

Photophysics and Optical Limiting of Platinum(II) 4'-Arylterpyridyl Phenylacetylide Complexes

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A series of platinum(II) 4'-aryl-2,2':6',2''-terpyridyl phenylacetylide complexes (**5–8**) with 4'-naphthyl, 4'-phenanthryl, 4'-anthryl, and 4'-pyrenyl substituents have been synthesized and characterized. The emission properties of these complexes and their corresponding platinum(II) 4'-aryl-2,2':6',2''-terpyridyl chloride complexes (**1–4**) at room temperature and 77 K have been systematically investigated. Except for the 4'-pyrenyl-2,2':6',2''-terpyridyl phenylacetylide complex that emits from an admixing state consisting of metal-to-ligand charge-transfer ($^3\text{MLCT}$), intraligand charge-transfer ($^3\text{ILCT}$), and $^3\pi,\pi^*$ characters, emissions of 4'-naphthyl, 4'-phenanthryl, and 4'-anthryl-2,2':6',2''-terpyridyl phenylacetylide complexes all originate from a $^3\text{MLCT}$ -dominant state. The emission lifetime of the 4'-pyrenyl-2,2':6',2''-terpyridyl phenylacetylide complex (**8**) is longer than 2 μs at room temperature, and more than 300 μs at 77 K, while the other three complexes possess an emission lifetime of 200–400 ns at room temperature and tens of microseconds at 77 K. Replacing the chloride ligand in the 4'-naphthyl, 4'-phenanthryl, and 4'-anthryl-2,2':6',2''-terpyridyl chloride complexes by a phenylacetylide ligand significantly increases the emission efficiency by an order of magnitude, and the emission lifetimes become longer. In contrast, such an alternation has no pronounced effect on the emission efficiency and lifetime of the 4'-pyrenyl-2,2':6',2''-terpyridyl complexes. In the transient difference absorption (TA) spectra of **5** and **6**, a moderately intense absorption band from 470 to 830 nm and a bleaching band between 400 and 470 nm were observed. For **7**, the TA spectrum features a narrow, weak bleaching band at ~ 380 nm and a strong, narrow band at ~ 420 nm, as well as a broad, structureless band from 470 to 750 nm. In addition, a fourth, positive band appears above 800 nm. Complex **8** exhibits a strong, narrow bleaching band at ~ 340 nm and a broad, positive band extending from 370 to 830 nm, with the band maximum appearing at ~ 520 nm. The lifetimes obtained from the kinetic transient absorption measurement coincide with those from the kinetic emission measurement, indicating that the transient absorption originates from the same excited state that emits or, alternatively, from a state that is in equilibrium with the emitting state. All complexes exhibit optical limiting for 4.1 ns laser pulses at 532 nm, with **8** giving rise to the strongest optical limiting, presumably because of the much longer triplet excited-state lifetime and the stronger transient absorption at 532 nm.

1. Introduction

Square planar platinum(II) complexes have been of great interest in recent years because of their potential applications in DNA intercalators,¹ protein probes,² chemosensors,³ photovoltaic cells,⁴ light-emitting devices,⁵ and optical limiters.⁶ Among these complexes, platinum terpyridyl complexes are particularly attractive for optical limiting applications, not only because of the presence of a planar configuration and multiple charge transfer states that could facilitate the electron delocalization, but also the excellent thermal and photochemical stabilities. In addition, the photophysical properties, such as the emission energy and the excited-state lifetime of these complexes can be readily tuned by varying the 4'-substituent on the terpyridyl ligand and by changing the monodentate ligand, as reported by many researchers in the literature.^{7,6b} McMillin and co-workers reported that both π -donating groups (such as NR_2) and π -accepting groups (such as CN) on the 4'-position of the terpyridyl ligand significantly increased the excited-state

lifetime,^{7a} and large conjugating aryl substituents such as pyrenyl even shifted the emitting state to a state involving metal-to-ligand charge-transfer ($^3\text{MLCT}$), intraligand charge-transfer ($^3\text{ILCT}$), and $^3\pi,\pi^*$ characters, which dramatically extended the excited-state lifetime to tens of microseconds.^{7c} Research conducted by the groups of Yam,^{7g} Wu,^{7h} and Sun^{6b} revealed that variations in the auxiliary substituents on the acetylide ligand drastically shifted the emission energy. Except for the profound effect of the 4'-substituents on the terpyridyl ligand and of the auxiliary substituents on the acetylide ligand on the photoluminescence characteristics, recent research by our group has found that variations in the arylacetylide ligand significantly change the excited-state absorption characteristics, and thus strongly impact the optical limiting performances of the complexes.^{6b} These results are intriguing; however, our previous study only focuses on the different arylacetylide ligands. The effect of the 4'-aryl substituent on optical limiting has not been investigated. Meanwhile, the influence of arylacetylide ligand on the photophysical properties of $\text{Pt}(4'\text{-Ar-trpy})\text{Cl}^+$ (trpy denotes 2,2':6',2''-terpyridine) systems has not been addressed in the literature.

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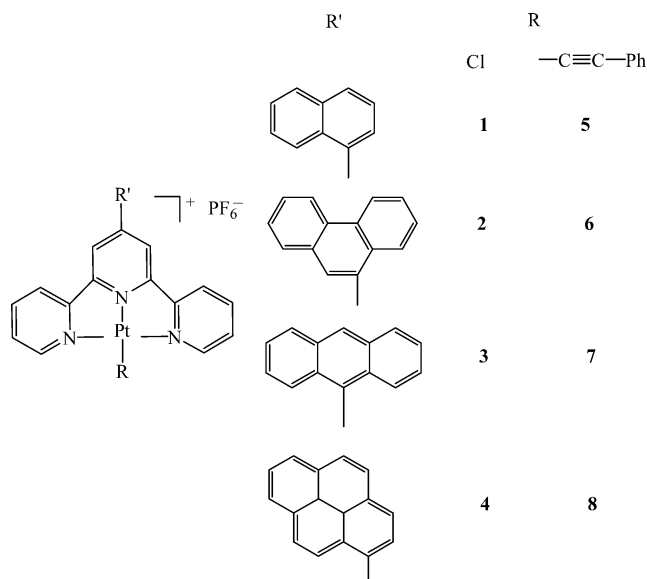


Figure 1. Structures of platinum(II) 4'-arylterpyridyl complexes.

To remedy these deficiencies, four platinum(II) 4'-Ar-terpy complexes (Ar = 1-naphthyl, 9-phenanthrenyl, 9-anthryl, and 1-pyrenyl) with a phenylacetylide ligand have been synthesized and characterized (structures shown in Figure 1). The phenylacetylide ligand was chosen based on our previous study on the platinum 4'-tolylterpyridyl arylacetylide complexes,^{6b} in which the complex with the phenylacetylide ligand exhibited the strongest optical limiting. The photophysical properties, including ultraviolet-visible (UV-vis) absorption, photoluminescence, transient difference absorption (TA), and the optical limiting properties of these four new complexes, have been systematically investigated and reported in this paper. For comparison purposes, $\text{Pt}(4'\text{-Ar-terpy})\text{Cl}\cdot\text{PF}_6$ complexes have also been synthesized and studied.

