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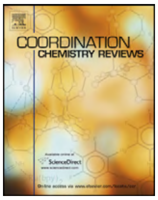

Review

Platinum(II) polypyridines: A tale of two axes

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ABSTRACT

There are many possible applications for luminescent platinum terpyridine (trpy) complexes, but the emission quantum yield and lifetime vary greatly depending upon the design. One reason is that potentially emissive metal-to-ligand charge-transfer (MLCT) states occur at relatively high energies because a planar coordination geometry is not the best supporting environment for a Pt(III) center. At the same time, strain in the Pt–N sigma bond framework often results in low-lying d–d excited states that effectively quench the emission. One way of differentially lowering the energy of the emitting state, and thereby reducing the effect of d–d states, involves delocalizing the π^*(trpy) acceptor orbital onto a 4′-aryl substituent. Delocalizing the 'hole' orbital is an alternative approach capable of producing dramatic results. Thus, with the addition of an electron-rich group like –NMe2 or 1-naphthyl to the 4′-position of trpy ligand, the emitting state takes on intraligand charge-transfer (ILCT) character and the excited-state lifetime extends to tens of microseconds in dichloromethane solution. In some systems introduction of a π-donating co-ligand enhances the emission yield, and when the co-ligand is a very electron-rich group like an ethynylarene, the emitting state takes on an admixture of ligand-to-ligand charge-transfer (LLCT) character. Finally, it is possible to destabilize deactivating states by incorporating an ethynylalkane as a strong-field co-ligand, or by utilizing a carbometalating derivative of the trpy ligand. Complexes of the latter support another type of ILCT excitation because of the presence of the formally anionic phenyl moiety, and the emission energy vary greatly depending upon which ligand axis contains the Pt–C bond.

1. Introduction

The 2,2′:6′,2″-terpyridine ligand (trpy) is a versatile tridentate polypyridine coordinating agent. Coordination to a metal center reinforces the planar shape, hence it is not surprising to find

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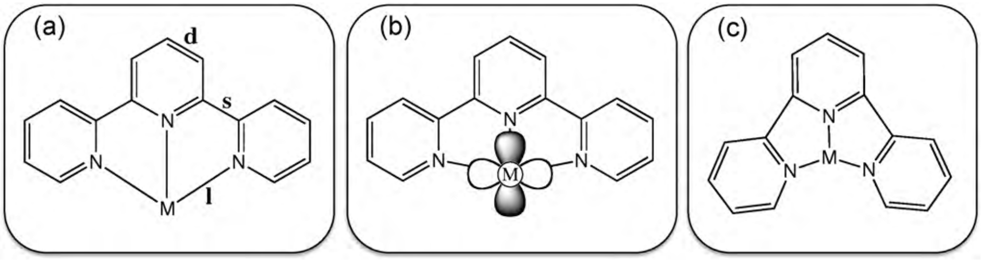


Fig. 1. (a) Structure of 2,2′:6′,2″-terpyridine (trpy) bound to a large metal center in which all M–N bonds are of equal length. (b) Structure of trpy bound to Pt(II) in which the central M–N bond is shorter than the latitudinal M–N bonds. (c) Theoretical structure of trpy bound to a small metal ion.

that the ligand coordinates well to the d^8 Pt(II) ion, a textbook example of a coordination center that prefers dsp^2 hybridization. What was not so obvious at the outset was that the electronic properties of platinum terpyridine complexes would prove to be quite interesting [1–4]. One important reason is low-energy π^* orbitals of the ligand give rise to metal-to-ligand charge-transfer (MLCT) excited states that can exhibit photoluminescence [5,6]. As discussed in more detail below, the emission energy and the excited-state lifetime are also often sensitive to the local environment. One reason is the accessibility of metal-centered, d–d excited states that are subject to distortion and rapid radiationless decay [1]. Although d–d states ordinarily occur at relatively high energies in complexes of a third-row transition ion, the story is different when there is a geometrically constraining ligand like trpy in place [7,8]. Fig. 1 reveals three conceivable ways trpy can coordinate to a metal center. Structure (**a**) in Fig. 1 is appropriate for a large polyvalent metal ion that engages in predominantly electrostatic bonding. In this limit it is possible for all three M–N distances to be of equal length. In fact, if the pyridine moieties have perfect hexagonal structures with sp^2 hybridization at all centers, edge lengths **d**, and pyridine-to-pyridine bonds of length **s**, the M–N bond distance is $\mathbf{l} = \mathbf{d} + \mathbf{s}$. For completeness, Fig. 1 includes structure (**c**) which may also support approximately equal M–N bond lengths. This hypothetical structure might be appropriate for trigonal covalent binding to a relatively small central atom but there would be considerable strain generated within the trpy ligand itself. Complexation to a metal center like platinum(II) actually results in structure (**b**) of Fig. 1, complete with a short bond to the 4′ nitrogen (ca. 1.92 Å) relative to the bonds to the other ligand nitrogen atoms (ca. 2.02 Å) [1,2,9–11]. The symmetry breaking within the M–N bond distribution is the joint result of coordinate–covalent bonding to the empty 5d orbital of platinum(II) and the rigidity of the trpy framework. For the same reason the N–Pt–N″ bond angle involving the outer pyridines is approximately 160° rather than the ideal value of 180° for a planar complex.

Similar bond lengths and angles occur in ruthenium(II) complexes such as $Ru(trpy)_2{}^{2+}$, and that is one reason why ruthenium systems serve as a paradigm for interpreting the photophysics of platinum(II) terpyridine complexes. The key result with $Ru(trpy)_2{}^{2+}$ is that a thermally accessible d–d state is responsible for the short lifetime of the MLCT excited state in room-temperature fluid solution [12,13]. Population of a d–d* excited state naturally induces bond weakening and gives rise to a measurable quantum yield for partial dissociation of a trpy ligand, at least in sterically crowded ruthenium(II) complexes [14]. Similarly, the lifetimes of the emissive CT excited states of platinum(II) terpyridines are typically quite temperature dependent [15]. The usual assumption is that here too thermally induced deactivation involves the population of a short-lived excited state with d–d* orbital parentage. However, supporting evidence in the form of net photoinduced ligand dissociation has been lacking. The difficulty may be that ligand recombination and/or chelate ring closure tends to be a relatively fast process in platinum(II) complexes because of easy access to open coordination sites [16].

