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Multiphotochromism in an Asymmetric Ruthenium Complex with Two Different Dithienylethenes

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S Supporting Information

ABSTRACT: An asymmetric bis(dithienylethene-acetylide) ruthenium(II) complex *trans*-Ru(dppe)₂(L1o)(L2o) (**100**) incorporating two different dithienylethene– acetylides (L1o and L2o) was designed to modulate multistate photochromism in view of the well separated ring-closing absorption bands between L1o and L2o. Upon irradiation with appropriate wavelengths of light, complex **1** undergoes stepwise photocyclization and selective photocycloreversion to afford four states (**100**, **1c0**, **10c**, **and 1cc**). As a contrast, symmetric complexes *trans*-Ru(dppe)₂(L1o)₂ (**200**) and *trans*-Ru(dppe)₂(L2o)₂ (**300**) with two identical dithienylethene-acetylides were synthesized, and the corresponding photochromic behavior was investigated. The photochromic properties of the oxidized species (**100**⁺/**1c0**⁺/**1cc**⁺/**1cc**⁺/**2co**⁺/**2co**⁺/**2co**⁺/**3co**⁺/**3co**⁺/**3co**⁺/**3co**⁺, **200**⁺, and **300**⁺ show obvious blue shifts relative to those of **100**, **200**, and **300**, respectively. The ring-closing absorption bands in both neutral and oxidized species grow progressively following **00** \rightarrow **0c**/**co** \rightarrow **cc**



and $\mathbf{oo}^+ \rightarrow \mathbf{oc}^+/\mathbf{co}^+ \rightarrow \mathbf{cc}^+$. As revealed by spectroscopic, electrochemical, and computational studies, complex 1 displays eight switchable states through stepwise photocyclization, selective cycloreversion, and a reversible redox process.

INTRODUCTION

Photochromic diarylethene (DTE) compounds that can undergo a light-induced reversible transformation between two isomers have attracted much attention due to their fast response, remarkable fatigue resistance, and excellent thermal reversibility¹⁻⁹ as well as their potential applications in optical memory storage systems and switching devices.¹⁰⁻²¹ During past decades, numerous research effort was devoted to the development of multiphotochromic systems that incorporate multiple DTE units into the same structures since they are of interest for the modulation of optoelectronic properties in materials and supramolecular systems.^{3,11,22-24} However, the resulting multiswitch systems often display partial photocyclization because of facile intramolecular energy transfer (ET) from the ring-open moiety to a ring-closed one that prevents further photocyclization.²⁵ Interestingly, when multi-DTE acetylides are inserted into a metal center, stepwise ringclosing is attainable, but the systems are still limited.²⁵ In most cases, the symmetric structures with two or more identical DTE moieties face difficulty in creating multistates and multicolors.^{25b,26-32} On the other hand, multistate and multicolor photochromism is likely achieved by incorporating DTE moieties with different structures into one organic molecule^{33,34} or a metal center.³⁵ The advantages of the asymmetric systems over those incorporating identical DTEs lie in their better feasibility in achieving stepwise and selective photochromism through irradiation with different wavelengths of light, but it is

still highly challenging to access all the possible switchable isomers. Particularly, the fully ring-closed isomers in the fused asymmetric organic molecules are always unattainable.^{33,34}

When ring-closing absorption maxima of two nonequivalent DTE moieties are sufficiently separated in asymmetric metalcoordinated systems, it is likely to obtain all four states (oo, co, oc, cc) through selective photocyclization and cycloreversion upon irradiation with suitable wavelengths of light.³⁵ Since the absorption positions of closed-ring DTEs are highly dependent on the π -conjugation, they can be conveniently modulated by change of the linking position of thienyl groups to a cyclopentene moiety.³⁶ In an attempt to obtain multistate and full color systems, two types of DTE-acetylides, L10 and L20 (Scheme 1), with a large energy gap between their ringclosing absorption peaks are elaborately designed for this study. For L1o, two 3-thienyl groups are bound to a perfluorocyclopentene moiety to achieve a ring-closing absorption peak at 605 nm. The π -conjugation of the closed-ring isomer of L1o is extended over the whole molecule through the DTE linkage with a pyrimidyl group. In contrast, the perfluorocyclopentene moiety in L20 is bound to one benzyl-containing 2-thienyl and one 3-thienyl so as to give a ring-closing absorption band centered at 506 nm with a much higher absorption energy than

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Scheme 1. Asymmetric Ruthenium(II) Complex 100 and Symmetric Complexes 200 and 300



that of L1o because the closed-ring form of L2o has a much shorter π -conjugated system.

A redox-active ruthenium(II) moiety is utilized to incorporate two nonequivalent DTEs (L1o and L2o) because the reversible oxidation of Ru(II) to Ru(III) can afford more addressable forms. We describe herein asymmetric ruthenium-(II) complex **100** with two different DTEs (L10 and L20) as well as symmetric complexes 200 and 300 with two identical DTEs (L10 for 200 and L20 for 300). The oxidized species 100⁺, 200⁺, and 300⁺ are also obtained through the oxidation of Ru(II) to Ru(III). As expected, stepwise photocyclization/ cycloreversion and a multistate are achieved. It is worth noting that eight states are accessible in asymmetric ruthenium(II) complex 100 through stepwise photocyclization, selective cycloreversion, and reversible redox processes. Interestingly, the oxidized species 100⁺, 200⁺, and 300⁺ exhibit near-infrared (NIR) absorption bands, strikingly different from those in 100, 200, and 300.

RESULTS AND DISCUSSION

Synthesis and Characterization. The synthetic routes to L10 and L20 as well as ruthenium(II) complexes 100-300 were depicted in Schemes S1 and S2. Asymmetric complex 100 (Scheme S1) was prepared by a two-step reaction procedure. The reaction of cis-Ru(dppe)₂Cl₂ with 1.2 equiv of L10 in the presence of $NaPF_6$ produced first ruthenium(II) vinylidene derivative Ru=C=C-DTE as a yellow intermediate. Stable complex *cis*-Ru(dppe)₂(L1o)Cl was then accessed in 56% yield as a yellow product by the addition of Et₃N as a base to the yellow intermediate through a deprotonation process. Further reaction of cis-Ru(dppe)₂(L10)Cl with 1 equiv of L20 in the presence of $NaPF_6$ (1.2 equiv) and NEt_3 resulted in the isolation of asymmetric complex 100 as a yellow solid in 55% yield. Treatment of cis-Ru(dppe)₂Cl₂ with 2.5 equiv of L10 or L20 in the presence of NaPF₆ and NEt₃ gave complex 200 (Scheme S1) or 300 (Scheme S2), respectively. Complexes 100-300 were readily purified through chromatography on short alumina columns using dichloromethane as an eluent.

