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Dark-Field Oxidative Addition-Based Chemosensing: New Bis-cyclometalated Pt(II) Complexes and Phosphorescent Detection of Cyanogen Halides

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Abstract: Heavy metal complexes that are phosphorescent at room temperature are becoming increasingly important in materials chemistry, principally due to their use in phosphorescent organic light-emitting devices (OLEDs). Their use in optical sensory schemes, however, has not been heavily explored. Homoleptic bis-cyclometalated Pt(II) complexes are known to undergo oxidative addition with appropriate electrophiles (principally alkyl halides) by either thermal or photochemical activation. We have applied this general reaction scheme to the development of a phosphorescence-based sensing system for cyanogen halides. To carry out structure−property relationship studies, a series of previously unreported Pt(II) complexes was prepared. Most of the complexes (excluding those that incorporated substituents on the ligands that forced steric crowding in the square plane) were strongly orange-red phosphorescent ($\Phi = 0.2-0.3$) in a room-temperature oxygen-free solution. These sterically demanding ligands also accelerated the addition of cyanogen bromide to these complexes but slowed the addition of methyl iodide, indicating that the oxidative addition mechanisms for these two electrophiles is different. The lack of solvent-polarity effect on the addition of BrCN suggests a radical mechanism. Oxidative addition of BrCN to the metal complexes in solution or dispersed in poly(methyl methacrylate) gave blue-shifted emissive Pt(IV) complexes. The blue-shifted products give a dark-field sensing scheme that is in sharp contrast to energy transfer-based sensing schemes, which have limited signal-to-noise because of the presence of lower-energy vibronic bands of the energy donor that can overlap with the emission of the acceptor.

Introduction

There has been an increasing interest in heavy metal complexes that phosphoresce strongly at room temperature. The principal reason behind this surge in research into novel and efficient phosphors is the development of phosphorescence-based organic light emitting devices (OLEDs), which can be more efficient than fluorescence-based devices because the majority of excitons created upon electron−hole recombination are triplets.[1] Phosphors are necessary to harness the energy of these triplet excitons and convert it into useful light output.

Among the most popular classes of heavy metal complexes used in phosphorescent OLEDs are those that are cyclometalated with bidentate ligands, such as 2-phenylpyridine.[2] These complexes are often highly emissive in fluid solution in the absence of oxygen. This property stems from the large ligand field induced by the metal−carbon bond, which raises the energy of the nonemissive d−d metal centered transitions above the triplet energy of the cyclometalated ligand.

The most commonly used metals in these complexes are iridium and platinum. The presence of the heavy metal serves to increase the intersystem crossing rate through spin−orbit coupling and reduce the forbidden character of emission from the triplet state of the ligand. The structures of the ligands are typically optimized to enhance emission intensity and color purity.

In addition to their simple light-emitting properties, the relatively underdeveloped bis-cyclometalated square-planar Pt(II) complexes can be highly reactive via oxidative addition to give the corresponding Pt(IV) products. This work was pioneered by von Zelewsky and Balzani, who investigated the oxidative addition reactions of simple bis-cyclometalated Pt(II) complexes, such as Pt(*ppy*)$_2$[3] or the strongly orange-emitting Pt(*thpy*)$_2$ (Figure 1).[4] They found that these complexes underwent facile oxidative addition reactions with reactive electrophiles, such as methyl iodine or benzyl bromide, under ambient conditions, principally by an S_N2-type mechanism, to give only one stereoisomeric Pt(IV) product out of a possible 11.[5] They

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[1] Baldo, M. A.; O'Brien, D. F.; Thompson, M. E.; Forrest, S. R. *Phys. Rev. B.* **1999**, *60*, 14422.

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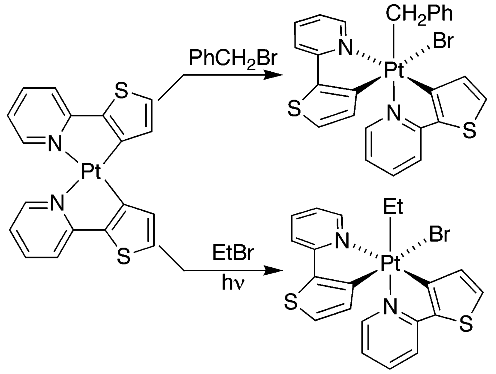

Figure 1. Oxidative addition reactions of the type described by von Zelewsky.

also found that less reactive molecules, such as chloroform, dichloromethane, or ethyl bromide, underwent a similarly clean oxidative addition reaction under photolytic conditions via a radical chain mechanism.[6]

von Zelewsky and co-workers also described that several of the Pt(IV) products of these reactions were strongly emissive, with a purely ligand-centered phosphorescence in the blue or green region of the visible spectrum.[6a,7] These emission signals were very distinct from those of the Pt(II) starting materials, where the contribution from a metal-to-ligand charge transfer (MLCT) state was much larger and gave a strongly red-shifted emission.[8] We became interested in this chemistry due to the fact that these compounds have the potential to react specifically with a wide variety of dangerous electrophilic chemicals, including some chemical weapons. The ability to make use of either thermal or photochemical reactions is very attractive and highlights this transformation and the accompanying photophysical changes as a potentially powerful chemosensing transduction scheme.

In addition, the blue-shifted phosphorescence of the Pt(IV) products of these reactions offers the advantage of negligible background signal. Most multicolor emission-based chemosensing schemes use red-shifting of the emission for signal transduction, often by the Förster energy transfer mechanism.[9] However, the lower energy vibronic bands of the donor chromophores often overlap with the acceptor emission, limiting the maximum observable signal-to-noise and decreasing the sensitivity of the measurement. Conversely, a blue-shifted signal transduction event (illustrated schematically in Figure 2) can allow for monitoring of a large portion of the desired signal with no background emission.

