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Luminescence that lasts from Pt(trpy)Cl^+ derivatives (trpy = 2,2′;6′,2″-terpyridine)

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Contents

Abstract

This report outlines progress to date in preparing Pt(trpy)Cl^+ derivatives that exhibit long-lived photoluminescence in solution (trpy = 2,2′;6′,2″-terpyridine). The trpy complex itself is a versatile binding agent/reporter probe for biological macromolecules but is non-emissive, except in solids or low-temperature glasses. Derivatives investigated are of the type Pt(4′-R-T)Y^+, where 4′-R-T denotes a 4′-substituted form of the trpy ligand and Y is a pseudohalide co-ligand. Simple halide replacement yields the Pt(trpy)OH^+ derivative which has facilitated luminescence-based DNA-binding studies. Other complexes with long-lived excited states in fluid solution include Pt(4′-NMe_2-T)Cl^+ and Pt(4′-Pyre1-T)Cl^+, where Pyre1 designates a 1-pyrenyl substituent. Due to intra-ligand charge-transfer character, Pt(4′-NMe_2-T)Cl^+ and Pt(4′-Pyre1-T)Cl^+ each exhibit relatively low energy absorption maxima. Open coordination sites support quenching by Lewis bases, however, the effect is less evident with increased intra-ligand orbital parentage in the excited state. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Charge-transfer states; DNA binding; Exciplex quenching; Luminescence; Photochemistry; Platinum(II); Polypyridine ligands; Quenching

1. Introduction

Polypyridine complexes of platinum(II) are receiving a great deal of attention. Unlike many other platinum(II) systems, polypyridine derivatives can exhibit photoluminescence from reasonably long-lived metal-to-ligand charge-transfer (MLCT) states in fluid solution [1–6]. More typically, the lowest energy excited state of a platinum(II) system is very short lived because excitation involves population of the dσ* orbital, significant metal-ligand bond weakening, and/or a large D_2 distortion [7]. Another reason for the interest in the d^8 polypyridine complexes is the profound influence open coordination sites have on the photophysical and photochemical processes, e.g. induction of strongly red-shifted emission in solution or the solid state [4,8–10]. Systems in which the uptake of small molecules modulates metal-metal interactions, therefore, offer promise for sensor development [11,12]. There are also reports of excimer emission or excimer quenching in fluid solution [13,14], and Lewis bases can attack the excited state and induce exciplex quenching [15,16]. Finally, reports that

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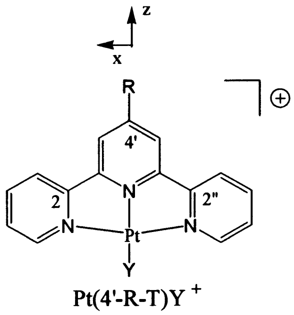


Scheme 1.

platinum polypyridines bind to biological macromolecules continue to fuel interest [17–25].

The following discussion focuses on studies of platinum(II) complexed to 2,2′;6′,2″-terpyridine (trpy) or derivatives thereof (Scheme 1). The presence of a trpy ligand inhibits D_{2d} distortions within the excited states. However, trpy complexes have relatively low energy d–d excited states that promote radiationless decay. Third-row, d^8 complexes usually have high-energy d–d states, but the bonds to the outer nitrogens of the trpy are weak because the ligand framework constrains the N–Pt–N″ angle to be around ca. 160° [1,4,10].

2. Pt(trpy)Y$^+$ systems

An absorption spectrum of the prototype system, Pt(trpy)Cl$^+$, natually breaks into two energy regimes (Fig. 1). As with the zinc(II) analogue, vibronically structured, intra-ligand π–π* bands dominate the spectrum at wavelengths shorter than about 350 nm. Weaker absorptions ($\varepsilon_{\text{max}} \approx 3000$ M^{-1} cm^{-1}) between 350 and 450 nm, not present in the spectrum of Zn(trpy)Cl$_2$, represent transitions with significant MLCT character [1,4]. Despite the presence of low-energy CT absorption, the complex is non-emissive in room-temperature (r.t.) acetonitrile solution, however, one can observe photoluminescence from the solid state [4,10,26]. For materials studied to date, the solid-state emission is broad, structureless, and occurs at relatively long wavelengths, characteristic of CT emission from a polypyridine complex of platinum involved in neighbor-neighbor interactions [8–10]. Strong d(z^2)–d(z^2) interactions result in emission from ^{3}dσ*π* states, often designated as ^{3}metal–metal-to-ligand charge-transfer (^{3}MMLCT) states. Low-temperature glassy solutions of Pt(trpy)Cl$^+$ are also emissive, but the signal is concentration dependent [10,26]. If the platinum concentration is ≤ 10 μM, the complex exhibits a structured emission with the highest energy band occurring at around 465 nm and a vibronic spacing of ca. 1400 cm^{-1} [26]. Assignment as slightly perturbed ^{3}π–π* emission from the coordinated trpy ligand is straightforward because an analogous zinc(II) complex exhibits the same type of vibronically structured emission beginning around 435 nm [3]. Glasses containing a ten-fold higher concentration of platinum also exhibit a broad emission in the 600–650 nm region that comes from aggregated forms involving metal–metal interactions [10,26]. In water concentrated solutions of the complex show evidence of aggregation even at r.t. [26,27].

