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Arylated versus Cyclometalated Platinum(II) Polypyridines: Photoluminescence from Pt(4′-R-trpy)Ph$^+$ Systems (R = NMe$_2$, N-Pyrrolidinyl, or 1-Pyrenyl)

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Supporting Information

ABSTRACT: Many platinum(II) polypyridine complexes are good luminophores, an enigmatic exception being Pt(trpy)Ph$^+$, where trpy denotes 2,2′:6′,2″-terpyridine. A new analysis suggests the complex is nonemissive due to ^{3}SBLCT (sigma-bond-to-ligand charge transfer) character in the lowest energy excited state. Bases for two distinct strategies for inducing emission from aryl derivatives become clear. The standard approach of incorporating a phenyl group into a ($N^\wedge N^\wedge C$) cyclometalating ligand relies in part on the rigidity of the ligand framework. An alternative strategy, which involves expanding the chromophore and altering the orbital parentage of the emitting state, is capable of suppressing radiationless decay even further. Indeed, the Pt(4′-pyren-1-yl-trpy)Ph$^+$ system emits from a low-lying $^3\pi-\pi^*$(pyrene) excited state that has a lifetime of 45 μs in fluid solution.

Chart 1. Ligands and Complexes

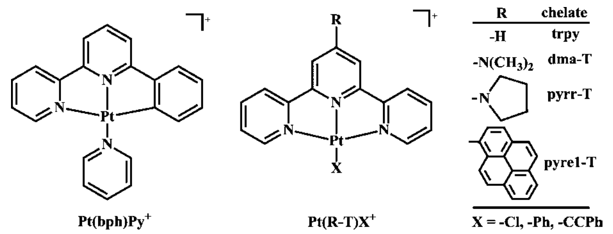

Table 1. Photophysical Data in Room-Temperature Acetonitrile, except as Noted

complex	λ_{Abs}, nm[a]	λ_{Em}, nm[a]	τ, μs[b]	Φ[c]
Pt(trpy)Cl$^+$	390sh			
Pt(dma-T)Cl^{+d}	420, 431sh, 440sh	560	1.9	0.08
Pt(pyrr-T)Cl^{+e}	423, 430sh, 445sh	575	4.5	0.079
Pt(trpy)Ph$^+$	400sh, 424			
Pt(dma-T)Ph$^+$	405sh, 428	564	0.04	0.0008
Pt(pyrr-T)Ph$^+$	405sh, 430	567	0.10	0.002
Pt(pyre1-T)Ph$^+$	430	570w, 650, 700	45	0.001
Pt(trpy)CCPh^{+f}	432	630	0.50	0.012
Pt(dma-T)CCPh^{+g}	436, 457	567	2.6	0.011
Pt(pyrr-T)CCPh$^+$	437, 456	575	3.9	0.064
Pt(bph)Py^{+h}	430sh	540	4.8	0.14

[a]Band maxima. [b]Excited state lifetime under N$_2$ atm. [c]Emission quantum yield under N$_2$ atm. [d]Ref 11a. [e]Green, R. L. MS thesis, Purdue University, West Lafayette, IN, 2005. [f]Ref 3c. [g]Ref 11c. [h]In dichloromethane.

Why Pt(trpy)Ph$^+$, where trpy denotes 2,2′:6′,2″-terpyridine and Ph represents a phenyl coligand,[1] is surprisingly nonemissive in fluid solution becomes clear from studies involving 4′-substituted-2,2′:6′,2″-terpyridine (R-T) analogues. The planar geometry at platinum and open coordination sites are useful design features for solution-based luminescent reporter probes,[2] even if applications for photoluminescent platinum(II) polypyridine complexes often relate to solid-state devices.[3] Predicting whether any given system will exhibit emission is still a challenge, despite an expanding base of luminophores. Especially in the case of platinum(II) terpyridines, photophysical properties vary markedly depending on substituents present as well as the coligand.[4] Thus, early reports showed that Pt(trpy)OH$^+$ and Pt(Ph-T)Cl$^+$, where Ph-T denotes 4′-phenyl-2,2′:6′,2″-terpyridine, are emissive in fluid solution, while the classical Pt(trpy)Cl$^+$ system exhibits no detectible emission under the same conditions.[5] Other complexes that exhibit easily detected emission signals include Pt(trpy)CCPh$^+$, where CCPh denotes the phenylethynyl coligand,[3c] and Pt(bph)Cl, where bph denotes cyclometalated ($N^\wedge N^\wedge C$) 6′-phenyl-2,2′-bipyridine.[6]

Chart 1 depicts the ligands and complexes involved in the current study, and the Supporting Information contains details regarding synthesis and characterization via cyclic voltammetry, X-ray crystallography, and various analytical methods. At wavelengths below about 375 nm, each complex in Table 1 exhibits a series of absorption bands, mainly attributable to $\pi-\pi^*$ bands of the chelating heteroaromatic $N^\wedge N^\wedge N$ or $N^\wedge N^\wedge C$ ligand. Weaker charge-transfer (CT) transitions, generally exhibiting some degree of platinum character, occur at wavelengths longer than 400 nm as in related complexes.[4,5] Figure 1 provides representative absorption spectra; see Table 1 for a compilation of data.