The absence of axial ligands in platinum(II) complexes also plays a prominent role in shaping other important photoproperties. In particular, the geometry is conducive to excimer formation [17], solvent-assisted exciplex quenching [1,18], as well as ground- or excited-state Pt–Pt interactions that occur in solution and/or the solid state [3,19–21]. On the other hand, a planar coordination geometry is not an ideal match for the Pt(III) oxidation state due to the extra sigma-bonding possible via the half-occupied orbital of the d^7 metal center. Largely for that reason, optically induced oxidation to the M(III) level is a less accessible process in platinum as compared with ruthenium complexes. Indeed, excited states with pure MLCT orbital parentage are simply not common in platinum complexes; a typical emitting state might exhibit ligand-centered (LC) character as well as MLCT character [1]. Excitations involving ligand-to-ligand charge-transfer (LLCT) or metal/metal-to-ligand charge-transfer (MMLCT) character are also possible [1,3,22]. MMLCT excitation in particular is possible when there are ground-state platinum–platinum interactions such that the ‘hole’ in the excited-state wavefunction delocalizes over both metal atoms [19].

To recap and set the stage, simple platinum terpyridine complexes often do not show emission in fluid solution because of two effects that act in concert. One is ligand-induced strain that lowers the energy of short-lived d–d excited states and promotes radiationless decay. Compounding the problem, potentially emissive MLCT states tend to occur at relatively high energies due to the planar bonding environment which is not ideal for the Pt(III) oxidation state. Fortunately, enhancement of the emission quantum yield is possible via a variety of modifications, especially those involving positions W through Z and R in Fig. 2. The sections to follow show that improvement of the emission yield often turns upon groups that lie on the axis connecting positions R, Z, and X.

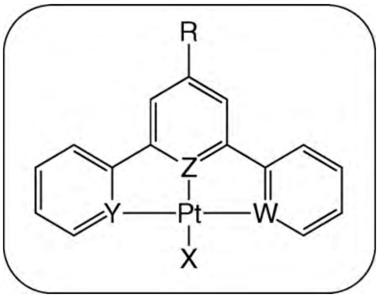
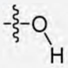
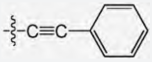
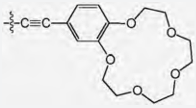
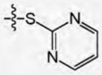
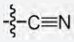
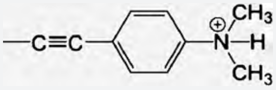


Fig. 2. Structure of platinum complexed to a terpyridine-like ligand and X; W–Z are the donor heteroatoms, and R is the substituent at the 4′-position.

Table 1
Emission data for $[Pt(trpy)X]^+$ complexes in acetonitrile.

X	Structure of X	λ_{max} (nm)	τ (μs), 298 K	Φ, 298 K	Reference
OH		621	0.17	2.1×10^{-3}	[5]
CCPh		630	0.5	0.0124	[27]
4-Ethynylbenzo-15-crown-5[a]		585	–	–	[27]
Pyrimidine-2-thiolate		650	0.34	6.1×10^{-4}	[35]
CN[b]		535	0.015	4×10^{-4}	[37]
CC–DMA·H⁺		560	0.62	4×10^{-4}	[32]

[a] Frozen glass.

[b] Data are in dichloromethane solution.

2. Variation of the co-ligand: $[Pt(trpy)X]^+$ complexes

2.1. $[Pt(trpy)OH]^+$

The well-known $Pt(trpy)Cl^+$ complex is worth revisiting at the outset as it serves as the prototypical non-emitting complex, at least in fluid solution, where facile non-radiative decay occurs via low-lying d–d excited states. On the other hand, the complex exhibits photoluminescence in the solid state and in low-temperature glasses, where the signal is concentration-dependent [1]. In the solid or an appropriate glass, significant $d(z^2)$–$d(z^2)$ interactions can occur between near neighbors and give rise to a red-shifted emission attributable to a metal–metal-to-ligand charge-transfer (^{3}MMLCT) excited state [10]. In effect, the platinum–platinum interaction stabilizes the emitting state relative to deactivating d–d states, and one can exploit the effect in a systematic way for vapor sensing applications [21]. Aggregation also occurs in fluid solution, especially aqueous solutions [10,22], and that may account for the observed concentration-dependent photoproduction of hydrogen in solutions containing $Pt(trpy)Cl^+$ and a sacrificial electron donor [24].

Strikingly, replacing chloride with the strongly π-donating hydroxide ligand produces the dramatically different $[Pt(trpy)(OH)]^+$ complex which exhibits photoluminescent and an excited-state lifetime of 170 ns in deoxygenated acetonitrile solution at room temperature [5]. In a dichloromethane solution containing about 5% acetonitrile, the lifetime increases by at least a factor of 10, consistent with a reduction in the rate of solvent-induced quenching in the less basic medium. Replacing chloride with hydroxide seems to stabilize the emissive MLCT excited state relative to deactivating d–d excited states, such that radiative decay becomes feasible. Indeed, the MLCT absorption of $[Pt(trpy)OH]^+$ extends beyond 450 nm in acetonitrile solution, whereas the corresponding absorption of $[Pt(trpy)Cl]^+$ drops to essentially zero by about 400 nm. Interestingly, in water, the CT absorption shifts back toward higher energy, and the complex is virtually non-emissive [25]. In water, hydrogen bond formation with the pπ lone pairs of the coordinated hydroxide probably weakens π-donation to platinum and induces the spectral shift. Isolation and characterization of the μ-hydroxy dimer $[(Pt(trpy))_2OH]^{3+}$ attest to the nucleophilicity of the coordinated hydroxide ligand [26]. However, it is possible to block out-of-plane interactions with the solvent by allowing $[Pt(trpy)OH]^+$ to intercalate between adjacent base pairs of double-helical DNA, regardless of whether water interacts by coordination to platinum and/or hydrogen bonding to the hydroxide ligand. Consequently, $[Pt(trpy)OH]^+$ acts as a “light switch” in that the complex becomes emissive when it intercalates between adenine–thymine or inosine–cytosine base pairs of a DNA host [25]. The complex actually preferentially intercalates along side of guanine–cytosine base pairs, but guanine residues are so reducing that they quench the emission by an electron-transfer process.

2.2. $[Pt(trpy)CC\text{-}Ar]^+$

Ethynyl co-ligands also act as strong π donors and are even stronger σ donors than hydroxide. Thus, it is not surprising that Yam and co-workers have found that the ethynylbenzene complex $[Pt(trpy)(CCPh)]^+$ is emissive with a lifetime of 500 ns in deoxygenated acetonitrile solution [27]; see Table 1 for structures. In DCM solution the emission lifetime extends to 1.9 μs [28,29]. Particularly with ethynylarene ligands, the co-ligand is part of the excitation process, according to calculations by Zhou et al. [22]. The results show that the orbital parentage of the emitting state exhibits a mixture of ligand–ligand charge-transfer (^{3}LLCT) and metal-to-ligand charge-transfer (^{3}MLCT) character. In ethynylalkane complexes, the emitting states contain less ^{3}LLCT character [22] and tend to exhibit higher emission yields and longer lifetimes [28,29]. Energy gap law considerations may provide part of the explanation, but structural relaxation within the electron-rich co-ligand is probably another factor [30]. Indeed, incorporation of strong electron-donating functions such as methoxy or amino groups on the aryl moiety generally quenches the emission in fluid solution [27,31].