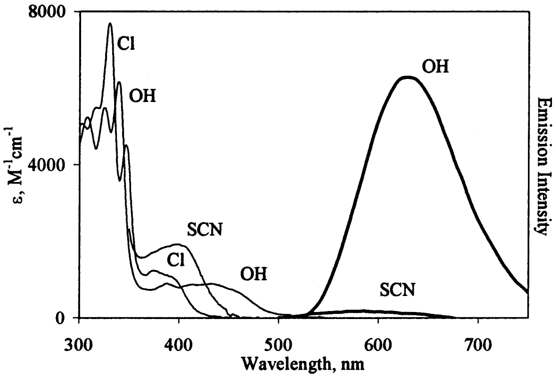


Fig. 1. r.t. spectra of Pt(trpy)Y$^+$ systems in acetonitrile. Thin lines, absorption spectra of the Y = chloro, hydroxo, and thiocyanato (truncated spectrum) complexes. Thick lines: corrected emission spectra of the thiocyanato and hydroxo complexes [1].

The Pt(trpy)SCN$^+$ complex, presumably S-bound, shows somewhat different behavior in fluid solution. The same type of CT absorption occurs, but the bands are broader and appear at slightly longer wavelengths (Fig. 1). More striking, the thiocyanato complex proves to be emissive in acetonitrile, but the signal is weak with an excited-state lifetime of only 3–4 ns [1]. On the other hand, in dichloromethane (DCM) the emission shifts to slightly longer wavelength, and the lifetime extends to 130 ns. In either solvent the emission is broad and unstructured with a maximum at about 590 nm, in keeping with CT, as opposed to intra-ligand, orbital parentage. The excitation is probably mainly metal-to-ligand CT, but may have S(thiocyanate)→π*(trpy) character as well, by analogy with systems Eisenberg and co-workers have studied involving bipyridine and dithiolate ligands bound to platinum(II) [2].

Due to the favorable lifetime, studies of Lewis base-induced, exciplex quenching of the thiocyanate complex are possible in DCM solution [15]. Consistent with quenching by adduct (exciplex) formation, Stern–Volmer analysis shows that the quenching constant increases monotonically with the base strength, measured in terms of the Gutmann donor number (DN). For the relatively weak donor acetone (DN = 17.0) the quenching rate constant is only 1.9×10^7 M^{-1} s^{-1}, however, it increases by three orders of magnitude to 2.7×10^{10} M^{-1} s^{-1} for the strong donor pyridine (DN = 33.1).

The Pt(trpy)OH$^+$ system has even more intriguing spectral properties in solution. As is evident in Fig. 1, the CT absorption extends to unusually long wave-

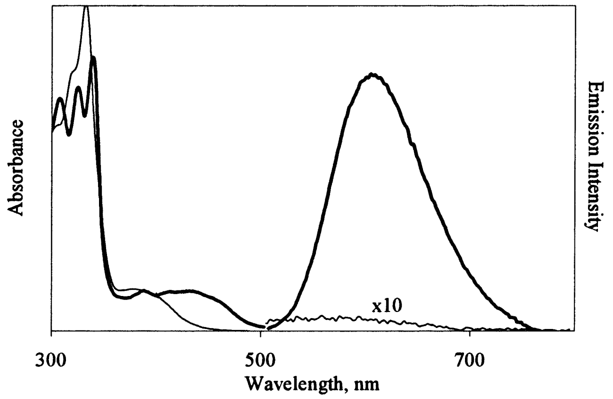


Fig. 2. Spectra of Pt(trpy)OH$^+$ in solution. Below 500 nm: absorption in acetonitrile (thick) and water. Above 500 nm: uncorrected emission in acetonitrile (thick) and water (× 10).

lengths in acetonitrile solution. The shift to lower energy is attributable to the short platinum–oxygen distance and the π-donor ability of the hydroxide ligand [1]. However, Fig. 2 reveals that the CT absorption shifts to much higher energy in aqueous solution where hydrogen-bonding interactions with the lone pairs of the hydroxide ligand weaken the π-donating ability [20]. Coordinated water evidently has a $pK < 5$ because the complex gives the same absorption spectrum from pH 5 to 9. The hydroxide complex is stable for periods of days in pH 9 aqueous solution, but in nonaqueous solvents spectral changes indicating replacement of the hydroxide ligand occur over a period of hours [20]. The Pt(trpy)OH$^+$ complex is luminescent in acetonitrile solution and exhibits an excited-state lifetime of 170 ns in the absence of dioxygen [1]. The excited state should be a good electron acceptor as a conservative energetic analysis suggests the potential is at least 0.8 V versus SCE [20]. Quenching studies by Cummings et al. confirm that Pt(trpy)OH$^+$ is a strong photooxidant [28].

