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Switching between Ligand-to-Ligand Charge-Transfer, Intraligand Charge-Transfer, and Metal-to-Ligand Charge-Transfer Excited States in Platinum(II) Terpyridyl Acetylide Complexes Induced by pH Change and Metal Ions

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Abstract: A series of platinum(II) terpyridyl alkynyl complexes, [Pt{4′-(4-R^1-C_6H_4)terpy}(C≡C-C_6H_4-R^2-4)]ClO_4 (terpy = 2,2′:6′,2″-terpyridyl; R^1 = R^2 = $N(CH_3)_2$ (**1**); R^1 = $N(CH_3)_2$, R^2 = *N*-[15]monoazacrown-5 (**2**); R^1 = CH_3, R^2 = $N(CH_3)_2$ (**3**); R^1 = $N(CH_3)_2$, R^2 = H (**4**); R^1 = CH_3, R^2 = H (**5**)), has been synthesized and the photophysical properties of the complexes have been examined through measurement of their UV/Vis absorption spectra, photoluminescence spectra, and transient absorptions. Complex **3** shows a lowest-energy absorption corresponding to a ligand-to-ligand charge-transfer (LLCT) transition from the acetylide to the terpyridyl ligand, whereas **4** shows an intraligand charge-transfer (ILCT) transition from the π orbital of the 4′-phenyl group to the π* orbital of the terpyridyl. Upon protonation of the amino groups in **3** and **4**, their lowest-energy excited states are switched to dπ(Pt)→π*(terpy) metal-to-ligand charge-transfer (MLCT) states. The lowest-energy absorption for **1** and **2** may be attributed to an LLCT transition from the acetylide to the terpyridyl. Upon addition of an acid to a solution of **1** or **2**, the amino group on the acetylide is protonated first, followed by the amino group on the terpyridyl. Thus, the lowest excited state of **1** and **2** can be successively switched from the LLCT state to the ILCT state and then to the MLCT state by controlling the amount of the acid added. Such switches in the excited state are fully reversible upon subsequent addition of a base to the solution. Sequential addition of alkali metal or alkaline earth metal ions and then an acid to a solution of **2** also leads to switching of its lowest excited state from the LLCT state, first to the ILCT state and then to the MLCT state. All of the complexes exhibit a transient absorption of the terpyridyl anion radical, which is present in all of the LLCT, ILCT, and MLCT states. However, the shape of the transient absorption spectrum depends on both the substitution pattern on the terpyridyl moiety and the nature of the excited state.

Keywords: alkyne ligands · charge transfer · excited states · platinum

Introduction

Square-planar platinum(II) complexes exhibit a wide range of fundamentally interesting and potentially useful excited-state properties.[1–19] Indeed, these complexes have demonstrated promise for various applications, including optical power limiting,[20–22] electroluminescence,[13,23–26] as photosensitizers for the generation of singlet oxygen[27] or hydrogen,[28] as molecular probes for biological macromolecules,[12,29] and as optical sensors.[17,18,30–34] In particular, platinum(II) complexes bearing terpyridyl and acetylide ligands have been extensively investigated in view of their rich photophysical properties.[12,17,20,21,28,31,35,36] The spectroscopic properties and low-energy absorptions of these complexes may arise from metal-to-ligand charge transfer (MLCT), intraligand charge transfer (ILCT), ligand-to-ligand charge transfer (LLCT), or intraligand (IL) transitions, depending very much on the substitution on their terpyridyl and/or acetylide ligands. In most instances, these complexes exhibit long-lived excited states with photophysical properties consistent with a dπ(Pt)→π*(terpyridyl) MLCT transition.[12,17] However, there are also ample examples whereby certain

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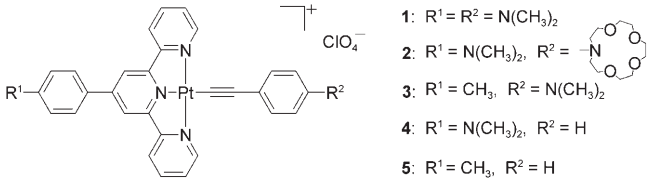
such complexes exhibit a low-lying intraligand $\pi\rightarrow\pi^*$ (IL) excited state that is derived from transition between π-type orbitals localized on the terpyridyl or acetylide ligand.[9,13,15,37] On the other hand, our group[35] has investigated the photophysical properties of platinum(II) terpyridyl acetylide complexes bearing amino or azacrown moieties on the acetylide ligands, [Pt(terpy)(C≡CC$_6$H$_4$-R-4)], where terpy = 2,2′:6′,2″-terpyridyl and R = N(CH$_3$)$_2$ or *N*-[15]monoazacrown-5. In neutral or basic solutions, these complexes exhibit a lowest-energy absorption band attributable to an LLCT transition from the amino-substituted acetylide to the terpyridyl acceptor. Upon protonation of the amino group, these complexes display a lowest-energy absorption in accordance with a $d\pi(Pt)\rightarrow\pi^*$(terpy) MLCT transition and a moderately intense emission from ^{3}MLCT states. For the complex bearing an azacrown group, complexation of this function with a metal cation also switches the lowest-lying LLCT to the MLCT excited state. Recently, Yam and co-workers[31] have used such complexes as colorimetric and luminescent pH sensors. Sun and co-workers have studied the optical limiting of such complexes.[21] It has also been established that introduction of an amino group (NR$_2$) at the 4-position of the phenyl in 4′-phenyl-substituted 2,2′:6′,2″-terpyridine, to give 4′-(4-NR$_2$-C$_6$H$_4$)-2,2′:6′,2″-terpyridine, results in the intramolecular charge-transfer (ICT) transition from the π orbital of the amino-substituted phenyl to the π^* orbital of the terpyridyl moiety becoming the lowest-energy absorption.[38] This substituted terpyridine has served as a ligand in the assembly of Pt^{II} complexes that display a low-lying ILCT excited state in which the amino-substituted phenyl acts as the electron donor and the metal-bound terpyridyl as the acceptor.[39] We postulate that platinum(II) terpyridyl acetylide complexes, which bear amino group(s) or azacrown group(s) on both their terpyridyl and acetylide ligands, might exhibit lowest-lying excited states having either ILCT or LLCT character. Furthermore, these excited states might be interchanged by a change of solvent or pH, or by the introduction of metal ions, thereby yielding a variety of interesting photophysical properties. In the present work, we set out to design two novel complexes, **1** and **2**. These complexes feature a low-lying LLCT excited state



