ELSEVIER
Coordination Chemistry Reviews
171 (1998) 125–150

Luminescent platinum complexes: tuning and using the excited state

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Received 7 July 1997; received in revised form 20 August 1997; accepted 19 November 1997

Contents

Abstract

The focus of recent research on square planar Pt(II) diimine dithiolate complexes has been to understand molecular factors that influence their excited state properties and to develop diad and triad systems based on them for use in light-driven reactions. Regarding the former, two series of Pt(diimine)(dithiolate) complexes have been synthesized and studied. All of the compounds display solvatochromic absorption bands and solution luminescence attributable to metal/dithiolate-to-diimine charge transfer excited states of the same orbital parentage. The excited-state energies can be tuned by approximately 1 eV through ligand variation.

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PII S0010-8545(98)00025-3

Excited-state redox potentials have been estimated for all of the complexes from spectroscopic and electrochemical data, and electron transfer quenching rate constants show the expected driving force dependence. Analogous Au(III) systems have been synthesized and characterized including molecular structure determinations of a cationic diimine dithiolate system and a neutral C-deprotonated-2-phenylpyridine derivative. Striking differences exist in the electronic structures of these Au(III) complexes from those of the Pt(II) systems, underscoring the key role of the metal in the excited state structure of the latter. The creation of diads and triads is being undertaken with ligand bridges capable of connecting the Pt(diimine)(dithiolate) moiety with other metal centers. Toward that end, complexes of dipyridocatecholate (dpcat) have been synthesized and characterized. These complexes may serve as models for the linking of chromophore and quencher components of a possible photosynthetic system. The dpcat complexes have been characterized by absorption and steady-state emission spectroscopies. Luminescence and redox properties of these and a related system containing a tetrapyridophenazine (tppz) bridge are described.

Keywords: Platinum metal complexes; Luminescence; Charge transfer excited states; Diimine; Dithiolate; Binuclear complexes

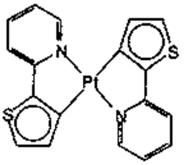
1. Introduction

The development of an artificial photosynthetic system for the conversion of light to chemical energy remains a continuing challenge to molecular photochemists despite extraordinary gains that have been made in understanding key system components and steps. The latter include chromophores for electron-hole creation, antennae for collecting and funneling photon energy, redox couples and electron transfer chains for efficient electron-hole separation, and dark catalysts for energy storing chemical reactions. Each of these components and the steps in which they play a role have been studied intensively since the initial reports on photochemically driven water splitting promoted by derivatives of $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) more than 20 years ago [1–6]. These early reports were based on multicomponent systems involving electron transfer quenching of the d^6 Ru^{2+} chromophore, subsequent electron transfer from the quencher to the dark catalyst, proton reduction to yield H_2 and irreversible reaction of a sacrificial electron donor [2–7]. Subsequent efforts have addressed every aspect of these systems including the back reaction, solar efficiency, the dark reaction catalyst and photo-stability of the chromophore. In recent studies by Graetzel and co-workers, a highly efficient and relatively durable system for solar photoconversion has been described that functions as a liquid junction photovoltaic with TiO_2 particles of high surface area and a $Ru(diimine)_2(SCN)_2$ photosensitizer spectroscopically similar to $Ru(bpy)_3^{2+}$ [8].

In the present paper, we describe efforts in our laboratory having the long-range goal of light-to-chemical energy conversion based on a molecularly designed system. The initial focus of our efforts and the main subject of this paper is a luminescent, platinum-based chromophore that has been investigated by us over the past decade [9–21]. The distinctive compositional feature of this chromophore is a square planar-coordinated Pt(II) ion having two different chelating ligands, one being an α,α′-diimine or heterocyclic aromatic and the other a 1,1- or a 1,2-dithiolate.

2. Background

Prior to 1986, luminescence from square planar complexes was relatively uncommon and restricted mainly to systems in rigid media at low temperature [22–28]. Beginning in the late 1980s, reports appeared of four-coordinate Pt(II) complexes that exhibited photoemission in fluid solution at ambient temperatures [29–36]. For nearly all of these systems, the excited states were assigned to intraligand or $\pi\pi^*$ excited states with only one complex, reported by von Zelewsky, Balzani and co-workers and shown as **1**, appearing to show metal orbital involvement in the excited state [32]. Our investigations into Pt(II) complexes at that time were stimulated by earlier work on luminescent Ir(I) dithiolates that exhibited highly structured emission in rigid media,[28] and led to the preparation of several Pt(diimine)(dithiolate) complexes. [9–13] These Pt(II) systems showed luminescence in room temperature fluid solution, structured or unstructured emission in rigid media depending on the dithiolate and a moderately intense solvatochromic transition (molar extinction coefficients ϵ of 5000–10000 M^{-1} cm^{-1}) in the 450–500 nm region of the spectrum. The initial complexes studied were relatively few in number because of solubility limitations and contained bipyridine (bpy), *o*-phenanthroline (phen) or an alkyl or aryl substituted derivative as the diimine and maleonitriledithiolate (mnt) or ethyl-2-cyano-3,3-dithiolatoacrylate (ecda) as the dithiolate.



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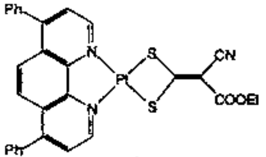
Based on spectroscopic changes as a result of simple ligand modification and semi-empirical molecular orbital calculations on model systems, the solvatochromic transition was assigned as a charge transfer from an orbital of mixed metal and dithiolate composition to a lowest unoccupied orbital localized on the diimine ligand [13]. This assignment which has been designated as MMLL'CT for "mixed metal–ligand-to-ligand" charge transfer, may be compared with a ligand-to-ligand charge transfer or LLCT assignment for related diimine dithiolate systems first described by Dance and later by Vogler [37,38]; the former differs in the notion that there is significant metal character in the HOMO and involvement in the transition. Because of solubility limitations, the first intensive study of the emission spectroscopy of Pt(diimine)(dithiolate) complexes concentrated on only two ecda complexes [9–11]. Both Pt(dpphen)(ecda) (**2**) and Pt(dmbpy)(ecda) (dpphen = 4,7-diphenylphenanthroline; dmbpy = 4,4'-dimethylbipyridine) were found to have multiple emitting states in low temperature solvent glasses. From relative emission quantum yields and solution lifetimes by single photon counting, the natural radiative lifetimes of these complexes were determined, indicating a degree of spin forbiddenness in the excited state and leading to assignment of the emission as ^{3}(Pt(d)/S(p)/dithiolate-π^*_{diimine}).



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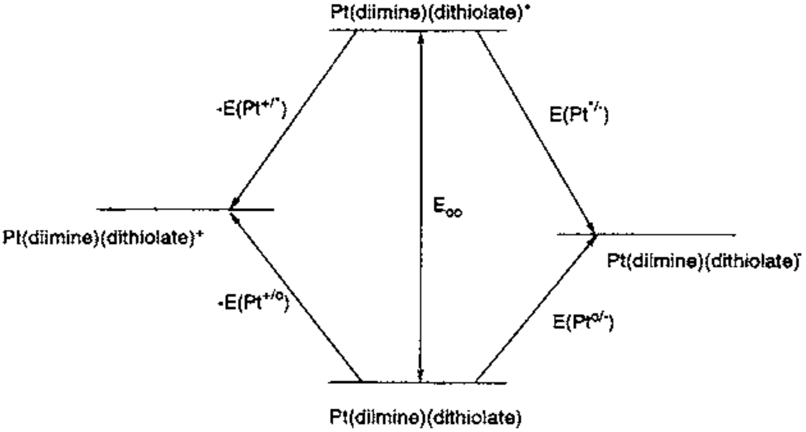
Initial observations of reductive and oxidative quenching of Pt ecda complexes were done using dimethylaniline (DMA) and nitrobenzaldehyde (ONB), respectively, as quenchers [10]. Both exhibited good Stern–Volmer kinetics. Based on excited state energies and electrochemical potentials of selected ecda complexes, it was possible to construct the simple thermochemical cycle shown in Scheme 1 to provide estimates of the excited state redox potentials of these systems. To obtain experimental confirmation of this approach, we concentrated on the excited state reduction potential $E(\text{Pt}^{*}/^{-})$ for Pt(dpphen)(ecda), **2**, and conducted a quenching study using a graded series of amines in combination with both fluorescence and lifetime measurements followed by a Rehm–Weller analysis of the quenching data. The experimentally determined value of 0.93 V versus SCE (1.17 V versus NHE) were found to agree well with the value of 0.98 V versus SCE (1.22 V versus NHE) estimated from the thermochemical cycle of Scheme 1, confirming the validity of the latter approach for estimating excited state redox potentials.



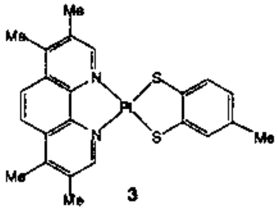
excited state reduction potential: $E(\text{Pt}^{*/-}) = E_{00} + E(\text{Pt}^{0/-})$

excited state oxidation potential: $-E(\text{Pt}^{+/*}) = E_{00} - E(\text{Pt}^{+/0})$

Scheme 1.

