Solvent Switching between Charge Transfer and Intraligand Excited States in a Multichromophoric Platinum(II) Complex

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The photophysical properties of a new multichromophoric platinum(II) complex, Pt(dbbpy)(C≡C−nap)$_2$ (**1**) (dbbpy = 4,4′-(di-*tert*-butyl)-2,2′-bipyridine; C≡C−nap = 1-ethynylnaphthalene), is reported in four different solvent systems of varying polarity: toluene, 2-methyltetrahydrofuran, dichloromethane, and acetonitrile. Since the low-energy dπ Pt → π^* dbbpy metal-to-ligand charge transfer (MLCT) transitions in this chromophore are negative solvatochromic in nature, increasing solvent polarity raises the energy of the MLCT state. At the same time, the low-lying, metal-perturbed π,π^* triplet intraligand (^{3}IL) state present within the molecule on the −C≡C−nap fragments are largely invariant to solvent polarity as evidenced by the absorption and emission properties of the model chromophore lacking the low-energy charge transfer state, Pt(dppe)(C≡C−nap)$_2$ (**2**) (dppe = 1,2-bis(diphenylphosphino)ethane). In solvents of low polarity, the static and dynamic absorption and luminescence spectroscopy of **1** are largely consistent with a dπ Pt → π^* dbbpy MLCT assignment. As the solvent polarity is increased, the excited-state absorption and emission properties of **1** are significantly altered, eventually resembling the spectral features seen in **2**. However, the excited-state decay kinetics for the structured emission measured in **2** is well beyond that observed for **1**. The discrepancy in lifetime indicates that the excited state of **1** in high polarity solvents is not composed of pure ^{3}IL character. In fact it is very likely that a significant electronic interaction exists between the ^{3}MLCT and ^{3}IL states in this molecule at ambient temperature. To further probe this possibility, static and dynamic luminescence experiments were performed on **1** and Pt(dbbpy)(C≡C−Ph)$_2$ (**3**), C≡C−Ph is phenylacetylene, at 77 K as a function of matrix polarity. In all glass matrixes at low temperature, the lowest-lying state in **1** is ^{3}IL, whose energy is nearly independent of the matrix. The reference molecule **3** possesses a low-lying ^{3}MLCT state, and we believe it reasonably models the ^{3}MLCT energy in **1** at low temperature. In essence, variation in the solvent glass changes the ^{3}MLCT−^{3}IL energy gap which modifies the observed excited-state lifetimes at 77 K, decreasing as the apparent energy gap decreases. The experimental results suggest stronger mixing of the two triplet states at room temperature relative to 77 K, but we cannot definitively rule out contributions from thermal equilibrium. Unfortunately, the relative energy separation of the two states in **1** does not permit a quantitative evaluation of potential configuration mixing of the two states. However, the close energetic proximity of the two triplets along with the solvent-dependent nature of the charge transfer state permits a wide variety of photophysical properties to be displayed by a single molecular system.

Introduction

The coupling of transition metals or transition-metal complexes with selected organic chromophores has generated new molecules and materials that exhibit a wide range of fundamentally interesting and potentially useful excited-state properties.[1−22] A significant amount of experimental work in this area has largely focused on d^6 metal polypyridine complexes of Ru(II), Os(II), and Re(I) which display metal-to-ligand charge transfer (MLCT) excited states. The general motivation for using these molecules as the “metal-containing” fragment in more complex systems lies in the widespread experience and knowledge gained in the field over the past 45 years.[23−41] In more recent history, MLCT chromophores have become appealing for a variety of technologies, including photovoltaics,[42] optical data storage,[9,11] luminescent sensors,[43,44] and electroluminescence displays.[45−48]

Over the past 15 years, there has been increasing interest in the properties of d^8 Pt(II) complexes of the general formulation Pt(diimine)L$_2$, where L is a monodentate ligand such as halide, nitrile, thiolate, or acetylide.[49−63] Several recent papers have appeared describing structure−photophysical property relationships in systems containing a diimine ligand such as 2,2′-bipyridine or 1,10-phenanthroline (and structurally related derivatives), where L is typically a substituted phenylacetylide.[53,56,57,62,63] In most cases, these molecules possess long-lived excited states with photophysical properties consistent with a dπ Pt → π^* diimine MLCT assignment. However, there are numerous examples within the work from several laboratories where the photophysical behavior of certain Pt(diimine)(C≡CR)$_2$ molecules is inconsistent with the MLCT assignment, which has indeed been recognized in several instances.[53,57] In those cases, it is believed that a low-lying intraligand $^3\pi-\pi^*$ (^{3}IL) excited state based within the diimine or acetylide ligand(s) contributes to the excited-state decay. Our group has recently recognized that the ^{3}MLCT excited state can be used to internally sensitize the formation of a low-lying ^{3}IL excited state on an appended pyrenylacetylide ligand, leading to the observation of extremely long-lived room-temperature phosphorescence

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in the red.[17] Clearly, the photophysical processes available in Pt(diimine)(C≡CR)$_2$ complexes warrant their further investigation. We postulate that proper selection of ligands and/or solvent medium in Pt(diimine)(C≡CR)$_2$ complexes may be able to produce either "pure" ^{3}MLCT or $^3\pi-\pi^*$ excited states in addition to equilibrated or configuration mixed excited states composed of varying degrees of ^{3}MLCT and $^3\pi-\pi^*$ character. This suite of accessible photophysical behavior can be expected to yield a wide range of excited-state absorptions, emissions, and associated dynamics. In related work, it has been shown that energy flow in [Ru(Pyr$_n$bpy)(CN)$_4$]$^{2-}$ (n = 1,2, Pyr = pyrene) is readily modulated with solvent, yielding a variety of excited-state decay behavior.[19]

