimethylthiophene rings were pointing in the opposite directions. The interplanar angles between the dimethylthiophene rings and the thienothiophene core are 46.817° and 47.834°, which are not orthogonal to each other. The platinum(II) center adopts a square planar geometry that is slightly distorted from its ideal geometry with the C−Pt−P bond angle in the range of 87−94°. The Pt−C bond distances (ca. 1.99 Å) and the Pt−P bond distances (ca. 2.30 Å) are comparable to the literature values reported in typical platinum(II) phosphine bis-alkynyl systems.[3a,4b,29] The

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(28) Clark, H. C.; Milne, C. R. *Can. J. Chem.* **1979**, *57*, 958–960.

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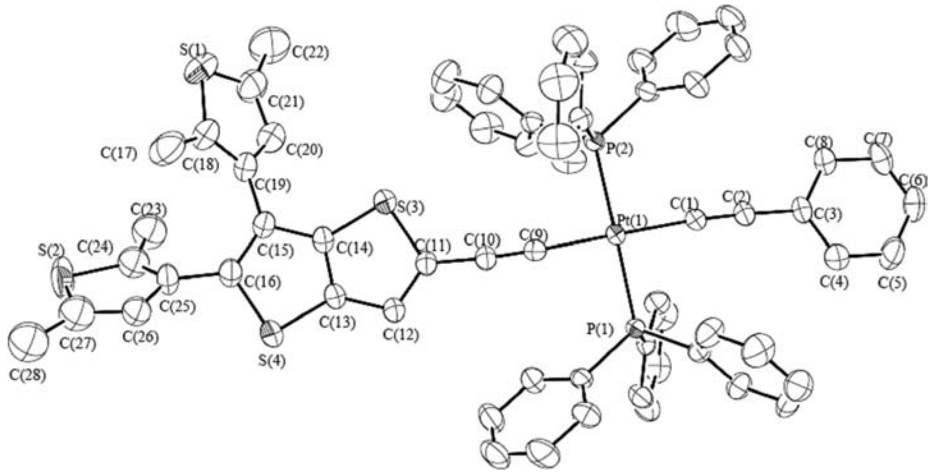

Figure 1. Perspective view of complex **2** with atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids were shown at the 30% probability level.

Pt−Pt separation between the two closest complexes is 8.196(1) Å, which indicates the absence of Pt−Pt interactions in the crystalline form.

Electronic Absorption and Emission Properties. All complexes are found to dissolve in benzene to give clear yellow solutions. The intense absorptions at about 300−350 nm with extinction coefficients in the order of 10^4 dm^3 mol^{-1} cm^{-1} are ascribed to intraligand transitions of the thiophene-containing alkynyl and phosphine ligands. The low-energy absorption bands at about 370−390 nm are found to be slightly red-shifted when the platinum center is coordinated to the more electron-rich triethylphosphine ligand (**1** vs **3**) or is coordinated to the more electron-donating phenyl alkynyl ligand (**1** vs **2** and **4** vs **5**). This suggests the possible involvement of a metal character in the highest occupied molecular orbital (HOMO). In addition, the absorption band is also found to be sensitive toward the nature of the thiophene-containing alkynyl ligands. Upon increasing the π-conjugation from thiophene in **4** and **5** to thienothiophene in **1** and **2**, respectively, the lower energy absorption bands at about 370 nm are also found to be red-shifted, suggesting the participation of the thiophene-containing alkynyl ligands in the transition. Thus, the low-energy absorption is tentatively assigned as the metal-to-ligand charge transfer MLCT [dπ(Pt) → π*(thiophene-containing alkynyl)] transition, with substantial mixing of an intraligand IL [π → π*(thiophene-containing alkynyl)] character, given the large extinction coefficients observed in the order of 10^4 dm^3 mol^{-1} cm^{-1}. This is consistent with the literature assignment and the computational studies on the related platinum(II) diphosphine bis-alkynyl system.[30] Thus, the low-energy intense absorptions of these complexes are best described as an admixture of IL [π → π*(alkynyl)]/MLCT [dπ(Pt) → π*-(alkynyl)] transition, or alternatively, as a metal-perturbed IL transition. The absorption data are summarized in Table 3. Figure 2 depicts the representative absorption spectra of complexes **1**, **2**, **4**, and **5**.