3. Tuning the excited state of Pt(diimine)(dithiolate) complexes

In order to understand the molecular design factors that influence the energy, lifetime, emission quantum yield and redox potentials of the emissive excited state with the purpose of developing the Pt(diimine)(dithiolate) chromophore for use in light-driven reactions, we have conducted a comprehensive study of the system [20]. Specifically, two series of Pt(diimine)(dithiolate) complexes, shown collectively as **3**–**15**, have been synthesized, characterized and investigated. The first consists of Pt(diimine)(tdt) complexes (**3**–**10**) where tdt = toluene-3,4-dithiolate and the diimines are substituted alkyl, aryl and carboalkoxy bipyridines and phenanthrolines, while the second (**4**, **11**–**15**) corresponds to Pt(dbbpy)(dithiolate) complexes where dbbpy = 4,4′-di-*t*-butyl-2,2′-bipyridine and the dithiolates are 1-(*t*-butylcarboxy)-1-cyanoethylene-2,2-dithiolate (tbcda), 1-diethylphosphonate-1-cyanoethylene-2,2-dithiolate (cpdt), 6,7-dimethyl-quinoxaline-2,3-dithiolate (dmqdt), mnt and tdt.



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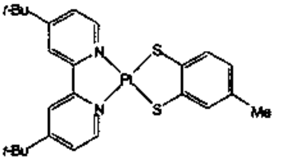

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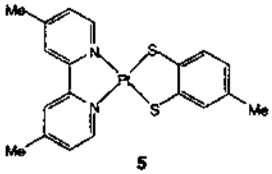

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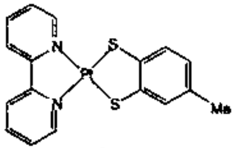

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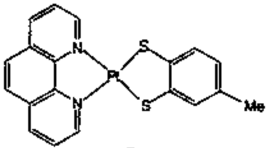

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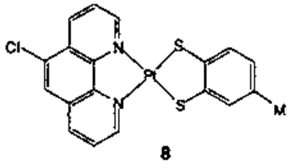

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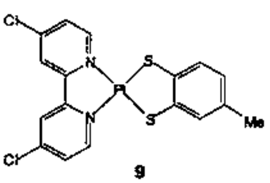

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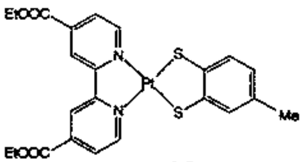

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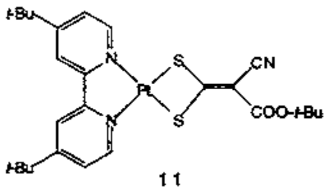
All of the compounds display solvatochromic absorption bands and solution luminescence. The solvatochromic shifts correlate well with Kosower's *Z* and Lees' E^*_{MLCT} solvent scales except for some deviations with dichloromethane and chloroform, with observed energies increasing with increasing solvent polarity. Fig. 1(a) and (b) show the absorption maxima for the two series of complexes and reveal the range over which the band energy is shifted as a function of ligand modification. For the Pt(diimine)(tdt) series, the results of Fig. 1(a) are particularly clear since the LUMO is nearly pure π^*_{diimine} in composition and the diimine substituents in going from **3** to **10** lower the energy of that orbital. A plot of the CT absorption energy versus the Hammett substituent constant of the 4,4′-X_2-2,2′-bpy ligand yields



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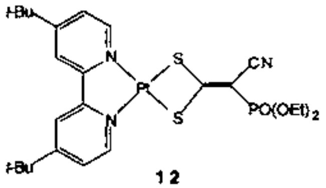

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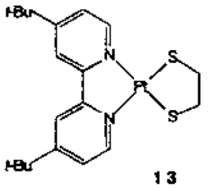

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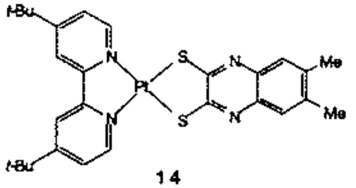

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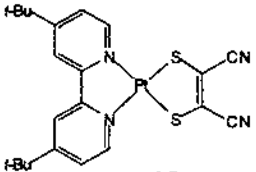

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an excellent correlation. For the Pt(dbbpy)(dithiolate) series, the change in energy spans 5000 cm^{-1} with the energies increasing according to the series tdt < mnt < dmqdt ~ edt < tbcda ~ cpdt. Since the dithiolates vary in structure, the shifts are harder to predict except that 1,1-dithiolates cause band energies to be higher than 1,2-dithiolates corresponding to a lowering of the HOMO in the former relative to the latter. The shifts of the solvent-sensitive absorption band for the two series of complexes are thus consistent with the assignment of the transition as MMLL′CT.

The emission maxima for the two series of complexes are presented in Table 1 and shown as Fig. 1(c),(d). It is evident that the emission energies shift with ligand modification in a manner that parallels very closely the absorption shifts. In all measurements, the solutions used were optically dilute with concentrations of 10^{-6}–10^{-5} M, and gave no evidence of excimer emission. Recently, Crosby has described evidence for excimer emission from the related complexes Pt(dpphen)(ecda) (**2**) and Pt(dmbpy)(ecda) in more concentrated low temperature glasses [39]. These observations follow reports of excimer emission from more concentrated room temperature solutions of Pt(dpphen)(CN)$_2$[36] and of concentration effects on solid state and frozen glass emissions from related diimine and triimine Pt(II) systems in which intermolecular bonding "turns on" in the excited state relative to the ground state [40,41].

We have carried out measurements similar to Crosby's on the *t*-Bu analog of **2**, [Pt(dpphen)(tbcda)], as well as another tbcda derivative, and find that whereas no change exists in room temperature emission spectra as a function of concentration (10^{-6}–10^{-3} M), clear changes occur in the 77 K emission consistent with the formation of an excited state dimer from a ground state aggregate or contact pair. Thus, while we confirm Crosby's assertion for 77 K samples of the ecda and tbcda complexes, the room temperature emissions, which do not change with concentration and are considerably blue-shifted from those assigned to the excimer (600 versus 670 nm), appear to be monomer based.

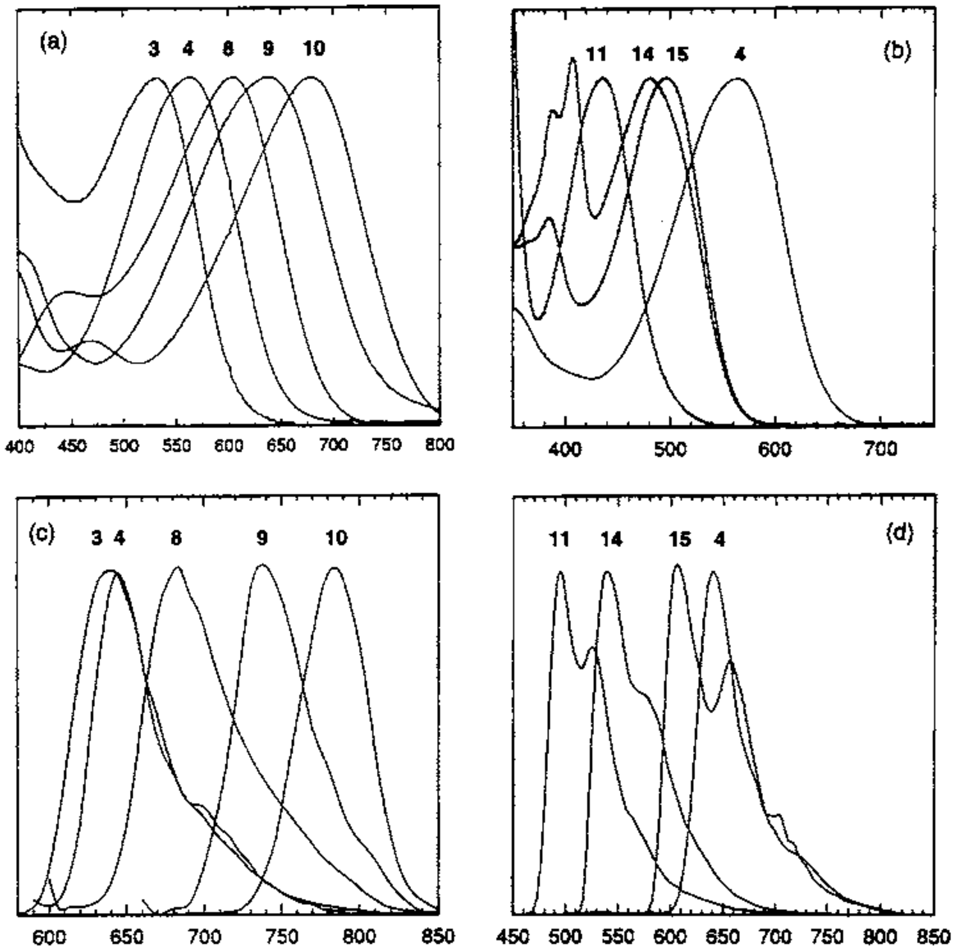


Fig. 1. Normalized absorption and emission bands for Pt(dimmine)(dithiolate) complexes: (a) solvatochromic absorption bands for Pt(diimine)(tdt) complexes in dichloromethane; (b) solvatochromic absorption bands for Pt(dbbpy)(dithiolate) complexes in dichloromethane; (c) emission bands for Pt(diimine)(tdt) complexes in frozen butyronitrile at 77 K; (d) emission bands for Pt(dbbpy)(dithiolate) complexes in frozen butyronitrile at 77 K.