2. Experimental Section

Materials. 1-Pyrenecarboxaldehyde and phenanthrene-9-carboxaldehyde were purchased from Aldrich Chemical Co. Phenylacetylene, 1-naphthaldehyde, 9-anthraldehyde, potassium *tert*-butoxide, copper iodide, potassium tetrachloroplatinate, ammonium hexafluorophosphate, 2-acetylpyridine, spectrophotometric-grade acetonitrile, butyronitrile, and ammonium acetate were obtained from Alfa Aesar.

Characterizations. The structures of the synthesized compounds were characterized by ^1H NMR, electrospray ionization mass spectrometry (ESI-MS), and elemental analyses. ^1H NMR spectra were measured on a Varian Oxford-400 VNMR spectrometer. ESI-MS analyses were performed with a 3-Tesla Finnigan FTMS-2000 Fourier transform mass spectrometer at the Ohio State University. Elemental analyses were performed on a Perkin-Elmer 2400 Series II CHNS/O Analyzer.

Synthesis. The 4'-aryl-2,2':6',2''-terpyridine ligands were synthesized according to a literature procedure reported by Maestri and co-workers⁸ for 4'-(9-anthryl)-2,2':6',2''-terpyridine. The $[(4'\text{-Ar-terpy})\text{PtCl}]\text{PF}_6$ complexes were then synthesized by modification of the procedure reported by Cummings et al. for the $[\text{Pt}(\text{Cl}_3\text{terpy})\text{Cl}]\text{PF}_6$ complex.⁹ Chloroform instead of methanol was used as the solvent to dissolve the reactants 4'-aryl-terpy and $\text{Pt}(\text{dmsO})_2\text{Cl}_2$ (prepared using a published method¹⁰), and the reaction was carried out at room temperature for 24 h. The solid was separated by centrifugation, washed with chloroform completely, and then dissolved in dimethylforma-

mide. After removal of the insoluble components by filtration, a methanol solution of NH_4PF_6 was added, and then water was added dropwise. The mixture was stirred for 1 h; after that, the red solid was isolated and recrystallized using acetonitrile and ether.

$[(4'\text{-Np-terpy})\text{PtCl}]\text{PF}_6$ (1). UV-vis (CH_3CN) λ : 255, 284, 321, 334, 388, 408 nm. ^1H NMR (400 MHz, CD_3CN) δ : 7.63–7.77 (m, 6H), 8.05–8.21 (m, 8H), 8.44 (s, 2H), 8.68 (d, J = 4.8 Hz, 1H) ppm. ESI-MS (m/z): calcd. for $[\text{C}_{25}\text{H}_{17}\text{N}_3\text{ClPt}^{194}]^+$, 588.0741; found, 588.0748 (68%); calcd. for $[\text{C}_{25}\text{H}_{17}\text{N}_3\text{ClPt}^{195}]^+$, 589.0761; found, 589.0753 (84%); calcd. for $[\text{C}_{25}\text{H}_{17}\text{N}_3\text{ClPt}^{196}]^+$, 590.0763; found, 590.0705 (100%). Anal. Calcd for $\text{C}_{25}\text{H}_{17}\text{N}_3\text{ClPtPF}_6\cdot\text{H}_2\text{O}$: C, 39.84; H, 2.52; N, 5.58. Found: C, 39.42; H, 2.37; N, 6.15.

$[(4'\text{-Phen-terpy})\text{PtCl}]\text{PF}_6$ (2). UV-vis (CH_3CN) λ : 254, 284, 296, 320, 334, 409 nm. ^1H NMR (400 MHz, CD_3CN) δ : 7.73–7.87 (m, 7H), 7.99–8.13 (m, 3H), 8.20–8.42 (m, 4H), 8.51 (s, 2H), 8.82–8.98 (m, 2H), 9.06–9.12 (m, 1H) ppm. ESI-MS (m/z): calcd. for $[\text{C}_{29}\text{H}_{19}\text{N}_3\text{ClPt}^{194}]^+$, 638.0898; found, 638.0952 (74%); calcd. for $[\text{C}_{29}\text{H}_{19}\text{N}_3\text{ClPt}^{195}]^+$, 639.0918; found, 639.0936 (98%); calcd. for $[\text{C}_{29}\text{H}_{19}\text{N}_3\text{ClPt}^{196}]^+$, 640.0920; found, 640.0937 (100%). Anal. Calcd for $\text{C}_{29}\text{H}_{19}\text{N}_3\text{ClPtPF}_6$: C, 44.33; H, 2.42; N, 5.35. Found: C, 43.91; H, 2.55; N, 5.31.

$[(4'\text{-Anth-terpy})\text{PtCl}]\text{PF}_6$ (3). UV-vis (CH_3CN) λ : 253, 276, 284, 304, 319, 332, 347, 363, 383, 447 nm. ^1H NMR (400 MHz, CD_3CN) δ : 7.54–7.66 (m, 4H), 7.80–7.84 (m, 5H), 8.22–8.37 (m, 6H), 8.47 (s, 2H), 8.85 (s, 1H), 9.06–9.07 (m, 1H) ppm. ESI-MS (m/z): calcd. for $[\text{C}_{29}\text{H}_{19}\text{N}_3\text{ClPt}^{194}]^+$, 638.0898; found, 638.0916 (74%); calcd. for $[\text{C}_{29}\text{H}_{19}\text{N}_3\text{ClPt}^{195}]^+$, 639.0918; found, 639.0885 (99%); calcd. for $[\text{C}_{29}\text{H}_{19}\text{N}_3\text{ClPt}^{196}]^+$, 640.0920; found, 640.0885 (100%). Anal. Calcd for $\text{C}_{29}\text{H}_{19}\text{N}_3\text{ClPtPF}_6\cdot 4\text{H}_2\text{O}$: C, 40.64; H, 3.15; N, 4.90. Found: C, 40.35; H, 2.55; N, 4.82.

$[(4'\text{-Pyren-terpy})\text{PtCl}]\text{PF}_6$ (4). UV-vis (CH_3CN) λ : 263, 275, 283, 310, 327, 338, 380, 438 nm. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 7.90–8.04 (m, 2H), 8.10–8.22 (m, 1H), 8.22–8.44 (m, 6H), 8.44–8.60 (m, 4H), 8.68–8.80 (m, 2H), 8.97 (s, 4H) ppm. ESI-MS (m/z): calcd. for $[\text{C}_{31}\text{H}_{19}\text{N}_3\text{ClPt}^{194}]^+$, 662.0898; found, 662.0863 (63%); calcd. for $[\text{C}_{31}\text{H}_{19}\text{N}_3\text{ClPt}^{195}]^+$, 663.0918; found, 663.0871 (87%); calcd. for $[\text{C}_{31}\text{H}_{19}\text{N}_3\text{ClPt}^{196}]^+$, 664.0920; found, 664.0947 (100%). Anal. Calcd for $\text{C}_{31}\text{H}_{19}\text{N}_3\text{ClPtPF}_6\cdot 2\text{H}_2\text{O}$: C, 44.34; H, 2.50; N, 5.01. Found: C, 44.90; H, 3.10; N, 4.80.

