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Anion-Sensitive 2,4-Dinitrophenylhydrazone-Containing Terpyridine Derivative and Its Platinum Chloride Complex

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Terpyridine derivative **1**, bearing 2,4-dinitrophenylhydrazone, and its platinum chloride complex **2** were synthesized and characterized. The UV/Vis, emission, and triplet transient difference absorption spectra of **1** and **2** were investigated. Both **1** and **2** exhibit broad and strong absorption in the visible spectral region (λ_{max} = 404 nm for **1** and 433 nm for **2**), which are dominated by the $^1\pi$–π^* transition of the ligand. When excited at the respective absorption band maximum, **1** and **2** exhibit charge-transfer fluorescence at approximately 550 nm. Compounds **1** and **2** also exhibit a broad and strong $^3\pi$–π^* excited-state absorption band in the visible region (λ_{max} = 520 nm with $\varepsilon_{\text{T1–T}n} = 4.74\times 10^4$ L mol^{-1} cm^{-1} for **1**, and λ_{max} = 590 nm with $\varepsilon_{\text{T1–T}n} = 3.45\times 10^4$ L mol^{-1} cm^{-1} for **2**). The triplet excited states of **1** and **2** are both long-lived, with lifetimes longer than 2 ms. Compounds **1** and **2** are sensitive to basic anions such as F^-, AcO^-, and $H_2PO_4^-$. Upon addition of these anions, the UV/Vis absorption spectra of these two compounds are significantly redshifted, which is reflected by the color change from yellow to purple for **1** and from yellow to blue for **2**. These anions also quench the charge-transfer emission band at 550 nm. Moreover, the triplet transient absorption of **1** and **2** in DMSO solution is quenched upon addition of these anions. These spectroscopic changes are attributed to the deprotonation of the hydrazone NH group, which causes intramolecular electron transfer. The deprotonation mechanism is supported by the upfield shifts of the ^{1}H NMR signals of the 2,4-dinitrophenylhydrazone group, the imine group, and the phenyl group, following the addition of excess F^-.

Introduction

The development of selective and sensitive anion sensors has attracted growing interest in the recent years because of the important roles anions play in biological systems and industrial applications.[1,2] Although a variety of anion receptors that can selectively bind to different anions have been reported in the past two decades,[3] it is still a challenge for chemists to improve the sensitivity of the sensors. For practical applications, colorimetric anion sensors, which would allow for naked-eye detection, are of particular interest.[4] Among various types of compounds, ruthenium bipyridine (bpy) complexes, with an amide functional group attached to one of the bipyridine ligands, have been widely investigated.[3] In most cases, the formation of a hydrogen bond between the hydrogen atom on the amide group and the anion increased the rigidity of the complex, thus inducing a significant enhancement of the ^{3}MLCT (metal-to-ligand charge transfer) emission of the complexes.[3] Only in a few recent reports, drastic color change was observed in bipyridine or terpyridine (tpy) complexes of Ru upon binding to F^-.[4b,5] Duan and co-workers recently reported two Ru complexes bearing 2,4-dinitrophenylhydrazone residues as fluoride sensors.[6] They revealed that the formation of a hydrogen bond between the quinonehydrazone tautomer and the highly electronegative F^- ion induced the formation of the azophenol tautomer, thus causing a dramatic color change in one case[6a] and deprotonation induced by F^- in the other case.[6b]

Although a vast amount of anion receptors, including Ru(bpy) or Ru(tpy) complexes, have been investigated, there are, to date, few reports on the use of the Pt(bpy) or Pt(tpy) motif as a signaling component for anion sensing. Chen and co-workers reported a series of platinum terpyridine complexes with phenolic ethynyl ligands as selective anion sensors.[7] The sensing mechanism is a two-step process: the formation of a hydrogen bond between the hydroxy hydrogen atom and the F^- anion at low concentrations of F^- is followed by a proton transfer from the hydroxy group to F^- upon further addition of F^-. A drastic color change and emission quenching were observed after addition of F^-. Recently, Wang and co-workers reported the binding of F^- by using Pt$^{\text{II}}$ bipyridine complexes containing boryl substituents.[8]

We were intrigued by this work and the growing interest in using platinum terpyridine complexes as potential pH sensors and sensors for cations or biomolecules. On the basis of the rich photophysics of these compounds and their

