

Study of the Heterocyclic-Substituted Platinum-1,2-Enedithiolate ³ILCT Excited States by Transient Absorption Spectroscopy

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The photoluminescent 1,2-enedithiolate complexes, (dppe)Pt{S₂C₂(2-quinoxaline)(H)}, [L₂Pt{S₂C₂(2-pyridinium)(H)}]⁺ where L₂ = dpmp and dppe, [L₂Pt{S₂C₂(4-pyridinium)(H)}]⁺, [L₂Pt{S₂C₂(N-Methyl-4-pyridinium)(H)}]⁺ and [L₂Pt{S₂C₂(CH₂CH₂-N-2-pyridinium)}]⁺ where L₂ = dpmp, dppe, and dppp are room temperature dual emitters where the emissions have thiolate to heterocycle π* intraligand charge transfer character (ILCT) singlet and triplet character. The pyridinium complexes have strong triplet-triplet absorption bands at approximately 400, 520 and 630 nm with a weaker band at 800 nm while (dppe)Pt{S₂C₂(2-quinoxaline)(H)} has strong triplet-triplet absorption bands at 385 and 550 nm with weaker bands at 610 and 805 nm. By fitting the decay of the transients to single exponential kinetics, the ³ILCT* lifetimes of the pyridinium complexes were determined to be 0.7 to 15.9 μs (DMSO) while the ³ILCT* lifetime of (dppe)Pt{S₂C₂(2-quinoxaline)(H)} was determined to be 2.8 μs (CH₃CN). The transient absorption spectra of the complexes is affected by the appended heterocycle rather than the bulk of ancillary phosphine ligand or whether the heterocycle is protonated or alkylated.

KEY WORDS: Transient absorption; platinum-1,2-enedithiolates; dual emitter; pyridinyl radical.

INTRODUCTION

Platinum-1,2-enedithiolates have emerged as an important new class of room temperature solution lumiphores [1–16]. Our group has focused on the study of heterocyclic-substituted complexes of the type L₂Pt{S₂C₂(Het)(R)} where L₂ = dpmp = 1,2-bis(diphenylphosphino)methane, dppe = 1,2-bis(diphenylphosphino)ethane, and dppp = 1,2-bis(diphenylphosphino)propane and Het = 2-quinoxalyl(ium), 2- or 4-pyridyl(ium) [1–3]. These complexes are a unique class of room temperature dual emitters with broad sensor applications [17,18].

The room temperature photoluminescence from these complexes has been assigned to a short-lived singlet and a long-lived triplet state with considerable thiolate to heterocycle π* intraligand charge transfer (ILCT) character [1–5]. The study of the triplet-triplet transitions by transient absorption (TA) spectroscopy is reported in this paper. The results from this study support a common ³ILCT* excited state where the heterocycle is the charge acceptor. Localized charge density upon the heterocycles in these complexes has led to proton state dependent emitters and photobasic complexes in this class [1–5]. A

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study of the photobasicity of $(dppe)Pt\{S_2C_2(2\text{-quinoxaline})(H)\}$ by TA spectroscopy is also reported.

EXPERIMENTAL

Materials. Complexes **1–12** were prepared according to or by modification of the established literature procedures [1–5]. Benzoic acid and DMSO were purchased from Acros and used without further purification. Acetonitrile was dried over CaH_2 and distilled prior to use.