The possibility of chemical elaboration is, nonetheless, a great advantage co-ligands such as ethynylbenzene offer. For example, Yam and co-workers showed that uptake of an alkali metal ion alters the absorption spectrum of $[Pt(trpy)(4\text{-ethynylbenzo-15-crown-5})]^+$ so that spectroscopically based ion sensing becomes possible [27]. The $[Pt(trpy)(4\text{-ethynylaniline})]^+$ analogue is also non-emissive in DCM solution, but protonation with a strong acid yields an emissive complex [32]. Finally, attaching an azo-crown function to the ethynylbenzene co-ligand yields a complex capable of spectrally responding to the uptake of the proton or a simple metal ion [33].

2.3. *[Pt(trpy)SR]$^+$*

In contrast to [Pt(trpy)(CCR)]$^+$ systems, a [Pt(trpy)(SR)]$^+$ complex is more apt to exhibit emission when the R group is an aryl as opposed to an alkyl group. Early on Lippard and co-workers found that [Pt(trpy)(SCH_2CH_2OH)]$^+$, abbreviated as [Pt(trpy)(HET)]$^+$, exhibits an unusually long-wavelength CT absorption band [23]. Later, Eisenberg and co-workers assigned analogous transitions as metal/sulfur-to-π*(diimine) transitions in Pt(diimine)(dithiolate) complexes [34]. Accordingly, Che and co-workers assigned ^{3}LLCT/^{3}MLCT character to the emission observed from complexes like [Pt(trpy)(pyrimidine-2-thiolate)]$^+$ [35]. In contrast, the HET analogue is non-emissive in solution. The difference in behavior may hinge, in part, upon the nature of the highest occupied orbital of the co-ligand. The degree of delocalization is greater when a conjugated thiol is present, and that may mean less ligand-centered structural distortion in the LLCT excited state to promote vibrationally assisted radiationless decay [30]. Predicting whether a particular design will emit nevertheless remains problematic. Thus, despite having an arenethiolate as co-ligand, the 4′-mercaptobenzo-15-crown-5 derivative studied by Yam and co-workers is completely non-emissive in solution [36]. The energy of the CT absorption band does, however, change with the uptake of a metal ion.

To summarize this section, the σ- and π-bonding properties of the co-ligand X can both play important roles in determining the photophysical properties of a [Pt(trpy)X]$^{n+}$ complex. Promotion of a photoluminescence signal in fluid solution requires stabilization of the potentially luminescent ^{3}CT excited state relative to d–d excited states that foster radiationless decay. The preponderance of evidence suggests that co-ligands that are both strong σ- and π-donating can be effective in that regard, provided the co-ligand itself does not introduce efficient pathways to radiationless decay. One rationale is that the energy required for CT excitation state is lower when the co-ligand provides electron density for the excitation process and the process is not entirely dependent on the generation of a Pt(III) metal center. To extend the argument, consider cyanide as an example of a strong σ-donating, π-accepting co-ligand. The [Pt(trpy)(CN)]$^+$ complex proves to be an improvement over [Pt(trpy)Cl]$^+$ in that the cyano derivative is emissive in DCM solution [37]. However, the emission is weak and originates in a ^{3}π–π*, ligand-centered (LC) state of the trpy ligand because the cyanide ligand destabilizes the MLCT state in addition to deactivating d–d states. That is not the end of the story, though, because work described below shows that cyano derivatives can exhibit very intense emission, when substituents on the trpy ligand assist in the CT excitation process. Two perturbations are sometimes better than one in improving the properties of the [Pt(trpy)Cl]$^+$ system.

3. Variation of terpyridine: [Pt(R-trpy)Cl]$^+$ complexes

A convenient way to modify [Pt(trpy)Cl]$^+$ and induce a photoluminescence signal in fluid solution involves introducing an aryl substituent in the 4′-position of the terpyridine ligand. The method works because delocalization of the π* orbital of terpyridine onto the substituent generally lowers the energy of the ligand LUMO and stabilizes potentially emissive ^{3}MLCT and ^{3}LC excited states vis à vis deactivating ^{3}d–d excited states [1,6,12]. Che and co-workers provided early results when they investigated the photophysical properties of a series of [Pt(4′-Ar–T)Cl]$^+$ derivatives, where 4′-Ar–T denotes 4′-aryl-2,2′:,6′,2″-terpyridine and aryl is either C_6H_4Me-*p*, C_6H_4Br-*p*, C_6H_4(OMe)-*p*, or C_6H_4(CN)-*p*. They found that the complexes showed triplet emission in acetonitrile solution with excited-state lifetimes that were on the order of a microsecond at room temperature [6]. The authors also found that the absorption maxima occurred at longer wavelength than that of [Pt(trpy)Cl]$^+$ and ascribed the emission to states with mixed ^{3}MLCT/^{3}LC character [6].

Later, Michalec et al. introduced easily ionized, fused-ring aryl groups such as 1-naphthyl, 2-naphthyl, 9-phenanthrenyl, and 1-pyrenyl at the 4′-position of trpy [38,39]. Interestingly, the lifetime systematically lengthened and the emission maximum shifted to lower energy as the number of fused rings within the arene increased. It is, however, not possible to explain the results in terms of simply extending conjugation within the LUMO. Thus, the 4′-(1-naphthyl)-trpy system exhibits a significantly longer excited-state