In light of the evidence for excimer emission from ecda and tbcda complexes at 77 K, the emission spectra of tdt complexes **3**, **4**, **7** and **8** have been collected over a range of concentrations at both ambient and low temperatures. In contrast with the ecda and tbcda systems, the room-temperature fluid and 77 K frozen solution emission and excitation spectra of the tdt complexes show little or no variation with concentration. However, since Pt diimine and triimine complexes exhibit a tendency to aggregate as shown by either excimer emission or self-quenching, [40,41] measurements described here in terms of emission energies, intensities and lifetimes are based on data obtained solely from dilute (10^{-6}–10^{-5} M) solutions.

Table 1
Photoluminescent properties of Pt(diimine)(dithiolate) complexes **3**–**15** in dichloromethane at 298 K

Compound	E_{em} (eV)[a]	Φ^{b}_{em}	τ (ns)[c]	τ_0 (ms)	k_r (μs^{-1})	k_{nr} (μs^{-1})
Pt(tmphen)(tdt) (**3**)	1.94	57.0	1020	178	0.0056	0.98
Pt(dbbpy)(tdt) (**4**)	1.93	10.8	504	565	0.0022	2.0
Pt(dmbpy)(tdt) (**5**)	1.87	7.4	381	517	0.0019	2.6
Pt(bpy)(tdt) (**6**)	1.86	3.1	291	933	0.0011	3.4
Pt(phen)(tdt) (**7**)	1.84	6.7	517	773	0.0013	1.9
Pt(Cl-phen)(tdt) (**8**)	1.81	2.6	315	1207	0.00083	3.2
Pt(Cl_2-bpy)(tdt) (**9**)	1.68	0.43	157	3639	0.00027	6.4
Pt(Ec-bpy)(tdt) (**10**)	1.58	0.04	68	18970	0.000053	15
Pt(dbbpy)(tbcda) (**11**)	2.51	12	2.0	1.6	0.62	499
Pt(dbbpy)(cpdt) (**12**)	2.50	2.2	1.5	0.6	0.15	690
Pt(dbbpy)(edt) (**13**)	1.97	2.8	10	32	0.028	111
Pt(dbbpy)(dmqdt) (**14**)	2.30	64	80	12.4	0.081	12.4
Pt(dbbpy)(mnt) (**15**)	2.04	1.0	3	29	0.035	333

[a] From emission maxima in butyronitrile at 77 K.
[b] $\times 10^{-4}$
[c] ±10%

The luminescence of complexes **3**–**15** is consistent with a common emissive state having the same orbital parentage as that responsible for the solvatochromic absorption band, namely a charge transfer-to-diimine or MMLL′CT. The results of Table 1 show that the energy of the excited state can be tuned by nearly 1 eV through systematic ligand modification. From emission lifetimes and quantum yields of emission, the radiative and nonradiative decay rate constants were calculated, leading to intrinsic radiative lifetimes for these complexes in the msec range (see Table 1). The photoluminescence thus arises from a formally spin-forbidden process with recognition of the fact that the purity of spin states and selection rules are substantially reduced in complexes of heavier metals such as platinum.

Additional support for the orbital nature of the emissive state in the Pt(diimine)(dithiolate) complexes is obtained from the electrochemical data given in Table 2. The formation of the emissive state formally involves oxidation of the HOMO having dithiolate and metal character and reduction of the LUMO which is diimine-localized. There should therefore exist a correlation between the energy of the excited state and the difference between the oxidation and reduction potentials for each complex. Indeed, such a correlation was found, as shown in Fig. 2 for the emission energies of the complexes; a similar correlation was obtained when absorption energies for the solvatochromic transition were plotted.

3.1. Excited state dynamics

In addition to their effects on emission energy, the diimines and dithiolates also influence the emission lifetime and quantum yield of the Pt(diimine)(dithiolate) chromophore. The complexes display lifetimes ranging from 1 ns to over 1 μs and

Table 2
Ground- and excited-state redox properties of Pt(diimine)(dithiolate) complexes **3**–**15**. All potentials in volts versus NHE unless otherwise noted

Compound	E_{em} (eV)	$E(\mathrm{Pt}^{0/-})^{a}$	$E(\mathrm{Pt}^{+/0})^{b}$	$E(\mathrm{Pt}^{*/-})^{c}$	$E(\mathrm{Pt}^{*/})^{d}$
Pt(tmphen)(tdt) (**3**)	1.94	−1.495	0.347	0.45	−1.60
Pt(dbbpy)(tdt) (**4**)	1.93	−1.398	0.389	0.54	−1.55
Pt(dmbpy)(tdt) (**5**)	1.87	−1.371	0.390	0.50	−1.48
Pt(bpy)(tdt) (**6**)	1.86	−1.339	0.376^{c}	0.52	−1.49
Pt(phen)(tdt) (**7**)	1.84	−1.319	0.376^{c}	0.52	−1.46
Pt(Cl-phen)(tdt) (**8**)	1.81	−1.257	0.359^{c}	0.56	−1.46
Pt(Cl_2-bpy)(tdt) (**9**)	1.68	−1.043	0.380	0.64	−1.30
Pt(Ec-bpy)(tdt) (**10**)	1.58	−0.962	0.412	0.62	−1.17
Pt(dbbpy)(tbcda) (**11**)	2.51	−1.302	0.963	1.21	−1.55
Pt(dbbpy)(cpdt) (**12**)	2.50	−1.274	0.957	1.23	−1.54
Pt(dbbpy)(edt) (**13**)	1.97	−1.484	0.431	0.49	−1.54
Pt(dbbpy)(dmqdt) (**14**)	2.30	−1.334	0.814	0.97	−1.49
Pt(dbbpy)(mnt) (**15**)	2.04	−1.266	0.944	0.77	−1.10

[a] $E_{1/2}$ from reversible couple.
[b] E_p anodic peak potential from irreversible couple.
[c] Quasi-reversible couple.
[d] Calculated from equation (4a).
[e] Calculated from equation (4b).

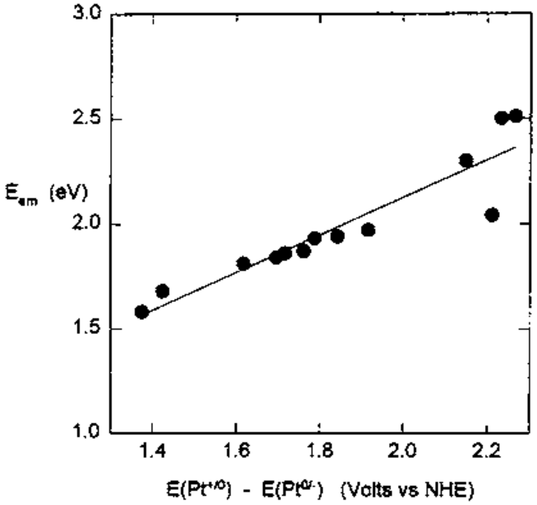


Fig. 2. Plot of E_{em} (77 K, butyronitrile) versus the difference between the ground state oxidation and reduction potentials for complexes **3**-**15** and linear least-squares fit to the data.

Φ_{em} ranging from $<10^{-5}$ up to 6.4×10^{-3}, indicating such an influence on the kinetics of excited-state decay (see Table 1). The tdt complexes have lifetimes that are significantly longer than those measured previously for other Pt(diimine)(dithiolate) complexes.

An analysis of the decay rates given in Table 1 shows that two trends are evident for the Pt(diimine)(tdt) series **3–10**. Nonradiative decay rate constants k_{nr} increase while radiative decay rate constants k_r decrease in going from the complex of highest excited state energy to lowest. These two effects can be understood in terms of the energy gap law and the Einstein equation for spontaneous emission, respectively. The energy gap law predicts that the rates of nonradiative decay increase as the energy gap separating the ground and excited state decreases. For a set of chromophores having excited states with a similar orbital basis and vibrational coupling, a simplified form of the law is obtained that predicts a linear relation between ln (k_{nr}) and E_{em}. This correlation has been observed for the nonradiative decay rates of the MLCT excited states of various d^6 diimine complexes of Ru, Os and Re in which the energies are varied by the chromophoric diimine ligand, the nonchromophoric ligand L, the solvent and the counter-ion [42–51]. The energy gaps for complexes **3**–**15** have been approximated using the low-temperature emission maxima. We find that a plot of $\ln(k_{nr})$ versus E_{em} for complexes **3–10** shown in Fig. 3 exhibits good qualitative agreement with the energy gap law with a slope of $-6.2\,\mathrm{eV}^{-1}$ that is similar in magnitude to those found for Os (II) and Ru (II) diimine complexes. This correlation suggests that the charge-transfer-to-diimine excited states of the tdt complexes all have similar vibrational and electronic components, although with very minor differences noted between the sets of tdt complexes where the diimine is a derivative of bpy versus a derivative of phen.