1: $R^1 = R^2 = N(CH_3)_2$
2: $R^1 = N(CH_3)_2$, R^2 =
3: $R^1 = CH_3$, $R^2 = N(CH_3)_2$
4: $R^1 = N(CH_3)_2$, $R^2 = H$
5: $R^1 = CH_3$, $R^2 = H$

corresponding to charge transfer from the acetylide to the terpyridyl moiety in neutral solution. Upon addition of one equivalent of acid to a solution of one of these complexes, its lowest excited state is switched to ILCT as a result of the transition from the π orbital of the 4′-phenyl group to the π^* orbital of the metal-bound terpyridyl. Addition of a second equivalent of acid to the solution results in a change of the lowest excited state to the $d\pi(Pt)\rightarrow\pi^*$(terpy) MLCT excited state. Similarly, complexation of the azacrown in **2** with a metal ion, followed by protonation of the amino group in the terpyridyl ligand, also leads to a switching of its lowest excited state from the LLCT state, first to the ILCT state and then to the MLCT state. Thus, we can adjust the relative energy levels of the various excited states in **1** and **2**. Although the interchange between two different excited states in platinum(II) complexes has been investigated previously,[15,31,35] reports of the successive modulation of several excited states and the obtainment of a variety of excited-state behaviors in a single molecular system are rare.

Results and Discussion

Synthesis: 4′-[4-N(CH$_3$)$_2$-C$_6$H$_4$]-2,2′:6′,2″-terpyridine was prepared according to a literature method.[38] Reaction of this substituted terpyridine with K_2PtCl_4 gave [Pt(4′-{4-N(CH$_3$)$_2$-C$_6$H$_4$}-terpy)Cl]Cl, in accordance with standard procedures.[35] This material was then reacted with two equivalents of 4-dimethylaminophenylacetylene and 4-ethynylphenyl-*N*-[15]monoazacrown-5 ether, respectively, in DMF in the presence of a catalyst system of CuI and triethylamine at room temperature, to yield **1** and **2**. After metathesis reaction with $LiClO_4$ and recrystallization of the crude products by vapor diffusion of diethyl ether into solutions in acetonitrile, complexes **1** and **2** were obtained as dark-blue crystals in yields of around 70%. These two complexes were structurally characterized on the basis of ^{1}H NMR, mass spectrometry, and satisfactory elemental analyses. For reference, complexes **3**–**5** were also prepared by following similar procedures.

Acid/base-controlled excited-state switching between the LLCT and MLCT states in 3 and between the ILCT and MLCT states in 4: Before discussing the successive excited-state switches from LLCT to ILCT and then to MLCT in **1** and **2** as a result of pH change and/or complexation to a metal ion, we present the absorption and emission changes of the reference complexes **3** and **4** upon protonation. Figure 1 shows the UV/Vis spectrum of a solution of **3** in acetonitrile. This complex exhibits intense vibronic-structured absorption bands at wavelengths below 350 nm with extinction coefficients (ε) of the order of 10^4 dm^3 mol^{-1} cm^{-1}, and less intense bands at 350–460 nm ($\lambda_{max} \approx 420$ nm) and 460–700 nm ($\lambda_{max} \approx 545$ nm) with ε of the order of 10^3 dm^3 mol^{-1} cm^{-1}. With reference to previous spectroscopic work on similar complexes reported by ourselves and others,[17,18,36,40–42] the absorption bands at wavelengths below 350 nm are assigned to the intraligand (IL) transition of the terpyridyl and acetylide ligands, while the absorption band at 350–460 nm is ascribed to the $d\pi(Pt)\rightarrow\pi^*$(terpy) MLCT transition. The lowest-energy absorption band in the region of 460–700 nm is consistent with an LLCT transition from the amino-substituted acetylide ligand to the terpyridyl acceptor. The relatively low energy of this LLCT absorption

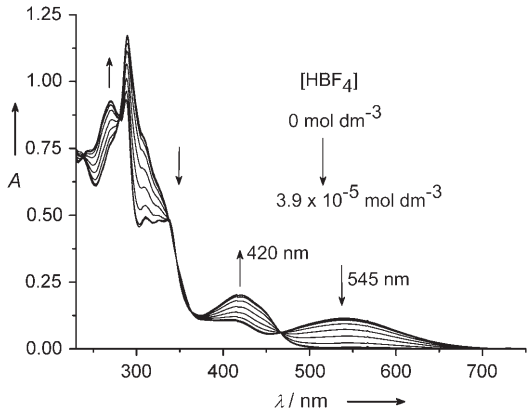
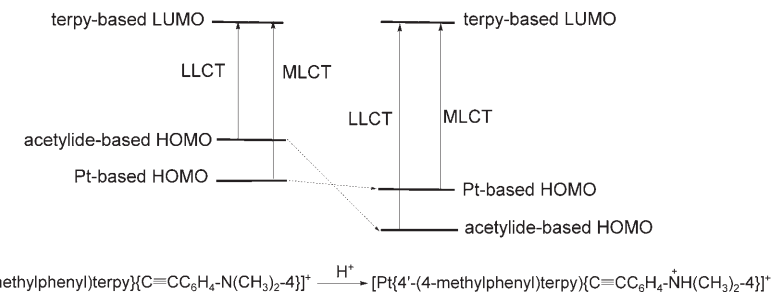


Figure 1. Changes in the absorption spectrum of complex **3** (2.55×10^{-5} mol dm^{-3}) upon addition of various concentrations (0–3.9×10^{-5} mol dm^{-3}) of HBF_4 in acetonitrile.

may be attributed to the good electron-donating ability of the amino group on the aryl alkynyl ligand.[35] Upon addition of an acid to a solution of **3**, a dramatic change in the absorption spectrum was observed. The absorption spectra of **3** (2.55×10^{-5} mol dm^{-3}) in acetonitrile as a function of added HBF_4 are shown in Figure 1. As HBF_4 is added to the solution, a decrease in the absorption band at 545 nm is accompanied by a growth in the band at 420 nm. Isosbestic points are observed at 466, 368, and 280 nm, indicative of the presence of only two absorbing species in the solution. Ultimately, only the MLCT absorption can be detected, and the absorption spectrum is almost identical to that of complex **5** in acetonitrile (the lowest-energy absorption band of **5** is in the region 350–500 nm with $\lambda_{max} \approx 430$ nm). This switching of the LLCT to MLCT excited state in **3** can evidently be attributed to protonation of the amino group on the acetylide ligand. As the amino receptor is protonated in the presence of HBF_4, its electron-donating ability is decreased. This can be expected to dramatically lower the highest occupied molecular orbital (HOMO) of the acetylide ligand. The Pt-based HOMO will also be lowered, but the extent of this lowering can be expected to be much less than that in the case of the acetylide ligand (Scheme 1). As a result, the LLCT transition from the amino-substituted acetylide ligand to the terpyridyl acceptor shifts to higher energy, and the dπ(Pt)→π*(terpy) MLCT transition becomes the lowest-energy transition.