There are multiple examples of phosphorescent complexes used as chemosensors.[10] The most notable is their use in the field of oxygen sensing.[11] The typically long-lived nature of the triplet excited state of metal complexes make them highly sensitive to even small concentrations of oxygen, which decreases the emission intensity and phosphorescence lifetime of most phosphors through triplet−triplet energy transfer to give singlet oxygen and the ground state of the complex. This reaction also forms the basis for photodynamic therapy, as the singlet oxygen produced in this reaction can be highly cytotoxic to cancer cells near the surface of the skin.[12] Square planar Pt(II) complexes have also been reported for the sensing of volatile organic compounds by reversible vapoluminescence.[13]

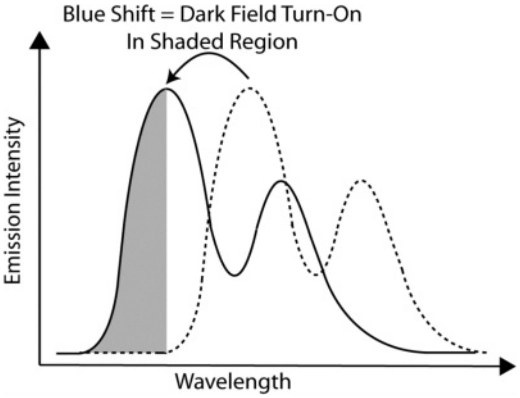

Figure 2. Schematic illustration of how a blue-shifting transduction event gives a significant dark-field turn-on signal.

Additionally, there have been phosphorescent complexes designed for the sensing of other vapors. One example is that of Pilato, who used a platinum 1,2-enedithiolate complex to detect fluoro and cyano phosphate esters by formation of a strongly phosphorescent complex.[14] The analytes activated a primary alcohol that subsequently intramolecularly alkylated a pyridine substituent to form a rigidified ligand around the platinum center. Our group has utilized a similar reaction to create a fluorescent turn-on sensor for these analytes, which are simulants for chemical weapons, including SARIN and SOMAN.[15] The primary advantages to this type of detection method for chemical weapons over others, such as surface acoustic wave or interferometry, are that it is functional group specific, simple, and highly portable.

Cyanogen halides (X−CN) are highly toxic blood agents that have an effect on the human body similar to that of hydrogen cyanide.[16] Cyanogen chloride, a gas under ambient conditions, is a military chemical weapon (abbreviation: CK). Reliable detection of these poisons at trace concentrations has obvious implications for homeland security. Herein we describe our studies of a series of bis-cyclometalated platinium(II) complexes as potential phosphorescent reporters of cyanogen halides via an oxidative addition reaction.

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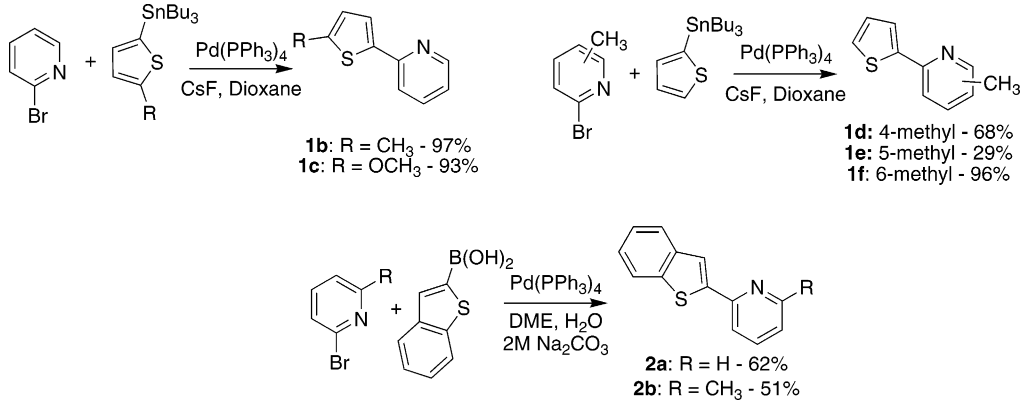
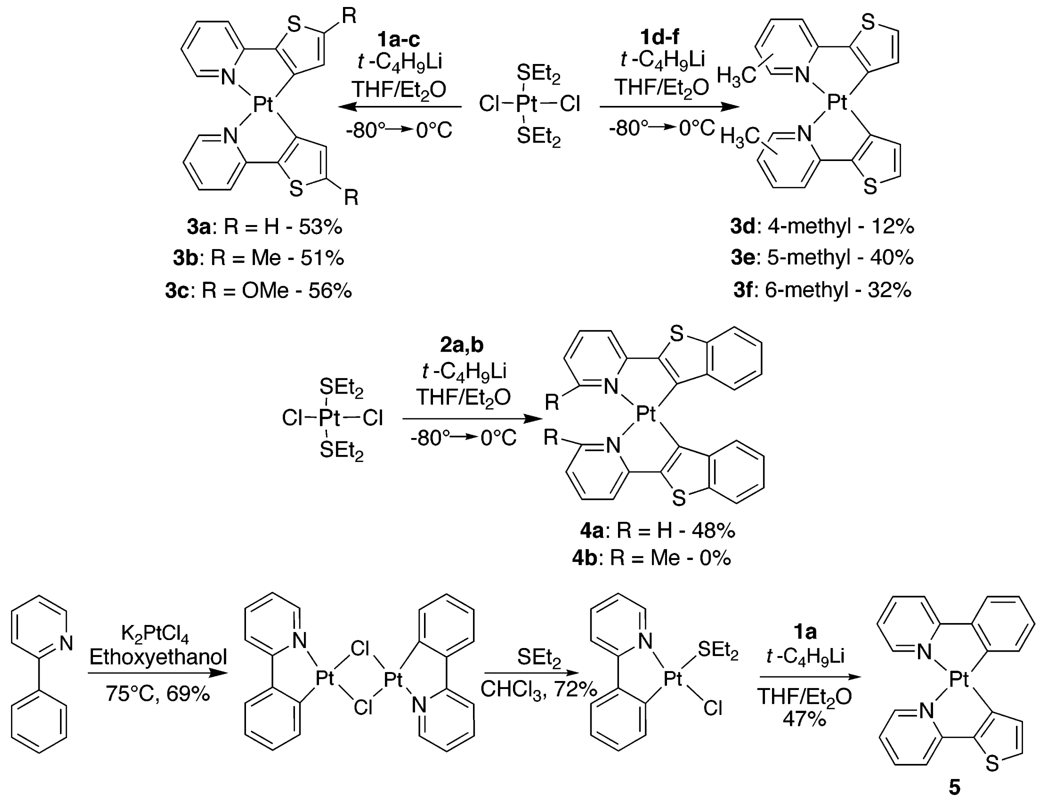
Scheme 1. Synthesis of *thpy* Ligands



