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Synthesis, tunable photophysics and nonlinear absorption of terpyridyl Pt(II) complexes bearing different acetylide ligands

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1. Introduction

Cyclometalated Pt(II) complexes have been attached huge attention in the past decade owing to their unique photophysical properties [1-3] and potential applications in probes [4-6], organic light-emitting devices (OLED) [7–11] and nonlinear optics [12–14]. Their rich properties and versatile applications are intrinsically based on the square-planar configuration of the cyclometalated Pt(II) complexes and the presence of multiple charge transfer excited states, such as metal-to-ligand charge transfer (MLCT), ligand-to-ligand charge transfer (LLCT), intraligand charge transfer (ILCT), in addition to the ligand localized π,π^* transitions. These features lead to long-lived triplet excited states, broadband excitedstate absorption (ESA) in the visible to the near-IR region, and room temperature phosphorescence. In addition, their photophysical properties can be readily tuned by structural modifications of the employed ligands to meet the specific requirements for each unique application [15–20].

ABSTRACT

A series of 4-phenyl-2,2'; 6',2"-terpyridyl Pt(II) complexes bearing different σ -alkynyl ancillary ligands (**1a–1f**) were synthesized and characterized. All complexes exhibit strong ${}^{1}\pi,\pi^{*}$ absorption bands in the UV region; and broad, structureless metal-to-ligand charge transfer (${}^{1}MLCT$)/ligand-to-ligand charge transfer (${}^{1}LLCT$) absorption bands in the visible region. When excited at the charge-transfer absorption band, the complexes exhibit yellow to red luminescence ($\lambda_{max} = 553-608$ nm) in CH₃CN at room temperature, which is attributed to the ${}^{3}MLCT$ / ${}^{3}LLCT$ state, except **1c**. The emitting state of **1c** exhibits a significant intraligand ${}^{3}\pi,\pi^{*}$ character, which is originated from the naphthalimide acetylide ligand. Complexes **1a–1c** exhibit moderate triplet transient absorptions from visible to NIR region, where reverse saturable absorption (RSA) occurs. The photophysical, electrochemical and nonlinear absorption properties of these Pt(II) complexes can be tuned drastically by the different acetylide ligand, which would be useful for rational design of broadband nonlinear absorption materials.

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Among these cyclometalated square-planar platinum complexes, 2,2'; 6',2"-terpyridyl (N^NN) Pt(II) acetylide complexes are particularly intriguing by virtue of their relatively intense emission, broadband nonlinear absorption and the ease of structural modification on both of the terpyridine ligand and acetylide ligand [12-18,20]. Previous studies on terpyridyl Pt(II) acetylide complexes demonstrated the ¹MLCT/¹LLCT absorption band energy and the emission energy of the complexes were significantly affected by the electron-donating or electron-withdrawing ability of the substituent(s) on the acetylide ligand. However, no monotonic trend was observed on the emission energy, lifetime and quantum yield when varying the substituents on the acetylide ligands, which might be caused by the admixture of multiple excited states in proximity. By modification of the acetylide ligands, the lowest triplet excited state of the terpyridyl Pt(II) complexes could be tuned to a ³MLCT state, a ${}^{3}\pi,\pi^{*}$ state localized on acetylide ligand, or a mixture of the ³MLCT and ³ π , π * states [12–14,16,17]. Moreover, the strong electron-donating substituent (such as a diphenylamino group) and strong electron-withdrawing substituent (such as the nitro group) on the acetylide ligands could change the nature of the lowest triplet excited state from a charge transfer triplet excited state to predominantly acetylide ligand-localized ${}^{3}\pi,\pi^{*}$ state [19,20].







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Intrigued by this preliminary study, we are interested in further understanding the effect of introducing aromatic substituents on the acetylide ligand of terpyridyl Pt(II) complexes. To the best of our knowledge, studies on the nonlinear optical properties and structure-property correlation of the terpyridyl Pt(II) complexes with extended π -conjugated substituents acetylide ligands are still limited. Understanding how the nature of these electron-donating or -withdrawing substituents influence the photophysics of Pt(II) complexes is essential for rational design of Pt(II) complexes as efficient photonic materials, such as electroluminescent materials and nonlinear absorbing materials.

In this work, a series of novel 4-phenyl-2,2'; 6',2"-terpyridyl Pt(II) complexes bearing different acetylide ligands (Scheme 1) were designed and synthesized. The nitro- and naphthalimidegroups were chosen as electron-withdrawing substituents, while the carbazolyl- and diphenylamino-groups were selected as electron-donating substituent. Their photophysical properties and excited-state absorption were systematically investigated in order to understand the structure-property correlations for developing efficient nonlinear absorbing materials and organic light-emitting materials.