UV–Vis Absorption Spectral Studies. The ring-closure absorption bands of L10 and L20 were well modulated by adjusting the linking position of thienyl groups to the perfluorocyclopentene moiety as well as introducing a substituent such as pyrimidine or benzyl at the 5-position of thienyl rings. When a CH_2Cl_2 solution of L10 was irradiated with 312 nm light, the colorless solution turned blue because the ring-closing absorption maximum appeared at 605 nm due to the formation of L1c. Similarly, the colorless CH_2Cl_2 solution of the ring-closing peak at 506 nm upon irradiation at 312 nm. As expected, the ring-closure absorption peaks of free ligands L1 and L2 (Figure S1) are well separated with a wavelength difference of ca. 100 nm.

Complexes **100–300** display intense absorption bands at ca. 290–370 nm, arising mainly from $\pi \to \pi^*$ IL (intraligand), 4d (Ru) $\to \pi^*$ (dppe) MLCT (metal-to-ligand charge transfer), and π (one C=C-DTE) $\to \pi^*$ (the other C=C-DTE) LLCT



Figure 1. UV–vis absorption spectral changes of **100** (a), **200** (b), and **300** (c) in toluene $(2 \times 10^{-5} \text{ M})$ at ambient temperature upon irradiation at 365 nm, and the absorbance change of **2** (d) at 701 nm upon alternate irradiation at 365 and 700 nm for five cycles.

(ligand-to-ligand charge transfer) states as supported by the computational studies (vide infra).

Upon irradiation at 365 nm, the colorless toluene solution of **100** turned blue as the new broad bands appeared increasingly at 426–850 nm. The broad absorption bands with maxima at ca. 696 and 524 nm (Figure 1a) originated from the ringclosing absorptions of L1c and L2c, respectively, due to the formation of a mixture of singly ring-closed species **1c0** and **10c**. When the solution was prolonged to be irradiated, the absorption maxima at 696 and 524 nm enhanced progressively due to further transformation of **1c0/10c** to **1cc**. At the photostationary state (PSS), the solution turned blue-black with a mixture of **1c0** and **1cc** as verified by NMR studies (Figure 2 and Figure 3a).



Figure 2. ¹H NMR spectral changes of 100 in C_6D_6 (5 × 10⁻³ M) upon irradiation at 365 nm to the PSS.

The photocycloreversion was also examined. On the one hand, when the solution at the PSS was irradiated with 730 nm light (Figure S2), the absorption band centered at 696 nm decreased rapidly and nearly disappeared. In contrast, although the band at 524 nm exhibited some extent of reduction, it still kept. Such spectral changes suggested that 1cc converted to loc through the cycloreversion of L1c to L1o with the blueblack solution turning red (Scheme 2). On the other hand, upon irradiation of the solution at the PSS with light at 530 nm (Figure S3), the absorption maximum at 524 nm decreased rapidly and bleached finally. By comparison, the band centered at 696 nm displayed some decrease but still remained without vanishing as 1cc was converted 1co through the cycloreversion of L2c to L2o with the blue-black solution turning blue. Therefore, selective ring-opening at L1c or L2c could be attained through irradiation at 730 or 530 nm, respectively, leading to the conversion of **1cc** to **1oc** or **1co** accompanied by a color change from blue-black into red (1oc) or blue (1co). Actually, when the solution at the PSS was irradiated at >460 nm, both ligands L1c and L2c exhibited cycloreversion reactions, resulting in stepwise $1cc \rightarrow 1oc/1co \rightarrow 1oo$ conversion with a color conversion of blue-black \rightarrow red/blue \rightarrow colorless. As depicted in Scheme 2, four states (100, 1co, 1oc,

and **1cc**) and four colors (colorless, blue, red, and blue-black) could be attained through stepwise photocyclization and selective cycloreversion processes upon irradiation of the solution at the PSS with appropriate wavelengths of light. The success to attain selective cycloreversion is attributed to the well-separated absorption bands of L1c and L2c.

When the colorless solution of 200 in toluene was irradiated at 365 nm (Figure 1b), three new bands generated at ca. 395, 474, and 694 nm with the decrease of the bands at 309 and 347 nm. Meanwhile, the solution turned cyan, suggesting the ongoing photocyclization of L10 \rightarrow L1c to the singly ringclosed species 2co (Scheme S3). Upon further irradiation at 365 nm, the absorption intensity of the band centered at 694 nm continually increased, and the absorption maximum progressively red-shifted to 701 nm, indicating a further photocyclization reaction of $2co \rightarrow 2cc$ at the second L1o to L1c. As depicted in Figure 1b, the ring-closed absorption maximum was red-shifted from the initial 694 to 701 nm, demonstrating unambiguously that stepwise photocyclization occurred indeed through the conversion process $200 \rightarrow 2co \rightarrow$ 2cc. On the other hand, the corresponding stepwise cycloreversion reaction of $2cc \rightarrow 2co \rightarrow 2oo$ was observed upon irradiation of the solution at the PSS with the light of 700 nm. Notably, stepwise photochromism of complex 2 was monitored by alternate irradiation at 365 and 700 nm for several cycles without appreciable photodegradation (Figure 1d).

Irradiation of a toluene solution of **300** at 365 nm resulted in an immediate increase in the absorption intensity at 522 nm with the colorless solution turning red (Figure 1c), which was assigned to the formation of singly ring-closed species **3co**. Further irradiation of the solution with 365 nm light did not show an obvious red-shift of the absorption peak, which could be elucidated from the NMR studies (Figure 3c and Figure S6). Since the species at the PSS was mainly **3co** (73%) with only a small amount of **3cc** (22%), an obvious red-shift could not be observed.

NMR Spectral Studies. The ¹H NMR spectral changes of 100 and the corresponding assignments are shown in Figure 2. The ¹H NMR spectrum of complex **100** displayed thienyl protons at 8.55, 6.73, 6.64, and 6.17 ppm together with four methyl signals at 1.85 (b), 1.75 (d), 1.74 (a), and 1.67 (c) ppm. When the solution of **100** in C_6D_6 was irradiated at 365 nm, the initial signals of thienyl and methyl protons attenuated gradually. Meanwhile, new peaks were observed at 7.89, 6.80, 6.15, and 5.60 ppm, which are ascribable to thienyl signals of the singly ring-closed 1co. Simultaneously, four relative weak signals occurred at 8.54, 6.67, 5.72, and 5.17 ppm, attributed probably to the thienyl signals of singly ring-closed 1oc. On the other hand, the new signals of methyl groups appeared at 2.48, 2.42, 1.75, and 1.65 ppm due to 1co together with four signals at 1.98, 1.82, 1.79, and 1.73 ppm due to loc. The assignment on the new peaks for 1co and 1oc is based on the integration area of the peaks as well as the absorption intensity in the UVvis absorption spectra in Figure 1a, in which the absorption intensity of 1co is much greater than that of 1oc. Thus, the content of 1co is much more than that of 1oc upon the UV irradiation of the solution. The obvious shifts of these thienyl and methyl protons imply that the process $100 \rightarrow 1co/1oc$ took place indeed. Upon further irradiation with 365 nm light, the thienyl and methyl signals of 1co and 1oc gradually decreased, and in fact the signals of loc disappeared finally following the $1co/1oc \rightarrow 1cc$ process. Three new thienyl signals were observed at 8.01, 6.82, and 6.70 ppm, whereas