Scheme 2. Synthesis of Bis-cyclometalated Pt(II) Complexes **3**−**5**



Results and Discussion

Synthesis. A total of eight platinum(II) complexes were synthesized and studied in this work. Scheme 1 summarizes the procedures used to synthesize the cyclometalating ligands. The bi- or tricyclic ligands were readily synthesized by standard palladium-catalyzed cross-coupling methods, except for 2-phenylpyridine, which is commercially available. Non-benzo-fused 2-thienylpyridine ligands, including the previously reported parent thienylpyridine (*thpy*, **1a**), were synthesized by either Suzuki couplings (**1a**) with thiophene 2-boronic acid and 2-bromopyridine or Stille couplings (**1b**−**1f**) with the appropriately substituted reactants that were either commercially available or readily prepared. Benzthiophene-based ligands **2a** and **2b** were prepared from the commercially available thianaphthene boronic acid and 2-bromopyridine by Suzuki coupling in 50−60% yield.

Scheme 2 summarizes the synthetic procedures used to prepare the bis-cyclometalated Pt(II) complexes. Most of the homoleptic complexes studied were synthesized by simple lithiation of the ligands with *tert*-butyllithium in a THF/Et_2O mixture, followed by metalation with $Cl_2Pt(SEt_2)_2$, as per the method of von Zelewsky.[4] Complex **4b** could not be synthesized, probably because of the steric congestion that would be present in the desired product. Also, the heteroleptic complex (**5**) was prepared by cracking the chloro-bridged *ppy*-ligated dimer intermediate with diethyl sulfide, followed by reaction with the lithiated *thpy* ligand. To our knowledge, this is the first heteroleptic bis-cyclometalated platinum complex that has been reported.[17] All final complexes were readily chromatographed under ambient conditions on silica gel and isolated as

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(17) For an example of a heteroletptic bis-cyclometalated palladium complex, see: Jolliet, P.; Gianini, M.; von Zelewsky, A.; Bernardinelli, G.; Stoeckli-Evans, H. *Inorg. Chem.* **1996**, *35*, 4883.

Table 1. Photophysical Parameters of Pt(II) Complexes **3**−**5**

	room-temperature solution (THF)				77 K glass (2-MeTHF)	
complex	λ_{max}(UV/vis)[a] (nm)	λ_{max}(phos) (nm)	τ_p (μs)	Φ_p	λ_{max}(phos) (nm)	τ_p (μs)
3a	306, 425	582	5.5	0.24	575	10.3
3b	312, 433	599	13.2	0.29	590	13.0
3c	317, 443	613	13.6	0.30	605	14.2
3d	306, 419	578	6.0	0.24	569	10.9
3e	309, 425	588	6.4	0.22	578	9.7
3f	311, 438	582	*b*	<0.01	572	15.2
4a	277, 458	630	*b*	<0.01	626	8.7
5	300, 415	581	*c*	0.05	567	13.2

[a] First maximum is ligand-centered absorption, and second is MLCT. [b] Not determined because of weakness of signal. [c] Multiexponential decay.

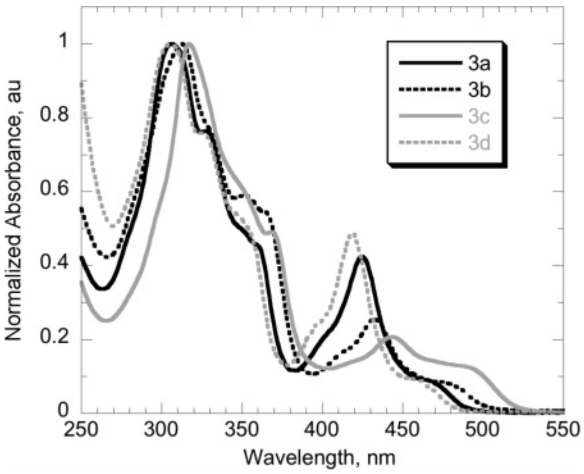

Figure 3. Normalized UV/vis spectra of complexes **3a**−**d** in THF.

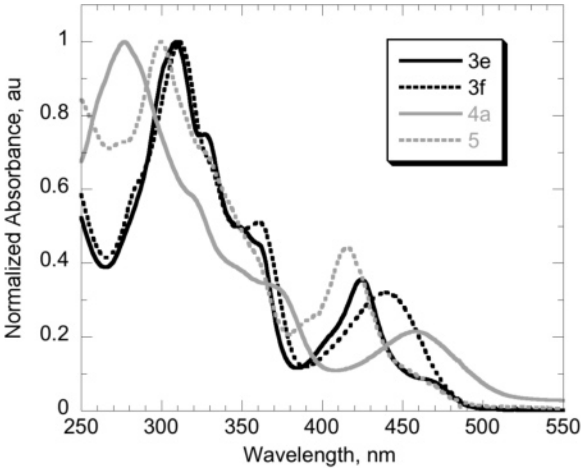

Figure 4. Normalized UV/vis spectra of complexes **3e**, **3f**, **4a**, and **5** in THF.

single stereoisomers, taken to be cis based on literature precedent and several X-ray crystal structures (vide infra).