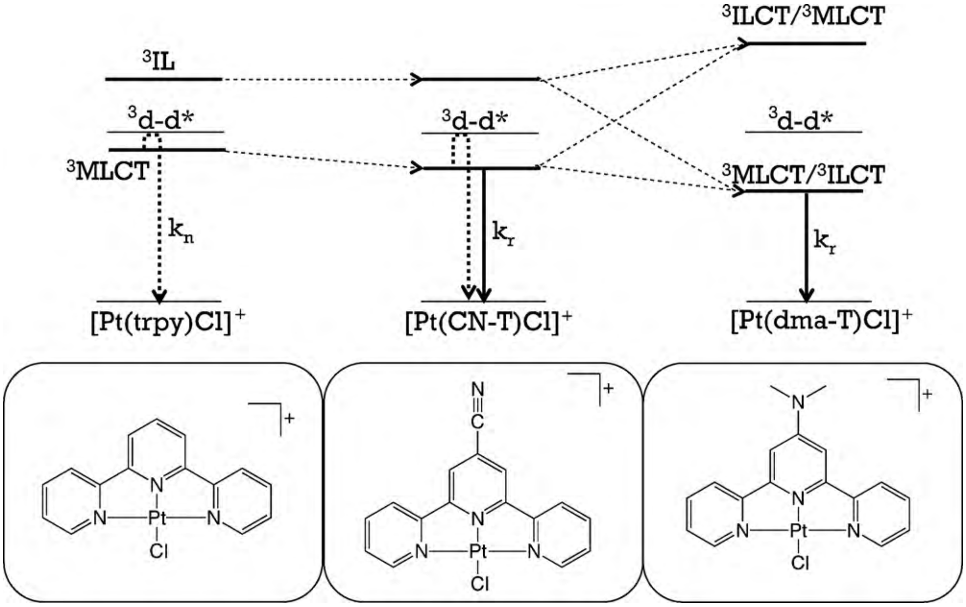


Fig. 3. Energy state diagram of [Pt(trpy)Cl]$^+$, [Pt(CN–T)Cl]$^+$, and [Pt(dma-T)Cl]$^+$ where the lines denote large radiative rate constant (thick solid), small radiative rate constant (thin solid), and large non-radiative rate constant (thick dashed).

lifetime than [Pt(4′-Ph-trpy)Cl]$^+$, even though the naphthyl derivative has to be a less planar ligand for steric reasons. The authors proposed that the emitting state takes on an admixture of ILCT character. Consistent with a decrease in heavy metal participation, the [Pt(4′-pyrenyl-trpy)Cl]$^+$ complex exhibits singlet and triplet emission signals. The triplet emission is very long-lived with a lifetime of 64 μs in dichloromethane solution. In that case the emitting state may reflect as many as three different types of orbital parentage, namely ^{3}MLCT, ^{3}ILCT, and $^3\pi$–π*(pyrene). The MLCT character is apt to be minimal because complexes within this series do not readily undergo base-induced exciplex quenching due to delocalization of the excitation 'hole' away from the metal center.

Alongside the results obtained with aryl substituents, McMillin and co-workers have also shown that introducing electron-withdrawing groups like SO_2Me and CN at the 4′-position can produce emissive platinum(II) terpyridine complexes by stabilizing the ^{3}MLCT state relative to deactivating d–d excited states [1,40]. See Fig. 3 for a schematic view of the change in the energy level diagram and representative structures. However, the complex with an electron-donating NMe_2 group in the 4′-position exhibits much more impressive photophysical properties ($\varphi = 0.11$ and $\tau = 1.9$ μs). The difference is that the electron-rich NMe_2 group provides the basis for low-lying ligand-based ILCT excitation. The positively charged platinum(II) center also has an important role in that it stabilizes the trpy anion formally generated by ILCT excitation. In actuality two CT states synergistically mix to give a low-lying ILCT/MLCT state that exhibits a long dipole length and relatively high molar absorptivity. The reactivity of the excited state is also consistent with the proposed ILCT character. Thus, in basic media the photoexcited state of [Pt(4′-NMe_2-trpy)Cl]$^+$, or [Pt(4′-NMe_2-T)CN]$^+$ for short, is much less susceptible to solvent-induced exciplex quenching than that of the [Pt(CN–T)Cl]$^+$ analogue, where CN–T denotes 4′-CN-trpy. The difference is that the excited state of the CN–T complex involves a greater degree of ^{3}MLCT character and therefore behaves more like a Pt(III) center.

4. Variation of terpyridine and co-ligand: [Pt(R-trpy)X]$^+$ complexes

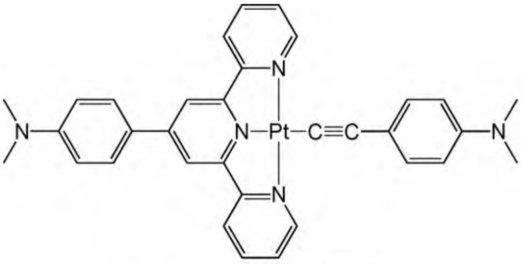
4.1. [Pt(R-trpy)CN]$^+$

Simultaneous modification of the trpy and co-ligand of [Pt(trpy)Cl]$^+$ is also feasible, but the perturbing elements have to work in concert in order to have a favorable impact. Consider [Pt(CN–T)Cl]$^+$ which exhibits ^{3}MLCT character but has an excited-state lifetime of only about 120 ns in dichloromethane solution due to fairly efficient deactivation via a thermally accessible d–d excited state. As noted above, in this case introducing cyanide as a co-ligand drives up the energies of d–d states as well as MLCT excited states [37]. As a consequence, the [Pt(CN–T)CN]$^+$ variant exhibits a structured ^{3}LC emission with a relatively low emission quantum yield in solution, due to the low radiative rate constant of a $^3\pi$–π* state (Fig. 3). The [Pt(4′-NMe_2-T)CN]$^+$ system turns out to be a much better emitter because of the ILCT character which suppresses the effect the co-ligand has on the absorption and emission energies. Thus, in dichloromethane solution the [Pt(4′-NMe_2-T)CN]$^+$ complex exhibits an impressive emission yield of $\varphi = 0.26$ and an excited-state lifetime of 22 μs [37]. The emission properties vary with the medium, however, and the complex is only weakly emissive in aqueous solution. Binding studies with B-form DNA were therefore of interest because platinum terpyridines often intercalate into DNA which limits solvent accessibility. Using results from absorption, emission, and circular dichroism spectroscopies as well as viscometry, Clark et al. showed that the favored mode of binding is, in fact, intercalation into DNA, except at high loading whereupon the complex aggregates on the polyanionic biomolecule [41]. As anticipated, the emission intensity increases when the complex intercalates into DNA and escapes solvent-induced quenching. However, the emission yield strongly depends on the base make up of the DNA because guanine–cytosine base pairs quench the emission very efficiently by some type of electron-transfer mechanism [41].