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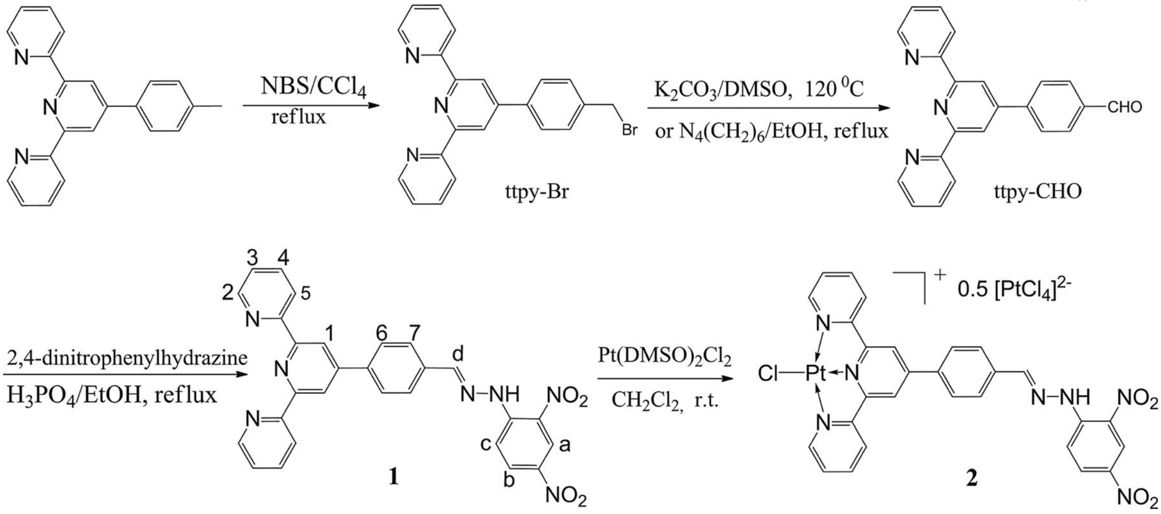

Scheme 1. Synthetic route and structures for **1** and **2**.

excited-state characteristics that can easily be tuned through chemical stimuli,[9] we became interested in designing new chromogenic and luminescent anion sensors that use terpyridine and platinum terpyridine moieties as the signaling unit and the 2,4-dinitrophenylhydrazone group as an anion-binding site. The structures of these compounds are shown in Scheme 1 together with the synthetic route for preparing them. The photophysics of **1** and **2** and their anion-sensing characteristics are reported in this paper.

Results and Discussion

Synthesis

4-(4′-Bromomethylphenyl)-2,2′:6′,2′′-terpyridine (ttpy-Br) and 4-formyl-2,2′:6′,2′′-terpyridine (ttpy-CHO) were synthesized according to literature procedures.[10] The reaction of ttpy-CHO and 2,4-dinitrophenylhydrazine in the presence of H_3PO_4 gave compound **1**. Ligand **1** is slightly soluble in dichloromethane, acetone, acetic acid, DMF, DMSO, and acetonitrile. Platinum complex **2** was synthesized from $Pt(DMSO)_2Cl_2$ and ligand **1** in dichloromethane. Compound **2** shows poor solubility in dichloromethane, chloroform, acetonitrile, and DMF.

UV/Vis Absorption Spectroscopy

The UV/Vis absorption of **1** and **2** obeys the Beer–Lambert law in the concentration range studied (2.5×10^{-6}–4.0×10^{-5} mol L^{-1}) in DMSO. Figure 1 presents the UV/Vis spectra of **1** and **2** in DMSO solutions. Compound **1** displays a strong absorption band at 404 nm (ε = 3.39×10^4 L mol^{-1} cm^{-1}), which is assigned to the $^1\pi$–π^* transition within the compound. Upon coordination to Pt^{II}, the absorption band maximum is redshifted to 433 nm (ε = 3.24×10^4 L mol^{-1} cm^{-1}). This could be attributed to the decreased electron density on the terpyridine component after complexation with Pt^{II}, which results in a more delocalized π system. A minor solvent effect was observed for the absorption bands of **1** and **2**. Considering the large extinction coefficient and the minor solvent effect, the absorption band of **2** likely originates from the metal-perturbed $^1\pi$–π^* transition of the ligand. However, contribution from the ^{1}MLCT transition and the intraligand charge-transfer transitions from the lone pair electron on the hydrazone nitrogen atoms to the 2,4-dinitrophenyl or terpyridine component could not be completely ruled out.

