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Functionalized Platinum(II) Terpyridyl Alkynyl Complexes as Colorimetric and Luminescence pH Sensors

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A series of platinum(II) terpyridyl alkynyl complexes that have been derivatized with basic amino functionalities, [Pt(tpy)(C≡C–C_6H_4–NR_2-4]X (X = OTf^-, R = CH_3 **1**, R = $CH_2CH_2OCH_3$ **2**, R = H **3**; X = Cl^-, R = CH_3 **4**, R = $CH_2CH_2OCH_3$ **5**, R = H **6**) (tpy = 2,2′:6′,2″-terpyridine), have been synthesized and characterized. Their photophysical responses at various acid concentrations were studied. The abilities of the complexes to function as colorimetric and luminescence pH sensors were demonstrated with dramatic color changes and luminescence enhancement upon introduction of acid.

Introduction

Platinum(II) terpyridyl complexes have attracted wide attention in recent years, mainly due to their intriguing spectroscopic and luminescence properties[1,2] as well as their biological activities, including their ability to bind and interact with DNA[1f,3] and protein substrates.[4] In addition, interesting aggregation[2,5] and vapoluminescence[6] properties of the square-planar platinum(II) system have also been reported recently. Despite examples on the use of this class of complexes for host−guest interactions and optical sensors being known,[1a,b,7] the utilization of the platinum(II) terpyridyl system for pH sensing has been rare. Over the past few decades, pH sensors based on organic molecules have been well-developed;[8] however, there is an increasing growth in

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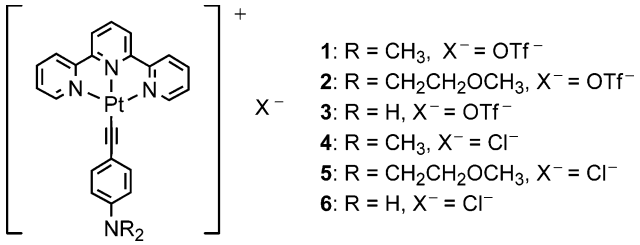
Chart 1



interest of the utilization of transition metal complexes as inorganic-based pH sensors.[9] Most of these metal complexes studied usually display pH-dependent luminescence properties; however, a significant change of the electronic absorption spectral properties at different pH has not been observed. Recently, we reported an interesting class of platinum(II) terpyridyl alkynyl complexes that display interesting photoluminescence and polymorphic behavior.[2a] Dramatic color changes were observed upon solvent-induced aggregation, and tuning of the electronic absorption and emission properties was shown to be readily achieved through a change in the ancillary ligands.[1a,2a] As an extension of this work, we now report the synthesis, electronic absorption, luminescence, and photophysical responses at various acid concentrations of a series of platinum(II) terpyridyl alkynyl complexes that have been derivatized with basic amino functionalities, [Pt(tpy)(C≡C−C_6H_4−NR_2-4]X (X = OTf^-, R = CH_3 **1**, R = $CH_2CH_2OCH_3$ **2**, R = H **3**; X = Cl^-, R = CH_3 **4**, R = $CH_2CH_2OCH_3$ **5**, R = H **6**) (tpy = 2,2′:6′,2″-terpyridine) (Chart 1). Crystals suitable for X-ray crystal structure determination were obtained for **2**. The present system has been demonstrated to show dramatic color change and emission enhancement upon the addition of acid, both in organic and in aqueous media, being completely reversible upon addition of a base. Their pK_a values have also been determined by pH titration studies in suitable buffer systems.

Experimental Section

Materials and Reagents. Dichloro(1,5-cyclooctadiene)platinum(II) and 2,2′:6′,2″-terpyridine were obtained from Strem Chemicals Inc. (Trimethylsilyl)acetylene, copper(I) iodide, and triethylamine were purchased from Lancaster Synthesis Ltd. Potassium fluoride was purchased from Aldrich Chemical Co. Lithium chloride was obtained from Merck. *N*-Iodosuccinimide was purchased from Acros Organics. Dichlorobis(triphenylphosphine)palladium(II),[10] 4-trimethylsilylethynyl-*N*,*N*-dimethylaniline (Me_3Si−C≡CC_6H_4−$N(CH_3)_2$-4),[11] and 4-trimethylsilylethynylaniline (Me_3Si−C≡CC_6H_4−NH_2-4)[12] were synthesized according to literature methods. [Pt(tpy)(MeCN)]$(OTf)_2$ was synthesized by modification of the literature method.[2g] Spectroscopic grade acetonitrile from Tedia Co. Inc. was used as received. All other reagents were of analytical grade and were used as received.

Synthesis. 4′-Iodo-*N*,*N*-bis(2-methoxyethyl)-benzamine. *N*,*N*-Bis(2-methoxyethyl)-benzamine[13] (2.09 g, 10 mmol) and *N*-iodosuccinimide (2.7 g, 12 mmol) were dissolved in 100 mL of benzene, and the mixture was refluxed for 12 h. After being cooled, the reaction mixture was filtered and the solid was extracted with benzene. The filtrate was then evaporated to dryness under reduced pressure to give a solid residue. The residue was then dissolved in chloroform and purified by column chromatography on silica gel, using chloroform as eluent. Yield: 60%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ = 7.44 (d, 2H, J = 8.7 Hz, $-C_6H_4-$), 6.50 (d, 2H, J = 8.7 Hz, $-C_6H_4-$), 3.52 (m, 8H, $-CH_2-CH_2-$), 3.34 (s, 6H, $-OCH_3-$). EI−MS: m/z 335 $[M]^+$. Anal. Calcd for $C_{12}H_{18}NO_2I$: C, 43.00; H, 5.41; N, 4.18. Found: C, 42.97; H, 5.43; N, 4.16.