In the present work, we set out to design a new molecule where the ^{3}IL states on the arylacetylide ligands would be energetically proximate to the luminescent ^{3}MLCT state. This motif features the possibility of observing radiative decay from two distinct triplet states at room temperature and permits the evaluation of potential excited triplet state interactions. Through well-established synthetic protocols, we were able to assemble the multichromophoric system, Pt(dbbpy)(C≡C−nap)$_2$ (**1**) (dbbpy = 4,4′-(di-*tert*-butyl)-2,2′-bipyridine; C≡C−nap = 1-ethynylnaphthalene), whose triplet energy levels were coarse-adjusted by design and synthetically imparted into the structure. Although several publications have commented on the strong negative solvatochromism displayed by the low-energy charge-transfer absorptions in Pt(diimine)(C≡CR)$_2$ chromophores,[53,62] to our knowledge nobody has attempted to use this dependence to systematically modulate the excited-state properties in this class of molecules. In this study we chose four different solvents to test this hypothesis: acetonitrile (CH$_3$CN), dichloromethane (CH$_2$Cl$_2$), 2-methyltetrahydrofuran (MTHF), and toluene. We postulated that the solvent polarity dependence could be used to fine-adjust the ^{3}MLCT energy relative to the $^3\pi-\pi^*$ levels in **1**, potentially accessing a variety of excited-state behaviors in a single molecular system. Indeed this is the case as the solvent polarity increases the nature of the excited-state becomes more ^{3}IL-like, as revealed by static and dynamic absorption and luminescence spectroscopy.

Experimental Section

General. All synthetic manipulations were performed under an inert and dry argon atmosphere using standard techniques. Anhydrous CH$_2$Cl$_2$, diisopropylamine, and diethylamine were obtained by distillation over CaH$_2$. All other reagents and materials from commercial sources were used as received. Silica gel used in chromatographic separations was obtained from EM Science (Silica Gel 60, 230−400 mesh). ^{1}H and ^{31}P NMR spectra were recorded on a Varian Unity 400 (400 MHz) spectrometer. All chemical shifts are referenced to residual solvent signals previously referenced to TMS, and splitting patterns are designated as s (singlet), d (doublet), t (triplet), q (quartet), m (multiplet), and br (broad). In the case of ^{31}P{^{1}H} NMR, chemical shifts are reported relative to 85% H$_3$PO$_4$, used as an external standard. Atmospheric pressure chemical ionization (APCI) mass spectra were measured at the University of Toledo using an Esquire-LC spectrometer. EI mass spectra were measured in-house using a Shimadzu QP5050A spectrometer. MALDI mass spectra were measured in-house using a Bruker-Daltonics Omniflex spectrometer. Elemental analyses were performed by Atlantic Microlab, Norcross, GA.

Preparations. Pt(dbbpy)Cl$_2$,[64] Pt(dppe)Cl$_2$,[65] and Pt(dbbpy)-(C≡C−Ph)$_2$[53,56] (**3**) were prepared according to literature procedures and yielded satisfactory mass and ^{1}H NMR spectra.

Pt(dbbpy)(C≡C−Nap)$_2$ (1). Pt(dbbpy)Cl$_2$ (0.25 g, 0.46 mmol) and CuI (8.8 mg, 0.046 mmol) were placed in the sealable reaction vessel, equipped with a Teflon screw-cap and O-ring. A solution of dichloromethane and diisopropylamine (3:1) (200 mL) was degassed for 15 min and added to the flask. 1-Ethynylnaphthalene (0.213 g, 1.39 mmol) was dissolved in a small volume of dichloromethane (10 mL), degassed for 15 min, and then added to the reaction mixture. The reaction vessel was sealed under argon with a Teflon screw-cap fitted with an O-ring, and stirred at room temperature for 3 days in the dark. The solvent was removed under vacuum and the residue was chromatographed on silica gel using dichloromethane as eluent. Evaporation of the solvent yielded the title compound as an orange solid (0.194 g, 54%). R_f = 0.52 (dichloromethane, silica gel).

^{1}H NMR (CDCl$_3$): δ 9.86 (d, 2H), 8.92 (d, 2H), 7.98 (d, 2H), 7.73−7.80 (m, 4H), 7.66 (d, 2H), 7.59 (m, 2H), 7.34−7.44 (br m, 6H), 1.46 (s, 18H). EI-MS (70 eV): m/z 766. APCI-MS (CHCl$_3$/MeOH): m/z 766. Anal. Calcd for C$_{42}$H$_{38}$N$_2$Pt•1.5 CH$_2$Cl$_2$: C, 58.44; H, 4.59; N, 3.13. Found: C, 58.95; H, 4.67; N, 3.23.

Pt(dppe)(C≡C−Nap)$_2$ (2). Pt(dppe)Cl$_2$ (1.0 g, 1.505 mmol) was placed in a sealable reaction vessel, equipped with a Teflon screw-cap and O-ring. A solution of freshly distilled diethylamine (300 mL) and dichloromethane (250 mL) was degassed for 15 min and added to the flask. 1-Ethynylnaphthalene (0.473 g, 3.311 mmol) was dissolved in diethylamine (10 mL) in a separate flask, degassed, and transferred to the reaction vessel. Copper iodide (15 mg, 0.150 mmol) was added and the reaction vessel was sealed under argon and stirred at room temperature for 20 h in the dark. The reaction mixture was filtered to remove unreacted Pt(dppe)Cl$_2$, and then solvents were removed under reduced pressure. Crude product was purified by column chromatography (silica gel) using 25 vol % hexane in dichloromethane as eluent. Evaporation of the solvents yielded the title compound as a yellow crystalline solid (0.153 g, 11%). R_f = 0.65 (25 vol % hexane in dichloromethane).

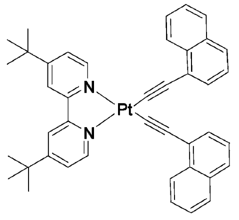
^{1}H NMR (CDCl$_3$): δ 8.31 (d, 2H), 7.98−8.07 (br m, 8H), 7.69 (d, 2H), 7.57 (d, 2H), 7.35−7.48 (br m, 14H), 7.30 (m, 4H), 7.09 (m, 2H), 2.46 (m, 4H). ^{31}P{^{1}H} NMR (162 MHz, CDCl$_3$):δ 41.826 ($J_{\mathrm{Pt-P}}$ = 2286.5 Hz). MALDI-MS: m/z 896.60 [M + H]$^+$. Anal. Calcd for C$_{50}$H$_{38}$P$_2$Pt: C, 67.03; H, 4.28. Found: C, 66.37; H, 4.31.

