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So-called “Dual Emission” for <sup>3</sup>MLCT Luminescence in Ruthenium Complex Ions: What is really happening?

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## ABSTRACT

Dual emission is a reality in many, but not all, ruthenium complex ions, even at room temperature and in fluid solution. It requires significantly different ligands and is more obvious in rigid media such as glasses at low temperature and crystalline powders. However, there are not just two unique lifetimes. Rather, there is a continuum of similar but slightly different lifetimes drawn from a bimodal distribution. In some of the cases that do not show dual emission, there still seems to be a continuum within a unimodal distribution. After reviewing a wide range of data, we describe possible interpretations. Most novel, but in our view most attractive, is a major role for ion pairing. If one admits that ions near charge transfer orbitals should have a stabilizing effect, and if one doubts that there would be any unique configuration for ion pairs, then it would seem that a continuous variation of excited state behavior is mandatory. This mechanism accounts for the fact that highly asymmetric substitutions at the 4- position of the phen ligand that most affects charge transfer always show dual emission and offer the most exaggerated differences between the two emissions. Other possibilities remain, given the data available at this time.

## 1. Introduction

In previous publications, we provided evidence that certain coordination compounds of ruthenium, even as dilute solutes in acetonitrile at room temperature, show phosphorescence from at least two distinct, spatially isolated metal-to-ligand triplet charge transfer ( $^3\text{MLCT}$ ) states that coexist for more than a microsecond but are not in thermal equilibrium [1,2]. The excited states had different emission spectra, different excitation spectra, and different lifetimes. This was very surprising. That it may also be significant was supported by the fact that reviewers and editors agreed: “That cannot be correct; but we cannot see where the problem lies, so go ahead and publish.” Despite several decades of intermittent previous reports of such behavior, which we review in this article, the suspicion remained that such observations were likely due to the presence of unrecognized impurities. In our two publications, after excluding any possibility of chemical impurities, we phrased our report carefully to read that two emissive  $^3\text{MLCT}$  states were adequate to account for data within the available precision of measurement. Many aspects, however, remained to be explained, even for the data then in hand. We address several of those here, taking advantage of the work of others before and after that time, along with refined measurements that reinforce and expand upon what we knew at that time. We are now convinced that whether a particular compound supports one, two, or even three different, localized and long-lived  $^3\text{MLCT}$  excited states, there is also some environmental heterogeneity that leads to a continuum of excited state properties, even in low viscosity liquid solutions. We suggest that ion-pairs, by themselves or as a part of small aggregates, could account for all observations. We admit other possibilities.

The initial observations occurred fortuitously in the course of preparing novel complex ions of ruthenium for use in supramolecular projects. The first examples featured dinuclear species consisting of two ruthenium centers connected by a bridge between two phenanthroline moieties [1]. Later we showed that a single ruthenium center could also show “dual” emission when a phenanthroline ligand was extended in specific ways with conjugated substituents [2]. Most of our attention at that time was devoted to exploring which substitution patterns gave the most convincing evidence for the novel behavior. Compounds had two bipyridyl (bpy) ligands and one substituted phenanthroline (phen) around either the one or each of the two ruthenium centers. The instances that showed dual (or perhaps multiple) emissions most clearly had asymmetric substitution only at the 4- position of the phenanthroline. Asymmetric substitution at the 3- or the 5- position did not give convincing evidence, and symmetric substitutions at both 4- and 7- were clearly not effective. Was that pattern, however, because certain structures are the only ones to exhibit this behavior? Or was it because “dual” emission is easier to recognize when two emission features are widely separated in wavelength, and those very asymmetric complexes exhibited unusually wide separation for two  $^3\text{MLCT}$  emission bands? Based on the structures that showed such clear evidence of “dual” emission, we speculated that two emission features were associated with orbitals spatially isolated on the two distinctly different types of ligands present in each complex. The state with greatly extended conjugation should emit at longer wavelengths. Yet, for some reason, a significant fraction of the total emission (sometimes even a majority) occurred at shorter wavelengths, near where one would expect complexes with only bipyridyl ligands to emit. Perhaps some localization was on one or both bpy ligands, although there could be other possibilities, as we will discuss below.

Even as we searched for substitution patterns that exhibited the most obvious anomalies, we devoted much effort to proving that the “dual” emission was not due to some unrecognized impurity or the coexistence of isomers. The problem was that the “dual” emissions showed exactly the properties that one would expect for two independent species: They had different emission spectra, different excitation spectra, different lifetimes, no measureable rise time for either component, and no evidence for excitation transfer from the short-lived component to the longer-lived component. In the decade since that initial effort we have explored more aspects of the novel behavior. We synthesized and characterized yet more compounds. They are not

included in this review, as they have not yet been reported in the primary literature. We also put great effort into assuring ourselves that observations were not compromised by nonlinearities in the detection electronics. After all this, we concluded and will prove below that two unique lifetimes are not sufficient to fit the phosphorescence decay curves. Instead, we need a distribution of decay times that is bimodal, peaking around two maxima but with variation. We use the term “multiple emission” at times to emphasize that two unique lifetimes are not sufficient. Any explanation for the behavior must, we stress, explain that feature. This is more strong evidence against simple dismissal of the behavior as due to contamination by impurities. One must explain the continuum distributions first; only after that may one even think about impurities. Another aspect that is difficult to explain away as an impurity effect was a dramatic change in different solvents. It may be tempting to wish for displays of emission spectra as they evolve over time. We did previously show data in that form. However, those were all constructed from the emission decay curves. Neither we nor anyone else has provided data that resolve measured time-resolved spectra into continuous distributions of many spectra. Since the critical data emerge from decay kinetics, we focus here on establishing the reliability of the raw data and not on reconfiguring data into derived spectra.

Even our earliest data were best fit by allowing exponential functions to have more than just two unique lifetimes. However, allowing more freedom in any fit will always improve the agreement between data and a fitting function. At the time, we had to admit that uncertainties in the data acquisition left open the (slight) possibility that there were just two unique decay rates, so that data curves at different wavelengths might be superpositions of those two in different amounts. That became more and more difficult to believe as we continued, even with the original apparatus. Finally, we built a new apparatus better suited to settling this issue. Our data are now far too good to allow fits at all emission wavelength to be just the sum of two unique decay rates. We also knew from the beginning that there were dramatic variations in luminescence spectra of our compounds when the solvent was changed. We will discuss that issue briefly, along with some results for the temperature dependence of emission features. We will mention also an exploration of the effects of adding exogenous salts at quite high concentrations.

Our goal here is primarily to offer a comprehensive review of phosphorescence decay kinetics sufficient to challenge others to propose explanations for the behavior observed—and to encourage them to do so. We cannot yet offer convincing proof for a single explanation. However, based on data presently available, we do propose a refinement of the conjecture offered previously. We suggest that the decades-old hypothesis of <sup>3</sup>MLCT excitation being localized on different ligands (or different parts of a sufficiently big ligand) can account for different spectra in heteroleptic compounds; but there is a need to explain why the spectral features are not in thermal equilibrium, as shown by phosphorescence decay profiles that are different over many microseconds, even though the species do, apparently, interconvert over minutes or hours, at least in liquid solutions. We suspect that a transient external factor is needed. Also required is an explanation for the fact that there are not just two unique decay rates. There is significant heterogeneity in excited state lifetimes. We conjecture that all or part of the explanation could be ion pairing. Might it be that ion pairing stabilizes one or another spatially localized <sup>3</sup>MLCT feature? A particular ion pair arrangement should stabilize excited state electron density that is localized on a particular ligand (or a portion of a ligand) and might persist for microseconds; and yet the ion pairs would reform over longer times, thereby accounting for the failure to observe any hint of two permanent molecular species. We are aware of no prior suggestion along these lines. Particular arrangements of surrounding solvent molecules might stabilize one or another localized orbital without invoking ion pairs and might be sufficient to explain phenomena in liquids over a few picoseconds or in glassy environments over longer times, but we do not see how simple solvent arrangements could persist for microseconds in solvents that are less viscous than water. Aggregation into dimers or small oligomers might

also be pertinent, but we point to some evidence against that. In any case, aggregation of ions would probably need to involve counterions.

During the decade since our first report other workers have reported what they called “dual” emissions of one sort or another. They worried about impurities, as we had. Whatever may be going on, it cannot all be simply a matter of obvious impurities. We hope that by relating our work to that of others, we may reach the point that all of us will agree that what was once unbelievable is, in fact, to be expected; and eventually we will agree that we knew it all along.

Since we write for an issue to honor Prof. Peter Ford, perhaps one of us (D. M.) may be forgiven for reminiscing about the first work he did with Peter. Four decades ago there was interest in understanding patterns of ligand substitution in metal complexes subsequent to photoexcitation into metal-centered  $d-d^*$  bands. Several treatments had been developed to explain why certain photosubstitution patterns should be expected to be favored over others, that is, to have faster rates of reaction. At the time the only experimental data were quantum yields (often just relative yields) for product formation. Peter was concerned that product yields are always the net result of competing processes. It is not sufficient to predict rates for the reactions of interest; one must also know the rates of competing processes. To obtain rates, one must measure lifetimes of reactive species, not just yields. So we began a collaboration to obtain nanosecond lifetimes for rhodium complexes, studies that involved a number of graduate students and continued with Prof. Leif Skibsted for several years. That and similar quantitative work by many others over four decades has changed inorganic photochemistry into a more quantitative science than it was in earlier days. Nonetheless, throughout all this progress, fundamental ideas about excited electronic states remained to a large extent based on ideas taken from the work of Prof. G. N. Lewis and Prof. Michael Kasha, who thirty years earlier had developed quantitative treatments for aromatic organic compounds. In this review, we suggest that it may be time to deemphasize the old insights that emerged during the study of aromatics if we are to understand the photophysics of transition metal complexes. Indeed, the best recent work has done precisely that.

## **2. History of dual emission**

It is timely to examine the history of dual emission because the term “dual emission,” which so troubled editors when we wrote a decade ago, has appeared regularly since, but usually as an isolated observation peripheral to other aspects of a study and without clarification of underlying issues. Dual emission can refer to many different phenomena. Only a restricted class is problematic. Editors and reviewers no doubt recognized this; but exactly what the problem is may not be known to all readers. Our summary here of the history of dual emission is illustrative of the principle issues, but still far from exhaustive. The citations offered, items 1 to 51, often include just one or two articles from laboratories that published extensively. When convenient, we cite a review article that can serve as a resource for finding earlier work; but in some cases, we wish to emphasize the first work from a laboratory. Including all the citations provided in the papers we do list would increase the bibliography several fold. Adding results from citation searches would increase the numbers further. We realize that we have omitted much that could be mentioned. We apologize both for lack of space and our own lack of knowledge. In addition, we report what authors stated without any attempt to verify or alter ancient interpretations. Early work used methods far inferior to what is available today, and some factors may have gone unrecognized. Some inferences may have been correct but not fully substantiated by the data then available; others might be incorrect. Nothing would be gained by pointing that out in each instance, and in most cases it would take new measurements to be sure. After writing this summary, we were struck by the fact that many pertinent issues were understood decades ago, but some work is now so old that it may not

be familiar to younger scholars. More importantly, we are amazed that we did not find a single instance in the entire library of work cited that so much as hints at key findings we report, or raises the possibilities that we now suggest may be crucial.

We are concerned here primarily with liquid solutions at room temperature. Glassy solutions at 77 K may be relevant, as they might exhibit essentially the same behavior minus only processes that require diffusive motion. We do not have space to give more than passing attention to the many early studies at that temperature that set the scene for later work. The situation at much lower temperatures, close to absolute zero, and especially in ordered environments, such as dilute doped crystals, most assuredly does involve additional concepts; but they do not enter our thinking here. We also give only brief mention of the consequences of internal rearrangements (photoisomerization), which may lead to multiple emitting states; for the most part, we assume that ground state geometries persist, aside from small changes in bond lengths or angles.

### 2.1. The Kasha-Vavilov Rule in the early years

Let us be clear: Dual emissions and even multiple emissions are not rare in atomic and molecular spectroscopy. They are common in atoms and very small molecules and occur in other instances. It is only within specific contexts that one may deem them surprising. For atoms and diatomic species, isolated from perturbing surroundings, emission varies with excitation wavelength and involves many different transitions among electronic states because there are no nonradiative channels available. For larger species, even in isolation but especially as solutes in some dense medium, the Kasha-Vavilov Rule for organic species asserts that within each different spin manifold it will be only the lowest state of that spin that exhibits appreciable emission yields—with some exceptions even then. Dual or multiple emissions that emanate from different spin manifolds are not at all surprising, quite the contrary. Kasha's seminal work with Prof. G. N. Lewis led subsequently to a paper from more than sixty years ago, which we mention because it is a good summary and because it includes ideas that had evolved during the years he was thinking about the issues [3]. What Kasha actually asserts is rather more limited than what one might gather from frequent references to him. Kasha was well aware that isolated atoms and diatomic molecules exhibit radiative transitions from many states. Kasha treats larger molecules, but he discusses only planar aromatic molecules and heterocyclic species such as dyestuffs. When Kasha makes an assertion about emission, he means "detectable emission" and he makes clear that he is referring to luminescence that can be recorded on photographic plates. He does not claim that the statement that only the lowest state within a spin manifold emits measurably is a novel insight. He knows the work of Vavilov and others; and he knows that molecular spectroscopists had ideas as to what chemical structures facilitate luminescence and which do not. He is more interested (in the paper referenced) in the converse, in using information about emission to distinguish two different families of transitions from each other: specifically,  $\pi \rightarrow \pi^*$  from  $n \rightarrow \pi^*$  transitions in heterocyclic species. Much of the paper discusses methods to tell those apart. He also takes some space to inform readers that quantum yields detectable on photographic plates must exceed approximately  $10^{-4}$  and, consequently, higher-energy states that are not luminescent but should have radiative rates near  $10^8 \text{ s}^{-1}$ , as expected for fully allowed transitions in the visible spectral region, must have lifetimes not more than a few picoseconds. For aromatic molecules and their close relatives, there is a sufficiently large energy gap between the ground state and the lowest energy excited state that radiative transitions can compete with nonradiative decay. In contrast, energy spacings among excited states are usually small enough that nonradiative decay competes effectively—except for the unique situation in which spin changes result in transitions so slow that fluorescence is observed from the lowest state of the originally populated manifold prior to eventual transition to even lower energy states of different spin, which may then phosphoresce, if they are not quenched. He does not concern himself with molecules different from aromatics

and dyestuffs. He does not address the possibility that there could be barriers other than spin change that inhibit transitions among excited states; nor does he worry about the possibility that spin changes might be very rapid in some different types of molecules. For the species he has in mind, he not only suggests that luminescence, both fluorescence and phosphorescence, is possible; he clearly expects that it will occur. Yet it was common understanding in that day that only rigid species, such as those he was discussing, commonly emit; “floppy” molecules were expected to decay by nonradiative pathways. Most transition metal compounds, likewise, were weakly emissive at best and were not of concern to Prof. Kasha.

In rare instances, large energy gaps exist between higher excited states of identical spin even for molecules of the sort Kasha was treating. In those cases anti-Kasha fluorescence can occur from higher excited states to the ground state, or between excited states within a particular spin manifold. It is all a matter of competing rates. Azulene is the well-known instance, along with a much less well known triazene [4]. This matter is still of some interest. Dual fluorescence was recently reported for an indocyanine dye molecule [5]. A few years ago, aggregation-dependent dual emissions of both S1 and S2 character were reported [6]. Beyond such instances, it is possible, with heroic efforts, to detect luminescence of very low quantum yield (below what Prof. Kasha considered measurable) from higher states that have large radiative rates but very short lifetimes. Prof. Michael Topp explored this last possibility at some length thirty to forty years ago. These cases show true “anti-Kasha” emission; but they are the exceptions that prove the rule. They refine the limits that Kasha himself taught us. Use of the term “anti-Kasha” in other contexts is by analogy and extension—and may be inappropriate.

## 2.2. The Crosby-DeArmond Corollary

Little more than a decade after the above-cited paper by Kasha, Prof. Glenn Crosby (who had worked with Prof. Kasha in a post-doctoral capacity) and his colleagues published a seminal review that offered a comprehensive treatment of the photophysics of Ru(bpy)<sub>3</sub> and Ru(phen)<sub>3</sub> [7]. Prior to that time, most work on the optical properties of transition metal compounds had dealt with cobalt or chromium. That review appears, from today’s perspective, much more modern in tone than does Kasha’s paper [3]. There is no mention of photographic recording. There are lifetime measurements—in solid matrices at low temperatures. Absorption and emission properties of the two complexes were reviewed based on earlier work in the Crosby lab. The paper and its predecessors distinguished among three different categories of excited electronic states in metal complexes: metal centered (or ligand field) d-d\* transitions, ligand-localized (or intraligand) transitions, and charge transfer transitions involving both the metal and the ligands. The last category involved charge transfer from metal to ligand (MLCT transitions) for the ruthenium compounds treated; but it could be ligand to metal in other cases. Each of those categories admitted of at least two spin manifolds, and possibly more for some metals. So by that time, we had the Crosby corollary (our name, not his) to Kasha’s rule: Only the lowest state within a spin manifold of any of the three categories of excited states would luminesce sufficiently to be detected by ordinary methods. Our impression is that most authors assume that only the lowest excited state of a particular spin among all three categories of states will emit, and that this would be in accord with the Kasha-Vavilov rule. It is not entirely clear to us that Crosby meant to insist upon that strong assertion as a universal principle, even though it was and remains the usual case. That would be the logical inference if spin transitions are always as slow as they are in the aromatics, and transitions among all categories having a given spin, even among the three different categories, are rapid; but we do not believe those conditions are universally in force. Spin changes in transition metal compounds often require only picoseconds and might be faster than transitions to other categories with the same spin. It is true that many transition metal compounds do not emit at all, as was also true of organic compounds; and those that do emit usually emit fairly strongly from only one

state; but that is not necessarily because spin changes are slow. It is worth considering that there might be, in principle, six different “lowest” spin states (or conceivably more if there are more spin options), each of which might emit detectable luminescence depending on the values of all the many rate constants for radiative decay, internal conversion, intersystem crossing, and other pathways for deactivation (and the sensitivity of one’s measurement), with the only prohibition being against emission by higher energy states within each unique category. Could there be even more than the six lowest states if some categories, the charge transfer states and the ligand localized states, could have multiple variations of each spin localized in different portions of the molecule?

