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Coordination Chemistry Reviews
208 (2000) 115–137

COORDINATION CHEMISTRY REVIEWS

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Platinum diimine complexes: towards a molecular photochemical device

Muriel Hissler, James E. McGarrah, William B. Connick, David K. Geiger, Scott D. Cummings, Richard Eisenberg *

Department of Chemistry, University of Rochester, Rochester, NY 14627-0216, USA

Received 3 September 1999; accepted 15 December 1999

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Abstract

Complexes having the general formula PtX_2(diimine) where X_2 = dithiolate, bis(acetylide) and diimine = bipyridine, phenanthroline and derivatives have been investigated for potential use as chromophores in the conversion of light-to-chemical energy. These complexes, like the analogous X = CN systems, are luminescent in fluid solution. Previous studies of the dithiolate derivatives reveal that they possess a charge transfer excited state involving a mixed metal–dithiolate donor orbital and a π*(diimine) acceptor function with excited state properties including emission energies, lifetimes and redox potentials that are tunable by ligand variation. The bis(acetylide) complexes are brightly luminescent in fluid solution, and their excited state is shown to be MLCT in character, consistent with an earlier proposal. Both sets of diimine complexes show evidence of self-quenching, and for Pt(phen)$(CCPh)_2$, weak excimer emission is observed. The mechanism of quenching has been probed through

* Corresponding author. Tel.: +1-716-2755573; fax: +1-716-4736889.
E-mail address: rse7@chem.rochester.edu (R. Eisenberg).

PII: S0010-8545(00)00254-X

cross-quenching experiments and is thought to involve Pt···Pt interactions. Efforts are now focussing on the use of the PtX_2(diimine) chromophores in dyads and triads with the goal of constructing a molecular photochemical device for light-to-chemical energy conversion. Connection of the Pt diimine chromophores to both a donor or reductive quencher and an acceptor is envisioned through new ligand bridges currently being synthesized using Pd-catalyzed coupling reactions and carbonyl condensations.

Keywords: Platinum diimine complexes; Chromophores; Quenching

1. Introduction

The development of a molecular-based system for light-to-chemical energy conversion remains a key research objective for molecular scientists focused on energy production and utilization [1–3]. It has been more than 20 years since the first reports appeared on the light-driven production of hydrogen with visible light using $Ru(bpy)_3^{2+}$ and its derivatives [4–9]. These initial investigations stimulated immense interest in artificial photosynthesis and served to foster efforts that continue to the present. These studies employed multiple component systems that involved electron transfer quenching of the 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 [5–10]. The most notable systems contained $Ru(bpy)_3^{2+}$ as the chromophore, a viologen quencher, a sacrificial amine donor (e.g. triethylamine (TEA), triethanolamine (TEOA) or ethylenediaminetetraacetic acid (EDTA)) and a colloidal metal catalyst. In the ensuing 20 years, considerable gains have been made in understanding key system components and steps including the excited state dynamics and quenching of the chromophore used for electron-hole creation, the redox couples and electron transfer chains for efficient electron-hole separation, and the dark catalysts for energy-storing chemical reaction [1,11–13]. Antennae systems for collecting and funneling photon energy to the system chromophore have also been designed and studied [14–18]. However, despite the greatly increased understanding of each step and component in the overall process, an efficient, practical, molecular-based system for visible light-driven hydrogen production from water still remains elusive. Problems with unproductive back-reaction, the bimolecular nature of the chemistry involved including quenching and electron transfer reactions, and the relative instability of the chromophore have even led to speculation that multiple-component homogeneous solution systems will never represent a viable approach for artificial photosynthesis and light-driven hydrogen production [1]. On the other hand, recent developments outlined below on the synthesis of integrated multi-component systems and supramolecular chemistry suggest that with proper design, a molecular-based system for light-to-chemical energy conversion can be achieved.

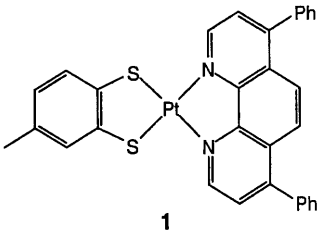
A major focus of chemistry in the past decade has been on the development of molecular assemblies and supramolecular systems containing different components

for the purpose of nano- and sub-nano-scale device construction [19–29]. In the realm of artificial photosynthesis and light-to-chemical energy conversion, elegantly formulated and daringly constructed molecules and assemblies have been reported to carry out fundamental steps of the overall photosynthetic process including the collection of photon energy, electron-hole creation and separation, charge accumulation and dark catalysis. A treatise by Balzani discusses the concept of supramolecular photochemistry and the assembly of molecular components to make *molecular photochemical devices* [30]. These devices include assemblies for vectorial transport of electrons, the generation of long-lived charge-separated states and the capture and migration of electronic energy [30]. Specific examples of each are found, respectively, in Mallouk's $Ru(bpy)_3^{2+}$/methylviologen/zeolite system for spontaneous triad assembly and charge separation [31–36], Gust and Moore's elegant quinone-porphyrin–carotenoid polyene triads and related systems for electron/hole creation and separation [37–44] and Meyer's investigations of charge separation using a Ru(II) chromophore-quencher triad and energy transfer along anthracene- and diimine-functionalized polymers and in helical proline arrays [45–56]. Additionally, energy-storing light-driven reaction chemistry has been demonstrated by Gust and Moore with ATP production employing an artificial photosynthetic membrane [57,58].

2. The platinum diimine chromophore

In the present paper, we describe efforts focused on the photochemical properties of luminescent platinum(II) diimine complexes with the long-range goal of designing a molecular-based system for light-driven, energy-storing reactions. The Pt diimine complexes are envisioned as the chromophore in these systems, having a directional charge transfer excited state for electron-hole creation and substituent flexibility for tuning of the excited state and connection to donor and acceptor groups. The Pt diimine complexes considered in this manner have either a dithiolate chelate or two acetylide ligands to complete the square planar coordination about the Pt(II) metal ion. The Pt(diimine)(dithiolate) complexes have been extensively studied by us for over a decade [59–68] and a brief review of their behavior is given here. The Pt(diimine)$(CCAr)_2$ (Ar = aryl) complexes are a relatively new set of compounds that have been synthesized and investigated over the last 3 years. The bis(acetylide) complexes are brightly luminescent in fluid solution with an emission that is significantly higher in energy than those of the corresponding dithiolates.

The observation of luminescence from square planar complexes in ambient temperature fluid solution is a relatively recent event. Prior to 1986, luminescence from square planar complexes was relatively uncommon and restricted mainly to systems in rigid media at low temperature [69–75]. During the past decade, we and others [76–83] have investigated solution emissive square planar complexes and in particular Pt(II) systems, with regard to the nature of their emitting state and their photophysical and photochemical properties. All of the solution luminescent complexes of Pt(II) found to date contain a diimine or related heteroaromatic chelating ligand.



