Determination of pK_a Values of 4-Phosphonato-2,2′:6′,2″-Terpyridine and Its Ruthenium(II)-Based Photosensitizer by NMR, Potentiometric, and Spectrophotometric Methods

Md. K. Nazeeruddin,* S. M. Zakeeruddin, R. Humphry-Baker, T. A. Kaden,† and M. Grätzel*

Institute of Photonics and Interfaces, Swiss Federal Institute of Technology, CH-1015 Lausanne, Switzerland

Received February 28, 2000

The dissociation constants of the 4-phosphonato-2,2′:6′,2″-terpyridine ligand were measured by pH−NMR and potentiometric titration methods. The 4-phosphonato-2,2′:6′,2″-terpyridine ligand shows three measurable pK_a values at 5.99, 4.65, and 3.55 using the latter method. The fourth pK_a was estimated to be below 2. Spectrophotometric titration of the ruthenium complex [Ru(P-terpy)(Me_2bpy)(NCS)] (**1**) (P-terpy = 4-phosphonato-2,2′:6′,2″-terpyridine and Me_2bpy = 4,4′-dimethyl-2,2′-bipyridine) exhibits two ground-state pK_a values at 6.0 and below 4.0, which can be assigned to pK_{a1} and pK_{a2}, respectively. The emission maximum of complex **1** shows a blue shift with decreasing pH, and apparent pH-dependent excited-state lifetimes. Complex **1** shows two excited-state pK^*_a values at 6.5 (pK^*_{a1}) and below 4.5 (pK^*_{a2}). Comparison of the ground- and excited-state pK_a values of complex **1** demonstrates that the excited state has metal to 4-phosphonato-2,2′:6′,2″-terpyridine ligand charge-transfer character.

1. Introduction

Ruthenium polypyridyl complexes have been studied most extensively during the last 30 years because of their long-lived metal-to-ligand charge-transfer (MLCT) excited states that can participate in electron- and energy-transfer reactions.[1] Recently, potential applications for these complexes that contain ligands with functional groups as photosensitizers have been reported in different laboratories.[2−4] The functional groups serve as grafting agents for the oxide surface of the TiO_2 films. The grafting of polypyridyl complexes onto the oxide surface, which allows for electronic communication between the complex and the substrate, is an important target in dye-sensitized solar cells and molecular electronics.[5] Several ruthenium complexes containing phosphonated polypyridyl ligands have been described in which the phosphonate functionality serves as an anchoring group to immobilize the complex on the nanocrystalline TiO_2 films.[6,7] The immobilized sensitizer absorbs a photon to produce an excited state, which efficiently transfers its electron onto the TiO_2 conduction band. Such electron-transfer processes (incident photon-to-current conversion efficiency) have been reported for ruthenium(II) polypyridyl complexes containing phosphonated and carboxylic acid functional groups, ∼80% and ∼90%, respectively.[8,9] These complexes were presumed to chelate through the functional groups onto TiO_2. On the basis of IR and Raman data, Woollfrey et al. have reported that the complexes containing 2,2′-bipyridine-4,4′-dicarboxylate ligands anchor on the surface of TiO_2 as bidentate chelates.[10] The phosphonate functional group is also postulated to attach in a similar fashion.

* To whom correspondence should be addressed. E-mail: nazeer@dcmail.epfl.ch (Md.K.N.). Phone: +41-21-693-6124. Fax: +41-21-693-4111.

† Institute of Inorganic Chemistry, University of Basel, Spitalstrasse 51, CH-4056 Basel, Switzerland.

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10.1021/ic000215+ CCC: $19.00
Published on Web 09/09/2000

However, during our studies we discovered that when TiO_2 electrodes containing phosphonated and carboxyl-functionalized dyes were dipped in water at pH 5−6, the dyes that contain carboxyl groups desorbed whereas phosphonated dyes remained intact on the surface.[11] Identification of the factors responsible for differences in the attachment properties of distinct functional groups is essential for the design of novel sensitizers. The difference in binding properties of the complexes containing carboxyl and phosphonate groups may stem from the differences in the pK_a values of the ligands. Knowledge of the pK_a values of ionizable groups may aid in indicating the possible nature of the attachment. The proton equilibrium constant for the 4,4-dicarboxy-2,2′-bipyridine ligand in various ruthenium complexes has been reported.[12] In this paper we report the dissociation constants of the 4-phosphonato-2,2′:6′,2″-terpyridine ligand and its ruthenium complex using different analytical techniques.