Scheme 2. Stepwise and Selective Photochromic Processes and Color Conversions of Complex 1 in Toluene Solution





Figure 3. ³¹P NMR spectral changes of 100 (a), 200 (b), and 300 (c) in C_6D_6 (5 × 10⁻³ M) under UV light irradiation at 365 nm to the PSS.

another one was overlapped with that of **1co** at 6.15 ppm. At the same time, two new methyl signals occurred at 2.40 (f) and 2.30 ppm (e), and the other two were observed at 1.75 (h) and 1.65 (g) ppm, which were overlapped with those of **1co**. At the PSS, only the signals of **1co** and **1cc** were observed (Figure 2).

The stepwise photocyclization $100 \rightarrow 1co/10c \rightarrow 1cc$ was also confirmed by the change of the ³¹P NMR spectrum (Figure 3a). The ^{'31}P NMR signal of 100 in C_6D_6 was first observed at 53.3 ppm. When the solution was irradiated at 365 nm, the signal at 53.3 ppm gradually decreased and ultimately disappeared. In the meantime, two new signals emerged at 52.3 and 52.1 ppm due to the photocyclization of L10 and L20 to generate mixed ring-open/closed species 1co and 1oc, respectively. Another new signal due to dually ring-closed species 1cc was observed at 51.4 ppm upon prolonged irradiation. Meanwhile, the signal of 1oc decreased and finally vanished at the PSS with gradual enhancement of the signal of 1cc at 51.4 ppm, suggesting the complete conversion of 1oc to 1cc. At the PSS, the percentages of 1co and 1cc were estimated as 51% and 49% (Table 1 and Figure 3a) as evidenced by the P signals of 1co and 1cc.

Conversely, photochemical cycloreversion at selective ligands (L1c or L2c) can be obtained by irradiation with specific wavelengths of light. As expected, when the toluene solution at the PSS was subsequently irradiated at 730 nm (Figure S4a), the signals at 51.4 ppm for 1cc and 52.3 ppm for 1co reduced

Table 1. C	Conversion 1	Maxima and	l Conversion	Percentages	at
PSS for 1-	-3				

	conversion maximum ^a	contents at PSS ^b
100	83% (→1co), 24% (→1oc)	1co (51%), 1cc (49%)
200	94% (→ 2co)	2co (12%), 2cc (88%)
300	85% (→3co)	300 (5%), 3c0 (73%), 3cc (22%)
Data	obtained with an uncer	tainty of ±10%. ^b Conversion
	11 373 65	

percentages measured by NMR spectroscopy in C_6D_6 solutions (5 × 10^{-3} M).

gradually, while those of **1oc** at 52.1 ppm and **1oo** at 53.3 ppm appeared and progressively enhanced, indicating that **1cc** and **1co** converted to **1oc** and **1oo** through selective ring-opening at L1c. Similarly, upon irradiation of the solution at the PSS with light of 530 nm (Figure S4b), the signal of **1cc** gradually decayed and finally disappeared. Meanwhile, the signal at 52.3 ppm due to **1co** emerged and increasingly enhanced, implying the selective cycloreversion at L2c, thus leading to the conversion of **1cc** to **1co**.

When **200** in C₆D₆ was irradiated with UV light at 365 nm (Figure S5 and Scheme S3), the signals of thienyl protons at 8.54 and 6.63 ppm attenuated gradually and disappeared finally. Concomitantly, four new signals at 8.52, 7.89, 6.70, and 5.60 ppm appeared and enhanced following **200** \rightarrow **2co**. Upon further irradiation at 365 nm to the PSS, two new signals at



Figure 4. Relative content changes of 100 (a), 200 (b), and 300 (c) in C_6D_6 (2 × 10⁻³ M) under UV light irradiation at 365 nm to the PSS.

7.90 and 5.68 ppm emerged, while the signals at 8.52, 7.89, 6.70, and 5.60 ppm gradually decreased and almost vanished, indicating further photocyclization of **2co** to **2cc**. Meanwhile, the methyl signals of **2oo** at 1.85 and 1.74 ppm decreased gradually with the formation of **2co**. Two methyl signals with low-field shifts appeared at 2.48 and 2.43 ppm, whereas another new methyl signal was observed at 1.83 ppm following **2oo** \rightarrow **2co**. Upon keeping irradiation at 365 nm, the methyl signals of **2co** weakened gradually, and two new signals enhanced progressively at 2.39 (a") and 2.45 (b") ppm due to the formation of **2cc**.

In the ³¹P NMR spectrum of **200** (Figure 3b), the P signal was observed at 53.3 ppm. Upon irradiation at 365 nm, this signal gradually reduced and finally vanished, while a new signal emerged at 52.2 ppm due to the formation of **2co**. Upon keeping irradiation, the signal at 52.2 ppm decreased gradually; another new signal at 51.3 ppm occurred and enhanced increasingly due to further conversion of **2co** to **2cc**. At the PSS (Table 1 and Figure 4b), the solution contained 12% **2co** and 88% **2cc**, as estimated by the relative area of P signals of **2co** (52.2 ppm) and **2cc** (51.3 ppm).

In the ¹H NMR spectrum of **300** (Figure S6, Scheme S4), the thienyl protons were observed at 6.89 (H_{10}) and 6.25 ppm (H_{20}) and the methyl signals appeared at 1.83 (a) and 1.97 ppm (b). Upon irradiation of 300 at 365 nm, both proton signals of thienyls (H₁₀ and H₂₀) and methyls (a and b) decreased gradually accompanied by four new thienyl proton signals at 6.88 (H'_{10}), 6.07 (H'_{1c}), 6.24 (H'_{20}), and 5.27 ppm (H'_{2c}) due to the formation of **3co**. In the same time, the methyl signals of ring-opened L2o occurred at 1.84 (c') and 1.97 ppm (d') with a slight high-field shift, whereas those of ring-closed L2c were observed at 1.83 (a') and 2.03 ppm (b'). Upon further irradiation, two new thienyl signals emerged at 6.04 and 5.25 ppm, and two new methyl signals at 2.06 and 1.93 ppm were also observed, indicating the further conversion of 3co to 3cc. Upon irradiation at 365 nm (Figure 3c), the P signal of 300 at 53.3 ppm gradually attenuated together with the appearance of a new signal at 52.8 ppm following $300 \rightarrow$ **3co**. Keeping irradiation of the solution resulted in another new signal at 51.8 ppm, suggesting the further formation of 3cc. At the PSS, the P signal integral ratio indicated the presence of 5% 300, 73% 3co, and 22% 3cc (Table 1 and Figure 4c).

