Coordination Chemistry Reviews, 111 (1991) 145–152
Elsevier Science Publishers B.V., Amsterdam

THE EFFECT OF LINEAR CHAIN STRUCTURE ON THE ELECTRONIC STRUCTURE OF PT(II) DIIMINE COMPLEXES

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ABSTRACT

In square planar d^8 complexes, the crystalline state can have a pronounced effect upon the electronic structure and photophysical parameters of the monomer due to electronic interactions between nearest neighbors. In this article, we discuss the luminescence behavior of Pt(II) diimine complexes in dilute monomeric environments and in linear chain solid state structures. In these complexes, triplet excited states of ligand field, metal-to-diimine charge transfer, and diimine (π-π^*) type lie at similar energies. Their relative ordering is influenced not only by intramolecular factors such as ligand field strength and diimine substituents, but also by the intermolecular structure of the crystal packing. The observed luminescence is a sensitive probe of these factors in the solid state.

1. INTRODUCTION

The unusual colors of many square planar d^8 complexes in the solid state has been known for a very long time, particularly those of double salts such as Magnus' Green, $[Pt(NH_3)_4][PtCl_4]$. In the early 1970's, interest in the low dimensional electrical conductivity and superconductivity of molecular materials sparked a renewed research effort in solid state d^8 materials [1-4]. Many of these materials were found to have highly anisotropic electrical and optical properties. X-ray crystal structures obtained for several anisotropic d^8 materials showed stack or slipped-stack structures in which the distances between metal ions along the chain was less than 4 Å.

The dependence of anisotropic properties such as conductivity on the intermolecular distance suggested that metal-metal interaction was important, but the electronic structure of these materials did not fit a classical semiconductor band model. Although early spectroscopic studies of linear chain materials [5-6] gave some insight into the solid state perturbations present, it was not until much subsequent work was done on the electronic structure of d^8 dimers [7-9] that the nature of axial metal-metal interactions began to be well understood.

Our interest in the spectroscopy of linear chain Pt(II) complexes began with experiments to test Pt(II) double salts as microheterogeneous photosensitizers to drive energy storage redox reactions [10]. The premise was that these insoluble microcrystalline materials might have some kind of cooperative excited state structure that would mimic a semiconductor particle photocatalyst, while their intense visible absorption spectra would allow high solar collection efficiency. Although a wide variety of highly colored salts ranging from yellow to purple were made, not all proved to be successful photosensitizers. The successful candidates all contained Pt(II) cations with bipyridyl ligand(s) and Pt(II) anions with strong-field ligands. This observation led us to focus on Pt(II) diimine complexes and on the effects of the solid state on their electronic structure [11-13]. Luminescence has proved to be a valuable probe of

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excited state structure, as most Pt(II) diimine complexes are emissive in both dilute glassy solution and crystalline forms, and the differences between these two environments is reflected markedly in both the luminescence spectra and photophysical properties.

The solid state Pt(II) diimine complexes to be discussed here are listed in Table 1 along with pertinent spectroscopic and photophysical data. Readers are referred to references 11-13 for a detailed description of synthetic and experimental procedures.

2. SOLID STATE STRUCTURE OF PT(II) DIIMINE COMPLEXES

For purposes of identification, we will define three categories of solid state structure in crystalline Pt(II) complexes. A complex is considered to be a *monomer* if it is in a lattice where the nearest Pt-Pt distance is > 4.5 Å and if the solid state emission spectrum is not significantly different from that in dilute solution or glass. An example of this structure is that of yellow Pt(bpy)Cl_2 [14]. A *linear chain* structure is one in which the Pt(II) complexes are stacked equidistantly along an axis that usually but not always perpendicular to the plane of the complex. This structure is known in both double salts and neutral complexes. In Pt(II) diimine complexes the Pt- Pt distance is typically in the range 3.2-3.4 Å (Table 1). Finally, a *dimer* structure contains pairs of complexes with an intermonomer distance that is clearly shorter than the distance to the next pair. Many dimer structures are known, among them [Pt$(phen)_2$]$Cl_2 \cdot 3H_2O$ [15], but no dimer structures have been established yet among double salts.

Several Pt(II) diimine complexes are known to be dimorphic, the best known example being the red and yellow forms of Pt(bpy)Cl_2 [14]. We have found polymorphism to be rather common in crystalline Pt(II) diimine complexes we have prepared. This results in luminescence properties that can vary widely among different sample preparations and also occasionally over time as a metastable material relaxes to a lower energy crystalline form. The optical properties of linear chain materials are also sensitive to factors that affect the Pt-Pt spacing [16] such as hydration number, counterion size, and temperature.