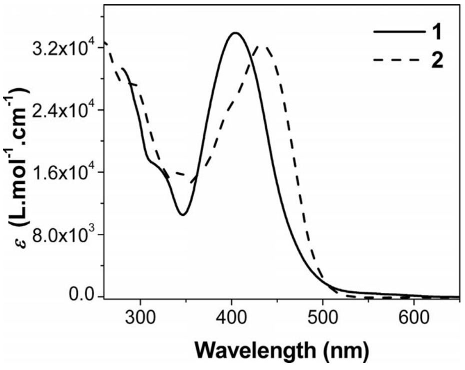

Figure 1. UV/Vis absorption spectra of **1** and **2** in DMSO solution.

Emission Spectroscopy

Compounds **1** and **2** exhibit weak emission at room temperature in DMSO solution. As shown in Figure 2, upon excitation at 404 nm, **1** emits at 551 nm; compound **2** emits at 553 nm when excited at 433 nm. Considering the fact that the emissions of **1** and **2** are insensitive to the presence of oxygen and that the lifetimes of the emissions are too short to be measured by our spectrometer (< 5 ns), we believe that the emission of both **1** and **2** emanates from the singlet excited state, which can be tentatively assigned to the intramolecular charge-transfer (^{1}ICT) emission from the lone pairs on the nitrogen atoms of the hydrazone motif to the 2,4-dinitrophenyl or the terpyridine component. The ^{1}ICT emission becomes stronger in platinum complex **2** because of the increased electron deficiency of the terpyridine component after complexation with Pt^{II}, which facilitates the ICT. Charge-transfer emission is commonly observed in molecules with donor–acceptor components, such as 4-aminobenzonitrile compounds.[11]

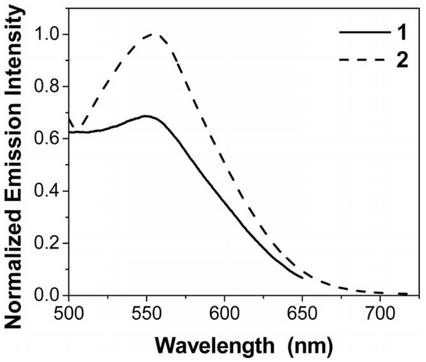

Figure 2. Normalized emission spectra of compounds **1** and **2** in DMSO at a concentration of 4.0×10^{-5} mol L^{-1} (λ_{ex} = 404 nm for **1** and 433 nm for **2**).

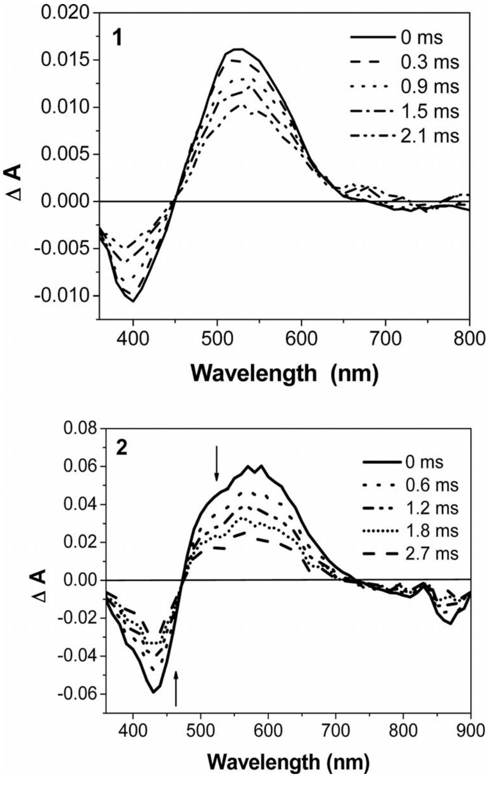

Figure 3. Time-resolved triplet transient difference absorption spectra of **1** and **2** in DMSO following excitation at 355 nm. The concentration of the solutions was 4.0×10^{-5} mol L^{-1}.

