Photophysics and Nonlinear Absorption of Cyclometalated 4,6-Diphenyl-2,2'-bipyridyl Platinum(II) Complexes with Different Acetylide Ligands

Rui Liu,^{†,‡} Yunjing Li,[†] Yuhao Li,[‡] Hongjun Zhu,[‡] and Wenfang Sun^{*,†}

Department of Chemistry and Biochemistry, North Dakota State University, Fargo, North Dakota 58108-6050, United States, and Department of Applied Chemistry, College of Science, Nanjing University of Technology, Nanjing 210009, People's Republic of China

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The photophysical properties of a series of 4,6-diphenyl-2,2'-bipyridyl platinum(II) complexes bearing different σ -alkynyl ancillary ligands (**1a**-**1k**) were systematically investigated. All complexes exhibit strong ${}^{1}\pi,\pi^{*}$ absorption bands in the UV region; and broad, structureless charge-transfer band(s) in the visible region, which systematically red-shift(s) when the electron-donating ability of the para substituent on the phenylacetylide ligand increases. All complexes are emissive in solution at room temperature. When excited at the charge-transfer absorption band, the complexes exhibit long-lived orange emission (λ_{max} : 555 - 601 nm), which is attributed to a triplet metal-to-ligand charge transfer/intraligand charge transfer emission (${}^{3}MLCT/{}^{3}ILCT$). Most of these complexes exhibit broad triplet transient difference absorption in the visible to the near-IR region, with a lifetime comparable to those measured from the decay of the ${}^{3}MLCT/{}^{3}ILCT$ emission. The reverse saturable absorption (RSA) of these complexes were demonstrated at 532 nm using nanosecond laser pulses. The degree of RSA follows this trend: $\mathbf{1k} \approx \mathbf{1a} > \mathbf{1c} > \mathbf{1f} \approx \mathbf{1i} > \mathbf{1h} \approx \mathbf{1b} > \mathbf{1e} > \mathbf{1d} > \mathbf{1g}$, which is mainly determined by the ratio of the triplet excited-state absorption cross section to that of the ground-state and the triplet excited-state quantum yield.

Introduction

Cyclometalated square-planar platinum(II) complexes have attracted a great deal of attention owing to their versatile photophysical properties and potential applications in lightemitting devices,^{1–5} photocatalysis,^{6–8} nonlinear optical devices,^{9–12} and chemosensors.^{13,14} Many of these complexes exhibit moderate charge-transfer absorption in the visible region and longlived emission at room temperature in solution. The squareplanar coordination geometry around Pt(II) reduces D_{2d} distortion that is likely to lead to radiationless decay.^{3,5} In addition, their photophysical properties can be tuned by structural modification of the ligands to meet the different requirements for diverse applications.

Among the cyclometalated square-planar platinum(II) complexes, 6-phenyl-2,2'-bipyridyl (C^N^N) platinum acetylide complexes are particularly intriguing by virtue of their relatively intense emission.^{1-3,15-17} The stronger emission from these complexes compared to their corresponding platinum terpyridyl complexes is partially attributed to the less-distorted squareplanar geometry that reduces the radiationless decay. Additionally, the ease of structural modification on the 4'-position of the central pyridine ring and on the 6-phenyl ring facilitates the tuning of the photophysical properties of the complexes. In the past, our group introduced alkoxyl substituent on the 6-phenyl ring¹¹ and fluorenyl substituent on the 4'-position of the central pyridine ring of the C^N^N ligand.^{9,18} These modifications not only improve the solubility of the complexes but also cause a pronounced effect on the photophysics of these complexes, which is reflected by their much larger molar extinction coefficients for their low energy charge-transfer absorption bands, longer triplet excited-state lifetimes, higher emission quantum yields, and significantly increased ratios of the excited-state absorption cross section to that of the ground state compared to those of their corresponding Pt complexes without these substituents.9,11 In these works we also demonstrated the influence of the monodentate ligand on the photophysics and nonlinear absorption of the C^N^N platinum complexes.^{9,11,18} A prior work reported by Che and co-workers studied the effect of substituent on the acetylide ligand on the UV-vis and emission properties of the Pt(II) C^N^N complexes as well.¹ The metal-to-ligand charge transfer (¹MLCT) absorption band energy and the emission energy of the complexes were systematically affected by the electron-donating or electronwithdrawing ability of the para substituent on the phenylacetylide ligand. In addition, our group have demonstrated that $(C^N^N)PtC \equiv CPh$ and $(C^N^N)PtC \equiv CC_3H_7$ exhibit broader triplet excited-state absorption, higher triplet excited-state quantum yield, and thus enhanced reverse saturable absorption for nanosecond laser pulses compared to their platinum terpyridyl analogues.^{17,19}

The reported work are quite intriguing, however, the study on the effect of monodentate ligand on the photophysics, especially on the nonlinear absorption of platinum C^N^N complexes is still limited. To remedy this deficiency, our groups have designed and synthesized a series of mononuclear cyclometalated platinum(II) 4,6-diphenyl-2,2'-bipyridyl acetylide complexes (Chart 1). Their photophysical properties have been systematically investigated with the aim to provide a basis for elucidating the structure—property correlations and developing new nonlinear absorbing materials.