In contrast, there appears to be no correlation between $\ln(k_{nr})$ and E_{em} for the series of Pt(dbbpy)(dithiolate) complexes (**11–15** and **4**), suggesting that factors in addition to the energy gap are important to the nonradiative decay pathways for this series of complexes. The Pt(dbbpy)(dithiolate) complexes differ a great deal in

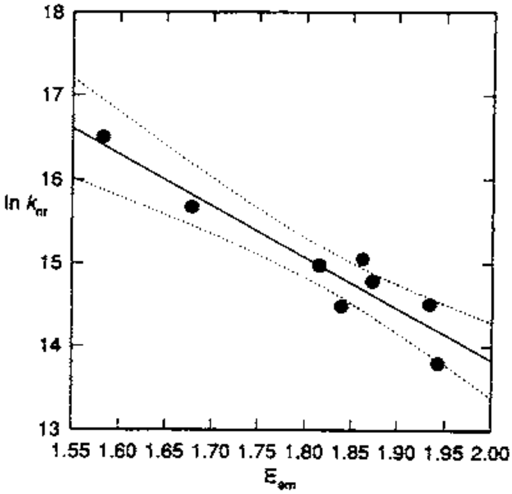


Fig. 3. Plot of $\ln(k_{nr})$ versus E_{em} for the series of complexes 3-10 showing an energy gap law correlation. The solid line corresponds to a linear least squares fit and the dotted lines denote 95% confidence limits.

the structure of the dithiolate, varying between 4- and 5-member chelate rings as well as in functional groups on the dithiolate backbone.

The second component of the lifetime is the radiative decay rate constant, k_r. Although the effect is smaller than the changes observed in k_{nr}, there is a correlation of k_r with E_{em} through the series of complexes **3–15**. The Einstein equation for spontaneous emission predicts that, for a series of related excited states, k_r scales with E_{em}^3, assuming that the electronic transition moment integral remains constant. For the complexes **3–15**, k_r increases with E_{em}^3 but a plot of the correlation exhibits curvature. Although the importance of k_r on the emission lifetimes increases at higher energies, for Pt(diimine)(dithiolate) complexes, the lifetimes of those systems having the highest E_{em} are still most strongly influenced by k_{nr} rather than k_r.

3.2. Excited state redox potentials

In view of the fact that the all of the Pt(diimine)(dithiolate) complexes undergo electron transfer quenching, excited state reduction and oxidation potentials for the two series of complexes Pt(diimine)(tdt) and Pt(dbbpy)(dithiolate) were estimated using the equations and thermochemical cycle outlined in Scheme 1. The E_{00} transitions were estimated using the energy maxima of the 77 K emission. The results obtained from this analysis are given in Table 2. For estimation of the excited state oxidation potentials, the irreversible oxidation waves of the complexes were employed while for calculation of excited state reduction potentials, the first reduction wave, which was reversible for all complexes, was used. The irreversible oxidation waves, while not rigorously correct for use in a thermochemical cycle, provide a good measure *within* the series of complexes of the *relative* ease of oxidation, and therefore we view the estimates of excited state oxidation potentials as valid for internal comparison.

Consider the excited state reduction potentials which probe the hole created in the metal/dithiolate HOMO upon excitation. For the Pt(dbbpy)(dithiolate) complexes **11–15** and **4**, $E(\mathrm{Pt}^{*/-})$ values decrease from 1.21 V for Pt(dbbpy)(tbcda) (**11**) to 0.54 V for Pt(dbbpy)(tdt) (**4**). This variation reflects the fact that the ground-state reduction potentials change very little with variation in the dithiolate, in accord with the diimine-localized nature of the reduction, while the E_{em} values for the series decrease substantially, thus leading to the large difference in $E(\mathrm{Pt}^{*/-})$. For the Pt(diimine)(tdt) complexes **3–10** having a similar HOMO, *both* the ground-state reduction potential and the emission energy E_{em} decrease as the diimine becomes more electron-withdrawing. These correlated changes effectively cancel in estimating the excited state reduction potentials $E(\mathrm{Pt}^{*/-})$, leading to a range of only 0.18 V for the tdt complexes. On the other hand, the excited-state oxidation potential $E(\mathrm{Pt}^{+/*})$ measures the ease of losing the electron that is placed in the π^*_{diimine} LUMO upon excitation. In accord with this notion, the Pt(diimine)(tdt) series of complexes **3–10** possess a large range of $E(\mathrm{Pt}^{+/*})$ values whereas the Pt(dbbpy)(dithiolate) series of complexes **11–15** and **4** having a fixed diimine ligand possess a small range of $E(\mathrm{Pt}^{+/*})$ values, with the exception of complex **15**.

In view of the fact that the excited-state redox potentials for the

Pt(diimine)(dithiolate) chromophore can be systematically tuned, oxidative and reductive quenching experiments were conducted to investigate if bimolecular electron-transfer rates are controllable in a similar manner. Eight complexes having the desired differences in their excited-state reduction or oxidation potentials were chosen. Complexes **11**, **14**, **15** and **4** were used for the reductive quenching experiments, since they have $E(\mathrm{Pt}^{*/-})$ values ranging from 1.23 to 0.54 V versus NHE. For the oxidative quenching experiments, complexes **3**, **4**, **7** and **8** were used, reflecting $E(\mathrm{Pt}^{*/})$ values estimated to range from −1.60 to −1.46 V versus NHE. The bimolecular electron-transfer rate constants obtained from the reductive quenching experiments are given in Table 3, and range from diffusion-limited rates to rates that are too slow to observe quenching. For a given electron donor, the electron transfer rate constants k_{el} increase in the order **4**<**15**<**14**<**11**, consistent with estimated increases in the excited-state reduction potentials. Completely analogous results were obtained in oxidative quenching experiments and the order for k_{el} thus obtained (**8**<**7**<**4**<**3**). A key difference that has been noted previously regarding oxidative and reductive electron transfer quenching of Pt(diimine)(dithiolate) complexes is that whereas the complexes decompose over several hours under oxidative quenching conditions, they appear to be relatively stable under reductive quenching [10]. This observation is consistent with the observed electrochemistry of these complexes.

From the results described above, it is evident that excited state properties of Pt(diimine)(dithiolate) complexes can be altered in a predictable manner through systematic ligand modification. These properties include excited state energies that have been varied by more than 1 eV and excited state redox potentials that show that diimine variation modulates $E(\mathrm{Pt}^{*/})$ while dithiolate change influences $E(\mathrm{Pt}^{*/-})$. Observed electron transfer quenching studies are totally consistent with these results and the driving force dependence of electron transfer.

3.3. *Au(III) diimine dithiolate complexes and related species*

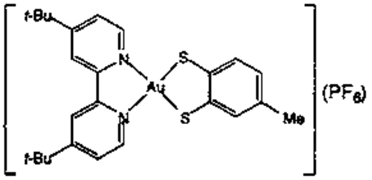
In order to probe the effect of metal ion on the excited state properties of square planar diimine dithiolate complexes, we have synthesized and characterized two

Table 3
Bimolecular electron transfer rate constants for selected Pt(dbbpy)(dithiolate) complexes with aromatic amine donors

	DMA[a]	TMB[b]	TMPD[c]
Pt(dbbpy)(tdt) (**4**)	4×10^6	3×10^7	5×10^9
Pt(dbbpy)(tbcda) (**11**)	4×10^9	9×10^9	2×10^{10}
Pt(dbbpy)(dmqdt) (**14**)	6×10^7	7×10^9	1.2×10^{10}
Pt(dbbpy)(mnt) (**15**)	$<10^7$	4×10^8	9×10^9

All values in units of $M^{-1}\,s^{-1} \pm 15\%$.
[a] DMA = N,N-dimethylaniline
[b] TMB = N,N,N,N-tetramethylbenzidine
[c] TMPD = N,N,N,N-tetramethyl-1,4-phenylenediamine

Au(III) systems. Prior to this effort, others had investigated Ni, Pd and Zn diimine dithiolates and observed the low energy solvatochromic absorption but no solution emission. For the Zn systems, which are tetrahedral, the solvatochromic absorption was substantially weaker in intensity indicating involvement of the metal and the role of its coordination geometry in coupling the donor and acceptor orbitals of the charge transfer transition. Extension of diimine dithiolate complexes to Au(III) would serve to investigate systems isoelectronic and isostructural with the Pt(II) systems. Towards this end, Au(III) complexes containing tdt and a diimine or orthometalating ligand with a C,N donor set have been prepared and investigated with respect to their photophysical properties. Specifically, [Au(dbbpy)(tdt)]PF_6 (**16**) and Au(η^2-C,N-ppy)(tdt) (**17**), where η^2-C,N-ppy = *o*-C-deprotonated-2-phenylpyridine, have been prepared from their dichloride precursors, [Au(dbbpy)Cl_2]PF_6 (**18**) and Au(η^2-C,N-ppy)Cl_2 (**19**), and characterized by electronic spectroscopy, ^{1}H-NMR spectroscopy, mass spectrometry and single crystal X-ray diffraction. The neutral C,N-ppy complex **17** exists in two isomeric forms denoted by the position of the Au-bound phenyl C atom relative to the tdt methyl substituent (cisoid or transoid - only the former is shown).