Transient Difference Absorption (TA) Spectroscopy

The time-resolved triplet transient difference absorption spectra of **1** and **2** in DMSO are shown in Figure 3. The TA spectrum of **1** possesses a bleaching band at 400 nm, which coincides with the $^1\pi$–π^* transition band in the UV/Vis absorption spectrum, and a broad positive absorption band in the visible region at approximately 520 nm with an extinction coefficient of $\varepsilon_{T1-Tn} = 4.74 \times 10^4$ L mol^{-1} cm^{-1} obtained by using the singlet depletion method.[12] The lifetime of the triplet excited state, deduced from the decay of the transient absorption, is 2.46 ms. The features of the TA spectrum of **2** are similar to that of **1**, with a bleaching band at 430 nm and a positive absorption band at 590 nm. The ε_{T1-Tn} for **2** is 3.45×10^4 L mol^{-1} cm^{-1} at 590 nm, and the triplet lifetime is 2.01 ms. In view of the ultra-long lifetime of the triplet excited state and the large extinction coefficient of the triplet-excited-state absorption at the respective TA band maxima, we tentatively attribute the transient absorption to the $^3\pi$–π^* state. The somewhat shorter lifetime of **2** could be due to the heavy-atom effect of Pt, which enhances the decay of the triplet excited state to the ground state through intersystem crossing.

Anion-Sensing Studies

Both **1** and **2** are sensitive to basic anions such as F$^-$, $H_2PO_4^-$, and OAc$^-$. As exemplified in Figure 4 for **1**, upon addition of F$^-$, $H_2PO_4^-$, or OAc$^-$ to the DMSO solutions of **1**, the color of the solutions changed drastically from yellow to purple (upper inset of Figure 4); the addition of NO_3^-, Cl$^-$, Br$^-$, or I$^-$ (all as tetra-*n*-butylammonium salts, TBA salts) has no effect on the color of the solution of **1**. A similar phenomenon was observed for **2** with a color change from yellow to blue upon addition of F$^-$, $H_2PO_4^-$, or OAc$^-$ (Figure 4). The titration of a DMSO solution of **1** with fluoride shows that with addition of F$^-$ anions, the intensity of the original absorption band of **1** at 404 nm gradually decreases, accompanied by the appearance of a new absorption band at 525 nm. A clear isosbestic point was observed at 451 nm (Figure 5), indicating that only two interconverting species are present in the solution upon addition of F$^-$ anions. The Job plot (Figure 5 inset) indicates that at a molar ratio [F$^-$]/[**1**] of 1, the absorption at 525 nm reaches a maximum. This implies that one F$^-$ anion interacts with one molecule of **1**. The binding constant estimated from the Job plot measurement is 3.3×10^6 M^{-2}, which is smaller than those of the Pt^{II} bipyridine complexes bearing diboryl substituents[8] and those of Pt^{II} terpyridine complexes with phenolic ethynyl ligands.[7] Similar phenomena were observed upon addition of $H_2PO_4^-$ and OAc$^-$ anions to the DMSO solutions of **1** with estimated binding constants of 3.4×10^5 and 2.5×10^6 M^{-2}, respectively (Supporting Information Figures S1 and S2).

For the platinum complex **2**, addition of F$^-$, $H_2PO_4^-$, or OAc$^-$ to the DMSO solution of **2** also causes a remarkable color change from yellow to blue, reflected by the appearance of a new absorption band at 580 nm at the expense of the 433 nm band in the UV/Vis spectrum; an isosbestic point occurs at 472 nm (Figure 6). Similar to **1**, the Job plot for **2** monitored at 580 nm shows an absorption maximum at a molar ratio of 1, indicating a 1:1 host–guest stoichiometry for the binding of F^-, $H_2PO_4^-$, or OAc^- anions to **2**. The binding constant estimated for F^- is 6.7×10^5 M^{-2}. The titration curves for the addition of $H_2PO_4^-$ and OAc^- to the DMSO solution of **2** are given in the Supporting Information (Figure S3).