The present authors have always thought of this analysis as the “Crosby Corollary.” However, in preparing this review, we were reminded that Prof. DeArmond was using the same insights in the analysis of absorption and emission at the same time, the very early 1970’s. The language was used also by others who put emphasis on photochemical reactions, notably by Prof. Arthur Adamson (possibly the most important figure in the United States, at least, in bringing ruthenium compounds to the interest of a broad community); but for our topic here, the detailed study of phosphorescence, it appears that Crosby and DeArmond were most involved in experimental studies that popularized the categorization of three sorts of excited states, each with two or more spin manifolds.

One may speculate that if one excites at high enough photon energies and detects emission with very low quantum yields, one may occasionally observe different emission features sequentially with distinct rise times and decay times, as in the aromatics. More than thirty years ago there was an article (one that included Prof. Ford among the authors, along with Dr. Douglas Sexton) having the term “dual emission” in the title that reported that prompt fluorescence from a singlet ligand field excited state in a rhodium complex seemed to persist for a few picoseconds prior to final equilibration into the triplet state [8]. In the same year, there was a report of prompt quartet fluorescence prior to slower, doublet phosphorescence in two chromium compounds [9]. Even earlier, Profs. Kirk and Porter, two prominent inorganic photochemists of the time, had reported thermally excited, delayed quartet fluorescence from chromium compounds [10]. (There were other chromium compounds in which the quartet state was lower than the doublet state, and those exhibited fluorescence, as expected.) Such measurements were difficult at the time and might be explored again with today’s superior tools. A recent article reported convincing evidence for prompt fluorescence from the <sup>1</sup>MLCT state in Ru(bpy)<sub>3</sub> [11]. We address other recent work below. These are all instances of dual emission; but they are entirely consistent with the Kasha-Vavilov-Crosby-DeArmond principle, in that the two features arose from different spin manifolds within the same category.

Even though typical behavior in metal complexes was fairly clear at the time of the Crosby review [7], evidence for the limits of what might be possible, but atypical, was not extensive then; and it remains uncertain even today. Is there a lowest excited state in every transition metal complex that is uniquely and very rapidly populated? Or are there some cases in which two (or more) excited states each persist long enough for both to be detectable, as in anthracene and its relatives? Since the radiative rates for emission from some states are very slow, one could imagine that some excited states might persist for picosecond or even nanosecond times and still not be obvious in emission. Even if multiple states do emit, the plethora of possible states of rather similar energies makes it difficult to distinguish among their emission spectra. Even if, however, very short-lived states might be detectable with fancy methods, could there really be multiple states in any single molecule that co-exist for many nanoseconds or even microseconds? In very large species, such as proteins, one may have two chromophores sufficiently isolated that they coexist and are independent enough that one may speak of energy or charge transfer between them. Is anything like that possible in complex ions that are



much smaller than proteins, but maybe large enough? As late as 1988, Prof. Balzani and his distinguished laboratory synthesized a series of nine mixed ligand ruthenium compounds and reported no exception among those, either at 77K or at room temperature, to the rule that only one, unique, lowest energy excited <sup>3</sup>MLCT state emits [12].

### 2.3. Observations attributed to dual emission from localized states

If a coordination compound of one of the heavier transition metals is to exhibit dual emission due to long-lived, localized chromophores in different portions of the same molecule, the most likely cases might involve ligand-localized excitations—those that involve  $\pi \rightarrow \pi^*$  (or  $n \rightarrow \pi^*$ ) transitions localized on different ligands only slightly influenced by the metal center. Such an interpretation was suggested more than 40 years ago by Prof. DeArmond for mixed ligand complexes of rhodium [13]. However, it was not only intraligand transitions that were implicated. In a 1989 report by Glezen and Lees (which expanded on work initially reported a year earlier) multiple emissions in a rhenium complex were attributed to a pair of thermally equilibrated <sup>3</sup>MLCT states, along with a much shorter lived triplet ligand field state [14]. Orthometalated complexes may add possibilities. Prof. Richard Watts, a post-doctoral student with Crosby and a colleague of Ford, noted ligand-field transitions along with intraligand transitions, or just multiple intraligand transitions, in orthometalated species. We list just one article by Watts and his coworkers from 1991 [15], which cited much earlier work. It began with the statement, “A wide variety of coordination complexes of the second- and third-row transition metals are now known to display dual emissions from thermally nonequilibrated excited states in rigid media.” Thirty citations were offered in confirmation of that bold assertion. Besides being in frozen glasses at low temperatures, the instances mostly involved iridium or other third-row metal atoms. Many involved different types of orbitals, and were described as “distinct orbital” as opposed to “spatially isolated” dual emissions. Although distinct orbitals were spatially separated in addition to other differences, apparently the term “spatially isolated” was to be reserved for instances in which the emitting states are of very similar orbital character, but differ in being spatially isolated in different regions of a molecule.

Known to us at the time of our first publication were the efforts of Prof. DeArmond and his collaborators, who worked throughout the 1970's and 1980's to catalog “spatially isolated” examples, with some emphasis on dual <sup>3</sup>MLCT transitions. We devote attention to DeArmond's work partly because it involved ruthenium, partly because much of it was earlier than most other work, and to acknowledge that it happened to attract the notice of one of us at the time. In 1986 DeArmond wrote, with Blakley and Myrick, the following explicit assertion in a paper having to do with emission from one particular ruthenium compound [16]: “Tris-chelated compounds ... have been shown to have single ligand-localized emitting states. Therefore, in mixed-ligand complexes a dual emission might be expected since localized states involving each type of ligand would exist. ... This type of emission is termed ‘spatially isolated’ since the emissions are from spatially distinct regions of the molecule.” He continues, however, by pointing out that detecting such dual emission would be difficult “due to the fact that the MLCT emissions would have virtually identical energies, contours, and lifetimes ...” He then argued that he had obtained data good enough to resolve such spatially localized <sup>3</sup>MLCT dual emission at 77 K in one particular case. Related studies had been summarized much earlier (in 1981) in a lengthy review by DeArmond and Carlin in this journal [17]. The emphasis in that 1981 review was not on the novelty of dual emission even then, but on establishing the spatially isolated nature of emitting states [17]. It seems to us that the earliest papers had often or always used the word “localized” to refer to metal-centered  $d \rightarrow d^*$  excited states, putting emphasis on how metal-containing compounds were different from organic compounds. Anything involving ligands was said to be delocalized. It may have been that authors at the time assumed that “delocalized” should mean that all ligands participate, but that is not

clear. In the homoleptic systems,  $^1\text{MLCT}$  absorption from the ground state seemed to offer good evidence for  $D_3$  symmetry, so that the initially formed  $^1\text{MLCT}$  Franck-Condon excited state must be delocalized in the sense of involving all three ligands; but some authors may have used “delocalized” in some cases only to assert that some orbital beyond the metal was involved. Eventually, custom changed and the term “localized” was employed also to refer to states involving orbitals on different ligands rather than just on the metal center. To DeArmond and his collaborators the question became whether the initial Franck-Condon state decayed to a localized triplet state spatially isolated on one ligand, and if so, how rapidly. Since they concluded that it did so and did it quickly, the question then arose whether subsequent behavior involved exciton hopping among ligands.

Strong evidence for localized excited  $^3\text{MLCT}$  states came in part from time-resolved resonance Raman studies of the excited states of  $\text{Ru}(\text{bpy})_3$ . Despite the fact that the three ligands were the same, time resolved Raman studies (quite novel in 1979) by Prof. Woodruff and collaborators were interpreted as requiring the co-existence of two species, identified as  $\text{bpy}$  and  $\text{bpy}^\square$ , even at room temperature and in liquid solution [18]. Eight years later Carroll and Brus extended the Raman work to frozen solutions and used different laser techniques to arrive at a similar conclusion [19]: The three ligands were not identical with nominal charges of  $\square 1/3$ ; instead, they were of two distinct charge properties, at least on time scales of Raman measurements. Studies using other techniques agreed. Electron paramagnetic resonance as well as polarized optical measurements and photoselection were reviewed and discussed in the DeArmond review [17], including both work from DeArmond’s own laboratory and work of others. Interest continues to the present day, with reports of results obtained by transient infrared spectroscopy appearing not long ago [20]. DeArmond’s review gave attention to how rapidly such localization occurs, and mentions exciton hopping that would transfer spatially localized excited states among ligands on some time scale. Originally, DeArmond thought he had evidence for such intramolecular exciton hopping from certain polarization studies, but that claim was retracted. Most relevant measurements from DeArmond’s laboratory were at liquid nitrogen temperatures. The aim was clearly to slow down thermally excited transfers and keep the spatially isolated state on the same ligand long enough to be identified. The conclusion in the review was that the molecular orbital involved in  $^3\text{MLCT}$  phosphorescent emission from any ruthenium complex, whether it contains one, two, or three bipyridyl ligands, is localized on a single ligand, at least enough to permit one to speak of exciton hopping, if not as long as it lived. Furthermore, the authors added, multiple state emissions must occur precisely because the emitting states “have near degenerate emitting energy levels.” For that logic to be valid, the authors must have believed that thermal processes can redistribute excitation among different, spatially isolated states. Evidently, DeArmond judged that populations would decay to the lowest energy  $^3\text{MLCT}$  state and any states accessible by Boltzmann equilibrium. Yet there have been intermittent reports of non-equilibrated behavior, as mentioned above.

Later, but already fifteen years ago, McCusker and co-workers offered evidence that localization onto a single ligand proceeds with a half-life of only about 100 fs in  $\text{Ru}(\text{bpy})_3$  [21]. They seem to have thought that was already a triplet state. They did not treat mixed ligand compounds in that effort. If the spin change really is so fast, or even a little bit slower, it becomes quite inappropriate to treat excited states in these compounds within a framework based on the Kasha-Vavilov Rule. McCusker and colleagues excited directly into the low energy side of the  $^1\text{MLCT}$  absorption, so they could not say how long it would take to make transitions between states of different parentage. More recent ultrafast work by McFarland and co-workers addressed the matter of exciting with higher energy photons [22]. They claimed to resolve behavior prior to or during thermalization, including observation of ultrashort-lived, spin-allowed fluorescence. The most recent work concerning such very early times will be treated at the end of section 2.4. Once we grant that localization is

prompt, the question still remains: After relaxation to a  $^3\text{MLCT}$  state, does excitation hop from ligand to ligand in mixed ligand species so that it quickly ends up either in the lowest energy state or a Boltzmann equilibrium among accessible low-energy states, or not? Ultrafast studies do not address that issue. Our own examples of dual emission (and a few other studies) answered, “Not!” to that question, at least not always. That is the real puzzle.

Let us return to the suspicion that anomalous dual emission might be due to “impurities.” Concern about the near-universal contamination that produces emission with one or two nanosecond decays whenever one searches hard enough is not relevant to features with microsecond lifetimes. Moderately intense emission with microsecond lifetimes must be charge transfer phosphorescence from some metal complex. Any “impurity” must be present at a concentration comparable to the intended species. Yet a variety of analytical procedures find nothing at levels even 1% of the principal feature. Isomers might be considered, but many examples do not admit of isomers. Finally, we found that irradiation by more than one watt at 532 nm for a few hours destroyed compounds by photodegradation, but failed to selectively bleach the longer-wavelength-emitting species, which had a noticeably greater excitation probability at that wavelength. One must conclude that we had, at least in that case, two (or more) emitting species that could not interconvert on the time scale of emission, but did interconvert over times of minutes or hours, as required by the photobleaching result.

Other authors reporting dual emission also defend their observations against charges that they are observing impurities. Returning, however, to the broad question of cataloging all ways in which the term “dual emission” has been used, there are phenomena that might be considered as pseudo-impurities, if they went unrecognized. We refer to photogenerated isomers that form on time scales such that multiple emissions are observed as the initially formed species evolves into a second structure. In suitable matrices, it is even possible that two such species might not just switch from one to the other but could coexist with distinct lifetimes and spectra. Reports of such phenomena are often described using the words “dual emission.” For example, “luminescence switching” and “dual emission” based on such behavior were described for a ruthenium complex in an organic crystal and even in liquid solutions [23]. We would suggest that even though this is dual emission from the point of view of the starting material, at the molecular level such dual emission is simply a matter of different molecular structures, each with its own characteristic behavior. Many such photoisomers involve twisted internal charge-transfer (TICT) states. They have been studied by physical chemists for their own interest; but given that dual emission in metal complexes is often pertinent to probes designed for some purpose, we might mention work toward that goal more than two decades ago by Prof. Marye Anne Fox and her co-workers [24]. That did not involve a metal complex, but the work that does involve TICT processes in metal complexes generally focuses on the behavior of some ligand, only moderately influenced by the metal center. Other reports described “dual emission” in copper compounds that involved ring inversion [25] or ring rotation [26]. Another possibility for species that might go unrecognized, are tautomeric species that involve proton transfer or species that may be protonated or deprotonated. Those have been described as showing dual emission [27]. More commonly, “switchable” luminescence is not of dual character, but simply of “on-off” behavior, frequently involving photoisomerization. Perhaps, with more effort, extra, weakly emitting species might be detectable in such cases. We pass over such matters with only a single mention of efforts by the distinguished laboratory of Prof. Harry Gray [28].

Returning to what might seem to be authentic dual or multiple emissions from a single structure, we note that Henry and coworkers reported multiple emissions from a rhenium compound with thiazole ligands [29]. Properties varied with excitation wavelength in a continuous fashion. Emission lifetimes varied but were on the nanosecond time scale, suggesting spin-allowed, intraligand transitions. The authors suggest that both

$\pi\pi^*$  and  $n\pi^*$  transitions occur, both having the same spin state. That would be “anti-Kasha.” Of particular interest to this review, Henry and his colleagues were very clear that two species with two distinct lifetimes were not sufficient to account for their data. There had to be more to the story; somehow more states were involved. Mixed states involving both charge transfer and ligand localized excitation were invoked. That work, however, also conceded a role for photo-generated isomers and perhaps even ground state isomers.

From work in the 1970's and early 1980's, one might think that it was well established that spatially localized excited states can coexist in the same molecule, and the only question left was to what extent they manifest themselves in detectable luminescence under various conditions. In 1998, Keyes and co-workers asserted [30], “In rigid media, a number of dual emissions have been documented. However, in solution such reports are rare, and to our knowledge no clear-cut cases have been reported ... for ruthenium polypyridyl compounds.” Two citations were listed for “rare” reports that were, they judged, not “clear-cut.” They then offered evidence for a mixed-ligand compound in which they did observe dual  $^3\text{MLCT}$  emissions that they assigned to a bpy ligand and a substituted pyrazine ligand. They noted different emission spectra, different excitation spectra, and different lifetimes. They worked in a mixed solvent, fluid solution. The dual emission was observed only between about 120 K and 260 K. Above and below that temperature, single (or unresolvable) features were noted. There are protonation concerns for their compound, but those were considered. An example of dual emission that did persist all the way to room temperature was reported by Song and co-workers in 2003 [31]. They claimed “first-time” observation of dual emission involving one  $^3\text{MLCT}$  state and one triplet intraligand charge transfer state. Different decay kinetics proved that the two states were not thermally equilibrated. This was shortly before our first paper that reported dual emission from two non-equilibrated  $^3\text{MLCT}$  states in acetonitrile at room temperature, but we did not know of their work.

Intraligand triplet transitions for most typical ligands in ruthenium compounds lie at higher energies than the  $^3\text{MLCT}$  transitions. Extending conjugation in ligands can lower the intraligand transition energies until the two are similar, or even make the intraligand excited state lowest. In 1998, Schmechl and co-workers reviewed work involving nearly isoenergetic states of the two sorts, concluding that in a few cases the coexistence of the two states was likely, usually or always in thermal equilibrium and, therefore, showing dual emission from different orbitals with a single lifetime [32]. One instance was their own work of a couple of years earlier [33]. Efforts to lower the energy of the triplet intraligand states by extending conjugation have continued to the present. Particularly prominent have been efforts from the laboratory of Prof. Castellano, of which we content ourselves with just two citations. One discusses multiple emissions at low temperature, and also reports thermal equilibrium among multiple states at room temperature [34]. Another raises the question whether such situations are best described as being independent states in equilibrium or as mixed states, with wave functions being intermediate and having characteristics of both [35].