The synthesis and structural characterization of the cyclometalated platinum(II) complexes with different acetylide ligands have been reported previously.²⁰ In this work, we focus on the

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^{*} To whom correspondence should be addressed. Phone: 701-231-6254. Fax: 701-231-8831. E-mail: Wenfang.Sun@ndsu.edu.

[†] North Dakota State University.

^{*} Nanjing University of Technology.

CHART 1: Structures for Pt(II) Complexes 1a-1k



photophysical and nonlinear absorption studies of these complexes for nanosecond laser pulses.

Experimental Section

Photophysical Measurements. An Agilent 8453 spectrophotometer was used to measure the UV-vis absorption spectra, and a SPEX fluorolog-3 fluorometer/phosphorometer was utilized to obtain the steady-state emission spectra. The emission quantum yields were determined by the comparative method,²¹ in which a degassed aqueous solution of [Ru(bpy)₃]Cl₂ ($\Phi_{em} =$ 0.042, excited at 436 nm)²² was used as the reference. An Edinburgh LP920 laser flash photolysis spectrometer was used to measure the excited-state lifetimes, the triplet transient difference absorption spectra and the triplet excited-state quantum yields and the molar extinction coefficients in degassed solutions. The excitation source was the third harmonic output (355 nm) of a Nd:YAG laser (Quantel Brilliant, pulsewidth ~4.1 ns, repetition rate was set at 1 Hz). Each sample was purged with Ar for 30 min before measurement.

The triplet excited-state molar extinction coefficient and triplet quantum yield were determined by the partial saturation method,²³ in which the optical density at the interested wavelength was monitored when the excitation energy at 355 nm was gradually increased. Saturation was observed when the excitation energy was higher than 10 mJ. The following equation was then used to fit the experimental data to obtain the ε_T and Φ_T^{23}

$$\Delta OD = a(1 - \exp(-bI_{\rm p})) \tag{1}$$

where ΔOD is the optical density at the interested wavelength, $I_{\rm p}$ is the pump intensity in Einstein cm⁻², $a = (\varepsilon_{\rm T} - \varepsilon_0)dl$, and $b = 2303 \varepsilon_0^{\rm ex} \Phi_{\rm T}/A$. $\varepsilon_{\rm T}$ and ε_0 are the absorption coefficients of the excited state and the ground state at the interested wavelength, $\varepsilon_0^{\rm ex}$ the ground-state absorption coefficient at the excitation wavelength of 355 nm, *d* the concentration of the sample (mol L⁻¹), *l* the thickness of the sample excited by the excitation beam (namely the diameter of the excitation beam), and *A* the area of the sample irradiated by the excitation beam.

Nonlinear Transmission Measurement. The experimental setup was similar to that described previously.²⁴ The light source

was the second harmonic output ($\lambda = 532$ nm) of a 4.1 ns (fwhm), 10 Hz, Q-switched Quantel Brilliant Nd:YAG laser. A f = 30 cm plano-convex lens was used to focus the laser beam to the center of a 2-mm-thick sample cuvette. The radius of the beam waist was ~75 μ m. Two Molectron J4–09 pyroelectric probes and an EPM2000 energy/power meter were used to monitor the incident and output energies.

Results and Discussion

Synthesis. The synthesis of the 4,6-diphenyl-2,2'-bipyridyl platinum(II) chloride complex ((C^N^N)PtCl) followed the procedures reported in the literature.²⁵ The (C^N^N)PtCl complex was then reacted with para-substituted ethynylbenzene with a base (diisopropylethylamine (DIEA)) and catalytical amount of CuI in degassed CH₂Cl₂ solution at room temperature for 12 h. The crude product was purified via recrystallization in CH₂Cl₂/Et₂O to yield the product for photophysical study. The complexes were characterized by ¹H and ¹³C NMR, HRMS, and elemental analysis. The detailed synthetic procedure and characterization data were reported earlier.²⁰