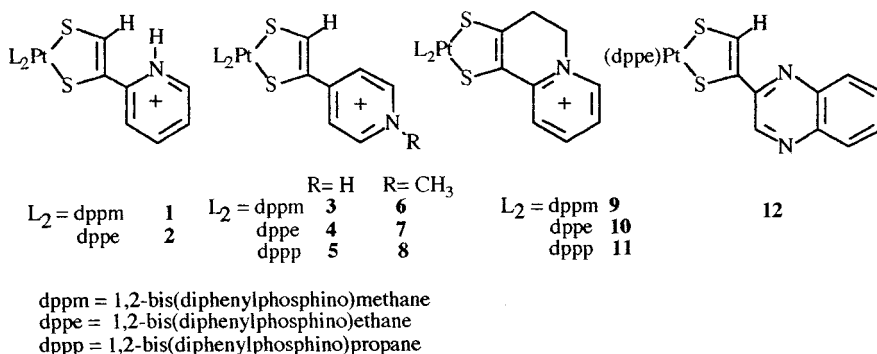
Physical Measurements. UV-visible spectra were recorded on a Perkin Elmer Lambda 2S spectrometer. Room-temperature excitation and emission spectra were acquired with a SLM AB2 fluorescence spectrometer. Emission spectra were corrected for instrumental response using factors supplied by the manufacturer. Oxygen free luminescence measurements were made on 10^{-5} M solutions of all complexes that were deoxygenated by three-freeze pump-thaw N_2 -backfill cycles in a fluorescence cell equipped with a reservoir and a Teflon valve. Quantum yields, ϕ , were calculated relative to $Zn(tpp)\{\phi_{std} = 0.04\}$ (tpp = tetraphenylporphyrinato) [36] in air and under Ar.

Nanosecond laser flash photolysis studies were conducted on solutions that were argon bubble-degassed for 30 minutes in a 5 mL recirculating cell to minimize the effects of sample decomposition during data acquisition. Data collection was repeated multiple times to assure consistent deoxygenation of samples. Excitation was achieved by using the third harmonic output of a Nd:YAG laser (Spectra Physics, GCR-14S, 355 nm, 10 ns fwhm, 10 mJ pulse $^{-1}$). The optical transients were monitored using a 75 W xenon arc lamp housed in an f/3.6 elliptical reflector housing (PTI ALH-1000), which is modulated with an in-house ms time scale, 100 A current pulser. The arc lamp is filtered with an IR filter (H_2O) and blocked

from the sample with a fast shutter between data acquisition cycles (Vincent Associates, Uniblitz). The laser and arc beams enter the 5 mL recirculating sample cell at a 90 degree angle, with apertures of 8×4 mm for the laser and 1×3 mm for the monitoring arc light. Thus, the effective path length of the experiment is defined by the laser beam width (8 mm), and the monitoring light beam is completely contained within the laser beam excitation path. Light not absorbed by the sample was collected through an ISA TRIAX 180 monochromator and detected with an R446 photomultiplier tube biased to -750 V and wired for high light intensity using a design reported in the literature [37]. Signals were collected with a Tektronix TDS 540 digitizing oscilloscope and processed on a 160 MHz pentium computer through a GPIB interface. Transient absorption spectra are generated from a series of transient decays taken at individual wavelengths. Laser, arc lamp pulser, and shutter control are achieved through in-house electronics, and computer control is afforded through a National Instruments PC DIO-24 Digital I/O interface. Factor analysis of the multi-wavelength transient absorption data array was performed with SPECFIT analysis software [38].

RESULTS AND DISCUSSION

Electronic Spectra. The complexes included in this study are shown in Scheme 1. All of the complexes have a UV-visible band assignable to a 1,2-enedithiolate π to heterocycle π^* intraligand charge transfer transition (ILCT) (Scheme 1) [1–5]. The ILCT band in $(dppe)Pt\{S_2C_2(2\text{-quinoxaline})(H)\}$ is found at $22,700$ cm^{-1} (CH_2Cl_2 , Table I) and shifts to $17,700$ cm^{-1} upon protonation. The ILCT band of the pyridinium complexes is found between $24,000$ – $20,000$ cm^{-1} (CH_2Cl_2 , Table I). In previous studies, the energy of the ILCT was found to correlate with the reduction potential of the heterocycle



Scheme 1.

Table I. UV-Visible Spectra of Complexes **1–12** recorded in CH₂Cl₂

Complex	Ligand (L ₂)	
[L ₂ Pt{S ₂ C ₂ (2-pyridinium)(H)}] ⁺		
1	dppm	334 (6500), 449 (5100)
2	dppe	336 (sh 280), 458 (6600)
[L ₂ Pt{S ₂ C ₂ (4-pyridinium)(H)}] ⁺		
3	dppm	334 (6600), 450 (7800)
4	dppe	342 (3800), 474 (5900)
5	dppp	334 (7200), 462 (8700)
[L ₂ Pt{S ₂ C ₂ (N-methyl-4-pyridinium)(H)}] ⁺		
6	dppm	346 (5800), 483 (7900)
7	dppe	358 (7000), 501 (9100)
8	dppp	357 (4300), 502 (5800)
[L ₂ Pt{S ₂ C ₂ (CH ₂ CH ₂ -N-2-pyridinium)}] ⁺		
9	dppm	350 (10700), 480 (3400)
10	dppe	344 (12400), 496 (3200)
11	dppp	349 (12000), 499 (3300)
L ₂ Pt{S ₂ C ₂ (2-quinoxaline)(H)}		
12	dppe	336 (9400), 442 (6000)