Photophysical Properties. Table 1 summarizes the photophysical properties of the platinum(II) complexes in deoxygenated, room-temperature fluid solution and in 77 K 2-methyltetrahydrofuran glasses. Figures 3 and 4 show normalized absorbance spectra of these complexes. Most of the complexes investigated here showed sharp and distinct MLCT transitions with extinction coefficients of approximately 10^4, as is characteristic for the parent Pt(*thpy*)$_2$ complex (**3a**). These bands also showed moderate negative solvatochromism, in that more polar solvents gave blue-shifted MLCT bands. One example is complex **3a**, which in acetone had an MLCT maximum at 419 nm but in toluene was red-shifted to 430 nm. Also, increasing the electron density (**3b**, **3c**) or the conjugation lengths (**4a**) of the ligands tended to cause a red shift in the absorbance bands.

In addition, most of the Pt(II) complexes displayed moderate to strong phosphorescence intensity (with quantum yields of emission between 0.05 and 0.30) in room temperature, deoxygenated fluid solution (Figure 5). All of the emissive complexes phosphoresce in the orange or red region of the visible spectrum with lifetimes on the time scale of 5−15 μs at ambient temperature. The lower quantum yield and biexponential character of **5** may be due to the presence of a competing, nonemissive state involving the phenylpyridine ligand.

All these Pt(II) complexes show only weak solvatochromism in their phosphorescence energy. The rigidochromic effect on the emission of these complexes is a small value of 9 ± 3 nm upon freezing the sample in a 2-methyltetrahydrofuran glass. The rigid glass does not allow reorganization of solvent dipoles upon generation of excited states and give strongly blue-shifted spectra of complexes that emit from charge-transfer states. These trends, coupled with the vibronic structure observed in the room-temperature phosphorescence spectra, suggest that the emissive state of these complexes is an admixture of an MLCT state and an intraligand $\pi-\pi^*$ state. This behavior is similar to other Pt(II) cyclometalated complexes.[2c]

Not all of the complexes, however, emit strongly at room temperature. Those complexes (**3f** and **4a**) have phosphorescence quantum yields less than 1%. Complex **3f** is a particularly striking example, as the inclusion of only a methyl group on the pyridine ring almost completely eliminated phosphorescence. The relatively small effect of including a more powerful donor in complex **3c** suggests that this phosphorescence attenuation is due to steric congestion of the square plane around the metal center. The strong room-temperature emission of **3d** and **3e** also supports the hypothesis that steric congestion is the reason for the very weak emission of **3f** and **4a**. Complex **3f** is very similar to **3d** and **3e**, the only difference being that the methyl groups *meta* or *para* to the pyridine nitrogen are not expected to have repulsive interactions in the square plane. Complexes **3f** and **4a** also gave broadened MLCT absorbance bands, suggesting that there is more conformational variation in these nonemissive complexes.

To directly observe the effects of interligand steric congestion around the platinum metal center, single-crystal X-ray structures were obtained for complexes **3c** and **3e**. ORTEP-style diagrams of these crystal structures are displayed in Figure 6, while crystallographic details and refinement statistics are included in the Supporting Information. Complex **3b** is only slightly distorted out of a square planar geometry, while **3f**, on the other hand, is severely distorted away from ideal square plane geometry because of the steric repulsion between the methyl groups *ortho* to the nitrogen on the pyridine ring. Although we were unable to grow suitable crystals from the benzthiophene-substituted complexes, simple molecular mechanics modeling indicates that the aryl hydrogen atoms in the 4-positions of the thianaphthene ring system in complex **4a** would have similar steric interactions in a square planar geometry, forcing the complex into a highly distorted conformation. Certain quinoline-substituted bis-cyclometalated heavy metal group 10 d^8 com-

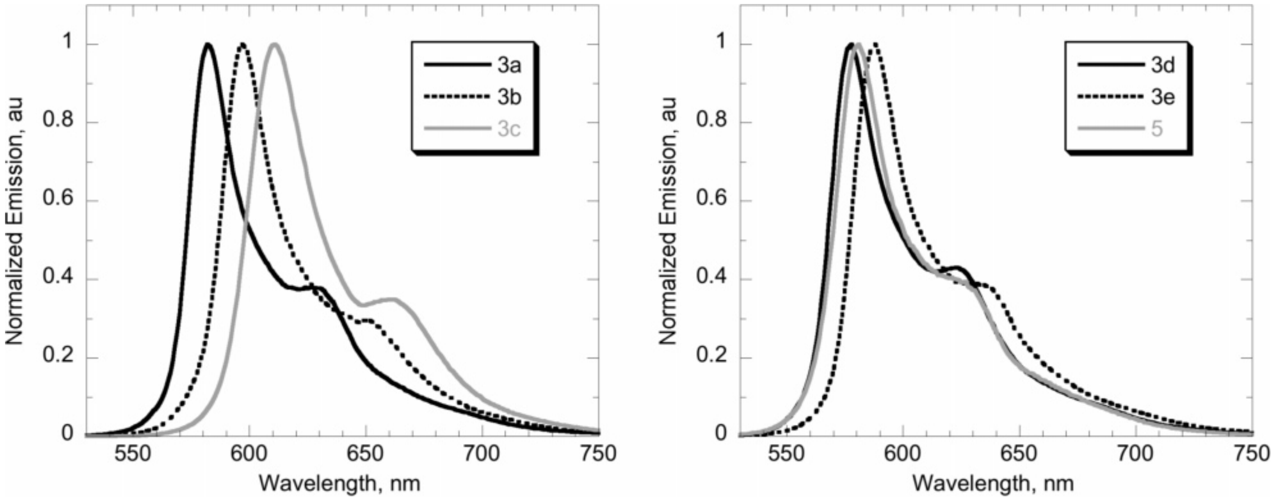

Figure 5. Room-temperature emission spectra of phosphorescent bis-cyclometalated Pt(II) complexes in THF.