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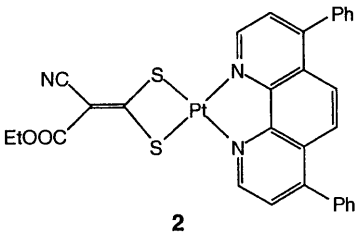

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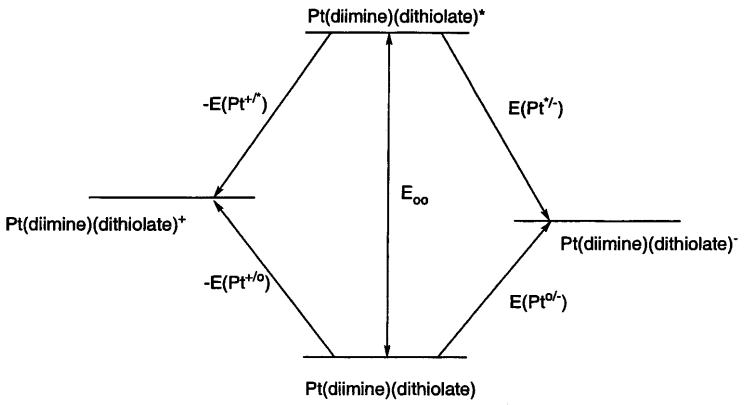
The Pt(diimine)(dithiolate) complexes studied by us and exemplified by **1** and **2** (Pt(dpphen)(tdt) and Pt(dpphen)(ecda)), respectively, are highly polar with a strong solvatochromic absorption in the visible region and a charge transfer luminescence from a state involving a mixed metal/dithiolate orbital and a π^*-orbital of the diimine ligand [59–67,84]. From relative emission quantum yields and excited state lifetimes in solution, 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)–π^*_{diimine}). The complexes were established to undergo both oxidative and reductive electron transfer quenching, with the former leading to slow photochemical decomposition of the system [60,63].

Tuning of the excited state in Pt(diimine)(dithiolate) complexes was demonstrated by systematic ligand variation and correlation of excited state properties [60]. Two series of complexes were investigated. The first were of the formula Pt(dbbpy)-(dithiolate) complexes where dbbpy = 4,4′-di-*t*-butyl-2,2′-bipyridine and the dithiolates were 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), toluene-3,4-dithiolate (tdt) and maleonitriledithiolate (mnt), while the second corresponded to Pt(diimine)(tdt) complexes where the diimines were substituted alkyl, aryl and carboalkoxy bipyridines and phenanthrolines. Through ligand variation, the excited-state energy was tuned by approximately 1 eV. Solution lifetimes ranged from 1 ns to over 1000 ns and relative emission quantum yields, ϕ_{em}, ranged from 6.4×10^{-3} to $< 10^{-5}$ in CH_2Cl_2. Based on these data, the non-radiative and radiative decay rate constants were calculated. For the Pt(diimine)(tdt) series, the non-radiative decay rate constants increased exponentially with decreasing excited state energy in agreement with the Energy Gap Law, while those for the Pt(dbbpy)(dithiolate) complexes did not exhibit a similar correlation owing to differences in structure and vibrational modes of the dithiolate.

For the two series of complexes Pt(diimine)(tdt) and Pt(dbbpy)(dithiolate), excited state reduction and oxidation potentials were estimated using electrochemical data and the simple thermochemical cycle shown in Fig. 1. The results given in the Table 1 show that the excited state oxidation potentials are sensitive to the nature of the diimine while the excited state reduction potentials are influenced by the dithiolate in a manner clearly consistent with the excited state assignment given above. The ability to vary excited state redox potentials systematically was also demonstrated by emission quenching studies of eight complexes with several electron donors and acceptors. Rates of electron transfer, k_{et}, ranged from diffusion controlled to ca. 10^6 M^{-1} s^{-1} and correlated with the driving force for the reaction.

3. Platinum diimine bis(acetylide) complexes

In 1994, Chan et al. described a platinum diimine bis(acetylide) compound that was found to luminesce brightly in fluid solution [85]. The complex, Pt(phen)-$(CCPh)_2$, showed a broad emission at 581 nm in MeCN solution which was proposed to arise from a metal-to-ligand charged transfer (MLCT). Details of the synthesis and characterization of the compound were not provided but the brightness of its solution luminescence proved intriguing. Independently, the general synthesis of platinum diimine bis(acetylides) was developed by James et al. [86] and by our laboratory using a copper iodide catalyst. While specifics of the reaction conditions such as solvent, temperature and the particular diimine may vary, the reactions shown as Eqs. (1) and (2) generally work. The CuI catalyst and the reaction conditions are similar to those used to synthesize other bis(acetylide) complexes, most notably with phosphine ligands [87–89].



excited state reduction potential: $E(Pt^{*/-}) = E_{oo} + E(Pt^{o/-})$

excited state oxidation potential: $-E(Pt^{+/*}) = E_{oo} - E(Pt^{+/o})$

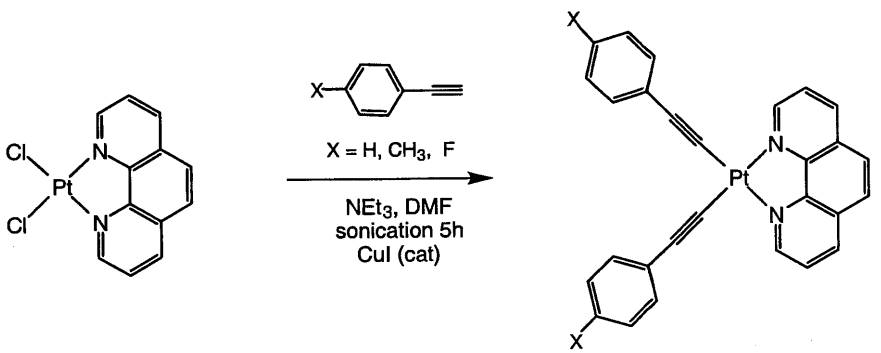
Fig. 1. A simplified thermochemical cycle for estimating the excited state reduction potentials for Pt(diimine)(dithiolate) complexes.

Table 1
Emission energy maxima and ground- and excited-state redox properties of Pt(diimine)(dithiolate) complexes[a,b]

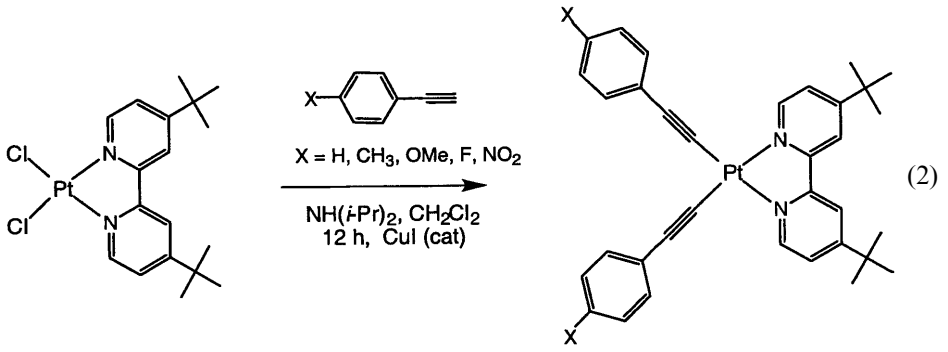
Compound	E_{em} (eV)	E ($Pt^{0/-}$)[c]	E ($Pt^{+/0}$)[d]	E ($Pt^{*/-}$)	E ($Pt^{+/*}$)
Pt(dbbpy)(tbcda)	2.51	−1.30	0.96	1.21	−1.55
Pt(dbbpy)(cpdt)	2.50	−1.27	0.96	1.23	−1.54
Pt(dbbpy)(edt)	1.97	−1.48	0.43	0.49	−1.54
Pt(dbbpy)(dmqdt)	2.30	−1.33	0.81	0.97	−1.49
Pt(dbbpy)(mnt)	2.04	−1.27	0.94	0.77	−1.10
Pt(dbbpy)(tdt)	1.93	−1.40	0.39	0.54	−1.55
Pt(tmphen)(tdt)	1.94	−1.49	0.35	0.45	−1.60
Pt(dbbpy)(tdt)	1.93	−1.40	0.39	0.54	−1.55
Pt(dmbpy)(tdt)	1.87	−1.37	0.39	0.50	−1.48
Pt(bpy)(tdt)	1.86	−1.34	0.38[e]	0.52	−1.49
Pt(phen)(tdt)	1.84	−1.32	0.38[e]	0.52	−1.46
Pt(Cl-phen)(tdt)	1.81	−1.26	0.36[e]	0.56	−1.46
Pt(Cl_2-bpy)(tdt)	1.68	−1.04	0.38	0.64	−1.30
Pt(EC-bpy)(tdt)	1.58	−0.96	0.41	0.62	−1.17