4′-Trimethylsilylethynyl-*N*,*N*-bis(2-methoxyethyl)-benzamine (Me_3Si−C≡CC_6H_4−$N(CH_2CH_2OCH_3)_2$-4). A mixture of 4′-iodo-*N*,*N*-bis(2-methoxyethyl)-benzamine (1.68 g, 5 mmol), bis(triphenylphosphine)palladium(II) chloride (70 mg, 0.1 mmol), and copper(I) iodide (22 mg, 0.2 mmol) distilled triethylamine (20 mL) and THF (20 mL) was deaerated with nitrogen. (Trimethylsilyl)-acetylene (0.6 g, 6 mmol) was then added to the reaction mixture and was stirred for 12 h at room temperature. The mixture was then filtered, and the filtrate was evaporated to dryness under reduced pressure to give a solid residue. The residue was then dissolved in chloroform and purified by column chromatography on silica gel, using chloroform as eluent. Yield: 56%. ^{1}H NMR (400 MHz, $CDCl_3$, 298 K, relative to Me_4Si): δ = 7.30 (d, 2H, J = 8.8 Hz, $-C_6H_4-$), 6.59 (d, 2H, J = 8.8 Hz, $-C_6H_4-$), 3.52 (m, 8H, $-CH_2CH_2-$), 3.34 (s, 6H, $-OCH_3-$), 0.22 (s, 9H, $-SiCH_3$). EI-MS: m/z 305 $[M]^+$. Anal. Calcd for $C_{17}H_{27}NO_2Si$: C, 66.84; H, 8.91; N, 4.58. Found: C, 66.80; H, 8.93; N, 4.56.

[Pt(tpy)(C≡CC_6H_4−$N(CH_3)_2$-4)](OTf) (1). A mixture of Me_3-Si−C≡CC_6H_4−$N(CH_3)_2$-4 (153 mg, 0.71 mmol) and potassium fluoride (82 mg, 1.41 mmol) in methanol was heated at reflux temperature for 30 min under nitrogen. This was followed by the addition of [Pt(tpy)(MeCN)]$(OTf)_2$ (450 mg, 0.59 mmol) to the reaction mixture, and the resulting dark purple solution was refluxed for 12 h under nitrogen. The solvent was evaporated under reduced pressure, and the solid residue was extracted with a dichloromethane−acetonitrile mixture (1:1 v/v). Any insoluble impurities were filtered off, and the filtrate was evaporated under reduced pressure to give the product as a solid. Recrystallization from diffusion of diethyl ether vapor into an acetonitrile solution of the product yielded dark purple crystals. Yield: 83%. ^{1}H NMR (400 MHz, CD_3CN, 298 K, relative to Me_4Si): δ = 8.86 (d, 2H, J = 5.3 Hz, tpy), 8.20 (m, 3H, tpy), 8.03 (m, 4H, tpy), 7.61 (t, 2H, J = 6.5 Hz, tpy), 7.19 (d, 2H, J = 8.8 Hz, $-C_6H_4-$), 6.73 (d, 2H, J = 8.8 Hz, $-C_6H_4-$), 3.01 (s, 6H, $-CH_3$). IR (KBr disk, ν/cm^{-1}): 2116 (w), ν (C≡C). Positive FAB-MS: m/z 572 $[M - OTf]^+$. Anal. Calcd for $C_{26}H_{21}F_3N_4O_3PtS\cdot CH_2Cl_2$: C, 40.21; H, 2.87; N, 6.95. Found: C, 40.45; H, 2.82; N, 6.93.

[Pt(tpy){C≡CC_6H_4−$N(CH_2CH_2OCH_3)_2$-4}](OTf) (2). Complex **2** was synthesized by a procedure similar to that of **1** except that Me_3Si−C≡CC_6H_4−$N(CH_2CH_2OCH_3)_2$-4 (215 mg, 0.70 mmol) was used in place of Me_3Si−C≡CC_6H_4−$N(CH_3)_2$-4 to give dark purple crystals. Yield: 83%. ^{1}H NMR (300 MHz, CD_3CN, 298 K, relative to Me_4Si): δ = 9.09 (d, 2H, J = 5.6 Hz, tpy), 8.31 (m, 3H, tpy), 8.18 (m, 4H, tpy), 7.71 (t, 2H, J = 6.7 Hz, tpy), 7.25 (d,

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2H, J = 8.9 Hz, $-C_6H_4-$), 6.73 (d, 2H, J = 8.9 Hz, $-C_6H_4-$), 3.58 (m, 8H, $-CH_2CH_2-$), 3.34 (s, 6H, $-OCH_3$). IR (KBr disk, ν/cm^{-1}): 2116 (w), ν (C≡C). Positive FAB-MS: m/z 660 [M − OTf]$^+$. Anal. Calcd for $C_{30}H_{29}F_3N_4O_5PtS\cdot0.5CH_2Cl_2$: C, 42.99; H, 3.55; N, 6.57. Found: C, 42.84; H, 3.52; N, 6.52.