2. Experimental Section

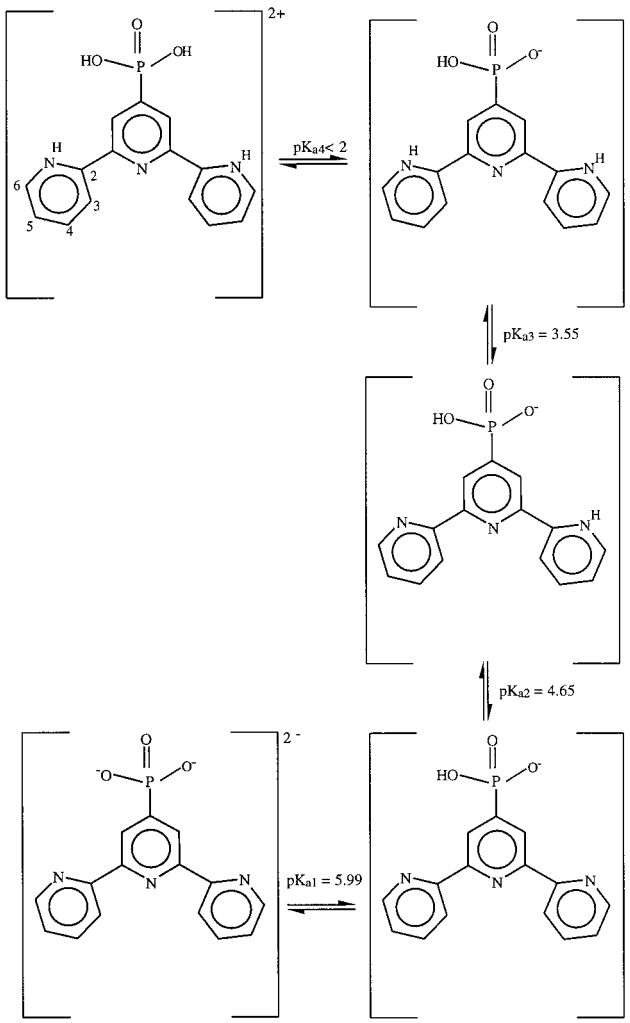
2.1. Materials. The solvents and chemicals were commercial puriss grade from Fluka and were used as supplied. $RuCl_3 \cdot 3H_2O$ was obtained from Johnson & Matthey. 4,4′-Dimethyl-2,2′-bipyridine (Me_2bpy) was a commercial sample from Aldrich and was recrystallized before use. The ligand 4-phosphonato-2,2′:6′,2″-terpyridine (P-terpy) and the complex [Ru^{II}(P-terpy)(Me2bpy)(NCS)] (**1**) were available from our previous studies.[9]

2.2. Methods. UV−vis and fluorescence spectra were recorded in a 1 cm path length quartz cell on a Cary 5 spectrophotometer and a Spex Fluorolog 112 spectrofluorometer, respectively. The emitted light was detected with a Hamamatsu R2658 photomultiplier operated in a single photon counting mode. The emission spectra were photometrically corrected using a calibrated 200 W tungsten lamp as the reference source. A dilute solution of quininesulfate was used as the quantum yield standard. The solutions were prepared to give approximate concentrations of 10 μM, and purged with nitrogen. The emission lifetimes were measured by exciting the sample with a pulse from an active mode-locked Nd:YAG laser, using the frequency-doubled line at 532 nm. The emission decay was followed on a Tektronix DSA 640 digitizing signal analyzer, using a Hamamatsu R928 photomultiplier to convert the light signal to a voltage waveform.