General Procedure for Synthesis of $[(4'\text{-Ar-terpy})\text{Pt}(\text{C}\equiv\text{CPh})]\text{PF}_6$. The corresponding $[(4'\text{-Ar-terpy})\text{PtCl}]\text{PF}_6$ (0.094 mmol), phenylacetylene (0.12 mmol), and CuI (5 mg) were dissolved in a mixture of 30 mL of CH_3CN and 15 mL of $\text{N}(\text{C}_2\text{H}_5)_3$. The mixture was stirred at room temperature under argon atmosphere for 24 h. The solvent was then removed under reduced pressure, and the residue was dissolved in 60 mL CH_3CN . The insoluble component was removed by filtration, and 100 mL of ether was added to the filtrate dropwise. After stirring for 1 h, the solid was filtered out and dried in a vacuum oven.

$[(4'\text{-Np-terpy})\text{Pt}(\text{C}\equiv\text{CPh})]\text{PF}_6$ (5). UV-vis (CH_3CN) λ ($\epsilon/\text{mol}^{-1}\cdot\text{dm}^3\cdot\text{cm}^{-1}$): 260 (3.85×10^4), 270 (3.67×10^4), 289 (3.08×10^4), 310 (1.38×10^4), 327 (1.17×10^4), 341 (1.33×10^4), 429 (5.77×10^3), 460 (4.89×10^3) nm. ^1H NMR (400 MHz, $\text{DMSO}-d_6$) δ : 7.20–7.30 (m, 3H), 7.40 (d, J = 6.8 Hz, 2H), 7.52–7.70 (m, 4H), 7.80 (t, J = 6.0 Hz, 2H), 7.90 (d, J = 7.6 Hz, 1H), 8.12 (dd, J_1 = 7.8 Hz, J_2 = 19.4 Hz, 2H), 8.36 (t, J = 7.8 Hz, 2H), 8.60 (d, J = 8.0 Hz, 2H), 8.78 (s, 2H), 8.98 (2H) ppm. ESI-MS (m/z): calcd. for $[\text{C}_{33}\text{H}_{22}\text{N}_3\text{Pt}^{194}]^+$, 654.1444; found, 654.1273 (69%); calcd. for $[\text{C}_{33}\text{H}_{22}\text{N}_3\text{Pt}^{195}]^+$, 655.1464; found, 655.1459 (100%); calcd. for $[\text{C}_{33}\text{H}_{22}\text{N}_3\text{Pt}^{196}]^+$, 656.1466;

found, 656.1365 (82%). Anal. Calcd for $C_{33}H_{22}N_3PtPF_6 \cdot 2H_2O$: C, 46.37%; H, 3.28%; N, 4.92%. Found: C, 46.07%; H, 2.95%; N, 4.92%.

[(4'-Phen-terpy)Pt(C≡CPh)]PF₆ (6). UV-vis (CH_3CN): λ ($\epsilon/mol^{-1} \cdot dm^3 \cdot cm^{-1}$): 253 (8.88×10^4), 270 (5.77×10^4), 284 (4.88×10^4), 296 (3.32×10^4), 326 (1.73×10^4), 339 (1.80×10^4), 412 (8.46×10^3), 458 (5.24×10^3) nm. 1H NMR (400 MHz, $DMSO-d_6$) δ : 7.18–7.30 (m, 2H), 7.45 (m, 1H), 7.62–7.88 (m, 7H), 7.90–7.97 (dd, $J_1 = 8$ Hz, $J_2 = 2.8$ Hz, 1H), 8.00–8.09 (m, 2H), 8.39 (t, $J = 7.8$ Hz, 2H), 8.63 (d, $J = 8$ Hz, 2H), 8.80–9.10 (m, 7H) ppm. ESI-MS (m/z): calcd. for $[C_{37}H_{24}N_3Pt^{194}]^+$, 704.1600; found, 704.1761 (71%); calcd. for $[C_{37}H_{24}N_3Pt^{195}]^+$, 705.1620; found, 705.1623 (100%); calcd. for $[C_{37}H_{24}N_3Pt^{196}]^+$, 706.1622; found, 706.1514 (96%). Anal. Calcd for $C_{37}H_{24}N_3PtPF_6 \cdot 4H_2O$: C, 48.15%; H, 3.47%; N, 4.56%. Found: C, 47.76%; H, 3.25%; N, 4.63%.

[(4'-Anth-terpy)Pt(C≡CPh)]PF₆ (7). UV-vis (CH_3CN): λ ($\epsilon/mol^{-1} \cdot dm^3 \cdot cm^{-1}$): 253 (1.62×10^5), 270 (4.48×10^4), 288 (3.48×10^4), 310 (1.67×10^4), 329 (1.68×10^4), 344 (2.03×10^4), 363 (1.19×10^4), 383 (1.09×10^4), 449 (6.86×10^3) nm. 1H NMR (400 MHz, $DMSO-d_6$) δ : 7.20–7.28 (m, 1H), 7.32 (t, $J = 7.2$ Hz, 2H), 7.48–7.64 (m, 6H), 7.78 (d, $J = 8.8$ Hz, 2H), 7.91 (t, $J = 6.2$ Hz, 2H), 8.25 (d, $J = 8.4$ Hz, 2H), 8.42 (t, $J = 7.6$ Hz, 2H), 8.60 (d, $J = 7.6$ Hz, 2H), 8.88 (s, 3H), 9.23 (d, $J = 4.8$ Hz, 2H) ppm. ESI-MS (m/z): calcd. for $[C_{37}H_{24}N_3Pt^{194}]^+$, 704.1600; found, 704.1670 (66%); calcd. for $[C_{37}H_{24}N_3Pt^{195}]^+$, 705.1620; found, 705.1616 (99%); calcd. for $[C_{37}H_{24}N_3Pt^{196}]^+$, 706.1622; found, 706.1759 (100%). Anal. Calcd for $C_{37}H_{24}N_3PtPF_6 \cdot H_2O$: C, 51.15%; H, 3.00%; N, 4.84%. Found: C, 51.17%; H, 3.28%; N, 4.63%.

[(4'-Pyren-terpy)Pt(C≡CPh)]PF₆ (8). UV-vis (CH_3CN): λ ($\epsilon/mol^{-1} \cdot dm^3 \cdot cm^{-1}$): 265 (4.11×10^4), 274 (4.61×10^4), 312 (2.05×10^4), 326 (2.68×10^4), 340 (3.21×10^4), 381 (5.81×10^3), 444 (9.88×10^3), 473 (8.02×10^3) nm. 1H NMR (400 MHz, $DMSO-d_6$) δ : 7.00–7.38 (m, 4H), 7.42–7.56 (m, 2H), 7.72–7.94 (m, 2H), 7.96–8.58 (m, 12H), 8.60–8.72 (m, 2H), 8.91 (s, 1H), 9.10 (s, 1H) ppm. ESI-MS (m/z): calcd. for $[C_{39}H_{24}N_3Pt^{194}]^+$, 728.1600; found, 728.1644 (50%); calcd. for $[C_{39}H_{24}N_3Pt^{195}]^+$, 729.1620; found, 729.1608 (75%); calcd. for $[C_{39}H_{24}N_3Pt^{196}]^+$, 730.1622; found, 730.1644 (62%). Anal. Calcd for $C_{39}H_{24}N_3PtPF_6 \cdot H_2O$: C, 52.47%; H, 2.91%; N, 4.71%. Found: C, 52.60%; H, 3.01%; N, 4.87%.