[Pt(tpy)(C≡CC$_6$H$_4$−NH$_2$-4](OTf) (3). Complex **3** was synthesized by a procedure similar to that of **1** except that $Me_3Si-C\equiv CC_6H_4-NH_2$-4 (133 mg, 0.70 mmol) was used in place of $Me_3Si-C\equiv CC_6H_4-N(CH_3)_2$-4 to give dark brown crystals. Yield: 80%. ^{1}H NMR (300 MHz, CD_3CN, 298 K, relative to Me_4Si): δ = 8.86 (d, 2H, J = 4.9 Hz, tpy), 8.23 (m, 3H, tpy), 8.07 (m, 4H, tpy), 7.62 (t, 2H, J = 6.7 Hz, tpy), 7.10 (d, 2H, J = 8.6 Hz, $-C_6H_4-$), 6.64 (d, 2H, J = 8.6 Hz, $-C_6H_4-$), 4.36 (s, 2H, $-NH_2$). IR (KBr disk, ν/cm^{-1}): 2116 (w), ν (C≡C). Positive FAB-MS: m/z 544 [M − OTf]$^+$. Anal. Calcd for $C_{24}H_{17}F_3N_4O_3PtS\cdot0.5CH_2Cl_2$: C, 39.98; H, 2.46; N, 7.61. Found: C, 39.94; H, 2.51; N, 7.66.

[Pt(tpy)(C≡CC$_6$H$_4$−N(CH$_3$)$_2$-4)]Cl (4). Complex **4** was prepared by metathesis reaction of complex **1** with lithium chloride in acetone. Yield: 75%. ^{1}H NMR (400 MHz, CD_3OD, 298 K, relative to Me_4Si): δ = 8.80 (d, 2H, J = 4.7 Hz, tpy), 8.20 (m, 7H, tpy), 7.65 (t, 2H, J = 6.1 Hz, tpy), 7.11 (d, 2H, J = 8.8 Hz, $-C_6H_4-$), 6.74 (d, 2H, J = 8.8 Hz, $-C_6H_4-$), 3.03 (s, 6H, $-CH_3$). IR (KBr disk, ν/cm^{-1}): 2116 (w), ν (C≡C). Positive FAB-MS: m/z 572 [M − Cl]$^+$. Anal. Calcd for $C_{25}H_{21}N_4PtCl\cdot0.5CH_2Cl_2\cdot H_2O$: C, 45.82; H, 3.62; N, 8.38. Found: C, 46.13; H, 3.68; N, 8.15.

[Pt(tpy)(C≡CC$_6$H$_4$−N(CH$_2$CH$_2$OCH$_3$)$_2$-4)]Cl (5). Complex **5** was prepared by metathesis reaction of complex **2** with lithium chloride in acetone. Yield: 71%. ^{1}H NMR (400 MHz, CD_3OD, 298 K, relative to Me_4Si): δ = 8.98 (d, 2H, J = 5.2 Hz, tpy), 8.31 (m, 7H, tpy), 7.73 (t, 2H, J = 5.7 Hz, tpy), 7.19 (d, 2H, J = 8.9 Hz, $-C_6H_4-$), 6.73 (d, 2H, J = 8.9 Hz, $-C_6H_4-$), 3.62 (m, 8H, $-CH_2CH_2-$), 3.34 (s, 6H, $-OCH_3$). IR (KBr disk, ν/cm^{-1}): 2116 (w), ν (C≡C). Positive FAB-MS: m/z 660 [M − Cl]$^+$. Anal. Calcd for $C_{29}H_{29}N_4O_2PtCl\cdot CH_2Cl_2\cdot 2H_2O$: C, 44.10; H, 4.32; N, 6.86. Found: C, 44.04; H, 4.36; N, 6.90.

[Pt(tpy)(C≡CC$_6$H$_4$−NH$_2$-4)]Cl (6). Complex **6** was prepared by metathesis reaction of complex **3** with lithium chloride in acetone. Yield: 68%. ^{1}H NMR (400 MHz, CD_3OD, 298 K, relative to Me_4Si): δ = 9.00 (d, 2H, J = 5.2 Hz, tpy), 8.32 (m, 7H, tpy), 7.73 (t, 2H, J = 7.3 Hz, tpy), 7.12 (d, 2H, J = 8.5 Hz, $-C_6H_4-$), 6.69 (d, 2H, J = 8.5 Hz, $-C_6H_4-$). IR (KBr disk, ν/cm^{-1}): 2116 (w), ν (C≡C). Positive FAB-MS: m/z 544 [M − Cl]$^+$. Anal. Calcd for $C_{23}H_{17}N_4PtCl\cdot0.5CH_2Cl_2\cdot H_2O$: C, 44.07; H, 3.15; N, 8.75. Found: C, 44.10; H, 3.23; N, 8.66.