and hence the electron affinity of the π^* accepting orbital of the heterocycle [3].

Luminescence. Excitation of **1–12** leads to a dual emission characteristic of this class of photoluminescent complexes (Fig. 1) [1–3,5]. The two emissions observed from deaerated solutions of these complexes have been assigned to fluorescence and phosphorescence from the ¹ILCT* and ³ILCT*, respectively. The emission quantum yields range from 0.001 to 0.007 for the fluorescence and from 0.003 to 0.020 for the phosphorescence (DMSO) (Table II). The fluorescence lifetimes range from 0.1–4 ns while the phosphorescence lifetimes range from 710 to 15,900 ns (DMSO).

Transient Absorption (TA) Spectroscopy. Given the ³ILCT* solution lifetimes of the photoluminescent complexes, the triplet-triplet transitions were readily studied by transient (TA) absorption spectroscopy. Flash excitation of the pyridinium complexes, **1–12**, in DMSO afforded the respective ³ILCT* excited states which show strong triplet-triplet absorption bands. The excited state absorption-difference spectra of **1, 2**, and **9–12** are shown for comparison (Fig. 2). The difference spectra of **1–11** all feature strong absorption bands at 400, 520 and 630 nm with a weaker band at 800 nm while that of complex **12** features strong triplet-triplet absorption bands at 385 and 550 nm with weaker bands at 610 and 805 nm. These absorption features are accompanied by bleaching of the ILCT ground state absorption band. The transient absorption of all the complexes decays with single exponential kinetics and no residual absorption or bleaching persists (Fig. 3). The ³ILCT* lifetimes as measured by the transient decays was in reasonable agreement with the life-

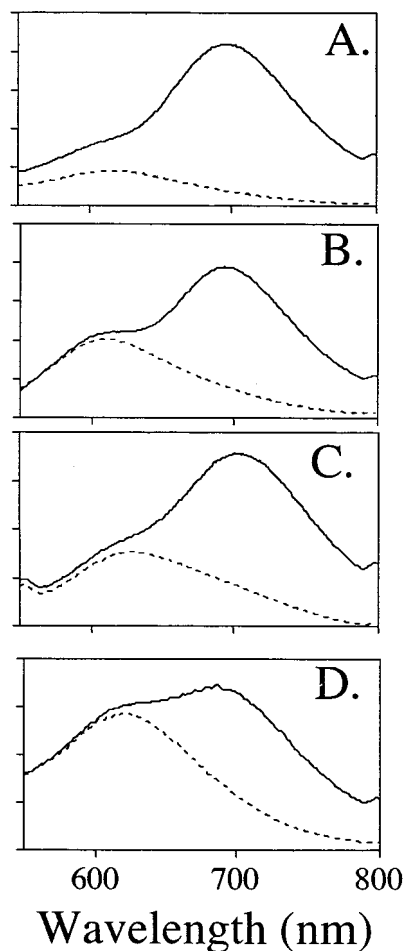


Fig. 1. Emission spectra of (A) **9**, (B) **10**, and (C) **11** (D) **12** in DMSO at 298K prior to instrument correction. Solid lines are deoxygenated samples showing the emission from both the ¹ILCT* and ³ILCT*. Dashed lines are aerated samples showing the emission from the ¹ILCT* only.

times measured by frequency modulation analysis of the phosphorescence decay kinetics [2].