Proton and ^{31}P NMR spectra were measured on a Bruker 250 MHz spectrometer, and the reported chemical shifts for ^{1}H and ^{31}P are given against TMS and 85% H_3PO_4, respectively. The details of the pH−NMR titration setup and the curve-fitting program used were described in our recent publication.[13] The potentiometric titration of the ligand and the complex was run on the automatic titrator consisting of a Metrohm 605 pH-meter, a Metrohm 665 buret, a thermostated titration vessel, and a 286-AT PC controlling the setup. The calibration method of the electrodes, the activity coefficient of the proton, a_H, and pK_w have been described elsewhere.[14]

The ground- and excited-state pK_a values of complex **1** were determined by UV−vis and emission measurements over the pH range 3.5−10.5. A stock solution (5×10^{-5} M) was prepared in 100 cm^3 of a 10:1 H_2O/DMSO mixture containing 0.1 M KCl. Since the neutral complex **1** was insoluble in water, 10% DMSO was added to avoid the precipitation. The initial pH of the solution was adjusted to 10.5 by adding 0.2 M NaOH solution. The pH of the solution was lowered by the addition of HCl solution. The acid was added in such a fashion that throughout the entire measurements the total volume of added acid was negligible. The UV−vis spectrum of each solution was obtained after adding acid and allowing the solution to equilibrate for 5 min. The emission spectra and the lifetime data were collected without degassing the solutions at room temperature by exciting into the lowest-energy MLCT band at 500 nm.

Scheme 1. Acid-Base Equilibria of 4-Phosphonato-2,2′:6,2″-terpyridine



3. Results and Discussion

3.1. Determination of the pK_a of the 4-Phosphonato-2,2′:6′,2″-terpyridine Ligand by ^{31}P NMR Titration. The ^{31}P NMR titration data of 4-phosphonato-2,2′:6′,2″-terpyridine show that it is protonated in four steps in the pH region of 1.5−7. Out of four protons, two are involved in protonation of pyridyl nitrogens of terpyridyl, and the remaining two protons are on the phosphonated group. Since the adjacent nitrogens of the 2,2′-bipyridyl ligand accept only one proton down to pH 1.6, it can be safely assumed that 4-phosphonato-2,2′:6′,2″-terpyridine accepts protons in nonadjacent positions as shown in Scheme 1.[15] The central nitrogen of the 4-phosphonato-2,2′:6′,2″-terpyridine is sterically restricted and less basic because of the doubly protonated form.

The phosphorus and proton resonance peaks are sensitive to pH due to the protonation and deprotonation of the ligand. The ^{31}P and ^{1}H NMR spectral data obtained for the free ligand containing different degrees of protonation are summarized in Table 1 (see the Supporting Information for Table 1). The dissociation constants, which were determined by potentiometric

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Table 2. Protonation Constants of 4-Phosphonato-2,2′:6′,2″-terpyridine and Complex **1**

species	pK_{a1}	pK_{a2}	pK_{a3}	method
ligand	6.20 ± 0.05	5.04 ± 0.02	3.70 ± 0.05	^{1}H/^{31}P, HYPNMR[a]
ligand	5.80 ± 0.05	4.64 ± 0.02	3.30 ± 0.05	^{1}H/^{31}P, corrected[b]
ligand	5.99 ± 0.01	4.65 ± 0.01	3.55 ± 0.03	potentiometric[c]
complex **1**	6.0 ± 0.1			spectrophotometric
complex **1**	6.5 ± 0.1[d]			spectrofluoromtric
complex **1**	6.87 ± 0.02			potentiometric[e]

[a] Temperature 25 °C, in D_2O, no control of ionic strength as obtained from HYPNMR. [b] Temperature 25 °C, in D_2O, no control of ionic strength, corrected with pH = pD − 0.4. [c] 25 °C, $I = 0.5$ mol dm^{-3} (KNO_3). [d] This value is an excited-state pK^*_{a1}. [e] Temperature 25 °C, in H_2O:DMSO = 1:1, $I = 0.5$ mol dm^{-3} (KNO_3).

and NMR titration methods, are gathered in Table 2. The neutral 4-phosphonato-2,2′:6′,2″-terpyridine ligand in DMSO solvent shows a phosphorus resonance signal at 9.51 ppm, with respect to an external standard, 85% H_3PO_4.