Some of the most intriguing emission results relate to aqueous solutions. The free hydroxide complex itself is virtually non-luminescent in water probably because of facile deactivation through a d–d excited state in view of the relatively high-energy CT absorption (Fig. 2). Upon adduct formation with DNA, however, the CT absorption shifts toward lower energy, and the complex is once again luminescent [20]. Like Pt(trpy)Cl$^+$ [17,29], in a kinetically controlled process Pt(trpy)OH$^+$ intercalates into DNA. The emission lifetime is 95 ns in a [poly(dA · dT)]$_2$ host and 135 ns in a [poly(dI · dC)]$_2$ host, where dA, dT, and dI designate deoxyadenosine, deoxythymine, and deoxyinosine, respectively [20]. The complex actually intercalates preferentially in guanine–cytosine (G≡C) rich sequences, but guanine residues quench the emission by an electron-transfer mechanism. Over a period of hours at r.t., any emission signal vanishes, and the platinum–terpyridine moiety converts to a thermodynamically more stable, covalently bound form. During this phase of the binding the CT absorbance shifts back to higher energy, consistent with replacement of the hydroxide ligand by a neutral donor center, most likely an N7 nitrogen from a purine residue of the DNA host.

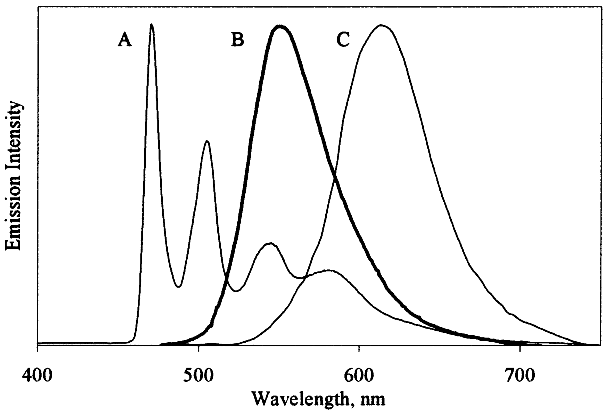


Fig. 3. Low-temperature emission from samples containing Pt(trpy)Cl$^+$. (A) Perturbed $^3\pi-\pi^*$ emission from the SbF$_6{}^-$ salt in a butyronitrile glass at 77 K; (B): (thick) ^{3}MLCT emission from solid [Pt(trpy)Cl]SbF$_6$ at 100 K [10]; (C): ^{3}MMLCT emission from solid [Pt(trpy)Cl]SO$_3$CF$_3$ at 100 K [10].

In summary, the photophysical properties of Pt(trpy)Y$^+$ systems are highly variable. Depending on the co-ligand and the medium, the trpy complex can exhibit dominant IL, MLCT or MMLCT emission (Fig. 3). Even when an emissive state occurs at lowest energy, a d–d excited state can play an important role in promoting radiationless decay. Two of the best behaved systems in r.t., fluid solution are Pt(trpy)SCN$^+$ and Pt(trpy)OH$^+$, where the emission has dominant MLCT character in each case. The thiocyanato complex exhibits an excited-state lifetime of 0.13 μs in DCM but is subject to exciplex quenching by Lewis bases. With hydroxide as the counterligand, the excited state is somewhat more resistant to exciplex quenching and is a good oxidant In aqueous solution, luminescence studies have been instrumental in characterizing DNA-binding interactions of Pt(trpy)OH$^+$.

3. Pt(4′-X-T)Cl$^+$ systems

As with the Ru(trpy)$_2^{2+}$ system [30], systematic exploration of substituent effects has led to the preparation of Pt(trpy)Cl$^+$ derivatives that are photoluminescent [31]. Introduction of substituents in the 4′ position of the trpy ligand (Scheme 1) to give a so called 4′-X-T derivative is straightforward with a number of synthetic routes available. For work in nonaqueous media, [Pt(4′-X-T)Cl]TFPB salts, where TFPB denotes the tetrakis[3,5-bis(trifluoromethyl)phenyl]borate anion, are convenient forms. The original premise was that intro-

Table 1
Reduction potentials, absorption and emission data from Pt(4′-X-T)Cl$^+$ systems in r.t. DCM [31]

X	$E_0(+/0)$ [a] vs. $F_c^{+/0}$	λ(Abs) (nm)	λ_{max}(Em) [b] (nm)	Φ [c]	τ [d] (ns)
CN	−0.92	311sh 323 345 366 405sh 428	550 590sh	0.005	116
SO_2Me	−0.98	325 348 380 430	542 577	0.002	21
H	−1.24	305 320 340 390 403			
SMe	−1.28	305 330 400 425	542 575 625sh	0.006	142
NMe_2	−1.53	282 316 346sh 420 444	535 570 635sh	0.08	1920