UV-Vis Absorption. The UV-vis absorption spectra of **1a-1k** in CH₃CN solution are presented in Figure 1, and the band maxima and molar extinction coefficients for each complex are compiled in Table 1. The absorption obeys Lambert-Beer's law in the concentration range studied (1 \times 10⁻⁶ through 1 \times 10⁻⁴ mol/L), suggesting no dimerization or oligomerization of the complexes within this concentration range. In line with the previous work on cyclometalated platinum(II) complexes, the intense absorption bands below 370 nm are assigned to the intraligand (IL) π,π^* transitions, while the broad, moderately intense absorption bands at 400-550 nm are assigned to the mixed ¹MLCT (metal-to-ligand charge transfer)/¹LLCT (ligandto-ligand charge transfer)/¹ILCT (intraligand charge transfer) transitions considering the similar energy and intensity of this band to those reported in the literature for other platinum C^N^N acetylide complexes.^{5,9,11,15,17,18} The involvement of the ¹ILCT and ¹LLCT characters into the low-energy absorption band of these complexes should be taken into account because of the π -donating ability of the 6-phenyl ring on the C^N^N ligand and the acetylide ligand, which has been suggested by the DFT calculation previously reported by our group for the 4,6diphenyl-2,2'-bipyridine platinum chloride complex and platinum 4,6-diphenyl-2,2'-bipyridine complexes with an alkoxyl



Figure 1. UV-vis absorption spectra of Pt(II) complexes 1a-1k in CH₃CN solution.

TABLE 1:	Photophysical	Parameters of	1a-1k	in	CH ₃ CN
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	$\lambda_{ m abs}~^{b}$ /nm	$\lambda_{\rm em}$ ^b /nm	$\lambda_{ m T1-Tn}/ m nm$			
	$(\varepsilon/10^3 \text{ L}\cdot\text{mol}^{-1}\cdot\text{cm}^{-1})$	$(\tau_{\rm em}/{\rm ns}, \Phi_{\rm em})$	$\overline{(\tau_{\mathrm{TA}}/\mathrm{ns}; \varepsilon_{\mathrm{T1-Tn}}/\mathrm{L}\cdot\mathrm{mol}^{-1}\cdot\mathrm{cm}^{-1}; \Phi_{\mathrm{T}})}$			
1a	285 (43.2), 332 (13.8), 365 (9.4), 432 (6.36), 450 (6.42)	584 (500, 0.048)	615 (510, 3004, 0.41)			
1b	289 (45.2), 332 (16.6), 365 (10.8), 429 (7.42), 448 (7.09)	570 (360,0.073)	615 (490, 10455, 0.18)			
1c	286 (50.0), 332 (25.2), 372 (31.0), 432 (22.1)	555 (380, 0.024)	610 (400, 9305, 0.16)			
1d	281 (42.7), 333 (12.0), 367 (8.0), 440 (5.18), 466 (5.40)	584 (90, 0.001)	С			
1e	290 (36.0), 366 (9.0), 436 (6.14), 455 (6.08)	592 (250, 0.018)	540 (450, 2422, 0.13)			
1f	289 (21.6), 327 (21.7), 422 (4.50), 440 (4.57)	582 (410, 0.062)	605 (840, 15873, 0.08)			
1g	287 (25.7), 322 (21.5), 437 (4.68), 472 (4.55)	601 (190, 0.003)	С			
1h	291 (10.4), 341 (3.2), 364 (1.8), 435 (1.33), 455 (1.28)	593 (70, 0.004)	С			
1i	287 (24.6), 332 (27.6), 430 (5.19), 453 (5.19)	568 (280, 0.015)	С			
1j	285 (10.4), 339 (9.6), 427 (1.73)	572 (550, 0.047)	580 (15480, 2758, 0.18)			
1k	282 (40.3), 319 (31.5), 340 (29.1), 430 (sh. 2.56)	569 (210, 0.021)	580 (260, 5432, 0.11)			

^a Measured at room temperature. ^b At a concentration of 5 \times 10⁻⁵ mol/L. ^c Too weak to be measured.

substituent on the 6-phenyl ring.¹¹ The transition energies in these complexes are quite similar to those of their corresponding platinum C^N^N complexes without the 4-phenyl substituent, especially for the low-energy charge-transfer bands. This indicates that the phenyl substituent has a negligible effect on the energy level of the bipyridine based LUMO ($\pi^*(N^N)$) for the Pt(C^N^N)X complexes.¹¹ However, introducing the 4-phenyl ring on the C^N^N ligand pronouncedly increases the molar extinction coefficients of the low-energy charge-transfer absorption band compared to those of their corresponding Pt complexes without the 4-phenyl substituent,¹ which is in line with the influence of the 4-tolyl substituent on the terpyridyl ligand on the UV-vis absorption of the corresponding platinum terpyridyl complexes.²⁶