Table 2. Selected Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations (e.s.d.s.) in Parentheses for Complex **2**

	Bond Distances/Å		
Pt(1)−P(1)	2.3016(13)	C(1)−C(2)	1.204(7)
Pt(1)−P(2)	2.3002(13)	C(2)−C(3)	1.434(7)
Pt(1)−C(1)	1.999(5)	C(9)−C(10)	1.199(7)
Pt(1)−C(9)	1.993(5)	C(10)−C(11)	1.420(7)
	Bond Angles/deg		
C(1)−Pt(1)−P(1)	86.80(14)	Pt(1)−C(1)−C(2)	176.3(5)
P(1)−Pt(1)−C(9)	92.96(14)	Pt(1)−C(9)−C(10)	178.0(4)
C(9)−Pt(1)−P(2)	86.38(14)	C(1)−C(2)−C(3)	177.1(6)
P(2)−Pt(1)−C(1)	93.85(14)	C(9)−C(10)−C(11)	175.7(6)

Upon excitation at λ = 360 nm, the open form of complexes **1**−**6** exhibited red emission at about 630−670 nm, with lifetimes in the range of microseconds. The long-lived emission and the large Stokes shift observed are suggestive of a triplet emissive origin. In other related platinum(II) diphosphine bis-alkynyl systems,[4a,b] the phosphorescence was believed to originate from the ^{3}IL [π → π*(alkynyl)]/^{3}MLCT [dπ(Pt) → π*(alkynyl)] state. It was believed that the emissions of complexes **1**−**6** were attributed to a similar origin. However, in view of the lack of an obvious trend in complexes **1**−**6**, it was suggested that the emissive origin was dominated by an IL character. As shown in Figure 3, it was found that the emission bands of complexes **1**−**6** were broad and of similar band shape and position, supportive of the predominant ^{3}IL assignment. The luminescence quantum yields of these complexes were found to vary from 0.0027 to 0.028. In general, complexes **1** and **3**, which contain the chloro ligand, showed a lower luminescence quantum yield. This is probably due to the presence of the low-lying ligand field excited state, which quenches the emission through non-radiative deactivation pathways.

Most complexes showed photoluminescence in the solid state at 77 K, 298 K, and glass at 77 K, with a blue shift in the emission maxima and well-defined vibrational progressional spacings, indicative of substantial involvement of the ligand orbitals in the emissive state. Thus, the emission is assigned as predominantly ^{3}IL [π → π*(alkynyl)] origin with mixing of ^{3}MLCT character, as a subtle trend of the emissive energy dependence on the electronic properties of the ancillary ligands is observable. The blue shift in emission maxima relative to the solution state is commonly observed

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Table 3. Electronic Absorption Data for **TMS—C≡C—TTh-DTE**, **TMS—C≡C—Th-DTE**, 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})
TMS—C≡C—TTh-DTE	open	336 (28070)
	close	326 (14480), 362 sh (30310), 378 (46210), 560 (8090)
TMS—C≡C—Th-DTE	open	322 (16350)
	close	348 sh (26200), 362 (32920), 572 (11820)
1	open	302 (16630), 356 (40360), 378 (35600)
	close	358 sh (34740), 384 (44400), 402 sh (38960), 534 sh (7140), 566 (7830)
2	open	340 sh (31490), 386 (54830)
	close	338 sh (29260), 388 (56570), 410 (52960), 532 sh (7530), 564 (8350)
3	open	314 (21940), 380 (66060)
	close	340 (35730), 356 (32680), 414 (103740), 536 sh (13730), 570 (15780)
4	open	346 (20010), 368 sh (15570)
	close	326 sh (18370), 362 (32240), 376 sh (29150), 534 sh (7326), 562 (8400)
5	open	336 sh (22870), 376 (44500)
	close	352 sh (39230), 368 (51280), 392 sh (37880), 530 sh (8820), 562 (10400)
6	open	366 (53040)
	close	306 sh (24730), 368 (59490) 382 sh (55650), 526 sh (10020), 556 (11770)

[a] Data obtained in benzene at 298 K.