More striking are the emission results obtained in fluid solution and reported in Table 1 as well as Figure 1. Indeed, Pt(dma-T)Ph$^+$, Pt(pyrr-T)Ph$^+$, and Pt(pyre1-T)Ph$^+$ are the first terpyridine complexes of platinum(II) to have a phenyl coligand and be photoluminescent in fluid solution. In terms of the excited-state lifetime, no complex in Table 1 compares with Pt(pyre1-T)Ph$^+$. Among the systems with amine substituents,

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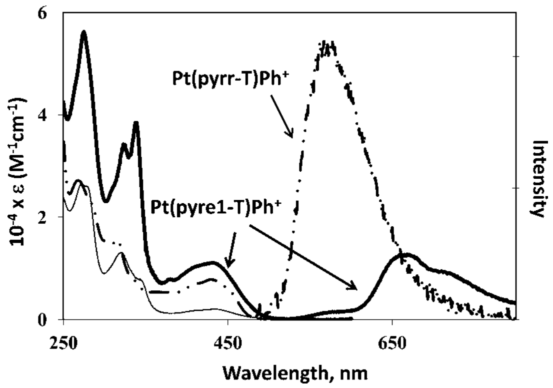

Figure 1. On the left: absorbance spectra of Pt(trpy)Ph$^+$ (—, thin), Pt(pyrr-T)Ph$^+$ (— ·· —), and Pt(pyre1-T)Ph$^+$ (—, thick) in acetonitrile. Corresponding emission spectra on the right, where the areas reflect relative quantum yields.

the emission lifetime increases in the order Pt(trpy)L$^+$ < Pt(dma-T)L$^+$ < Pt(pyrr-T)L$^+$, whether the coligand L is phenylethynyl or simply phenyl. In terms of the emission quantum yield, however, Pt(bph)Py$^+$ stands apart in Table 1, in keeping with the fact that a cyclometalating (N$^\wedge$N$^\wedge$C) ligand frequently yields a highly emissive platinum derivative.[3b,7] That the isomeric form, Pt(trpy)Ph$^+$, is only emissive in a rigid glass has been somewhat of a mystery.[1] The tacit understanding has been that a thermally accessible metal-centered excited state mediates decay, as in other photoexcited Pt(trpy)L$^+$ systems.

However, strong sigma-bonding ligands like carbanions tend to drive up the energy of d−d excited states,[8] the very rationale typically offered for the observation of emission from *cyclometalated* forms.[3b] More likely, the problem is, as discussed in a recent review,[7] that a coligand cannot be effective at promoting emission if the presence of the coligand itself introduces efficient pathways to radiationless decay. In light of results obtained with other Pt−C bonded systems, one can expect the excited state of Pt(trpy)Ph$^+$ to exhibit sigma-bond-to-ligand charge-transfer (SBLCT) character simply because the coligand *is* such a strong donor.[9] The charge redistribution that takes place in the excited state naturally paves the way to a significant elongation of the Pt−C bond, which in turn can promote vibrationally assisted radiationless decay. In extreme cases, photoinduced homolysis of the platinum−carbon bond may even occur.

Fortunately, there are ways of avoiding the problem. Consider Pt(trpy)CCPh$^+$, which exhibits a comparatively long-lived excited state. SBLCT character fades in this case because the CCPh coligand presents an sp-hybridized carbon center. (Note that the gas-phase ionization of a lone pair electron is a 2.1 V higher energy process for the anion of CCPh vis-à-vis the C_6H_5 anion.[10]) Cyclometalated N$^\wedge$N$^\wedge$C complexes exhibit even longer lived excited states, presumably because a rigid chelate framework restricts the range of motion of the Pt−C bond as well as the efficiency of vibrationally assisted decay. The motivation for installing electron-rich groups at the 4′ position of the trpy ligand is to alter the lowest energy excited state by introducing intraligand charge-transfer (ILCT) character.[11] The proof of concept is that the simplest amine-substituted product isolated, Pt(dma-T)Ph$^+$, is emissive in fluid solution, although the excited-state lifetime is only 40 ns. The emission yield and excited-state lifetime increase more than a factor of 2 in the analogous Pt(pyrr-T)Ph$^+$complex due to the presence of the more strongly donating pyrrolodinyl substituent.[12]

Also consistent with increasing ILCT character, the emission lifetime lengthens within the series Pt(trpy)CCPh$^+$ < Pt(dma-T)CCPh$^+$ < Pt(pyrr-T)CCPh$^+$ (Table 1). That ILCT character dominates is also evident from the fact that the emission maxima occur at a similar wavelength for the entire series of dma-T and pyrr-T complexes, regardless of the coligand (Table 1). By way of comparison, the emission maximum of Pt(trpy)CCPh$^+$ falls at longer wavelengths, presumably due to larger structural relaxation of an excited state with coligand-to-trpy charge-transfer (LLCT) character.[3c,13]