Physical Measurements and Instrumentation. ^{1}H NMR spectra were recorded on either a Bruker DPX-300 (300 MHz) or a Bruker DPX-400 (400 MHz) FT-NMR spectrometer in $CDCl_3$, CD_3CN, or CD_3OD at 298 K, and chemical shifts were reported relative to Me_4Si. Positive-ion FAB-mass spectra and EI-mass spectra were recorded on a Finnigan MAT95 mass spectrometer and IR spectra as KBr disks on a Bio-Rad FTS-7 Fourier transform infrared spectrophotometer (4000−400 cm^{-1}). Elemental analyses of the new complexes were performed on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences. UV/vis spectra were obtained on a Hewlett-Packard 8452A diode array spectrophotometer, and steady-state excitation and emission spectra were obtained on a Spex Fluorolog 111 spectrofluorometer. All solutions for photophysical studies were degassed on a high-vacuum line in a two-compartment cell consisting of a 10 mL Pyrex bulb and a 1 cm path length quartz cuvette sealed from the atmosphere by a Bibby Rotaflo HP6 Teflon stopper. The solutions were subject to no less than four freeze−pump−thaw cycles. Solid-state photophysical studies were carried out with solid samples contained in a quartz tube inside a quartz-walled Dewar flask. Excited-state lifetimes of solution samples were measured using a conventional laser system. The excitation source was the 355 nm output (third harmonic, 8 ns) of a Spectra-Physics Quanta-Ray Q-switched GCR-150 pulsed Nd:YAG laser (10 Hz). Luminescence quantum yields were measured by the optical dilute method reported by Demas and Crosby.[14] A degassed acetonitrile solution of $[Ru(bpy)_3]Cl_2$ (ϕ = 0.062, excitation wavelength at 436 nm) was used as the reference.[15]

Crystal Structure Determination. Single crystals of **2** were obtained by vapor diffusion of diethyl ether into an acetonitrile solution of the complex. A purple crystal of dimensions 0.5 mm × 0.25 mm × 0.03 mm in a glass capillary was used for data collection at −20 °C on a MAR diffractometer with a 300 mm image plate detector using graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). The images were interpreted and intensities integrated by use of the DENZO program.[16] The structure was solved by direct methods employing SIR-97 program[17] on a PC. The positions of H atoms of the complex were calculated on the basis of a riding mode with thermal parameters equal to 1.2 times that of the associated C atoms, and participated in the calculation of final R-indices.[18] One crystallographic asymmetric unit consists of one formula unit. In the final stage of least-squares refinement, only Pt and S atoms on the molecule were refined anisotropically; other non-hydrogen atoms were isotropic. The H atoms were generated using the SHELXL-97 program.[19] All 2432 independent reflections (R_{int} equal to 0.0697, 1199 reflections larger than $4\sigma(F_o)$) from a total 6694 reflections were used in the full-matrix least-squares refinement against F^2, where $R_{int} = \sum|F_o^2 - F_o^2(\text{mean})|/\sum[F_o^2]$. These reflections were in the range $-24 \le h \le 24$, $-6 \le k \le 7$, $-31 \le l \le 32$ with $2\theta_{max}$ equal to 45.40°. Convergence ($(\Delta/\sigma)_{max}$ = 0.001, av. 0.001) for 189 variable parameters by full-matrix least-squares refinement on F^2 reaches R_1 = 0.0575 and wR_2 = 0.1453 with a goodness-of-fit of 0.87. Crystallographic and structural refinement data are given in Table 1.

Results and Discussion

Synthesis and Characterization. Reaction of [Pt(tpy)(MeCN)](OTf)$_2$, which was synthesized by modification of literature procedures,[2g] with $Me_3Si-C\equiv CC_6H_4-N(CH_3)_2$-4, $Me_3Si-C\equiv CC_6H_4-N(CH_2CH_2OCH_3)_2$-4, and $Me_3Si-C\equiv CC_6H_4-NH_2$-4, respectively, in the presence of an excess of potassium fluoride in methanol yielded complexes **1**−**3** as dark purple or dark brown crystals. Metathesis reactions

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(18) Because the structure refinements are against F^2, R-indices based on F^2 are larger than (more than double) those based on F. For comparison with older refinements based on F and an OMIT threshold, a conventional index R_1 based on observed F values larger than $4\sigma(F_o)$ is also given (corresponding to intensity ≥ $2\sigma(I)$). w$R_2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$, $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$. The goodness of fit is always based on F^2: GOF = $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined. The weighting scheme is: $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where P is $[2F_c^2 + \max(F_o^2, 0)]/3$.
(19) SHELXL97: Sheldrick, G. M. *SHELX97*, Programs for Crystal Structure Analysis (Release 97-2); University of Goetingen: Germany, 1997.

Table 1. Crystallographic and Structural Refinement Data for Complex **2**

empirical formula	$C_{30}H_{29}F_3N_4O_5PtS$
fw	809.72
temperature	253(2) K
wavelength	0.71069 Å
cryst syst	monoclinic
space group	*C*2/*c*
unit cell dimens	$a = 28.546(6)$ Å, $b = 7.090(1)$ Å, $c = 31.623(6)$ Å, $\beta = 95.21(3)°$
volume	6374(2) Å^3
Z	8
density (calcd)	1.688 g cm^{-3}
abs coeff	4.530 mm^{-1}
F(000)	3184
cryst size	0.5 mm × 0.25 mm × 0.03 mm
data collection range	1.29−22.70°
index ranges	$-24 \le h \le 24$, $-6 \le k \le 7$, $-31 \le l \le 32$
no. of reflns collected	6694
no. of indep reflns	2432 [R(int)[a] = 0.0697]
completeness to $\theta = 22.70°$	56.8%
absorp corr	none
refinement method	full-matrix least-squares on F^2
no. of data/restraints/params	2432/0/189
goodness-of-fit[b] on F^2	0.870
final R indices [$I > 2\sigma(I)$][c]	$R_1 = 0.0575$, w$R_2 = 0.1453$
R indices (all data)	$R_1 = 0.1212$, w$R_2 = 0.1896$
largest diff peak and hole	1.076 and −1.638 e Å^{-3}