In most (or all) instances of claimed equilibrium and a single lifetime cited above, it is not clear to what extent instrumental capabilities could have distinguished lifetimes that were similar but not identical. Was equilibrium proved or just assumed for lack of convincing evidence to the contrary?

All this digression into the history of “dual emission” sharpens the issue raised in our two papers [1,2]. We postulated two emitting states that were both  $^3\text{MLCT}$  states, somehow “localized.” Despite the work of DeArmond and others over the decades prior to our work, as outlined above, dual emission did not seem to be taken very seriously. We had the impression that there were doubts about the reliability of much of the work. DeArmond's review conceded that questionable conclusions had been made in the 1970's by several different investigators; but claimed that all confusion had been corrected by 1981 [16]. Perhaps memories of those old

problems lingered on. Still, our instances, which involved  $^3\text{MLCT}$  states rather than intraligand states, ruthenium rather than heavier atoms, fluid solutions, and room temperature, were in the area that had the fewest previous examples and the most skepticism. Most importantly, even if there could be two localized states, why would there not be some communication between them over times longer than a microsecond? Finally, there was the nagging problem that we did not address in our reports, that maybe there were not just two lifetimes and, therefore, two well defined states. Further heterogeneity was likely. What might that be telling us about complex ions?

#### 2.4. The period after 2007: dual emissions of many sorts

Much work has appeared between our reports and this writing. Some of that was mentioned above in the context of particular issues [23,25,26,29]. We summarize next, in chronological order, 16 more articles that reported observations of dual emission, passing over other good work that focused mostly on syntheses or theoretical quantum calculations. Do any of these address the problem we raised?

In 2008, Fan and coworkers reported investigations of relatively large, multinuclear compounds with extended linkages [36]. For compounds having platinum and ruthenium centers, excitation decayed exclusively to the ruthenium moiety; but when platinum and rhenium centers were present, dual emission was observed. In the same year, Gafney and coworkers described novel ruthenium diimines [37]. They asserted, rightly or not, and in contradiction to some assertions quoted above, that, "All [previous] emissive ruthenium complexes appear to undergo intersystem crossing ... to an emissive triplet MLCT state localized on the lowest energy metal-ligand pair." They claimed that their work in fluid solution at ambient temperature suggested to them two emissive states localized on two different ligands. They did cite our first report involving dinuclear complexes, but were unaware of our 2007 report of identical phenomena in mononuclear systems. Their pyrazine-based ligands raise some issues related to the complications of protonation; but their observation adds weight to our proposals nonetheless. Also in 2008, Lo and coworkers reported dual emission at room temperature from several cyclometalated iridium compounds, adding that dual emission in iridium complexes is common in rigid matrices at low temperature but rare in ambient solutions [38]. They assigned one emission feature to an intraligand excited state and the other to a state of mixed intraligand/charge transfer character. Proportions of the two emissions were sensitive to the environment, a property that they asserted should be useful in "biological probes."

In 2010, Siebert and coworkers reported dual emission from terpyridine complexes of the congeners iron, ruthenium, and osmium, all of which had greatly extended conjugation of one ligand [39]. Their ultimate goal was "white emitters." They attributed one emission feature to singlet fluorescence from a transition internal to the extended ligand and a second, longer wavelength feature to a charge transfer state formed with only modest yield following short-wavelength excitation. Also in 2010 came two more reports of extending ligand conjugation in ruthenium compounds with the goal of lowering intraligand triplet energies, increasing the lifetimes of the lowest states, and making luminescent probes that are more sensitive to oxygen concentration [40,41]. Dual emission was not reported, and is not apparent in published spectra; but it is not clear that much effort was expended in excluding the possibility of a minor component at shorter wavelengths. In the same year, Chao, Ji, and their coworkers studied complexes of ruthenium that contained two bpy ligands and one triazine ligand. They observed dual emission in rigid media at low temperature that switched to single emission at somewhat higher temperatures before disappearing at room temperature [42]. They suggested that the simplest explanation was that one feature may be associated with a state localized on a bipyridyl and the other on the triazine.

In 2011, Prof. Lippard and collaborators reported an iridium complex useful as a sensor for copper ions [43]. Dual emission was noted, with the assertion that it facilitates ratiometric measurements. In the same year, Sen and coworkers reported dual emission using only the homoleptic Ru(bpy)<sub>3</sub> compound [44]. It was incorporated into an anionic metal-organic framework. Different sites produced different emission spectra. This reminds us that site heterogeneity is known to affect state energies and should always be considered.

In 2012, Menzel and coworkers added to the growing library of ligands by synthesizing some new thiazoles [45]. In certain cases they resolved two distinct emission bands in glasses at 77 K; in other cases only a single, broad band was evident. They could detect no luminescence at room temperature. They emphasized the need for time-resolved studies and reiterated the difficulty of resolving broad emission features that occur close together. They used “elaborate quantum mechanical calculations” in order to clarify the nature of the excited states, as did much of the recent work by others—all something of a change from the tendency 40 years ago to categorize very quickly within the three Crosby-DeArmond categories.

In 2013, Shan and coworkers reported metal organic frameworks incorporating two different copper clusters that exhibited dual emission [46]. The same year saw Zhan and coworkers report yet another metal-organic framework with copper-based chromophores exhibiting dual emission, which they attributed to different microenvironments [47]. Again, it is not surprising to find well-defined matrices showing multiple emissions when they incorporate completely different clusters and/or have heterogeneous sites. In the same year, Bhattacharya and colleagues observed another of the few, but ever-increasing examples of dual emission at room temperature in fluid solution [48]. Dinuclear rhenium compounds showed the coexistence of a triplet  $\pi\text{-}\pi^*$  intraligand state along with a <sup>3</sup>MLCT state. For one compound, peaks in emission were fully 50 nm apart and not at all difficult to resolve. Also noteworthy was a lengthy review article (33 pages, 206 references) that treated many different ideas for using “metal coordination in photoluminescence sensing” and pointed to an emerging role for compounds that exhibit dual luminescence [49].

In recent months, while this review was being finalized, two articles appeared that merit special attention. They illustrate well that contemporary investigations of transition metal complex ions have indeed moved well beyond simplistic extensions of ideas developed to explain behavior in aromatic molecules. Profs. Lever and Carlos led an international team that characterized four *cis*-[Ru(□-diimine)<sub>2</sub>(4-aminopyridine)<sub>2</sub>]<sup>2+</sup> complexes [50]. The monodentate ligands permit reasonably facile photosolvolytic, which is different from the work emphasized above. The photochemical studies were combined with photophysical characterization of absorption and emission spectra, transient absorption on the nanosecond time scale, and sophisticated luminescent decay measurements. These were interpreted with the aid of extensive quantum calculations of excited state energies based on density functional theory (DFT). The language of Crosby-DeArmond to describe three distinctly different types of excited states still applies very well, probably because it focuses on location of and changes in charge density, which is the goal also for DFT. The DFT calculations found two low-lying metal centered states, which were of special interest for photosolvolytic, but also pertinent to other excited state decay mechanisms. The many low-lying excited states may or may not communicate and may or may not be evident in emission, as was proposed long ago. Although it was only a minor issue in that article, what is of most interest to us here is that dual emission was detected. It did not show up in either excitation or emission spectra. Only very precise luminescence decay measurements revealed two distinct lifetimes at 660 nm, after excitation at 460 nm, in all four complexes in two different solvents at ambient conditions. All decays would have looked like perfectly good single exponentials not long ago. The published spectra show subtle, barely noticeable curvature when a reader lays a straightedge along the plot, but otherwise, even a careful reader would not notice the nonexponential decay. The measurements were made with photon

counting; and statistical analysis left no doubt that two lifetimes were needed. This sort of evidence for dual or multiple emissions will be considered at length below; but the fact that there was no spectral evidence for dual emission and only very good decay measurements revealed it opens huge holes in forty years of work on similar compounds that did not notice evidence for dual emission. The dual emission observed by Lever and Carlos may be, and quite likely is, a case of conformers, although it might be conceivable that other ideas introduced below play some role. The two monodentate ligands can arrange themselves in different orientations relative to the two bidentate ligands. Two configurations have energy minima, one slightly lower than the other, with the favored configuration switching in different states. The two conformers were not distinguishable in spectra but apparently did differ in their lifetimes. Presumably, the two arrangements interconvert over long times, but not over times less than the decay times.

The most recent article we review, like much recent work, emphasized a potential practical application, namely, hydrogen-evolving photocatalysis [51]. The article treated a mononuclear compound that had two bpy ligands along with a terpyridine moiety (2,2':5',2''-terpyridine, tpy) as the third ligand. It appears that all work was done in acetonitrile. Substantial efforts were made to measure underlying photophysical processes. Indeed, the authors have been quite active in that area for some years. They showed very nice resonance Raman spectra and ultrafast transient absorption spectra and inferred that localization of charge transfer onto different ligands started already in femtoseconds for  $^1\text{MLCT}$  states that evolved into  $^3\text{MLCT}$  states within a few picoseconds. Those persisted on different ligands at least out to a major fraction of a nanosecond. In addition to the ultrafast studies, data were presented for phosphorescence decay over three microseconds. Single exponential decay at 635 nm was obtained over at least six half-lives with an impressive signal-to-noise ratio. However, even if there were two different states co-existing over the entire microsecond time range, it is not obvious that they would appear as distinct in either spectra or lifetime in that compound, which had only slightly extended conjugation at the 3- position. Usually, a more significant change to the third ligand seems to be necessary, as we shall demonstrate below. The paper did not report decay curves at wavelengths other than 635 nm. Often the first evidence of unusual behavior is a decay that might be fit to a single exponential at each wavelength but exhibits slightly different lifetimes at different wavelengths. The real interest of the paper, however, was not the mononuclear compound, but in comparing that mononuclear compound to a dinuclear species that included both ruthenium and palladium centers, and then studying electron transfer in the latter. The dinuclear compound showed obvious nonexponential phosphorescence decay. Although not directly addressing the issues we raise here, that work confirmed and refined earlier work on the picosecond photophysics and also revealed microsecond behavior entirely consistent with our claims.

### **3. Critical problems in making luminescence lifetime measurements**

What did not attract concern in our earlier reports was the reliability of the opto-electronic measurements of luminescent emission. That is somewhat surprising, as we could cite a fairly long list of premature claims in the field of inorganic photophysics based on instrumental artifacts. We were always convinced (and apparently others agreed) that non-exponential phosphorescence decays were not simply due to nonlinearities in the detection system. We were not, however, so sanguine when it became time to go beyond the initial measurements into the question of whether two exponentials are sufficient. That is a much more demanding question. Even though it is not too difficult to demonstrate (with today's methods) that fits to single exponential decays are not adequate, it is quite another matter to establish whether there are two components or more than two, determine their parameters, and decide how those may or may not change slightly for different excitation wavelengths or with changes in temperature, solvent, or other conditions. One

must have great confidence in the linearity of the detection apparatus in order to put much faith into complex decay measurements.

### 3.1. Hardware issues

In our original work and for some time after that, excitation for our phosphorescence decays was accomplished with pulses of about 10 ns duration at about one pulse per second, either from a Nd:YAG laser or a XeCl-pumped dye laser. We used wavelengths of 355 nm, 445 nm, or 532 nm. Pulse energies at the sample were in the range 0.02 to 2 mJ. A monochromator with 5 nm bandpass isolated the wavelength to be detected. Low-luminescing Schott glass filters further attenuated excitation light. Additional glass filters were used for the longest wavelength detection (>700 nm) to attenuate short wavelengths of the phosphorescence.

The photomultiplier (Amperex TUVP46, with an S-20 photocathode) was designed to output large anode currents. Then we wired it with generous capacitance between and very close to the dynodes, and constructed a remote capacitor bank with much larger capacitors to provide constant voltage between dynodes even out to milliseconds. We devoted much effort to exploring how much current we could extract. For tens of microseconds, as much as 5 mA gave highly linear performance. That allowed 50 ohms of load resistance with a dynamic range of up to 1000 to 1 in voltage measurements. In most cases, from 50 to 200 laser shots were summed in a LeCroy 9361 digital oscilloscope for each measurement run. The challenge was to have enough linearity with good enough signal-to-noise ratio to untangle what may be fits to three or four exponentials. In the end, we converted to single-photon pulse counting to do even better. Photon counting was initially introduced for the same nanosecond laser excitation, with the repetition rate increased to 10 pulses per second. For that work, instead of fifty laser shots, we used something of order fifty thousand shots. Thus, it took one to two hours per measurement to capture something approaching one million photon counts.

Subsequently, we switched to the higher rep rate, photon counting system outlined next. A continuous green laser (a frequency doubled, diode-pumped Nd:YVO<sub>4</sub>, Coherent Verdi) operated at 532 nm to give about 2 watts in a cw beam, often attenuated. The continuous laser traversed a double-pass Pockels Cell. The Pockels Cell acts as a capacitance load to an electronic pulse generator. A square pulse of about 200 volts was sufficient to switch the small aperture, “transverse field” Pockels Cell from “blocking” to “transmitting.” The rejection ratio between “on” and “off” was close to 10<sup>5</sup>. The “on” duration was typically 120 ns, but could be varied from below 100 ns to 1  $\mu$ s or more. The repetition rate was always more than 1000 and less than 10000 pulses per second, adjusted to minimize collection time while avoiding any overlap. The electronic pulses were generated with a Hewlett-Packard 8012B pulse generator that gave complete control over duration and repetition rate. Its output of somewhat more than 5 volts was sent to a pre-amplifier capable of supplying the quite large currents needed to drive a high voltage FET that could switch up to 400 volts with low nanosecond transition times. Both the pre-amp and the high voltage FET amplifier were home-built using commercial prototyping boards. Considering losses in the optical path, the excitation energy at the sample was always less than 100 nJ per pulse, which amounts to an average excitation power below 1 mW.

Phosphorescence was collected over a fairly large solid angle (about f:4) and sent through a 0.5 meter spectrograph (Spex 1870), operated as a monochromator with a five nanometer band pass. There was a low-emission glass filter (Schott KV550) before the monochromator to reduce scattered green excitation light. When recording decays far into the red, where the photomultiplier was less sensitive and the transmission of the monochromator was lower, an additional long-pass, red cutoff filter was inserted to discriminate against any residual scattering of the strong, shorter-wavelength portion of the phosphorescence. The photomultiplier



was a Hamamatsu R374HA, with thermoelectric cooling to about 0°C. Anode pulses were amplified 100-fold with a Pacific Precision AD6 pulse amplifier-discriminator. Pulses were sent to a multi-channel analyzer/scalar (Model MSA-3F ADC from FAST ComTec GmbH, Germany), which is a plug-in board for a personal computer. Pulses are counted and stored in “bins” at well-defined times after a trigger signal. With multichannel scaling, one can record many photons for each excitation flash, unlike the case for time-correlated single-photon methods. Consequently, we had full digital, statistically well-defined counting of photons without the nonlinearities inherent in analog methods. The bin width of the analyzer was always 100 ns. Photon counts were recorded almost to the next excitation pulse before the scalar was reset to await the next trigger. Triggers were provided by a simple photodiode that monitored transmission through the Pockels Cell. The scalar was capable of counting pulses at rates in excess of 200 MHz, so it was safe to allow more than one count in the one or two bins coincident with the excitation pulse. Once past the excitation, the average count rate was not more than a single pulse per 100 ns bin per laser “shot.” Each experimental run included at least several hundred thousand “sweeps” and often as many as four or eight million.

### 3.2. Curve fitting and statistics

Best fits to sums of exponentials were computed using the method of Marquardt as described in Bevington [52], with his FORTRAN code translated into C code. With that method, if the uncertainty in each data point is random and known, each data point can be weighted properly and the deviations from the best fit may be compared with the expectation for deviations due solely to the random uncertainties. This ratio is the reduced  $\chi^2$  statistic; it should be close to unity for an adequate fit. [Bevington [52], p. 190.] A value of unity does not prove that a measurement is a good measurement; it merely reveals that the fit is compatible with the measurement uncertainty. A sufficiently bad (noisy) measurement may be compatible with almost any model. A major advantage of high-repetition-rate, low peak power excitation with photon counting is that we can prove unambiguously that the uncertainty in each datum is given exclusively by photon statistics, the so-called shot noise. The entire experiment can be performed with excitation blocked before the sample to generate exactly the same trigger signals with no phosphorescence. Then, random dark counts or ambient light, if any, can be detected. Either of those will be uncorrelated with excitation and should yield a “flat baseline” with each datum obeying Poisson statistics, for which the variance should be equal to the mean of the photons detected. This was confirmed. A possible question is whether excitation through the switched Pockels Cell had any “tail” that added a fixed component to some “early” detection channels. This could be, and was, tested by detecting either laser light from a colloidal scatterer or emission from a short-lived fluorescent species, one of the rhodamine dyes. It was below 0.1% of the peak signal, of concern only for extremely small components of the decay profile. It was also quite repeatable, so that deconvolution was practical, if desired. Data reported below did not require deconvolution, although runs were analyzed using deconvolution as a check. When the uncertainties are known perfectly, one can even go one step further. When comparing two models, each of which is characterized by a  $\chi^2$  statistic for the goodness of fit, the “ratio of the reduced chi-squares ... is distributed according to the  $F$  distribution.” [Bevington [52], p. 196] To be very conservative, one should, as we did, consider a three-exponential fit rather than just a two-exponential fit only if the likelihood that a two exponential fit was sufficient was less than 0.01 according to the  $F$  statistic. The testing of the need to include an additional parameter in a fit is discussed nicely by Bevington [52] on page 198.