Scheme 1. Switching of the low-lying excited state of **3** as a result of pH change.

The change in the luminescence response of complex **3** towards protons was found to be even more pronounced. In neutral or basic solution, **3** is nonemissive. The lack of emission upon excitation of the MLCT band may be attributed to the transfer of an electron from the electron pair on the amino group to the Pt center, resulting in an LLCT excited state. Because of its low energy, the ^{3}LLCT excited state decays via a nonradiative pathway. However, in an acidic medium, **3** exhibits a structureless emission band with a maximum at around 550 nm. Figure 2 shows the change in

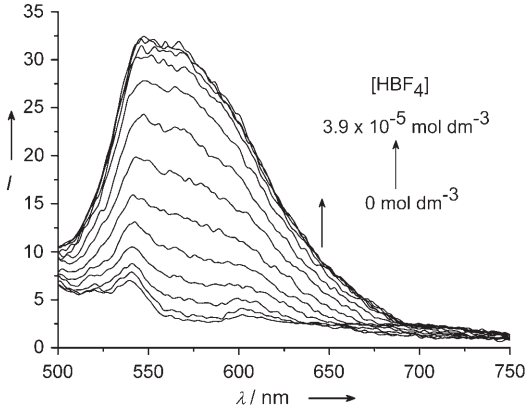


Figure 2. Changes in the luminescence spectrum of complex **3** (2.55×10^{-5} mol dm^{-3}) upon addition of various concentrations (0–3.9×10^{-5} mol dm^{-3}) of HBF_4 in acetonitrile.

the emission spectrum of **3** as a function of the HBF_4 concentration. Throughout the titration, the excitation wavelength corresponds to the isosbestic point found at 466 nm in Figure 1. The emission intensity is noticeably enhanced on increasing the HBF_4 concentration, with saturation being observed towards the end of the titration, while the shape and energy of the emission band remain unchanged. With reference to previous work on the emission of platinum(II) terpyridyl acetylide complexes,[17,36,40,43] this emission may be assigned as being due to the dπ(Pt)→π*(terpy) ^{3}MLCT excited state. Evidently, the emission of complex **3** on addition of HBF_4 originates from protonation of the amino group. As mentioned above, upon protonation the ^{3}MLCT excited state becomes the lowest-lying state and displays luminescence.

The changes in the absorption and emission behavior for complex **3** are fully reversible. For example, subsequent addition of a base (e.g., triethylamine) to an acidic solution of **3** in acetonitrile resulted in the observation of the reverse trends: the luminescence was gradually quenched, and the absorbance at 420 nm diminished with a concomitant rise in the absorption at 545 nm. Eventually, the LLCT band in

the absorption spectrum was fully recovered. This result is indicative of the reversible nature of the protonation and deprotonation processes for the amino group in complex **3**.

Acids and bases can also induce excited-state switching in complex **4**. The absorption spectrum of this complex in acetonitrile is presented in Figure 3. In addition to the IL transition bands at wavelengths below 350 nm, **4** exhibits an intense low-energy absorption band at 400–600 nm with λ_{max} at 490 nm. Compared with the absorption of **3**, the long tail of this band is shifted to shorter wavelengths by about 100 nm. We have tentatively ascribed this band to an ILCT transition from the π orbital of the amino-substituted phenyl group to the π^* orbital of the metal-bound terpyridyl moiety, probably mixed with some $d\pi(Pt)\rightarrow\pi^*$(terpy) MLCT contribution.[39] This assignment was made on the following grounds. First, it has been established that the absorption and fluorescence spectra of the ligand, 4′-[4-N-$(CH_3)_2$-C_6H_4]-2,2′:6′,2″-terpyridine (4′-aminophenyl-terpy), are observed at much longer wavelengths compared with those of 4′-phenyl-2,2′:6′,2″-terpyridine (4′-phenyl-terpy), which has no amino substituent at the 4-position of the phenyl group.[38] The maximum of the lowest-energy absorption band of 4′-phenyl-terpy in dichloromethane is at around 278 nm, while that of 4′-aminophenyl-terpy appears at a 62 nm longer wavelength. The redshift in the case of fluorescence is even more significant. The fluorescence maxima for 4′-phenyl-terpy and 4′-aminophenyl-terpy in dichloromethane are at 348 nm and 469 nm, respectively. Semiempirical molecular orbital calculations have indicated that the second HOMO (HOMO−1), the HOMO, and the LUMO for 4′-phenyl-terpy are mainly localized on the phenyl (π_{Ph}), terpyridyl (π_{terpy}), and terpyridyl (π^*_{terpy}) moieties, respectively. Thus, its lowest-energy absorption is the local excitation $\pi_{terpy}\rightarrow\pi^*_{terpy}$. In the case of 4′-aminophenyl-terpy, the electron-donating substituent (amino group) on the 4′-phenyl group elevates the energy level of the π_{Ph}, but has little effect on the π_{terpy} and π^*_{terpy}. Thus, π_{Ph}, rather than π_{terpy}, becomes the HOMO, and the lowest-energy absorption is the intramolecular charge-transfer (ICT) transition $\pi_{Ph}\rightarrow\pi^*_{terpy}$. Upon complexation of this ligand with Pt^{II} (complex **4**), the ILCT absorption is substantially redshifted (Figure 3), suggesting considerable σ donation of the terpyridyl electron density to the Pt^{II} center. Secondly, this lowest-energy absorption shows a strong solvent dependence. The λ_{max} of the absorption band in dichloromethane is 524 nm, and this shifts to 490 nm in acetonitrile. This negative solvatochromism is consistent with the nature of the charge-transfer transition and a greater ground-state dipole moment compared with the excited state. Thirdly, upon addition of HBF_4 to a solution of **4** in acetonitrile, the low-energy band at 490 nm decreases monotonically throughout the addition, and at the end of the titration a less intense band is seen in the region 400–550 nm (Figure 3). The latter band may be assigned to a $d\pi(Pt)\rightarrow\pi^*$(terpy) MLCT transition. This observation may evidently be attributed to protonation of the amino group on the terpyridyl ligand. As the amino group is protonated in the presence of HBF_4, the energy level of π_{Ph} is lowered, and the $\pi_{Ph}\rightarrow\pi^*_{terpy}$ ILCT band shifts to higher energy, and hence the $d\pi(Pt)\rightarrow\pi^*$(terpy) MLCT transition becomes the lowest-energy transition. As in the case of **3**, complex **4** is nonemissive in neutral solution. However, in acidic solution, **4** exhibits moderately intense emission from the ^{3}MLCT state with λ_{max} at 625 nm. Again, the changes in the absorption and emission behavior for **4** are fully reversible. Addition of a base to an acidic solution of **4** results in luminescence quenching and the recovery of the ILCT band in the absorption spectrum.