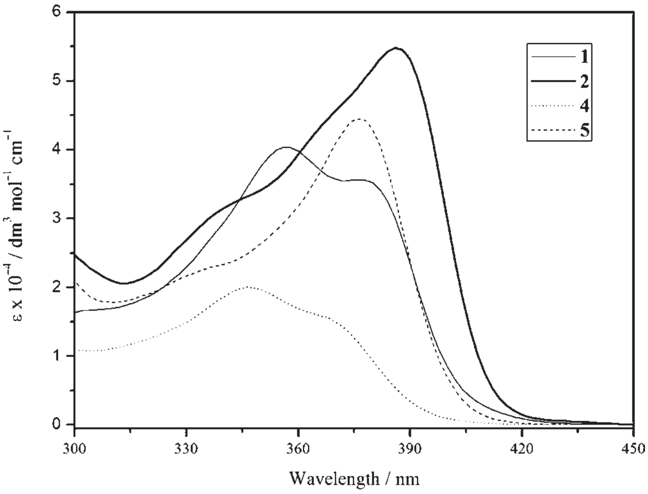

Figure 2. Electronic absorption spectra of complexes **1**, **2**, **4**, and **5** in benzene at 298 K.

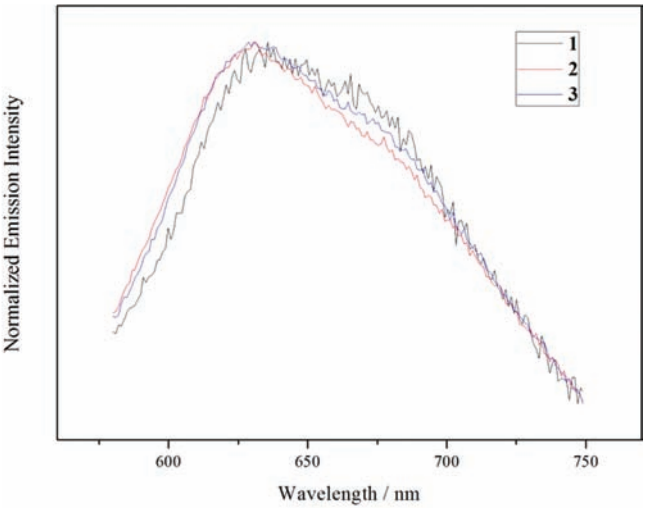

Figure 3. Normalized corrected emission spectra of the open forms of **1**−**3** in degassed benzene at 298 K.

in related systems[31] because of the presence of luminescence rigidochromism.[32] The energies of the vibrational progressional spacings have been determined and are listed in Table 4. The vibrational progressional spacings of about 1080 cm^{-1} are assigned as C−C vibrational modes.[4b] In additional, other vibrational progressional spacings of about 1370 and 1500 cm^{-1} are typical of CH_3 bending and aromatic ring C=C stretching modes.[4b,30a,33]

Photochromic Properties. Upon photoexcitation at λ = 320 nm for ligands and λ = 370 nm for complexes **1**−**6**, the solutions turned purple, with the emergence of low-energy absorption bands at about 560 nm, attributed to the ring closed form of the *8a*,*8b*-dimethyl-1,8-thia-*as*-indacene moiety. The absorption pattern of complexes **1**−**6** is comparable to that of TMS-protected ethynylthiophene, simple dithienylethene-containing thiophene, thienothiophene,[12c] and dithienopyrrole,[12e] suggesting that the absorption is only slightly perturbed by the incorporation of the platinum center. For complex **6**, which contains two pairs of photochromic dithienylethene moieties, it did not undergo dual cyclization as evidenced by the existence of well-defined isosbestic points at about 349 and 357 nm as shown in Figure 4. The lack of photocyclization of the second dithienylethene moiety is probably due to the rapid energy transfer to the low-lying excited state resulting from the closed form that quenches the second photocyclization step.[34] Upon photoexcitation into the absorption bands at about 470−600 nm in the closed form, the UV−vis absorption spectral changes were reversed, resulting in the regeneration of the open form. The cyclo-reversibility has been demonstrated in complex **6** as depicted in Figure 5.