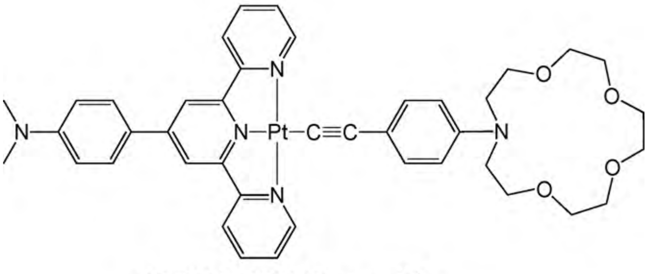
4.2. [Pt(R-trpy)(CC-Ar)]$^+$

Sun and co-workers investigated a similar series of 4′-substituted-trpy complexes of platinum(II) with chloride or phenylacetylide as co-ligand [42]. They found enhanced emission from the complexes with CC–Ph as the co-ligand due in part to a decreased influence of deactivating ^{3}d–d states [41,42]. Moreover, Ji et al. discovered a similar trend in platinum(II) 4′-(5‴-R-pyrimidyl-trpy) complexes, where R denotes H, OEt, Ph, Cl, or CN, and chloride or phenylacetylide is the co-ligand [43]. Whenever the CC–Ph co-ligand is present, the emitting state exhibits CC–Ph → trpy LLCT charge-transfer character, but the orbital parentage also depends on the 4′ substituent of the trpy ligand. Thus, the emissive states in [Pt(Cl–T)CC–Ph]$^+$ and [Pt(CN–T)CC–Ph]$^+$ have both ^{3}MLCT and ^{3}LLCT character, while the emission from [Pt(NMe_2-T)CC–Ph]$^+$ involves an admixture of ^{3}MLCT, ^{3}ILCT, and ^{3}LLCT character [42].

Tung and co-workers recently have recently investigated in a series of platinum(II) CC–Ph complexes that also exhibit varying degrees of LLCT, ILCT, and MLCT character as well as interesting excited-state switching behavior [32]. As a case in point, they report that the lowest energy absorption of [Pt(DMA–T)(CC–DMA)]$^+$, where DMA–T denotes 4′-[4-$N(CH_3)_2$-C_6H_4]-2,2′:6′,2″-terpyridine and CC–DMA denotes the $C{\equiv}CC_6H_4$-p($N(CH_3)_2$) co-ligand, is due to a non-emissive excited state with significant LLCT character.



[Pt(DMA-T)(CC-DMA)]$^+$



[Pt(DMA-T)(CC-Ph-crown)]$^+$

Upon protonation of the CC–DMA nitrogen in acetonitrile solution, the lowest energy excited state becomes a DMA-T based, ^{3}ILCT state which is likewise non-emissive. Addition of more acid leads to the protonation of the aniline nitrogen of the DMA-T ligand at which point the lowest energy excited state switches to a ^{3}MLCT state that is emissive with a lifetime of 36 ns. It is worth noting that transient absorption studies reveal that the non-emissive ^{3}LLCT and ^{3}ILCT states both have longer lifetimes, at 69 and 88 ns, respectively [32]. The low radiative rate constants ($k_r < 10^4$ s^{-1}) associated with the latter states probably reflect in

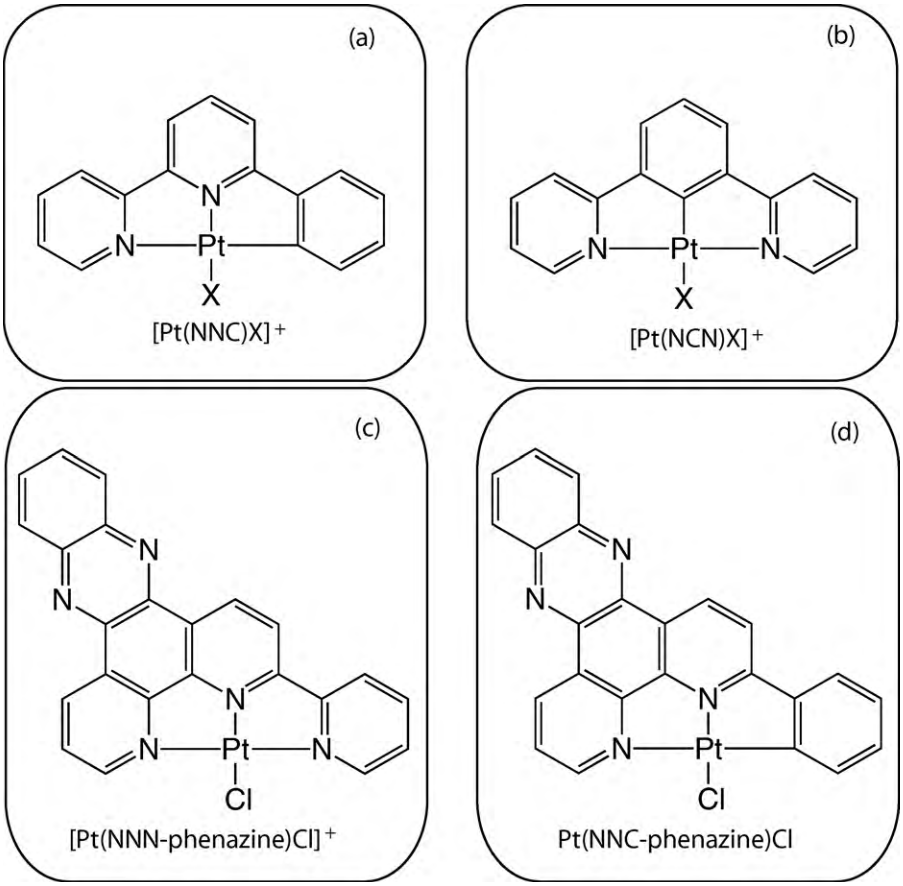
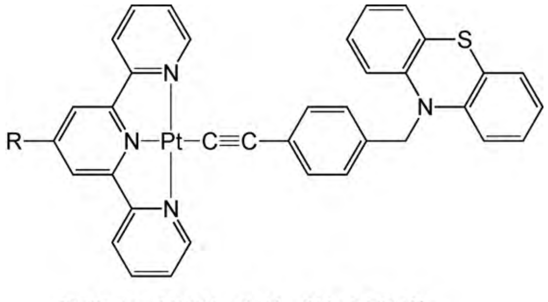


Fig. 4. (a) Structure of [Pt(6-phenyl-2,2′-bipyridine)X]$^+$, where 6-phenyl-2,2′-bipyridine is abbreviated NNC. (b) Structure of [Pt(1,3-dipyridylbenzene)X]$^+$, where 1,3-dipyridylbenzene is abbreviated NCN. (c) Structure of [Pt(6-(2-pyridyl)-dipyrido[3,2-a:2′,3′-c]phenazine)Cl]$^+$, where 6-(2-pyridyl)-dipyrido[3,2-a:2′,3′-c]phenazine, is abbreviated NNN-phenazine. (d) Structure of Pt(6-phenyl-dipyrido[3,2-a:2′,3′-c]phenazine)Cl, where 6-phenyl-dipyrido[3,2-a:2′,3′-c]phenazine is abbreviated NNC-phenazine.

part the absence of significant heavy metal orbital participation in the excitation processes. The same group studied the analogous complex [Pt(DMA-T)(CC–Ph-crown)]$^+$, where CC–Ph-crown denotes the C≡C(p-C_6H_4-(N-[15]azacrown-5) anion [32]. Capture of Mg^{2+}, Ba^{2+}, Ca^{2+}, or Sr^{2+} by the [15]azacrown-5 ring system of the co-ligand induces a switch from LLCT absorption to ILCT absorption in acetonitrile solution. In the presence of excess alkaline earth metal ion, a further switch to MLCT absorption occurs with the addition of acid and protonation of the aniline nitrogen on the coordinated DMA-T ligand.