Physical Measurements. UV−Vis absorption spectra were measured with a Hewlett-Packard 8453 Diode array spectrophotometer, accurate to ±2 nm. Uncorrected steady-state photoluminescence spectra were obtained with a single photon counting spectrofluorimeter from Edinburgh Analytical Instruments (FL/FS 900). The excitation was accomplished with a 450 W Xe lamp optically coupled to a monochromator (±2 nm) and the emission was gathered at 90° and passed through a second monochromator (±2 nm). The luminescence was measured with a Peltier-cooled (−30°C), R955 red-sensitive photomultiplier tube (PMT). Excitation spectra were corrected with a photodiode mounted inside the fluorimeter that continuously measures the Xe lamp output. All photophysical experiments used optically dilute solutions (OD = 0.09−0.11) prepared in spectroscopic grade solvents unless otherwise stated. All luminescence samples in 1 cm^2 anaerobic quartz cells (Starna Cells) were deoxygenated with solvent-saturated argon for at least 30 min prior to measurement. Photoluminescence quantum yields were determined as previously described,[5,66] using [Ru(bpy)$_3$]$^{2+}$ in CH$_3$CN (Φ_{em} = 0.062) as the quantum counter.[32] Frozen glass emission samples at 77 K were prepared by

TABLE 1: Photophysical Data at Room Temperature[a]

compound	solvent	λ_{abs}, nm	λ_{em}, nm	τ_{em},[b] μs	τ_{TA},[c] μs	Φ_{em}[d]	k_r, $\times10^{-5}$ s^{-1}[e]	k_{nr}, $\times10^{-5}$ s^{-1}[f]
1	CH_3CN	392	548m	2.8	3.5	0.046	0.16	3.41
			591					
	CH_2Cl_2	404	562m	3.0	2.7[g]	0.11	0.36	2.97
			591					
	toluene	427	591	0.87	0.75	0.168	1.93	9.56
	MTHF	422	593	0.54	0.52	0.023	0.43	18.09
3	CH_3CN	386	561	0.69	0.60	0.15	2.20	12.29
	CH_2Cl_2	396	562	1.36		0.34	2.50	4.85
	toluene	425	569	1.05	1.02	0.307	2.92	6.60
	MTHF	416	573	0.16	0.15	0.047	2.94	59.56
2	MTHF	330	542m	100	69			
		350	587					

[a] Argon-degassed solutions. [b] Emission intensity decay lifetime, ±5%. [c] Absorption transient lifetime, ±10%. [d] Quantum yield of photoluminescence relative to $[Ru(bpy)_3]^{2+}$ in CH_3CN ($\Phi_{em} = 0.062$). [e] Radiative decay rate, calculated by $k_r = \Phi_{em}/\tau_{em}$. [f] Nonradiative decay rate, calculated by $k_{nr} = (1 - \Phi_{em})/\tau_{em}$. [g] Measured in 1,2-dichloroethane.



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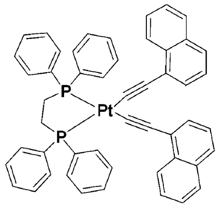

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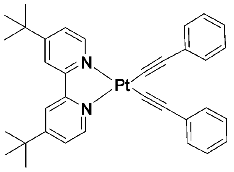

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inserting a 5 mm inner diameter NMR tube containing a 10^{-5} M solution of the appropriate compound into a quartz-tipped finger dewar containing liquid nitrogen.

Emission lifetimes were measured by means of a nitrogen-pumped broadband dye laser (2−3 nm fwhm) from PTI (GL-3300 N_2 laser, GL-301 dye laser). BPBD (360−395 nm) and Coumarin 460 (440−480 nm) laser dyes were used to tune the excitation. Pulse energies were typically attenuated to ~50 μJ/pulse, measured with a Molectron Joulemeter (J4−05). The luminescence was collected at 90° through a long pass optical filter, focused through a lens system, and passed through a monochromator (±4 nm). The emission was detected with a Hamamatsu R928 PMT. The PMT signal was terminated through a 50 ohm resistor to a Tektronix TDS 300 digital oscilloscope (400 MHz). The data from the oscilloscope represented an average of 128 laser shots collected at 2−3 Hz, were transferred to a computer, and processed by Origin 6.1 software.

The experimental apparatus for nanosecond transient absorption spectroscopy, operating under the control of LabView, has been described previously.[5,7] Transient absorption spectra and decay kinetics were obtained using the unfocused second or third harmonic provided by a Continuum Surelite I Nd:YAG laser (532 or 355 nm, 5−7 ns fwhm). Alternatively, the third harmonic was used to pump an in-house constructed high-pressure Raman shifter filled with H_2 gas (400 psi) and the first Stokes line isolated ($\lambda_{ex} = 416$ nm, 3 mJ/pulse). The data consisting of a 32-shot average were analyzed by Origin 6.1 software. All flash photolysis measurements were conducted at the ambient temperature 22 ± 2 °C. All samples were thoroughly degassed prior to measurements with high purity argon and kept under argon atmosphere throughout the experiment.

Results and Discussion

Structures. All of the Pt(II) complexes used in this study were prepared in accordance with standard procedures with final purification achieved by chromatography over silica. All complexes are stable solids at room temperature and are readily soluble in a variety of organic solvents. Compounds **1**−**3** were structurally characterized by NMR, mass spectrometry, and elemental analysis. Multichromophoric **1** possesses a combination of low-lying ^{3}MLCT and ^{3}IL excited states, whereas **2** is a reference compound containing the metal-perturbed naphthaleneacetylide chromophores arranged in a cis-geometry around the Pt(II) center, enforced by the bidentate dppe ligand. Structure **2** lacks a low-lying charge transfer state and will be used to model the ^{3}IL manifold resident on the naphthaleneacetylide ligands, whereas compound **3** is intended to represent the ^{3}MLCT state in **1**.