As shown in Figure 1 and Table 1, the low-energy absorption band for most of the complexes appears to show two distinct transitions. The transitions occurring in the region of 424-440 nm are not quite sensitive to the ancillary substituents on the phenyl ring of the acetylide ligand, which likely emanate from the $d\pi$ (Pt) $\rightarrow \pi^*(N^N)$ MLCT excited state. In contrast, the transitions appearing at lower energies are influenced significantly by the nature of the ancillary substituents. Electrondonating substituents, such as OBu, NPh₂, and 9H-carbazolyl, cause a pronounced red-shift of this transition, while electronwithdrawing substituents such as SAc and NO2 induce a blueshift compared to complex 1a. A linear correlation is observed between the energy of this band and the Hammett constant ($\sigma_{\rm p}$) of the substituent on the phenyl ring (see Figure S1 of Supporting Information). Considering the sensitivity of the lower-energy transition to the para-substituent at the phenylacetylide ligand, we tentatively assign this transition to a spin allowed LLCT transition (¹LLCT). However, the ¹ILCT may also contribute to this region. Because of the inductive and resonant effects from the para substituent, the energy of the acetylide-based HOMO is affected, which in turn causes the change of the lowest excited-state energy. An electron-donating substituent raises the acetylide-based HOMO, while an electronwithdrawing substituent stabilizes the acetylide-base HOMO. Consequently, the energy difference between the acetylide-based HOMO and the bipyridine (N^N)-based LUMO will be varied and the bathochromic shift or hypsochromic shift occurs. Although the influence of the para substituent at the phenylacetylide ligand on the MLCT transition is not as pronounced as it does on the LLCT transition, a similar trend was observed for the MLCT transition. A linear correlation also exists between the energy of the ¹MLCT band and the Hammett constant ($\sigma_{\rm p}$) of the para substituent (see Figure S1 of Supporting Information). This is because an acetylide ligand with electron-donating substituent is more electron rich and raises the Pt d orbital energy, which leads to a decrease of the energy gap between the bipyridine-based LUMO and the Pt-based HOMO and results in the red-shift. In contrast, an electron-withdrawing substituent would have the opposite effect. A similar effect of the para substituent at the phenylacetylide ligand on the charge-transfer band energy has been reported by Che group for $Pt(C^N N)$ complexes without the 4-phenyl substituent¹ and by our group and Yam group for platinum terpyridyl complexes.^{26,27}

In addition, it is noted that complex **1c** has an additional intense absorption band at $\lambda_{max} = 378 \text{ nm} (\varepsilon \approx 3.5 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$. With reference to the work reported by Eisenberg²⁸ and Che¹ groups, this band is attributed to the intraligand charge-transfer transition (¹ILCT) within the 4-nitrophenylacetylide ligand. It is also worthy of mention that extension of the conjugation of the acetylide ligand affects the charge transfer band pronouncedly. In comparison of the spectra for **1a**, **1f** and **1j**, and **1i** and **1k**, we notice that with the increased conjugation



Figure 2. UV-vis absorption spectra of 1f in different solvents

of the oligoyne ligand the charge-transfer band blue-shifts and the molar extinction coefficient decreases. Especially the lowerenergy transition corresponding to the ¹LLCT transition is significantly weakened. This phenomenon could probably be ascribed to the lowering of the oligoyne ${}^{1}\pi,\pi^{*}$ transition energy with the increased conjugation length, which could change the parentage of the lowest excited state by mixing some ${}^{1}\pi,\pi^{*}$ character into the lowest excited state for 1i and 1k. The participation of the acetylenic π,π^* character in the emissive state of C^N^N complexes bearing oligoyne ligand has been suggested by Che previously.¹ We believe it is also likely to be the case for the lowest singlet excited state of 1j and 1k.

The charge transfer nature of the low-energy absorption bands in 1a-1k is supported by the solvent-dependency studies. As exemplified in Figure 2 for 1f, the low-energy absorption band bathochromically shifts to longer wavelengths in solvents with lower polarity (i.e., hexane and toluene) compared to those in more polar solvents (i.e., CH₃CN and CH₃OH). This negative solvatochromic effect is indicative of a charge-transfer transition, in which the dipole moment of the ground state is larger than that of the excited state. This phenomenon is also in accordance with that observed in many of the platinum C^N^N or terpyridyl complexes reported in the literature.^{9-14,17,18,24,26-28} The same solvent effect is observed for all of the other complexes studied in this work, and the results are provided in the Figures S2-S11 of the Supporting Information.