Eisenberg and co-workers have studied yet another series of platinum complexes with 4′-substituted-trpy ligands and CC–Ph derivatives as co-ligands [44]. When C≡C(p-C_6H_4-CH_2-PTZ) anion is the co-ligand, where PTZ is N-phenothiazine, the complexes are non-emissive due to electron-transfer quenching by the phenothiazine moiety.



[Pt(R-trpy)(CC(p-C_6H_4-CH_2-PTZ))]$^+$

On the other hand, the complex exhibits an emission signal in a low-temperature glass because a rigid matrix interferes with the necessary solvent reorganization. The authors also attached the systems to semiconducting TiO_2 via the trpy ligand and identified conditions under which the covalently attached chromophores sensitize the photogeneration of H_2 upon excitation by visible light [44].

5. Carbometalated complexes

5.1. Pt(NNC)Cl

Replacing nitrogen for carbon in the ligand framework is another strategy used to affect the electronic properties of platinum(II) complexes [45,46]. As with an ethynyl co-ligand, introducing a strong-field carbanion donor center should raise the energy of the deactivating metal-centered states and produce complexes that are emissive in fluid solution at room temperature. However, the introduction of new electronic states into the excited-state manifold is also a possibility [30,47]. Constable first introduced the 6-phenyl-2,2′-bipyridine (NNC) ligand, the simplest analogue of 2,2′:6′,2″-terpyridine (trpy or NNN), and Che and co-workers later reported photophysical studies of Pt(NNC)Cl and derivatives thereof; see Fig. 4 for structures [48]. They found that Pt(NNC)Cl exhibits a broad, unstructured emission, centered at ∼565 nm, in fluid solution. The quantum yield ranges from 0.025 to 0.068, depending upon substitution pattern, with lifetimes between 0.5 and 1 μs; see Table 2. They ascribed the emission to a

Table 2
Photophysical properties of carbometalated derivatives.

Complex	λ_{max}[a], 298 K	τ (μs), 298 K	Φ, 298 K	Reference
Pt(NCN)Cl[b]	491	7.2	0.6	[51]
Pt(NCN-tolyl)Cl[b]	516	9.2	0.59	[51]
Pt(NNC-tolyl)Cl[b]	562	0.62	0.064	[49]
Pt(NNC)Cl[c]	565	0.51	0.025	[49]
Pt(NNN-phenazine)Cl[b]	570	5.0	0.003	[47]
Pt(NNC-phenazine)Cl[d]	585	0.27	0.002	[47]
Pt(NNC-et-tolyl)Cl[b]	584	1.15	0.06	[30]

[a] Highest energy maximum.
[b] Dichloromethane.
[c] Acetonitrile.
[d] 2-Chloronaphthalene.

^{3}MLCT state that has a long lifetime due to the fact that carbometalation drives up the energy of deactivating ^{3}d–d states [48,49]. They also noted that self-quenching is evident at high concentration, but did not observe excimer emission [49]. Stacking and self-quenching become facile due to the reduction in charge from monocationic to neutral by the addition of an anionic ligand. The observation of ^{3}MMLCT based emission is often possible in the solid state, vide supra.

5.2. *Pt(NCN)Cl*

Interestingly, moving the carbanion from a peripheral site to the central ligation site in the trpy framework has significant consequences on the orbital parentage of the excited state [46,50–52]. Thus, Williams and co-workers have found that Pt(NCN)L (where L = Cl) exhibits solution phase ^{3}LC emission from a long-lived excited state with high quantum yield [50–52]. Fig. 5 illustrates the differences in the spectra of the NNC and NCN systems. Thus, the emission from an NCN complex occurs at a shorter wavelength than that of an NNC analogue, and vibronic structure also becomes apparent. The authors attribute the spectral differences to a change in the nature of the HOMO from metal-centered, in NNC complexes, to ligand based in NCN complexes, due, in part, to the unusually short Pt–C bond distance in NCN systems [51]. DFT calculations support the idea that the lowest energy state has mixed ^{3}LC/^{3}MLCT character [53,54]. A recent report employing high resolution cryogenic spectroscopy largely confirms the assignment as ^{3}LC emission with a degree of ^{3}MLCT character, as the zero field splitting of the triplet state is only ~10 cm^{-1} [52]. The authors also suggest the high quantum yield and emission lifetime result from the rigidity of the NCN ligand in the excited state.

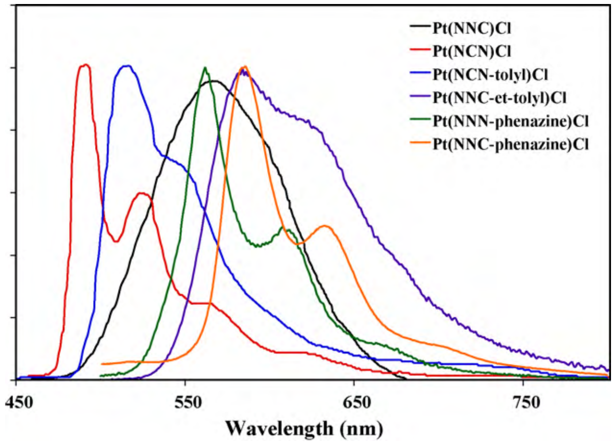


Fig. 5. Emission spectra of carbometalated platinum complexes. Pt(NNC)Cl in MeCN, 298 K, from Ref. [49]. Pt(NCN)Cl and Pt(NCN-tolyl)Cl in DCM, 295 K, from Ref. [51]. Pt(NNC-et-tolyl)Cl in DCM at RT, from Ref. [30]. Pt(NNN-phenazine)Cl in DCM at RT and Pt(NNC-phenazine)Cl in 2-chloronaphthalene at RT, from Ref. [47].