Several points are of interest with respect to the triplet-triplet absorption spectra of the L₂Pt{S₂C₂(Het)(R)}, complexes. Variations in the TA difference spectra for the ³ILCT* state of [(dppe)Pt{S₂C₂(2-pyridinium)(H)}]⁺ and (dppe)Pt{S₂C₂(2-quinoxaline)(H)} are consistent with a charge-transfer assignment where the heterocycle is the acceptor [1–3,5]. Interestingly, pyridinyl radicals, produced by one-electron reduction of pyridinium ions, typically absorb in the region >600 nm [19–21]. Thus, we suggest that the visible excited state absorption bands observed for the [L₂Pt{S₂C₂(2-pyridinium)(R)}]⁺ and [L₂Pt{S₂C₂(4-pyridinium)(R)}]⁺ complexes may arise from allowed transitions associated with a “pyridinyl radical” which

Table II. Fluorescence and Phosphorescence Maxima, Quantum Yield and Lifetimes for Complexes 1–12 (DMSO)

Complex	1_{ϕ}	3_{ϕ}	$1_{\lambda_{\max}}$ (nm)	$3_{\lambda_{\max}}$ (nm)	1_{τ}^a (ns)	3_{τ} (ns)
1 [(dppm)Pt{S ₂ C ₂ (2-pyridinium)(H)}] ⁺	0.001	0.003	550	680	0.05	710 ^a
2 [(dppe)Pt{S ₂ C ₂ (2-pyridinium)(H)}] ⁺	0.002	0.009	677	732	4.3	2010 ^b
3 [(dppm)Pt{S ₂ C ₂ (4-pyridinium)(H)}] ⁺	0.003	0.009	553	731	0.3	3520 ^b
4 [(dppe)Pt{S ₂ C ₂ (4-pyridinium)(H)}] ⁺	0.003	0.03	589	742	3.1	7500 ^b
5 [(dppp)Pt{S ₂ C ₂ (4-pyridinium)(H)}] ⁺	0.003	0.004	585	764	0.1	2800 ^b
6 [(dppm)Pt{S ₂ C ₂ (N-methyl-4-pyridinium)(H)}] ⁺	0.003	0.011	572	740	0.2	15900 ^b
7 [(dppe)Pt{S ₂ C ₂ (N-methyl-4-pyridinium)(H)}] ⁺	0.003	0.016	578	758	0.2	12500 ^b
8 [(dppp)Pt{S ₂ C ₂ (N-methyl-4-pyridinium)(H)}] ⁺	0.002	0.010	586	775	0.2	11100 ^b
9 [(dppm)Pt{S ₂ C ₂ (CH ₂ CH ₂ -N-2-pyridinium)}] ⁺	0.004	0.020	610	730	0.2	8500 ^b
10 [(dppe)Pt{S ₂ C ₂ (CH ₂ CH ₂ -N-2-pyridinium)}] ⁺	0.002	0.010	677	732	0.2	8660 ^b
11 [(dppp)Pt{S ₂ C ₂ (CH ₂ CH ₂ -N-2-pyridinium)}] ⁺	0.007	0.020	620	700	0.1	4500 ^b
12 [(dppe)Pt{S ₂ C ₂ (2-quinoxaline)(H)}]	0.006	0.002	660	748	0.2	4700 ^b

^a Lifetimes in ns determined by frequency modulation.

^b Lifetimes determined by transient absorption spectroscopy.

can be produced, in a one-electron sense, from the thiolate to pyridinium intramolecular charge transfer. This is analogous to the strong ligand-based radical-ion type absorptions that are typically observed for the metal-to-ligand charge transfer excited states of d⁶, d⁸ and d¹⁰ metal pyridyl and polypyridyl complexes [22–30].