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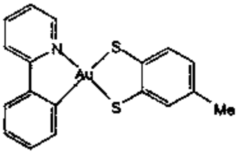


17

The solid state structures of both **16** and **17** confirm the square planar coordination geometry typical for d^8 metal complexes with all ligand donor atoms essentially coplanar in both molecules. The planarity of these molecules promotes stacking in the solid state which is observed for both complexes. However, the interplanar distances and Au···Au contacts of ≥ 3.60 Å between neighboring molecules are too great to indicate any significant interplanar bonding. On the other hand differences in color for the Au(III) tdt complexes from yellow in solution to orange in the solid state indicate the possibility of weak electronic interactions.

Whereas the precursor dichloride complexes **18** and **19** do not exhibit absorptions in the visible region of the spectrum, the Au(III) tdt complexes possess mildly solvatochromic absorptions in the visible region with molar extinction coefficients of 2300 $M^{-1}\,cm^{-1}$ (**16**) and 3200 $M^{-1}\,cm^{-1}$ (**17**) in CH_2Cl_2. These absorptions at 444 nm and 408 nm, respectively, are tentatively assigned as charge transfer-to-diimine transitions in both complexes. Unlike their Pt(II) analogs, neither of the Au(III) complexes, **16** or **17**, luminesces in solution or in rigid media at low temperature when $\lambda_{excit} \geq 300$ nm. Both observations suggest that Au(III) orbitals are substantially more stabilized than the Pt(II) orbitals, leading to a reduced intensity in the solvatochromic absorption and the absence of emission. On the other hand, complexes **18** and **19** do exhibit luminescence in low temperature glass matrices, but in both cases, the emission is at high energy with significant vibrational structure showing spacings between 1300–1500 cm^{-1}, characteristic of $C=C$ and $C=N$ vibrational modes of the diimine or phenylpyridine ligand. This high energy emission is tentatively assigned to an intraligand π–π^* transition in both complexes.

In terms of electrochemistry, the Au(III) tdt complexes **16** and **17** exhibit irreversible reduction waves at -0.255 and -1.339 V, respectively. Whereas the diimine complex, **16**, undergoes an irreversible oxidation at 1.589 V, the phenylpyridine complex exhibits a quasi-reversible oxidation at a significantly less positive potential with $E_{p,ox}=0.925$ V ($\Delta E_p=0.124$ V). The monoanionic phenylpyridine ligand in **17**, therefore, results in a more facile oxidation and a more difficult reduction relative to its cationic congener **16** containing the diimine ligand.

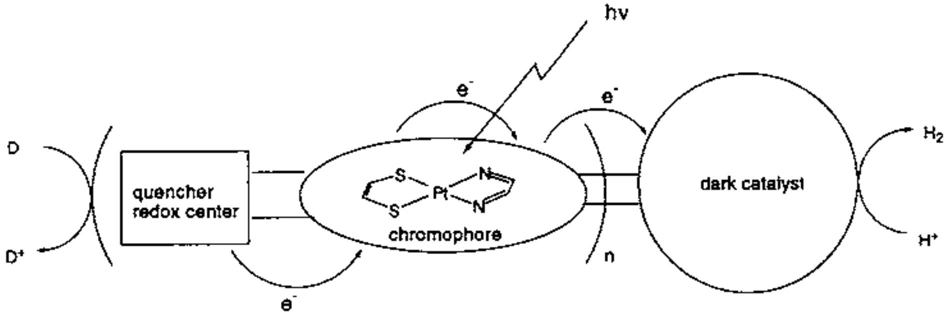
While the Au(III) complexes are isostructural with their Pt(II) analogs in a molecular sense, the electronic structures of these systems exhibit significant differences that can be tied to the relative energies of the metal valence orbitals in these systems. The absence of solution emission and a substantially weakened low energy charge transfer both attest to reduced metal character in the HOMO of these complexes, and they underscore the influence of the metal center on the lowest excited state of these complexes.

4. Towards using the excited state of Pt(diimine)(dithiolate) complexes

Based on the fact that the charge transfer of the platinum diimine dithiolate chromophore is necessarily directional, we consider its incorporation into a multi-component photosynthesis system as highly desirable. Other factors are also important in stimulating the formulation of this objective, notably the visible region of the spectrum from which the excited state can be accessed, the intensity of the absorption band, the electron transfer quenching of the excited state and the stability of the chromophore under reductive quenching conditions. Finally, we note that the reduced Pt(diimine)(dithiolate) complex has sufficient reducing power to catalyze proton reduction. All of these considerations serve to stimulate use of the Pt(diimine)(dithiolate) chromophore in the context of light-to-chemical energy conversion and lead to the system proposed in Scheme 2 for H_2 production from aqueous protons, light and electrons supplied by a sacrificial donor.

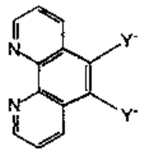
In the scheme, the Pt(diimine)(dithiolate) chromophore is connected to a reductive quencher on one side and a hydrogen generating dark reaction catalyst on the other. Because of the nature of the charge transfer from the dithiolate side of the complex to the π^*_{diimine} orbital, it is envisioned that the quencher connects to the dithiolate while the diimine is linked to the dark catalyst. The latter may be molecular, colloidal or bulk material for which it is known that H_2 evolution occurs in aqueous solution at low negative overpotential. Since multi-electrons are needed for this and related bond-forming and energy-storing processes, we envision multiple chromophores attached to the dark catalyst centers.

One of the most challenging aspects in the development of a system according to Scheme 2 is the connection of the chromophore to the other elements in the scheme.



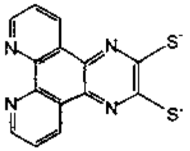
Scheme 2.

We envision this to be accomplished using multi-functional ligands that serve to bridge the components and connect them electronically. Since charge separation is a crucial aspect of a photosynthetic system, we view that the ligand bridges must be polar in their linking function. These considerations have led us to the next stage in the development of Scheme 2, the construction of diad and hetero-binuclear systems containing appropriate bridging ligands. Structures **20–22** are several candidate ligand systems that would be able to serve as suitable bridges between system components.



Y = O, S, NH

20



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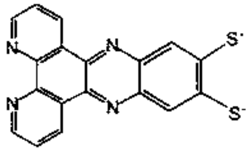
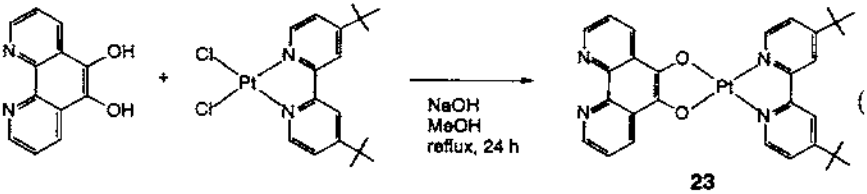


22

4.1. Dipyridocatecholate (dpcat) and its Pt(dbbpy) complex as a mononuclear precursor

One of the simplest and most interesting of the polar bridging ligands is dipyridocatecholate or dpcat, shown as **20** with $Y=O$. This ligand is obtainable in principle by two-electron reduction of the corresponding quinone, 1,10-phenanthroline-5,6-dione, which has been known for many years [52,53]. The dual chelating ability of **20** as either a diimine or a catecholate was first noted in 1975 by Balch,[54] and bi- and tri-metallic complexes utilizing dpcat have been reported recently by Pierpont and Doherty.[55,56] In both of these studies, the formation of the dpcat-bridged complexes was accomplished starting with 1,10-phenanthroline-5,6-dione and using an oxidative addition of the quinone to generate the catecholate. This approach thus required a low valent metal precursor for the oxidative addition reaction to generate the catecholate chelate.

In our studies we have reduced 1,10-phenanthroline-5,6-dione prior to coordination, with the resultant dipyridocatechol (dpcatH_2) being easily deprotonated and coordinated to a Pt(II) center without a change in metal oxidation state. This is noted in equation 1 which involves reaction with $PtCl_2$(dbbpy) leading to Pt(dpcat)(dbbpy) (**23**) which is an interesting and versatile precursor complex for the synthesis of bi- and tri-metallic systems [57].