Photophysical Measurements. The electronic absorption spectra were measured on a CARY 500 dual beam scanning UV-vis-NIR spectrophotometer. The samples were dissolved in CH_3CN . The emission and excitation spectra were measured in acetonitrile solutions on a SPEX Fluorolog-3 fluorimeter/phosphorimeter or a SPEX Fluorolog 1680 0.22 m double spectrometer. The excitation wavelength was 436 nm for all of the samples. The solutions were purged with argon for at least 20 min before each measurement. The emission quantum yields of the samples were determined by the comparative method,¹¹ in which eq 1 was used for calculation:

$$\phi_s = \phi_r(A_r/A_s)(n_s/n_r)^2(D_s/D_r) \quad (1)$$

where the subscripts s and r refer to the sample and reference solutions respectively; A is the absorbance at the excitation wavelength, n is the refractive index of the solvent, and D is the integrated emission intensity. A degassed aqueous solution of $[Ru(bpy)_3]Cl_2$ ($\phi_{em} = 0.042$ at 436 nm excitation)¹² was used as the reference. The emission lifetime at room temperature and 77 K and the nanosecond TA spectra were measured on an Edinburgh LP920 laser flash photolysis spectrometer. The

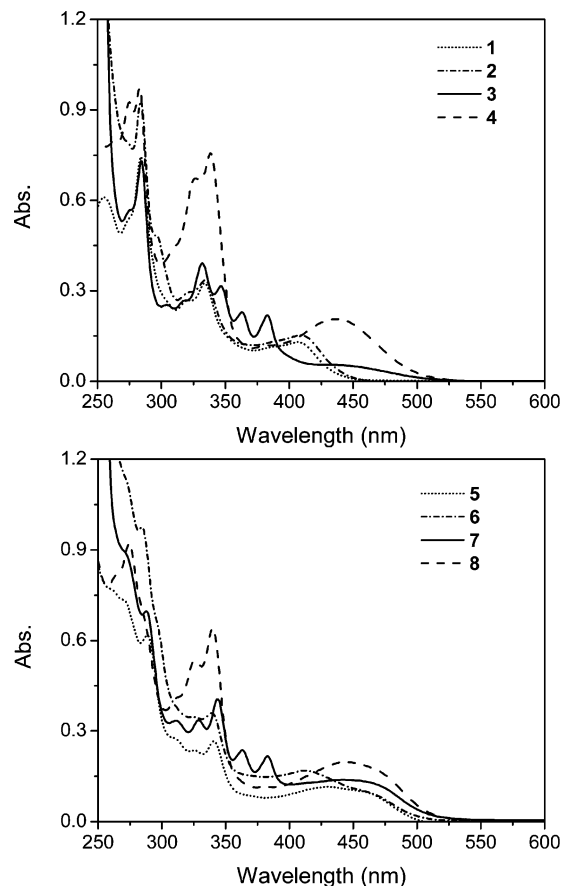


Figure 2. Electronic absorption spectra of complexes 1–8 in acetonitrile at 2.0×10^{-5} mol/L in a 1-cm cuvette.

samples were excited by a 4.1 ns (fwhm) Quantel Brilliant Nd:YAG laser at its third-harmonic output (355 nm) with a repetition rate of 1 Hz. The samples were placed in a 1-cm quartz cell, and the solutions were degassed with argon for at least 20 min before each measurement.

Optical Limiting Measurement. The optical limiting measurements were carried out using a setup that has been described previously.^{6b,c} A Quantel Brilliant Nd:YAG laser was used as the light source and was operated at its second-harmonic output (532 nm) with a 10 Hz repetition rate.

3. Results and Discussion

3.1. Electronic Absorption Spectra. Figure 2 shows the electronic absorption spectra of 1–8 in acetonitrile, and the absorption data are presented in Table 1. All of the spectra exhibit intense absorption bands below 350 nm, which can be assigned to the $^1\pi, \pi^*$ transitions within the 4'-Ar-terpy ligand.^{7c} For 1, 2, 5, and 6, the moderately intense bands around 330 nm mainly arise from the $^1\pi, \pi^*$ transitions of the cis-cis form of terpy moiety,^{7c,13,14} while the more intense bands between 320 and 400 nm for 3, 4, 7, and 8 predominately stem from the anthracene and pyrene moieties, probably with some contributions from the terpy $^1\pi, \pi^*$ transition to the band around 330 nm. Similar to other platinum polypyridine complexes, all of the complexes exhibit a broad low-energy band in the range of 400–500 nm, which can be attributed to a $d\pi(Pt) \rightarrow \pi^*(terpy)$ MLCT transition.^{6b,7} These bands are affected profoundly by the 4'-substituents on the terpy ligand. Large substituents, such as anthryl and pyrenyl, induce a pronounced redshift of the MLCT band. In addition, pyrenyl substituent significantly increases the intensity of this band. Comparing the spectra of 5–8 to their

TABLE 1: Photophysical Parameters of 1–8

complex	$\lambda_{\text{abs}}/\text{nm}^a$ ($\epsilon/\text{dm}^3\text{mol}^{-1}\text{cm}^{-1}$)	emission (r.t.) ^a λ/nm (τ/ns ; Φ_{em})	emission (77 K) ^b λ/nm ($\tau/\mu\text{s}$)	TA (r.t.) ^c $\tau_{\text{TA}}/\text{ns}$
1	255 (30570), 284 (37240), 321 (13420), 334 (16280), 388 (5740), 408 (6490)	578 (169); 0.0011	546 (90.7, 84%; 26.4, 16%), 587 (sh., 73.4, 90%; 5.1, 10%)	194 ^d
2	254 (73210), 284 (46500), 296 (24250), 320 (14680), 334 (16780), 409 (7670)	582 (202); 0.0016	549 (68.9, 92%; 17.5, 8%), 592 (sh., 66.9, 90%; 4.4, 10%)	238 ^e
3	253 (178840), 276 (28430), 284 (36580), 304 (12710), 319 (13460), 332 (19600), 347 (15810), 363 (11500), 383 (10990), 447 (2600)	600, 712; 0.0002	493 (11.8), 578 (11.1), 690	2748 ^d
4	263 (39930), 275 (46340), 283 (48640), 310 (22130), 327 (33690), 338 (37780), 380 (5990), 438 (10330)	658; 0.0013	510 (13.3), 565 (sh.), 633 (sh.), 656 (286.9), 710 (sh., 332.1)	4077 ^e
5	260 (38490), 270 (36710), 289 (30810), 310 (13820), 327 (11740), 341 (13340), 429 (5770), 460 (4890)	603 (274); 0.0151	543 (16.5), 586 (sh.), 637 (2.2)	255 ^e
6	253 (88760), 270 (57670), 284 (48780), 296 (33180), 326 (17330), 339 (17990), 412 (8460), 455 (5240)	603 (373); 0.0167	548 (15.9), 584 (sh.), 626 (18.2, 30%; 2.2, 70%)	408 ^e
7	253 (161580), 270 (44840), 288 (34830), 310 (16680), 329 (16780), 344 (20270), 363 (11860), 383 (10850), 449 (6860)	603 (349); 0.0012	537 (13.2), 570 (13.5), 685 (2.1)	384 ^e
8	265 (41050), 274 (46080), 312 (20530), 326 (26760), 340 (32080), 381 (5810), 444 (9880), 473 (8020)	668 (2000); 0.0013	637 (315.6), 690 (369.7)	2540 ^e