[a] All potentials in V vs. NHE.
[b] Abbreviations not defined above: edt, ethane-1,2-dithiolate; tmphen, 3,4,7,8-tetramethyl-1,10-phenanthroline; dmbpy, 4,4′-dimethyl-2,2′-bipyridine; Cl-phen, 5-chloro-1,10-phenanthroline; Cl_2bpy, 4,4′-dichloro-2,2′-bipyridine; EC-bpy, 4,4′-bis(ethoxycarbonyl)-2,2′-bipyridine.
[c] $E_{1/2}$ from reversible couple.
[d] E_p anodic peak potential from irreversible couple.
[e] Quasi-reversible couple.

The Pt(diimine)$(CCAr)_2$ complexes have all been characterized spectroscopically and by elemental analyses. The structure of the Pt(phen)$(CCTol)_2$ derivative is shown in Fig. 2 and confirms the anticipated square planar coordination geometry characteristic of Pt(II). The Pt–C(acetylide) and Pt–N(diimine) distances average 1.948 (3) and 2.063 (3) Å, respectively, in reasonable agreement with other Pt–C and Pt–N distances for the same or related ligands. In the solid state, the square planar complexes are well separated and not aligned in a stacking arrangement, while a close π-stacking contact is noted between the aryl rings of the acetylide ligands on nearest neighbor complexes.



(1)



(2)

The electronic structure of the emissive state in the Pt(diimine)$(CCAr)_2$ complexes has been probed by systematic ligand variation in conjunction with excited state lifetime and luminescence quantum yield measurements. The data are summarized in Table 2. The Pt(diimine)$(CCAr)_2$ complexes in Table 2 comprise two series, one in which the diimine is held fixed as di-*t*-butylbipyridine while the arylacetylide ligand is varied in the para position, and the other in which the acetylide ligand is maintained constant as CCPh and the diimine is a phen derivative varied in the 5-position. Fig. 3 shows the room temperature solution emission spectra for both series of complexes. In panel A of Fig. 3, the absorption and room temperature and 77 K emission spectra of Pt(5-Mephen)$(CCPh)_2$ are presented. From the dbbpy series, it can be seen that the room temperature emission shifts to lower energy as X becomes more electron-donating (panel B of Fig. 3); the extent of this shift is

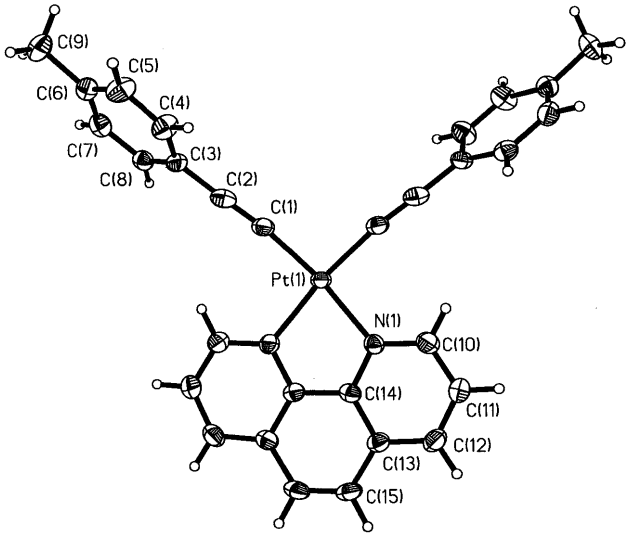


Fig. 2. A perspective drawing of the molecular structure of Pt(phen)$(CCTol)_2$.

Table 2
Excited-state properties of Pt(diimine)$(CCAr)_2$ complexes

Compound	λ_{max} (nm)	ϕ_{em}[a]	τ (ns)[b]	k_r ($\times 10^6$ s^{-1})	k_{nr} ($\times 10^6$ s^{-1})
Pt(dbbpy)$(CCC_6H_4F)_2$	570	0.14	663	0.21	1.3
Pt(dbbpy)$(CCPh)_2$	570	0.11	691	0.15	1.2
Pt(dbbpy)$(CCTol)_2$	592	0.07	440	0.16	2.1
Pt(dbbpy)$(CCC_6H_4OMe)_2$	640	0.002	14[c]	0.14	71
Pt(5Me-phen)$(CCPh)_2$	575	0.098	980	0.10	0.9
Pt(phen)$(CCPh)_2$	580	0.090	907	0.10	1.0
Pt(5Cl-phen)$(CCPh)_2$	605	0.040	375	0.10	2.5
Pt(5Br-phen)$(CCPh)_2$	605	0.036	350	0.13	3.4

[a] ϕ_{em} values are relative to $Ru(bpy)_3(PF_6)_2$ in MeCN ($\Phi = 0.062$) and extrapolated to infinite dilution.
[b] Excited state lifetimes in MeCN with λ_{ex} at 406 nm are extrapolated to infinite dilution ($\tau = 1/k_o$).
[c] This lifetime was measured using single-photon counting with λ_{ex} at 420 nm.

relatively minor and much less than that seen with dithiolate variation published previously. The series in which the acetylide remains fixed exhibits a decrease in emission energy as the 5-phen substituent becomes more electron-withdrawing (panel C of Fig. 3) but the change is even more modest than for the dbbpy series of complexes. Both sets of changes are consistent with a HOMO that is primarily metal based and a LUMO composed mainly of π*(diimine). Changes that influence the former are provided by the series in which the acetylide is varied — as donicity of the ligand increases, the metal-based HOMO rises in energy leading to a shift of the emission to longer wavelengths. The spectral shifts are thus consistent with the proposal of Chan et al. of a metal-to-diimine charge transfer for the excited state [85]. It is interesting to note that the absorption spectra of the Pt(diimine)$(CCAr)_2$ complexes all exhibit a band in the range 385–400 nm in MeCN that is attributed to an MLCT transition of the same orbital parentage but different multiplicity (singlet for the absorption and triplet for the emission (vide infra)). However, the observed spectral shifts in the MLCT absorption band as a function of ligand variation are very small for the systems examined.