Room-Temperature Absorption and Photoluminescence. The room-temperature spectroscopic and photophysical properties of all the complexes investigated in this study are collected in Table 1. Figure 1 displays the absorption spectra of Pt(dbbpy)(C≡C−nap)$_2$ measured in different solvents. It is clear that the low-energy MLCT absorption ($\epsilon_{CH_3CN} = 7900$ M^{-1} cm^{-1} @ 386 nm) blue shifts with increasing solvent polarity. This is not surprising as negative solvatochromism has been previously observed for Pt(dbbpy)(C≡C−Ph)$_2$ (and structurally related molecules),[53,62] resulting from a large ground-state dipole moment. We have performed density functional theory (DFT) calculations on the ground states of **1** and **3** to estimate each dipole moment.[67] Using optimized structures in Gaussian 98 (BP86 functional with a double-ζ basis set using an effective core potential for Pt),[67] the calculated values of the ground-state dipole moments are 10.8 and 10.6 D, respectively, consistent with the transient DC photoconductivity study performed by Hupp and co-workers in a structurally related Pt(II) diimine dithiolate complex.[68] In both cases the ground-state dipole moment vector directly opposes that produced by MLCT excitation. The higher-energy ligand-localized π−π* transitions between 300 and 350 nm resulting from electronic transitions within the naphthaleneacetylide fragments are not significantly perturbed by solvent polarity. These observations are easily confirmed by the absorption spectra in Figure 1 as well as that displayed by the structural model **2**. In essence, solvent polarity can be used to tune the MLCT energy in relation to the π−π* energy on the C≡C−nap chromophores in **1**.

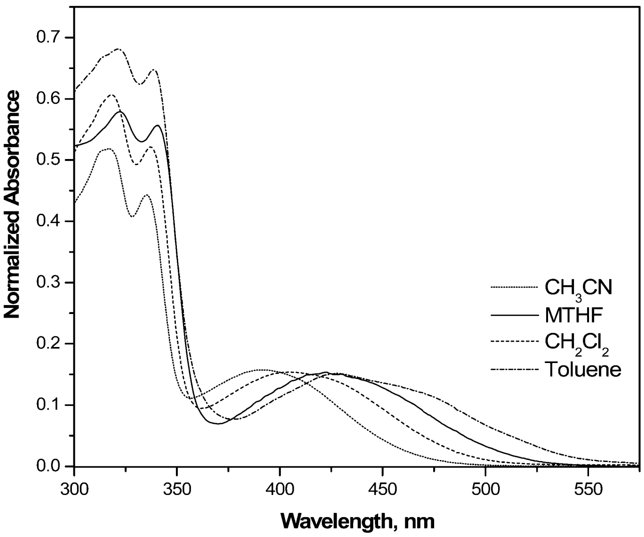

Figure 1. UV−Vis absorption spectra of **1** in CH_3CN, MTHF, CH_2Cl_2, and toluene.

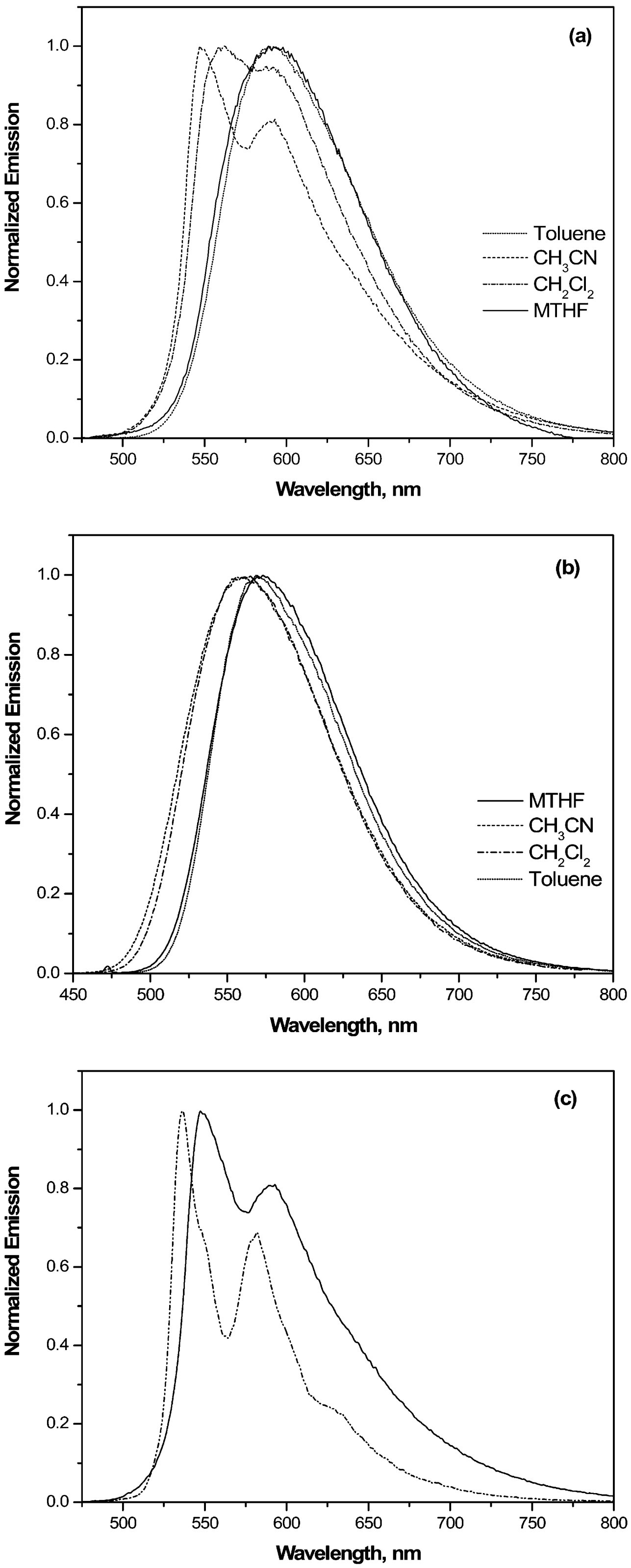

Figure 2. Static photoluminescence spectra of (a) **1** and (b) **3** in CH_3CN, MTHF, CH_2Cl_2, and toluene. (c) Photoluminescence spectra of **1** (solid line) and **2** (dashed line) in CH_3CN.