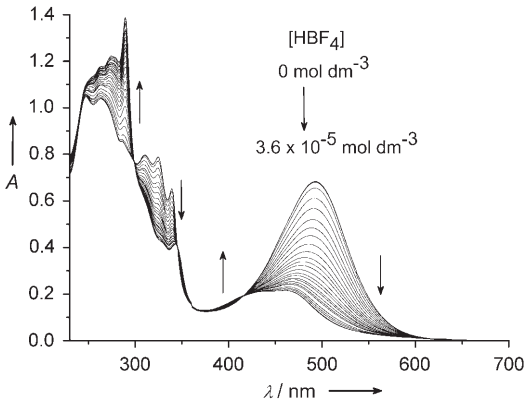


Figure 3. Changes in the absorption spectrum of complex **4** (2.25×10^{-5} mol dm^{-3}) upon addition of various concentrations (0–3.6×10^{-5} mol dm^{-3}) of HBF_4 in acetonitrile.

Successive excited-state switching between LLCT, ILCT, and MLCT states in 1 and 2 induced by acids/bases: The lowest-energy absorption of **1** and **2** can be successively switched from the LLCT to the ILCT, and then to the MLCT transition by the addition of an acid. Figure 4a shows the absorption spectrum of **1** in acetonitrile. In addition to the intense vibronic-structured IL absorption bands at $\lambda <$ 350 nm, **1** shows a moderately intense band at 350–700 nm. The location of the long tail of this band is comparable with that of **3**, but at longer wavelengths than that of **4**. With reference to the absorption spectrum of **3**, this band is tentatively assigned to an LLCT transition from the amino-substituted acetylide ligand to the terpyridyl acceptor, probably mixed with some character of the ILCT transition from the π orbital of the amino-substituted phenyl to the π^* orbital of the terpyridyl moiety, and the MLCT transition $d\pi(Pt)\rightarrow\pi^*$(terpy). Upon addition of HBF_4 to the solution, the absorbance at $\lambda > 520$ nm decreases, while that in the region 445–520 nm increases until one equivalent of the acid has been added (Figure 4a). Well-defined isosbestic points at 445 and 520 nm are observed, indicative of the presence of only two absorbing species in the solution. After the addition of one equivalent of HBF_4, the longer wavelength band is centered at 490 nm. In view of the fact that its shape and location are similar to those of the lowest-energy absorption band of **4** in the absence of acid (see Figure 3), this band is

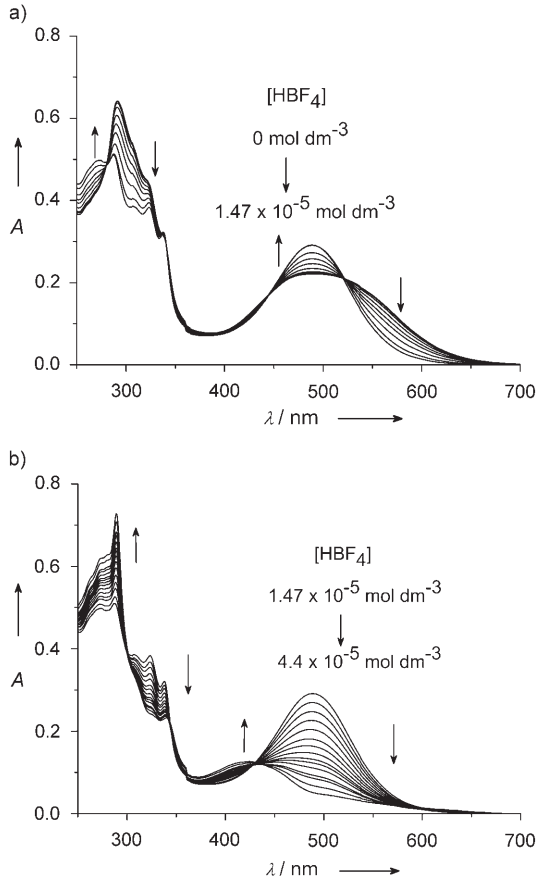


Figure 4. Changes in the absorption spectrum of complex **1** (1.47×10^{-5} mol dm^{-3}) upon addition of various concentrations of HBF_4 in acetonitrile. a) [HBF_4]: 0–1.47×10^{-5} mol dm^{-3}; b) [HBF_4]: 1.47–4.4×10^{-5} mol dm^{-3}.

assigned to an ILCT transition from the π orbital of the amino-substituted phenyl group to the π* orbital of the terpyridyl moiety. Evidently, the basicity of the amino group on the acetylide ligand in **1** is different from that of the amino function of the terpyridyl. In the presence of a small amount (less than one equivalent) of HBF_4, the former amino group is protonated, whereas the latter is not. As a result, the electron-donating ability of the acetylide is dramatically decreased, and the HOMO of this ligand is lowered. On the other hand, the π* orbital of the terpyridyl moiety and the π orbital of the phenyl group of the terpyridyl are little affected. Thus, the LLCT transition from the acetylide ligand to the terpyridyl acceptor shifts to higher energy, and the ILCT transition from the phenyl π orbital to the π* orbital of the terpyridyl moiety becomes the lowest-energy transition. Further addition of HBF_4 to the solution results in a decrease in the absorption band at 490 nm and an increase in the absorbance in the region 380–430 nm (Figure 4b), with a well-defined isosbestic point at 430 nm. At the end of the titration, a less intense band in the region 380–550 nm is clearly visible (Figure 4b). Because this band is very similar in shape to the lowest-energy absorptions of **3** and **4** in the presence of an acid, as well as to that of **5**, we assign this band to an MLCT transition from dπ(Pt) to π*-(terpy). Obviously, in the presence of a sufficient amount of acid, the amino group of the terpyridyl moiety is also protonated. As in the case of **4**, the HOMO of the phenyl group of the terpyridyl is lowered, and the lowest-energy absorption is switched from the ILCT to the MLCT transition. Again, while the ^{3}LLCT and ^{3}ILCT excited states of **1** are nonemissive, protonated **1** shows luminescence from its ^{3}MLCT state with λ_{max} at 575 nm.