Electrochemical Studies. The electrochemical properties of 1-3 were in situ monitored under UV irradiation at 365 nm using a cyclic voltammogram (CV) and differential pulse voltammogram (DPV) in 0.1 M ["Bu₄N][PF₆] dichloromethane solutions. The data are summarized in Table 2.

As illustrated in Figure 5, the redox waves of **100** were observed at 0.47 V as a quasi-reversible process and 1.20 V as an irreversible one, attributed to the oxidation of $Ru^{II} \rightarrow Ru^{III}$ and ring-open DTEs, respectively. Upon irradiation of **100** with 365 nm light, while the waves at 0.47 and 1.20 V reduced

Table 2. Electrochemical Data for Complexes 1-3 with Various Forms in 0.1 M Solutions of $[^nBu_4N][PF_6]$ in Dichloromethane

	$E_{1/2} \left(\Delta E_{\rm p}\right)^{a,b}$		
	Ru-centered	DTEs ^c	
100	0.47 (0.06)	1.20 ^d	
1co	0.44 (0.07)	0.94, ^d 1.14	
200	0.48 (0.06)	1.21^{d}	
2co	0.45 (0.07)	0.95, ^d 1.16	
2cc	0.43 (0.08)	0.81, 0.96	
300	0.43 (0.05)	1.18^{d}	
3co	0.45 (0.08)	$0.89^{d}, 1.19^{d}$	

^{*a*}Potential data in volts were recorded relative to Ag/AgCl as a reference electrode. ^{*b*} $\Delta E_p = E_a - E_c$, where E_a and E_c are the anodic and cathodic potentials, respectively. ^{*c*}Potential data from differential pulse voltammogram (DPV). ^{*d*}Anodic potential.



Figure 5. Plots of cyclic voltammograms (a) and differential pulse voltammograms (b) of 100, 1c0, and 1cc in 0.1 M solutions of $["Bu_4N][PF_6]$ in dichloromethane.

gradually and disappeared finally, three new oxidation waves emerged at 0.44, 0.94, and 1.14 V. The reversible wave at 0.44 V corresponds to the oxidation of the Ru^{II} center, whereas the waves at 0.94 and 1.14 V are ascribable to the ring-closed L1c and the ring-opened L2o of singly ring-closed species **1co**, respectively. The redox wave for **1oc**, however, was not detected because of the low content (<25%) in the mixture. Upon keeping irradiation of the solution of complex **1** at 365 nm, three waves at 0.80, 0.95, and 1.13 V were observed at the PSS. Since the singly ring-closed **1co** (51%) and the fully ringclosed **1cc** (49%) coexisted at the PSS (Table 1), it is unattainable to separate them as pure samples through chromatography. At this stage, it is difficult to thoroughly investigate the electrochemical property of **1cc**.

The voltammogram plots of **200**, **2co**, and **2cc** (Figure S7) showed a quasi-reversible wave at ca. 0.40-0.50 V (vs Ag/AgCl), respectively, due to the oxidation of Ru^{II} to Ru^{III}. Species **200** also displayed an irreversible wave at 1.21 V, most likely corresponding to the L10-centered oxidation process. For **2co**, ligand-centered redox process showed two one-electron



Figure 6. (a) The UV–vis–NIR spectra of switchable eight forms for complex 1 in CH_2Cl_2 . (b) The UV–vis–NIR spectral changes of 100^+ upon irradiation at 365 nm. (c) Eight states of complex 1 from stepwise photochemical and electrochemical reactions.



Figure 7. UV–vis–NIR spectra of complexes 2 (a) and 3 (b) in various states in CH_2Cl_2 solutions (2 × 10⁻⁵ M).

oxidation waves at 0.95 and 1.16 V with lower potentials, ascribed to L1c and L1o in **2co**, respectively. Dually ring-closed species **2cc** showed two waves at 0.81 and 0.96 V due to the sequential oxidation of two ring-closed L1c's, implying an obvious electronic interaction between two identical ring-closed DTE moieties.³⁰ Species **3oo** (Figure S8) also displayed a reversible wave at 0.43 V stemming from the oxidation of the Ru^{II} center together with an irreversible wave at 1.18 V due to the ring-opened DTE moiety. Compound **3co** showed three oxidation waves at 0.45 (Ru), 0.89 (L2c), and 1.19 V (L2o). Unfortunately, the low conversion percentages of **3co** to **3cc** (ca. 22%) resulted in the absence of distinct electrochemical changes upon further irradiation of **3co** solution at 365 nm.

Spectroscopic Studies on Oxidized Species. In order to achieve multistate systems, monocationic species were obtained through the oxidation of Ru^{II} into Ru^{III} . On the basis of electrochemical studies, they $(100^+/1c0^+/1cc^+, 200^+/2c0^+/2c0^+/3c0^+/3c0^+)$ were accessed by the addition of 1 equiv of $[N(C_6H_4Br-4)_3](SbCl_6)$ as an oxidant to the corresponding solutions of complexes 100-300.

Complex **100⁺** (Figure 6a) displayed a near-infrared (NIR) absorption band centered at 1273 nm, which was mainly attributed to L1o/L2o/dppe \rightarrow Ru(III) LMCT states. By comparison, both complexes **10c⁺** and **1co⁺** exhibited a new band centered at 908 nm with a distinct attenuation of the NIR

band at ca. 1273 nm. The ring-closing absorption band occurred at 515 nm for $1oc^+$ and 657 nm for $1co^+$. In the case of $1cc^+$, three low-energy bands were observed at 908, 657, and 515 nm. The NIR bands at ca. 908 nm in $1co^+/1cc^+/1cc^+$ showed an obvious blue-shift compared with that in $10o^+$ (1273 nm), ascribed to their differences in transition character between ring-closed $1co^+/1oc^+/1cc^+$ and ring-open $1oo^+$ as revealed by computational studies (vide infra). Moreover, the ring-closed absorption bands in the visible region due to L1c and L2c in one-electron oxidized complexes $1co^+$ (657 nm), $1oc^+$ (515 nm), and $1cc^+$ (657 and 515 nm) showed distinct blue-shifts in comparison with those in 1co (696 nm), 1oc (524 nm), and 1cc (696 and 524 nm), respectively.