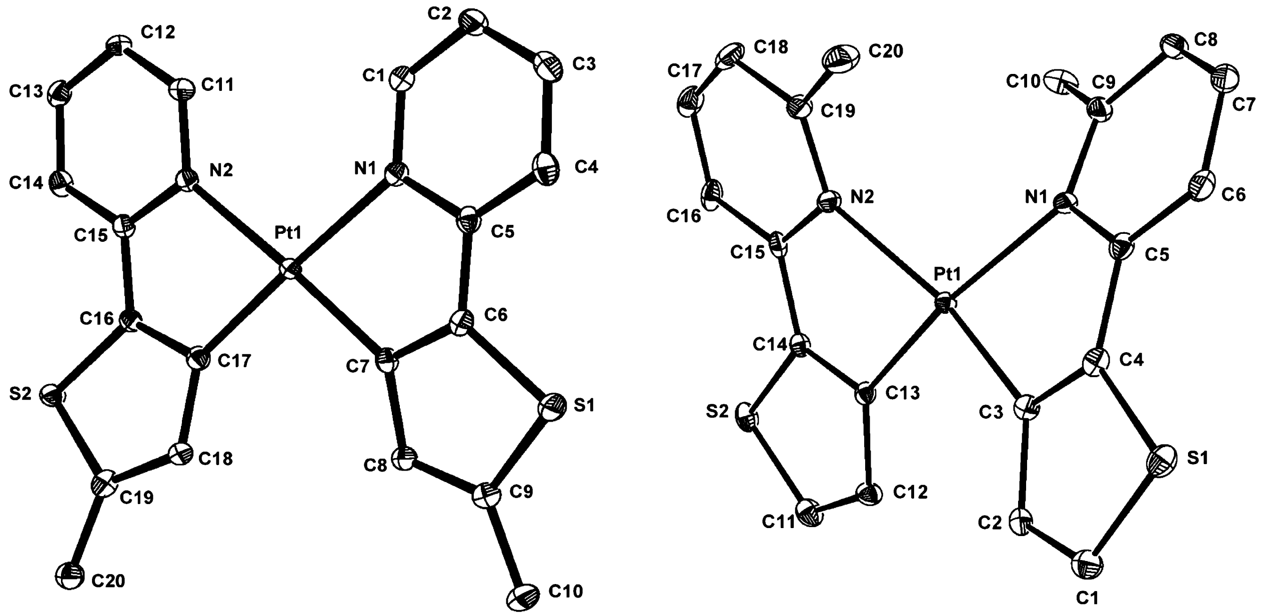

Figure 6. 50% probability representation of X-ray crystal structures of **3b** (left) and **3f** (right).

plexes have been shown to have a severely twisted geometry for similar reasons.[17] These intramolecular repulsions may lead to enhanced nonradiative relaxation of the excited state through additional twisting and vibration.

Oxidative Addition In Solution. All of the reported complexes take part in oxidative addition reactions under ambient conditions as described by von Zelewsky.[5] Figure 7 shows the progress of a reaction with **3b** with methyl iodide under pseudo-first-order conditions in benzene as followed by absorbance spectroscopy. Well-behaved isosbestic points, in addition to well-behaved pseudo-first-order kinetics (Figure 8), characterize this reaction. There is also a strong solvent dependence on the rate of reaction, which is indicative of a highly polar transition state and an S_N2-type mechanism.

Upon adding cyanogen bromide to these complexes under similar conditions, several important differences were apparent. The first is that the reaction with cyanogen bromide was much faster than with methyl iodide. Figure 9 compares the percent conversion as a function of reaction time for cyanogen bromide (0.00013 M) and methyl iodide (1.0 M) with **3a**. The cyanogen bromide reaction goes to completion well before the reaction with MeI, even though the concentration of BrCN is almost 10^4 times smaller. The nonpolar solvent benzene was used to

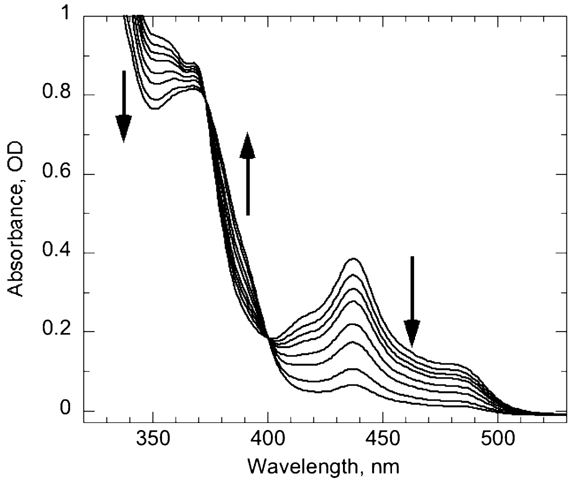

Figure 7. UV/vis spectra of **3b** during its reaction with 1.0 M MeI in benzene. Times elapsed, in seconds, are 15, 30, 45, 60, 90, 120, 180, 240, and 300.

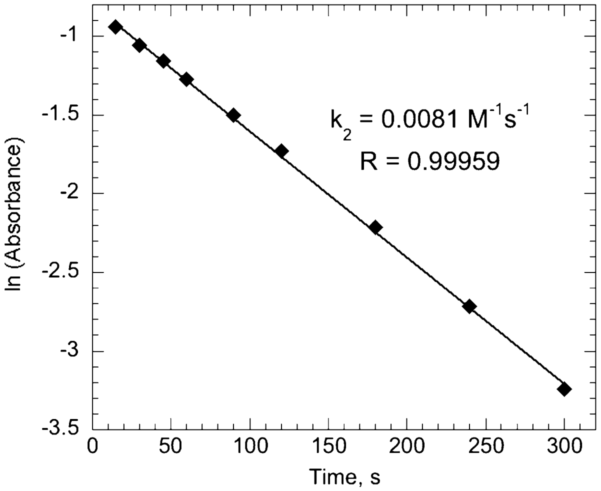

Figure 8. Pseudo-first-order rate plot for **3b** in 1.0 MeI/benzene. The calculated bimolecular rate constant was 0.0081 M^{-1} s^{-1}.