The excited state lifetime measurements, done using time-correlated spectroscopy as described elsewhere, reveal that the emission has a significant degree of spin-forbiddenness consistent with a ^{3}MLCT assignment. Luminescence quantum yields for the complexes of Table 2 show that some of the systems are brightly emissive with luminescence intensities nearly twice that of absorbance-matched $Ru(bpy)_3^{2+}$ solutions in comparable solvents. From both lifetime and emission quantum yields, the radiative and non-radiative rate constants can be calculated using Eqs. (3) and (4). The short lifetime and low emission quantum yield for the electron-donating *p*-$MeOC_6H_4$ acetylide derivative are consistent with the Energy Gap Law from a plot of $\log k_{nr}$ vs. E_{em}^{max} for the ddbpy series of complexes.

$$k_r = \phi_{em} \times \tau^{-1} \quad (3)$$

$$k_{nr} = k_r(\phi_{em}^{-1} - 1) \quad (4)$$

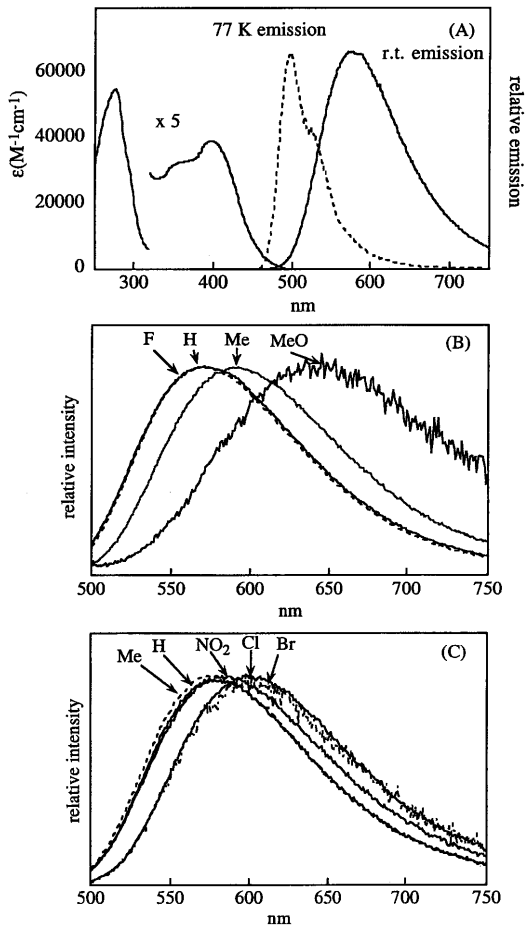


Fig. 3. Solution emission spectra of Pt(diimine)$(CCAr)_2$ complexes in MeCN solutions. Panel A: 298 K absorption and emission spectra and the 77 K emission spectrum for Pt(5-Mephen)$(CCPh)_2$. Panel B: emission spectra for the Pt(dbbpy)$(CCC_6H_4X)_2$ complexes. Panel C: emission spectra for the Pt(5-X′phen)$(CCPh)_2$ series.

The Pt(diimine)$(CCAr)_2$ complexes undergo electron transfer quenching of both reductive and oxidative types. As with the corresponding diimine dithiolate complexes, the systems are relatively photostable in the presence of an electron donor whereas photodegradation occurs under oxidative quenching. For Pt(dbbpy)$(CCPh)_2$, reductive quenching was examined quantitatively using 10-methylphenothiazine and *N*,*N*,*N*′,*N*′-tetramethylbenzidine as electron donors. Good Stern–Volmer behavior was seen for both quenchers with essentially diffusion-controlled k_q values of 9.6×10^9 and 1.3×10^{10} M^{-1} s^{-1} and τ_o of 715 ± 20 ns. All of the complexes exhibit reversible reduction waves by cyclic voltammetry. The $E_{1/2}$ reduction potentials for the dbbpy series are close in value, reflecting the fact that upon reduction the same π*-orbital of the diimine is occupied in each case.

Table 3
Ground- and excited-state redox properties of Pt(diimine)$(CCAr)_2$ complexes[a]

Compound	E_{oo} (eV)	$E_{1/2}$ (red, V vs. NHE)[b]	E (Pt^*/Pt^-)
$Pt(dbbpy)(CCPh)_2$	2.55	−1.38	1.17
$Pt(dbbpy)(CCTol)_2$	2.52	−1.37	1.15
$Pt(dbbpy)(CCC_6H_4F)_2$	2.55	−1.36	1.19
$Pt(dbbpy)(CCC_6H_4OMe)_2$	2.38	−1.39	0.99

[a] All potentials in V vs. NHE.
[b] $E_{1/2}$ from reversible couple.

Through the use of a thermochemical cycle analogous to that shown in Fig. 1 involving the excited-state energies E_{oo} and the reversible reduction potentials $E_{1/2}$, the excited-state reduction potentials for the Pt(diimine)$(CCAr)_2$ complexes have been estimated. Table 3 presents the results which show that the smallest $E(Pt^*/Pt^-)$ value corresponds to the most electron donating of the bis(acetylide) derivatives, reflecting the ease with which the hole in the HOMO is filled upon reduction of the excited configuration.

4. Self-quenching of Pt(diimine) complexes

In the course of measuring excited state lifetimes of Pt diimine dithiolate and bis(acetylide) complexes, it was seen that the lifetimes exhibited a concentration dependence. This observation, indicative of more than simple radiative and non-radiative decay paths from the excited state, stimulated a study that demonstrated the existence of self-quenching in platinum(II) diimine systems [90]. Plots of excited state lifetime versus complex concentration yielded linear correlations in accord with Eq. (5) obtained from a modified Stern–Volmer analysis where k_{obs} is the observed first order decay rate and k_o is the first order decay rate at infinite dilution. Two examples are shown in Fig. 4 for Pt(phen)$(CCTol)_2$ and Pt(tmphen)(tdt) (tmphen = tetramethylphenanthroline), yielding second-order quenching rate constants k_q that are essentially diffusion controlled.

$$k_{obs} = k_o + k_q[Pt] \quad (5)$$

Self-quenching for the systems described here involves the interaction of an excited Pt diimine molecule with one in the ground state leading to a reduction in emission from the former. If the two molecules associate for a period that is long on the vibrational time scale, an excimer or excited state dimer is formed. The observation of emission from the excimer thus serves as additional proof of self-quenching. For the related Pt diimine complexes Pt(dpphen)$(CN)_2$ and Pt(dbbpy)$(CN)_2$, excimer emission was reported nearly 10 years ago [91–93]. In these studies by Vogler and Che, it was seen that in dilute solutions, these complexes exhibited high-energy, structured emissions assignable to a $^3\pi\pi^*$ state, but that in more concentrated solutions, a broad red-shifted emission was seen [91,92]. For

both di(cyanide) complexes, Beer's Law behavior was followed in their respective absorption spectra indicating that ground state aggregation was not occurring over the concentration ranges investigated. Emission decay profiles for the Pt-(dbbpy)$(CN)_2$ system also revealed a rise time for the broad red-shifted emission, leaving little doubt that it arose from bimolecular chemistry (i.e. excimer formation) after excitation of the Pt(dbbpy)$(CN)_2$ chromophore [92].

Analysis of emission spectra for Pt(phen)$(CCPh)_2$ at 0.01 and 0.50 mM concentrations suggested a slight but significant difference at long wavelength (750 nm) relative to the emission maximum at ca. 570 nm. The results are shown in Fig. 5. A difference spectrum provided evidence of excimer emission which was confirmed when the decay profiles at 570 and 750 nm were measured independently (Fig. 5 inset). The latter shows an initial rise consistent with formation of an excimer whose lifetime is ca. 100 ns. The excimer emission thus seen for Pt(phen)$(CCPh)_2$ establishes the existence of self-quenching for the bis(acetylide) complexes [90]. To date, however, a corresponding excimer emission has not been observed for the analogous tdt complex; its excimer emission would be expected at wavelengths beyond current detector sensitivity (>825 nm) with an intensity thought to be extremely weak.