As depicted in Figure 6b, upon irradiation of one-electron oxidized species 100^+ with UV light at 365 nm, while the NIR band centered at 1273 nm decreased gradually, a new NIR band at 908 nm occurred and grew increasingly. Meanwhile, a broad composite band composed of the ring-closing absorption peaks at 515 nm (L2c) and 657 nm (L1c) emerged and increased progressively following the stepwise photocyclization $100^+ \rightarrow 10c^+/1co^+ \rightarrow 1cc^+$. As a result, complex 1 displays eight switchable states $(100/1c0/10c/1cc \text{ and } 100^+/1co^+/1co^+)$ through optical and electrochemical stimuli (Figure 6c).

Similarly, complex **200**⁺ exhibited an intense NIR band at ca. 1261 nm (Figure 7a) due to the L10/dppe \rightarrow Ru(III) LMCT state.³⁰ In contrast, **2co**⁺ displayed a weaker NIR band at ca. 1261 nm together with a ring-closing band at 654 nm and another NIR band at 920 nm. Relative to that in **2co**⁺, the NIR band at 920 nm became stronger, and the ring-closing band was shifted to 661 nm in **2cc**⁺ with the complete disappearance of the NIR band at ca. 1261 nm. The red-shift of the ring-closing band from 654 nm (**2co**⁺) to 661 nm (**2cc**⁺) reflects a more extended π system in **2cc**⁺ than that in **2co**⁺.

Complex 300^+ displayed a NIR band centered at ca. 1265 nm (Figure 7b). For $3c0^+$, a ring-closing band centered at 516 nm and a NIR band at 960 nm were observed, but the NIR band at ca. 1265 nm became much weaker relative to that of 300^+ . The corresponding absorption bands in $3cc^+$ were not detected due to the low conversion percentage.

Computational Studies. TD-DFT computational studies were performed on 100/1c0/1cc, 200/2co/2cc, and 300/3co/3cc together with monocationic 100⁺/1co⁺/10c⁺/1cc⁺ (Tables S1–S14). For 100–300, the HOMO is distributed on 4d orbitals of ruthenium and two ring-open DTE–acetylides, whereas the LUMO is localized at one of the ring-open ligands. The low-energy absorption bands are ascribable to Ru \rightarrow DTE–acetylide (MLCT) and DTE–acetylide (IL) centered transitions, mixed with some LLCT character from one DTE–acetylide to the other.

For 1co, both the HOMO and LUMO are mostly populated at ring-closed L1c. The LUMO+1 is mostly populated at L2o, which is responsible for further ring closure.²⁵ The low-energy absorption of 1co results mainly from the $\pi \to \pi^*$ (L1c) IL state, mixed with minor $4d(Ru) \rightarrow \pi^*$ (L1c) MLCT character. Similarly, both HOMO and LUMO for loc are mostly distributed on L2c. The LUMO+1 responsible for further ring-closure is populated on L10. The electronic transition from HOMO to LUMO is typical of the $\pi \to \pi^*$ (L2c) IL state, mixed with some 4d(Ru) $\rightarrow \pi^*$ (L2c) MLCT character. For 1cc, the HOMOs are mainly contributed by two ring-closed L1c and L2c, while the LUMO and LUMO+1 are mainly localized on L1c and L2c, respectively. The calculated ringclosure absorption at 691 nm (L1c) is featured with $\pi \to \pi^*$ (L1c) IL and π (L2c) $\rightarrow \pi^*$ (L1c) LLCT transitions, mixed with some 4d(Ru) $\rightarrow \pi^*(L1c)$ MLCT state. Similarly, the calculated ring-closure absorption at 531 nm is primarily assigned to $\pi \to \pi^*$ (L2c) IL and π (L1c) $\to \pi^*$ (L2c) LLCT states, mixed with a minor $4d(Ru) \rightarrow \pi^*(L2c)$ MLCT state. The large separation of the two ring-closure absorption bands at 691 nm (L1c) and 531 nm (L2c) implies that the mixed ringopen/closed species 1co or 1oc could be obtained experimentally through selective cycloreversion at L2c or L1c, respectively. However, the calculated ring-closure absorption of L2c at 531 nm (oscillator strength of 0.6422) is much weaker than that of L1c at 691 nm (oscillator strength of 1.0125), coinciding with the fact that a much smaller content of loc than of 1co could be generated upon irradiation of 100 under UV light.

For 2co and 3co, both the HOMO and LUMO are mostly located at ring-closed L1c and L2c, respectively. Thus, the lowenergy absorption due to electron promotion from HOMO to LUMO is typical of L1c and L2c centered states for 2co and 3co, respectively. The LUMO+1 populated primarily on L1o for 2co and L2o for 3co is favorable for further photocyclization. The calculated UV absorption bands at 303 nm for 2co and 329 nm for 3co indeed involve HOMO-3 \rightarrow LUMO +1. The greater involvement of HOMO-3 \rightarrow LUMO+1 for 2co (48%) than that for 3co (10%) gives a reasonable explanation to the experimental fact that further ring closure of 2co to 2cc (conversion percentage 88%) is much more facile than that of 3co to 3cc (conversion percentage 22%). For 2cc and 3cc, the HOMO/HOMO-1 is uniformly distributed on the two ring-closed DTE moieties along with a minor population at the Ru center, while the LUMO/LUMO+1 is mainly populated on one of the two ring-closed DTE moieties. The calculated low-energy absorption bands at 706 nm for 2cc and 543 nm for 3cc due to HOMO \rightarrow LUMO/LUMO+1 and HOMO-1 \rightarrow LUMO/LUMO+1 are all typical of IL and LLCT (from one DTE to the other) character. The oscillator strength of low-energy absorption of 3cc is weaker than that of 2cc, implying a smaller portion of 3cc can be obtained upon irradiation of 3co under UV light.

For 100⁺, the calculated NIR absorption at 1053 nm is typical of a LMCT state (Lo/dppe to Ru center). The NIR absorptions of 1co⁺ are mainly featured with a LLCT state of L2o \rightarrow L1c and MLCT transition of Ru \rightarrow L1c. Likewise, the NIR absorptions of 1oc⁺ are primarily assigned to LLCT character from L1o \rightarrow L2c and MLCT transition of Ru \rightarrow L2c. For 1co⁺ and 1oc⁺, the bands in the visible region are typical of ring-closing absorption of L1c and L2c, respectively, mixed with some LLCT state from the ring-opened DTE moiety to the ring-closed one and MLCT transition of Ru \rightarrow ring-closed DTE. For 1cc⁺, the NIR absorption bands result mainly from Ru \rightarrow L1c MLCT, $\pi \rightarrow \pi^*$ (L2c centered), and L2c \rightarrow L1c LLCT states. Due to their difference in transition character, the NIR absorptions in 1co⁺/1oc⁺/1cc⁺ exhibit distinct blue-shifts relative to that in 100⁺.