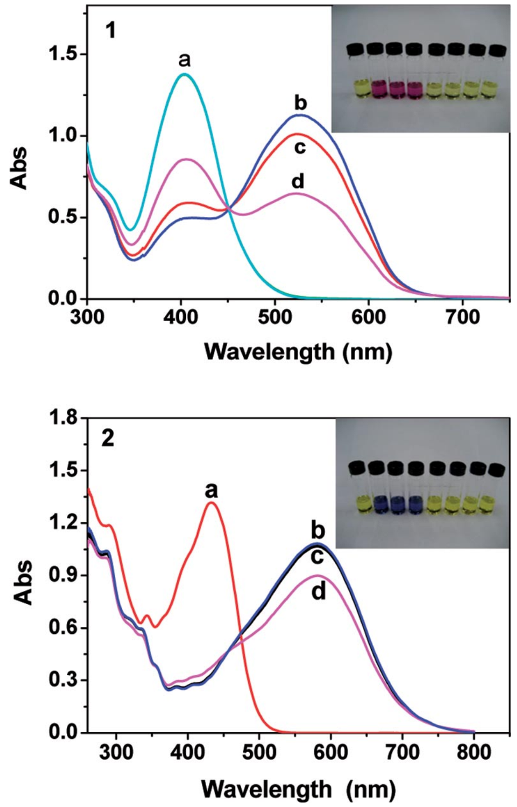

Figure 4. UV/Vis absorption spectra of 4.0×10^{-5} mol L^{-1} DMSO solutions of **1** (top) and **2** (bottom) after addition of 10 equiv. of either Cl^-, Br^-, I^-, NO_3^-, or HSO_4^- (a), 1 equiv. F^- (b), 1 equiv. AcO^- (c), or 1 equiv. $H_2PO_4^-$ (d). Insets show the color pictures of the original solutions of **1** (top) and **2** (bottom) (4×10^{-5} mol L^{-1}) and the solutions with different anions [from left to right: original solution, solutions with F^- (1 equiv.), AcO^- (1 equiv.), $H_2PO_4^-$ (1 equiv.), Cl^- (10 equiv.), Br^- (10 equiv.), I^- (10 equiv.), and NO_3^- (10 equiv.)].

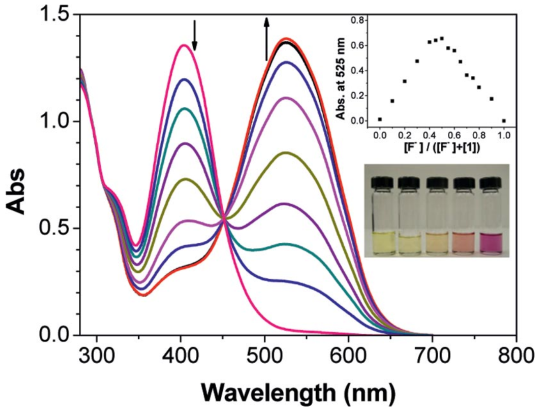

Figure 5. UV/Vis spectral changes of a DMSO solution of **1** (4.0×10^{-5} mol L^{-1}) upon addition of a solution of $(Bu_4N)F$ (1.0×10^{-2} mol L^{-1}). The inset shows the Job plot for the binding of **1** to F^- monitored at 525 nm ($[F^-] + [\mathbf{1}] = 4.0\times 10^{-5}$ mol L^{-1}) and the color change of DMSO solutions of **1** upon addition of (from left to right) 0, 0.25, 0.5, 0.75, and 1.0 equiv. F^-.

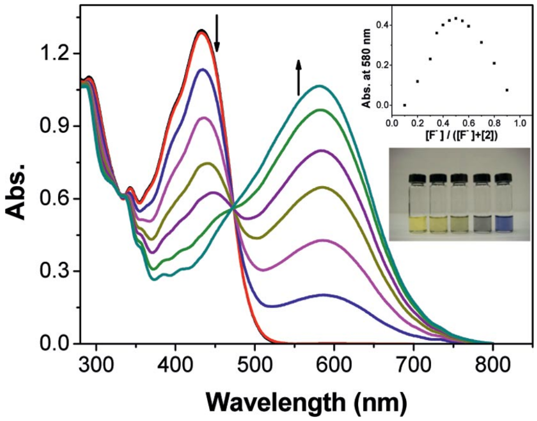

Figure 6. UV/Vis spectral changes of a DMSO solution of **2** (4.0×10^{-5} mol L^{-1}) upon addition of a solution of $(Bu_4N)F$ (1.0×10^{-2} mol L^{-1}). The inset shows the Job plot for the binding of **2** to F^- monitored at 580 nm ($[F^-] + [\mathbf{2}] = 4.0\times 10^{-5}$ mol L^{-1}) and the color change of DMSO solutions of **2** upon addition of (from left to right) 0, 0.25, 0.5, 0.75, and 1.0 equiv. F^-.

Addition of F^-, $H_2PO_4^-$, or OAc^- into the DMSO solutions of **1** and **2** also induces substantial changes in their respective emission spectra. As exemplified in Figure 7, upon addition of F^- the emission intensity of **1** and **2** at approximately 550 nm gradually decreases. The emission is completely quenched upon addition of 1 equiv. F^-.