23

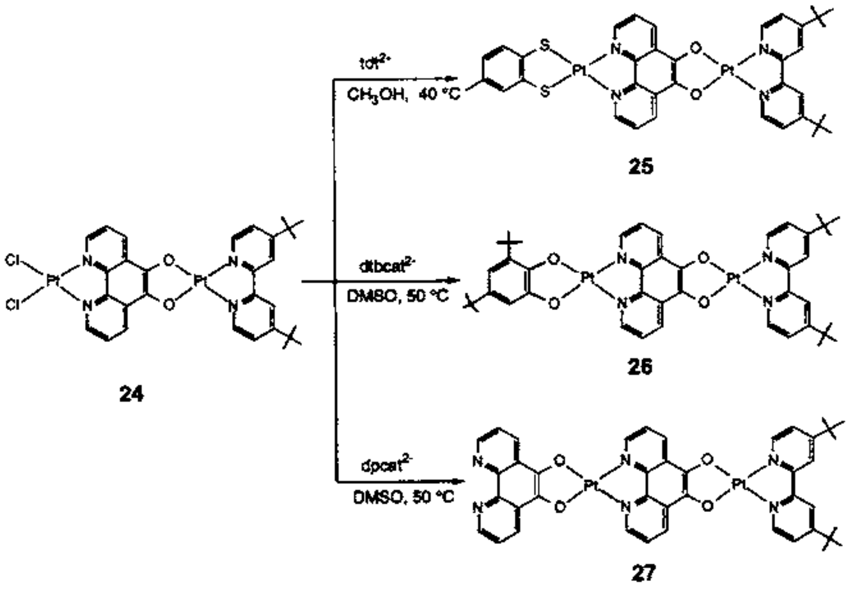
(1)

The complex Pt(dpcat)(dbbpy) (**23**) displays significant solvatochromism, a property ascribed to a charge transfer-to-diimine transition and reminiscent of the Pt(II) diimine dithiolate complexes. Two reversible redox processes are observed in the cyclic voltammetry of **23** corresponding to oxidation of the dpcat ligand and a diimine-based reduction. However, Pt(dpcat)(dbbpy), unlike the Pt(dithiolate)(diimine) complexes, does not display a low energy (> 500 nm) emission band of the same charge transfer type in either ambient temperature solution or low temperature butyronitrile glass.

4.2. Binuclear systems

In view of the fact that it possesses an uncoordinated phenanthroline moiety, the Pt(dpcat)(dbbpy) complex is a convenient starting material for the construction of bi- and polynuclear systems. The reaction of Pt(dpcat)(dbbpy) with $PtCl_2(PhCN)_2$ yields Cl_2Pt(dpcat)Pt(dbbpy) (**24**), which can be reacted further with diolate or dithiolate ligands to yield the binuclear complexes **25**–**27** having toluenedithiolate (tdt), di-*t*-butylcatecholate (dbcat) and dipyridocatecholate (dpcat) as terminal ligands, as shown in equation (2).

The UV–vis spectra of (tdt)Pt(dpcat)Pt(dbbpy) (**25**) and (dbcat)Pt(dpcat)Pt(dbbpy) (**26**) complexes each show a broad, unsymmetrical band in the visible region [Fig. 4(a)]. These complexes, like the mononuclear precursor Pt(dpcat)(dbbpy), do not exhibit low energy (> 500 nm) emission at room temperature. This situation contrasts with that found for Pt(diimine)(dithiolate) complexes and is particularly notable for **25** since the closely related system Pt(phen)(tdt) (**7**) displays characteristic fluid solution emission at 730 nm. However, unlike Pt(dpcat)(dbbpy), which does not emit even in frozen glass, both (tdt)Pt(dpcat)Pt(dbbpy) and (dbcat)Pt(dpcat)Pt(dbbpy) display a very weak emission under these conditions [Fig. 4(b)]. In both cases a band at 700 nm is observed and it is therefore assigned to the (dpcat)Pt(dbbpy) chromophore. No other band is observed for (dbcat)Pt(dpcat)Pt(dbbpy). The additional band at 650 nm in the spectrum of (tdt)Pt(dpcat)Pt(dbbpy) can be assigned to the (tdt)Pt(*N*,*N*-dpcat)



(2)

chromophore, but the analysis is uncertain because of the close proximity of the absorption energies of (tdt)Pt(*N,N*-dpcat), (dbcat)Pt(*N,N*-dpcat) and (*O,O*-dpcat)Pt(dbbpy) chromophores.

In analogy with Pt(dpcat)(dbbpy), the complex (dpcat)Pt(dpcat)Pt(dbbbpy) (**27**) can in principle serve as a diimine equivalent to coordinate to other metal centers. However, low solubility of this species has, thus far, precluded practical synthesis of species containing more Pt(II) centers.

4.3. Platinum–ruthenium heterobimetallic systems

In the context of connecting a reductive quencher to the Pt(diimine)(dithiolate) chromophore, we employed dpcat as a dithiolate analog and sought to have it bridge to a redox active metal through the diimine side of the ligand. Estimations of the $Ru^{3+/2+}$ oxidation potential indicated that with appropriate ligands the value of this couple will be such that it can serve as a reductive quencher of the Pt(diimine)(dithiolate) excited state. The linking of Pt(dpcat)(dbbpy) to Ru(II) centers was carried out in a manner that led to several bimetallic complexes having different numbers of Pt(dbbpy) moieties for a given Ru(II) center. Specifically, complexes **28**–**30** were obtained in excellent yields starting from $Ru(dbbpy)_2Cl_2$, $Ru(dbbpy)(dmso)_2Cl_2$ and $Ru(dmso)_4Cl_2$, respectively, according to equation (3). Together with the mononuclear complexes Pt(dpcat)(dbbpy), $Ru(dbbpy)_3^{2+}$ and $Ru(phen)_3^{2+}$, **28**–**30** provide an interesting series for spectroscopic and electrochemical investigation and analysis.

The connectivity crystal structure $[(dbbpy)_2Ru(dpcat)Pt(dbbpy)](PF_6)_2$ (**28**) is

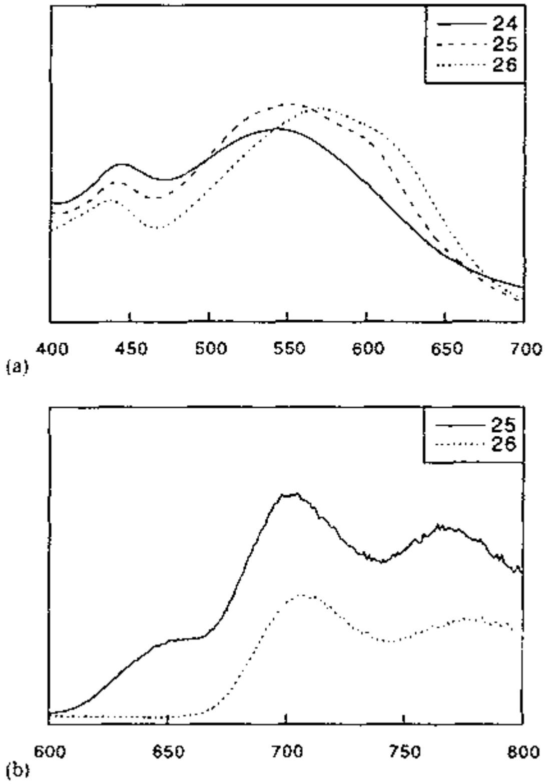
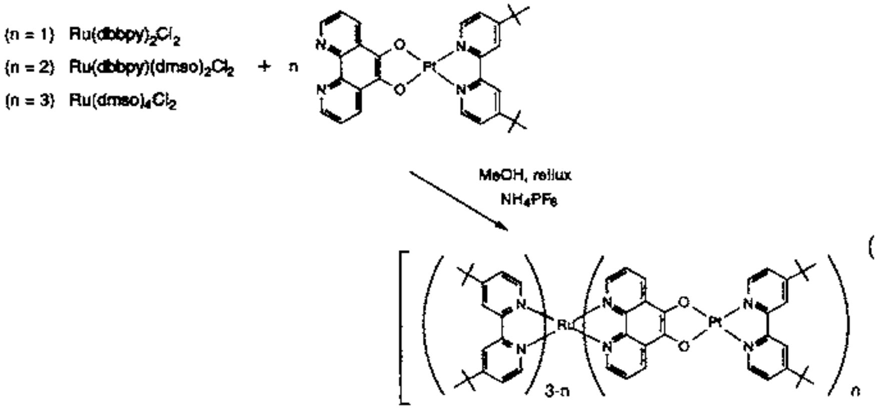


Fig. 4. Absorption and emission spectra of binuclear Pt(II) complexes containing diimine, diolate and dithiolate ligands. (a) UV-visible absorption (CH_2Cl_2) of Cl_2Pt(dpcat)Pt(dbbpy) (**24**), (tdt)Pt(dpcat)Pt(dbbpy) (**25**) and (dbcat)Pt(dpcat)Pt(dbbpy) (**26**); (b) low temperature emission (butyronitrile glass) of (tdt)Pt(dpcat)Pt(dbbpy) (**25**) and (dbcat)Pt(dpcat)Pt(dbbpy) (**26**).

shown in Fig. 5. The electrochemical data are presented in Table 4 and display the presence of a reversible oxidation associated with the dpcat ligand and a reversible reduction for the Pt(dbbpy) moiety in addition to other voltammetric waves. The additional processes are assigned as Ru centered oxidation and reductions of the Ru(dbbpy) and Ru(N,N-dpcat) moieties. The absorption spectra of these complexes in CH_2Cl_2 [Fig. 6(a)] show a progression as *n* goes from 0 to 3 of an increase of absorption intensity at ca. 540 nm and a shift of the 460 nm maximum to 440 nm. The former reflects the increasing number of (dpcat)Pt(dbbpy) chromophores in the molecule while the latter corresponds to a change in the Ru coordination from tris(dbbpy) to tris(*N*,*N*-dpcat). The emission spectra of these complexes show key differences between room temperature CH_2Cl_2 solution [Fig. 6(b)] and 77 K butyronitrile glass [Fig. 6(c)]. With irradiation at 440 nm in fluid solution at room temperature, a strong emission for Ru(dbbpy)$_3^{2+}$ ($n=0$) at 620 nm is seen but this decreases significantly upon the introduction of one (dpcat)Pt(dbbpy) unit and is quenched completely for $n \geq 2$ with no other emission bands observed. Irradiation of solution