The above-described excited-state switching induced by acid is fully reversible. Subsequent addition of a base (triethylamine) to an acidic solution of **1** in acetonitrile results in successive switching of the lowest-energy absorption band from the MLCT to the ILCT and then to the LLCT transition, suggesting that the amino group of the terpyridyl is deprotonated first, followed by that on the acetylide. The photophysical responses to pH of **2** are very similar to those of **1**.

Excited-state switching from LLCT to ILCT by metal ions and subsequent switching to MLCT by acid in 2: The azacrown ether moiety in **2** is capable of complexing metal cations, resulting in an excited-state switch. Addition of Mg^{2+}, Ca^{2+}, Sr^{2+}, or Ba^{2+}, as their perchlorate salts, to a solution of **2** in acetonitrile leads to changes in the absorption spectrum. Figure 5a shows the changes in the UV/Vis spectrum of **2** upon addition of Ca^{2+}. The absorbance at $\lambda > 532$ nm decreases monotonically throughout the course of the addition, while the band at 453–532 nm concomitantly develops with increasing Ca^{2+} concentration. Well-defined isosbestic points at 532 and 453 nm are clearly observed. Similar changes were observed upon addition of other cations to a solution of **2**. This phenomenon evidently arises from complexation of the cation by the azacrown ether receptor on the acetylide ligand, which decreases the electron-donating ability of the latter, thereby lowering the acetylide-based HOMO. Thus, the LLCT transition from the azacrown-containing acetylide ligand to the terpyridyl acceptor shifts to higher energy and the ILCT transition from the phenyl π orbital to the π* orbital of the terpyridyl moiety becomes the lowest-energy absorption. Indeed, control experiments with the crown-free analogues, complexes **1** and **3**–**5**, showed no such changes in their absorption spectra upon addition of the cations under identical conditions. The inset in Figure 5a shows a plot of $A_0/(A_0-A)$ versus $[Ca^{2+}]^{-1}$, where A and A_0 refer to the absorbance of complex **2** at 490 nm in the presence and absence of Ca^{2+}, respectively. The straight line suggests that the complexation of the cation to the azacrown ether occurs in a 1:1 ratio. The bonding constants (log K) determined from such plots for the various cations are Na^+ (2.43), Ba^{2+} (4.14), Ca^{2+} (3.77), Mg^{2+} (2.91), and Sr^{2+} (3.41), and their absolute values are very similar to those of other [15]azacrown-5 ionophores reported in the literature.[44]

Subsequent addition of HBF_4 to a solution of **2** containing an excess of Ca^{2+} ions in acetonitrile led to a decrease in

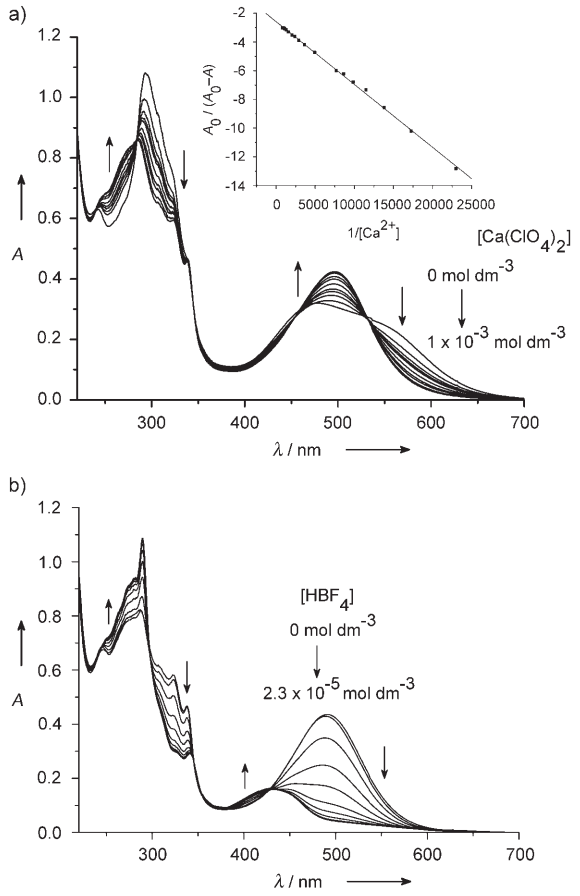


Figure 5. Changes in the absorption spectrum of complex **2** (1.78×10^{-5} mol dm^{-3}) a) upon addition of various concentrations of $Ca(ClO_4)_2$ ($0–1\times10^{-3}$ mol dm^{-3}), then b) upon addition of various concentrations ($0–2.3\times10^{-5}$ mol dm^{-3}) of HBF_4 in acetonitrile.

the absorbance of the ILCT band centered at 490 nm and to an increase in the absorbance at $\lambda < 430$ nm (Figure 5b). An isosbestic point at 430 nm is clearly evident. With reference to the absorption spectra of **1** and **2** in the presence of an excess of HBF_4, the newly appeared band in the region 380–550 nm may be ascribed to a $d\pi(Pt)\rightarrow\pi^*$(terpy) MLCT transition. It is worthy of note that during the titration, the addition of HBF_4 immediately leads to a decrease in the ILCT absorbance and to an increase in the MLCT absorbance. To complete the excited-state switch from the ILCT to the MLCT, only about one equivalent of HBF_4 is needed. This observation suggests that the added HBF_4 reacts with the amino group of the terpyridyl ligand, not with the amino group on the cation-complexed azacrown. Upon cation complexation and subsequent protonation, **2** shows a moderately intense emission from the ^{3}MLCT state when excited, with λ_{max} at 580 nm.