The photocyclization quantum yields are larger than that of the photocycloreversion quantum yields, commonly observed in photochromic diarylethene systems.[12a,c−e] It was

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Table 4. Emission Data for **TMS—C≡C—TTh-DTE**, **TMS—C≡C—Th-DTE**, and Complexes **1**−**6** in Various Media

	medium	emission		
compound	(T/K)	$\lambda_{em}{}^{a}$/nm (τ_o / μs)	vibrational progressional spacing ν/cm^{-1}	$\phi_{lum}{}^{b}$
TMS—C≡C—TTh-DTE	benzene (298)	402		-[e]
TMS—C≡C—Th-DTE	benzene (298)	403		-[e]
1	benzene (298)	640 (2.0)		0.0095
	solid (298)	646 (9.8)		
	solid (77)	641 (59.1)		
	glass[c] (77)	574, 625 (135.3)	1420	
2	benzene (298)	630 (16.6)		0.0222
	solid (298)	573, 612 (21.8)	1110	
	solid (77)	573, 614 (65.4)	1170	
	glass[c] (77)	572, 620 (190.2)	1350	
3	benzene (298)	632 (17.8)		0.0162
	solid (298)	*d*		
	solid (77)	635, 670 (6.4)		
	glass[c] (77)	578, 632 (145.3)	1480	
4	benzene (298)	647 (0.1)		0.0027
	solid (298)	570 (8.5)		
	solid (77)	568 (23.8)		
	glass[c] (77)	577 (99.2)		
5	benzene (298)	640 (2.4)		0.0276
	solid (298)	567 (5.3)		
	solid (77)	562 (93.9)		
	glass[c] (77)	567 (122.4)		
6	benzene (298)	677 (2.0)		0.0077
	solid (298)	*d*		
	solid (77)	562 (58.2)		
	glass[c] (77)	547, 581 (226.2)	1070	

[a] Emission maxima are corrected values. [b] Luminescence quantum yields are reported using a degassed aqueous solution of [Ru(bpy)$_3$]Cl$_2$ as standard at 298 K. [c] Butyronitrile. [d] Non-emissive. [e] Not determined.

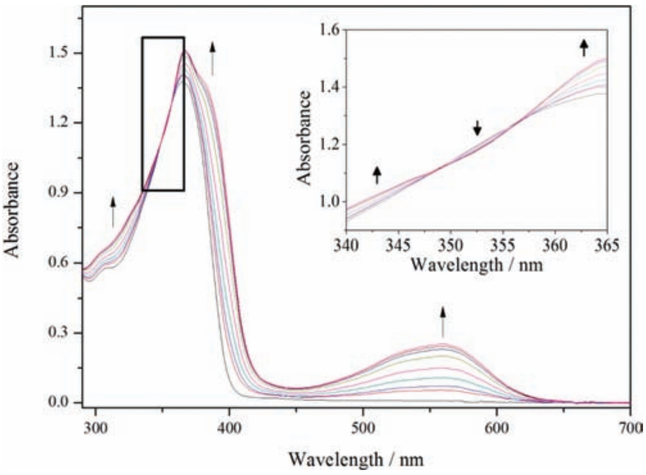

Figure 4. Electronic absorption spectral change of complex **6** in benzene upon irradiation at λ = 370 nm at 298 K. Inset shows the expanded spectral change in the region of 340−365 nm.

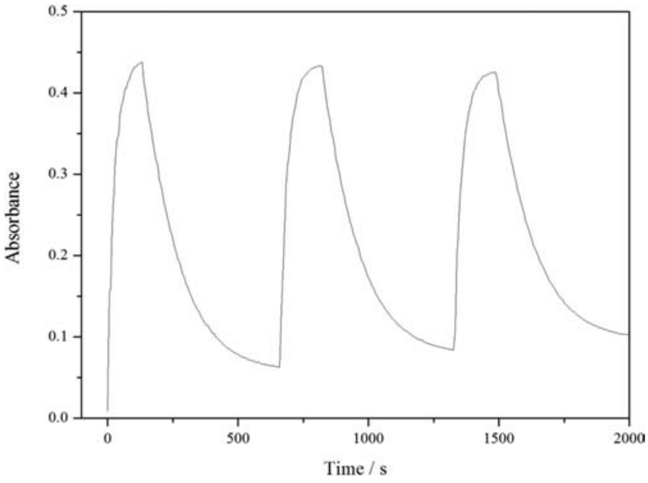

Figure 5. UV−vis absorbance changes of complex **6** at 560 nm on alternate excitation at 365 and 560 nm over three cycles in degassed benzene solution at 293 K.