The pH−NMR titration of the protonated ligand was carried out in D_2O solution using a fully automated pH−NMR titration setup, which allows one to obtain at each titration point ^{31}P and ^{1}H NMR spectra with the same solution. The ligand solution at pH 2.3 shows a ^{31}P resonance peak at 6 ppm. Upon increasing the pH to 5, the phosphorus resonance line moves from 6 to 8.5 ppm. The ∼2.5 ppm downfield shift reflects the extent of deshielding due to deprotonation of the pyridyl nitrogens. Upon further increasing the pH to 12, the phosphorus resonance signal moves to high field (7.5 ppm) due to the increased electron density caused by the deprotonation of the phosphonate group. Figure 1 (top panel) shows the chemical shifts for ^{31}P as a function of pH that were determined using the peak search subroutine of WinNMR.[16] The bottom panel of Figure 1 shows the ^{31}P NMR shift change with pD, and calculated chemical shifts are shown as a solid line, which exhibit good agreement with the experimental results. The data were fitted using the HYPNMR program,[17] which gave three pK_a values at 5.80 ± 0.05, 4.64 ± 0.02, and 3.30 ± 0.05 assigned to pK_{a1}, pK_{a2}, and pK_{a3}, respectively (Table 2). We could not resolve the pK_{a4}, which is below 2, beyond the detection limit of our system. On the basis of the shift of the phosphorus resonance signal, we assigned 4.64 and 3.30 values to the pK_{a2} and pK_{a3} coming from pyridyl nitrogen protonation, and pK_{a1} and pK_{a4} are from the phosphonate protonation as shown in Scheme 1. Kim and Nancollas have reported the pK_a values of 2,2′:6,2″-terpyridine at 3.42 and 4.64.[18] Our data for 4-phosphonato-2,2′:6′,2″-terpyridine are in full agreement with their values.

3.2. Determination of the pK_a of the 4-Phosphonato-2,2′:6′,2″-terpyridine Ligand by ^{1}H NMR Titration. The proton NMR specrum of the fully deprotonated ligand shows a lowest field doublet centered at δ 8.68 ppm, which is assigned to the H6 proton of the 4-phosphonato-2,2′:6′,2″-terpyridine ring. The remaining doublet at δ 8.67 and the two triplets at 8.05 and 7.55 ppm are assigned to the H3, H4, and H5 protons, respectively (for proton numbering, see the first structure in Scheme 1). The most characteristic feature of the central pyridine H3′ proton of the 4-phosphonato-2,2′:6′,2″-terpyridine ligand is its coupling with the phosphorus atom (10.8 Hz) that gives a doublet centered at δ 8.3 (not shown in Table 1). The pK_a values were obtained by plotting the change in chemical shift of the different proton resonance signals against pH and fitting the points with HYPNMR.[17] Figure 2 shows a plot of the H6, H5, H4, and H3 resonance shifts with pH. There is a significant change in the proton resonance signals up to pH 5, due to the deprotonation of the pyridyl nitrogens. After pH 5, the changes are marginal because the deprotonation is occurring at the phosphonate group, which is far from the pyridyl protons. It is quite interesting to note the considerable upfield shift of the H4 proton (0.79 ppm) from changing the pH from 2.5 to 8 compared to that of the H6 proton (0.34 ppm), though the latter is very close to the protonation site, i.e., the pyridyl nitrogen.