3. ELECTRONIC STRUCTURE OF MONOMERS

The electronic structure of monomeric Pt(II) diimine complexes has been discussed in detail elsewhere [11]. Briefly, three types of absorption bands are observed in the near uv-visible region; these are intraligand $\pi \rightarrow \pi^*$ (IL), Pt -> diimine(π^*) charge transfer (MLCT), and ligand field (LF). Each of these types of absorption can have luminescence associated with the lowest spin-forbidden state if it is lowest in energy.

3.1. Intraligand (IL) Transitions

The IL manifold is characteristic of a given diimine ligand and transition energies are not much affected by the other ligands on Pt. Bipyridyl complexes have an intense ^{1}IL absorption at 310-330 nm that shows vibronic structure to higher energy with spacings of ~1200-1500 cm^{-1}. The singlet-triplet splitting is very large, on the order of 9000 cm^{-1}. Weak ^{3}IL absorption with analogous vibronic structure is observable in the region of 450 nm in favorable spectra such as that of Pt(bpy)$(en)^{2+}$ [11] and Pt(5,5'-Me_2bpy)$(CN)_2$ [12]. In Pt(bpy)$(en)^{2+}$ we estimate the (0,0) transition to the ^{3}IL state to be at 452 nm, and our spectroscopic data for complexes with ^{3}IL luminescence indicate that the range of (0,0) energies is only ~452-455 nm in Pt (II) bipyridyl complexes [11-13]. In phenanthroline complexes, a similar IL situation is found where structured ^{1}IL absorption occurs at ~380 nm and poorly-resolved ^{3}IL absorption is observed at ~450 nm.

Emission from a lowest ^{3}IL diimine state is characterized by a small Stokes shift from absorption (420 cm^{-1} for Pt(5,5'-Me_2bpy)$(CN)_2$, 670 cm^{-1} for [Pt(bpy)(en)]$(ClO_4)_2$). Vibronic structure is usually well-resolved at room temperature and the relatively large Franck-Condon factor gives the spectrum a characteristic "glove" lineshape reminiscent of aromatic organic compounds. At low temperature, the maximum shifts slightly to higher energy. ^{3}IL emission has a radiative rate constant of the magnitude 10^4 s^{-1}; we have calculated k_r = 53,000 s^{-1} for $[Pt(bpy)(en)](ClO_4)_2$ at 300 K [11] and Ballardini, *et al.* have measured k_r = 20,000 s^{-1} for $Pt(bpy)(NH_3)_2^{2+}$ in butyronitrile at 77 K [17]. ^{3}IL emission can also show the effect of excimeric interaction between diimine ligands on nearest neighbor complexes. Excimer emission appears as a broad structureless band to the red of the monomer emission maximum. We have documented [11] excimeric emission from $[Pt(phen)_2]Cl_2 \cdot 3H_2O$ and from $[Pt(bpy)_2](ClO_4)_2$. The former is known to have a dimer structure as the trihydrate [15] while the structure of the latter is unknown. Similar emission has also been seen from adducts of $Pt(bpy)(NH_3)_2^{2+}$ with aromatic crown ethers [17].

3.2. Ligand Field (LF) Transitions

Ligand field (LF) states are difficult to observe in Pt(II) diimine complexes because they are usually masked by intense IL and MLCT absorption. In strong field complexes such as $Pt(bpy)(en)^{2+}$, the lowest ^{3}LF state is expected to be much higher energy than the lowest ^{3}IL state discussed above, but in weaker field complexes such as $Pt(diimine)Cl_2$, the energies are comparable. We have never observed ^{3}IL emission from any dihalo complex but have observed LF emission from many dichloro complexes and also from $Pt(bpy)I_2$ [13] (Table 1). LF emission is always broad and Gaussian in shape, with a maximum that is nearly temperature-independent. The observed Stokes shift of 3-4000 cm^{-1} is typical of LF emission. Although ^{3}LF emission from these complexes can sometimes be intense at room temperature in crystalline materials, the radiative rate constant is only on the order of 10^3 s^{-1}, consistent with the Laporte-forbidden nature of the transition. For example, we have measured k_r = 5100 s^{-1} for crystalline $Pt(5,5'\text{-}Me_2bpy)Cl_2$ at 300 K [13]. As expected, the energy of the lowest ^{3}LF excited state is very sensitive to any factors affecting the ligand field. While ligand σ-donating effects are dominant, the secondary effects of varying the diimine or substituents on a given diimine can also be seen by comparing the LF emission maxima among dichloro complexes in Table 1. From our spectroscopic data on these complexes, we estimate the position of the ^{3}LF (0,0) transition to be in the range 18,000-19,500 cm^{-1} for $Pt(diimine)Cl_2$ complexes.