Transient absorption of complexes 1–4: The evidence for the above-described excited-state switching in complexes **1**–**4** based on absorption spectroscopy and photoluminescence is further corroborated by studies of their transient absorptions. Pulsed laser photoexcitation of these complexes in degassed acetonitrile using light of wavelength 355 nm leads to strong absorption throughout the near-UV and visible region. Figure 6a–f illustrate the time-resolved absorption difference spectra for complex **1**, **1**·H (**1** with the amino group on the acetylide protonated), **1**·2H (**1** with the amino groups on both the acetylide and terpyridyl protonated), **3**·H (protonated **3**), **4**, and **4**·H (protonated **4**), respectively. As reported by Sun and co-workers, the transient absorption from **3** was too weak to be observed.[21] Each spectrum in Figure 6 features an absorption band in the near-UV, a bleaching in the 430–540 nm region, and a broad absorption throughout the visible region. In all cases, the decay of the absorption transients throughout the absorption region and the recovery of the bleach occur on the same time scale, indicating that a single type of excited state is responsible for the experimental observations. Both the decay of the absorption and the recovery of the bleach can be well described by a monoexponential function. The lifetime (τ) for each transient decay is given in Figure 6a–f. With reference to previous transient absorption spectroscopy work on platinum(II) terpyridyl acetylide[21] and diimine platinum(II) bisacetylide complexes,[37] the bleaching in the 430–540 nm region of each spectrum may be attributed to ground-state absorption. Indeed, the bleaching for each complex occurs in the corresponding region of its absorption spectrum (Figure 1 and Figures 3–5). The transient absorptions in the near-UV and visible regions arise from the terpyridyl anion radical, which is present in the LLCT, ILCT, and MLCT states. Close inspection reveals that the shape of the transient absorption spectrum is dependent on both the structure of the terpyridyl moiety and the nature of the excited state. For example, the transient absorption spectra of **1**·H and **4** (Figure 6b and e) are remarkably similar, because these species have the same terpyridyl ligand, 4′-[4-N$(CH_3)_2$-C_6H_4]-2,2′:6′,2″-terpyridyl, and ILCT excited state, and hence have the same terpyridyl anion radical coordinated to the Pt^{II} center. The same phenomenon is observed for **1**·2H and **4**·H (Figure 6c and f), which have the same protonated 4′-[4-N$(CH_3)_2$-C_6H_4]-2,2′:6′,2″-terpyridyl and MLCT excited state, and hence have the same terpyridyl anion radical coordinated to the Pt^{III} center. It is noteworthy that the transient for **4**·H has a longer lifetime compared to those for the other complexes. Evidently, the form of the transient absorption spectra of these complexes is not only dependent on their terpyridyl ligands, but also on the nature of their excited states. Since the complexes with an MLCT state as the lowest-energy excited state (complexes **1**·2H, **3**·H, and **4**·H) are emissive, we also measured their luminescence lifetimes. The luminescence lifetimes of **1**·2H, **3**·H, and **4**·H were found to be about 34, 80, and 600 ns, respectively. The lifetimes obtained from the decays of the absorption transients, as well as from the bleach recoveries, are in quantitative agreement with those derived from the luminescence intensity decays.

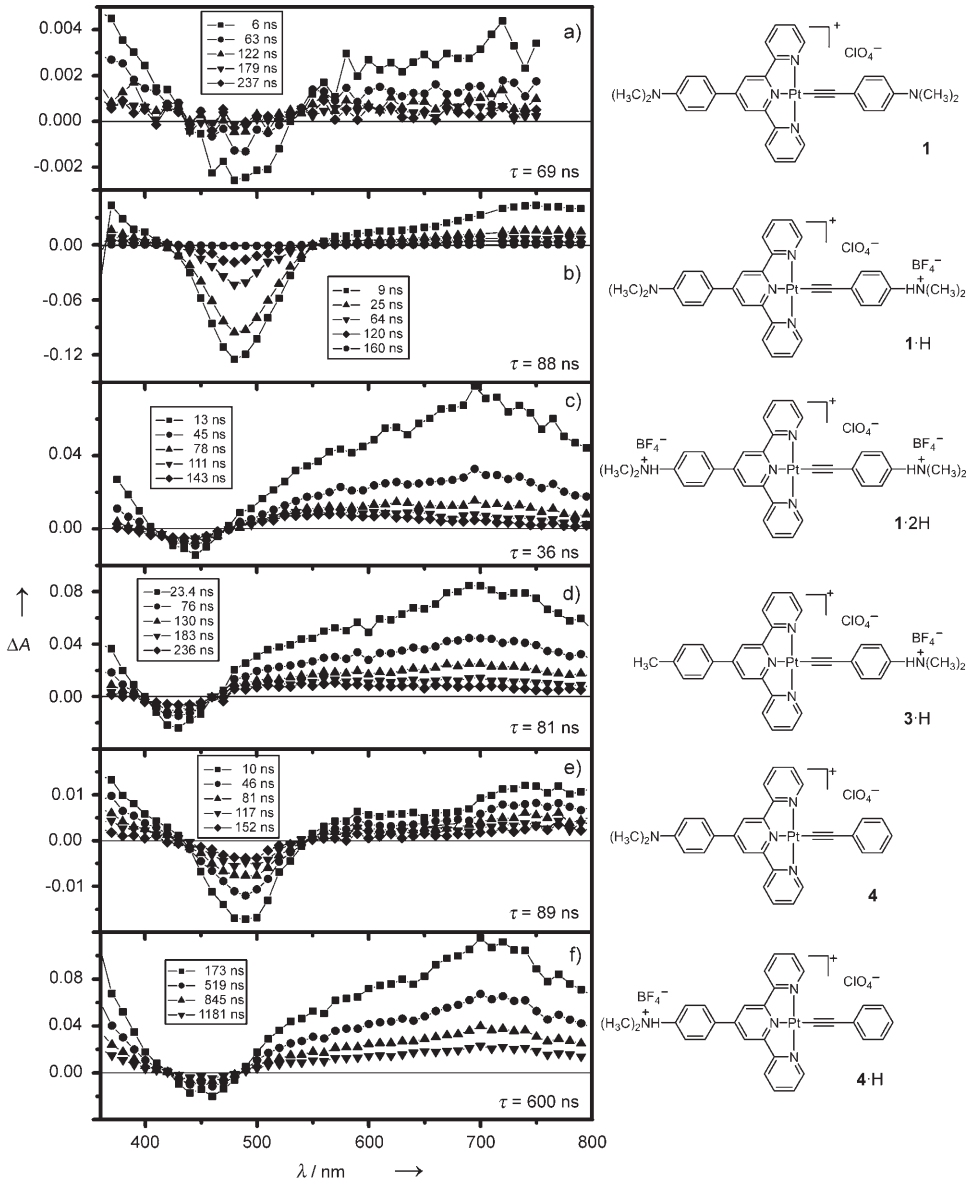


Figure 6. Transient absorption difference spectra for solutions of a) **1**, b) **1**·H, c) **1**·2H, d) **3**·H, e) **4**, and f) **4**·H in acetonitrile at ambient temperature following excitation at 355 nm. The delay times are specified on each spectrum. τ denotes the lifetime of the transient absorption.