Emission. The emission characteristics of complexes 1a-1k in a variety of solvents and at different concentrations in CH₂Cl₂ at room temperature were investigated, and the normalized emission spectra of these complexes in CH₃CN at a concentration of 1×10^{-5} mol/L are illustrated in Figure 3. The emission



Figure 4. Normalized emission spectra of 1f in different solvents. The excitation wavelength was 468 nm for CH2Cl2, toluene, and hexane solutions, 450 nm for CH₃CN solution, and 420 nm for CH₃OH solution.

lifetimes and the emission quantum yields are summarized in Table 1. As shown in Figure 3 and Table 1, excitation of these complexes in CH₃CN solution at their respective charge-transfer band at room temperature results in orange to red luminescence, corresponding to a Stokes shift of 4220-5940 cm⁻¹. The emission lifetimes in degassed CH₃CN solutions are all several hundred nanoseconds except for 1d and 1h. The drastic Stokes shift and relatively long lifetime suggest that the observed emission from these complexes is from a triplet excited state. With reference to the other platinum C^N^N complexes reported in the literature, the emission could be tentatively assigned to the ³MLCT/³ILCT emission.^{1,2,9–11,15} The charge transfer nature of the emitting state could be supported by the structureless feature of the emission spectra and the solvent-dependency study. Except for 1g and 1h, all of the other complexes exhibit a negative solvatochromic effect (exemplified in Figure 4 for complex 1f and in Figures S12-S21 of Supporting Information for the other complexes), i.e., when the dielectric constant (ε) or $E_{\rm T}(30)$ value of the solvent increases, the emission energy of the complexes decreases, which is a characteristic of the ³MLCT excited state. However, no linear correlation is observed between the ε or $E_{\rm T}(30)$ value and the emission energy. For complex 1g, a positive solvatochromic effect was observed (see Figure S17 of Supporting Information), indicating that the excited state is more polar than the ground state. This suggests that the emitting state for 1g could possibly be dominated by the intraligand charge-transfer character. For complex 1h, minor solvatochromic effect was observed, which probably reflects the interplay of the ³MLCT and ³ILCT configuration. In addition to the solvatochromic effect discussed above, the different



Figure 3. Normalized emission spectra of complexes 1a-1k in CH₃CN solution (1 × 10⁻⁵ mol/L). The excitation wavelength was 450 nm for 1a, 1b, 1e, 1f, 1h, and 1j; 421 nm for 1c, 420 nm for 1d, 466 nm for 1g and 1i, and 436 nm for 1k.

solvents also influence the emission lifetime and quantum yield pronouncedly. As shown in Table 2, all of the complexes exhibit a longer emission lifetime and a higher quantum yield in noncoordinating solvents, such as CH₂Cl₂ in comparison to those in coordinating solvents like CH₃CN and CH₃OH. This solvent induced quenching by coordinating solvents is commonly seen in Pt(II) complexes with a ³MLCT emitting state, which provides another piece of evidence for the involvement of the ³MLCT character in the emitting state of these complexes.

The emission energies (λ_{max}/nm) of **1a-1k** are influenced by the electron-donating ability of the para substituent on the phenylacetylide ligand, which increase in the order of $NPh_2 >$ carbazolyl > BuO > SAc > NO_2 . This trend is consistent with that observed for the ¹MLCT band in the UV-vis absorption spectra. It provides another piece of evident that the emission has ³MLCT character. Similar to that observed for the lowenergy charge-transfer band(s) in the UV-vis absorption spectra, the emission energy for 1a, 1b, 1c, 1d, 1e, and 1g exhibits a linear correlation to the Hammett constant (σ_p) of the para substituent on the phenylacetylide ligand (see Figure S22 of Supporting Information). The effects of the π -conjugation length of the oligo phenylacetylide ligands on the emission of $(C^N^N)Pt(C \equiv CC_6H_4)_n$ -R in CH₃CN solution is salient. When the conjugation length of the phenylacetylide ligand increases from ethynylbenzene monomer in 1a to phenylene ethynylene trimer in 1j, the corresponding emission energy blue-shifts from 584 nm (1a) to 572 nm (1j). The same trend was observed for complexes 1d and 1k. For complexes with stronger electrondonating substituent on the phenylacetylide ligand, i.e., 1d, 1g, and 1h, the lifetimes are much shorter and the emission quantum yields are much lower. This could be attributed to the presence of low-lying nonemissive ³LLCT state, which adds an additional decay pathway.