CONCLUSIONS

Two different dithienylethene-acetylides, L1o and L2o, that display a large separation between their ring-closing absorption peaks were utilized to construct an asymmetric ruthenium(II) complex 100 and two symmetric ones 200 and 300. The oxidized ruthenium(III) species 100^+ , 200^+ , and 300^+ were also accessible by the oxidation of Ru^{III} to Ru^{III}. They display distinctly stepwise photocyclization and selective photocycloreversion upon irradiation with suitable wavelengths of light. The one-electron oxidized Ru^{III} species exhibit NIR absorption and distinctly blue-shifted ring-closing absorption bands in the visible region relative to the corresponding Ru^{II} ones. Complex 1 presents unique stimuli-responsive features, including (1) multicolor, four different colors by using light as a trigger; (2) multistate, eight interconvertible states through light or redox stimulation; and (3) double addressing modes, via light irradiation and a reversible redox process. It is concluded that when the ring-closing absorption bands of two different DTE moieties are well-separated, four states and four colors can be achieved upon irradiation with different wavelengths of light. This asymmetric ruthenium complex with two types of DTE switches represents an eight-state system triggered simultaneously by optical and electrochemical stimuli. Such multistate and multicolor photochromic switches have potential applications in photoswitchable full-color displays and multifrequency of three-dimensional optical memory media.

EXPERIMENTAL SECTION

General Procedures and Materials. The operations were performed by Schlenk techniques and vacuum-line systems under a dry argon atmosphere. Solvents were dried (sodium/benzophenone for THF and calcium hydride for dichloromethane) and distilled under an argon atmosphere. *cis*-Ru(dppe)₂Cl₂,³⁷ 2,5-dibromo-3-methylthiophene,³⁸ 3-bromo-2-methyl-5-thienyl boronic acid,³⁹ and ((4-(3,3,4,4,5,5-hexafluorocyclopent-1-en-1-yl)-5-methylthiophen-2-yl)ethynyl)trimethylsilane⁴⁰ were prepared by procedures described in the literature. Other chemicals were commercially purchased and used as received.

2-(5-Bromo-4-methylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane. A dried 250 mL two-neck flask was charged with 2,5-dibromo-3-methylthiophene (5.2 g, 20 mmol) and dry THF (100 mL) at -78 °C under an argon atmosphere. The mixture was stirred at -78 °C for 1 h after n-BuLi (8.8 mL, 22 mmol, 2.5 M) was dropwise added. Then, the isopropoxyboronic acid pinacol ester (5.3 mL, 26 mmol) was added dropwise and the mixture stirred for 2 h. After the temperature rose to room temperature, the mixture was stirred overnight. Then, the mixture was quenched by the addition of a saturated aqueous solution of NH₄Cl (50 mL) and extracted with ethyl acetate three times. The combined extracts were dried over MgSO4. The crude product was purified with silica-gel column chromatography using ethyl acetate as an eluent to afford the compound (4.3 g, 70%) as a yellow oil. ¹H NMR (CDCl₃, ppm): δ 7.32 (s, 1H, CH), 2.22 (s, 3H, CH₃), 1.34 (s, 12H, 2-OC(CH₃)₂). ¹³C NMR (CDCl₃, ppm): δ 139.1, 138.6, 116.9, 84.2, 24.7, 14.9. HRMS (ESI) m/z calcd for $[C_{11}H_{16}BBrO_2SNa]^+$: 326.9981 $[M + Na]^+$. Found: 326.9629.

2-(2-Pyrimidyl)-4-bromo-5-methylthiophene. 2-Bromopyrimidine (2.29 g, 14.4 mol), 2-(4-bromo-5-methylthiophen-2-yl)-4,4,5,5tetramethyl-1,3,2-dioxaborolane (3.97 g, 13.1 mol), and tetrakis-(triphenylphosphine)palladium(0) (0.76 g, 0.66 mmol) were dissolved in THF (100 mL) with stirring for 15 min. An aqueous (50 mL) solution of sodium carbonate (12.5 g, 118 mmol) was then added. The mixture was refluxed with vigorous stirring for 8 h. The reaction process was monitored by TLC. The product was extracted with ethyl acetate three times. The combined extracts was dried with MgSO4 and then concentrated. The residue was purified by silica gel column chromatography using dichloromethane-petroleum (1:1, v/v) as an eluent. Yield: 81% (2.7 g). ¹H NMR (CDCl₃, ppm): δ 8.67 (d, J = 4.88 Hz, 2H), 7.81 (s, 1H), 7.09 (t, J = 4.88 Hz, 1H), 2.46 (s, 3H). ¹³C NMR (CDCl₃, ppm): δ 160.5, 157.2, 139.5, 139.4, 131.5, 118.6, 110.6, 15.3 (CH₃). HRMS (ESI) *m*/*z* calcd for [C₉H₈BrN₂S] ⁺: 256.9492 [M + H]⁺. Found: 256.9565.

2-Benzyl-5-bromo-4-methylthiophene. Benzyl chloride (1.30 mL, 11.3 mol), 2-(4-bromo-5-methylthiophen-2-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (3.12 g, 10.3 mol), and tetrakis-(triphenylphosphine)palladium(0) (0.60 g, 0.52 mmol) were added to DME (80 mL) with stirring for 15 min. An aqueous (30 mL) solution of sodium carbonate (7.5 g, 71 mmol) was then added. The mixture was refluxed with stirring overnight. The reaction process was monitored by TLC. The product was extracted with ethyl acetate three times. The combined organic was dried with Na_2SO_4 and concentrated. The product was purified by chromatography on a silica gel column using petroleum as an eluent. Yield: 59% (1.6 g). ¹H NMR (CDCl₃, ppm): δ 7.30–7.21 (m, 5H), 6.46 (s, 1H), 3.99 (s, 2H), 2.09 (s, 3H). ¹³C NMR (CDCl₃, ppm): δ 143.6, 139.6, 136.9, 128.7, 128.6, 127.2, 126.7, 106.9, 36.4 (PhCH₂), 15.2 (CH₃). HRMS (ESI) m/z calcd for $[C_{12}H_{12}BrS]^+$: 268.9743 $[M + H]^+$. Found: 268.9802