^a Measured at a complex concentration of 1.0×10^{-4} mol/L in CH_3CN . ^b Measured at a complex concentration of 1.4×10^{-4} mol/L in butyronitrile glass. ^c Measured at a complex concentration of 1.0×10^{-4} mol/L in CH_3CN . ^d Monitored at 800 nm. ^e Monitored at 680 nm.

corresponding chloride complexes **1–4**, it is clear that the introduction of the phenylacetylide ligand induces an obvious bathochromic shift along with an intensity increase in the MLCT bands in **5–8**. More specifically, in addition to the redshift of the original MLCT band, a shoulder appears in the range of 450–520 nm. These somewhat structured MLCT bands are consistent with the feature observed in platinum 4'-tolylterpyridyl arylacetylide complexes reported by Wu et al.^{7h} and our group,^{6b} as well as by Schanze and co-workers for diimine platinum(II) bis-acetylide complexes.¹⁵ This indicates the presence of two orbitally distinct MLCT transitions, for example, $d_{xz}(\text{Pt}) \rightarrow \pi^*(\text{trpy})$ and $d_{yz}(\text{Pt}) \rightarrow \pi^*(\text{trpy})$ (assuming that the acetylide ligand is along the x axis with z perpendicular to the coordination plane) in these phenylacetylide complexes. Consistent with the charge-transfer nature, this low-energy band is very sensitive to the polarity of the solvent. Less polar solvent, such as CH_2Cl_2 , shifts the MLCT band to a longer wavelength, suggesting that the dipole moment of the ground state is larger than that of the excited state.^{7c,e}

3.2. Emission Properties. Figure 3 presents the emission spectra of **1–8** in CH_3CN at room temperature, and the emission data are provided in Table 1. In comparison with the excitation spectra, the Stokes shift of the complexes varies from 110 to 220 nm, and the emission lifetimes are all in the range of hundreds of nanoseconds to microseconds. In line with other platinum complexes,^{3–7} the large Stokes shift and the relatively long lifetime suggest that the emitting state should be a triplet excited state. For complexes **1**, **2**, **3**, **5**, **6**, and **7**, the emitting state could be attributed to a ³MLCT-dominated state, which is consistent with the literature report for similar complexes.^{7c} For complexes **4** and **8**, the emission should originate from a state

that mixes several configurationally distinct excitations, such as ³ILCT, ³MLCT and ³ π, π^* , in view of the emission energy for these complexes being similar to that of the [4'-(1-pyrenyl)-terpyridyl]platinum chloride complex reported by McMillin and co-workers.^{7c} The assignment of the emitting state to an admixing state for **4** and **8** can be further supported by the fact that these two complexes possess much longer emission lifetimes in comparison to those of **1**, **2**, **5**, **6**, and **7**, and the fact that the introduction of phenylacetylide ligand exhibits a negligible effect on the emission energy and emission quantum yield comparing **8** to that of **4**. This is easy to understand because both the ILCT and π, π^* transitions are all within the 4'-aryl-trpy ligand, on which the phenylacetylide ligand shows a negligible effect. In contrast, emission arising from the ³MLCT-dominated state exhibits a pronounced bathochromic shift upon introduction of the phenylacetylide ligand by comparing the emission energies of **1** and **5**, as well as **2** and **6**, which raises the energy of the metal-based highest occupied molecular orbital (HOMO) and thus reduces the energy gap between the HOMO and the terpyridine-based lowest unoccupied molecular orbital (LUMO). In addition, the emission quantum yields of **5** and **6** exhibit a 1 order of magnitude increase in comparison to those of their corresponding chloride complexes **1** and **2**. For **3**, at the concentration used for the measurement ($\sim 1.0 \times 10^{-4}$ mol/L), the emission possesses two bands. The band at ~ 600 nm is similar in energy to those of **1** and **2**, suggesting a ³MLCT-dominated emitting state. The low-energy band at ~ 712 nm could be attributed to an excimeric emission due to its concentration-dependence nature. With an increase in the concentration, the intensity of this band increases. Moreover, the excitation spectrum monitored at 712 nm coincides with

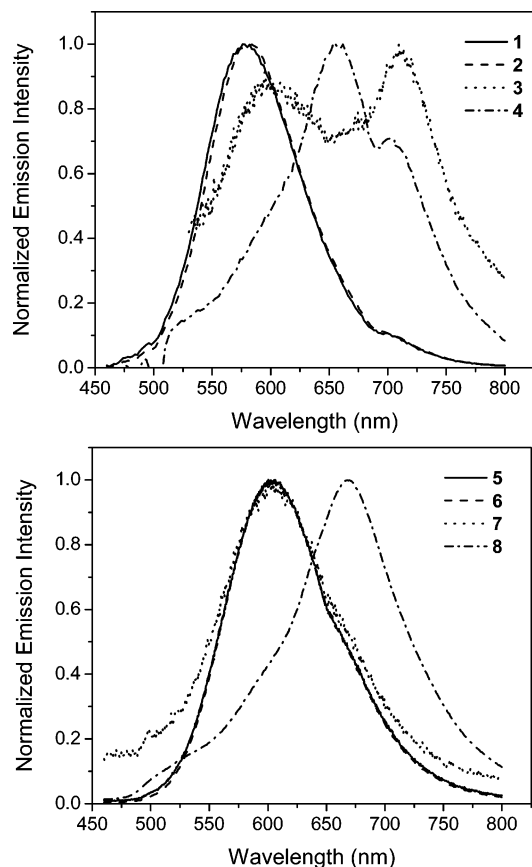


Figure 3. Normalized emission spectra of complexes **1–8** in degassed acetonitrile solutions at room temperature. The complex concentration is approximately 1.0×10^{-4} mol/L. The excitation wavelength is 436 nm. The shoulders around 700 nm for **1**, **2**, and **4** are due to instrumental artifact. The spectra of **1** and **2**, and **5** and **6** overlap.