Concentration-dependency study in CH₂Cl₂ reveals that from 2.5×10^{-6} mol/L to 5×10^{-5} mol/L the intensity of the emission keeps increasing with the increased concentration. However, the lifetime keeps decreasing at higher concentrations, indicating a self-quenching effect. The self-quenching rate constant deduced from the Stern–Volmer plot is 1.63×10^9 for **1a**, 5.19×10^9 for **1c**, 5.40×10^9 for **1f**, and 4.04×10^9 for **1k**, which are of the same order as those reported for many other platinum terpyridyl or C^N^N complexes by our group and several other groups.^{1,9,11,26,29}

It is also interesting to note that the emission energies for all the complexes are similar to their respective platinum C^N^N congeners without the 4-phenyl substituent.^{1,2} This feature is consistent with that observed from the UV–vis absorption study, indicating the twist of the phenyl substituent from the plane of the (C^N^N)Pt component. In X-ray diffraction crystallography study of complex **1b**,²⁰ the dihedral angle between the phenyl ring at the 4-position of the C^N^N ligand and the plane of the (C^N^N)Pt moiety is 142.8°. Obviously, electronic interaction between the phenyl substituent and the C^N^N ligand is minimized. However, introducing the phenyl substituent on the C^N^N ligand pronouncedly enhances the emission efficiency and increases the emission lifetime for these complexes compared to their respective Pt complexes without the phenyl substituent in CH₂Cl₂.^{1.2}

Transient Difference Absorption. Transient difference absorption (TA) spectroscopy measures the absorption difference between the ground state and the excited state. A positive TA band indicates stronger excited-state absorption than that of the ground-state, while a negative band (bleaching band) suggests stronger ground-state absorption than that of the excited state. Additionally, when monitoring the decay of the TA at a given wavelength, the lifetime of the excited state contributing to the TA can be obtained. Because many of the platinum C^N^N complexes exhibit broad and moderately strong excited-state absorption in the visible to the near-IR region,^{9,11,17,18} and the lifetimes measured from the decay of the emission of 1a-1k suggest that the triplet excited state is much more long-lived than the excitation pulsewidth (4.1 ns). Therefore, triplet excitedstate absorption is expected to be observed for these complexes. Figure 5 displays the triplet TA spectra of 1a, 1e, 1j, and 1k at the zero-time delay and the time-resolved TA spectra of 1c in degassed CH₃CN solution. The TA spectra of 1b and 1f are similar to that of 1k (see Figure S23 of Supporting Information). The TA absorption band maxima, the excited-state lifetimes deduced from the decay of the TA, the excited-state absorption coefficients, and the triplet quantum yields for these complexes are listed in Table 1. The TA spectra of 1d, 1g, 1h, and 1i were unable to be measured partially due to the shorter excited-state lifetime as indicated by the emission lifetime. Another possible reason could be related to their lower triplet excited-state quantum yields, which is suggested by their significantly lower emission quantum yields compared to the other complexes in this series.

The spectral features for these complexes are quite different. **1a** and **1c** exhibit a bleaching band below 475 nm and broad, structureless absorption bands in the visible to the NIR region. The bleaching bands occur at the similar position as the lowestenergy absorption bands in their respective UV-vis absorption spectrum. The lifetimes obtained from the decay of the TA in CH₃CN are in line with those measured from the decay of the emission. These facts suggest that the TA for **1a** and **1c** possibly emanate from the same excited state that emits or a state in

TABLE 2:	Emission	Energy,	Lifetime,	and	Quantum	Yield of 1	la–1k in	Different	Solvents a	t Room	Temperature
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	$\lambda_{ m em}/ m nm~(au_{ m em}/ m ns;~\Phi_{ m em})$								
	CH ₃ CN	CH ₃ OH	CH ₂ Cl ₂	hexane	toluene				
1a	584 (500; 0.048)	582 (150; 0.014)	588 (750; 0.073)	604 (^{<i>a</i>} ; 0.002)	592 (670; 0.084)				
1b	570 (360; 0.073)	575 (100; 0.011)	576 (1060; 0.127)	587 (^a ; 0.0005)	577 (430; 0.103)				
1c	555 (380; 0.024)	a	558 (1060; 0.180)	571 (; 0.0004)	565 (470; 0.185)				
1d	584 (90; 0.0007)	593 (^a ; 0.0008)	576 (430; 0.003)	a	618 (210; 0.004)				
1e	592 (250; 0.018)	593 (180; 0.014)	595 (390; 0.034)	592 (370; 0.001)	600 (510; 0.035)				
1f	582 (410; 0.062)	584 (210; 0.021)	588 (820; 0.072)	602 (540; 0.001)	591 (740; 0.110)				
1g	601 (190; 0.003)	595 (^a ; 0.0007)	576 (530; 0.007)	a	578 ^a				
1ĥ	593 (70; 0.004)	576 (60; 0.007)	595 (170; 0.016)	а	595 (390; 0.051)				
1i	568 (280; 0.015)	589 (200; 0.016)	595 (460; 0.036)	594 (480; 0.003)	599 (660; 0.076)				
1j	572 (550; 0.047)	583 (270; 0.02)	586 (890; 0.078)	592 (^{<i>a</i>} ; 0.001)	589 (530; 0.082)				
1k	569 (210; 0.021)	578 (140; 0.01)	583 (890; 0.101)	609 (800; 0.003)	588 (1040; 0.105)				