[a] $R_{int} = \sum|F_o^2 - F_o^2(\text{mean})|/\sum[F_o^2]$. [b] GOF = $\{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$, where n is the number of reflections and p is the total number of parameters refined. The weighting scheme is $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where P is $[2F_c^2 + \max(F_o^2, 0)]/3$. [c] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, w$R_2 = \sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$.

of complexes **1**−**3** with lithium chloride in acetone gave the respective complexes **4**−**6**. Complexes **1**−**6** have been characterized by ^{1}H NMR spectroscopy, IR spectroscopy, and FAB-mass spectrometry and gave satisfactory elemental analyses. Complex **2** was also characterized crystallographically.

Crystal Structure Determination. The crystal structure of the complex cation of **2** is depicted in Figure 1. Selected bond distances and angles are tabulated in Table 2. The platinum(II) metal center adopts a distorted square-planar geometry due to the geometric constraints imposed by the terpyridyl ligand. The N−Pt−N angles [N(1)−Pt(1)−N(3) 160.4°; N(2)−Pt(1)−N(3) 76.8°; N(1)−Pt(1)−N(2) 83.6°] deviate from the idealized values of 90° and 180° due to the steric demand of the terpyridine ligand. The bond distance of Pt−C is 2.07 Å and that of C≡C is 1.22 Å, which are comparable to other related platinum(II) alkynyl complexes.[1a,c,2a,20] The crystal packing of **2** shows a head-to-tail stacking between pairs of complex cations, with alternating intermolecular Pt···Pt distances of 3.59 and 3.96 Å.

Electronic Absorption Spectroscopy. The electronic absorption spectra of complexes **1**−**3** in acetonitrile solutions at 298 K show intense absorption bands at 286−342 nm and less intense bands at 412−414 nm and 510−546 nm. With reference to previous spectroscopic studies on platinum(II) terpyridyl complexes,[1,2,7] the high-energy intense absorption band at 286−342 nm is assigned to intraligand (IL) transition

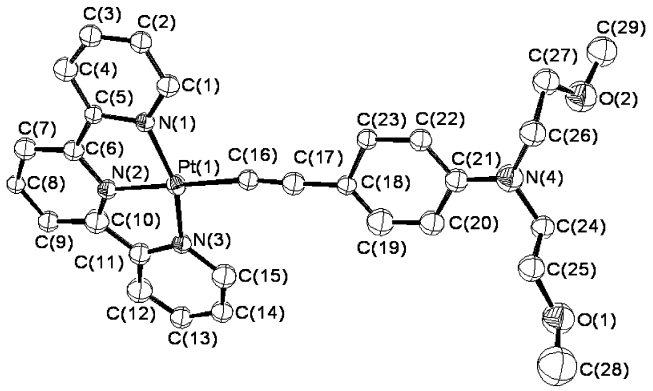

Figure 1. Perspective drawing of the complex cation of **2** with the atomic numbering scheme. Thermal ellipsoids were shown at the 30% probability level.

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

Pt(1)−N(1)	2.06(2)	Pt(1)−C(16)	2.07(3)
Pt(1)−N(2)	2.04(2)	C(16)−C(17)	1.22(3)
Pt(1)−N(3)	2.01(19)		
N(2)−Pt(1)−N(1)	83.6(8)	N(2)−Pt(1)−C(16)	179.7(9)
N(3)−Pt(1)−N(2)	76.8(8)	N(1)−Pt(1)−C(16)	96.4(9)
N(3)−Pt(1)−N(1)	160.4(7)	C(17)−C(16)−Pt(1)	168.0(3)

of the terpyridine ligands. The bands at 412−414 nm are assigned to a dπ(Pt) → π^*(tpy) metal-to-ligand charge-transfer (MLCT) transition, while the lowest energy absorption bands at 510−546 nm are assigned to a π(C≡C) → π^*(tpy) ligand-to-ligand charge-transfer (LLCT) transition, probably mixed with some MLCT contribution. The relatively low energy of the LLCT absorptions is attributed to the good electron-donating ability of the amino moieties. Alternatively, the transition can be viewed as an intramolecular charge-transfer transition from the strongly donating amino group on the arylalkynyl to the good π-accepting terpyridine ligand through the platinum metal center. Our assignment has been made on the basis of the following grounds. According to the previous spectroscopic studies on related platinum(II) terpyridyl systems, $[Pt(tpy)X]^+$ involving X = Cl, Br, SCN, N_3, NH_3, PPh_2R, $NC_5H_4C{\equiv}CR$,[1b,2e] no significant shifts in the energy of the low-energy dπ(Pt) → π^*(tpy) MLCT absorption band at ca. 400 nm was observed upon a change in the nature of the ligand X. In contrast, the low-energy absorption band was found to shift dramatically to the red for the complexes $[Pt(tpy)X]^+$ when X = I and SR, and such low-energy absorption was tentatively assigned as LLCT transition.[2e,f,7] Thus, the dependence of the lowest energy absorption on the nature of the alkynyl ligands is suggestive of the assignment of a transition of predominantly LLCT character with some mixing of a MLCT character. In addition, a plot of the energy of this low-energy absorption band versus the Hammett σ^+ value[21] for $[Pt(tpy)(C{\equiv}C{-}C_6H_4{-}R\text{-}4)]^+$ shows a straight line with a slope of ca. 2200 cm^{-1}/unit change in σ^+ ($r = 0.99$) as shown in Figure 2. This demonstrates the sensitive dependence of the absorption energy on the R substituents of the alkynyl ligands, signifying

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(21) March, J. *Advanced Organic Chemistry*: *Reactions, Mechanism, and Structure*, 4th ed.; John Wiley & Sons: New York, 1992.