2. Experimental section

2.1. Materials

 K_2 PtCl₄ was purchased from Jiulin Shanghai Company, and all the other reagents were purchased from Aladdin. Tetrahydrofuran (THF) and *N*,*N*-diisopropylethylamine (DIEA) were distilled under N_2 over sodium benzophenone ketyl. Acetonitrile were purified by redistillation. Tetra-n-butylammonium perchlorate (TBAP) and ferrocene were purified by recrystallization twice from ethanol. All other reagents were used as received. 4-phenyl-2,2'; 6',2"-terpyridyl [21,22] and arylacetylide ligands [23–26] were synthesized according to literature methods.

2.2. Measurements

Synthesis and Characterization. All complexes were characterized by ¹H NMR, elemental analysis, and MS. ¹H NMR spectra were recorded on a Bruker 300 MHz or 400 MHz spectrometer using DMSO- d_6 as the solvent, with tetramethylsilane as internal standard. The elemental analyses were performed with a Vario El III elemental analyzer. Mass analyses were performed on an Agilent 1100 mass spectrometer.

Photophysical Measurements. Optical absorption spectra were obtained by using a Cary-5000 UV/vis/near-IR Spectrophotometer. Photoluminescence spectra were carried out on a Fluoro-Max 4 fluorometer/phosphorometer. The nanosecond transient difference absorption spectra, triplet excited-state lifetimes and triplet excited-state quantum yields were measured on an Edinburgh LP920 laser flash photolysis spectrometer. The excitation source was the third harmonic output (355 nm) of a Nd:YAG laser (Quantel Brilliant, pulsewidth ~4.1 ns, 1 Hz). Before each measurement, the sample solutions were degassed with Ar for 30 min.

Electrochemical Measurements. The electrochemical experiments were carried out using a CHI 660C electrochemistry workstation (CHI-USA). A standard one-compartment three-electrode cell was used with a Pt electrode as the working electrode, a Pt wire as the counter electrode and a Ag/Ag⁺ electrode (Ag in 0.1 M AgNO₃ solution) as the reference electrode. TBAP (0.1 M) was used as the supporting electrolyte. The films of these complexes were coated on the Pt working electrode and the scan rate was 100 mVS⁻¹.

Nonlinear Transmission Measurement. A plano-convex lens (f = 40 cm) was used to focus the beam to the sample cuvette. The radius of the beam waist at the focal point was approximately 96 μ m. A Quantel Brilliant nanosecond laser (4.1 ns pulses) with a repetition rate of 10 Hz was used as the light source.

2.3. Synthesis

2.3.1. Synthesis of complex [Pt(tpy)Cl]Cl (2)

4-Phenyl terpyridine (0.0619 g, 0.2 mmol) was dissolved in 30 mL hot CH₃CN and K₂PtCl₄ (0.0830 g, 0.2 mmol) was dissolved in 10 mL H₂O. The solutions were then mixed, and heated to reflux for 24 h. After cooling to room temperature, the mixture was filtered, washed with water (10 mL), ether (5 mL) and CH₂Cl₂ (20 mL) to afford a brown solid (0.086 g, 79.5%). ¹H NMR (500 MHz, DMSO-*d*₆): δ ppm 8.93 (s, 2H), 8.83 (d, *J* = 7.95, 2H), 8.70 (d, *J* = 5.1 Hz, 2H), 8.45–8.42 (m, 2H), 8.20–8.18 (m, 2H), 7.84 (t, *J* = 6.32, 2H), 7.68–7.65 (m, 3H).

2.3.2. General procedure for synthesis of complexes 1a-1f

Arylacetylide compound (0.1 mmol) and KOH (11.2 mg, 0.2 mmol, 2.0 equiv.) were dissolved in MeOH (20 mL) under stirring at room temperature for 30 min. Then complex **2** (57.4 mg, 0.1 mmol, 1.0 equiv.) and CuI (1.2 mg, 0.06 mmol, 0.6 equiv.) were



Scheme 1. Synthetic routes for Pt(II) complexes 1a-1f.

added. The mixture was purged under N₂ for 30 min, and then stirred at room temperature for 18 h. After the reaction, the reaction mixture was concentrated, and ether was added. The precipitants were separated by filtration. The solid was dissolved in 20 mL MeOH, then 20 mL saturated aqueous solution of NH₄PF₆ was added at room temperature. The mixture was stirred at room temperature for 3 h, then the solid was filtered, washed with ether and CH₂Cl₂ to give the desired product.