[a] Potential vs. ferrocene couple in DMF.
[b] Uncorrected.
[c] Emission quantum yield.
[d] Lifetime.

duction of an appropriate substituent would result in a lowering of the energy of the emissive MLCT state relative to deactivating d–d excited states. Electrochemical data can provide insight into the energy of a CT state that formally entails oxidation of the metal center and reduction of the ligand [32,33]. Unfortunately, solvent limitations have so far prevented direct observation of the Pt(III)–Pt(II) potential. However, as with other systems of this type [34–36], the first reduction is generally a kinetically controlled process involving injection of an electron into the lowest energy π* orbital of the trpy moiety, i.e. reduction of the coordinated ligand. In line with this model, the results in Table 1 reveal that the potential shifts positive (negative) upon introduction of electron-withdrawing (-donating) substituents. Substituents can also influence the energies of d–d states and other important excited states, vide infra.

The influence substituents have on the photophysical properties of a Pt(4′-X-T)Cl$^+$ systems is evident in absorbance and emission data that appear in Table 1 and Fig. 4. In accordance with expectations, the CT absorption maximum shifts to longer wavelength with the introduction of an electron-withdrawing cyano or methylsulfonyl substituent. Furthermore, both derivatives exhibit emission in r.t. DCM solution. Each emission signal exhibits vibrational structure but originates at a significantly longer wavelength than the $^3\pi$–π* emission of the free 4′-X-T ligand. Therefore, on energy grounds the most reasonable state assignment is emission from a ^{3}MLCT state, although the emitting state must have some admixture of $^3\pi$–π* character as well [3]. The emission from the 4′-CN-T (4′-cyano-2,2′;6′,6″-terpyridine) derivative has an excited-state lifetime of 0.12 μs in DCM solution. As depicted in Fig. 5, the presence of the electron-withdrawing sub-

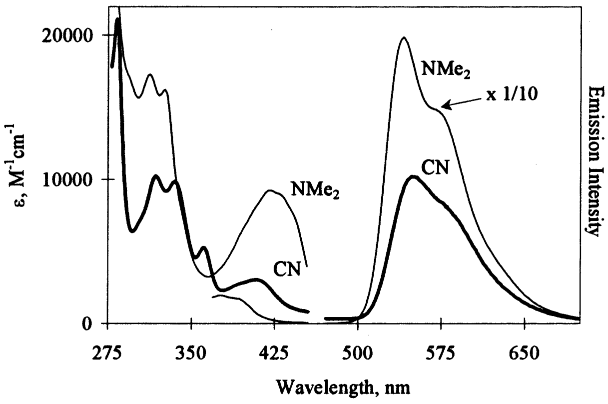


Fig. 4. r.t. spectra of Pt(4′-X-T)Cl$^+$ systems [31]. Below 500 nm: absorption spectra of the 4′-NMe$_2$-T, 4′-CN-T (thick) and trpy (truncated) complexes in acetonitrile. Above 500 nm: uncorrected emission spectra of the 4′-NMe$_2$-T and 4′-CN-T (thick) complexes in deoxygenated DCM (same absorbance at excitation maximum).

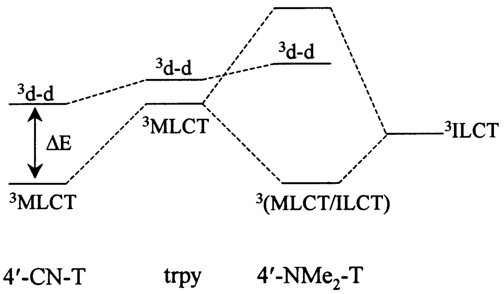


Fig. 5. Proposed excited-state energies in Pt(4′-X-T)Cl$^+$ complexes. Left to right: 4′-CN-T, trpy, and 4′-NMe$_2$-T complexes. Far right: ILCT state that mixes into the emitting of Pt(4′-NMe$_2$-T)Cl$^+$. ΔE is the minimum barrier to deactivation via a ^{3}d–d state.

stituent probably inhibits thermal population of d–d excited states that would otherwise facilitate radiationless decay.