## 4. Evidence for dual, or multiple, $^3\text{MLCT}$ phosphorescence in ruthenium compounds

Compounds treated here are either well known and commercially available or were prepared and characterized by methods described previously in detail [1,2]. Although we have since prepared additional

compounds, some of which show dramatic “dual” emissions, this is a review of previously reported species. Structures are illustrated in Figure 1. For these, we offer some data for emission at liquid nitrogen temperatures, where so much of the early work was done. We address additional possibilities for artifacts or impurity effects and show that there could be problems in specific cases, if one is careless, but not in general. Ultimately, we show that luminescence decay curves for many compounds require distributions of lifetimes, specifically, continuous distributions that are bimodal, that is, cluster around two mean values. Two unique lifetimes are not adequate. Some compounds, however, are still well described by a single lifetime at the present limit of resolution. Most of those require continuous distributions, albeit ones that are unimodal.

#### 4.1. Two possible artifacts excluded

One observation, although only qualitative, is pertinent to the question of the reliability of our measurements and those of other workers. One might imagine that an apparent second emission could be due to some degradation product. That is not the case. Even some of the original measurements [1] were made on samples that had been synthesized two or more years earlier for an entirely different project. We were not looking for anomalous emission; nature forced herself upon us. When anomalies were found, new batches were synthesized. They appeared the same as the older batches. Now, again, some of the later measurements reported here were made on exactly the same lots used in initial reports almost a decade ago. In some cases, the compound was saved as the solid; but some new measurements were made even on liquid solutions that had been saved for four years or more. None of the compounds were refrigerated. None were protected from oxygen in air. No effort was made to keep them dry. Most samples were kept in the dark, but some bottles of solutions in clear glass were left exposed to low levels of laboratory light. At the same time, some of the compounds were freshly synthesized. In those cases, measurements were mostly made within a week or two of synthesis. There was no difference in emission properties between freshly synthesized preparations in fresh solutions and those that had been left sitting for years. It is, of course, possible that there could have been some small fraction of degradation into products that have no absorption in the visible spectrum and would be invisible in emission studies; but it is not possible that degradation products are responsible for the phenomenon of “dual” emission.

A second possible concern in studies that employ high powered lasers could relate to nonlinear optical processes. Most of our studies using nanosecond pulsed lasers were carried out at peak powers of about 1 to 4 MW cm<sup>-2</sup> or a bit less, which is lower than what is usually employed to study multiphoton processes. Just to be certain such power levels were not excessive, we made a few measurements on compound **6** (a mononuclear species that had previously given convincing evidence for dual emission) using excitation at 532 nm at powers of 10, 75, 150, and 600 MW cm<sup>-2</sup>. We did this by increasing the pulse energy up to 25 mJ per pulse and then decreasing the beam diameter. Only at 600 MW cm<sup>-2</sup> may there have been some slight change in the phosphorescence signal detected. That assured us that our routine measurements were made under conditions that were safe by two orders of magnitude. The new photon counting methods operate at peak excitation powers seven or eight orders of magnitude lower than the pulsed laser studies and completely eliminate any possible concerns about nonlinear effects.

#### 4.2. Emission from glasses at liquid nitrogen temperatures

The cryostat was quite simple. A liquid nitrogen reservoir cooled a copper cylinder surrounding a cylindrical cuvette made of Suprasil fused silica with dimensions of 3 mm internal diameter and 10 mm sample depth. Direct measurement showed that the temperature within the sample cell was above 77 K but

below 80 K. The solvent for all low temperature measurements was tributyl nitrile. We expected that to make a reasonable glass. The glass was perfectly adequate for luminescence work, even if not always what one would prefer for transmission studies. Preliminary efforts examined emission from the solvent alone and also from free ligand either by itself or in the presence of zinc, which was expected to coordinate. Signals were always far below what we would later obtain for ruthenium complexes. Plain solvent gave emission only at short times, dominated by Raman scattering but with lesser signals from impurities that emit with lifetimes around one to two nanoseconds. For the free ligand, phenanthroline with extended conjugation at the 4- position, with or without added zinc, only UV excitation gave much of a signal. That signal persisted for many milliseconds, as one would expect for phosphorescence from an organic heterocycle. Of course, long-lived emitters such as triplet state aromatics have low radiative rates per microsecond; so even if one thinks there might be some tiny fraction of free ligand in the samples, it would contribute far smaller signals than did the ruthenium complexes, and it would be just a constant offset for the time range of interest. Furthermore, it should contribute nothing with blue or green excitation.

We recorded altogether a few hundred decay curves for phosphorescence from ruthenium complexes at liquid nitrogen temperatures. In the end, the work did not lead to a simple explanation for the so-called “dual emission”; but it did confirm basic ideas of dual emission that had been observed by others forty years ago. It showed, however, that the older work was incomplete. “Dual emission” is not the full story. An example from some of the very earliest work, selected at random, is illustrated in Figure 2 for compound **4**.

In that particular run, we used the older laser apparatus to record phosphorescence decays at 570, 580, 590, 620, 650, 680, 710, and 740 nm following excitation with nanosecond laser pulses at 455 nm and averaging with a digital oscilloscope. Both Table 1 and the Figure 2 show clearly that the shorter wavelength emission decays more quickly. We found that adequate fits very clearly demanded more than two exponentials; and the fits varied with wavelength in a continuous manner. It is sufficient to list fits for just three wavelengths to make the points we wish to make. Table 1 shows fits to two, three, and four exponentials at three emission wavelengths. If we had had more noisy data than we did, we might have been misled into thinking that this measurement showed simple dual emission. However, the  $\chi^2$  statistic judging goodness-of-fit is improved significantly by using three exponentials and improves further with four exponentials. Note that this fitting allows the lifetimes to be different at different wavelengths; but even with that freedom, decays are not just double exponentials. Examination of the residuals between data and fit made a convincing case that two exponentials are not adequate and that four is an improvement over three. We do not want to devote too much space to this matter as we do not assign any particular significance to each exponential. It is unlikely that there are three or four distinct species. The only point is that decays are very heterogeneous. The  $\chi^2$  values calculated are “reduced,” meaning that we made some effort to predict what the noise should be so that a perfect fit (that is, an adequate fit, given the noise in the data) would exhibit a  $\chi^2$  value near unity. That is not so easy to do for oscilloscope recordings; but we tried. Even if the absolute numbers might be questioned, the relative values should be reliable. We considered that the photocurrent noise should include a term for shot noise proportional to the square root of the current magnitude plus a term that is a constant for any particular oscilloscope setting. Over hundreds of measurements two exponentials are not sufficient for glassy solutions when the data are at their best. Either there are systematic distortions in the data, which miraculously know which molecule is measured and which wavelengths are used for excitation and for emission or, much more likely, the decay curves are heterogeneous in a complex pattern. The same sort of analysis to justify fits to more than two exponentials applies to many cases below; but the one quantitative example given in Table 1 will have to suffice as illustrative of all.

Heterogeneous decay kinetics for molecules dissolved in a solid glass solvent should be no surprise to experienced spectroscopists. Investigators thirty years ago or more did fine work just to establish that something like dual emission was present in rigid glasses at 77 K, even if there is more to the story in some cases. What is important today is that our own measurements confirmed that behavior at low temperatures is really not much different from results at room temperature, except to be even more convincing in showing a need for more than two discreet lifetimes. They swayed us further to the idea that the “dual” emission was not, strictly speaking, just dual.

While we were making cryogenic measurements, we thought it worthwhile to investigate a second issue that had worried us. Would the non-single-exponential emission be confined to dinuclear species and a few exotic, highly asymmetric mononuclear species; or would it turn out to be characteristic of all mixed ligand ruthenium complexes, but just be difficult to detect when different ligands are not greatly different? Still working at 80 K, we investigated five compounds, all in tributyl nitrile, all of which might be expected to show only single decay lifetimes: **2**, **3**, **9**, **10**, and **12**. Of these, **2** is the parent (bpy)<sub>2</sub>Ru(phen) and **10** and **12** have all three ligands the same and would exhibit single exponential decays by the arguments of the 1970s, even those that postulated charge localization. In contrast, **3** and **9** do have two bpy ligands along with a phen with greatly extended conjugation, but did not show dual emission in our earlier study [2]. For all five of these, two exponential fits were required at liquid nitrogen temperatures, mostly with lifetimes of 5–6 μs and 10–12 μs in approximately equal amounts. For these compounds, the lifetimes are similar enough and the change with wavelength is so small that no convincing evidence emerged for a need for more than two exponentials. The departures from single exponentials are certainly not large enough to have been convincing 40 years ago. We even looked at a sixth compound, Ru(bpy)<sub>3</sub> itself. Although one might argue for a better fit with two exponentials even in that case, the measurements we made did not (at that time and with the old apparatus) provide convincingly better  $\chi^2$  statistics for more than a single exponential with a lifetime  $5.5 \pm 0.1$  μs. One good aspect of this result for Ru(bpy)<sub>3</sub> is that the finding makes a very strong argument against any notion that all our results are simple instrumental distortions. Better measurements later, however, did show that even Ru(bpy)<sub>3</sub> can, at times, reveal heterogeneous lifetimes.

#### 4.3. Crystalline powders

One possibility for heterogeneous environments in glasses could be precipitation of aggregates of some sort, or even nanocrystals, as the solvent cools. We decided to characterize emission from crystalline powders at room temperature and above. Would they also show heterogeneous decays? These were investigated several times over some years using both the pulsed laser apparatus and the newer Pockels Cell method. Powders were placed into fused silica cuvettes of dimensions 2 × 10 × 40 mm<sup>3</sup> with a long neck and a tightly fitting stopper that allowed flushing with argon gas for 30 minutes. We quickly proved that deoxygenation had little, if any, effect for crystals; but we thought it best to eliminate any concern that quenching by dioxygen at crystal surfaces could produce varied lifetimes for emission. The last and some of the best data are displayed in Figure 3 for compound **3**. That particular compound in acetonitrile solution, according to our earlier report [2], gave only monoexponential decay from a single state (or, as we wrote at the time, perhaps two states in thermal equilibrium). We excited with pulses of duration about 200 ns at 532 nm from the new apparatus. We collected emission decay curves at 580, 610, 650, 690, 730, and 770 nm. We made measurements at ten degree intervals from ambient up to 80 °C.

Figure 3 shows luminescence decays for **3** on a log-linear plot as recorded at 30 °C. This choice of temperature is arbitrary; any other would serve as well. The curves are arranged by wavelength from 580 nm at

the top to 770 nm at the bottom. The curves have been normalized. Each should start at a zero on the vertical scale. The curves, however, are displaced to enhance visualization. The strongest signal occurred at 690 nm. For that curve, the total photon count at time zero was 87 000 recorded in a 0.1  $\mu\text{s}$  bin. Over the entire time record 4 773 966 photon counts were recorded from 2 million excitation sweeps. The full trace extended to 102.5  $\mu\text{s}$ , more than enough to prove that the constant background is perfectly flat, and that the random noise is due to shot noise proportional to the square root of the number of counts per bin. For the purposes of the figure (but not for curve fitting) the mean background was subtracted from the data. At 690 nm and the adjacent 650 nm and 730 nm curves, data are quite good over more than eight half-lives. The signals are much larger than the noise. Emission at 580 nm and at 770 nm is weaker. All assertions about amplitudes refer to data uncorrected for spectral response. The data acquisition employed was very good for constant response over each sweep of about 100  $\mu\text{s}$ ; but not so good for comparing measurements made hours apart. There can be slow drift. One should be cautious in comparing amplitudes at different wavelengths. It was, therefore, pointless to worry about trying to correct for detection sensitivity at each wavelength.

What is clear in Figure 3 is that the decays were not single exponentials. Two or more lifetimes were needed to fit the data. A log plot over so many cycles tends to compress the early, larger signals. At 580 nm, almost exactly half the emission is in the faster component, while at 770 nm barely one quarter is in the faster component. Almost all the curves displayed were fit adequately by using two exponential decays. “Adequately” means that the reduced chi-squared values are all less than 1.1, except for the case of 650 nm, where the value was 1.52. What is not so immediately apparent from the figure is that the two exponentials used in the fits cannot have the same lifetimes at all wavelengths. In order to obtain satisfactory fits with only two decays at each wavelength, the lifetimes must be allowed to vary. The faster component lengthened substantially, from 0.74  $\mu\text{s}$  at 580 nm to 2.93  $\mu\text{s}$  at 770 nm. The slower component increased from 4.82  $\mu\text{s}$  to 5.41  $\mu\text{s}$  over that range. When forced to a global fit having the same two lifetimes over the entire spectrum, the reduced  $\chi^2$  statistic increased to 6.6, which is intolerable. The virtue of rigorous photon counting is that we know the statistical uncertainty at each datum and we know that a reduced  $\chi^2$  value much more than unity means that the model is not fitting the data in the presence of the known noise. (Very noisy data give a  $\chi^2$  statistic close to unity for any model.) If the reduced  $\chi^2$  value is much above unity, the model is not correct; the fit is not adequate. The problem could conceivably be systematic noise that is not accounted for; but it cannot be random noise. Of course, exactly two decay components changing systematically at wavelengths measured every 30 to 40 nm across a broad spectrum seem unlikely, to say the least. Much more likely is a continuous distribution of lifetimes for single exponential decays, overlapping in various proportions at any particular wavelength. In that regard, the failure of even two exponentials, optimally selected, to yield a satisfactory reduced  $\chi^2$  value at 650 nm is diagnostic. That is reminiscent of the fits at liquid nitrogen temperatures described above. That 650 nm wavelength had a strong signal with good signal-to-noise, and it was in the middle of the wavelength range, where one might expect that any need for more than two decays would be most apparent.

Consider next how phosphorescence decays changed with temperature for this powdered sample. Initial amplitudes of the luminescence changed little or not at all (but we caution that we cannot compare amplitudes of runs collected hours apart). Proportions of fast and slow components changed only slightly with temperature changes. To make that quantitative, we fit all six wavelengths at each temperature to two exponentials, constrained to use the same two lifetimes at all wavelengths, in different proportions, for a given temperature. Lifetimes were allowed to vary at different temperatures, of course, as that is the whole point. Even though this is not the way to find the best fits at each temperature, it permitted some crude estimate of trends. The lifetimes obtained in this way changed at different temperatures and so did the relative fractions.

The fractions assigned to the faster component at six wavelengths and five temperatures are shown in Figure 4. It is apparent that longer wavelengths favor the longer-lived component; and there is not much change at different temperatures. All lifetimes get shorter, and decay rates get faster, at higher temperatures, as is illustrated in Figure 5. The plot could be used for analysis in terms of an Arrhenius model, although it can be deceptive to do that unless one is confident the rates being considered characterize a well-defined, unique process. In any case, lifetimes changed by less than a factor of two between ambient and 80 °C for compound **3** as a powder. Any activation energy for whatever is rate limiting must be small. Since we already argued that the evidence is against two unique lifetimes at any particular temperature, it is risky to try to ask whether two components change in parallel or one is more affected than the other. The problem with fitting multiple exponentials is that the parameters are not mathematically independent. We emphasize that this compound, **3**, offered no apparent evidence for “dual” emission in acetonitrile solution in our earlier study. As a powder, and with new and better methods, dual—actually multiple—emission was quite apparent. For the dinuclear species, attachments at the 3- position always did give dual emission; but the dinuclear species might involve different issues.

Consider the case of **1**, Ru(bpy)<sub>3</sub> itself. Figure 6 displays decay curves for a crystalline powder of that compound. As before, this is a log-linear plot for six wavelengths, with curves offset. The time axis displayed is only 10 μs, although data were collected over a much longer interval. The sample crystals were deoxygenated with argon sparging; but results in air were not significantly different. The figure shows data collected at 50 °C, selected arbitrarily from measurements made at ten degree intervals from ambient up to 80 °C. As with compound **3** powder, two-exponential fits were required to obtain satisfactory reduced  $\chi^2$  parameters for goodness of fit, and lifetimes must be allowed to vary with both wavelength and temperature. Fast and slow components differ in lifetime by only a factor of two. The figure shows that shorter wavelengths have somewhat more of the faster decaying portion, but it is only a modest difference. For the data in the figure, the shorter lifetimes were all close to 0.6 μs and the longer components all close to 1.2 μs. There was only a slight change with temperature. Over the entire range, the change was about 200 ns decrease for the longer component and about 100 ns for the shorter component. There was, however, a shift in relative proportions. The fraction of the fast component decreased from about 0.6 at ambient down to about 0.35 at 80 °C. At the intermediate temperature illustrated in Figure 6, the two components were very close to equal in amplitude. In the past, no kineticist would attempt to fit two lifetimes so close together; but with photon counting and two million sweeps, there is no question that at least two lifetimes are needed to fit each curve and they must be allowed to vary; there cannot be just two unique times in different proportions. More likely, there is a continuum of lifetimes that change with wavelength.