2.3.2.1. Complex [*Pt*(*tpy*)(*C*=*C*-*C*₆*H*₅)]*PF*₆ (**1a**). Yield was 77.3% as red solid. ¹H NMR (DMSO-*d*₆, 300 MHz): δ ppm 9.20 (d, *J* = 3.1 Hz, 2H), 9.05 (s, 2H), 8.88 (d, *J* = 4.7 Hz, 2H), 8.55 (t, *J* = 4.8 Hz, 2H), 8.18 (d, *J* = 3.8 Hz, 2H), 7.95 (d, *J* = 4.0 Hz, 2H), 7.69 (d, *J* = 4.0 Hz, 3H), 7.51 (d, *J* = 4.4 Hz, 2H), 7.35 (t, *J* = 4.5 Hz, 2H), 7.28 (t, *J* = 4.5 Hz, 1H). ESI-MS: *m*/*z* calcd for [C₂₉H₂₀N₃Pt]⁺, 605.1; Found 605.1. Anal. Calcd. (%) for C₂₉H₂₀F₆N₃PPt: C, 46.41; H, 2.69; N, 5.60. Found: C, 46.32; H, 2.73; N, 5.52.

2.3.2.2. Complex $[Pt(tpy)(C \equiv C - C_6H_4 - NO_2)]PF_6$ (**1b**). Yield was 81.6% as orange solid. ¹H NMR (DMSO-*d*₆, 500 MHz): δ ppm 8.89 (s, 2H), 8.82 (d, J = 5.3 Hz, 2H), 8.76 (d, J = 8.0 Hz, 2H), 8.42 (t, J = 7.4 Hz, 2H), 8.04 (d, J = 8.3 Hz, 4H), 7.72 (t, J = 6.4 Hz, 2H), 7.59 (d, J = 6.7 Hz, 3H), 7.53 (d, J = 8.5 Hz, 2H). ESI-MS: *m/z* calcd. for $[C_{29}H_{19}N_4O_2Pt_{195}]^+$, 650.12; Found 650 (100%). Anal. Calcd. (%) for $C_{29}H_{19}F_6N_4O_2PPt$: C, 43.78; H, 2.41; N, 7.04; found C, 43.73; H, 2.64; N, 7.12.

2.3.2.3. Complex [*Pt*(*tpy*)(*C*=*C*-*C*₆*H*₄−*NI*)]*PF*₆ (**1***c*). Yield was 78.1% as orange solid. ¹H NMR (DMSO-*d*₆, 500 MHz): δ ppm 9.09 (s, 1H), 8.98 (s, 2H), 8.88 (s, 3H), 8.74 (d, *J* = 8.1 Hz, 1H), 8.50–8.59 (m, 3H), 8.37 (d, *J* = 8.1 Hz, 1H), 8.00 (s, 1H), 8.04 (s, 2H), 7.91–8.01 (m, 3H), 7.68 (d, *J* = 3.2 Hz, 1H), 7.61 (s, 2H), 4.05 (d, *J* = 8.5 Hz, 2H), 1.65 (t, *J* = 6.0 Hz, 2H), 1.37 (t, *J* = 7.6 Hz, 2H), 0.96 (t, *J* = 7.6 Hz, 3H). ESI-MS: *m/z* calcd. for [C₃₉H₂₉N₄O₂Pt]⁺, 780.2; Found 780.2. Anal. calcd. (%) for C₃₉H₂₉F₆N₄O₂PPt: C, 50.60; H, 3.16; N, 6.05; Found C, 50.47; H, 3.22; N, 6.07.

2.3.2.4. Complex [Pt(tpy)($C \equiv C - C_6 H_4 - C_2$)]PF₆ (**1d**). Yield was 71.3% as brown solid. 1H NMR (DMSO- d_6 , 500 MHz): δ ppm 9.15 (d, J = 4.5 Hz, 1H), 8.79 (d, J = 8.1 Hz, 1H), 8.62 (s, 1H), 8.42 (t, J = 7.1 Hz, 1H), 8.37 (s, 1H), 8.25 (d, J = 7.8 Hz, 2H), 8.12 (d, J = 6.8 Hz, 2H), 7.93–7.89 (m, 2H), 7.84 (d, J = 7.3 Hz, 1H), 7.67–7.60 (m, 5H), 7.53 (d, J = 8.6 Hz, 2H), 7.48–7.42 (m, 4H), 7.30 (t, J = 7.3 Hz, 2H), 7.18 (t, J = 7.3 Hz, 1H), 7.13 (t, J = 7.3 Hz, 1H). ESI-MS: *m/z* calcd. for [C₄₁H₂₇N₄Pt]⁺, 770.2; Found 770.2. Anal. calcd. (%) for C₄₁H₂₇F₆N₄PPt: C, 53.78; H, 2.97; N, 6.12; Found C, 53.74; H, 2.92; N, 6.22.