In addition to the changes in the UV/Vis absorption and emission spectra induced by F^-, $H_2PO_4^-$, or OAc^-, these anions quench the triplet transient absorptions of **1** and **2** as well. The TA of **1** is completely quenched upon addition of 0.5 equiv. F^-. In contrast, the intensity of the TA of complex **2** at zero-delay is reduced to approximately 1/6 of the original intensity upon addition of 1.5 equiv. F^- (Figure 8), accompanied by a remarkable decrease of the triplet lifetime from the original 2.01 ms to 0.62 ms.

To understand the spectroscopic changes induced by these anions, a ^{1}H NMR spectroscopic titration experiment was carried out, which is often used for studying the chemical sensing mechanism. As shown in Figure 9, upon addition of an excess amount of fluoride as the TBA salt, the peaks assigned to protons on the 2,4-dinitrophenylhydrazone group, the imine group, and the phenyl group shift to high field significantly (0.1–0.85 ppm), while the signals of the terpyridine moiety only exhibit a slight shift. The substantial upfield shift of protons a–d, 6, and 7 suggests that the fluoride anion causes deprotonation of the NH group, which increases the electron density on the 2,4-dinitrophenylhydrazone group, the imine group, and the phenyl group. Subsequently, the NMR signals for the protons on these components shift to high field. The upfield shift of the corresponding protons on the 2,4-dinitrophenylhydrazone

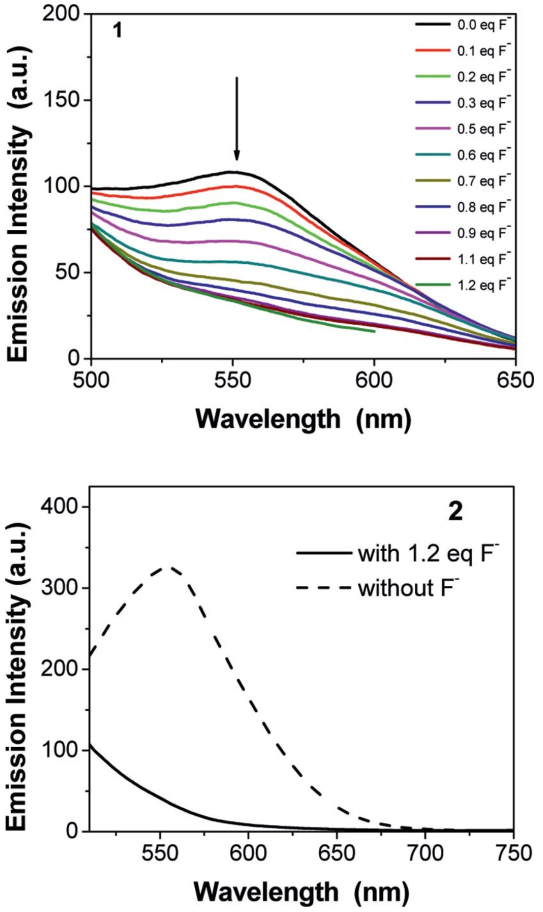

Figure 7. Changes in the emission spectra of **1** and **2** in DMSO solution ($4.0\times\ 10^{-5}$ mol L^{-1}) upon addition of $(Bu_4N)F$ (λ_{ex} = 404 nm for **1** and 430 nm for **2**).

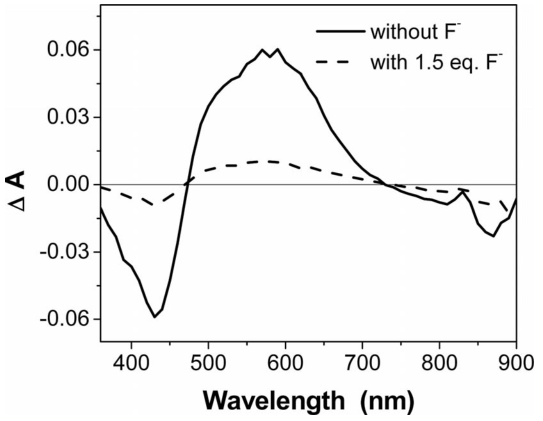

Figure 8. Triplet transient difference absorption spectra of **2** in $4.0\times\ 10^{-5}$ mol L^{-1} DMSO solutions without $[Bu_4N]F$ and with 1.5 equiv. $[Bu_4N]F$ immediately after the 355 nm excitation.