3.3. Metal-to-Ligand Charge Transfer (MLCT) Transitions

Pt -> diimine(π^*) ^{1}MLCT absorption occurs in the near-uv region of the spectra of these complexes, significantly lower in energy than Pt -> amine [18] or Pt -> CN^- [18] ^{1}MLCT absorption bands. Although they are of comparable intensity to ^{1}IL absorption, ^{1}MLCT absorption bands are often difficult to locate due to overlap with ^{1}IL absorption. One characteristic that unambiguously identifies ^{1}MLCT transitions in monomeric complexes is their marked solvent-sensitivity; for example, the lowest ^{1}MLCT band in the spectra of $Pt(bpy)X_2$ (X = Cl, Br, I) shifts ~4000 cm^{-1} to lower energy upon going from aqueous to chloroform solution [19]. This identification technique is severely limited by the low solubility of most Pt(II) diimine complexes in a sufficiently wide range of solvents to demonstrate the effect. However, the majority of bipyridyl complexes show a shoulder at 330-360 nm in acetonitrile or aqueous solution which may be assigned to the lowest energy Pt -> diimine(π^*) ^{1}MLCT. In phenanthroline complexes, the picture is complicated by the more complex ^{1}IL absorption manifold, and we have not been able to unambiguously identify ^{1}MLCT bands in these complexes.

The position of ^{3}MLCT absorption features is similarly obscured by overlap with ^{3}IL and in some cases ^{3}LF absorption. However, we recently examined [13] one compound, $Pt(3,3'\text{-}(CO_2Me)_2bpy)Cl_2$, in which the position of ^{1}MLCT absorption, ^{3}MLCT absorption, and ^{3}MLCT solid state emission can be clearly identified (Table 1). The crystal structure of this material [13] shows a monomeric environment.

Table 1. Photophysical Data for Pt(II) Diimine Complexes in the Solid State

Compound	Form[a] (Pt-Pt spacing)	Emission Maxima (nm)	Emission FWHM (cm^{-1})	Emission Lifetime	Quantum Yield[b] or Intensity	Type
$[Pt(bpy)(en)](ClO_4)_2$ yellow	monomer (unknown)	461, 482sh, 492, 521, 530sh, 569sh, 607sh	structured	1.4 μs	0.074 very intense at RT	IL
$[Pt(phen)_2]Cl_2 \cdot 3H_2O$ yellow	dimer (3.71 Å)[c]	630 excimeric	5800	<20 ns	very weak at RT	IL
$Pt(5,5''Me_2bpy)(CN)_2$ yellow	monomer (ref 25)	455, 488, 518, 557, 600sh	structured	1.82 μs	0.038	IL
$Pt(bpy)(CN)_2$ orange	linear chain (3.3296 Å)[d]	600 (652, 30K)	1500 (1020, 30K)	160 ns	0.041	MLCT
$Pt(phen)(CN)_2$ red	linear chain (unknown)	691 (755, 30K)	2300 (960, 30K)	130 ns	0.012 intense at RT	MLCT
$Pt(bpy)Cl_2$ red form orange	linear chain (3.40 Å)[e]	615 (650, 10K)	2000 (1050, 10K)	155 ns	intense at RT	MLCT
$Pt(bpy)Cl_2$ yellow form yellow	monomer (>4.5 Å)[e]	(624, 77K) (630, 10K)	(2800, 77K) (2400, 10K)	(23 μs, 77K) (3.4 μs, 10K!)	undetectable at RT	LF
$Pt(5,5'-Me_2bpy)Cl_2$ yellow	monomer (ref. 13)	645 (647, 10K)	3900 (2600, 10K)	1.24 μs (5.1 μs, 10K)	0.0063 moderate at RT	LF
$Pt(4,4'\text{-}t\text{-}Bu_2bpy)Cl_2$ yellow	monomer (unknown)	645 (645, 10K)	3900 (2600, 10K)	<20ns (~50ns, 10K)	very weak at RT	LF
$Pt((3,3'-CO_2Me)_2bpy)Cl_2$ orange	monomer (ref. 13)	550sh, 595 (555, 595, 645sh, 10K)	structured	350 ns (1.1 μs, 10K)	moderate at RT	MLCT (xz)