2.3.2.5. *Complex* [*Pt(tpy)*($C \equiv C - C_6 H_4 - t - BuCz$)]*PF*₆ (**1e**). Yield was 70.6% as brown solid. ¹H NMR (DMSO-*d*₆, 500 MHz): δ ppm 8.89 (s, 2H), 8.86 (d, *J* = 6.5 Hz, 2H), 8.79–8.82 (m, 4H), 8.69 (d, *J* = 8.0 Hz, 2H), 8.64–8.66 (m, 2H), 8.31 (t, *J* = 3.6 Hz, 1H), 8.09–8.11 (m, 2H), 7.79 (t, *J* = 6.0 Hz, 2H), 7.63–7.66 (m, 4H), 7.54 (t, *J* = 2.0 Hz, 2H), 7.14 (d, *J* = 8.2 Hz, 2H), 2.50 (s, 18H). ESI-MS: *m/z* calcd. for [C₄₉H₄₃N₄Pt]⁺, 882.3; Found 887.3. Anal. calcd. (%) for C₄₉H₄₃F₆N₄PPt: C, 57.25; H, 4.22; N, 5.45; found C, 57.29; H, 4.31; N, 5.43.

2.3.2.6. *Complex* [*Pt(tpy)*($C \equiv C - C_6H_4 - NPh_2$)]*PF*₆ (**1***f*). Yield was 79.3% as black solid. ¹H NMR (DMSO-*d*₆, 500 MHz): δ ppm 9.07 (d, *J* = 4.6 Hz, 2H), 9.02 (s, 2H), 8.84 (d, *J* = 7.6 Hz, 2H), 8.51 (t, *J* = 7.4 Hz, 2H), 8.17 (d, *J* = 3.1 Hz, 2H), 7.89 (t, *J* = 6.5 Hz, 2H), 7.66 (d, *J* = 2.1 Hz, 3H), 7.34 (t, *J* = 7.7 Hz, 6H), 7.03-7.11 (m, 6H), 6.92 (d, *J* = 8.0 Hz, 2H). ESI-MS: *m/z* calcd. for [C₄₁H₂₉N₄Pt]⁺, 772.2; Found 772.2

(100%). Anal. calcd. (%) for $C_{41}H_{29}F_6N_4PPt$: C, 53.66; H, 3.19; N, 6.10; Found C, 53.61; H, 3.22; N, 6.16.

3. Results and discussion

3.1. Synthesis and characterization

Scheme 1 outlines the synthesis of the Pt(II) 4-phenyl-2,2'; 6',2"-terpyridyl acetylide complexes. Pt(II) acetylide complexes derived from these precursors were prepared by employing Sonogashira's conditions (terminal alkynes, CuI/KOH/CH₃OH) and were obtained in 70–81% yield. All complexes are air-stable and soluble in acetone, acetonitrile, dimethyl formamide and dimethyl sulfoxide. The complexes were characterized by ¹H NMR spectra, MS, and elemental analyses to confirm their structures. All of the complexes have distinct, well-resolved patterns in their aromatic proton resonances, which are attributable to the protons of the pyridine rings and phenyl substituents. ¹H NMR spectra showed obvious changes of chemical shifts for pyridine protons (δ 7.8–9.9 ppm) after coordination with the Pt(II) metal ion and upon exchange of chloride for acetylide, particularly the protons nearest to the acetylide moiety.

3.2. Optical properties

3.2.1. Electronic absorption spectra

The UV-vis absorption spectra of complexes 1a-1f were measured in CH₃CN at different concentrations. No ground-state aggregation was observed in the concentration range investigated $(1 \times 10^{-6} \text{ to } 1 \times 10^{-4} \text{ mol } L^{-1})$, which is reflected by the compliance of the absorbance with the Beer's law. The UV-Vis absorption spectra of complexes 1a-1f in CH₃CN solution are presented in Fig. 1, and the optical characteristics are summarized in Table 1. All of the spectra exhibit intense absorption bands below 380 nm, which can be assigned to the $\pi - \pi^*$ transition within the acetylide and terpyridyl ligands, while the broad, moderately intense absorption bands at 380-600 nm are assigned to the mixed ¹MLCT/¹LLCT/¹ILCT transitions. These are also in line with the terpyridyl Pt(II) acetylide complexes reported previously [12–14,16,17,20]. The charge transfer nature of the low-energy absorption bands in 1a-1f is also supported by the solventdependency studies. As exemplified in Fig. 2 for 1a, these lowenergy absorption bands bathochromically shift to longer wavelengths in solvents with lower polarity (*i.e.*, toluene and THF)



Fig. 1. UV-vis absorption spectra of 1a-1f in CH₃CN solution.