The luminescence spectra of **1** obtained in various solvents are displayed in Figure 2a. The spectra observed in MTHF and toluene are broad and structureless, closely resembling the breadth and shape measured for **3** in the same solvents, Figure 2b. Therefore, we tentatively assign the photoluminescence of **1** in those solvents as MLCT-based. The photoluminescence spectrum of **1** measured in CH_3CN is qualitatively similar to the spectrum observed for **2**, Figure 2c. In this case, the emission appears to be most consistent with ^{3}IL phosphorescence emanating from a naphthaleneacetylide moiety. The luminescence spectrum of **1** measured in CH_2Cl_2 is intriguing as it lies somewhat between that observed in CH_3CN and MTHF, Figure 2a. The static luminescence data at room temperature strongly suggest that the ^{3}MLCT and ^{3}IL states cross over in energy as the solvent polarity is increased from MTHF to CH_3CN. In low polarity solvents the emission is dominated by the MLCT state, whereas in higher polarity media the emission appears to be dictated by the ^{3}IL state residing on one of the C≡C−nap ligands. With the notable exception of MTHF, the photoluminescence quantum yields observed for **1** are significantly lower than those measured for **3**, Table 1. When the quantum yields and excited-state lifetimes (see below) are taken into account in both molecules, the calculated values of k_r and k_{nr} (Table 1) provide evidence of the proposed state inversion in **1**. The radiative decay rates observed for **1** in CH_3CN and CH_2Cl_2 are an order of magnitude smaller than those measured for **3** in the same solvents, while the k_{nr} values are respectively smaller. This drop in k_r and k_{nr} may reflect more of a ^{3}IL character in the excited-state decay.[57] In toluene, where the ^{3}MLCT is lower in energy, the k_r and k_{nr} values measured for **1** are of the same magnitude as those seen for **3**, suggesting that the ^{3}MLCT manifold is largely responsible for the radiative decay. The data obtained in MTHF cannot be readily interpreted as the emission spectrum and lifetime are consistent with a ^{3}MLCT excited state but values of k_r and k_{nr} are both smaller than the values obtained for **3** in the same solvent. We note that the emission spectrum of **1** is symmetrically quenched in all solvents investigated when the solution environment changes from argon-purged to air-saturated. This seemingly simple result is important as it suggests that either the emission manifold is comprised of one state or two closely lying states in rapid thermal equilibrium.

Photoluminescence Dynamics. The excited-state luminescence lifetimes of **1** measured in optically dilute (10^{-6}−10^{-5} M) deaerated solutions of MTHF, toluene, CH_2Cl_2, and CH_3CN are 0.54, 0.87, 3.0, and 2.8 μs, respectively. The recovered lifetimes were invariant at the low sample concentrations used in these experiments. In all cases the emission intensity decays were well modeled by single exponential kinetics, and lifetimes were constant as a function of the emission monitoring wavelength. This suggests that in every solvent there is only one type of emitting state, consistent with the static data described above. However, all of our results are also compatible with a solvent-dependent fast equilibrium (relative to excited-state decay) between ^{3}MLCT and ^{3}IL excited states. In MTHF and toluene, we believe that the lifetimes are most consistent with a lowest excited state composed primarily of ^{3}MLCT character. Indeed, these lifetimes are in the range of values typically observed in Pt(diimine)(C$\equiv$CR)$_2$ complexes, whose excited states are derived from MLCT composition.[52,53,56,57,63] In CH$_2$Cl$_2$ and CH$_3$CN the lifetimes of the emissions increase to $\sim$3.0 μs, suggesting that significant ^{3}IL character is present in the excited-state manifold. The lifetime of **2** measured in CH$_3$CN with 337 nm excitation is 100 μs. This value is $\sim$30 times larger than the similar radiative decay process in **1**. Although the static emission spectrum appears to be consistent with a ^{3}IL assignment, the observed dynamics suggest that there is some degree of MLCT character in the excited-state decay of **1**, which substantially shortens the lifetime relative to a purely ^{3}IL excited state. This is quite different than what we have observed previously in Pt(dbbpy)(C$\equiv$C-pyrene)$_2$, where the excited state could be readily interpreted as largely ^{3}IL (pyrenylacetylide) in nature.[17] The major difference is that in the latter multichromophoric system, the pyrenylacetylide triplet states were substantially lower in energy relative to the ^{3}MLCT manifold, preventing any mixing or thermal equilibration between the two triplets. On the basis of the luminescence data, it appears that the ^{3}MLCT and ^{3}IL states in **1** are interacting in some manner at room temperature and that the solvent medium dictates the extent of the interaction.

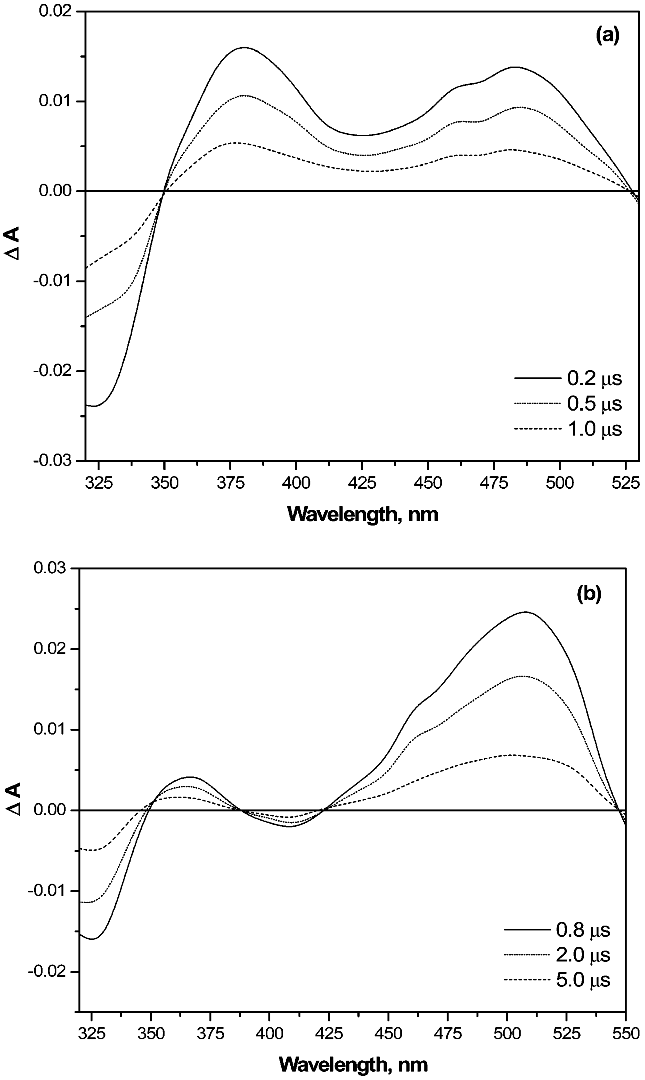

Figure 3. Excited-state absorption difference spectra of **1** in (a) toluene and (b) CH$_3$CN following 416 nm excitation. The delay times are specified on each spectrum.