To probe the basis of self-quenching in Pt diimine complexes further, a series of quenching experiments was conducted [90]. First, it was found that free phenanthroline or free naphthalene, known for their ability to engage in π-stacking, had no effect on the emission spectrum or excited state lifetime of Pt(tmphen)(tdt). Second, in a cross-quenching experiment, solutions containing both Pt(phen)$(CCPh)_2$ and

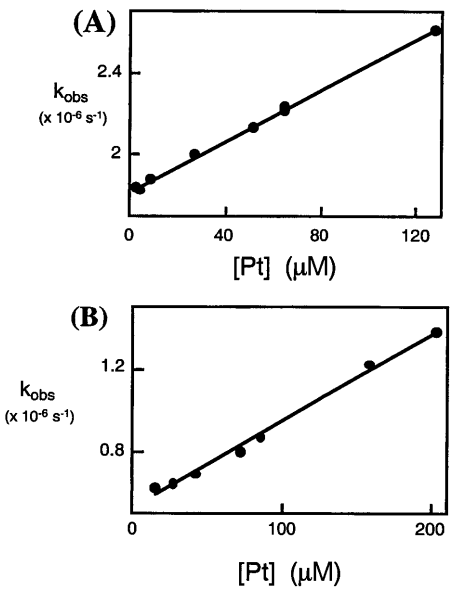


Fig. 4. Stern–Volmer plots of excited state lifetimes vs. metal complex concentration for Pt-(phen)$(CCTol)_2$ (A) and Pt(tmphen)(tdt) (B).

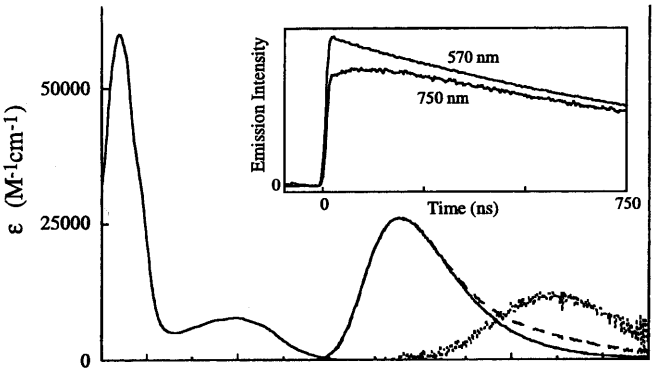


Fig. 5. Absorption and emission spectra for Pt(phen)$(CCPh)_2$ (solid line, 0.01 mM; dashes, 0.5 mM; dots, difference emission spectrum × 5) in CH_2Cl_2. The inset shows the emission intensities at 570 and 750 nm after laser flash excitation (λ_{ex} 460 nm). Emission spectra are arbitrarily scaled.

Pt(tmphen)(tdt) were found to give reduced lifetimes for both complexes. While partial quenching of the higher energy excited state (that of the bis(acetylide) complex) can be rationalized by energy transfer to the lower energy excited state (that of the tdt species), the same analysis could not be applied to the tdt complex, which yielded a near diffusion-controlled k_q for quenching by Pt(phen)$(CCPh)_2$. Finally, quenching was noted when a non-emissive complex, Pt(dbbpy)Cl_2, was employed with Pt(phen)$(CCPh)_2$ and a Stern–Volmer plot of the latter's emission intensity yielded k_q of 2×10^9 M^{-1} s^{-1} for the non-emissive, slightly more hindered Pt diimine quencher.

The results indicate that self-quenching is a general phenomenon for Pt diimine complexes which possess a variety of emitting states from $^3\pi\pi^*$ at high energy for the di(cyanide) systems to ^{3}MLCT for the bis(acetylide) complexes and ^{3}MMLLCT (mixed metal/ligand-to-ligand charge transfer) for the lower energy dithiolate derivatives. The basis of self-quenching appears to involve association between excited state and ground state molecules, and from the experiments conducted, we conclude that this takes place by Pt···Pt interaction, though π-stacking interactions between aromatic ligands could also play a role. The proposed arrangements are shown in Fig. 6. It is evident that self-quenching and excimer formation should be considered when the solution photochemistry and photophysics of Pt diimine complexes at higher concentrations (> ca. 0.2 mM) are examined.

5. A molecular photochemical device based on the platinum diimine chromophore

Analysis of photosynthesis and the problem of light-to-chemical energy conversion leads to a number of considerations in the design of any system to accomplish this goal. They include photon capture, electron-hole creation, electron-hole separation, charge storage and accumulation, and dark reaction catalysis of the desired

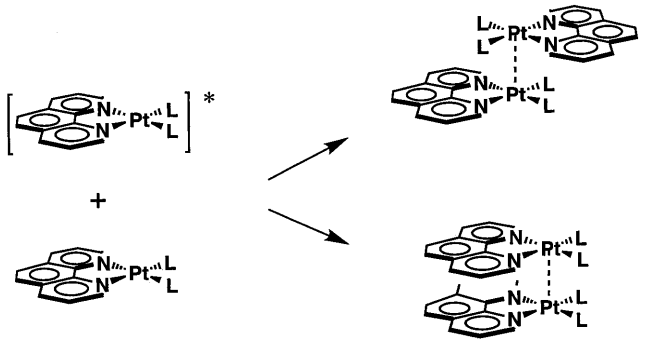
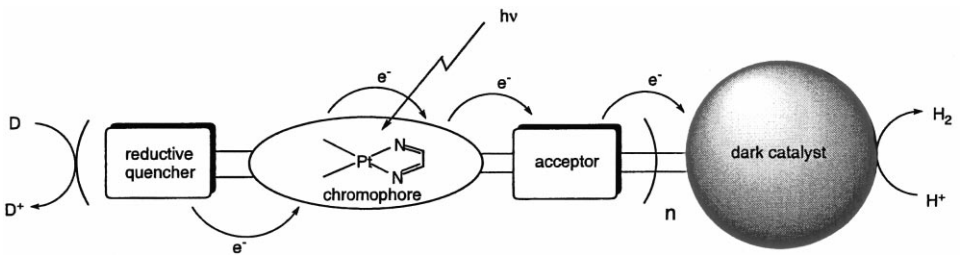


Fig. 6. Proposed interactions between excited and ground state Pt diimine complexes leading to excimer formation and self-quenching.

reaction. For electron-hole creation and separation, one needs a visible light absorber that undergoes a charge transfer excitation in a manner that will allow the electron-hole pair to become spatially separated through an electrochemical gradient. The latter corresponds to vectorial electron transfer. Following Balzani's analysis [30], a molecular photochemical device (MPD) based on the platinum diimine chromophore can be envisioned as in Scheme 1. Since the Pt diimine complexes are photostable under reductive quenching conditions, the proposed MPD is formulated to function by rapid electron transfer from a donor to the Pt diimine chromophore with the donor connected to the anionic ligands of the square planar moiety. The donor may be either an organic molecule or a coordination complex with the only requirements being that it can reductively quench the Pt diimine excited state and that it is relatively stable upon oxidation to the corresponding cation.