(3)

28 n = 1
29 n = 2
30 n = 3

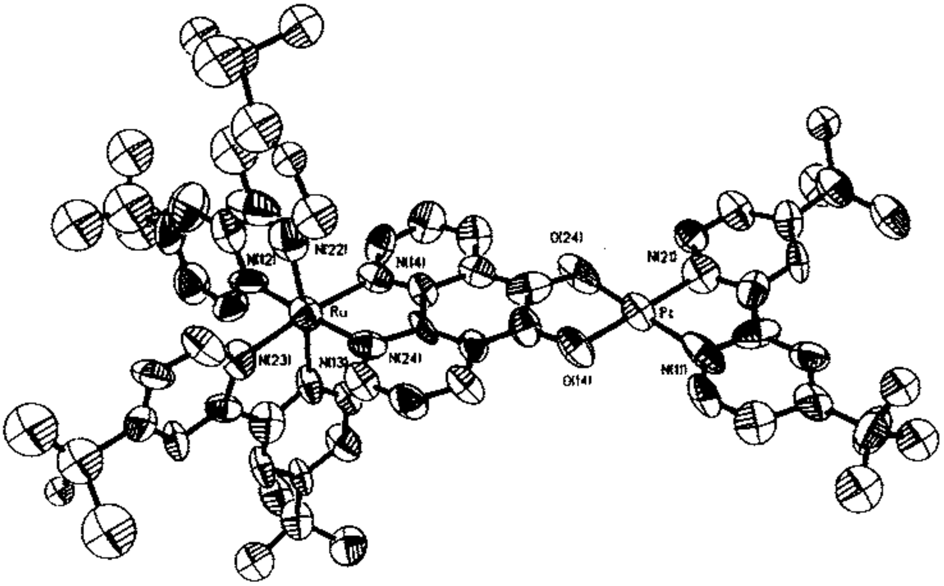


Fig. 5. Connectivity crystal structure of $[(dbbpy)_2Ru(dpcat)Pt(dbbpy)](PF_6)_2$ (**28**).

samples of **28–30** at 540 nm yields no emission. At 77 K, irradiation at 440 nm for the complex with one (dpcat)Pt(dbbpy) unit (**28**) results in a relatively weak Ru-based emission at 570 nm and a more intense emission at 670 nm assignable to the (diolate)Pt(dbbpy) moiety. The 570 nm emission is completely quenched for the n = 2,3 systems, $[(dbbpy)Ru((dpcat)Pt(dbbpy))_2]^{2+}$ and $[Ru((dpcat)Pt(dbbpy))_3]^{2+}$,

Table 4
Electrochemical data of mixed $RuPt_n$ systems ($n=0$-3) $[(dbbpy)_{3-n}Ru((dpcat)Pt(dbbpy))_n](PF_6)_2$, $[Ru(dbbpy)_3](PF_6)_2$ (Ru), and Pt(dpcat)(dbbpy) (Pt) in CH_3CN. All potentials in volts versus NHE

	Ru(II)/(III)	dpcat(−2/−1)	Pt(dbbpy)	Ru(dbbpy)	Ru(dbbpy)	Ru(dpcat)
Ru	+1.14			−1.48[a]	−1.64[a]	
Pt (**23**)		+0.21	−1.37			
RuPt1 (**28**)	+1.4[a]	+0.57[b]	−1.33	−1.49	−1.70	−2.00
RuPt2 (**29**)	+1.5[a]	+0.58[b]	−1.33	−1.55		−1.86
RuPt3 (**30**)	+1.7[a]	+0.62[b]	−1.37			−1.74

[a] Irreversible, anodic or cathodic peak potential reported.
[b] Quasi-reversible.

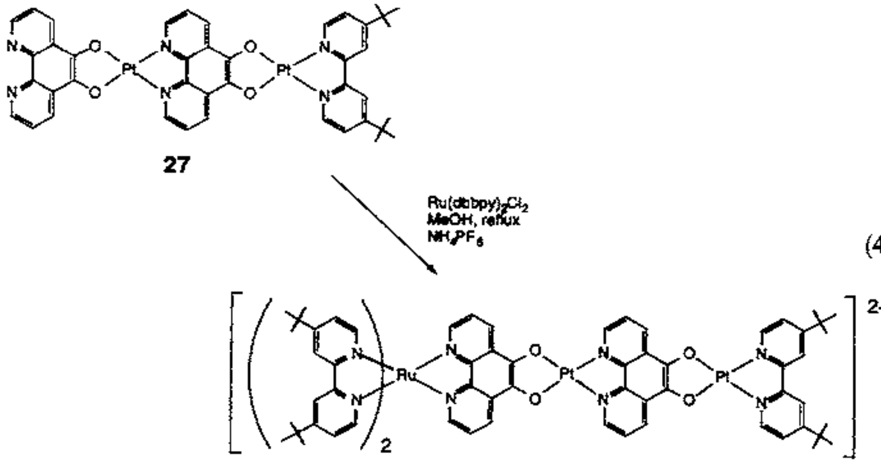
and both exhibit Pt-based emissions at 670 nm. This 670 nm emission is also observed for all three complexes upon irradiation at 570 nm.

The irradiations at 440 nm and 570 nm result mainly in excitations of the $Ru(diimine)_3^{2+}$ and (dpcat)Pt(dbbpy) chromophores, respectively, and lead to emissions in the 570–620 nm and 670 nm regions. It appears that energy transfer from the higher energy Ru*Pt state (* denotes excitation) to the lower energy RuPt* state is quite efficient at low temperature and it may occur as well at room temperature with the absence of any Pt-based emission due to non-radiative decay of the Pt(diolate)(dbbpy) excited state. It is extremely likely that the Pt(diolate)(dbbpy) chromophore is non-emissive in fluid solution as has been found for the mononuclear, "unbound" complex Pt(dpcat)(dbbpy) and other Pt(catecholate)(diimine) complexes. However, whereas Pt(dpcat)(dbbpy) exhibits no low energy emission in frozen solution at 77 K, the bound Pt(diolate)(dbbpy) units appear to be emissive.

Extension of the reaction chemistry of dpcat-containing complexes to yield a different type of "$RuPt_2$" system was found in the reaction of $Ru(dbbpy)_2Cl_2$ with (dpcat)Pt(dpcat)Pt(dbbpy) (**27**) to yield the soluble trinuclear complex $[(dbbpy)_2Ru(dpcat)Pt(dpcat)Pt(dbbpy)]^{2+}$ (**31**) shown in equation 4. However, detailed spectroscopic studies of this complex have been hampered by the presence of emissive impurities.

4.4. Tetrapyridophenazine as a bridging ligand

The use of tetrapyridophenazine (tppz) as a bridging ligand has been recently described [58]. This ligand, while symmetrical, offers interesting potential as a bridge between dissimilar metals and it was with this objective in mind that $[(dbbpy)_2Ru(tppz)](PF_6)_2$ was prepared and the reaction sequence shown as equation 5 carried out to yield successively $[(dbbpy)_2Ru(tppz)PtCl_2]^{2+}$ (**32**) and $[(dbbpy)_2Ru(tppz)Pt(tdt)](PF_6)_2$ (**33**). The absorption spectrum of **33** [Fig. 7(a)] clearly shows two absorptions associated with the two chromophores of the complex. The low energy band arising from the (tppz)Pt(tdt) part of the complex is clearly revealed with a maximum at 610 nm by subtracting the spectrum of the precursor complex **32** in which the absorption is absent. The 610 nm maximum can be com-



(4)

pared to 583 nm and 605 nm for unbound (phen)Pt(tdt) and (5-Cl-phen)Pt(tdt), respectively. The emission spectrum of $[(dbbpy)_2Ru(tppz)Pt(tdt)](PF_6)_2$ at room temperature in CH_2Cl_2 shows only one band corresponding to the emission from the $(dbbpy)_2Ru(tppz)^{2+}$ center [Fig. 7(b)] but at 77 K in butyronitrile glass, a band assignable to the (tppz)Pt(tdt) chromophore is revealed. This latter band at 760 nm appears to be more intense than the one associated with the Ru center at 600 nm, with the latter substantially decreased. Emission from the Pt(II) diimine dithiolate center of **33** after irradiation of the Ru tris(diimine) absorption band is evidence of energy transfer across the tppz bridge in this system. These results are thus similar to those described above for the dpcat-bridged system $[(dbbpy)_2Ru(dpcat)Pt(dbbpy)]^{2+}$ (**28**). Complex **33**, however, differs from **28** in the placement of the Ru tris(diimine) moiety relative to the directionality of charge transfer in the Pt(diimine)(dithiolate) or (diolate) chromophore. In **33**, the Pt-based charge transfer is towards the bridging ligand whereas in **28** it is away from the dpcat bridge.