Pt(phen)Cl_2 yellow	monomer (unknown)	630 (630, 10K)	3700 (3000, 10K)	2.4 μs (13.3 μs, 10K)	intense at RT	LF
Pt(bpy)I_2 red	monomer (unknown)	695 (695, 10K)	2650 (2300, 10K)	5.62 μs (30.7 μs, 10K)	intense at RT	LF
[Pt(bpy)(en)][Pt$(CN)_4$] bright yellow	linear chain (3.34 Å)[f]	560 (584,640sh, 30K)	2600 (2050, 30K)	160 ns	0.17 (0.32, 30K)	MLCT
[Pt(phen)(en)][Pt$(CN)_4$] bright yellow	linear chain (unknown)	560	2600	150	moderate at RT	MLCT
[Pt$(bpy)_2$][Pt$(CN)_4$] · $2H_2O$ yellow orange	linear chain (unknown)	570	2800	<15 ns	weak at RT	MLCT
[Pt$(bpy)_2$][Pt$(CN)_4$] red orange	linear chain (est. 3.2 Å)[f]	620 (658, 730sh 20K)	3000 (1550, 20K)	8 ns	0.002 moderate at RT	MLCT
[Pt$(phen)_2$][Pt$(CN)_4$] · xH_2O magenta	linear chain (unknown)	628	2600	~15 ns	weak at RT	MLCT
[Pt$(phen)_2$][Pt$(CN)_4$] blue violet	linear chain (unknown)	650	2200	<15 ns	very weak at RT	MLCT
[Pt(4,4-Me_2bpy$)_2$][Pt$(CN)_4$] yellow	linear chain (unknown)	(576, 77K)	(1950, 77K)	98 ns	intense at RT	MLCT
[Pt$(bpy)_2$][Pt$(ox)_2$] xH_2O blue violet	linear chain (unknown)	660	2200	<15 ns	weak at RT	MLCT
[Pt$(bpy)_2$][Pt$(ox)_2$] red orange	linear chain (unknown)	605	2800	<15 ns	very weak at RT	MLCT
[[Pt$(bpy)_2$][PtCl_4] yellow	linear chain? (unknown)	(770, 77K)[g]	(2000, 77K)[g]	(70 μs, 77K)[g]	extremely weak at RT	LF

Microcrystalline powders in quartz sample holders, front surface orientation, room temperature. See refs. 11-13 for details of measurements. a) Deduced from spectral and photophysical data unless otherwise noted. b) Obtained by the method of Wrighton, *et al.*, *J. Phys. Chem.* **78**, 2229 (1973). c) Ref. 15. d) Ref 25. e) Ref. 14. f) Ref. 12. g) Measured by C. Craig and Prof. R.J. Watts, U.C. Santa Barbara.

We have used the ordering of Pt(II) d-orbitals calculated by Textor and Ludwig [20] to assign the emissive state as Pt(d_{xz}) -> bpy(π^*) ^{3}MLCT (z-axis normal to the coordination plane, x-axis bisecting bpy), hereafter referred to as ^{3}MLCT(xz). The singlet-triplet splitting can be estimated to be ~3800 cm^{-1} with a Stokes shift of ~1600 cm^{-1} between absorption and emission. These values can be used to estimate the position of the lowest ^{3}MLCT(xz) (0,0) transition as ~390 nm in crystalline [Pt(bpy)(en)]$(ClO_4)_2$ and ~490 nm in chloroform solutions of Pt(bpy)Cl_2 (for comparison, Textor and Oswald [14] assigned a band maximum at 475 nm in the methylene chloride solution spectrum of Pt(bpy)Cl_2 as ^{3}MLCT(xz)). In the former compound, ^{3}IL is lower in energy but in the latter, ^{3}MLCT could be the lowest excited state. We searched unsuccessfully for luminescence from Pt(bpy)Cl_2 in dilute chloroform at low temperature. If indeed ^{3}MLCT(xz) is the lowest excited state, it is strongly quenched even at 77K. We suspect that a ^{3}LF excited state is in fact lower.