Table 1

Photophysical parameters of complexes 1a-1f .					
Complex	$\lambda_{abs}/nm \ (\epsilon/10^4 \ L \ mol^{-1} \ cm^{-1})^a$	$\lambda_{\rm em}/{\rm nm}~(au_{\rm em}/{\rm ns};~\Phi_{\rm em})$ R.T. ^b	$\lambda_{ m T1-Tn}/ m nm~(au_{ m TA}/ m ns;~arepsilon_{ m T1-Tn}/ m 10^{4}~ m L~ m mol^{-1}~ m cm^{-1};~arPsi_{ m T})^{c}$		
1a	264 (5.54), 309 (2.91), 341 (1.55), 454 (0.79)	604 (820; 0.003)	705 (815, 4.20, 0.92)		
1b	288 (3.31), 337 (3.10), 421 (1.21)	553 (30, 0.001)	650 (40, 2.73, 0.51)		
1c	284 (5.43), 331 (2.37), 387 (2.08), 450 (1.02)	621 (10, 0.011), 674 (sh)	560 (8370, 1.94, 0.85)		
1d	290 (5.03), 307 (3.74), 404 (0.64), 468 (0.42)	608 (^c)	c		
1e	283 (4.74), 331 (2.82), 404 (0.87), 482 (0.18)	608 (^c)	с		
1f	290 (4.95), 312 (4.72), 409 (0.57), 512 (0.56)	c	c		

^a Electronic absorption band maxima and molar extinction coefficients in CH₃CN at room temperature.

^b Room temperature emission band maxima and decay lifetimes measured in CH₃CN at a concentration of 1 × 10⁻⁵ mol/L. A degassed aqueous solution of [Ru(bpy)₃]Cl₂ $(\Phi_{\rm em} = 0.042,$ excited at 436 nm) was used as the reference.

Too weak to be measured.

^d Nanosecond TA band maxima, triplet extinction coefficients, triplet excited-state lifetimes and quantum yields in CH₃CN/DMF mixture (9:1, v/v). SiNc in C₆H₆ was used as the reference. ($\varepsilon_{590} = 70,000 \text{ Lmol}^{-1}.\text{cm}^{-1}, \Phi_{\text{T}} = 0.20$).



Fig. 2. Normalized UV-vis absorption spectra of complex 1a in different solvents. The concentration of each solution was adjusted in order to obtain A = 0.08 at 436 nm in a 1 cm cuvette.

compared to those in more polar solvents (*i.e.*, CH₃CN and CH₂Cl₂). This negative solvatochromic effect is indicative of a chargetransfer transition, in which the dipole moment of the ground state is larger than that of the excited state. The same solvent effect is observed for all of the other complexes studied in this work, and the results are provided in Fig. S1-S6 of the Supporting Information.

For most of the complexes, except 1b, the low-energy absorption band appears to be two distinct bands in this region. The band at about 380–430 nm appears to be insensitive to the ancillary substituents of the acetylide ligand, which emanate from the $d\pi$ (Pt) $\rightarrow \pi^*(N^N)^{1}$ MLCT excited state. However, in the region of about 430-600 nm, the lower energies transitions are influenced significantly by the nature of the ancillary substituents. Electrondonating substituents, such as carbazole, 3,6-di-tert-butyl-carbazole and NPh₂, cause a pronounced red-shift of this transition, while electron-withdrawing substituents such as NO2 and naphthalimide induce a blue-shift compared to complex 1a. Considering the sensitivity of the lower-energy transitions to the substituents at the acetylide ligands, we assigned these transitions to ¹LLCT transition. The calculation results indicate that the LUMO is almost exclusively π^* (terpyridine) based for the terpyridyl Pt(II) acetylide complexes; while the compositions of the HOMO are delocalized on both of the Pt metal and acetylide ligand (Fig. S7 and Table S1).

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 electron-withdrawing substituent stabilizes the acetylidebase HOMO. Consequently, the energy difference between the acetylide-based HOMO and the terpyridine-based LUMO will be varied and the bathochromic shift or hypsochromic shift occurs [18,19]. These results are also in line with the bi/terpyridine Pt(II) acetylide complexes reported previously [12–14,16–20].