However, the phenyl complex with by far the longest excited state lifetime in Table 1 is Pt(pyre1-T)Ph$^+$ (Figure 2), which also exhibits the longest-wavelength emission maximum. The absorption maximum of the pyre1-T complex occurs at 430 nm and is attributable to ILCT excitation in view of the ease of ionization of pyrene.[14] However, the extremely red-shifted emission is incompatible with a ^{3}ILCT state assignment, as is the calculated radiative rate constant, $\varphi/\tau \approx 20$ s^{-1} (3 orders of magnitude smaller than corresponding estimates for the dma-T and pyrr-T analogues). The energy, lifetime, and residual vibronic structure of the emission are consistent with a substituent-based $^3\pi-\pi^*$(pyrene) state assignment, instead, analogous with the signal Castellano and co-workers have reported for a dipyrenylethynyl complex of platinum(II).[15] The emission spectrum of the latter exhibits more vibronic structure than that of the pyre1-T system, perhaps because neither steric nor bonding forces absolutely fix the torsion angle subtended by the 4-terpyridyl moiety. Another contributing factor to the band shape could be that the excited state of Pt(pyre1-T)Ph$^+$ has an element of ^{3}ILCT character. In fact, Figure 1 reveals that the emission spectrum reveals a weak shoulder at around 570 nm. In view of the energy, this component of the emission could originate from a near lying ^{3}ILCT.[16]

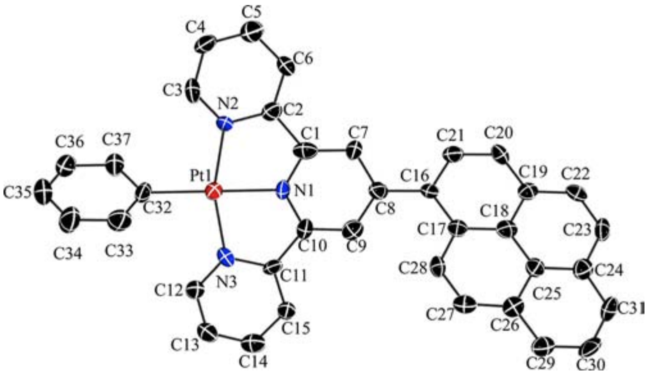

Figure 2. The molecular structure of a representative molecule of [Pt(pyre1-T)Ph]$^+$ from the asymmetric unit with thermal ellipsoids set at 50% probability. Selected bond lengths (Å) and angles (deg) associated with the metal center: N1−Pt1 1.984(7), N2−Pt1 2.024(7), N3−Pt1 2.024(7), Pt−C32 2.011(9); N1−Pt1−N2 80.5(3), N1−Pt1−C32 177.5(3), N2−Pt1−C32 98.7(3), N2−Pt1−N3 161.3(3), N1−Pt1−N3 80.7(3), N3−Pt1−C32 100(3).

In summary, rapid deactivation of photoexcited Pt(trpy)Ph$^+$ is due to intrinsically efficient radiationless decay from the lowest energy ^{3}SBLCT excited state. The weak emission exhibited in a low-temperature glass actually originates from a higher lying $^3\pi-\pi^*$(trpy) state.[1] In cyclometalated analogues, the suppressed rate of radiationless decay is attributable to the rigidity of the ligand framework. Work described herein shows that expanding the chromophore and altering the orbital parentage of the emitting state is also an effective way of promoting photoluminescence. The best example is Pt(pyre1-T)Ph$^+$, which exhibits $^3\pi-\pi^*$(pyrene) emission with a lifetime of 45 μs in room-temperature solution.[17] Supplanting ^{3}SBLCT character could have the same effect in complexes with *alkyl* coligands as well, although electron transfer from an alkyl anion is a relatively low energy process.[10] Weakly or nonemissive alkyl or aryl complexes could, on the other hand, be useful as photoinitiated DNA-nicking agents,[18] if they undergo photoinduced homolytic bond cleavage. Finally, understanding the dynamics of the Pt(trpy)Ph$^+$ system in greater detail will require state-of-the-art computational methods for mapping excited-state potential energy surfaces.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Synthesis, characterization, and cyclic voltammetry for all compounds as well as crystallographic data for [Pt(bph)Py]$^+$ (CCDC 884587) and [Pt(R-T)Ph]$^+$ (R = dma-T, pyre1-T, and pyrr-T, CCDC 884588−884590) can be obtained free of charge via the Internet at http://pubs.acs.org or Cambridge Crystallographic Data Centre via http://www.ccdc.cam.ac.uk/data_ request/cif.

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Notes

The authors declare no competing financial interest.

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