4.5. *Linking the chromophore to the dark catalyst*

The focus to this point has been on connection of the Pt diimine dithiolate chromophore to the reductive quencher or a redox active complexed metal center. In this approach, a well-defined structural arrangement has been sought through the use of rigid cyclic structures in the bridge. For the purpose of connecting the Pt-based chromophore to a colloid or related dark catalyst, a simpler synthetic approach is being examined that will join these two components by a more flexible single point of attachment achieved through a condensation or a coupling reaction. Towards this end, complexes containing 5-substituted phenanthroline derivatives such as **34** and **35** have been synthesized by Schiff base condensation of the

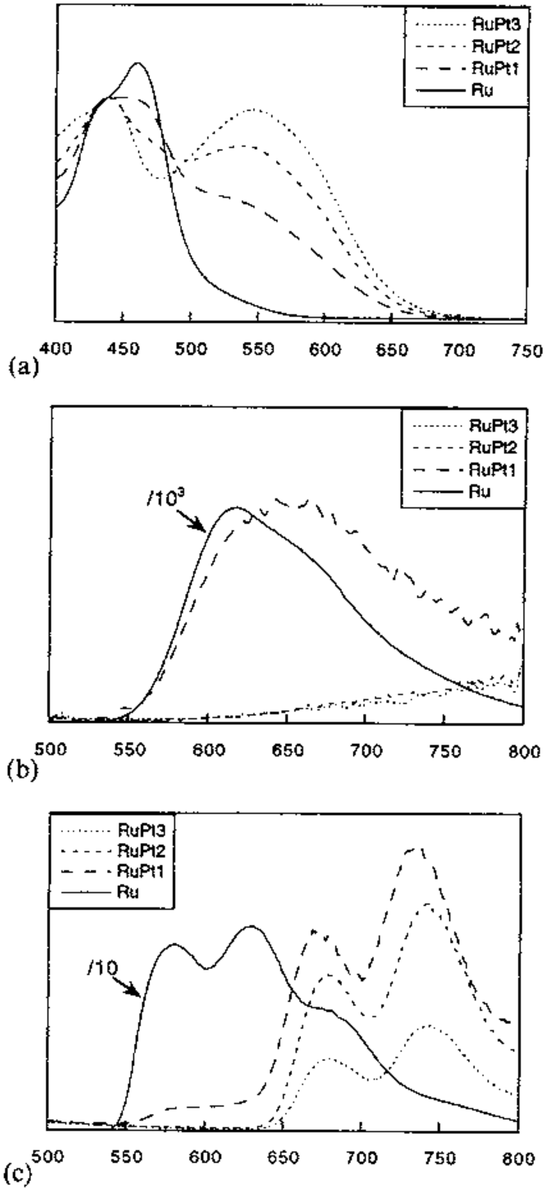
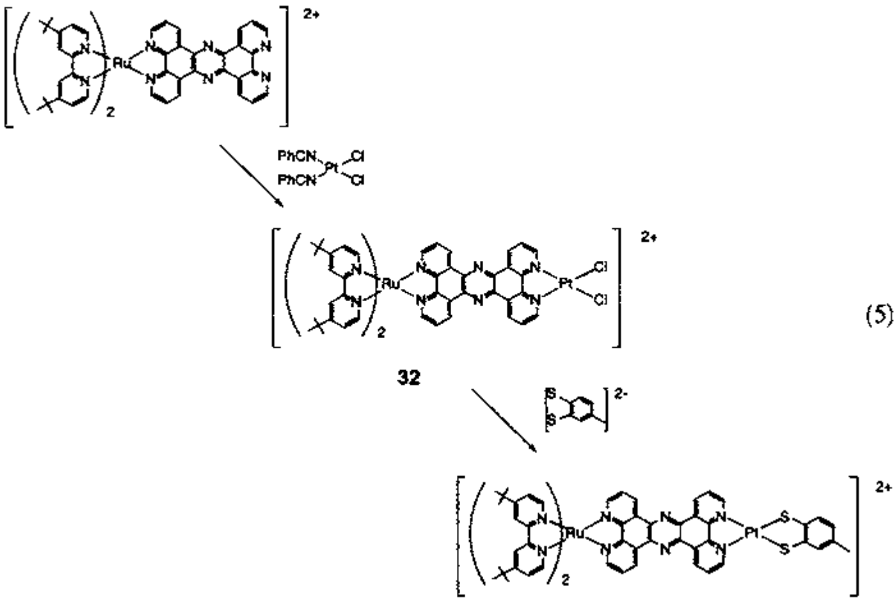


Fig. 6. Absorption and emission spectra of [(dbbpy)$_{3-n}$Ru((dpcat)Pt(dbbpy))$_n$](PF$_6$)$_2$ (RuPtn, $n = 1$–3, **28**–**30**) and [Ru(dbbpy)$_3$](PF$_6$)$_2$ (Ru). (a) UV-visible absorption in CH$_2$Cl$_2$; (b) room temperature emission in CH$_2$Cl$_2$; (c) low temperature emission in butyronitrile glass.

5-aminophenanthroline complexes with the corresponding hetero-aromatic aldehydes. Both complexes exhibit a low energy charge transfer transition that varies in λ_{max} with solvent polarity and both show luminescence in fluid solution. The



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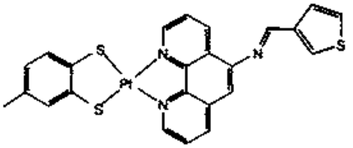
(5)

incorporation of these complexes into diads and their connection to colloids via the appended hetero-aromatic substituents is under investigation.



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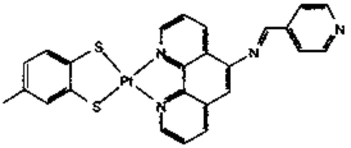

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5. Conclusions

The results described here of studies on solution-luminescent Pt(II) diimine dithiolate complexes suggest that these chromophores are excellent candidates for applications to photocatalysis. The complexes absorb strongly in the visible region resulting in a highly directional charge transfer. The complexes undergo electron transfer quenching of the emissive excited state and are stable under reductive quenching conditions. The reduced Pt(diimine)(dithiolate) species thus produced have sufficient reducing power to catalyze proton reduction and related energy storing reactions.

Application of the directional character of the Pt(II) diimine dithiolate chromophore is envisioned in a covalently bound multicomponent system containing the quencher and a dark reaction catalyst attached to the dithiolate and diimine parts

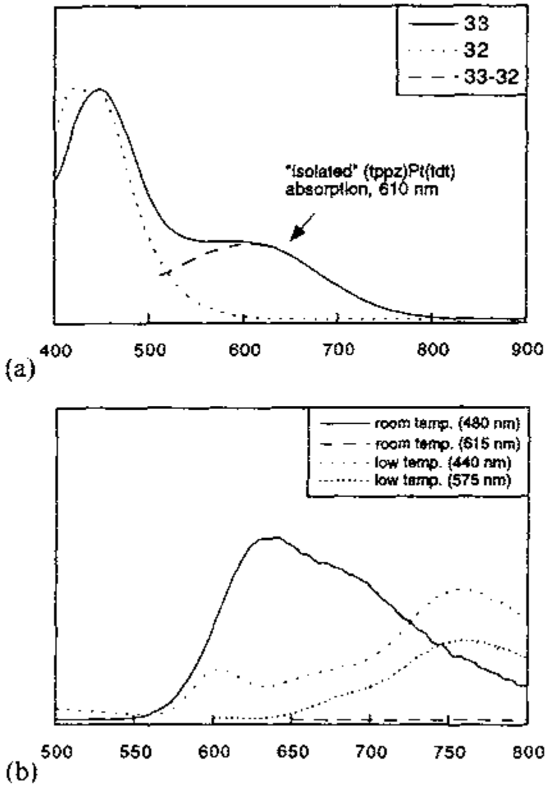

Fig. 7. Absorption and emission spectra of $[(dbbpy)_2Ru(tppz)PtCl_2](PF_6)_2$ (**32**) and $[(dbbpy)_2Ru(tppz)Pt(tdt)](PF_6)_2$ (**33**). (a) UV-visible absorption in CH_2Cl_2 and (b) emission spectra of **33** at room temperature in CH_2Cl_2 and at 77 K in butyronitrile glass.

of the chromophore, respectively. Since multiple reducing equivalents are required by the reduction of protons, the dark catalyst would bind to at least two quencher-chromophore diads. A sacrificial electron donor would enable the process to be catalytic.

Model diad systems are being constructed and studied in order to probe electronic communication between the components and assess elements of the photocatalytic system to be constructed. To date, systems utilizing dipyridocatecholate and tetrapyridophenazine as bridging ligands have been investigated. Although fluid solution emission is not observed from the Pt-based chromophores in these complexes, evidence of electronic communication between metal centers is clearly seen in low temperature glasses. The results also underscore the importance of the Pt(II) diimine dithiolate chromophore rather than the corresponding Pt(II) diolate in the photocatalytic system since the latter have greatly reduced solution luminescence. Synthetic methodologies for linking system components are being developed, including the preparation of luminescent Pt(II) diimine dithiolate complexes having heteroaromatic substituents capable of binding to a colloidal surface.

Acknowledgements

We wish to thank the Department of Energy, Division of Chemical Sciences for support of this research. A generous loan of platinum salts from Alfa/AESAR Johnson Matthey Co. is also gratefully acknowledged. We also wish to thank Dr Brian Cleary and Dr Steven Atherton for helpful discussions and experimental assistance.

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