For complex **1b**, it is noted that it has an intense structureless absorption band at $\lambda_{max} = 421 \text{ nm} (\varepsilon \approx 1.21 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1})$, which is significantly different from those of the other complexes. This band is attributed to the ¹MLCT/¹LLCT transitions mixed with a significant ${}^{1}\pi,\pi^{*}$ transition component. This phenomenon could also observed in the absorption spectrum of complex 1c, which exhibits an additional intense absorption band at 387 nm $(\varepsilon \approx 2.08 \times 10^4 \text{ L mol}^{-1} \text{ cm}^{-1})$. In addition, considering the extended π -conjugation of the acetylide ligands and the strong electron-withdrawing ability of the NO₂ substituent in **1b**, ¹ILCT within the 4-nitrophenylacetylide ligand is also likely to contribute to this band [19,27,28].

3.2.2. Photoluminescence

The emission characteristics of Pt(II) complexes 1a-1f were investigated in different solvents at room temperature. The normalized emission spectra of Pt complexes in CH₃CN at the



Fig. 3. Normalized emission spectra of Pt(II) complexes ($\lambda_{ex} = 436$ nm) in degassed CH₃CN solution ($c = 1 \times 10^{-5}$ mol L⁻¹).

concentration of 1×10^{-5} mol L⁻¹ are illustrated in Fig. 3, and the emission lifetimes and the emission quantum yields are provided in Table 1. Except for **1f**, excitation of these Pt(II) complexes at their respective charge-transfer band at room temperature results in yellow to red luminescence. The emissions exhibit significant Stokes shifts, and the emission lifetimes in degassed CH₃CN solutions vary from tens to hundreds of ns. In addition, the emission is quite sensitive to oxygen quenching. Taking all these facts into account, we believe that their emissions emanate from a triplet excited state (T₁ excited state).

As shown in Fig. 3, 1a, 1b, 1d and 1e exhibit structureless emission in CH₃CN solution, suggesting a charge transfer character of their emitting state. Based on the literature precedents for the reported bi/terpyridine Pt(II) acetylide complexes, such emission could be attributed to the ³MLCT/³LLCT states [12–14,16,17,19,20]. The charge transfer nature of the emitting state could be supported by the solvent-dependency study (Fig. S8-12). For complex 1a, the nature of emitting state could be ³MLCT/³LLCT mixed with some ${}^{3}\pi,\pi^{*}$ character, which is supported by the minor solvatochromic effect (Fig. 4a). Complex 1b exhibit a negative solvatochromic effect (Fig. S9), *i.e.*, when the dielectric constant (ε) or $E_T(30)$ value of the solvent increases, the emission energy of the complex decreases. This negative solvatochromic effect indicates a charge-transfer transition of the complex, in which the dipole moment of the ground state is larger than that of the excited state, that is also a characteristic of the ³MLCT excited state [13,14,19,20,27,28]. In contrast, the emission spectrum of **1c** is not only red-shifted and more structured than the other complexes (with a vibronic spacing of approximately 1264 cm^{-1} in CH₃CN), but also exhibits minor solvatochromic effect (Fig. 4b). This is indicative of an emitting state with significant intraligand ${}^{3}\pi,\pi^{*}$ character originated from the naphthalimide acetylide ligand. It is also noted that complex 1d and 1e only exhibit very weak emission bands in CH₃CN, which was ascribed to the enhanced ICT (intramolecular charge transfer) state, particularly the ³LLCT state caused by the electron-donating carbazoyl group and 3,6-di-tert-butyl-carbazole groups [19,27,28]. Similarly, no emission was observed for complex **1f** by virtue of the strong electron-donating NPh2 group which quenches the radiative pathway [29]. In addition, 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 and toluene in comparison to those in coordinating solvents (the solvents which are able to coordinate with ions, like CH₃CN). The quenching of the emission in coordinating solvent like CH₃CN, suggests that the emitting state has Pt metal involved. This solvent induced quenching by coordinating solvents is commonly seen in Pt(II) complexes with a ³MLCT emitting state, which provides another solid evidence for the involvement of the ³MLCT character in the emitting state of these complexes.

Since **1a–1f** all contain the same terpyridyl ligand, their photoluminescent properties are influenced significantly by the natures of the acetylide ligands, especially the electron-donating or electron-withdrawing ability of the substituents on the ligands. Compared to **1a**, complex **1b** with electron-withdrawing substituent exhibits pronounced blue-shifted emission with structureless feature. Meanwhile, when electron-donating substituents are introduced, complex **1d** and **1e** show slight red-shifted and structureless emission bands with relative weak emission character. This trend is consistent with that observed for the ¹MLCT band in the UV–vis absorption spectra, which provides another piece of evident that the emission has ³MLCT character. For complex **1c**, the nature of its emitting state is altered to a ${}^{3}\pi,\pi^{*}$ excited states by replacing the phenylacetylide ligand with the naphthalimide acetylide ligand.