1-(5-Methyl-2-(2-pyrimidyl)-4-thienyl)-2-(2-meth-yl-5-trimethylsilylethynyl-3-thienyl)- perfluorocyclopentene. To a dry THF (40 mL) solution of 2-(2-pyrimidyl)-4-bromo-5-methylthiophene (500 mg, 1.96 mmol) at -78 °C was added dropwise *n*butyllithium (1.6 M in hexane, 1.2 mL, 1.9 mmol) with stirring for 1 h. A dry THF (5 mL) solution of 2-(5-(4-trimethylsilylethynyl)-2methylthiophen-3-yl)perfluorocyclopentene (757 mg, 1.96 mmol) was then added to the above solution. The reaction mixture was stirred at -78 °C for another 2 h and then put aside at room temperature overnight before being quenched by the addition of an aqueous NH₄Cl solution. The product was extracted with ethyl acetate and dried with MgSO₄ and then concentrated. The product was purified through silica gel column chromatography using dichloromethanepetroleum ether (v/v = 1:2) as an eluent to afford the product as a yellow solid. Yield: 40% (425 mg). ¹H NMR (CDCl₃, ppm): δ 8.71 (d, *J* = 4.92 Hz, 2H), 8.00 (s, 1H), 7.26 (s, 1H), 7.15 (t, *J* = 4.88 Hz, 1H), 1.99 (s, 3H), 1.93 (s, 3H), 0.27 (s, 9H). ¹³C NMR (CDCl₃, ppm): δ 160.6, 157.3, 146.3, 143.3, 141.1, 132.1, 128.4, 126.0, 124.7, 121.7, 118.9, 99.9, 96.2, 14.9 (CH₃), 14.5 (CH₃), -0.2 (SiCH₃). HRMS (ESI) *m*/*z* calcd for [C₂₄H₂₁F₆N₂S₂Si]⁺: S43.0820 [M + H]⁺. Found: S43.0814. IR (KBr): 2146 cm⁻¹ (C=C).

1-(5-Methyl-2-(2-pyrimidyl)-4-thienyl)-2-(2-meth-yl-5-ethynyl-3-thienyl)perfluorocyclo-pentene (L10). To a THF-methanol (30 mL, v/v = 1:1) solution of 1-(5-methyl-2-(2-pyrimidyl)-4-thienyl)-2-(2-methyl-5-trimethylsilylethynyl-3-thienyl)perfluorocyclopentene (550 mg, 1.01 mmol) was added an excess of anhydrous potassium carbonate, and the mixture was stirred overnight. Upon removal of the solvent, the residue was dissolved in dichloromethane (30 mL). The product was purified by chromatography on a silica gel column using dichloromethane-petroleum ether (v/v = 1:1) as an eluent to afford to the product as a yellow solid. Yield: 90% (428 mg). ¹H NMR (CDCl₃, ppm): δ 8.71 (d, J = 4.92 Hz, 2H), 7.99 (s, 1H), 7.27 (s, 1H), 7.13 (t, J = 5.12 Hz, 1H), 3.35 (s, 1H), 1.96 (s, 3H), 1.93 (s, 3H). ¹³C NMR (CDCl₃, ppm): δ 160.6, 157.3, 146.3, 143.7, 141.2, 132.7, 128.4, 125.9, 124.7, 120.5, 118.9, 82.2, 75.8, 14.9 (CH₃), 14.5 (CH₃). HRMS (ESI) m/z calcd for $[C_{21}H_{13}F_6N_2S_2]^+$: 471.0424 $[M + H]^+$. Found: 471.0421. IR (KBr): 2106 cm⁻¹ (C≡C).

1-(5-Methyl-2-benzyl-4-thienyl)-2-(2-methyl-5-trimethylsilylethynyl-3-thienyl)perfluoro-cyclopentene. To a dry THF (40 mL) solution of 2-benzyl-4-bromo-5-methylthiophene (570 mg, 2.13 mmol) at -78 °C was added slowly n-butyllithium (1.6 M in hexane, 1.4 mL, 2.3 mmol). Upon stirring at -78 °C for 1 h, to the above solution was then added a dry THF (5 mL) solution of ((4-(3,3,4,4,5,5-hexafluorocyclopent-1-en-1-yl)-5-methylthiophen-2-yl)ethynyl)trimethyl-silane (823 mg, 2.13 mmol). The reaction mixture was stirred at -78 °C for 2 h and put aside at room temperature overnight before being quenched by the addition of an aqueous hydrochloric acid solution. The product was extracted with ethyl acetate and dried with Na₂SO₄ and then purified by chromatography on a silica gel column using dichloromethane-petroleum ether (v/v =1:4) as an eluent. The product was isolated as a yellow solid. Yield: 53% (625 mg). ¹H NMR (CDCl₃, ppm): δ 7.34–7.20 (m, 5H), 7.19 (s, 1H), 6.51 (s, 1H), 4.06 (s, 2H), 1.88 (s, 3H), 1.67 (s, 3H), 0.25 (s, 9H). ¹³C NMR (CDCl₃, ppm): δ 148.5, 143.4, 141.2, 139.1, 132.5, 129.2, 128.7, 128.6, 126.9, 125.1, 121.4, 121.1, 99.7, 96.4, 36.1 (PhCH₂), 15.5 (CH₃), 14.2 (CH₃), -0.2 (SiCH₃). HRMS (ESI) m/z calcd for [C₂₇H₂₄F₆S₂SiNa]⁺: 577.0891 [M + Na]⁺. Found: 577.0883. IR (KBr): 2153 cm⁻¹ (C≡C).

1-(5-Methyl-2-benzyl-4-thienyl)-2-(2-methyl-5-ethynyl-3-thienyl)perfluorocyclopentene (L2o). An excess of anhydrous potassium carbonate was added to a THF–methanol (30 mL, v/v = 1:1) solution of 1-(5-methyl-2-benzyl-4-thienyl)-2-(2-methyl-5-trime-thylsilylethynyl-3-thienyl)perfluorocyclopentene (571 mg, 1.03 mmol). The mixture was stirred at ambient temperature overnight. The product was purified by chromatography on a silica gel column using dichloromethane–petroleum ether (v/v = 1:3) as an eluent to afford the product as a yellow solid. Yield: 92% (457 mg). ¹H NMR (CDCl₃, ppm): δ 7.34–7.22 (m, 5H), 7.20 (s, 1H), 6.52 (s, 1H), 4.06 (s, 2H), 3.33 (s, 1H), 1.90 (s, 3H), 1.67 (s, 3H). ¹³C NMR (CDCl₃, ppm): δ 148.7, 143.7, 141.3, 139.1, 133.1, 129.2, 128.7, 128.6, 126.9, 125.1, 121.1, 120.2, 82.0, 75.9, 36.1 (PhCH₂), 15.4 (CH₃), 14.3 (CH₃). HRMS (ESI) *m*/*z* calcd for [C₂₄H₁₆F₆S₂Na]⁺: 505.0495 [M + Na]⁺. Found: 505.0490. IR (KBr): 2108 cm⁻¹ (C≡C).