#### 4.4. Suspensions of colloidal particles in liquids

If crystals always show “dual” (and now it seems a continuum of) lifetimes, we were driven to ask: Could apparently anomalous observations in liquid solutions be due to aggregates, either colloidal nanocrystals or smaller entities? We investigated that question in several solvents, including some that are not good solvents for our compounds. The ruthenium complex ions dissolve quite well in acetonitrile and a number of other polar organic solvents, but they do not dissolve so well either in water or in nonpolar liquids such as tetrachloromethane—and how certain are we about the species actually present even in “good” solvents?

We studied phosphorescence decay kinetics in different solvents for **1**, Ru(bpy)<sub>3</sub>, as one of the last projects carried out with the old nanosecond pulsed laser excitation. Our choice of this compound was partly due to curiosity as to whether even it would show some evidence for dual or multiple emissions in solution, as

it quite clearly did as a crystalline powder; but it was also because other compounds that already show “dual” emission in solution might not reveal much further difference due to any possible suspended colloids. The Ru(bpy)<sub>3</sub> complex does not absorb well at 530 nm, but we wanted to excite at that wavelength in order to favor any long-wavelength, slow decaying component that might exist. We made solutions as concentrated as 2 mM (when possible) and dilutions thereof in various solvents. We investigated 10 polar solvents along with two nonpolar solvents, at various concentrations. We measured air-saturated solutions and deoxygenated solutions. We also used that opportunity to compare argon sparging with multiple-cycle freeze-pump-thaw methods for deoxygenation. We convinced ourselves that at least out to a few tens of microseconds, thorough sparging and multiple-cycle freezing were equally effective at removing oxygen. We also investigated the effects of filtering solutions through fine filters, which should remove large colloids.

For the polar solvents tested, there was no convincing evidence for anything other than single lifetimes in **1**. This is persuasive evidence that our methods do not produce multiple exponential fits unless the data require them. It was reassuring that in the case for which monoexponential decay kinetics were most likely, that is all that we saw, at least with the capabilities of the old apparatus, which was probably comparable to or better than any used in prior studies. Were there, however, any subtle hints of a need for more than single exponentials? In deoxygenated acetonitrile, the lifetime was 0.91  $\mu\text{s}$  within 0.01 or 0.02  $\mu\text{s}$  at all wavelengths. Any second exponential allowed in the fit contributed less than 1%. At that level, one might, perhaps, postulate an impurity or a small aggregate. Difficulties in determining tiny amounts of very slow decays represent one of the problems with oscilloscope methods that led us to turn to photon counting. In deoxygenated methanol, fits behaved the same with a lifetime of 0.736  $\mu\text{s}$  varying no more than 0.002  $\mu\text{s}$  at different wavelengths from 580 nm to 750 nm. In water, with added sodium chloride salt, good single exponential fits gave a lifetime of 0.66  $\mu\text{s}$  at all wavelengths. In deoxygenated *n*-butanol, the single lifetime was always very close to 0.776  $\mu\text{s}$ . Deoxygenated solutions in *n*-propanol gave lifetimes of 0.71  $\mu\text{s}$  with some evidence for slightly shorter lifetimes at shorter wavelengths and slightly longer lifetimes at longer wavelengths over the range 590 nm to 710 nm. Isopropanol solutions gave single lifetimes between 0.71 and 0.68  $\mu\text{s}$  over the range 590 nm to 720 nm, but with the slightly longer lifetimes at shorter wavelengths, contrary to all other known instances. Ethanol gave lifetimes between 0.709 and 0.717  $\mu\text{s}$  for seven wavelengths between 580 nm and 720 nm, increasing slightly toward longer wavelengths. Very few lifetime studies attempt to make arguments dependent upon 1% or 2% changes in the lifetimes. A second series in ethanol, similarly sparged, but perhaps with more complete removal of oxygen, gave values between 0.720 and 0.723  $\mu\text{s}$  over the same wavelength range, with no pattern. Measurements in dimethylformamide gave lifetimes near 0.91  $\mu\text{s}$ . In dichloroethane under deoxygenated conditions fits gave a major component at 0.64  $\mu\text{s}$  and sometimes used a second exponential to accommodate less than 1% of a slower decay. However, fits sometimes converged to a two quite similar lifetimes, each just slightly longer or shorter 0.64  $\mu\text{s}$ , which might hint at slight heterogeneity. When fit to single exponentials, moreover, there was a trend from slightly shorter to slightly longer lifetimes between 580 nm and 750 nm. Such a trend is often the first hint of heterogeneity. Chloroform, which is not very polar, gave lifetimes that scattered slightly more than did the other polar solvents, but still with values between 0.85 and 0.87  $\mu\text{s}$ . Fits for chloroform were not really satisfactory singles, and did provide some hints of a need for double exponential fits. It may be significant that what little evidence there was for anything anomalous came with this solvent; but it was all very subtle. In air-saturated solutions of all these solvents, single exponentials were always adequate; but then one expects that quenching would make slightly different lifetimes become even more similar. Filtering solutions in these polar solvents had no significant effect. We caution that filters can introduce artifacts. Many are designed for aqueous solutions. Water and ethanol solutions generated no problems. We had more than one filter type available, including some intended for organic solvents. Some of

the solvents (chloroform and *n*-propanol among others) produced poor data with some filter materials. Filters can release fluorescent impurities, albeit with nanosecond lifetimes; they can retain solutes by adhesion; they can dissolve and fail completely. After this effort, we are confident that data showing “dual” emission in any reasonable solvents are not just measuring emission from colloidal particles that are large enough to behave like crystalline powders.

In nonpolar solvents, such as tetrachloromethane, things were quite different, even for Ru(bpy)<sub>3</sub>. We suggest that this is a poor solvent and we probably had aggregates that are not evident in better solvents. Mixed hexanes and even a higher alcohol, *n*-hexanol, were similar. Plots of decay kinetics were not single exponential, being obviously curved on semi-log plots. Two components for tetrachloromethane solutions had lifetimes of about 0.14 and 0.84 μs, but varied somewhat from run to run. It is noteworthy that these values applied to samples equilibrated with air as well as deoxygenated samples, which is strong evidence that we were not observing molecular solutes. These samples in poor solvents, prepared initially at quite high nominal concentrations, were solubilized by extended sonication. Initially, they were often cloudy, but they clarified overnight, either by slow dissolution or by sedimentation of the largest particles or both. We made some measurements soon after sonication, but mostly we waited overnight. We also tried filtering with micropore filters down to pore diameters of 200 nm in order to eliminate large colloidal particles. Of the filter materials we tried, Teflon filters gave the cleanest data, which is no surprise. In all cases, fits for these poor solvents, even after settling and/or filtering, clearly required two or more lifetimes, although what the best fits were varied from run to run. From this effort, we infer that with enough effort (or by being sufficiently careless) one may get large colloids that show powder-like luminescence, if one fails to wait for sedimentation and does not filter. Much worse, there can be very small colloids that pass filters and show non-single-exponential behavior, even for compounds like Ru(bpy)<sub>3</sub>. This is, however, not a concern in any but the poorest solvents. In very poor solvents, the aggregates, if that is what they are, must be rather tiny nanocrystals or oligomers. Efforts using dynamic light scattering to characterize the size of any nanocrystals present in apparently clear solutions were not successful. That would be consistent with the fact that the solutions had passed through fine filters. Neither light scattering nor filtration can identify dilute aggregates only a few nanometers in size.

#### 4.5. Solvent effects on molecular spectra for good solvents

Should “dual” emission be affected by solvent? Aside from concerns about solubility in nonpolar solvents, there are, in some cases, dramatic effects due to changes in solvent. It is surprising that our literature review above did not turn up mention of this. Perhaps we missed something, but it is clear this is not well known—and that we still have much to learn about ruthenium complex ions even after almost 50 years. Figure 7 illustrates luminescence spectra for an extreme case, the dinuclear compound, **13**. Excitation was at 450 nm in the blue, which favors the shorter wavelength emission feature. These are corrected spectra, using manufacturer supplied factors, and cannot be compared in detail with amplitudes in kinetic measurements. In acetonitrile, emission was predominately the shorter wavelength, faster decaying feature. In dichloromethane, emission was biased toward the long wavelength, slower decaying feature. Two different alcohols and water fall in between, showing comparable signals at both wavelengths. This behavior does not have an obvious, simple interpretation in terms of relative amounts of solvent stabilization of excited and ground states. Charge transfer transitions often do change with solvent, but the expected behavior is a shift in the position of the transition due to preferential stabilization of either the excited or the ground state. Here, we do not have much of a shift of the transition energies; rather we have a change in the relative amounts of two features, each of which is affected only slightly. Furthermore, the two peaks move in opposite directions in different solvents. There is a blue shift with increasing solvent polarity for the short wavelength feature and a red shift for the



long wavelength feature. Yet they both involve charge transfer states. That the two emission peaks are two different features was demonstrated conclusively by lifetime studies. That was the beginning of the entire project. More studies of various effects on emission spectra were provided in another place along with data about changes seen also in absorption spectra [53]. The spectra in Figure 7 were obtained for concentrations of  $2.2 \times 10^{-6}$  M. At that low concentration, there are no inner filter effects, although such do come into play and distort emission spectra at higher concentrations. One might worry about aggregation. In these good solvents (but not in the “bad” solvents discussed above), NMR spectra were recorded at concentrations a hundred to a thousand times more concentrated without evidence of anything but monomeric solutes. Absorption spectra at higher concentrations, likewise, gave no evidence for aggregation in these solvents.

#### 4.6. Phosphorescence decay kinetics of dinuclear compounds

We turn finally to where we started, the matter of phosphorescence decay kinetics of ruthenium complex ions in fluid solution, near and somewhat above ambient temperature. In all cases below, except as noted explicitly, we are discussing samples deoxygenated by multiple freeze-pump-thaw methods and using high-repetition-rate Pockels Cell methods with photon counting. We begin with dinuclear compound **13**, one from our first report, and the one with the phosphorescence spectra shown in Figure 7.

We measured decay kinetics for compound **13** at six or seven wavelengths from 590 nm to 770 nm in acetonitrile, dichloromethane, methanol, and water, all under oxygen-free conditions. We expected dual emission, but would there be evidence for a continuum of decay rates, as there had been in cold glasses and in powders? This was one of many instances in which we tested both long-stored solutions and freshly synthesized and dissolved samples—and found no differences. We also explored the effect of adding excess amounts of different salts. Aqueous solutions required added salt for acceptable solubility of the compound, which had been isolated as the  $\text{PF}_6^-$  salt. Figure 8 shows eight decay curves recorded in methanol at ambient temperature for seven different wavelengths, 590, 610, 650, 680, 710, 740, and 770 nm. The curve for 680 nm was measured first and then repeated at the end. The two superimpose themselves on the plot to such an extent that one cannot see any difference whatsoever. This repetition was done mostly to ensure that there was no oxygen leakage during the run, but it also tested the stability of the optical setup. We recorded while skipping back and forth in wavelength in order to avoid any artifact introduced by measuring progressively from shorter to longer wavelengths, or vice versa. For the purposes of the figure, the small, constant baseline offset was subtracted so that single exponential curves must be perfectly linear on the semilog plot vs. time. For the actual curve fitting, the offset is included in the fit itself. Furthermore, data before excitation and at long times were removed from the figure. As always, the reduced  $\chi^2$  statistic should be near unity for good fits. If we insist that there should be only one, unique lifetime at all wavelengths, the global fit yields a lifetime of  $1.48 \mu\text{s}$  with  $\chi^2 = 131$ . If two unique exponentials are used in a global fit of all eight curves, the lifetimes derived are 1.24 and  $3.95 \mu\text{s}$ , in various proportions, with  $\chi^2 = 7.56$ , still quite poor—indeed, totally unacceptable by the F-statistic. The shorter decays predominate at all wavelengths in this solvent, and there is a monotonic increase in the fraction of the longer-lived component as one goes to longer wavelengths. One must not make too much of the exact values of fits in cases like this. On another day, the general behavior was similar, but both the lifetimes were faster but the fraction of the faster portion was smaller to compensate. This is to be expected. Multiple exponentials do not constitute orthogonal basis functions. In fitting, one can change one parameter slightly and the other parameters adjust to compensate. Whatever the exact parameter values are, the important point is that the fit constrained to two unique lifetimes for a global analysis at all wavelengths is not close to adequate. Acceptable fits require either allowing two lifetimes to vary at different wavelengths, or using more than two decay times at some or all wavelengths, or both. If there is in reality a single lifetime for each individual solute

molecule, but it changes from molecule to molecule, distributed with a continuous, but bimodal, distribution, then we would expect that the extreme wavelengths (590, 610, 740, 770 nm) might be adequately fit by only two exponentials, because at the extremes, the lifetimes for the opposite extreme would have little amplitude. It is for the middle wavelengths that contributions would be expected from the middle lifetime values along with components also from both the shorter and longer extremes. That is exactly what we find. If we try to fit with two exponentials plus the base offset, allowing lifetimes to vary, even the extremes of 590 and 770 nm do not have really good  $\chi^2$  values, as they are above 1.5; but such modest deviation from unity gives only a weak argument from F-statistic analysis for any need for a third component. The intermediate wavelengths, however, were very poorly fit by using just a double exponential. The worst case was the fit at 650 nm, where  $\chi^2 = 4.8$  for a double exponential, while it was 0.93 for a triple. Fits at 610, 680, 680 (repeated), and 710 for double exponentials all gave  $\chi^2$  values above 3 and even at 740 nm, it was still well above 2. Of course, the middle wavelengths are also the ones at which the noise is least and the signal is best. If one's data are noisy enough, then one can always get by with just double exponentials—or even single exponentials, if data are truly deficient.

Still, no matter how convincing the statistics of one half-day run might be, we would not draw conclusions from that alone. It was dozens of runs over months and years all giving similar results that convinced us that something in solution was causing truly heterogeneous decay curves. The better were the data by independent criteria, the more evidence there was for this hypothesis. Measurements have to be truly wretched to believe that two unique lifetimes could suffice for dinuclear compound **13**.

The effect of changing solvents among the four listed above was to vary the distribution between longer and shorter emitting components and the exact values of lifetimes; but otherwise, all solvents listed behaved in similar fashion. Dichloromethane gave more of the slow component (or components) and acetonitrile gave even more of the fast component than did the methanol used for Figure 8. Both results are consistent with the spectra in Figure 7. In contrast, the effect of added salts was modest—disappointing, if one hoped for some dramatic effect. Even so, the effort to vary conditions widely led to many measurements, all supporting the argument in the preceding paragraph. This dinuclear compound does not just show “dual” emission; it exhibits something more complicated, namely, lifetimes varying in a continuous distribution that is bimodal, that is, centered around two distinct maxima.

We knew from our very first work that the dinuclear complexes would probably not fit two, unique lifetimes when data were improved. In our first report [1], we asserted that two exponentials may be adequate, only because we took a conservative view when proposing novel behavior.

#### 4.7. Phosphorescence decay kinetics of mononuclear compounds

With the question of “dual” vs. a “continuum of” emissions settled for the dinuclear cases, the next question was whether the phenomenon is limited to dinuclear and, perhaps, some few mononuclear species, or all ruthenium compounds might show such heterogeneous behavior, even if it may be easy to overlook unless one's apparatus is very good and the emission peaks around two very distinct wavelengths and lifetimes.

The first compound investigated with the new apparatus was **6**. This compound, which had shown dual emission in acetonitrile solution in our previous report [2], was investigated this time in methanol, in methanol with added NaCl, and in water with 0.1 M KNO<sub>3</sub>. All were similar, but the last received the most attention. Satisfactory fits required not only three exponentials but liberty to vary all three lifetimes, even if they did not vary much. Decay curves were collected for 570, 610, 650, 690, 740, and 790 nm. Global fits constrained to

use three exponentials with the same lifetimes at all wavelengths plus a constant offset were tried and gave lifetimes of 0.93, 4.21, and 7.50  $\mu\text{s}$ . The fastest decay contributed 55% of the initial amplitude at 570 nm and decreased dramatically through 35%, 10%, 6%, 6%, and 3.6% as wavelengths increased. Almost all of the remaining amplitude was assigned to the middle component. The slowest piece contributed 2% at 690 nm and almost as much at 650 nm, decreasing to less than 0.1% at the extreme limits. This global fit constrained to use three unique lifetimes (plus a constant offset), even with the freedom to exploit seven variable parameters, was not at all good in a statistical sense, as it gave a  $\chi^2$  value of 38. Allowing lifetimes to vary at each wavelength reduced  $\chi^2$  dramatically, but did not alter the lifetimes very much from those of the global fit, which demonstrates that the noise was so small that curve fitting provides a very critical test of any proposed model—and that lifetimes are probably drawn from a continuous distribution and not any small number of exponential decays. The two other solvents gave almost identical results. Some instances were improved using four exponentials, but this has no interpretation beyond a further proof that lifetimes are not unique values but are drawn from a continuous distribution.

Since this was the first effort with the new apparatus, and since it worked so well, we examined the same samples using the old apparatus and obtained the same results, despite its limitations. This was, in fact, the sample used to test for any nonlinear effects due to peak excitation irradiance at very high power, as described in Section 4.1. We also took advantage of the excellent statistics to search for any changes with concentration (over a modest range around the values we were using, in the micromolar regime). There were no concentration effects for this system, at least at the low micromolar level.