3.2.3. Electrochemical properties

The electrochemical behaviors of **1a-1f** were investigated by cyclic voltammetry (CV). The electrochemical properties of these complexes were summarized in Table 3, and their CV curves were provided in Fig. S13. The reduction process occurring at -1.27to -1.62 V presumably corresponds to the one-electron reduction of the terpyridyl ligand. This process must be affected by the electron-donating ability of the para-substituent on the phenylacetylide ligand. The reduction waves are shifted to more negative direction by the electron-donating groups on the phenylacetylide ligand. For example, carbazole shift the reduction peak to -1.41 V, and diphenylamino shift the reduction peak to -1.62 V for **1d** and 1f. Meanwhile, compared to 1a, the complexes bearing electronwithdrawing groups on the acetylide ligands show more positive reduction waves (-1.31 for 1b and -1.27 for 1c). All complexes show an irreversible oxidation wave at 0.72-0.76 V, which can be tentatively assigned to a Pt^{II/III} process [30].

3.2.4. Transient absorption

The nanosecond (ns) transient absorption (TA) spectra of the complexes were studied to understand the excited-state behaviors of the triplet excited states and to predict the spectral region where reverse saturable absorption (RSA, *i.e.* transmission decreases with increased incident energy) occurs. Fig. 5 displays the triplet TA spectra of **1a**–**1c** at the zero-time delay and the time-resolved TA spectra of **1a**–**1c** in degassed CH₃CN solution. The triplet excited-state lifetimes deduced from the TA decay profile are listed in Table 1. The TA spectra of **1d**–**1f** were unable to be measured due to the shorter excited-state lifetime and lower triplet excited-state quantum yields as indicated by the emission lifetime and emission quantum yields (Table 1).

As presented in Fig. 5, all complexes exhibit bleaching bands below 480 nm. However, the spectral features of 1a-1c are



Fig. 4. Normalized emission spectra of (a) complex **1a** and (b) complex **1c** in different solvents at room temperature, $\lambda_{ex} = 436$ nm.

Table 2	
Emission energy, lifetime and quantum yield of 1a-1f in different solvents at room temperature	•

	$\lambda_{\rm em}/{\rm nm} (\tau_{\rm em}/{\rm ns}; \Phi_{\rm em}^{\rm a})$				
	CH ₃ CN	CH ₂ Cl ₂	THF	Toluene	
1a	604 (820; 0.003)	607 (2000; 0.009)	608 (200, 0.003)	612 (1500; 0.012)	
1b	553 (30, 0.001)	564 (360, 0.020)	b	570 (80, 0.005)	
1c	621 (10, 0.011)	623 (200, 0.018)	622 (15,0.012)	626 (1030, 0.006)	
1d	608 (^b)	608 (^b , 0.003)	b	b	
1e	608 (^b)	600 (^b , 0.001)	b	b	
1f	b	b	b	b	

^a A degassed aqueous solution of $[Ru(bpy)_3]Cl_2$ ($\Phi_{em} = 0.042$, excited at 436 nm) was used as the reference.

^b Too weak to be measured.

Table 3Electrochemical properties^a of complexes 1a-1f.

Complex	Oxidation E_{OX}^{peak} (V)	Reduction E_{re}^{peak} (V)
1a	0.73	-1.35, -1.62 ^b
1b	0.75	-1.31
1c	0.72	-1.27
1d	0.76	-1.41
1e	0.73	-1.46
1f	0.73	-1.62

^a Cyclic voltammetry of complex 1a–1f in CH₃CN at 298 K with 0.1 M Bu₄NClO₄ as supporting electrolyte; scanning rate: 100 mV/s; Value versus $E_{1/2}$ (Cp₂Fe^{+/0}) [0.08–0.10 V versus Ag/AgNO₃ (0.1 M in CH₃CN) reference electrode].

^b Irreversible under experimental conditions.

of the emission, implying that the TA of **1a** and **1b** likely emanates from the same excited state that emits or a state in equilibrium with the emitting state. Thus, the triplet excited state giving rise to the observed TA for **1a** and **1b** could be assigned to the ³MLCT/³LLCT/³ π,π^* excited state for **1a** and ³MLCT/³LLCT/³ILCT excited states for **1b**, respectively. For complex **1c**, the lifetime that obtained from the decay of the TA in CH₃CN is ~8.4 µs, 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. Thus, the TA for **1c** arises from the ³ π,π^* state of the naphthalimide acetylide ligand, possibly mixed with some ³MLCT/³LLCT characters.