found that complexes **2** and **6** had similar photocyclization quantum yield with their corresponding TMS-protected ligands. On the other hand, complexes **1**, **3**, and **4**, which contain the chloro ligand, showed lower photocyclization quantum yields than their corresponding alkynyl analogues (**2** and **5**). This is in line with the results from the studies on the luminescence quantum yield. The presence of the weak field chloro ligand gives rise to a low-lying ligand field excited state that undergoes facile non-radiative deactivation, competing over luminescence and photochromic processes. Similar observation was also found in complexes **5** and **6**, with complex **6** showing higher photocyclization quantum yield but lower luminescence quantum yield than complex **5**. The percentage conversion of the TMS-protected ethynylthiophene, ethynylthienothiophene and complexes **1**−**6** was determined. It was found that the percentage conversion to the closed form at photostationary state of complexes **2**, **5**, and **6**, which do not contain the chloro ligand, was higher, and was enhanced when compared with the chloro-containing complexes (**1**, **3**, and **4**), probably because of the enhanced photocyclization quantum yield. The results are summarized in Table 5.

A study on the thermal stability of the closed form was carried out on a representative sample of complex **6**. At room temperature, the half-life was found to be about

Table 5. Photochemical Quantum Yields and the Percentage Conversion at Photostationary State (PSS) for **TMS—C≡C—TTh-DTE**, **TMS—C≡C—Th-DTE**, and Complexes **1**−**6** in Degassed Benzene Solution at 298 K

	photochemical quantum yield/ϕ^a		
compound	photo-cyclization	photo-cycloreversion	conversion at PSS (%)
TMS—C≡C—TTh-DTE	0.204[b]	0.009[d]	60[b]
TMS—C≡C—Th-DTE	0.226[b]	0.009[d]	47[b]
1	0.118[c]	0.026[d]	48[d]
2	0.243[c]	0.015[d]	> 95[d]
3	0.117[c]	0.010[d]	44[d]
4	0.063[c]	0.061[d]	22[d]
5	0.170[c]	0.025[d]	94[d]
6	0.242[c]	0.029[d]	> 95[d,e]

[a] Data obtained with estimated ±10% error. [b] Data obtained using 320 nm as the excitation source. [c] Data obtained using 370 nm as the excitation source. [d] Data obtained using 500 nm as the excitation source. [e] Based on singly cyclized product.

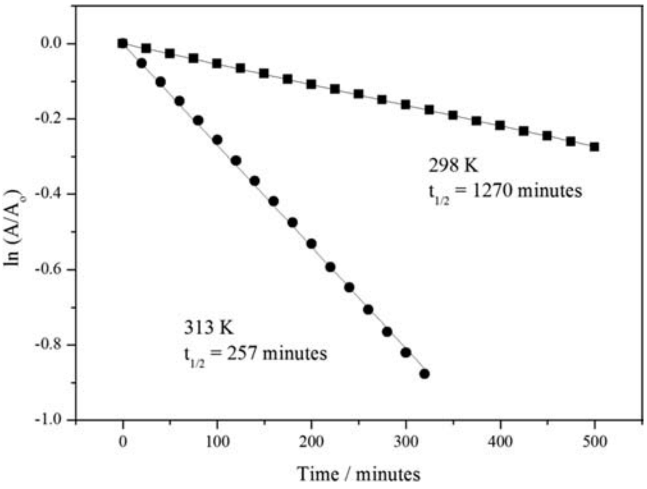

Figure 6. A plot of ln(A/A_o) versus time for the absorbance decay of complex **6** at 560 nm at various temperatures in argon-flushed toluene solution; A denotes absorbance at time t, and A_o denotes the initial absorbance; solid lines represent the theoretical linear fits.

21 h while at 313 K, the half-life was found to be less than 5 h. A plot of the ln(A/A_o) versus time at various temperatures is depicted in Figure 6.

Table 6. Electrochemical Data for **TMS—C≡C—TTh-DTE**, **TMS—C≡C—Th-DTE**, and Complexes **1**−**6** in Acetonitrile Solution (0.1 mol dm^{-3} ^{n}Bu$_4$NPF$_6$) at 298 K[a]

	$E_{1/2}{}^b$/V vs SCE (ΔE_p / mV)^c	
	oxidation	reduction
compound	[$E_{pa}{}^d$/V vs SCE]	[$E_{pc}{}^e$/V vs SCE]
TMS—C≡C—TTh-DTE	[+1.25], [+1.74]	[−2.20], [−2.32]
TMS—C≡C—Th-DTE	[+1.37], [+1.96]	–[f]
1	+0.80 (80), [+1.20]	[−1.69]
2	+0.78 (57), [+1.17, +1.36]	[−1.68]
3	+0.75 (75), [+0.96, +1.20, +1.44]	[−1.70]
4	+0.86 (95), [+1.28]	[−1.68]
5	+0.82 (75), [+1.24, +1.44]	[−1.66]
6	+0.80 (113), [+1.07, +1.46, +1.59]	[−1.67]

[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] ΔE_p = (E_{pa} − E_{pc}). [d] E_{pa} is reported for irreversible oxidation wave. [e] E_{pc} is reported for irreversible reduction wave. [f] No reduction wave was observed.