The more striking finding is that a complex with an electron-donating thioether or dimethylamino substituent exhibits even brighter, longer-lived emission (Table 1). Thus, the Pt(4′-NMe$_2$-T)Cl$^+$ complex has a lifetime of 1.9 μs in r.t. DCM solution. (4′-NMe$_2$-T = 4′-(dimethylamino)-2,2′;6′,2″-terpyridine) This result is quite remarkable because electron-donating substituents *destabilize* the MLCT state relative to deactivating d–d states in Ru(4′-X-T)$_2$$^{2+}$ systems [30]. In platinum–terpyridine complexes, other types of excitation influence the energetics and dynamics of the emitting state. One indication is that the 4′-NMe$_2$-T complex has the lowest energy CT absorption maximum in the series despite having the ground state with the most negative (least accessible) reduction potential. Part of the explanation is probably that an electron-donating substituent drives up the energy of the occupied orbital(s) from which the CT excitation originates. Perhaps more importantly, the electron-rich –SMe and –NMe$_2$ substituents both have lone pairs that conjugate with the π system of the trpy core and give rise to new π–π* transitions with considerable intra-ligand, substituent-to-trpy charge-transfer (ILCT) character. The ILCT transitions occur in the UV spectrum of the free ligands, but they shift to lower energy in complexes as a consequence of the coulomb field of the metal ion [31,37]. Since two type of excitation with nominally similar energies are possible, the lowest energy CT transition inevitably has a mixed-orbital parentage that includes MLCT as well as ILCT/π–π* character (Fig. 5) [3,31,38].

Two quite different observations support the idea of a mixed-orbital parentage. One is that mixing can account for the dipole strength of the lowest energy excitation in the 4′-NMe$_2$-T complex [31]. The second argument revolves around the reactivity of the excited state, specifically the susceptibility to exciplex quenching. As noted above, the CT excited state of Pt(trpy)SCN$^+$ is subject to exciplex quenching by Lewis bases, and Fig. 6 reveals that the quenching constant increases with the DN of the quencher. Lewis bases also quench the emission of the 4′-SMe-T and 4′-NMe$_2$-T systems, however, the quenching constants for DMSO and pyridine are noticeably smaller for Pt(4′-SMe-T)Cl$^+$ or Pt(4′-NMe$_2$-T)Cl$^+$ than Pt(trpy)SCN$^+$ (Fig. 6). Along with smaller quenching constants, the Stern–Volmer plots for photoexcited Pt(4′-SMe-T)Cl$^+$ and Pt(4′-NMe$_2$-T)Cl$^+$ show saturation at higher quencher concentrations with weak bases [15]. Quenching is much less efficient because weak bases do not directly attack the metal center. Instead, they first combine with the excited state to form an outer-sphere complex from which the excited state can either escape or convert to the exciplex with relaxation back to the ground state. A limiting rate, therefore, occurs at high quencher concentrations, when outer-sphere complex formation is complete. One reason the emissive excited states of Pt(4′-SMe-T)Cl$^+$ and Pt(4′-NMe$_2$-T)Cl$^+$ are relatively weak electrophiles is that ILCT character provides for delocalization of the ‘hole’ away from the metal and onto the ligand.

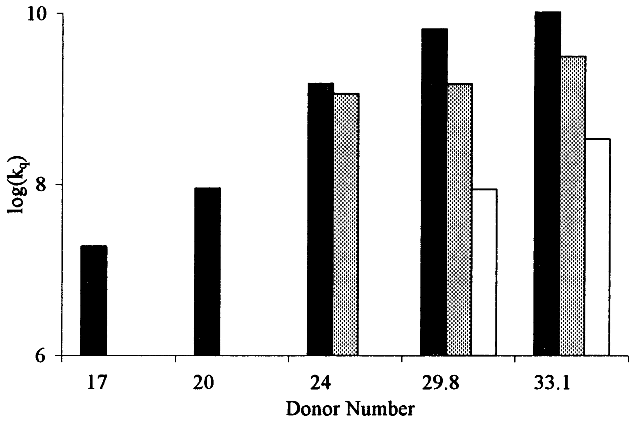


Fig. 6. Kinetics data for quenching of photoexcited Pt(4′-X-T)Y$^+$ systems by Lewis bases in r.t. DCM. Second-order rate constants (k_qs) for quenching of Pt(trpy)SCN$^+$ (solid bars), Pt(4-SMe-T)Cl$^+$ (hatched bars) and Pt(4′-NMe$_2$-T)Cl$^+$ (unshaded bars) increase with the base strength (DN) [15]. DNs: 17.0 (acetone), 20.0 (THF), 24.0 (DMF), 29.8 (DMSO) and 33.1 (pyridine).

In summary, the addition of an electron-withdrawing or an electron-donating substituent at the 4′ position of the trpy ligand results in a lower energy CT absorption in Pt(4′-X-T)Cl$^+$ systems. The excited-state lifetime and emission yield increase because of a net increase in the barrier against deactivation via low-lying ^{3}d–d excited states, most dramatically in Pt(4′-NMe$_2$-T)Cl$^+$ where the lowest energy excited state exhibits a mixed ^{3}ILCT–^{3}MLCT orbital parentage. Diminution of MLCT character renders the reactive excited state less susceptible to exciplex quenching by Lewis bases. In principle, ILCT excitation can also occur when an electron-withdrawing substituent is present, however, in Pt(4′-X-T)Cl$^+$ systems the effect is less important because the coulomb field of platinum destabilizes trpy-to-substituent excitation.