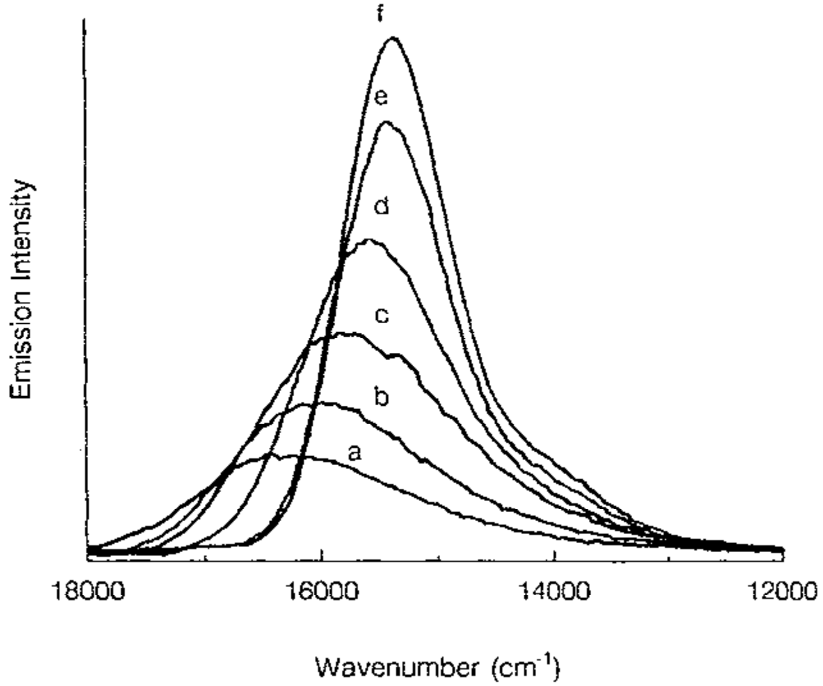
4. ELECTRONIC STRUCTURE OF LINEAR CHAINS

When square planar Pt(II) complexes are stacked in a linear chain crystal structure, the interaction of z-directed orbitals on adjacent units causes marked changes in the electronic structure from that of the isolated monomer. The interactions are analogous to those that take place in axial d^8 dimers such as $[Pt_2(H_2P_2O_5)_4]^{4-}$ [7-9]. The net bonding interaction that results from overlap of filled Pt(d_{z^2}) and empty Pt(p_z) orbitals explains the predilection for Pt(II) complexes to crystallize in linear chain structures. In Pt(II) diimine complexes, linear chain structure has a profound effect on the energy of MLCT transitions involving z-directed orbitals. Although the Pt(d_{xz}) and Pt(d_{yz}) orbitals should be raised in energy somewhat, the Pt(d_{z^2}) orbital should be much more strongly affected, and should become the highest occupied orbital below some critical Pt-Pt distance.

Textor and Oswald [14] were the first to propose that the red color of linear chain Pt(bpy)Cl_2 was due to the red-shift of Pt(d_{z^2}) -> bpy(π^*) ^{3}MLCT absorption (hereafter called ^{3}MLCT(z^2)) to 520 nm, even below Pt(d_{xz}) -> bpy(π^*) ^{3}MLCT(xz). We have confirmed this assignment by observing ^{3}MLCT(z^2) emission from red Pt(bpy)Cl_2 (Figure 1) in contrast to the ^{3}LF emission observed from yellow Pt(bpy)Cl_2 [11]. As with ^{3}MLCT(z^2) from linear chain Pt(bpy)$(CN)_2$ [21] and Pt(phen)$(CN)_2$ [22], a distinctive red-shift is observed in the emission from red Pt(bpy)Cl_2 as the Pt-Pt spacing shortens with decreasing temperature. This is a signature of ^{3}MLCT(z^2) emission; the ^{3}MLCT(xz) emission from Pt(3,3'-$(CO_2Me)_2$bpy)Cl_2 mentioned above does not show such a red-shift. Another difference between ^{3}MLCT(xz) and ^{3}MLCT(z^2) emission is in the vibronic structure of the spectrum. In the emission spectrum of Pt((3,3'-$CO_2Me)_2$bpy)Cl_2, vibronic structure with a Huang-Rhys constant of ~1 is evident at room temperature and well resolved at 10K. In red Pt(bpy)Cl_2, asymmetry is noticeable in the room temparature spectrum but vibronic structure only becomes clear at low temperature, where a progression with a Huang-Rhys constant (I(1,0)/I(0,0)) of only ~0.25 is observed at 10 K. A small Huang-Rhys constant seems to be typical of ^{3}MLCT(z^2) emission [12].