component due to deprotonation of the N–H group was reported by Duan, Bai and co-workers[6b] and was also observed in other deprotonated compounds, such as a urea derivative.[13]

The deprotonation of the N–H group upon addition of F^-, $H_2PO_4^-$, or OAc^- increases the electron density on the nitrogen atom, which enhances photoinduced electron transfer (PET) from the lone-pair electrons on N to the electron-deficient component(s). Therefore, a significantly redshifted absorption band appears at longer wavelengths for both **1** and **2**. Meanwhile, the PET also quenches the emission at approximately 550 nm, which is in line with the quenching of emission after deprotonation in platinum terpyridine complexes with phenolic ethynyl ligands reported by Chen and co-workers.[7]

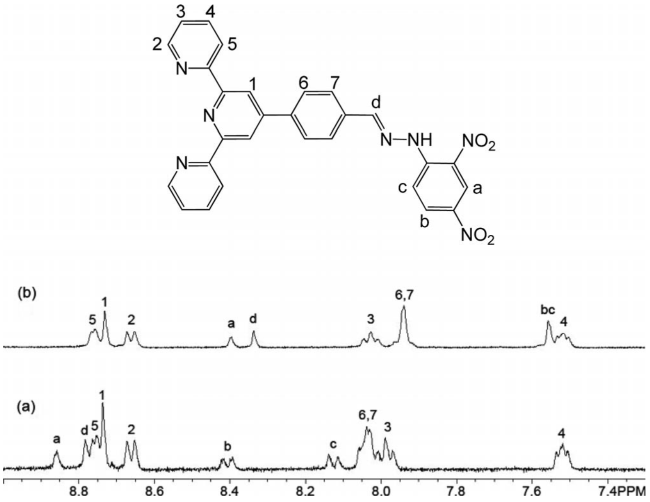

Figure 9. The downfield ^1H NMR (400 MHz) spectra of **1** in $[D_6]$DMSO at 25 °C without $(Bu_4N)F$ (a) and with excess $(Bu_4N)F$ (b).

Conclusions

Terpyridine derivative **1**, bearing 2,4-dinitrophenylhydrazone, and its platinum chloride complex **2** exhibit broad and strong $^1\pi$–π^* absorptions in the visible spectral region (λ_{max} = 404 nm for **1** and 433 nm for **2**). They display weak charge-transfer fluorescence at approximately 550 nm. A broad and strong $^3\pi$–π^* excited-state absorption band in the visible spectral region was observed for **1** (λ_{max} = 520 nm with $\varepsilon_{T1-Tn} = 4.74\times\ 10^4$ L mol^{-1} cm^{-1}) and **2** (λ_{max} = 590 nm with $\varepsilon_{T1-Tn} = 3.45\times\ 10^4$ L mol^{-1} cm^{-1}). Addition of F^-, AcO^-, or $H_2PO_4^-$ anions to the DMSO solutions of **1** and **2** causes a drastic color change: **1** changes from yellow to purple, and **2** changes from yellow to blue. The charge-transfer emission band of **1** and **2** at 550 nm as well as their triplet transient absorptions are quenched upon addition of these anions. The sensing mechanism for **1** and **2** is attributed to the deprotonation of the hydrazone NH group, which is supported by the upfield shifts of the ^1H NMR signals on the 2,4-dinitrophenylhydrazone group, the imine group, and the phenyl group after addition of an excess amount of F^-.

Experimental Section

Syntheses and Characterization: All reagents were purchased from Aldrich or Alfa Aesar and used as received. 4-(4′-Bromomethylphenyl)-2,2′:6′,2′′-terpyridine (ttpy-Br) and 4-formyl-2,2′:6′,2′′-

terpyridine (ttpy-CHO) were synthesized according to literature procedures.[10] The target compounds were characterized by ^{1}H NMR spectroscopy, high-resolution mass spectrometry (ESI-MS), and elemental analysis. ^{1}H NMR spectra were measured with a Varian Oxford-400 VNMR spectrometer. ESI-MS analyses were performed with a Bruker BioTOF III mass spectrometer. Elemental analyses were conducted by NuMega Resonance Laboratories, Inc. in San Diego, California.