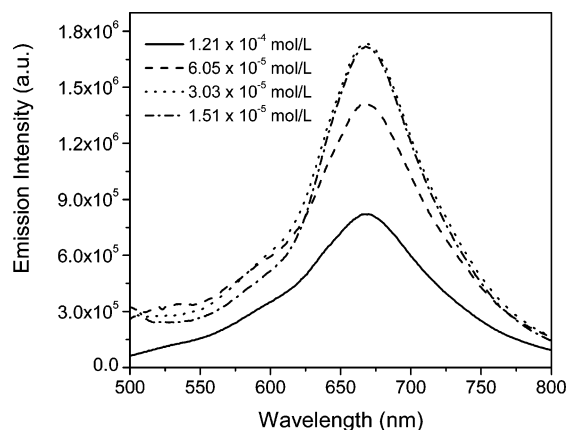


Figure 4. Emission spectra of **8** at different concentrations in degassed CH_3CN at room temperature. The excitation wavelength is 436 nm. that monitored at 600 nm. This further confirms the excimeric nature of the 712 nm band. However, the emission efficiency of **3** is very weak ($\Phi_{\text{em}} = 0.0002$ in CH_3CN), preventing us from obtaining the emission lifetime. Incorporating phenylacetylide ligand onto **3** slightly shifts the emission to a longer wavelength, while the emission quantum yield has been drastically increased to 0.0012 for **7**. It is noted that, except for **3**, the emission of the other complexes are all independent of the concentrations of solutions. As exemplified by **8** in Figure 4, the maximum position of the emission spectra remains the same from concentrations of $\sim 1.0 \times 10^{-5}$ mol/L to 5.0×10^{-4} mol/L, indicating that no aggregation or excimer forms at high complex concentrations at room temperature.

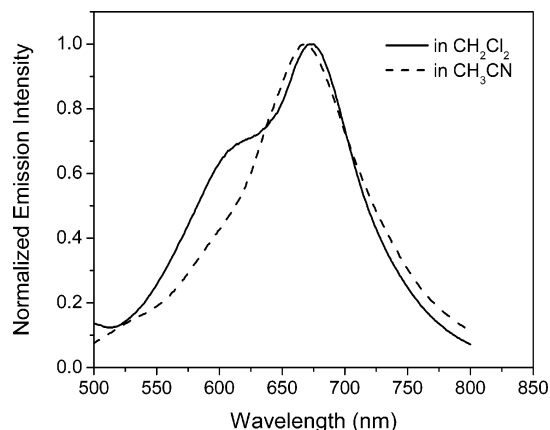


Figure 5. Normalized emission spectra of degassed solutions of **8** at different solvents at room temperature. The complex concentration is approximately 1.0×10^{-4} mol/L, and the excitation wavelength is 436 nm.

It is worth mentioning that, in line with the substituent effect on UV–vis spectra, the emission energies at room temperature are also remarkably sensitive to the 4'-substituent. Larger aryl substituents, such as pyrenyl, drastically reduce the emission energy of the complex because of the admixture of the $^3\text{ILCT}$ and $^3\pi, \pi^*$ characters into the emitting state, as discussed in the previous paragraph. In addition, because of the charge-transfer nature of the emitting state, the emission bands are affected by the polarities of the solvents. Less polar solvents, such as CH_2Cl_2 , cause a noticeable bathochromic shift of the emission bands. The maxima of the emission bands appear at 612 nm for **5**, 611 nm for **6**, 615 nm for **7**, and 673 nm for **8**. This feature could be attributed to the decreased dipole moment in the excited state, which is consistent with other platinum terpyridyl complexes.^{7c,e} For **8**, as shown in Figure 5, in addition to the redshift of the emission maximum, a shoulder appears clearly at ~ 620 nm. However, these two bands originate from the same excited state in view of the similar emission lifetimes and the same excitation spectra monitored at these two different wavelengths.

At 77 K, all the emissions shift to higher energies and exhibit a clear vibronic structure (shown in Figure 6). Except for **3**, the vibronic progression spacing is approximately 1100–1300 cm^{-1} , which corresponds to the aromatic vibrational mode of the terpyridyl ligand.^{7g} For **1**, **2**, **5**, **6**, and **7**, they all exhibit a relatively large thermally induced Stokes shift (i.e., the rigidochromic shift) $\Delta E_s \sim 1010\text{--}1830$ cm^{-1} , which is a characteristic of the charge-transfer emission, and have been seen in several platinum(II) 4'-tolylterpyridyl phenylacetylide complexes.^{6b} Therefore, the emitting state at 77 K for these five complexes can be assigned to the $^3\text{MLCT}$ state. In contrast, complex **8** lacks a significant rigidochromic shift ($\Delta E_s \sim 500$ cm^{-1}), suggesting that the 77 K emission does not originate from a pure MLCT manifold. Rather, it likely arises from a state that involves three configurationally distinct excitations: $^3\text{MLCT}$, $^3\text{ILCT}$, and $^3\pi, \pi^*$, similar to what has been proposed by McMillin and co-workers for the platinum 4'-pyrenylterpyridyl chloride complex.^{7c} For complexes **3** and **4**, the assignment of the emission at 77 K appears to be more complicated. They all exhibit high-energy bands with a large rigidochromic shift and low-energy bands with a small rigidochromic shift. In reference to the assignment of the emission at 77 K for the other complexes, the high energy bands for **3** and **4** could be tentatively attributed to a $^3\text{MLCT}$ -dominant state, while the low-energy emission for **4** might stem from an admixture state of $^3\text{MLCT}$, $^3\text{ILCT}$, and $^3\pi, \pi^*$. The different parentage of the high-

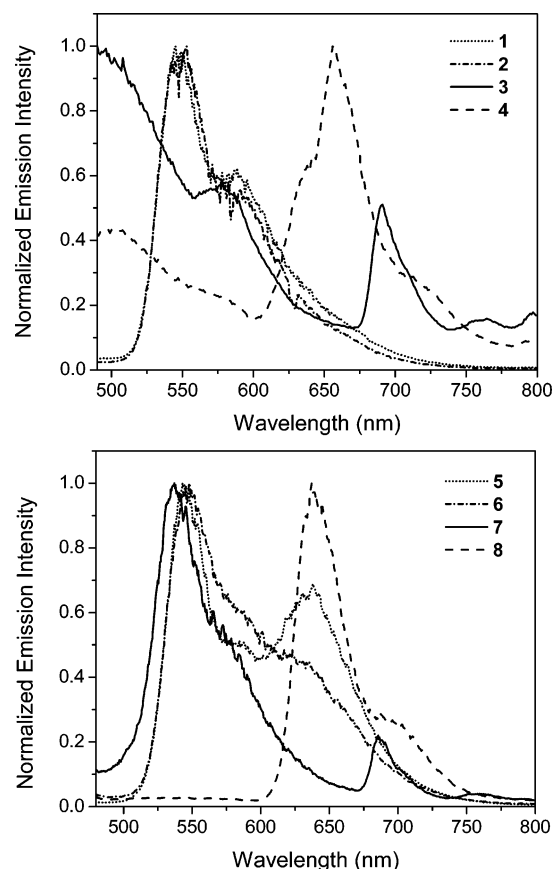


Figure 6. Normalized emission spectra of complexes **1–8** in degassed butyronitrile glass at 77 K. The complex concentration is approximately 1.4×10^{-4} mol/L, and the excitation wavelength is 436 nm.