^a Signal too weak to be detected.



Figure 5. (a) Triplet transient difference absorption spectra of 1a, 1e, 1j, and 1k at zero delay after the laser excitation in CH₃CN solution. (b) Time-resolved TA spectra of 1c in CH₃CN solution. $\lambda_{ex} = 355$ nm.

equilibrium with the emitting state. Thus, this state possibly consists of ³MLCT/³ILCT characters. The TA spectra of **1b**, **1f**, and **1k** are quite similar, with two absorption bands at 400 and 600 nm respectively. Almost no bleaching was observed for these three complexes. The TA lifetime and the emission lifetime for these three complexes are of the same order, but the lifetime deduced from the decay of TA is somewhat longer than that obtained from the decay of emission. This implies that the emitting state and the TA state possibly have different compositions of the ³MLCT and ³ILCT characters. Alternatively, there could be some extent of configurationally mixing of the acetylenic ${}^{3}\pi,\pi$ character. The TA spectrum of **1e** composes of two obvious absorption bands, one appearing at \sim 395 nm and another broad, somewhat structured one from 500 to 800 nm. The TA lifetime of **1e** is also longer than the emission lifetime, which could be attributed to the similar reason as we just discussed for **1b**, **1f** and **1k**.

The TA spectrum of 1j is drastically different from all the aforementioned complexes, with a bleaching band in the UV region and a relatively narrow positive band at 580 nm. The bleaching band occurs in the region of the acetylenic ligand $\pi^{1}\pi,\pi^{*}$ absorption band, and the lifetime of **1** j obtained from the decay of the TA in CH₃CN is \sim 15.5 μ s, which is much longer than that for a charge-transfer band and is quite distinct from that obtained from the decay of the emission for this complex. Taking these facts into account, we believe that the TA for 1j arises from the ${}^{3}\pi,\pi^{*}$ state of the oligo phenylene ethynylene ligand. Although it is unusual that the emitting state (³MLCT) and the excited state giving rise to the TA $({}^{3}\pi,\pi^{*})$ is different for 1j, this phenomenon is not unprecedented. The presence of an emissive ³MLCT state and a nonemissive lower-lying ${}^{3}\pi,\pi^{*}$ state than ³MLCT state has been reported by Turro and coworkers for a [Ru(bpy)₂(dppn)]²⁺ complex.³⁰ Unfortunately, the reason for this phenomenon is still not well understood.

Reverse Saturable Absorption. The TA spectra discussed above show that most of the complexes studied in this work exhibit broad positive absorption band in most of the visible to the near-IR region. This implies that their excited-state absorption is stronger than the ground-state absorption. Therefore, reverse saturable absorption (RSA) are expected to occur from these complexes under the irradiation of nanosecond laser pulses. To demonstrate this, the nonlinear transmission experiment was conducted for these complexes in CH_2Cl_2 solution. The experiment results are illustrated in Figure 6. Except for **1j** that has too low solubility in CH_2Cl_2 to obtain solution with 80% linear transmission; thus the data was not included for comparison, all of the other 10 complexes exhibit moderate to strong



Figure 6. Transmittance vs incident fluence curves for 1a-1k in CH₂Cl₂ for 4.1-ns laser pulses at 532 nm. The linear transmission was adjusted to 80% for each sample in a 2-mm cell.