3.3. Determination of the pK_a of the 4-Phosphonato-2,2′:6,2″-terpyridine Ligand by the Potentiometric Method. The

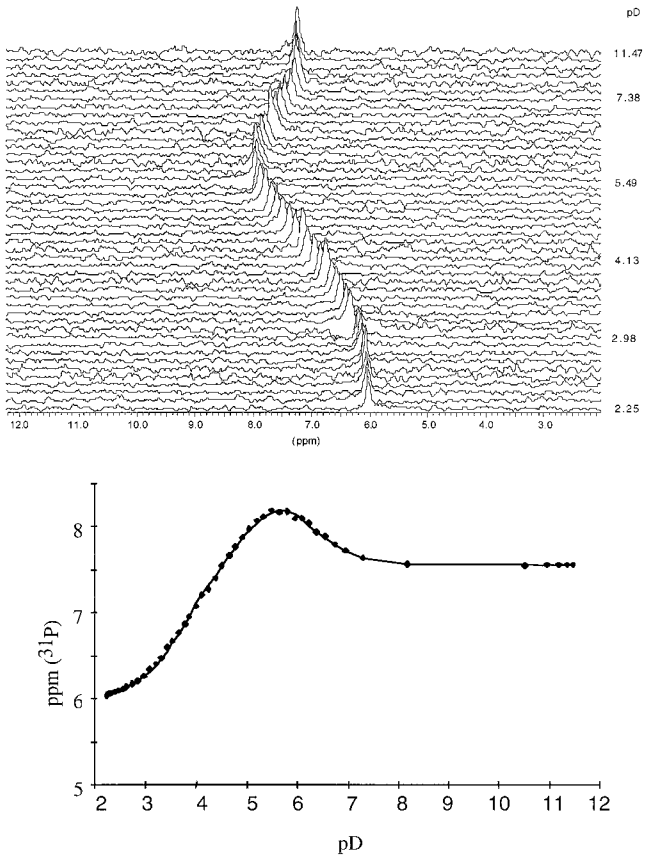

Figure 1. ^{31}P NMR spectra of 4-phosphonato-2,2′:6′,2″-terpyridine as a function of pD (top panel). The bottom panel shows δ_P as a function of pD. The experimental points are indicated by ◆, and the solid line is calculated with the δ_P values of Table 1 obtained from HYPNMR.

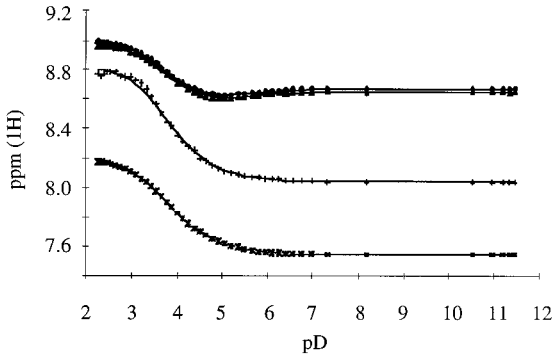

Figure 2. Chemical shifts taken from the ^{1}H NMR spectra of 4-phosphonato-2,2′:6′,2″-terpyridine as a function of pD. Experimental points: (◆) H_6, (▲) H_3, (+) H_4, (*) H_5.The solid lines are calculated with the δ_H values of Table 1 for the corresponding protons that were obtained from HYPNMR.

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protonation constants of the ligand were determined by titration of an aqueous solution of the fully protonated ligand containing 0.5 M KNO_3 at 25 °C with a 0.4 M NaOH solution. Figure 3 (top panel) shows a titration curve of the ligand in the 2−11 pH range (see the Supporting Information for Figure 3). The titration curve was fitted with the program TITFIT[19] assuming that the ligand has three acidic protons above pH 2. The fourth proton has a pK_a value that is below 2 and not measurable under our conditions. The results of the two titrations are in good agreement and are gathered in Table 2. Figure 3 (bottom panel) shows the abundance of species distributed at different pH values. The fully protonated ligand is LH_4, from which other species are formed by deprotonation as shown in eq 1. It is quite rewarding that the values obtained by the potentiometric method are in good agreement with those obtained by the NMR titration (Table 2).

$$LH_4^{2+} \overset{pK_{H4}}{\rightleftharpoons} LH_3^{+} \overset{pK_{H3}}{\rightleftharpoons} LH_2 \overset{pK_{H2}}{\rightleftharpoons} LH^{-} \overset{pK_{H1}}{\rightleftharpoons} L^{2-} \quad (1)$$

Dissociation constants of aminopolyphosphonate ligands have been studied by many groups using phosphorus NMR and potentiometric methods.[13,20] The pK_a values of these ligands depend very much on the number of phosphonate groups owing to the negative charge. However, *N*,*N*-dimethylaminomethylphosphonic acid and 4-pyridylmethylphosphonic acid, which have two protons each, will be the ideal candidates for comparison with the 4-phosphonato-2,2′:6′,2″-terpyridine ligand. *N*,*N*-Dimethylaminomethylphosphonic acid shows two pK_a values due to the phosphonic group at 5.16 and 1.3.[20] Kostka and Ochocki have reported three pK_a values for 4-pyridylmethylphosphonic acid, out of which two at 7.44 and 1.12 are assigned to phosphonic acid pK_{a1} and pK_{a2}, respectively.[21] The ∼2 pK_a unit difference between the aliphatic and aromatic phosphonic acid groups displays the extent of basisity in the latter case. The experimentally found pK_{a1} of the 4-phosphonato-2,2′:6′,2″−terpyridine ligand is 5.8, which is ∼1.64 pK_a less basic than the pyridine phosphonic acid. The difference could be due to the delocalization of electron density on the three pyridyl rings of the terpyridine, which modifies the pK_a value, causing the phosphonic acid group to be less basic compared to the pyridine phosphonic acid.