Fig. 5. Triplet transient difference absorption spectra of **1a**–**1c** in CH₃CN at 0 time delay and time-resolved transient difference absorption spectra of **1a**–**1c**. ($A_{355} = 0.4$ in CH₃CN in a 1 cm cuvette, excited with a 355 nm pulsed-laser).

different. Complex **1a** exhibit a broad and structured absorption band in the visible to the NIR region, while complex **1b** shows a broad and structureless absorption band in this region.

The lifetimes of **1a** and **1b** obtained from the decay of the TA in CH_3CN (Table 1) are consistent with those measured from the decay

3.2.5. Nonlinear absorption

The positive TA bands of 1a-1c indicate stronger triplet excitedstate absorptions with respect to the ground-state absorptions at these wavelengths. Therefore, RSA is anticipated to occur in the visible or near-IR spectral region for these complexes. It is well known that reverse saturable absorption can lead to optical limiting, which reduces the transmittance when the laser intensity is higher than the limiting threshold. In addition, optical limiting of nanosecond laser pulses is generally dominated by the triplet excited-state absorption when the intersystem crossing time is shorter than the laser pulse width [31,32]. Thus, the optical limiting of nanosecond laser pulses by terpyridyl Pt(II) complexes should be dominated by the triplet excited-state absorption. In this case, complexes 1a-1c would be expected to enhance the optical limiting of nanosecond laser pulses.

To demonstrate this, a nonlinear transmission experiment in CH₃CN solution in a 2 mm cuvette was carried out using 4.1 ns laser pulses at 532 nm. The concentration of each complex solution was adjusted in order to obtain a linear transmission of 90% for easy comparison, Fig. 6 depicts the optical limiting curves for complexes **1a–1c**. With increased incident fluence, the output fluence of 1a–1c decreases drastically, which clearly indicates the occurrence of RSA at 532 nm. The strength of the RSA at 532 nm for these complexes follows the trend of 1a > 1c > 1b. Among these, 1a exhibits the strongest RSA, with an RSA threshold (defined as the incident fluence at which point the transmittance drops to 70% of the linear transmittance) of 0.30 J/cm², and the output fluence decreases to 0.97 I/cm^2 when the incident energy reaches ~2.5 I/cm^2 $cm^2 \mu$]. The optical limiting performances of these complexes are influenced by the different acetylide ligand, and the electronwithdrawing groups may advance the ability of the reverse saturable absorption. The strong optical limiting of **1a** could be related to its higher triplet excited-state absorption. The relatively high emission quantum vield, broad excited-state absorption, and strong nonlinear transmittance performance at 532 nm for 1a-1c suggest that these complexes could be promising candidates as nonlinear absorbing materials.

4. Conclusions

In summary, a series of 4-phenyl-2,2'; 6',2"-terpyridyl Pt(II) complexes bearing different aryl-acetylide ligands were synthesized and characterized. Their photophysical and electrochemical properties were investigated systematically with the aim of understanding the structure-property correlations and developing



Fig. 6. Optical limiting curves for complexes **1a–1c** in CH₃CN for 4.1 ns laser pulses at 532 nm.

novel photofunctional materials. The complexes exhibit ligandcentered ${}^{1}\pi,\pi^{*}$ transitions in the UV spectral region, and broad, structureless ¹MLCT/¹LLCT absorption bands in the visible spectral region. All complexes show yellow to red phosphorescence in solution at room temperature, which is mainly attributed to ${}^{3}\pi,\pi^{*}$ state for **1c** and ³MLCT/³LLCT state for other complexes. The nanosecond TA spectroscopic study indicates that these complexes exhibit moderate excited-state absorption from the visible to the near-IR region. Due to the stronger triplet excited-state absorption as compared to the ground-state absorption at 532 nm, moderate to strong RSA was observed at 532 nm for ns laser pulses from some of these complexes with a trend of 1a > 1c > 1b. It is found that the photophysical and electrochemical properties of these complexes were profoundly influenced by the electron-donating ability of the substituents on the acetylide ligands. We hope these complexes would serve as a model system for investigating structure-property relationships with respect to the nonlinear optical properties of cyclometalated square-planar Pt(II) complexes.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at http://dx.doi.org/10.1016/j.dyepig.2015.11.021.

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