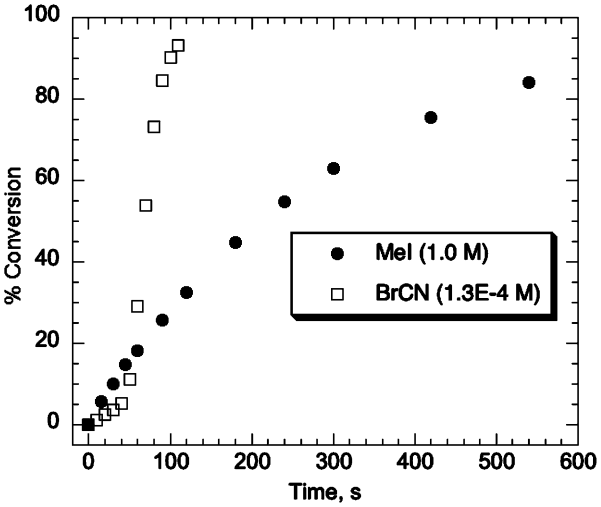

Figure 9. Conversion versus time, as determined by UV/vis, for **3a**, with either MeI or BrCN (in benzene). A much smaller concentration of BrCN is necessary to achieve rapid conversion.

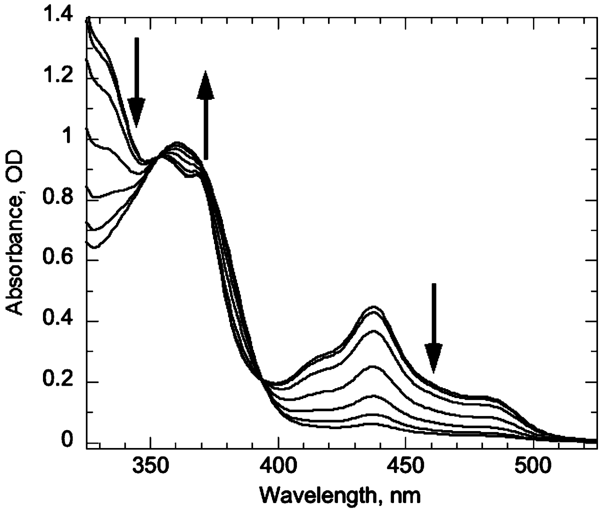

Figure 10. UV/vis spectra of **3b** during its reaction with 0.00013 M BrCN in benzene. Times elapsed are in 20 s intervals.

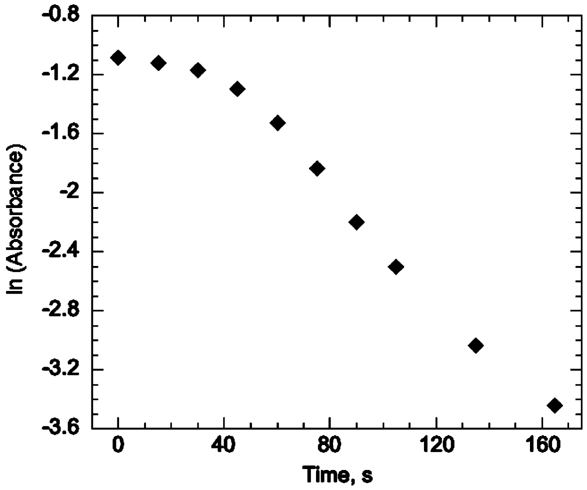

Figure 11. First-order kinetic plot for the reaction of **3b** with BrCN (2.4 × 10^{-4} M) in benzene. The reaction accelerates after an initial induction period.

more effectively mimic a solid-state environment, which would be used for sensing purposes, than a more polar solvent. The UV/vis profiles of these reactions (Figure 10 for **3b**) also show well-behaved isosbestic points, disappearance of the Pt(II) MLCT band, and growth of an absorbance at approximately 350 nm, characteristic of bis-cyclometalated Pt(IV) complexes.

In addition to a much faster reaction rate in solution, the kinetic profiles of these reactions with CNBr do not follow a simple kinetic model. Figure 11 shows the pseudo-first-order rate plot for the reaction of **3b** with 0.00024 M CNBr in benzene. The reaction accelerates very quickly following an initial induction period. This difference in kinetic behavior suggests a different mechanism than the S$_N$2 type invoked for the oxidative addition with methyl iodide.

A third significant difference between the reactions with CNBr and MeI is the lack of strong solvent polarity dependence on the rate of reaction with the Pt(II) complexes and CNBr. Upon switching from toluene to acetone, the initial reaction rate only increased by approximately 50%. The key differences in these reactions are indicative of a radical, potentially chain, mechanism operating in this reaction. von Zelewsky has reported these reaction properties occurring between **3a** complexes and certain benzylic halides and also ascribed them to a radical mechanism. This is further supported by the observation that the reaction goes to completion much faster in benzene than in toluene (Figure 12), suggesting that an intermediate radical may abstract a benzylic hydrogen atom from toluene, thereby inhibiting the reaction.

To ensure that oxidative addition, and not complex decomposition, was occurring, the reaction between **3a** and BrCN was performed on a preparative (~30 mg) scale. Upon mixing the two in THF, a colorless product immediately precipitated. The major product (of the two by TLC) was isolated by filtration and washing with dichloromethane. Mass analysis of the isolated product showed the desired molecular ion for Pt(*thpy*)$_2$(Br)(CN) with the expected fragmentation pattern. NMR analysis was not possible because of the very limited solubility of the complex. No free ligand was observed upon addition of BrCN. Although the product was not emissive in room temperature fluid solution, it was strongly emissive at 77 K with photophysical parameters consistent with a bis-cyclometalated Pt(IV) complex.[7a] This included a highly structured emission spectrum with a maximum in the green region of the visible spectrum and an excited-state lifetime of about 400 μs.