cis-Ru(dppe)₂(L1o)Cl. cis-Ru(dppe)₂Cl₂ (137 mg, 0.142 mmol) and L10 (80 mg, 0.17 mmol) were dissolved in CH₂Cl₂ (15 mL). Upon the addition of NaPF₆ (29 mg, 0.17 mmol), the solution was stirred at room temperature for 12 h and then concentrated to 2 mL. To the solution was added 40 mL of anhydrous diethyl ether, which produced a precipitate. Upon filtration, the solid was dissolved in 30 mL of CH₂Cl₂, followed by the addition of NEt₃ (1 mL). When the solution was stirred for 30 min, the solvent was removed under a vacuum. The residue was chromatographed over a short alumina column using CH₂Cl₂ as an eluent. The product was recrystallized from dichloromethane—hexane to give a yellow solid. Yield: 56% (111

mg). ¹H NMR (CDCl₃, ppm): δ 8.71 (d, J = 4.88 Hz, 2H), 8.06 (s, 1H), 7.46–6.94 (m, 40H), 7.13 (t, J = 4.90 Hz, 1H), 6.06 (s, 1H), 2.66 (s, 8H), 1.94 (s, 3H), 1.79 (s, 3H). ³¹P NMR (CDCl₃, ppm): δ 48.9. HRMS (ESI) m/z calcd for $[C_{73}H_{59}F_6N_2P_4RuS_2]^+$: 1367.1950 [M–Cl]⁺. Found: 1367.2034. IR (KBr): 2056 cm⁻¹ (C≡C).

100. To a dichloromethane (20 mL) solution of cis-Ru-(dppe)₂(L1o)Cl (100 mg, 0.071 mmol) and L2o (41.0 mg, 0.085 mmol) were added NaPF₆ (14.3 mg, 0.085 mmol) and triethylamine (1 mL). The reaction mixture was stirred in the dark at ambient temperature for 1 day. The reaction was monitored by TLC. The solution was concentrated and chromatographed on a short alumina column using dichloromethane as an eluent. The yellow-green product was further purified through recrystallization by layering *n*-hexane onto the dichloromethane solution. Yield: 55% (72 mg). ¹H NMR (CDCl₃, ppm): δ 8.55 (s, 1H), 8.04 (d, J = 4.80 Hz, 2H), 7.66–6.90 (m, 45H), 6.73 (s, 1H), 6.64 (s, 1H), 6.17 (s, 1H), 6.03 (t, J = 4.80 Hz, 1H), 3.66 (s, 2H), 2.43 (s, 8H), 1.84 (s, 3H), 1.75 (s, 3H), 1.74 (s, 3H), 1.67 (s, 3H). ³¹P NMR (CDCl₃, ppm): δ 53.2. ¹³C NMR (CD₂Cl₂, ppm): δ 160.6, 157.3, 146.3, 141.2, 136.0, 134.7, 133.7, 128.7, 128.6, 127.2, 127.1, 126.6, 123.7, 123.4, 118.9, 103.6 (C≡C), 30.6 (m, CH₂P), 14.9 (CH_3) , 14.3 (CH_3) . HRMS (ESI) m/z calcd for $[C_{97}H_{74}F_{12}N_2P_4RuS_4Na]^+$: 1871.2429 $[M + Na]^+$. Found: 1871.2453. IR (KBr): 2050 cm⁻¹ (C≡C).

200. To a dichloromethane (20 mL) solution containing cis-Ru(dppe)₂Cl₂ (93.9 mg, 0.097 mmol) and L10 (100 mg, 0.213 mmol) were added NaPF₆ (35.8 mg, 0.213 mmol) and triethylamine (1 mL). The mixture was stirred at ambient temperature for 1 day, and the reaction was monitored by TLC. The solution was filtrated and concentrated, which was then chromatographed on a short alumina column to give a pale green solid using dichloromethane as an eluent. The product was further purified through recrystallization by layering *n*-hexane onto the dichloromethane solution. Yield: 50% (89 mg). ¹H NMR (CDCl₃, ppm): δ 8.54 (s, 2H), 8.05 (d, J = 4.84 Hz, 4H), 7.57– 6.95 (m, 40H), 6.64 (s, 2H), 6.04 (t, I = 4.86 Hz, 2H), 2.43 (s, 8H),1.85 (s, 6H), 1.74 (s, 6H). ³¹P NMR (CDCl₃, ppm): δ 53.3. ¹³C NMR (CDCl₃, ppm): δ 147.7, 140.9, 139.3, 136.4, 135.9, 134.1, 129.6, 129.0, 128.8, 128.7, 128.6, 127.1, 126.8, 124.2, 121.9, 107.9 (C=C), 36.2 (PhCH₂), 31.4 (m, CH₂P), 15.5 (CH₃), 14.3 (CH₃). HRMS (ESI) m/z calcd for $[C_{94}H_{70}F_{12}N_4P_4RuS_4Na]^+$: 1859.2178 $[M + Na]^+$. Found: 1859.2201. IR (KBr): 2050 cm⁻¹ (C \equiv C).

300. This compound was prepared by the same synthetic procedure as that of **200** except for the use of L20 in place of L10. Yield: 52% (91 mg). ¹H NMR (CDCl₃, ppm): δ 7.62–6.99 (m, 50H), 6.89 (s, 2H), 6.25 (s, 2H), 3.73 (s, 4H), 2.48 (s, 8H), 1.97 (s, 6H), 1.83 (s, 6H). ³¹P NMR (CDCl₃, ppm): δ 53.2. ¹³C NMR (C_6D_6 , ppm): δ 160.8, 156.7, 148.1, 146.4, 141.6, 141.0, 139.2, 134.7, 133.0, 130.5, 130.2, 130.1, 129.1, 129.0, 128.9, 127.2, 126.8, 126.7, 124.6, 124.5, 124.3, 124.1, 122.1, 118.2, 108.1 ($C \equiv C$), 37.2 (PhCH₂), 31.4 (m, CH₂P), 15.3 (CH₃), 14.6 (CH₃), 14.3 (CH₃), 14.1 (CH₃). Yield: 52% (91 mg). HRMS (ESI) *m*/*z* calcd for [$C_{100}H_{78}F_{12}P_4RUS_4Na$]⁺: 1883.2681 [M + Na]⁺. Found: 1883.2706. IR (KBr): 2050 cm⁻¹ ($C \equiv C$).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.7b02023.

Tables and figures giving additional spectroscopic, computational, and electroluminescent data (PDF)

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Notes

The authors declare no competing financial interest.

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