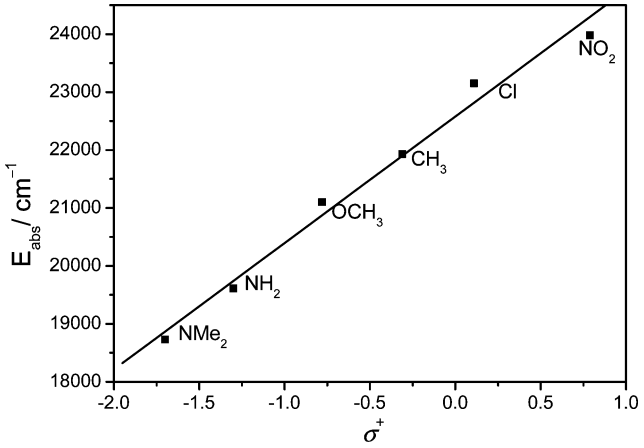

Figure 2. Plot of the energy of the lowest energy absorption band versus the Hammett σ^+ value for $[Pt(tpy)(C{\equiv}C{-}C_6H_4{-}R\text{-}4)]^+$ (■) and its linear least-squares fit (−). For R = OCH, CH_3, Cl, NO_2, the absorption energies were taken from ref 1a.

the substantial involvement of the alkynyl ligand in the transition. For a related neutral platinum(II) bipyridyl system, [Pt(4,4′-R_2-bpy)(tdt)] (bpy = 2,2′-bipyridine, tdt = toluene-3,4-dithiolate), a similar plot of the charge-transfer-to-diimine emission energy versus the Hammett constant gave a slope of ca. 4900 cm^{-1}/unit change in σ, upon variation of the substituent groups R.[22] Because there are two R substituents on the 4,4′- positions of the 2,2′-bipyridine ligand, such a value for the slope is comparable to that observed in the $[Pt(tpy)(C{\equiv}C{-}C_6H_4{-}R\text{-}4)]^+$ complexes. On the other hand, a plot of emission energy versus the Hammett σ^+ value on the related rhenium(I) polypryidyl system, $[Re(bpy)(CO_3)(NC_5H_4{-}R\text{-}4)]^+$, in which transitions of a pure MLCT character are well-documented, gave a smaller slope of 790 cm^{-1}/unit change in σ^+, indicating a smaller influence of the remote R group on the transition energy.[23] Thus, the significant decrease in the low-energy absorption energy in the $[Pt(tpy)(C{\equiv}C{-}C_6H_4{-}R\text{-}4)]^+$ system from 23 980 to 18 730 cm^{-1} upon changing the remote R group from $-NO_2$ to $-NMe_2$ suggests that the role of the R group is one that has a more direct involvement in the transition. Accordingly, a transition of predominantly LLCT character mixed with some MLCT contribution has been assigned to the lowest energy absorption band. However, one should be aware that the assignments of electronic transitions between metal and/or ligand localized orbitals are only rough approximations because of the possible extensive orbital mixing in these complexes. The electronic absorption spectra of complexes **4**−**6** in water show intense absorption bands at 280−290 nm and low-energy absorption bands at 488−520 nm. Similar to complexes **1**−**3**, the high-energy intense absorption bands at 280−290 nm are assigned to IL transition of terpyridine ligand, while the low-energy absorption bands at 488−520 nm are assigned to LLCT transition mixed with MLCT character. The UV−vis absorption spectral data for complexes **1**−**6** are summarized in Table 3. The energy trend of

Figure 3. Solutions of **2** (concentration = 1.8×10^{-4} M) in acetonitrile with various concentrations of *p*-toluenesulfonic acid (from left to right): 0, 0.11, 0.16, 0.18, 0.22, 0.27, 0.33, 0.44 mM, demonstrating the drastic color change at different acid concentrations.

Table 3. UV−vis Absorption Spectral Data for Complexes **1**−**6**

complex	medium (*T*/K)	absorption λ_{max}/nm (ϵ_{max}/dm^3 mol^{-1} cm^{-1})
1	MeCN (298)	288 (51 750), 342 (14 760), 412 (2705), 534 (5080)
2	MeCN (298)	288 (50 185), 342 (15 160), 412 (2760), 546 (5285)
3	MeCN (298)	286 (46 755), 342 (12 300), 414 (2900), 510 (4680)
4	H_2O (298)	284 (41 730), 496 (3975)
5	H_2O (298)	290 (40 905), 520 (4255)
6	H_2O (298)	280 (34 135), 488 (3535)

the LLCT absorption bands follows the electron-richness of the amino groups, $N(CH_2CH_2OMe)_2 > NMe_2 > NH_2$. The more electron-donating amino group would render the alkynyl groups more electron-rich and result in the raising of the $\pi(C{\equiv}C)$ orbital energy and lowering of the LLCT absorption energy. Similar to other Pt(II) polypyridine complexes,[1h,2f,20b,22,24] negative solvatochromic behavior has been observed, in which the low-energy LLCT absorption bands are blue-shifted in water as compared to acetonitrile, in line with the expected decrease in dipole moment on going from the ground to the excited state.