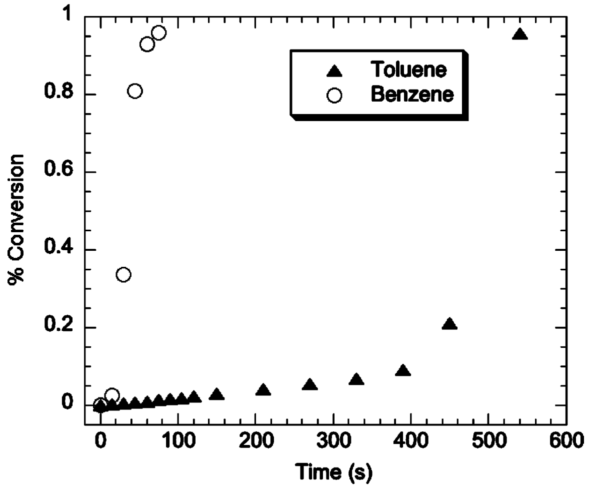

Figure 12. Percentage conversion of **3a**, in either toluene or benzene, in the presence of 0.00024 M BrCN.

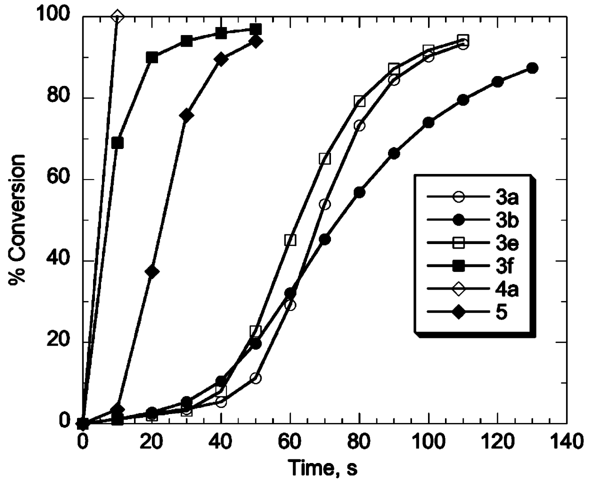

Figure 13. Conversion percentages of several Pt(II) complexes as a function of time in 0.00013 M BrCN/benzene.

Table 2. Bimolecular Rate Constants of Platinum Complexes with MeI in Benzene

complex	k ($M^{-1}\ s^{-1}$)
3a	3.4×10^{-3}
3b	8.1×10^{-3}
3c	4.8×10^{-3}
3d	8.8×10^{-3}
3e	5.1×10^{-3}
3f	0.82×10^{-3}
4a	0.93×10^{-3}
5	5.8×10^{-3}

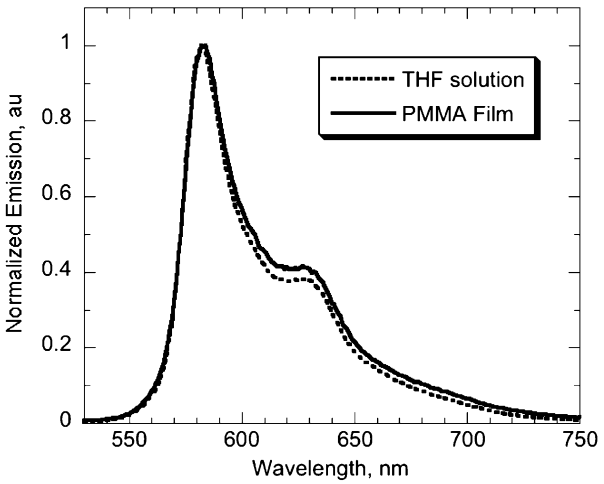

Figure 14. Normalized emission spectra of **3a** in degassed THF solution and doped into PMMA films (10% w/w).

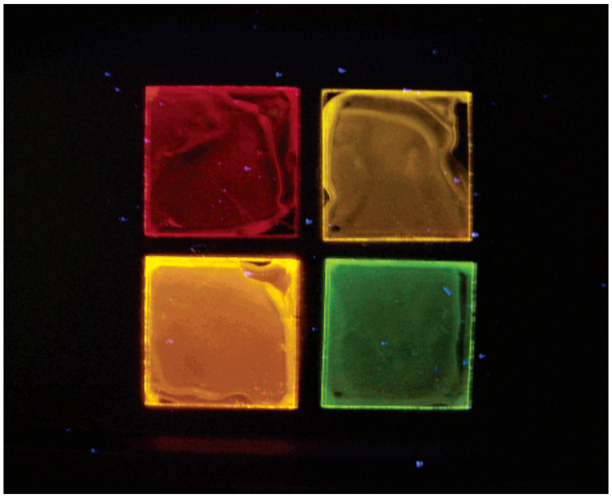

Figure 15. PMMA/Pt(II) spun-cast films of **4a** (top) and **3a** (bottom) under UV light. Films on the left are unexposed, while films on the right have been exposed to saturated BrCN for 15 s.

Analysis of the structure–reactivity trends between different Pt(II) complexes and BrCN yielded similar results to the study of photophysical properties. The most reactive complexes were those that incorporated interligand steric congestion into the square plane of the complex (**3f**, **4a**) even at stoichiometric concentrations of BrCN. Figure 13 shows the conversion as a function of time (in 0.00013 M BrCN/benzene) of several members of the Pt(*thpy*)$_2$ family. Therefore, the increase in the energy of the sterically crowded complexes decreases the activation barrier for oxidative addition, increasing the rate at which these heavily distorted complexes go to octahedral products. The fact that the least emissive Pt(II) complexes are the most reactive toward oxidative addition with BrCN will likely be beneficial to any turn-on phosphorescence-based sensing scheme, since excessive phosphorescence from the starting "off" state may increase the background signal on top of which the measurement must be made. The heteroleptic complex **5** also goes to completion faster than the parent homoleptic complex **3a**, but the reason for this is presently unclear.

In contrast to the structure–reactivity trend with BrCN, the more sterically hindered complexes (**3f**, **4a**) show bimolecular rate constants with methyl iodide (in benzene) that are approximately 4–10 times smaller than the unstrained systems (Table 2). An electronic effect for this behavior was ruled out because **3d** and **3e**, which have methyl groups in different positions on the pyridine ring, do not show behavior similar to that of **3f**. This suggests that the transition state for S_N2 type oxidative addition to these complexes exacerbates the preexisting steric congestion, possibly by forcing the complex into a square-pyramidal geometry, whereas the transition state for the reaction with BrCN relieves the unfavorable interactions. This difference is particularly useful for sensing, as it could impart additional selectivity for cyanogen halides over interferents that react by the S_N2-type mechanism.