Conclusion

The photophysical properties of Pt complexes **1** and **2** have been examined and compared with those of model complexes **3**–**5**. In neutral or basic solution, **1** and **2** show a lowest-lying LLCT transition from the amino-substituted acetylide to the aminophenyl-substituted terpyridyl acceptor. Upon addition of an acid to the solution, first the amino group on the acetylide is protonated, and the lowest-lying excited state of these complexes is switched from the LLCT to the ILCT state, based on the transition from the π orbital of the phenyl to the π^* orbital of the metal-bound terpyridyl. In the presence of a sufficient amount of acid, the amino group of the terpyridyl is also protonated, and the lowest-lying excited state is further switched to the $d\pi(Pt)\rightarrow\pi^*$-(terpy) MLCT state. This switching of the excited states is fully reversible. Subsequent addition of a base to the protonated **1** or **2** leads first to switching of the MLCT state to the ILCT state, and then to the LLCT state. The excited state of complex **2** can also be switched in the presence of metal ions and acids. All of the complexes studied in the present work show transient absorption of the terpyridyl anion radical, which is present in the LLCT, ILCT, and MLCT excited states. The character and shape of the transient absorption spectra of these complexes are not only dependent on the structure of their terpyridyl ligands, but also on the nature of their lowest-lying excited states.

Experimental Section

Materials: 4′-(4-Dimethylaminophenyl)-2,2′:6′,2″-terpyridine,[38] 4′-(4-methylphenyl)-2,2′:6′,2″-terpyridine,[21] 4-dimethylamino-phenylacetylene,[35] and 4-ethynylphenyl-*N*-[15]azacrown-5 ether[35] were prepared according to literature methods. Phenylacetylene was purchased from Acros Co. Inc. Spectroscopic grade acetonitrile and dichloromethane were used as received in the spectroscopic studies. All other reagents were of analytical grade and were used as received.

Caution: Perchlorate salts are potentially explosive. All compounds containing perchlorate should be handled with great care and in small amounts.

[Pt(4′-{4-N(CH$_3$)$_2$-C$_6$H$_4$}terpy)Cl]Cl: This complex was synthesized according to a literature procedure.[35,45] A mixture of 4′-(4-dimethylaminophenyl)-2,2′:6′,2″-terpyridine (352 mg, 1.0 mmol) and K_2PtCl_4 (415 mg, 1.0 mmol) was taken up in acetonitrile/water (1:1, v/v, 60 mL) and the solution was refluxed for 36 h. The reaction mixture was then filtered and the solid was washed successively with water and diethyl ether. The obtained orange solid was dissolved in excess dichloromethane. The resulting solution was filtered and the filtrate was concentrated to a volume of about 5 mL. Addition of diethyl ether to the concentrated solution led to precipitation of the product (441 mg, 71.4%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 3.04 (s, 6H), 6.76 (d, 2H), 7.80 (t, 2H, J = 6.8 Hz), 8.0 (d, 2H, J = 8.8 Hz), 8.4 (t, 2H, J = 8.0 Hz), 8.60 (s, 2H, J = 7.9 Hz), 8.72 (d, 2H, J = 8.0 Hz), 8.76 ppm (d, 2H, J = 6.8 Hz); MS (FAB): m/z calcd for $[C_{23}H_{20}N_4PtCl]^+$: 583; found: 583; elemental analysis calcd (%)

for $C_{23}H_{20}Cl_2N_4Pt{\cdot}H_2O$: C 43.4, H 3.48, N 8.80; found: C 43.4, H 3.46, N 8.47.

[Pt(4′-{4-N(CH$_3$)$_2$-C$_6$H$_4$}terpy){C≡C-C$_6$H$_4$-N(CH$_3$)$_2$-4}]ClO$_4$ (1): A mixture of [Pt(4′-{4-N(CH$_3$)$_2$-C$_6$H$_4$}terpy)Cl]Cl·H$_2$O (63.6 mg, 0.1 mmol), 4-dimethylaminophenylacetylene (29 mg, 0.2 mmol), CuI (10 mg), DMF (3 mL), and triethylamine (6 mL) was sonicated under nitrogen for 8 h. Thereafter, excess aqueous $LiClO_4$ solution was added. Dark-blue crystals were obtained after stirring for 1 h. The product was filtered off and washed with water and diethyl ether. Subsequent recrystallization by diffusion of diethyl ether vapor into a solution of the product in acetonitrile gave **1** as dark-blue crystals (60 mg, 76%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 3.07 (s, 6H), 3.22 (s, 6H), 6.76 (d, 2H, J = 8.0 Hz), 6.93 (d, 2H, J = 8.0 Hz), 7.36 (d, 2H, J = 7.6 Hz), 7.90 (t, 2H, J = 5.6 Hz), 8.12 (d, 2H, J = 7.6 Hz), 8.51 (t, 2H, J = 6.2 Hz), 8.80 (d, 4H), 9.08 ppm (d, 2H); MS (FAB): m/z calcd for $[C_{33}H_{30}N_5Pt]^+$: 690; found: 690; elemental analysis calcd (%) for $C_{33}H_{30}ClN_5O_4Pt{\cdot}H_2O$: C 48.98, H 3.99, N 8.65; found: C 48.73, H 3.94, N 8.61.