Electrochemical Studies. The electrochemical data for **TMS—C≡C—TTh-DTE**, **TMS—C≡C—Th-DTE,** and complexes **1**−**6** in acetonitrile (0.1 mol dm^{-3} ^{n}Bu4NPF$_6$) are tabulated in Table 6. Representative cyclic voltammograms of complex **2** are depicted in Supporting Information, Figure S1. The cyclic voltammograms of **TMS—C≡C—TTh-DTE** (+1.25, +1.74 V vs SCE) and **TMS—C≡C—Th-DTE** (+1.37, +1.96 V vs SCE) showed two irreversible oxidation waves, which were found to be sensitive toward the different extent of π-conjugation of the ethynylthiophene or ethynylthienothiophene core. In addition, it was found that only **TMS—C≡C—TTh-DTE** possessed two irreversible reduction waves at about −2.2 and −2.3 V versus SCE. No reduction waves were found in **TMS—C≡C—Th-DTE** within the potential of the solvent window though one could not completely exclude the possibility that similar reductive waves might occur beyond the solvent windows. Thus, the oxidative and reductive waves were tentatively assigned as the ethynylthiophene- or ethynylthienothiophene-centered oxidations and reductions, respectively. On the other hand, complexes **1**−**6** showed several oxidation waves at about +0.75 to +0.86 V, +0.96 to +1.28 V and +1.36 to +1.59 V versus SCE. The first oxidation wave is quasi-reversible and is sensitive toward the nature of the thiophene-containing alkynyl ligands. For instance, upon going from the chloro ligand in **1** and **4** to the stronger electron-donating phenyl alkynyl ligand in **2** and **5**, the platinum center becomes more electron-rich and the first oxidation wave is shifted to less positive potential, indicating that the species is easier to be oxidized. Similar trend could be observed on different alkynyl ligands, in which complexes with more electron-rich 2-ethynylthienothiophene ligand in **1** and **2** are easier to be oxidized than complexes with 2-ethynylthiophene ligand as in **4** and **5**. Thus, it is likely that the HOMO contains both the alkynyl ligand and the metal character, and the first oxidation wave should be assigned as the ethynylthiophene-centered oxidation with mixing of Pt(II) to Pt(III) oxidation, which is commonly observed in other related systems.[4a,b,35] The second irreversible oxidation wave is tentatively assigned as Pt(III) to Pt(IV) oxidation, which also appeared in other related systems.[35] Other irreversible oxidative waves might probably be attributed to the thiophene alkynyl-centered oxidations, which also appeared in the TMS-protected ligands. In addition, complexes **1**−**6** showed one irreversible reduction wave at about −1.68 V, which is slightly sensitive to the nature of the ethynylthiophene ligands, with the more electron-rich ethynylthienothiophene shown to be less easy to be reduced. Moreover, this reduction

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(35) Younus, M.; Kohler, A.; Cron, S.; Chawdhury, N.; Al-Mandhary, M. R. A.; Khan, M. S.; Lewis, J.; Long, N. J.; Friend, R. H.; Raithby, P. R. *Angew. Chem., Int. Ed.* **1998**, *37*, 3036–3039.

wave is found to be absent in other platinum(II) bis-phosphine systems that do not contain the thiophene moiety.[4b] Thus, the reduction wave is tentatively assigned as thiophene-centered reduction.

Conclusion

A new class of photochromic dithienylethene alkynes has been successfully synthesized. The photophysical, photochromic and electrochemical studied have been carried out on their corresponding platinum(II) phosphine complexes. They show red phosphorescence and reversible photochromism. The existence of labile chloro ligands in complexes **1**, **3**, and **4** demonstrated their capability to function as building blocks for further functionalization.

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Supporting Information Available: Experimental description for crystal structure determination, tables of crystal data, atomic coordinates, thermal parameters, and a full list of bond distances and angles for complex **2**. This material is available free of charge via the Internet at http://pubs.acs.org.