In simple Pt(II) diimine complexes, the crossover of ^{3}MLCT(z^2) emission to the lowest excited state does not often occur in the solid state. While Pt(bpy)$(CN)_2$, Pt(phen)$(CN)_2$, and red Pt(bpy)Cl_2 have ^{3}MLCT(z^2) solid state emission, the majority of complexes we have studied do not. Double salts are a notable exception to this observation. We have examined the emission of a large number of double salts of Pt(II) diimine cations (Table 1) including those of our original photosensitization study [10]. ^{3}MLCT(z^2) emission occurs in every case where the anion is reasonably strong-field, such as $Pt(CN)_4^{2-}$ or $Pt(ox)_2^{2-}$ (ox = oxalato). (If the counterion is $PtCl_4^{2-}$ then LF emission from this anion is observed.) The observed ^{3}MLCT(z^2) emission is typically shortlived and intense at room temperature; we calculate

Figure 1. Emission from red Pt(bpy)Cl_2 as a function of temperature. a) 300 K b) 200 K c) 150 K d) 100 K e) 50 K f) 10 K. Excitation 457.9 nm, 2 μW-cm^{-1}.



k_r = 1,060,000 s^{-1} for [Pt(bpy)(en)][Pt$(CN)_4$] and 250,000 s^{-1} for [Pt$(bpy)_2$][Pt(CN)] at room temperature [12]. The Stokes shift between the lowest diffuse reflectance feature and emission maximum is typically >3000 cm^{-1}, larger than in the case of ^{3}MLCT(xz) emission. We have determined [12] the unit cell parameters of one diimine-containing double salt, [Pt(bpy)(en)][Pt$(CN)_4$], which are consistent with a linear chain structure having a Pt-Pt spacing of 3.34 Å. As this salt is yellow, the orange-to-purple colors of other salts listed in Table 1 suggest shorter Pt-Pt spacing [23]. (Each case needs to be examined individually, however, as d-orbital energies are also sensitive to the electron donor/acceptor capacity of the ligands, which is quite variable among the double salts listed in Table 1.) We surmise that the strong attraction between cation and anion in the double salts may act as a driving force for a linear chain strucuture and/or a short Pt-Pt spacing.

The energy of the ^{3}MLCT(z^2) state is expected to increase as a function of increasing Pt-Pt distance until at some point it is no longer the lowest excited state. Although it is difficult to estimate the Pt-Pt distance at which a crossover should occur in a given linear chain material, we have observed one instance of a dynamic crossover in Pt (5,5′-Me_2bpy)$(CN)_2$, a material in which polymorphism has been documented [25]. Freshly prepared samples of this yellow solid exhibit ^{3}MLCT(z^2) emission. After several weeks, however, the same samples exhibit emission that is clearly ^{3}IL. We suspect that some factor such as a slow structural relaxation of the lattice causes a lengthening of the Pt-Pt distance, which is probably already rather long due to the presence of the methyl groups on bipyridyl.

It is likely that the photosensitizing behavior of the successful Pt double salts is due to their lowest excited state being ^{3}MLCT(z^2). Not only is CT excitation inherently redox in nature, but the participation of the z-directed orbitals may confer some delocalization or mobility. To test the mobility of this excited state along the chain, we doped the prototype sensitizer [Pt(bpy)$_2$][Pt(CN)$_4$] with known amounts of the dark trap Ni(CN)$_4^{2-}$ and studied the emission yield as a function of quencher concentration [12]. Following the theoretical treatment by Simon, *et al.* [26] of exciton quenching in linear chains, we determined that the excitation travels over <50 units within its lifetime of 8 ns at room temperature. This undoubtedly enhances the effectiveness of linear chain materials as heterogeneous photosensitizers, as the probability of bulk ^{3}MLCT(z^2) excitation travelling to the surface of a submicron-sized particle is significant. We would predict that double salts with longer lifetimes and higher quantum yields such as [Pt(bpy)(en)][Pt(CN)$_4$] should be even better redox photosensitizers.

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23. A few double salts exhibit behavior that is contrary to the majority. For example, hydrated [Pt(bpy)$_2$][Pt(oxalate)$_2$] shows a blue-shift of both diffuse reflectance and emission upon dehydration, implying a *longer* Pt-Pt distance in the anhydrate. We therefore hesitate to claim linear chain structure for all of the double salts listed in Table 1. It is known, for example in *cis*-bis(2-phenylpyridine)Pt(II) [24], that a dimer structures can also give rise to highly colored solids with MLCT emission.
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