The distinct differences between Pt(NNC)Cl and Pt(NCN)Cl are intriguing, and electrochemical data provide additional insight. The first reduction potential of Pt(NNC)Cl has not been reported however, similar Pt(NNC)X complexes exhibit reduction potentials (vs. ferrocene) of ca. −1.50 V [55], while that of Pt(NCN)Cl is −2.03 V [51]. The more cathodic potential needed to reduce Pt(NCN)Cl may reflect the lack of direct conjugation between the two pyridine moieties, which are meta to each other on the central benzene ring. Note that in NNC complexes, calculations show the LUMO orbital tends to localize on the bipyridine motif which presents an α,α′-diimine arrangement [22]. Strong coupling between the two pyridine moieties may explain why charge-transfer excitation is more facile in the Pt(NNC)X system, and the emission occurs at lower energy.

5.3. *Pt(R-NCN)Cl and Pt(R-NNC) complexes*

Introduction of substituents on the phenyl ring, para to the bond to platinum in NCN complexes, can tune the excited-state energy over a range of 5000 cm^{-1} [51,53]. The introduction of aniline alters the excited-state parentage from mainly ^{3}LC to ^{3}ILCT, due to the ease of oxidation of the substituent [51]. The emission maximum shifts to 588 nm, and the excited-state lifetime increases to 12.4 μs. Protonation of the aniline nitrogen leads to a switch in excited-state parentage back to ^{3}LC emission, similar to the parent complex. Interestingly, the emission of the protonated aniline complex closely matches that of the unsubstituted NNC complex. Fu and co-workers have demonstrated the same effect by introducing aniline into [Pt(NNC)(PPh$_3$)]$^+$, where NNC is 4-*p*-dimethylaminophenyl)-6-phenyl-2,2′-bipyridine [56]. Additionally, they provide support for the ^{3}ILCT assignment in the form of DFT calculations.

It is illustrative to compare the effect of adding a 4′-tolyl group to the central C4 position of the NNC complex and the analogous position of a NCN-derived complex. In going from Pt(NNC)Cl to Pt(NNC-tolyl)Cl, there is a small shift in the emission maximum, but the quantum yield increases by more than a factor of two, from 0.025 to 0.064 [49]. In the case of the NCN complex the emission yield is much higher and does not change much; however, the emission maximum shifts from ~495 nm to ~515 nm, and the band shape noticeably broadens [51]. The shift is consistent with an increase in the ^{3}CT character of the excited state [51]; however, it may relate to an enhancement of the ^{3}ILCT character. Comparison of the gas phase ionization energies of benzene (9.25 eV) and biphenyl (7.95 eV) reveal that it is easier to ionize biphenyl than benzene as a result of increased π delocalization. The spectral broadening may be a reflection of the fact that the dihedral angle between the tolyl group and the mean plane of the NCN framework changes in going from the ground to the excited state. Here, the introduction of ^{3}ILCT character is analogous to what one observes with the introduction of a 4′-dimethylamino into the [Pt(NNN)Cl]$^+$ system, vide supra.

Other work has also shown that ligand elaboration may lead to a change of orbital parentage. As a case in point, Clark et al. have introduced large electron-donating groups such as ethynyl *p*-toluene and ethynyl (trialkyl)gallate at the C4 position of the NNC framework [30]. In both cases substitution results in longer wavelength and longer lived emission relative to the control. For example, λ_{max} for the luminescence from the Pt(NNC-et-tolyl)Cl complex is 584 nm, versus 515 nm and 562 nm for Pt(NCN-tolyl)Cl and Pt(NNC-tolyl)Cl, respectively. The Pt(NNC-et-tolyl)Cl complex also exhibits an excited-state lifetime of 1.15 μs and an emission quantum yield of 0.06, both intermediate values. The authors attribute the changes in photophysical properties to enhanced ^{3}LC character in the emitting state of Pt(NNC-et-tolyl)Cl compared with

Pt(NNC-tolyl)Cl [30]. Indeed, the radiative rate constant (estimated as ϕ/τ) of the et-tolyl derivative is very similar to that calculated for the Pt(NCN-tolyl)Cl system. The emitting state of Pt(NNC-et-tolyl)Cl exhibits two kinds of ^{3}ILCT character to the extent that the et-tolyl and coordinated phenyl groups participate more in the HOMO as opposed to the LUMO, which localizes more on the coordinated bipyridine moiety.

The potential of the et-tolyl group as a π electron donor is evident when it functions as co-ligand, albeit in the form of a carbanionic ligand. Thus, in Pt(NNC)Cl systems replacing the chloride with an ethynylarene as co-ligand induces a red shift in the emission and decrease in the excited-state lifetime. As in the [Pt(trpy)(CCPh)]$^+$ systems described above, these results are consistent with inclusion of an admixture of charge-transfer (^{3}LLCT) character in the emitting state [30]. By way of contrast, replacing the chloride ligand of [Pt(trpy)Cl]$^+$ with an ethynylarene dramatically *enhances* the excited-state lifetime in fluid solution. The difference is that the overriding effect in trpy complexes is deactivation via a ^{3}d–d excited state that becomes less accessible when the ethynyl co-ligand is present. In Pt(NNC)X complexes, of course, the ^{3}d–d excited state is not much of a factor, so the intrinsic properties of the ^{3}LLCT state come to the fore. The change in orbital parentage lowers the energy gap, but that only partly accounts for the decrease in lifetime. In simplified terms Clark et al. have proposed that excitation-induced oxidation of the co-ligand promotes a new type of structural relaxation in the excited state. The resulting distortion, in turn, alters vibrational overlap with the ground-state surface and thereby facilitates radiationless decay [30]. When the co-ligand is an ethynyl (trialkyl)gallate, the effect is large enough that the emission signal effectively vanishes in fluid solution [30].

5.4. [Pt(NNN-phenazine)Cl]$^+$ and Pt(NNC-phenazine)Cl

McGuire et al. have investigated a ligand which is formally a fusion product of phenyl-bipyridine (NNC) and phenazine with the goal of introducing nucleophilic sites for excited-state reactivity as complements of the open coordination sites available at the metal center [47]. Since the complex contains Pt(II) and a coordinated phenyl anion, the lowest energy excited state is capable of exhibiting ^{3}MLCT as well as ^{3}ILCT character. However, the NNC-phenazine derivative is largely insoluble in most conventional solvents. The corresponding [Pt(NNN-phenazine)Cl]$^+$ complex, involving the fusion product of terpyridine (NNN) and phenazine, is more soluble and easier to investigate due to an ionic composition. In dichloromethane, the [Pt(NNN-phenazine)Cl]$^+$ complex exhibits an excited-state lifetime of 5 μs and an emission quantum yield of 0.003. The emitting state therefore has an estimated radiative rate constant of only 600 s^{-1}. The excited state appears to have a degree of Pt(III) character because Lewis bases quench the emission. However, the quenching constants obtained with Lewis bases are on the order of 10^6 to 10^7 M^{-1} s^{-1}, well below the diffusion limit [47]. Both observations suggest that the reactive excited state has at best moderate ^{3}MLCT character. The expectation was that exciplex quenching by Lewis acids would also be possible, on the assumption that there is a build-up of negative charge on the phenazine moiety in the excited state. However, acetic acid does not noticeably quench the emission of [Pt(NNN-phenazine)Cl]$^+$ in dichloromethane [47]. The conclusions are that the excited state has little charge-transfer-to-phenazine character and most likely involves $^3\pi$–π^* excitation, occurring mainly on the phenazine moiety.