Emission Properties. Unlike most other platinum(II) terpyridyl complexes,[1a−f,2] which usually exhibit intense ^{3}MLCT luminescence, complexes **1**−**3** do not emit in acetonitrile solutions or in the solid state. The lack of emissive behavior is probably a result of the presence of the amino functionalities, which leads to the quenching of the ^{3}MLCT state by the lower-lying nonemissive ^{3}LLCT state, as well as by reductive electron transfer.

Acid−Base Titration Studies. Complexes **1**−**3** exhibit drastic color changes from purple through orange to yellow upon addition of *p*-toluenesulfonic acid to the complex solutions in acetonitrile. Figure 3 demonstrates the remarkable color change of complex **2** with increasing acid concentration in acetonitrile solutions. Electronic absorption titration studies showed that the lowest energy absorption bands at 534 nm in complex **1** and 546 nm in complex **2** decrease in absorbance while the higher energy absorption band at 412 nm increases in absorbance with increasing acid concentration in acetonitrile solutions, with a well-defined isosbestic point at 460 nm, indicative of a clean conversion of complexes **1** and **2** to their respective protonated forms.

(22) Cummings, S. D.; Eisenberg, R. *J. Am. Chem. Soc.* **1996**, *118*, 1949−1960.
(23) Sacksteder, L. A.; Zipp, A. P.; Brown, E. A.; Streich, J.; Demas, J. N.; DeGraff, B. A. *Inorg. Chem.* **1990**, *29*, 4335−4340.
(24) Pomestchenko, I. E.; Castellano, F. N. *J. Phys. Chem. A* **2004**, *108*, 3485−3492.

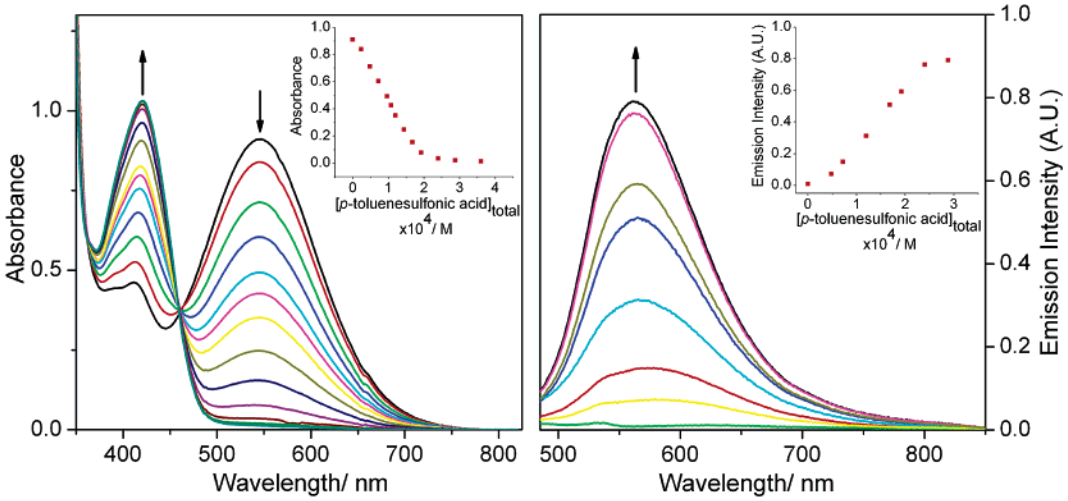

Figure 4. UV−vis absorption changes of **2** (concentration = 2.0×10^{-4} M) in acetonitrile (0.05 M $^{n}Bu_4NPF_6$) with increasing *p*-toluenesulfonic acid concentration (left). Inset: Plot of absorbance at 546 nm against the total concentration of *p*-toluenesulfonic acid. Emission spectral traces of **2** (concentration = 1.8×10^{-4} M) in acetonitrile (0.05 M $^{n}Bu_4NPF_6$) with increasing *p*-toluenesulfonic acid concentration (right). Inset: Plot of relative emission intensity at 563 nm against the total concentration of *p*-toluenesulfonic acid.

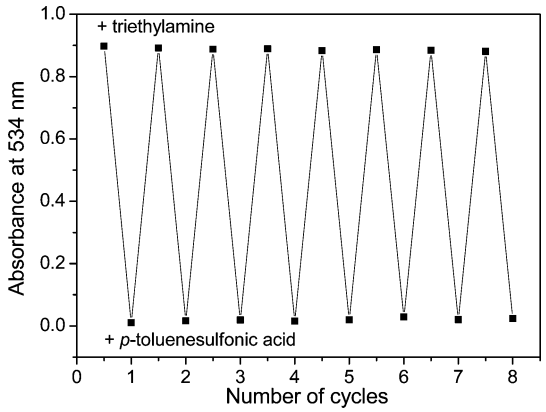

Figure 5. UV−vis absorption changes of **1** (concentration = 1.7×10^{-4} M) in acetonitrile (0.05 M $^{n}Bu_4NPF_6$) with alternate addition of *p*-toluenesulfonic acid and triethylamine for eight repeating cycles.