We went on to other mononuclear compounds. Compound **8** was measured in propylene carbonate at temperatures up to 80  $^{\circ}\text{C}$ . It had previously shown dual emission in acetonitrile [2]. This time, it showed predominately a long lifetime of about 5.5  $\mu\text{s}$  at seven wavelengths at room temperature, but definitely needed a shorter component of about 2  $\mu\text{s}$  for the shorter wavelengths of 590 and 610 nm. The long lifetime decreased to 4.55  $\mu\text{s}$  at 80  $^{\circ}\text{C}$ . It is almost impossible to obtain precise values for a small amplitude, short lifetime component when it appears on top of a large, slow signal, which has its statistical noise obscuring the small fast signal. At 70 and 80  $^{\circ}\text{C}$ , fits did not really need a fast component. Although this is an asymmetric compound with substitution at the 4- position, extended conjugation is minimal. Even so, there is dual emission. Were two unique lifetimes sufficient? Not at all. If fits were constrained at each temperature to require the same two lifetimes in various proportions at all wavelengths, the  $\chi^2$  values are not good. At some temperatures, they were above 30.

Compound **7**, with extended conjugation at the 4- position of the phen, should offer strong evidence for dual emission, and so it did. In propylene carbonate a longer lifetime of about 5.25  $\mu\text{s}$  predominated at all wavelengths at 22  $^{\circ}\text{C}$  but there was 28% of a 1.1  $\mu\text{s}$  lifetime at 590 nm and 14% at 610 nm. Fitting to a variable single exponential gave  $\chi^2$  values above 5 at all wavelengths, whereas fitting to two variable exponentials reduced  $\chi^2$  to values slightly above or below unity. Essentially the same was true at all temperatures. There was no need for triple exponentials. Even fitting with the constraint that two unique lifetimes be used for all wavelengths at a given temperature gave quite nice fits, with  $\chi^2$  only moderately above unity. This is one case in which a conventional dual emission model would be adequate. In terms of a continuous distribution, it suggests that the bimodal distribution is sharply peaked around two modes. With two lifetimes shown to be sufficient for a global fit it was reasonable to think of analyzing the temperature dependence. The longer lifetime, which was 5.25  $\mu\text{s}$  at 22  $^{\circ}\text{C}$  decreased strictly monotonically until it was 4.71  $\mu\text{s}$  at 80  $^{\circ}\text{C}$ . The shorter lifetime also decreased strictly monotonically over the same range, from 1.11  $\mu\text{s}$  to 0.17  $\mu\text{s}$ . The long lifetime shows a rather small change that requires minimal activation energy for whatever

is rate limiting. The shorter component has a larger activation energy, possibly due to decay through a higher-lying state.

We already knew, however, that asymmetric substitutions at the 4- position of the phenanthrene ligand, gave “dual emission” (now probably “multiple emissions” in many, if not all, cases); but what about substitution in the 3- position? What about compound **3** in solution? It did not show convincing dual emission in our earlier report [2]. That compound was the subject of Figure 3 for a crystalline powder. We examined it also as a solute in propylene carbonate. This solvent allows the broad temperature range needed for compounds that change so little with temperature. Not only did we now resolve dual emissions, attempts to fit all wavelengths at a given temperature with just two lifetimes failed badly, except at 60 °C and above. That is no doubt due to the fact that at those high temperatures, the fast component reduces to a short lifetime and a small amplitude. When lifetimes were allowed to vary, two exponential fits gave lifetimes slightly above 5  $\mu$ s for the longer component and near or below 1  $\mu$ s for the shorter in complex patterns that suggested that the fits are really more complex. So with improved methods, at least some compounds that we could not say showed dual emission in the past now turn out to have such. This one, **3**, is asymmetric, but at a position that is less influential than the 4- position.

One of the most important issues was whether there might also be small, but measurable amounts of dual or multiple emission in solution even for symmetric species, as there was for their powders. Compound **9** was investigated. It has extended conjugation at both 4- and 7- positions of the phenanthrene. Similar substitution was effective in spawning dual emission for the asymmetric case that involved only the 4- position (compound **4**); but **9** differs in having the same substituent also at the 7- position. In previous work in acetonitrile, **9** gave only a single exponential decay [2]. We measured **9** this time in five different solvents. In acetonitrile, as before, single exponentials provided excellent fits at 590, 610, 650, 680, 710, 740, and 770 nm, along with a repetition of the 680 nm run. Lifetimes determined by fits to a single exponential plus a constant offset were 6.57, 6.58, 6.56, 6.55, 6.58, and 6.58  $\mu$ s in that order, along with 6.59  $\mu$ s for the extra run at 680 nm. That was impressive consistency. The first evidence of dual emission is usually that lifetimes change with wavelength; these did not. The  $\chi^2$  values were all near unity, with some slightly above and some slightly below, as they should be for random statistics. The decay curves are shown in Figure 9. For the figure (but not for the curve fitting), the constant baseline offset was subtracted and the file was truncated at both ends. In methanol, the story was the same as in acetonitrile, with single lifetimes all between 5.46 and 5.51  $\mu$ s. In water, the single lifetimes were shorter, between 2.56 and 2.58  $\mu$ s. In dichloroethane, lifetimes were much longer, near 10.2  $\mu$ s, but still single exponentials. In propylene carbonate, lifetimes varied somewhat more, ranging from 4.17 to 4.53  $\mu$ s. There was even some suggestion of a small amount of a fast component, but it was statistically significant only at middle wavelength values. That solvent was used for measurements at seven temperatures ranging from 22 °C to 80 °C. All behaved much the same; and there was almost no change in lifetimes. Whatever mechanism is rate limiting and accounts for the lifetime, it appeared to have only a small activation energy. We also studied temperature variations in other solvents, but aside from water the accessible range is rather limited. In all cases, lifetimes did shorten at higher temperatures but only very modestly.

Compound **11**, which is similar to **9** but without the extra ethynyl linkers, gave rather similar results, albeit with slightly more evidence for nonexponential behavior, but only modest evidence for two distinct states. It was more suggestive of site heterogeneity in a single feature. In water, single lifetimes all fell within the range 1.62 to 1.68  $\mu$ s for seven measurements between 590 and 740 nm and gave acceptable  $\chi^2$  values in most cases. There was a trend toward shorter lifetimes at shorter wavelengths and longer lifetimes at longer wavelengths. In methanol, single exponentials with lifetimes near 2.03  $\mu$ s were mostly adequate except at the

longest wavelengths, where a small admixture of something slower might be indicated. In acetonitrile, single exponentials gave excellent fits at wavelengths from 590 to 740 nm and temperatures from 22 °C to 50 °C. Lifetimes at the lowest temperature ranged from 2.34 to 2.36 μs. They decreased to become 1.44 or 1.45 μs at 50 °C. For **9** in dichloromethane, however, single exponentials were not adequate. The  $\chi^2$  statistics were all between 2 and 3. Double exponentials gave 90% or more of a lifetime near 1.25 μs and 3 to 11% of a longer lifetime of about 2 μs. Perhaps dichloromethane shows some slight evidence for the behavior that was more prominent in chloroform and very prominent in tetrachloromethane, in which we saw evidence for aggregation.

Of course, we also had to try Ru(bpy)<sub>3</sub> in solution yet again. We studied this compound, **1**, with the Pockels Cell apparatus using “good” solvents and focusing on the effect of changing the sample temperature. We found very similar results for acetonitrile, our favorite solvent, and for propylene carbonate, a pretty good solvent useful over a wider temperature range. In both cases, single exponentials were almost adequate and showed no wavelength variation. In acetonitrile, the decay time was about 0.90 μs at 22 °C, and became steadily shorter as temperature increased until it was about 0.51 μs at 50 °C. In propylene carbonate, the decay lifetime was about 0.95 μs at 22 °C and decreased monotonically to 0.15 μs at 80 °C. The only hint of anything unusual was about one per cent, or even a little more, of a slower decay at ambient conditions, very roughly 1.5 μs in acetonitrile and about 3 μs in propylene carbonate. It would be tempting to attribute such a tiny piece to deficiencies in the “turn-off” of the Pockels cell. We cannot exclude that possibility altogether; but there are two arguments against such an artifact. It would be coincidence that the longer artifact appeared in the case for which the main decay time was also longer; but it is possible. More noteworthy is the fact that as the temperature was raised, the amount of the slow piece always decreased ten-fold, down to 0.1 or 0.2%. Since the optics were aligned at the beginning, and the temperature started at ambient and then increased, one would expect any drift to get worse, not better, over the course of a few hours. In contrast, any minute fraction of mysterious aggregates might well be reduced at high temperature. We do not want to overemphasize such subtleties. The main point is that any heterogeneity is at the level of fractions of a per cent. This is very different from the situation with Ru(bpy)<sub>3</sub> in powders or poor solvents. We investigated other compounds in a variety of solvents, with and without added salts; but we do not have space here for more.

## 5. Weighing the options to explain dual or multiple emissions

How should we understand the heterogeneous decay kinetics of phosphorescence in ruthenium complex ions, even in good solutions at ambient conditions? A definitive conclusion is not yet available, but we have new ideas to propose. Let us frame this discussion as a series of questions.

1. For the rather typical ruthenium complex ions discussed in our own work, whenever dual emission is observed, should one assign all emission to spin forbidden phosphorescence originating in <sup>3</sup>MLCT states? Yes, microsecond lifetimes with respectable luminescence yields cannot be due to any other species. With more extended conjugation, one might observe phosphorescence from intraligand states or mixed states; but unless they are predominately <sup>3</sup>MLCT in character, they will have smaller radiative rates and either markedly longer lifetimes or much lower quantum yields.

2. When dual emissions occur, is each <sup>3</sup>MLCT state localized somehow on a single ligand? Yes, there is no other way to distinguish multiple <sup>3</sup>MLCT states of similar energy except to involve orbitals localized in different places, either on different ligands or different portions of the same ligand, at least for simple compounds. This terminology, however, may be overly simplistic in explaining emission from dinuclear compounds.

3. Over microsecond times, surely excited states of the same character localized on different ligands must interconvert by exciton hopping, right? No. Some may, but the dual emitters we investigated have different decay times at different wavelengths. There cannot be interconversion on time scales less than microseconds. For the homoleptic cases and a few others that do not show apparent dual emission in fluid media, we do not know whether localized excitation might hop from ligand to ligand, if all would have the same spectra and the same lifetimes. There were suggestions decades ago (and more recently, in some cases) that such states will interconvert; but that may be assumption more than experimental data. It is not clear that older work was able to distinguish lifetimes that differ only slightly.

4. Why speak of dual emission at times, but then insist that the emission is not simply dual? Emission in some complexes, in glasses, in crystals, and in ambient solutions, shows bimodal spectra centered around two obviously distinct wavelength maxima, which have different lifetimes and different excitation spectra. The evidence, however, is overwhelming in most, if not quite all, cases that there are not two unique lifetimes but rather distributions of lifetimes. There is, presumably, also a continuous range of subtly different, overlapping spectra for both excitation and emission, but that is more difficult to measure directly.

5. For the homoleptic species and those heteroleptic cases that did not show bimodal distributions, are there subtle variation of lifetimes around unimodal means? Some cases clearly did show detectable variations in lifetimes. This was true for crystalline powders, for what appears to be nanocrystalline colloidal powders in “bad” solvents, and even in some cases for solutes in what appear to be good solutions. However, a few cases do present only single exponential lifetimes at the best precision we have yet achieved.

6. What is the reason to propose a distribution of lifetimes with exponential decays that are different for each different emitter, rather than complex, nonexponential decay of identical emitters? At the ensemble level, the observed signals can be described as nonexponential; but can that apply to an individual molecule? It might be conceivable that something about an individual molecule changes either the radiative or the nonradiative rate constants during the lifetime of the excited states. That does occur with TICT behavior, slow excited state tautomerism, and the like; but those are not possible in the examples we are stressing. Furthermore, they usually show rise and fall times as one species evolves into another, which our examples do not. The heterogeneous behavior we measure is most apparent in rigid media where such processes are inhibited. One might also invoke a bimolecular process such as triplet-triplet annihilation; but that again is not possible in rigid media and should not be possible at the low concentrations used in our studies. It does not fit the full decay profiles and so could be only a partial contribution in any case. We cannot think of a reason for consistently nonexponential decays that would apply broadly. If someone else can, we welcome the suggestion. For now, heterogeneous lifetimes in a continuous distribution centered on one (sometimes) or two (often) main species seems most plausible. Continuous distributions can be characterized in various ways, but that is a topic not yet treated in the primary literature and, therefore, not appropriate for this review.

7. What was learned from rigid glasses at liquid nitrogen temperatures and from crystalline powders, either neat or present as colloids in bad solvents? All these, even something as simple and symmetric as  $\text{Ru}(\text{bpy})_3$ , can show multiexponential decay in some instances. We look for an explanation in terms of site heterogeneity.

8. When there are two  $^3\text{MLCT}$  species with distinct spectra, as in Figure 7, and distinct lifetimes, where are the two states localized? In our earlier reports we proposed, albeit tentatively, that at least for the mononuclear species one (lower energy) emitting state might be localized on the substituted phen ligand and the other on one or both of the bpy ligands [1,2]. Others have proposed the same, as

reviewed above. Additional support for that idea comes from very recent ultrafast studies that gave evidence for one compound that localization occurred in less than a picosecond in approximately equal amounts to either one of two bpy ligands or the third ligand, a tpy [51]. Subsequently this initial branching ratio relaxed to a distribution that favored the tpy state more, but still left significant occupation on the bpy. That was complete in less than 20 ps, a time that may suggest that solvent reorientation participates. The populations then remained unchanged at least out to hundreds of picoseconds. Those data are consistent with our conjecture, made before the data were known. There remains, however, a huge difference between one nanosecond and tens of microseconds. Why does excitation in our compounds not settle eventually into the lowest available state or a Boltzmann equilibrium among all accessible states and then decay with a single lifetime? In fact, the authors of that ultrafast work explicitly assert that they expect Boltzmann equilibrium eventually. How can we have two states that look for all purposes like they belong to two different molecules? And why do the proportions of the two states change with solvent polarity (or other solvent properties)? And why do we almost always find a continuum of states with slightly different decay profiles?

9. Could both localized excited states be centered on the phen ligand? That may be a possibility. It could be that excitation does evolve onto the phen over some picoseconds or a few nanoseconds but that there are variations possible in the orbitals. This might account for the fact that asymmetric substitution at the 4- position of the phen ligand gives prominent dual emission in all cases, while symmetric substitution at both the 4- and the 7- positions gives no evidence for anything but one phosphorescent emitter, in five different solvents. This idea would have the benefit that phosphorescence would always occur from what we expect to be the lowest state, localized on the phen ligand, of any given molecule. It is just something about the environment that dramatically changes the character of that lowest state in different molecules in the ensemble. We do assume that in any individual molecule, excitation does end up on the lowest excited state, whatever that is.

10. How, ultimately, does one account, in so many compounds, for two populations of low-lying excited states that have different excitation spectra and different emission spectra, in proportions that are different in different solvents, and also have markedly different lifetimes, which proves that they do not interconvert on the time scale of emission? Furthermore, how does one also account for the fact that the lifetimes (and, presumably, the spectra) of the two species are heterogeneous within the two main types, and that even species that have single (or unresolvable) emissive states sometimes show heterogeneity in their lifetimes? We believe that nature is providing a hint: the same explanation must explain all features. We hypothesize that environmental heterogeneity certainly exists in solids, both crystals and glass solutions, and also exists even in good liquid solvents, so that for many microseconds they act almost like rigid glasses; but at longer times they rearrange as a proper liquid should. Some of the otherwise identical ruthenium complex ions have an excited state at lower energies and others have an excited state at higher energies because they exist in different environments. There is no exciton hopping, because the states really are on different molecules. These are not excimers, because their excitation spectra are different and there is no slow risetime. Furthermore, whether there are one or two basic forms, there are no well-defined structures, so that there are small variations in spectra and decay rates around the mean values. This may not be so farfetched. We should expect solution environments to have some slight variations. Much ultrafast work has explored solvent relaxation in the picosecond time regime. The unusual thing here is that the solvent environments persist so long. These environments seem to be analogous to different environments in crystals or in glasses, if one can judge by the decay kinetics. In other words, there really are different populations in solution, but for a reason different from previous suggestions, which

focused exclusively on chemical impurities and isomers. The heterogeneous species must interconvert on sufficiently long time scales, so that any attempt to isolate them by separation, or any effort at preferential photobleaching is doomed to fail. There is one other clue. The states involved are charge transfer states. They may be very sensitive to counterions that might be present in ion pairs. We teach freshman chemistry students that van't Hoff factors for colligative properties of ionic solutes in solution are never really as large as one expects from naïve stoichiometry, even in water. Glucose has a unity factor, but even NaCl has a factor below two. Workers in photophysics tend to ignore this unless there is an obvious change in the absorption spectra. Perhaps we need to give it more thought. If ion pairing is readily measurable even for alkali halides in water, what should we expect for large, complex ions in organic solvents? An anionic counterion positioned near a ligand would destabilize electron transfer toward that ligand and encourage transfer to some other ligand. This would affect both excitation and emission spectra. If this is possible, would it not be expected that the detailed properties could, and probably should, vary in a continuous fashion, but be centered around two main alternatives when two alternatives clearly exist? On what time scale would ion pairs rearrange?