The acceptor component is attached to the diimine and provides a facile, downhill path for electron transfer from the π^*(diimine) orbital into which the charge-transfer electron has been excited. The free energy change ΔG used to drive the electron transfer onto the acceptor component serves to effect spatial electron-hole separation. Additional or secondary acceptors can also be envisioned in this model, each with a reduction potential slightly more favorable than the previous acceptor. The electrochemical gradient thus developed serves to facilitate charge



Scheme 1.

separation and inhibit unproductive back-reaction. However, with each electron transfer, some of the energy input to the system through photoexcitation is consumed, making less chemical potential available for the ultimate energy storing reaction.

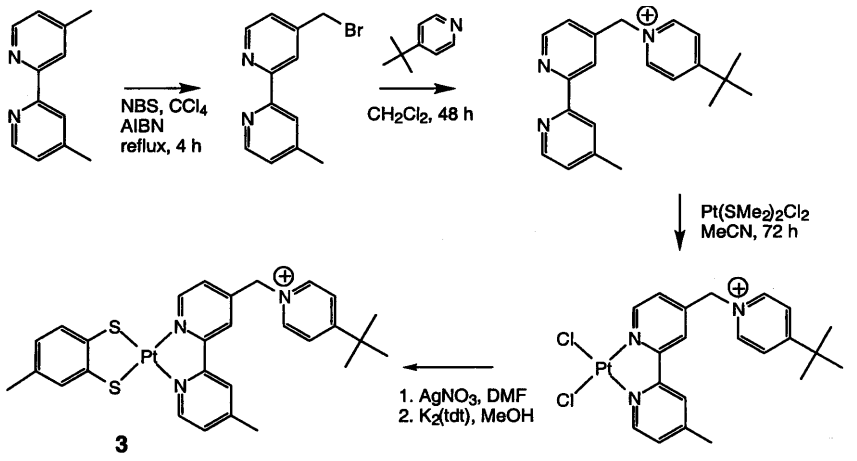
Charge accumulation is an essential part of any system for light-to-chemical energy conversion since bonds, formed or broken, involve electron pairs whereas photoexcitation under solar radiation is in general a single electron event. Owing to the multi-electron nature of desirable energy-storing reductions — i.e. $n = 2$ for H_2, while $n = 2, 4, 6$ or even 8 for CO_2 [94] — the dark catalyst will have a number of Pt(diimine) chromophores attached to it. The dark catalyst is envisioned as a metal colloid functioning as a 'microelectrode' in which charge can be accumulated and the desired reaction promoted. In the particular MPD envisioned in Scheme 1, the energy-storing reaction is H_2 generation from protons supplied by water and electrons supplied by a sacrificial donor. While multiple component reaction systems containing mixtures of compounds have been used in the past to effect this reaction, the stability of these systems, as well as their relative inefficiencies as a consequence of bimolecular chemistry, render them unsuitable for practical application. The notion of an MPD to achieve this reaction in a more efficient and durable way thus becomes a highly desirable objective.

The challenge to designing and constructing an MPD concerns mainly the connections or bridges used to link components and how they will be put in place. Synthetic strategy is thus of paramount importance. The bridges are required to facilitate electronic communication between system components and will allow their controlled positioning and orientation. A number of recent efforts on the study of donor–bridge–acceptor systems have been reported and have shown that for rapid charge separation, the energies of bridge orbitals relative to those of donor and acceptor must be considered [11,37,39,41,44,46,48,52,53,55]. Specifically, Wasielewski and co-workers have demonstrated that bridge orbitals for optimized electron transfer should closely match to those of the donor, and lie at only very slightly higher energies [95]. The use of carotenoids as bridges has been described in elegant studies by Gust and Moore [37,39–41,44].

6. Dyads and triads

In order to address the challenge posed by building the MPD envisioned in Scheme 1, we are carrying out studies to synthesize two- and three-component systems, dyads and triads, for charge separation upon photoexcitation. The dyads have either a reductive donor connected to the Pt diimine chromophore through the anionic ligands of the Pt coordination sphere or an acceptor attached to the diimine part of the molecule.

The simplest — and earliest — dyad synthesized by us in this context is shown in Scheme 2 in which dimethylbipyridine (dmbpy) is brominated and then reacted with *t*-butylpyridine to form a pyridinium acceptor prior to diimine complexation. Subsequent substitution of the chloride ligands by toluenedithiolate yields the dyad



Scheme 2.

shown as **3**. Initial study of this system showed that partial quenching of the Pt(dmbpy)(tdt) excited state does occur. Fig. 7 provides a simple thermochemical analysis for **3** based on the excited state energy E_{oo} and the redox potentials for the pyridinium/pyridine and Pt(dmbpy)(tdt)$^{0/+}$ couples (with the caveat that Pt-(dmbpy)(tdt) does not undergo oxidation reversibly so that the value of $+1.7$ V for the back reaction is not well based), to indicate that the driving force for forward electron transfer (charge separation) is much less than that of back-electron transfer (charge recombination). In **3**, light-driven charge separation corresponds to oxidative quenching. The observation that **3** exhibits decomposition upon prolonged irradiation underscores one of the important considerations in designing the MPD of Scheme 1, namely that the excited Pt(diimine) chromophore be quenched reductively rather than oxidatively.

The strategy we are currently pursuing in the synthesis of dyads and triads employs well-documented Pd-catalyzed coupling reactions involving aryl halides and alkynes. The conditions for these coupling reactions were developed by Hagihara and co-workers [96,97]. The types of dyads envisioned by this strategy are illustrated by **4**–**7** with **4** and **5** leading to reductive quenching of the excited chromophore, and **6** and **7** achieving charge separation via oxidative quenching.

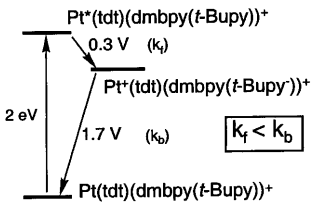


Fig. 7. Simplified thermochemical cycle for estimating the driving force for forward and back electron transfers in dyad **3**.

In Scheme 3, the synthesis of a donor–chromophore dyad based on a Pd-catalyzed coupling strategy is outlined with phenothiazine (PTZ) as the donor. Phenothiazine and its derivatives have been used previously as donors in dyads and triads containing tris diimine-chelated Ru^{2+} chromophores [55,98,99]. The redox potentials for the oxidation of PTZ and 10-MePTZ are 0.60 and 0.72 V versus NHE, respectively. Dyad **8** in Scheme 3 connects the PTZ moiety to the bridge at the N atom of the thiazine ring. The synthesis proceeds in good yield from PTZ and *p*-bromobenzyl bromide by initial *N*-alkylation followed by Pd-catalyzed coupling to give the TMS-protected alkyne. Deprotection of the alkyne and CuI-catalyzed reaction with $Pt(dbbpy)Cl_2$ yields the desired product.

Dyad **8** exhibits a charge transfer band in the absorption spectrum similar to that seen for other Pt diimine bis(acetylide) derivatives, and reversible electrochemical waves corresponding to dbbpy reduction at -1.39 V and PTZ oxidation at 0.81 V. The presence of the PTZ group leads to efficient quenching of the MLCT emission. Fig. 8 shows the emission spectra of the model compound $Pt(dbbpy)(CCPh)_2$ and dyad **8**. The nearly complete quenching of the latter is thought to occur by rapid electron transfer from PTZ to the excited Pt diimine chromophore. The charge-separated species, however, has not been detected on timescales down to 20 ns, presumably because of efficient and rapid back electron transfer.