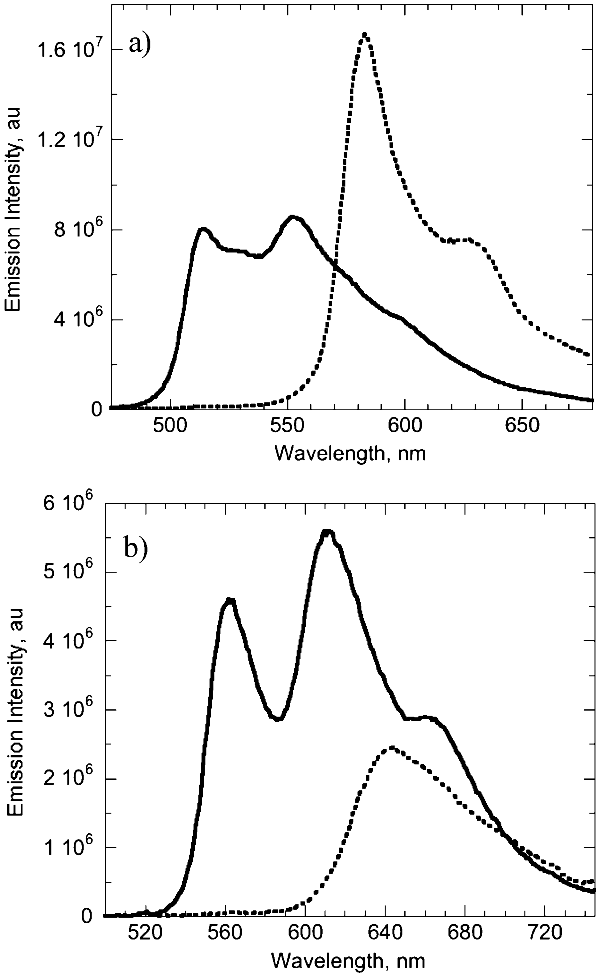

Figure 16. PMMA film emission spectra of **3a** (a) and **4a** (b) before (dotted) and after (solid) exposure to BrCN vapor for 15 s.

Solid State Phosphorescence Sensing. Solid-state materials are essential for the fabrication of effective vapor-phase sensory devices. This can be readily achieved with conjugated polymer sensors, neat thin films of which can be highly emissive when the polymer structure is properly designed to prevent aggregation. These platinum complexes, however, were doped into a polymer matrix in order to create a substance with desirable material properties that could be readily cast into films. By spin-casting from a dichloromethane solution that contained a mixture of poly(methyl methacrylate) (PMMA) and the desired Pt(II) complex (10% w/w relative to PMMA), transparent, glassy, highly phosphorescent thin films were readily prepared. Many of these films were highly emissive even under ambient conditions because the glassy PMMA excluded enough oxygen to allow radiative decay of the triplet excited states to be kinetically competitive with oxygen-induced quenching. As illustrated in Figure 14, these films showed very similar shapes of their emission spectra to the solution data. This indicates that at 10% loading the amount of intermolecular communication between the metal complexes was negligible. In addition, those complexes that were not emissive in room-temperature solution (**3f**, **4a**) showed phosphorescence spectra in the PMMA films that were in the same spectral region as at 77 K. This is presumably because the rigid PMMA matrix inhibits the intramolecular conformational changes that lead to nonradiative deactivation of the excited states of these strained molecules.

Upon exposing these doped PMMA films to saturated BrCN vapor, complete conversion to the corresponding platinum(IV) complexes occurred within seconds. The blue-shifted emission of the product is apparent both spectroscopically and visually. The spectral features of the products in the solid state are consistent with the characteristic ligand-centered platinum(IV) emission, both in spectral position and in the relative intensities of the vibronic bands. Figure 15 shows a picture in which PMMA films containing **3a** and **4a** have been exposed to saturated BrCN vapor for 15 s. The spectra in Figure 16 illustrate how using a strong spectral blue-shift as the sensing signal gives a turn-on signal with virtually no background (dark field). This feature is desirable in any sensing system for maximum sensitivity to trace quantities of analyte. Current experiments are focused on demonstrating trace (part per million) sensitivity to the cyanogen halides. Preliminary experiments have shown modest sensitivity to 10 ppm BrCN vapor. We are also focusing on extending this type of chemosensing mechanism to other dangerous chemicals, such as explosives.

Conclusion

A new dark-field turn-on optical chemosensing scheme has been developed using bis-cyclometalated platinum complexes. A series of these complexes was synthesized, most of which have not been previously reported in the literature. The ligands were chosen so that structures with a variety of electronic and steric properties could be investigated. Most of these Pt(II) complexes were strongly phosphorescent at room temperature in fluid solution. It was found that cyanogen halides oxidatively add readily to these Pt(II) complexes to give the corresponding Pt(IV) products. Investigations of the structure−property relationships showed that those complexes that were twisted out of the square planar geometry (and were also not phosphorescent at room temperature in solution) reacted faster with CNBr than those that were not. The relative lack of solvent polarity dependence on the reaction kinetics as well as the strong difference in kinetics between toluene and benzene strongly suggests a radical mechanism for this reaction. Thin polymer films containing these complexes, which were phosphorescent at room temperature, also reacted with cyanogen halide vapors to give the blue-shifted Pt(IV) products which were also emissive under these conditions, giving a dark-field turn-on of the product phosphorescence, an advantageous characteristic for improving sensitivity toward any potential analyte. Current efforts are directed at improving the sensitivity of cyanogen halide detection, as well as applying this new chemosensing technique to other potential analytes.

Acknowledgment. This work was supported by the Army Research Office and the Institute for Soldier Nanotechnologies.

Supporting Information Available: Experimental and synthetic details. Crystallographic information files (CIF) for **3b** and **3f**. Crystal structure and CIF file for **5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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