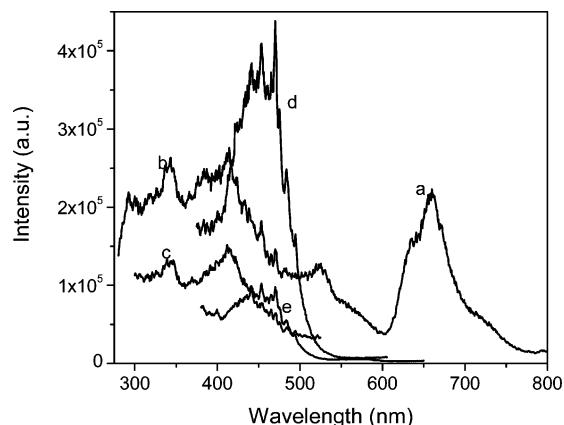


Figure 7. The emission and the excitation spectra of **4** in degassed butyronitrile glass at a concentration of $\sim 1.4 \times 10^{-4}$ mol/L at 77 K: (a) the emission spectrum at an excitation wavelength of 436 nm; (b) excitation spectrum monitored at 524 nm; (c) excitation spectrum monitored at 570 nm; (d) excitation spectrum monitored at 660 nm; (e) excitation spectrum monitored at 720 nm.

and low-energy emissions of **4** could be further demonstrated from the excitation spectra shown in Figure 7.

The low energy peak at ~ 690 nm for **3**, 637 nm for **5**, and 626 nm for **6** likely arise from a ground-state complex. This notion is supported by the study of the excitation spectra of these complexes at different emission wavelengths, in which the excitation spectrum monitored at the low-energy band is different from those monitored at the high-energy structured bands. In addition, the lifetime of this low-energy state is quite distinct from those of the high-energy emission bands. In reference to the work reported by Yam and co-workers for the

platinum(II) 2,6-biphenylpyridyl complexes¹⁶ and our previous work on the 4'-tolylterpyridyl arylacetylide complexes,^{6b} the broad low-energy band at 77 K for **3**, **5**, and **6** could be assigned to an emissive state resulting from ground-state aggregation of the complexes. In addition, the appearance of the low-energy emission band(s) at 77 K but not at room temperature for **5** and **6** at a similar concentration indicates that the association constant for the aggregation process could be too small to be observed at room temperature for these two complexes.

3.3. Nanosecond Transient Absorption. The nanosecond TA study can provide information on the triplet excited-state absorption characteristics and the lifetime of the triplet excited state that gives rise to the transient absorption. A positive band in a TA spectrum suggests a stronger excited-state absorption than that of the ground state, which may result in reverse saturable absorption and is useful for optical limiting of nanosecond laser pulses. In contrast, a negative band implies a significant ground-state bleaching. Therefore, from the triplet excited-state TA studies, one can obtain valuable information on the spectral region that could be useful for optical limiting. For this purpose, the TA spectra of **1–8** have been measured, and the lifetimes of the triplet excited state have been deduced. Although the transient absorption of **1–4** has been found to be very weak, **5–8** exhibit moderately strong and characteristic transient absorption. Figure 8 shows the transient absorption spectra of **5**, **7**, and **8** in acetonitrile at room temperature. The shape of the transient absorption spectrum of **6** is similar to that of **5**; therefore, is not shown in Figure 8. The spectrum of **5** exhibits a shallow bleaching band from 400 to 470 nm, which is consistent with the spectral region corresponding to the ¹MLCT transition in the UV–vis absorption spectrum, and a broad, moderately intense positive band above 470 nm and extending to the near-IR region. With reference to the transient absorption spectrum of the platinum 4'-tolylterpyridyl phenylacetylide complex reported by our group previously,^{6b} and considering the coincidence of the τ_{TA} with τ_{em} , we can conclude that the transient absorption spectrum should originate from an excited state with ³MLCT character. Or, alternatively, the absorbing state is in equilibrium with the emitting state. In line with our previous study,^{6b} the broad, positive absorption band in the visible to the near-IR region could arise from the terpyridyl anion that is present in the MLCT state. For **8**, a narrow and strong bleaching band appears between 320 and 370 nm, corresponding to the spectral region of ¹ π, π^* transition in the UV–vis absorption spectrum. In addition, a broad, positive band extends from 370 to 830 nm, with a band maximum appearing at ~ 520 nm. The lifetime of the absorbing transients τ_{TA} also coincides with the emission lifetime. Therefore, the nature of the transient absorbing state for **8** should possess MLCT, ILCT, and π, π^* characters, in line with the parentage of the emitting state. The TA spectrum of **7** is quite distinct from those of **5**, **6**, and **8**. It features a narrow, weak bleaching band at ca. 380 nm, and a strong, narrow band at ca. 420 nm, as well as a broad, structureless band from 470 to 750 nm. An additional positive band appears above 800 nm. Although the definite assignment of the absorbing state for **7** is not clear at this time, the consistency of the transient absorption lifetime with the emission lifetime suggests that the excited state absorption of **7** likely arises from the ³MLCT state, probably mixed with some ³ILCT and ³ π, π^* characters considering the bleaching band in the near UV region.

3.4. Optical Limiting. As discussed in the previous sections, complexes **5–8** possess relatively long triplet excited-state lifetimes and moderately strong and broad triplet excited-state