The change in the UV−vis absorption spectra of **2** upon addition of acid is illustrated in Figure 4 (left). A corresponding titration study was not performed for complex **3** due to precipitate formation in the presence of *p*-toluenesulfonic acid. The drastic color changes are ascribed to the protonation of the amino group in **1** and **2** upon introduction of acid, which decreases the electron-donating ability of the alkynyl ligand, shifting the low-energy LLCT band to the blue, causing a drop in the absorbance of the 534−546 nm band and an increase in the intensity of the 412 nm band. This acid-dependent color change is found to be fully reversible upon alternate addition of *p*-toluenesulfonic acid and triethylamine, with at least eight repeating cycles. Figure 5 illustrates the reversibility of complex **1** upon alternate addition of *p*-toluenesulfonic acid and triethylamine.

The emission properties in the presence of acid were also studied. Dramatic emission intensity enhancement was observed with increasing *p*-toluenesulfonic acid concentration in the acetonitrile solutions of **1** and **2** at 560 and 563 nm, respectively, at room temperature. Both complexes are nonemissive in the absence of acid. The emission intensity enhancement of **2** with increasing acid concentration is shown in Figure 4 (right). The switching on or revival of emission is probably a result of the shift of the ^{3}LLCT state to higher energies as well as the elimination of reductive electron-transfer quenching pathway upon protonation of the amino group, giving rise to a ^{3}MLCT [dπ(Pt) → π^*(tpy)] emission. The luminescence quantum yields of protonated **1** ([**1**] = 3.0×10^{-5} M; [*p*-toluenesulfonic acid] = 6.1×10^{-5} M) and **2** ([**2**] = 3.0×10^{-5} M; [*p*-toluenesulfonic acid] = 6.1×10^{-5} M) in acetonitrile were found to be ca. 4×10^{-4} and 7×10^{-4} respectively, measured at room temperature using $[Ru(bpy)_3]^{2+}$ as standard. Their lifetimes under these conditions were found to be 0.62 ± 0.02 and 0.56 ± 0.03 μs, respectively.

pK_a Determination. Complexes **4**−**6**, the chloride salts of **1**−**3**, were used for the determination of the pK_a in aqueous buffer solutions. Different pH buffer solutions with 0.01 M ionic strength were prepared by the literature method.[25] The buffer solutions ranging from pH 2.2 to 6.2 were prepared from solutions of different organic acids in potassium hydroxide, with pH 2.2 to pH 3.1 from chloroacetic acid/potassium hydroxide mixture, pH 3.2 to pH 4.1 from formic acid/potassium hydroxide, and pH 4.2 to pH 6.2 from succinic acid/potassium hydroxide mixtures. Like the UV−vis absorption and emission titration studies of **1** and **2** in acetonitrile, buffer solutions of **4**−**6** show similar UV−vis spectral changes upon a change in pH. The absorbance of the low-energy LLCT bands decreases, while that of the MLCT bands increases with decreasing pH. Luminescence enhancement was also observed. Complexes **4**−**6** do not emit in aqueous solutions, while their protonated forms emit. The pK_a values of **4**, **5**, and **6** were found to be 3.55, 2.29, and 3.22, respectively, from the inflection point of the plot of absorbance at λ_{max} against pH. These findings were consistent with the pK_a values determined according to eq 1,[9b]

(25) Perrin, D. D. *Aust. J. Chem.* **1963**, *16*, 572−578.

$$\log[(A_{max} - A)/(A - A_{min})] = pH - pK_a \quad (1)$$

in which the pK_a values for **4**, **5**, and **6** were found to be 3.54 ± 0.02, 2.30 ± 0.01, and 3.20 ± 0.04, respectively (Supporting Information). The electron-richness of the amino groups is in the order of: $N(CH_2CH_2OMe)_2 > NMe_2 > NH_2$. The higher p$K_a$ value of complex **4** as compared to complex **6** shows that the protonated form of complex **4** is more favorable due to the presence of the more electron-donating methyl groups. According to the pK_a values, the protonated form of complex **5** is least favorable; however, the $-CH_2CH_2OMe$ group is the most electron-donating out of the three. Thus, the steric bulk of the two $-CH_2CH_2OMe$ groups may play an important role in this case because this may hinder protonation of the amino group, because the change in configuration at the nitrogen atom on protonation may lead to greater internal strain in the protonated form than in the unprotonated species. In addition, the two bulky $-CH_2CH_2OMe$ groups in **5** may also result in the poorer solvation of the conjugate acid, and thus the pK_a value is lowest. A similar trend in the pK_a values was also reported for a related ruthenium(II) polypyridyl system.[9a]

Conclusion

A series of platinum(II) terpyridyl alkynyl complexes were successfully synthesized and characterized, and their pH sensing property has been studied. The complexes exhibit dramatic and reversible color change and luminescence switching upon addition of acid, as a result of the protonation of the amino group which decreases the electron-donating ability of the alkynyl ligand and results in a blue shift of the low-energy LLCT absorption and the corresponding shift of the ^{3}LLCT state to higher energy. The reversibility of color changes was studied upon alternate addition of *p*-toluenesulfonic acid and triethylamine. These findings suggest that with a suitable design of the ligands and complexes, and a sound understanding of the spectroscopic properties of these complexes, promising potential colorimetric and luminescence pH sensors could be developed.

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Supporting Information Available: Tables of atomic coordinates, thermal parameters, a full list of bond distances and angles for **2** and fitting curves of **4**−**6** for pK_a determination, and crystallographic data in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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