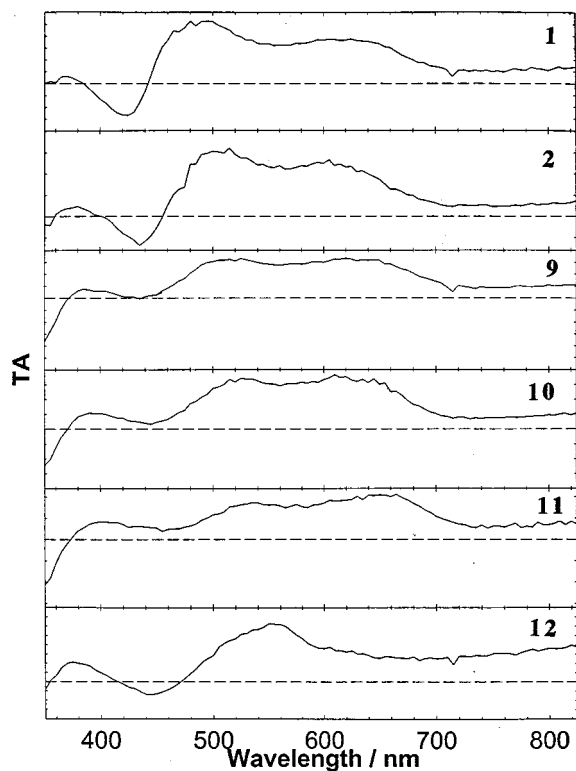


Fig. 2. Transient absorption spectra of **1**, **2** and **9–12** in DMSO immediately following 355 nm excitation. The dashed line represents a transient absorption of zero.

In addition to the TA studies of the photolumiphores, TA studies of [(PPh₃)₂Pt{S₂C₂(2-pyridinium)(H)}]⁺ and [(dppe)Pt{S₂C₂(2-pyridinium)(CH₂CH₂OH)}]⁺ were undertaken since these complexes are representative of nonemissive molecules which have lowest lying ILCT transitions. Consistent with the TA of **1–12** being associated with an emissive long-lived triplet state, there were no transients detected following excitation of either [(PPh₃)₂Pt{S₂C₂(2-pyridinium)(H)}]⁺ or [(dppe)Pt{S₂C₂(2-pyridinium)(CH₂CH₂OH)}]⁺.

Photobasicity of (dppe)Pt{S₂C₂(2-quinoxaline)(H)}, **12**. Unlike the excitation of **12**, the excitation of **12H**⁺ does not lead to luminescence in the visible region of the spectrum. This is not unexpected since the ILCT absorption for **12H**⁺ is at 17,700 cm⁻¹. Assuming a Stokes shift for **12H**⁺ that is similar to **12**, the ³ILCT* emission of **12H**⁺ is expected to be < 8500 cm⁻¹ and well beyond visible detection. As such, the presence of an ³ILCT* for **12H**⁺ was studied by transient absorption spectroscopy. In addition to lack of a visible emission, excitation of **12H**⁺ did not lead to an excited states that was observable by TA spectroscopy. Moreover, flash photolysis of **12** in the presence of 5 × 10⁻⁴ M benzoic acid, a proton source insufficient to protonate the ground state but an effective ³ILCT* quencher [2], produced a TA spectrum with only bands assignable to the ³ILCT* of **12**. Analysis of the TA decay in the presence of 5 × 10⁻⁴ M benzoic acid shows that the lifetime of the ³ILCT* state has been substantially shortened from 2.8 to 1.1 μs. From the decrease in the ³ILCT* lifetime the second order rate constant for quenching of the ³ILCT* by benzoic acid is determined to be k_q = 1.3 × 10⁹ M⁻¹s⁻¹, which is in good agreement with the values reported earlier obtained by phosphorescence quenching [2].