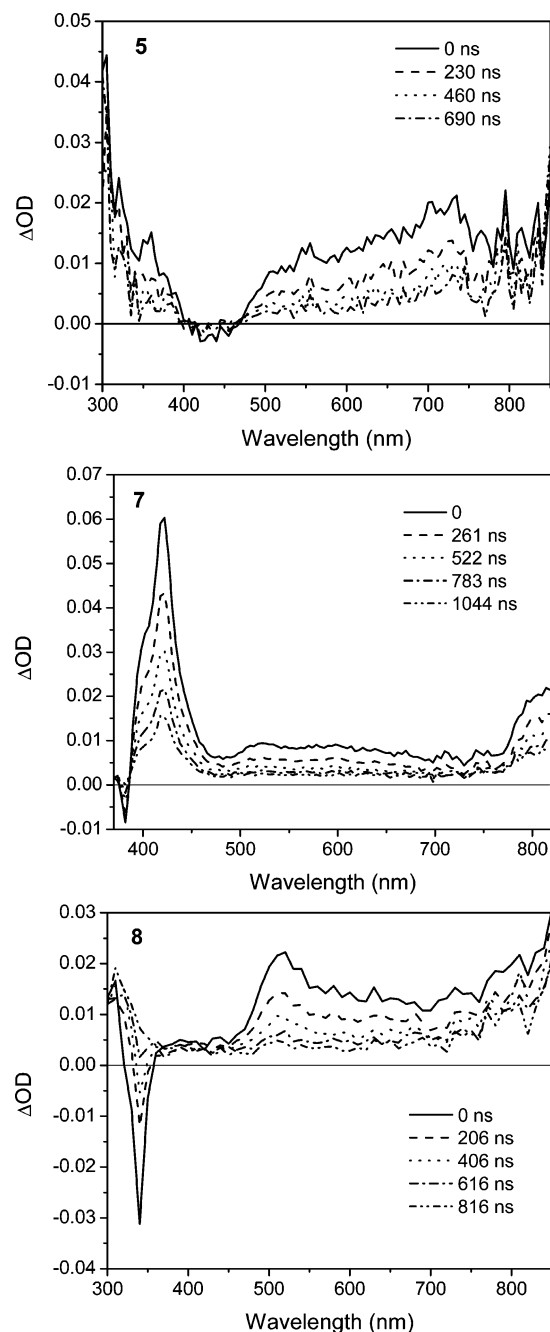


Figure 8. Time-resolved triplet TA spectra of **5**, **7**, and **8** in degassed acetonitrile at room temperature following 355 nm excitation. The complex concentration is approximately 2×10^{-5} mol/L.

absorption in the visible to the near-IR region; therefore, a significant optical limiting of nanosecond laser pulses is expected from these complexes. To demonstrate this, nonlinear transmission measurements were conducted at 532 nm using 4.1 ns (fwhm) laser pulses. The concentrations of the solutions were adjusted to obtain the same linear transmission of 70% for all these samples at 532 nm in a 2-mm cell. In this case, the different optical limiting performances of these complexes should only be related to their excited-state characteristics, such as the excited-state absorption cross-section, the excited-state lifetime, and the quantum yield of the excited state. The nonlinear transmission results are shown in Figure 9.

It is quite obvious that the absorption curves for all of the complexes deviate significantly from the linear absorption curve, suggesting the occurrence of optical limiting. The limiting threshold at $T/T_0 = 0.9$ and the nonlinear transmittance at an

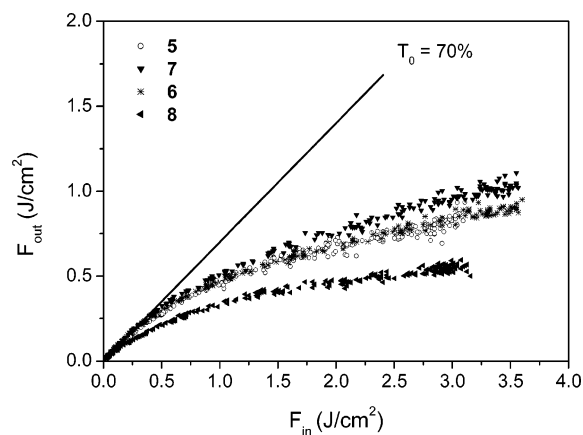


Figure 9. Optical limiting of complexes **5–8** in acetonitrile in a 2-mm cell for 532 nm, 4.1 ns laser pulses. The linear transmission of the solutions is 70%.

TABLE 2: Optical Limiting Parameters of 5–8 in CH₃CN at $T_0 = 70\%$

complex	σ_0^a (cm ²)	F_{th}^b (mJ/cm ²)	T_{lim}^c	σ_{eff}/σ_0
5	1.81×10^{-18}	250	0.27	>3.7
6	4.30×10^{-19}	370	0.27	>3.7
7	1.76×10^{-18}	490	0.32	>3.2
8	1.34×10^{-18}	52	0.18	>4.8

^a Ground-state absorption cross-section at 532 nm. ^b Optical limiting threshold when the transmittance drops to 90% of the linear transmittance. ^c Nonlinear transmittance at incident fluence of 3.0 J/cm²

incident fluence of 3.0 J/cm² are listed in Table 2. The optical limiting characteristics of these complexes are influenced significantly by the 4'-substituent. **8** exhibits the lowest limiting threshold and limiting throughput among these four complexes, with a transmittance drop to 18% at 3.0 J/cm². The trend of the optical limiting appears to be **8** > **5** > **6** > **7**. The strong optical limiting of **8** could be related to its longer triplet excited-state lifetime and the larger excited-state absorption cross-section at 532 nm, as demonstrated by its TA spectrum in Figure 8. The relatively weak optical limiting of **7** should be attributed to its low triplet excited-state absorption at 532 nm.

To quantitatively compare the strength of optical limiting of the complexes, a figure of merit σ_{eff}/σ_0 can be used, where σ_{eff} is the effective excited-state absorption cross-section, and σ_0 is the ground-state absorption cross-section. At a incident fluence of 3.0 J/cm², which is much higher than the saturation fluence $F_{sat} = h\nu/\sigma_g\Phi_t$,¹⁷ the ground state has been greatly bleached, and the molecules mainly populate at the excited states. In this case, σ_{eff}/σ_0 can be defined as $\sigma_{eff}/\sigma_0 = \ln T_{sat}/\ln T_0$,¹⁷ where T_{sat} is the transmittance at the saturable fluence, and T_0 is the linear transmittance. Although the damage threshold of the quartz cell (5.0 J/cm²) limited the maximum incident fluence that could be used in our experiments to obtain the saturable transmittance, the transmittance at 3.0 J/cm² could be used to calculate the lower bound of σ_{eff}/σ_0 for these complexes. The results are shown in Table 2. It is very clear that this ratio is much higher for **8** than the other complexes.

4. Conclusion

The results and discussion in Section 3 have clearly demonstrated that the 4'-substituent on the terpyridyl ligand and the phenylacetylide ligand exhibit significant effects on the photo-physical properties and the optical limiting performances. Large aryl substituents, such as anthryl and pyrenyl, induce a pronounced bathochromic shift of the low-energy MLCT band

in the UV–vis spectra along with a significant intensity increase in the pyrenyl-substituted complex **8**. The pyrenyl substituent also causes a remarkable redshift of the emission bands at room temperature in comparison to those containing naphthyl, phenanthryl, and anthryl substituents, and admixes some $^3\text{ILCT}$ and $^3\pi,\pi^*$ characters in the emitting state. Because of the admixing feature of the emitting state, the lifetime of **8** becomes much longer (on the order of 2 μs) in acetonitrile solution at room temperature. The introduction of phenylacetylide ligand to corresponding chloride complexes **1–4** reduces the energy of the lowest-energy transition in the UV–vis spectra. For complexes containing naphthyl, phenanthryl, and anthryl substituents, the emission energies have been reduced upon incorporation of phenylacetylide ligand, with a 1 order of magnitude increase of the emission efficiency. The effect of the 4'-aryl substituent has also been reflected by the different features and origin of the triplet TA spectra, and has been further demonstrated by the optical limiting behavior. Because of the much longer lifetime of the triplet excited state and the stronger triplet excited-state absorption cross-section at 532 nm for the 4'-pyrenyl containing complex, **8** exhibits the strongest optical limiting for nanosecond laser pulses at 532 nm. These excited-state characteristics, along with the broad optical window in the UV–vis absorption spectrum, suggest that complex **8** could be a promising broadband optical limiting material.

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