TABLE 3: Ground-State (σ_0) and Excited-State (σ_{ex}) Absorption Cross Sections of the Platinum Complexes in CH₃CN at 532 nm

	1a	1b	1c	1d	1e	1f	1g	1i	1j	1k
$\sigma_0/10^{-18} \text{ cm}^2$	1.53	1.76	1.27	4.13	1.83	1.37	7.65	3.83	1.53	0.63
$\sigma_{\rm ex}/10^{-18}~{\rm cm}^2$	6.91	39.2	20.7		10.3	50.4			7.15	19.3
$\sigma_{\rm ex}/\sigma_0$	4.52	22.3	16.3		5.63	36.8			4.67	30.6
$\Phi_{\rm T}\sigma_{\rm ex}/\sigma_0$	1.85	4.01	2.61		0.73	2.94			0.84	3.37

transmission decrease with the increased incident fluence, indicating the occurrence of RSA. Among these complexes **1a** and **1k** exhibit the strongest RSA, with a RSA threshold (defined as the incident fluence at which point the transmittance drops to 70% of the linear transmittance) of 0.14 J/cm² and the transmission decreases to 0.28 when the incident fluence reaches 1.73 J/cm². The strength of the RSA for these ten complexes follows this trend: $1\mathbf{k} \approx 1\mathbf{a} > 1\mathbf{c} > 1\mathbf{f} \approx 1\mathbf{i} > 1\mathbf{h} \approx 1\mathbf{b} > 1\mathbf{e} > 1\mathbf{d} > 1\mathbf{g}$.

Our previous studies on RSAs reveal that two of the key factors that determine the strength of RSA are the ratio of the excited-state absorption cross section to that of the ground-state and the triplet excited-state quantum yield. The ground-state absorption cross sections at 532 nm for these complexes are listed in Table 3, which are deduced from the ε values obtained from their UV-vis absorption spectra and the conversion equation $\sigma = 2303\varepsilon/N_A$, where N_A is the Avogadro constant. The triplet excited-state absorption cross sections at 532 nm are estimated from the Δ OD at zero time delay and the $\varepsilon_{T_1-T_n}$ at the TA band maximum according to the method described previously by our group.³¹ The results are also compiled in Table 3. The $\Phi_T \sigma_{es}/\sigma_0$ value follows this trend: **1b** > **1k** > **1f** > **1c** >

1a > **1j** > **1e**. This trend essentially parallels the RSA trend except for **1a** and **1b**, implying that extending the conjugation length of the acetylide ligand and introducing electronwithdrawing substituent on the acetylide could reduce the ground-state absorption cross section while improving the triplet excited-state absorption cross section, which consequently increases the ratio of the σ_{ex}/σ_0 and improves the RSA. The disparity between the $\Phi_T \sigma_{ex}/\sigma_0$ value and the RSA result for **1a** and **1b** could be due to the fact that the σ_{ex}/σ_0 values listed in Table 3 are measured or estimated in CH₃CN solution, while the RSA measurement was conducted in CH₂Cl₂. Both the ground-state absorption and the excited-state absorption parameters could vary in different solvents.

Conclusions

The photophysics of mononuclear cyclometalated platinum(II) 4,6-diphenyl-2,2'-bipyridyl acetylide complexes 1a-1k were systematically investigated. The broad, moderately intense ¹MLCT/¹ILCT/¹LLCT absorption bands at 400-550 nm are systematically red-shifted in accordance with the electrondonating ability of the para substituent on the phenylacetylide ligand. Excitation of these complexes in solution at their respective charge-transfer band at room temperature results in orange luminescence, which can be assigned as ³MLCT/³ILCT emission. Except for 1d, 1g, 1 h, 1i, and 1j, all of the other complexes exhibit broad and relatively strong triplet excitedstate absorption in the visible extending to the near-IR region, which is tentatively attributed to the ³MLCT, ³ILCT, and/or ${}^{3}\pi,\pi^{*}$ states. Most of the complexes exhibit reverse saturable absorption for nanosecond laser pulses at 532 nm, with the RSA strength decreases following this trend: $1k \approx 1a > 1c > 1f \approx 1i$ > 1h \approx 1b > 1e > 1d > 1g, which is mainly determined by the ratio of the triplet excited-state absorption cross section to that of the ground state and the triplet excited-state quantum yield. Introducing electron-withdrawing substituent or extending the conjugation length of the acetylide ligand could reduce the ground-state absorption cross section while increasing the triplet excited-state absorption cross section. Consequently, the RSA for these complexes is improved. Moreover, introducing the phenyl substituent on the C^NN ligand pronouncedly increases the molar extinction coefficients for the low energy chargetransfer absorption band, enhances the emission efficiency and increases the emission lifetime.

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Supporting Information Available: The linear correlation between the various excited-state energies and the Hammett constant (σ_0), UV-vis absorption spectra and emission spectra

at room temperature for 1a-1e and 1g-1k in different solvents, and the time-resolved triplet transient difference absorption spectra of 1a, 1b, 1e, 1f, 1j, and 1k in CH₃CN. This material is available free of charge via the Internet at http://pubs.acs.org.

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