3.4. Determination of the Ground-State pK_a of Complex 1 by the Spectrophotometric Method. Complex **1** is highly colored due to intense MLCT transitions in the visible region (see Figure 4 in the Supporting Information for the structure of complex **1**). The absorption spectrum of complex **1** measured in ethanol solution at room temperature shows a maximum at 506 nm. Besides the intense lowest-energy MLCT band, the spectra possess additional absorption features at lower and higher energies. Complex **1** shows UV bands at 318 and 282 nm due to the intraligand $\pi-\pi^*$ transition of 4-phosphonato-2,2′:6′,2″-terpyridine and Me_2bpy, respectively.

The lowest-energy MLCT absorption band in complex **1** is red shifted compared to those of the corresponding homoleptic complexes of the types $[Ru^{II}(terpy)_2]$ and $[Ru^{II}(Me_2bpy)_3]$.[22] The apparent red shift is attributed to an increase in the energy of the metal t_{2g} orbital due to the donor properties of the thiocyanate ligand. The broad absorption in the 400−500 nm range is a composite of MLCT transitions involving 4-phosphonato-2,2′:6′,2″-terpyridine and Me_2bpy ligands. The longer wavelength band of complex **1** is 20 nm blue shifted in water (at pH 3.5) compared to that in ethanol due to the solvato chromism. Deprotonation of the phosphonate groups in complex **1** slightly blue shifts the $\pi-\pi^*$ and MLCT charge-transfer bands.

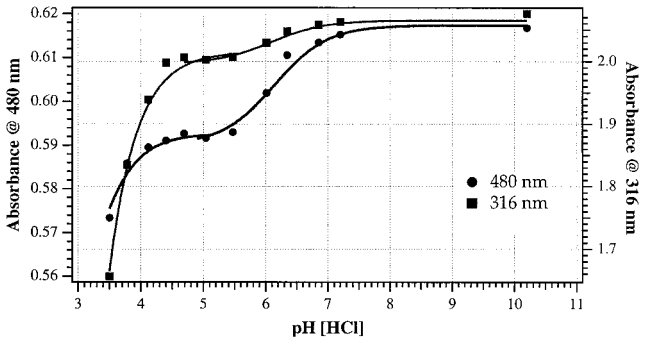

Figure 5. Absorbance changes as a function of pH in complex **1** at λ 480 and 316 nm. The solid lines are calculated using the pK_a values 6.0 and 3.5.

Complex **1** at pH 10.5 shows an MLCT band at 483, two distinct shoulders at 436 and 358 nm, and two high-energy $\pi-\pi^*$ bands at 316 and 282 nm. When acid is added to an alkaline solution of complex **1**, changes in the absorbance occur as shown in Figure 5. Upon lowering the pH from 10.5 to 3.5, the MLCT transition band shifts from 483 to 488 nm. The intraligand ($\pi-\pi^*$) transition shifts from 316 to 319 nm with an isosbestic point at 305 nm. The ground-state pK_a values were obtained from the relationship between the change in the optical density or the peak maximum with the pH for a given wavelength. Figure 5 shows a titration curve, obtained by plotting the change in absorbance at λ 480 and 316 nm vs pH for complex **1**. The plot shows a clear inflection point at pH 6.0 ± 0.1, giving the ground-state pK_a value, which is assigned to the pK_{a1} of the 4-phosphonato-2,2′:6′,2″-terpyridine ligand. However, at pH below 3.5, precipitation of the complex becomes apparent and the second pK_a can not be resolved. Recently, Montalti et al. have reported ground- and excited-state pK_a values of ruthenium tris complexes containing different phosphonated ligands. In their studies they found two ground-state pK_a values at 6.3 and ∼2.[7a] The measured pK_{a1} value of 4-phosphonato-2,2′:6′,2″-terpyridine is comparable to that of the 4-phenylphosphonato-2,2′-bipyridine ligand.