4. Pt(4′-Ar-T)Cl$^+$ systems

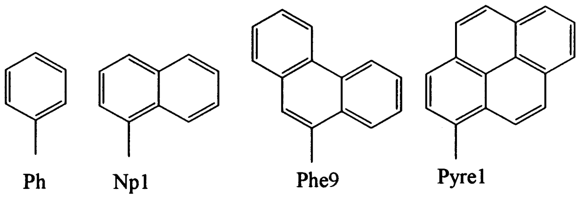
Introduction of aryl substituents at the 4′ position of the trpy ligand also dramatically affects the photophysical properties [3,39]. One could anticipate that Pt(4′-Ar-T)Cl$^+$ complexes would prove interesting on the basis of previous work on metal polypyridine complexes [40,41]. Thus, delocalization of the π* acceptor orbital of the trpy ligand onto the substituent can result in a lower energy ^{3}MLCT state relative to deactivating ^{3}d–d states as well as a less distorted excited state. However, as with the 4′-X-T series, ILCT character becomes a factor when the aryl subtituent is a large, easily ionized, fused-ring system. Scheme 2 depicts a series of four substituents used. Illustrative absorption and emission data for two Pt(4′-Ar-T)Cl$^+$ systems appear in Fig. 7, while Table 2 contains a summary of emission data.

Parallel studies of Zn(4′-Ar-T)Cl$_2$ systems have also been informative. For the zinc complexes the emissions vary with the aryl substituent (Fig. 8) and they appear at shorter wavelengths. In the case of the parent complex Zn(trpy)Cl$_2$, the vibronically structured emission corresponds to ^{1}π–π* fluorescence from the coordinated trpy moiety. However, the broad, unstructured emission from Zn(4′-Pyre1-T)Cl$_2$ has a much lower energy than the ^{1}π–π* fluorescence of either terpyridine or pyrene. The reason is that the Zn(4′-Pyre1-T)Cl$_2$ system exhibits ^{1}ILCT emission on account of the ease of ionization of the pyrenyl substituent [3].

Assigning orbital parentage to the emission from the platinum complexes is not as straightforward. The simplest possible treatment of charge-transfer excitation assumes the participation of one orbital from each center involved [42,43]. For a low-valent metal in combination with a π-acid ligand like trpy, they correspond to the first two terms of Eqs. (1) and (2):

$$\Psi_{\mathrm{u}} = f|5\mathrm{d}_{yz}\rangle + g|\pi^*_{\mathrm{T}}\rangle + h|\pi^*_{\mathrm{Ar}}\rangle + k|\pi_{\mathrm{T}}\rangle + l|\pi_{\mathrm{Ar}}\rangle + m|6\mathrm{p}_z\rangle \quad (1)$$

$$\Psi_{\mathrm{f}} = a|5\mathrm{d}_{yz}\rangle + b|\pi^*_{\mathrm{T}}\rangle + c|\pi^*_{\mathrm{Ar}}\rangle + d|\pi_{\mathrm{T}}\rangle + e|\pi_{\mathrm{T}}\rangle + e|6\pi_{\mathrm{Ar}}\rangle \quad (2)$$



Scheme 2.

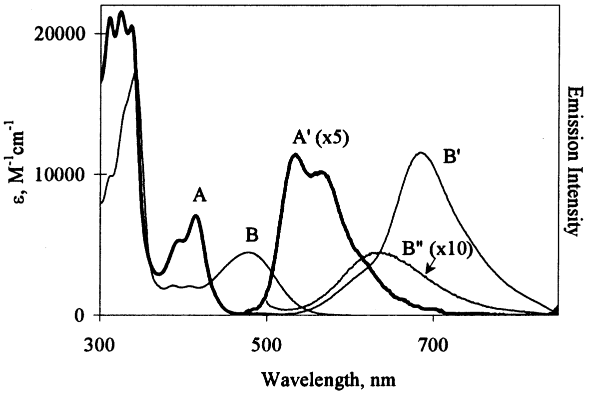


Fig. 7. Spectra of Pt(4′-Ar-T)Cl$^+$ systems in r.t. DCM solution [3]. Absorption spectra, (A) (thick), Pt(4′-Ph-T)Cl$^+$; (B) Pt(4′-Pyre1-T)Cl$^+$. Uncorrected emission spectra: A′ (thick), Pt(4′-Ph-T)Cl$^+$; B′ and B″, Pt(4′-Pyre1-T)Cl$^+$. Emissions from deoxygenated solutions except B″ which is aerobic.