Transient Absorption. The transient absorption spectra of **1** following visible excitation at 416 nm in toluene and CH$_3$CN are displayed in Figure 3. This excitation wavelength was chosen in order to preferentially pump the low-energy MLCT transitions. The flash photolysis data obtained in the other solvents are available as Supporting Information. In these experiments, the concentrations used were slightly larger than in the luminescence experiments, and minor variations in excited-state lifetime were observed, Table 1.[55] It is apparent that the relative intensities in the observed absorption transients markedly change with solvent, while the positions of the same bands do not shift dramatically, Figure 3. In toluene, the excited-state absorptions occur at $\sim$380 and $\sim$485 nm, with the 380 nm band possessing slightly more intensity, Figure 3a. The absorption signatures obtained for **1** in CH$_3$CN tell a different story as the band positions are slightly shifted $\sim$365 and $\sim$510 nm, and most of the transient absorption intensity can be found in the low-energy band at $\sim$510 nm, Figure 3b. It is now worthwhile to make direct spectroscopic comparisons to the reference chromophores **2** and **3**. Compound **3** in toluene, believed to possess a low-energy MLCT excited state, features excited-state absorptions at $\sim$360 and $\sim$485 nm, with most of the intensity present in the high-energy 360 nm band, Figure 4a. These data are consistent with the excited-state difference spectra measured by Schanze and co-workers in structurally related Pt(II) systems.[57] The first-order kinetics displayed by the absorption transients as well as the bleach recoveries for **1** and **3** in deaerated toluene were in quantitative agreement within experimental error of their respective luminescence intensity decays, Table 1. If the solvent is changed to CH$_3$CN, the absorption transients observed in **3** both experience a $\sim$10$-$15 nm blue shift relative to toluene, with peak band positions at $\sim$350 and $\sim$470 nm, Figure 4b. However, the relative intensities of the bands are comparable to that observed for **3** in toluene. The same is true in the other solvents investigated (see Supporting Information), illustrating that **3** possesses a lowest energy ^{3}MLCT state in all solvents investigated, in agreement with the literature.[53,56,57] The excited-state absorption difference spectrum obtained for **2** in MTHF ($\lambda_{ex} = 355$ nm) exhibits a strong absorption transient near 530 nm along with a strong ground-state bleaching signal below 375 nm, Figure 4c. We note that there is no significant solvent dependence for the transient absorption spectrum of **2**, so only the data obtained in MTHF will be discussed. The absorption at 530 nm is assigned to the triplet-to-triplet absorption of the naphthaleneacetylide chromophore, as no other absorption transients are expected for this model system. The single-exponential lifetime of the absorption transients measured for **2** are well beyond that observed in **1**, mirroring the kinetic behavior seen in the time-resolved photoluminescence experiments, Table 1.

The entire collection of transient absorption data yields significant insight into the proposed solvent-induced reordering of the lowest excited state in **1**. Similar to that observed in the luminescence intensity decays, in all instances the transients self-consistently exhibit similar lifetimes throughout the absorption envelope, illustrating that a single type of excited state is probably responsible for the experimental observations. We note that the nanosecond flash photolysis data do not yield any insight

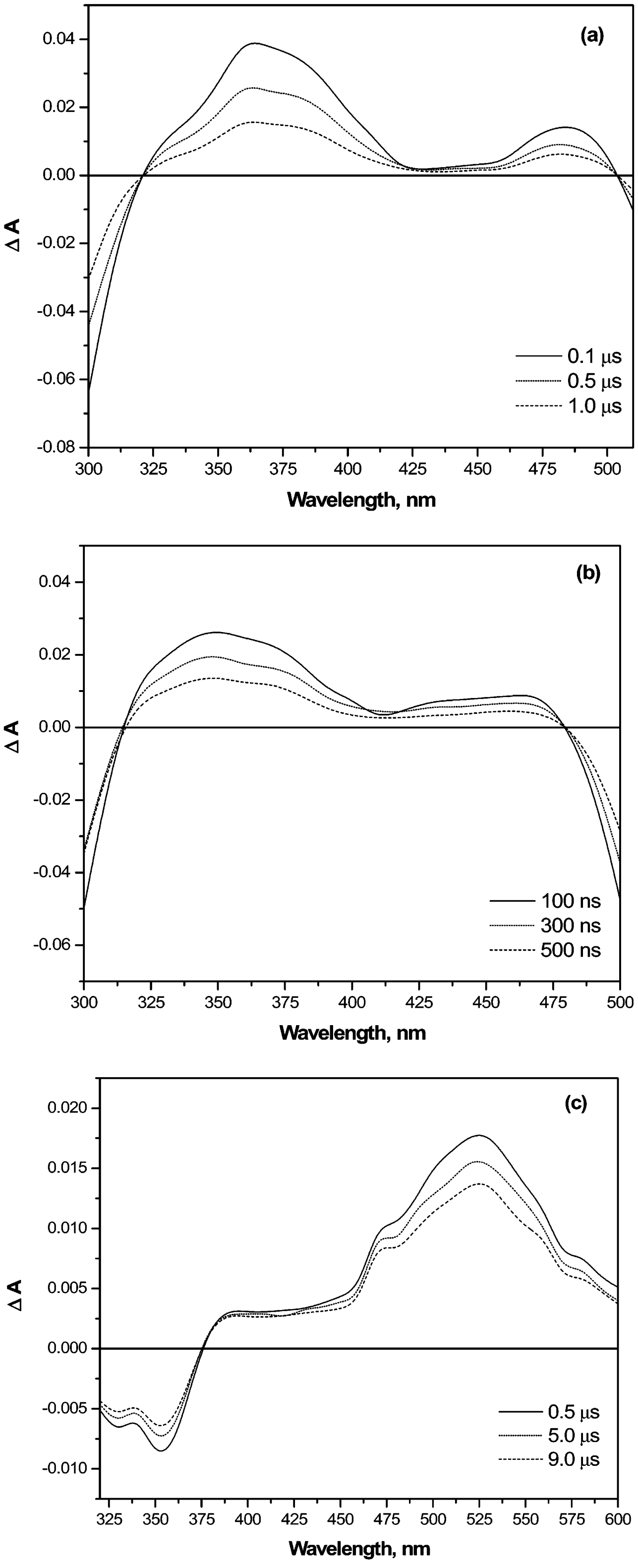

Figure 4. Excited-state absorption difference spectra of **3** in (a) toluene and (b) CH_3CN following 416 nm excitation. (c) Excited-state absorption difference spectrum of **2** in MTHF following a 355 nm laser flash. The delay times are indicated on each spectrum.