[Pt(4′-{4-N(CH$_3$)$_2$-C$_6$H$_4$}terpy){C≡C-C$_6$H$_4$-(*N*-[15]azacrown-5)-4}]ClO$_4$ (2): Complex **2** was prepared according to a procedure similar to that described for **1**, except that 4-ethynylphenyl-*N*-[15]azacrown-5 ether was used in place of 4-dimethylaminophenylacetylene. Yield: 77 mg (79.7%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 3.22 (s, 6H), 3.66 (m, 16H), 3.78 (t, 4H), 6.70 (d, 2H, J = 8.0 Hz), 6.93 (d, 2H, J = 7.2 Hz), 7.32 (d, 2H, J = 8.0 Hz), 7.87 (t, 2H), 8.12 (d, 2H), 8.49 (t, 2H), 8.80 (d, 4H), 9.03 ppm (d, 2H); MS (MALDI-TOF): m/z calcd for $[C_{41}H_{44}N_5PtO_4]^+$: 865; found: 864.5; elemental analysis calcd (%) for $C_{41}H_{44}ClN_5O_8Pt{\cdot}1.5\,H_2O$: C 49.62, H 4.77, N 7.06; found: C 49.65, H 4.69, N 6.68.

[Pt{4′-(4-CH$_3$-C$_6$H$_4$)terpy}{C≡C-C$_6$H$_4$-N(CH$_3$)$_2$-4}]ClO$_4$ (3): Complex **3** was prepared according to a procedure similar to that described for **1**, except that 4′-(4-methylphenyl)-2,2′:6′,2″-terpyridine was used in place of 4′-(4-dimethylaminophenyl)-2,2′:6′,2″-terpyridine. Yield: 59 mg (77.7%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.45 (s, 3H), 2.93 (s, 6H), 6.60 (d, 2H, J = 8.2 Hz), 7.18 (d, 2H, J = 8.2 Hz), 7.44 (d, 2H, J = 8.7 Hz), 7.75 (t, 2H, J = 6.0 Hz), 8.00 (d, 2H, J = 8.7 Hz), 8.40 (t, 2H, J = 7.6 Hz), 8.72 (d, 2H, J = 7.6 Hz), 8.84 (s, 2H), 8.90 ppm (m, 2H); MS (MALDI-TOF): m/z calcd for $[C_{32}H_{27}N_4Pt]^+$: 661.5; found: 661.7; elemental analysis calcd (%) for $C_{32}H_{27}ClN_4O_4Pt{\cdot}CH_2Cl_2{\cdot}CH_3CN$: C 47.33, H 3.63, N 7.89; found: C 47.40, H 3.53, N 7.70.

[Pt(4′-{4-N(CH$_3$)$_2$-C$_6$H$_4$}terpy)(C≡C-C$_6$H$_5$)]ClO$_4$ (4): Complex **4** was prepared according to a procedure similar to that described for **1**, except that phenylacetylene was used in place of 4-dimethylaminophenylacetylene. Yield: 50 mg (77.2%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 3.05 (s, 6H), 6.80 (d, 2H, J = 8.8 Hz), 7.25 (t, 1H, J = 7.9 Hz), 7.30 (t, 2H, J = 7.6 Hz), 7.41 (d, 2H, J = 7.6 Hz), 7.78 (t, 2H, J = 6.4 Hz), 8.00 (d, 2H, J = 8.8 Hz), 8.38 (t, 2H, J = 7.6 Hz), 8.69 (d, 2H, J = 8.8 Hz), 8.71 (s, 2H), 9.00 ppm (d, 2H); MS (FAB): m/z calcd for $[C_{31}H_{25}N_4Pt]^+$: 648; found: 648; elemental analysis calcd (%) for $C_{31}H_{25}ClN_4O_4Pt{\cdot}0.5\,H_2O$: C 49.18, H 3.46, N 7.40; found: C 49.06, H 3.37, N 7.00.

[Pt{4′-(4-CH$_3$-C$_6$H$_4$)terpy}(C≡C-C$_6$H$_5$)]ClO$_4$ (5): Complex **5** was prepared according to a procedure similar to that described for **1**, except that 4′-(4-methylphenyl)-2,2′:6′,2″-terpyridine and phenylacetylene were used in place of 4′-(4-dimethylaminophenyl)-2,2′:6′,2″-terpyridine and 4-dimethylaminophenylacetylene, respectively. Yield: 55 mg (76.4%). ^{1}H NMR (400 MHz, [D$_6$]DMSO): δ = 2.44 (s, 3H), 7.27 (m, 1H), 7.32 (m, 2H), 7.45 (m, 4H), 7.84 (m, 2H), 8.04 (d, 2H, J = 8.2 Hz), 8.45 (m, 2H), 8.77 (d, 2H, J = 7.8 Hz), 8.91 (s, 2H), 9.02 ppm (d, 2H, J = 5.5 Hz); IR: $\tilde{\nu}$ = 2119 cm^{-1}; HRMS: m/z: calcd for $[C_{30}H_{22}N_3Pt^{194}]^+$: 618.1435; found (%): 618.1432 (70) [M^+]; calcd for $[C_{30}H_{22}N_3Pt^{195}]^+$: 619.1456; found (%): 619.1454 (100) [M^+]; calcd for $[C_{30}H_{22}N_3Pt^{196}]^+$: 620.1457; found (%): 620.1465 (83) [M^+], 516.0975 (48) [M^+ − C≡CC$_6$H$_5$], 517.0993 (69) [M^+ −C≡CC$_6$H$_5$], 518.1010 (58) [M^+−C≡CC$_6$H$_5$]; elemental analysis calcd (%) for $C_{30}H_{22}ClN_3O_4Pt$: C 50.10, H 3.06, N 5.85; found: C 50.01, H 2.97, N 5.34.

Physical measurements and instrumentation: UV/Vis spectra were measured on a Shimadzu UV-1601 PC spectrophotometer. Steady-state emission spectra were recorded on a Perkin Elmer LS50B spectrofluorimeter. Luminescence lifetimes were measured by using an Edingburge LP920 apparatus from Analytical Instruments. Elemental analyses were performed by using a Carlo Erba 1106 elemental analyzer. ^{1}H NMR spectra were recorded on a Bruker 400 FT-NMR spectrometer and chemical shifts are given relative to tetramethylsilane. FAB mass spectra were acquired on a KYKY-ZHP mass spectrometer. In the transient absorption spectroscopy experiments, the samples were purged with argon for 30 min. Excitation was provided by using an Nd:YAG laser (third harmonic, 10 ns) at 355 nm. The detector was a xenon lamp on the Edingburge LP920 apparatus from Analytical Instruments.

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