The addition of the other terms in Eqs. (1) and (2) permits a still crude, but more realistic theoretical description of the molecular orbitals (MO's) involved in the case of a Pt(4′-Ar-T)Cl$^+$ system. MO's ψ_{u} and ψ_{f} involve contributions from 5d$_{yz}$ and 6p$_z$ atomic orbitals on platinum, π and π* orbitals of the trpy core, and orbitals from the arene substituent, where a-m are appropriate mixing coefficients. (See Scheme 1 for the orientation of the Cartesian axes.) In the model the original excitation formally entails injecting an electron into ψ_{u}, in which a π* orbital of trpy, the $|\pi^*_{\mathrm{T}}\rangle$ term, is almost certainly the dominant component. Beyond that, Eq. (1) reveals other influences on ψ_{u} including coupling to the π system of the substituent and conjugation with a dπ orbital of the metal, as well as—electrochemistry data suggest—platinum 6p$_z$ [34,35]. Eq. (1) also allows for metal-induced mixing with other MO's of the trpy moiety. A further assumption of the model is that the 'hole' in the excited state occurs in a lower-energy, companion orbital that also has π symmetry (Eq. (2)). The transition probability then depends on the integral $\langle\psi_{\mathrm{u}}|D|\psi_{\mathrm{f}}\rangle$ which expands into a number of integrals of the type $\langle\pi^*_{\mathrm{T}}|D|5\mathrm{d}_{yz}\rangle$, $\langle\pi^*_{\mathrm{T}}|D|\pi_{\mathrm{T}}\rangle$, etc., where D is an appropriate dipole moment operator. The mixed parentage is evident because the $\langle\pi^*_{\mathrm{T}}|D|\pi_{\mathrm{T}}\rangle$ term signifies π–π*(trpy) character, the $\langle\pi^*_{\mathrm{T}}|\mathrm{D}|\pi_{\mathrm{Ar}}\rangle$ term represents ILCT character, and so on. Mixing coefficients determine the weight each factor has in shaping the overall transition probability. For example, if g is the dominant coefficient in Eq. (1) and a is dominant in Eq. (2), the excitation has principally MLCT character. The discussion that follows focuses on two limiting cases, the 4′-Ph-T and 4′-Pyre1-T systems.

In Pt(4′-Ph-T)Cl$^+$ the phenyl moiety only weakly influences the chromophore because the HOMO/LUMO gap of benzene is much greater than that of

Table 2
Photophysical data from Pt(4'-Ar-T)Cl$^+$ systems in deoxygenated DCM [3]

Pt(4′-Ar-T)Cl$^+$	λ_{max} (nm) [a], 298 K	τ (μs), 298 K	Φ, 298 K	k_r [b] (s^{-1}), (Φ/τ)
Pt(4′-Ph-T)Cl$^+$	535, 570sh, 608sh [538, 572(s), 610(s)]	0.085	0.0021	2.5×10^4
Pt(4′-Npl-T)Cl$^+$	588 [600]	16.6	0.047	2.8×10^3
Pt(4′-Phe9-T)Cl$^+$	595 [610]	21.0	0.070	3.3×10^3
Pt(4′-Pyrel-T)Cl$^+$	640 [650] [c]	1.0 ns [c]	0.001 [c]	1.0×10^6 [c]
	640sh, 685 [700]	64.0	0.034	5.3×10^2

[a] Corrected emission maxima in brackets.
[b] Radiative rate constant calculated as Φ/τ.
[c] Data from aerobic solution.

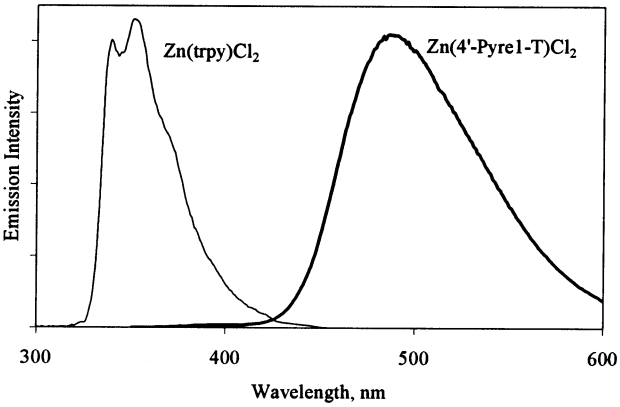


Fig. 8. Uncorrected fluorescence from zinc(II) complexes. Thin trace, Zn(trpy)Cl$_2$; thick trace, Zn(4′-NMe$_2$-T)Cl$_2$. DCM solution at r.t.

the more extended trpy moiety. As a consequence, coefficients *c*, *e*, *h* and *l* in Eqs. (1) and (2) are small. Even so, the orbital parentage of the Pt(4′-Ph-T)Cl$^+$ excited state is mixed in that the excitation has both ^{3}d–π* and ^{3}π–π(trpy) character, not to mention the possibility of ^{3}π–p (ligand-to-metal charge transfer) character due to the participation of platinum's 6p$_z$ orbital (Eq. (1)). Delocalization onto the phenyl substituent is modest, but the CT absorption shifts to longer wavelength, and the emitting state evidently drops in energy relative to deactivating ^{3}d–d states. As a result, in contrast to the parent trpy complex, Pt(4′-Ph-T)Cl$^+$ shows photoluminescence in DCM solution.