into the dynamics occurring within the 7 ns laser pulse so it is possible that these data reflect transients associated with the lowest of two states connected together via thermal equilibrium. This possibility is currently being explored with ultrafast transient absorption spectroscopy. Figure 3 shows that in the two extremes of solvent polarity (toluene versus CH_3CN), the major difference in the observed transients is in the relative magnitude of their absorption intensities, the band in the red being greatly enhanced as the solvent polarity is increased. The enhancement of this low-energy band is most consistent with the formation of ^{3}IL states in the naphthaleneacetylide chromophore(s), as can be easily ascertained by the data provided in the model system **2**, Figure 4c. What is interesting is that in all solvents investigated, the relative intensities of the two transient absorption bands vary but they never approach the ratio seen in **3**, which is expected for a "pure" ^{3}MLCT excited state,[57] see Figures 3 and 4 and Supporting Information. These data imply that in all solvents, the excited-state manifold in **1** can best be described as something intermediate of ^{3}MLCT and ^{3}IL. However, we do believe that the transient absorption data reveal the proposed reordering of the lowest excited state in **1** from predominately ^{3}MLCT to ^{3}IL as the solvent polarity is increased. Since the absorption bands characteristic of both triplet states severely overlap, we cannot definitively say that one state or the other (or a combination of the two) solely exist in any given solvent at room temperature. However, the independently measured excited-state dynamics support the notion that both triplet states interact at room temperature and the photophysical properties observed as a function of solvent likely represent different composites of the two states.

Low-Temperature Photoluminescence. Luminescence spectra obtained at 77 K also yield some insight into the nature of the lowest excited state in **1**. All low-temperature luminescence data are cataloged in Table 2. Figure 5 presents the room temperature and 77 K spectra of compounds **1**−**3** measured in MTHF, selected because of its low polarity and capacity to readily form high-quality, low-temperature glasses. Immediately one notices that the thermally induced Stokes shifts ($\Delta E_s = E_{00}(77\text{ K}) - E_{00}(298\text{ K})$) observed for **3** are extraordinarily large in the nonpolar MTHF solvent ($\Delta E_s = 2470$ cm^{-1}), consistent with previous observations from the Schanze laboratory in related complexes (Figure 5a).[57] This indicates the likelihood of a charge-transfer excited state in **3**, as there are clearly large differences in ground- and excited-state dipole moments.[35] In the model system **2**, ΔE_s plummets to ~170 cm^{-1} (Figure 5b), signaling the low level of charge redistribution typically associated with $\pi-\pi^*$-based intraligand transitions, such as those expected from the phosphorescence of the naphthaleneacetylide ligands. Therefore, the magnitude of ΔE_s serves as an indicator for the nature of the luminescence from the lowest excited state. Interestingly, the ΔE_s values are very distinct in complex **1**, varying from 1490 cm^{-1} in MTHF (Figure 5c) to 230 cm^{-1} in BuCN (see Supporting Information). We interpret this result in much the same manner as all previous data in the manuscript. In more polar solvents, the ΔE_s values in **1** are small and within experimental error of that measured in reference system **2**, more consistent with a ^{3}IL naphthaleneacetylide-based lowest excited state. In low-polarity solvents, the ΔE_s values in **1** are large, but not nearly as large as the values obtained in model system **3**. This latter result suggests that the excited state is composed mainly of ^{3}MLCT character, but there are likely contributions from the ^{3}IL manifold as well. In any case, the ΔE_s values are much smaller in **1** relative to **3** and the emission profiles at low temperature are markedly different, signaling a fundamental difference in the excited-state composition of the two Pt(II) chromophores.

To further investigate potential triplet state electronic interactions in **1**, we measured the static and dynamic luminescence properties of this complex at 77 K and compared these data to those measured for **3**.[31,69−71] Table 2 presents the static and