Compound 1: Compounds 2,4-dinitrophenylhydrazine (40.0 mg, 0.20 mmol) and ttpy-CHO (67.0 mg, 0.20 mmol) were dissolved in 6 mL and 30 mL of ethanol/H_3PO_4 (ethanol/H_3PO_4 = 2:1), respectively. These two solutions were mixed and heated at reflux for 2 h. A red precipitate formed and was collected by filtration, then washed with ethanol, water, ethanol, and ether, and finally dried in air. The crude product was purified by recrystallization from DMF to yield crystalline orange needles (66.0 mg, yield: 65%). ^{1}H NMR ([D$_6$]DMSO): δ = 8.86 (s, 1 H), 8.78 (d, J = 8.0 Hz, 2 H), 8.75 (d, J = 8.0 Hz, 2 H), 8.74 (s, 2 H), 8.66 (d, J = 8.0 Hz, 2 H), 8.40 (d, J = 9.0 Hz, 1 H), 8.12 (d, J = 9.0 Hz, 1 H), 8.04 (m, 4 H), 7.99 (t, J = 8.0 Hz, 2 H), 7.51 (t, J = 8.0 Hz, 2 H) ppm. ESI-HRMS: calcd. for $[C_{28}H_{19}N_7O_4 + Na]^+$ 540.1391; found 540.1388. $C_{28}H_{19}N_7O_4$ (517.50): calcd. C 64.99, H 3.70, N 18.95; found C 64.60, H 4.03, N 18.72.

Compound 2: Compound **1** (51.7 mg, 0.10 mmol) and Pt(DMSO)$_2$Cl$_2$ (42.2 mg, 0.10 mmol) were dissolved in CH_2Cl_2 (50 mL), and the reaction mixture was stirred at room temperature for 1 day. An orange solid formed and was collected by filtration, washed with CH_2Cl_2, and dried in air. The reaction afforded 62.0 mg of pure product (Yield: 55%). ^{1}H NMR ([D$_6$]DMSO): δ = 9.02 (s, 2 H), 8.96 (d, J = 7.6 Hz, 2 H), 8.88 (d, J = 8.0 Hz, 2 H), 8.86 (s, 1 H), 8.75 (s, 1 H), 8.56 (t, J = 8.0 Hz, 2 H), 8.38 (d, J = 9.0 Hz, 1 H), 8.29 (d, J = 9.0 Hz, 2 H), 8.13 (d, J = 8.0 Hz, 1 H), 7.99 (m, 4 H) ppm. ESI-HRMS: calcd. for $[C_{28}H_{19}N_7O_4PtCl]^+$ 747.0829; found 747.0808. $C_{28}H_{19}ClN_7O_4Pt\cdot 0.5PtCl_4\cdot 2.5CH_2Cl_2$ (1128.8): calcd. C 32.45, H 2.14, N 8.69; found C 32.33, H 2.36, N 8.85.

Photophysical and Anion-Sensing Studies: UV/Vis spectra were measured with a UV-2501 spectrophotometer in 1-cm quartz cuvettes. The concentration of the solutions of **1** and **2** in DMSO for sensing measurements was 4.0×10^{-5} mol L^{-1}. For Job plot measurements, this represents the total concentration of F$^-$ and compound in solution. The steady-state emission spectra were acquired with a SPEX fluorolog-3 fluorometer/phosphorometer. The triplet transient difference absorption (TA) spectra and triplet-excited-state lifetimes were measured in degassed DMSO solutions with an Edinburgh LP920 laser flash photolysis spectrometer. The third harmonic output (355 nm) of a Nd:YAG laser (Quantel Brilliant, pulse width ca. 4.1 ns, repetition rate set at 1 Hz) was used as the excitation source. Each sample was purged with Ar for 30 min before the measurement. The triplet-excited-state absorption coefficient (ε_{T1-Tn}) was determined by the singlet depletion method,[12] in which the optical density changes at the minimum of the bleaching band (ΔOD_S) and at the maximum of the positive band (ΔOD_T) in the TA spectrum, and the ground-state molar extinction coefficient (ε_s) at the wavelength of the bleaching band minimum are used to calculate the ε_{T1-Tn} according to the following equation.[12]

$$\varepsilon_{T1-Tn} = \frac{\varepsilon_S\left[\Delta OD_T\right]}{\Delta OD_S}$$

Supporting Information (see footnote on the first page of this article): UV/Vis absorption spectra of DMSO solutions of **1** and **2** recorded upon addition of [Bu$_4$N]AcO and [Bu$_4$N]H$_2$PO$_4$ and the respective Job plots.

Acknowledgments

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