3.5. Determination of the Excited-State pK^*_a of Complex 1 by the Spectrofluorometric Method. When complex **1** is excited at 298 K in an air-equilibrated ethanolic solution, within the MLCT absorption band, it exhibits a luminescence maximum at 780 nm and a lifetime of 29(±1) ns. The emission spectral profile is independent of the excitation wavelength, and the excitation spectrum matches well with the absorption spectrum. It is remarkable that complex **1** is strongly emitting at room temperature with an excited-state lifetime of 29 ns. Under similar conditions, ruthenium bisterpyridine complexes show an excited-state lifetime of less than 2 ns.[9,23] The reason for such a long excited-state lifetime for complex **1** compared to the ruthenium bisterpyridine complexes is due to the strong splitting of the t_{2g} and e_g level of metal orbitals caused by thiocyanate anionic ligands. Consequently, the dd states may not be thermally accessible at room temperature.[24]

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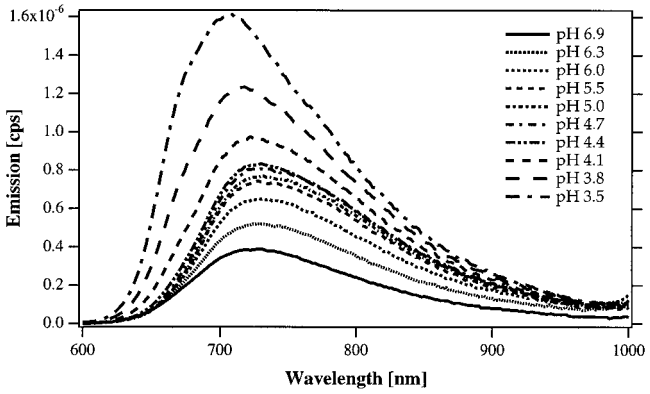

Figure 6. Emission spectral changes of complex **1** as a function of pH between 3.5 and 6.9. For clarity purposes, spectral data at higher pH are not shown in the figure.

The emission maxima of complex **1** are strongly solvent dependent, because of formation of hydrogen bonds with the lone pair electrons on the sulfur of the thiocyanate ligand. In water the emission maximum (718 nm at pH 11) is blue shifted compared to that in ethanol. The emission spectra were also blue shifted with decreasing pH (705 nm at pH 3.5). Figure 6 shows emission spectra of complex **1** measured at room temperature at different pH values, by excitation into the lowest-energy MLCT band (500 nm). Several observations can be made from Figure 6 on the emission behavior of complex **1**. The emission from the acid form is at a higher energy and is more intense as compared with that observed from the basic form. The excited-state lifetime data are consistent with the trend observed in emission intensities. The intense emission from the protonated form of the complex can be rationalized considering that in the acid form the differences in the emitting MLCT and the MC states are larger than those in the basic form. In their studies Barigelletti et al. have observed similar behavior for a ruthenium complex that contains protonatable sites.[25] The lifetime of complex **1** in water at pH 10 is 14 ns, and increases to 44 ns by decreasing the pH to 3.5. The plot of emission intensity vs pH shows an approximate inflection point at pH 6.0 (see Figure 7 in the Supporting Information). By using eq 2

$$\mathrm{pH} = \mathrm{p}K^*_a - \log(\tau_{acid}/\tau_{base}) \qquad (2)$$

developed by Ireland and Wyatt, one could calculate the excited-state pK^*_a values.[26] pH = value of the inflection point; τ_{acid} and τ_{base} are the experimentally measured lifetimes in the protonated and deprotonated forms. Using eq 2, we were able to estimate an excited-state pK^*_a of 6.5 for complex **1**, which is in agreement with the reported complexes containing phosphonated ligands.[7a] Our data show that the excited-state pK^*_a value is slightly basic compared to the ground-state pK_a value, suggesting that in the excited state the ligand electron density is higher because of charge-transfer transition from the metal to the 4-phosphonato-2,2′:6′,2″-terpyridine ligand. Nevertheless, the second excited-state pK^*_a is difficult to obtain because of the precipitation of complex **1** at pH below 3.5.

Comparison of ground-state and excited-state pK_a values provides valuable information for the identification of the ligand involved in the lowest-energy MLCT transition, which is essential for the design of photosensitizers for nanocrystalline solar cells based on TiO_2 films. The difference in the ground- and excited-state pK_a values can be considered as a measure of localization of charge on the ligand that contains protonatable sites. Wrighton et al. have investigated the ground- and excited-state pK_a values of the $[Ru(bpy)_2(4,7\text{-dihydroxy-}1,10\text{-phen})]^{2+}$ complex and found that the excited-state pK_a values are lower than the ground-state pK_a, indicating that in the excited state the charge is localized on the bipyridine ligand away from the 1,10-phenanthroline.[27] In a related system, $[Ru(bpy)_2(4,4'\text{-dicarboxy-}2,2'\text{-bipyriden})]^{2+}$, we and others found that the excited-state pK_a is ~1.5 units higher than the ground-state pK_a, implying that the ligand electron density is significantly higher in the excited state because of charge-transfer transition from the metal to the 4,4′-dicarboxy-2,2′-bipyridine ligand.[28]