11. What was learned from measurements in which anions like  $\text{Cl}^-$ ,  $\text{PF}_6^-$ , and  $\text{NO}_3^-$  were added to solvents in amounts ranging from 0.01  $M$  to 1  $M$ ? We found that we had to add NaCl to water to obtain suitable solubility of some Ru(II) complexes that had been isolated as  $\text{PF}_6^-$  salts. That suggested investigating what salts might do more generally. One idea was that perhaps one of the two emission features was from ion pairs and the other from solutes without nearby ion partners. Then adding salt would favor one or the other feature. That did not turn out to be the case, at least not in any very dramatic way. Extra salt caused modest effects, even at concentrations orders of magnitude higher than the ruthenium ion concentration. This suggested that if ion pairing has anything to do with dual emission, then a large fraction, perhaps even a majority, of solutes exist as ion pairs, even without added salt. Unfortunately, we were unable to work in water without added salt. That might have been the one case that would have had the best chance to minimize ion pairing.

12. Did variable temperature studies clarify what ultimately determines the lifetimes of the emitting states? Well known decay mechanisms have been discussed elsewhere in more detail, including a summary by one of us [53]. The studies reported here revealed slight temperature dependence over as much as a 60  $^{\circ}\text{C}$  range. If the mechanism always involved return to a higher state, usually thought to be a metal-centered  $d^1d^*$  state, one might expect a larger activation energy and particularly so for the lower lying states that emit at longer wavelengths. That is not the case in general. All changes with temperature are small and the lower lying state usually shows the smaller change with temperature. Direct deactivation by nonradiative intersystem crossing from the emitting states to the ground state might have small activation energies. Although one expects lower lying states to decay more rapidly by that mechanism, that need not apply to the relatively small energy differences between the states involved in dual emission in these compounds. (Some of the largest, albeit still modest, changes with temperature were for the shorter wavelength emissions. Conceivably, if that involved excitation localized on bpy, perhaps it could decay by way of thermal excitation to a metal localized state while excitation on an extended phen system might not.) A lesson from these studies is that we should be cautious in accepting any data for temperature dependence that depend on decay profiles measured at only a single wavelength. It is essential to prove that several wavelengths give the same result, if one wants to propose a mechanism common to all molecules in the sample.

13. Do the correlations with structures for unimolecular systems that were emphasized earlier [2] hold up after more work? In general, yes, except that even more structures do show dual and heterogeneous lifetimes if one builds a better apparatus. Mononuclear species with asymmetric



substitution in at the 4- position of phen always give dual emissions, especially with extended conjugation, as we asserted. With better methods, substitutions at 3- and 5- positions now also show subtle dual emission in fluid solution and obvious dual emission in rigid environments, both glasses and crystals. In contrast, symmetric substitution at 4- and 7- still gives no sign of dual emission in fluid solvents, even though it can lead to heterogeneous lifetimes clustered around one mean value in glasses and crystals. Even homoleptic species show heterogeneous decay in solids, and occasionally in fluid solution, if one's tools are adequate. The dinuclear species we looked at before seem always to give dual emission with heterogeneous, continuous distributions of lifetimes; but they may involve different or additional issues, not addressed here.

14. Is there more to the story than ion pairing? One might invoke dimers or oligomers, especially given the data that suggests a continuum of behavior from crystals through glasses and bad solvents to good solvents. In bad solvents, nanocrystals small enough to pass fine filters but large enough to be unaffected by oxygen do seem to be present. Perhaps smaller aggregates persist even in good solvents. Furthermore, some solvents seem to be intermediate between good and bad in their behavior. One needs something that persists for microseconds to milliseconds in fluid solution, but not for minutes or hours. That might be true for dimers or other very small oligomers, but probably not for larger nanocrystals. Aromatic and heterocyclic species with extended conjugation, as some ligands have, do sometimes dimerize. It is difficult to imagine dimers of ions overcoming electrostatic repulsion without counterions being involved, so ion pairing may still be part of the story. Efforts mentioned above and reported elsewhere in more detail were thought to offer evidence against aggregation as it is commonly observed [53]; but perhaps loosely organized aggregates of two or a few ions could be possible even in good solvents.

15. Can one account for the failure of past research efforts to notice dual emissions at ambient conditions more often than they did, let alone heterogeneous multiple decay kinetics? Only the dinuclear species and a few very asymmetric mononuclear species show behavior obvious enough that it might have been easily detectable in the past with crude methods like Polaroid photos of oscilloscope traces, and those compounds were not synthesized until recently. Even if there were hints at unusual behavior, it is unlikely that the effort needed to demonstrate exotic effects would have been attractive to major research groups. Prejudice based on Kasha-Vavilov principles would be against it; and funding to obtain advanced instrumentation to make the needed measurements would be difficult to obtain. Efforts by smaller, but dedicated, research groups may deserve more attention than they received at the time.

## 6. Conclusion and suggestions for further study

Dual emission is a reality in many, but perhaps not all, heteroleptic ions of ruthenium, even at room temperature and in fluid solution. It is more obvious in rigid media such as glasses at low temperature and in crystalline powders. However, there are not just two unique lifetimes. Rather, there is a continuum of slightly different lifetimes drawn from what is, in those cases, a bimodal distribution. In other cases that do not show dual emission, there is still in some cases a continuum of lifetimes within a unimodal distribution. One possibility might be that photoexcitation can create different, distinct, localized and spatially isolated  $^3\text{MLCT}$  states that persist, but are not in thermal equilibrium, in otherwise identical solute species. This hypothesis has great difficulty explaining why the states are not in thermal equilibrium, some difficulty predicting the branching ratios under different conditions, such as different solvents, and a great deal of difficulty accounting for a continuum of different decay lifetimes. Two other explanations postulate site heterogeneity in solids and even in liquid solution. One invokes an exclusive role for ion pairing. If one admits that ions near charge

transfer orbitals should have an influence, and if one doubts that there would be well-defined, unique configurations for ion pairs, then it would seem that a continuous variation of excited state energies is mandatory. We suspect that ion pairs in solution are far more common and important than photophysical chemists have wanted to bother with. They should be even more common in solids. The other possibility invokes aggregation to dimers or small oligomers, although these might also involve counterions to overcome electrostatic repulsion.

If one wants to distinguish among these hypotheses, more might be done with instrumentation similar to our present apparatus with some further improvements; or one might try two other approaches. Better than our Pockels Cell apparatus would be a pulsed laser with a repetition rate of 1 to 10 kHz and tunability to permit excitation over a wide range, perhaps a parametric oscillator. Photon counting is mandatory. Investigations of temperature dependence are not likely to be very helpful until other issues are resolved. It would be interesting to investigate complexes with three very distinct ligands. Correlating spectra with solvent properties over a wide range of solvents should be helpful. Exploring salt effects very carefully, using rigorous ion exchange rather than just flooding with excess salts, might be worthwhile. All measurements must be precise. It will not be helpful to carry out inferior measurements and show that they fail to distinguish multiple species. A second option is to try other optical approaches. Transient photobleaching by powerful laser pulses at different wavelengths might be helpful in proving that there are different ground states that interconvert on long time scales; but such measurements will be difficult when all features are likely to be very broad. Polarization studies like those used by DeArmond decades ago might be revisited. Initial efforts in that direction for fluid solutions at picosecond times were described more than a decade ago by McCusker and Shank and their colleagues [54] and more efforts were described recently [51]. Additional insights might be gained by combining polarization studies with photobleaching by powerful laser pulses. How such experiments differ from more familiar polarization anisotropy studies in the low intensity limit was treated by one of us long ago [55]. Time-resolved vibrational studies out to microseconds, either Raman or IR, would be useful, especially if they could be done well enough to resolve heterogeneity beyond just two species. Work in glasses, at both room and low temperatures over long times would be helpful, although it might be futile to try to untangle continuous distributions of almost identical spectra for large molecules. All these seem like difficult experiments, especially when one has to do them for dozens of structures, several solvents, different salts, and a variety of temperatures. Finally, there might be a third option. We hope that some readers may be stimulated to think of clever experimental approaches that have escaped us but can offer direct evidence for or against the hypotheses we presented. Computational studies could be very helpful; but those are also likely to be time consuming, if they are to give convincing results that take into account both solvent effects and ion pairs while extending molecular dynamics out to microsecond times for such large molecules. It may well be that the problem is not really to explain dual emission but rather to explain what ionic species actually exist in different solvents. Computations for simplified models might tell us something useful without having to include the full molecular complexities of complex ions.

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Ruthenium; MLCT; phosphorescence; dual emission; ion pairs

Table 1. Fits for percentage amplitudes and lifetimes to phosphorescence decay curves at 80 K for compound **4** at three wavelengths, using sums of two, three, or four exponentials. Five other wavelengths are similar.

$\lambda$ / nm	Amp1	$\tau$ 1 / $\mu$ s	Amp2	$\tau$ 2 / $\mu$ s	Amp3	$\tau$ 3 / $\mu$ s	Amp4	$\tau$ / $\mu$ s	$\chi^2$
580			68%	4.7			32%	19.7	8.1
	11%	1.0	58%	5.1			30%	19.5	7.8
	7%	0.4	19%	2.6	47%	5.9	27%	20.3	2.1
620			29%	4.6			71%	25.2	8.9
	19%	2.8			15%	9.3	66%	25.8	2.1
	4%	0.6	22%	3.9	19%	16.3	54%	26.9	1.4
680			26%	5.8			74%	23.8	3.5
	14%	2.9			22%	11.2	64%	24.8	1.1
	9%	2.2	14%	6.0	37%	18.0	40%	27.0	1.0

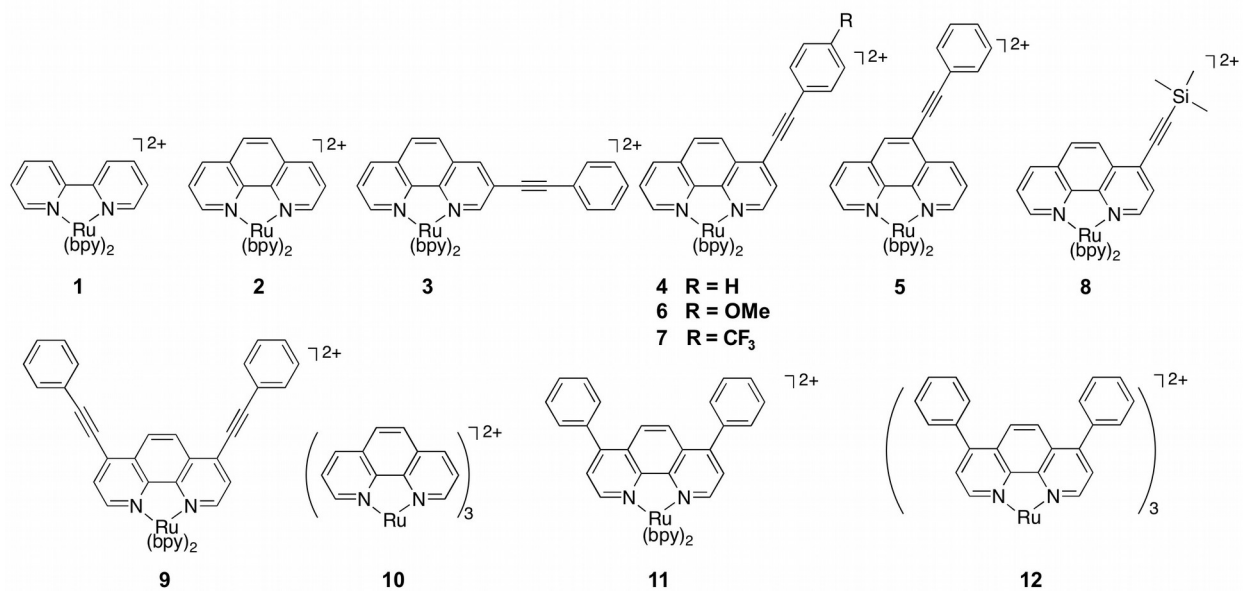


Figure 1. Structures of compounds discussed in this review. Compound **13** is shown elsewhere.

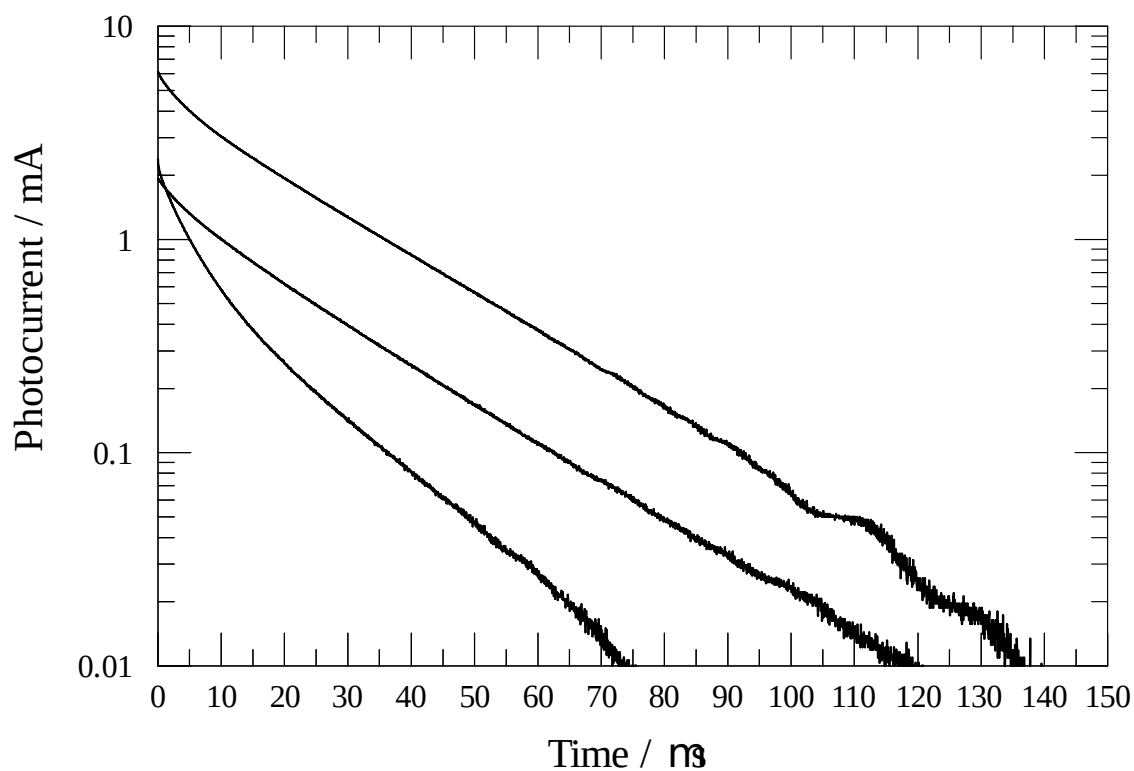


Figure 2. Phosphorescence decay at 80 K for **4** in tributyl nitrile glass displayed as a log-linear plot of photocurrent versus time. Decays are clearly not single exponentials. The top curve was recorded at 620 nm, the middle at 680 nm, and the lowest at 580 nm. At long times noise is evident. At short times noise is less than the width of the lines. About eight or nine half-lives are displayed.



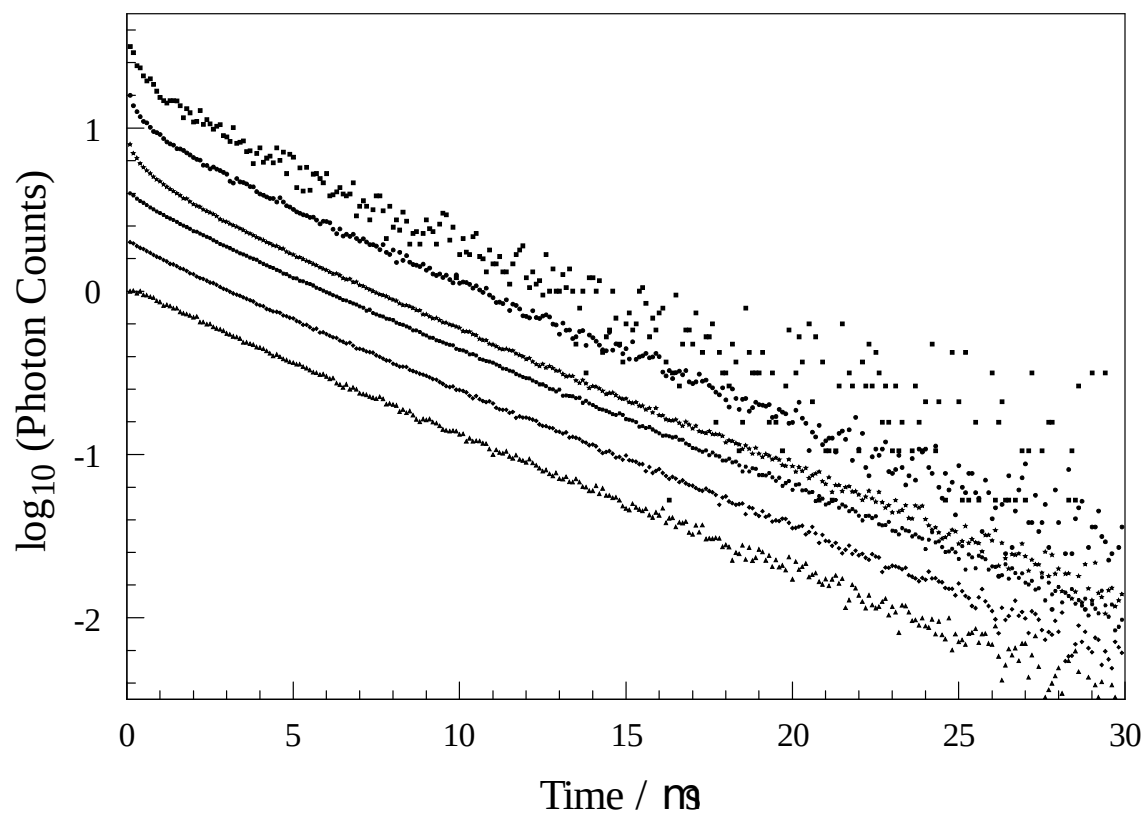


Figure 3. Log-linear plot of luminescence decay of **3** as powdered crystals at six wavelengths: from the top down, 580, 620, 650, 690, 730, and 770 nm. Photon counts are normalized and the displays offset by 0.3 log units. The weak signals at short wavelengths are scattered dots because points are not connected.