A more general approach to donor–chromophore dyads is outlined in Scheme 4 that is currently being followed in our laboratory. In this approach, an aldehyde-functionalized donor undergoes a Horner–Wadsworth–Emmons reaction with a phosphonate ester derived from *p*-bromobenzylbromide prior to the Pd-catalyzed coupling. In this way, the donor remains in conjugation with the alkyne and the Pt center. Different donors can be employed in this approach, the sole synthetic requirement being aldehyde functionality on the donor. At present, dyads **9** having ferrocene (Fc), phenothiazine (PTZ) and tetrathiafulvalene (TTF) as donors are being synthesized via Scheme 4. The synthesis of the Fc-containing dyad is complete, while the other two have progressed through the Pd-catalyzed coupling stage. The Fc-containing dyad exhibits significant quenching of the Pt chro-

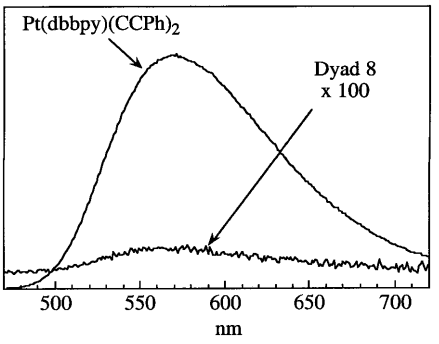
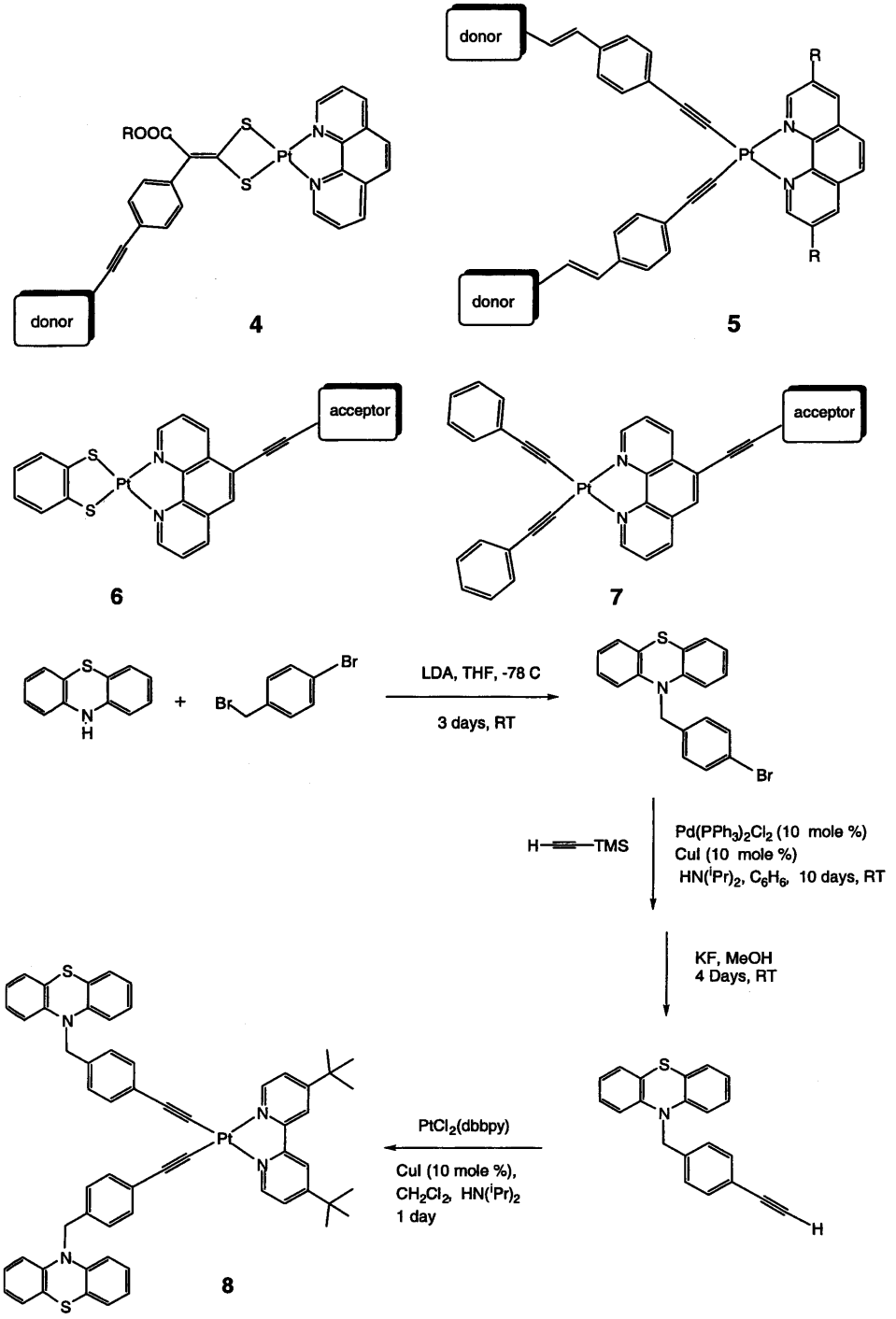


Fig. 8. The emission spectra of $Pt(dbbpy)(CCPh)_2$ and dyad **8**.


donor
ROOC
S
S
Pt
N
N
donor
4
donor
R
N
Pt
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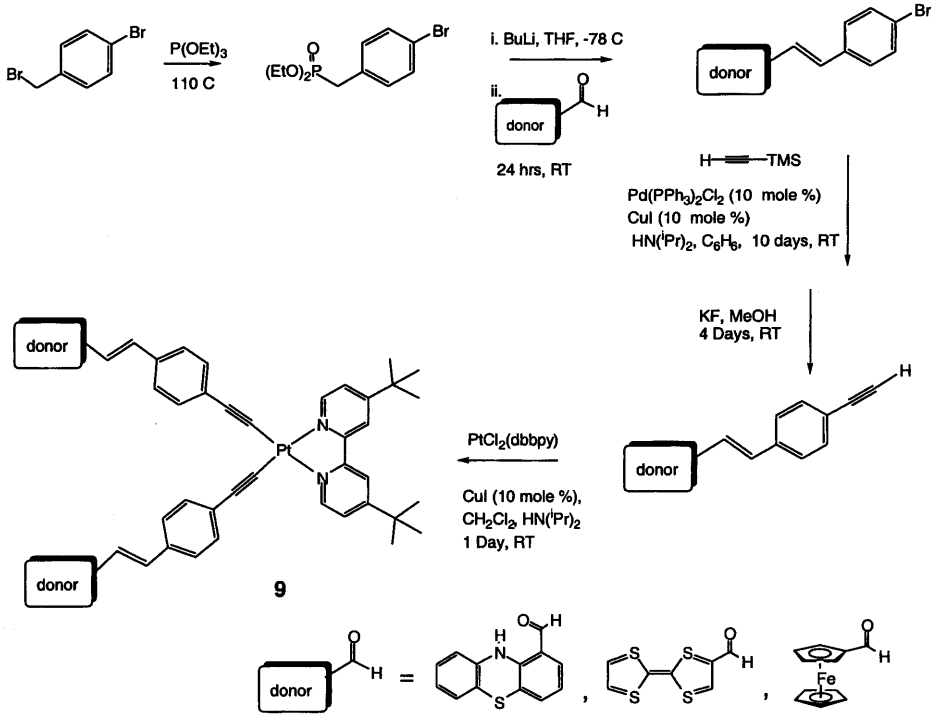
R
donor
5
acceptor
S
S
Pt
N
N
6
acceptor
Pt
N
N
7
S
N
H
+
Br
Br
LDA, THF, -78 C
3 days, RT
S
N
Br
H—≡—TMS
Pd(PPh3)2Cl2 (10 mole %)
CuI (10 mole %)
HN(iPr)2, C6H6, 10 days, RT
KF, MeOH
4 Days, RT
S
N
H
PtCl2(dbbpy)
CuI (10 mole %),
CH2Cl2, HN(iPr)2
1 day
S
N
Pt
N
N
N
S
8