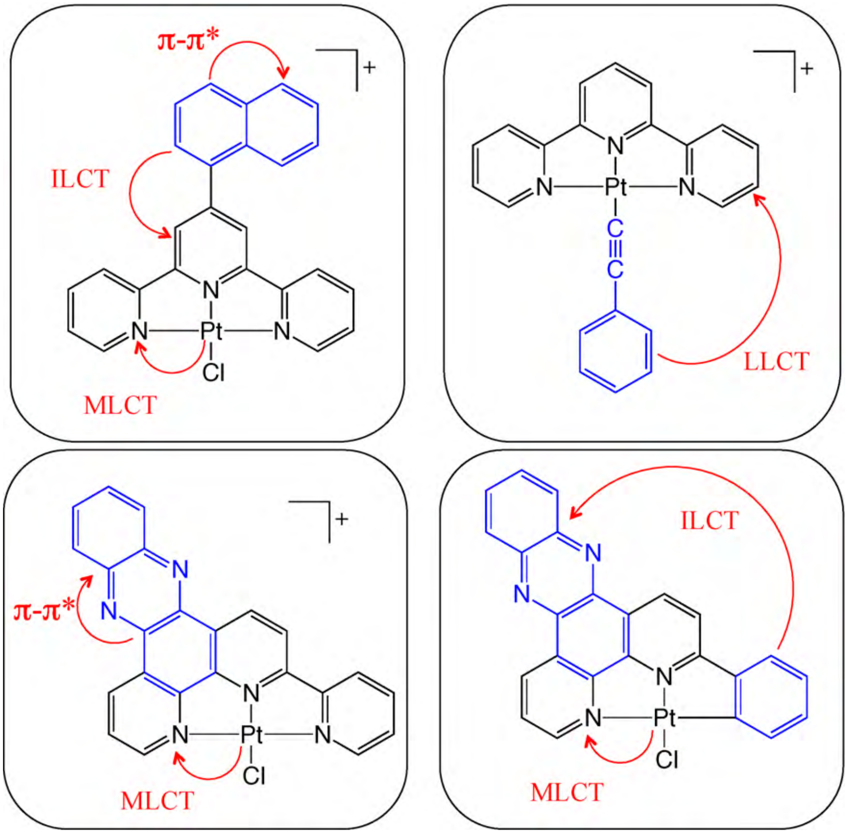


Fig. 6. Summary of the various excited-state transitions in the chemical toolbox used to tune the photophysics and photochemistry of platinum(II) complexes derived from the trpy ligand.

In contrast, acetic acid is an effective quencher of the emission from [Pt(NNC-phenazine)Cl]$^+$ in 2-chloronaphthalene. Base-induced quenching at the metal center is, however, diminished relative to [Pt(NNN-phenazine)Cl]$^+$, because only very strong donors like dmso and dmf are capable of quenching the emission of the NNC-phenazine complex [47]. That probably means that the degree of ^{3}MLCT character in the excited state is very limited. DFT calculations of the free ligands are also suggestive. They reveal the NNN-phenazine ligand has a very delocalized HOMO while more of the electron density localizes on the 6-phenyl component of NNC-phenazine [47]. On the other hand, in each case the ligand LUMO tends to localize on the phenazine moiety. Both theoretical work and quenching results are therefore consistent with the idea that the charge-transfer character in the reactive excited state of [Pt(NNC-phenazine)Cl]$^+$ is mainly ^{3}ILCT(phenyl → phenazine) in nature.

In summary carbometalation has proven to be a successful strategy for enhancing the photophysical and photochemical properties of platinum(II) complexes for specific applications [55]. A paramount effect is certainly that substituting carbon for nitrogen in the chelate ring system raises the energy of the deactivating ^{3}d–d states. Additionally, ligand-based excited states come into play. Thus, recent efforts have shown that incorporating large electron-donating substituents within the NNC framework leads to emitting states with ^{3}LC and mixed ^{3}MLCT/^{3}ILCT character, lower energies, and extended lifetimes [30]. Introduction of phenazine into the NNC framework realizes a molecule that is capable of dual reactivity in the excited state, namely exciplex quenching by both Lewis acids and bases at spatially distinct sites. Additionally, the resulting ligand framework supports a new type of ^{3}ILCT state [47].

6. Conclusions

In platinum terpyridine complexes the metal center lies at a crossroad of two axes. Sigma bond formation is relatively weak along the axis that extends toward the trpy ligand's outer nitrogen atoms, but there are many possibilities for electronic tuning along the other axis which extends toward the N′ nitrogen of trpy and the opposite co-ligand. Low-lying π^* orbitals of the trpy ligand introduce the possibility of MLCT excitation and potentially photoluminescent Pt(II) complexes; on the other hand, low-lying d–d excited states can quench the emission by promoting non-radiative decay. The parent complex [Pt(trpy)Cl]$^+$ is non-luminescent in fluid solution, but it is possible to modify the system in many ways and induce a signal by stabilizing the emitting state relative to neighboring quenching states (Fig. 6). One option involves replacing the chloride with a co-ligand that is a stronger σ and π donor, such as hydroxide or an acetylide. Augmenting the ligand framework by incorporating large aryl substituents at the 4′-position delocalizes the π^* orbitals and also stabilizes the emitting state, which may have mixed LC/MLCT parentage as a result. Additionally, electron-donating substitution at the 4′-position produces excited states with a large percentage of intraligand CT character. Simultaneous modification of both the co-ligand and the terpyridine can produce molecules with exceptionally high quantum yields and long lifetimes, [Pt(dma-T)CN]$^+$, for example. Lastly, replacement of one of the nitrogen donors of the terpyridine framework with a deprotonated carbon atom leads to a new class of complexes and another type of intraligand charge-transfer excitation in which the formally anionic phenyl group acts as the donor moiety. Interestingly, the position of carbometalation has a dramatic effect, possibly due to changes in the nature of the acceptor orbital. All of these strategies reveal a large and expanding chemical toolbox for tuning the electronic and photophysical properties of platinum(II) terpyridine based complexes for a variety of applications.

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