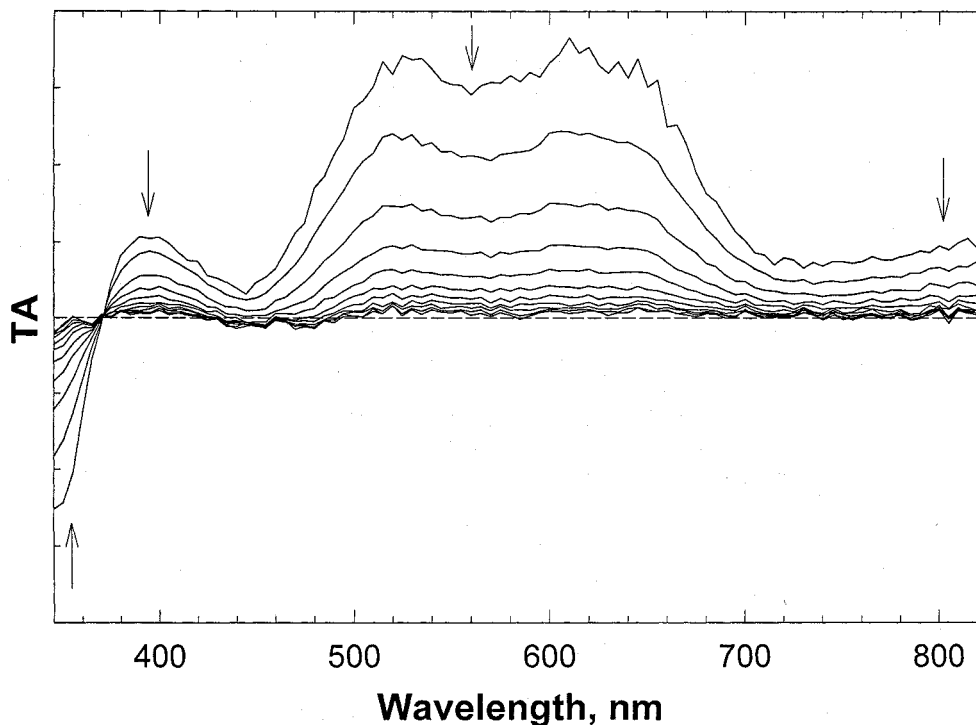


Fig. 3. Transient absorption spectrum of **10** in DMSO. Traces shown are from 0 to 40 μs in 4 μs interval following 355 nm excitation. The arrows denote the absorbance decreases (\downarrow) and increases (\uparrow), respectively. The dashed line represents a transient absorption of zero.

The lack of luminescence and transient absorption for **12H⁺** demonstrates that direct excitation of the protonated complex does not afford a long-lived excited state. Moreover, the fact that a new transient is not observed following benzoic acid quenching of the $^3\text{ILCT}^*$ indicates that protonation of the $^3\text{ILCT}^*$ of **12** does not produce the long-lived $^3\text{ILCT}^*(\text{H})^+$. Collectively, these observations strongly support the premise that the protonated form of the triplet excited state is very short lived ($\tau < 1$ ns) due to rapid non-radiative decay. This is consistent with the Energy Gap Law, since protonation of the quinoxaline acceptor significantly reduces the energy of the charge transfer state, which increases the vibrational overlap factors between the excited and ground states [31]. The increased vibrational overlap results in an increase in the rate of non-radiative decay [31]. Similar significant enhancement of non-radiative decay rates are observed concomitant to protonation of heterocyclic nitrogens in polypyridyl ruthenium(II) and rhenium(I) complexes [32–34]. Unfortunately, rapid release of the proton from the short-lived $^3\text{ILCT}^*(\text{H})^+$ excited state will likely preclude the use of **12** as a catalytic photobase in a large number of chemical applications.

CONCLUSION

The study of the triplet excited state of the heterocyclic-substituted platinum 1,2-enedithiolates by TA spectroscopy has confirmed the intraligand nature of the transition. Variations in the TA spectra for pyridinium complexes **1–11** and the quinoxaline complex **12** support the heterocycle being the acceptor in the charge transfer in agreement with our previous studies. The similarity of the triplet transitions for these complexes with the absorption spectra of pyridinyl radicals is also consistent with an ILCT excited state where the heterocycle is the electron acceptor. In this regard, the ILCT excited states of the heterocyclic-substituted platinum 1,2-enedithiolates are similar to the MLCT excited states of tris(bipyridyl) and tris(phenanthroline) ruthenium(II) and osmium(II) complexes. In previous studies, it was demonstrated that increasing the steric bulk of the 1,2-enedithiolate functional groups as well as the steric bulk of the ancillary phosphine ligands bound to the metal can lead to a loss of emission [5,35]. However, in this study it has been demonstrated that for those complexes which are emissive, the steric bulk of the phosphine and whether the pyridyl group is protonated or alkylated has only a

subtle effect upon the energy and intensity of the triplet-triplet transitions. However, the failure to generate the $^3\text{ILCT}^*$ of $\mathbf{12H}^+$ either by direct excitation or proton quenching of the $^3\text{ILCT}^*$ of $\mathbf{12}$ suggests protonation of the quinoxaline (unlike the pyridines) leads to rapid non-radiative decay and the loss of emission.

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