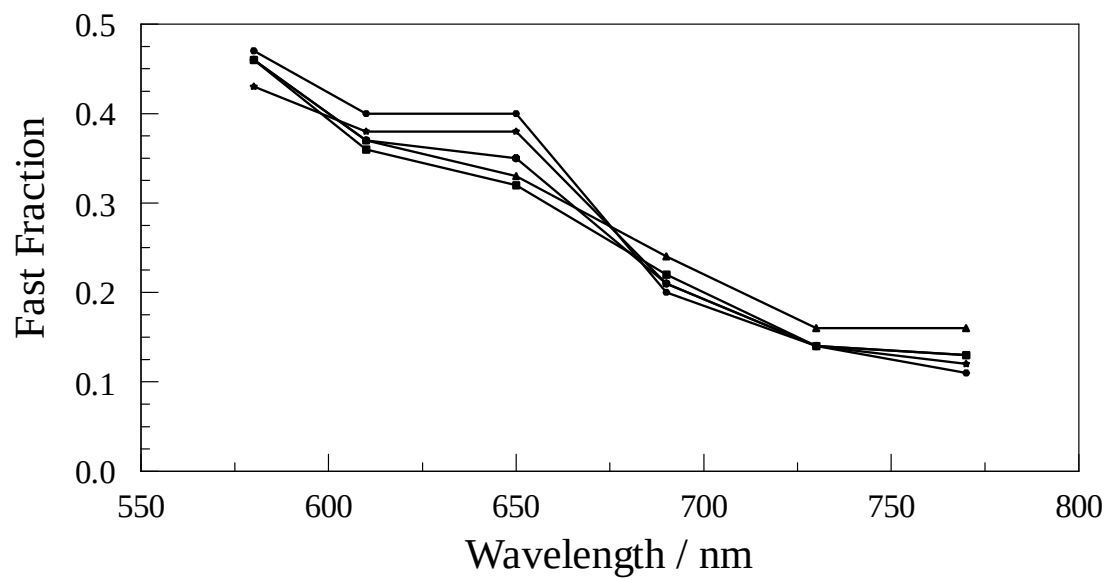


Figure 4: The fraction of the faster decay at six wavelengths for **3** as powdered crystals for temperatures near or above ambient. At 650 nm, the temperatures are in order from the top down, 22, 30, 50, 80, and 65 °C. Short wavelengths have more fast decay; but any variation with temperature is not statistically significant.

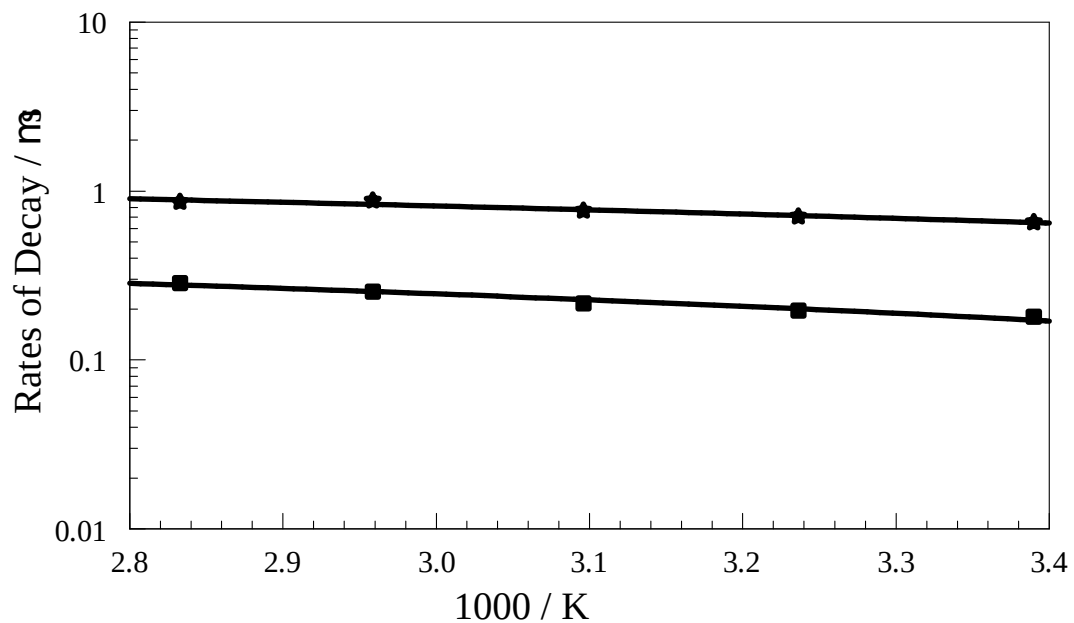


Figure 5: Log-linear plot of reciprocal lifetimes for fits to 3 as powdered crystals plotted against reciprocal Kelvin temperatures corresponding to 22 to 80 °C. The faster rates, triangles, have a somewhat smaller temperature dependence on a log scale, but the changes in rates are very small. This and Figure 4 is shown as illustrative of most or all other cases.

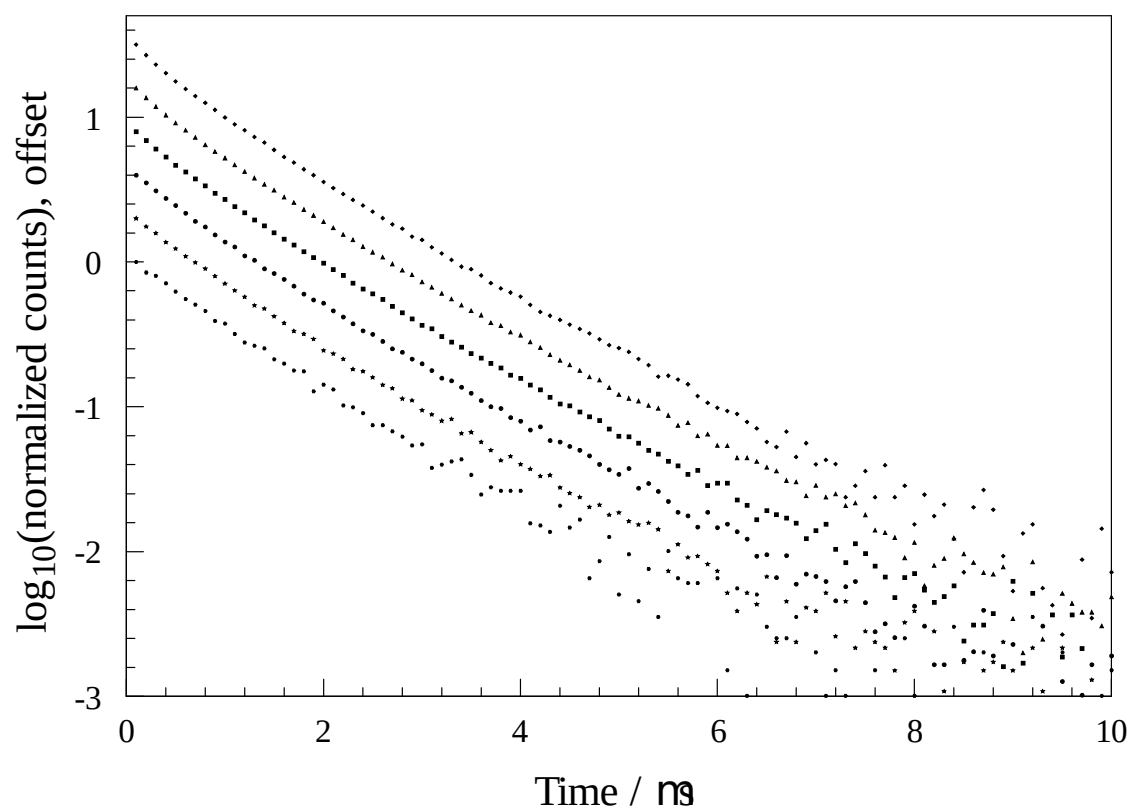
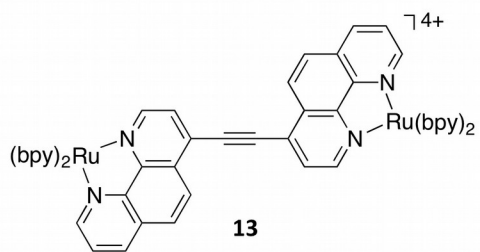


Figure 6. Luminescence decay curves for powdered crystals of  $\text{Ru}(\text{bpy})_3$  at six wavelengths: from the top, 580, 610, 650, 690, 730, and 770 nm. These are in an argon atmosphere and at 50 °C. They are normalized and offset. Even these are clearly not single exponentials on the log-linear plot.

A)



B)

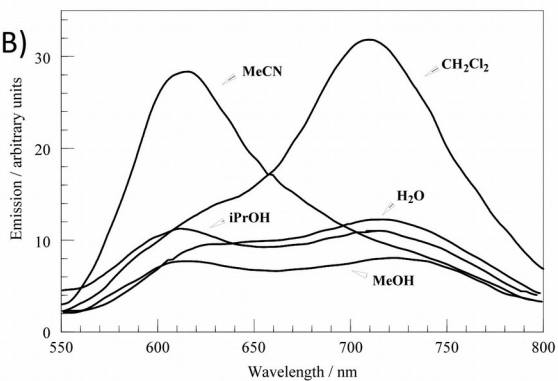


Figure 7: A) Structure of dinuclear ionic complex **13**. B) Proportions of short wavelength (fast) and long wavelength (slow) emission features change dramatically for this compound as solvent is changed.

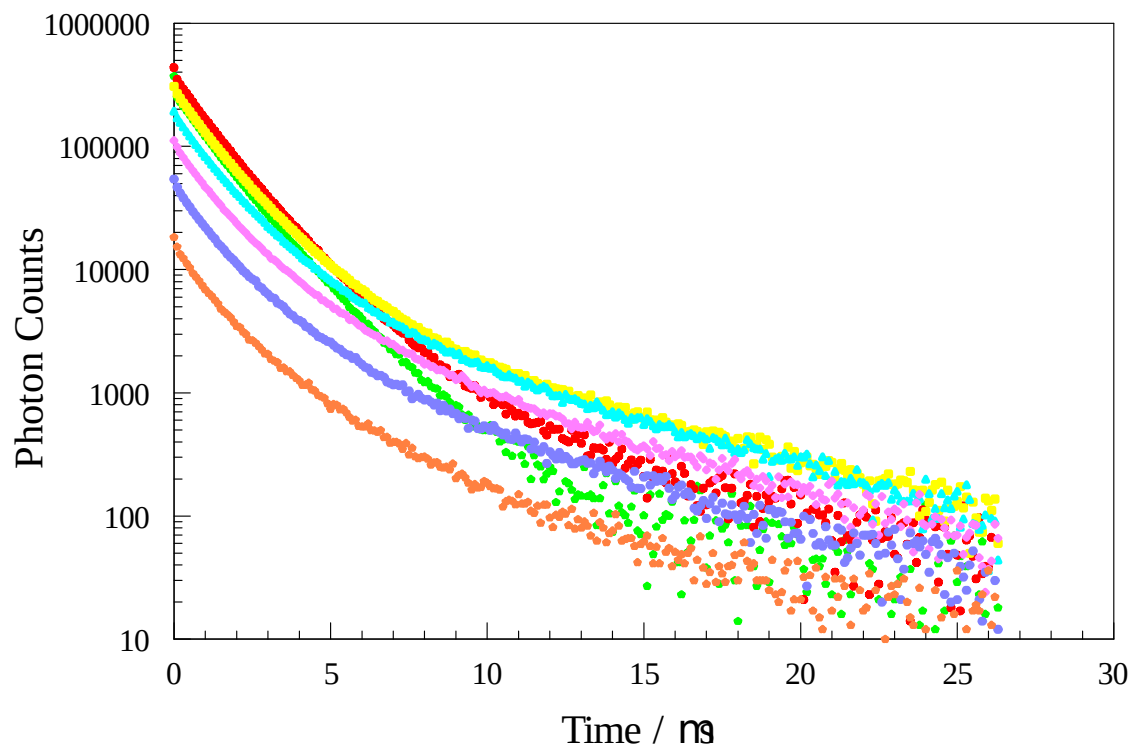


Figure 8: Log-linear plot of phosphorescence decay of methanol solutions of **13**. The structure of this dinuclear compound is shown in Figure 7. There are eight curves plotted, showing the actual numbers of photons detected. They may be difficult to distinguish, but the point is that single exponentials would be perfectly straight lines. These are not, and they vary with wavelength. Green, 590 nm; red, 610 nm; yellow, 650 nm; light blue, 680 nm (two identical curves overlaid); pink, 710 nm; dark blue, 740 nm; tan, 770 nm. The text explains that these cannot be fit even by double exponentials. Contrast this with Figure 9.

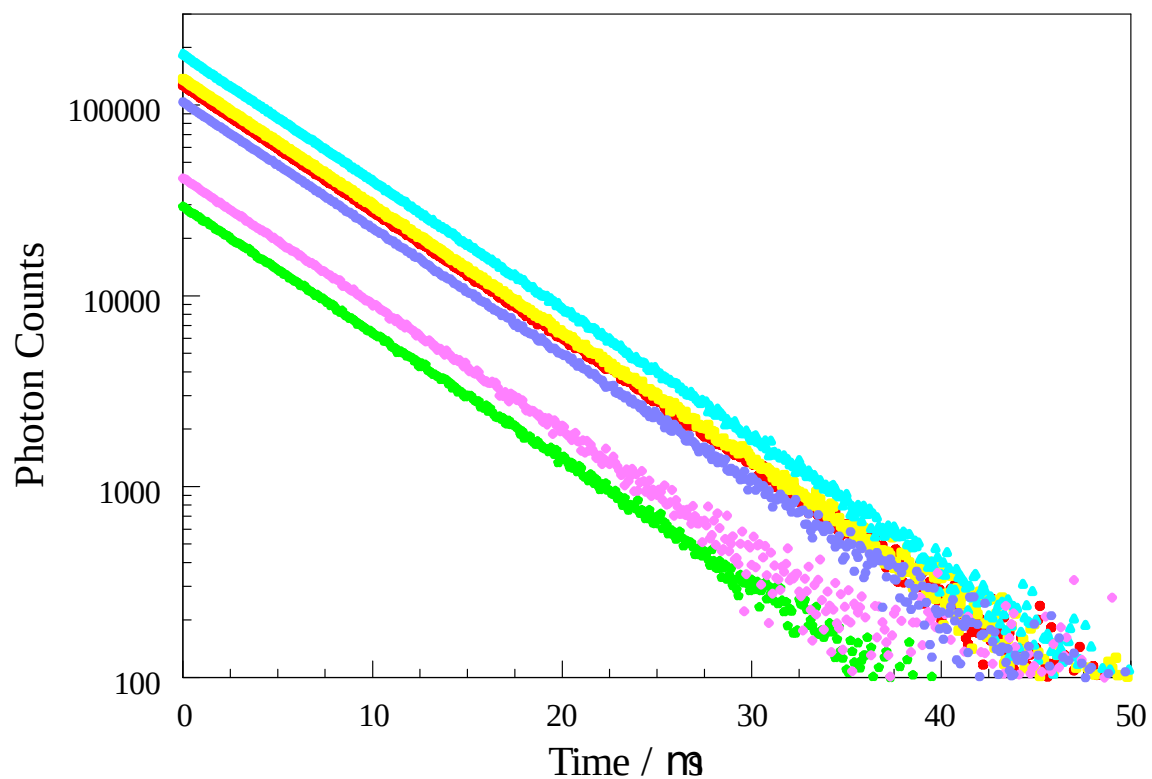


Figure 9: Phosphorescence decay curves for **9** in acetonitrile on a log-linear plot. Wavelengths in nm shown are, from the top down, blue, 680; yellow, 650; red, 610; dark blue, 710; pink, 740; green, 590. Single exponentials are statistically sufficient for fits over as many as ten half-lives for the largest signals. Contrast this with Figure 8.