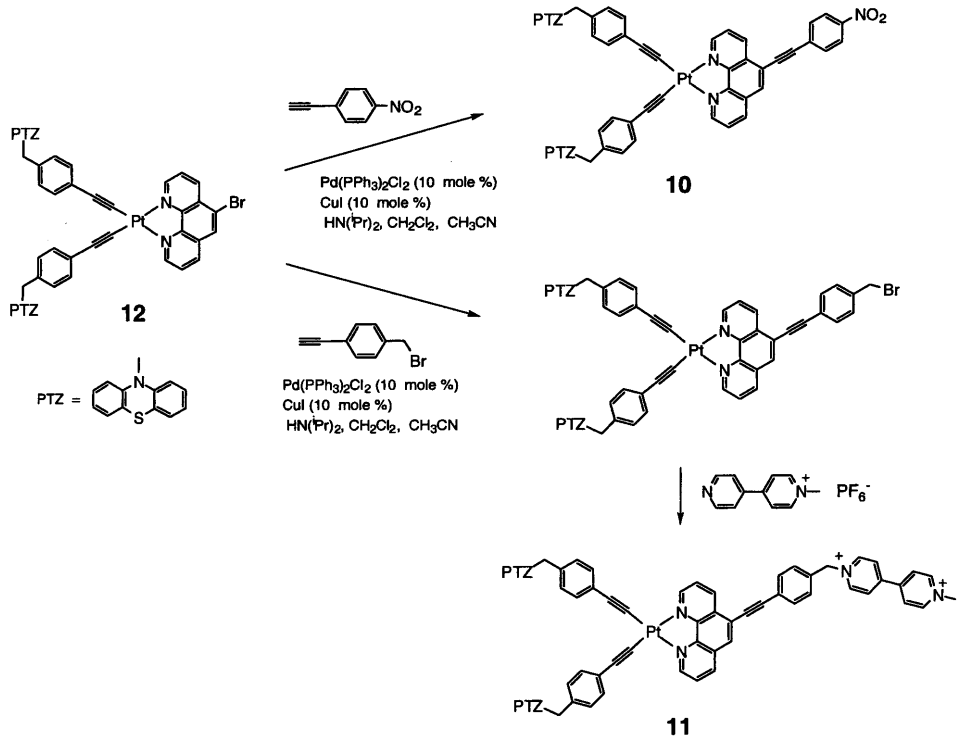
Scheme 3.



Scheme 4.

mophore. As in the case of the PTZ dyad, no charge-separated species is observed on timescales down to 20 ns.

The attachment of an acceptor to the diimine side of the chromophore proceeds by Pd-catalyzed coupling reactions as well. Examples of these couplings using bromo-substituted hetero-aromatic chelating ligands have been described recently by Ziessel and Tor [100–105], and the viability of our approach has been supported by the synthesis of Pt(5-phenCCPh)$(CCPh)_2$ from the corresponding bromo-derivative [106]. Studies are now in progress for dyad and triad construction using other 5-Brphen derivatives of Pt diimine chromophores. One specific example involves the synthesis of triads **10** and **11** as envisioned in Scheme 5. Complex **12** has been synthesized and characterized with elaboration into a triad now underway. As in the case of the PTZ–$Ru(bpy)_3^{2+}$–MV^{2+} triad reported by Meyer and Elliot [98], **10** and **11** are expected to have long-lived charge-separated states, thus achieving one of the key goals in the development of an MPD for light-to-chemical energy conversion. Other approaches to triads in which a Pt diimine moiety serves as the chromophore are also in progress.



Scheme 5.

7. Conclusions

Over the last decade, platinum diimine complexes have been found to luminesce in fluid solution. The energy and nature of the emitting state vary with the anionic ligand from the highest energy $^3\pi\pi^*$ of the di(cyanide) derivatives to the lowest energy ^{3}MMLLCT of the dithiolate systems. Tuning of the excited state energies and properties through systematic ligand variation has been demonstrated for the latter. The bis(acetylide) complexes Pt(diimine)$(CCAr)_2$ have been found to be brightly luminescent in fluid solution with relative emission quantum yields greater than $Ru(bpy)_3^{2+}$ and have emission energies between those of the di(cyanide) and dithiolate derivatives. The excited state for Pt(diimine)$(CCAr)_2$, originally proposed to be ^{3}MLCT, has been confirmed through diimine and arylacetylide substitution and emission measurements. For each set of Pt diimine complexes, the LUMO is a $\pi^*_{diimine}$ orbital, while the HOMO varies depending on the electron-donating properties and orbital energies of the anionic ligands. The bis(acetylide) complexes have been established to undergo electron-transfer quenching, and like the dithiolate derivatives, are photostable in the presence of electron donor quenchers but unstable under oxidative quenching conditions.

A general feature of all of the Pt diimine complexes is that they show evidence of self-quenching. For the bis(acetylide) and dithiolate derivatives, excited state lifetimes in fluid solution are found to decrease with increasing concentrations. For the di(cyanide) systems, it was previously reported that higher concentrations result in red-shifted excimer emission. A recent study has established the generality of self-quenching for these square planar complexes by carrying out cross-quenching experiments involving mixtures of Pt diimine systems and by observing weak excimer emission for $Pt(phen)(CCPh)_2$. The mechanism of self-quenching is thought to proceed via interaction between excited state and ground state molecules through the Pt centers.

The directionality of the charge transfer excited state in Pt diimine bis(acetylide) and dithiolate complexes and the relative photostability of these systems under reductive quenching conditions make them of interest for incorporation into molecular photochemical devices for photoinduced charge separation and light-driven energy-storing reactions. In the desired molecular photochemical devices, the Pt diimine chromophore is attached to the reductive quencher through the anionic ligands of the square planar coordinated metal center and to an electron acceptor through the diimine ligand.

The synthetic strategy being followed in the construction of the target MPDs and in related dyads and triads involves the use of Pd-catalyzed coupling reactions between alkynes and aryl halides. Several dyads have been synthesized in this manner, one in which the donor is phenothiazine and a second with ferrocene as the donor. Other systems are currently under construction. The dyads prepared to date exhibit efficient quenching of the excited state. Elaboration of these systems into triads is expected to increase the lifetime of charge separated excited states for ultimate use in a Pt diimine based system for artificial photosynthesis.

Acknowledgements

We wish to thank the Department of Energy, Division of Chemical Sciences, for support of this research.

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