The fact that in complex **1** the excited-state pK^*_a is slightly more basic than the ground-state pK_a indicates that in the excited state the electron is localized on the 4-phosphonato-2,2′:6′,2″-terpyridine ligand. Our findings are consistent with resonance Raman data of complex **1**, where the energy levels of the two ligands are very close, and in the excited state mostly 4-phosphonato-2,2′:6,2″-terpyridine peaks are enhanced compared to those of the 4,4′-dimethyl-2,2′-bipyridine ligand.[9] The other supporting evidence for an MLCT transition to the 4-phosphonato-2,2′:6,2″-terpyridine ligand comes from the incident photon-to-electron injection efficiency (IPCE) measurements on a nanocrystalline TiO_2 electrode. Using complex **1** as a charge-transfer sensitizer, we have obtained near-quantitative IPCE values.[11]

There is a striking difference between the emission intensity of complex **1** and the analogous ruthenium complexes that contain 4,4′-dicarboxyl-2,2′-bipyridine and 4-phenylphosphonato-2,2′-bipyridine ligands. In the latter case, the emission intensity decreases with decreasing pH and the lifetime of the MLCT excited state also decreases,[7a,28] whereas in the case of complex **1** the emission intensity and the lifetime increase with decreasing pH from 11 to 3.5. The other notable difference is the excited-state pK^*_a of the ruthenium complex that contains a 4,4′-dicarboxyl-2,2′-bipyridine ligand, which is 1.5 pK_a units more basic than the ground-state pK_a. However, in complex **1** the difference is only 0.5 pK_a unit, which reflects the extent of conjugation between the pyridyl units and the functional groups. In other words, the carboxylate functional group LUMO has a large overlap with the LUMO of the bipyridine compared to the LUMO of the phosphonate group, which facilitates the electron delocalization more efficiently in the former.

3.6. Determination of the pK_a of Complex 1 by the Potentiometric Method. The proton dissociation constant of complex **1** was found by titration in 1:1 aqueous and DMSO solution. The DMSO solvent was added to dissolve complex **1**, and no attempts were made to find the activity coefficient of the proton in this solution mixture. Hence, the observed pK_{a1} value is indicative rather than absolute. The titration curve of complex **1** between pH 4 and pH 13 was fitted assuming that the complex has one acidic proton above pH 4, and the obtained pK_{a1} value is gathered in Table 2. The difference in the pK_a value of the spectrophtometric and potentiometric methods is

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attributed to the presence of 50% DMSO solvent in the latter method compared to 10% DMSO in the former method.

Conclusions

An examination of the acid−base properties of 4-phosphonato-2,2′:6′,2″-terpyridine and complex **1** compared to the complexes that contain 4,4′-dicarboxy-2,2′-bipyridine shows that the strong anchoring property of complex **1** is due to the difference in the pK_a values, where the former is 3 pK_a units more basic than the latter. Hence, the complexes containing phosphonated functional groups provide the way for the design of new sensitizers that increase the binding to the oxide surfaces.

Acknowledgment. We acknowledge financial support of this work by the Swiss National Funds for Scientific Research (FNRS), Swiss Federal Office for Energy (OFEN), and National Institute for Applied Photovoltaic Research (INAP), Gelsenkirchen, Germany. We thank Mrs. L. Siegfried for running the NMR titrations and Dr. P. Bonhôte for providing the 4-phosphonato-2,2′:6′,2″-terpyridine ligand.

Supporting Information Available: Table 1 listing the chemical shifts of the different protonated species and Figures 3, 4, and 7 showing the structure of complex **1**, potentiometric titration of 4-phosphonato-2,2′;6′,2″-terpyridine, distribution diagram of various protonated species as a function of pH, and pH dependence of the emission intensity for complex **1** in a 10: 1 water/DMSO mixture containing 0.1 M NaCl, excited at 500 nm. This material is available free of charge via the Internet at http://pubs.acs.org.

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