With the large, fused-ring pyrenyl substitutent, coefficients *c*, *e*, *h* and *l* of Eqs. (1) and (2) are certainly not negligible, and the emission from the Pt(4′-Pyre1-T)Cl$^+$ complex essentially has ILCT character. This is evident from the fact that the difference in the trpy-based, first reduction potentials almost completely accounts for the disparity between the emission energies of the Zn(4′-Pyre1-T)Cl$_2$ and Pt(4′-Pyre1-T)Cl$^+$ complexes [3]. The photochemistry and the photophysics of the 4′-Pyre1-T complex are also consistent with the proposed intraligand character. Although the observation of fluorescence is unusual for a heavy metal complex, the emission from Pt(4′-Pyre1-T)Cl$^+$ consists of a combination of singlet and triplet components, in accordance with minimum participation of metal orbitals in the excitation. In aerated DCM solution the otherwise dominant 685 nm component, attributable to ^{3}ILCT emission, all but vanishes, but a 640 nm component persists with a lifetime of 1 ns with no change in the excitation spectrum (Fig. 7). Moreover, the short-lived component exhibits a radiative rate constant of ca. 10^6 s^{-1} that compares favorably with values reported for other platinum complexes exhibiting ^{1}ILCT emission [44,45]. The intra-ligand character also explains why the emission from Pt(4′-Pyre1-T)Cl$^+$ persists in a donor solvent like acetonitrile, where it retains an impressive lifetime of 18 μs. For an MLCT state, the availability of open coordination sites, the increase in the formal oxidation state at the metal center, and the switch from a d^8 to a d^7 configuration all would promote exciplex quenching by a basic solvent [15]. In the 4′Pyre1-T complex, as with the 4′-NMe$_2$-T system described above, delocalization of the hole onto the substituent sharply reduces solvent-induced quenching.

Although the emitting states of Pt(4′-Pyre1-T)Cl$^+$ clearly have dominant ILCT orbital parentage, there are important caveats to keep in mind. One is that metal-centered orbitals play a role in the long-lived triplet excitation. Purely ligand-centered excitation would not permit such efficient triplet emission because of the spin conservation rule. Secondly, the notion that emission entails a simple electron jump from one orbital to another is a very naive one. A single electronic configuration with, say, ψ_f as the highest occupied MO, may conceivably provide a reasonable description of the ground state, but the excited state wavefunction certainly involves multiple configurations. Perturbation theory guarantees that no one orbital arrangement can possibly minimize electron–electron repulsions when multiple configurations exist with nominally similar energies. The final caveat is that other non-emissive excited states can also influence the results. For example, population of a potentially close-lying pyrenelocalized $^3\pi-\pi^*$ state could inhibit decay and extend the life of the emission signal [46–48]. Simultaneous multiple emissions from neighboring IL and CT excited states can also occur when internal conversion is slow as reported for platinum(II) dithiooxamide complexes that Rosace et al. have investigated [56].

5. Conclusions

As with the ground-state chemistry, vacant coordination sites have a profound influence on the photochemistry and photophysics of platinum(II) systems. Here the focus has been on Pt(trpy)Cl^+ and related systems. The parent ion is essentially non-luminescent in fluid solution, but various derivatives including Pt(4′-Pyre1-T)Cl^+ and Pt(4′-NMe_2-T)Cl^+ are emissive and exhibit microsecond excited-state lifetimes in non-coordinating solvents like DCM. By comparison with Pt(trpy)Cl^+, the derivatives that show emission in fluid solution all have lower energy excited states. This is somewhat surprising because the energy gap law is normally an important factor influencing excited-state lifetimes [2,49–51]. For Pt(trpy)Cl^+ and related systems with relatively high energy excited states, non-radiative decay via thermally accessible ^{3}d–d excited states complicates the picture. In line with this model, some solids containing related compounds exhibit short-lived ^{3}d–d emission at low temperatures [52]. Long-lived excited states occur in Pt(4′-R-T)Y^+ systems when the orbital parentage of the emissive excited state has significant intra-ligand character, usually involving easily oxidized substituent groups. In a one-electron picture, simple covalent bonding naturally imparts intra-ligand character to the ground and excited states. However, configuration interaction also influences orbital participation, especially in excited states [53–55]. Due in part to the stability of the neutral Pt(4′-R-T)Y reduction product, the emissive excited states can be a potent oxidant. For example, Pt(trpy)OH^+ intercalates into B-form DNA duplexes, but is non-emissive amidst guanine-cytosine rich sequences because a guanine residue is capable of transferring an electron to the excited state. Excited states with significant MLCT character are also susceptible to quenching by Lewis bases. The systems with the longest-lived excited states are Pt(4′-Ar-T)Cl^+ systems with large fused-ring aryl substituents such as the pyrenyl group, however, these systems exhibit poor solubility in water. To sum up, the design of emissive analogues of Pt(trpy)Cl^+ depends upon stabilization of the emitting state versus deactivating ^{3}d–d states, and incorporating intra-ligand character into the excited state can be a very effective strategy.

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