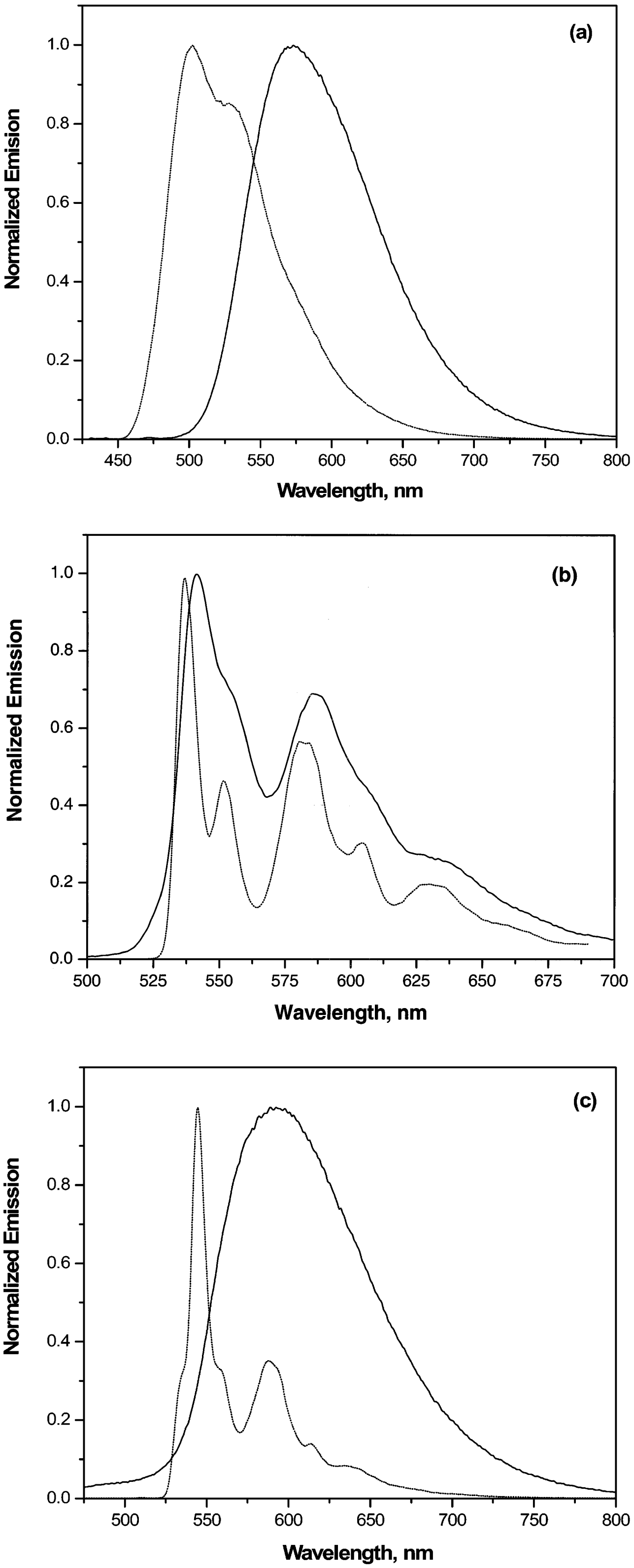

Figure 5. Static photoluminescence spectra of (a) **3**, (b) **2**, and (c) **1** in MTHF at room temperature (solid lines) and 77 K (dashed lines).

TABLE 2: Luminescence Data at 77 K.

compound	solvent matrix[a]	$\lambda_{em.}$, nm (cm^{-1})[b]	τ, μs[c]	^{3}MLCT-^{3}IL gap, cm^{-1} [d]
1	EtOH/MeOH	542 (18450)	100	1960
	BuCN	541 (18480)	95	2050
	MTHF	545 (18350)	65	1570
	3MP	546 (18310)	61	1640
3	EtOH/MeOH	490 (20410)	3.51	
	BuCN	487 (20530)[e]	3.20	
	MTHF	502 (19920)	3.35	
	3MP	501 (19960)	2.58	
2	MTHF	537 (18620)	470	

[a] EtOH/MeOH = 4:1 EtOH/MeOH; BuCN = butyronitrile; 3MP = 3-methylpentane. [b] Emission maximum, ±2 nm.
[c] Emission decay lifetime, ±10%.
[d] ^{3}MLCT/^{3}IL gap, calculated by the difference in the E_{00} energies of **3** and **1** at 77 K in each matrix, ±~200 cm^{-1}.
[e] High-energy shoulder.

dynamic photophysical data obtained for these complexes at 77 K in each solvent glass. In all glass matrixes studied, the emission at 77 K in **1** is derived exclusively from the C≡C−nap fragment(s) and its spectrum is largely invariant to the polarity of each matrix. In other words, the apparent state reordering seen at room temperature is no longer observed at low temperature. The measured low-temperature lifetimes are independent of monitoring wavelength, implying the presence of one type of emitting state. The 77 K spectral data obtained for **3** vary with the nature of the matrix, blue-shifting with increasing polarity. Therefore, we rationalized that the only energy levels that significantly shift with solvent matrix in **1** are those associated with dπ Pt → π^* dbbpy MLCT states. Interestingly, the excited-state lifetimes measured at 77 K for **1** are much longer and vary as a function of matrix, whereas those measured for **3** are nearly constant and are relatively short-lived in comparison. Qualitatively, as the ^{3}MLCT/^{3}IL energy gap becomes larger (see Table 2), the lifetimes measured for **1** increase, suggesting that there is indeed a perturbation induced on the ^{3}IL level by the ^{3}MLCT state. We believe that the extent of this interaction dictates the lifetime observed from the lowest excited state.[69−71] Unfortunately, the relative energy levels available in the present case prevent a true test of this model because the two relevant states at 77 K never really approach "resonance". In MTHF, the solvent with the smallest measured triplet energy gap, the states are separated by ~1570 cm^{-1}, well beyond that required for significant configuration interaction.[31] In any case, our data appear to be qualitatively consistent with the first-order perturbation model proposed by Crosby and coworkers over 30 years ago, used to describe electronic interactions between charge transfer and ligand localized triplet states in Ir(III) diimine complexes at low temperature.[31,69−71]

Conclusion

The photophysical properties of **1** have been explored and compared to the model chromophores **2** and **3** as a function of solvent and two extremes of temperature. The excited-state properties of **1** at room temperature can best be described as possessing a combination of charge transfer and intraligand character, where the lower-lying state dominates the behavior and solvent medium allows transitioning between these two limits. The data obtained in solvents of low polarity are consistent with an excited state composed of primarily ^{3}MLCT character, whereas the situation becomes inverted in solvents of higher polarity. In the latter cases, the static and dynamic optical data are most consistent with an excited state whose photophysics is largely determined by the ^{3}IL states resident on the naphthaleneacetylide unit(s). Interestingly, in solvents of higher polarity, excited-state decay is not exclusively determined by the ^{3}IL level(s), as the lifetimes are significantly shorter than one would expect for a pure $^3\pi-\pi^*$ intraligand state. These results suggest that the ^{3}MLCT state actively influences the decay of the excited state at room temperature, most likely due to mixing of the triplet states, although we cannot rule out contributions from thermal equilibrium.[1,5−8,12,13,15,19] We are currently investigating the ultrafast transient absorption properties of the complexes described in this study and anticipate these data will yield significant insight into whether state mixing or thermal equilibrium is responsible for the current experimental observations. The magnitude of the thermally induced Stokes shifts indicates a lack of "purity" in the emission properties of **1**, i.e., "pure ^{3}MLCT" versus "pure ^{3}IL". The luminescence data obtained at low temperature as a function of glass matrix are qualitatively consistent with a ^{3}IL excited-state decay whose rate is influenced by the presence of an energetically proximate ^{3}MLCT state, suggestive of an electronic perturbation occurring between the two triplets. To quantitatively examine the perturbation model, we are preparing new structures that will maintain the ^{3}IL level and simultaneously lower the ^{3}MLCT level. These minor structural and energetic changes should yield additional insight into the photophysics of $\mathrm{Pt(diimine)(C{\equiv}CR)_2}$ chromophores containing multiple, nearly isoenergetic triplet states.

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Supporting Information Available: Additional transient absorption and low-temperature luminescence spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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